

Development of poly(vinylidene fluoride) electrospun fibers and films for sustainable applications

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Abstract

The work presented in this thesis focuses on electrospinning of homopolymer PVDF solutions and PVDF solutions blended with a specialty novel polyampholytic copolymer called r-PAC. The structural and thermal properties of the prepared electrospun fiber mats were carefully analyzed. Since the quantitative analysis of the electroactive phases (β - and γ -phases) of PVDF is quite important due to their piezoelectric nature, using a novel method called Fourier Self Deconvolution (FSD), the relative fraction of β - and γ -phases was determined in the PVDF electrospun fiber mats and electrosprayed non-fibrous mats. FSD is a method used to synthetically narrow broad and complex infrared absorbance spectra. The relative fractions of β - and γ -phase crystals were determined by resolving the peak at 840 cm^{-1} in the IR absorbance spectra. When the overall level of crystallinity is known, as it is here from X-ray analysis, then FSD allows determination of the absolute content of the polar β and γ phases. Comparing results from wide-angle X-ray scattering and FTIR/FSD, we show that γ -phase dominates over β -phase in both electrospun and electrosprayed materials, with relative γ to β ratios of 55/45 and 81/19, respectively.

Membrane fouling is a major problem in the filtration industry as it causes high operational costs and more environmental pollution due to the frequent replacement of filtration membranes. This study reports the fabrication of fouling resistant non-woven fibrous membranes from electrospinning blended solutions of PVDF with a novel polyampholytic copolymer called r-PAC. Polyampholytes are macromolecules that have both positive and negative charged units in different side groups attached to the backbone. The r-PAC is synthesized by our collaborators by co-

polymerizing a hydrophobic monomer in addition to the positive and negative charged monomer units, to reduce the fouling propensity of PVDF electrospun membranes while preserving its inherent hydrophobicity. Blends of PVDF/r-PAC were electrospun across the full range of compositions from 0/100 to 100/0. Adsorptive fouling experiments with a fluorescently labeled protein confirmed that the fiber mats obtained from the PVDF/r-PAC blends resist protein adsorption, exhibiting highly enhanced fouling resistance compared to the fibers obtained from homopolymer PVDF. The thermal degradation kinetics of four different variants of the r-PAC were determined by analyzing the IR absorbance spectra and comparing to results of thermogravimetry. The dynamic fragility index and the glass transition temperature of the four r-PAC variants were determined by fast scanning calorimetry.

Processing PVDF solutions for electrospinning involves dissolving the PVDF resin in solvents such as N,N-dimethylacetamide (DMAc), N,N-dimethylformamide (DMF), and N-methyl-2-pyrrolidone (NMP). These hazardous solvents exhibit various risks, such as reprotoxicity, corrosivity, liver and kidney damage, and skin and eye irritation. Therefore, it is a timely requirement to find alternative eco-friendly and safe solvents to process PVDF solutions. γ -valerolactone (GVL) is a low-toxic, biorenewable, and environmentally friendly solvent obtained from biomass hydrolysis that shows promising potential for use in PVDF processing. However, electrospinning PVDF solutions made with GVL is quite a complex process because they undergo a sol-to-gel transition much faster than solutions made with other hazardous solvents. This work, with its comprehensive oscillatory rheological analysis of PVDF solutions of three different concentrations, provides crucial insights into how the temperature and the shear rate affect sol-to-gel transition in PVDF/ GVL solution systems. The successful electrospinning of PVDF/LiCl in

GVL/Acetone solutions to obtain nano-scale fibrous mats, based on the rheological test results, demonstrates the practical application of these findings.

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Chapter 1: Introduction

1.1 Polymers

1.1.1 *Polymer basics*

Polymers are very large molecules constructed as a chain of a repeated smaller unit called a monomer. Polymers either occur naturally or are synthesized artificially, depending on the requirement. Cellulose, rubber, wool, silk, and the proteins found in living organisms can be categorized as naturally occurring polymers or bio-polymers. On the other hand, polymers like poly(ethylene) (PE), poly(propylene) (PP), poly(styrene)(PS), poly-para-phenylene teraphthalamidean (Kevlar), and poly(vinylidene fluoride) (PVDF) are examples of synthetically derived polymers.

Polymers are of utmost importance in the modern era. Their unique properties have made them impossible to replace. Polymers are lightweight and flexible. Some polymers show extremely strong mechanical properties (Kevlar) while some exhibit tremendous thermal stability, such as poly(tetrafluoroethylene), which is commonly known as Teflon. Polymers like PVDF show excellent electric properties such as piezo and pyroelectricity. Polymers are easy to mass produce, and the cost of production is relatively low compared to other alternatives.

The formation of a long chain of repetitions of a monomer unit is called polymerization. A monomer unit usually has a double bond between two carbon atoms. As shown in Figure 1.1-A, a propylene molecule has a double bond between two of its three C atoms. Upon excitation (chemically or by irradiation), one bond in this double bond breaks, creating the opportunity for

the molecule to bond with another to form a polymer chain. The polymer (poly(propylene)) is denoted by the monomer unit between square brackets, as shown in Figure 1.1-B. The subscript n denotes the number of monomer units in a polymer chain. The molecular weight of the polymer is given by,

$$M_w^{monomer} \times n = M_w^{polymer} \quad (1.1)$$

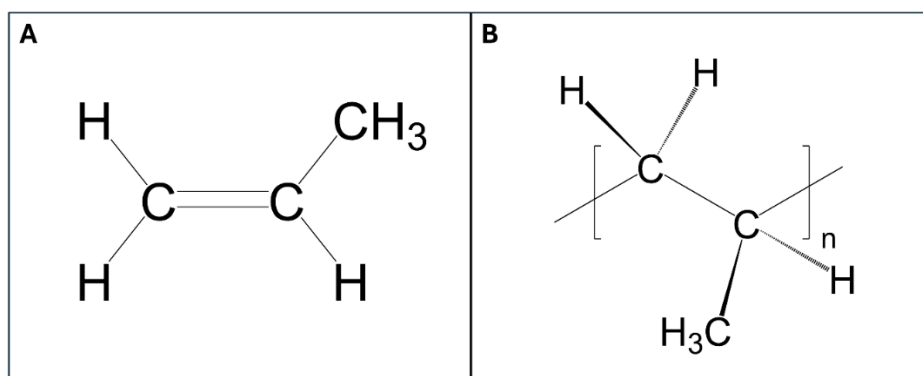


Figure 1.1: A) Structure of propylene; B) Monomer unit of poly(propylene).

Free radical polymerization is performed by adding radicals into a monomer unit solution with carbon-carbon double bonds. These radicals are generated by homolytic cleavage of covalent bonds. Radicals can be generated by homolysis in three different ways. 1) Azo initiators, where radicals are initiated by breaking C-N or O-N bonds; 2) peroxide initiators, where highly reactive peroxides are decomposed to form radicals; and 3) persistent initiators, where either a C-C bond is broken, or an azo compound is decomposed to form a radical. Once the radicals are added to the monomer solution, primary propagating radicals will be generated. These radicals will propagate further to initiate a polymer chain. This is the most common method of polymerization [1].

Polymers can be categorized into two main groups based on their monomer composition. A polymer chain made up of a single type of monomer is known as a homopolymer, while a chain that consists of at least two different types of monomers is referred to as a copolymer. When two (or more) distinct monomers are combined, they can be copolymerized in various ways to create different polymer chains, all with the same monomer composition. One approach is to connect the monomer units randomly, resulting in a random copolymer. An alternating copolymer, as the name implies can be formed if the monomer units are arranged in an alternating pattern. A block copolymer occurs when two oligomers—shorter polymer chains composed of multiple monomer units—are created from the different monomers and then polymerized together. Another method of copolymerization involves grafting one monomer onto the chain of another. In Figure 1.2, a homopolymer and examples of the different types of copolymers are shown. The copolymers illustrated in the figure represent the simplest forms, featuring two distinct monomer units, which are depicted as blue and brown circles.

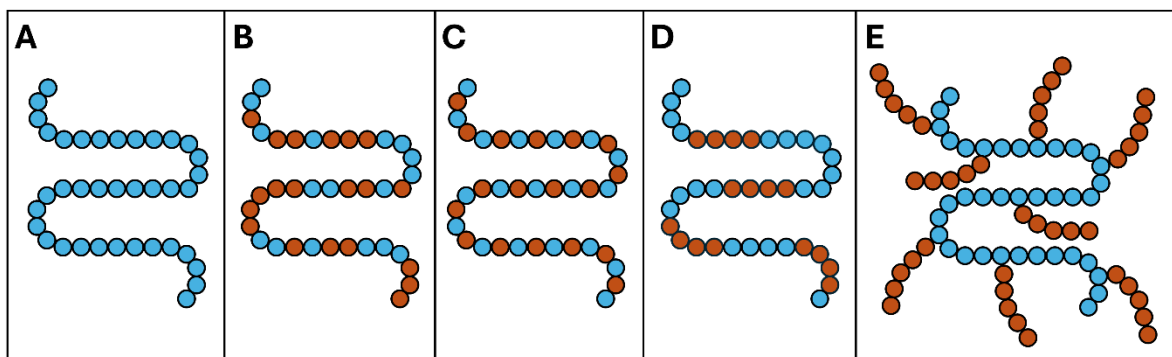


Figure 1.2: A) A homopolymer; B) a random copolymer; C) an alternating copolymer; D) a block copolymer; and E) a grafted copolymer. The two distinct monomer units are shown in blue and brown circles.

Polymer chains can exist as linear chains (unbranched) and branched chains. High-density poly(ethylene) (HDPE) is a good example of a linear polymer with little to no branching, whereas low-density poly(ethylene) (LDPE) has branched chains of various lengths. Even though they have the same chemical structure, they exhibit different physical properties, such as the degree of crystallinity or opacity due to the presence or absence of the branches [2]. Figure 1.3 shows a linear polymer chain and a branched polymer chain.

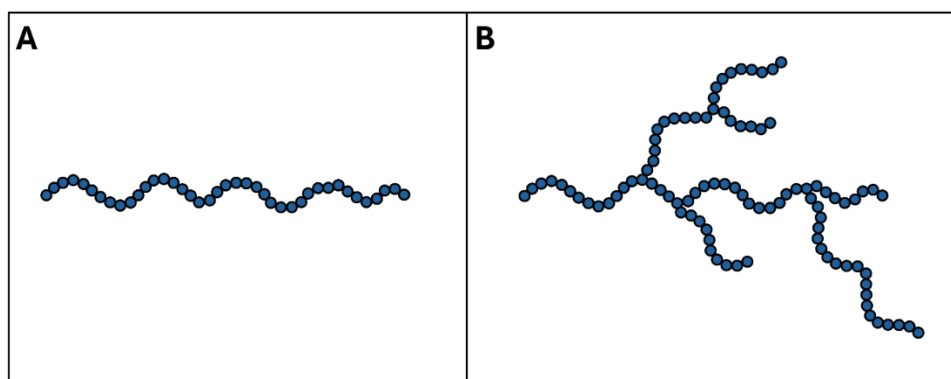


Figure 1.3: Schematic of A) A linear polymer chain; B) a branched polymer chain.

The long chain of carbon atoms in a polymer chain is often called its backbone. Any other molecule or a chain (not a branch) is called a side group or a pendant group and is usually denoted by R (Figure 1.4). For example, if the R group is $-\text{CH}_3$, the polymer takes the form of poly(propylene), as shown in Figure 1.1-B. The nature of the R group can significantly influence the properties of a polymer, such as the crystal formation, degree of crystallinity, defects, cross-linking, and charged nature.

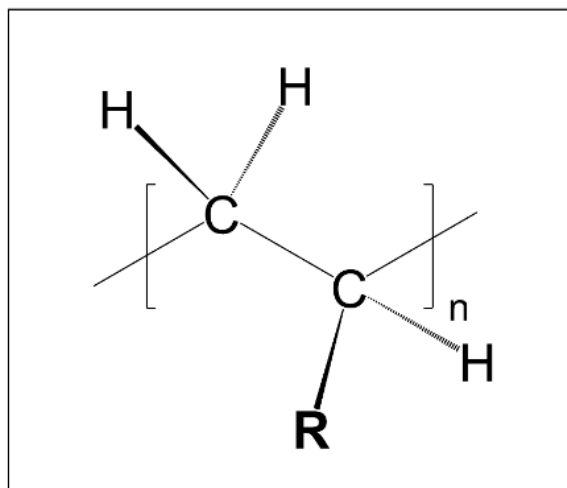


Figure 1.4: Monomer unit with R group (pendant group) attached to one of the carbon atoms in the backbone.

The stereoregularity of the polymer's pendant group in the repeat unit is called the tacticity. If the R group is on the same side of the backbone in all repeat units, it is called isotactic, while if the R group alternates its side, the polymer chain is said to be syndiotactic. Atactic polymer chains do not have such regularity and where the pendant group is randomly connected to the backbone [3]. The different tacticities of a polymer with a pendant group R are shown in Figure 1.5. Due to their excellent regularity, the isotactic and syndiotactic polymers tend to form crystalline structures. However, atactic polymers do not form crystals as the unit cell of a crystal needs to be in a highly regular ordered structure [4]. Polymer crystals and crystallization dynamics in polymers are discussed briefly in the following sections.

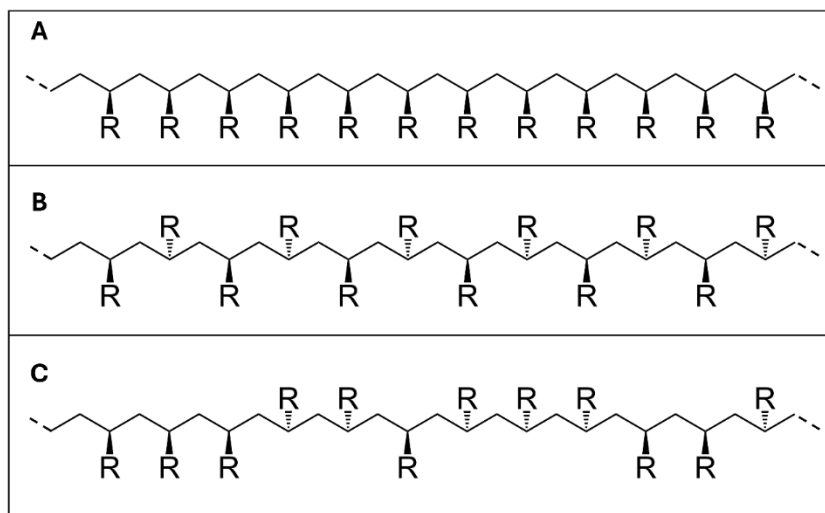


Figure 1.5: A) Isotactic configuration (pendant group on the same side of the backbone); B) syndiotactic configuration (pendant group alternates on either side of the backbone); C) atactic configuration (no regularity).

1.1.2 Phases in polymers

Matter can exist in three phases: solid, liquid, and gaseous. Polymers can also be classified according to the arrangement of their chains. The polymer chains are randomly oriented in the liquid state and have high mobility due to thermal excitation. The molecules constantly move around the space that they acquire when they are in their liquid state. When the polymers are cooled, the molecules' (chains') mobility is reduced, and the motion is restricted to molecular vibrations [5]. If the polymer is non-crystalline, a.k.a. amorphous, this transition occurs at a critical glass transition temperature T_g . The randomly oriented polymer chains in the liquid state are frozen as a polymer goes through its glass transition. If the polymer forms crystals, some polymer chains attain a highly ordered structure below a critical temperature called the crystallization point T_c . Polymers hardly undergo comprehensive crystallization all over the material because of chain

entanglements. Hence, the polymers that can form crystals are deemed to be semi-crystalline polymers. The crystalline domains are densely packed and have reduced volumes and mobility, whereas the amorphous regions have relatively higher mobility. Therefore, this intermediate state is called the rubbery state. If it is cooled further, it will also undergo its glass transition, freezing the amorphous fractions where now the mobilities of both the non-crystallized and crystallized chains are restricted. This state is called the glassy state. The change in specific volume and the enthalpy for an amorphous polymer and a semi-crystalline polymer during phase transitions is shown in Figure 1.6.

In Figure 1.6, the phase transitions at T_c (crystallization while cooling) and T_m (crystal melting while heating) for the semi-crystalline polymer show abrupt changes in specific volume or enthalpy and, therefore, discontinuity. Hence, these are called first-order phase transitions [6]. However, the specific volume and enthalpy change at T_g for the amorphous polymer is smooth and continuous through the transition. These are called second-order phase transitions; T_g also depends on the heating and cooling rates [6, 7]. Therefore, the glass transition is known as a quasi-second-order phase transition. It can be seen in Figure 1.6 that there is no overlap in T_c and T_m ($T_c < T_m$) for semi-crystalline polymers. This is called supercooling, and it is caused due to the crystal formation mechanism in polymers. It is discussed in detail in the following sections.

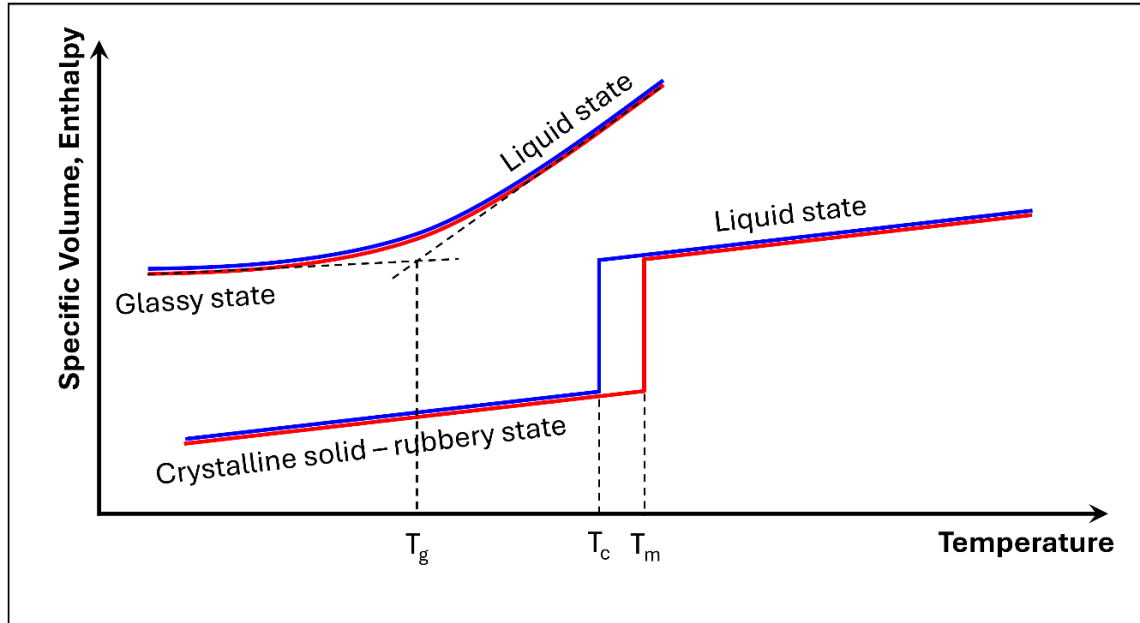


Figure 1.6: The schematic diagram of specific volume, enthalpy vs. temperature for an amorphous polymer at the glass transition temperature T_g (top); and at the melting point T_m and the crystallization point T_c for a semi-crystalline polymer (bottom). The heating curves and the cooling curves are shown in red and blue, respectively.

1.1.3 Crystals in polymers

1.1.3.1 Crystal basics

Crystals are long-range ordered structures. They are aggregates of atoms or molecules that are arranged in a repeating pattern in space. When a symmetry operation is applied to the system, it transforms into an indistinguishable state, meaning it looks the same as before the symmetry operation was applied [8]. A schematic of crystalline and amorphous structures is shown in Figure 1.7.

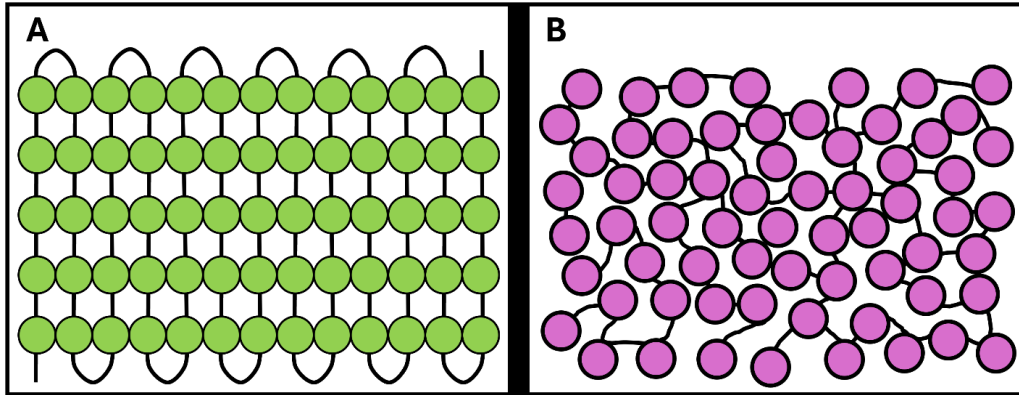


Figure 1.7: Schematic diagram of A) highly ordered crystal structure showing chain folding; B) randomly oriented amorphous structure with no long-range order.

Figure 1.7-A shows a simple crystal structure if one green circle is imagined as one atom or small molecule repeated in the lengthwise direction. One such repeating unit can be identified as a motif or basis. The crystal structure can simply be described as a lattice structure extended infinitely with motifs located at lattice points [8]. A translational lattice is shown in Figure 1.8.

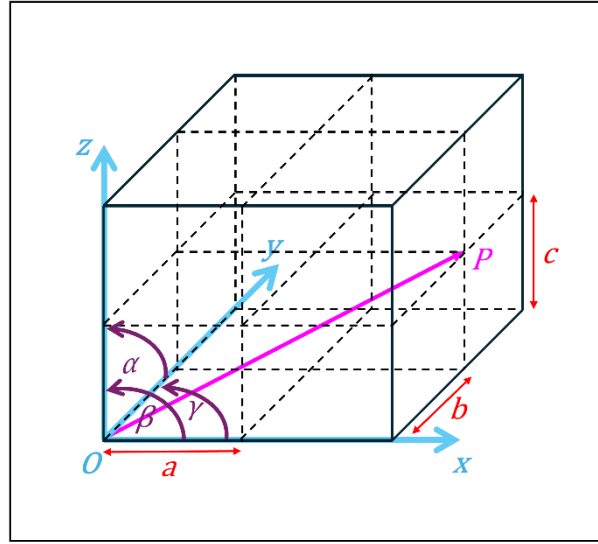


Figure 1.8: A translational lattice. $Oxyz$ axes are shown in light blue. The fundamental vectors along Ox , Oy , and Oz directions are **a**, **b**, and **c**, respectively (shown in red). P is a lattice point with a position given by the vector **OP** (shown in magenta). Figure adapted from [8].

The coordinates **a**, **b**, and **c** when multiplied by integers can give any lattice point and hence are defined as primitive vectors. For example, the lattice point P can be given by (shown in Figure 1.8 by a magenta vector),

$$\overrightarrow{OP} = 2\vec{a} + \vec{b} + \vec{c} \quad (1.2)$$

The different types of translational lattices are given in Table 1.1.

.

Table 1.1: Transitional lattice types and their axes and angles. Table adapted from [8].

Lattice Type	Crystal Systems	
	Axes	Angles
Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$
Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma$
Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90^\circ \neq \beta$
Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$
Trigonal	$a = b = c$	$\alpha = \beta = \gamma \neq 90^\circ$
Hexagonal	$a = b \neq c$	$\alpha = \beta = 90^\circ, \gamma = 120^\circ$

1.1.3.2 Polymer crystals

Unlike crystal formation in elemental compounds (for example, pure metals or intrinsic semiconductors) or small molecules (e.g., salts, extrinsic semiconductors), crystal formation in polymers takes a very different approach. Polymer molecules are extremely large compared to the size of an atom. Therefore, highly ordered crystal domains in polymers may contain sections from multiple polymer chains. When forming a crystal, the polymer chains reduce their lengths in multiple magnitude scales. Crystal formation in polymers initiates through a process called nucleation. Wunderlich's [9] classical nucleation approach suggests that the difference between the free energy of the crystalline state and the melt state becomes negative, as shown in the equation 1.3,

$$\Delta G = G_c - G_m \quad (1.3)$$

where G_c and G_m are the Gibbs free energy of the crystalline state and the melt state, respectively.

ΔG is defined as the Gibbs free energy of crystallization. Here, G_c can be written as,

$$G_c = G_{bulk} + \sum \gamma A \quad (1.4)$$

G_{bulk} represents the crystal's free enthalpy, excluding any surface effects, which are included by the second term on the right side of the equation where γ (γ is positive for all temperatures that are of interest for crystallization) is the specific surface free energy, and A is the corresponding area of the crystal, and the summation is extended over all surfaces with different surface energies.

Then equation 1.3 can be rewritten as,

$$\Delta G = \Delta G_c + \sum \gamma A \quad (1.5)$$

ΔG_c is the bulk-free energy difference, which is negative for all temperatures below T_m . Hence, ΔG takes a maximum corresponding to a critical nucleus size that can initiate crystallization. Random thermal fluctuations in the polymer chains overcome this positive energy barrier. This process, also known as primary nucleation, occurs by folding chains in a repeating manner that creates a highly ordered structure. A folded chain nucleus formed due to thermal fluctuations is shown in Figure 1.9-A. Then, secondary nucleation, the crystal growth phase, kicks off in the same chain folding mechanism.

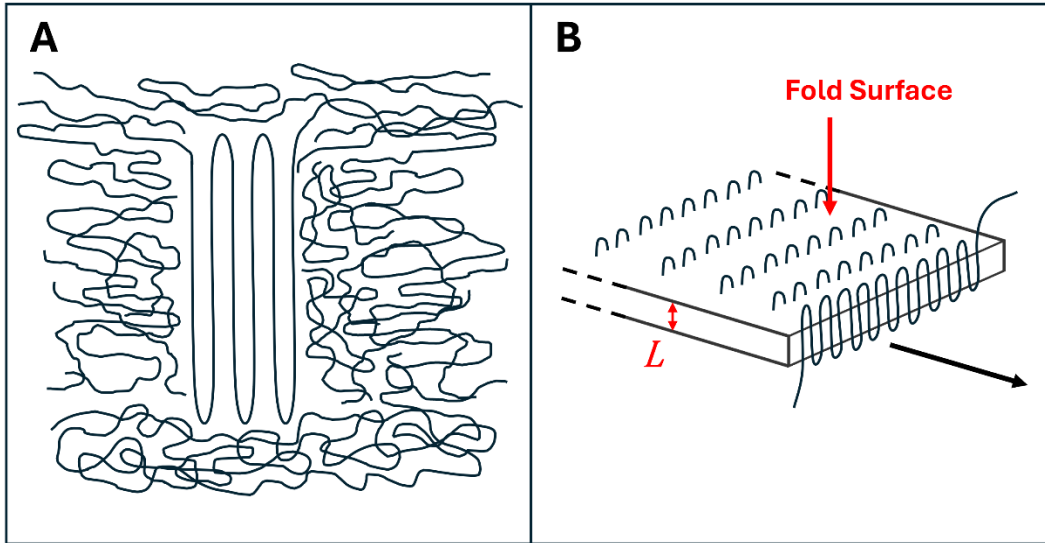


Figure 1.9: A) Folded chain nucleus (ordered polymer chains) in a pool of randomly oriented polymer chains (disordered/randomly oriented polymer chains); B) Crystalline lamella structure constructed by chain folding dynamics. The black arrow indicates the growth direction. L is the lamellar thickness.

Polymer crystals grow as crystalline lamellae. One such lamella is shown in Figure 1.9-B. The lamellar thickness L (see Figure 1.9-B), also known as the fold length, is an important parameter as it is a metric of how perfect the crystal is [10]. Lamellar thickness is inversely related to the supercooling (ΔT); when ΔT increases/decreases, L decreases/increases. Lamellar thickness can also be increased without changing orientation. It is also possible to thicken lamellae by changing the orientations of the chains. However, the temperature must be greater than the original crystallization temperature T_c . The thickening of lamellae is generally termed polymer crystal perfection [10].

A single crystal of a polymer can be obtained from its dilute solutions [11]. However, the crystals formed during the crystallization from the melt are far more complex. Many lamellae form these bulky crystals. As Keller *et al.* [12] describe these lamellae can branch via screw dislocation mechanisms and grow as more lamellae in a dendritic pattern. These bulky structures can be identifiable in polarized light microscopy due to the symmetrical aggregation of birefringent units [13]. Figure 1.10-A shows the PVDF α -phase spherulitic crystals as seen through a polarized light microscope. The birefringence in the crystalline structure shows the Maltese cross pattern. The growth of a spherulitic domain is limited by impingement into another domain. The crystalline lamellae are uniformly spread throughout the spherulite. The density of the crystalline structures is significantly high at the center of the spherulite. However, as they grow out, the space between the lamellae increases, and the amorphous structures fill in the space between lamellae (see Figure 1.10-B) [14].

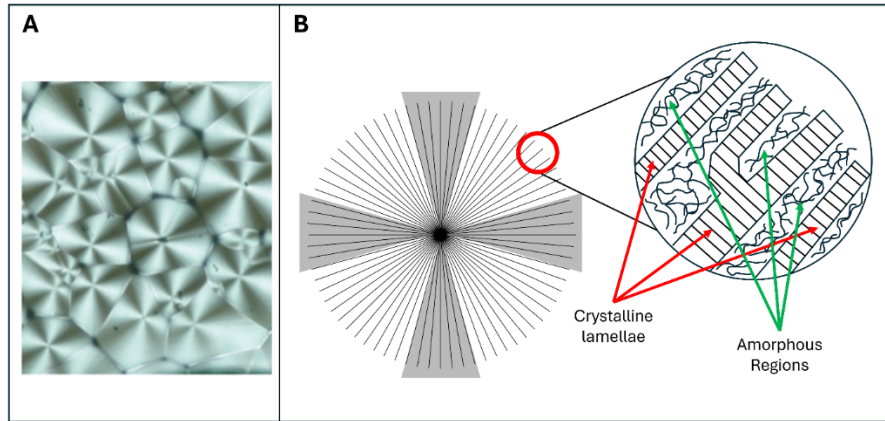


Figure 1.10: A) Spherulites of α -PVDF crystals observed through polarized light (analyzer $\perp$ polarizer) exhibiting the Maltese cross pattern. Figure adapted from [15]; B) Schematic of the spherulitic structure (left) with a zoomed-in view of the lamellae (right). The amorphous structures are located between the crystalline lamellae.

Due to various irregularities in its chains, a polymer will never achieve a 100% crystalline structure. These irregularities can result from chain branching, bulky side (pendant) groups, stereotypical conformations such as tacticity, and defects. Defects may occur either within the chain or at the ends. Two common types of defects in polymers are head-to-head and tail-to-tail defects (Figure 1.11). As a result, the maximum crystallinity a polymer can reach is about 70%. Typically, the degree of crystallinity in polymers ranges from 35% to 70%.

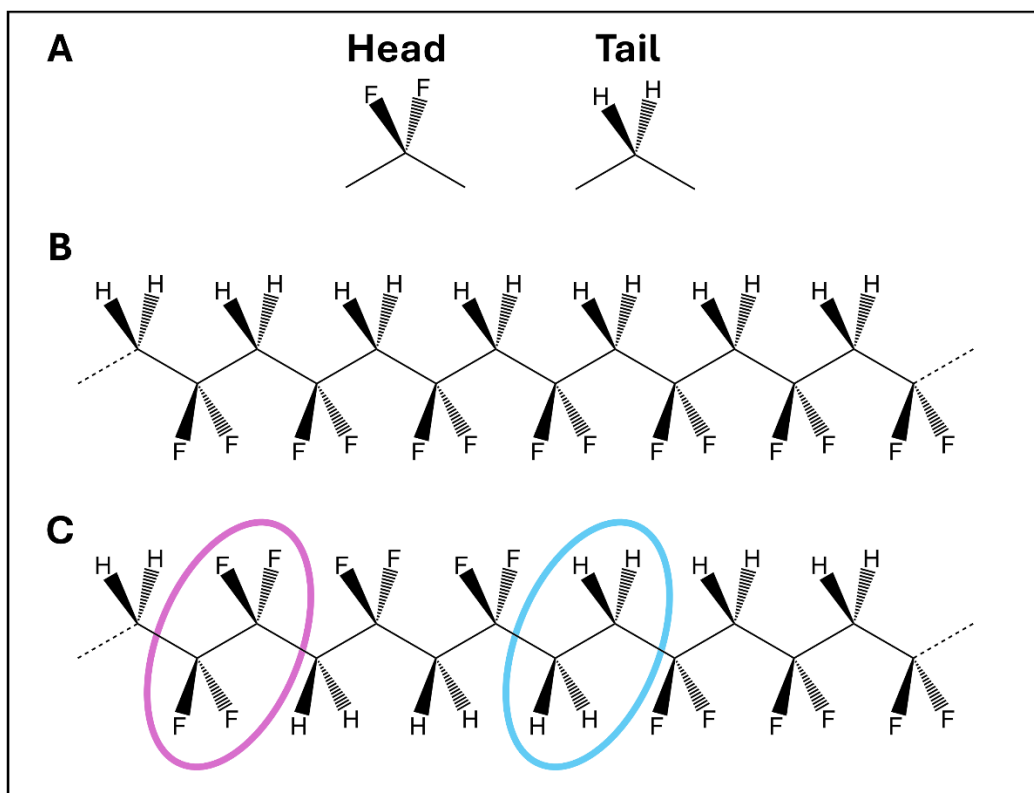


Figure 1.11: A) Head unit and the tail unit in PVDF; B) PVDF chain with no defects; C) PVDF chain with an H-H defect (circled in magenta) and a T-T defect (circled in cyan).

1.2 Poly (vinylidene fluoride)

Poly (vinylidene fluoride) (PVDF) is a commodity polymer manufactured by many companies worldwide by polymerizing vinylidene fluoride (shown in Figure 1.12) by free radicals generated through peroxide initiators using batch polymerization processes in aqueous emulsion or suspension [16].

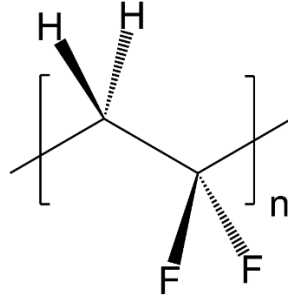


Figure 1.12: Vinylidene fluoride, the monomer unit of PVDF.

PVDF is a semi-crystalline polymer. In addition, it is one of the polymers that shows polymorphism. In other words, PVDF can crystallize into different crystallographic forms (namely, five). Among these five, three are quite common: alpha (α), beta (β), and gamma (γ) [17]. These three are referred to as phase II, phase I, and phase III, respectively, in many studies [18]. The α -phase crystals have TGT $\bar{G}$ chain conformation, where T stands for a trans bond, and G and $\bar{G}$ for gauche bonds. β -phase has the all-trans planar TTTT chain conformation [19], and the γ -phase's chain conformation is TTTGTTT $\bar{G}$ [20]. The chain conformations of all three phases are shown in Figure 1.13.

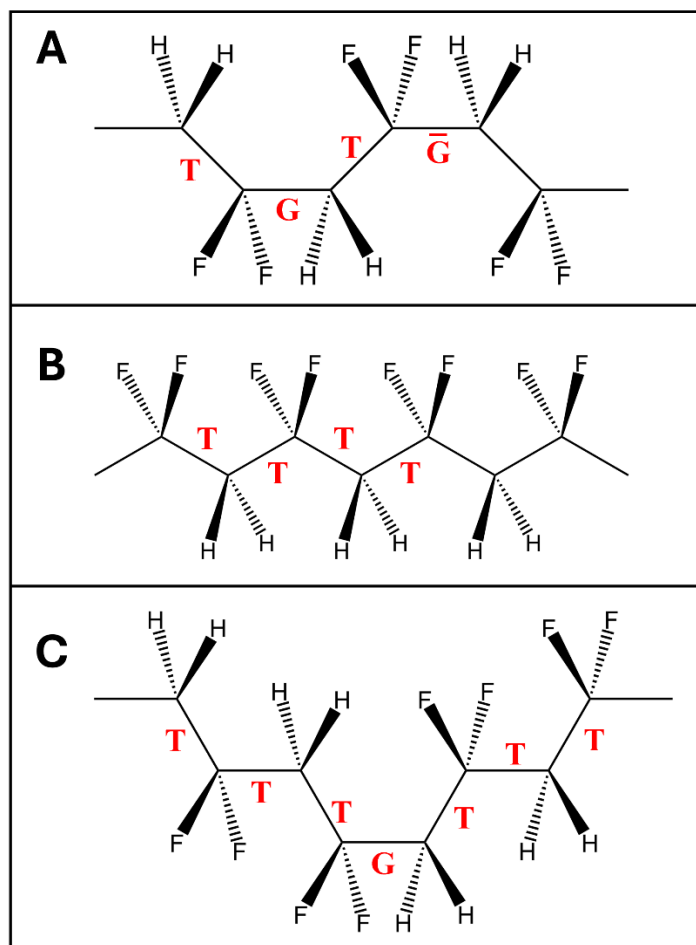


Figure 1.13: Chain conformations of A) α -phase; B) β -phase; C) γ -phase PVDF. The letters in red indicate the trans (T) and the gauche (G, $\bar{G}$) bonds.

The α -phase is the most thermodynamically stable crystalline morphology in PVDF [21]. Therefore, when PVDF crystallizes from the melt, it tends to form α -phase crystals [19]. Melt crystallized α -phase crystals form spherulites, as seen in Figure 1.10-A. The unit cell of the α crystal takes the orthorhombic form with $\mathbf{a} = 4.96 \text{ \AA}$, $\mathbf{b} = 9.64 \text{ \AA}$, and $\mathbf{c} = 4.62 \text{ \AA}$. The schematic of the α unit cell is shown in Figure 1.14 as seen from the $\mathbf{c}$ direction (chain growth direction). The α -phase chains show a non-zero dipole moment. However, the chain configuration in the unit cell

cancels out the dipole moments along the chain direction as well as the dipole moments perpendicular to the chain, as shown in Figure 1.14. Therefore, the α -phase crystal is non-polar[19].

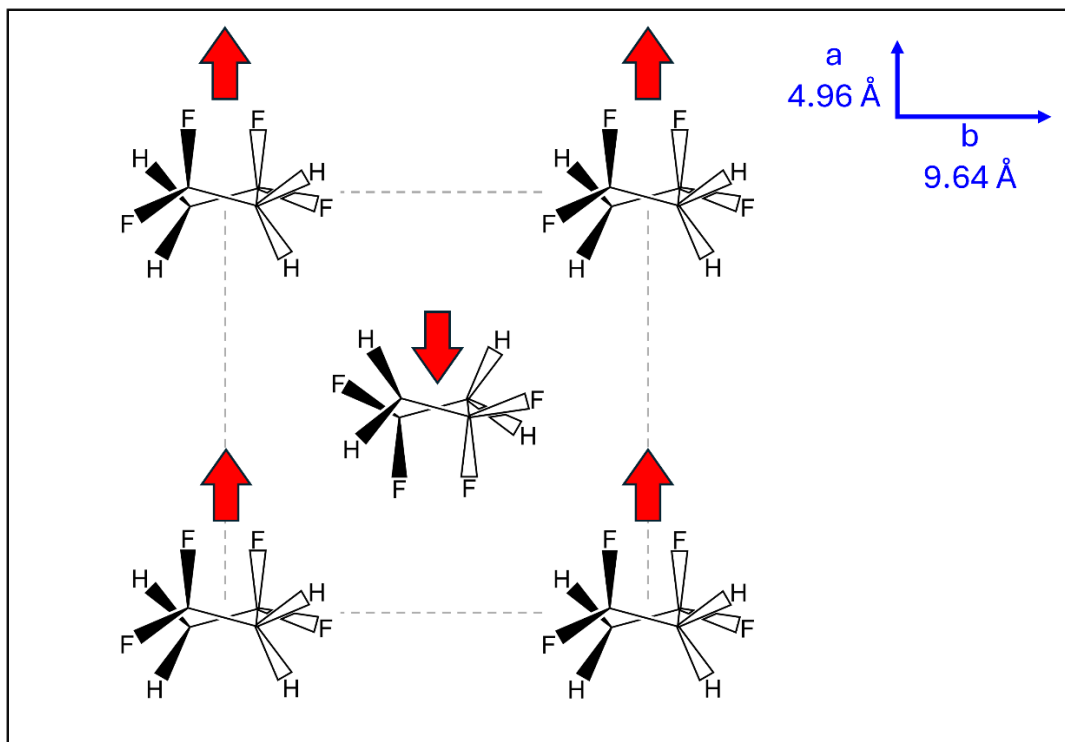


Figure 1.14: Unit cell of monoclinic PVDF α -phase crystal as seen from the c direction outlined in dashed grey lines. Carbon atoms are not indicated. a and b axes are shown by the blue arrows in the top right corner. Foreground bonds are shown by white blocks.

All-trans planar β -phase crystals have an orthorhombic unit cell with a , b , and c magnitudes of 8.58 Å, 4.91 Å, and 2.56 Å, respectively [19]. As shown in Figure 1.15, the β -phase unit cell shows strong non-zero dipole moments due to all F atoms on one side of the chain. Hence, the β -phase is the most essential crystalline form in PVDF, as it gives rise to strong piezoelectric and pyroelectric

properties [19, 22, 23]. The dipole moment in β -phase crystals is 7×10^{-28} Ccm and is essentially normal to the chain axis.

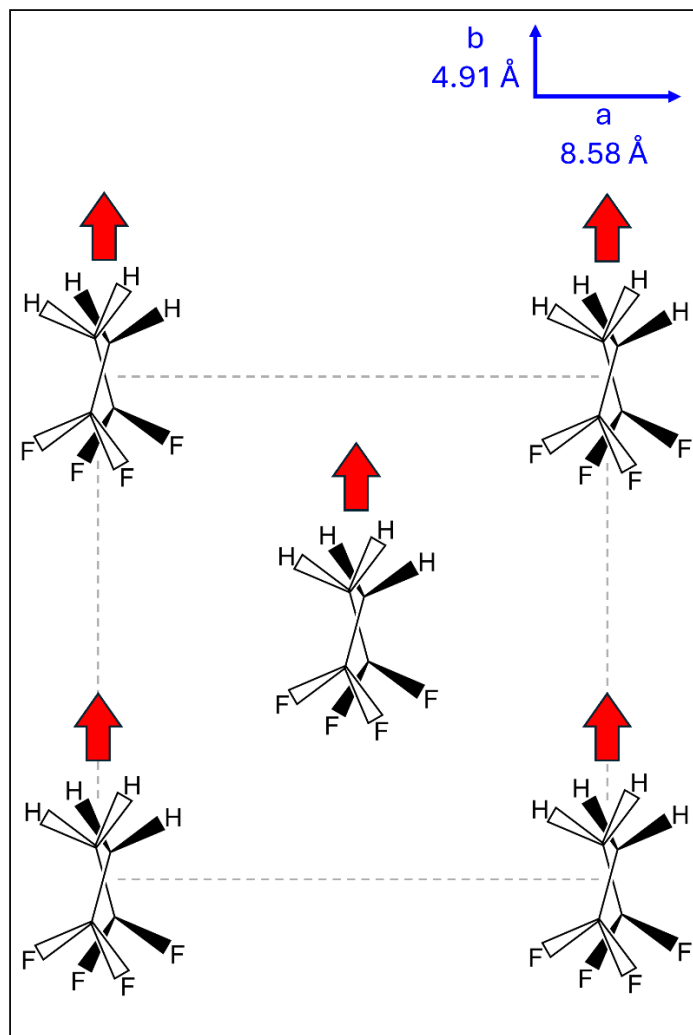


Figure 1.15: Unit cell of orthorhombic PVDF β -phase crystal as seen from the c direction outlined in dashed grey lines. Carbon atoms are not indicated. a and b axes are shown by the blue arrows in the top right corner. Foreground bonds are shown by white blocks.

The most efficient and common method to obtain β -phase crystals is by stretching PVDF films which were formed initially in the α -phase. In industry, this is done by roll-to-roll stretching at an

elevated temperature. During the drawing process, the α -phase spherulites undergo a necking behavior to form fibrillar β -phase crystals when the α_c relaxations, also known as crystalline segmental relaxations (not to be confused with the crystalline phase α), are activated [24]. The longitudinal sliding motion of the polymer chains in the crystalline lamellae is known as α_c relaxation [25]. The crystalline lamellae experience homogenous shearing, orienting the chains in the draw direction and tilt the lamellae fold surface toward the draw axis. The transformation to fibrillar form is initiated during the heterogenous shearing that takes place on the tilted lamellae at the yield point. The initial lamellae break into blocks of crystals that are rapidly oriented in the draw direction, resulting in β -phase crystals [24]. The schematic of the effect of the drawing process beyond α_c (*i.e.* α_c relaxations are active) is shown in Figure 1.16.

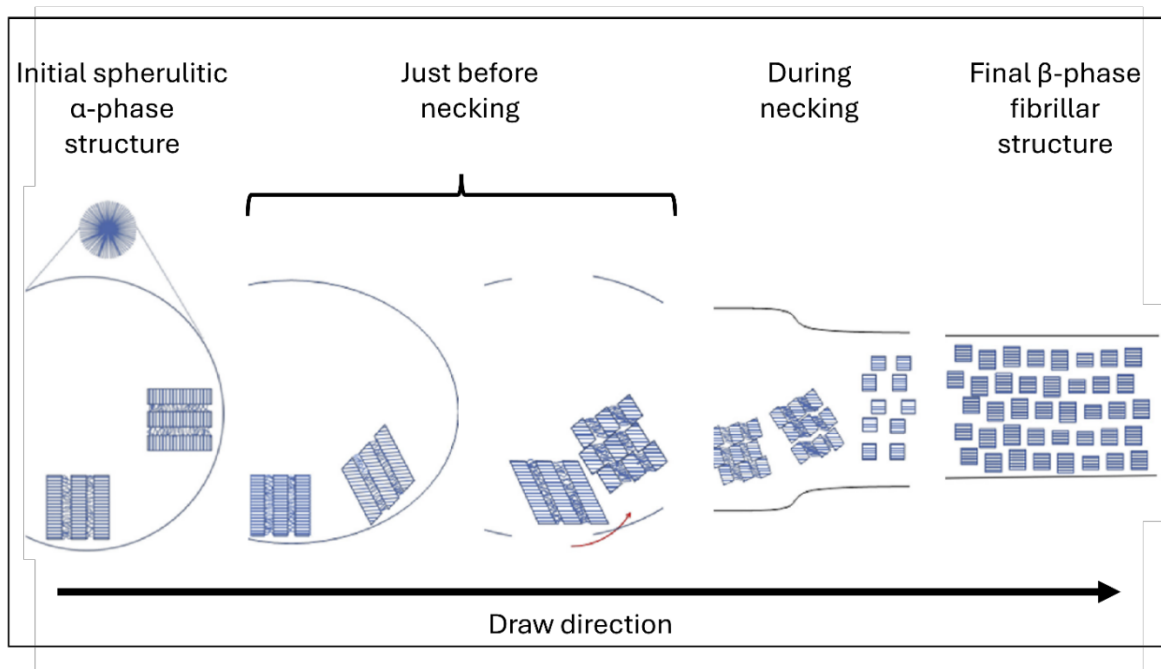


Figure 1.16: The reorganization of crystalline lamellae during the α -phase to β -phase transition of PVDF by uniaxial drawing when the α_c relaxations are activated. Figure adapted from [24].

Hence, increasing the β -phase fraction in PVDF is very important to harness its potential as a good piezoelectric material. There are other mechanisms to enhance the β -phase content in PVDF, such as copolymerization of vinylidene fluoride with trifluoro ethylene (TrFE) to obtain PVDF-co-TrFE [26], blending PVDF with nanoparticles such as organically modified silicate (clay) [27, 28], or carbon nanotubes (CNTs). However, electrospinning PVDF solutions have been proven to increase the β -phase fraction quite well in the past few years [17, 29-31]. A detailed theoretical outline of electrospinning is provided in section 2.7. In electrospinning, a very strong electric field parallel to the chain direction stretches the chains to form an all-trans planar β -phase. We hypothesize that either the nearly completely dry polymer jet experiences extensive tensional force, which reorients already formed crystals into fibrillar β -phase crystals, or a different type of nucleus, specifically an extended chain nucleus, initiates the nucleation process, resulting in a high fraction of β -phase crystals.

The γ -phase crystals have the TTTTGT $\bar{T}$ T $\bar{T}$ G chain conformation, which shows a strong dipole moment along the chain direction. Hence, it also shows a non-zero polarity, but not as strong as the β -phase. The unit cell of γ -phase (Figure 1.17) takes the monoclinic form with $\mathbf{a} = 4.98 \text{ \AA}$, $\mathbf{b} = 9.66 \text{ \AA}$, and $\mathbf{c} = 9.20 \text{ \AA}$ and $\beta = 93^\circ$. γ -phase also makes spherulites and can be transformed from α -phase at both higher and lower supercooling with the help of organically modified silicate [32, 33]. It is observed that PVDF crystallizes from solution into γ -phase when certain solvents such as dimethylformamide, dimethylacetamide, and dimethylsulfoxide are used [19].

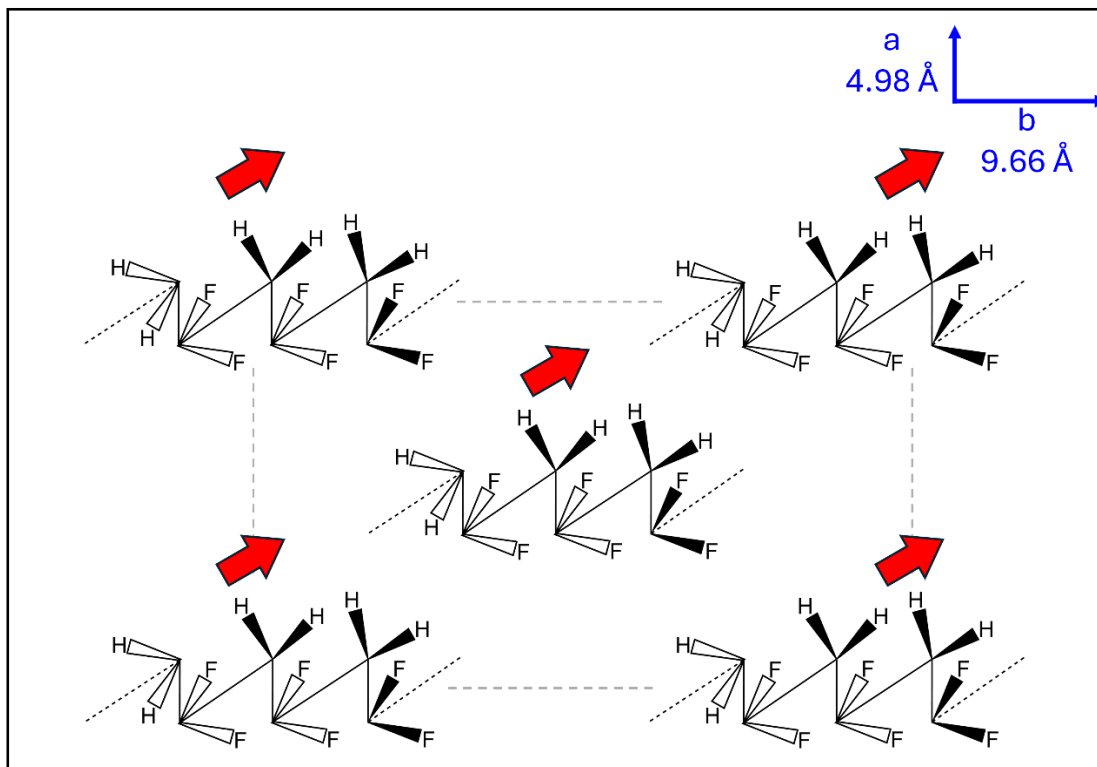


Figure 1.17: Unit cell of orthorhombic PVDF γ -phase crystal as seen from the c direction outlined in dashed grey lines. Carbon atoms are not indicated. a and b axes are shown by the blue arrows in the top right corner. Foreground bonds are shown by white blocks.

Therefore, increasing the polar crystal fractions in PVDF (preferably β -phase) and quantifying the relative fractions of PVDF crystal polymorphs is extremely important. All three morphologies can coexist [34], which makes quantifying the relative fractions of each crystal phase quite challenging. Few techniques quantify the degree of crystallinity of polymers, such as thermal analytical (differential scanning calorimetry) and structural analytical (wide-angle X-ray scattering and Fourier-transform infrared spectroscopy) methods. Providing good measures of the relative phase fractions, absolute crystallinity is the motivation for the study described in Chapter 4.

1.3 Membrane Filtration

Membranes play a significant role in modern times because they can selectively transport many substances through them. These substances could be chemical units, air molecules, liquid molecules, etc.; therefore, they are used in many filtration applications. For example, membranes serve as a drug-delivery mechanism that controls the drug's permeation rate through them, and in filtration (separation) applications like waste-water filtration and safety masks, membranes allow one component of a mixture to permeate through it freely while prohibiting the permeation of other components [35]. Membrane technology has come a long way from its initial use during the Second World War [35].

An isotropic membrane is one in which the transport rate of a species through the membrane is uniform. There are three types of filters such as 1) microporous, 2) non-porous, and 3) electrically charged [35]. Microporous and electrically charged membranes are important in this thesis; hence, no further discussion of non-porous membranes is provided [35].

Microporous membranes feature a highly voided structure with pores of varying sizes. These pores are randomly distributed and interconnected. The relative size of the species influences its transport through the membrane (see Figure 1.18). Transport is not allowed if a species is larger than the largest pore in the membrane. However, permeation is permitted but limited if the species is smaller than the largest pore but larger than the smallest pore. Permeation is allowed for species smaller than the membrane's smallest pore. These membranes are further categorized as microfiltration (MF), ultrafiltration (UF), and nanofiltration (NF) membranes [35]. Electrically

charged membranes are often microporous with even finer porosity. However, the membrane's surface and the pores' walls contain either positively charged or negatively charged entities or both [35]. These can bind the respective counter-ionic components in the species, restricting their flow through the membrane.

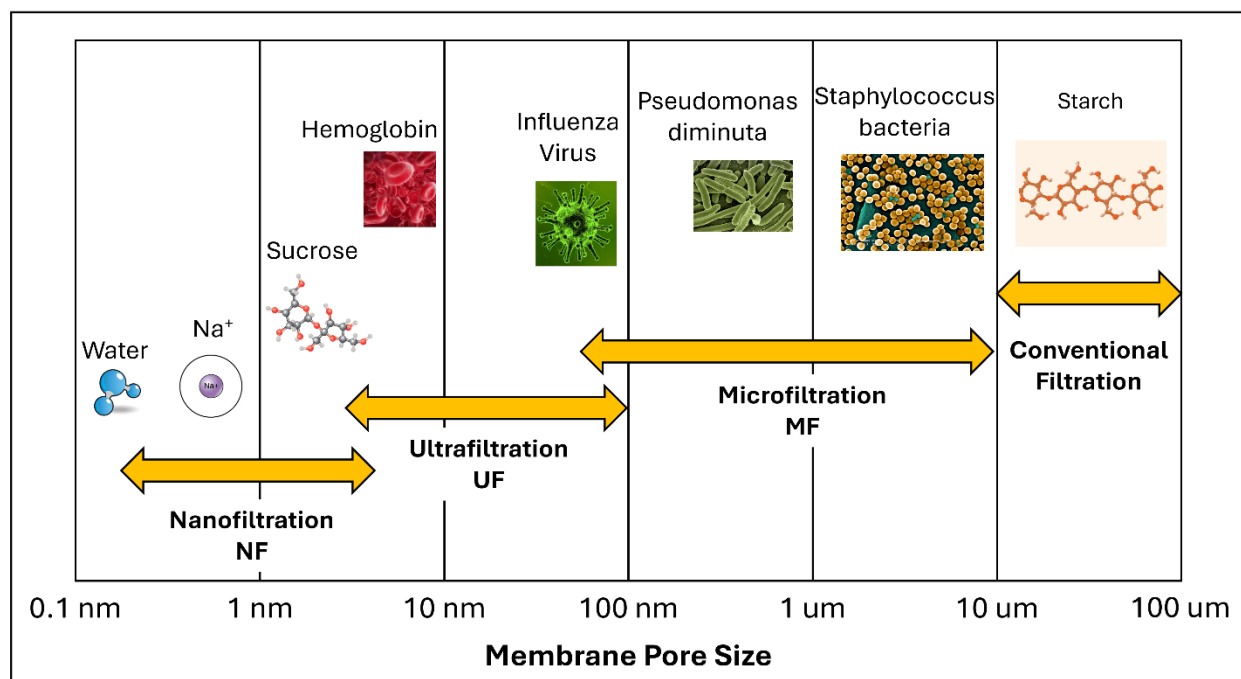


Figure 1.18: Permeation of molecules of different sizes through microporous membranes and the respective microporous membrane category. Figure adapted from [35].

Membranes can be manufactured from many materials such as ceramics, polymers and glasses, and metals. Out of all of them, polymeric membranes are very important because they are flexible, easily tunable, and cost efficient. There are many ways of fabricating polymeric membranes.

Phase separation methods have caught a lot of attention in membrane fabrication [36]. Non-solvent induced phase separation (NIPS) is the most common method of membrane making. NIPS is a

ternary method where three components are in play, polymer-solvent-nonsolvent. First, a polymer solution (a homopolymer or a blend of polymers) is cast over a mechanical substrate. Then the polymer cast substrate is immersed in a bath of a poor solvent (non-solvent) of the polymer. The non-solvent and the solvent must be miscible in this case. Therefore, the solvent is ejected out of the solution leaving the polymer to solidify in the non-solvent medium and the rapid ejection of the solvent leaves pores in the solidified membrane [36]. The other widely used phase separation method is called thermally induced phase separation (TIPS). In TIPS, the polymer is dissolved in a solvent that has a low molecular weight and a high boiling point at an elevated temperature. Then it is cast on a substrate and allowed to cool down in a controlled manner to induce phase separation to precipitate the polymer. The membrane is extracted via solvent extraction methods [37]. Our collaborators Mazzaferro *et al.* [38-40] prepared polyampholytic membranes using the NIPS method.

Electrospinning is also an efficient way to obtain microporous membranes [41-44]. Wide pore size variation in the electrospun fiber mats and the high surface area-to-volume ratio is extremely advantageous in filtration applications as it intensifies the surface properties of the membrane [45]. PVDF is a widely used polymer in membrane fabrication due to its inherent hydrophobicity due to the low surface energy and its excellent thermal, mechanical, and chemical stability [46]. It is a great material to fabricate membranes to filter out substances mixed with water as it does not readily interact with water. However, this is not favorable in the long run since water cannot then be used to clean the membranes made out of PVDF. This leads to membrane fouling and affects the durability of the PVDF membranes causing extensive operational costs [45].

The study described in Chapter 5 is motivated by addressing this timely issue. Hydrophobic PVDF and a hydrophilic polyampholyte (r-PAC) are blended together to obtain solutions and subsequently electrospun to fabricate fouling-resistant fibrous membranes. In Chapter 6, the properties of the r-PACs, such as degradation dynamics and their glass-forming ability (fragility), are discussed.

1.4 PVDF processing by green solvents

The previous sections highlighted two crucial applications of PVDF: its use in fabricating piezoelectric devices and hydrophobic filtration membranes. Additionally, PVDF is used in various other applications due to its outstanding thermal, mechanical, and chemical stability [47-49]. Therefore, the processing of PVDF is crucial, especially in electrospinning.

PVDF solutions are typically prepared for electrospinning by dissolving PVDF resin, whether in powder or pellet form, in a strong solvent. The solvents often used are N,N-dimethylacetamide (DMAc), N,N-dimethylformamide (DMF), and N-methyl pyrrolidone (NMP). These solvents are incredibly hazardous to the human body and to the environment. Exposure to these solvents through oral, dermal, and inhalation routes can harm the liver, digestive system, and reproductive system [50-52].

Therefore, exploring alternatives to the hazardous solvents mentioned above is important for PVDF processing. One such solvent is γ -valerolactone (GVL). It is derived from starch; therefore, it is biorenewable. It is soluble in water and possesses minimal risk in handling [53-55]. GVL can

dissolve PVDF effectively above a critical temperature [56]. However, as the solution cools below the critical temperature, it goes through a gradual thermoreversible gelation process. Although it is a gel at room temperature it can be reformed into a solution if heated above the critical temperature which is 60 °C [56]. This restricts its ability to be continuously electrospun, as the typical electrospinning process lacks temperature control to prevent the solution from making a gel. Figure 1.19 shows a PVDF 10 wt.% solution made with GVL. Figure 1.19-A shows the solution when it is at 100 °C. The solution is transparent hence it is a homogeneous solution. The solution is flowing at 100 °C. However, when it was taken out of heat and kept at 20 °C for 12 hours, it becomes a translucent gel which indicates that the solution is inhomogeneous, and phase separated. Furthermore, GVL is less volatile than DMAc, DMF, and NMP. Therefore, acquiring dry fibers on the collector plate during electrospinning is also difficult.

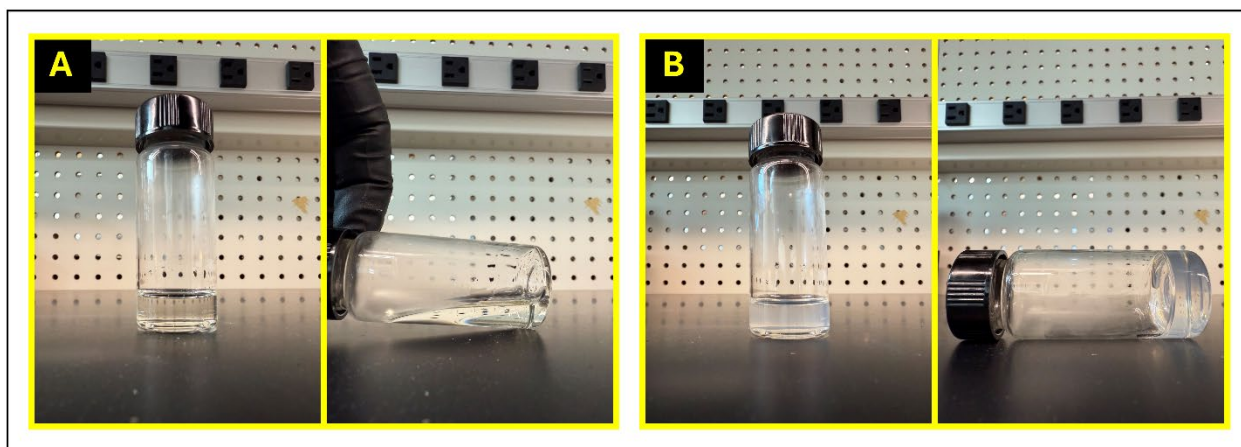


Figure 1.19: PVDF 10 wt.% solution in GVL. A) At 100 °C; B) After 12 hours at 20 °C.

These challenges motivate the study discussed in Chapter 7. The sol-to-gel transition information was verified by analyzing the rheological properties of the PVDF solutions prepared with GVL, including temperature and shear rate (frequency) effects on the solutions' flow properties. The best

flow parameters determined from rheological analysis were applied to electrospinning, and PVDF fibers were obtained successfully.

1.5 References

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Chapter 2: Theory

This chapter provides theoretical frameworks for all experimental work discussed in this thesis. First, the theory and techniques of Fourier-transform infrared spectroscopy will be examined, followed by wide-angle X-ray diffraction. Next, theory on thermal analytical work will be presented, including differential and fast scanning calorimetry, and thermogravimetric analysis. The rheological analysis will then be discussed in detail. Finally, a brief discussion of contact angle measurements and a section on polymer electrospinning will conclude this chapter.

2.1 Fourier-transform infrared spectroscopy (FTIR)

2.1.1 *FTIR basics*

FTIR is a great analytical tool for characterizing materials. It is a vibrational spectroscopic method that characterizes molecular vibrations in a sample when infrared light is shining upon it. In this case, the material can be treated as a collection of atoms in a molecule connected by springs acting as harmonic oscillators representing the chemical bonds. These bonds and the angles are not rigid; hence, they undergo deformation when a force or a torque is applied to them. Therefore, when the atoms are disturbed from their equilibrium position, they vibrate. These vibrations can be observed as a superposition of numerous vibrations in which all the molecules in the material vibrate harmonically at the same frequency, known as normal modes [1].

If a molecule has N number of atoms, then the total number of degrees of freedom that molecule has can be defined as $3N$. Three of these correspond to the translational motion of the center of mass along the three orthogonal axes Ox , Oy , and Oz (shown in Figure 2.1), and another three can be identified as the rotational motion around the same axes for a nonlinear molecule. The number of rotational degrees of freedom for a linear molecule becomes two, which is an exception. Therefore, the rest of the degrees of freedom are considered the molecule's vibrational modes. Hence, the total number of vibrational modes n_{vib} of a nonlinear molecule that has N number of atoms can be written as:

$$n_{vib} = 3N - 6 \quad (2.1)$$

For a linear molecule, n_{vib} becomes:

$$n_{\text{vib}} = 3N - 5 \quad (2.2)$$

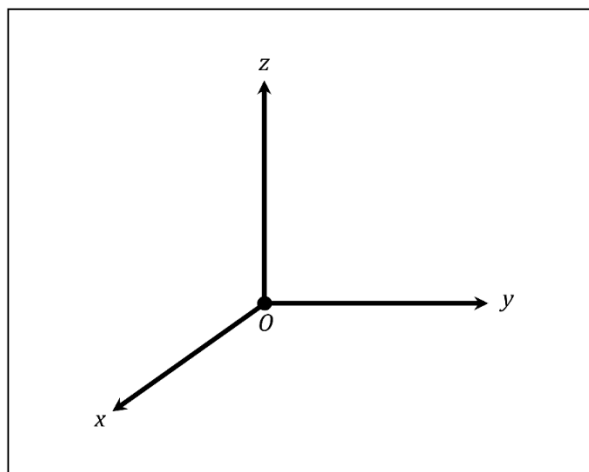


Figure 2.1: Axes representation for this section. Ox is perpendicular to the plane of the page (yz plane), Oy is horizontal in the yz plane, and Oz is vertical in the yz plane. The origin is the center of mass of the collection of atoms in the molecule.

Since these vibrations are considered approximately harmonic, the vibrational energy of each harmonic vibrational state can be given as:

$$V_n = h\nu_n \left(n + \frac{1}{2} \right) \quad (2.3)$$

Here n is the vibrational quantum number, h is Planck's constant, and ν_n is the frequency corresponding to the n^{th} vibrational mode. The energy difference for the transitions between the ground state ($n = 0$) and the first excited state ($n = 1$) typically falls within the 4000 cm^{-1} to 400 cm^{-1} range. In FTIR, the traditional unit for frequency, Hz, is dropped and instead the frequency is expressed in terms of wavenumber (ν), which is the number of waves in a centimeter.

Hence, the unit cm^{-1} is adapted for frequency. The equation is only valid for low values of n ($n = 0, 1$, and 2) because, at higher n values the anharmonicity of the vibrations becomes significant. For higher n values, Morse potential would be a better model to analyze the molecular vibrations [2].

As discussed in Chapter 1, a polymer molecule typically consists of around 100,000 monomer units, resulting in a total number of atoms that is approximately 600,000 (~six atoms per monomer unit). Thus, the number of vibrational modes in a polymer, as indicated by equation 1.1, is extremely large. However, an FTIR spectrum of a polymer typically shows a simple limited number of peaks corresponding to molecular vibrations. A homopolymer typically consists of chemically identical units containing 10 or fewer atoms, significantly reducing the complexity of FTIR spectra [1].

If a polymer has crystalline regions, only a few normal modes vibrate, so all repeating units in a molecule vibrate in phase. The other vibrational modes are standing-wave modes that are similar across all repeating units but vibrate in alternating phases that ultimately cancel out over the length of the chain. The molecule's symmetry significantly influences this property. Based on the molecule's symmetry, two or more normal modes may share the same frequency. These normal modes are referred to as degenerate modes [1].

In a non-degenerate mode, all atoms in a molecule move through their equilibrium positions at the same time. When a symmetry operation is performed on a molecule during one of its non-

degenerate vibrations while its atoms are displaced from their equilibrium positions, the new vibration must be identical to the initial one. However, its phase may change by π radians. In other words, even though the vibrational energy or the frequency of vibration does not change when a symmetry operation is applied, its phase may either remain unchanged or change by π , making the vibration either symmetric with the initial one or antisymmetric, respectively. Therefore, the atomic displacements of a non-degenerate mode must be symmetric or antisymmetric, depending on the symmetry operation. Thus, it is evident that the symmetry of a molecule restricts many vibrational modes, decreasing the intricacy of FTIR spectra [1]. For example, the water molecule's symmetric stretching vibration is symmetric under a 180° rotation (C_2 symmetry operation) around the Oz axis, while the asymmetric stretching vibration is asymmetric under the same symmetry operation as shown in Figure 2.2.

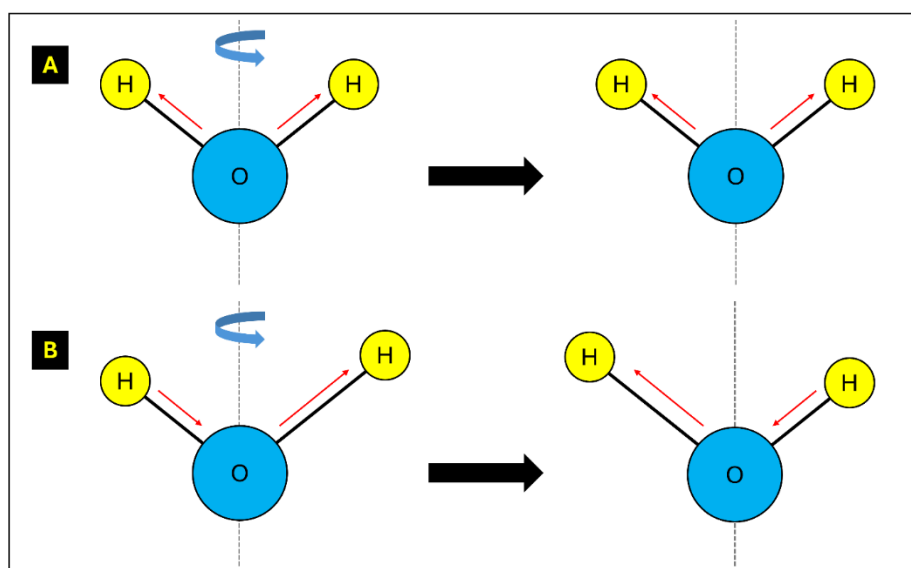


Figure 2.2: A) Symmetric stretching vibration of the water molecule; B) Asymmetric stretching vibration of the water molecule. The C_2 rotational symmetry around the Oz axis is indicated by the

turning arrow on the diagrams on the left. The molecule after the symmetry operation is shown on the right.

The polymer's amorphous (non-crystalline) regions do not show any molecular symmetry. Even though the chemical repeat units are not geometric physical repeat units, the coupling forces are no longer the same. In a case like this, the side group vibrations are more dominant than the backbone vibrations. Broad peaks in the FTIR spectrum can be observed due to the group vibrations that occur in the same mode but at different frequencies due to the different physical environments in which each unit is located [1].

All atoms in a molecule carry some effective charge such that a sinusoidal electric field can create a periodic distortion in the molecule, called a vibration. In the classical picture, if the frequency of the electric field is matched up with the frequency of the vibrational mode, the molecule will vibrate at its maximum amplitude due to resonance. Yet, not every mode can take in energy to vibrate in this way. A mode can only absorb energy from infrared radiation if it is polarized parallel to an axis (Ox, Oy, or Oz), where the mode belongs to a symmetry species with a translation parallel to the same axis. This is called the selection rule for infrared absorption [1].

The Beer-Lambert law quantifies the absorption of the material's infrared radiation. If the transmittance of radiation of a frequency ν through a material is defined as $T(\nu)$, then

$$T(\nu) = \frac{I}{I_0} = \exp[\alpha(\nu) \times b] \quad (2.4)$$

Here I_0 is the intensity of the incident radiation on the front face of a sample, and I is the intensity of the transmitted radiation from the back face of the sample (see Figure 2.3)

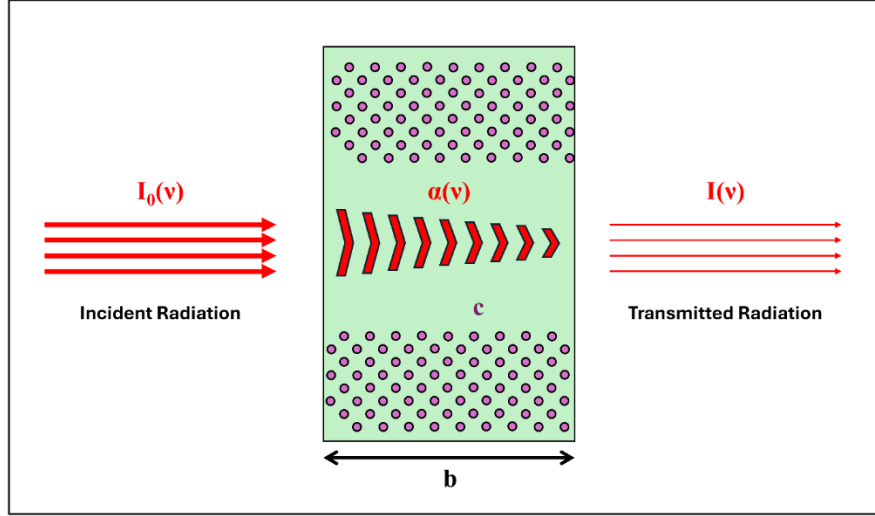


Figure 2.3: A sample of thickness b and concentration of the absorbing species c with an incident IR radiation intensity of $I_0(\nu)$ and transmitted radiation $I(\nu)$. The green block shows the sample, where its linear absorption coefficient is given by $\alpha(\nu)$.

Then, the absorbance in the material is given by the base 10 logarithm of $T(\nu)^{-1}$

$$A(\nu) = \log_{10} \left(\frac{1}{T(\nu)} \right) \quad (2.5A)$$

$$A(\nu) = \frac{1}{\ln 10} \times \alpha(\nu) \times b \quad (2.5B)$$

Here, the quantity $\alpha(\nu)/\ln 10$ is defined as the material's absorptivity for radiation of frequency ν , $a(\nu)$. A sample of absorbing component concentration c can be written as:

$$A(\nu) = a(\nu) \times b \times c \quad (2.5C)$$

This is the Beer-Lambert law [3]. From equation 2.5C, The absorption of radiation in a material depends on the absorptivity, the path length, and the concentration of the absorbing species. Thus, absorption spectra are significantly more effective than the transmittance spectra for quantitative analyses of samples.

2.1.2 The role of the interferometer in FTIR spectrometer

FTIR spectrometers gather data as interferograms and convert them into spectra using Fourier transformation, which is the FT in FTIR. Therefore, the component that records interferograms, the interferometer, plays a significant role in FTIR. As the name suggests, the interferometer measures the interference between two rays. Most modern FTIR spectrometers are equipped with interferometers similar to Michelson interferometers. A Michelson interferometer typically consists of four main components: a radiation source, a beam splitter, a movable mirror, and a fixed mirror. A schematic diagram of a Michelson interferometer is shown in Figure 2.4-A. The positions of the fixed and movable mirrors are indicated by the letters F and M, respectively. The letter O indicates the point where the radiation from the source strikes the beam splitter [2].

For a monochromatic IR source, the wavenumber ν_0 can be defined as:

$$\nu_0 = \frac{1}{\lambda_0} \quad (2.6)$$

Then, the intensity of the IR source can be defined as $I(\nu_0)$.

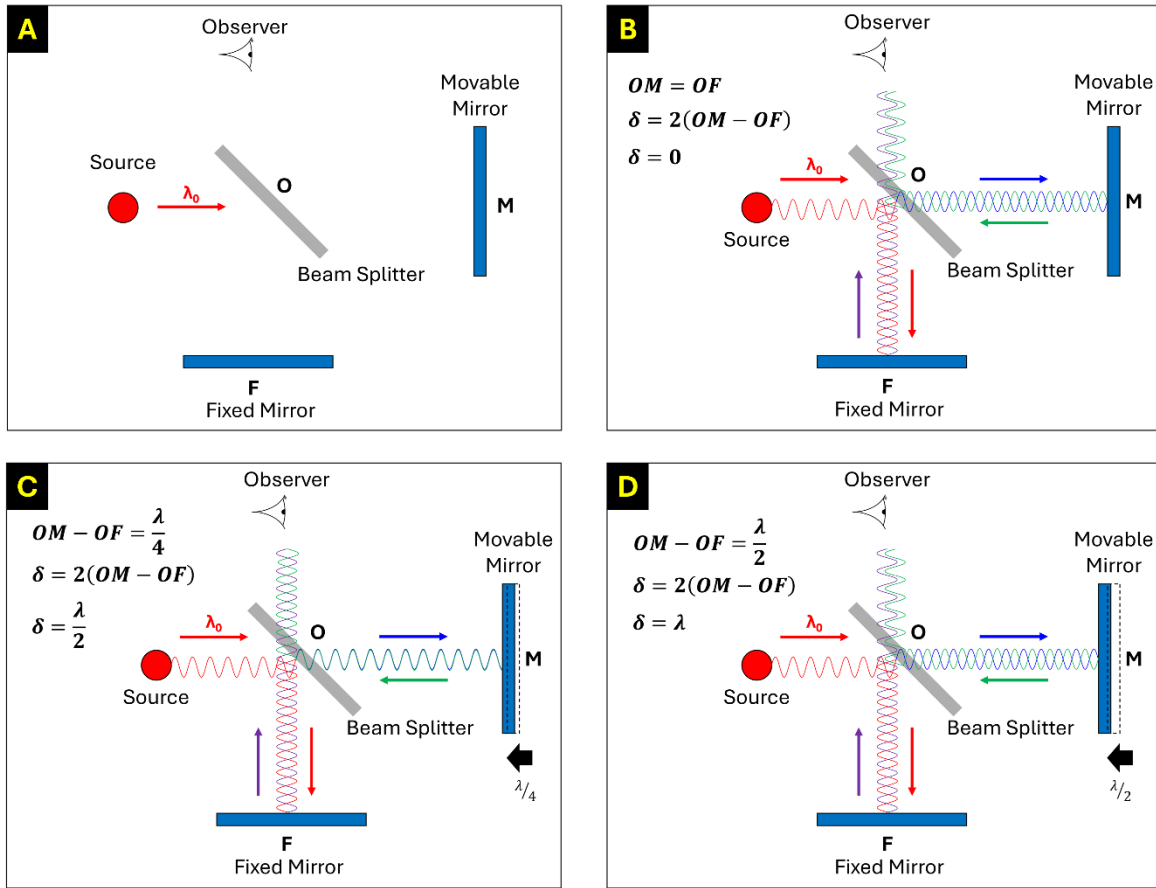


Figure 2.4: A) Schematic diagram of a Michelson interferometer; B) Zero path difference where $OM = OF$ where $\delta = 2(OM - OF) = 0$. δ is the optical path difference. Observer sees constructive interference; C) When the movable mirror is shifted by $\lambda/4$, $\delta = 2(OM - OF) = \lambda/2$. The observer sees destructive interference; D) When the movable mirror is shifted $\lambda/2$, $\delta = 2(OM - OF) = \lambda$. The observer sees constructive interference again.

When the source is turned on, the radiation is incident on the beam splitter at point O (red wave from the source to O), and a fraction of it is reflected toward the fixed mirror F (red wave from O to F) while the other fraction is transmitted through the beam splitter and travels toward the

movable mirror M (blue wave from O to M). These rays undergo a π phase change as they get reflected from the mirrors and travel toward point O (the purple ray from F to O and the green ray from M to O) [2]. The ray that travels to the fixed mirror completes a distance of $2 \times OF$; similarly, the one that travels to the movable mirror completes a $2 \times OM$ distance. Then, the optical path difference between the two rays (δ) can be defined as:

$$\delta = 2(OM - OF) \quad (2.7)$$

When $OM = OF$, $\delta = 0$. This is called the zero path difference. In this case, the observer sees constructive interference between the two rays reflected back from the mirrors Figure 2.4-B. When the movable mirror is shifted a distance of $\lambda_0/4$ from this position, then

$$OM - OF = \frac{\lambda_0}{4} \quad (2.8)$$

making $\delta = \lambda_0/2$. The observer will then see destructive interference between the two reflected rays from the mirrors, as seen in Figure 2.4-C. Thus, if M is moved at a constant velocity, the observer will see a sinusoidal variation of the intensity in which a maximum will be observed when $\delta = n\lambda$ and a minimum when $\delta = (2n+1) \lambda/2$ where n is an integer ($n = 0, 1, 2, \dots$). Therefore, the observed intensity $I'(\delta)$ is given by:

$$I'(\delta) = A \times I(\nu_0) \times (1 + \cos(2\pi\nu\delta)) \quad (2.9)$$

Where A is related to the efficiency of the beam splitter. In an ideal beam splitter $A = 0.5$. The modulated part of equation 2.9 is the important component in spectroscopic analyses (given in equation 2.10) and it is generally referred to as the interferogram $I(\delta)$ [2].

$$I(\delta) = A \times I(\nu_0) \times \cos(2\pi\nu\delta) \quad (2.10)$$

The $I(\delta)$ function can be modified with the correction factors from the amplifiers and detector sensitivity. These factors coupled with A and $I(\nu_0)$ in equation 2.10, $I(\delta)$ can be written as:

$$I(\delta) = E(\nu_0) \times \cos(2\pi\nu\delta) \quad (2.11)$$

$I(\delta)$ is the cosine Fourier transform of $E(\nu_0)$. The spectrum in an FTIR spectrometer is generated by the cosine Fourier transformation of the interferogram. The interferogram produced by a monochromatic source is simply a cosine wave with the same intensity at every maximum, making it indistinguishable from the zero path difference maximum. Hence, polychromatic IR radiation is used in FTIR spectrometers as it is advantageous in spectrometry [2]. The cosine wave functions of two narrow spectral lines that have slightly different frequencies and their interferogram are shown in Figure 2.5-A,B.

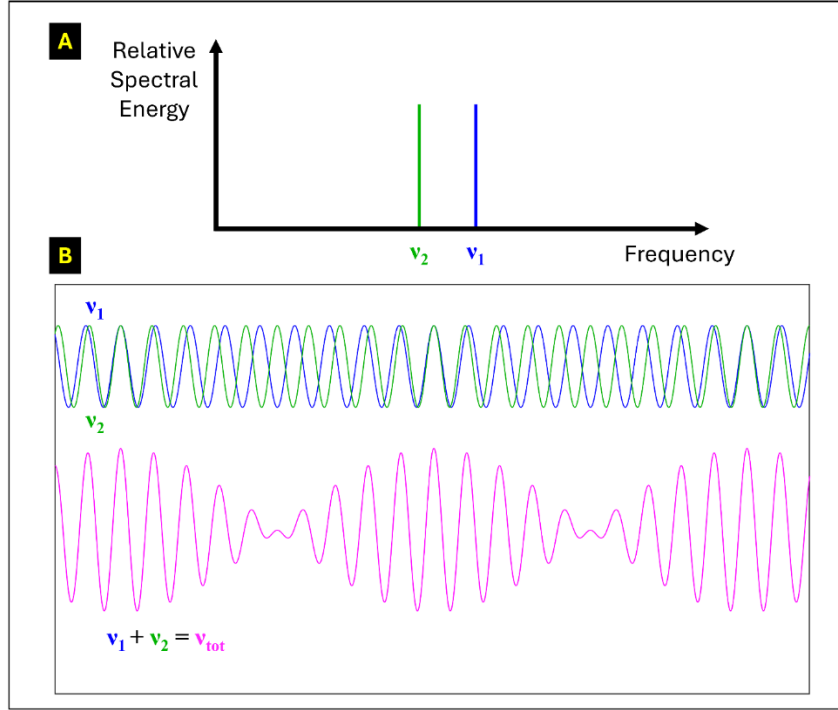


Figure 2.5: A) Two narrow spectral lines with equal intensity where $\Delta\nu = |\nu_1 - \nu_2| = 0.1$. B) The cosine waves of the two lines (blue ν_1 and green ν_2) and their interferogram (magenta ν_{tot}) are shown. Figure adapted from [2].

Therefore, $I(\delta)$ can be shown as an integral for a polychromatic source.

$$I(\delta) = \int_{-\infty}^{\infty} E(\nu) \times \cos(2\pi\nu\delta) d\nu \quad (2.12)$$

Then, by taking the Fourier transform of this signal (interferogram), the spectrum $E(\nu)$ is given by:

$$E(\nu) = \int_{-\infty}^{\infty} I(\delta) \cos(2\pi\nu\delta) d\delta \quad (2.13)$$

2.1.3 *Peak broadening in FTIR spectra*

If the interferogram depicted in Figure 2.5 (wave shown in magenta) is Fourier transformed to obtain its spectrum, it should resemble the top diagram in Figure 2.5 with narrow spectral lines. However, in reality, the spectra do not resemble sharp, narrow peaks; instead, they appear as peaks with some width. This is called spectral peak broadening. Peak broadening is caused by the spectrometer's (or interferometer's) finite resolution and the material's properties (homogeneous and inhomogeneous broadening). The latter significantly affects peak broadening, ultimately impacting the quantitative spectra analysis. Both mechanisms will be discussed in detail in the following subsections.

2.1.3.1 *Peak broadening due to the finite resolution of the instrument*

Consider the interferogram and the cosine wave functions shown in Figure 2.5-B. An enlarged image of a selected range is shown in Figure 2.6.

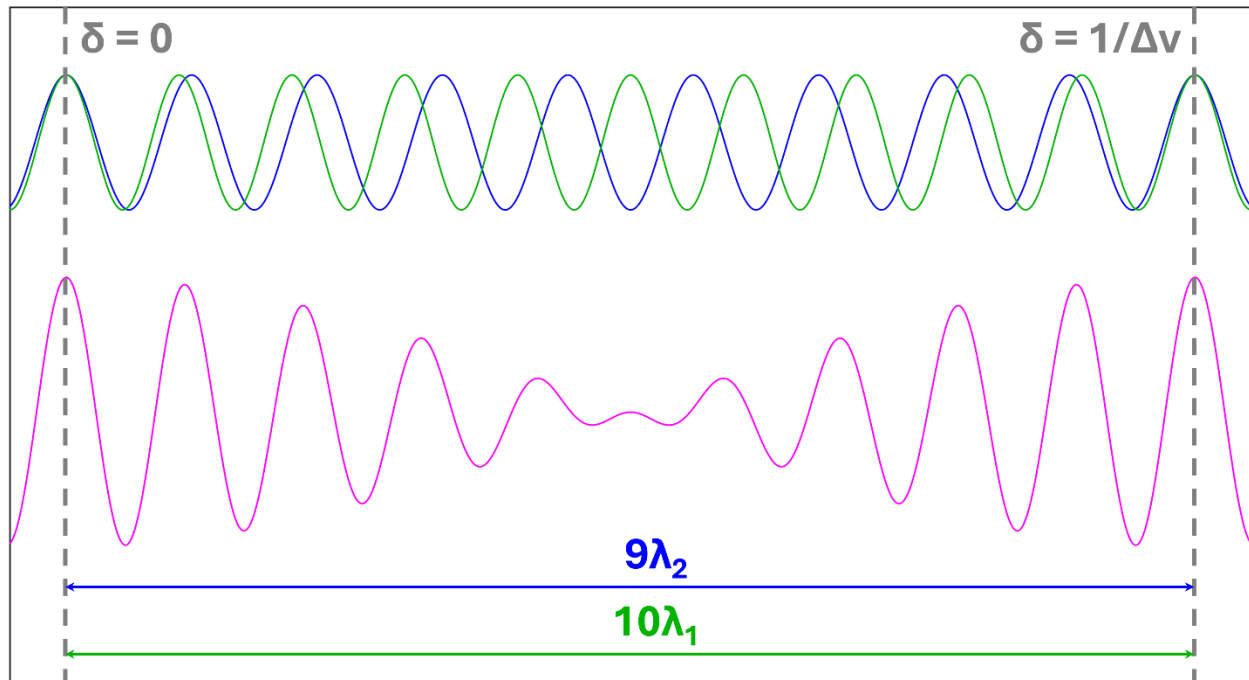


Figure 2.6: An enlarged image of Figure 2.5-B, where the optical path difference δ changes from 0 (zero path difference) to the first δ maximum. Figure adapted from [2].

The difference in wavenumber of the two cosine waves is $\Delta\nu = |\nu_1 - \nu_2| = 0.1\nu_1$. They go out of phase at the halfway point, specifically $\delta = 0.5 \times (1/\Delta\nu)$, and become in phase after $\delta = 1/\Delta\nu$. Therefore, to span through one period of the beat frequency, at least δ should be equal to $\delta = 1/\Delta\nu$. Any δ value less than that could not resolve the two spectral lines in Figure 2.5-A. Thus, it is evident that instrument resolution is constrained by the maximum δ – value permitted by the instrument. To resolve the two spectral lines, the δ – value must be at least shifted to the point where the two cosine wave functions become in phase for the first time ($\delta = 1/\Delta\nu$) after the zero path difference (ZPD) ($\delta = 0$) as shown in Figure 2.6. Thus, if the maximum δ value permitted by the instrument is $\delta_{\max}$, then the maximum wavenumber resolution attainable by the instrument is given by

$$\Delta\nu = \frac{1}{\delta_{max}} \quad (2.14)$$

This restriction of δ to δ_{max} is usually applied to the $E(\nu)$ (spectrum function – equation 2.13) by an apodization function $D(\delta)$. The apodization function either takes the form of a box car function or a triangular function [2], as given below:

Box car apodization function:

$$D(\delta) = \begin{cases} 1 & -\delta_{max} < \delta < +\delta_{max} \\ 0 & \delta < |\delta_{max}| \end{cases} \quad (2.15)$$

Triangular apodization function:

$$D(\delta) = \begin{cases} 1 - \frac{\delta}{\delta_{max}} & -\delta_{max} < \delta < +\delta_{max} \\ 0 & \delta < |\delta_{max}| \end{cases} \quad (2.16)$$

Then equation 2.13 can be rewritten considering the instrument limits as,

$$E(\nu) = \int_{-\infty}^{\infty} I(\delta) \cos(2\pi\nu\delta) d\delta \times D(\delta) \quad (2.17)$$

2.1.3.2 Spectral line shape variation due to homogeneous and inhomogeneous broadening

From the previous sections, it is clear that the interferograms of the IR radiation with continuous frequencies are Fourier-transformed to obtain the absorption spectra of a sample. The vibrational modes are excited by absorbing the incoming radiation which has a frequency ($\omega_{0 \rightarrow 1}$) matching the energy gap between the two states (typically the ground state E_0 and the excited state E_1).

$$\omega_{0 \rightarrow 1} = \frac{E_1 - E_0}{\hbar} \quad (2.18)$$

The ground state and the excited state can exist together as a superposition. If the phase difference between the two states is well-defined, then the two states are said to be coherent. The phase coherence decays with time due to the molecule's interactions with its surrounding environment. This is called dephasing [4, 5].

If the surrounding environment is viewed as a bath, one can assume that the bath is in thermal equilibrium with the molecule and that the interaction between them is weak. This is known as the Markovian approximation. Typically, the interactions between the bath and the molecule manifest in the form of hydrogen bonding, other dipole-dipole interactions, or long-range Coulomb forces. Thermal fluctuations in the bath induce perturbations ($\delta\omega(t)$) in the transition frequency ($\omega_{0\rightarrow 1}(t)$), which are time-dependent [4].

$$\omega_{0\rightarrow 1}(t) = \omega(t) = \omega_0 + \delta\omega(t) \quad (2.19)$$

Here, ω_0 is the time-averaged frequency. Then, the variance of the frequency of thermal fluctuations ($\Delta\omega$) and a correlation time (τ_c) can be defined as [4]:

$$\Delta\omega = \sqrt{\langle\delta\omega^2\rangle} \quad (2.20)$$

$$\tau_c = \frac{1}{(\Delta\omega^2)} \int_0^\infty \langle\delta\omega(t)\delta\omega(0)\rangle dt \quad (2.21)$$

The product of these quantities ($\Delta\omega\tau_c$) is the modulation that describes the correlation between the transitions. When $\Delta\omega\tau_c \ll 1$, known as the rapid modulation limit, the interactions between the molecule and its surroundings decay exponentially, resulting in homogeneous broadening. It can be shown that the line shape is, in fact, a Lorentzian function when the rapid modulation limit is

applicable [4, 5]. In addition to dephasing, homogeneous broadening is caused due to the finite lifetime of the transitions [6] particularly in gases.

Inhomogeneous broadening occurs when the slow modulation limit holds. That is $\Delta\omega\tau_c \gg 1$. This results in a Gaussian line shape function [4]. However, according to Oxtoby [5], a truer kind of inhomogeneous broadening occurs when the energy exchange between definite types of molecules, such as different lattice sites in a crystal, is slow compared to the time scale of the experiment. This inhomogeneous broadening is a convolution of many Lorentzian (homogeneous) line shapes rather than a Gaussian line shape function. The Doppler effect is also another cause for inhomogeneous broadening [6].

Therefore, the spectral function $E(\nu)$ (equation 2.17) can be modified to include the homogeneous and inhomogeneous broadening function $L(\delta)$:

$$E(\nu) = \int_{-\infty}^{\infty} I(\delta) \cos(2\pi\nu\delta) d\delta \times L(\delta) \times D(\delta) \quad (2.22)$$

2.1.4 Fourier self-deconvolution (FSD)

Due to the $L(\delta)$ and the $D(\delta)$ functions in equation 2.22, the spectrum of absorbed IR bands will not consist of intense spectral lines. Instead, it will consist of peaks of some width. This is the result obtained from the FTIR spectrometer as the output. Equation 2.22 can be written as a convolution of a line shape function $L(\nu)$ due to homogeneous and inhomogeneous broadening

and a spectrum function $E'(v)$. The spectrum function $E'(v)$ contains the cosine wave function and the apodization function on the right-hand side of the equation 2.22 [7], and $E(v)$ is rewritten as:

$$E(v) = L(v) \otimes E'(v) \quad (2.23)$$

Here $\otimes$ is the convolution operator. Then, by taking the inverse Fourier transformation ($\mathcal{F}^{-1}$) of the equation 2.23, the interferogram $I(\delta)$ can be obtained. $I(\delta)$ here is the same interferogram given by equation 2.12.

$$I(\delta) = \mathcal{F}^{-1}\{L(v)\} \times \mathcal{F}^{-1}\{E'(v)\} = \mathcal{F}^{-1}\{L(v)\} \times I'(\delta) \quad (2.24)$$

$I'(\delta)$ is the interferogram corresponding to the deconvoluted spectrum, or:

$$I'(\delta) = \frac{1}{\mathcal{F}^{-1}\{L(v)\}} \times I(\delta) \quad (2.25)$$

The deconvoluted spectrum can be obtained by Fourier transforming ($\mathcal{F}$) equation 2.25 to yield:

$$E'(v) = \mathcal{F}(I'(\delta)) = \mathcal{F}\left(\frac{1}{\mathcal{F}^{-1}\{L(v)\}} \times I(\delta)\right) \quad (2.26)$$

It can be seen from equation 2.25 that the interferogram corresponding to the deconvoluted spectrum is obtained by removing the effects from homogeneous and inhomogeneous broadening by dividing the interferogram corresponding to the observed experimental spectrum by its own line shape function $\mathcal{F}^{-1}(L(v))$. Hence, this method takes the name Fourier self-deconvolution [8]. Figure 2.7 shows the FTIR absorbance spectrum of an electrospun PVDF fiber sample, an enlarged region where the electroactive (EA) peak (840 cm^{-1}) is located, and the Fourier self-deconvoluted version of the same peak. The resolution of the EA peak is enhanced quite well by FSD. The instrumental line shape is still present in the deconvoluted spectrum, as shown in equation 2.26

and Figure 2.7-C. Then, the deconvoluted spectrum is curve-fitted using Voigt functions (a mix of Gaussian and Lorentzian functions) to analyze spectra quantitatively [9]. This method is different from curve fitting the experimental spectrum using either Gaussian, Lorentzian, or Voigtian functions because, by Fourier self-deconvolution, the spectra are synthetically narrowed down to improve resolution [10].

2.1.5 Post-processing of spectra

Manipulation of experimental IR absorption spectra before analysis is called post-processing. Post-processing is quite important in obtaining valuable information from the raw experimental spectra. The key reasons for post-processing are to enhance the appearance of the spectra and extract more information from them. A couple of very common post-processing techniques are baseline correction and spectra normalization. Baseline correction must be performed to obtain flat baselines for spectra with sloped or curved baselines caused by scattering, inappropriate background choice, and instrumental drift [11].

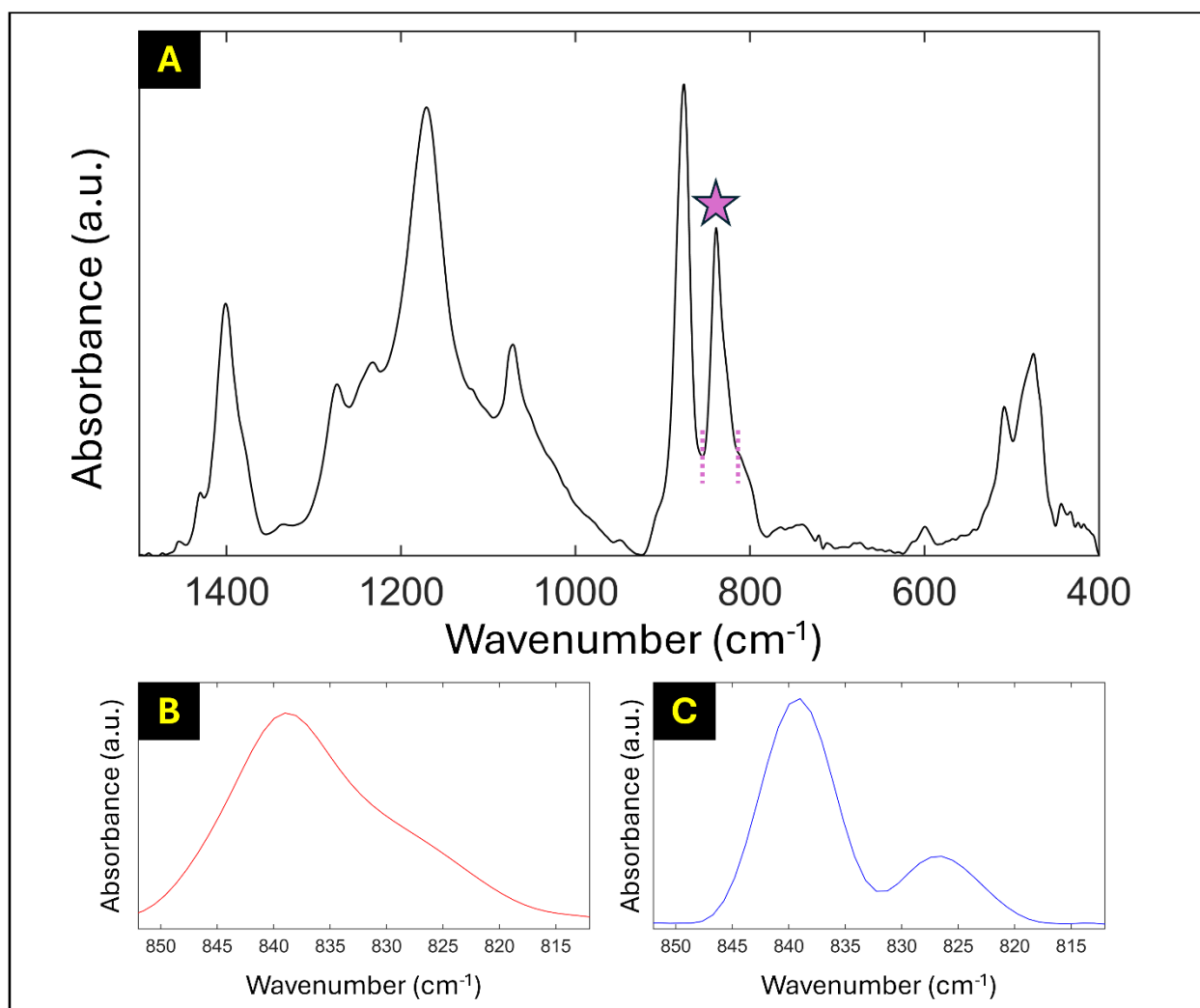


Figure 2.7: A) FTIR absorbance spectrum of PVDF electrospun fibers. The electroactive (EA) peak at 840 cm⁻¹ is indicated by the magenta star and the peak boundaries are indicated by the dashed lines; B) an enlarged view of the EA peak in the original spectrum; C) Fourier self-deconvoluted spectrum of the EA peak with enhanced resolution.

Normalization in FTIR spectroscopy is a crucial step in post-processing. The spectra are adjusted to a common scale, allowing for better comparisons between different sampling conditions of the same sample and across different samples [12]. It is quite common to normalize spectra using a

specific peak. The selection of this peak is based either on the uniqueness of its vibrational mode or on the most intense peak of the spectrum. However, this method is inconsistent throughout different samples or sampling conditions of the same sample type. Therefore, an advanced spectral normalization technique called Standard Normal Variate (SNV) method is used to normalize spectra. In SNV, the mean value of the spectrum is subtracted by each spectral point and then divided by the standard deviation of the full spectrum as in equation 2.27. This brings all spectra to the same level by removing constant offset terms. Since this method is consistent with all samples, it is very popular in spectra post-processing [13].

$$A_{ni} = \frac{A_i - \bar{A}}{\sigma} \quad (2.27)$$

Here, A_{ni} is the i^{th} spectral point in the spectrum normalized by the technique described above, A_i is the i^{th} spectral point in the original spectrum, $\bar{A}$ and σ are the mean and the standard deviation of the full spectrum [12].

All IR absorbance spectra in this thesis are normalized by the SNV method. Since the SNV method is a consistent normalization technique for all spectra and does not depend on arbitrary features like the tallest peak or the total area under the curve, direct comparisons between the intensities of peaks in different spectra are made.

2.2 Wide-angle X-ray scattering (WAXS)

2.2.1 *X-ray scattering and Fourier analysis*

Wide-angle X-ray scattering is an X-ray diffraction (XRD) technique used to obtain crucial information on a material's structural properties, especially if the material is crystalline. X-rays interact with matter elastically and inelastically. When an X-ray photon collides with an electron and transfers all its energy to the electron, the electron will be emitted if the energy is sufficient. This is an inelastic interaction, and it is called the photoelectric effect. However, the X-rays can scatter with or without losing energy to electrons. When X-rays lose partial energy to electrons during scattering, it is referred to as the Compton effect; when they do not lose energy, it is known as coherent scattering.

Coherent scattering is the principal physical concept behind WAXS. All materials are built with atoms, and these atoms have electron clouds. If the material is crystalline, then these electron clouds are periodic such that any translation along any direction makes the electron number density invariant. If the electron number density is $n(\mathbf{r})$, where $\mathbf{r}$ is a position vector, we can write:

$$n(\mathbf{r}) = \sum_{\mathbf{G}} n_{\mathbf{G}} \exp(i\mathbf{G} \cdot \mathbf{r}) \quad (2.28)$$

$\mathbf{G}$ is a set of vectors that satisfies the invariance condition under any translation in a crystal. $n_{\mathbf{G}}$ is the set of Fourier coefficients that determines the scattering amplitude [14]. The set of vectors is given by:

$$\mathbf{G} = A\mathbf{a}' + B\mathbf{b}' + C\mathbf{c}' \quad (2.29)$$

$\mathbf{a}'$, $\mathbf{b}'$, and $\mathbf{c}'$ are the primitive vectors of the reciprocal lattice (similar to $\mathbf{a}$, $\mathbf{b}$, and $\mathbf{c}$ which are the primitive vectors of the crystal lattice, as shown before in Figure 1.8). The two sets of primitive vectors are related as shown below:

$$\mathbf{a}' = 2\pi \frac{\mathbf{b} \times \mathbf{c}}{\mathbf{a} \cdot \mathbf{b} \times \mathbf{c}} \quad (2.30A)$$

$$\mathbf{b}' = 2\pi \frac{\mathbf{c} \times \mathbf{a}}{\mathbf{a} \cdot \mathbf{b} \times \mathbf{c}} \quad (2.30B)$$

$$\mathbf{c}' = 2\pi \frac{\mathbf{a} \times \mathbf{b}}{\mathbf{a} \cdot \mathbf{b} \times \mathbf{c}} \quad (2.30C)$$

If the incident ray's wavevector is $\mathbf{k}$ and the scattered ray's wave vector is $\mathbf{k}'$ (see Figure 2.8) then the scattering amplitude (F) is given by:

$$F = \int n(\mathbf{r}) \exp(i\Delta\mathbf{k} \cdot \mathbf{r}) dV \quad (2.31)$$

$\Delta\mathbf{k} = \mathbf{k}' - \mathbf{k}$ is also known as the scattering vector. When the equation 2.31 is substituted into equation 2.28, we get:

$$F = \sum_G \int n_G \exp(i(\mathbf{G} - \Delta\mathbf{k}) \cdot \mathbf{r}) dV \quad (2.32)$$

When $\Delta\mathbf{k} = \mathbf{G}$, F takes a maximum value as the exponential becomes 1. Therefore, when the scattering vector equals a reciprocal lattice vector, it satisfies the diffraction condition.

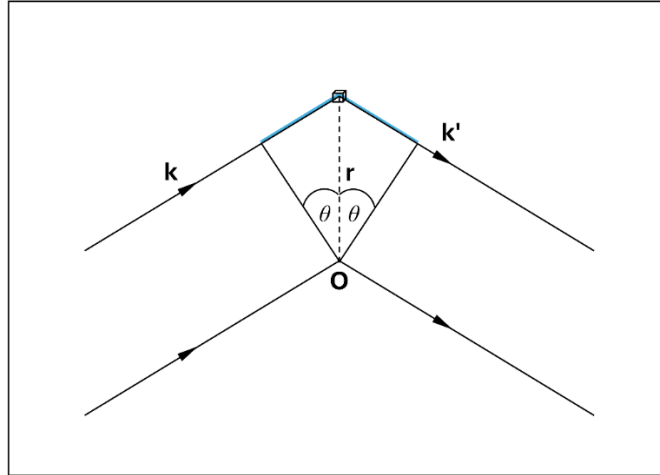


Figure 2.8: Scattering of photons by a small crystal volume (dV) located at r distance away from the origin O . The incident wavevector is $\mathbf{k}$ and the scattering wavevector is $\mathbf{k}'$. The scattering angle is θ . The path difference between the two rays is shown by the blue shaded section.

The primitive cell defined in Chapter 1 is repeated to construct the entire crystalline lattice. Based on the location of lattice sites, lattice planes can then be defined. These lattice planes can be uniquely identified using a set of indices called Miller indices, as shown in Figure 2.9. The Miller indices are denoted by (hkl) .

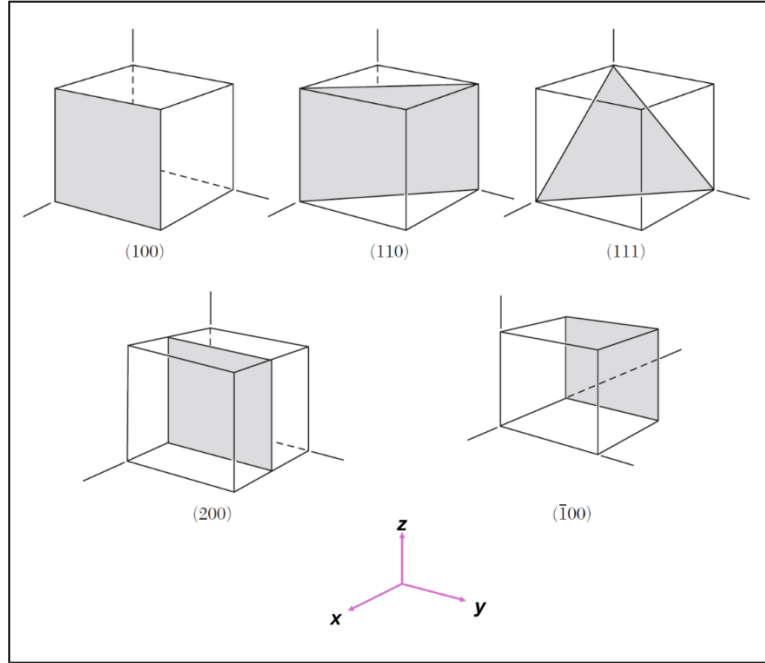


Figure 2.9: Different lattice planes of a cubic crystal are shown with their respective Miller indices below each diagram. The axes system is shown in magenta. Image reproduced from [14].

2.2.2 Bragg's law

The spacing between two consecutive crystal lattice planes is defined as d_{hkl} if the planes are normal to a lattice vector $\mathbf{G}$ given by:

$$\mathbf{G} = h\mathbf{a}' + k\mathbf{b}' + l\mathbf{c}' \quad (2.33A)$$

$$|\mathbf{G}| = |\Delta\mathbf{k}| = 2k \sin \theta = 2 \times \frac{2\pi}{\lambda} \times \sin \theta \quad (2.33B)$$

$$d_{hkl} = \frac{2\pi}{|\mathbf{G}|} \quad (2.33C)$$

Then,

$$2d_{hkl} \sin \theta = \lambda \quad (2.33D)$$

When the common factor n is associated with the Miller indices, the equation 2.33D can be written as,

$$2d_{hkl} \sin \theta = n\lambda \quad (2.34)$$

Equation 2.34 is Bragg's law of diffraction. In a physical sense, as shown in Figure 2.10, when X-rays are incident on a crystal lattice in which lattice planes are defined by Miller indices (hkl) they scatter at an angle 2θ . The path difference between the two rays is equal to $AB + BC$. $AB = BC = d_{hkl} \times \sin\theta$. Therefore, the two rays interfere constructively if the path difference is equal to an integer (n) multiple of the wavelength of the incident radiation.

$$AB + BC = 2d_{hkl} \sin \theta = n\lambda \quad (2.35)$$

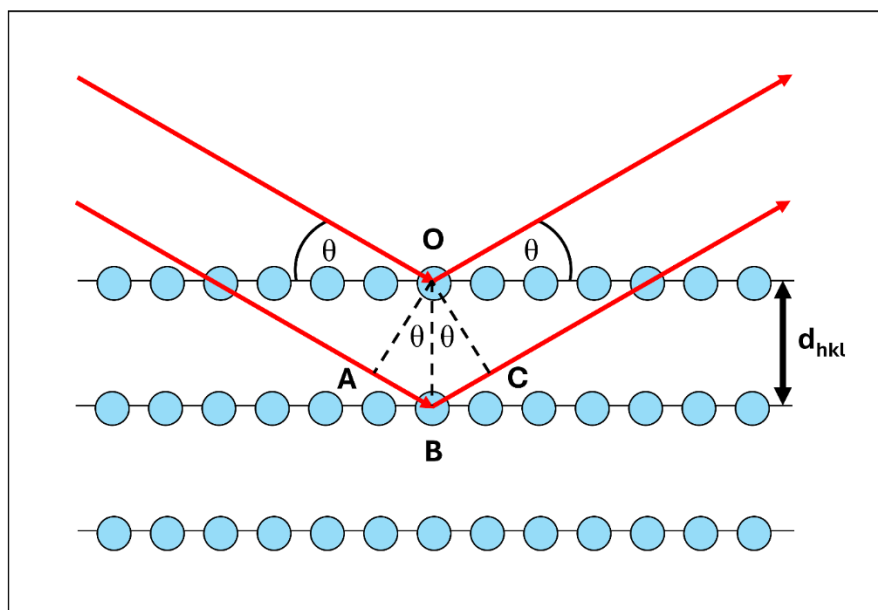


Figure 2.10: Diffraction of X-rays from two different lattice planes denoted by (hkl)

2.2.3 *X-ray generation and determination of crystalline fraction*

In WAXS, monochromatic X-rays are generated by accelerating electrons between two metal electrodes, the cathode and the anode. The cathode is heated to generate the electrons, and due to the high voltage applied between the two, the generated electrons will accelerate toward the anode. If the accelerated electrons have sufficient kinetic energy to eject electrons from an inner shell of the anode material, another electron at a higher energy level will fill that void by transitioning to the lower level and emitting an X-ray with an energy corresponding to the transition energy [15]. The common anode material used in WAXS is copper (Cu). An electron in the s orbital in the K shell (1s) is ejected by collision with fast electrons. If an electron from a p orbital in the L shell

(2p) fills that void in 1s, the X-ray emitted by that electron is known as K_α . Cu- K_α X-ray photon has a characteristic wavelength of 1.54 Å.

Even though X-ray scattering is represented in 2D in Figure 2.8, the scattered X-rays travel in spherical wavefronts. However, the detector only captures a very small area of these spherical wavefronts. Therefore, the obtained WAXS reflections must be “corrected” for accurate quantitative analysis. This is called the Lorentz correction. In the Lorentz correction, the scattered intensity (I) is expressed in terms of the scattering vector ($\mathbf{q}$)

$$|\mathbf{q}| = q = \frac{4\pi}{\lambda} \sin \theta \quad (2.36)$$

$I(q) \cdot q^2$ is called the Lorentz-corrected intensity. A plot of $I(q) \cdot q^2$ vs. q is called a Lorentz-corrected intensity plot, as shown in Figure 2.11 (blue line). Such a plot is very useful in quantitative analyses, such as determining the total crystalline fraction of a sample [16]. A Lorentz-corrected WAXS intensity plot can be deconvoluted and curve-fitted by Gaussian peaks using the following equation (black solid peaks for crystal reflections and black dashed peaks for amorphous halos in Figure 2.11),

$$I(q) \cdot q^2 = \sum_i \left(A_i \exp \left(\frac{(q-q_0)^2}{\sigma_i} \right) \right) + Bq + Cq^2 \quad (2.37)$$

A_i is the amplitude of the Gaussian peak, q_0 is the mean q vector or the peak position, σ_i is the standard deviation or the full width of the peak at half maximum (FWHM). B and C are the coefficients of q and q^2 , respectively. $Bq + Cq^2$ constructs the quadratic baseline (green solid line in Figure 2.11). The peak positions must be known for crystalline reflections and ideal values for

FWHM must be chosen such that a good fit is obtained. The fitted curve (equation 2.37) for the original data is shown in red solid line in Figure 2.11.

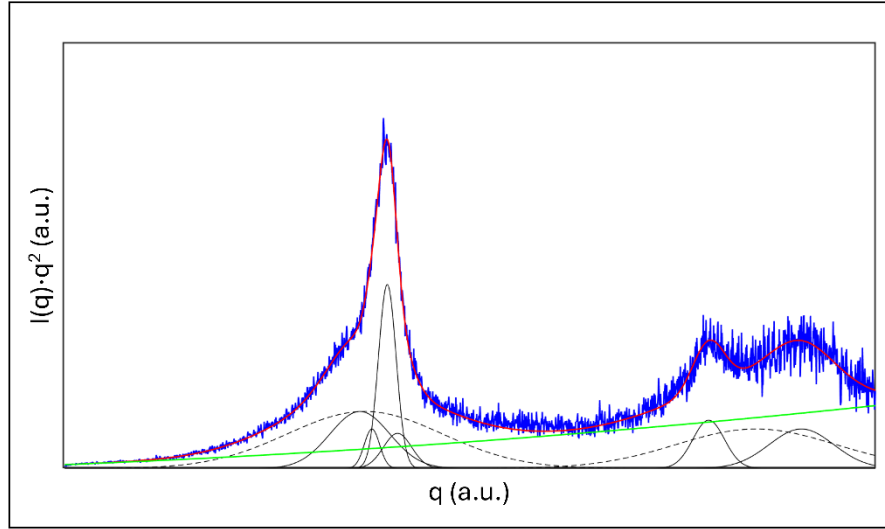


Figure 2.11: Lorentz corrected WAXS intensity plot $I(q) \cdot q^2$ vs q . Blue data points are original data, black solid peaks are crystalline peaks, black dashed peaks are amorphous halos, the red solid line is the fitted data, and the green solid line is the quadratic baseline.

The total crystalline fraction (Φ_c) is then determined by the equation 2.38 calculating the areas of each peak.

$$\Phi_c = \frac{\sum A_c}{\sum A_c + \sum A_a} \times 100\% \quad (2.38)$$

A_c is the crystalline peak area, and A_a is the amorphous peak area [17]. Deconvolution and curve fitting of WAXS intensity plots were performed using the MATLAB program developed by Matthew Reveley, a former undergraduate student of the Cebe Group.

The total crystalline index of electrospun PVDF fibers and electrosprayed PVDF thick films is estimated using the above mentioned program in Chapter 4.

2.3 Thermal analysis

2.3.1 Calorimetry

Calorimetry can be simply defined as the measurement of heat flow. The heat exchanged by a system with its surroundings can be measured using calorimeters. This section discusses two advanced calorimeters: the differential scanning calorimeter (DSC) and the fast scanning calorimeter (FSC).

2.3.2 Heat capacity

The first law of thermodynamics states:

$$dU = \delta Q - \delta W \quad (2.39)$$

Equation 2.39 is simply the principle of conservation of energy where the change in energy in a system (dU) is equal to the amount of heat added to the system (δQ) and the amount of work done by the system (δW) during a thermal process where the system is taken from one state (U_1) to another (U_2). The energy of the system (U) describes the state of the system whereas Q and W depend on the path taken between the two states. Hence, a change in energy can be shown as a differential (dU), but heat and work exchange are shown as infinitesimal changes (δQ and δW) [18].

The work done during a change in volume (dV) at equilibrium pressure (p) is given by:

$$\delta W = p dV \quad (2.40)$$

When the pressure and volume are at equilibrium, then it is fixed by the state of the material as well as it is the maximum work done [19]. Therefore, equation 2.39 can be rewritten as,

$$dQ = dU + p dV \quad (2.41)$$

If the work required to create a volume V at constant pressure p is $p \cdot V$, then the enthalpy of the system is defined as:

$$H = U + pV \quad (2.42)$$

Then, a change in enthalpy of the system (dH) can be given as:

$$dH = dU + p dV \quad (2.43)$$

Combining equations 2.40 and 2.43 to obtain:

$$dQ = dH \quad (2.44)$$

From equation 2.44, for a closed system at isobaric conditions, the heat capacity (C_p) is defined as:

$$\left(\frac{dQ}{dT}\right)_{N,p} = \left(\frac{dH}{dT}\right)_{N,p} = C_p \quad (2.45)$$

The subscripts N and p indicate no exchange in matter (closed system described by N particle) and constant pressure (isobaric). C_p is called the heat capacity at constant pressure, and it is extremely useful in solid and liquid calorimetry as these materials undergo significant volume expansions (or contractions) when the temperature changes.

2.3.3 Heat capacity measurements

The simple definition of heat capacity C_p is the amount of heat required to raise the temperature of a system by one degree of Kelvin at a constant pressure. Therefore, the variation of a material's heat capacity C_p with temperature (T) can provide tremendous information. A typical schematic of a C_p vs T plot for a polymer on heating is shown in Figure 2.12. The polymer is in its glassy state below the glass transition temperature (T_g), and the amorphous regions in the polymer undergo a quasi-second-order phase change during the glass transition and enters the rubbery state or semi-solid state. The change in the heat capacity takes a sigmoidal shape during the glass transition. The inflection point of the transition is defined as the glass transition temperature T_g .

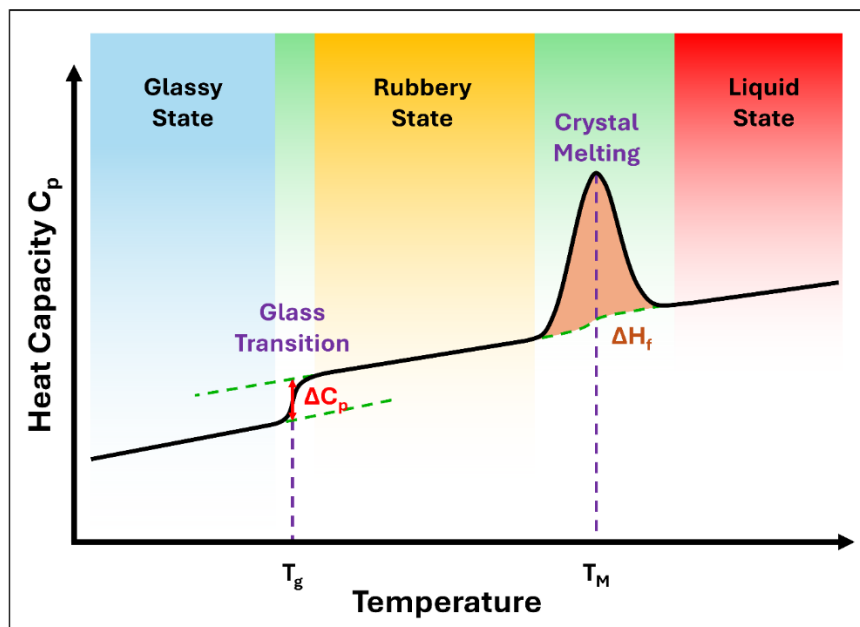


Figure 2.12: Heat capacity C_p vs temperature for a polymeric material on heating. T_g and T_M are glass transition temperature and melting point, respectively.

The glassy state C_p baseline is shown by the tangent drawn to the curve below T_g and the rubbery state baseline is shown by the tangent drawn to the curve above it (green dashed lines). The change in C_p at T_g (ΔC_p shown in red double arrows at T_g in Figure 2.12) is a measure of the polymer's mobile amorphous content (Φ_a). Φ_a is given by [20, 21],

$$\Phi_a = \frac{\Delta C_p^{SC} \text{ at } T_g}{\Delta C_p^{Am} \text{ at } T_g} \times 100\% \quad (2.46)$$

ΔC_p^{SC} is the change in heat capacity of a semi-crystalline polymer at T_g and ΔC_p^{Am} is the change in heat capacity at T_g for a fully amorphous polymer. The dynamics during the glass transition can be very complicated if enthalpic relaxation is involved. It will be discussed in section 2.3.3.1.1.

Crystal melting can be observed at the melting point T_M . At this point, the system's enthalpy is governed by the latent heat of fusion of the crystals, where the crystalline domains (lamellae) transition to the liquid phase while keeping the temperature constant. This is a first order phase transition. According to equation 2.45, the heat capacity is diverging to infinity at T_M as there is no change in temperature. Therefore, the heat capacity curve rises sharply at first melting a fraction of crystals. The molten crystals now have the heat capacity of the liquid state. Hence, the rise in heat capacity during crystal melting is finite in reality as the molten proportion of the polymer increases every time a crystal melts. As the molten proportion increases, the heat capacity curve approaches the liquid state heat capacity by lowering the heat capacity curve, giving rise to a peak at T_M in the thermograph shown in Figure 2.12. This is called the melt peak, and it is endothermic. The total degree of crystallinity (Φ_c) can be determined by measuring the peak area using a sigmoidal baseline (green dotted line under the peak). During the transition, the sigmoidal baseline accounts for the heat capacities of both crystals and liquid-state polymer chains. Φ_c is given by:

$$\Phi_c = \frac{\Delta H_f}{\Delta H_f^0} \times 100\% \quad (2.47)$$

ΔH_f is the enthalpy of fusion of the semi-crystalline polymer at T_M , which can be measured by calculating the endothermic melt peak area, and ΔH_f^0 is the equilibrium heat of fusion, *i.e.*, the melting enthalpy of a 100% crystalline sample.

2.3.3.1 Glass transition and polymer fragility

2.3.3.1.1 Glass transition and fictive temperature

The structure of a polymer in its liquid state (usually at elevated temperatures) remains constant at equilibrium temperature values because the random fluctuations in the system average out the total rearrangements in the structure. The rearrangement of the structure is called the structural relaxation. With decreasing temperature, the rate of structural relaxations also decreases. When the time scale of the relaxation is too slow to measure experimentally, the state is said to be a “frozen” state. This “frozen” state is called the glassy state, and the transition from a highly mobile liquid (rubbery for semi-crystalline polymers) state to the glassy state is called the glass transition.

If τ is the structural relaxation rate, it follows an Arrhenius relationship as follows:

$$\tau = \tau_0 \exp \left(\frac{\Delta H^*}{RT} \right) \quad (2.48)$$

Figure 2.13 shows the variation of the enthalpy (H) and the volume (V) of a glass forming sample such as a polymer with temperature while cooling and heating. If the sample is cooled at a rate of β_1 (solid blue line in curve 1 in the figure), the equilibrium enthalpy H_e (or the equilibrium volume

V_e) follows the measured enthalpy at high temperatures when in the liquid state. According to equation 2.48, as the temperature decreases the structural relaxation time increases. At some temperature range the experiment time scale Δt falls in the proximity of τ ($\Delta t \sim \tau$). This temperature range is called the transition range. When the temperature decreases even further, τ attains larger values compared to Δt . At this point the enthalpy (or V) of the sample falls out of equilibrium and enters the glassy state. In other words, the structural relaxation lags behind as it is too slow to follow the measurement. If the sample is reheated after entering the glassy state (solid red line in curve 1 in the figure), the enthalpy will trace along the cooling curve until the transition range as $\Delta t < \tau$. When the sample enters the transition range on heating, the measured enthalpy of it is greater than the equilibrium enthalpy thus relaxes downwards showing a departure from the cooling curve. Then it relaxes upwards again when the equilibrium enthalpy increases past the measured enthalpy of the sample. Eventually at high temperatures, when $\Delta t > \tau$, the measured enthalpy is matched with the equilibrium enthalpy, hence the heating curve starts to trace the cooling curve at high temperatures. Therefore, the cooling curve and a heating curve of a glass forming material show a hysteresis near the glass transition. The temperature value where the structural relaxation rate becomes too slow to measure is defined as the fictive temperature (T_f). The value of T_f can be found using the H (or V) vs T plot as shown in Figure 2.13 by the intersection point of the extrapolated glassy and liquid state baselines (black dashed lines in Figure 2.13) [22].

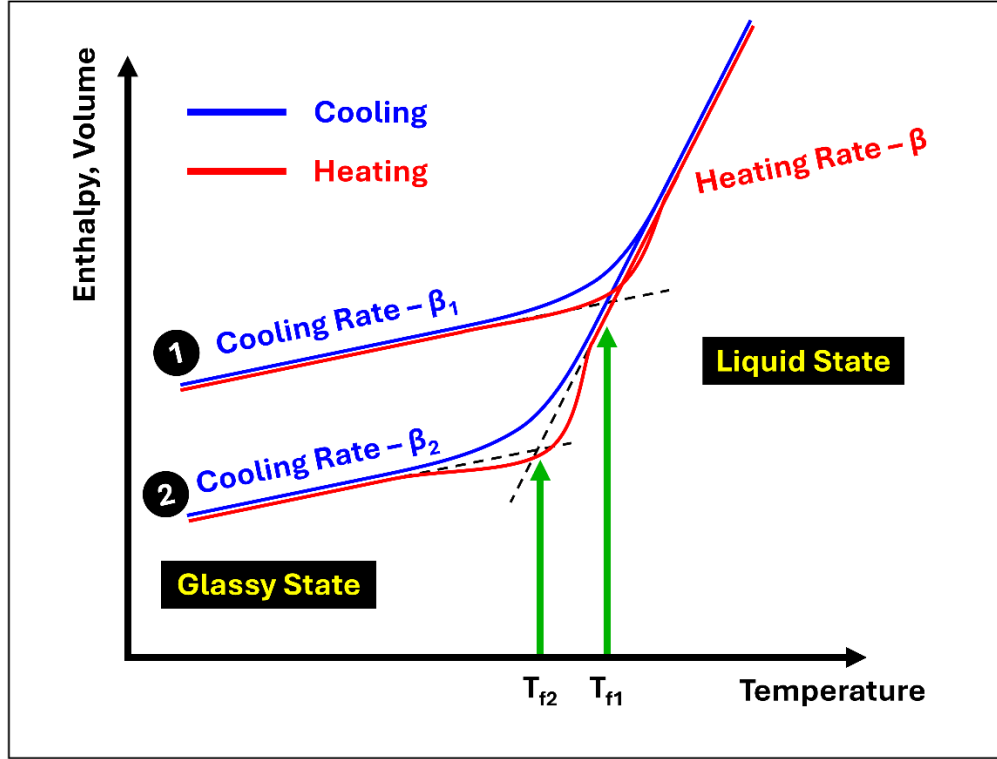


Figure 2.13: Variation of the enthalpy (H) and the volume (V) of a glass forming material when cooling and reheating. The curves 1 and 2 represent two instances where the material sample is cooled at two different rates β_1 and β_2 ($\beta_1 > \beta_2$) and reheated at the same rate β . T_{f1} and T_{f2} are the limiting fictive temperatures for the two curves. The glassy state and the liquid state baselines are drawn shifted from each other for clarity.

The glass transition and the value of the fictive temperature are rate-dependent [22, 23]. The experiment time scale Δt can be expressed as the ratio between the temperature difference during heating or cooling (ΔT) and the cooling/ heating rate (β),

$$\Delta t = \frac{\Delta T}{\beta} \quad (2.49)$$

Then, Δt_1 and Δt_2 are the experimental time scales for curves 1 and 2 (cooling rates are β_1 and β_2 , where $\beta_1 > \beta_2$), respectively. When the cooling rate is slow, then the structural relaxations will follow the equilibrium line for an extended temperature range before falling out of it, lowering the value of T_f (as shown for curve 2 in Figure 2.13). Because of this, when the sample is reheated, the departure from the cooling curve is quite noticeable. The fictive temperature T_f is quite often regarded as the glass transition temperature T_g on heating and if the heating rate is equal to the prior cooling rate T_g and T_f are equal. The WLF (Williams-Landel-Ferry) model is ideal for describing the rate dependence of T_g , and it is given by [24]:

$$\log_{10} \left(\frac{\beta}{\beta_{ref}} \right) = \frac{C_1(T_f - T_{f_{ref}})}{C_2 + T_f - T_{f_{ref}}} \quad (2.50)$$

β and β_{ref} are the cooling rate prior to heating and the reference cooling rate, respectively. T_f and $T_{f_{ref}}$ are the fictive temperature and the fictive temperature for the reference cooling rate, respectively. C_1 and C_2 are fit parameters. A key assumption in the WLF model is that the polymer is not degrading during the heating and cooling cycles. Therefore, the slowest cooling rate that the sample does not show any degradation must be chosen as the reference cooling β_{ref} .

Figure 2.14 shows the heating curve of a glass former with structural relaxation in the realm of heat capacity (C_p). Since all advanced thermal analyses were done using the heat capacity curves, it is quite important to determine the fictive temperature using them. The most efficient method to determine T_f is the Moynihan method, as shown below [22, 25]:

$$\int_{T_f}^{T \gg T_g} (C_{pl} - C_{pg}) dT = \int_{T \ll T_g}^{T \gg T_g} (C_p - C_{pg}) dT \quad (2.51)$$

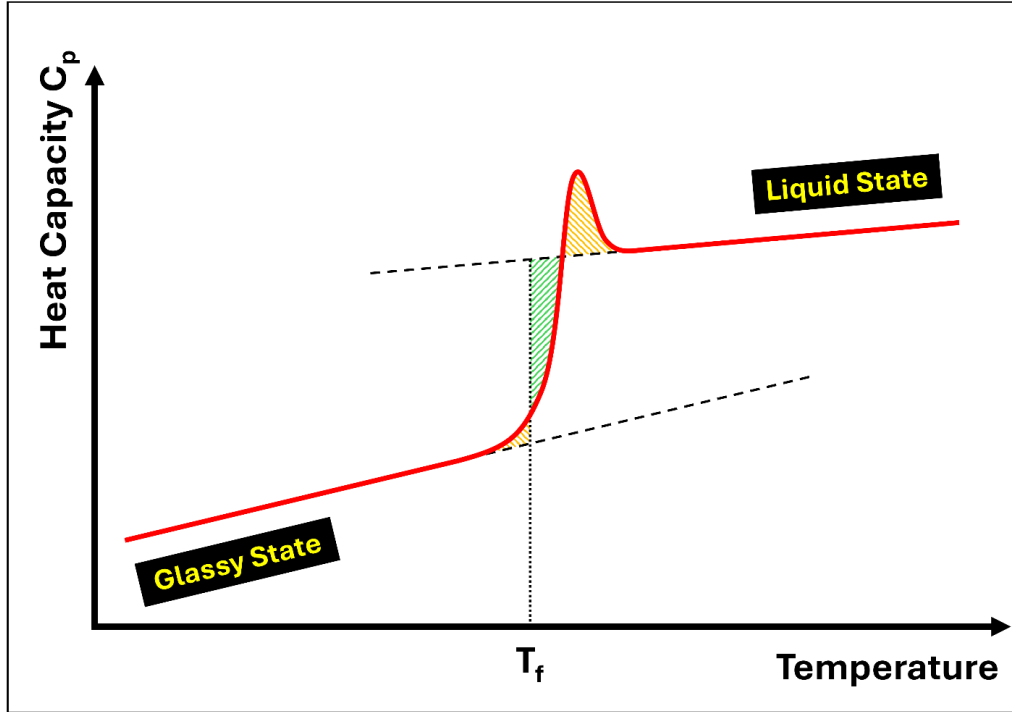


Figure 2.14: The heat capacity curve of a glass former with a structural relaxation in the glass transition range. The fictive temperature T_f is determined when the values of the green and the two yellow shaded areas are equal.

C_{pl} and C_{pg} are the extrapolated heat capacity baselines in the liquid and glassy states, respectively.

C_p is the heat capacity curve. The equation 2.50 simply means the value of T_f is determined by finding its limits where the green shaded area is equal to the sum of the two yellow shaded areas in the heat capacity plot shown in Figure 2.14.

2.3.3.1.2 Dynamic fragility of polymers

The fragility of a polymer (in general, of a glass former) can have dynamic (kinetic) or thermodynamic meanings. In this section, the dynamic fragility of polymers is discussed. The dynamic fragility m is defined as how quickly the dynamic properties of a liquid change as its glass transition temperature is approached [26]. It is given by:

$$m = \frac{d(\log_{10} \tau)}{d\left(\frac{T_g}{T}\right)} \bigg|_{T=T_g} \quad (2.52)$$

τ is the rate of structural relaxation, T_g is the glass transition temperature, and T is the temperature.

If the structural relaxation rate τ in the equation 2.52 is replaced by the prior cooling rate β , the dynamic fragility can be determined from [25]:

$$m = \frac{d(\log_{10} \beta)}{d\left(\frac{T_{fref}}{T_f}\right)} = \frac{C_1}{C_2} T_{fref} \quad (2.53)$$

C_1 and C_2 fit parameters can be estimated by rearranging the WLF equation (equation 2.51) and plotting T_f vs $\log_{10}(\beta)$.

2.3.3.2 Differential scanning calorimetry

Differential scanning calorimetry (DSC) is a precise technique for measuring how a material's physical properties change with respect to temperature. In DSC, the temperature changes continuously, and the heat absorbed or released by the sample is recorded by taking the heat flow difference between the sample and a reference [27]. There are two types of DSC instruments: heat-flux and power-compensation differential scanning calorimeters. Both measure heat flow, but they

use different mechanisms which are described later in this section. DSC is extremely important because it makes all the above thermal analytical methods possible. A typical thermograph obtained from a DSC instrument is shown in Figure 2.15. As it is evident from Figure 2.15 DSC thermographs can be used to qualitatively and quantitatively analyze phase transitions and a material's thermal history.

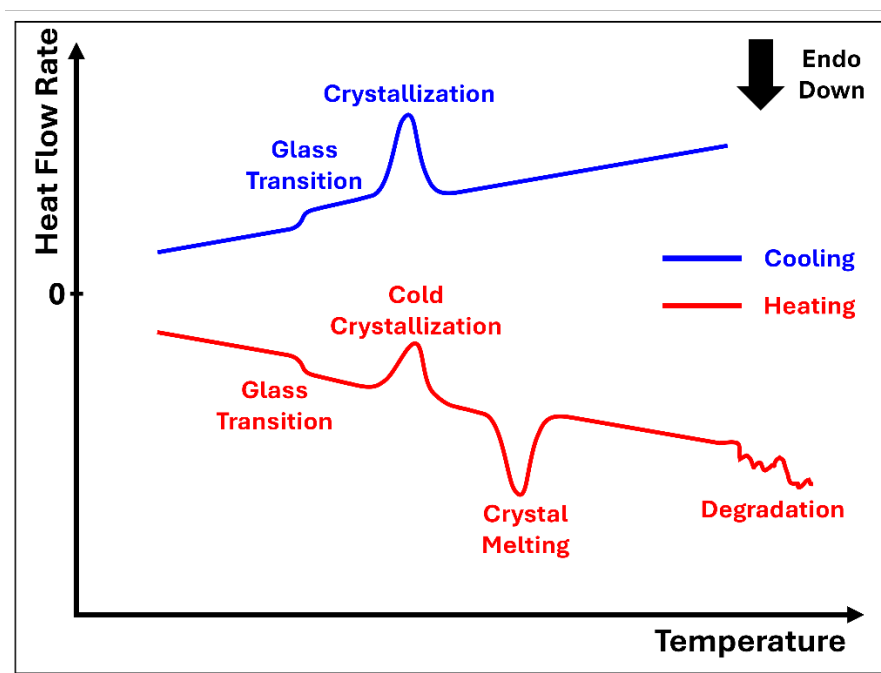


Figure 2.15: An example DSC thermograph with important phase transitions indicated with their respective characteristic signal.

At temperatures well below T_g , the polymer is in its glassy state. The previous section provides a detailed discussion of this state. Since the polymer chains are “frozen” and immobile in this state, the heat flow rate is growing with increasing temperature (red curve in Figure 2.15). After the glass transition, the polymer enters the rubbery state, increasing the heat flow into the sample, an endothermic event, where amorphous chains are conditionally mobile. Their kinetic mobility is

restricted only by the crystalline domains. Further increase of temperature would result in cold crystallization if the polymer sample had been cooled at a rate at which crystal formation was restricted or limited. At such cooling rates, nucleation sites could still form, but crystal growth is hindered. At a temperature above T_g , viscosity decreases and these nucleation sites could grow into crystals. Since this process is happening while increasing temperature, it is called cold crystallization. Since heat is transferred out of the system during cold crystallization, this creates an exothermic peak in the thermograph. The crystals formed either during prior cooling or during cold crystallization will start to melt at the melting point. Heat is absorbed by the crystals to break the crystalline lattices. Therefore, the crystal melting signal would be an endothermic peak in the DSC thermograph. At very high temperatures, the polymer will degrade by breaking the molecular chains. This will result in random fluctuations in the thermograph.

If the sample were cooled before degradation, the cooling curve would look like the blue curve in Figure 2.15. Since the polymers undergo supercooling as described in Chapter 1, the crystallization peak appears at a lower temperature relative to the melting temperature. Further cooling will make the sample transition into its glassy state. As described above, at faster cooling rates, the crystallization process can be hindered, allowing all polymer chains to be amorphous. In that case, the step height at the glass transition would be greater than that for the semicrystalline sample.

Schematic diagrams of heat flux and power-compensating DSCs are shown in Figure 2.16. A power-compensation DSC measures the heat flow in and out of the sample by regulating the temperature between the sample and the reference. The sample and the reference are placed on

two separate heating elements and furnaces. According to the operational program, the instrument delivers power to both sample and reference at the same rate. During the transitions described above, the temperature of the sample deviates from the set value – increases when the signal is exothermic and decreases when it is endothermic, thus requiring it to provide heat or withdraw it, in other words, compensate power with respect to the temperature of the reference. Earlier DSCs adapted this technique.

The heat flux DSCs have one furnace for the sample and the reference. The sample and the reference platforms are mounted on a constantan base where its temperature T_b is regulated. The sample temperature T_s and the reference temperature T_r are measured separately. The heat flux is proportional to ΔT the difference between T_s and T_r . Then the heat flow rate into the sample platform ($\dot{q}_s$) and the reference platform ($\dot{q}_r$) can be expressed as:

$$\dot{q}_s = \frac{T_b - T_s}{R_s} - C_s \frac{dT_s}{dt} \quad (2.54A)$$

$$\dot{q}_r = \frac{T_b - T_r}{R_r} - C_r \frac{dT_r}{dt} \quad (2.54B)$$

R_s and R_r are the thermal resistance of the sample and reference platforms, C_s and C_r are the heat capacities of the sample and reference platforms, respectively.

Then the difference between the two heat flows is given by:

$$\dot{q} = -\frac{\Delta T}{R_r} + \Delta T_0 \left(\frac{1}{R_s} - \frac{1}{R_r} \right) + (C_r - C_s) \frac{dT_s}{dt} - C_r \frac{d\Delta T}{dt} \quad (2.55)$$

The first term on the right-hand side is equivalent to the conventional DSC heat flow rate. The second and third terms result from the imbalances between the thermal resistance and the heat capacities of the sample and reference platforms. Finally, the fourth term results from the heating rate differences between the sample and the reference platforms.

Since the samples cannot be placed directly on the sample platform, they are encapsulated in enclosed pans made of a material with a high thermal conductivity, such as aluminum. An empty enclosed pan with a similar mass is used as the reference. To obtain data with high precision, a difference of ± 0.02 mg between the sample pan and the reference pan is allowed. The DSC used in the thermal analysis in this thesis is a heat flux DSC.

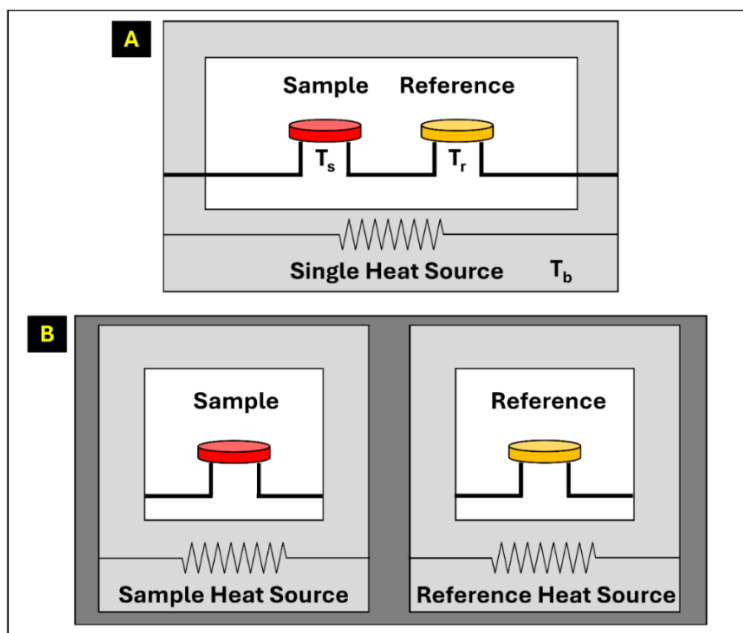


Figure 2.16: Schematic diagrams of A) Heat flux DSC; B) Power compensation DSC.

2.3.3.3 *Fast scanning calorimetry (FSC)*

2.3.3.3.1 *FSC basics*

The modern DSC instruments are vital in characterizing thermal properties of materials, but their scanning rates range from 0.1 K/min – 500 K/min. This could lead to many uncertainties as the slow scanning rates could allow matter to diffuse and rearrange resulting in misinterpretations in the DSC measurements. In addition, the cooling rates in real life applications, like casting and melt extrusion, are extremely high (~1000 K/s) and the scanning rates in DSC instruments are unable to match that. Hence, a new fast scanning technique was introduced in which the samples can be heated and cooled at rates that are several orders of magnitudes greater than a conventional DSC. This technique was developed by Prof. Christoph Schick and his student Evgeny Zhuravlev at University of Rostock [28]. The commercially available instrument is called the Flash DSC manufactured by Mettler-Toledo (Greifensee, Switzerland) and this instrument can scan a sample at slow rates like 0.5 K/s and as high as 40000 K/s [29].

To obtain ultra-fast scanning rates as above, the samples need to be very thin (typically < 10 μm) and must be in good thermal contact with the heating element. The calorimeter is designed in such a way that the heat capacity of the calorimeter is very small. It is surrounded by a gas and the thermal resistance between the calorimeter and the gas is small. The calorimeter is made out of a thin membrane made of Si_3N_x with an electrically controlled furnace. Two such identical furnaces are built in an FSC chip sensor for the sample and the reference, and each furnace is about 0.5 mm wide in diameter. Using eight thermocouples, the temperature of the FSC furnace or the heating element is measured. The sensors operate on the power compensated mode, as described in a previous section, by regulating the temperature between the sample and the reference [30]. A

schematic of the Mettler Toledo UFS2 sensor is shown in Figure 2.17 and an actual one in Figure 2.18-A and an enlarged image of the sensor area is shown in Figure 2.18-B.

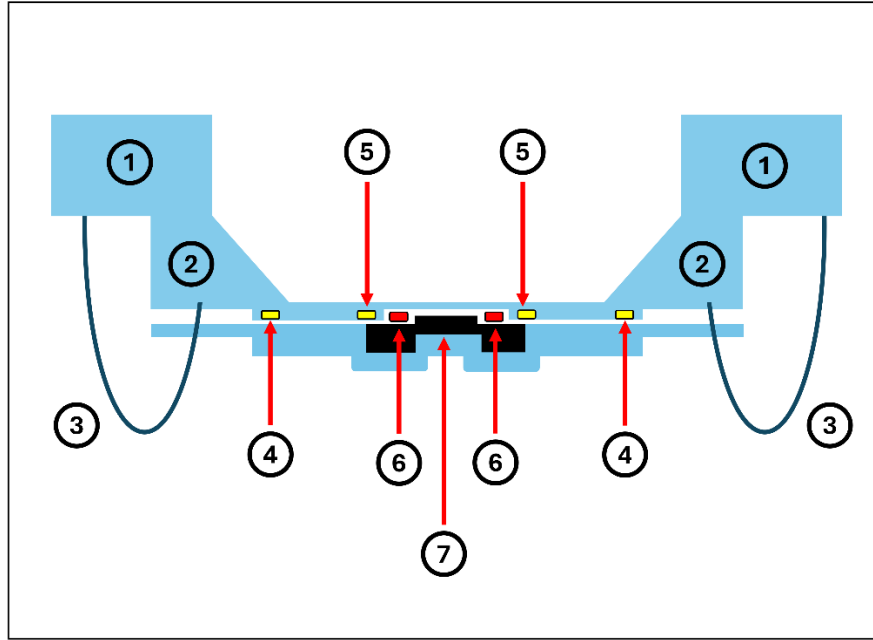


Figure 2.17: Schematic of the UFS2 sensor (not to scale). (1) Ceramic plate; (2) Silicon frame; (3) Bonding wire; (4) Cold junction; (5) Hot junction; (6) Heating resistor; (7) Aluminum plate. Image reproduced from [30].

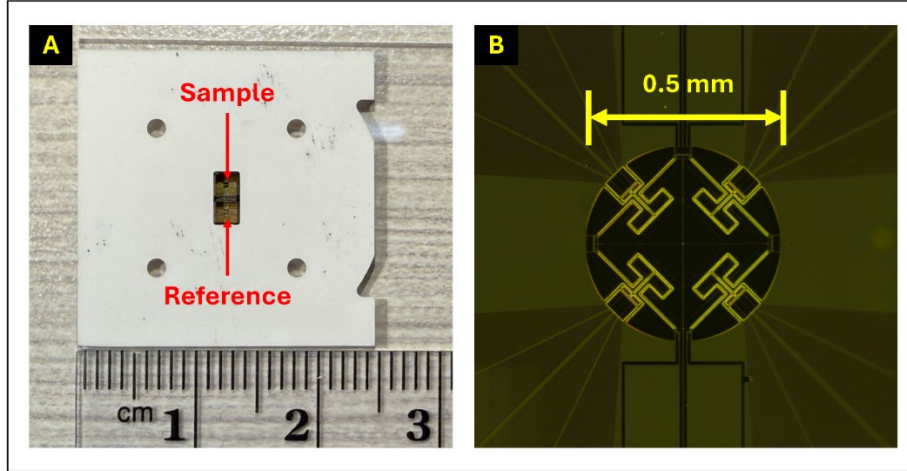


Figure 2.18: A) Mettler Toledo UFS2 FSC chip sensor with a scale. The sample sensor and the reference sensors are indicated; B) An optical microscopic image of the heating element of the calorimeter (sensor area is the circular part with electrical connections).

The heat balance equations in power compensation mode for the reference sensor and the sample sensor are given by:

$$C_0^{ref}(T) \cdot \frac{dT^{ref}}{dt} = P_0^{ref}(T) - P_{loss}^{ref}(T) \quad (2.56A)$$

$$(C_0^s(T) + C_{sample}(T)) \cdot \frac{dT^{sample}}{dt} = P_0^{sample}(T) + P_{diff} - P_{loss}^{sample}(T) \quad (2.56B)$$

where, P_0^{sample} , P_0^{ref} are the power applied to the two sensors and P_{loss}^{sample} and P_{loss}^{ref} are the power lost from the two sensors to the surroundings, respectively. The superscripts “sample” and “reference” refer to the respective sensors. C_0^{ref} , C_0^{sample} , and C_{sample} are the heat capacities of the reference sensor, sample sensor, and the sample itself. P_0^{sample} is intentionally left to vary between 0.8 – 1.2 times of P_0^{ref} to compensate for the linear asymmetry of the two sensors and, usually, the

power applied to the two sensors is an average of P_0^{sample} and P_0^{ref} , and it is P_0 . C_0^{ref} and C_0^{sample} are the same for both sensors [28]. However, the power lost to the surrounding from the sample sensor $P_{\text{loss}}^{\text{sample}}$ is not the same as that of the reference $P_{\text{loss}}^{\text{ref}}$. If the scanning rate dT/dt is the same for both sensors an expression for the sample heat capacity C_{sample} can be obtained [28]:

$$C_{\text{sample}}(T) \cdot \frac{dT}{dt} = P_{\text{diff}} - P_{\text{diff}}^{\text{loss}}(T) \quad (2.56C)$$

where $P_{\text{loss}}^{\text{diff}}$ is the difference in power lost to the surrounding by the two sensors. The $P_{\text{loss}}^{\text{diff}}$ function needs to be determined to symmetry-correct the thermographs obtained from the FSC.

2.3.3.3.2 Symmetry correction of FSC data

In a conventional DSC, the sample is encapsulated in an aluminum pan with an aluminum lid and a similar aluminum pan and lid system is used as the reference. Therefore, the heat lost to the surrounding from the sample and the reference in a DSC is very similar to each other. Thus, the data obtained in the DSC has already accounted for the heat loss and the heating and cooling curves are symmetric. However, in the FSC the sample is not encapsulated but is exposed to the ambient conditions of the FSC unit such as the purge gas unlike the DSC. Therefore, the heat loss function needs to be determined manually for symmetry correction of data.

The heat flow rates of the empty sensor are subtracted from the sample heat flow rates prior to symmetry-correction to eliminate the effects arising from the addenda (heated area of the membrane). Then, the heat flow data can be symmetry-corrected easily by considering common ranges of the glassy state baseline (below T_g) and liquid state baseline (above crystal melting for

a semi-crystalline polymer or above T_g for an amorphous polymer). When selecting the data ranges for symmetry corrections, the transition regions such as glass transition, crystallization, and crystal melting need to be strictly avoided to prevent introducing uncertainties. The heat flow vs. temperature for an amorphous polymer obtained from FSC is shown in Figure 2.19-A. The selected data ranges in both glassy and liquid states are shown by the dashed black lines on both heating and cooling curves. Then, the averages of the glassy and liquid state data ranges (on heating and cooling) are calculated. These are shown in black solid lines in Figure 2.19-A. The heat loss function can then be constructed by extrapolating the average data ranges in both states. This function often is a third order polynomial [28, 29]. The constructed heat loss function is shown by the solid green line in Figure 2.19-A. The heat loss function is then subtracted from both heating and cooling raw data to obtain the symmetry corrected heating and cooling data as shown in Figure 2.19-B.

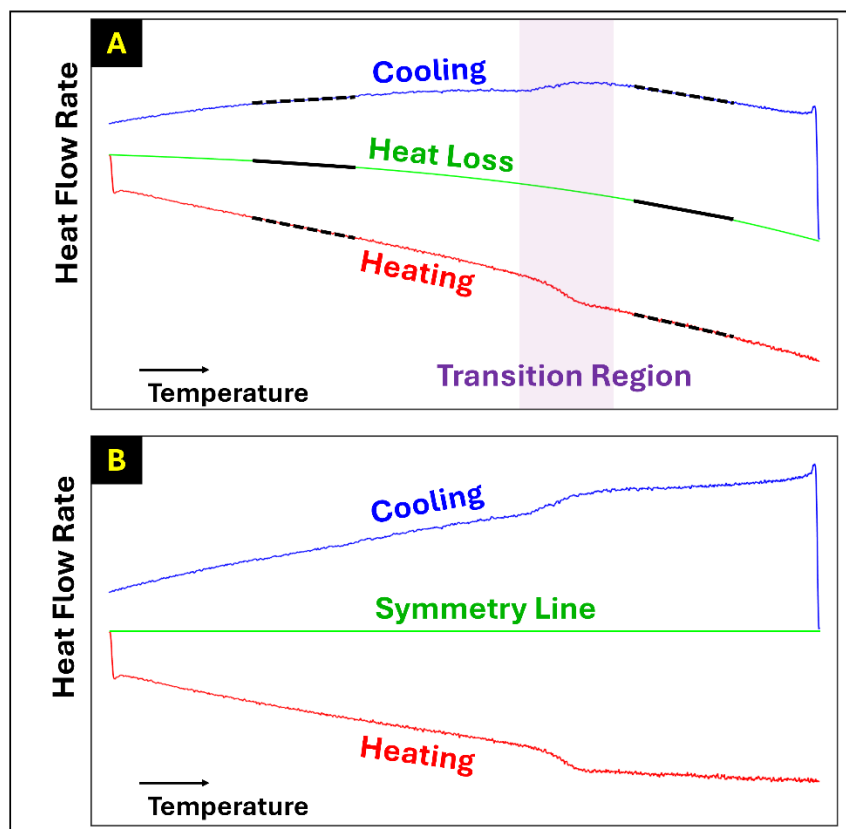


Figure 2.19: Heat flow rates in FSC for an amorphous polymer. A) Raw heating (red) and cooling data (blue). Selected data ranges in the glassy state and the liquid state for symmetry correction are indicated by the black dashed lines on heating and cooling curves. The transition range is shown by the purple band, and it is strictly avoided when selecting the ranges for symmetry correction. The average ranges in glassy and liquid states are shown by the black solid lines. The heat loss function constructed by extrapolating the black solid lines and fitting a third order polynomial is shown by the solid green line; B) The symmetry corrected heating (red) and cooling (blue) data.

2.3.4 *Thermogravimetric analysis (TGA)*

Materials exhibit different properties as they are heated. The thermodynamic changes can be measured by DSC and FSC, whereas the changes in mass can be measured by thermogravimetry. The mass of a material can be increased or decreased based on the reaction that occurs with increasing temperature. If the sample shows an absorbing or an oxidizing reaction, the mass of the sample is increased. However, the materials often show mass loss with increasing temperature as they undergo various reactions that decrease mass such as the evaporation of solvents or water and thermal or oxidative decomposition [31].

Figure 2.20 shows a schematic diagram of a thermogravimetric analyzer. The sample placed on a platinum pan is lowered into the furnace by a hang down wire. There is another similar pan with equal mass to counter the weight of the sample pan. Hence, the instrument will only measure the mass of the sample if tared properly against the empty sample pan. The furnace heats up the sample according to the set temperature program. The atmosphere in the furnace is maintained inert by purging N_2 gas, hence degradation by oxidation is minimized. Thus, the data collected is solely corresponding to the thermal degradation of the sample.

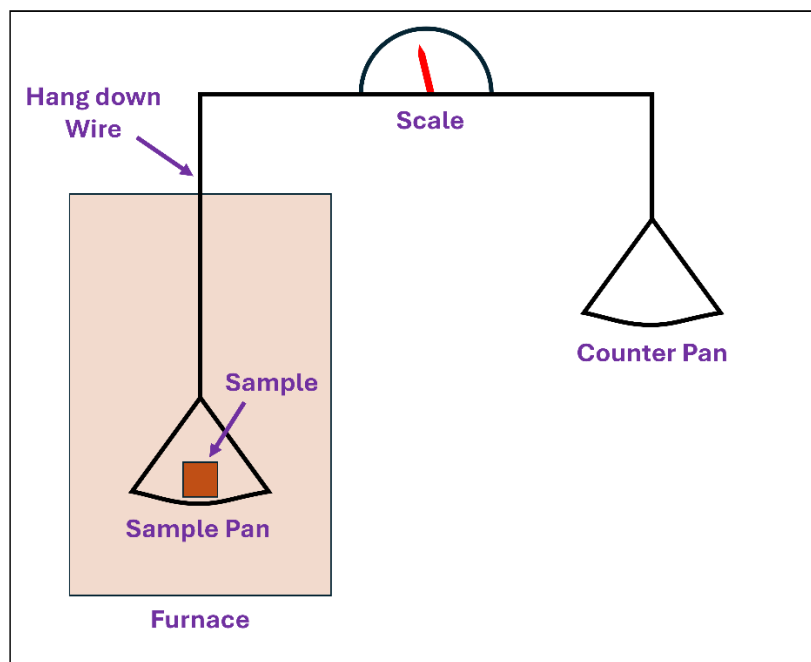


Figure 2.20: Simple schematic diagram of a thermogravimetric analyzer (TGA).

A typical thermograph obtained from TGA is shown in Figure 2.21. The data are shown by the solid red line. The initial mass loss at low temperatures often corresponds to the ejection of solvents or bound water from the sample. As temperature increases, the significant mass loss is caused by the thermal degradation. The onset temperature of the thermal degradation (T_d) of the sample can be computed by extrapolating tangent lines drawn to the data before and after the inflection point and taking the intersection of them. The value of T_d is an important quantity as it determines the upper limit operational temperature range of a material and is used as a guide in performing DSC.

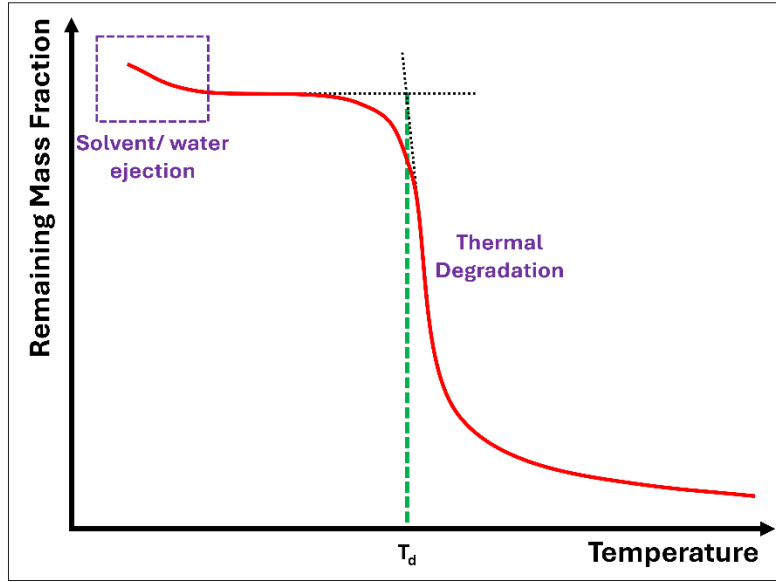


Figure 2.21: Features of a TG thermograph. The remaining mass fraction vs. temperature is shown by the solid red line during heating, at a fixed rate. The onset temperature of thermal degradation T_d is determined by the intersection point of the two tangents drawn to the data curve before and after the inflection point.

2.4 Scanning electron microscopy (SEM)

Scanning electron microscopy is a popular technique to obtain surface topography of a material. In an SEM, an electron beam is used to characterize the surface features instead of an optical beam. The Abbe's equation gives the theoretical resolution (d) of an ideal optical system [32]:

$$d = 1.22 \frac{\lambda}{2n \sin \alpha} \quad (2.57)$$

The numerical aperture (NA) is given by $n \cdot \sin \alpha$ term. In an optical microscope it is related to the refractive index (n) of the medium that the optical beam is traveling and the angular aperture ($\sin \alpha$) of the objective lens. Therefore, typically an optical microscope has a resolution of 200 – 300 nm.

However, in SEM accelerated electrons traveling at very high velocities can attain very short wavelengths. According to the de Broglie formula, the wavelength of an electron traveling at a very high momentum is given by:

$$\lambda = \frac{h}{p} \quad (2.58)$$

Therefore, by accelerating the electrons their momentum can be increased thus decreasing the wavelength. An electron accelerated through a 10 kV applied voltage has a wavelength around 0.01 nm. Hence, the resolution of an SEM is very high compared to an optical microscope according to equation 2.57. Typical resolution is about 200 nm in SEM.

A schematic of an SEM is shown in Figure 2.22. The filament is an electron gun that emits electrons. The anode is set to a very high voltage (~ 10 kV) thus the emitted electrons will accelerate towards the anode and attain a very high speed. The fast electrons are then focused onto the sample using electromagnetic lenses (condenser and objective). To increase the mean free path of the fast moving electrons, the SEM is kept under a vacuum. When the electron beam reaches the sample, the electrons scatter elastically and inelastically. This generates a wide range of signals such as secondary electrons, back scattered electrons, and X-rays. There are several types of detectors in an SEM to detect these signals. The collected signals are then transferred to a computer for processing [32].

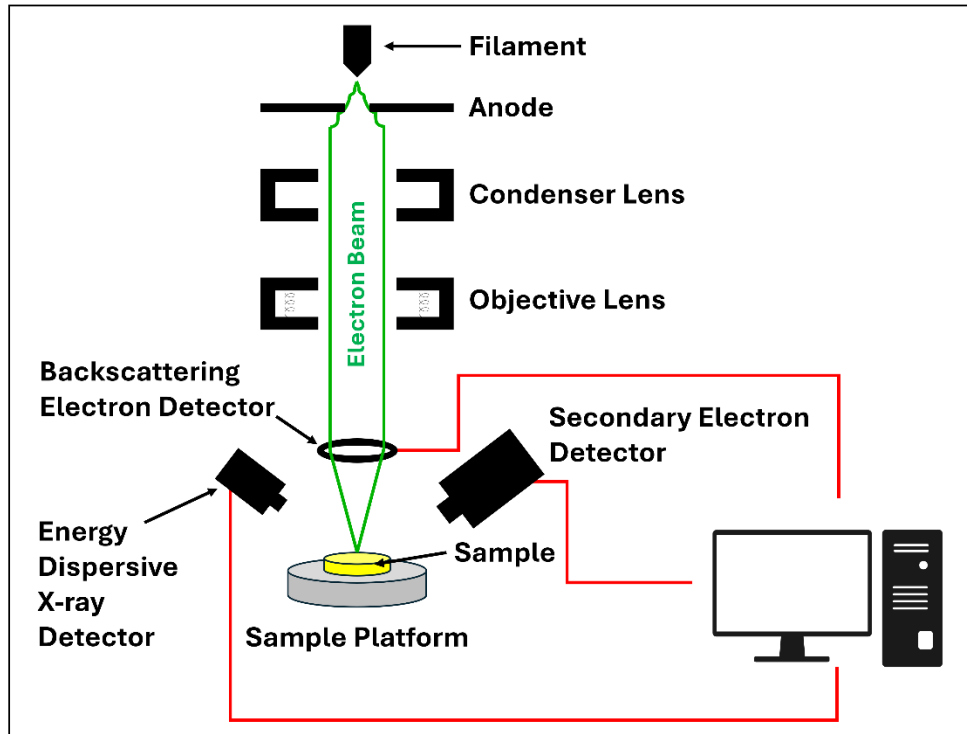


Figure 2.22: Schematic diagram of an SEM microscope.

The electron beam does not get confined on the surface of the sample. Instead, the electron beam travels deep into the sample and interacts with a much larger volume of the sample. This volume is called the interaction volume and takes a teardrop shape as shown in Figure 2.23. The size of the interaction volume depends on the energy of the incident beam, atomic number Z of the sample, and the density of the sample [32].

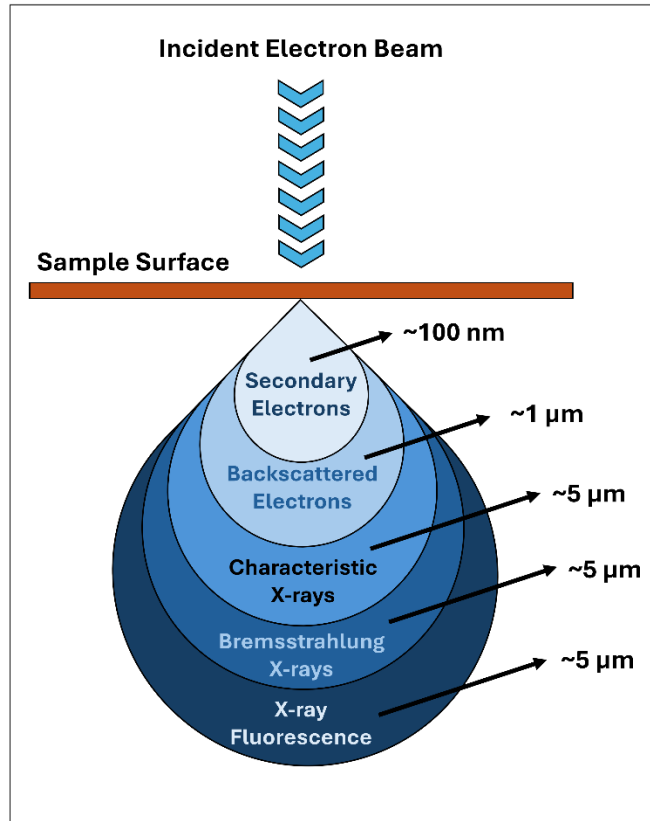


Figure 2.23: Schematic representation of the interaction volume of the sample with the incident electron beam. The various signals generated at different depths of the sample are shown. Figure reproduced from [33].

The wide range of signals emitted by the electron beam interaction with the sample can be used to measure different contrasts in the sample. The secondary electrons are emitted from the sample when the electron beam interacts inelastically with the atoms in close proximity of the surface. These electrons have very low kinetic energy ($\sim 50 \text{ eV}$) and since they arise from the surface, they are useful in constructing a high resolved image of the surface. Thus, topographical contrast is measured using the secondary electrons. Backscattered electrons occur further deep in the sample due to the elastic interaction and have almost the same energy as the incoming electron beam. The

incoming electrons scatter at an angle more than 90° due to the positive charge (number of protons, aka atomic number Z) in the nuclei of the sample. Hence, backscattering electrons give composition contrast. X-rays are generated at much deeper levels when a fast moving electron collides with an inner shell electron (such as K or L shell) and ejects it. Then an outer shell electron will fill that void by emitting the energy difference between the shells as an X-ray. Since this transition energy is characteristic of each element, the X-ray signal can be used to measure the composition contrast. These X-rays are detected by the energy dispersive X-ray (EDS) detector [32].

In this thesis, SEM was used to image the surface morphology of the electrospun fiber mats, electrosprayed thin films, and doctor-bladed thin films using the secondary electrons. The SEM images were further analyzed using an image analysis software called ImageJ and its plugin called DiameterJ to obtain the diameter and porosity statistics of the fiber mats and thin films.

2.5 Rheometry

2.5.1 *Rheology basics*

Rheology is the science of flow. Materials deform when forces are applied on them. These forces are either body forces or shear forces. The shear deformation of materials results from the shear forces applied on them while the extensional deformation is caused by body forces. Flow behavior of materials is mainly caused by the shear deformations. The measurement of flow behavior of the materials is called rheometry. Rheometry can be performed by rotational rheometers either in steady or oscillatory modes.

The shear deformation of a cubic block placed on a surface, under a force F is shown in Figure 2.24. The force F is acting on the top surface with an area of A and at a height of h from the bottom surface. In this model the whole block can be assumed to be constructed by many layers. The bottom layer is stationary as it is in contact with the surface under it. The resistance between each layer to become displaced with the applied force F causes the block to deform in to a parallelepiped shown on right. The top surface is displaced Δy distance making it the maximum deformation. Thus, the shear strain can be expressed as γ :

$$\gamma = \frac{dy}{dz} = \frac{\Delta y}{h} \quad (2.59)$$

The shear stress σ is defined as:

$$\sigma = \frac{F}{A} \quad (2.60)$$

The shear stress is proportional to the shear strain. It is given by:

$$\sigma = G\gamma \quad (2.61)$$

Here, G is a proportionality constant and is defined as the rigidity modulus or the shear modulus.

Equation 2.61 shows the elastic behavior of materials when a shear stress is applied.

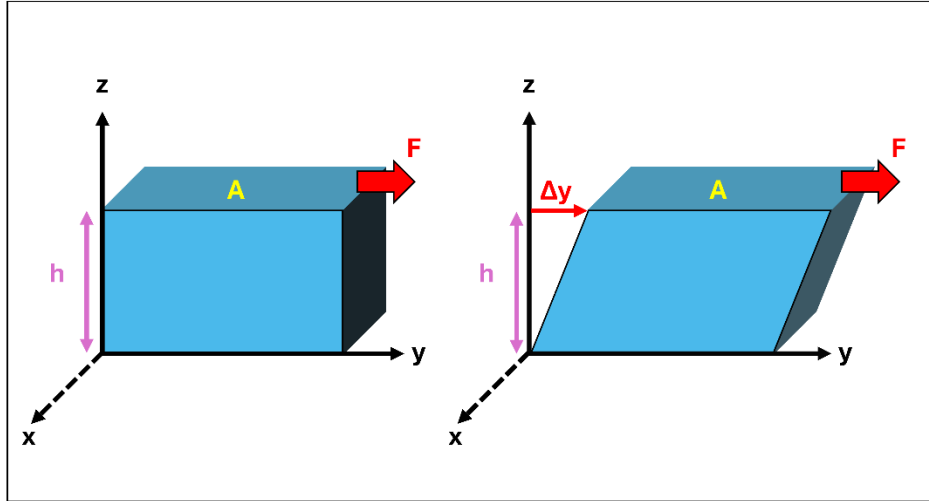


Figure 2.24: Shear deformation of a block under a force F applied on its top surface (area of the top surface is A).

When a liquid flows in a laminar flow as shown in Figure 2.25, it can be analyzed using the shear stress and the deformation in the y direction analogous to the deformation of the block discussed previously. In a flowing material such as a liquid, the layer in contact with the bottom surface is stationary and the top layer travels at a velocity v . Hence, there is a velocity gradient along the z direction in a flowing liquid under shear. Therefore, the shear stress is proportional to the velocity gradient [34].

$$\sigma = \eta \frac{dv}{dz} \quad (2.62A)$$

η is the viscosity coefficient or the dynamic viscosity of the material. Simply, viscosity is the resistance to flow.

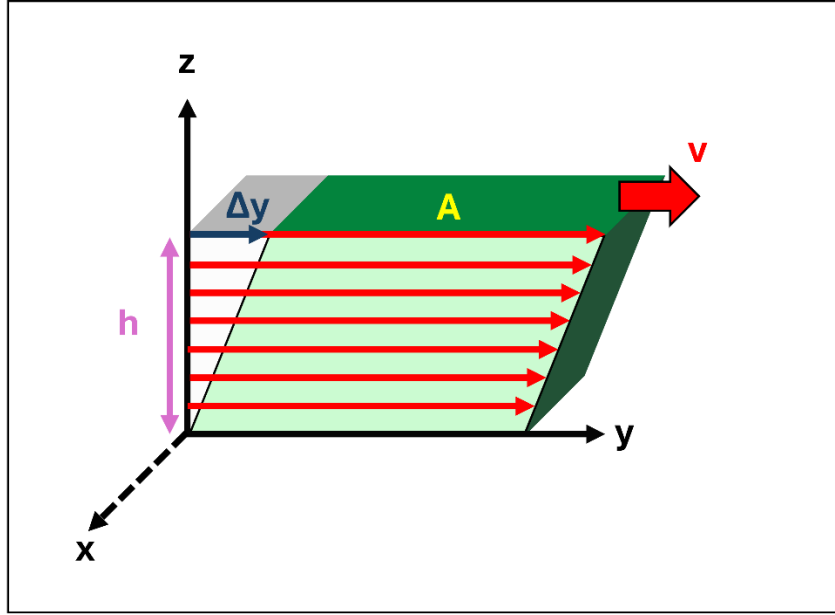


Figure 2.25: Laminar flow of a material of height h and a lateral area A . The top layer is flowing at a velocity of v . The bottom layer is stationary. The red arrows indicate the layers in the liquid under shear flow and the length of each arrow is an indication of the velocity of the respective liquid layer.

Velocity v is the rate of change of displacement along the y direction.

$$v = \frac{dy}{dt} \quad (2.62B)$$

Then substituting from equation 2.59,

$$\sigma = \eta \frac{d}{dz} \left(\frac{dy}{dt} \right) = \eta \frac{d}{dt} \left(\frac{dy}{dz} \right) = \eta \frac{d}{dt} \gamma \quad (2.62C)$$

$$\sigma = \eta \dot{\gamma} \quad (2.62D)$$

Equation 2.62D shows that the dynamic viscosity is a function of the shear stress and the rate of change in shear strain or the strain rate. This corresponds to the viscous behavior of a flowing material.

A Newtonian liquid has a viscosity that varies linearly with the applied shear stress and strain rate. If the viscosity decreases or increases non-linearly then that liquid is defined as a non-Newtonian liquid. If the viscosity decreases with the strain rate, then it is called a shear-thinning liquid (ketchup) and the viscosity of a shear-thickening liquid (corn starch slurry) increases with the strain rate. The variation of the shear stress and the dynamic viscosity of the three types of liquids with the strain rate is shown in Figure 2.26.

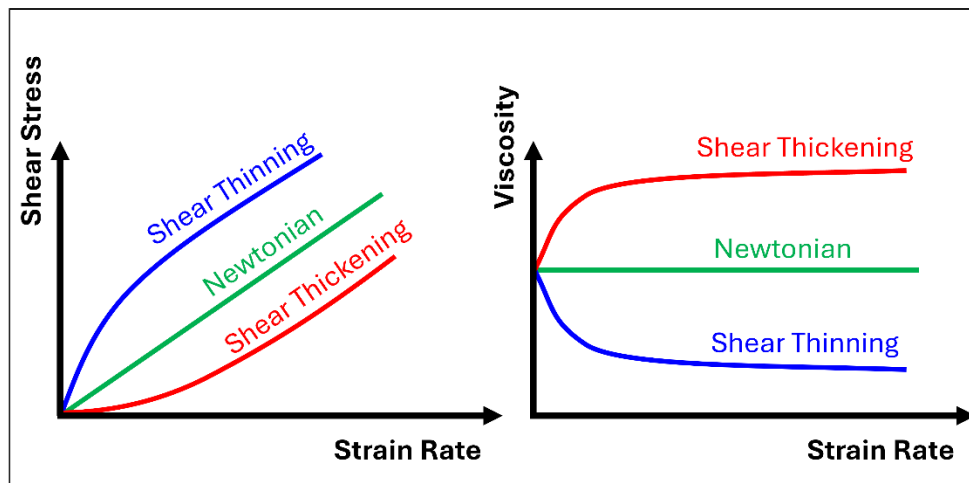


Figure 2.26: Variation of the shear stress (left) and the dynamic viscosity (right) with the strain rate of a Newtonian liquid (green), shear-thinning liquid (blue), and a shear-thickening liquid (red).

Polymers in any of their states (glassy, rubbery, liquid, or in solution) show both elastic and viscous properties. These materials are called viscoelastic materials. Oscillatory rheometry tests are often

used in characterizing the viscoelastic behavior of polymers. In the oscillatory mode, the sample is trapped between an oscillating top plate and a stationary bottom plate as shown in Figure 2.27.

The top plate oscillates at a frequency ω . Then the shear stress is a function of time given by:

$$\sigma(t) = \frac{F \sin \omega t}{A} = \sigma_0 \sin \omega t \quad (2.63)$$

σ_0 is the maximum shear stress F/A .

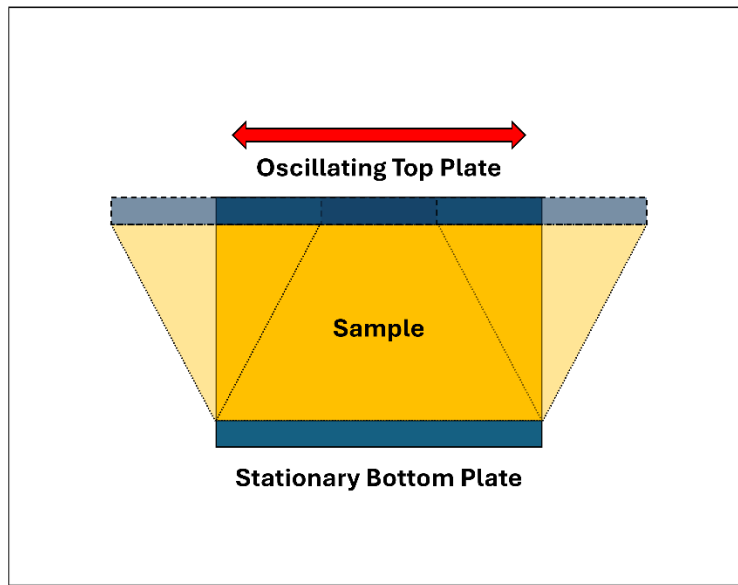


Figure 2.27: Schematic of the oscillatory rheometry setup. The top plate is oscillating while the bottom plate is stationary. The sample is trapped between the two plates.

If the material is ideally elastic (no viscous properties) then the shear strain shows no phase difference between the shear stress *i.e.* the shear strain shows instantaneous response to the shear stress [35], or:

$$\gamma(t) = \gamma_0 \sin \omega t \quad (2.64A)$$

where γ_0 is the maximum shear strain. For a viscoelastic material under an oscillating strain, the shear stress can be written as:

$$\sigma(t) = G^* \gamma(t) \quad (2.64B)$$

G^* is the complex shear modulus. For an ideally elastic material, G^* is same as G in equation 2.61.

An ideally viscous material shows a shear strain with a phase difference of 90° with the applied shear stress. Then it can be deduced that the shear stress and the shear strain are completely out of phase in an ideally viscous material. However, the shear stress is in phase with the strain rate.

$$\dot{\gamma}(t) = \gamma_0 \omega \sin \omega t \quad (2.65A)$$

$$\sigma(t) = \eta^* \dot{\gamma}(t) \quad (2.65B)$$

η^* is the complex viscosity. It is the same as η in equation 2.62D for an ideally viscous material.

The shear strain response to an oscillating shear stress in a viscoelastic material is quite complex. Due to the presence of both elastic and viscous properties, the phase difference δ between shear stress and the shear strain is greater than 0° and less than 90° ($0^\circ < \delta < 90^\circ$) [34, 35]. Therefore, the complex modulus and the complex viscosity have real and imaginary components. The applied shear stress and the corresponding shear strain response in each material is shown in Figure 2.28.

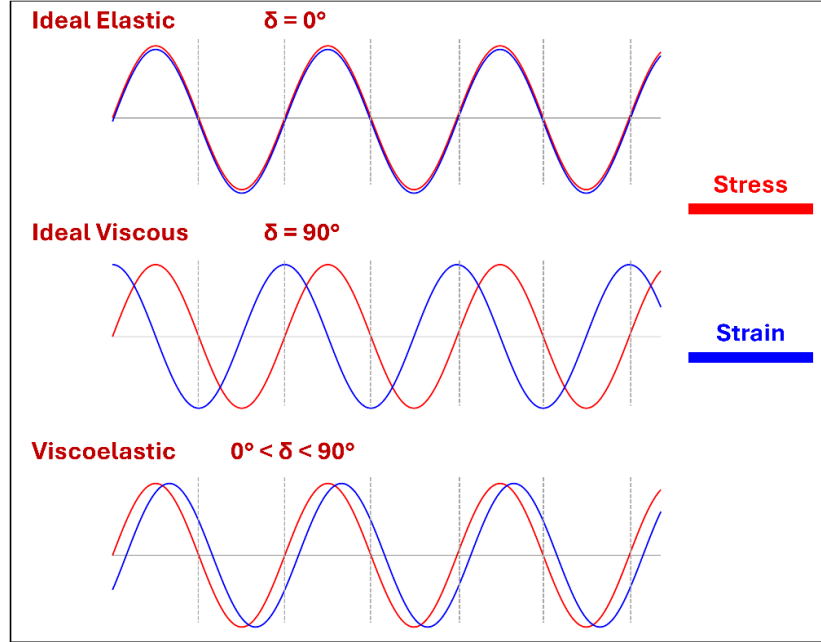


Figure 2.28: Shear stress (red) and the corresponding shear strain response (blue) in ideally elastic material (top), ideally viscous material (middle), and a viscoelastic material (bottom).

The real part of the complex modulus is called the storage modulus G' and it corresponds to the elastic properties of the material while the imaginary component, the loss modulus, G'' corresponds to the viscous properties. The vector diagram depicting the relationship between G^* , G' , and G'' is shown in Figure 2.29.

$$G^* = \sqrt{G'^2 + G''^2} \quad (2.66A)$$

$$G' = \frac{\sigma_0}{\gamma_0} \cos \delta \quad (2.66B)$$

$$G'' = \frac{\sigma_0}{\gamma_0} \sin \delta \quad (2.66C)$$

Similarly,

$$\eta^* = \sqrt{\eta'^2 + \eta''^2} \quad (2.67A)$$

$$\eta' = \frac{\sigma_0}{\gamma_0 \omega} \sin \delta \quad (2.67B)$$

$$\eta'' = \frac{\sigma_0}{\gamma_0 \omega} \cos \delta \quad (2.67C)$$

Real part of the complex viscosity η' corresponds to the viscous nature of the material and the imaginary component η'' corresponds to the elastic nature of the material.

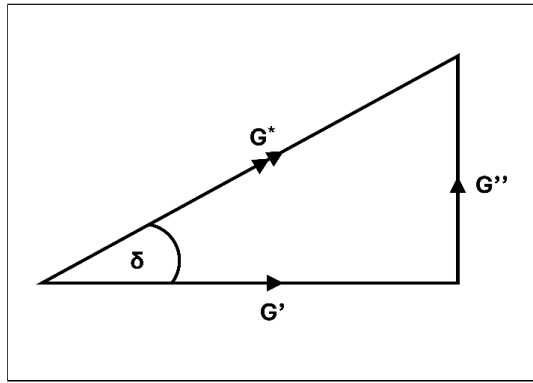


Figure 2.29: Vector diagram of G^* , G' , and G'' .

The loss factor ($\tan \delta$) is defined as,

$$\tan \delta = \frac{G''}{G'} = \frac{\eta'}{\eta''} \quad (2.68)$$

The $\tan \delta$ value is very important as it is a measure of viscous and elastic proportions of the material. Especially in polymer solutions, $\tan \delta$ value is used in estimating the sol-to-gel transition point. If $G' > G''$ the solution behaves as a viscoelastic solid or in other words having more gel-like properties whereas when $G'' > G'$, the solution is a viscoelastic liquid that shows liquid-like

properties. Thus, the cross-over point is called the sol-to-gel transition point and $\tan \delta$ is equal to 1. An example frequency sweep analysis is shown in Figure 2.30.

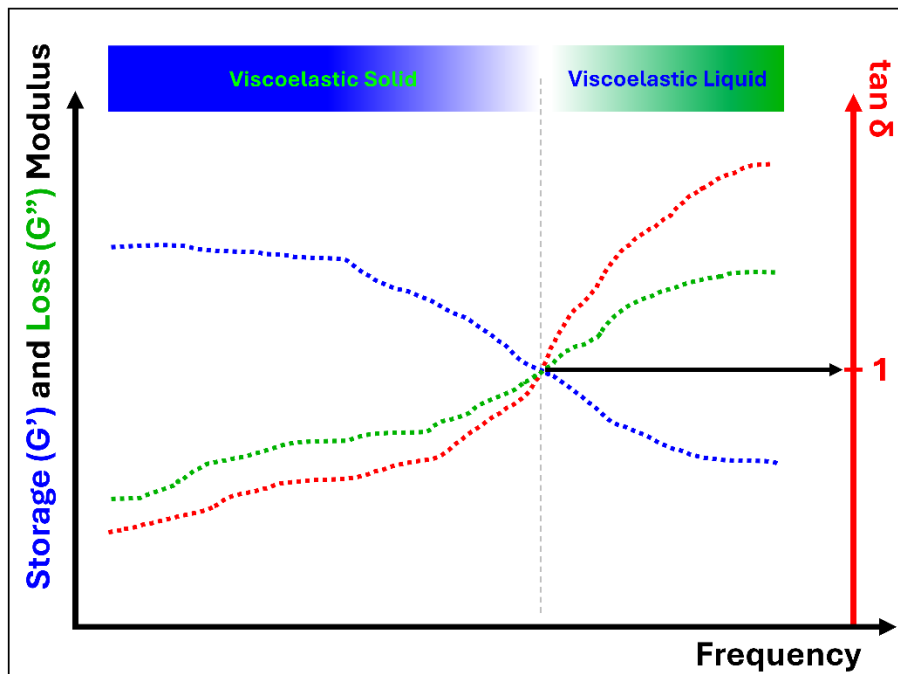


Figure 2.30: Schematic frequency sweep data exhibiting sol-to-gel transition. The storage modulus G' (blue) and the loss modulus G'' (green) cross over during the transition. The loss factor $\tan \delta$ (red) is equal to 1 at the transition point.

2.5.2 Data collection in rheology

Rheometric data are collected using a single or a double headed rheometer using different types of geometries. These geometries act as the top plate shown in Figure 2.27. Commonly used geometries are parallel-plate, cone-plate, and concentric cylinders. These geometries are shown in Figure 2.31.

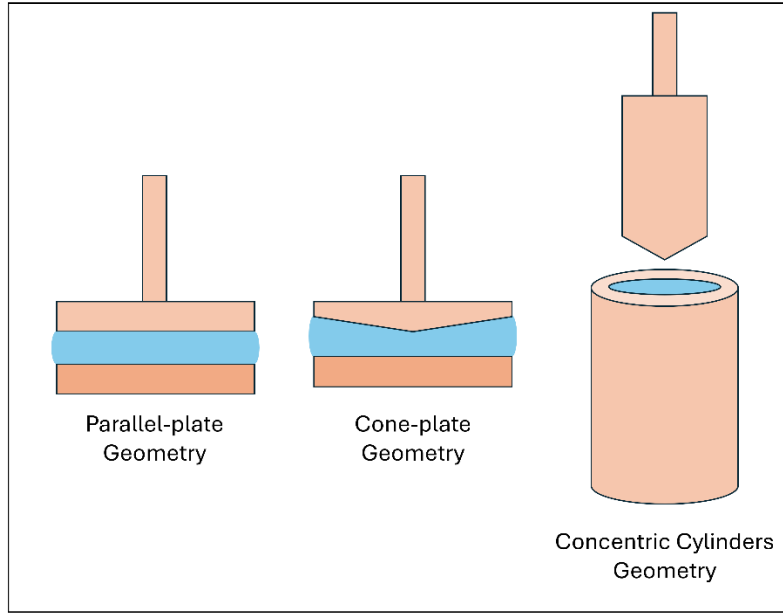


Figure 2.31: Common geometries used in rheometers. The sample is shown in blue.

Each geometry has its unique properties, and a suitable geometry must be chosen according to the desired experiment and the nature of the sample. The parallel-plate geometry and the cone-plate geometry have very similar properties and are often used in many rheometric applications. However, the shear rate is a function of the radial distance r from the center of the geometry to the edge in the parallel plate geometry whereas the cone-plate geometry applies a constant shear rate on the sample at every point. Concentric cylinder geometry is suitable for volatile samples, but it requires a large volume of the sample.

The oscillatory rheometric experiments are often conducted in the linear viscoelastic range of a material. In the linear viscoelastic region, the deformations are sufficiently mild that the perturbations in molecules when they transition from their equilibrium configuration to an

entangled one are negligible [34]. Determination of the linear viscoelastic region of the polymeric material is done by the amplitude sweep mode. In this mode, the strain amplitude is varied while keeping the temperature and the frequency constant. Since the storage modulus is very sensitive to the linear viscoelastic properties, the point where G' decreases by 5% in an amplitude sweep is determined as the end of linear viscoelastic region.

Frequency sweeps are the most common type of rheometric tests. The variation of the storage and the loss moduli of the sample with frequency can be observed by the frequency sweeps. The strain amplitude must be maintained at a constant value that is in the linear viscoelastic region. According to the Cox-Merz rule, the complex viscosity vs. frequency can be regarded as the frequency vs. strain rate [34]. Therefore, the variation of the viscosity of a material (polymer melt/ solution) with the strain rate can also be observed in a frequency sweep test.

In the temperature ramp tests, the temperature of the sample is changed at a constant rate while keeping the frequency and the amplitude (strain) constant. The variation of G' and G'' with temperature is measured in temperature ramps. Time sweeps are another common oscillatory rheological test where the variation of G' and G'' is measured as a function of time.

In the study discussed in Chapter 7, the linear viscoelastic region of the solutions was estimated by analyzing the amplitude sweeps. The frequency sweeps were obtained and then analyzed to determine the shear rates at which the solutions remain to be in the viscoelastic liquid state. Using the temperature ramps, the temperature range where the solutions show viscoelastic liquid

behavior was estimated. The effect of addition of salt into the solutions is determined by the time sweeps.

2.6 Surface wettability of membranes and contact angle

The surface wettability of a filtration membrane is a crucial factor in determining its performance. For example, if a membrane is wetted by water then it is a hydrophilic membrane. Similarly, a hydrophobic membrane repels water and thus it is not wetted by water. Therefore, surface wettability must be considered when choosing a filtration membrane for a desired application.

The surface wettability is caused by the free energy minimization at the interface between the membrane surface and the liquid. Starting from the first law of thermodynamics (equation 2.39) the Gibbs free energy (G) for a surface can be expressed as:

$$dG = \gamma dA \quad (2.69)$$

where γ is the excess surface energy density and A is the area. When a droplet of a liquid is placed on a surface, it takes a shape that minimizes the overall surface energy at all of its interfaces, liquid-solid, solid-vapor, and liquid-vapor as shown in Figure 2.32. The angle θ formed between the liquid-solid interface and the liquid-vapor interface at the foot of the droplet is defined as the contact angle of the droplet. It can be geometrically measured by drawing a tangent along the liquid-vapor interface until it intersects the liquid-solid interface. The Young's equation states that [33]:

$$\gamma_{LV} \cos \theta = \gamma_{SV} - \gamma_{LS} \quad (2.70)$$

where γ denotes the interfacial free energy and the subscripts indicate the interfaces (SV – solid-vapor, LV – liquid-vapor, and LS – liquid-solid). The contact angle is also a good measure of the cohesive and adhesive forces at the interface. If the cohesive forces (inter-molecular forces between the same species of molecules such as water-water or glass-glass) are stronger than the adhesive forces (inter-molecular forces between different species of molecules such as water-glass), then the contact angles take an obtuse value ($\theta > 90^\circ$) and the liquid does not wet the surface. On the other hand, if the adhesive forces are dominant, the contact angle takes an acute value ($\theta < 90^\circ$), and the liquid wets the surface.

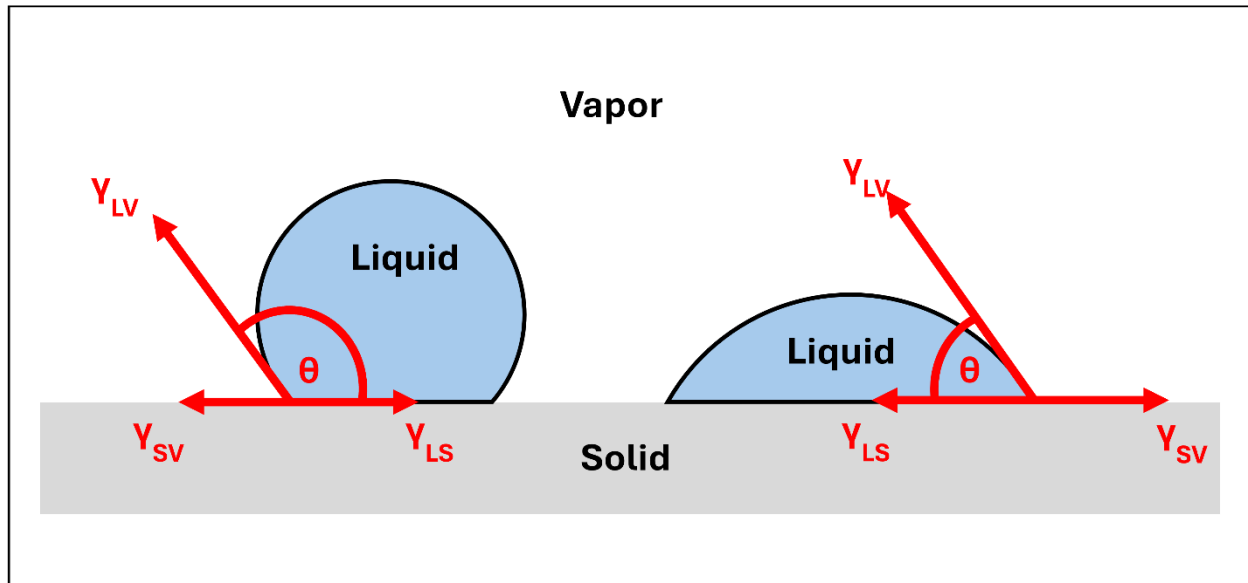


Figure 2.32: Shapes attained by liquid droplets in order to minimize the overall interfacial energy. The contact angle is obtuse when cohesive forces are dominant (left) and acute when adhesive forces are dominant (right). The surface forces between each interface are shown by the red arrows. The subscripts denote the interface (SV – solid-vapor, LV – liquid-vapor, and LS – liquid-solid).

2.7 Polymer electrospinning

Often polymers exist as melt extruded resins in powder, pellets, film or filament form. These can be processed to change the morphology according to the desired application. Polymers in their fibrous form are used in many applications such as wound dressings, tissue engineering, filtration applications, and sensors [10, 36, 37]. Polymers can be fabricated as fibers by numerous methods such as but not limited to wet spinning, dry spinning, melt extrusion, and electrospinning. This section discusses the process of electrospinning.

Electrospinning is an electrohydrodynamic process that elongates a polymer droplet by electric forces to obtain fibers. In electrospinning, first the polymer solution is charged by applying a very high potential (around 5 kV – 30 kV) either by direct contact or charging the extruder. The polymer solution is typically loaded into a syringe and the extruder is the needle connected to the syringe. The syringe is mounted on a pump (electrically driven or pressure driven) to extrude the polymer solution through the needle at a controlled rate. At the tip of the needle the charged polymer solution stretches out as a straight line at first forming a polymer jet due to the high electric field present between the needle tip and the grounded collector plate. The polymer jet undergoes whipping (bending) instabilities and starts to whip forming a helix with an increasing diameter. During flight the polymer jet ejects the solvent and dry fibers are deposited on the collector plate. A typical electrospinning setup [38] is shown in Figure 2.33.

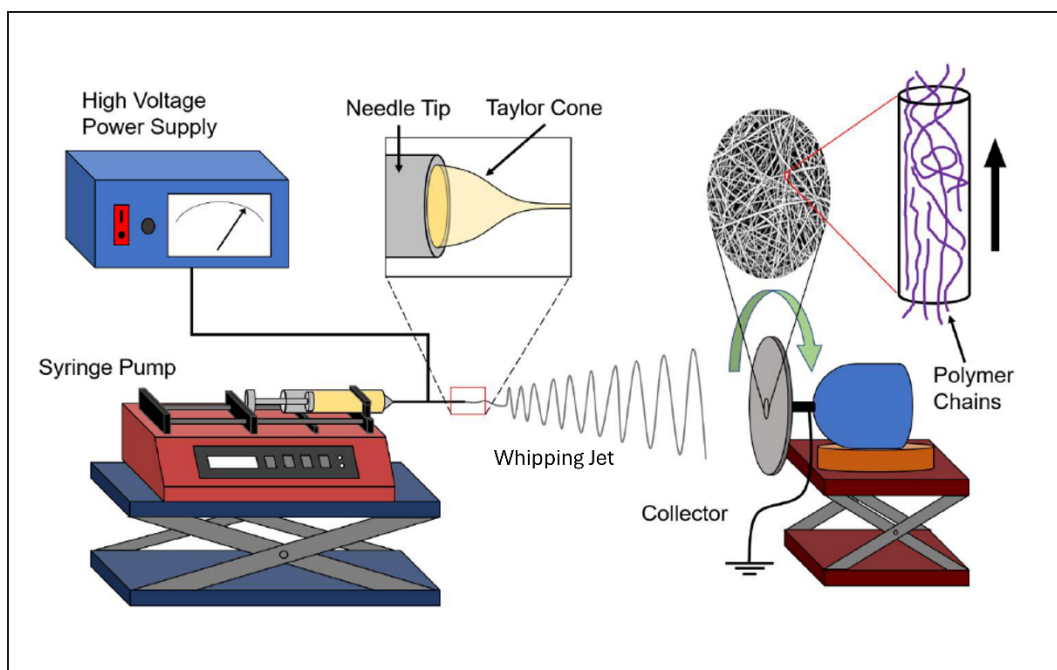


Figure 2.33: Schematic diagram of the electrospinning setup. Image adapted from [38].

If the electric field is not present, then the polymer solution pumped through the needle will simply drip from the tip without forming a jet. Without the high applied voltage, the polymer solution forms a droplet at the tip of the needle when pumped out. To minimize the surface energy the droplet will take a nearly spherical shape. When a high voltage is applied to the needle, the polymer solution gets charged and similar charges will repel and get accumulated in the droplet. These accumulated charges build a high electric repulsive force increasing the electrostatic energy. To minimize the overall effect of the electrostatic and the surface free energies, the droplet deforms into a conical shape which is called the Taylor cone. The critical voltage (V_c) at which the electrostatic pressure overcomes the capillary pressure is given by [39]:

$$V_c^2 = \frac{4H^2}{h^2} \left(\ln \left(\frac{2h}{R} \right) - 1.5 \right) \times (1.3\pi R\gamma)(0.09) \quad (2.71)$$

H and h are the distance from the needle tip to the collector plate (working distance) and the length of the needle, respectively. R is the outer radius of the needle and the γ is the surface tension of the solution. Once this condition is satisfied, a charged polymer jet is ejected from the tip of the Taylor cone accelerating towards the grounded collector plate. Near the tip of the needle, this jet takes the shape of a straight line. Hence, it is called the near-field range. As it moves further away from the needle tip (high potential), it undergoes an axisymmetric (Rayleigh) instability and a non-axisymmetric instability. The viscoelastic properties of the polymer jet should withstand the axisymmetric instability in order to elongate without breaking into droplets. If the polymer jet breaks into droplets, then it is called electrospraying, which is also a highly useful technique to fabricate ultra-thin films. The non-axisymmetric instability makes the jet bend or whip as it propagates through air. This occurs as a result of aerodynamics and the repulsion of the surface charges in the jet. Whipping of the jet significantly reduces its diameter. This is called the thinning

of the jet. Once the solvent is evaporated the jet cannot further reduce its diameter. This terminal diameter (d_t) value of the jet is given by [39]:

$$d_t = \left(\gamma \varepsilon \frac{Q^2}{I^2} \frac{2}{\pi(2\ln\chi-3)} \right)^{1/3} \quad (2.72)$$

γ and ε are the surface tension and the dielectric constant of the polymer solution, respectively. Q is the pump rate, or the deposition rate, and I is the current through the jet. χ is the wavelength of the bending instability. It is proportional to the ratio between the bending perturbation and the jet radius. Finally, the dry fibers are deposited on the collector plate.

The electrospinning process is governed by many parameters. These parameters can be mainly classified into solution parameters, process parameters, and ambient parameters. The solution parameters include conductivity, concentration, viscosity, molecular weight, and surface tension. The process parameters are the applied voltage, deposition rate, needle diameter (gauge), and working distance (needle tip to collector distance). Temperature and relative humidity are the ambient parameters. By tweaking one or many such parameters, the morphology of the deposited fibers can be manipulated. Table 2.1 shows how each parameter could possibly affect the morphology of the deposited fibers [40]. However, electrospinning is a very complicated process in which an accurate prediction of the morphology of the deposited fibers is difficult to make.

The deposited fibers have many novel properties such as the structure of the fibers, pore size and distribution, molecular orientation, and mechanical properties due to their nano-scale dimensions and high surface area to volume ratio [10, 41-43]. The obtained fibers can be further treated to modify them according to the desired use [37].

Table 2.1: Effect of different electrospinning parameters on the deposited fibers

Type	Parameter	Effect
Solution	Concentration (C)	Low C could lead to the formation of beads. High C can lead to needle clogging.
	Molecular weight (M_w)	Low M_w polymer leads to bead formation and high M_w polymer forms fibers with larger diameters.
	Viscosity (η)	Low η can form discontinuous fibers while high η is difficult to pump out.
	Surface tension (γ)	Low γ leads to fiber formation while high γ could introduce instabilities and result in electrospraying
	Conductivity (σ)	High σ leads to small fiber diameters and low σ may cause bead formation.
Process	Applied voltage (V)	V could increase or decrease the fiber diameter and formation of the beads depending on the solution concentration and working distance.
	Deposition rate (Q)	Q should be kept at a minimum. Increased Q could result in an increase in fiber diameter or incomplete drying during flight
	Working distance (WD)	Short WDs can result in wet fibers. Long WDs can lower the electric field ($E = V/WD$ in the simplest form)
Ambient	Temperature (T)	Viscosity of the solution is affected.
	Relative humidity (RH)	At higher RH drying process of the jet may happen quicker and jets can be discharged faster as well

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Chapter 3: Materials, Sample Preparation, & Experimental Techniques

This chapter outlines the experimental techniques employed in the studies presented in this thesis. It begins with a detailed listing of the materials used in each study, followed by a description of how they were prepared for experimentation, either in film or fiber form. The chapter first addresses the microscopic imaging techniques used to observe surface properties. Next, it presents structural analytical techniques, including vibrational and scattering spectroscopic methods, constituting a significant portion of the experimentation. Following this, the chapter discusses thermal analytical methods, which provide critical insights into phase transitions and the kinetics of the materials, as well as how the preparation techniques influenced these characteristics. The rheology testing methods, which were the main focus of the last study, are discussed next. Finally, application-based techniques are described to validate the intended use of the prepared materials.

3.1 Materials

3.1.1 PVDF

As mentioned in Chapter 1, PVDF is used in many industries due to its excellent properties. PVDF in its powder form was used in all the studies presented in this thesis. The breakdown of PVDF used in each study is given below.

For the experiments discussed in Chapter 4 and Chapter 5, PVDF Kynar® (Grade 301F) powder was used. This material was kindly provided by Arkema Inc. (King of Prussia, PA, USA). Kynar® 301F is a finely milled powder with a melting point ranging from 155°C to 165°C. The melt flow index (ASTM D1238) for Kynar® 301F is between 2.0 and 6.0. Additionally, the specific gravity of Kynar® 301F is approximately 1.77 to 1.79 g/mL.

In the study presented in Chapter 7, another powdered form of PVDF was used. PVDF Kynar® 761, also kindly provided by Arkema Inc., has a melt flow index similar to grade 301F, ranging between 2.0 and 6.0. The melting point of grade 761 falls between 165 °C and 172 °C, and its specific gravity is 1.75 g/mL.

3.1.2 *Randomly polymerized amphiphilic co-polymers (r-PACs) - polyampholytes*

The randomly polymerized amphiphilic co-polymers (r-PACs) discussed in Chapter 5 and Chapter 6 were synthesized by Dr. Luca Mazzaferro while he was a graduate student in Professor Ayse Asatekin's group in the Chemical and Biological Engineering department at Tufts University.

Chapter 5 provides a detailed account of the synthesis of r-PACs. The chemical structure of the r-PACs is shown in Figure 3.1.

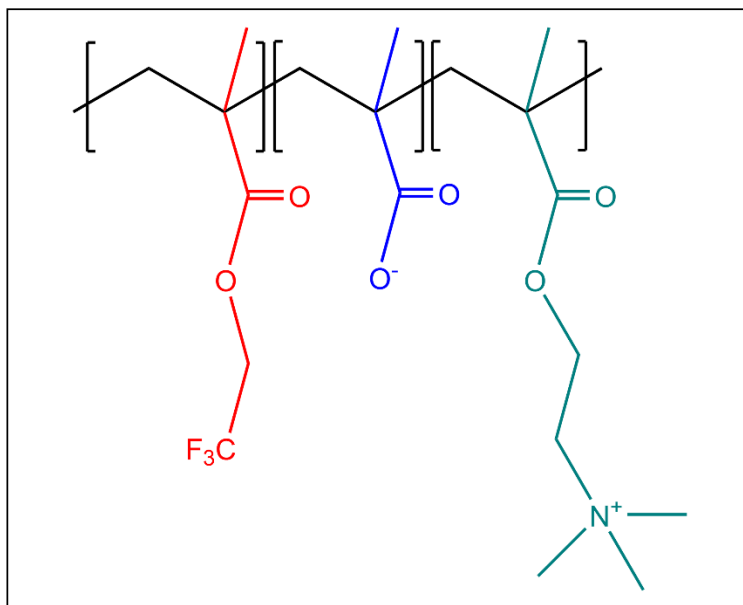


Figure 3.1: Chemical structure of r-PACs. The hydrophobic unit (TFEMA) is shown in red, the negatively charged unit (MAA) is shown in blue, and the positively charged unit (MAETA) is shown in green.

R-PACs belong to a subclass of polyelectrolytes known as polyampholytes. Polyampholytes are charged macromolecules that differ from polyzwitterions—another subclass of polyelectrolytes—because they have positive and negative charged units on separate side groups, rather than both types of charge on the same side group.

In addition to the charged groups, r-PACs also contain a hydrophobic unit, making them terpolymers synthesized from the random copolymerization of three repeat units: methacrylic acid

(MAA), which is negatively charged; [2-(methacryloyloxy)-ethyl]trimethylammonium chloride (MAETA), which is positively charged; and 2,2,2-trifluoroethyl methacrylate (TFEMA), which is hydrophobic. The absence of a specific order among the repeat units during polymerization justifies the term “randomly copolymerized.”

Chapter 6 discusses a study examining the thermal and structural properties of four varieties of r-PACs, which are co-polymerized with different monomer unit compositions. It provides a detailed description of these varieties.

3.2 Sample Preparation

3.2.1 *Solution preparation*

3.2.1.1 *Solution preparation for the estimation of the relative degree of crystallinity of PVDF electrospun and electrosprayed samples*

For the experiment described in Chapter 4, PVDF powder was dissolved in a mixture of N,N-dimethylacetamide (DMAc), and acetone, purchased from Oakwood Chemicals Inc. (Estill, SC, USA). The resulting solutions had a concentration of 15 wt.%, with a solvent composition of DMAc and acetone in a 1:1 volume ratio. Initially, PVDF was dissolved in DMAc while stirring continuously at 60 °C for several hours. Once the PVDF was dissolved entirely, acetone was added to the solution and the temperature was lowered to 30 °C.

3.2.1.2 Solution preparation for the fabrication of fouling-resistant hydrophobic filtration membranes

For the experiment discussed in Chapter 5, both PVDF and r-PAC were dissolved in a mixture of N,N-dimethylformamide (DMF), and methanol (MeOH), which were also purchased from Oakwood Chemicals Inc. PVDF and r-PAC were mixed in different ratios, ensuring that the total polymer concentration was maintained at 10 wt.%. DMF and MeOH were combined at a constant ratio of 13:1 (v/v). Chapter 5 provides a detailed description of the polymer blend ratios.

3.2.1.3 Solution preparation for the study of properties of r-PACs (polyampholytes)

For the experiment discussed in Chapter 6, as received r-PAC variants were dissolved in N,N-dimethylformamide (DMF) to create 10 wt.% solutions for doctor blading.

3.2.1.4 Solution preparation for the estimation of the rheological properties of PVDF solutions prepared with an environmentally friendly green solvent γ -valerolactone

For the rheological experiments discussed in Chapter 7 (time sweeps, amplitude sweeps, frequency sweeps, and temperature ramps), PVDF 761 powder was dissolved in γ -valerolactone (GVL) (biorenewable, purity $\geq 99\%$) (Millipore Sigma, Waltham, MA, USA). For rheological experiments, solutions were prepared at three different concentrations: 10 wt.%, 12.5 wt.%, and 15 wt.% by dissolving PVDF in GVL stirring continuously at 100 °C for few hours. 10 wt.% solutions of PVDF/LiCl (16:1 and 16:2) mixtures were also prepared in the same way. For the electrospinning and doctor-blading experiments, PVDF and PVDF/LiCl mixtures were dissolved

in a mixture of GVL and acetone (GVL/Acetone – 50/50, and 40/60) to obtain 10 wt.% solutions at 100 °C. Chapter 7 provides a comprehensive description of the solvent compositions.

3.2.2 Electrospinning and electrospraying of polymer solutions

A thorough discussion of electrospinning and electrospraying is presented in Chapter 2. The following procedure was followed in all electrospinning experiments discussed in this thesis. The details of the electrospinning parameters for each experiment are provided in their respective chapters.

The electrospinning chamber is a Teflon (PTFE)- lined polymethylmethacrylate (PMMA) box (see Figure 3.2) that prevents the user from electric shock and the polymer jet from turbulent airflow. Its left wall has a long vertical window for the positioning of the needle and its right wall is hinged to its roof such that it could act as a door. The collector plate setup is moved into the chamber through this side by opening the door. It also has a small window cut out from the Teflon lining on the side, so the user can observe the deposition safely without opening the chamber while the high voltage is on.

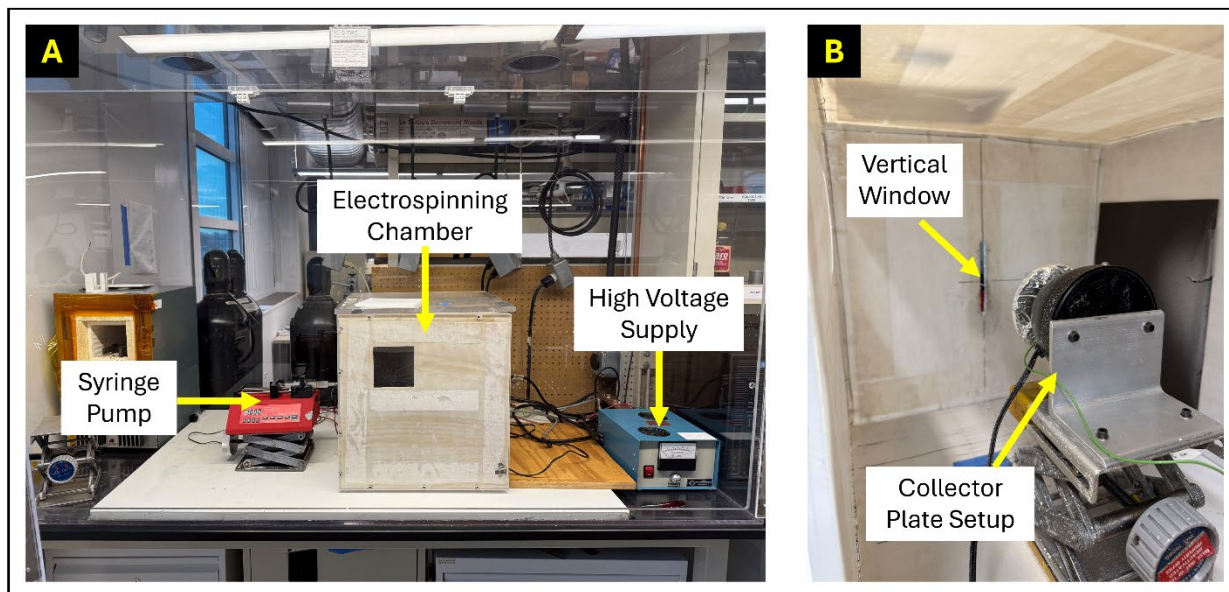


Figure 3.2: A) Complete electrospinning setup; B) Inside of the electrospinning chamber with the collector plate setup as seen from the right side of the chamber.

First, a collector plate of choice was wrapped in very flat, unwrinkled aluminum foil, electrically grounded, and mounted on a rotating motor (rotating at 1 rpm) held on a lab jack. This entire motor and collector plate setup was then moved into the electrospinning chamber. It was positioned at a total distance equal to the working distance plus 1 cm from the opposite wall of the chamber, where the needle would be positioned. Typical working distance values are 15 cm, 22.5 cm, and 30 cm. The different sizes of collector plates are shown in Figure 3.3-A. An aluminum foil wrapped collector plate mounted on the motor with the ground connection is shown in Figure 3.3-B.

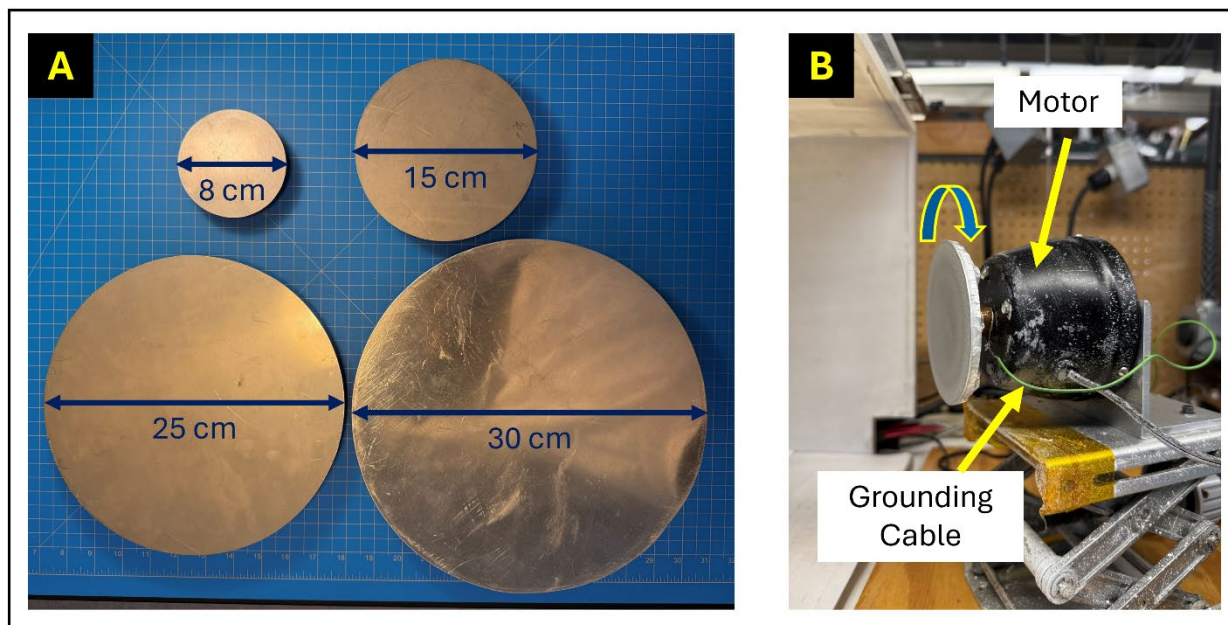


Figure 3.3: A) Collector plates of different sizes without the aluminum foil. The diameter of each plate is indicated by the value below the double-headed arrow on the plates; B) A grounded collector plate wrapped in aluminum foil and mounted on the motor. The curved arrow above the plate shows the rotational direction of the motor.

The prepared polymer solutions were loaded into dissolved gas analysis (DGA) syringes (Cadence Science, Cranston, RI, USA). Depending on the specific requirements, two types of syringes were used. One syringe had an inner diameter of 14.67 mm and a maximum volume of 10 mL, while the other had an inner diameter of 0.84 mm and a maximum volume of 5 mL. Once the polymer solution was loaded into the syringe, a 2-inch long stainless-steel needle (McMaster-Carr, Robbinsville, NJ, USA) was attached using a luer lock connection. As shown in Figure 3.4, the syringe was held upright, allowing air bubbles to rise to the top. Finally, the bubbles were removed by slowly pumping them out.

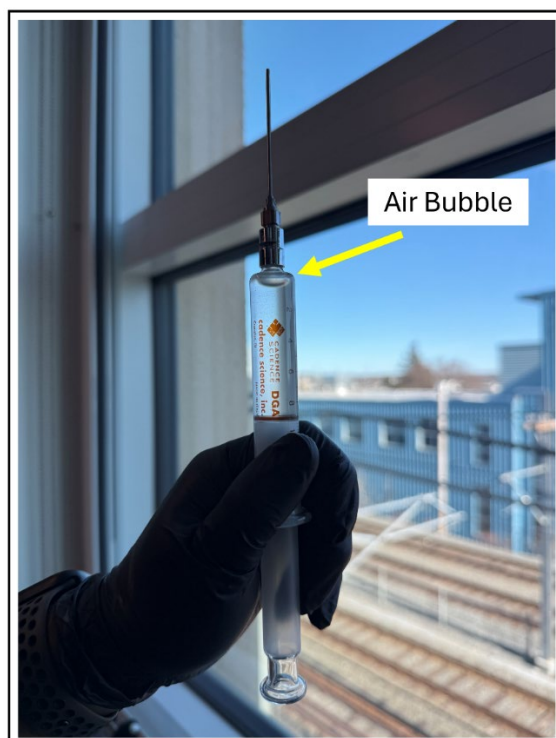


Figure 3.4: A DGA syringe filled with a polymer solution held upright to remove air bubbles. A large air bubble trapped in the syringe is shown.

The loaded syringe with the needle setup is then mounted on a syringe pump system (NE-1000, New Era Pump Systems Inc., Farmingdale, NY, USA) as shown in Figure 3.5. Once all parameters were set, such as the pump rate (deposition rate), syringe diameter, and desired volume to pump, the entire setup was adjusted so that the needle extended 1 cm into the electrospinning chamber. The added 1 cm when positioning the collector plate compensates for the needle extension, ensuring that the distance from the needle tip to the collector plate matches the working distance. Then, the smooth flow of the polymer solution through the needle is confirmed by pumping it a few times at the desired pump rate.

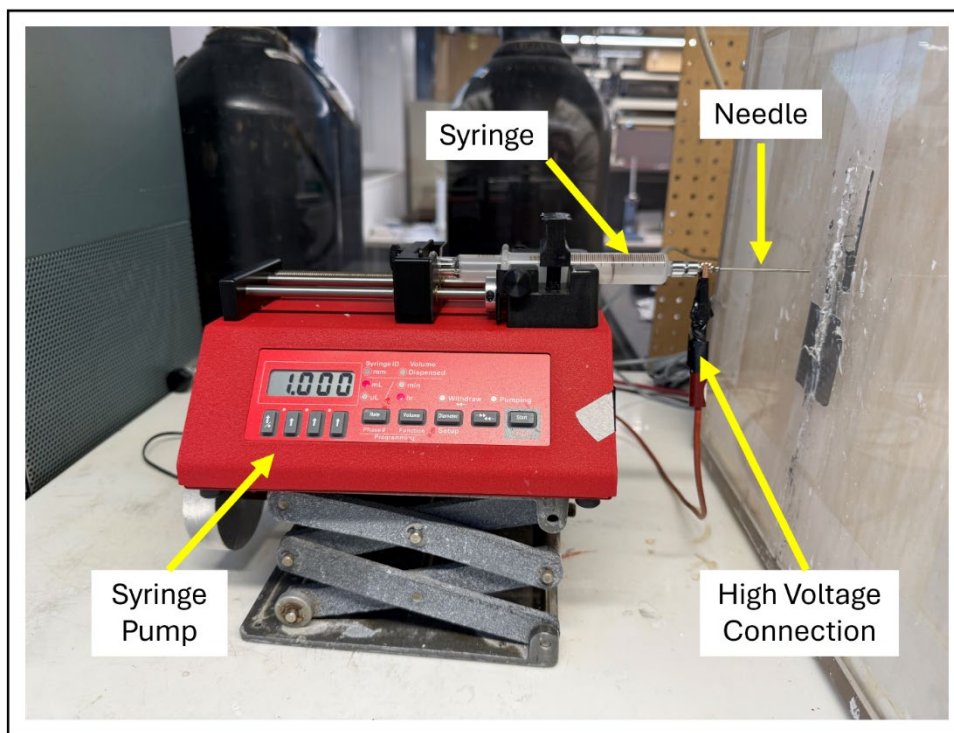


Figure 3.5: The DGA syringe loaded with the polymer solution mounted on the syringe pump. The high voltage is connected to the base of the needle by an alligator clip.

After that, the high-voltage connection is connected to the base of the needle, where it is the strongest, by an alligator clip so that the weight of the clip would not deform the needle which could eventually lead to disruptions in pumping. After turning on the syringe pump, the high voltage is set to the desired value but the supply is still off, and the chamber doors are closed. The high voltage is turned on once all the safety measures are met and the experimental setup is completed. While observing the deposition through the window, a 15-minute test period is initiated to ensure the deposition is satisfactory, and the pumping process is continuous. If the results are satisfactory, the electrospinning process will continue until the desired volume is pumped or the fiber mat has attained the desired thickness.

The thickness of the deposited fiber mat is crucial for successful separation from the aluminum foil. A thicker fiber mat can be easily removed, while a mat that is too thin becomes very difficult to separate. Therefore, maintaining adequate thickness is essential. In most electrospinning experiments, using a smaller collector plate is preferable because its reduced surface area allows a specific volume of polymer to accumulate and form a thicker fiber mat more efficiently. However, if the experimental conditions are too extreme such as formation of hairs along the edge of the collector plate as shown in Figure 3.6, a larger collector plate must be used, the resulting fiber mat may not achieve the same thickness as it would on a smaller plate with the same polymer volume. In such cases, if the fibers cannot be removed, the fiber mats that adhere to the aluminum foil are utilized for further studies. This scenario is illustrated in the experiment discussed in Chapter 5.



Figure 3.6: Accumulation of fibers along the edge of the collector plate. This is caused when the diameter of the cone shaped whipped fiber jet is greater than the diameter of the collector plate.

Image courtesy: Ryo Shimada.

3.2.3 Doctor-blading polymer solutions to obtain thin films

Doctor-blading is a widely used technique for preparing thin films in the materials science field. To begin, the polymer solutions are applied to a clean glass plate, which is secured in place using a vacuum draw down table. A metric film applicator (Gardco, Columbia, MD, USA) is then adjusted by its micrometers to the desired height and dragged to spread the polymer solution evenly across the glass plate, creating a thin film of uniform thickness. The Gardco film applicator measures thickness in mils where,

$$1 \text{ mil} = 0.001 \text{ inches} = 25.4 \mu\text{m} \quad (3.1)$$

The doctor-bladed thin films were either allowed to dry under constant airflow or immersed in a deionized (DI) water bath for non-solvent-induced phase separation (NIPS). In the NIPS method, the solvent and non-solvent must be highly miscible. During this process, the solvent is expelled from the solution, leaving the polymer thin film in the water bath. All solvents and solvent mixtures used in this study, including dimethylacetamide, dimethylformamide, acetone, methanol, and γ -valerolactone, are highly miscible in water. In contrast, PVDF and other polymers used in the study are not soluble in water. When the solvent is removed from the sample by NIPS, it creates pores. Therefore, NIPS is a widely used method for fabricating porous membranes extensively used in filtration applications.

3.2.4 Spin-casting polymer solutions to obtain ultra-thin films

Spin-casting, also known as spin-coating, is a commonly used technique for preparing ultra-thin films. This process typically involves applying a low-concentration solution (around 3 wt.%). A chosen substrate, such as a glass slide or silicon wafer, is mounted on a rotating vacuum base. The rotational speed is set to the desired level, usually around 2000 rpm, and the Headway research grade spin caster (Garland, TX, USA) is turned on.

The low-concentration polymer solution is drop-cast onto the substrate's surface as it spins at a constant high speed. The high centrifugal force generated during spinning drives the solvent out of the solution, resulting in a very thin polymer film coating the substrate. This method is

particularly effective for preparing samples for fast scanning calorimetry, provided that the sample can be separated from the substrate. To improve the separation of the ultra-thin film from the substrate, a sugar solution is spun cast on the substrate before the polymer solution. By immersing the substrate in a DI water bath, the sugar coating between the substrate and the thin film can be dissolved and the thin film could be lifted off from water.

As detailed in Chapter 6, the r-PAC variants were spin-coated onto silicon wafers to measure their contact angle.

3.2.5 Compression molding of as-received polymer

Compression molding is a well-known technique for processing raw polymers into workable samples. The process begins with the raw polymer, which can be in powder or pellet form, being placed between two metal plates covered with Kapton[®] (polyimide) films (American Durafilm, Holliston, MA, USA). This entire polymer-Kapton[®]-metal plate assembly is then inserted into the Carver hydraulic hot press shown in Figure 3.7, where the plates are brought slightly together until resistance is felt, indicating that the metal plates are flattened with the polymer inside.

The plates are heated electrically to around 20 °C above the polymer's melting point. Once the desired temperature is reached, a pressure of 2000 psi is applied by pumping up the lower platen for about two minutes. This process causes the molten polymer to spread evenly between the Kapton[®] covered metal plates. After two minutes, the metal plates are immersed in a room-

temperature water bath. Finally, the solidified polymer sample is retrieved by carefully removing the metal plates and the Kapton[®] films.



Figure 3.7: Hydraulic hot press for compression molding.

3.2.6 *Special solution casting technique to obtain ultra-thin polymer films*

Casting polymer solutions onto a substrate is another method for obtaining thin films. The polymer solution is typically applied to the substrate dropwise and allowed to dry at a specific temperature and under constant airflow. This process generally results in thin films at the micron scale. However, a specialized solution casting method was introduced as an alternative to spin casting. This method is particularly useful for producing ultra-thin films when spun cast films cannot be separated from the substrate.

In this unique method, two glass slides were prepared as substrates by applying a polytetrafluoroethylene (PTFE, or Teflon®) film to one side of each slide using double-sided Scotch tape. Once the PTFE film was securely adhered to the glass slides, a few droplets of the polymer solution were applied to the PTFE side of one slide along its length. The other glass slide was then placed on top of the first slide, sandwiching the solution between the PTFE-coated sides of the two slides. Pressure was applied by hand to spread the solution between the slides evenly, and a weight about 5 kg was placed on top of them to ensure stability. After a few hours, the weight was removed, and one slide was dragged along the other to smear the remaining solution evenly on both slides. Once the moving slide was entirely off the other slide, both were left to dry in the fume hood. The thin coated film is sliced under a microscope to obtain fast scanning calorimetry (FSC) samples. Since almost no substances adhere to PTFE, a suitable sample for FSC can be easily peeled off from the substrate.

3.3 Experimental Approaches

3.3.1 Microscopic Analysis

3.3.1.1 Scanning electron microscopy (SEM)

Scanning electron microscopy is an essential tool for observing the surface morphological properties of materials. Characterizing polymer samples prepared by electrospinning is especially significant, as fiber diameters can be measured. The electrospun fiber samples were cut carefully using a scalpel blade in a rolling motion (Figure 3.8) so that the cut was clean and would not damage the sample. Each sample was cut into a distinct shape so that they were distinguishable. Metal (Al) SEM stubs were prepared by applying conductive double-sided carbon tapes, and the samples were carefully mounted to the stub.

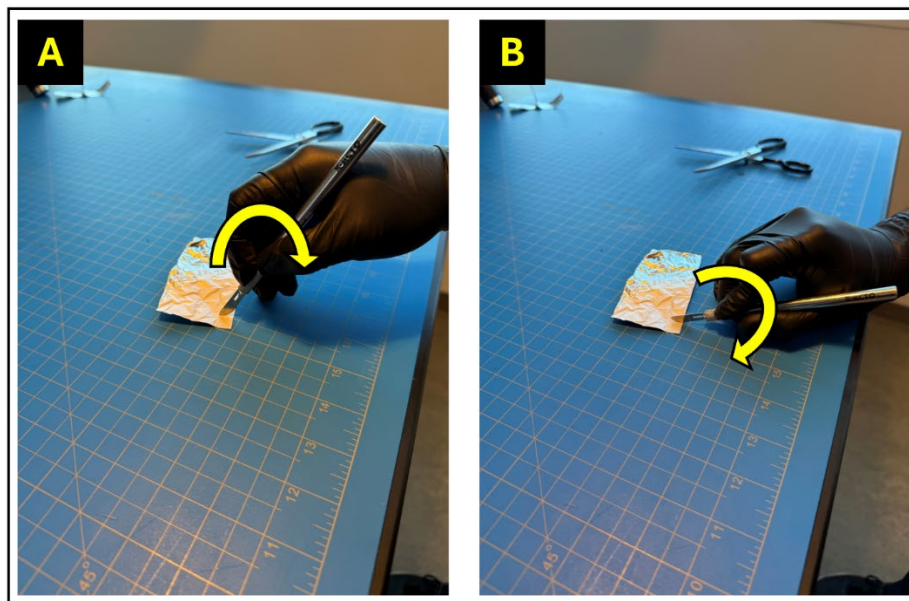


Figure 3.8: The correct sample cutting method in SEM sample preparation. A and B show the rolling motion of the scalpel blade.

The prepared SEM stubs were then transferred to the sputter coater located in the Asatekin Lab in the Department of Chemical and Biological Engineering at Tufts University (Cressington 108 Manual sputter coater, Ted Pella Inc., CA, USA), which is an essential step in SEM characterization. In sputter coating, the samples are coated with a metal alloy to ensure a clean connection between the sample's surface and the conductive carbon tape. This way, the electrons from the SEM electron beam do not accumulate on the fiber surface, resulting in an image with excellent resolution. The accumulation of electrons on the fibers could result in fiber motion; hence, the image will be blurry. The sputter coater uses an alloy made from gold (Au) and palladium (Pd) in a 60:40 ratio of Au to Pd. Pure gold can create large agglomerates on the sample, which may interfere with morphological measurements. In contrast, the Au/Pd alloy provides a uniform coating on the sample, avoiding the formation of large agglomerates.

A Phenom Delphi desktop SEM located in the Kaplan Lab in the Department of Biomedical Engineering at Tufts University (Eindhoven, Netherlands) shown in Figure 3.9-A was used to obtain images of all samples discussed in this thesis. The operating voltage was set to 10 kV for all imaging. The live viewing was set to the best resolution mode, and the high-resolution images were captured at an exposure time of 6 seconds. An SEM image of a fibrous mat obtained from Phenom Delphi is shown in Figure 3.9-B.

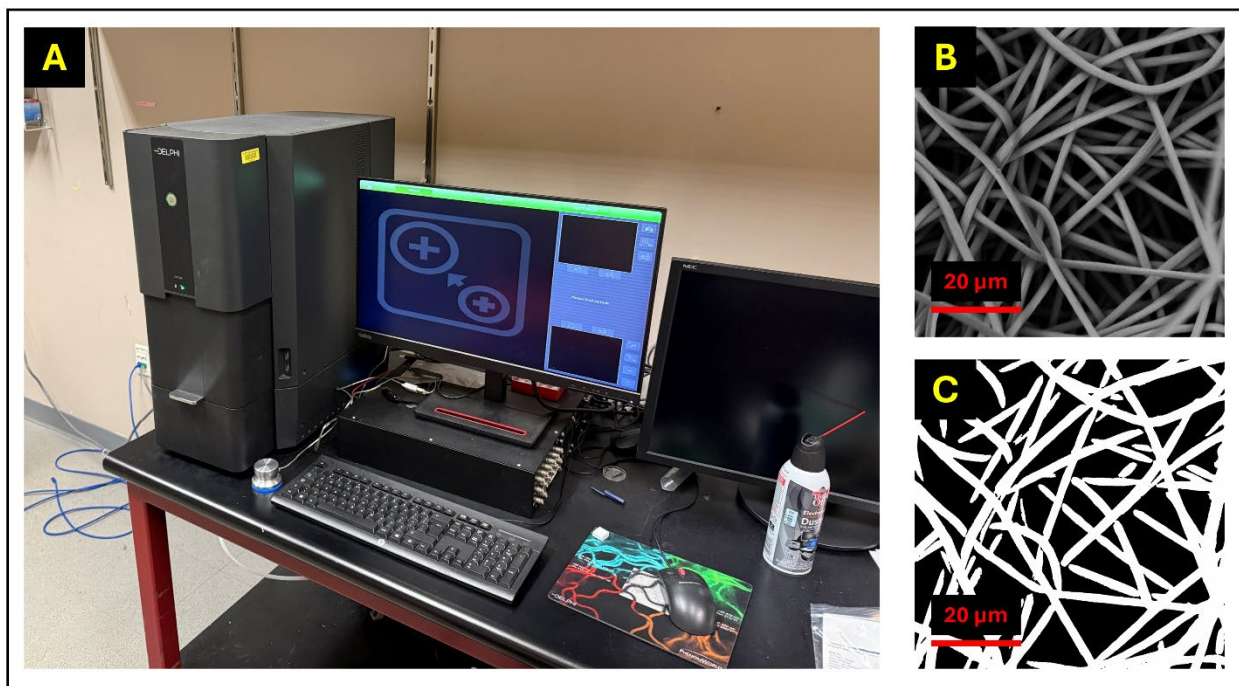


Figure 3.9: A) Phenom Delphi desktop SEM machine; B) An SEM image of a fiber sample; C) Black and white pixelated image of B segmented by DiameterJ plugin of ImageJ software.

The DiameterJ plugin (v1.54m) of ImageJ software was utilized to measure the average diameter of fibers in the electrospun fiber samples. Since SEM (scanning electron microscopy) images are typically in greyscale, it is essential for the fibers to be highly resolved, well-focused, and exhibit high contrast for effective analysis using DiameterJ.

The process begins with DiameterJ segmenting the SEM image into 24 pure black-and-white pixels. The image that best matches the original SEM image is selected from these segments for further analysis. The user must input several parameters into DiameterJ for segmentation, including the width and length of the image in pixels. Cropping coordinates must also be provided

if a specific area of interest in the SEM image is to be analyzed. The same SEM image shown in Figure 3.9.B was segmentalized into a pure black and white pixelated image as shown in Figure 3.9-C.

The user must select a segmentation algorithm for the segmentation process. In all the analyses conducted in this thesis, the "Stat. Region Merged" algorithm and the "Mixed" algorithm were used. To obtain statistics on fiber diameters, the user must input the length of the scale bar in the SEM image in both pixels and actual units. In all the studies presented in this thesis, the SEM images were taken at a magnification of $\times 7500$, with the scale bar measuring 10 μm . To determine the pixel length of the scale bar, the user needs to open the SEM image in ImageJ and employ the rectangle tool. After measuring the scale bar, the DiameterJ analysis is conducted. This analysis provides vital statistics for the fiber mat, including fiber diameter and porosity.

3.3.2 *Structural Analysis*

3.3.2.1 *Fourier-transform infrared spectroscopic analysis (FTIR)*

3.3.2.1.1 *Data collection*

A Jasco 6200 infrared spectrometer located in the Kaplan Lab in the Department of Biomedical Engineering at Tufts University (Tokyo, Japan) equipped with a MIRacle KRS-5 diamond crystal (Pike Technologies, Madison, WI, USA) (Figure 3.10-A,B) in the attenuated total reflection (ATR) mode was used to obtain FTIR spectra of all samples discussed in this thesis. Samples were cut into pieces that were relatively larger than the size of the exposed crystal for the FTIR analysis. Initially, a background scan was collected using the test parameters: data acquisition range of 1800

cm^{-1} to 400 cm^{-1} , a resolution of 4 cm^{-1} , and the number of scans set to 256 to remove any effect from background radiation. Then, the sample data were collected immediately using the same test parameters.

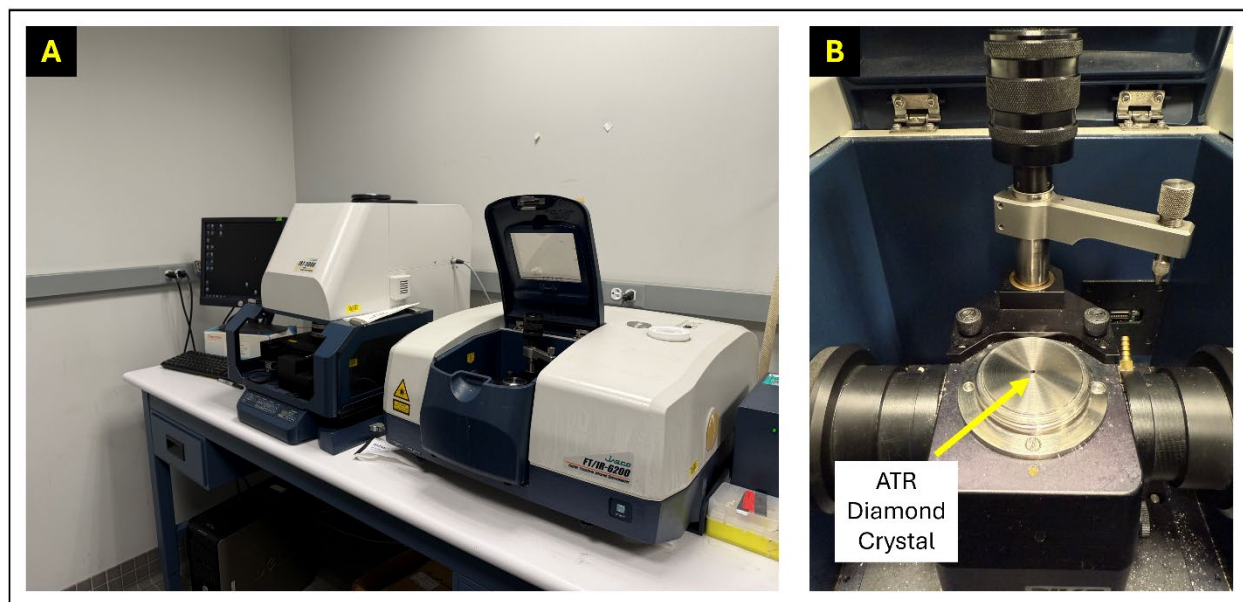


Figure 3.10: A) Jasco 6200 FTIR spectrometer; B) ATR diamond crystal used to obtain spectra.

3.3.2.1.2 Data analysis

The software Spectra Manager (v2.0, Jasco Corporation) was used for post-processing acquired data. First, the spectrum was baseline-corrected. If Fourier self-deconvolution is required, the spectrum is truncated to the desired range, and then deconvolution is performed. The highest possible integer value allowed by the software is used as the entire width of half maximum in deconvolution to resolve the convoluted peak in the spectrum to a minimum number of deconvoluted peaks. The data files were then exported as ASCII (txt) files for further analysis, such as normalization and plotting in MATLAB using customized codes.

3.3.2.2 *Wide angle X-ray scattering (WAXS)*

One-dimensional Wide-Angle X-ray Scattering (WAXS) data for all samples were collected using a Philips PW 1830 X-ray generator (Panalytical, Almelo, Netherlands) (shown in Figure 3.11) with a Cu K α wavelength ($\lambda = 0.154$ nm). The generator operated at 30 kV and 55 mA at room temperature. All samples were sufficiently large, ensuring only the sample was exposed to the X-ray beam. The samples were either mounted on aluminum (Al) holders or single-crystal <100> silicon (Si) wafers (Ted Pella, Redding, CA, USA). Data were collected by scanning from 5° to 40° or 45° or 60° with a step scan interval of 0.02° steps with a collection time of 1 second per step. Background scans were collected before analyzing the samples by scanning the substrates. These scans were then subtracted from the sample data to eliminate background effects. The collected data were subsequently exported as ASCII files for further analysis in MATLAB[™]. The total crystalline fraction of the samples was estimated using the deconvolution steps discussed in Chapter 2.

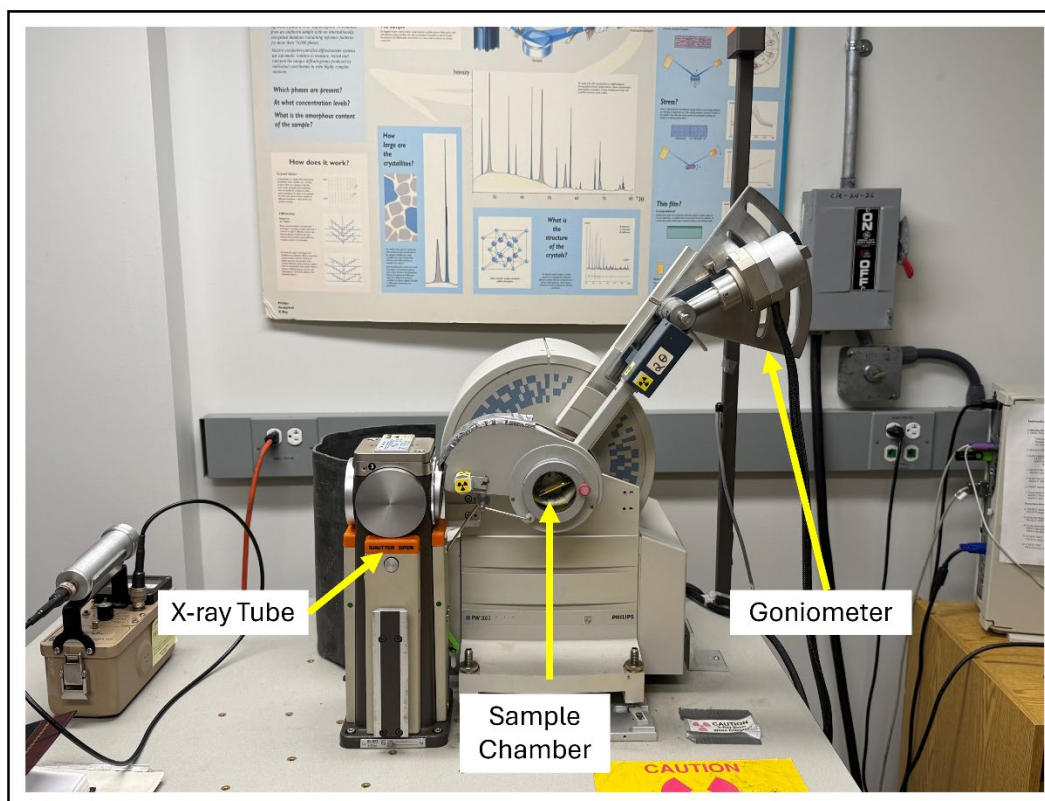


Figure 3.11: Philips PW 1830 X-ray generator and diffractometer.

3.3.3 Thermal Analysis

3.3.3.1 Thermogravimetric analysis (TGA)

A thermogravimetric analyzer (TGA) from TA Instruments (New Castle, DE, USA) Q500 (Figure 3.12-A) was utilized to conduct TGA analyses on all samples presented in this thesis. The furnace is purged with protective nitrogen (N_2) gas at a flow rate of 50 mL/min. A zoomed in image of the furnace area with the platinum basket and the thermocouple is shown in Figure 3.12-B.

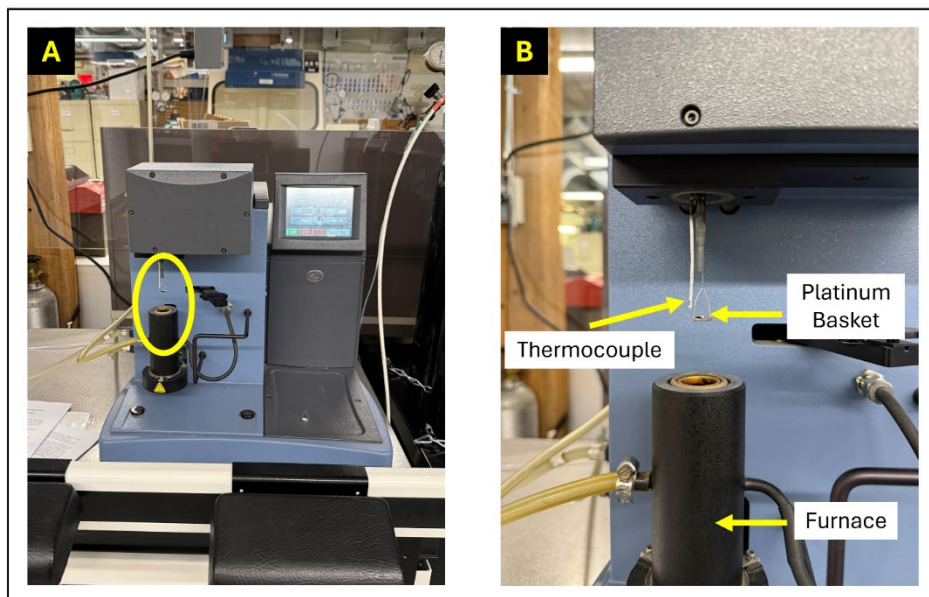


Figure 3.12: A) TA Instruments Q500 TGA ; B) Enlarged image of the yellow circled area in A.

The operating temperature range for the samples varied according to their nature. Free-standing samples were heated from 50 °C to 1000 °C at 10 °C/min or 20 °C/min. Samples adhered to aluminum foil were heated from 50 °C to 600 °C at the same rates. The typical masses of the samples ranged from 3 g to 10 g.

3.3.3.2 *Differential scanning calorimetry (DSC)*

All experiments discussed in this thesis were analyzed using a TA Instruments Q100 differential scanning calorimeter (Figure 3.13-A). The heating chamber of the DSC is purged with nitrogen (N₂) gas at a flow rate of 50 mL/min. The thin film samples were cut into pieces that fit into aluminum DSC pans, as shown in the figure. The fiber samples for the DSC experiments were prepared by cutting a long, thin strip from the fiber mat and rolling it up, holding one end with

tweezers. This technique, known as the free-end method [1], ensures that the sample has an appropriate mass for DSC analysis and maintains good thermal contact with the aluminum pan. This results in data with a high signal-to-noise ratio. Additionally, another aluminum pan with a similar mass to the sample's (within ± 0.01 mg) was prepared to serve as the reference. The mass of the samples typically ranged between 3 g and 10 g. The inside of the DSC furnace is shown in Figure 3.13-B.

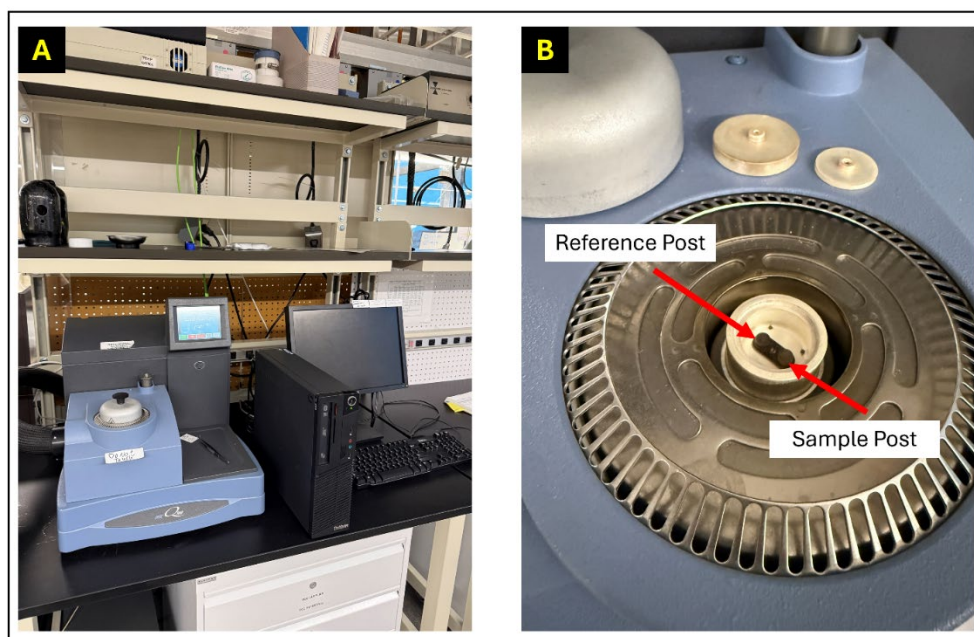


Figure 3.13: TA Instruments Q100 DSC; B) An image of the inside of the DSC furnace. The posts where the reference and the sample are placed are indicated.

The DSC scans for all PVDF samples were conducted by heating at a constant rate of 10 °C/min. The first heating involved equilibrating the sample at -80 °C before gradually raising the temperature to 220 °C. This initial heating provides crucial information about the sample's thermal history. As the material undergoes crystal melting and transitions into its liquid state, that thermal

history is erased, and a new one is established during cooling. Therefore, subsequent heating scans will give general insights about the material itself, depending on the rate at which the sample was cooled previously. The subsequent heating scans were performed from 0 °C to 220 °C. After every heating scan, all samples were cooled from 220 °C to 0 °C at the same rate of 10 °C/min.

3.3.3.3 *Heat treatment for degradation tests*

For the experiment discussed in Chapter 6, r-PAC samples were doctor-bladed on glass slides and heated to temperatures at which a stable mass value is observed after a degradation process as seen in their TGA thermographs using a hot stage (Mettler-Toledo, Greifensee, Switzerland). The samples were heated at 20 °C/min up to the desired temperature value and then immediately cooled under ambient conditions.

3.3.3.4 *Fast scanning calorimetry (FSC)*

Differential fast scanning calorimetry was performed on r-PAC samples using a Flash DSC 1 (Mettler-Toledo, Greifensee, Switzerland) at Pennsylvania State University, Behrend. We thank Prof. Alicyn Rhoades and Dr. Xiaoshi Zhang for their generous support in making it available. All r-PAC variant samples were prepared using the method described in section 3.2.6 and were mounted on empty Mettler Toledo UFS2 chips (Figure 3.14-A,B), which were conditioned and calibrated according to the manufacturer's recommended procedures. An enlarged image of the sensor area on the sample side (shown in red in Figure 3.14-B) of the chip is shown in Figure 3.14-C. The samples underwent cooling and heating cycles from -90 °C to 300 °C at customized heating and cooling rates ranging from 4000 K/s to 30 K/s (shown in Figure 3.15). Before scanning the

samples, background scans were conducted in the same temperature range using empty sensors and the same procedures. These background scans were then subtracted from the sample scans to eliminate any effects caused by the empty sensors. The heat flow curves were subsequently symmetry-corrected (as described in section 2.3.3.3) to improve the data quality.

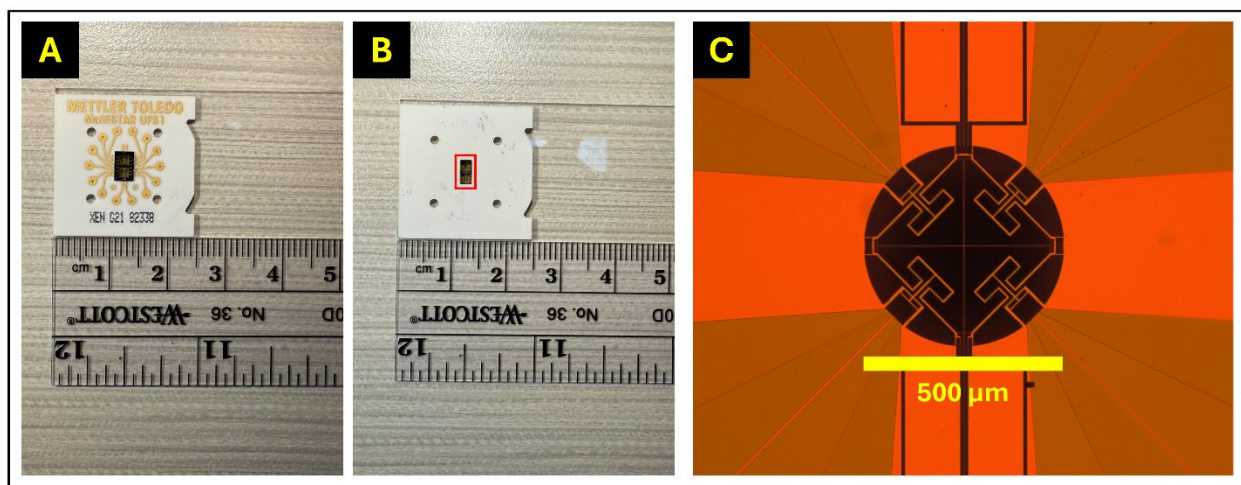


Figure 3.14: Mettler Toledo UFS2 fast scanning chip. A) Side with the electronic leads; B) sensor side (red square); C) enlarged image of the FSC sensor on the sample side.

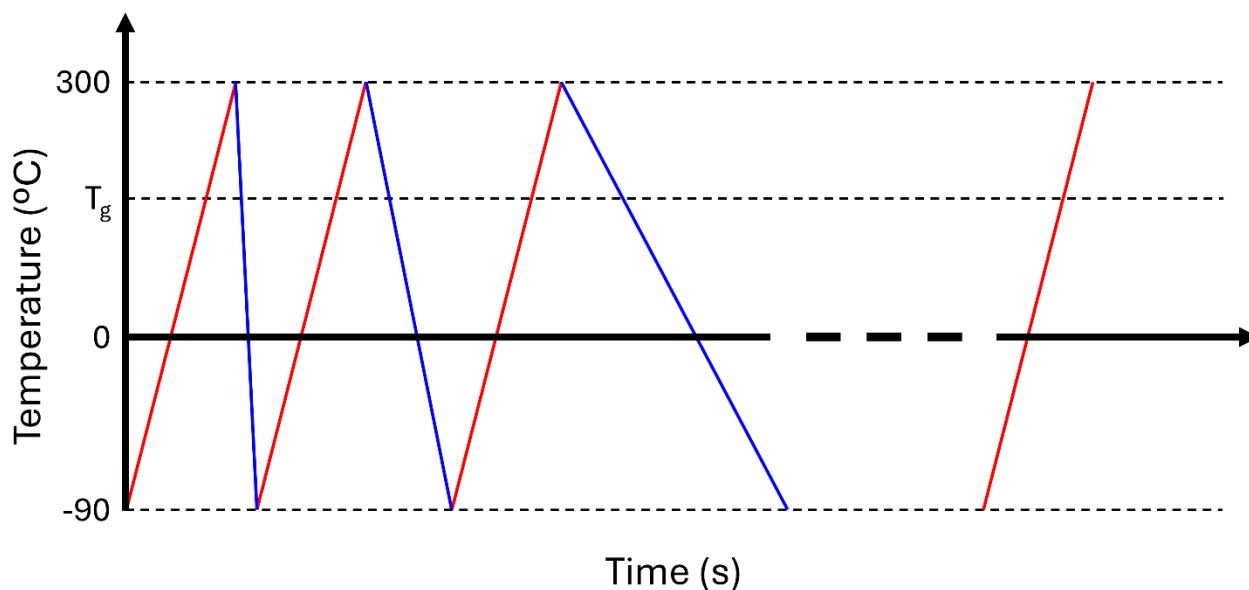


Figure 3.15: Schematic temperature vs. time variation of the fast-scanning calorimetry program for fictive temperature measurements of r-PAC variants. The heating rate (red line) is set to 2000 K/s while the cooling rates (blue lines) are varied from 4000 K/s down to 30 K/s.

3.3.4 Performance Analysis

3.3.4.1 Contact angle measurements

The electrospun fiber mats and thin films prepared in the experiments in Chapters 5 and 6 are tested for their surface wettability with water and an oil-like hydrocarbon called dodecane by the sessile drop contact angle measurements using a Ramé-Hart (Succasunna, NJ, USA) contact angle (CA) goniometer in the Kaplan Lab in the Department of Biomedical Engineering at Tufts University (Figure 3.16-A). The samples were prepared for contact angle measurements by spin casting or taping the fiber mats on glass slides with double-sided adhesive tape. Then, the sample was placed on the sample stage of the CA goniometer, and a known volume of water or dodecane was placed on it as a droplet as shown in Figure 3.16-B. The droplet is observed through the camera

as a dark, contrasting object in the bright field created by the lamp (see Figure 3.16-C). Then, the droplet image is captured by the camera and analyzed on the computer screen, and the contact angle is measured using the software. This experiment was performed for five droplets of each liquid for every sample, and the average value was taken as the contact angle.

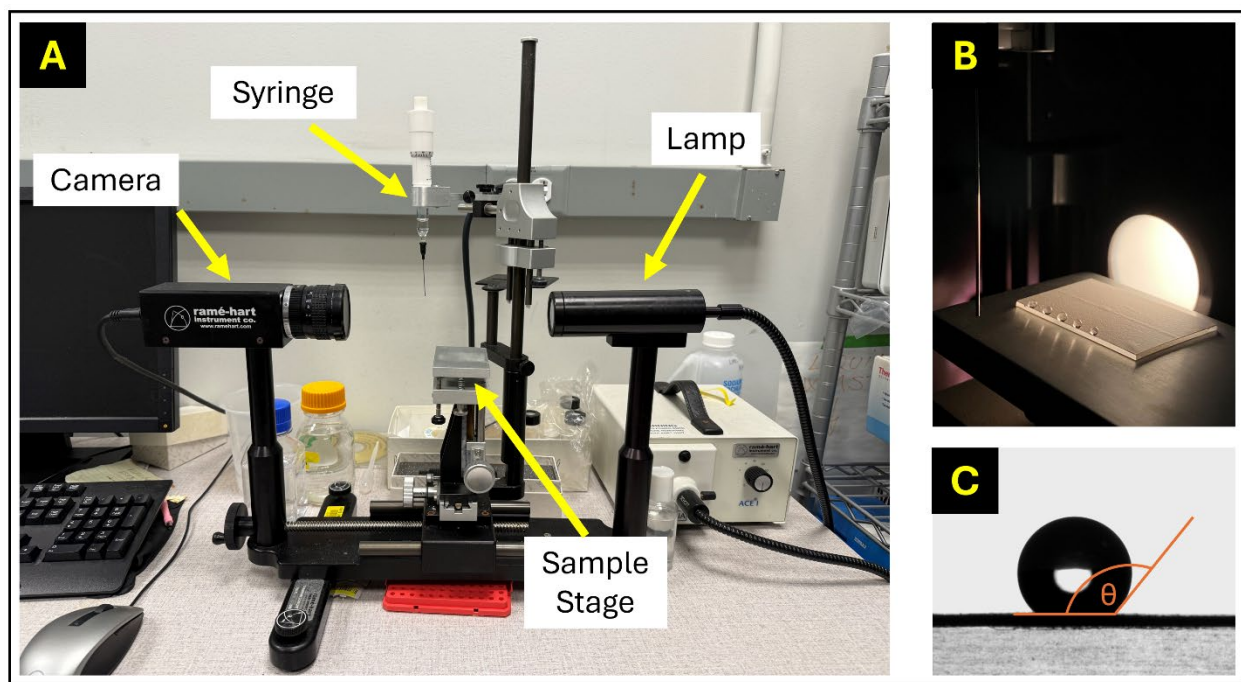


Figure 3.16: A) Ramé-Hart contact angle goniometer; B) Five water droplets on a fibrous mat adhered to a glass slide; C) A water droplet as seen through the camera. The contact angle of water with the sample surface is shown by θ .

3.3.5 Rheological Analysis

All rheological data in the study discussed in Chapter 7 were obtained using a DHR-20 single-head rotational hybrid rheometer in the Kaplan Lab in the Department of Biomedical Engineering at Tufts University (TA Instruments, New Castle, DE, USA) shown in Figure 3.17-A. Oscillatory

rheological tests were conducted on PVDF solutions of three concentrations prepared as described in 3.2.1.4, utilizing a hard-anodized aluminum parallel plate geometry with a diameter of 40 mm. First, about 2 mL of the PVDF solution at 100 °C was poured onto the bottom Peltier plate. Then, the parallel plate geometry was carefully lowered manually from its loading gap of 4.5 cm to its trim gap of 1.05 mm, ensuring that no air bubbles were trapped in the solution. Then, the gap was set to the operational gap, which is 1 mm. The excess solution was meticulously removed with a PTFE tool blade. The setup ready for experiment is shown in Figure 3.17-B.

All oscillatory rheological tests were performed in the linear viscoelastic region of the solutions. Frequency sweeps and temperature ramps were performed to understand the flow properties of the solutions. Frequency sweeps were performed on all solutions at three different temperatures 25 °C, 45 °C, and 65 °C. The solutions were stabilized for 60 minutes at the temperatures before performing the frequency sweeps. The frequency varied from 500 rad/s to 0.1 rad/s at a strain amplitude of 1%. In temperature ramps, PVDF solutions were heated and cooled between 25 °C and 80 °C at 5 °C/min while oscillating at 10 rad/s and with a strain of 1%. The sample was initially kept at 25 °C for 60 minutes before heating, and as the temperature reached 80 °C, the cooling cycle was initiated immediately to avoid any evaporation.

To test the effect of the addition of salt, time sweeps were performed at 25 °C on three different solutions which were prepared as described in section. The hot solutions were loaded on the Peltier plate and the parallel plate geometry was set up as described above. The time sweeps were performed for 4 hours at 1% strain and 10 rad/s frequency.

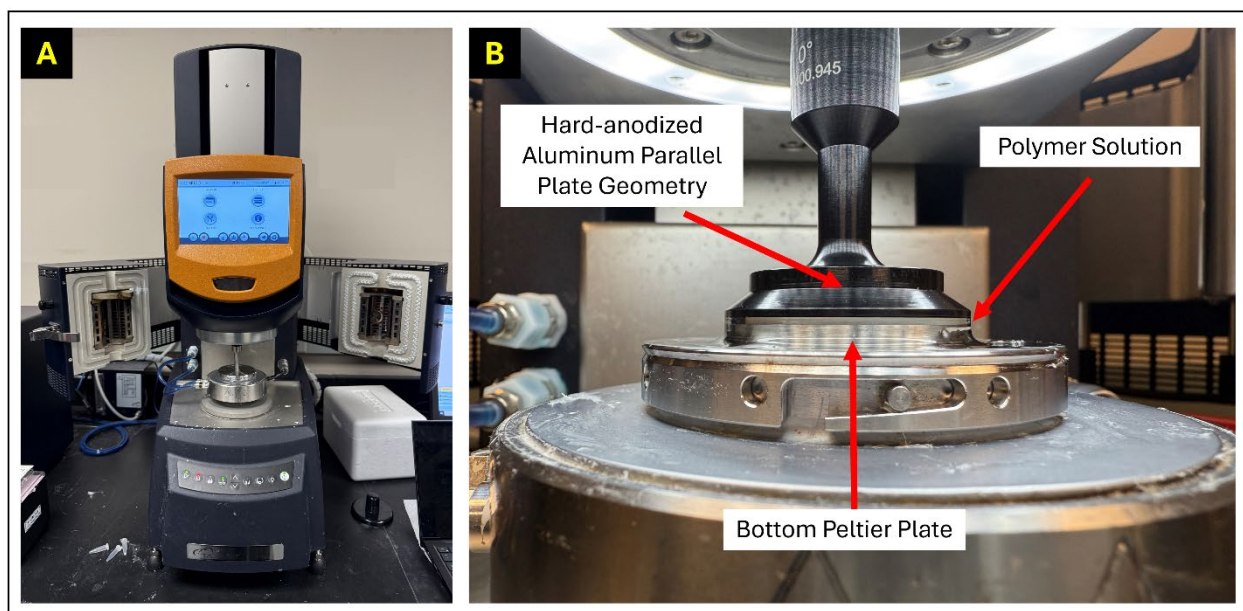


Figure 3.17: A) TA Instruments DHR 20 Rheometer; B) Polymer solution trapped between the parallel plate geometry (hard-anodized) and the Peltier plate. The gap between the parallel plate geometry and the Peltier plate is set to the geometry gap of the test (1 mm).

3.4 References

1. Ma, Q., Pyda, M., Mao, B., and Cebe, P., *Relationship between the Rigid Amorphous Phase and Mesophase in Electrospun Fibers*. Polymer, 2013. **54**(10): p. 2544-2554.

**Chapter 4: Quantitative analysis of polar crystalline fractions in poly(vinylidene fluoride)
electrospun fibers and electrosprayed films**

This section is based on the following publication

Anuja S. Jayasekara, Peggy Cebe, Quantitative analysis of polar crystalline fractions in poly(vinylidene fluoride) electrospun fibers and electrosprayed films, Polymer, Volume 281, 2023, 126140, ISSN 0032-3861, <https://doi.org/10.1016/j.polymer.2023.126140>.

4.1 Introduction

Electrospinning is a widely implemented technique to obtain nano-scale polymer fibers [1-3]. Electrospinning is considered as an effective technique to obtain polar β -phase crystals in poly(vinylidene fluoride) (PVDF) [4, 5]. In electrospinning, the polymer solution is subjected to both a shear force by the flow of solution through a capillary and a high Coulombic force by the high electric field applied [6]. These forces cause the molecular chain axis of PVDF to align preferentially with the fiber axis resulting in formation of the β crystallographic form [6]. During the electrospinning process, if the polymer jet undergoes Rayleigh-Plateau instabilities and breaks into droplets, the deposition is called electrospraying [7]. Several studies have shown that β -phase crystals can be obtained by either electrospraying PVDF solutions or by electrospinning [8, 9]. Obtaining solely β -phase crystals in PVDF is extremely difficult because the other two common crystalline morphologies, non-polar α -phase and polar γ -phase, often co-exist with β -phase crystals [1, 10]. However, the presence of γ -phase in electrospun fibers has been widely overlooked even though its characteristic features can be observed in both wide angle X-ray scattering and the vibrational spectrum of PVDF [11-13]. Since the piezoelectric effects in PVDF are governed by the polar crystal phases [10, 14], quantitative analysis of their crystalline fraction is very important.

Identifying the presence of a particular crystalline morphology in a polymer can be done by observing and analyzing features in wide-angle X-ray scattering (WAXS) intensity plots and Fourier-transform infrared (FTIR) absorbance spectra. Since each crystallographic phase has different and distinct d-spacings, they scatter X-rays at unique scattering angles. This allows one to assign distinct peaks corresponding to each crystallographic phase. Due to the distinct chain

packing in each crystal phase, some molecular vibrations in the crystals make unique absorption peaks in their FTIR spectra as well. PVDF β -phase crystals have an all-trans (TTTT) zig-zag chain conformation [1, 15, 16] and PVDF γ -phase crystals have TTTGTTTG' chain conformation [1, 16, 17]. Because of the repetitive trans bond structure in both types of polar crystals, some features in WAXS intensity plots and FTIR spectra of β -PVDF and γ -PVDF have strong overlap [1, 18].

Difficulties of infrared absorbance band overlap can be obviated by use of Fourier Self-Deconvolution (FSD). Deconvoluting a spectrum results in a much-resolved version of itself making it convenient to identify peaks corresponding to a particular crystalline phase. FSD has been used by our group to assess the fraction of protein secondary structures in silk fibroin, by analysis of the Amide I spectral region. FSD enhances the resolution of an IR spectral band by synthetically narrowing the band in the phase space of the interferogram, and by inverse Fourier transform returns a better resolved peak in absorbance space [19]. In the case of the PVDF, the electro-active peak at 840 cm^{-1} results from both β - and γ -phase vibrations which have close wavenumbers [20] contributing to the broad and complex shape of this vibration band. FSD allows the relative fractions of β - and γ -phases to be estimated reliably. To our knowledge, FSD has not been applied to estimate the different fractions of the electro-active phases of PVDF before.

In this study, electrospun fiber mats and electrosprayed non-fibrous mat prepared from N,N-dimethylacetamide and acetone solutions were investigated and compared with melt-crystallized PVDF samples. The focus of this study is the application of FSD to determine the relative fractions of β - and γ -phase PVDF crystals in different samples containing both crystal phases. Hence,

optimization of fibers for more β -phase crystals in electrospinning is not discussed in this manuscript, but details can be found in reference [5]. Mats were characterized using WAXS, FTIR, scanning electron microscopy (SEM), and differential scanning calorimetry (DSC). By analyzing WAXS intensity and FSD-FTIR spectra, the relative and absolute crystalline fractions of both β - and γ -phases of PVDF were determined.

4.2 Experimental

4.2.1 *Materials*

The solutions were prepared as described in section 3.2.1.1. For comparison, a bulk film was created using compression molding at 2000 psi and 200°C.

4.2.2 *Characterization*

4.2.2.1 *SEM analysis*

Prepared polymer solutions were subjected to electrospinning and electrospraying under an applied voltage of 20 kV as discussed in section 3.2.2. The PVDF solutions were drawn into a glass syringe of inner diameter 14.67 mm. The syringe was mounted on a syringe pump system and an 18-gauge (inner diameter 0.84 mm) needle was attached to it. The flow rate was adjusted to 2 mL/hr and an aluminum foil covered collector plate (10 cm in diameter) rotating at 1 rpm was placed 15 cm from the needle tip. A thick electrosprayed film was formed at the center of the collector plate when a needle with a reduced diameter was attached. The electrospinning processing parameters were

chosen based on the findings of the previous collaborative work [5]. The electrospun fiber mat and electrosprayed non-fibrous mat are shown in Figure 4.1-A,B, respectively.

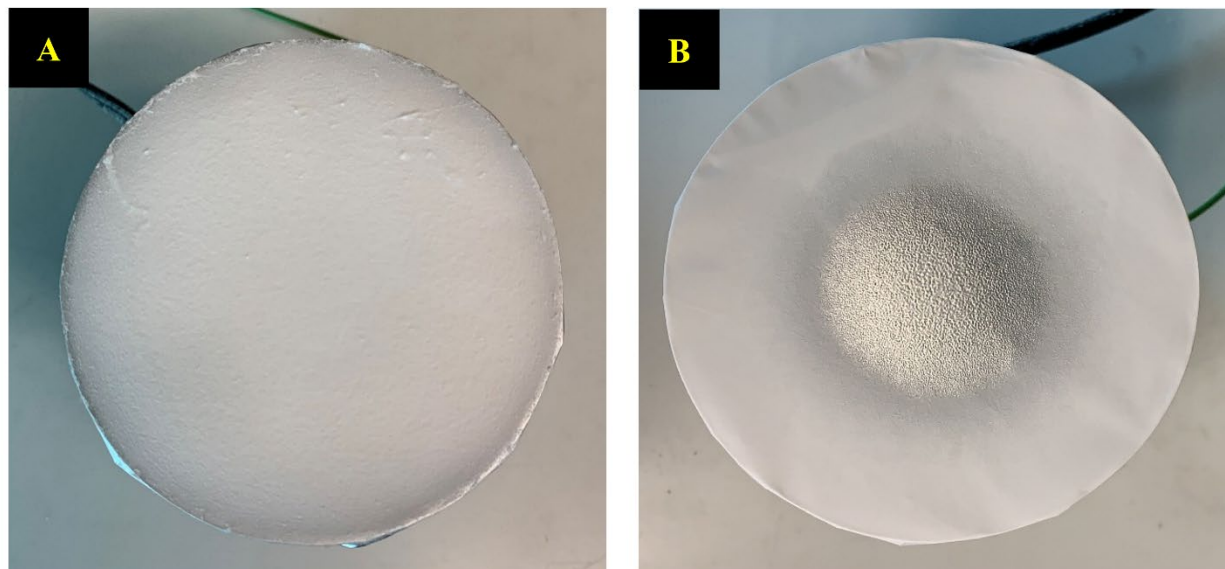


Figure 4.1: A) Electrospun fiber mat; B) electrosprayed mat shown on the collector plate immediately after deposition. The central part of B has a thick non-fibrous (electrosprayed) layer of PVDF surrounded by a fibrous region. Samples from the circular collector plate were about 10 cm in diameter.

4.2.2.2 *Structural analysis*

4.2.2.2.1 *FTIR analysis*

FTIR data were collected as mentioned in section 3.3.2.1. Fourier self-deconvolution was performed according to section 3.3.2.1.2.

Fourier self-deconvolution (FSD) was performed after background subtraction on the 840 cm^{-1} peak using Jasco Spectra Analysis software. FSD is a specific case of Fourier deconvolution (FD) where the peak convolution due to homogeneous and inhomogeneous broadening is fully inverted [1]. An IR spectrum $E(\nu)$ of one single band can be written as [1]:

$$E(\nu) = A\delta(\nu - \nu_0) \otimes L(\nu) \otimes R(\nu) \quad (4.1)$$

where A is the area of the band, $\delta(\nu - \nu_0)$ is a delta function centered at ν_0 , $L(\nu)$ is the line shape function of the band due to homogeneous and inhomogeneous broadening, and $R(\nu)$ is the line shape function of the band due to instrument broadening. The convolution operator is shown by $\otimes$ symbol. FSD is a different technique of peak deconvolution compared to conventional mathematical deconvolution. In mathematical peak deconvolution, which can be performed using various analytical software such as OriginPro or WiRE v.5, a curve is fitted by assuming a curve shape (either Gaussian or Lorentzian) and number of such peaks to be used in the fitting of a complex peak. This is also considered as a “deconvolution” because a single complex peak can be fitted by a summation of individual peaks. However, according to Oxtoby [2], peaks in vibrational spectra undergo homogeneous and inhomogeneous broadening. In FSD, the vibrational peaks in an FTIR spectrum are synthetically narrowed by taking out the homogeneous and inhomogeneous broadening factors as explained below.

Since instrumental broadening $R(\nu)$ has a smaller effect than the homogeneous and inhomogeneous broadening, $L(\nu)$, the band can be narrowed significantly by inverting $L(\nu)$ [1, 3]. To perform the deconvolution of $L(\nu)$, the spectrum needs to be inverse Fourier-transformed ($\mathcal{F}^{-1}$) into its interferogram $I(x)$, using:

$$I(x) = \mathfrak{F}^{-1}E(v) = \mathfrak{F}^{-1}(A\delta(v - v_0) \otimes L(v) \otimes R(v)) = \mathfrak{F}^{-1}(A\delta(v - v_0))L(x)R(x) \quad (4.2)$$

$L(x)$ is often modeled by a Lorentzian function. Dividing $I(x)$ by $L(x)$, and Fourier-transforming the result, gives the resolution enhanced spectrum, $E(v')$ [1]. FSD is available as a tool in Jasco Spectra Analysis software. It performs FSD on IR spectra after the full widths at half maximum (FWHM) of the resulting bands have been entered manually. In this study, the highest value allowed by the software (21 cm^{-1}) is used to avoid over deconvolution.

The secondary structures in proteins have been studied by using FSD to analyze the amide I region [3-5]. Using FSD, the beta sheet content in silk was successfully determined by Hu, *et al.* [3]. However, to our knowledge, FSD has never been used in estimating the relative crystalline fractions in PVDF. To perform the FSD on our PVDF materials, we use a mixture of Gaussian and Lorentzian bands, based on the recommendation of Lorenz-Fonfria *et al.* [6]. In their study, these authors state that the use of a mixture of Gaussian and Lorentzian bands to curve-fit Fourier self-deconvoluted spectra significantly reduces the bias induced for some bands by the use of Gaussian or Lorentzian bands individually. The self-deconvoluted spectra of PVDF electrospun fiber mat and the electrosprayed non-fibrous mat in this study were curve-fitted using WiRE 5.0 analysis software. The relative β and γ crystalline fractions were estimated using the following [7]:

$$F_{EA} = \frac{I_{EA}}{\left(\frac{K_{840}}{K_{762}}\right) \times I_{762} + I_{EA}} \times 100\% \quad (4.3)$$

$$F(i) = F_{EA} \times \left(\frac{A_i}{A_i + A_j} \right) \quad (4.4)$$

where F_{EA} is the relative fraction of electrically active polar phases (β and γ) in PVDF; I_{EA} and I_{762} are the absorbances at 840 cm^{-1} and 762 cm^{-1} , respectively; K_{840} ($7.7 \times 10^4\text{ cm}^2\text{ mol}^{-1}$) and K_{762} ($6.1 \times 10^4\text{ cm}^2\text{ mol}^{-1}$) are the absorption coefficients at 840 cm^{-1} and 762 cm^{-1} , respectively [8]. The relative crystalline fraction of crystalline phase type i is given by $F(i)$ where A_i and A_j are areas under each peak in the Fourier self-deconvoluted spectra of the 840 cm^{-1} peak [9].

4.2.2.2.2 WAXS analysis

Wide angle X-ray scattering experiments were setup as described in section 3.3.2.2. Samples were mounted on single crystal silicon wafers and investigated in $\theta/2\theta$ reflection mode. The scattering angle (2θ) was varied from 5° - 45° . The resulting X-ray intensity plots were then plotted as Lorentz corrected intensity to determine the total crystalline fraction (ϕ_C) according to section 2.2.2.

4.2.2.3 Thermal analysis

DSC scans were performed on all samples according to section 3.3.3.2. Samples of mass $\sim 4\text{-}5\text{ mg}$ were encapsulated in Al pans and lids.

4.3 Results and Discussion

The SEM images for the electrospun fiber mat and the electrosprayed non-fibrous mat are shown in Figure 4.2-A, B, respectively. The electrospun fiber mat resulted in uniform smooth fibers (Figure 4.2-A). The fiber diameters were measured using DiameterJ plugin in the ImageJ application software [10]. DiameterJ segmentalizes the SEM image into pure black and white pixels and then determines the diameter distribution. The average fiber diameter was $0.73\ \mu\text{m} \pm 0.41\ \mu\text{m}$. The SEM image of the electrosprayed non-fibrous mat shows a colloid-like morphology (Figure 4.2-B) which can be expected in electrospraying as droplets are collected on the collector plate. However, on the top edge and the top right corner in Figure 4.2-B, there are some poorly developed fiber-like structures, which appear squashed. This is an indication that some partially wet fibers are also hitting the collector plate as well as droplets during the electrospraying process. The diameters of the dried droplets are in the sub-micron scale.

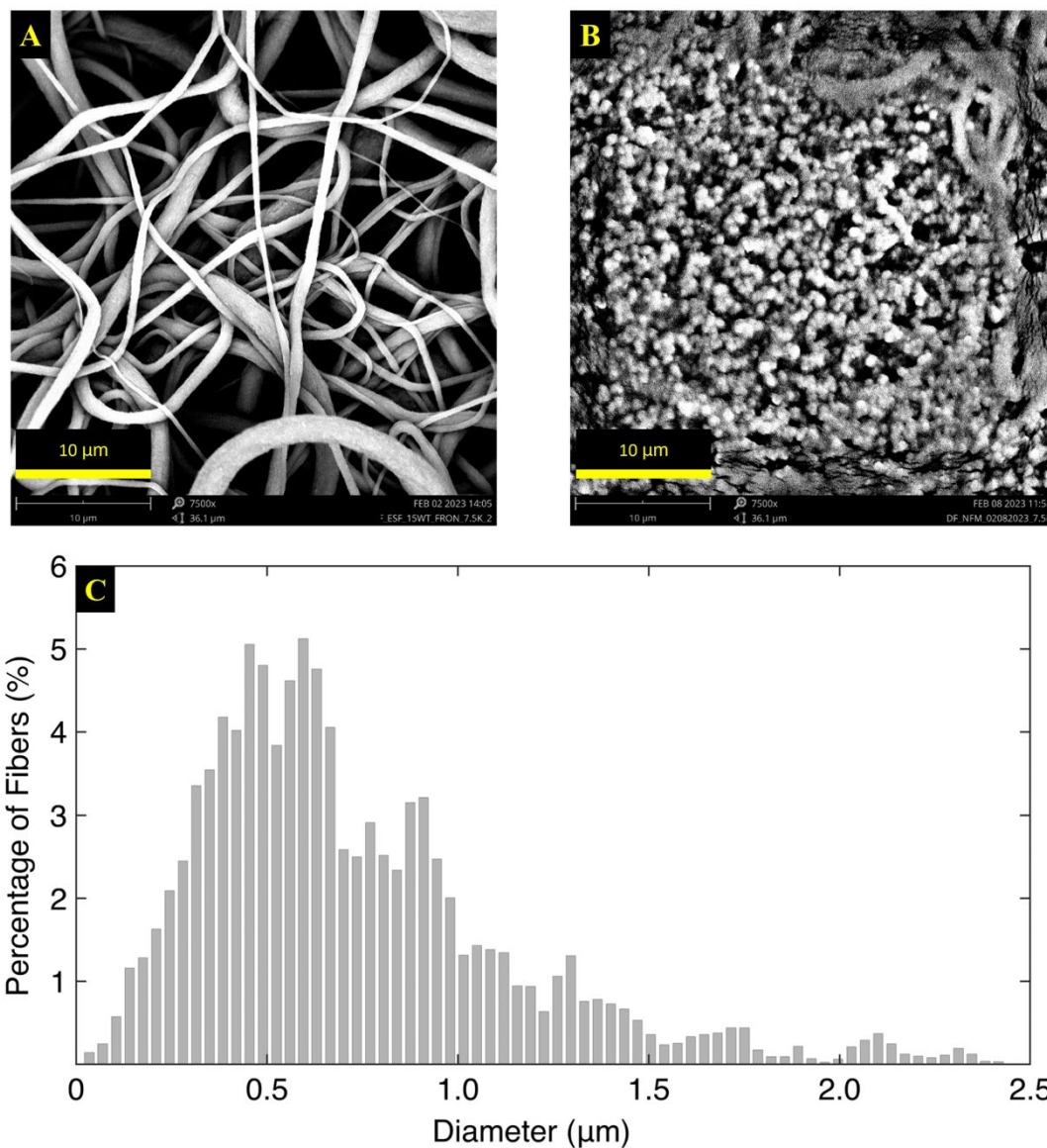


Figure 4.2: SEM images at 7500 $\times$ magnification of: A) electrospun fiber mat; B) center portion of electrosprayed non-fibrous mat; C) histogram of the fiber diameter distribution in the electrospun fiber mat shown in (A). Scale bars are 10 μm .

Figure 4.3-A shows WAXS data for both the electrospun fiber mat (center, green) and the electrosprayed non-fibrous mat (top, black) along with a WAXS intensity plot of a compression

molded film of PVDF (bottom, blue) for comparison. All scans are normalized to the maximum intensity of each scan. Since PVDF crystallizes into non-polar α -phase when crystallizing from the melt [9, 11], the compression molded film shows intense α -phase reflections such as the peaks at 2θ values of 17.6° ($d_{100}^\alpha = 0.49$ nm), 18.3° ($d_{020}^\alpha = 0.48$ nm), 19.9° ($d_{110}^\alpha = 0.44$ nm), and the triplet of peaks at 25.8° ($d_{120}^\alpha = 0.34$ nm), 26.7° ($d_{021}^\alpha = 0.33$ nm), and 28.1° ($d_{111}^\alpha = 0.32$ nm) [12, 13]. The absence of characteristic alpha reflections in the other two plots gives a strong indication of the presence of only the polar phases (β and γ) in the electrospun fiber mat and the electrosprayed non-fibrous mat. The characteristic peaks for polar phases are seen as peaks at $2\theta = 20.7^\circ$ ($d_{200/110}^\beta = 0.43$ nm) and 36.5° ($d_{310/020}^\beta = 0.25$ nm) for β -phase [12] and at $2\theta = 18.5^\circ$ ($d_{020}^\gamma = 0.48$ nm), 20.5° ($d_{021}^\gamma = 0.43$ nm), and 37.9° ($d_{004}^\gamma = 0.23$ nm) for γ -phase [12, 14]. These can be seen in the green and black curves in Figure 4.3-A indicating the presence of the electroactive phases of PVDF in both samples. Both scans for fibers and the thick mat show two amorphous halos, one centered at 21° and the other at 40° .

The Lorentz corrected scattered intensity profiles for electrospun fiber mat and the electrosprayed non-fibrous mat are shown in Figure 4.3B and Figure 4.3C, respectively. Peaks in the Lorentz corrected plots were fitted with Gaussian peaks and a quadratic baseline, using:

$$I(q)q^2 = \sum \left\{ A_i \exp \left(\frac{(q - q_{0i})^2}{2\sigma_i^2} \right) \right\} + Bq + Cq^2 \quad (4.5)$$

where the amplitude is given by A_i ; the mean q -vector is given by q_{0i} ; the standard deviation is given by σ_i ; and B and C are the coefficients of q and q^2 , respectively, which characterize the quadratic baseline.

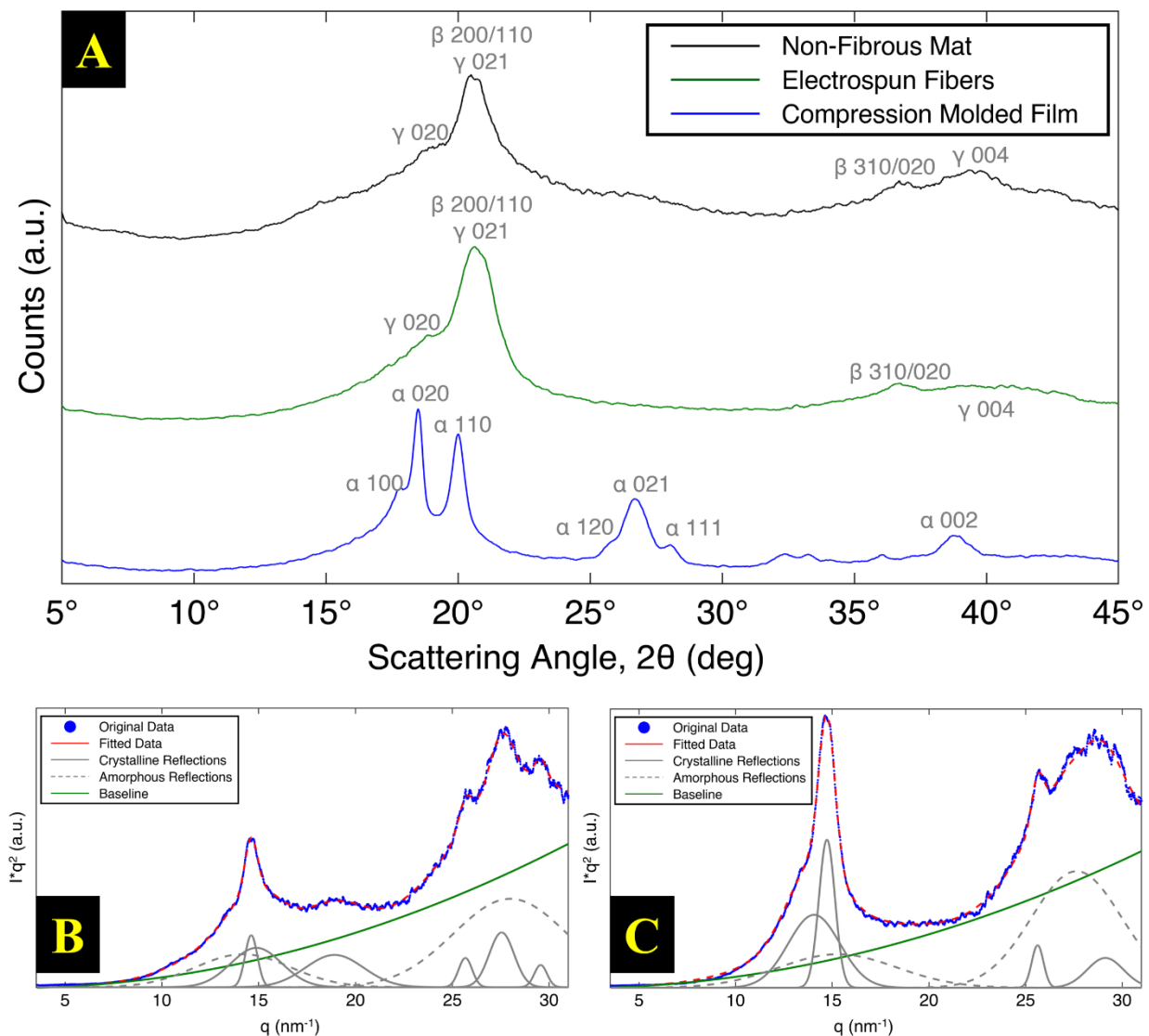


Figure 4.3: A) WAXS intensity vs. scattering angle plots of electrospayed non-fibrous mat (top, black), electrospun fiber mat (center, green), and compression molded film (bottom, blue); B, C) Deconvolution of Lorentz-corrected WAXS intensity using Gaussian wavefunctions: B) electrospun fiber mat; C) electrospayed non-fibrous mat. The crystalline peaks and amorphous peaks are shown in solid and dotted lines, respectively. Green curve is the quadratic baseline. Raw data is shown in blue dots and the fitted data is shown by the red dashed trace.

The curves shown in Figure 4.3-B,C were used to determine total crystalline fraction, and the relative fractions of the β and γ phases. The total crystallinity (ϕ_C) was calculated from:

$$\phi_C = \frac{A_C}{A_C + A_A} \quad (4.6)$$

where A_C and A_A are the areas under the crystalline and amorphous peaks, respectively. The peaks at $q = 14.7 \text{ nm}^{-1}$ and 25.6 nm^{-1} are β -phase reflections and the γ -phase reflections are seen as peaks at $q = 14.1 \text{ nm}^{-1}$ and 29.1 nm^{-1} . The relative fractions of β and γ phases were estimated from:

$$\phi_i^{rel} = \frac{\sum A_i}{\sum A_i + \sum A_j} \quad (4.7)$$

where A_i and A_j are the areas under each of the two polar crystal phases' peaks. The total crystallinity (ϕ_C) of both samples is shown in Table 4.1 along with the relative crystallinities (ϕ_i) of each phase ϕ_β^{rel} and ϕ_γ^{rel} . Because of the close proximity of the (021) gamma peak to the (200/110) beta peak, the relative phase fractions are not as reliable as the total crystalline fraction. A larger error can be expected in the relative values of the gamma and beta fractions.

Table 4.1: Total degree of crystallinity and relative β and γ phase fractions from X-ray and infrared analysis

Sample	WAXS			FSD/FTIR	
	ϕ_C (± 0.05)	ϕ_β^{rel} (± 0.15)	ϕ_γ^{rel} (± 0.15)	F_β^{rel} (± 0.05)	F_γ^{rel} (± 0.05)
Electrospun fiber mat	0.41	0.37	0.63	0.45	0.55
Electrosprayed non-fibrous mat	0.41	0.16	0.84	0.19	0.81

FTIR spectra obtained for the electrospun fiber mat (center, green) and the electrosprayed non-fibrous mat (top, black) are shown in Figure 4.4-A. The IR spectrum of the compression molded PVDF film (bottom, blue) is also presented for comparison. The characteristic vibrational peaks for β -phase PVDF crystals appear at 1276 cm^{-1} and 468 cm^{-1} (shown in green dashed lines) corresponding to the strong symmetric stretching and wagging vibrations of CF_2 , respectively [13, 15-17]. The peaks at 1234 cm^{-1} (CF_2 anti-symmetric stretching and CH_2 twisting), 811 cm^{-1} (CH_2 rocking) and 483 cm^{-1} (CF_2 bending and wagging) (shown in black dashed lines) [13, 15-17]. These three peaks are characteristic of γ -phase PVDF. On the other hand, characteristic vibration peaks for non-polar α -phase can be seen at 976 cm^{-1} (CH_2 twisting) and 762 cm^{-1} (CF_2 bending) (shown in blue dashed lines) [13, 15, 17]. The absence of the α -phase characteristic peaks and the presence of polar crystalline phase peaks in the center green and the top black spectra confirm the presence of only β and γ crystals in the two samples, complementing the WAXS results. The increased intensity of the peak at 1234 cm^{-1} and the presence of the sharp peak at 811 cm^{-1} in the upper black spectrum indicate large gamma crystal content in the electrosprayed non-fibrous mat. Since neither sample contains any alpha phase crystals, the value of I_{762} in equation (1.3) becomes zero making $F_{\text{EA}} = 1$. Hence, equation (1.4) takes the form,

$$F_i^{rel} = \left(\frac{A_i}{A_i + A_j} \right) \quad (4.8)$$

According to Cai, *et al.* the peaks at 840 cm⁻¹ and 510 cm⁻¹ correspond to both β and γ phases [18]. Hence, they are called the electro-active (EA) peaks (and are indicated by the red dashed lines). The EA peak at 840 cm⁻¹ was curve-fitted by Fu, *et al.* without Fourier Self Deconvolution prior to the fitting to estimate the relative crystalline fraction of β and γ phases [8]. According to their analysis, the fitted peak centered at 840 cm⁻¹ corresponds to β -phase vibrations and the one centered at 835 cm⁻¹ corresponds to γ -phase vibrations. Lorenz-Fonfria, *et al.* advises that reliable results cannot be obtained by curve-fitting the original spectrum as it contains noise and errors due to imperfect fitting [6]. We believe this is especially true for bands that are broad and indistinct such as the 840 cm⁻¹ band of PVDF which contains contributions from overlapping and unresolved β and γ peaks. For comparison, the reader is referred to Figure Appx. A.1 (Appendix A), which shows zoomed-in spectra in the vicinity of the 840 cm⁻¹ band, which can be compared to the self-deconvoluted spectra shown in Figure 4.4-B,C. Furthermore, curve-fitting the deconvoluted spectra results in an enhanced robustness that leads to a more reliable analysis, according to reference [6].

Hence, in our study, we chose the peak at 840 cm⁻¹ for analysis over the 510 cm⁻¹ peak since the region below 600 cm⁻¹ is inherently noisy. Fourier self-deconvolution was performed on the 840 cm⁻¹ peak and analyzed for relative fraction of β - and γ -phases using equation (2.8). The deconvoluted 840 cm⁻¹ peaks for electrospun fiber mat and for the electrosprayed non-fibrous mat are shown in Figure 4.4-B,C, respectively. The Fourier deconvoluted 840 cm⁻¹ peak was then curve-fitted using a mixture of Gaussian and Lorentzian functions. When the EA peak was

deconvoluted using FSD, the shoulder at 825 cm^{-1} was synthetically narrowed and resulted in a distinct separate peak. Koenig, *et al.* in 1979 presented in their work the presence of a shoulder at 815 cm^{-1} that corresponds to γ -phase vibrations [19]. Furthermore, many studies have considered the shoulder at 825 cm^{-1} as a part of the γ peak at 835 cm^{-1} or the EA peak at 840 cm^{-1} in the analyses of non-deconvoluted spectra [7-9, 18]. In consideration of these prior studies, we also attribute the peak at 825 cm^{-1} to γ -phase vibrations.

The estimated relative fractions of β and γ phases, F_{β}^{rel} and F_{γ}^{rel} , are shown in Table 4.1. Comparison of the relative beta and gamma fractions from FTIR also shows that there is a significant amount of γ -phase crystals present in the electrospun fiber mat, $F_{\gamma}^{\text{rel}} = 0.55$. The gamma phase crystal fraction in the electrosprayed non-fibrous mat is extremely high, $F_{\gamma}^{\text{rel}} = 0.81$ relative to the amount of beta phase crystals present ($F_{\beta}^{\text{rel}} = 0.19$). Hence, the results from the FTIR spectra analysis using Fourier self-deconvolution are consistent with the results from WAXS data. Low β -phase fractions could have resulted from the non-optimized fibers (average fiber diameter $> 0.50\text{ }\mu\text{m}$). However, He, *et al.* [20] reported that the diameter of the fibers does not directly correlate to the β -phase fraction in the fibers [20]. According to Lovinger [21], γ -phase is favored in PVDF when crystallized from dimethylacetamide. The high γ -phase fraction in both electrospun fiber mat and electrosprayed non-fibrous mat may be the result of our solvent choice.

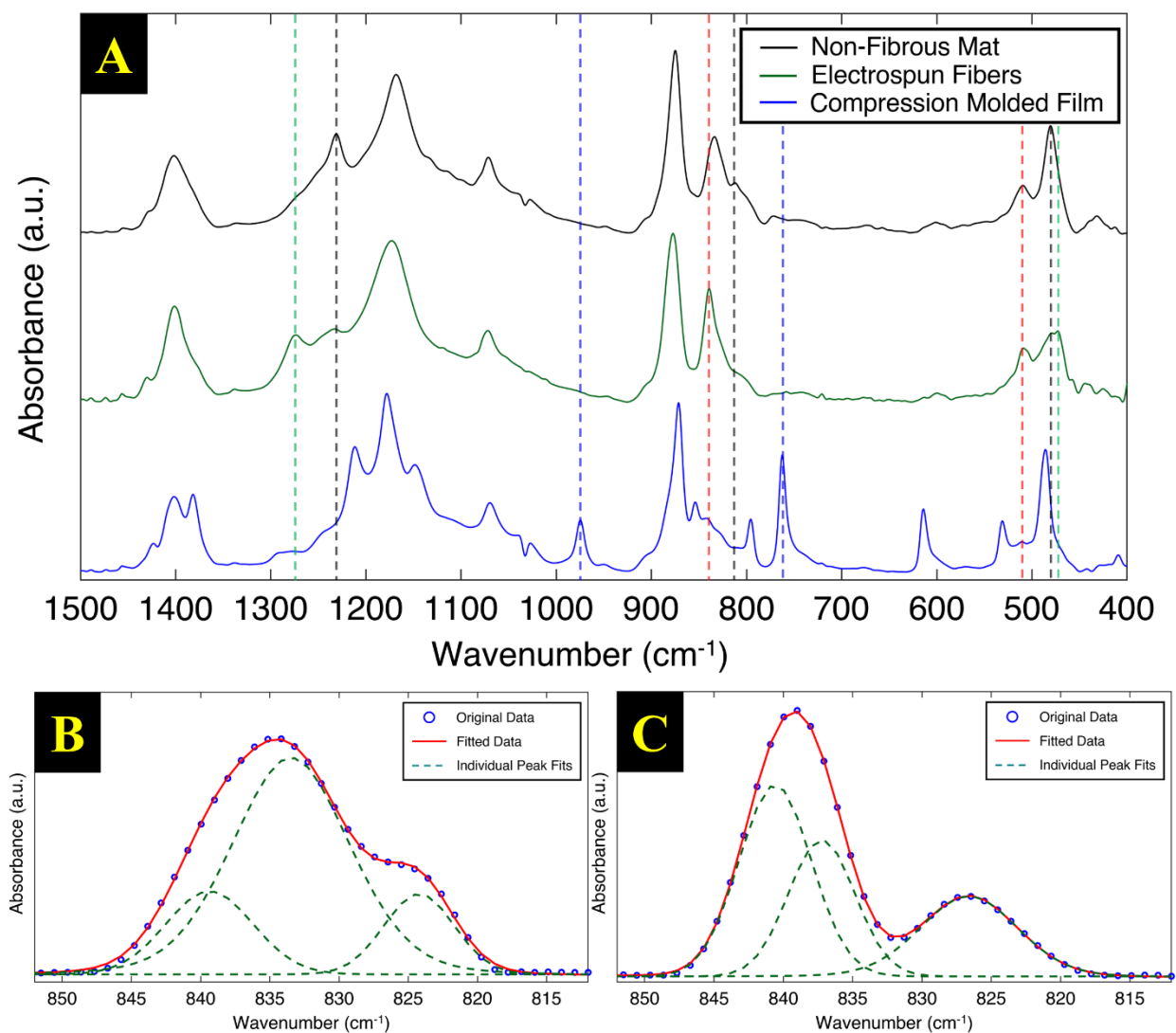


Figure 4.4: A) FTIR spectra of electrospayed non-fibrous mat (top, black), electrospun fiber mat (center, green), and compression molded film (bottom, blue). The dashed lines in the same color as the spectra show the position of characteristic peaks for each crystalline phase: The red dashed lines show the electro-active (EA) peaks of PVDF. B,C) Fourier self-deconvoluted spectra of the peak at 840 cm^{-1} for; B) electrospun fiber mat; C) electrospayed non-fibrous mat. Deconvoluted spectral data are shown in blue circles. The fitted spectrum is shown in solid red, and the green dashed curves are individually fitted peaks.

Evidence from thermal analysis of these samples confirms the relative phase structure of electrospun fiber mat and the electrosprayed non-fibrous mat. Figure 4.5 shows the apparent specific heat capacity data obtained from differential scanning calorimetric experiments for PVDF electrospun fiber mat (center, green) and electrosprayed PVDF electrosprayed non-fibrous mat (top, black), along with the compression molded PVDF film (bottom, blue). Since the compression molded film contains only α -PVDF according to both WAXS intensity plots and FTIR absorbance spectra, the blue curve shows only one melting peak at 159 °C which is mainly caused by melting α -phase crystals. The shoulder at 156 °C in the blue curve suggests melting and reorganization process leading to crystal perfection by the variation of lamellar thickness [22].

Both the electrospun fiber mat and electrosprayed non-fibrous mat show two partially resolved melting peaks at 157 °C and 161 °C (center, green) and at 159 °C and 163 °C (top, black), respectively. The presence of multiple peaks suggests crystal polymorphism [22]. According to Fu, *et al.* β -phase crystals transform into α -phase crystals upon heating and then melt [8]. Therefore, the lower melting peak was attributed to β -phase crystals [23]. γ -phase crystals usually melt at a higher temperature than either β - or α -phase crystals [13, 14, 23]. Therefore, the high temperature melting peak was attributed to γ -phase crystals. The total crystalline fraction of PVDF was not estimated using the endothermic areas of DSC plots because each crystalline phase has a different equilibrium heat of fusion value [24, 25].

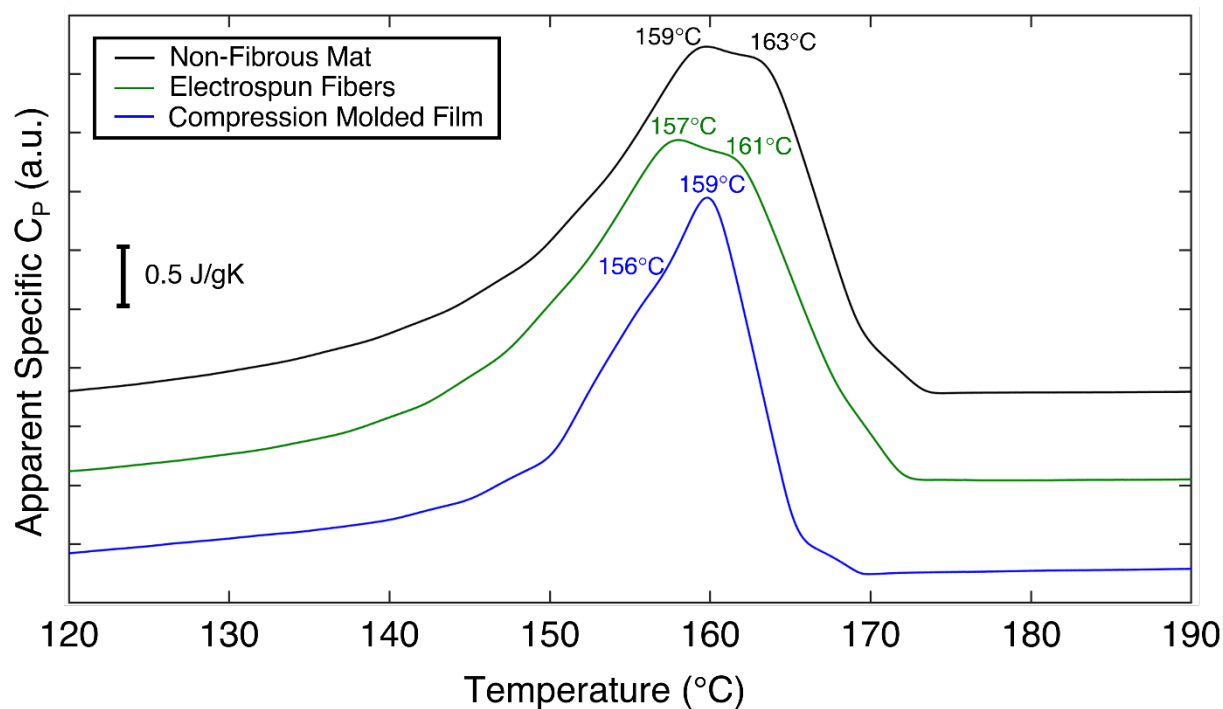


Figure 4.5: Apparent specific heat capacity (C_p) vs. temperature at a heating rate of 10 $^{\circ}\text{C}/\text{min}$ for electrospayed non-fibrous mat (top, black), electrospun fiber mat (center, green), and compression molded film (bottom, blue).

The total crystalline fraction in polymers can be determined either from the analysis of the WAXS intensity or by analyzing differential scanning calorimetric (DSC) heat flow vs. temperature. To employ the thermal method, the equilibrium heat of fusion of the crystal must be known. In the special case of PVDF, only the equilibrium heat of fusion of its non-polar α -phase (TGTG' chain conformation) is known (104.6 J/g) [7, 11, 12, 26]. A few studies have shown that β -phase crystals have a higher equilibrium heat of fusion than that of α -phase [24, 25]. However, it is often also assumed that the γ -phase shares the same equilibrium heat of fusion as the α -phase [7, 12, 27, 28]. Due to the uncertainty of the heat of fusion for β and γ phases, in this work we prefer to use WAXS

to obtain the overall degree of crystallinity of samples containing the polar crystal phases of PVDF. Lorentz corrected WAXS intensity plots have been used before to estimate all crystalline phases in PVDF [29, 30]. Hence, the total crystalline fraction can be estimated by analyzing the Lorentz corrected WAXS pattern, with results shown in Table 4.1.

4.4 Conclusions

In this study, we estimated the relative fractions of β - and γ -phase crystals in PVDF by the application of Fourier self-deconvolution to the absorbance peak at 840 cm^{-1} in the FTIR spectra of electrospun fiber mat and electrosprayed non-fibrous mat. Crystal polymorphism was observed in both samples and the presence of only electro-active polar phases (β and γ) in the samples was confirmed by WAXS intensity plots and FTIR absorbance spectra. The relative crystalline fractions of β and γ crystal phases in PVDF estimated by the analysis of Fourier self-deconvoluted spectrum of the absorbance peak at 840 cm^{-1} suggest electrospinning ($F_{\beta}^{\text{rel}} = 0.45$ and $F_{\gamma}^{\text{rel}} = 0.55$) and electrospraying ($F_{\beta}^{\text{rel}} = 0.19$ and $F_{\gamma}^{\text{rel}} = 0.84$) PVDF solutions result in mostly γ -phase crystals. A dramatic increase in γ -phase crystals was seen in the electrosprayed non-fibrous mat. Analysis of the Lorentz corrected WAXS intensity profiles confirms that both preparations result in larger proportion of gamma phase crystals.

In addition, the total crystallinity was determined by analyzing the Lorentz corrected WAXS intensity profiles of both samples, yielding $\phi_c = 0.41$ for both electrospun fiber mat and electrosprayed non-fibrous mat. Therefore, our FSD analysis of PVDF can be extended to determine the absolute crystalline fractions of the β and γ phases. For our materials, we find

absolute phase fraction by multiplying the total crystallinity by the relative phase fractions from Table 4.1. This results in absolute β ($\phi_{\beta}^{\text{abs}}$) and γ ($\phi_{\gamma}^{\text{abs}}$) fractions in the electrospun fiber mat of $\phi_{\beta}^{\text{abs}} = 0.19$, $\phi_{\gamma}^{\text{abs}} = 0.22$. In the electrosprayed non-fibrous mat, the absolute fractions are $\phi_{\beta}^{\text{abs}} = 0.08$, $\phi_{\gamma}^{\text{abs}} = 0.33$.

The electrospun fiber mat had diameters in sub-micron scale (average diameter $0.73 \mu\text{m}$) whereas electrospraying resulted in droplets and partially wet fibers. The DSC apparent specific heat capacity vs. temperature plots showed two partially resolved melting peaks for both electrospun fiber mat and electrosprayed non-fibrous mat indicating crystal polymorphism. The results from WAXS and FTIR analysis were complemented by thermal data.

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Chapter 5: Hydrophobic fouling-resistant electrospun nanofiber membranes from poly(vinylidene fluoride)/polyampholyte blends

This chapter is based on the following publication

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5.1 Introduction

Membrane filtration is an energy-efficient, simple, compact process for many purification challenges, from removing bacteria and other microorganisms to generate safe drinking water to wastewater treatment to the purification of biologic drugs [1, 2]. Poly(vinylidene fluoride), PVDF, is a highly preferred material for membrane filters due to its chemical and physical stability, mechanical strength, and processability. However, its high hydrophobicity leads to membrane fouling [3-5], which affects the life span of the filtration membrane by reducing the flux significantly and adding to the operational costs [6-8]. Several methods exist for improving the fouling resistance of a membrane.

One of the most efficient methods of making a membrane fouling-resistant is increasing its surface hydrophilicity [6, 9]. Blending PVDF with hydrophilic materials including polymers and nanoparticles, and surface modification of PVDF membranes by grafting or coating hydrophilic segments, are broadly studied techniques directed toward improving its hydrophilicity [6, 8]. Blending mechanisms have significant advantages such as allowing convenient operation from fewer number of steps [10, 11], improving the hydrophilicity in the whole membrane matrix instead of only the surface, and cost effectiveness [12]. In addition, unlike surface modification [11], blending techniques do not affect the porosity of the membrane. Successful polymer additives for decreasing fouling in membranes are often amphiphilic, with hydrophobic segments anchoring hydrophilic, anti-fouling groups or brushes to the surface of the membrane [13, 14]. In this work, we use polyampholytes blended with PVDF to decrease membrane fouling.

Polyampholytes are defined as polymers that comprise anionic and cationic groups in different monomer units on the same chain. Polyampholytic materials can prevent fouling of surfaces by the adsorption of proteins and other organic macromolecules. This is believed to be due, in part, to a strong hydration shell layer created by the charged groups on the polymer chain [15-18]. Leng, *et al.*[19] state that the hydration layer on the surface is tightly bound to the surface by electrostatic-induced hydrogen bonding between water molecules and ether oxygen atoms. Because of this strong attachment, the hydration layer acts as a physical barrier as well as an energy barrier for biomolecular foulants such as proteins. Yet, there are only a few previous reports of polyampholytes being used to enhance fouling resistance on commercial membrane surfaces [20, 21] . Recently, Mazzaferro, *et al.* [22] introduced a family of novel amphiphilic polyampholyte copolymers that could be coated on a porous support to serve as the “selective layer” of membranes with tunable selectivity and remarkable fouling resistance. These polymers were designed to be insoluble in water to avoid dissolution during use and comprised three types of monomers: a hydrophobic monomer to provide stability, and the combination of an anionic and a cationic monomer to create the ampholytic, fouling-resistant behavior as well as enable water permeation. However, to our knowledge, there are no reports of blending amphiphilic polyampholytes to a commodity polymer (*e.g.*, PVDF) during manufacturing to create more fouling-resistant membranes.

Non-woven fibrous membranes can be obtained by the process of electrospinning. Electrospinning is an efficient method to obtain nanoscale fibers[23] which show excellent surface area-to-volume ratios and enhanced porosity, making make them good options for liquid filtration mechanisms [23-25]. Non-woven *fibrous* membranes help overcome some of the limitations found in *non-*

fibrous membranes in filtration applications, such as lower mechanical stress and non-uniform pore distribution [23]. PVDF is a widely used polymer in electrospinning applications as well [26-29]. Electrospun PVDF membranes are already in extensive use in filtration applications [25, 27, 30-32] such as air-borne particle filtration[33], heavy metal filtration[34], and oil-water filtration[7]. Blends of PVDF with various copolymers have been used to create electrospun mats with improved filtration capabilities, including but not limited to zwitterionic copolymers for enhanced organic fouling resistance, or fluorinated copolymers for high hydrophobicity and selective oil permeation [27, 35, 36]. However, polyampholytes are not often used as electrospinnable materials. To the best of our knowledge, only two groups reported on electrospinning of polyampholytes[37, 38]. Mincheva, *et al.* [37] report electrospinning a variety of polyampholytes in combination with non-ionogenic polymers to associate and stabilize the electrospinning process.

In this study, we electrospun nanofiber membranes from PVDF and its blends with a random polyampholyte amphiphilic copolymer (r-PAC) containing methacrylic acid, and [2-(methacryloyloxy)-ethyl]trimethylammonium chloride, and 2,2,2-trifluoroethyl methacrylate. This r-PAC is similar to the one used by Mazzaferro, *et al.* [22] as self-assembled membrane selective layers shown to have remarkable fouling resistance. Despite the similarity of its chemical structure, the hydrophobic TFEMA units are not fully miscible with PVDF due to the repulsive dipolar interactions between fluorine atoms in both polymer chains [39]. As a result, PVDF and the r-PAC incorporating these hydrophobic units had to be dissolved in a mixture of dimethylformamide (DMF) and methanol to ensure good solubility. The membranes were characterized using scanning electron microscopy (SEM), wide angle X-ray scattering (WAXS), thermogravimetric (TG) analysis, and sessile drop contact angle measurements. The fouling

resistance was documented using a common protein foulant, bovine serum albumin (BSA) tagged with fluorescein isothiocyanate (FITC) for visualization.

5.2 Experimental

5.2.1 *Materials*

The solutions for this study were prepared as mentioned in section 3.2.1.2. PVDF powder and as received r-PAC were mixed in the following ratios (PVDF/r-PAC): 100/00, 95/05, 90/10, 75/25, 50/50, 25/75, and 00/100 in DMF/MeOH mixture. A short label format is used to identify the samples with different ratios. For example, PVDF/r-PAC 75/25 sample is labelled as PVDF75. Phosphate buffered saline (PBS) powder and Albumin from Bovine Serum (BSA), fluorescein isothiocyanate conjugate (FITC-BSA) were purchased from Thermo Fisher Scientific (Waltham, MA, USA) and used after mixing with ultra-pure DI water as instructed by the recipe, resulting in a pH 7.4 solution.

5.2.1.1 *Synthesis of r-PAC*

A random terpolymer with three monomeric units was synthesized using methacrylic acid (MAA, Sigma Aldrich), [2-(methacryloyloxy)ethyl]trimethylammonium chloride (MAETA, Sigma Aldrich), and 2,2,2-trifluoroethyl methacrylate (TFEMA, ACROS Organics). The first two monomers were passed through a column of neutral activated alumina (Sigma Aldrich) to remove the inhibitor, while the last monomer was passed through a column of basic activated alumina (VWR). MAA (1.46 g, 17.0 mmol), MAETA (3.54 g, 17.0 mmol), and 2,2,2-trifluoroethyl methacrylate (5.00 g, 29.7 mmol) were dissolved in this order in dimethyl sulfoxide (DMSO, 40

mL, Fisher). Azobisisobutyronitrile (AIBN, 0.01 g, Sigma Aldrich) was added to the flask. The flask was sealed with a rubber septum. Nitrogen was bubbled through the reaction mixture for 30 min to purge any dissolved oxygen. The flask was then kept at 60 °C while stirring at 300 rpm for 17 h. After the reaction, 1 g of 4-methoxyphenol (MEHQ, Sigma Aldrich) was added to terminate the synthesis. The reaction mixture containing DMSO and the polymer was poured in 600 mL of acetone to precipitate the polymer. After the removal of the precipitation solvent the polymer was washed by stirring two fresh portions of 1:3 ethanol to hexane volume ratio for at least 5 h, and two fresh portions of acetone for at least 5 h; all portions were around 500 mL. Finally, the terpolymer was dried in a vacuum oven for 72 h at 60 °C. The composition of the terpolymer was calculated from the ^1H -NMR spectrum (Figure 5.1), using the ratio of protons from the three different monomer units. The calculated composition was: 25 mol% MAA, 25 mol% MAETA, and 50 mol% TFEMA. The final conversion of this reaction was 57%.

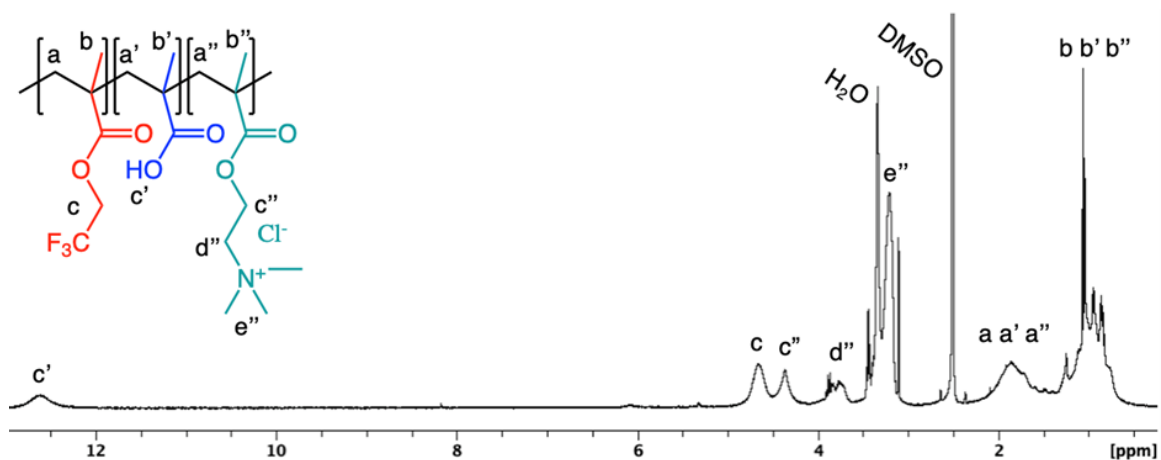


Figure 5.1: NMR spectrum of r-PAC chemical structure indicating copolymerization of the three monomer units. Inset shows the structure of r-PAC. The subgroups are: TFEMA (red, left); MAA (blue, middle); MAETA (green, right).

5.2.1.2 Electrospinning

Prepared solutions were electrospun as mentioned in section 3.2.2 by using a glass syringe of internal diameter 14.67 mm, an 18G (inner diameter 0.84 mm) needle, and a large collector plate of diameter 25 cm. The applied voltage and the working distance between the needle tip and the collector plate varied between 25 kV – 27.5 kV and 15 cm – 22.5 cm, respectively. The solution was pumped at a flow rate between 0.5 mL/h – 1.0 mL/h. These variables were adjusted to address the variation of the viscosity of the solution and the subtle changes in the relative humidity of the atmosphere. Examples of the obtained electrospun fiber mats, and the electrospinning set up, are shown in Figure 5.2.

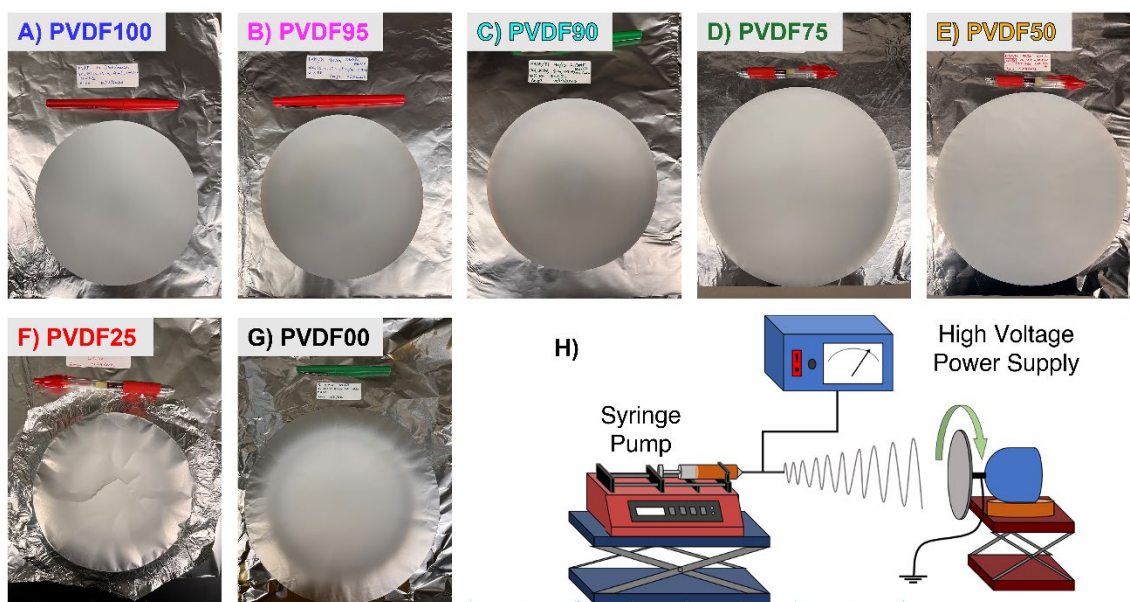


Figure 5.2: Optical images of electrospun fiber mats of: A) PVDF100; B) PVDF95; C) PVDF90; D) PVDF75; E) PVDF50; F) PVDF25; G) PVDF00; H) Schematic of the electrospinning setup, showing syringe pump, high voltage source, fiber whipping, and rotating grounded collector plate from Govinna [40]. A pen (~15 cm) is used to indicate the scale in A-G.

5.2.2 *Characterization*

5.2.2.1 *SEM analysis*

All SEM images were obtained as described in section 3.3.1.1. A detailed description of the fiber diameter analysis, and the method for removal of the beads, is provided in Appendix B.

5.2.2.2 *WAXS analysis*

Wide angle X-ray scattering intensity (WAXS) vs. scattering angle, 2θ , was obtained for all electrospun mats as described in section 3.3.2.2. All samples were mounted on Al sample holders. The scattering angle varied from 5° - 40° .

5.2.2.3 *TGA analysis*

Thermogravimetric (TG) analysis was conducted on all samples as described in section 3.3.3.1. The samples were heated at a rate of $10^\circ\text{C}/\text{min}$ from 25°C – 600°C . The sample mass varied from 3 mg – 10 mg . To determine the degradation onset temperatures, the intersection point of the extrapolated line in the dry undegraded states, and the tangent line drawn along the degradation step was used. We recorded the degradation onset temperature with an uncertainty of $\pm 1^\circ\text{C}$.

5.2.2.4 *Contact angle measurements*

Sessile drop contact angle measurements were performed on all samples according to section 3.3.4.1. All contact angle values are reported with an uncertainty of $\pm 3^\circ$.

5.2.2.5 Membrane fouling tests

Fouling samples were prepared by punching out circular samples (10 mm diameter) from electrospun fiber mats adhered to aluminum foil. These samples were attached to a 35 mm polystyrene petri dish with double-sided tape, which was filled with 5 mL of phosphate buffered saline (PBS) and kept covered to prepare the sample surface for protein fouling. After 1 h, the PBS was removed, and 5 mL of a 0.1 mg/mL solution of FITC-BSA in PBS was added. Samples were kept in the dark to reduce photobleaching and moved to an oven at 37 °C for 1.5 h. The FITC-BSA solution was then removed and replaced with fresh PBS 3 times, followed by soaking the samples in fresh PBS for 15 min on a rocker plate 3 more times. The samples were then washed once with DI water to reduce PBS crystallization during imaging. Background samples were also prepared following the same protocol; however, these samples did not come into contact with the FITC-BSA solution. Epifluorescence micrographs of the fouled electrospun fibers were obtained using an Olympus BX51 microscope (Olympus Corp., Center Valley, PA, USA) equipped with a DP70 microscope digital camera, 10x objective lens, and a standard green (U–N31001) filter set (Chroma Technology Corp., Rockingham, VT, USA). Exposure was optimized to be 1/5 sec to prevent background signal and pixel intensity overflow. Relative fluorescence intensity was calculated using ImageJ's mean grey value function on each image of the fouled and unfouled samples and calculated using Equation 1.1. The sample background intensity was subtracted from the fouled sample intensity, normalized to the difference between the PVDF100 fouled sample and background intensities, and converted to a percent.

$$\text{Relative Fluorescence Intensity (\%)} = \frac{I_{\text{Sample Fouled}} - I_{\text{Sample Background}}}{I_{\text{PVDF100 Fouled}} - I_{\text{PVDF100 background}}} * 100\% \quad (5.1)$$

5.3 Results and Discussion

SEM images obtained for each sample are shown in Figure 5.3 (A-G). As evident in Figure 5.3-G, homopolymer r-PAC was successfully electrospun to form fibrous membranes with an average fiber diameter of $0.28\ \mu\text{m} \pm 0.19\ \mu\text{m}$. To the best of our knowledge, this is the first time a polyampholyte has been electrospun to obtain fibers without incorporating another polymer to stabilize the electrospinning process. The fibers contain a significant number of beads. The shape of the beads is more spherical when the PVDF fraction is high. This is caused by the low viscosity of the solutions with higher PVDF contents and as a result some electrospraying could occur. On the other hand, when the r-PAC fraction becomes greater the solution viscosity is increased significantly, and the beads become elongated and form along with the fibers. The presence of beads is rare in the PVDF50 electrospun mat. The average diameter of the fibers obtained for all samples was estimated using the DiameterJ plugin in the ImageJ application. Table 5.1 reports the average fibril diameter after exclusion of the beads, in comparison to the average bulk fiber diameter including the beads. After exclusion of the beads, PVDF75 and PVDF50 showed the two smallest fibril diameter values of $0.09 \pm 0.02\ \mu\text{m}$ and $0.12 \pm 0.03\ \mu\text{m}$, respectively. (see Appendix B: Figure Appx. B.2 (A-G) for histograms of the fiber diameter distributions).

As shown in Figure 5.3-H, the average fibril diameter initially decreases from PVDF100 to PVDF75 with the addition of r-PAC and then increases again from PVDF50 to PVDF00. Fiber diameter can be affected by several different parameters of the electrospinning process and by the properties of the polymer solution. Electrospinning processing variables include deposition rate (or, the pumping speed), Taylor cone stability, and the applied voltage. The effect of

electrospinning parameters on the fiber diameter is a widely studied area as the diameters of the fibers produced by electrospinning are distributed over a wide range[41-46]. According to Cramariuc, *et al.*[42] and Fridrikh, *et al.*[43], the terminal diameter of the polymer jet that eventually determines the fiber diameter is controlled by the deposition rate, electric current due to bulk motion of surface charges in the polymer solution and conduction through the solution[44], and the surface tension of the solution.

During electrospinning, the pumping rate was varied. PVDF100 solution was pumped at 1 mL/hr and the rest of the solutions were pumped at 0.5 – 0.6 mL/hr because the applied electric field was too weak to form a stable jet when electrospinning PVDF/r-PAC blends and homopolymer r-PAC. The variation of deposition rate might be one reason for the gradual reduction of fibril diameters observed from PVDF100 to PVDF75.

Properties of the solutions also affect the fiber diameters. For example, surface charge density and conductivity of the polymer fluid, which directly influences the electric current of the polymer jet, has an inverse effect on fiber diameter, as discussed by Cramariuc, *et al.*[42] and Fridrikh, *et al.*[43]. As the fraction of r-PAC is increased the fiber diameter decreases because the surface charge density and conductivity of the solution increase with the introduction of the ionic r-PAC units. The applied electric field also affects the electric current, but the variations we made in the working distance and the applied voltage make the variations in the electric field negligible.

As shown in Figure Appx. B.6 in Appendix B, the dynamic viscosity and the average fibril diameters show an inverse relationship between them. Addition of r-PAC to the solution increases the dynamic viscosity of the solution first, and then as the r-PAC fraction increases and starts to dominate, the viscosity begins to decrease. Accordingly, as r-PAC fraction increases, the average fibril diameter first decreases and then starts to increase again. The low viscosity of the solutions with high r-PAC fractions such as PVDF25 and PVDF00 may have caused the bead formation observed in their respective fiber mats. It is observed that the Taylor cone was slightly unstable when electrospinning PVDF25 and PVDF00. The Taylor cone was periodically varying its size during the electrospinning process which could be another cause why PVDF25 and PVDF00 exhibited beading in the fibers as Singh, *et al.*[45] state that the instabilities of the Taylor cone have a complex effect on the fiber diameters.

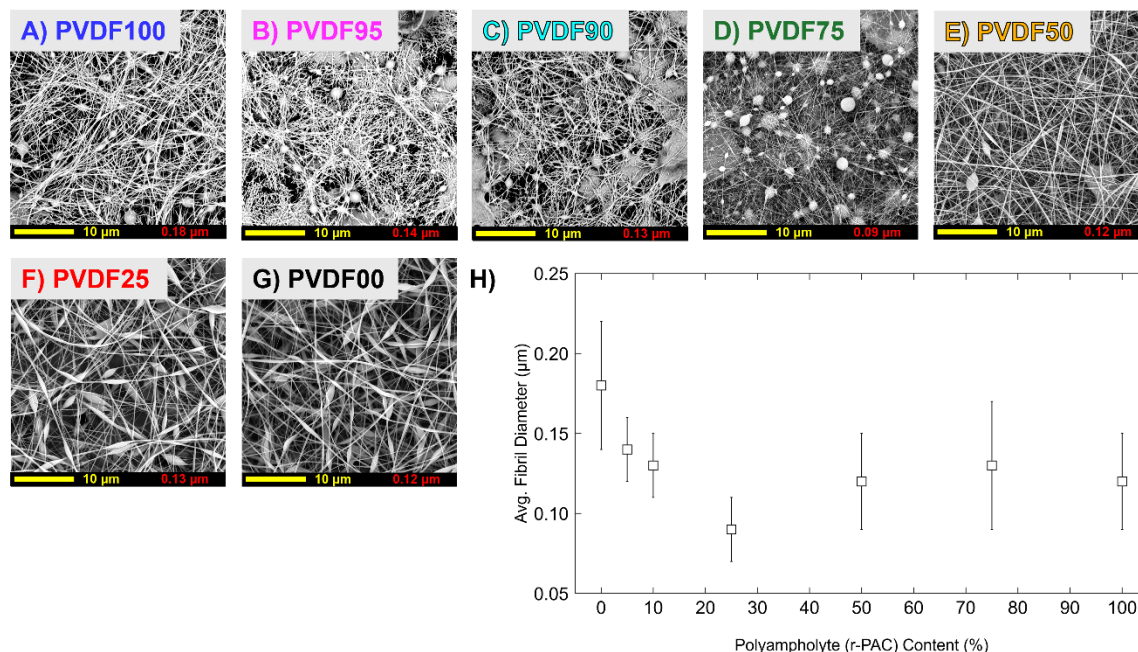


Figure 5.3: SEM images of the electrospun fibers. A) PVDF100; B) PVDF95; C) PVDF90; D) PVDF75; E) PVDF50; F) PVDF25; G) PVDF00; H) Variation of fibril diameters in all electrospun mats. All images were obtained at a magnification of 7500x and scale bars are 10 μm. Average fibril diameter is shown on each image at the lower right.

The porosity of each fibrous mat was also estimated using DiameterJ. As shown in Table 5.1, PVDF75 and PVDF50 showed the two smallest mean pore areas $0.26 \pm 0.02 \mu\text{m}^2$ and $0.27 \pm 0.01 \mu\text{m}^2$, respectively. PVDF75 and PVDF50 also showed the two highest pore densities $14.0 \times 10^5 \text{ mm}^{-2}$ and $15.3 \times 10^5 \text{ mm}^{-2}$, respectively. About 75% of the pores in each sample had areas below the mean pore area indicating high porosity with smaller pore sizes.

Table 5.1: Average diameters and pore data of electrospun fibers of PVDF/r-PAC Blends

Sample Name	Average Bulk Fiber Diameter ^a (μm)	Average Fibril Diameter ^b (μm)	Mean Pore Area ^c (μm^2)	Pore Density ^d ($\times 10^5 \text{ mm}^{-2}$)
PVDF00	0.27 ± 0.18	0.12 ± 0.03	0.72 ± 0.03	6.35
PVDF25	0.25 ± 0.17	0.13 ± 0.04	0.48 ± 0.02	8.62
PVDF50	0.20 ± 0.11	0.12 ± 0.03	0.27 ± 0.01	15.3
PVDF75	0.17 ± 0.14	0.09 ± 0.02	0.26 ± 0.02	14.0
PVDF90	0.29 ± 0.17	0.13 ± 0.06	0.49 ± 0.04	6.95
PVDF95	0.29 ± 0.15	0.14 ± 0.02	0.46 ± 0.03	6.06
PVDF100	0.28 ± 0.14	0.18 ± 0.04	0.43 ± 0.02	8.13

^a Bulk diameter includes the beads – See Appendix B: for description of this calculation

^b Fibril diameter does not include the beads – See Appendix B: for description of this calculation

^c The nine images shown in Figure Appx. B.1 were examined for pores and the average number of pores per image is listed in Table Appx. B.1. The magnification of the images was the same for all samples.

^d SEM images were converted from pixel units to mm^2 .

Figure 5.4 shows the WAXS intensity vs. scattering angle of all samples. PVDF00 (bottom, black) shows a broad peak centered at 16.5° (dotted purple line) and none of the narrow intense peaks characterizing a crystalline material. This confirms that homopolymer r-PAC was not able to form any crystalline domains due to its bulky structure and lack of stereoregularity. However, a narrow intense peak emerges around 20° – 21° as the PVDF fraction increases (from PVDF25 to PVDF100). This peak is a convolution of two peaks centered at 20.4° ($d_{021}^\gamma = 0.431 \text{ nm}$ – long-dashed purple line) and 20.7° ($d_{200/110}^\beta = 0.427 \text{ nm}$ – short-dashed purple line) which correspond, respectively, to the γ - and β -crystallographic phases of PVDF [47, 48]. These two phases, γ and β , are the electroactive (EA) phases of PVDF [26, 29, 49], hence the presence of EA crystal phases in the electrospun fiber mats is confirmed. Electrospinning is known to produce EA crystal phases of PVDF as it simultaneously applies electrical and mechanical forces to stretch the polymer chain

[50]. The absence of the triplet of peaks between 25° - 30° (at 25.8° ($d_{120}^{\alpha} = 0.344$ nm), 26.7° ($d_{021}^{\alpha} = 0.334$ nm), and 28.1° ($d_{111}^{\alpha} = 0.318$ nm)) in all samples confirms that there are no α -phase crystals in any of the electrospun fiber samples [48, 51].

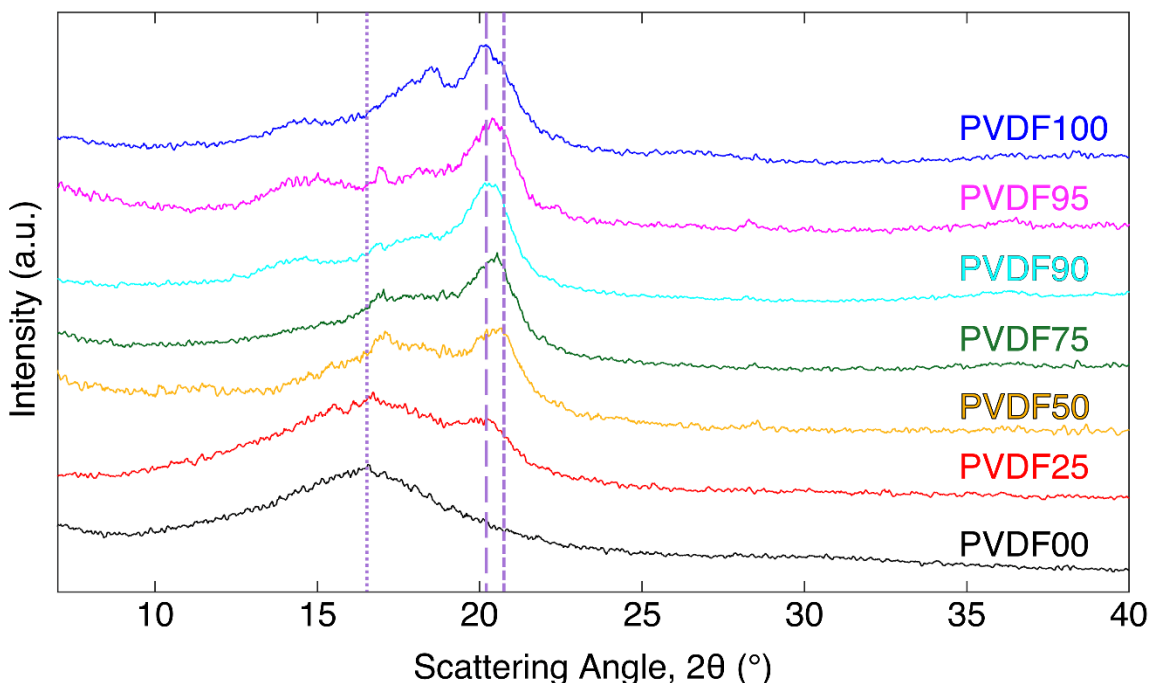


Figure 5.4: WAXS intensity vs. scattering angle of: PVDF100 (homopolymer PVDF, top, blue); PVDF95 (magenta); PVDF90 (cyan); PVDF75 (green); PVDF50 (yellow); PVDF25 (red); PVDF00 (r-PAC, bottom, black). The vertical purple lines show the scattering angle at the following reflections: r-PAC amorphous halo (dotted line); γ -phase reflection (long-dashed line); β -phase reflection (short-dashed line).

Figure 5.5 shows the results of thermogravimetric (TG) analysis of each sample. Homopolymer PVDF sample, PVDF100 (top, blue), shows excellent thermal stability with only one degradation onset point around 450°C which is typical for PVDF [35]. Homopolymer r-PAC (bottom, black)

and its blends with PVDF show complex TG curves with multiple degradation steps. The blends show thermal stability up to 180 °C and their first significant mass loss occurs from 180 °C to 200 °C. A second mass loss can be seen from 240 °C to 250 °C, followed by a third degradation step, which can be seen around 400 °C. Goel, *et al.* [52] and Shukla, *et al.* [53] report that pMAETA possess super hygroscopic properties. Hence, the initial mass loss at lower temperatures which is evident in r-PAC and its blends with PVDF can be accounted for by ejection of the bound water.

At temperatures above the ejection of bound water, the observed degradation steps in the blends containing r-PAC correspond to the degradation of charged side groups in the r-PAC. Supeno, *et al.* [54] and Goel, *et al.* [52] reported that polymerized MAETA (pMAETA) (the positively charged side group in r-PAC) degrades around 230 °C and 400 °C. Ho, *et al.* [55], Bajaj, *et al.* [56], and McNeil, *et al.* [57] report that polymerized MAA (pMAA) (negatively charged side group in r-PAC) also shows a two-step degradation process comprising a first step around 200 °C – 230 °C and a second step around 400 °C. Polymerized TFEMA is reported to have a significant mass loss around 360 °C – 400 °C according to Xu, *et al.* [58], Fang, *et al.* [59], and Li, *et al.* [60]. The blends also show a fourth degradation step at 450 °C which is caused by the degradation of the PVDF component.

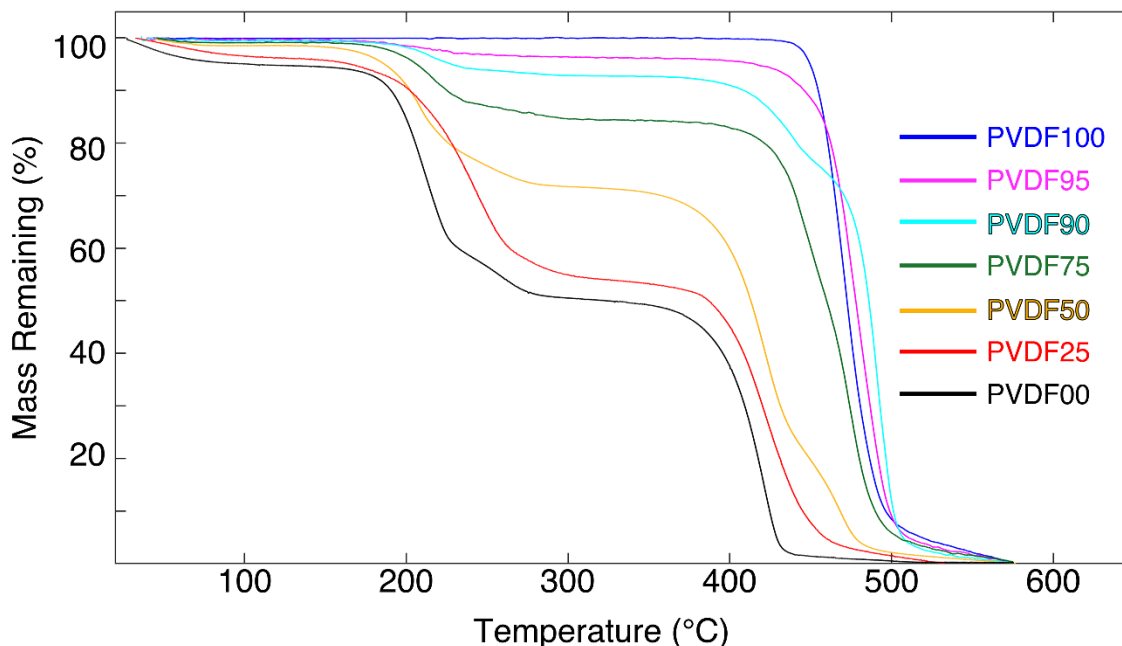


Figure 5.5: Thermogravimetric analysis showing the remaining mass fraction vs. temperature for: PVDF100 (top, blue); PVDF95 (magenta); PVDF90 (cyan); PVDF75 (green); PVDF50 (yellow); PVDF25 (red); PVDF00 (bottom, black). The initial mass loss for temperatures below 100 °C is due to bound water ejection. The r-PAC homopolymer and its blends with PVDF show multiple thermal degradation steps whereas homopolymer PVDF show single-step thermal degradation.

The sessile drop contact angle measurements conducted with water on all samples are shown in Figure 5.6. PVDF100 fibers exhibited a water contact angle of 128°, indicating a significant increase in hydrophobicity compared to its thin film form, which has a contact angle of 95° [61, 62]. This is obvious because the fibers of a material have a higher surface area-to-volume ratio which leads to a higher surface energy compared to the material's thin film form. PVDF95 and PVDF90 show no significant change in the contact angle with water compared to PVDF100. Their contact angles were 127° and 129°, respectively. However, when the PVDF content drops to 75%

or less (r-PAC content 25% or greater), the contact angle increases to 136° indicating a significant increase in hydrophobicity as the hydrophobic content increases drastically as TFEMA (the hydrophobic unit in r-PAC) fraction in the fibers rise and the fiber diameters rapidly decrease. The contact angle maintains this higher value and does not vary significantly with further increase of r-PAC content. The highest contact angle was observed for PVDF00 (the homopolymer r-PAC), with a value of 139° - a substantial increase from its thin film form, which had a contact angle of 82°. Hence, all electrospun fibrous mats are very hydrophobic.

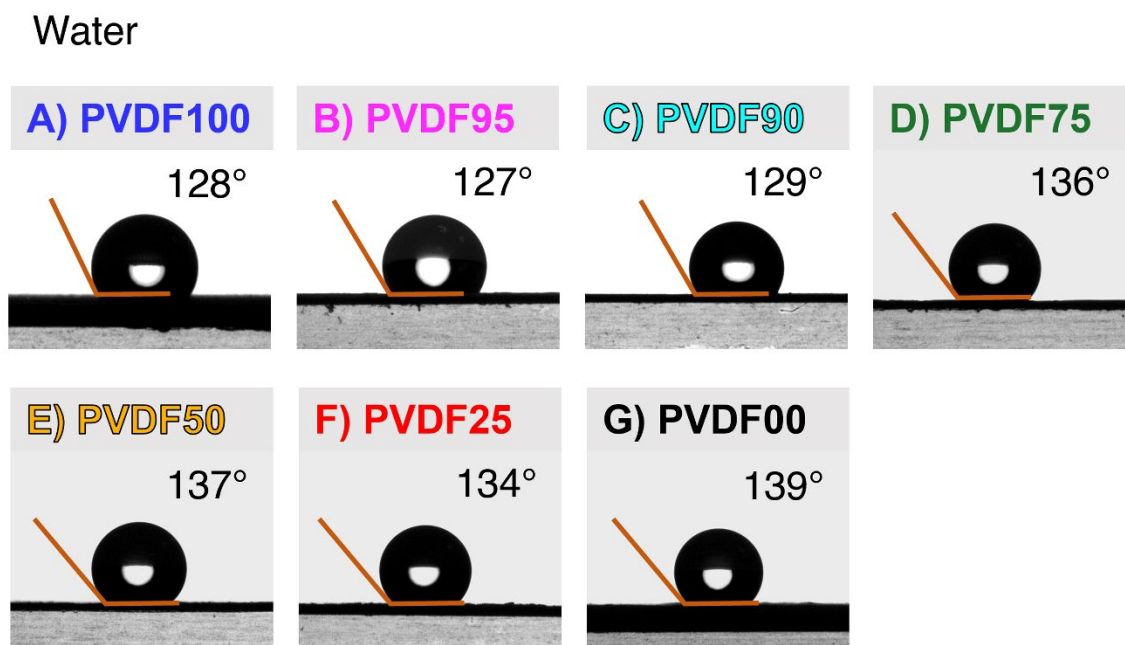


Figure 5.6: Sessile drop contact angle measurements for a water droplet on electrospun fiber mats of: A) PVDF100; B) PVDF95; C) PVDF90; D) PVDF75; E) PVDF50; F) PVDF25; G) PVDF00 at room temperature (25 °C). The water droplet is shown by the black orb and the angle between the orange lines indicates the contact angle. The measured values are shown on each figure.

The contact angle measurements were also taken using dodecane, an oil-like substance, and are presented in Appendix B: B.4 A-G. All fibrous mats showed very small contact angles indicating that they are super-oleophilic. The oil droplets dispersed over the surface of the fibrous mats within seconds after deposition. This implies that the electrospun fiber mats would be well suited for applications in oil/water separation, where oil is selectively absorbed into the mat.

Proteins are one of the most significant biomacromolecular foulants found in many water and wastewater treatment applications, and are often used as key probes for testing fouling resistance. Therefore, to quantify the fouling resistance of PVDF/r-PAC electrospun mats, we performed static adsorption experiments of a common, highly fouling protein, bovine serum albumin (BSA), labeled with the fluorescent dye fluorescein isothiocyanate (FITC). Each electrospun mat was immersed in a solution of this labeled protein, FITC-BSA, for 1.5 h. After rinsing to remove any unbound protein, the mats were imaged using fluorescence microscopy to determine how much protein remained adsorbed to the surface (Figure 5.7). Total fluorescence intensity in each image, quantified by image analysis, is correlated with the amount of FITC-BSA. The pure PVDF mat, PVDF100, exhibited the highest protein adsorption, and was thus used as the reference material for calculating differences in fouling propensity. Therefore, “relative fluorescence intensity” was defined to indicate the amount of protein adsorbed on each mat normalized by the amount on PVDF100 (Equation 1.1). All PVDF/r-PAC samples, PVDF95, PVDF90, PVDF75, PVDF50, and PVDF25, as well as PVDF00, showed a significant decrease in fluorescence intensity of at least 50% (Figure 5.7-H). PVDF50, PVDF25, and PVDF00 showed a relative fluorescence intensity of less than 10%, indicating that despite being hydrophobic, these electrospun mats have excellent fouling resistance and can resist nearly all protein adsorption.

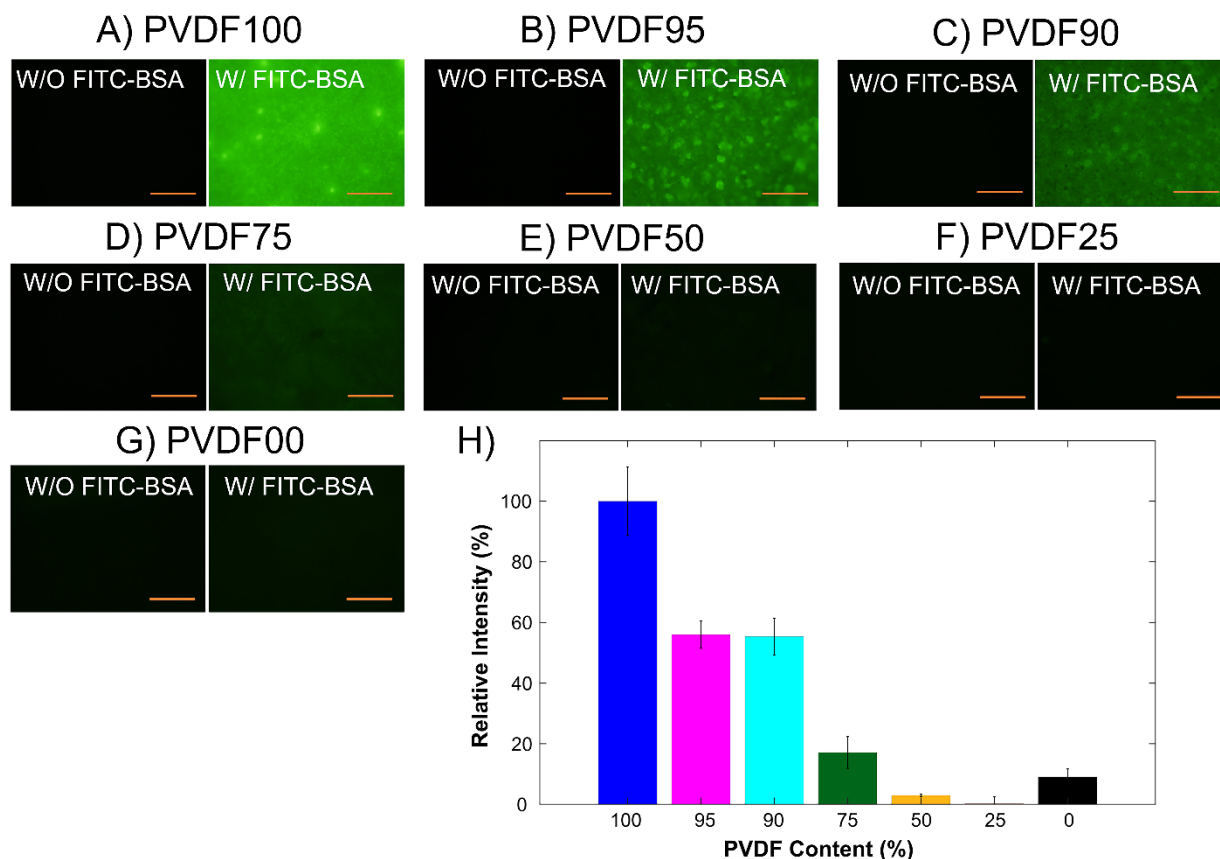


Figure 5.7: A-G) Epifluorescence micrographs of electrospun fiber mats after fouling with the fluorescently labeled protein FITC-BSA (W/FITC-BSA) on the right sides, compared with images of mats that were not exposed to the protein as a control (W/O FITC-BSA) on the left sides. Scale bars are 200 μm. Selected micrographs are representative images of the whole sample. H) Relative extent of protein adsorption reported as relative fluorescence intensity compared to fouled pure PVDF samples. Fluorescence intensity, which is proportional to the amount of adsorbed protein, was quantified by calculating the mean grey value for each image in ImageJ and normalized with the extent of fouling of PVDF samples (Eqn. 1.1). At least 4 randomly selected images were taken per mat. Error bars were calculated using propagation of uncertainty.

5.4 Conclusions

In this study, we report successful use of electrospinning to obtain fibrous membranes of a random polyampholyte ter-copolymer (r-PAC) and its blends with PVDF. The average diameter of homopolymer r-PAC fibrils was 0.12 μm . Fibers made from blends with PVDF also had sub-micron scale fibrils, with minimum diameter (0.09 μm) occurring in PVDF75. Fiber formation was enhanced with increasing r-PAC fraction. Minimal beading was seen in PVDF50, *i.e.*, when PVDF and r-PAC were blended in equal parts. The average fibril diameters showed an inverse relationship with the solution viscosity. The solution viscosity increased as the r-PAC content was raised, peaking in PVDF75, after which the viscosity began to decrease. On the other hand, the fibril diameter first decreased and then increased for compositions beyond PVDF75. The mean pore area also showed a variation similar to that of fiber diameters with increasing r-PAC fraction. Higher pore densities were observed in PVDF75 and PVDF50 compared to the other electrospun mats because of small fibril diameters and reduced tendency for beading.

While all the blends of PVDF/ r-PAC and the homopolymer PVDF crystallized into the electroactive (EA) crystal phases as detected in WAXS, homopolymer r-PAC was completely amorphous. The TG curves showed that PVDF/r-PAC blends and homopolymer r-PAC are thermally stable below 180 °C. Above 180 °C, the blends and homopolymer r-PAC show a complex multi-step thermal degradation process whereas homopolymer PVDF showed excellent thermal stability up to 450 °C.

The sessile drop contact angle measurements showed that fibrous mats obtained from all materials, including homopolymer r-PAC and PVDF, and all PVDF/r-PAC blends, are very hydrophobic with contact angles over 120° with water. However, they showed very low contact angles with dodecane (oil) and the oil droplets were immediately dispersed on the surface after deposition confirming that the mats are super-oleophilic. These properties confirm that electrospun fibers of PVDF/r-PAC may be ideal materials for oil-water filtration.

The addition of r-PAC to PVDF led to significant, even drastic, decreases in protein adsorption when the r-PAC content was 25% or greater. This indicates that, in addition to being highly hydrophobic, these materials are highly resistant to fouling by biomacromolecular solutes.

In summary, our findings in this study highlight the applications of r-PAC and its blends with PVDF as potential materials for wastewater treatment processes displaying high hydrophobicity and excellent fouling resistance over a broad composition range. In a future study, we will report on the thermal properties of these materials such as their heat capacities and melting behavior.

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Chapter 6: Thermal degradation and dynamic fragility of a novel series of polyampholytes

A manuscript is under preparation for the study discussed in this chapter.

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6.1 Introduction

Polyampholytes are macromolecules with oppositely charged units attached to different side groups on the backbone [1]. They show both acidic and basic properties and, due to the presence of charged side groups, they are hydrophilic. Hence, polyampholytes are often used in fabricating fouling resistant filtration membranes [2-4]. However, for certain applications like the filtration of oil–water mixtures, the filtration membranes should contain a hydrophobic component. Usually this is attained by blending polyampholytes with a hydrophobic polymer like poly(vinylidene fluoride), PVDF [5]. In this study a novel series of polyampholytes was synthesized by copolymerizing a hydrophobic monomer (2,2,2-trifluoroethyl methacrylate – TFEMA), a positively charged monomer [2-(methacryloyloxy)-ethyl] trimethylammonium chloride – MAETA), and a negatively charged monomer (methacrylic acid – MAA) [5]. Since the monomer units are randomly copolymerized to obtain the polyampholytes, they are called random polyampholyte amphiphilic copolymers or r-PACs in short. The quaternary amine unit in the MAETA is said to disrupt the cell membranes of bacteria, thus the novel synthesized r-PACs have antibiotic characteristics as well [6]. Understanding the thermal behavior of the r-PACs is very important since they are novel polymers synthesized to fabricate fouling resistant filtration membranes [2, 5]. Due to the presence of both positive and negative charged units, it can be hypothesized that the glass transition temperature of polyampholytes could be very high as the electrostatic interactions between the charged units cause dipole-dipole crosslinking. The synthesis of the r-PAC is presented in our previous work [5].

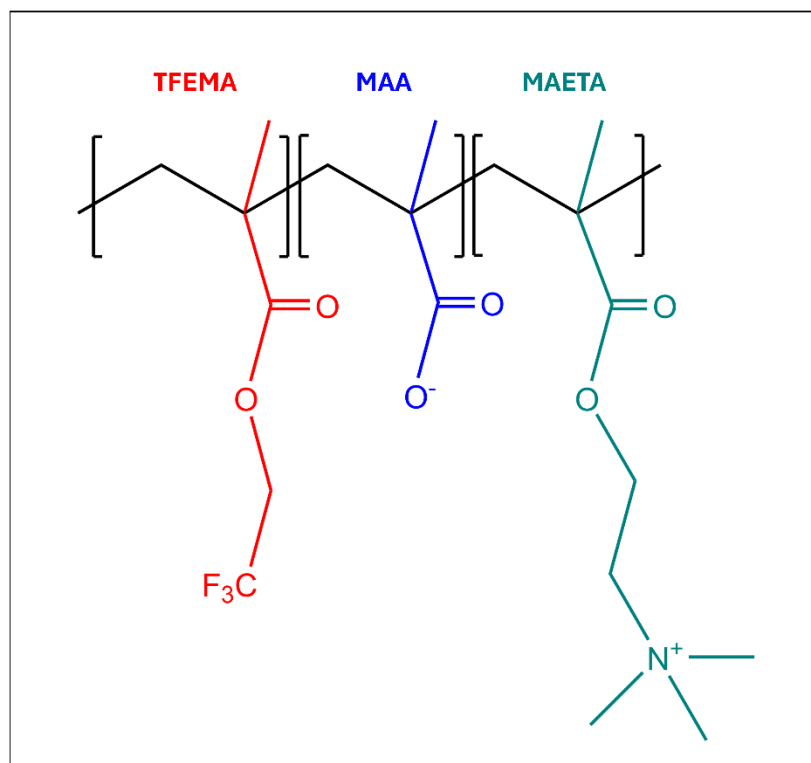


Figure 6.1: Chemical structure of r-PAC. The hydrophobic unit TFEMA is shown in red, the anionic unit MAA is shown in blue, and the cationic unit MAETA is shown in green.

Thermal degradation is the process by which a material's chemical structure breaks down when exposed to high temperatures. The onset temperature of thermal degradation is very important in polymer processing techniques [7] or applications where polymeric materials are used at very high temperatures as it can be considered to be the upper limit of the operational temperature range of the polymer [8]. In addition to that, heat treatment is one of the most efficient methods to enhance the properties and performance of a polymer [9, 10]. Another important aspect of thermal degradation is the effective waste management through increasing the rate of degradation of bulk produced polymers as a solution for the ever increasing volume of plastic waste [11, 12]. Thus,

determination of the onset temperature of thermal degradation and understanding the thermal degradation process of a polymer is of utmost importance.

Dynamic fragility of a polymer is a measure of the rate of change of its structural relaxation dynamics when the temperature approaches its glass transition temperature T_g and as introduced by Angell it is a valuable tool for gaining insights into the glass formation in liquids [13, 14]. Liquids that form strong glasses show an Arrhenius relationship with the relaxation dynamics (relaxation time or viscosity) while those that form fragile glasses show non-Arrhenius relationships. Dynamic fragility index (m) value can be expressed as:

$$m = \left. \frac{d(\log_{10}(X))}{d\left(\frac{T_g}{T}\right)} \right|_{T=T_g} \quad (6.1)$$

Here X can either be τ (relaxation time) and η (viscosity) and T is the temperature. m is also considered as the degree of non-Arrhenius behavior or the deviation of the relaxation time from an Arrhenius behavior. According to Clark *et al.* [15] higher m value would imply that the relaxation time of the polymer liquid will increase as the temperature approaches the glass transition temperature T_g forming a fragile glass ($m > 120$). When the m value is small ($16 < m < 60$) the polymer liquid forms a strong glass as the relaxation time does not increase as much as in a fragile glass forming polymer, giving ample time to the chains to relax and efficiently pack as the temperature approaches T_g .

Fast scanning calorimetry (FSC) is one of the most prominent thermal analysis methods as samples can be heated and cooled at extremely high rates in the scale of 1000 K/s. Heating and cooling at such high rates allows the sample to undergo thermal transitions like the glass transition or crystal melting that take place at very high temperatures minimizing the chance of thermal degradation. FSC has been used in estimating the dynamic fragility of charged polymers such as polyelectrolytes by Clark *et al.* [15], an uncharged polymer like polyether ether ketone (PEEK) by Govinna *et al.* [16] and ionic liquids by Simon *et al.* [17]. Therefore, it is an ideal method of thermal analysis for polymers that have high glass transition temperatures since slow cooling rates (~ 10 °C/min) in conventional differential scanning calorimeters (DSC) could more readily degrade the sample.

In this study, four variants of r-PAC were synthesized by varying the composition of each monomer unit as shown in Table 6.1. The thermal degradation dynamics of the four r-PAC variants were studied using thermogravimetric analysis and Fourier-transform infrared (FTIR) absorbance spectra. The dynamic fragility of the four r-PAC variants was estimated by analyzing the heat flow data obtained from FSC.

Table 6.1: Monomer compositions of polyampholyte variants and their overall charged nature

R-PAC Variant	Hydrophobic / Charged Weight ratio, %		Positive / Negative Molar ratio, %		Overall Charged Nature
	TFEMA	MAETA + MAA	MAETA	MAA	
P1	50	50	50	50	Neutral
P2	70	30	50	50	Neutral
P2+	70	30	70	30	Positive
P2-	70	30	30	70	Negative

6.2 Experimental approaches

6.2.1 *Sample preparation*

As received P1, P2, P2+, and P2- crumbs were dissolved in N,N-dimethylformamide to prepare 10 wt.% solutions as described in section 3.2.1.3. The prepared solutions were then doctor bladed as explained in section 3.2.3 to obtain samples for TG, FTIR, and heat treatment.

Thin samples (thickness 10 – 20 μm) of all four r-PAC variants were prepared for fast scanning calorimetry by the method discussed in section 3.2.6.

6.2.2 *TG*

As received pellets of all four variants of r-PAC were analyzed by thermogravimetry as described in section 3.3.3.1.

6.2.3 FTIR analysis

FTIR absorbance spectra of the doctor bladed r-PAC thin films before and after heat treatment were collected using the methods described in 3.3.2.1.

6.2.4 Heat treatment

The doctor bladed thin films of the four r-PAC variants were heat treated as described in section 3.3.3.3. The P2 variants (P2, P2+, and P2-) were heated at 280 °C or 375 °C (different samples). Based on the TG results, the P1 films were only heat treated at 375 °C. Figure 6.2 shows three P2 films before heat treatment, heat treated at 280 °C, and heat treated at 375 °C. The discoloration observed in the samples is due to the thermal degradation.

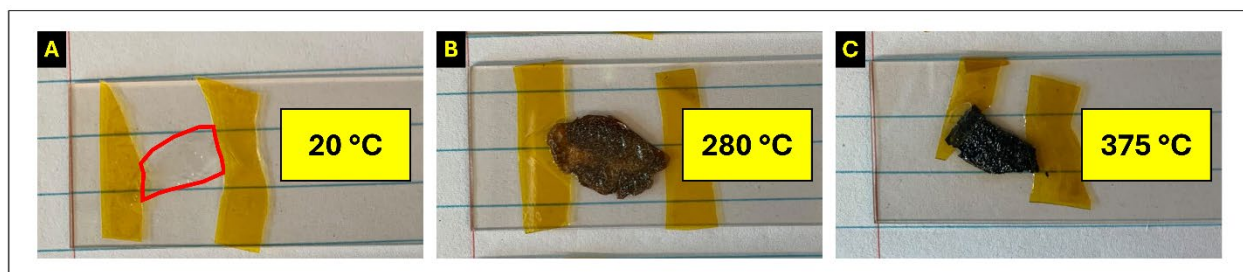


Figure 6.2: Three doctor bladed P2 films. A) No heat treatment (left). Sample outlined in red; B) heat treated at 280 °C (middle); and C) heat treated at 375 °C (right). Kapton® high temperature tape is shown in orange.

6.2.5 Fast scanning calorimetry (FSC)

Ultra-thin samples of the four r-PAC variants were heated and cooled in FSC using the temperature program given in section 3.3.3.4. The samples were cooled at 12 different cooling rates (4000,

3500, 3000, 2500, 2000, 1500, 1000, 500, 300, 100, 50, and 30 K/s) and heated at a constant rate of 2000 K/s from -90 °C to 300 °C. As the cooling rate decreased, more pronounced enthalpic relaxation at the glass transition region was observed in the subsequent heating cycle. Using the Moynihan method [18] described in section 2.3.1.3.1 but using the heat flow rate data instead of heat capacity, the fictive temperatures for each cooling rate were estimated for each r-PAC variant by solving this equation for the lower limit of the left-side integral:

$$\int_{T_f}^{T \gg T_g} (\dot{Q}_l - \dot{Q}_g) dT = \int_{T \ll T_g}^{T \gg T_g} (\dot{Q} - \dot{Q}_g) dT \quad (6.2)$$

$\dot{Q}_l$ and $\dot{Q}_g$ are the extrapolated heat flow rate baselines in the liquid and glassy states, respectively. $\dot{Q}$ is the heat flow rate data curve.

6.3 Results and discussion

6.3.1 Thermogravimetric analysis

The TG analysis of each doctor bladed sample is shown in Figure 6.3-A. Out of all variants, P1 (black) showed a slight initial mass loss below 200 °C. This can be attributed to the ejection of bound water in P1 since the high composition of charged units results in high affinity for water. All other variants (P2 (red), P2+ (green), and P2- (blue)) were stable over the temperature range below 200 °C since their hydrophobic composition is very high. All variants show a complex degradation process with multiple degradation steps. The degradation profile of P1 (black) shows two main steps, at 240 °C and 465 °C. The three P2 variants show three degradation steps.

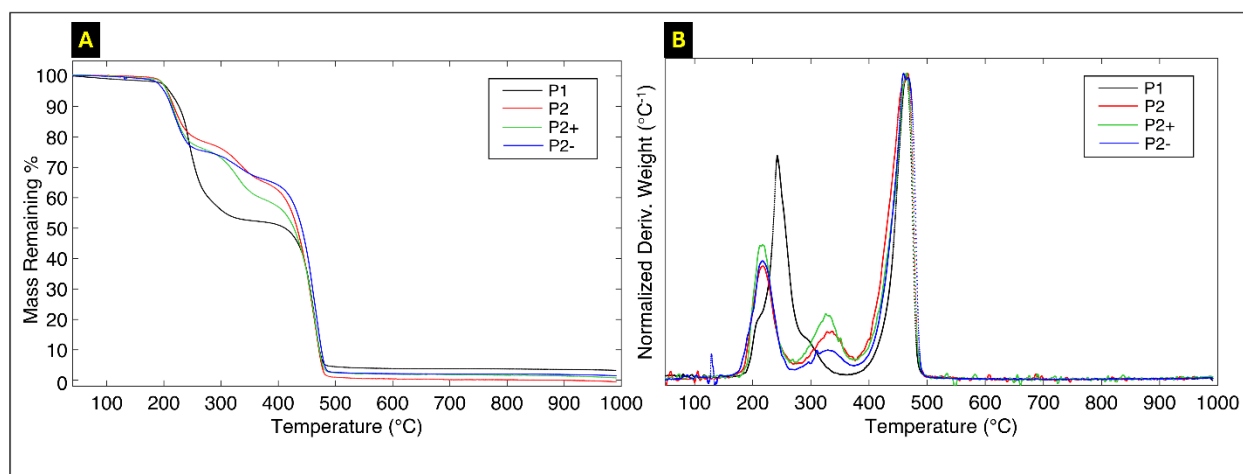


Figure 6.3: A) Thermogravimetric analysis showing percent mass remaining vs. temperature at a rate of 10 °C/min; B) Normalized first derivative of mass remaining vs. temperature: P1 (black), P2 (red), P2+ (green), P2- (blue). The derivative of the mass remaining is normalized to the value of the tallest peak observed at 450 °C.

To obtain clearer insight into the degradation profiles, the first derivative of the fraction of remaining mass is plotted against the temperature in Figure 6.3-B. All P2 variants show an intense peak that corresponds to the first major mass loss around 215 °C. On the other hand, P1 shows its first major mass loss at a higher temperature, around 240 °C. However, this peak has two shoulders on either side with apparent peak values at 215 °C and 290 °C. All P2 variants show a second mass loss at 330 °C. The next, and final, major mass loss for P1 occurs at 465 °C at which the other variants show their third and final significant mass loss. Between the major degradation steps, a few temperature zones can be identified at which only a little further degradation is taking place. These occur near 280 °C for all P2 variants and near 375 °C for all polyampholytes. With these

results in mind, thin film samples of P2, P2+, and P2- were then annealed at 280 °C or 375 °C, and P1 thin films were annealed only at 375 °C.

6.3.2 *Analysis of IR vibrational spectra*

Figure 6.4 shows the FTIR absorbance spectra of each polyampholyte variant at room temperature before any heating. The characteristic peaks for each monomer unit in the polyampholyte were identified using available databases [19, 20]. The peaks of interest that we observed, and which match literature for positions of the monomers, are listed in **Table 2**. The monomer peaks serve as references for peak assignment in the terpolymers.

All spectra before heat treatment show a complex peak around 1700 cm^{-1} which corresponds to the stretching vibration of C = O. The characteristic peaks of $\text{N}^+ - \text{C}$ in MAETA can be seen at 954 cm^{-1} and 1230 cm^{-1} . Other unique characteristic peaks for MAETA can be seen at 1480 cm^{-1} as a doublet and at 1416 cm^{-1} . At 1280 cm^{-1} , 666 cm^{-1} , and 650 cm^{-1} the characteristic peaks for C - F stretching and bending vibrations, respectively, can be observed in TFEMA. The doublet seen around 1140 cm^{-1} is a characteristic feature of TFEMA. However, the rightward peak of the doublet coincides with a characteristic peak of MAA at 1133 cm^{-1} . More characteristic peaks for MAA are observed at 1455 cm^{-1} , 1390 cm^{-1} , 1008 cm^{-1} , 966 cm^{-1} , and 950 cm^{-1} .

Next, we examined the IR absorbance spectra obtained for polyampholytes after annealing at 280 °C or 375 °C as shown in Figure 6.5. In the spectra obtained for P2, P2+, and P2- at 280 °C (Figure

6.5-B,C,D), the doublet at 1480 cm^{-1} , and the peaks at 1230 cm^{-1} , and 1416 cm^{-1} seen in the unannealed sample are no longer visible indicating that the MAETA monomer has been degraded. However, peaks at 1455 cm^{-1} , 1390 cm^{-1} , and 966 cm^{-1} show stronger intensities and a new peak appears at 1008 cm^{-1} showing strong presence of MAA in the sample partially degraded at $280\text{ }^{\circ}\text{C}$. Since the peaks at 1280 cm^{-1} , 666 cm^{-1} , and 650 cm^{-1} and the doublet at 1140 cm^{-1} are present at $280\text{ }^{\circ}\text{C}$ but at much lower intensity, it is evident that TFEMA has also begun degrading but is not fully degraded at $280\text{ }^{\circ}\text{C}$ in the P2 variants.

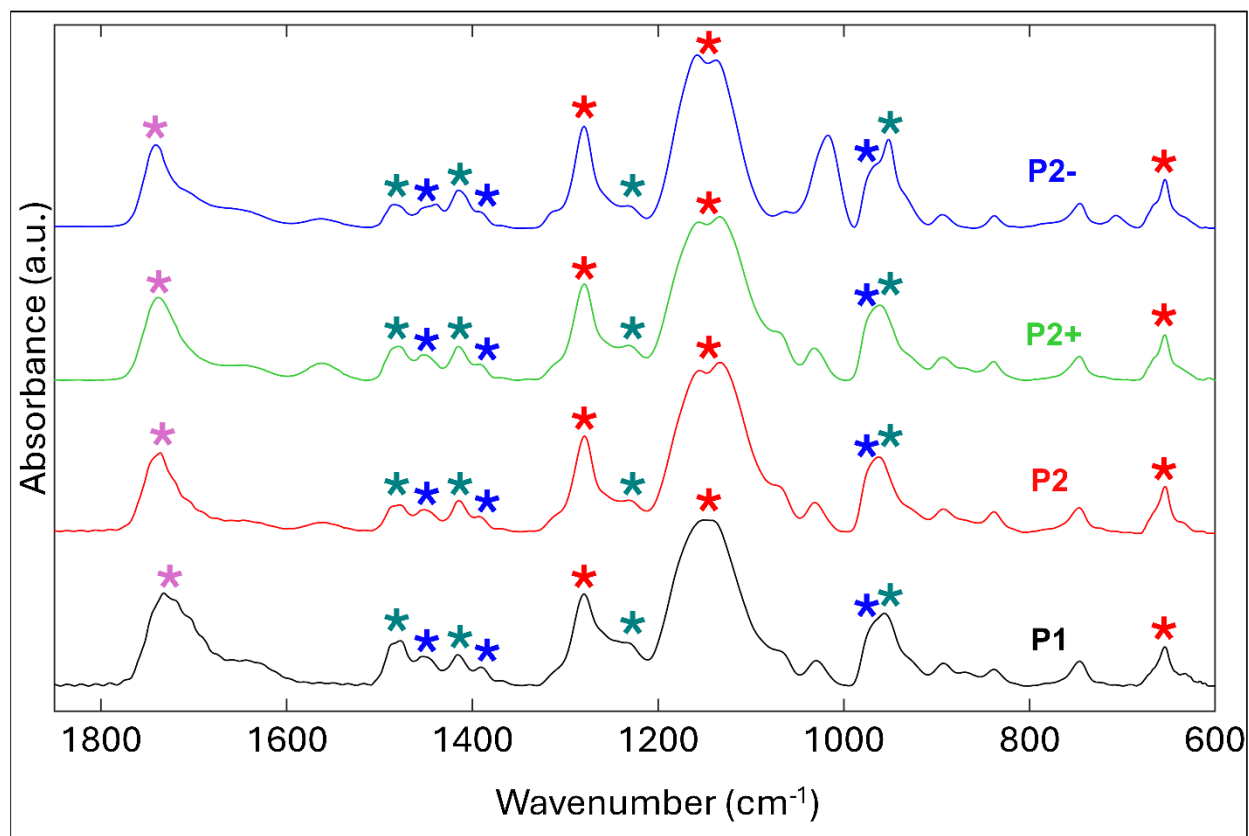


Figure 6.4: Room temperature FTIR absorbance spectra vs. wavenumber of unannealed PAs: P1 (bottom, black), P2 (red), P2+ (green), P2- (top, blue). Characteristic peaks of MAETA, MAA, and TFEMA units are labelled by green, blue, and red * signs, respectively.

Table 6.2: Observed IR frequencies of monomer units, in cm^{-1} (d – doublet).

* Peaks labelled in Figure 6.4

TFEMA	MAA	MAETA
	1767	
1739		
		1725
	1706	
		1645
	1480	*1480 - d
		1474
1453	*1455	
1417		*1416
	*1390	
*1280		
		*1230
*1140 - d	1133	
1075		
1034		1034
	*1008	
968	*966	
	950	954
		748
*666		
*650		

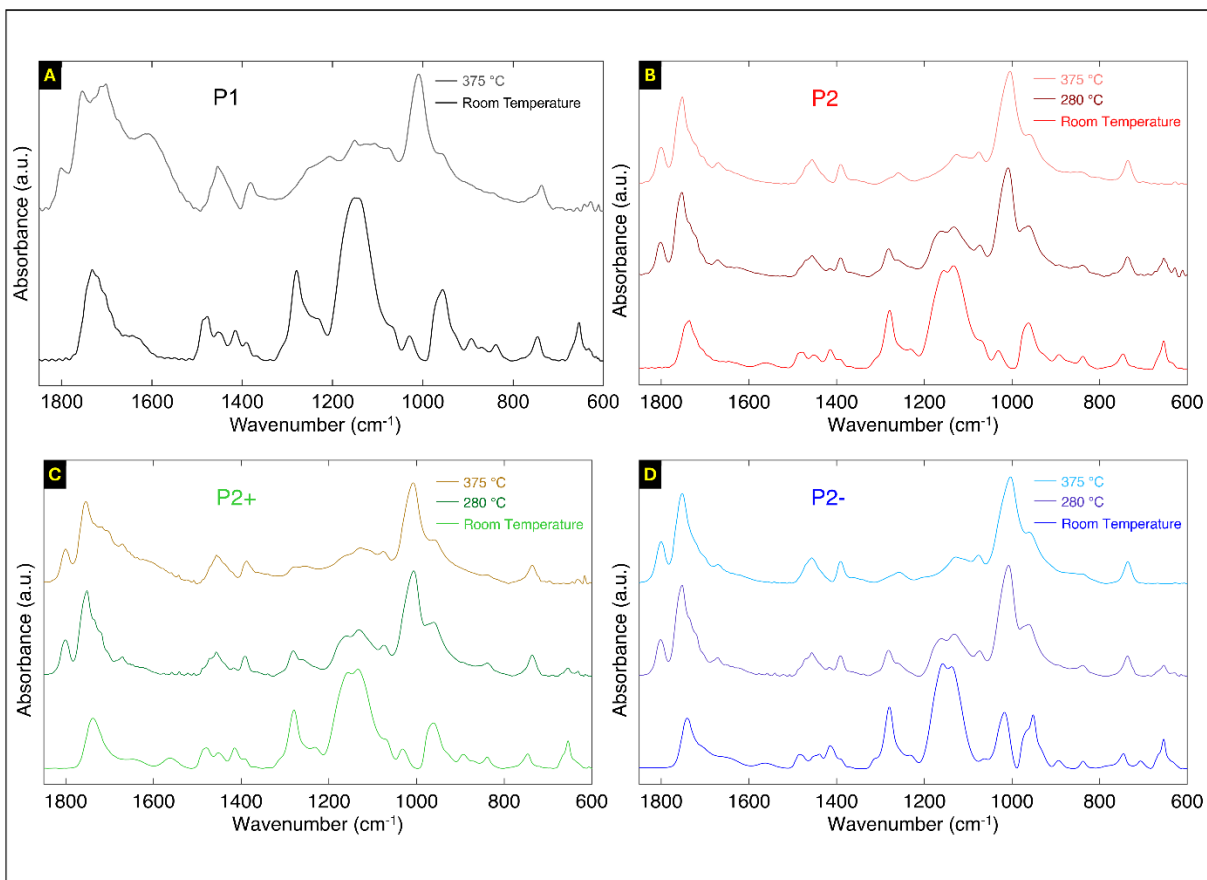


Figure 6.5: Room temperature FTIR spectra of both unheated (Room Temperature) samples and annealed PAs, characterized by highest sample annealing temperature. A) P1; B) P2; C) P2+; D) P2-. Unheated samples, 25 °C – bottom scans; Samples annealed at 280 °C – middle scans; Samples annealed at 375 °C – topmost scans.

At 375 °C, all characteristic peaks of TFEMA have diminished in all polyampholytes including the doublet at 1140 cm^{-1} leaving the characteristic MAA peak at 1133 cm^{-1} . The remaining peaks seen between 1800 cm^{-1} and 1700 cm^{-1} (at 1455 cm^{-1} , 1390 cm^{-1} , 1008 cm^{-1} , and 966 cm^{-1}) further confirm the presence of MAA in the samples at 375 °C. Hence, it can be confirmed that MAETA

units degrade first at 280 °C, followed by TFEMA units at 375 °C, and finally the rest of the polymer along with MAA units degrade at 465 °C (peak labelled by a blue star in Figure 6.6). By comparing this result with derivative TGA plots, the first mass loss observed in all P2 variants at 215 °C corresponds to the degradation of MAETA (peak labelled by a green star in Figure 6.6) and the second observed at 330 °C corresponds to the degradation of TFEMA units (peak labelled by a red star in Figure 6.6). From this observation, the complex degradation peak observed at 240 °C in derivative TGA thermographs of P1 can be explained. The shoulder at 215 °C corresponds to the MAETA degradation and it triggers TFEMA to degrade simultaneously giving rise to the peak observed at 240 °C (peak labelled by an orange star in Figure 6.6). Once all MAETA is degraded, the remaining TFEMA degrades at 290 °C.

6.3.3 *Fast scanning calorimetry*

The heat flow thermographs of FSC for each r-PAC variant are shown in Figure 6.7. The glass transition region can be clearly observed in the heating scans for all four r-PAC variants. The fictive temperature corresponds to the glass transition temperature, when determined during a heating process conducted at the same rate used in the preceding cooling curve. Since the heating rate is fixed at 2000 K/s in this study, the measured fictive temperature during heating subsequently to the cooling scan at 2000 K/s represents the glass transition temperature. The calculated T_g s for all r-PAC variants are shown in Table 6.3.

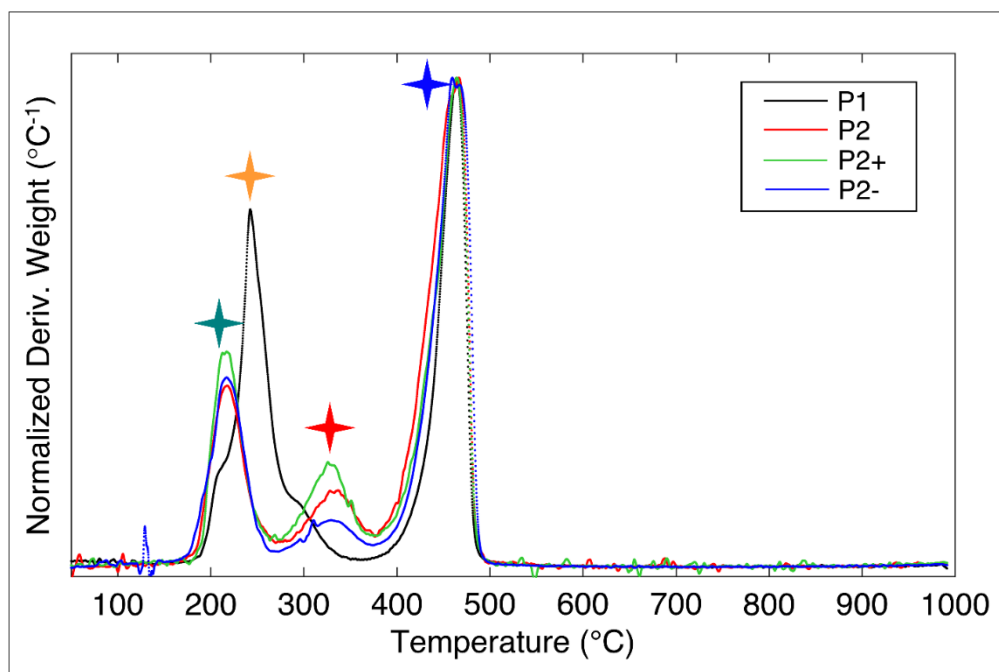


Figure 6.6: Normalized first derivative of mass remaining vs. temperature: P1 (black), P2 (red), P2+ (green), P2- (blue). Stars above each peak indicate the components degrading at the respective temperatures, Green – MAETA, red – TFEMA, blue – MAA and the rest of the polymer, and orange – simultaneous degradation of MAETA and TFEMA in P1.

Table 6.3: Glass transition temperature, WLF fit parameters, and dynamic fragility index of each r-PAC variant

r-PAC Variant	Glass Transition Temperature (°C)	C_1	C_2	Fragility Index ^a m
P1	174	28	114	108 ± 5
P2	132	7	27	95 ± 9
P2+	129	7	26	104 ± 18
P2-	147	10	41	104 ± 7

^a The standard deviation of the fragility index estimated using a bootstrap method with 10000 resampling iterations is taken as the uncertainty.

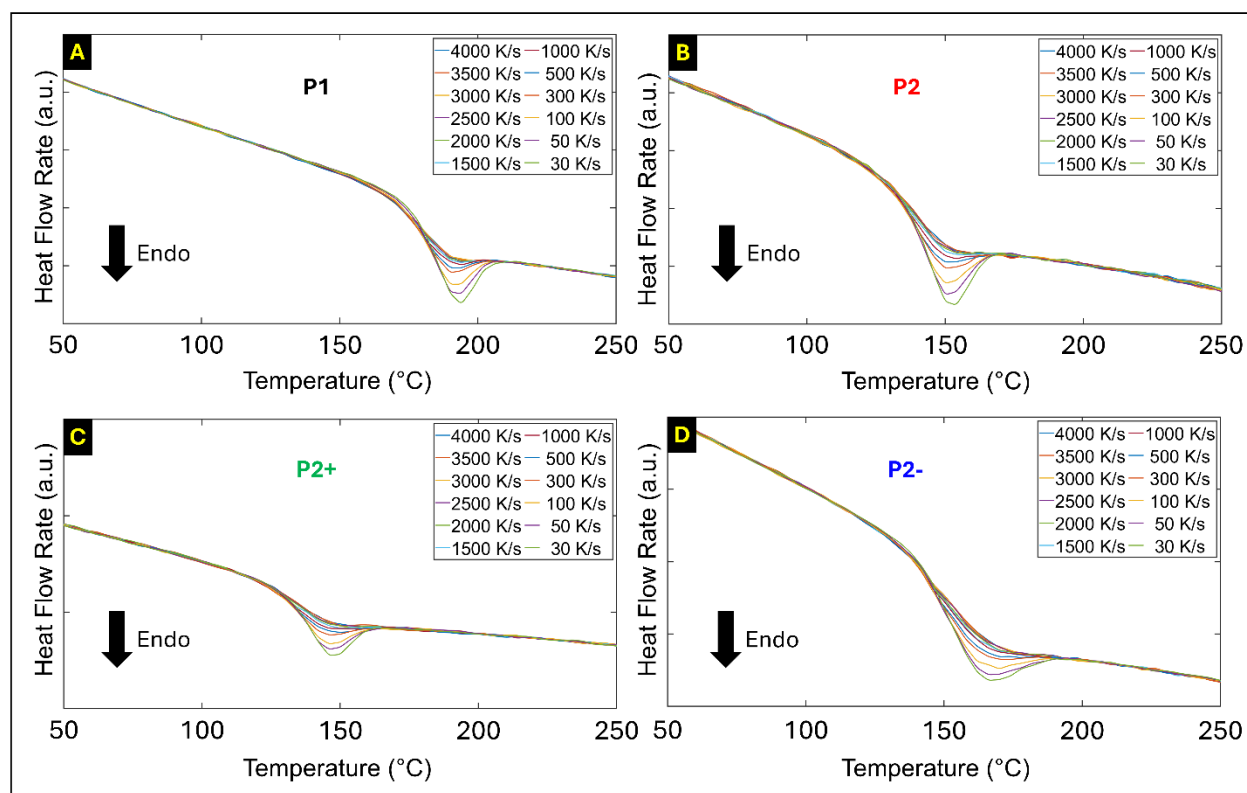


Figure 6.7: Heat flow rate vs. temperature for A) P1; B) P2; C) P2+; and D) P2- on heating at 2000 K/s. The prior cooling rates are shown in the legend. The endothermic peak in the glass transition temperature range corresponds to the enthalpic relaxation.

From Table 6.3, it is understood that T_g is decreased by a significant amount with the increase of TFEMA composition. The highest T_g value is observed for P1 (174 °C) and as the TFEMA fraction (hydrophobic) is increased, the T_g value has decreased by ~40 °C as evident in P2 and P2+. An increase in the hydrophobic units results in relatively less cross linking due to electrostatic interactions between the charged units thus decreasing the glass transition temperature. The P2 variants could also possess longer chains made out of TFEMA units. Hence, the intrinsic T_g of TFEMA (~70 °C [21]) could lower the T_g of the P2 variants. The glass transition temperature of

P2 and P2+ is ~130 °C and it is the lowest among the r-PACs. The low MAA composition (anionic unit) results in significantly less hydrogen bonding lowering the interactions between the chains thus lowering the T_g value as well. The T_g value increases again to 147 °C when MAA units are added as seen in P2-. It further confirms that the introduction of the hydrogen bonds increases the T_g .

The dynamic fragility of r-PAC variants was estimated using the rate dependence of T_f by the William-Landel-Ferry (WLF) model [22] given by equation 6.3:

$$\log_{10} \left(\frac{\beta}{\beta_{ref}} \right) = \frac{C_1(T_f - T_{fref})}{C_2 + T_f - T_{fref}} \quad (6.3)$$

Here T_f and T_{fref} are the calculated fictive temperature and the fictive temperature of the cooling rate chosen as the reference. β and β_{ref} are the prior cooling rates and the reference cooling rate, respectively. It is common practice to choose the slowest cooling rate where no degradation was observed as the reference. In this study, no degradation was observed even at the slowest cooling rate of 30 K/s, hence it is chosen as the reference. C_1 and C_2 are fitting parameters that need to be estimated. By rearranging the terms in equation 6.3, WLF equation is fitted to T_f vs $\log_{10}(\beta)$ plot of all r-PAC variants as shown in Figure 6.8 to obtain C_1 and C_2 fit parameters.

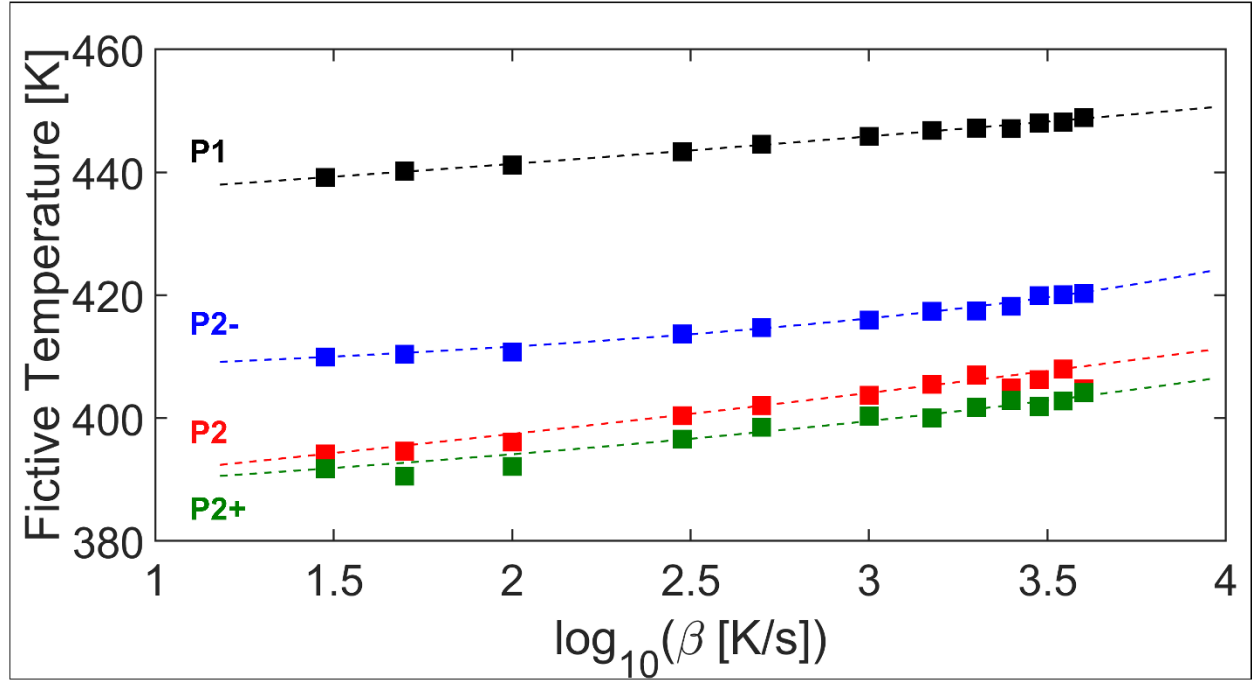


Figure 6.8: Calculated fictive temperatures T_f vs logarithm of prior cooling rate for P1 (black - top); P2 (red); P2+ (green - bottom); and P2- (blue).

Then the fragility index m can be determined by [15]:

$$m = \frac{d(\log_{10}(\beta))}{d\left(\frac{T_{fref}}{T_f}\right)} = \frac{C_1}{C_2} T_{fref} \quad (6.4)$$

The estimated values for C_1 , C_2 , and the calculated values of fragility index for each r-PAC variant are shown in Table 6.3. All r-PACs exhibited a fragility index close to 100 indicating that they form moderately strong glasses. Since they also show high T_g s, according to Clark *et al.* they form rigid and fragile glassy structures with a lower packing efficiency [15].

6.4 Conclusions

The newly synthesized series of polyampholytes (r-PACs) have complex degradation mechanisms related to their monomeric structures. All materials showed multi-step degradation, with major mass loss steps at 215 °C, 330 °C, and 465 °C, depending on the variant. FTIR spectra of freshly prepared r-PACs were compared to spectra of r-PACs heat treated at intermediate, nearly stable temperature regions. This comparison showed that the positively charged unit (MAETA) degrades first, followed by the hydrophobic unit (TFEMA), and finally the negatively charged unit (MAA).

The glass transition temperature of P1 shows the highest value as it has more charged units, both positive and negative in equal parts, resulting in high cross linking due to the electrostatic interactions. On the other hand, when the neutral and hydrophobic monomer (TFEMA) fraction is increased the T_g decreases due to fewer electrostatic interactions present in P2 variants relative to P1. Addition of MAA forms more hydrogen bonding interactions and raises the T_g again. All r-PACs indicated moderately strong fragility indices (~ 100) exhibiting high temperature rigid and fragile glass forming ability with a low packing efficiency.

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Chapter 7: Rheological analysis and electrospinning of poly(vinylidene fluoride) solutions prepared with environmentally friendly gamma-valerolactone

A manuscript is under preparation for the study discussed in this chapter.

Jayasekara, A. S., Buyea, L., Wyatt, K., O'Hara, R., Asatekin, A., & Cebe, P. Rheological analysis and electrospinning of poly(vinylidene fluoride) solutions prepared with environmentally friendly gamma-valerolactone. Applied Rheology. (2025) – In preparation

7.1 Introduction

Poly(vinylidene fluoride) (PVDF) is a versatile commodity polymer with a wide range of applications, thanks to its unique properties [1-5]. Its excellent piezoelectric properties make it ideal for fabricating sensors and actuators [1, 6-9]. Furthermore, its high natural hydrophobicity makes it a popular choice for filtration applications [10-15]. PVDF's strong adhesive qualities and remarkable durability also make it a preferred binder in lithium-ion batteries [2, 9, 16]. With excellent thermal, mechanical, and chemical stability, PVDF is used to make coatings, linings, and sheets in various industries, including nuclear waste management, the aviation industry, and construction [2, 16].

PVDF is a polymorphic polymer that exists in three common crystalline phases: alpha (α – Type II), beta (β – Type I), and gamma (γ – Type III) [1, 17-19]. Among these three polymorphs, the β and γ phases are considered electro-active because their unit cell conformations result in non-zero dipole moments [1, 7]. Thermodynamically favorable α -phase has a unit cell conformation that results in a net zero dipole moment [20, 21]. The β -phase features a planar zigzag chain conformation, which generates a high dipole moment of approximately 2.1 D (7×10^{-30} Cm) that is oriented perpendicular to the chain direction [6, 7]. Therefore, it is essential to focus on obtaining the β -phase, as it significantly contributes to the piezoelectric properties of PVDF. A widely used method to prepare PVDF is by electrospinning PVDF solutions which is known to achieve the β -phase in PVDF [21-29]. Electrospinning is a technique used to produce non-woven mats with fibers at the nanoscale [30, 31]. The electrospun fiber mats of PVDF demonstrate significant

hydrophobicity compared to its thin film form, making them ideal candidates for filtration applications [10].

PVDF solutions for electrospinning are made by dissolving PVDF resin, either in powder or pellet form, using strong solvents. Common solvents for preparing PVDF solutions include N,N-dimethylacetamide (DMAc), N,N-dimethylformamide (DMF), and N-methyl-2-pyrrolidone (NMP) [1, 8, 22, 32-34]. PVDF demonstrates excellent solubility in these solvents at room temperature. However, improper handling of these solvents presents significant risks to human health and the environment. They are toxic, corrosive, and can cause serious health issues to the human reproductive and respiratory systems if they enter the bloodstream [35, 36]. Therefore, it is of utmost importance to find alternative solvents that do not pose such extreme hazards in PVDF processing. γ -Valerolactone (GVL) is a solvent produced by reducing levulinic acid, which can be obtained through the acid hydrolysis of cellulose, a common polysaccharide found in plants [37-42]. GVL is biorenewable, has very low toxicity, and readily dissolves in water, with a boiling point of 207 °C. It has been used in several recent studies to dissolve PVDF, facilitating the production of membranes through non-solvent induced phase separation (NIPS) techniques [37-43]. As such, GVL presents a promising green alternative for processing PVDF.

To our knowledge, there have been no studies investigating the use of GVL for electrospinning PVDF. Unlike other hazardous solvents, GVL presents a significant challenge in preparing PVDF solutions due to the rapid sol-to-gel transition that occurs [40]. The solubility of PVDF in GVL can be estimated with the help of Hansen solubility parameters (HSPs) δ_D , δ_P , and δ_H which

represent the contributions to the molar vaporization energy from dispersion, polarity, and hydrogen bonding, respectively [36, 39, 40, 44]. The Hansen solubility parameters (HSPs) for polyvinylidene fluoride (PVDF) and its common solvents are presented in Table 7.1, along with the relative energy difference (RED) for each solvent. The RED value is calculated using the following equation:

$$RED = \frac{R_a}{R_0} \quad (7.1)$$

Here, R_0 is the radius of interaction of the Hansen solubility parameter sphere for a solute *i.e.* the polymer. R_a is the relative affinity or the molecular interaction distance between the polymer and the solvent which is calculated from equation 7.2:

$$R_a = \sqrt{4(\delta D_P - \delta D_S)^2 + (\delta P_P - \delta P_S)^2 + (\delta H_P - \delta H_S)^2} \quad (7.2)$$

where subscript P corresponds to the HSP of the polymer, and subscript S corresponds to the HSP of the solvent. The RED value indicates how effectively a solvent can dissolve a solute. The solvent is considered good if the RED value is close to 0 [35, 42, 45]. Conversely, as the RED value approaches 1, the solubility of the solute in that solvent decreases. If the RED value exceeds 1, the solvent cannot dissolve the solute. GVL has a RED value of 0.7, indicating that it needs external support like heat to dissolve PVDF efficiently [44]. Therefore, the PVDF/GVL solutions attain an entangled form when the heat is removed, eventually leading to gelation. Hence, the investigation of the flow properties of PVDF/ GVL solutions and how temperature and shear rate (frequency) affect them is extremely important when it comes to electrospinning.

Table 7.1: Hansen solubility parameters of PVDF and its solvents.

Polymer/ Solvent	δD (MPa ^{0.5})	δP (MPa ^{0.5})	δH (MPa ^{0.5})	R_0 (MPa ^{0.5})	R_a (MPa ^{0.5})	RED	Ref.
PVDF	17.2	12.5	9.2	9.6			[44]
DMAc	16.8	11.5	10.2	- ^a	1.8	0.2	[46]
DMF	17.4	13.7	11.3	-	2.6	0.3	[46]
NMP	18.0	12.3	7.2	-	2.3	0.2	[46]
GVL	19.0	16.6	7.4	-	6.4	0.7	[44]

^a – indicated data are not available

This study performed a detailed oscillatory rheological analysis using temperature ramps and frequency sweeps on three PVDF/GVL solutions with varying concentrations. The addition of salt to polymer solutions is a widely used technique to disrupt entanglements. Thomas *et al.* [47] has shown that the addition of LiCl can disrupt the electrostatic crosslinking in charged polymers like polyelectrolytes. Therefore, to determine the effect of salt in gelation kinetics in PVDF/GVL solutions time sweeps were performed on solutions prepared with and without LiCl. Based on the results of the rheological tests, suitable electrospinning parameters, such as flow rate and temperature, were established and applied in the electrospinning process to produce nanoscale fibers successfully. To the best of our knowledge, this is the first time PVDF fibers have been obtained through electrospinning solutions made with GVL. Then, the obtained fiber mats were characterized using scanning electron microscopy (SEM), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), Fourier-transform infrared spectroscopy (FTIR), wide-angle X-ray scattering (WAXS).

7.2 Experimental

7.2.1 *Solution preparation*

PVDF powder and PVDF/LiCl mixtures were dissolved in GVL and GVL/Acetone mixtures as described in 3.2.1.4.

7.2.2 *Rheological analysis*

Oscillatory rheological tests were performed on PVDF and PVDF/LiCl solutions made from GVL as described in 3.3.5 to determine the ideal solution concentration for electrospinning. Since a parallel plate geometry is used in this experiment, the strain rate $\dot{\gamma}$ is measured at the edge of the geometry. This is the maximum strain rate, and all data in this study are expressed in terms of that.

7.2.3 *Electrospinning*

PVDF solutions and PVDF/LiCl solutions made from GVL/Acetone mixtures were electrospun as described in 3.2.2 and the spinning parameters are as follows: Applied voltage, 30 kV; working distance, 30 cm; needle gauge, 18; and pump rate, 0.6 mL/hr.

7.2.4 *Characterization*

Scanning electron microscopy, Fourier-transform infrared spectroscopy and wide angle X-ray scattering were performed on electrospun samples as described in sections 3.3.1.1, 3.3.2.13.3.2.1.1, and 3.3.2.2.

7.3 Results and discussion

7.3.1 Rheological analysis

7.3.1.1 Frequency sweeps

The variation of the storage modulus (G') and the loss modulus (G'') with the oscillation frequency is obtained for the PVDF/GVL solutions with PVDF concentrations of 10 wt.%, 12.5 wt.% and 15 wt.% at 25 °C, 45 °C, and 65 °C as shown in Figure 7.1. The full data set is shown in Figure 7.1. Data at high frequencies are impacted by effects of inertia in the plate geometry. The limits of reliability for the G' and G'' vs. frequency plots have been calculated and are presented in Figure Appx. C.1.

The 10 wt.% and the 12.5 wt.% solutions (Figure 7.1-A,B) show a sol-to-gel transition around 0.7 – 0.8 rad/s at 25 °C indicated by the crossover point where G' goes below G'' . This result indicates that at 25 °C and low frequencies the solutions with these concentrations behave like viscoelastic solids or as a gel. As the frequency is increased, they start to break the entanglements in the gel and after a critical frequency value they start to behave as viscoelastic liquids (at very high frequencies G' shows a small decrease due to the presence of inertial effects arising at very high frequencies). When the temperature is increased (for example, to 45 °C and 65 °C), these two solutions showed well defined G'' values and very noisy G' values below the reliable data limit. This result indicates that at elevated temperatures the liquid-like behavior of the solutions is dominant relative to the solid-like behavior. Using the frequency sweep data, a value for the critical volume flow rate V_c was calculated as 0.55 mL/hr (see Appendix C: C.1). Since the pump rate

used in electrospinning is 0.6 mL/hr, the solutions maintained their viscoelastic liquid behavior without undergoing gelation.

The 15 wt.% solution (Figure 7.1-C) shows viscoelastic solid behavior at 25 °C throughout the entire frequency range except at very high frequencies. Data obtained at high frequencies is unreliable due to the high inertial effects as mentioned in the previous paragraph. Therefore, it can be concluded that the solution has become a gel at 25 °C. As the temperature increased to 45 °C, a sol-to-gel transition can be observed at a similar frequency (*i.e.* 0.7 rad/s) to that seen in the lower concentration solutions. The solution behaves as a viscoelastic liquid at 65 °C since no defined G' values are observed at that temperature in the reliable data range.

G' and G'' data vs. frequency can be unreliable at high frequency. To explore solution behavior in the high frequency regime we measured the dynamic viscosity. Figure 7.2 shows the variation of the dynamic viscosity with the oscillating strain rate for the three solutions at three different temperatures obtained from the frequency sweep analysis. The dynamic viscosity increases with increasing concentration and decreases with increasing temperature. According to Cox-Merz rule the variation of the apparent dynamic viscosity of a liquid with shear rate is the same as the variation of the dynamic viscosity with frequency [48]:

$$\eta_{(\dot{\gamma}=\omega)} = |\eta^*|(\omega) \quad (7.1)$$

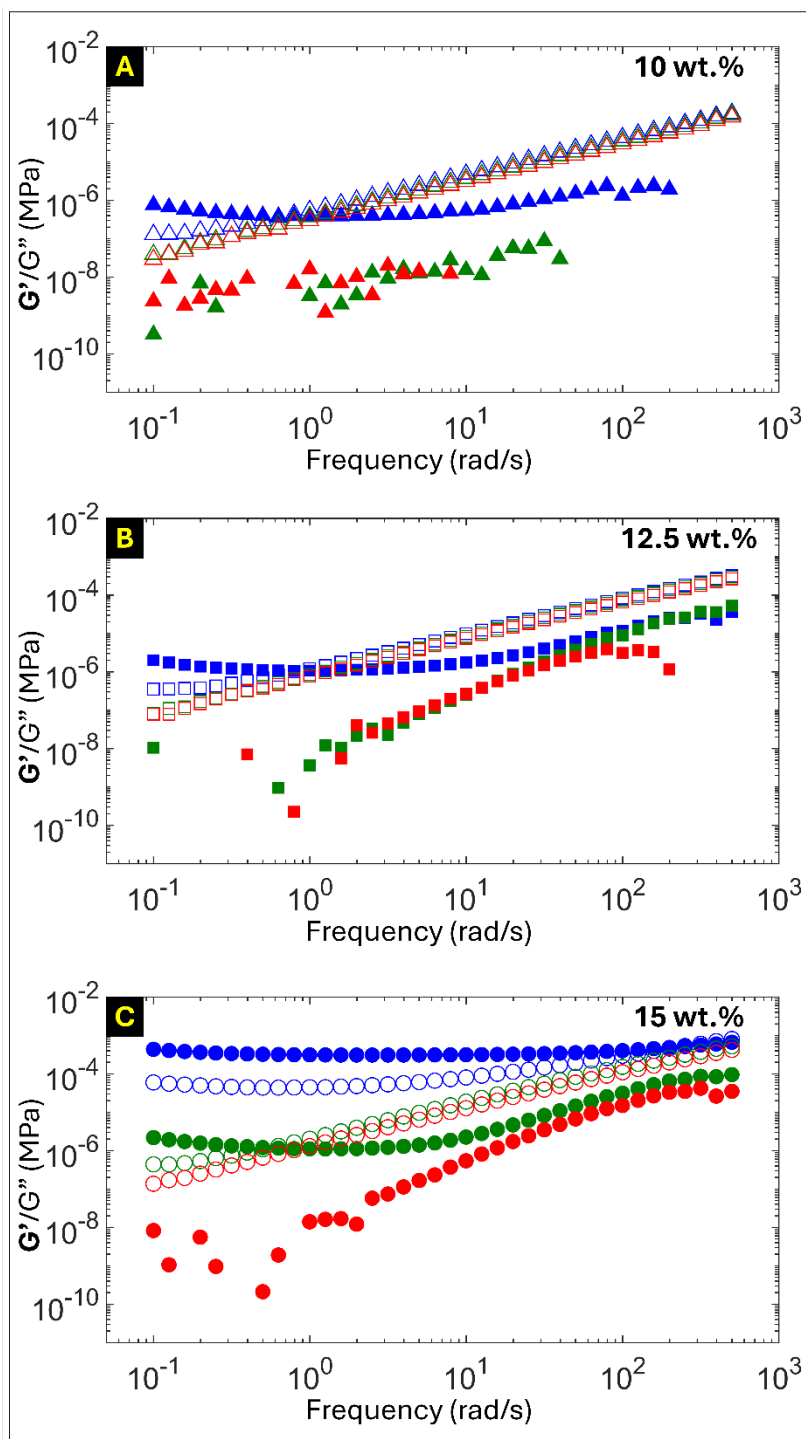


Figure 7.1: Variation of the storage modulus (G' – solid shapes) and the loss modulus (G'' – empty shapes) of A) 10 wt.% solution (triangles); B) 12.5 wt.% solution (squares); C) 15 wt.% solution (circles) at 25 °C (blue), 45 °C (green), and 65 °C (red) with the oscillating frequency.

Equation 7.1 is the Cox-Merz rule [48]. The left hand side is the apparent viscosity (η) as a function of the shear rate ($\dot{\gamma}$) and the right hand side is the dynamic viscosity (η^*) measured as a function of the frequency (ω). Dynamic viscosity values at lower frequencies are influenced by low torque effects, where the measured torque approaches the rheometer's minimum detectable limit. The reliable dynamic viscosity data ranges (above the low torque limit) are shown in Figure Appx. C.2. Therefore, the dynamic viscosity data at high frequencies are valuable for understanding the flow behavior of PVDF/GVL solutions, as G' and G'' measurements can be distorted by instrument inertia at those frequencies and complement the shear modulus data.

The viscosity of the 10 wt.% and 12.5 wt.% solutions at all temperatures showed an almost constant value with the variation of frequency (or shear rate) indicating nearly Newtonian behavior. However, the 15 wt.% solution at 25 °C showed shear thinning behavior as the viscosity was decreased with the increase of the frequency. At higher temperatures (45 °C and 65 °C), even the 15 wt.% solution showed nearly Newtonian behavior.

7.3.1.2 *Temperature ramps*

Figure 7.3 shows the variation of the storage modulus G' and the loss modulus G'' of the three PVDF/GVL solutions with temperature. The 10 wt.% solution shows well defined G'' values over the full temperature range during heating and it is above the G' values indicating viscoelastic liquid behavior. The G' values lose definition around 50 °C on heating. This shows that the elastic properties (solid-like properties) of the solution are diminishing at this temperature while the liquid-like properties dominate above it. During subsequent cooling, G'' values trace the heating

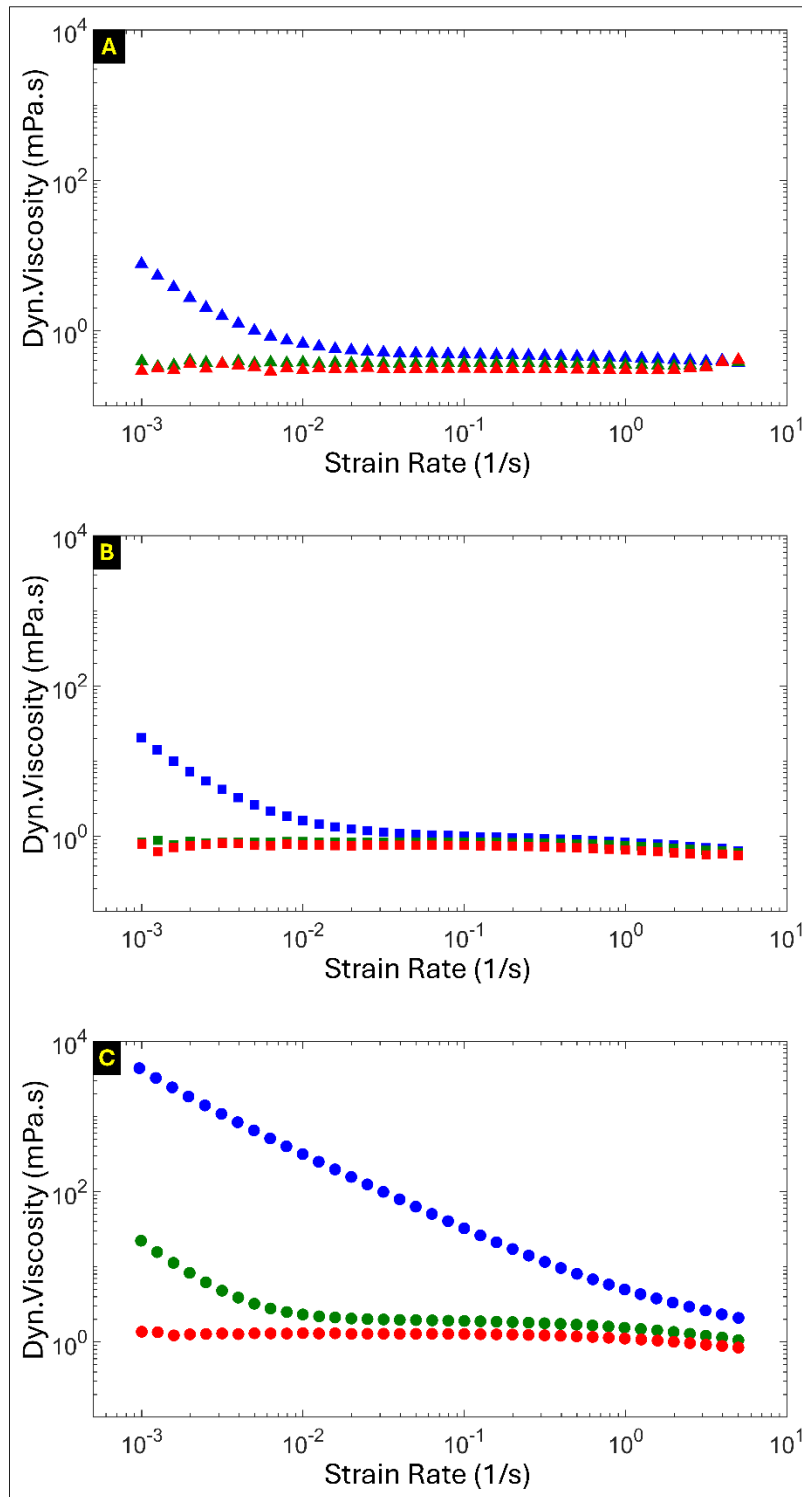


Figure 7.2: Variation of dynamic viscosity with strain rate in: A) 10 wt.% solution; B) 12.5 wt.%; and C) 15 wt.% solution at 25 °C (blue), 45 °C (green), and 65 °C (red).

values indicating that the solution still shows the same liquid-like behavior observed during heating. However, the G' values during cooling do not attain clear definition until the solution is cooled to 30 °C. From this result, it is evident that the hot 10 wt.% solution exhibits viscoelastic liquid behavior for a longer temperature range while cooling.

The 12.5 wt.% solution also shows viscoelastic liquid behavior during heating and cooling since the G'' values are greater than G' values over the entire temperature range. During heating, the solution's G' values lose definition around 65 °C. G'' values on cooling trace the G'' values observed on heating, and they are greater than the G' values indicating that the solution shows similar viscoelastic liquid properties in both heating and cooling. However, unlike the 10 wt.% solution, the 12.5 wt.% solution attains a well-defined G' value during cooling at the same temperature that it loses definition during heating (around 65 °C). Therefore, the 12.5 wt.% solution has a higher tendency to form a very viscous liquid quickly on heating.

The 15 wt.% solution shows a G' value greater than G'' value at the start of the heating cycle showing viscoelastic solid properties at low temperatures. Then it crosses below the G'' values at 65 °C showing a sol-to-gel transition on heating. This value is very close to the sol-to-gel transition temperature of PVDF/GVL solutions reported by Ravikumar *et al.* [40] which is 60 °C. On the cooling cycle, the 15 wt.% solution shows a well-defined G' value right away and it is very much the same as the G' values observed at 80 °C on heating. The G' values do not cross over the G'' values throughout the entire temperature range while cooling. However, G' shows an upward trend towards the G'' values at lower temperatures (below 30 °C) and a possible cross over point (sol-

to-gel transition on cooling) can be assumed to occur at a temperature below 25 °C which is the lower limit of the experimental temperature range.

As evident from the frequency sweeps and temperature ramps, the 10 wt.% solution shows more liquid-like properties even at room temperature above a critical frequency and it does not form significant crosslinks thus remain in liquid form when cooling from 100 °C until near room temperature. Hence, the 10 wt.% PVDF/GVL solution is chosen for electrospinning.

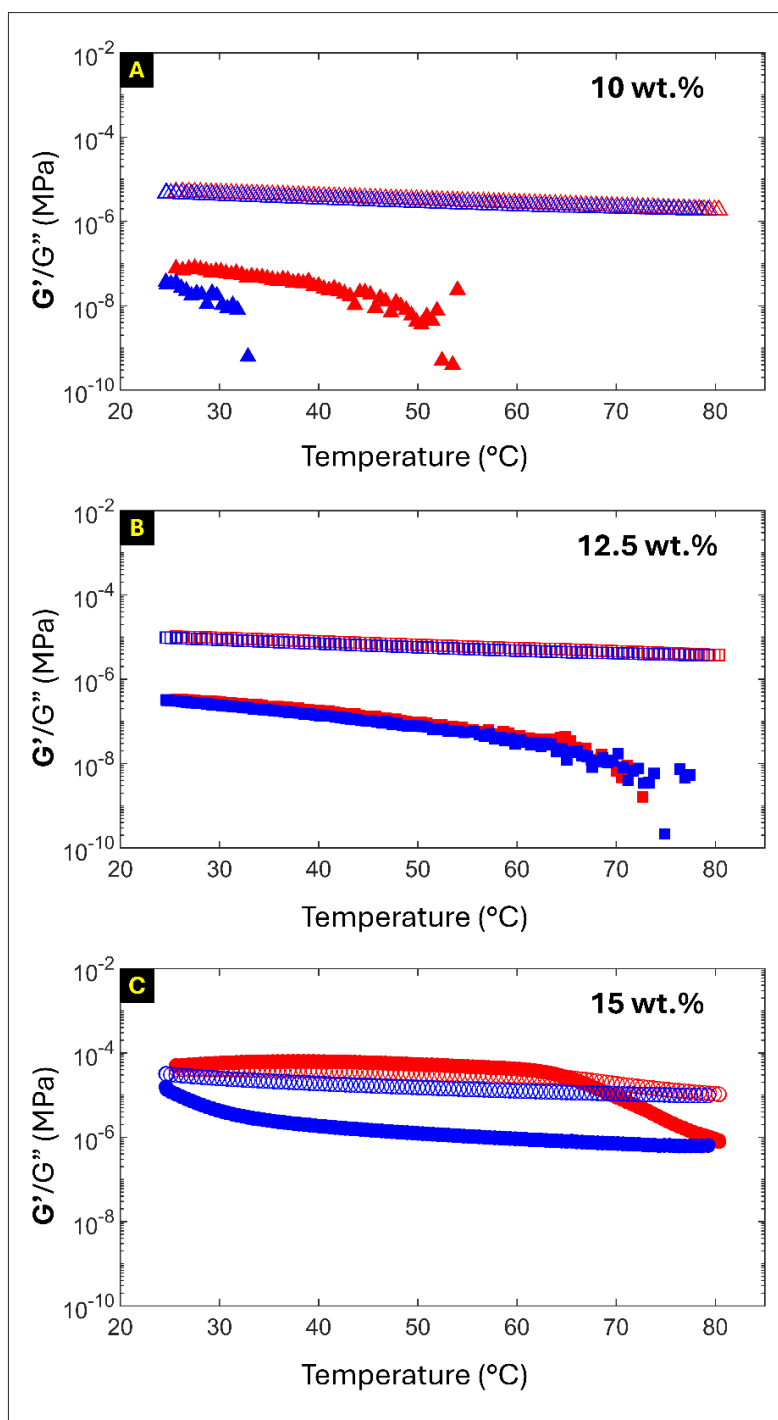


Figure 7.3: Variation of storage modulus (G' – solid shapes) and loss modulus (G'' – empty shapes) of: A) 10 wt.% solution; B) 12.5 wt.% solution; C) 15 wt.% solution with temperature while heating (red) and cooling (blue).

7.3.1.3 Time sweeps

The variation of G' and G'' of the 10 wt.% PVDF/GVL solutions prepared with and without LiCl with time is shown in Figure 7.4. Both solutions initially showed a good liquid-like behavior ($G' < G''$) with noisy G' values and well-defined G'' values. This result is as expected since the solutions are at elevated temperatures initially. Noisy G' values in the solution without LiCl (Figure 7.4-A) spanned well over one hour while the solution with salt showed noisy G' values for about 30 minutes. Thereafter, both solutions started to show a well-defined and rising G' values indicating solid-like features are appearing due to the formation of crosslinks. The solution without salt showed a crossover point after two hours and the solution with salt showed a crossover point after an hour. According to this result, addition of salt accelerated the gelation in PVDF/GVL solutions.

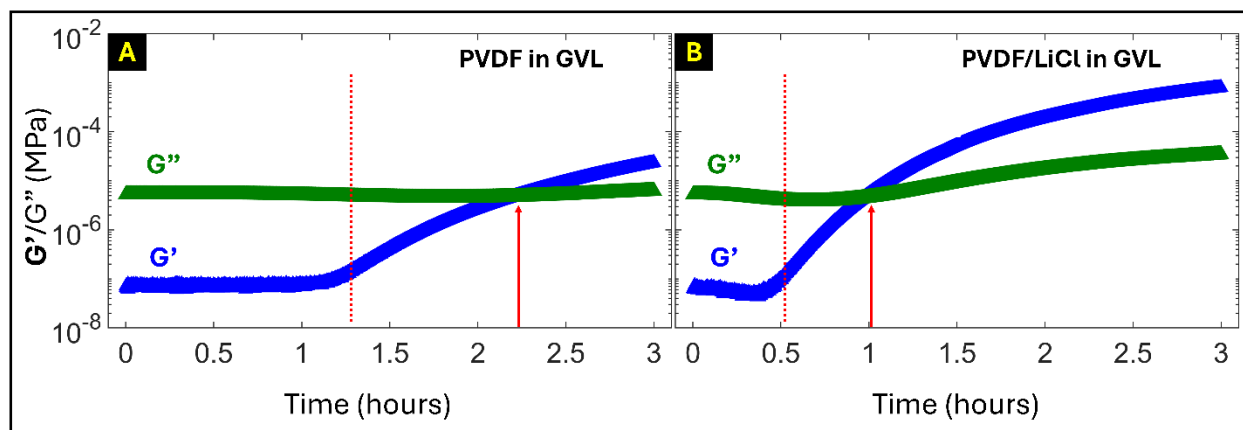


Figure 7.4: Variation of storage modulus (G' – blue) and loss modulus (G'' – green) of 10 wt.% solutions of: A) PVDF in GVL; B) PVDF/LiCl in GVL with time. The red dashed line and the red arrow indicate the starting point of the well-defined G' values and the crossover point, respectively.

7.3.2 *Electrospinning*

The PVDF solutions made with GVL/Acetone mixtures resulted in a translucent thin film as shown in Figure 7.5-A. No whipping jet was observed during the electrospinning process of these solutions and as a result the wet jets were deposited on the collector plate resulting in a thin film. The whipping jet is essential in forming fibers as explained in Chapter 2. The addition of salt enhances the formation of the whipping jet due to the increase in the free charge density. Because of that the jet undergoes bending instabilities to enhance whipping motion. The electrospun fiber mat collected by electrospinning with salt added to the solution is shown in Figure 7.5-B.

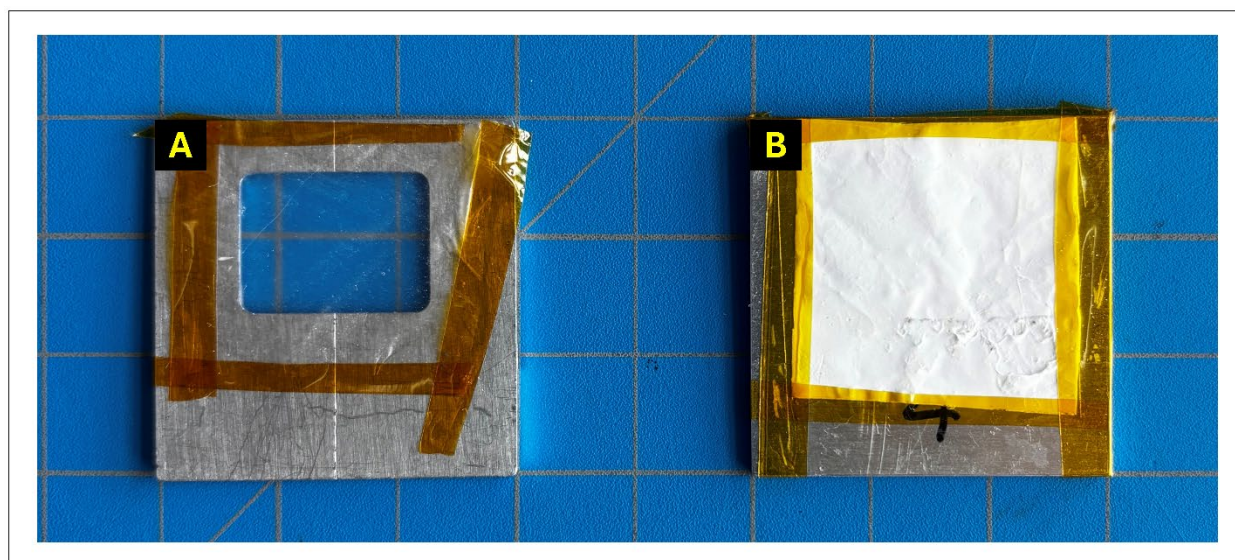


Figure 7.5: A) Thin transparent film resulted from electrospinning PVDF in GVL/Acetone solutions; B) Electrospun fiber mat resulted from PVDF/LiCl in GVL/Acetone solutions. The samples are mounted on Al sample holders for X-ray scattering experiments and are secured by Kapton™ tape (orange).

The SEM images of the thin film and the electrospun fiber mat are shown in Figure 7.6. The thin film shows features like streaks indicating wet jet deposition and the streaks eventually merged with each other (Figure 7.6-A). In Figure 7.6-B, the fibers formed by electrospinning the PVDF/LiCl solutions made from GVL/Acetone solutions are shown. This confirms that the addition of LiCl salt resulted in bending instabilities in the polymer jet which eventually lead to the formation of well-defined dry fibers.

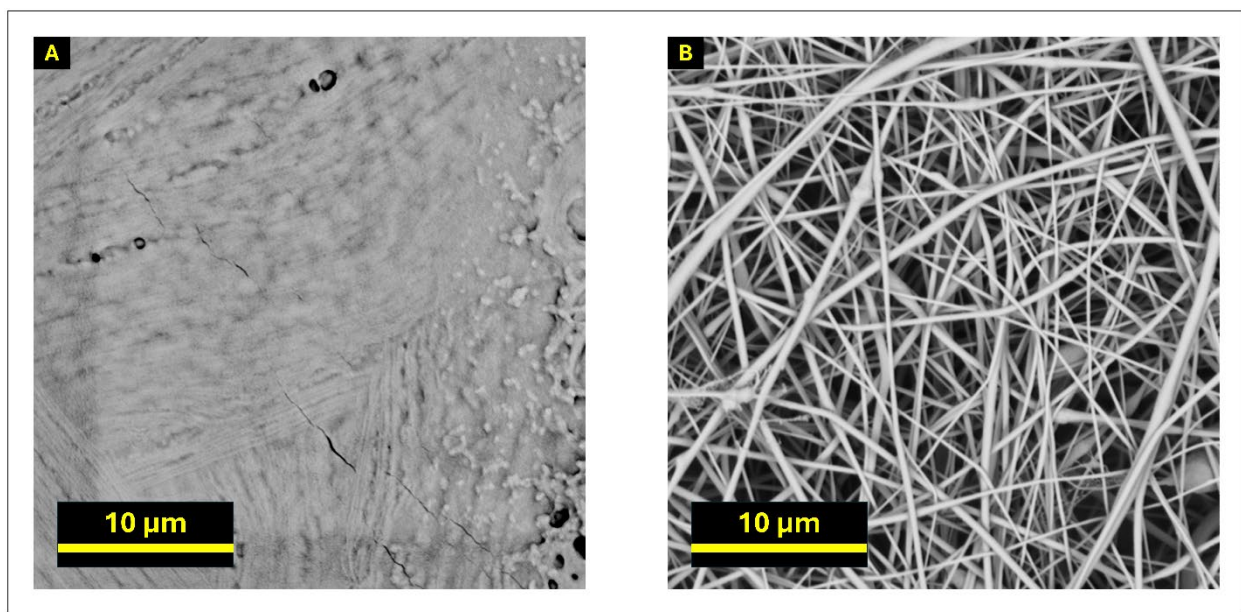


Figure 7.6: The SEM images of: A) thin splattered film resulted from electrospinning PVDF in GVL/Acetone; B) well-defined fibers resulted from electrospinning PVDF/LiCl in GVL/Acetone.

The diameters of the fibers in the mat obtained from electrospinning PVDF/GVL/LiCl solutions were analyzed using the DiameterJ plug-in of ImageJ software. The average fiber diameter was estimated as $0.35 \pm 0.16 \mu\text{m}$. The error in the average fiber diameter is estimated from a bootstrap

analysis with a resampling iteration of 1000. Figure 7.7 shows the distribution of the fiber diameters observed in Figure 7.6-B.

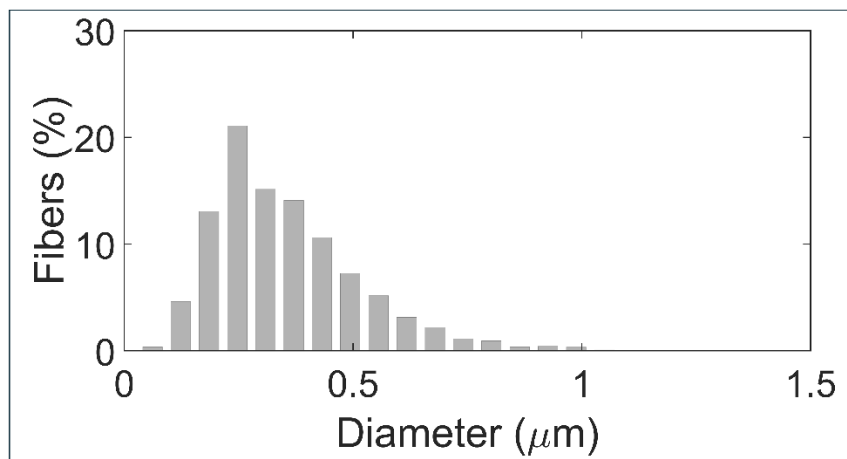


Figure 7.7: Distribution of the diameters of the fibers observed in the electrospun mat obtained from PVDF/GVL/LiCl solutions.

Figure 7.8-A shows the IR absorbance spectra of the thin film sample and the electrospun fiber sample. The characteristic β and γ peaks are seen in both spectra at 1276 cm^{-1} and 1233 cm^{-1} , respectively, indicating the presence of both β -phase and γ -phase crystals in both samples. However, the peak at 1276 cm^{-1} is much more intense in the electrospun fiber sample than in the thin film sample thus showing increased beta phase fraction in the fibers, as expected. On the other hand, the 1233 cm^{-1} peak is more intense in the thin film sample compared to the electrospun sample indicating high gamma phase crystal fraction in the film. It has been shown by Lovinger [49] that PVDF prefers forming γ -phase when it crystallizes from solutions made from DMF, DMAc, and DMSO. Our result shows that the PVDF solutions made from GVL also prefer to form γ -phase crystals. Thus, GVL proves to be a great alternative for PVDF processing and can suitably

replace hazardous solvents while still yielding the electroactive β - and γ -phases. In addition to that, the IR absorbance spectra show no α -phase peaks. The characteristic α peaks should appear at 976 cm^{-1} and 762 cm^{-1} (the wavenumber positions are highlighted in cyan in Figure 7.8-A). Absence of these peaks confirms that both samples have no alpha phase crystals.

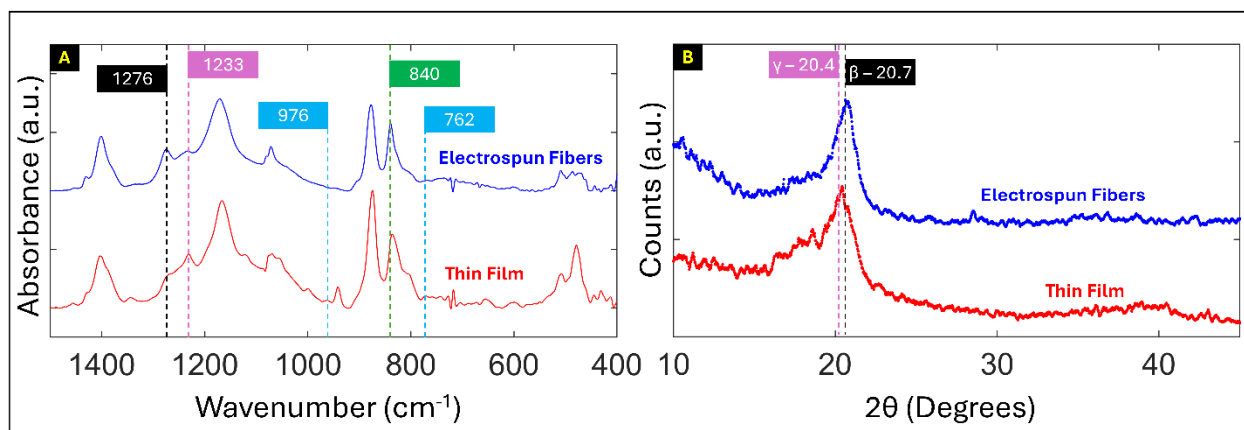


Figure 7.8: A) IR absorbance spectra; B) wide-angle X-ray scattering intensity plots of the thin film (red) and the electrospun fiber mat (blue). Wavenumbers corresponding to specific vibrations (in A) and X-ray crystalline reflections (in B) are labelled: β phase – black, γ phase – magenta, α phase – cyan, and electroactive (β and γ) phases – green.

Figure 7.8-B shows the WAXS intensity plots of the thin film and the electrospun fibers. The characteristic peaks of γ -phase crystals and β -phase crystals are seen at 20.4° (γ^{021}) and 20.7° ($\beta^{200/110}$), respectively. The broad intense peak seen around $20^\circ - 21^\circ$ in the WAXS intensity plots of both samples shows the presence of both β and γ phase crystals. However, the peak position of the electrospun fiber mat is at 20.7° characteristic of β whereas it is observed at 20.4° which is characteristic of γ in the thin film sample. This result confirms the enhanced formation of β phase in electrospun fibers and enhanced γ phase crystals in the thin film sample.

7.4 Conclusions

As seen in frequency sweep tests the PVDF solutions made from GVL with concentrations 10 wt.% and 12.5 wt.% showed viscoelastic liquid behavior above 0.6 – 0.7 rad/s at 25 °C while the viscoelastic liquid behavior was preserved in the low frequency domain at higher temperatures like 45 °C and 65 °C. At these concentrations, PVDF/GVL solutions showed nearly Newtonian liquid properties in the high frequency domain at all temperatures. The 15 wt.% solution showed viscoelastic solid behavior at 25 °C in the low frequency domain and shear thinning behavior in the high frequency domain. At 45 °C, the 15 wt.% solution showed a viscoelastic liquid behavior above a critical frequency (~ 0.6 rad/s) similar to the lower concentration solutions at 25 °C. It also showed nearly Newtonian behavior in the high frequency domain at elevated temperatures. The temperature ramp tests show that the 10 wt.% solution and the 12.5 wt.% solution behave as viscoelastic liquids throughout the entire temperature range and the 15 wt.% solution behaves as a viscoelastic solid at lower temperatures but undergoes a sol-to-gel transition at 65 °C. Based on the results of the frequency sweeps and temperature ramps, the solutions with a PVDF concentration of 10 wt.% solutions are chosen to electrospin since the solutions remain in liquid form above a critical frequency (~ 0.7 rad/s) at 25 °C and gelation does not occur until hot solutions reach about 30 °C giving ample time to electrospin.

The PVDF solutions made from GVL/Acetone mixtures resulted in a thin film when subjected to electrospinning due to the poor whipping motion of the jet. The PVDF/GVL/LiCl solutions resulted in well-developed fibers when electrospun since the addition of LiCl resulted in high free charge density that enhanced whipping motion of the jet. The electrospun fibers showed high β -

phase crystal formation with little γ -phase and no α -phase as seen in IR absorbance spectra and WAXS intensity plots. The electrospun fibers obtained from PVDF/GVL/LiCl solutions resulted in nanoscale fibers with an average fiber diameter of 0.35 μm .

7.5 References

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Chapter 8: Future work

This chapter explores the potential studies that can be carried out in the future on PVDF processing by solutions made from green solvents and on estimation of relative crystalline fractions in PVDF by Raman spectra analysis.

8.1 Potential studies on processing of PVDF solutions made from green solvents

8.1.1 Dilute viscometry and dynamic light scattering to understand the polymer-solvent interactions in PVDF/GVL mixtures

As evident from the work discussed in Chapter 7, PVDF/GVL solutions form a gel below 60 °C and the temperature needs to be elevated to enhance the solubility of PVDF in GVL. This indicates that GVL is showing θ solvent properties for PVDF *i.e.* above a certain temperature ($T > \theta$), the solvent shows excellent solubility for a polymer [1]. This property can be characterized by estimating the Huggins constant K_H [2]. As Chae *et al.* [2] discussed in their work, K_H can be estimated by the slope of the reduced viscosity vs. the concentration of dilute solutions of PVDF according the equation below. Reduced viscosity (η_{red}) is given by:

$$\eta_{red} = \frac{\eta_{sp}}{C} \quad (8.1)$$

$$\frac{\eta_{sp}}{C} = [\eta] + K_H[\eta]^2 C \quad (8.2)$$

where C is the concentration of the solution, $[\eta]$ is the intrinsic viscosity of the solution, and η_{sp} is the specific viscosity of the solution which can be estimated by:

$$\eta_{sp} = 1 - \frac{\eta}{\eta_0} \quad (8.3)$$

where η is the dynamic viscosity of the solution and η_0 is the dynamic viscosity of the pure solvent. The K_H values for good, theta, and poor solvents are shown in Table 8.1. Dilute viscometry can be performed using an Ubbelohde capillary viscometer to measure the dynamic viscosities of the solutions and the pure solvent.

Table 8.1: K_H values for good, θ , and poor solvents

Nature of solubility	Good	θ	Poor
K_H	$\ll 0.5$	~ 0.5	$\gg 0.5$

Dynamic light scattering experiments could be performed to understand the polymer-solvent interactions by estimating the diffusion coefficient of the polymer chains in dilute solutions. This experiment can be extended to estimate the molecular weight distribution of the polymers by determining Mark-Houwink exponents [3]. It can also be used to confirm the dilute viscometric analysis.

8.1.2 Investigation of gelation kinetics

The gelation kinetics of PVDF/GVL mixtures need to be investigated thoroughly to delay the gelation.

8.1.3 Use of other green solvents for PVDF processing

There are many other green solvents that are readily available for PVDF processing as shown in Table 8.2 [4]. The possibility of using these solutions for electrospinning PVDF could be investigated. Especially, PolarClean is a synthetic solvent developed by Solvay [5] that has shown promising results in membrane fabrication.

Table 8.2: Potential green solvents for PVDF processing along with their water solubility

Based/ Derived on	Solvent	Name	Water Solubility
Ester based	TEP	Triethyl Phosphate	Slow, sinks in water
	ATBC	Acetyl-tributyl Citrate	Soluble
	TBC	Tributyl Citrate	Insoluble
	ATEC	Acetyl-triethyl citrate	Soluble
	GBL	γ -Butyrolactone	Miscible
	PolarClean		Soluble
	PC	Propylene Carbonate	Soluble
	EC	Ethylene Carbonate	Soluble
	BC	1,2-Butylene Carbonate	NA
Cellulose/ Starch Derived	Cyrene	Dihydrolevoglucosenone	Soluble
Biosolvents	DMI	Dimethyl Isosorbide	Soluble

8.2 Estimation of the relative crystalline fractions of PVDF by temperature controlled

Raman spectra analysis

IR absorbance spectra are very useful in estimating the relative crystalline fractions in PVDF as discussed in Chapter 4. Raman scattering is another vibrational spectroscopic analysis technique that can be used to obtain valuable information on the structure of materials, especially polymers. Since the sample does not have to be placed on the detector as in an FTIR spectrometer, Raman spectroscopy gives tremendous flexibility in obtaining data while heating. This way the structural changes that take place in the polymer with the variation of temperature can be observed and then analyzed in temperature-controlled Raman spectroscopy.

Figure 8.1 shows the Raman spectra obtained for a PVDF sample melt-crystallized into α -phase at 30 °C and heated to 250 °C. The characteristic peaks of α -phase are indicated on the spectrum for the semi-crystalline sample (blue). At very high temperatures, above the infinite crystal melting point for PVDF ($T_M^\infty = 200$ °C [6]) most of the peaks such as 1296 cm^{-1} , 1200 cm^{-1} , and 611 cm^{-1} in the semi-crystalline sample lose definition and therefore can be assigned to crystalline vibrations.

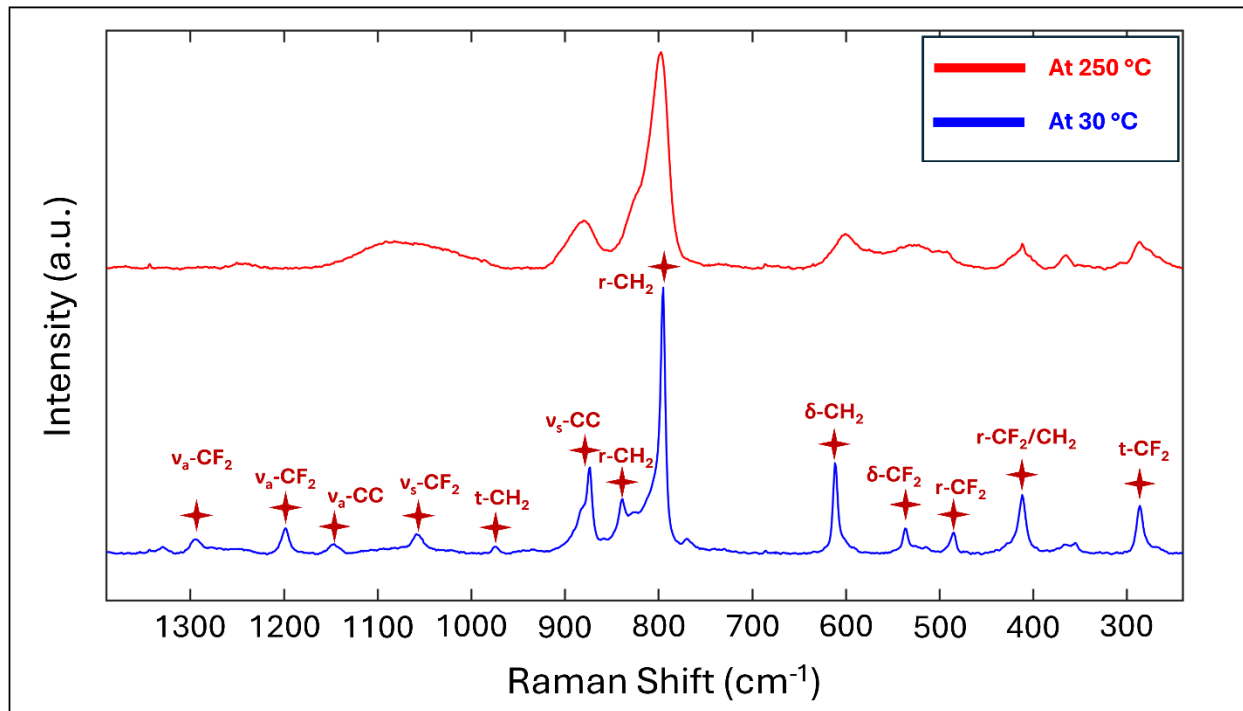


Figure 8.1: Raman spectra obtained for melt crystallized α -phase PVDF samples at 30 °C (blue, bottom) and at 250 °C (red – top). The vibrational modes of α -phase are shown on the peaks of the blue curve: v_s – symmetric stretching; v_a – asymmetric stretching; t – twisting; δ – bending; r – rocking [7, 8].

Figure 8.2 shows the continuous variation of the logarithmic intensities of Raman peaks with temperature for the α -phase sample. From this plot, the peaks corresponding to the crystalline and amorphous vibrations can be easily identified. Using statistical techniques like Principal Component Analysis (PCA), the correlation of the features (area or intensity) of amorphous and crystalline peaks can be estimated. Since the equilibrium heat of fusion of α -phase PVDF is known ($\Delta H_F^0 = 104.6 \text{ J/g}$ [9]), the endothermic crystal melting peak area of DSC heat flow rate thermographs of the same α -phase samples can be used to estimate the total degree of crystallinity. WAXS intensity plots can also be used to estimate the crystalline index as melt crystallized samples form only α -phase crystals [10]. Using the degree of crystallinity data obtained either from DSC or from WAXS analysis and coupled with Raman spectroscopic data, a new method can be developed to obtain the degree of crystallinity of PVDF α -phase only by analyzing the features of its Raman spectra. This method can then be developed to estimate the absolute crystalline fractions of β - and γ -phases in electrospun and electrosprayed samples.

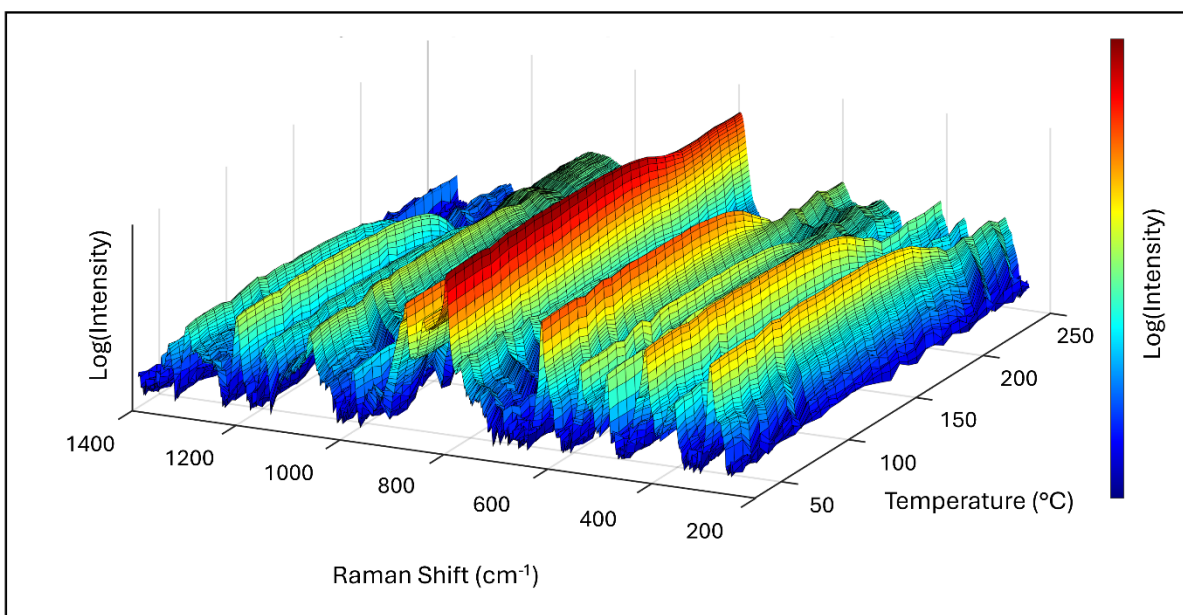


Figure 8.2: 3D surface plot of log of Raman intensity variation with Raman shift frequency and temperature for melt crystallized α -phase PVDF sample.

Figure 8.3 shows the 2D surface plot of the variation of the logarithmic Raman intensities with temperature at different Raman shifts. Some crystalline peaks such as 1296 cm^{-1} , 1200 cm^{-1} , 1150 cm^{-1} , 976 cm^{-1} , and 611 cm^{-1} lose their definition around $200\text{ }^{\circ}\text{C}$ (equilibrium melting point of PVDF [6]) instead of $160\text{ }^{\circ}\text{C}$ where DSC heat flow rate thermographs shows a melting peak as discussed in Chapter 4. This strongly suggests the existence of the self-nucleating agents in the polymer melt even after the end of the melting event observed in DSC scans. Investigation of crystallization dynamics of PVDF through self-nuclei by analyzing temperature-controlled Raman spectra is also a potential area of research.

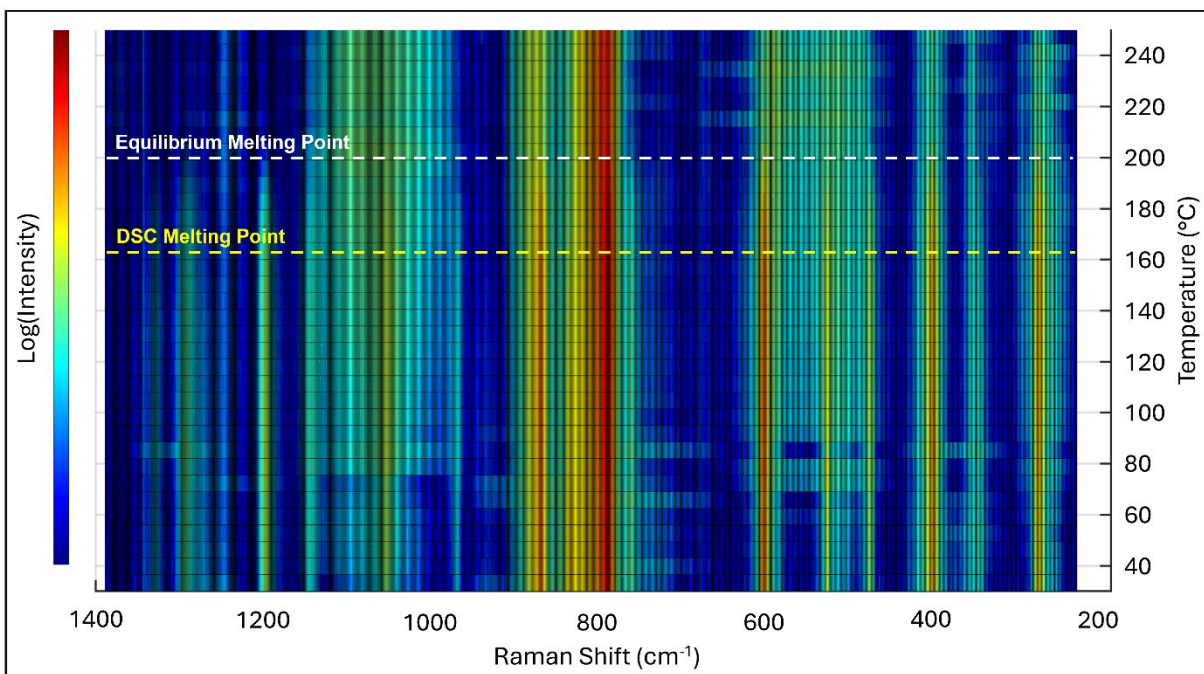


Figure 8.3: 2D surface plot of plot of log of Raman intensity variation with Raman shift frequency and temperature for melt crystallized α -phase PVDF sample.

8.3 References

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Appendix A: Supplementary information for Chapter 4

A.1 PVDF FTIR absorbance spectra before Fourier self-deconvolution

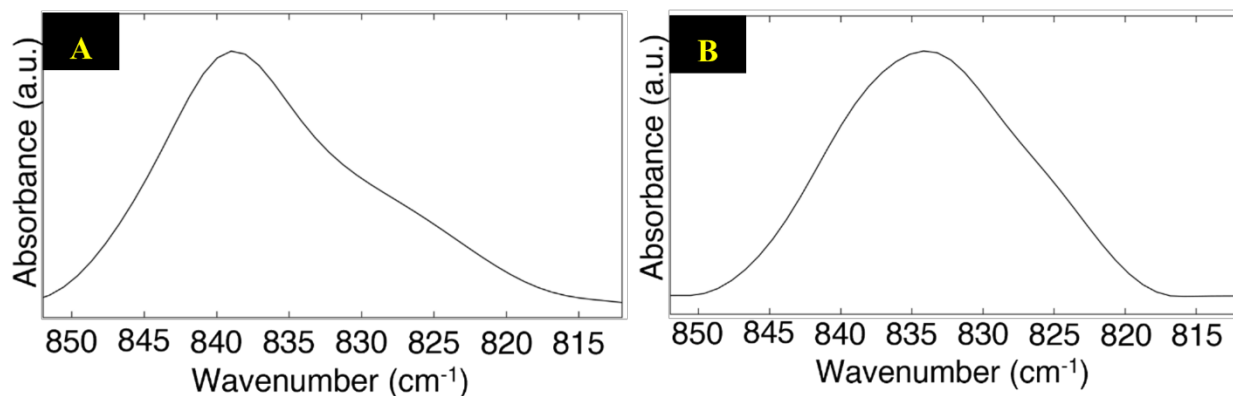


Figure Appx. A.1: The original broad and complex electro-active peak at 840 cm⁻¹ in the FTIR absorbance spectra of PVDF samples: A) electrospun fibers; B) electrospayed thick film. The absorbance spectra in this frequency range contain contributions from β -phase near 840 cm⁻¹ and γ -phase near 835 cm⁻¹ and 825 cm⁻¹ [1-5]. To determine the relative phase composition, this absorbance feature is synthetically narrowed using Fourier self-deconvolution which results in better separation of the contributions of β and γ phases, as shown in Figure 4B, C in the main manuscript.

A.2 References

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Appendix B: Supplementary information for Chapter 5

B.1 SEM Fiber Diameter Analysis

The fiber images in our study show that beads are often observed. Depending upon the number and size of beads, it is possible that beads contain a lot of polymer mass, leading to thinner fibers in between the beads. For proper fiber diameter analysis, the SEM images should be examined in two ways: case 1, to determine the bulk average size of both fibers and beads taken together (Figure Appx. B.1, Figure Appx. B.2); and case 2, to determine the size of fibrils alone under conditions where the beads are excluded (Figure Appx. B.3). We will refer to case 1 as “bulk fiber diameter” analysis and case 2 as “fibril diameter” analysis. Figure Appx. B.1 illustrates the method used for Case 2, bulk fiber analysis, and Figure Appx. B.2 shows the histograms of the bulk fiber diameter distribution in each electrospun fiber mat.

B.1.1 Case 1: Bulk fiber diameter measurements

In DiameterJ analysis, an SEM image (Figure Appx. B.1-A) is first segmented into 24 images with pure black and white pixels (three categories with eight images in each category) as shown in Figure Appx. B.1-B. A set of three images from each category was selected by the authors, using their best judgment, to represent the true fiber structure in the sample. These nine images are shown in Figure Appx. B.1-B with a red outline. Using these nine segmented images, the average diameter of the bulk (including beads) was determined for each sample using the DiameterJ plug in of ImageJ. Histograms of the bulk fiber diameters, including the beads, are shown for each electrospun fiber mat in Figure Appx. B.2 (A-G).

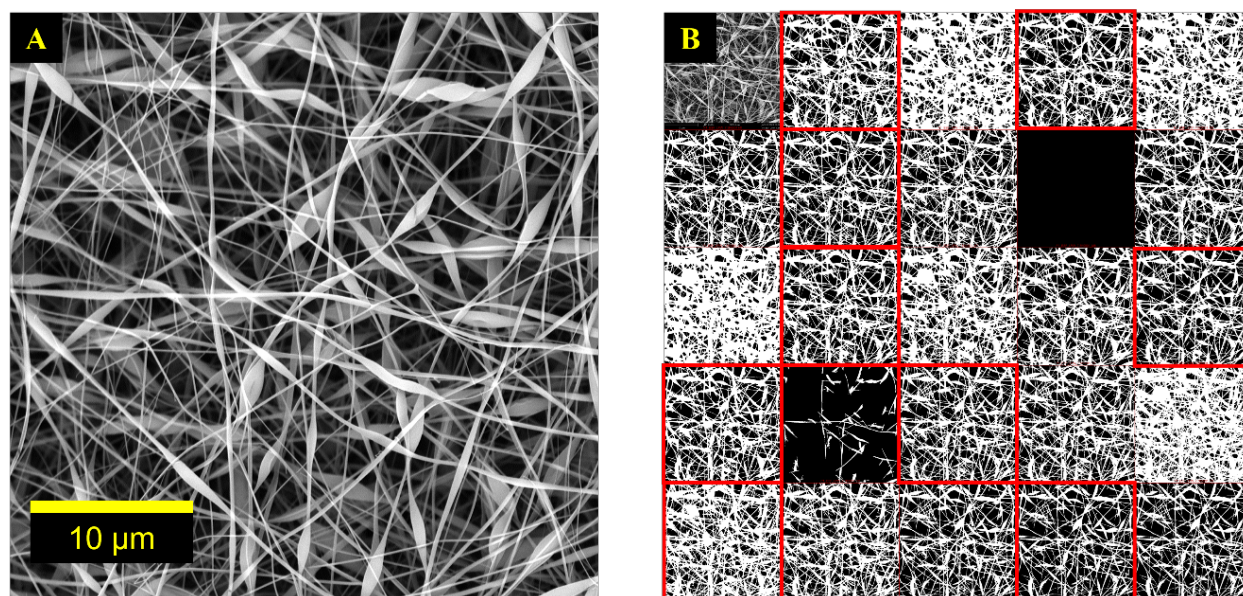


Figure Appx. B.1: A) SEM image of PVDF00 at $\times 7500$ magnification; B) Montage of the segmented black and white pixelated images of the same SEM image but with the scale bar removed. The nine segmented images that were considered in the DiameterJ analysis are outlined in red boxes.

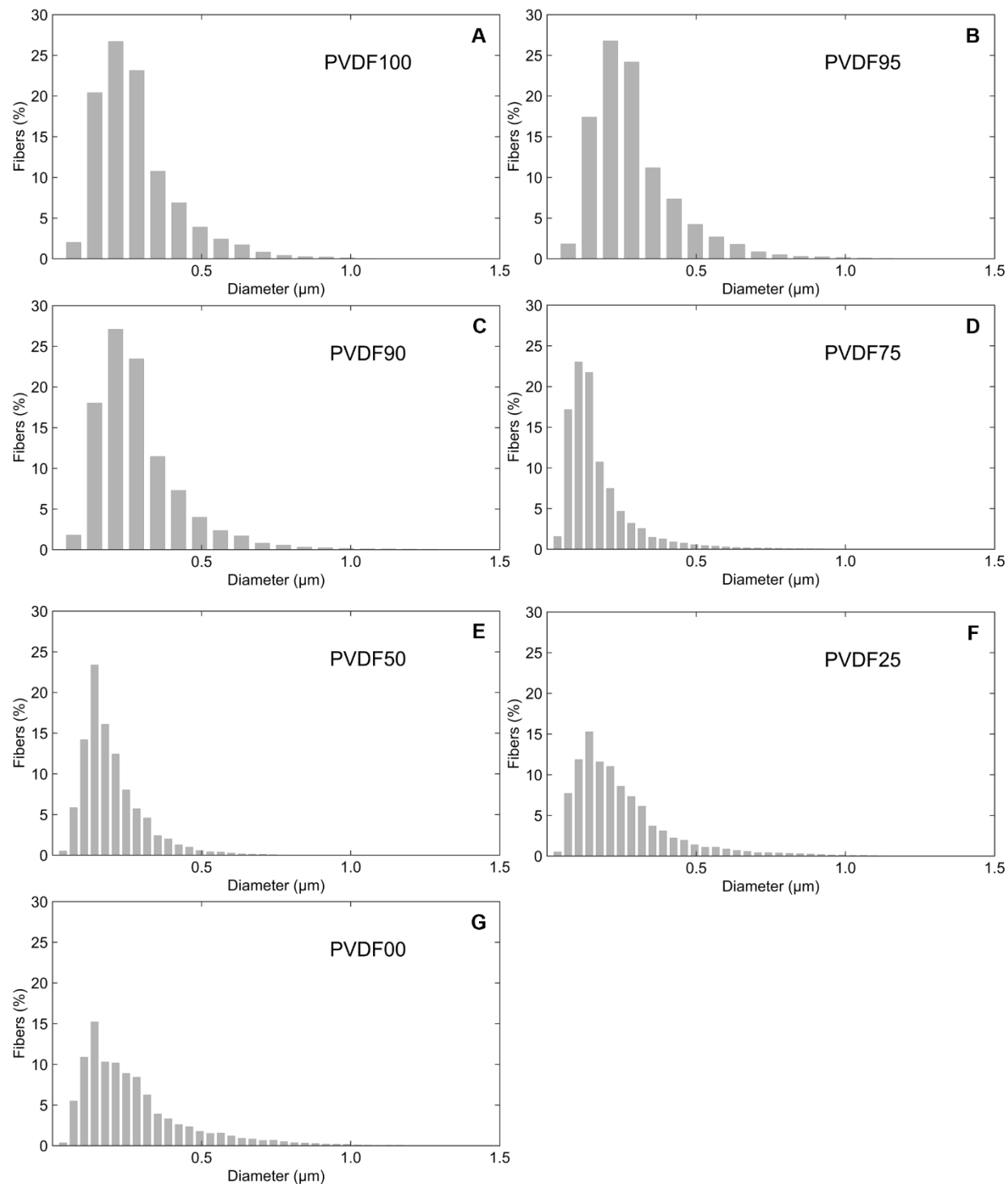


Figure Appx. B.2: Histograms of bulk fiber diameter distribution, including beads, for: A) PVDF100; B) PVDF95; C) PVDF90; D) PVDF75; E) PVDF50; F) PVDF25; G) PVDF00.

B.1.2 Case 2: Fibril diameter measurements.

Next, an in-depth analysis was done to determine the case 2 “fibril diameter” distribution. Since the bulk fiber diameter values include the bead diameters, a method to eliminate the beads was carried out to determine the fibril diameter values. As shown in Figure Appx. B.3 (A-B), a cut-off diameter value was measured and defined for a fiber as it widens to form a bead. A line was drawn along the fiber passing into the bead (Figure Appx. B.3-B, red dashed line PQ) and then another line was drawn perpendicular to PQ at the critical point where the fiber starts to flare out and turn into a bead (Figure Appx. B.3-B, double arrow line RS). The length of RS is defined as the cut-off diameter value, the largest diameter that can still be considered to be a fiber and not a bead. Using the Specific Radius Identifier in DiameterJ, the fibers with diameters below the cut-off diameter value (defined as “fibrils”) are highlighted in red in the segmented images. As shown in Figure Appx. B.3-C, this analysis has successfully excluded the beads and avoids considering them in the analysis of the fibril diameter.

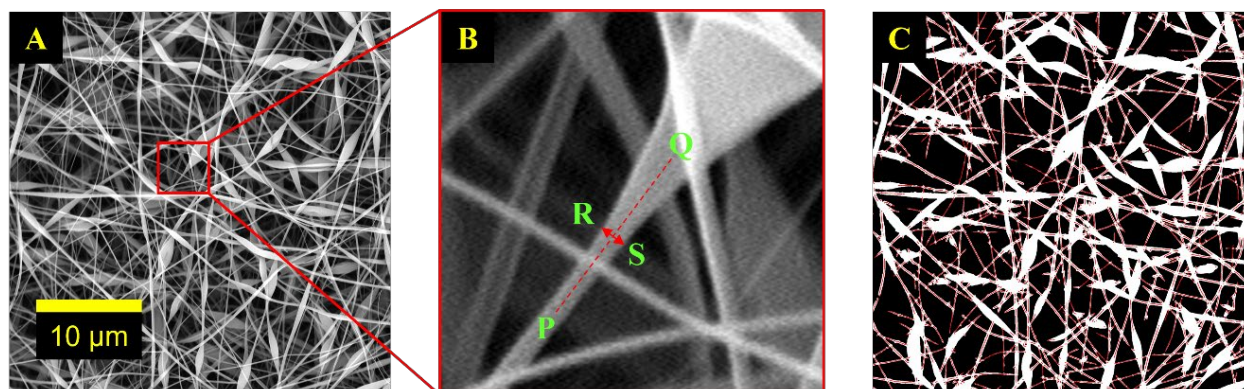


Figure Appx. B.3: A) SEM image of PVDF00 at $\times 7500$ magnification; B) Zoomed in image of a fiber turning into a bead. Red dashed line PQ is drawn along the fiber into the bead and double arrow RS is the cut-off diameter drawn normal to PQ; C) Segmented image of the same SEM image with scale bar removed, and with fibrils highlighted in red.

Then the average fibril diameter (without beads) was determined by taking the mean value of the diameters below the cut-off diameter value. The standard deviations of the bulk and fibril diameter distributions are presented as the uncertainty of the average bulk fiber diameter and the average fibril diameter measurements. This data is presented in Table 5.1 in Chapter 5.

B.2 SEM Porosity Analysis

The same set of nine segmented images used for diameter analysis in each sample was also used for the porosity analysis. An example SEM image is shown in Figure Appx. B.4-A for PVDF00. One of the nine segmented images is shown in Figure Appx. B.4-B. Figure Appx. B.4-C shows

the DiameterJ output image of the SEM image with every pore marked in red. Large black void areas in Figure Appx. B.4-B are counted as “pores” if they are interior to the image; they are not counted as “pores” if they appear at the edge of the image.

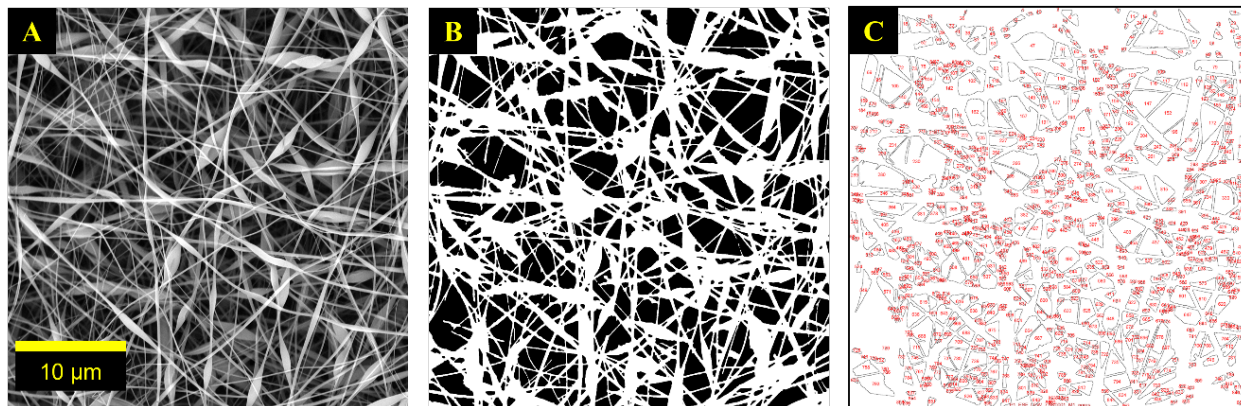


Figure Appx. B.4: A) SEM image of PVDF00 at $\times 7500$ magnification; B) Segmented image of the same SEM image with scale bar removed; C) Pores present in the segmented image. Each pore is numbered in red.

Pore data from all segmented images were used in estimating the average pore area. To estimate the uncertainty in mean pore area, a bootstrapping technique was used because the data are highly skewed. Pore data histograms are shown in Figure Appx. B.5 (A-G). Pore data is shown in Table Appx. B.1.

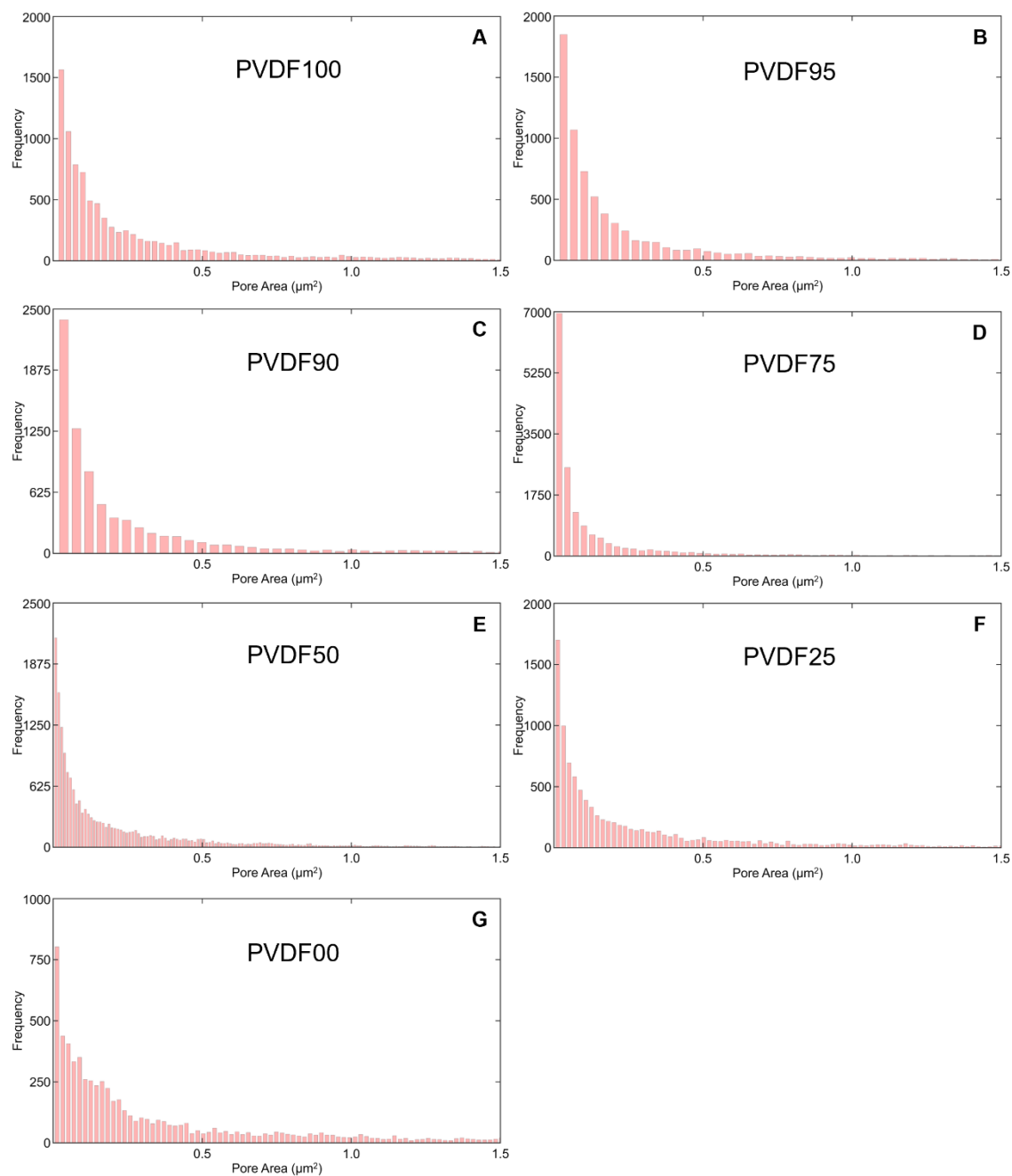


Figure Appx. B.5: Histograms of pore area distribution for: A) PVDF100; B) PVDF95; C) PVDF90; D) PVDF75; E) PVDF50; F) PVDF25; G) PVDF00.

Table Appx. B.1: Pore data values of PVDF/r-PAC blends

Sample	Average No. of Pores per Image ^a	Pore Density ^b ($\times 10^5 \text{ mm}^{-2}$)	Average Pore Area (μm^2)	Pores with Areas below the Avg. Pore Area (%)
PVDF00	828	6.35	0.67 ± 0.03	74
PVDF25	1125	8.62	0.48 ± 0.02	77
PVDF50	1996	15.3	0.27 ± 0.01	73
PVDF75	1828	14.0	0.26 ± 0.02	83
PVDF90	907	6.95	0.49 ± 0.04	82
PVDF95	791	6.06	0.46 ± 0.03	82
PVDF100	1061	8.13	0.43 ± 0.02	77

^a The nine images shown in Fig. S1 were examined for pores and the average number of pores per image is listed in the table. The magnification of the images was the same for all samples.

^b SEM images were converted from pixel units to mm^2 .

All SEM images can be found via the following link

<https://doi.org/10.17605/OSF.IO/E683P>

B.3 Viscosity Analysis

The viscosity of each electrospinning solution was measured using a rotational viscometer (IKA lo-vi, Wilmington, NC). A volume of 2.1 mL from each solution (10 wt.% of solid polymer in dimethylformamide/methanol 13/01 v/v) was poured into the viscosity chamber and the spindle was rotated at a rate of 200 rpm for 10 minutes and the dynamic viscosity was measured every 30 s. The chamber was maintained at a constant temperature of 18 °C. The mean dynamic viscosity

was calculated averaging all viscosity values collected over 10 mins and shown in Table Appx.

B.2. The standard deviation of the viscosities is presented as the uncertainty.

Table Appx. B.2: Mean dynamic viscosity of sample solutions

Sample	Mean Dynamic Viscosity (mPa.s)
PVDF00	240.8 ± 2.1
PVDF25	359.4 ± 2.0
PVDF50	477.6 ± 2.5
PVDF75	554.9 ± 3.3
PVDF90	568.9 ± 5.3
PVDF95	399.1 ± 2.2
PVDF100	394.0 ± 3.7

The relationship between the average fibril diameter (black squares) and the solution viscosity (red circles) is shown in Figure Appx. B.6 as a function of r-PAC content. The viscosity increases with the addition of r-PAC up to PVDF90 which shows the highest mean dynamic viscosity of $568.9 \text{ mPa.s} \pm 5.3 \text{ mPa.s}$. PVDF75 also shows a similar viscosity as PVDF90. The average fibril diameter decreases from PVDF100 to PVDF75. The viscosity decreases as more r-PAC is introduced to the solution and at the same time, the average fibril diameter increases.

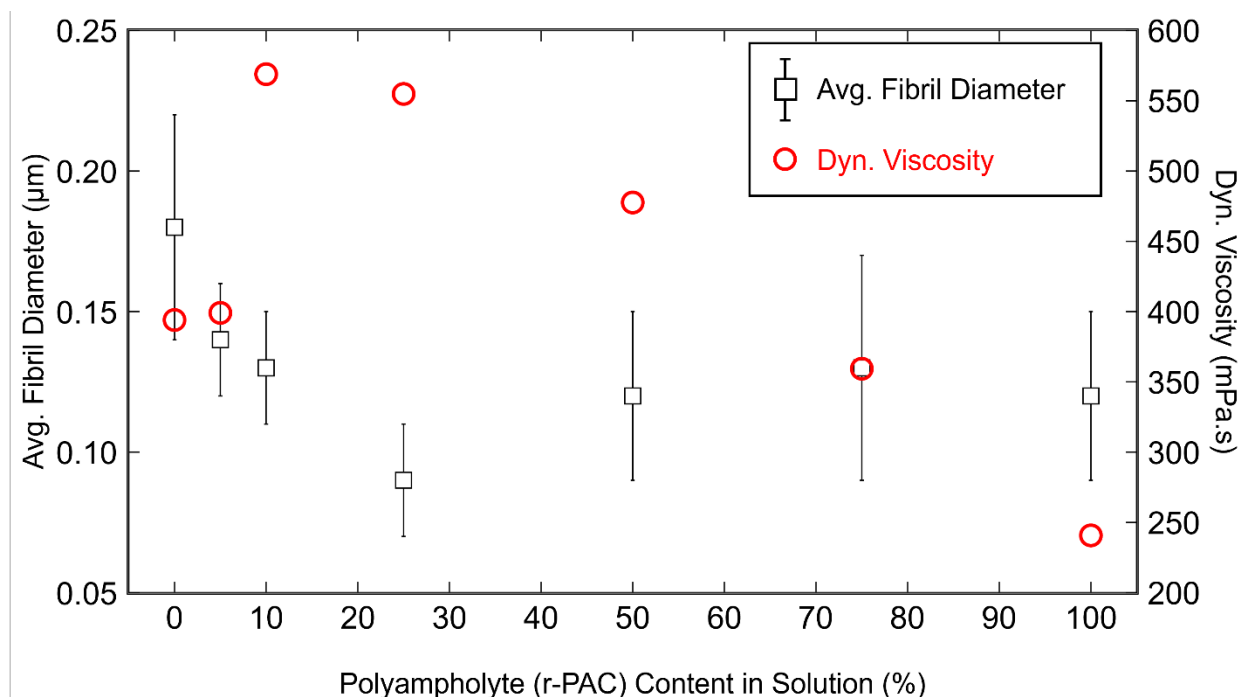


Figure Appx. B.6: The variation of the mean fibril diameter of electrospun mats (black squares, left axis) and the dynamic viscosity of the solutions (red circles, right axis) with the polyampholyte (r-PAC) percentage in each blend. The percentage refers to the comparison of the r-PAC weight to the total polymer weight (PVDF and r-PAC) in the blends.

B.4 Please follow the link to access the videos of the contact angle measurements of each sample with oil (dodecane)

<https://doi.org/10.17605/OSF.IO/E683P>

Appendix C: Supplementary information for chapter 7

C.1 Determination of the critical pump rate (deposition rate) for electrospinning using the frequency sweeps

The G' and G'' frequency sweeps of the PVDF/GVL solutions with three different concentrations are shown in Figure Appx. C.1. The instrumental limitations caused by low torque and by inertia are shown in black dashed lines. According to Ewoldt, *et al.* [1] the low torque limit of the modulus value (regardless of whether one is using G' or G'') in the low frequency domain is given by:

$$G_{min} = \frac{F_{\tau} T_{min}}{\gamma_0} \quad (\text{Appx. C.1})$$

And the inertial limit of G (regardless of G' or G'') in the high frequency domain is given by:

$$G_{min} = \frac{I F_{\tau}}{F_{\gamma}} \omega^2 \quad (\text{Appx. C.2})$$

In the above equations, I is the total moment of inertia of the instrument and the parallel plate geometry; F_{τ} and F_{γ} are the stress and strain constants of the parallel plate geometry, respectively; T_{min} is the smallest torque that can be measured by the rheometer; γ_0 is the oscillating strain amplitude; and ω is the oscillation frequency. Measured data are reliable only above the low torque limit and to the left of the inertial limit. Since the sol-to-gel transition of the solutions in the low frequency domain satisfies the above conditions, the critical frequency at which the sol-to-gel transition undergoes is reliably measured. This frequency corresponds to a critical strain rate, which can be used to determine a critical pump rate (Q_c), such that electrospinning can proceed at pump rates $Q > Q_c$.

The oscillating strain rate ($\dot{\gamma}$) is related to the oscillation frequency by:

$$\dot{\gamma} = F_{\gamma}\omega \quad (\text{Appx. C.3})$$

From equation 2.62A, the strain rate of a liquid flowing under laminar flow is given by:

$$\dot{\gamma} = \frac{dv}{dz} \quad (\text{Appx. C.4})$$

where v is the velocity and z is along the radial direction. According to Munson, *et al.* [2] if the fluid is flowing in a cylindrical tube, then the maximum velocity of the fluid $v_{\max}$ is observed at the center of the tube and the fluid layer in contact with the inner wall of the tube is considered stationary. Then, equation Appx. C.4 can be written as:

$$\dot{\gamma} = \frac{v_{\max}}{R} \quad (\text{Appx. C.5})$$

Here R is the radius of the cylindrical tube. The average velocity of the fluid $\bar{v}$ is expressed in terms of $v_{\max}$ as [2]:

$$v_{\max} = 2\bar{v} \quad (\text{Appx. C.6A})$$

From Hagen-Poiseuille equation, the volume flow rate Q of the fluid in the cylindrical tube is given by [2]:

$$Q = \bar{v}\pi R^2 \quad (\text{Appx. C.7A})$$

$$\bar{v} = \frac{\Delta p R^2}{8\eta L} \quad (\text{Appx. C.7B})$$

Here Δp is the pressure difference on either side of the tube; η is the viscosity coefficient of the fluid; and L is the length of the tube.

Combining the equations from Appx. C.3 to Appx. C.7, an expression for volume flow rate Q in terms of oscillating frequency is developed as follows:

$$Q = \frac{\pi R^3 F_\gamma \omega}{2} \quad (\text{Appx. C.8})$$

Then the volume flow rate Q_c at the critical oscillating frequency ω_c is calculated using Appx. C.8 using the following parameters: $R = 0.042$ cm (18G needle inner radius), $\omega_c = 0.7$ rad/s, and $F_\gamma = 20$ /rad. Then for the parameters of our experiment we find $Q_c = 0.55$ mL/hr.

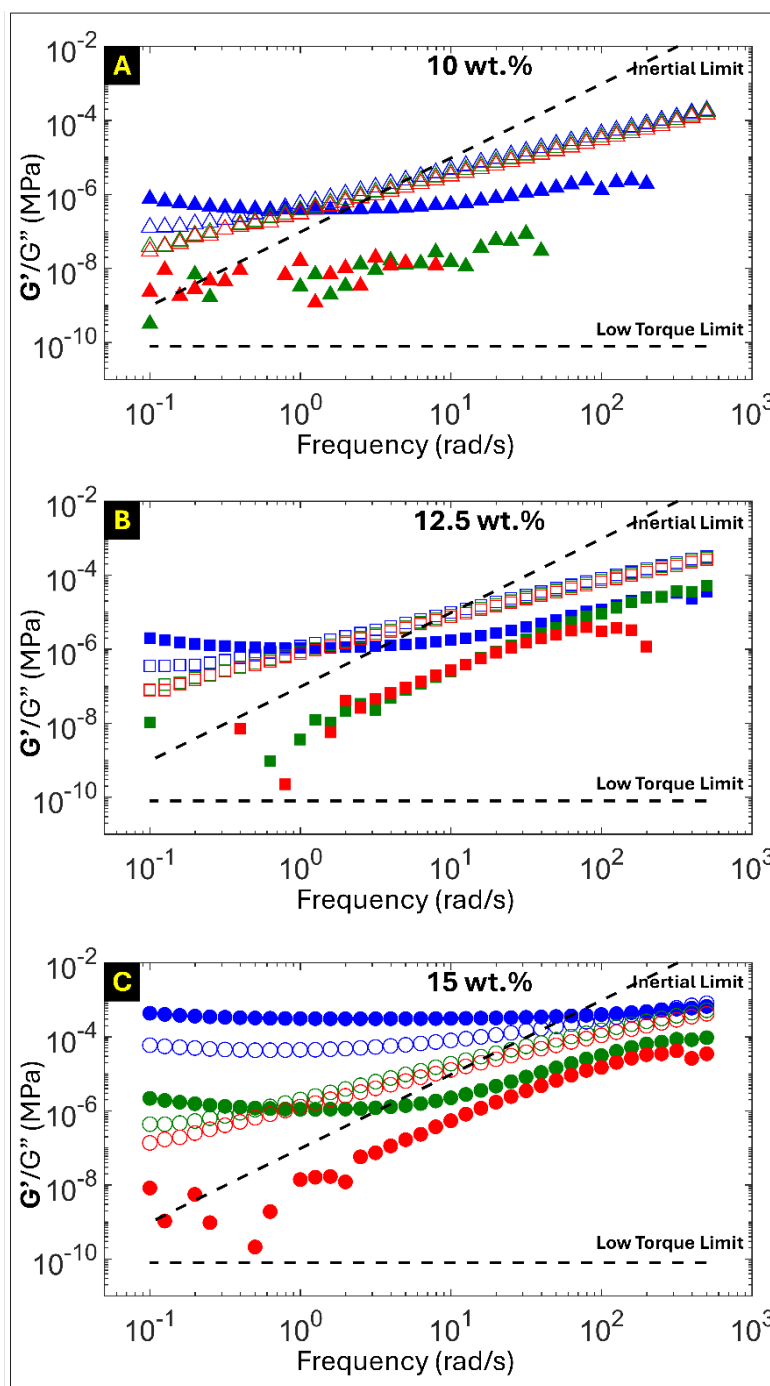


Figure Appx. C.1: Variation of the storage modulus (G' – solid shapes) and the loss modulus (G'' – empty shapes) of A) 10 wt.% solution (triangles); B) 12.5 wt.% solution (squares); C) 15 wt.% solution (circles) at 25 °C (blue), 45 °C (green), and 65 °C (red) with the oscillating frequency. The instrumental limitations (inertial and low torque) are shown in black dashed lines.

C.2 Variation of dynamic viscosity with frequency

The variation of the dynamic viscosity of the PVDF/GVL solutions with three different concentrations obtained from frequency sweep analysis is shown in Figure Appx. C.2. The black dashed line represents the low torque limit for the dynamic viscosity obtained from equation Appx. C.9 as given in Ewoldt *et al.* [1]

$$\eta > \frac{F_{\tau} T_{min}}{\dot{\gamma}} \quad (\text{Appx. C.9})$$

Dynamic viscosity values to the right of the black dashed lines are reliable. The shear thinning behavior observed below the dashed line in Figure Appx. C.2-A,B, and C is possible due to the uncertainty of low torque measured at very low frequencies.

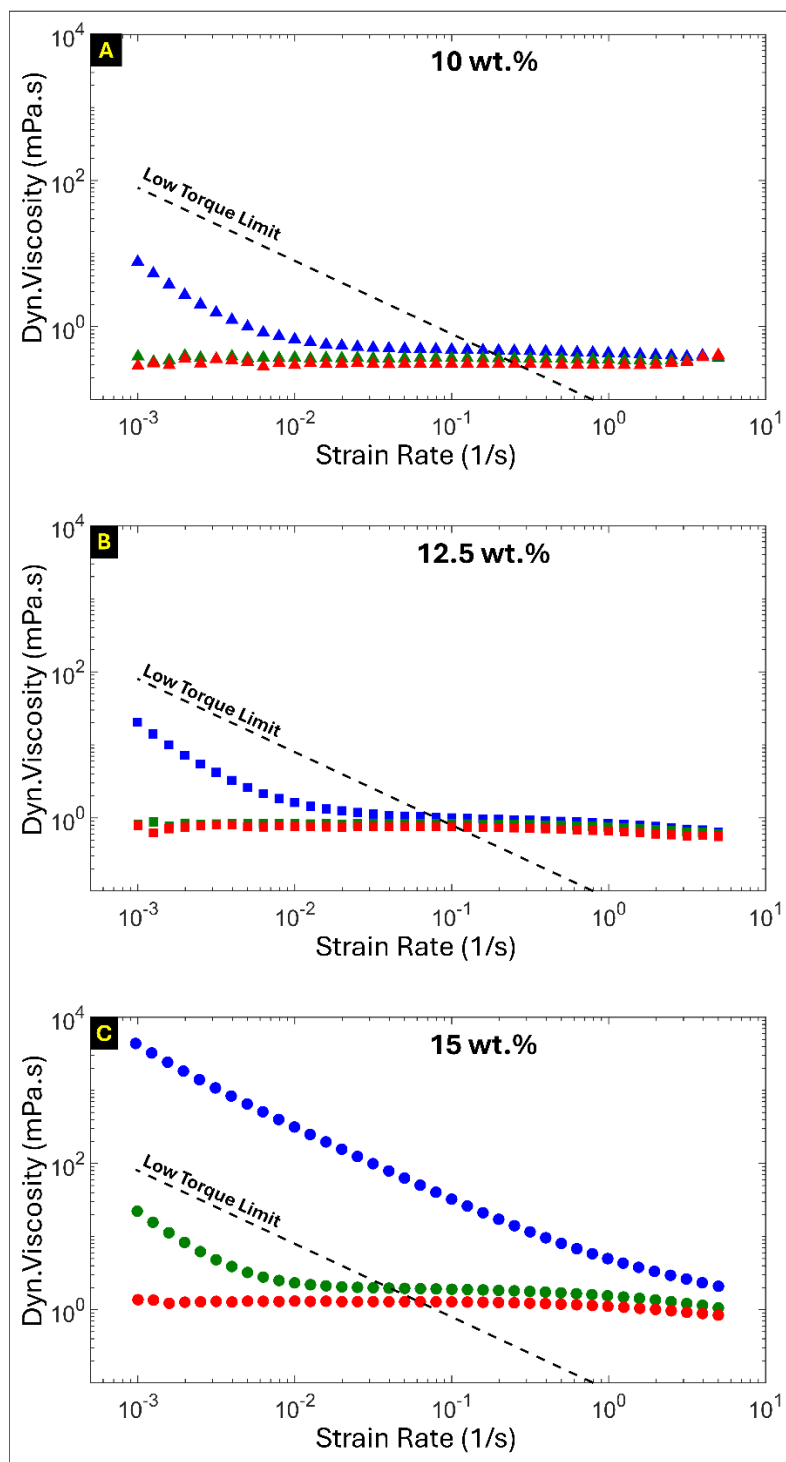


Figure Appx. C.2: Variation of dynamic viscosity with strain rate in: A) 10 wt.% solution; B) 12.5 wt.%; and C) 15 wt.% solution at 25 °C (blue), 45 °C (green), and 65 °C (red). Black dashed line shows the low torque limit.

C.3 *References*

1. Ewoldt, R.H., Johnston, M.T., Caretta, L.M., and Spagnolie, S.E., *Experimental Challenges of Shear Rheology: How to Avoid Bad Data*. 2015, Springer New York: New York, NY. p. 207-241.
2. Munson, B.R., Gerhart, P.M., Gerhart, A.L., Hochstein, J.I., Young, D.F., and Okiishi, T.H., *Munson, Young, and Okiishi's Fundamentals of Fluid Mechanics*. Eighth ed. 2016, Hoboken, NJ: Wiley.

Appendix D: MATLAB codes

D.1 Analysis of the average fiber diameter and the mean porosity of fiber mats

```
% Import All Summary File Values as P (table) because we will be analyzing pore
% data here
% This code only works in the Combined Files folder created by DiameterJ
% operation
% Input the sample details - this will ask you to provide the Sample Name,
% Length of the scale bar (both in um and px), and the maximum radius value
% to avoid beads in the analysis

SampleDetails = {'Sample Name','Length of the scale bar (um)','Length of scale bar
(px)','Length of a side (px)','Enter the max radius value before beads (px)'}; % this
is the prompt
dlgtitle = 'Sample Details'; % title of the input dialog box

Input = inputdlg(SampleDetails,'dlgtitle'); % opens the Input dialog box

sclbar = Input(2,1); % grabs the length of the scale bar in um
sclbar = cell2mat(sclbar); % these two steps convert the string to a number
sclbar = str2num(sclbar);

npx = Input(3,1); % grabs the number of pixels along the length of the scale bar
npx = cell2mat(npx);
npx = str2num(npx);

res = Input(4,1); % grabs the number of pixels along a side of the SEM image
res = cell2mat(res);
res = str2num(res);

maxR = Input(5,1); % grabs the max Radius of a fiber right before a bead
maxR = cell2mat(maxR);
maxR = str2num(maxR);
cFD = 2*maxR*(sclbar/npx);

WorkspaceName = "Workspace_"+Input{1,1}; % Sets the workspace name
%%

%%%%%%%%%% Diameter Analysis %%%%%%%%%%%

R = readtable('All_Radius_Values.csv','VariableNamingRule','preserve'); % Imports the
.csv file with radius data
R = table2array(R);
DiameterProfiles.AllRadiusData = R;
DiameterProfiles.AggregateDiameterData = [R(:,2)*2, R(:,12)]; % converts diameter
profiles from radius profiles and stores in a struct

% this loop converts occurrences to frequency as a percentage

for i = 1:length(DiameterProfiles.AggregateDiameterData)
```

```

        DiameterProfiles.AggregateDiameterData(i,3) =
(DiameterProfiles.AggregateDiameterData(i,2)/sum(DiameterProfiles.AggregateDiameterData(:,2)))*100;
end

% Bar Graph Creation - Creates bar graphs labelled and unlabelled and saves
% them in .m and .tiff formats

% Labelled

figure ()
box on
pl
bar(DiameterProfiles.AggregateDiameterData(:,1),DiameterProfiles.AggregateDiameterData(:,3),'BarWidth',0.7,'FaceColor',[0.7 0.7 0.7],'EdgeColor',[0.5 0.5 0.5]);

xlabel('Diameter (\mum)')
ylabel('Fibers (%)')
xlim([0 1.5]);
ylim([0 30]);

set(gca,'linewidth',2,'fontsize',60)
set(gcf,"Units","normalized","OuterPosition",[0 0 1 1])

FigureName_L = Input{1,1} + "_Labelled";
FigureName_Ltiff = Input{1,1} + "_Labelled.tiff";

saveas(gcf,FigureName_L,'fig')
exportgraphics(gcf,FigureName_Ltiff,'Resolution',600);

% Average Bulk Fiber Diameter Analysis

for i = 1:length(DiameterProfiles.AggregateDiameterData)
    temp(i,1) = DiameterProfiles.AggregateDiameterData(i,1); % diameter values (X)
    temp(i,2) = DiameterProfiles.AggregateDiameterData(i,3); % frequencies (F)
    temp(i,3) =
DiameterProfiles.AggregateDiameterData(i,1)*DiameterProfiles.AggregateDiameterData(i,3); % X*F

    DiameterProfiles.BulkDiameterStatistics = temp;
end

Sum_Frequency = sum(DiameterProfiles.BulkDiameterStatistics(:,2)); % sum of the frequency%
Sum_Diameter_Frequency = sum(DiameterProfiles.BulkDiameterStatistics(:,3)); % sum of X*F

DiameterMeasurement_Bulk_Mean = Sum_Diameter_Frequency/Sum_Frequency; % stores bulk fiber diameter

for i = 1:length(DiameterProfiles.BulkDiameterStatistics)

```



```

        DiameterProfiles.BulkDiameterStatistics(i,4) =
        ((DiameterProfiles.BulkDiameterStatistics(i,1)-
        DiameterMeasurement_Bulk_Mean))^2*DiameterProfiles.BulkDiameterStatistics(i,2);
    end

    Sum_DiameterminBulkAveragesq = sum(DiameterProfiles.BulkDiameterStatistics(:,4));

    DiameterMeasurement_Bulk_SD = sqrt(Sum_DiameterminBulkAveragesq/Sum_Frequency); %
    stores bulk fiber SD

    % Reconstruct the original dataset from the frequency distribution
    Bdiamdataboot = repelem(DiameterProfiles.AggregateDiameterData(:,1),
    DiameterProfiles.AggregateDiameterData(:,2));

    % Number of bootstrap samples
    BdiamnumBootstrapSamples = 1000;

    % Initialize an array to store the bootstrapped means
    bootstrappedBDiamMeans = zeros(BdiamnumBootstrapSamples, 1);

    % Perform bootstrapping
    nBDiam = numel(Bdiamdataboot); % Number of data points
    for i = 1:BdiamnumBootstrapSamples
        % Resample with replacement
        bootstrapBDiamSample = Bdiamdataboot(randi(nBDiam, nBDiam, 1));

        % Compute the mean of the bootstrap sample
        bootstrappedBDiamMeans(i) = mean(bootstrapBDiamSample);
    end

    % Calculate the 95% confidence interval
    BDiamPercentiles = prctile(bootstrappedBDiamMeans, [2.5 97.5]);

    BDiamMeanUpperlim = BDiamPercentiles(1,2);
    BDiamMeanLowerlim = BDiamPercentiles(1,1);

    % Calculate the bootstrap mean
    DiameterMeasurement_Bulk_bootstrap_Mean = mean(bootstrappedBDiamMeans);

    DiameterMeasurement_Bulk_unc_upperlim = round(abs(DiameterMeasurement_Bulk_Mean-
    BDiamMeanUpperlim),3);
    DiameterMeasurement_Bulk_unc_lowerlim = round(abs(DiameterMeasurement_Bulk_Mean-
    BDiamMeanLowerlim),3);

    % Average Fibril Diameter Analysis

    % this loop finds the diameter range lower than the cutoff diameter -
    % fibril diameters

    DiameterProfiles.FibrilDiameterStatistics = [];

    for i = 1:length(DiameterProfiles.BulkDiameterStatistics)
        if cFD - DiameterProfiles.BulkDiameterStatistics(i,1) >= 0

```

```

        DiameterProfiles.FibrilDiameterStatistics(i,1) =
DiameterProfiles.BulkDiameterStatistics(i,1); % diameter values (x)
        DiameterProfiles.FibrilDiameterStatistics(i,2) =
DiameterProfiles.BulkDiameterStatistics(i,2); % frequencies% (f%)
        DiameterProfiles.FibrilDiameterStatistics(i,3) =
DiameterProfiles.BulkDiameterStatistics(i,3); % x*f%

        continue
    else
        break
    end
end

Sum_Fibril_Frequency = sum(DiameterProfiles.FibrilDiameterStatistics(:,2)); % sum of
fibril frequency
Sum_Fibril_Diameter_Frequency = sum(DiameterProfiles.FibrilDiameterStatistics(:,3));
% sum of x*f

DiameterMeasurement_Fibril_Mean = Sum_Fibril_Diameter_Frequency/Sum_Fibril_Frequency;
% stores average fibril diameter

for i = 1:length(DiameterProfiles.FibrilDiameterStatistics)
    DiameterProfiles.FibrilDiameterStatistics(i,4) =
(((DiameterProfiles.FibrilDiameterStatistics(i,1)-
DiameterMeasurement_Fibril_Mean))^2)*(DiameterProfiles.FibrilDiameterStatistics(i,2))
;
    DiameterProfiles.FibrilDiameterStatistics(i,5) =
DiameterProfiles.AggregateDiameterData(i,2); % f
end

Sum_DiameterminFiberAveragesq = sum(DiameterProfiles.FibrilDiameterStatistics(:,4));

DiameterMeasurement_Fibril_SD =
sqrt(Sum_DiameterminFiberAveragesq/Sum_Fibril_Frequency); % stores fibril diameter SD

% Standard deviation and MAD (median absolute deviation) values do not
% make sense in this case. We implement a bootstrapping method to find
% the uncertainty. Bootstrapping for 5000 diameter distributions

% Reconstruct the original dataset from the frequency distribution
Fdiamdataboot = repelem(DiameterProfiles.FibrilDiameterStatistics(:,1),
DiameterProfiles.FibrilDiameterStatistics(:,5));

% Number of bootstrap samples
FdiamnumBootstrapSamples = 1000;

% Initialize an array to store the bootstrapped means
bootstrappedFDiamMeans = zeros(FdiamnumBootstrapSamples, 1);

% Perform bootstrapping
nFDiam = numel(Fdiamdataboot); % Number of data points
for i = 1:FdiamnumBootstrapSamples
    % Resample with replacement

```

```

bootstrapFDiamSample = Fdiamdataboot(randi(nFDiam, nFDiam, 1));

% Compute the mean of the bootstrap sample
bootstrappedFDiamMeans(i) = mean(bootstrapFDiamSample);
end
% Calculate the 95% confidence interval
FDiamPercentiles = prctile(bootstrappedFDiamMeans, [2.5 97.5]);

FDiamMeanUpperlim = FDiamPercentiles(1,2);
FDiamMeanLowerlim = FDiamPercentiles(1,1);

% Calculate the bootstrap mean
DiameterMeasurement_Fibril_bootstrap_Mean = mean(bootstrappedFDiamMeans);

DiameterMeasurement_Fibril_unc_upperlim = round(abs(DiameterMeasurement_Fibril_Mean-
FDiamMeanUpperlim),4);
DiameterMeasurement_Fibril_unc_lowerlim = round(abs(DiameterMeasurement_Fibril_Mean-
FDiamMeanLowerlim),4);

%%
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
P = readtable('All Summary File Values.csv','VariableNamingRule','preserve'); %
imports the .csv file with all summary values
Q = readtable('All Pore Area Values.csv','VariableNamingRule','preserve'); % imports
the .csv files with all pore data

[lengthP, widthP] = size(PorePercentiles);
[lengthQ, widthQ] = size(Q);

Q = table2array(Q(:,1:widthQ-1));
PoreAreaVals = Q(:,2);

Pp = [P(13:18,3:widthP)]; % extracts necessary pore data from all summary values
Pp = table2array(Pp);
Pp = Pp';
PoreData.PercentPorosity = Pp(:,5);
PoreData.NumberPores = Pp(:,6);

Porosity_averagePores = mean(PoreData.NumberPores); % average number of pores
Porosity_SDPores = std(PoreData.NumberPores); % standard deviation of the number of
pores

Porosity_averagePercentPorosity = mean(PoreData.PercentPorosity); % porosity %

% Binning pore area values into 1000 bins

% Define the number of bins or bin edges
numBins = 1000; % Number of bins
binEdges = linspace(min(PoreAreaVals), max(PoreAreaVals), numBins+1); % Alternatively,
specify custom edges

% Calculate the frequency of each bin

```

```

[counts, binEdges] = histcounts(PoreAreaVals, binEdges);

% Calculate the bin centers for plotting
binCenters = (binEdges(1:end-1) + binEdges(2:end)) / 2;

PoreData.PorosityStatistics(:,1) = binCenters; % (x pores)
PoreData.PorosityStatistics(:,2) = counts; % (f pores)

for i = 1:length(PoreData.PorosityStatistics)
    PoreData.PorosityStatistics(i,3) =
PoreData.PorosityStatistics(i,1)*PoreData.PorosityStatistics(i,2); % (x pores * f
pores)
end

Porosity_averageMeanPoreArea =
sum(PoreData.PorosityStatistics(:,3))/sum(PoreData.PorosityStatistics(:,2)); %
calculating and storing mean pore area

for i = 1:length(PoreData.PorosityStatistics)
    PoreData.PorosityStatistics(i,4) = ((PoreData.PorosityStatistics(i,1) -
Porosity_averageMeanPoreArea)^2)*PoreData.PorosityStatistics(i,2);
end

Porosity_PoreAreaSD =
sqrt(sum(PoreData.PorosityStatistics(:,4))/sum(PoreData.PorosityStatistics(:,2))); %
calculates the standard deviation

% Standard deviation and MAD (median absolute deviation) values do not
% make sense in this case. We implement a bootstrapping method to find
% the uncertainty. Bootstrapping for 10000 pores

% Reconstruct the original dataset from the frequency distribution
poredataboot = repelem(PoreData.PorosityStatistics(:,1),
PoreData.PorosityStatistics(:,2));

% Number of bootstrap samples
porenumBootstrapSamples = 5000;

% Initialize an array to store the bootstrapped means
bootstrappedPoreMeans = zeros(porenumBootstrapSamples, 1);

% Perform bootstrapping
npores = numel(poredataboot); % Number of data points
for i = 1:porenumBootstrapSamples
    % Resample with replacement
    bootstrapPoreSample = poredataboot(randi(npores, npores, 1));

    % Compute the mean of the bootstrap sample
    bootstrappedPoreMeans(i) = mean(bootstrapPoreSample);
end

% Calculate the 95% confidence interval
PorePercentiles = prctile(bootstrappedPoreMeans, [2.5 97.5]);

```

```

PoreMeanUpperlim = PorePercentiles(1,2);
PoreMeanLowerlim = PorePercentiles(1,1);

% Calculate the bootstrap mean
Porosity_bootstrapMean = mean(bootstrappedPoreMeans);

Porosity_unc_upperlim = round(abs(Porosity_averageMeanPoreArea-PoreMeanUpperlim),3);
Porosity_unc_lowerlim = round(abs(Porosity_averageMeanPoreArea-PoreMeanLowerlim),3);

Pore_frequency_sum = sum(PoreData.PorosityStatistics(:,2));

indicesBelowPoreMean = PoreData.PorosityStatistics(:,1) <
Porosity_averageMeanPoreArea;

indcount = 0;
for i = 1:length(indicesBelowPoreMean)
    if indicesBelowPoreMean(i,1) == 1
        indcount = indcount +1;
        continue
    else
        break
    end
end

Pore_frequency_sum_belowmean = sum(PoreData.PorosityStatistics(1:indcount,2));

Porosity_PercentageofPoresBelowMean =
round((Pore_frequency_sum_belowmean/Pore_frequency_sum)*100);

%%
% Creating bar graphs - labelled
figure ()
box on;
bar(PoreData.PorosityStatistics(:,1),
PoreData.PorosityStatistics(:,2), 'BarWidth',0.7, 'FaceColor',[1
0.7], 'EdgeColor',[0.5 0.5 0.5]);
xlabel('Pore Area (\num^{2})');
ylabel('Frequency');
xlim([0 1.5]);

% setting y limits

numPoreyTicks = 5;
ydataUPlim = max(PoreData.PorosityStatistics(:,2));
yaxisUPlim = ceil(ydataUPlim / 500) * 500;
ylim([0 yaxisUPlim]);

yLimits = ([0 yaxisUPlim]);

% Generate evenly spaced y-tick values
yTicks = linspace(yLimits(1), yLimits(2), numPoreyTicks);

```

```

set(gca,'linewidth',2,'fontsize',40)

set(gcf,"Units","normalized","OuterPosition",[0 0 1 1])

PoreFigureName_L = Input{1,1} + "_PoreData_Labelled";
PoreFigureName_Ltiff = Input{1,1} + "_PoreData_Labelled.tiff";

saveas(gcf,PoreFigureName_L,'fig')
exportgraphics(gcf,PoreFigureName_Ltiff,'Resolution',600);

% creating bar graphs - unlabelled
figure ()
box on;
bar(PoreData.PorosityStatistics(:,1),
PoreData.PorosityStatistics(:,2),'BarWidth',0.7,'FaceColor',[1
0.7],'EdgeColor',[0.5 0.5 0.5]);

xlim([0 1.5]);
ylim([0 yaxisUPlim]);

yLimits = ([0 yaxisUPlim]);

% Generate evenly spaced y-tick values
yTicks = linspace(yLimits(1), yLimits(2), numPoreyTicks);

% Set the y-axis ticks
yticks(yTicks);

set(gca,'fontsize',24,'linewidth',2,'XTickLabel',[],'yticklabels',[])

set(gcf,"Units","normalized","OuterPosition",[0 0 1 1])

PoreFigureName_uL = Input{1,1} + "_PoreData_noLabel";
PoreFigureName_uLtiff = Input{1,1} + "_PoreData_noLabel.tiff";

saveas(gcf,PoreFigureName_uL,'fig')
exportgraphics(gcf,PoreFigureName_uLtiff,'Resolution',600);

% the following stores all important porosity values

% from all summary values
Porosity_averagePores = round(mean(PoreData.NumberPores));
Porosity_averagePercentPorosity = round(mean(PoreData.PercentPorosity)*100);

% other information from pore data histogram
Porosity_averageMaxPoreArea = max(PoreAreaVals);
Porosity_averageMinPoreArea = min(PoreAreaVals);
[Porosity_modePoreArea, Porosity_modePoreFrequency] = mode(PoreAreaVals);

% Pore density calculation
AreaofImage = (sclbar/(npx*1000))^2*(res^2); % in mm^2
% AreaofImageum = (sclbar/npx)^2*(res^2); % in um^2

```

```
PoreDensity = Porosity_averagePores/AreaofImage; % # of pores in 1 sq mm

% save workspace
save(WorkspaceName)
```

D.2 FTIR absorbance spectra SNV normalization

```
FTS = importFiles('FTIR'); % Importing data files using John Thomas' import function

% SNV Normalization & Non-negativity satisfaction
% SNV (Standard Normal Variate) is a normalization technique for
% vibrational spectra. The SNV transformation was introduced by Barnes et al.
% to reduce multiplicative effects of scattering and particle size, and also to reduce
% differences in the global intensities of the signals. Each spectrum is centered
% and then scaled by dividing by its standard deviation.

%  $X(\text{snv}) = (X(i) - X(\text{ave})) / \text{SD}(X(i))$ 

% X(snv) - SNV normalized absorbance
% X(i) - Experimental absorbance
% X(ave) - Mean absorbance
% SD(X(i)) - Standard deviation of absorbance

% For the MCR-ALS analysis, the spectra need to have non-negative
% absorbance. There is a step to fulfill this requirement in the code
% below.

for i = 1:length(FTS)
    for j = 1:length(FTS(i).data)
        FTS(i).data(j,3) = (FTS(i).data(j,2) - mean(FTS(i).data(:,2))) /
std(FTS(i).data(:,2)); % SNV normalization

        % Normalized values are stored in the 3th column in samples.spectra{p,1}

        FTS(i).data(j,4) = FTS(i).data(j,3) - min(FTS(i).data(:,3)); % non-negativity
satisfaction
        % Non-negative values are stored in the 4th column in samples.spectra{p,1}
    end
end

end
```

D.3 Analysis of fast scanning calorimetric data

D.3.1 FSC data unpacking

```
% Add Dr. John Thomas' FSC importFiles.m and resolutionincrease.m functions
% to the directory to unpack FSC data using the following code

% Prompt user for a struct name and RGB values
prompt = {'Enter the name to be used for the struct:', 'Enter RGB values as a matrix
(e.g., [1,0,0]):'};
dlgtitle = 'Input Name and RGB Matrix';
dims = [1 50];
userInput = inputdlg(prompt, dlgtitle, dims);

% Check if the user provided valid inputs
if ~isempty(userInput)
    structName = strtrim(userInput{1}); % Store the name as a string
    color = str2num(userInput{2}); % Convert RGB input to a matrix

    % Validate RGB input
    if isempty(color) || size(color, 2) ~= 3 || any(color(:) < 0) || any(color(:) >
255)
        disp('Invalid RGB input. Please enter a matrix with three columns (values
between 0 and 255).');
    else
        disp(['The struct will be named: ', structName]);
        disp('RGB Matrix:');
        disp(color);

        % Import files and store them in the struct
        importedStruct = importFiles; % Assuming importFiles function returns a struct

        % Dynamically assign the struct to the variable with user-defined name
        assignin('base', structName, importedStruct);

        % Store the RGB matrix separately in the workspace
        assignin('base', 'RGB_Matrix', color);
    end
else
    disp('No name entered. Operation cancelled.');
```

```
end

Work_Struct = importedStruct;

% Background correction

% Reverse the rates
tempHC_var = zeros(1:length(Work_Struct));
tempC_var = zeros(1:length(Work_Struct));

tempH_CVar = flip(Work_Struct(1).ratesHeating(:,1));
tempC_CVar = flip(Work_Struct(1).ratesCooling(:,1));
```



```

fields = {'heating', 'cooling'};

% Compute BL_CVar in a single loop
for f = 1:length(fields)
    field = fields{f};

    % Select the appropriate reversed rates for BL_HCVar
    if strcmp(field, 'heating')
        rates_CVar = tempH_CVar;
    else
        % rates_HCVar = tempC_HCVar;
        rates_CVar = tempC_CVar;
    end

    % Compute BL_CVar
    x = 0;
    for numruns = 2:length(Work_Struct)
        x = x+1;
        for k = 1:length(Work_Struct(numruns).(field))
            BL_CVar(x).(field){k,1} = [Work_Struct(numruns).(field){k,1}(:,1),
smooth(Work_Struct(numruns).(field){k,1}(:,2) - Work_Struct(1).(field){k,1}(:,2), 21,
'sgolay', 1)];
            BL_CVar(x).(field){k,2} = rates_CVar(k); % Store the corresponding rate
        end
    end
end

```

D.3.2 Background correction and generation of symmetry-corrected FSC heat flow rate data

```

%% Cool cycles - various rates // Heat cycles - 2000 K/s
% Creating the average cooling plot at 2000 K/s
% Gridded Interpolants for all cooling and heating
% numPairs = length(BL_CVar.cooling); % Assuming equal number of cooling and heating
curves

for numruns = 1:length(BL_CVar)
    numPairs = length(BL_CVar(numruns).cooling); % Assuming equal number of cooling
and heating curves
    cAVG = (BL_CVar(numruns).cooling{5,1}(:,2) + BL_CVar(numruns).cooling{end-
1,1}(:,2) + BL_CVar(numruns).cooling{end,1}(:,2))/3; % average cooling curves cooled
at 2000 K/s

    BL_CVar(numruns).averagecooling(:,2) = cAVG;
    BL_CVar(numruns).averagecooling(:,1) = BL_CVar(numruns).cooling{5,1}(:,1);

    F = figure();
    F.WindowState = 'maximized';
    box on;
    hold on;

    plot(BL_CVar(numruns).averagecooling(:,1), BL_CVar(numruns).averagecooling(:,2),
'b'); % Cooling curve

```

```

    plot(BL_CVar(numruns).heating{5, 1}(:, 1), BL_CVar(numruns).heating{5, 1}(:, 2),
'r'); % Heating curve

% Display instructions and get 4 points once for all curves
disp('Select 4 points: First: 2 for glassy region, Second: 2 for liquid region');
g = ginput(4); % Get points once

for pairIndex = 1:numPairs-1
    % Create interpolants for current cooling and next heating curve
    Fcvar = griddedInterpolant(flip(BL_CVar(numruns).averagecooling(:,1)),
flip(BL_CVar(numruns).averagecooling(:,2)));
    Fhvar = griddedInterpolant(BL_CVar(numruns).heating{pairIndex + 1, 1}(:, 1),
BL_CVar(numruns).heating{pairIndex + 1, 1}(:, 2));

    % Anonymous functions for easier interpolation
    FcFunc = @(t) Fcvar(t);
    FhFunc = @(t) Fhvar(t);

    % Plot current cooling and next heating curves
    F = figure();
    F.WindowState = 'maximized';
    box on;
    hold on;
    plot(BL_CVar(numruns).averagecooling(:,1),
BL_CVar(numruns).averagecooling(:,2), 'b'); % Cooling curve
    plot(BL_CVar(numruns).heating{pairIndex + 1, 1}(:, 1),
BL_CVar(numruns).heating{pairIndex + 1, 1}(:, 2), 'r'); % Heating curve

    % Find indices for glassy and liquid regions in cooling curve
    xC = BL_CVar(numruns).averagecooling(:, 1); % X-axis values in cooling
    G1C = find(xC >= g(1, 1) & xC <= g(2, 1)); % Glassy region indices in cooling
    L1C = find(xC >= g(3, 1) & xC <= g(4, 1)); % Liquid region indices in cooling

    % Find indices for glassy and liquid regions in heating curve
    xH = BL_CVar(numruns).heating{pairIndex + 1, 1}(:, 1); % X-axis values in
heating
    G1H = find(xH >= g(1, 1) & xH <= g(2, 1)); % Glassy region indices in heating
    L1H = find(xH >= g(3, 1) & xH <= g(4, 1)); % Liquid region indices in heating

    % Create common x-values for interpolation in both regions
    dummyValsG = linspace(max(min(xC(G1C)), min(xH(G1H))), min(max(xC(G1C)),
max(xH(G1H))), 100); % Glassy region
    dummyValsL = linspace(max(min(xC(L1C)), min(xH(L1H))), min(max(xC(L1C)),
max(xH(L1H))), 100); % Liquid region

    % Sort cooling data
    [xC_sorted, sortIdxC] = sort(xC); % Sort x-values in ascending order
    yC_sorted = BL_CVar(numruns).averagecooling(sortIdxC, 2); % Reorder
corresponding y-values

    % Sort heating data
    [xH_sorted, sortIdxH] = sort(xH); % Sort x-values in ascending order
    yH_sorted = BL_CVar(numruns).heating{pairIndex + 1, 1}(sortIdxH, 2); % Reorder
corresponding y-values

```

```

% Create interpolants using sorted data
Fcvar = griddedInterpolant(xC_sorted, yC_sorted); % Cooling interpolant
Fhvar = griddedInterpolant(xH_sorted, yH_sorted); % Heating interpolant

CsG = Fcvar(dummyValsG); % Cooling glassy region values
HsG = Fhvar(dummyValsG); % Heating glassy region values
CsL = Fcvar(dummyValsL); % Cooling liquid region values
HsL = Fhvar(dummyValsL); % Heating liquid region values

% Store results (including common x values)
Results_CVar(numruns).Runs{pairIndex,1}.GlassyRegion.dummyVals = dummyValsG';

Results_CVar(numruns).Runs{pairIndex,1}.GlassyRegion.Cooling = CsG';
Results_CVar(numruns).Runs{pairIndex,1}.GlassyRegion.Heating = HsG';

Results_CVar(numruns).Runs{pairIndex,1}.LiquidRegion.dummyVals = dummyValsL';
Results_CVar(numruns).Runs{pairIndex,1}.LiquidRegion.Cooling = CsL';
Results_CVar(numruns).Runs{pairIndex,1}.LiquidRegion.Heating = HsL';

% Midpoint calculation
midx = [Results_CVar(numruns).Runs{pairIndex,1}.GlassyRegion.dummyVals;
Results_CVar(numruns).Runs{pairIndex,1}.LiquidRegion.dummyVals];
midx = midx;

midy = [(Results_CVar(numruns).Runs{pairIndex,1}.GlassyRegion.Cooling +
Results_CVar(numruns).Runs{pairIndex,1}.GlassyRegion.Heating)/2;
(Results_CVar(numruns).Runs{pairIndex,1}.LiquidRegion.Cooling +
Results_CVar(numruns).Runs{pairIndex,1}.LiquidRegion.Heating)/2];

% Polynomial fitting (3rd-degree)
Results_CVar(numruns).Runs{pairIndex,1}.FitP3mid = polyfit(midx, midy, 3); %
Fit the midpoint data with a 3rd-degree polynomial

Results_CVar(numruns).Runs{pairIndex,1}.FitV3midC =
polyval(Results_CVar(numruns).Runs{pairIndex,1}.FitP3mid, xC); % Evaluate the
fitted 3-polynomial over the full x range in cooling
Results_CVar(numruns).Runs{pairIndex,1}.FitV3midH =
polyval(Results_CVar(numruns).Runs{pairIndex,1}.FitP3mid, xH); % Evaluate the
fitted 3-polynomial over the full x range in heating

% Plot the fitted curve for symmetry line over the full range of x
hold on
Fit3C = plot(xC, Results_CVar(numruns).Runs{pairIndex,1}.FitV3midC, '--c',
'LineWidth', 1.5); % Symmetry line (fitted curve)
Fit3H = plot(xH, Results_CVar(numruns).Runs{pairIndex,1}.FitV3midH, '--m',
'LineWidth', 1.5); % Symmetry line (fitted curve)

% Add legend for clarity
legend('Cooling', 'Heating', 'Cooling Symmetry Line (Fitted)', 'Heating
Symmetry Line (Fitted)', 'Location', 'Northwest');

hold off;
close

```

```

    end
    close
end

%% Symmetry Corrected Plots

for numruns = 1:length(Results_CVar)
    Fsym = figure('units','normalized','outerposition',[0 0 1 1]);
    Fsym.WindowState = 'maximized';
    box on;
    hold on;
    colors = lines(numPairs); % Generate distinct colors for each pair
    p = gobjects(numPairs-2, 1); % Preallocate plot handles array

    for pairIndex = 1:numPairs-2
        % Symmetry corrected heating and cooling values
        Results_CVar(numruns).Runs{pairIndex,1}.SymCorH(:,2) =
BL_CVar(numruns).heating{pairIndex + 1,1}(:,2) -
Results_CVar(numruns).Runs{pairIndex,1}.FitV3midH;
        Results_CVar(numruns).Runs{pairIndex,1}.SymCorH(:,1) =
BL_CVar(numruns).heating{pairIndex + 1,1}(:,1);

        % Plot heating curve
        p(pairIndex) = plot(Results_CVar(numruns).Runs{pairIndex,1}.SymCorH(:,1),
Results_CVar(numruns).Runs{pairIndex,1}.SymCorH(:,2), ...
        'color', colors(pairIndex,:), 'linestyle', '-', 'linewidth', 2,
'DisplayName', ['Heating ', num2str(pairIndex)]);

        xlim([50 250])
        % ylim([-0.4 -0.2])
        set(gca, 'yticklabel', [], 'linewidth', 2, 'fontsize', 45)

        % Create legend labels with units
        legendLabels = strcat(num2str(-tempC_CVar(1:numPairs-2,1), '%.0f'), ' K/s');
    end

    % Add a multi-column legend after the loop
    L = legend(p, legendLabels, 'Location', 'northeast');
    L.NumColumns = 2; % Set the number of columns for the legend
    L.FontSize = 36;

    % Save figures with unique filenames
    savefig(structName + "_Symmetry_Corrected_Figure_CVar_Run" + num2str(numruns) +
".fig");
    saveas(Fsym, structName + "_Symmetry_Corrected_Figure_CVar_Run" + num2str(numruns)
+ ".png"); % Save as PNG for easy viewing

    close(Fsym); % Close the figure to free up memory
end

```

D.3.3 Determination of the fictive temperature of heating cycles using Moynihan's method

```
% Moynihan method to obtain the fictive temperature
for numruns = 1:length(Results_CVar)
    xf = zeros(length(Results_CVar(numruns).Runs) - 1, 3);
    xf(:,1) = -tempC_CVar(1:(end-2),1);

    Fm_base = figure();
    Fm_base.WindowState = 'maximized';
    box on
    hold on

    X_inc = linspace(min(Results_CVar(numruns).Runs{5,1}.SymCorH(:,1)),
max(Results_CVar(numruns).Runs{5,1}.SymCorH(:,1)),
length(Results_CVar(numruns).Runs{5,1}.SymCorH(:,1)) * 5)';
    Y_inc = interp1(Results_CVar(numruns).Runs{5,1}.SymCorH(:,1),
Results_CVar(numruns).Runs{5,1}.SymCorH(:,2), X_inc);
    %
    p_base = plot(X_inc, sgolayfilt(Y_inc, 1, 21), ...
'color', 'r', 'linestyle', '-', 'linewidth', 2);

    LiqRegionIdx = ginput(2);
    LiqBd_Lo = min(LiqRegionIdx(1,1), LiqRegionIdx(2,1));
    LiqBd_Hi = max(LiqRegionIdx(1,1), LiqRegionIdx(2,1));

    GlsRegionIdx = ginput(2);
    GlsBd_Lo = min(GlsRegionIdx(1,1), GlsRegionIdx(2,1));
    GlsBd_Hi = max(GlsRegionIdx(1,1), GlsRegionIdx(2,1));

    for numSymCor = 1:length(Results_CVar(numruns).Runs) - 1

        Fm = figure();
        Fm.WindowState = 'maximized';
        box on
        hold on

        X_inc = linspace(min(Results_CVar(numruns).Runs{numSymCor,1}.SymCorH(:,1)),
max(Results_CVar(numruns).Runs{numSymCor,1}.SymCorH(:,1)),
length(Results_CVar(numruns).Runs{numSymCor,1}.SymCorH(:,1)) )';
        Y_inc = interp1(Results_CVar(numruns).Runs{numSymCor,1}.SymCorH(:,1),
Results_CVar(numruns).Runs{numSymCor,1}.SymCorH(:,2), X_inc);

        FH = griddedInterpolant(X_inc, Y_inc);

        FHfunc = @(t) FH(t);

        p = plot(X_inc, Y_inc, ...
'color', 'r', 'linestyle', '-', 'linewidth', 2);

        xL = find(X_inc >= LiqBd_Lo & X_inc <= LiqBd_Hi);
        xG = find(X_inc >= GlsBd_Lo & X_inc <= GlsBd_Hi);

        x_dummyL = X_inc(xL);
        y_dummyL = Y_inc(xL);
```

```

x_dummyG = X_inc(xG);
y_dummyG = Y_inc(xG);

[pL, SL, muL] = polyfit(x_dummyL, y_dummyL, 1);
x_extrp = linspace(min(x_dummyG), max(x_dummyL), length(x_dummyL));
[yL_extrp, ~] = polyval(pL, x_extrp, SL, muL);

FyL = griddedInterpolant(x_extrp, yL_extrp);
FyL_func = @(t) FyL(t);

pL_b1 = plot(x_extrp, yL_extrp, '--k', 'LineWidth', 2);

% Error in Liq state baseline

[yL_err, deltaL] = polyval(pL, x_dummyL, SL, muL);

% Error in Glc state baseline

[pG, SG, muG] = polyfit(x_dummyG, y_dummyG, 1);
[yG_extrp, ~] = polyval(pG, x_extrp, SG, muG);

FyG = griddedInterpolant(x_extrp, yG_extrp);
FyG_func = @(t) FyG(t);

pG_b1 = plot(x_extrp, yG_extrp, '--k', 'LineWidth', 2);

% Error in Glc state baseline

[yG_err, deltaG] = polyval(pG, x_dummyG, SG, muG);

tolerance = 0.001; % Define the critical value

% Initialize flags and solution storage
flagMid = false;
flagLo = false;
flagHi = false;

for x_incr = (min(x_extrp):0.01:max(x_extrp))
    % Calculate RHS and LHS values
    RHS_mid = integral(FHfunc, min(x_extrp), max(x_extrp)) -
integral(FyG_func, min(x_extrp), max(x_extrp));
    LHS_mid = integral(FyL_func, x_incr, max(x_extrp)) - integral(FyG_func,
x_incr, max(x_extrp));

    % Check stopping conditions
    if ~flagMid && (RHS_mid == LHS_mid || abs(RHS_mid - LHS_mid) < tolerance)
        xf(numSymCor, 2) = x_incr; % Store the result
        flagMid = true;
    end
end

```

```

        % Break if all flags are set
        if flagMid && flagLo && flagHi

            end
        end

        % Optional: Check if xf was found
        if all(isnan(xf))
            disp('No solution found within the tolerance.');
```

else

```

            fprintf('Solution found: xf = [%.1f, %.1f]\n', xf(numSymCor, 1),
xf(numSymCor, 2));
            end
            close
            for i = 1:length(xf)
                xf(i,3) = log10(xf(i,1));
            end
        end
        close
        Results_CVar(numruns).FictiveT = xf;
    end
end

```

D.3.4 Fragility index calculation

```

%% Fragility calculation

%  $T_f = ((C2*x - C2*K) / (C1 - x + K)) + T_{ref}$ 
Frag = figure ();
Frag.WindowState = 'maximized';
box on

for numruns = 1:length(Results_CVar)

    % Define your X and Y data
    x = Results_CVar(numruns).FictiveT(:,3); % Independent variable
    Y_vals = Results_CVar(numruns).FictiveT(:,2)+273; % Dependent variable

    % Define initial guesses for C1 and C2

    initial_C = [100 3500]; % Initial guess for C values

    % Use the given values for K and T_ref from xf_P1
    K = Results_CVar(numruns).FictiveT(end,3);
    T_ref = Results_CVar(numruns).FictiveT(end,2)+273;

    % Combine parameters into an initial guess vector

    initialParams_mid = [initial_C(1), initial_C(2)];

```

```

% Define the model

fit_func = fitttype(@(C1, C2, x) (((x - K)*(C2 - T_ref)))+(C1 * T_ref))./(C1 - x +
K));
[fit_model, gof, op] = fit(x, Y_vals, fit_func, 'StartPoint', initial_C, 'Upper',
inf, 'Lower', 1);
coeff = coeffvalues(fit_model);
conf_intervals = confint(fit_model, 0.95); % 95% confidence interval

x_fit = linspace(min(x)*0.8, max(x)*1.1, 1000);
y_fit = feval(fit_model, x_fit);

Results_CVar(numruns).Fragility.FitData(:,1) = x_fit;
Results_CVar(numruns).Fragility.FitData(:,2) = y_fit;
Results_CVar(numruns).Fragility.C_val = coeff;
Results_CVar(numruns).Fragility.C_CI = conf_intervals; % Store confidence
intervals

Results_CVar(numruns).Fragility.M =
(Results_CVar(numruns).Fragility.C_val(1,1)/Results_CVar(numruns).Fragility.C_val(1,2
)) * T_ref;
Results_CVar(numruns).M =
(Results_CVar(numruns).Fragility.C_val(1,1)/Results_CVar(numruns).Fragility.C_val(1,2
)) * T_ref;

p_data = plot(Results_CVar(numruns).FictiveT(:,3),
Results_CVar(numruns).FictiveT(:,2)+273, 's', 'MarkerFaceColor', color,
'MarkerEdgeColor', color, 'MarkerSize', 25);
hold on
p_fit = plot(Results_CVar(numruns).Fragility.FitData(:,1),
Results_CVar(numruns).Fragility.FitData(:,2), '--', 'Color', color, 'LineWidth', 2);

ylim([435 450])
xlabel('log_{10}(\beta [K/s])')
% ylabel('Fictive Temperature [K]')

set(gca, 'LineWidth', 2, 'FontSize', 45)

savefig("Fragility" + structName);
saveas(Frag, structName + "_Fragility" + ".png"); % Save as PNG for easy viewing

end

```


D.3.5 Estimation of the error of the fragility index by bootstrap method

```
% Number of bootstrap samples
numBootstrap = 10000;

% Loop over all runs
for numruns = 1:length(Results_CVar)

    % Define your X and Y data
    x = Results_CVar(numruns).FictiveT(:,3); % Independent variable
    Y_vals = Results_CVar(numruns).FictiveT(:,2) + 273; % Dependent variable

    % Define initial guesses for C1 and C2
    initial_C = [10 100]; % Initial guess for C values

    % Use the given values for K and T_ref from xf_P1
    K = Results_CVar(numruns).FictiveT(end,3);
    T_ref = Results_CVar(numruns).FictiveT(end,2) + 273;

    % Initialize array to store fragility values from bootstrap samples
    fragility_bootstrap = zeros(numBootstrap, 1);

    % Perform bootstrap resampling
    for i = 1:numBootstrap
        % Resample x and Y_vals with replacement
        idx = randi(length(x), length(x), 1);
        x_resampled = x(idx);
        Y_resampled = Y_vals(idx);

        % Define the model
        fit_func = fittype(@(C1, C2, x) (((x - K)*(C2 - T_ref)) + (C1 * T_ref)) ./ (C1
- x + K));

        % Fit the model to the resampled data
        [fit_model, gof, op] = fit(x_resampled, Y_resampled, fit_func, 'StartPoint',
initial_C, 'Upper', inf, 'Lower', 1);

        % Extract fitted coefficients
        coeff = coeffvalues(fit_model);

        % Calculate fragility M for the resampled data
        fragility_bootstrap(i) = (coeff(1) / coeff(2)) * T_ref;
    end

    % Calculate the standard deviation (error) of fragility from bootstrap samples
    fragility_error = std(fragility_bootstrap);

    % Store the fragility and error in the results struct
    Results_CVar(numruns).M_BootStrap = mean(fragility_bootstrap); % Mean fragility
    Results_CVar(numruns).M_BootStrapError = fragility_error; % Bootstrap error

    % Display the results
    fprintf('Run %d: Fragility = %.2f, Bootstrap error = %.2f\n', numruns,
mean(fragility_bootstrap), fragility_error);
```

```

% Plot the data and fit (optional)
Frag_bootstrap = figure('Units','normalized','OuterPosition',[0 0 1 1]);
Frag_bootstrap.WindowState = 'maximized';

p_data = plot(Results_CVar(numruns).FictiveT(:,3),
Results_CVar(numruns).FictiveT(:,2) + 273, '^', 'MarkerFaceColor', color,
'MarkerEdgeColor', color, 'MarkerSize', 25);
hold on
x_fit = linspace(min(x)*0.8, max(x)*1.1, 1000);
y_fit = feval(fit_model, x_fit);
p_fit = plot(x_fit, y_fit, '--', 'Color', color, 'LineWidth', 2);

% Customize plot
ylim([435 450])
xlabel('log_{10}(\beta [K/s])')
ylabel('Fictive Temperature T_{f} [K]')
set(gca, 'LineWidth', 2, 'FontSize', 45)

% Save figure
savefig("Fragility_Bootstrap" + structName);
saveas(gcf, structName + "_Fragility_Bootstrap" + ".tif"); % Save as TIFF for easy
viewing
end

save(structName + "_new_BS" + ".mat")

```

D.4 Rheology data import function

```

function data = importRheo_beta()

MinTorque = 1e-9; % minimum torque of the instrument DHR 20

% Select multiple CSV files using a file selection dialog
[fileNames, pathName] = uigetfile('*.csv', 'Select CSV Files', 'MultiSelect', 'on');

% Convert fileNames to a cell array if only one file is selected
if ischar(fileNames)
    fileNames = {fileNames};
end

% Initialize a struct to hold each file's data, procedure type, and metadata
RheoData = struct();

% Helper function to find and extract data from a specified keyword row
function value = extractDataByKeyword(rawData, keyword)
    rowIdx = find(strcmp(rawData(:, 1), keyword), 1);
    if ~isempty(rowIdx)
        % Extract the cell content from the rawData
        extractedData = rawData{rowIdx, 2};
    end
end

```

```

        % Check if keyword matches any specific constants that need numeric values
        if any(strcmp(keyword, {'Diameter', 'Stress constant', 'Strain constant',
'Geometry Inertia', 'Instrument inertia'}))
            numericPart = regexp(extractedData, '\d+(\.\d+)?', 'match'); % Extract
numbers
            value = str2double(numericPart{1}); % Convert to double
        else
            value = extractedData; % Return as-is for other keywords
        end
    else
        value = []; % Return empty if keyword is not found
    end
end

% Helper function to convert a cell array to a numeric array, handling scientific
notation and non-numeric entries
function numericArray = cellArrayToNumeric(cellArray)
    % Initialize output as NaN array
    numericArray = NaN(size(cellArray));
    for i = 1:numel(cellArray)
        if isnumeric(cellArray{i}) && ~isempty(cellArray{i})
            numericArray(i) = cellArray{i}; % Keep valid numeric entries as is
        elseif ischar(cellArray{i})
            % Attempt to convert scientific notation strings to double
            numericValue = str2double(cellArray{i});
            if ~isnan(numericValue)
                numericArray(i) = numericValue; % Assign numeric value if
conversion is successful
            else
                numericArray(i) = NaN; % Assign NaN for non-numeric or
unconvertible entries
            end
        else
            numericArray(i) = NaN; % Assign NaN for other non-numeric entries
        end
    end
end

% Loop through each selected file to extract procedure info and data
for k = 1:length(fileNames)
    % Full path of the current file
    fullFileName = fullfile(pathName, fileNames{k});

    % Import data from the CSV file as a cell array to capture text and numeric data
    rawData = readcell(fullFileName);

    % Extract procedure type, geometry type, and diameter using helper function
    procedureType = extractDataByKeyword(rawData, 'Procedure name');
    geometryType = extractDataByKeyword(rawData, 'Geometry Type');
    diameter = extractDataByKeyword(rawData, 'Diameter'); % Now stores diameter as a
number
    StressConst = extractDataByKeyword(rawData, 'Stress constant');
    StrainConst = extractDataByKeyword(rawData, 'Strain constant');

```

```

GeoInertia = extractDataByKeyword(rawData, 'Geometry Inertia');
InsInertia = extractDataByKeyword(rawData, 'Instrument inertia');

% Detect the row that contains 'Storage modulus' in the first cell
DataRow = find(strcmp(rawData(:, 1), 'Storage modulus'), 1);

% If no target row is found, generate a warning and continue to the next file
if isempty(DataRow)
    warning('No valid column names found with "Storage modulus" in file: %s.
Skipping this file.', fileNames{k});
    continue;
end

% Extract and clean column names
columnNames = rawData(DataRow, :);
for i = 1:length(columnNames)
    if isempty(columnNames{i}) || ~ischar(columnNames{i})
        columnNames{i} = sprintf('Column_%d', i);
    end
end
columnNames = cellstr(columnNames); % Ensure they are in cell array format

% Read the table data
dataTable = readtable(fullFileName, 'VariableNamingRule', 'preserve');

% Identify the columns for Temperature, Storage Modulus, Loss Modulus, and Complex
Viscosity
targetColumns = {'Temperature', 'Storage modulus', 'Loss modulus', 'Complex
viscosity', 'Angular frequency', 'Oscillation displacement', 'Tan(delta)',
'Oscillation strain', 'Oscillation strain rate', 'Oscillation torque', 'Step time'};
structFieldNames = {'Temperature', 'StorageModulus', 'LossModulus',
'ComplexViscosity', 'AngularFrequency', 'Amplitude', 'TanD', 'Oscillationstrain',
'Oscillationstrainrate', 'Oscillationtorque', 'Steptime'};

columnIndices = struct('Temperature', 0, 'StorageModulus', 0, 'LossModulus', 0,
'ComplexViscosity', 0, 'AngularFrequency', 0, 'Amplitude', 0, 'TanD', 0,
'Oscillationstrain', 0, 'Oscillationstrainrate', 0, 'Oscillationtorque', 0,
'Steptime', 0);

% Loop to populate column indices based on column names
for i = 1:length(targetColumns)
    colIdx = find(strcmp(columnNames, targetColumns{i}), 1);
    if ~isempty(colIdx)
        columnIndices.(structFieldNames{i}) = colIdx; % Store in struct
    end
end

% Store the data into the struct
RheoData(k).fileName = fileNames{k};
RheoData(k).procedureType = procedureType; % stores the procedure type
RheoData(k).geometryType = geometryType; % stores the geometry type
RheoData(k).StressConst = StressConst; % stores the stress constant of the geometry
RheoData(k).StrainConst = StrainConst; % stores the strain constant of the geometry
RheoData(k).GeoInertia = GeoInertia; % stores the geometry inertia

```

```

RheoData(k).InsInertia = InsInertia; % stores the instrument inertia

% Organize data according to the procedure type
numHeaderLines = DataRow + 1;
switch procedureType
    case 'Temperature ramp' % scans the temperature ramps and stores the values
        xData = dataTable{2:end, columnIndices.Temperature};
        yData1 = cellArrayToNumeric(table2cell(dataTable(2:end,
columnIndices.StorageModulus))));
        yData2 = cellArrayToNumeric(table2cell(dataTable(2:end,
columnIndices.LossModulus))));
        yData3 = cellArrayToNumeric(table2cell(dataTable(2:end,
columnIndices.TanD))));

        RheoData(k).Data(:,1) = xData; % Temperature
        RheoData(k).Data(:,2) = yData1; % Storage Modulus
        RheoData(k).Data(:,3) = yData2; % Loss Modulus
        RheoData(k).Data(:,4) = yData3; % Tan Delta

        yData4 = [];
        if columnIndices.ComplexViscosity > 0
            yData4 = cellArrayToNumeric(table2cell(dataTable(2:end,
columnIndices.ComplexViscosity))));
        end
        RheoData(k).Data(:,5) = yData4; % Viscosity

    case 'Frequency sweep' % scans the frequency sweeps and stores the values
        xData = dataTable{numHeaderLines:end, columnIndices.AngularFrequency};
        yData1 = cellArrayToNumeric(table2cell(dataTable(numHeaderLines:end,
columnIndices.StorageModulus))));
        yData2 = cellArrayToNumeric(table2cell(dataTable(numHeaderLines:end,
columnIndices.LossModulus))));
        yData3 = cellArrayToNumeric(table2cell(dataTable(numHeaderLines:end,
columnIndices.TanD))));

        RheoData(k).Data(:,1) = xData; % Frequency rad/s
        RheoData(k).Data(:,2) = yData1; % Storage Modulus
        RheoData(k).Data(:,3) = yData2; % Loss Modulus
        RheoData(k).Data(:,4) = yData3; % Tan Delta

        yData4 = [];
        if columnIndices.ComplexViscosity > 0
            yData4 = cellArrayToNumeric(table2cell(dataTable(numHeaderLines:end,
columnIndices.ComplexViscosity))));
        end
        RheoData(k).Data(:,5) = yData4; % Viscosity

        yData5 = cellArrayToNumeric(table2cell(dataTable(numHeaderLines:end,
columnIndices.Oscillationstrain))));
        RheoData(k).Data(:,6) = yData5; % Strain

```

```

        yData6 = cellArrayToNumeric(table2cell(dataTable(numHeaderLines:end,
columnIndices.Oscillationstrainrate)));
        RheoData(k).Data(:,7) = yData6; % Strain Rate

        yData7 = cellArrayToNumeric(table2cell(dataTable(numHeaderLines:end,
columnIndices.Oscillationtorque)));
        RheoData(k).Data(:,8) = yData7; % Torque

        RheoData(k).Data(:,10) = ((StressConst *
MinTorque)./RheoData(k).Data(:,6)) * 1e-6; % Low Torque Limit for G at Low Frequencies
        RheoData(k).Data(:,11) = ((InsInertia + GeoInertia)*1e-6 *
(StressConst/StrainConst) * ((RheoData(k).Data(:,1)).^2)) * 1e-6; % Inertial Limit for
G at High Frequencies
        RheoData(k).Data(:,12) = ((StressConst *
MinTorque)./RheoData(k).Data(:,7)) * 1e3; % Low Torque Limit for n (viscosity) at Low
Frequencies

        case 'Amplitude sweep' % scans the amplitude sweeps and stores the values
            xData = dataTable(numHeaderLines:end, columnIndices.Oscillationstrain);
            yData1 = cellArrayToNumeric(table2cell(dataTable(numHeaderLines:end,
columnIndices.StorageModulus)));
            yData2 = cellArrayToNumeric(table2cell(dataTable(numHeaderLines:end,
columnIndices.LossModulus)));
            yData3 = cellArrayToNumeric(table2cell(dataTable(numHeaderLines:end,
columnIndices.TanD)));

            RheoData(k).Data(:,1) = xData;
            RheoData(k).Data(:,2) = yData1;
            RheoData(k).Data(:,3) = yData2;
            RheoData(k).Data(:,4) = yData3;

            yData4 = [];
            if columnIndices.ComplexViscosity > 0
                yData4 = cellArrayToNumeric(table2cell(dataTable(numHeaderLines:end,
columnIndices.ComplexViscosity)));
            else
                yData4 = [];
            end

            case 'Time sweep' % scans the time sweeps and stores the values
                xData = dataTable(2:end, columnIndices.Steptime);
                yData1 = cellArrayToNumeric(table2cell(dataTable(2:end,
columnIndices.StorageModulus)));
                yData2 = cellArrayToNumeric(table2cell(dataTable(2:end,
columnIndices.LossModulus)));
                yData3 = cellArrayToNumeric(table2cell(dataTable(2:end,
columnIndices.TanD)));

                RheoData(k).Data(:,1) = xData; % Time
                RheoData(k).Data(:,2) = yData1; % Storage Modulus
                RheoData(k).Data(:,3) = yData2; % Loss Modulus
                RheoData(k).Data(:,4) = yData3; % Tan Delta

```

```
        otherwise
            warning('Unknown procedure type: %s', procedureType);
            continue;
        end
    end

    % Return the data struct as the output
    data = RheoData;

end
```