Study of the Miscibility, Morphology, Crystallization, 
and Melting Behavior of Blends of Poly(3-hydroxybutyrate) 
and Poly(vinylidene fluoride) 

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(ABSTRACT)

This thesis reports on the results of thermal, optical, and spectroscopic studies on poly(vinylidene fluoride)/poly(3-hydroxybutyrate) (PVDF/PHB) blends prepared by melt and solution blending techniques. The blends exhibit a single, composition dependent T_g. Dynamic crystallization studies indicate that PVDF crystallizes first in all blends containing more than 30% PVDF, and that the blends exhibit single phase behavior in the liquid state. Studies of the melting of isothermally crystallized samples indicate a melting point depression for melt blended PVDF/PHB but no equilibrium melting point depression for the solution blends. Growth rate studies on the \(\alpha\) phase of PVDF reveal that its radial growth rate decreases with increasing PHB blend content. Morphological studies demonstrate that the ring spacing of the PVDF \(\alpha\) phase increases with increasing temperature and PHB blend content. The different behavior of the melt and solution blends and the previous findings on the thermooxidative degradation behavior of PHB by Kunioka and Doi [1] indicated that PHB may
have degraded during the melt blending process. NMR spectra reveal that PHB's chemical composition had not been affected by either blending procedure, but intrinsic viscosity studies indicate a dramatic decrease in PHB's viscosity average molecular weight after melt blending and a smaller decrease after solution blending. FT-IR studies were conducted to determine if PHB did crystallize in the same temperature range as PVDF. FT-IR spectra reveal PHB does crystallize in the same temperature range as PVDF in the solution but not in the melt blends, and the PVDF γ phase content is higher in the solution blends. Finally, TGA studies were performed to determine the effect of PVDF on the degradation of PHB. These findings indicate that PVDF retards the rate of PHB degradation in both types of blends.
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Chapter 1. Introduction

Polymer blending has become an increasingly important technique in creating new materials with novel properties relatively inexpensively in comparison to the synthesis of new polymers or copolymers. Immiscible blends are more commonly encountered in industry and in research and require the presence of another component to prevent phase separation. Such blends yield the additive properties of the parent components. Miscible blends, on the other hand, have a one phase structure in the liquid state with intermediate physical properties. These blends yield an average of the homopolymers' properties. Unfortunately, such blends are rare and often contain chemically similar polymers.

The compatibility of poly(vinylidene fluoride) and poly(3-hydroxybutyrate) was explored due to PVDF's history of forming miscible blends with polymers containing carbonyl groups. Both PVDF and PHB are semicrystalline. Such a blend, if miscible, would improve the mechanical properties, melt processibility, and chemical resistance of PHB. From a fundamental standpoint, it would be
interesting to study a blend of two semicrystalline polymers since such blends are rarely encountered.

This thesis reports on the research conducted to blend the two polymers, to subsequently prove their miscibility, and to determine how blending affects the crystallization and melting behavior of the two polymers. Melt and solution blending techniques were utilized in blend preparation, and thermal, optical, and spectroscopic techniques were utilized in the blend and homopolymer characterization.

The first chapter is a review of miscibility and crystallization theory, as well as of the pertinent literature. The second chapter discusses the experimental methods employed to blend the two polymers and to subsequently characterize the blends and the homopolymers. The third chapter discusses the results and compares the solution and melt blending techniques. The last two chapters state the conclusions and report possible future work.
Chapter 2. Literature Review

2.1 Miscibility and Crystallization Theory

2.1.1 Introduction

In the following sections, the theoretical basis for miscibility will be discussed, as well as polymer crystallization theory. A fundamental understanding of these two areas is necessary before embarking on a study of the miscibility and crystallization of blends of poly(vinylidene fluoride) (PVDF) and poly(3-hydroxybutyrate) (PHB).

2.2 Miscibility

2.2.1 Introduction

When attempting to blend two or more homopolymers, it is possible to obtain either a miscible (a one phase system with homogeneous mixing on the molecular level) or an immiscible blend (a structure with at least two
macroscopic phases). The latter, an immiscible blend, is sometimes more desirable since such a blend exhibits the additive properties of the components.

For example, in the case of polybutadiene and polystyrene, it is necessary to have the two phase structure in order to improve the impact resistance of polystyrene[2]. Polybutadiene is a rubber with a glass transition temperature well below room temperature (-101°C, [3]), and the resulting high chain mobility enables it to absorb stresses. By blending small amounts of polybutadiene with polystyrene, which has a Tg of 100°C[3], it is possible to create a material with improved impact resistance from room temperature conditions to around 100°C. Above 100°C, polystyrene begins to soften and may begin to degrade at temperatures well above 100°C.

Because the polymers are immiscible, however, there is interfacial tension at the phase boundaries, and with time the polymers begin to phase separate further, leading to a decrease in the interfacial surface area. Furthermore, since there is little mixing between the phases, cracks resulting from thermal or mechanical stresses can easily propagate along the interfaces. Therefore, to create a stable material with good mechanical properties, it is necessary to improve the adhesion between the phases by reducing the interfacial surface tension[4].

One method is to graft/cross-link the two polymers at the interface. After grafting, it would be necessary to break chemical bonds in order for further phase separation to occur or for cracks to propagate along the interface[4].

The addition of a compatibilizer can also limit further phase separation. Compatibilizers, normally in the form of a copolymer composed of segments of the two blend components, not only mix with both polymers but also migrate to
the interfaces thereby lowering the surface free energy. This improves the adhesion between the two phases, lessens interfacial surface tension, and results in a decrease in the driving force for phase separation[4].

It is also desirable, in certain systems, to obtain the average of the homopolymers' properties. This is only possible in a miscible system, where the polymers are homogeneously mixed on the molecular level. This could help with the processability of materials with high viscosities or with a high susceptibility to degradation, allow materials with novel properties to be produced, or help reduce cost in the case of an expensive polymer[4].

Examples of situations where it is advantageous to average the polymers' properties are the following. A polymer with a high glass transition temperature can be made processable by the addition of a compatible blend component which has a lower glass transition temperature. This is especially important when the polymer degrades at a temperature close to the temperature where it begins to flow[4]. A product with novel properties is produced in the case of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) and polystyrene (PS). These blends exhibit miscibility in all blend compositions, good mechanical properties, and excellent optical clarity[5]. In other cases, a blend can improve the radiation or abrasion resistance of one polymer, or simply lower the product cost[4].

In polymer processing, a miscible system may lead to product with better physical properties. This is true in the case of extrusion or injection molding. In the extrusion process, the low viscosity component tends to migrate to the surface thus leading to phase separated materials. In injection molding,
incomplete mixing of immiscible polymers may lead to poor mechanical properties at the "weld line"[4].

Most polymer systems studied thus far appear to be immiscible due to the high molecular weights involved. This results in a low entropy of mixing term in the free energy equation and if there are unfavorable polymer-polymer interactions, there is also a positive enthalpy of mixing[6]. Because of the difficulty of successfully stabilizing an immiscible system, and the desire in some cases to attain average properties rather than additive properties, an intensive effort has been made over the last thirty years to understand the causes of miscibility, how to prove whether a system is miscible, how to improve the degree of miscibility, and how to predict miscibility of a given polymer system.

2.2.2 Thermodynamic Criteria for Miscibility

In order to obtain miscibility in any system, it is necessary to have a negative free energy of mixing. Several theories have been developed to describe the free energy of mixing ($\Delta G_{\text{mix}}$) in a solution. In the case of an ideal solution, Raoult's law is employed to describe $\Delta G_{\text{mix}}$. It states that the vapor pressure of component A in the mixture is the product of the mole fraction of component A in the liquid phase and the vapor pressure of pure component A. Such a solution has an ideal entropy of mixing ($\Delta S_{\text{mix}}$), a zero enthalpy of mixing ($\Delta H_{\text{mix}}$), which indicates the absence of either net favorable or unfavorable interactions between the two components, and a negative $\Delta G_{\text{mix}}$. Because $\Delta G_{\text{mix}}$ will only reflect the changes in chemical potential upon mixing,
Racalt's law relates the change in the chemical potential upon mixing to \( \Delta G_{\text{mix}} \)\[7\].

In real solutions, however, there are net favorable or disfavorable interactions. Henry's law was developed for the case of real solutions that appear ideal at dilute concentrations. It defined an empirical constant that related the vapor pressure of component A in the mixture to its mole fraction at dilute concentrations. From the vapor pressure, the chemical potential and thus the free energy of mixing could be calculated\[7\].

Hildebrand introduced the concept of a lattice to describe the non-zero enthalpy of mixing encountered in non-ideal mixtures. He assumed, in spite of possible favorable or unfavorable interactions, that the kinetic energy of the molecules in the mixture would enable them to occupy the same number of positions and, consequently, have the same entropy as an ideal solution. The enthalpy of mixing was computed utilizing a lattice model\[4\].

The solution is represented by a lattice. Hildebrand assumed that each solute molecule was surrounded by \( zn_1 \) solute molecules and \( zn_2 \) solvent molecules, where \( n_i \) is the mole fraction of molecule \( i \) \( (n_i = N_i/N, \) where \( N_i \) is the total number of molecules \( i \) and \( N \) is the total number of molecules in the system) and \( z \) is the coordination number of the lattice. It is assumed that the specific volume of the solvent and solute are equal\[4\].

The enthalpy of mixing is found in the following manner. The interaction energy between the solute molecule and the surrounding solvent and solute molecules is described as:

\[
zn_1\varepsilon_{11} + zn_2\varepsilon_{12}
\]
where $\varepsilon_{ij}$ is the interaction energy between molecules i and j. If there are a total of N molecules in the system, the total energy contribution of this type of interaction is:

$$Nn_1(zn_1\varepsilon_{11} + zn_2\varepsilon_{12})$$

[2]

In addition, there is an energy contribution from the solute and solvent molecules surrounding the solvent[4]:

$$Nn_2(zn_2\varepsilon_{22} + zn_1\varepsilon_{12})$$

[3]

When the pure component interaction energies ($zn_1N\varepsilon_{11}$ for the solute and $zn_2N\varepsilon_{22}$ for the solvent) are subtracted from the sum of the interaction energies described in equations 2 and 3, the enthalpy of mixing can be described by:

$$\Delta H_{Mix} = Nzwx_1x_2$$

and $w = 1/2\varepsilon_{11} + 1/2\varepsilon_{22} - \varepsilon_{12}$

[4]

where w is the exchange energy[4].

Early work on polymer-solvent systems revealed that the vapor pressure of the solvent was much less than that predicted from Hildebrand's theory. It was decided that volume fractions rather than mole fractions would more accurately describe the amount of polymer and solvent in the mixture[4].

Thus, Flory and Huggins independently developed a lattice theory in which the enthalpy expression is identical to that of Hildebrand, except $\phi_i$ (the volume fraction of component i) is used instead of $n_i$[4]. Thus, the enthalpy of mixing is:

$$\Delta H_{mix} = zN\phi_1\phi_2w$$

[5]
where \( zw = \chi_{RT} \) (\( \chi \) is the Flory-Huggins chi parameter and a negative \( \chi \) parameter indicates strong specific interactions), \( T \) is the experimental temperature, and \( R \) is the molar gas constant[3].

The entropy expression derived from the Flory-Huggins theory recognizes the connectivity of the polymer segments, and it assumes the concentration of vacant lattice sites in the bulk is equal to that near the polymer molecule examined. This latter assumption results in a theory which works best for concentrated polymer solutions[3].

For simplicity's sake, this theory assumes that the polymer is monodisperse with \( n \) segments per molecule, and there are \( N \) sites in the lattice which can be occupied by either solvent molecules or polymer segments. The length of these polymer segments is chosen such that the segmental volume equals the solvent molecular volume. When polymer molecule \( i+1 \) is placed in the lattice, \( N - ni \) lattice sites are available to the first segment. The second segment can only occupy \( z \) (the lattice coordination number) sites adjacent to the first, and the concentration of empty sites ((\( N - ni \))/\( N \)) available to it is assumed to be unaffected by the addition of the previous segment. Therefore, the total number of ways the second segment can be placed are \( z(N - ni)/N \). The third segment can occupy only \( z - 1 \) lattice sites surrounding the second segment. The total number of ways it can be placed are \([(z - 1)(N - ni))/N]3 \).

Because the concentration of empty sites surrounding a segment of the polymer molecule is unaffected by the total number of segments of that molecule already placed down on the lattice, each event is independent of the previous one. Therefore, the total number of ways (\( \omega_{i+1} \)) the \( i + 1 \) polymer molecule can occupy the lattice are:
\[
\omega_{i+1} = (N - ni)z \left( \frac{N - ni}{N} \right)^i \left( z - 1 \right)^{\left( \frac{N - ni}{N} \right)^{n-2}}
\]

and the total number of ways (\(\Omega\)) of placing \(N_2\) polymer molecules in the lattice is:

\[
\Omega = \frac{1}{N_2!} \prod_{i=1}^{N_2} \omega_i
\]

where \(N_2!\) is included to account for the fact that polymer molecules are interchangeable[3].

Now an expression describing the entropy of mixing can be derived. Using the Boltzman Equation, entropy is defined as:

\[
S = k_B \ln \Omega
\]

where \(k_B\) is Boltzman's constant. After much manipulation of the expression for \(\Omega\), the following expression is derived:

\[
\Omega = \frac{z^{N_2} (z - 1)^{N_2} (n - 2)!^{nN_2}}{N_2! N_2^{n(N - 1)} (N/n)! (N/n - N_2)!^n}
\]

After equation 9 is substituted into equation 8, the resulting expression can be simplified using Sterling's approximation \(|\ln y| = y\ln y - y\) to give:

\[
\frac{S_{\text{mix}}}{k_B} = -N_2 \ln \left( \frac{nN_2}{N} \right) - N_1 \ln \left( \frac{N_1}{N} \right) + N_2 \left[ \ln z + (n - 2) \ln (z - 1) + (1 - n) \right] + \ln n]
\]

where \(S_{\text{mix}}\) is the entropy of the mixed solution. After entropy expressions for the pure polymer and the pure solvent are formulated, the \(\Delta S_{\text{mix}}\) can be calculated by subtracting these expressions from equation 10. This gives:
\[ \Delta S_{\text{mix}} = -k_B \left[ N_1 \ln \left( \frac{N_1}{N} \right) + N_2 \ln \left( \frac{nN_2}{N} \right) \right] \]

Since the solvent and the polymer repeat units are assumed to occupy the same volume, \( N_1/N \) and \( nN_2/N \) can be converted to volume fractions to give[3]:

\[ \Delta S_{\text{mix}} = -k(N_1 \ln \phi_1 + N_2 \ln \phi_2) \]

Finally, the Flory-Huggins expression describing the free energy of mixing is obtained by adding equations 5 and 12 (remember \( \chi \) equals \( zw/RT \)):

\[ \Delta G_{\text{mix}} = RT \left[ n_1 \ln \phi_1 + n_2 \ln \phi_2 + N_A \chi \phi_1 \phi_2 \right] \]

where \( n_i = N_i/N \). This assumes the total number of molecules in the system equals Avogadro's number \( (N_A) \)[3].

The Flory-Huggins theory has been extended to polymer-polymer systems by replacing \( V_1 \) with the interacting segment volume \( (V_s) \)[4]. Polymer molecules by definition have high molecular weights which give rise to a almost zero entropy of mixing \( (N_i \ll N \text{ due to the high molecular weights involved}) \). Therefore, in order for the system to exhibit miscibility, the \( \chi \) parameter must be negative. In contrast, small molecule mixtures often have a large and positive \( \Delta S_{\text{mix}} \) and a negative \( \chi \) parameter is not necessary for miscibility.

Polymer/polymer mixtures normally exhibit lower critical solution temperature (LCST) behavior, and polymer solutions generally exhibit upper critical solution temperature (UCST) behavior. In polymer solutions, as the temperature is lowered, the \(-T \Delta S_{\text{mix}}\) term decreases and phase separation occurs. Since specific interactions are responsible for a negative \( \chi \) parameter and miscibility in polymeric systems, a rise in temperature will weaken such interactions and lead to phase separation.
Flory-Huggin's theory can be used to predict such UCST or LCST behavior. However, it has been found that it can't predict bimodality (cases where more than one minimum or maximum exist in the phase diagram) and, consequently, partial miscibility in some polymer systems[4].

Therefore, other theories have been developed. The empirical modifications by Koningsveld are able to predict such behavior, but these provide no explanation for such behavior[4]. Other theories, such as Flory's Equation of State and Sanchez-Lacombe's equation of state, have also been developed to describe the free energy of mixing and more accurately predict the polymer-polymer, and polymer-solvent phase diagrams[4].

These later theories have other disadvantages, however. In the case of Flory's equation of state, the calculations are tedious and require precise data on thermal expansion coefficients and compressibility coefficients[8]. Sanchez-Lacombe's equation of state appears simpler, but the necessary experimental data is not yet available for most polymers[8]. McMaster has stated that Flory-Huggins' theory works well when the thermal expansion coefficients of the two polymers are similar[9]. Therefore, it appears Flory-Huggins theory will be the most commonly used in the near future.

The Flory-Huggins theory can be utilized to construct a phase diagram. From such a phase diagram, it is clear that in order to achieve a stable miscible system, not only must the free energy of mixing be negative as mentioned in the beginning of this section, but the second derivative of the free energy of mixing with respect to composition \( \partial^2 G_{\text{mix}}/\partial \phi^2 \) (which will be noted as \( \partial^2 G/\partial \phi^2 \) from here on) must also be positive[6]. In Figure 1, the region between points \( \alpha \) and \( \beta \) is the unstable region because any small fluctuation in composition leads to a
Figure 1. Free energy diagram illustrating an unstable phase[4].
decrease in the free energy and hence to phase separation. In this region \( \partial^2 G / \partial \phi^2 \) is negative. A decrease in the total free energy of the system can be accomplished by changing the composition slightly, while maintaining an average composition equal to the initial blend composition, until the state of lowest possible free energy is attained[4].

The metastable region is separated from the unstable region by the spinodal. The spinodal connects those points where \( \partial^2 G / \partial \phi^2 \) is zero. In the metastable region, \( \partial^2 G / \partial \phi^2 \) is positive. In figure 2, it is demonstrated that a large change in composition about \( C_0 \) is needed for the free energy to be lowered. The phase change proceeds through several steps, each with an average composition equal to the initial blend composition, until the lowest free energy state is achieved[4].

Phase separation occurs by a nucleation and growth mechanism in this region. In figure 2, it is demonstrated that the initial steps result in a free energy greater than that of the initial blend. As a result, an activation energy is required to form a nucleus. Since growth is necessary to stabilize the nuclei's excess surface free energy, like molecules diffuse to the nucleus in a downhill concentration gradient. This nucleation and growth mechanism leads to phase separation.

The most important features of the phase diagram are the binodal, the spinodal, and the critical point. The metastable region is bound by the binodal which connects those points where \( \partial^2 G / \partial \phi^2 \) is positive and \( \partial G / \partial \phi \) is zero. A one phase or miscible structure exists in the region outside of the binodal. Between the binodal and spinodal, two phases may exist under the right conditions, and
Figure 2. Free energy diagram of a metastable phase[4].
within the spinodal, two phases exist. The critical point of the phase diagram is the point where $\frac{\partial^3 G}{\partial \phi^3}$ is zero[4]. Below this point, in the case of a lower critical solution temperature diagram, or above this point, in the case of an upper critical solution temperature diagram, one phase exists[8]. This phase diagram can be used to determine the state of the blend at a given composition, temperature, molecular weight, etc. and may be a useful tool for anticipating blend behavior[4].

As mentioned previously, the Flory-Huggins theory can be used to construct a phase diagram. However, before it has any predictive capability, it is necessary to know the sign and magnitude of the $\chi$ parameter. One method of determining the $\chi$ parameter is by Hildebrand's solubility parameter approach:

$$\chi = (\delta_1 - \delta_2)^2$$  \[14\]

where $\delta_i$ is defined as the solubility parameter of the polymer $i$ and represents the square root of the cohesive energy density. $\delta$ can be determined experimentally by extrapolation of data from analogues of the polymer which range in size from small molecules to molecules with molecular weights close to that of the polymer[4].

Another approach is that of Small. Small calculated $\delta$ using energy values derived from group contributions to the cohesive energy. He was able to tabulate such group contributions and provide an easy method of estimating the solubility parameter without the need of experimentation[4].

Once the $\delta$ values of each polymer have been determined by one of the above methods, the $\chi$ parameter can be calculated with equation 14. If the $\chi$
parameter results in a negative free energy of mixing, there is a possibility that the blend may be miscible. The drawback of these approaches is that they don't account for strong intermolecular interactions which would result in a negative $\chi$ parameter[4].

Scientists in the field of polymer blends have discovered that it is difficult to predict whether or not a blend will be miscible. As a result, one must often resort to determining a blend's miscibility by experimental methods[8]. Such characteristics as the glass transition temperature(s) of the blend, as well as the melting and crystallization behavior of one or more of the blend components, are often studied in order to prove miscibility. However, before experimental methods of determining miscibility are discussed, the theory of polymer crystallization will be described.

2.3 Crystallization

2.3.1 Introduction

Since the blend studied in this project contains two semicrystalline polymers, it is necessary to understand crystallization theory in order to better understand how such a miscible system will affect the crystallization of one or more of the blend's components.

2.3.2 Crystallization Theory

At equilibrium, the melting point of such a polymeric crystal is a first-order transition as in the case of small molecule systems. That is, the melting transition is infinitely sharp and is independent of the amounts of the two
phases (the liquid and crystalline phases) in equilibrium. In a polymer system, the equilibrium situation would consist of a perfect polymer crystal, without any defects and with a large volume to surface ratio, in equilibrium with the melt[10]. Such a crystal would minimize any excess contribution of the side and end surface free energies to the overall free energy caused by the juxtaposition of the crystal and the melt[11]. It would take an infinite period of time to crystallize the polymer at the equilibrium melting temperature[10].

However, unlike small molecule systems where crystallization is observed a few degrees below the equilibrium melting temperature, crystallization normally occurs at least 20° below the equilibrium melting temperature in polymer systems. This is due in part to the high activation energy for nucleation resulting in part from the high interfacial free energy associated with the basal plane or side surface of the polymer crystallites, and in part to the difficulty in extracting crystallizable sequences of sufficient length from the isometric melt[11].

Therefore, the modern theories of crystallization are primarily kinetic theories. These assume that the observed lamellar thickness is that which grows fastest, not that corresponding to the most stable crystal. In addition, nucleation is the rate controlling step in crystallization at crystallization temperatures close to the equilibrium melting temperature[12]. This latter assumption has been confirmed by studies of the temperature dependence of the crystallization rate in the vicinity of the equilibrium melting temperature. A low crystallization rate is observed directly below the equilibrium melting temperature, and the rate increases until it reaches a maximum. After it passes through the maximum, it decreases once more. Therefore, crystallization is a
nucleation controlled process at temperatures close to the equilibrium melting temperature and a diffusion controlled process at temperatures close to \( T_g \)[11].

In the kinetic theory, growth begins from a primary nucleus which may be either heterogeneous or homogeneous. Nuclei can be formed homogeneously by statistical fluctuations of the polymer chain conformation in the melt, but more often nucleation is catalyzed by the presence of foreign particles which gives rise to heterogeneous nucleation[10].

The following model sufficiently accurately describes the asymmetric nucleus found in polymer systems. This model assumes the crystal is of a finite size, making side and surface free energy contributions significant. The free energy of formation (\( \Delta G \)) of an asymmetric nucleus, which has a thickness of \( \zeta \) and \( n \) chains a distance \( a \) apart in a square array, is described by the following equation:

\[
\Delta G = 4\zeta a v^{1/2} \sigma_u + 2va^2 \sigma_e - va^2 \zeta \Delta f
\]

where:

\[
\Delta f = \Delta h - T_X \Delta s = \frac{\Delta h \Delta T}{T_m^0}
\]

\[
\Delta T = T_m^0 - T_X
\]

where \( \Delta f \) is the free energy of crystallization of a perfect crystal of size \( va^2 \zeta \). \( \sigma_e \) is the interfacial free energy per molecule at the cylinder end, \( \Delta h \) is the enthalpy of fusion per unit volume at the equilibrium melting temperature \( T_m^0 \), \( T_X \) is the crystallization temperature, and \( \sigma_u \) is the side surface free energy per unit area. The first two terms of the equation describe the surface free energy of the nucleus, and the third term describes the bulk free energy[12].

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ΔG initially increases as the nucleus increases in size. It then reaches a maximum (ΔG*) and eventually decreases and becomes negative which leads to the formation of a stable nucleus. The nucleus at this saddie point (where ΔG = ΔG*) is the critical nucleus and has a ΔG of[12]:

\[
ΔG = ΔG^* = \frac{32\sigma_0^2\sigma_e}{\Delta t^2}
\]

Turnbull and Fisher have developed a theory for the nucleation rate of a condensed monomer system

\[
\dot{N} = N_0 \exp\left( -\frac{U^*}{k_BT_x} \right) \exp\left( -\frac{\Delta G^*}{k_BT_x} \right)
\]

where \( N_0 = \frac{N_Ak_BT_x}{h} \)

where \( \dot{N} \) is the rate of homogeneous nucleation, \( U^* \) is the activation energy for the transport of crystallizable segments across the liquid-nucleus interface, and \( h \) is Planck’s constant. After substitution of equation 16 for ΔG*, the nucleation rate of homogeneous nucleation in a polymeric system is shown to be[12]:

\[
\dot{N} = N_0 \exp\left[ -\frac{U^*}{RT_x} - \frac{32\sigma_0^2\sigma_eT_m^2}{(\Delta h)^2k_BT_x(\Delta T)^2} \right]
\]

The free energy of formation of a heterogeneous nucleus (ΔG_{h}^*) is related to ΔG* by the following equation:

\[
ΔG_{h}^* = f(θ)ΔG^*
\]

where \( f(θ) \) has a value between 0 and 1. The lower free energy of formation of a heterogeneous nucleus results in a higher rate of heterogeneous nucleation. Therefore, nucleation will preferably occur heterogeneously[10].
Experimental findings reveal secondary, rather than primary nucleation, is more relevant in determining lamellar thickness. In secondary nucleation, it is assumed the thickness of the nucleus is not greater than that of the substrate. If the secondary nucleus is in contact with the substrate along one side, the free energy of formation is:

\[ \Delta G = 2va^2\sigma_e + 2a^2\zeta \sigma_u - va^2\zeta \Delta f \]

After solving for \( \partial \Delta G / \partial v = \partial \Delta G / \partial \zeta = 0 \), the thickness and free energy of the secondary nucleus are[12]:

\[ \zeta^* = \frac{2\sigma_e}{\Delta f} \]

\[ \Delta G^* = \frac{4a^2\sigma_u^* \sigma_e}{\Delta f} \approx \frac{4a^2\sigma_u \sigma_e T_m^0}{\Delta h \Delta T} \]

The Gibbs Thompson Tammann equation is used to relate the observed melting point to the equilibrium melting point and the lamellar thickness. The free energy of fusion is:

\[ \Delta G_f = -\Delta G_{cry} = -2va^2\sigma_e - 2a^2\zeta \sigma_u + va^2\zeta \Delta f \]

\[ = -2va^2\sigma_e - 2a^2\zeta \sigma_u + va^2\zeta \Delta h (T_m^0 - T_m) / T_m^0 \]

From now on \( \Delta h \) and \( \Delta f \) will refer to the fusion process. It is assumed the free energy of formation is zero. Therefore:

\[ 0 = 2va^2\sigma_e + 2a^2\zeta \sigma_u - va^2\zeta \Delta h^0 + va^2\zeta (T_m \Delta h^0 / T_m) \]

After dividing through by \( va^2\zeta \Delta h^0 \) the following equation is derived:

\[ T_m = T_m^0 \left( 1 - \frac{2\sigma_e}{\Delta h^0 \zeta} - \frac{2\sigma_u}{\Delta h^0 \sigma_u va} \right) \]

For most polymers, \( va \) is >> \( \zeta \) and \( \sigma_e \) is >> \( \sigma_u \) and:
\[ T_m = T_m^\circ(1 - 2\sigma_e/\Delta h\zeta) \]  

(\(\Delta h\) is equal to \(\Delta h^\circ\)) which is the Gibbs Thompson Tamman equation. If:

\[ \zeta = \frac{2\sigma_e}{\Delta f} \approx \frac{2\sigma_e T_m^\circ}{\Delta h\Delta T} \]

is substituted into equation 20, the free energy will never become negative, and from equation 22, it results in \(T_m = T_X\). This is not observed. Therefore, in order for crystallization to occur, \(\zeta > 2\sigma_e/\Delta f\). That is:

\[ \zeta = \frac{2\sigma_e}{\Delta f} + \delta\zeta \]

The nature of the \(\delta\zeta\) has been the subject of debate for quite some time[12].

Various theories predict the thickness of the chain-folded strip to fluctuate. A general theory formulated by Lauritzen, DiMarzio and Passaglia, allows for the fluctuation of thickness for every fold stem. However, in this theory, \(\delta\zeta\) goes to infinity at finite undercoolings. This has never been observed and has been referred to as the \(\delta\zeta\) "catastrophe"[13].

This \(\delta\zeta\) "catastrophe" has been avoided in the later Lauritzen and Hoffman theory which assumes the thickness is invariant after nucleation. Each successive attachment and detachment of segments have well defined activation energies and the free energy of crystallization is apportioned between these two events. Eventually these steps will lead to a negative free energy and a stable nucleus. This theory defines the lamellar thickness as:

\[ <\zeta>_{av} = \frac{2\sigma_a}{\Delta f} + \left( \frac{k_BT_x}{2b_0\sigma_u} \right) \frac{4\sigma_u}{a + \Delta f} \]
where \( b_0 \) is the layer thickness. Lauritzen and Hoffman postulate that the molecule will become attached to the face with zero momentum perpendicular to the crystal face before adopting the extended chain conformation required for crystallization. That is, a surface free energy term will be created before the free energy of crystallization is released[14].

Once nucleation has occurred, ribbon-like lamellae will begin to form. In these structures, the chain axis of polymer molecules is generally aligned perpendicular to the plane of the lamella as a result of chain folding at the surface of the lamella[15]. Growth begins at the nucleus, and bundles of lamellae fan out from the nucleus like wheat sheaves[10].

The original expression which described the radial growth rate, \( G \), of these lamellae was an equation developed by Turnbull and Fisher for monoatomic substances:

\[
G = G_0 \exp(-\Delta \phi^*/kT_x) \exp(-U^*/kT_x) \tag{29}
\]

where \( G_0 \) is a front factor, and \( \Delta \phi^* \) is the free energy of activation required to form a critical-sized nucleus from the melt[16].

Turnbull and Fisher's equation was modified by Lauritzen and Hoffman. They recognized that the growth rate was not related simply to the nucleation rate because of successive surface nucleations. In regime I, after one nucleus is formed, the growth layer is completed before another nucleus forms, and the growth rate is given by:

\[
G = b_0 L S_T/a N_A \tag{30}
\]

where \( L \) is the lamellar width, \( b_0 \) is the thickness of the growth layer, and \( S_T \) is the total flux of crystallizable segments to the growth front. Since the term
$S_T/aN_A$ is equal to the secondary nucleation rate, $G = b_0LN$. The growth rate is given by:

$$G = G_0\exp[-U^*/R(T_x - T_\infty)]\exp(-4b_0\sigma_u\sigma_e/\Delta f_k BT_x)$$

where: $G_0 = b_0(k_B T_x/h)n_sJ_1(P/\zeta_u)\exp(2ab_0\sigma_e\phi/k_BT_x)$,

$$J_1 = \exp(-\Delta G^\dagger/RT_x),$$

and,

$$P = \left(\frac{k_BT_x}{2b_0\sigma_u - ab_0\Delta f} - \frac{k_BT_x}{2b_0\sigma_u + (1 - \phi)ab_0\Delta f}\right)$$

where $n_s$ is the number of sites or step elements corresponding to the substrate, $\Delta G^\dagger$ includes any free energy barriers not included in $U^*$ (such as orientation and "parking" effects that occur as segments migrate to the crystallization site), $\phi$ deals with the relative rates of the forward and backward reactions discussed earlier, $\zeta_u$ is the length of a repeat unit, $T_\infty$ is the temperature at which all molecular motion ceases ($T_\infty = T_g - 30$), and the other terms are as described previously[14].

In regime II, nuclei form in large numbers at a rate $\dot{N}$, and spread slowly at a velocity $g$. The growth rate is described as:

$$G = b_0(\dot{N}g)^{1/2} = \zeta(S_T g/aN_A)^{1/2}$$

This gives:

$$G = G_0\exp[-U^*/R(T_x - T_\infty)]\exp(-2b_0\sigma_u\sigma_e/\Delta f_k BT_x)$$

where: $G_0 = b_0(k_BT_x/h)J(1/PQ/\zeta_u)^{1/2}\exp(ab_0\sigma_e(2\phi - 1)/k_BT_x)$,

and $Q = \exp(ab_0\phi\Delta f\zeta/k_BT_x) - \exp[-ab_0(1 - \phi)\Delta f\zeta/k_BT_x]$

where all terms are as defined previously. The terms $P/\zeta_u$ and $Q$ are approximately unity[14].

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A third growth regime, regime III, has also been identified. Here the nucleation rate is much greater than the growth rate[11].

The lamellae grow at this rate and eventually begin to branch noncrystallographically. That is, the angles of branching aren't directly related to the geometry of the crystal lattice, and the crystallographic orientation of the parent lamella isn't carried onto the daughter lamella. This branching mechanism leads to a space filling spherulitic structure[17]. This branching mechanism is not well understood at the present time.

As the polymer crystal grows, lamellar thickening behind the growth front takes place. This is believed to reduce the amount of disorder on the lamellar fold surface as will be discussed later on in this section, and it allows a more thermodynamically stable crystal to form. Thus far, only an empirical relationship has been developed relating the actual lamellar thickness to that of the initial strip:

\[ \zeta = \gamma \zeta^* = \frac{2\sigma_0 T_m^0}{\Delta h(T_m^0 - T_x)} \]

where \( \gamma \) is the thickening coefficient, and \( \zeta^* \) is the thickness of the initial strip. If this is substituted into:

\[ T_m = T_m^0(1 - 2\sigma_0/\Delta h\zeta) \]

the following expression is obtained:

\[ T_m = T_m^0\left(1 - \frac{1}{\gamma}\right) + T_x\left(\frac{1}{\gamma}\right) \]

Such an expression can be utilized to find the equilibrium melting point[12].

The stress brought on by the overcrowded fold surface, however, is not relieved quickly enough by the lamellar thickening process which is slow in
comparison to the crystal growth. This stress has been utilized to explain the lamellar twisting observed in electron microscopy and in the concentric banding observed in polarized optical microscope micrographs. The disordered surface (see figure 3b) results from nonregular chain folding, such as loops formed during adjacent chain folding, nonadjacent chain folding which may incorporate large loops, and tie molecules (a polymer chain which is incorporated in two adjacent lamella), as well as from noncrystallizable portions of the chain (atactic portions, branches, etc.) that are rejected from the lattice, and chain ends rejected from the lamella during the crystallization process[18]. The incidence of nonregular chain folding increases at higher undercoolings, where the crystallization rates increase[10].

It is believed that the fold surfaces are not equally disordered. This leads to a difference in the longitudinal (along the length of the fold surface) and transverse (normal to the fold surface) surface stresses. S-bending as well as superimposed twisting (helicoidal twisting) near the free ends (Figures 4a and b) result from these longitudinal and transverse bending moments acting simultaneously[18].

The surface stresses can be relieved by lamellar thickening which follows the growth front. In the lamellar thickening process, the chain segments move in a direction normal to the fold surface, which allows for readjustment of the folds, and relaxation as well as equalization of the surface stresses. As a result of this process, the lamellar core will begin to relax and the lamella will begin to flatten out[18].

In spite of these relaxation processes, the twisting will still be preserved. Keith and Padden propose this is due to a locking mechanism that occurs
Figure 3. Schematic diagram of (a) the lamellar crystallite with regularly folded chains and (b) the switchboard model.
Figure 4. Schematic diagrams of (a) S-bending and (b) helicoidal twisting[18].
during the growth process. Since the lamella is surrounded by other lamellae in a close vicinity and each undergo helicoidal twisting, at some point during the growth, the lamellae impinge and lock. This locking mechanism preserves the observed twisting and forces the lamellae to continue to grow in a coordinated manner. After the point of impingement, growth continues, and as before, surface disorder, S-bends, helicoidal twisting, and impingements are observed until the spherulite impinges upon a neighboring spherulite, or the melt is depleted of the crystallizable material[18].

This theory based on the coordination of the lamellae in the crystal has recently been challenged by the observations of Briber and Khoury. In their poly(ethyl acrylate)/poly(vinylidene fluoride) (PEA/PVDF) blends of low PVDF content, no such coordination is observed. After the PEA is removed by the addition of solvent, PVDF spherulites are observed in which the lamellae are clearly separated, and exhibit a fanlike splaying. The former observation indicates such locking and subsequent coordination would be impossible. Optical micrographs reveal the same periodic ring spacing reported by other researchers and it coordinates with the branching observed in electron micrographs. It is uncertain whether their observations indicate a general phenomenon since it has only been observed in this blend[19].

The following section will discuss how the crystallization of the polymer is influenced by the presence of a second component as in the case of a miscible system where there is mixing on the molecular level.
2.4 Experimental Proof of Miscibility

As mentioned previously, it is not always possible to predict whether or not a given polymer pair will be miscible. Thus, it is necessary to prepare the blend, and to determine the miscibility by investigating the possible composition dependence of key physical properties. Researchers commonly study the glass transition as well as the melting and crystallization behavior in the case of blends containing one or more semicrystalline polymers to determine whether or not a blend is miscible.

A single, composition dependent glass transition temperature is indicative of a miscible blend[4]. The glass transition temperature is the temperature below which the motions in the amorphous liquid are frozen, giving rise to the formation of a glassy amorphous solid. This transition is also defined as the onset of cooperative movement of several repeat units of a segment along the polymer chain[3]. In order to observe a single glass transition in a polymer blend, it is necessary for the environment surrounding these segments to be homogeneous. It is believed that the segment size responsible for the glass transition observed by differential scanning calorimetry is approximately 150 Å[20].

Several theories have been developed which relate the glass transition temperature to blend composition. The Fox relationship states:

\[
1/T_{g,b} = w_A/T_{g,A} + w_B/T_{g,B}
\]

where \( w_A \) and \( w_B \) are the weight fractions and \( T_{g,A} \) and \( T_{g,B} \) are the glass transition temperatures of polymers \( A \) and \( B \) respectively. The Gordon-Taylor equation states:

\[
T_g = [w_AT_{g,A} + k(1 - w_A)T_{g,B}]/[w_A + k(1 - w_A)]
\]
where \( k = (\alpha_{IB} - \alpha_{gB})/(\alpha_{IA} - \alpha_{gA}) \)

where \( \alpha_{li} \) and \( \alpha_{gi} \) are the coefficients of thermal expansion of the rubbery and glassy states of the component polymer \( i \)[4]. Other commonly used relationships are the Kelley-Bueche and Gibbs-Dimarzio expressions[5]. Most polymer blends only roughly fit these types of expressions.

If, however, two distinct glass transition temperatures are observed, either partial or complete phase separation has occurred, and the position and appearance of the glass transition temperature(s) can determine which. In the case where the glass transition temperatures of the two polymers have not been affected by blending, no molecular mixing has occurred[5]. In the case where partial phase separation has occurred, phases containing different concentrations of each polymer result, and two \( T_g \)'s are observed. Each \( T_g \) is shifted from that of the homopolymer. In this case, the types of analysis mentioned above can be used to estimate the composition of each phase and to determine the extent of mixing[4]. If upon blending the two polymers some mixing has taken place (interfacial mixing), the single glass transition temperature would be broader than that observed for a one phase system[4].

In the case of a blend containing at least one semicrystalline component, the equilibrium melting point of one component both as a homopolymer and in the blend can be determined to conclude whether or not there is an equilibrium melting point depression. As mentioned previously, at the equilibrium melting temperature, a perfect crystal melts and crystallizes simultaneously. The following equation, discussed previously, is utilized to find the equilibrium melting temperature:
\[ T_m = T_m^0 \left( 1 - \frac{1}{\gamma} \right) + T_x \left( \frac{1}{\gamma} \right) \]

To obtain the equilibrium melting temperature of a given crystalline form of polymer A, the melting temperature of the polymer, \( T_m \), crystallized at a given crystallization temperature, \( T_x \), is plotted against \( T_x \) (Hoffman-Weeks plot). The line is extrapolated back to the point where \( T_m \) equals \( T_x \) which is the equilibrium melting temperature. In a miscible blend the melting point will be depressed from that of the pure polymer. This melting point depression results from thermodynamic factors[21].

The chemical potential of component A in a blend will be less than that of pure component A (Raoult's law)[7]. If it is assumed that the second component doesn't enter the crystals of component A, then only the chemical potential of the liquid phase is altered upon blending[10]. The chemical potential of component A can be plotted against temperature, and the temperature at which the chemical potential of the crystalline phase of component A is equal to that of the liquid or amorphous phase is the equilibrium melting temperature[7]. Figure 5 demonstrates this temperature will decrease upon blending.

The thermodynamic expression describing the melting point depression can be derived from the Flory-Huggins equation where the chemical potential per repeating unit of polymer i (\( \mu_{i\text{u}} \)) is equal to \( (\partial G_{\text{mix}}/\partial n_{i\text{u}})_{p,T,n_i+1,...} \)[3]. This leads to the following expression describing the change in the liquid polymer's chemical potential upon blending:

\[ \mu_{\text{Au}}^1 - \mu_{\text{Au}}^0 = \frac{RTV_{\text{Au}}}{V_{\text{Bu}}} \left[ \ln \frac{V_A}{m_A} + \left( \frac{1}{m_A} - \frac{1}{m_B} \right) x \right] \]

\[ (1 - V_A) + \chi (1 - V_A)^2 \]
Figure 5. Schematic diagram of the change in chemical potential upon blending.
where \( V_{iu} \) is the molar volume per repeating unit of polymer \( i \), \( m_i \) is the degree of polymerization of polymer \( i \), \( V_i \) is the volume fraction of polymer \( i \), and all other terms are as described previously[22].

The difference between the chemical potential of the crystalline and liquid form of polymer \( A \) is:

\[
\mu_{Au}^C - \mu_{Au}^O = -(\Delta h_A - T_m \Delta s_A)
\]

where \( \Delta h_A \) and \( \Delta s_A \) are the enthalpy and entropy of fusion per repeating unit of polymer \( A \). The term \( \Delta h_A/\Delta s_A \) is assumed to be temperature independent and equal to the equilibrium melting temperature, \( T_m^\circ \). Since at the equilibrium melting temperature, \( \Delta s_A = \Delta h_A/T_m^\circ \):

\[
\mu_{Au}^C - \mu_{Au}^O = -\Delta h_A(1 - (T_m/T_m^\circ))
\]

At the melting point of the mixture, the chemical potential of polymer \( A \) in its crystalline and liquid states is equal, and as a result:

\[
\frac{1}{T_m} - \frac{1}{T_m^\circ} = -\frac{RV_{Au}}{\Delta h_A V_{Bu}} \left[ \ln V_A - \left( \frac{1}{m_A} - \frac{1}{m_B} \right) \chi \right] (1 - V_A) + \chi(1 - V_A)^2
\]

In the case of a polymer blend where the molecular weights of polymers \( A \) and \( B \) are large, the first and second terms in the brackets vanish. The resulting equation is[22]:

\[
\frac{1}{T_m} - \frac{1}{T_m^\circ} = -\frac{RV_{Au}}{\Delta h_A V_{Bu}} \chi(1 - V_A)^2
\]

In a miscible blend, where the \( \chi \) parameter is negative, this theory predicts the equilibrium melting temperature of a polymer crystallized from the...
blend will be depressed from the equilibrium melting temperature of the polymer crystallized from the pure liquid. The magnitude of this depression will depend on the $\chi$ parameter as well as the volume fraction of the second component.

Another way to test the miscibility of the blend is through growth rate analysis. The equation below describes the radial growth rate:

$$ G = G_0 \exp(-U^*/R(T_x - T_\infty)) \exp(-K_g/(T_x \Delta T f(T_x))) $$

where $f(T_x) = 2T_m^\circ/(T_m^\circ + T_x)$ and $K_g = n b_0 (\sigma u \sigma_e) T_m^\circ/(\Delta h_l) k_B$

where $n$ is a constant dependent on the growth regime, and $f(T_x)$ is a correction factor accounting for the temperature dependence of the heat of fusion[23].

$G_0$, the growth rate constant, will be affected by blending, since this term includes the dilution effect. The dilution effect is the increase in the difficulty of extracting crystallizable segments from the melt as the weight fraction of the crystallizable blend component decreases with the addition of the second component.

The activation energy for diffusion term, the first exponential term in the equation, is affected by the blending process since it is dependent on $U^*$ and the $T_g$. $U^*$ is expected to vary with composition since the transport properties of the two polymers are generally not equivalent at the crystallization temperature. The activation energy for transport would expect to increase with the $T_g$ and lead to an overall decrease in the radial growth rate[24]. The $T_g$ is composition dependent, as discussed earlier.

Finally, the second exponential term, the activation energy for secondary nucleation term, is affected by the blending process due to its dependence on
$K_g$ and on $T_m$. $K_g$ will be affected by an equilibrium melting point depression and the composition dependence of the product $\alpha_u \sigma_e$ if the blend is miscible[23]. The term $\alpha_u$ is related to the entropy difference between the amorphous melt and the crystal. Since this term is related to the entropy change in the melt which occurs after the introduction of a second component, it is expected to be composition dependent. Similarly, the fold surface free energy may be expected to be slightly dependent on the blend composition.

2.5 Poly(vinylidene fluoride)

2.5.1 Introduction

Now that the theoretical basis behind miscibility and crystallization has been explained, the two polymers, which will be the subject of this project, and their blend history will be discussed beginning with poly(vinylidene fluoride) (PVDF).

PVDF has been particularly of interest over the past few decades due to its excellent chemical and physical properties, its polymorphism, its electrical activity, and its ability to form homogeneous mixtures in the amorphous state with noncrystalline polymers over a wide range of compositions.

PVDF is polymerized by emulsion or suspension polymerization of vinylidene fluoride utilizing peroxide initiators[25, 26], and it has the following structure:

$$\left(-\text{CF}_2\text{CH}_2\right)_n$$

PVDF is a ferroelectric polymer with an equilibrium melting point of 175-185°C [27, 28, 29], high chemical resistance[30], good thermooxidative stability[30], a
T\textsubscript{g} of -35°C as determined by Hsu and Geil on unquenched films [31], excellent mechanical properties (i.e., high tensile strength and compressive strength, good Izod impact, and superior abrasion resistance)[30], high crystallinity (50 to 65%)[32], and electrical activity[33].

2.5.2 Poly(vinylidene fluoride)’s Morphology

PVDF has sparked a great deal of interest in academic circles as a result of its polymorphism. This comes as a result of many factors. First, it doesn’t have any bulky substituents which would keep it from crystallizing. Second, because of the similarity in the size of the van der Waals radii of its fluorine and hydrogen atoms, PVDF can adopt three different conformations which have similar potential energy--trans (T), gauche (G), and gauche’ (G’). However, unlike polyethylene in which the rotational barriers are so low that the chain can easily form the lowest energy, all trans conformation, PVDF’s rotational barriers between the three conformations are high enough for it to adopt chain conformations which will minimize electrostatic and steric interactions. Third, because PVDF lacks an asymmetric carbon, it does not have different tacticities[34].

As a result of these various factors, PVDF has five reported polymorphs: \(\alpha\), \(\beta\), \(\gamma\), \(\delta\), and \(\varepsilon\). The \(\alpha\) phase chain conformation is TGTG’ with a monoclinic unit cell[35] in which two chains pack in a statistical arrangement of up and down chains such that their dipoles cancel which gives rise to a nonpolar crystalline phase[36]. The \(\alpha\) phase is formed at atmospheric pressure[37] at high to intermediate undercoolings[38] (see figure 6a).
Figure 6. Unit cells of (a) the \( \alpha \) phase, (b) the \( \beta \) phase, and (c) the \( \delta \) phase of PVDF shown in a projection parallel to the chain axes[34]. The arrows indicate the direction of the dipole moments.
The β phase is the most polar of the different crystalline modifications of PVDF[33], and the least thermodynamically stable[39]. It consists of chains of a slightly distorted TTTT conformation[40-43] in an orthorhombic cell (see figure 6b)[37]. Its low thermodynamic stability is due to the highly unfavorable steric and electrostatic interactions which result from the close proximity of the fluorine atoms in the all trans conformation[34].

The β phase is formed in four ways. First, it is formed by poling films under high electric fields[33]. Second, the extended all trans conformation characteristic of β-PVDF is easily formed by mechanically deforming other phases of PVDF to give elongated uniaxially oriented chains[37, 43]. This must be done at fairly low temperatures. Under deformation at high temperatures, molecular chains simply slide past one another while retaining their original conformation[34], but at low temperatures, the stiff chains are forced into their all trans conformation[34]. Third, the β phase is formed from the melt under high pressure conditions[44]. Finally, it is formed by the efficient quenching of thin films of PVDF[31]. The cause of this latter phenomena is unknown.

The δ phase is a polar form of the α phase and is obtained by poling the α phase under intermediate electric fields[31]. This results in the reversal of the dipole moments of the α phase. Most likely, intramolecular rotations alter the TGTG' conformation to TG'TG (see figure 6c)[45].

The polar γ phase consists of chains in a T3GT3G' conformation[46, 47] in a monoclinic unit cell (see figure 7a)[48]. Its unit cell has the same base dimensions as that of the α phase. This facilitates the formation of the γ phase from transformation of the α phase by annealing at high pressures[43], initiated
Figure 7. Unit cells of the PVDF (a) $\gamma$ phase[44], and (b) $\varepsilon$ phase [36] shown in a projection parallel to the chain axes. The arrows indicate the direction of the dipole moments.
by adjoining \( \gamma \) spherulites\[36, 49\], beginning at the \( \alpha \) nucleus at very high temperatures \[36, 49\], and an accelerated transformation of \( \alpha \) as it is heated through its melting point in the presence of a surfactant\[38\]. These are all accomplished by means of intramolecular motions\[49\]. The \( \gamma \) phase is also formed by crystallization from the melt at high temperatures and pressures \[42, 50\], from a transformation of \( \delta \) to \( \gamma \) at high temperatures\[36\], from crystallization from dimethyl sulfoxide, dimethylacetamide, and dimethylformamide solutions\[51, 54\], and from an accelerated transformation from \( \beta \) to \( \gamma \) as the \( \beta \) phase is heated through its melting point in the presence of a surfactant\[38\].

The \( \varepsilon \) phase (see figure 7b), an antipolar form of \( \gamma \), is formed by the transformation of \( \delta \) to \( \gamma \) and then to \( \varepsilon \) at high annealing temperatures\[36\].

2.5.3 Poly(vinylidene fluoride)'s Relaxation Behavior

These different crystalline phases as well as the amorphous phase respond in dielectric and dynamic mechanical testing. This leads to several different relaxations: \( \alpha_c \), \( \alpha_a \), \( \gamma \), and \( \beta' \)[55]. The \( \alpha_c \) transition is due to molecular motion in the crystalline region and is affected by lamellar thickness, sample morphology, as well as defects in the crystalline phase (i.e., head-to-head defects included in the crystalline phase)[56-59]. The \( \alpha_a \) transition is attributed to the micro-Brownian motion of the amorphous main chains[56, 57]. The \( \gamma \) relaxation is related to local oscillations of the amorphous phase below the \( T_g \)[56, 57]. The \( \beta' \) relaxation is related to fold motions in the amorphous regions[58, 60, 61]. The \( \alpha_c \) transition occurs at the highest temperature followed by the \( \beta' \), \( \alpha_a \), and \( \gamma \)[56, 57, 60].
2.5.4 Poly(vinylidene fluoride)'s Electrical Activity

Due to PVDF's electrical activity, there has been a great deal of interest in PVDF in the electronics industry[33]. The polymer is electrically active for several reasons. First, as stated earlier, it doesn't have "tacticity." Second, it has a lower degree of head-to-head addition than other fluorine containing polymers (eg. poly(vinyl fluoride) and poly(trifluoroethylene))[62, 63]. Such defects result in reduced net dipole moment. In addition, as discussed above, PVDF is capable in crystallizing in the $\beta$, $\gamma$, and $\delta$ forms all of which have a permanent net dipole moment.

These qualities make PVDF a piezoelectric, pyroelectric and ferroelectric material[64, 65]. The first two result from the fact PVDF's $\beta$, $\gamma$, and $\delta$ phases do not contain a center of symmetry. Therefore, these phases are capable of developing polarization when under stress and give rise to a piezoelectric material[34]. Because PVDF has permanent net dipole moments in these phases, it is also pyroelectric[34, 64, 65]. Pyroelectric polymers will develop polarization with changes in temperature.

PVDF is ferroelectric because it has a unique polar axis in the $\beta$ and $\delta$ crystalline phases and the direction of this axis can be reoriented in an electric field[34]. This reversibility in the $\beta$ phase is believed to be a result of the pseudohexagonal nature of its lattice combined with the fact that PVDF contains no bulky groups in the main chain or as pendant groups[66, 67]. The resulting high chain flexibility would allow the dipoles to reorient themselves more easily under an electric field. The $\delta$ phase doesn't have a pseudohexagonal lattice, and its ferroelectric nature may result from the same chain flexibility[45, 68].
However, these polar crystals are randomly dispersed in an amorphous melt. Therefore, in order to impart a strong piezo- and pyroelectric response to the film, it is necessary to first stretch the film to orient the crystals then to pole the film to orient the dipoles. One method of poling the film is to subject an electroded film to a high electric field, and a nearly permanent polarization is achieved. A second method is to subject the film, which has been either electroded on one side or not at all, to a corona discharge. This produces polarization in a much shorter period of time than poling[33].

2.5.5 Blends with Poly(vinylidene fluoride)

PVDF blends studied have exhibited some very unique properties. Because of the high fluorine content in PVDF, it is capable of strongly interacting with other polymers in such a way that the heat of mixing is negative.

Many PVDF blends studied in the past six years exhibit an interphase between the crystal and amorphous regions which has different dielectric and mechanical relaxations. These blends have a transition in the neighborhood of -40°C and this transition temperature does not vary with composition[69-72]. This has been seen in blends with poly(vinyl pyrrolidone)[69, 70], and poly(methyl methacrylate) (PMMA)[71, 72].

Flory and other researchers have shown that this transition is produced by an interphase between the crystalline and amorphous regions. The flux of chains from the crystal face is large and must be diminished in order for the chains to attain the conformational disorder characteristic of the amorphous region. Therefore, some chains will reenter the crystal face at adjacent or
nonadjacent points, and a region of partial order results. This is called the interphase[73, 74].

Hahn has expanded on this theory to account for the observations in the case of blends[71, 72]. It is believed that the partner polymer in the blend will be rejected from the interphase to better reduce the chain flux. This would account for the similarity in the interphase and the crystalline homopolymer. Furthermore, the width of the interphase is related to the percentage of chain defects in PVDF. These defects affect the ability of the chains to reenter the crystalline phase and consequently increase the width of the interphase. Hahn, et. al. believe the origin of the large dielectric constant in PVDF must be associated solely with the lamellar crystalline features (the crystal as well as the interphase) and not the amorphous phase as previously thought. The interphase would explain the fast reorienting component of PVDF observed under high electric fields[72].

As previously mentioned, the other unique feature of PVDF blends is the splaying of PVDF lamellae. This has been observed in PVDF blends with poly(ethyl acrylate) at low PVDF blend content[19]. These results and their implications have been discussed in section 2.3.2.

Finally, PVDF is unusual in that it is capable of forming miscible blends with many chemically dissimilar polymers. This has been attributed to its high fluorine content which enables it to engage in dipole-dipole as well as in hydrogen bonding interactions. PVDF forms miscible blends with many oxygen containing polymers[75-78]. Several groups have confirmed poly(methyl methacrylate) (PMMA)[17, 71, 72, 79-90], poly(ethyl methacrylate) (PEMA)[91], poly(ethyl acrylate) (PEA)[19, 75], poly(vinyl acetate) (PVAc)[76, 92] and
poly(methyl acrylate) (PMA)[75] are miscible with PVDF. The cause of miscibility was narrowed down to an interaction between PVDF and the carbonyl groups on the partner polymer after the researchers discovered poly(vinyl methyl ether) is not miscible with PVDF, but poly(vinyl methyl ketone) is[77, 78]. It was also discovered that the degree of this interaction is weakened as the length of the hydrocarbon chain between the carbonyl groups increases[75]. As a result, blends of poly(ethyl acrylate) and poly(methyl acrylate) are miscible with PVDF but poly(isopropyl acrylate) is not[75].

Later, results from FTIR[92] and NMR[93] studies led to the conclusion that miscibility resulted from a hydrogen bonding interaction between the electropositive hydrogens on PVDF and the electronegative carbonyl group on the partner polymer.

Because of the ester functionality on poly(3-hydroxybutyrate) (PHB) and of its short hydrocarbon segment, the possibility of miscibility between it and PVDF was explored.

### 2.6 Poly(3-hydroxybutyrate)

#### 2.6.1 Introduction

Poly(3-hydroxybutyrate) (PHB)

\[
\begin{align*}
\text{CH}_3 & \quad \text{O} \\
\text{(C-CH}_2\text{C-O)}_n & \quad \text{H}
\end{align*}
\]

is synthesized by a variety of bacteria by the condensation of D-(-)-β-hydroxybutyl coenzyme A[94]. It is then stored in a membrane containing
polymerase and depolymerase enzymes[95] and here it functions as a source of energy and as a carbon supply[96].

Normally PHB constitutes only 10% by weight of the cells. Nevertheless, it is possible for PHB to be accumulated at a much higher rate and ICI has patented such a process. ICI forced the cells to accumulate PHB at a higher rate by limiting one of the nutrients vital to cell growth but not necessary for PHB accumulation. In addition, to make the production of PHB economically feasible, a mutant strain of Alcaligenes eutrophus was developed which processes glucose instead of pure carbon dioxide and hydrogen. This new process allows for 50-60% accumulation of PHB[97].

PHB is a piezoelectric polymer[98, 99] with 60-90% crystallinity[100], optical activity[101], a reported glass transition temperature in the range of -5 to 5°C[100], a higher tensile strength than isotactic poly(propylene)[102, 103], biodegradability[102], but poor mechanical properties due to its brittle nature caused by radial and circumferential cracking of the spherulites under applied stress[104].

2.6.2 Poly(3-hydroxybutyrate)'s Morphology

PHB is polymorphic and exists in the α and β crystalline forms. The α form is orthorhombic with a 2₁ helix in which trans ester groups are piled up and the carbonyl groups are nearly perpendicular to the chain axes and point out from them[105]. In this orthorhombic unit cell, there are two antiparallel chains[106] and the ester groups of each chain are nearly at the same level with a 60° angle between the dipoles to minimize dipole-dipole interactions (see figure 8)[105].
Figure 8. Unit cell of the $\alpha$ phase of PHB viewed along the helix axis[105].
The β phase (see figure 9) is formed upon film orientation. It is believed that the formation of the β phase is a strain induced crystallization of the amorphous regions. The unit cell is characterized by a 4.60Å rise per residual which must result from a nearly planar zigzag structure. On account of unfavorable van der Waals interactions, the methyl groups must twist away from each other, and the resulting net dipole moment is different from that of the α form[107].

2.6.3 Blends with Poly(3-hydroxybutyrate)

PHB has formed miscible blends with poly(ethylene oxide) (PEO). Both polymers are semicrystalline, and the researchers avoided the complexities of a blend consisting of two crystalline phases and a coexisting amorphous phase by crystallizing PHB above the equilibrium melting point of PEO. They observe an equilibrium melting point depression as well as a decrease in the growth rate as the weight fraction of PEO increases. In addition, while pure PHB crystallizes in regime III, it crystallizes in regime II in the blend. The authors conclude the miscibility is a result of an interaction between the carbonyl group in PHB and the ethylene hydrogens in PEO[108].

2.7 Poly(vinylidene fluoride)/Poly(3-hydroxybutyrate) Blends

A blend of PVDF with PHB would be interesting to study from both a practical and a fundamental standpoint. From a practical standpoint, such a
Figure 9. Chain conformation of the $\beta$ phase of PHB (a) perpendicular to the chain axis and (b) down the chain axis[107].
blend would improve PHB’s chemical and radiation resistance, mechanical properties, and processability in the melt state. In addition, it might improve the piezoelectric properties of PVDF based materials. From a fundamental standpoint, the blend might prove interesting to study, since very little is known about the crystallization process and morphologies of blends of two semicrystalline polymers.

2.8 Blends of Two Semicrystalline Polymers

If a blend of PVDF and PHB was truly miscible, it would be one of the few blends of two semicrystalline polymers studied. The only known miscible blends of two semicrystalline polymers are that of poly(ethylene terephthalate)/poly(butylene terephthalate) (PET/PBT)[109, 110], poly(caprolactone)/poly(vinylidene chloride-vinyl chloride) (PCL/P(VCl₂-VC)), PCL/poly(vinylidene chloride-vinyl acetate) (PCL/P(VCl₂-VA)), PCL/poly(vinylidene chloride-acrylonitrile) (PCL/P(VCl₂-AN)[111, 112], poly(aryl-ether-ether-ketone)/poly(aryl-ether-ketone) (PEEK/PEK), poly(aryl-ether-ketone-ketone)/PEK (PEKK/PEK)[113], and PHB/PEO[108].

Studies of PET/PBT blends have been performed by Escala and Stein. Miscibility was determined by Fourier Transform Infrared Spectroscopy (FTIR) as well as Differential Scanning Calorimetry (DSC) studies. A single, composition dependent Tg was observed for all blend compositions. The crystallization rate of PET and PBT were determined by FTIR and depolarized light intensity (DPI) and density studies. These techniques revealed the
crystallization rate of each component is affected by the overall blend Tg. Morphological studies by polarized optical microscopy indicated two crystalline populations and two overlapping crystallization exotherms were observed in DSC. Therefore, the authors concluded the blend is miscible and both components crystallize in the same matrix. No cocrystallization occurs. One of the problems of this study is that transesterification is unavoidable and copolymers result[109, 110].

A later study by Zhang and Prud'homme employed the now commonly accepted Hoffman-Weeks extrapolation method which is used to determine the miscibility of a system of one or more semicrystalline polymers. In particular, they studied blends of PCL/P(VCl2-VC), and PCL/P(VCl2-VA) which they had already shown to be miscible. They found such a system allowed the determination of the \( \chi \) parameter (a measure of the level of specific interactions) over a full range of compositions. In addition, for the first time, the self consistency of the Hoffman-Weeks analysis for the determination of the \( \chi \) parameter was tested[111, 112].

Zhang and Prud'homme were aware of a possible limitation of the Hoffman-Weeks analysis in this case. The theory assumes an equilibrium state in the melt surrounding the crystal growth front. The crystallization of the second component would create a nonequilibrium situation and the precise nature of the melt's composition would be unknown. Zhang and Prud'homme avoided this problem by crystallizing the blend in such a manner that only one component would crystallize. The \( \chi \) parameter was calculated for all blend compositions using the Hoffman-Weeks equation. This analysis revealed it was composition dependent, and the plot of the \( \chi \) parameter versus composition
was continuous. Thus the Hoffman-Weeks analysis appeared to be consistent. However, the authors predicted an equilibrium situation in the case where both components crystallized would result in a eutectic melting point. This was not observed[111].

In Avella and Martuscelli’s study of PHB/PEO blends, the problem of a nonequilibrium situation arising from two crystalline populations was also avoided. The results of the work have been discussed in section 2.6.4. Like Zhang and Prud’homme, they observed a composition dependent $\chi[110]$. 
Chapter 3. Experimental Methods

3.1 Introduction

As described in the previous chapters of this thesis, the main objective was to gain a fundamental experimental understanding of the blending of poly(vinylidene fluoride) (PVDF) and poly(3-hydroxybutyrate) (PHB), to prove the blends' miscibility, and to characterize the polymers' properties in the blend matrix to determine how they vary as a function of blend composition, blending technique, and temperature. The experimental details of the characterization and preparation of melt and solution blends of (PVDF/PHB) will be discussed in the following sections.

3.2 Materials

Emulsion polymerized PVDF (commercial grade KYNAR 710 with a $M_w$ of 140,000 g/mole and $M_n$ of 45,000 g/mole and 5 weight percent head-to-head defects), was generously donated by ATOCHEM North America Corporation
and was ground to a fine powder and used without further purification. A fine powder of PHB (commercial grade BX-G04), synthesized by the continuous fermentation of glucose utilizing a mutant strain of *Alcaligenes eutrophus*, was generously donated by Marlborough Biopolymers (England).

### 3.3 Blend Preparation

PHB undergoes chain scission by an ester hydrolysis mechanism due to the high thermal and shear stresses experienced during melt blending[1]. Therefore, both melt and solution blending techniques were used to study the effect the molecular weight of PHB had on the blends' miscibility, morphology, and degradation.

#### 3.3.1 Melt Blending

Melt blends were prepared in a Haake Inc. Rheomix Model 600 Melt Blender attached to a Digital Pyrometer. The blending was performed by mixing approximately 50 grams of material at a rate of 50 rpm for 5 minutes at 180°C. The hot polymer blend was scraped from the blender and quenched in air.

#### 3.3.2 Solution Blending

Solution blends were prepared at a concentration of 2.5 to 10% (w/v) in N,N-dimethylformamide (DMF) at 120°C under nitrogen flow for 20 minutes with agitation followed by 30 minutes without agitation. The clear solution was pipetted into an ice water bath. The blend precipitated out and was washed with
3000 mls of distilled water to remove any residual DMF, allowed to air dry overnight, and then dried in a vacuum oven at 40°C for 12 hours.

To prepare samples to measure the growth rates of the α phase of PVDF by light microscopy studies, it was necessary to use filtered water instead of distilled water to minimize the amount of impurities introduced into the system. In addition, before the blend was pipetted into the filtered water, the hot solution was filtered twice through a gas tight syringe with a coarse filter tip. This procedure produced blends with fewer cell walls from the PHB and less impurities from the PVDF and an overall lower nucleation density.

3.4 Film Preparation

In order to perform thermal analysis, optical microscopy, and spectroscopic studies on the blends, it was necessary to prepare thin films of the blends. Therefore, compression molding (0.1 mm), and solvent casting (0.05 mm) techniques were developed.

3.4.1 Compression Molding

A Carver Hydraulic press was preheated to 175°C. Two one quarter inch thick steel plates were covered with Reynolds wrap heavy duty aluminum foil. Kimwipes soaked with isopropanol were then used to yield a clean, wrinkle free, smooth surface. After the solvent evaporated, approximately 0.25-1 g of the blend was placed between the two plates, and the assembly was inserted between the preheated press plattens. The bottom platten was raised several times, each time incrementally increasing the pressure to allow for the formation
of bubble free film. Thirty seconds after the maximum load was reached, the lower platen was quickly dropped and the assembly was cooled in air. The total time in the press was less than one minute. Such short times were necessary to prevent substantial degradation of the PHB.

3.4.2 Solution Casting

For FT-IR experiments, it was necessary to develop a procedure to drive off the DMF while preventing bubbles from forming in the film, and furthermore to remove residual cell walls from the PHB. Hence, a 1.5 w/v% blend was made using the procedure for light microscopy studies (see section 3.2.2), except while still hot, two to three drops of the twice-filtered solution was pipetted onto KBr disks and placed in a vacuum oven (10 in Hg) for twelve hours at 40 to 50°C. The KBr plates were then placed in a second vacuum oven (10 in Hg) at 100°C and dried for an additional 2 hours.

3.5 PHB Characterization

Nuclear Magnetic Resonance (NMR) Spectroscopy and intrinsic viscosity studies were performed in order to characterize the chemical changes that PHB had undergone during solution and melt blending, and to determine the extent of degradation.

3.5.1 Nuclear Magnetic Resonance

$^1$H and proton decoupled $^{13}$C Nuclear Magnetic Resonance (NMR) Spectroscopy were performed on as-received PHB and PHB subjected to the
same conditions as the melt and solution blended samples. The polymers were dissolved in CDCl₃ along with a few drops of trifluoroacetic acid (TFA). Tetramethylsilane (TMS) was utilized as a reference. ¹H NMR required a less concentrated solution (2%) than ¹³C NMR (5%). Spectra were taken with a Bruker WP 200 spectrometer.

3.5.2 Intrinsic Viscosity Studies

Intrinsic viscosity studies were performed on as-received PHB and PHB subjected to the same conditions as the melt and solution blended samples. Measurements were obtained with a 50 bore Cannon-Ubbelohde diluting viscometer immersed in a constant temperature water bath (25°C). Three flow times each of chloroform, the stock solution (a one to two percent solution of PHB in chloroform), and three dilutions of the stock solution were measured.

The intrinsic viscosities (dl/g) were calculated by a computer program which uses both the Huggins equation and the Kraemer equation. The Huggins equation relates the intrinsic viscosity to the flow times and concentration in the following manner:

\[
\frac{1}{c}\left(\frac{t}{t_0} - 1\right) = [\eta] + k_H[\eta]^2c
\]

where \(c\) is the concentration in g/ml, \(t\) is the flow time of the polymer solution in seconds, \(t_0\) is the flow time of the solvent, \(k_H\) is the Huggins constant, related to the breadth of the molecular weight distribution, and \([\eta]\) is the intrinsic viscosity. The Kraemer equation has the following form:

\[
c^{-1}\ln(\eta/\eta_0) = [\eta] - k_H[\eta]^2c
\]
where \( \eta_0 \) is the intrinsic viscosity of the solvent, and all other values are defined as before. In both cases, if the left hand term is plotted against \( c \), the intrinsic viscosity can be found from the intercept. The average of the intrinsic viscosities obtained from the two plots is taken and the viscosity average molecular weight (\( M_v \)) can be determined by the Mark-Houwink-Sakurada (MHS) equation since both the exponent \( a \) and the prefactor \( K \) are known for the polymer solvent pair[2]:

\[
[\eta] = KM_v^a
\]

\( K = 1.18 \times 10^{-4} \text{ dl/g} \) and \( a = 0.78 \) for PHB under these solvent and temperature conditions[114].

### 3.6 Blend Characterization

The melt and solution blends were characterized by Differential Scanning Calorimetry (DSC) and Polarized Optical Microscopy (POM) in order to prove the blends’ miscibility and to determine the blends’ properties. Thermogravimetric analysis (TGA) was performed to determine the effect PVDF has on PHB’s degradation.

#### 3.6.1 Differential Scanning Calorimetry

All experiments were performed on a Perkin Elmer Thermal Analysis Station 2 Differential Scanning Calorimeter (DSC) operated under a \( \text{N}_2 \) atmosphere. The furnace was heated to \( 180^\circ\text{C} \) before the samples were inserted. The melting points of indium (3.7 mg with \( T_m = 156.61^\circ\text{C} \) and \( \Delta h_f = 6.8 \text{ cal/g} \)) and lead (3.3 mg with \( T_m = 327.50^\circ\text{C} \) and \( \Delta h_f = 5.9 \text{ cal/g} \)) were used.
as standard references to periodically check the temperature calibration as well as the heat of fusion calibration[115].

3.6.1.1 Tg measurements

The DSC furnace was preheated to 180°C, and a 15-20 mg portion of the film (blend) was placed in the furnace and melted for 1 minute. The film was then quenched to -40°C at the fastest rate available on the DSC with a dry ice-isopropanol bath, and then reheated to 20°C at 10°C/minute. The Tg was recorded as the inflection point in the DSC trace.

3.6.1.2 Dynamic Cooling Experiments

An 8.0 ± 0.3 mg portion of the film was melted in the furnace for 1-2 minutes at 180°C. After thermal equilibrium had been reached, the sample was cooled at 10°C/minute to 40°C. The minima in the crystallization exotherms were recorded as $T_{\text{max}}$, the temperature at the maximum crystallization rate for each semicrystalline polymer.

3.6.1.3 Melting Study of Isothermally Crystallized Samples

A 4.0 ± 0.1 mg portion of the film of approximately 0.2 mm in thickness was melted for 1 minute at 180°C, quenched at the fastest rate available to the crystallization temperature, and allowed to crystallize to a crystallinity of 10% in the $\alpha$ phase (1.25 cal/g for 50/50 PVDF/PHB) of PVDF in the melt and solution blends. The film was heated at a rate of 10°C/min. and the maximum in the melting endotherm was recorded for the $\alpha$ phase of PVDF (which has the melting endotherm at the lowest temperature). The 70/30 PVDF/PHB melt and
solution blends and pure PVDF were allowed to crystallize either for the same period of time or the same level of crystallinity. Afterwards, they were heated as before, and the melting point of the α phase was recorded.

The melting point of the α phase of PVDF was plotted against the crystallization temperature for pure PVDF, 50/50 and 70/30 PVDF/PHB blends. From this plot, it was possible to extrapolate back to the equilibrium melting temperature in each case in order to determine if there was an equilibrium melting point depression.

3.6.2 Polarized Optical Microscopy

In the following experiments, a Zeiss Axioplan Polarized Optical Microscope operated under crossed polarizers was used in conjunction with a Linkham THM 600 hot stage operating with N₂ flow. TMX ASA 100 Kodak film was used in the Zeiss MC100 camera, with a reciprocity setting of 3.

3.6.2.1 Growth Rate Studies

The film was ramped to 190°C at the fastest rate available on the hot stage, held there for 1 minute to achieve melting of both polymers' crystals and quenched at the fastest rate to the desired crystallization temperature. Once nucleation had occurred and the spherulites had reached approximately 32 μm in diameter, photographs were taken for growth rate measurements. A micrometer scale was utilized to convert to the exact length scale. A mean growth rate at a given crystallization temperature was calculated by averaging the slopes from various radius versus time plots taken from 8 different radii of the same spherulite.
3.6.2.2 Morphology Studies

The film was brought to the crystallization temperature, as described in the previous section, and allowed to fully crystallize. Optical micrographs were taken of the fully crystallized film at that crystallization temperature.

3.6.3 Fourier Transform Infrared Spectroscopy

Fourier Transform Infrared Spectroscopy (FTIR) experiments were performed in order to determine the differences in the crystallization rates of both PVDF and PHB in the solution and melt blends. These investigations were conducted on a Nicolet 800 FTIR spectrometer at a 4 cm\(^{-1}\) resolution. A cell heated with a GC 7000 Nicolet Instrument Corporation light pipe was employed to conduct the crystallization experiments. This heat cell fit into the sample chamber.

Two clean, dry, clear KBr disks from International Crystal were inserted into the heat cell and the assembly was placed in the FTIR sample chamber. A background spectrum which contained water and carbon dioxide was taken. Later this spectrum would be used to subtract out water and carbon dioxide bands in the blends’ spectra.

In order to observe the crystallization of both PVDF and of PHB, fairly thick films were needed. Therefore, a 50/50 (w/w) PVDF/PHB blend was cast onto KBr disks from a 2.5% (w/v) solution (see section 3.4.2). Forty-eight scans were averaged over a one minute period to give a spectrum. Five spectra were taken at room temperature, and spectra were taken at one minute intervals as the cell was heated to 180°C at an average rate of 31°C/min.. Spectra were recorded at one minute intervals as the cell was cooled to 148°C at the same
rate, and once this temperature was reached approximately 180 spectra were recorded.

3.6.4 Thermogravimetric Analysis

Thermogravimetric analysis (TGA) was utilized to determine whether the presence of PVDF enhanced or inhibited the degradation of PHB. It was necessary to control the films' surface area in each case in order to quantitatively compare the isothermal degradation rates. Therefore, compression molding was employed to prepare thin films (0.315-0.325 mm thick) of as-received PHB, PHB subjected to "melt" and "solution blending" conditions, and 50/50 and 30/70 PHB/PVDF melt and solution blends. Portions of the films were cut with a cork borer.

A Perkin Elmer TGA model 7 was used in all isothermal degradation investigations. The onset of the Curie transition of nickel in a nitrogen atmosphere was used to periodically check the temperature calibration of the TGA. The samples were placed in an oxygen atmosphere and were heated at the fastest rate available to the desired temperature and held there for one hour. The percent weight loss was then monitored at that temperature.
Chapter 4. Results and Discussion

4.1 Introduction

Over the past several decades, polymeric blends have given industry the ability to create new materials with novel properties at a cost relatively low in comparison to the synthesis of a new polymer or copolymer. However, as discussed in section 2.2.1, such a blend must either be miscible, or immiscible with a suitable compatibilizer. Such a compatibilizer should prevent further phase separation in order to result in a product with good mechanical properties. A good compatibilizer is sometimes difficult to find however, and may increase the cost of producing a useful immiscible blend. Therefore, the situation is simplified if a miscible blend is accessible.

The primary goal of this project is to prove whether or not blends of poly(vinylidene fluoride)/poly(3-hydroxybutyrate) (PVDF/PHB) are miscible. In this chapter, the results of thermal, optical, and spectroscopic studies on (PVDF)/(PHB) blends will be discussed. If the blend did prove to be miscible, it would be interesting both from a practical and a fundamental standpoint. Such
a blend might improve the chemical and thermal resistance, as well as the mechanical properties of PHB and might improve some of the piezoelectric properties of PVDF based materials. In addition, if miscible, the blend would be one of the few miscible blends of two semicrystalline polymers studied.

The blends were prepared by melt and solution blending techniques. Characterization of these blends included thermal analysis by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA), growth rate and morphological studies by polarized optical microscopy (POM), and analysis of the crystallization of the two polymers in the blends by fourier transform-infrared spectroscopy (FT-IR)

4.2 Differential Scanning Calorimetry

As discussed in the literature review, there are many ways to study a blend's miscibility. One of the easiest and quickest methods of investigating miscibility is by differential scanning calorimetry. In this work, the DSC was utilized in dynamic cooling studies to examine the crystallization rate of the two blend components and in Hoffman-Weeks analysis to study the melting behavior of isothermally crystallized samples, and in the subambient mode, it was utilized to measure the blends' glass transition temperature.

4.2.1 Subambient Experiments

If a blend is miscible, it will exhibit a single composition dependent glass transition temperature (T_g). Because both PVDF and PHB have T_g's below room temperature (-35[31] and 5°C[100] respectively), it was necessary to
perform subambient experiments to observe the blends' Tg's, and thus test the blend's miscibility.

The data are listed in Table 1 and are plotted in Figure 10. The blends did show a single composition dependent Tg at all compositions. At both high and low PVDF weight fractions (greater than 70% and less than 30% PVDF), a broad Tg was observed (see Figure 11).

The broadening may be explained in two ways. First, it may result from the semicrystalline nature of the blend. This causes the Tg to be broadened by molecular motions of the cilia and loose loops on the crystal surfaces[91]. However, at intermediate blend compositions this broadening is not as pronounced. This may be due to the fact the equilibrium melting temperature of each component is depressed in this region, and crystal growth is slow. Therefore, during the quenching process, a smaller fraction of the blend will crystallize, and more pronounced, narrower Tg's will be observed.

Second, the broad Tg may result from small scale phase separation[4]. Such broadening would result from polymer-polymer phase separation creating phases smaller than 150Å[20] as discussed in section 2.4 of the literature review. At high PVDF weight fractions, it could be caused by the interphase rather than polymer-polymer incompatibility. This interphase is commonly observed in PVDF blends (see section 2.5.5) and would result in partial phase separation in the melt at high PVDF blend contents[4].

In Figure 10, the results were only compared with the predictions of the Fox equation since thermal expansion coefficients for PHB were unavailable. The poor fit is due to several assumptions inherent in the Fox equation. First, the equation is based on the idea of random mixing, and doesn't account for
Table 1. Tg Data from Melt and Solution Blended PVDF/PHB.

<table>
<thead>
<tr>
<th>Weight Fraction of PVDF</th>
<th>Tg of the Melt Blends (°C)</th>
<th>Tg of the Solution Blends (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2.4</td>
<td>5</td>
</tr>
<tr>
<td>0.3</td>
<td>-0.1</td>
<td>-1.2</td>
</tr>
<tr>
<td>0.4</td>
<td>-0.9</td>
<td>-2.9</td>
</tr>
<tr>
<td>0.5</td>
<td>-2.5</td>
<td>-3.0</td>
</tr>
<tr>
<td>0.6</td>
<td>-4.0</td>
<td>-3.8</td>
</tr>
<tr>
<td>0.7</td>
<td>-6.0</td>
<td>-7.5</td>
</tr>
<tr>
<td>0.8</td>
<td>-8.2</td>
<td>-8.4</td>
</tr>
<tr>
<td>0.9</td>
<td>-11.4</td>
<td>NA</td>
</tr>
<tr>
<td>1</td>
<td>-35[31]</td>
<td>-35[31]</td>
</tr>
</tbody>
</table>
Figure 10. Tg versus weight fraction of PVDF in melt and solution blended PVDF/PHB.
Figure 11. DSC traces of the glass transition temperatures of the (a) 10/90, (b) 40/60, (c) 50/50, (d) 60/40, (e) 70/30, and (f) 90/10 PVDF/PHB melt blends.
specific interactions[116] such as hydrogen bonding which has been observed for other PVDF blends[92, 93]. Second, PVDF crystallization during the quenching process results in a somewhat more PHB rich amorphous phase than is suggested by the overall composition. This would explain the observation of a single $T_g$ which is slightly lower than that of pure PHB. This has also been observed in other PVDF blends due to PVDF’s high level of crystallinity[91].

It is clear there is a negligible difference between the $T_g$’s of the PVDF/PHB melt and solution blends. The $T_g$ increases with the number average molecular weight according to the following equation:

$$T_g = T_g^\infty - u/M_n$$

where $T_g^\infty$ is the $T_g$ of an infinitely long polymer chain, $u$ is a constant that is composition dependent, and $M_n$ is the number average molecular weight. The $T_g$’s level off within the experimental degree of uncertainty at molecular weights above 40,000 g/mole for vinyl polymers[2]. Since the molecular weight of PHB is well above this range, and the molecular weight of PVDF is assumed to be the same in both cases, a large difference between the $T_g$’s of the melt and solution blends is not expected.

The scatter of the $T_g$’s of the solution blends is within the experimental degree of uncertainty.

4.2.2 Dynamic Cooling Studies

In addition to glass transition measurements, dynamic cooling studies were performed to check the miscibility of PVDF and PHB. At high
undercoolings, the crystallization rate of the crystallizable component in a miscible blend will decrease at a given temperature as the weight fraction of the second component with a higher T_g increases. At low undercoolings where the crystallization temperature is much greater than the glass transition temperature, the growth rate decreases as a result of the melting point depression. Finally, at all temperatures the growth rate of the PVDF α phase crystals decreases with increases in PHB blend content as a result of dilution effects.

Since the temperature range studied in these experiments fits in the latter category, it is necessary to crystallize at higher undercoolings for crystals to grow to a noticeable extent in the time scale of the experiment. This can be explained by the following equations:

\[ k = A G_i \dot{N} \]  
\[ \dot{N} = N_0 \exp \left[ \frac{U^*}{RT_x} - \frac{32\alpha^2 \sigma_0 T_m^2}{(\Delta h)^2 k_B T_x (\Delta T)^2} \right] \]

\[ G_i = G_0 \exp[-U^*/R(T_x - T_i)] \exp[-K_g(i)/T_x \Delta T f(T_x)] \]

where \( K_g(i) = 2b_o \sigma_0 \sigma_r (T_m^o/k_B \Delta h_i) \) and \( f(T_x) = 2T_m^o/(T_m^o + T_x) \)

where \( k \) is the crystallization rate, \( A \) is a constant dependent on the polymer studied, \( n \) is a constant dependent on the geometry of the crystal, and all other terms are as defined previously. As the volume fraction of the second blend component increases, the second exponential term in the radial growth rate and nucleation rate equations decrease as a result of the decrease in the equilibrium melting temperature. A decrease in the equilibrium melting temperature alone results in a decrease in the crystallization rate, and it will be
necessary to go to lower temperatures before crystallization will occur[10, 12, 14].

It seems that the blend should crystallize at the same undercooling and consequently at the same rate as the homopolymer. However, this is not observed due to two factors. First, a change in the glass transition temperature upon blending may affect the growth rate of the blend at a given crystallization temperature. If the Tg of the blend is higher than that of the crystallizable homopolymer, the blend will crystallize at a lower rate at a given temperature, and it may even be necessary to go to higher temperatures (lower undercoolings) for crystallization to proceed at a reasonable rate. Second, there is a dilution effect. The decrease in the concentration of the crystallizable polymer at the growth front increases the difficulty of extracting crystallizable segments from the melt and decreases the growth rate. This gives rise to a decrease in the crystallization rate at a given temperature, and it may even be necessary to go to lower temperatures for crystallization to proceed at a reasonable rate. In practice, these two factors give rise to broader crystallization exotherms[10].

Therefore, in the dynamic cooling experiments, miscible blends should exhibit the following. The crystallization exotherm of the semicrystalline component will shift to lower temperatures as the weight fraction of the amorphous component increases. Dilution effects result in broader crystallization exotherms than those of the homopolymer, unless the crystallizable component in the blend is forced to crystallize at lower temperatures where crystallization will proceed at a reasonable rate. A blend
with a $T_g$ higher than that of the crystallizable homopolymer will exhibit even broader crystallization exotherms.

This type of behavior is observed for PVDF in the case of both the melt and solution blends (see table 2, and figures 12, 13, and 14). PHB's broader crystallization exotherms result from the dilution effect alone since the $T_g$ of the blend is lower than that of the homopolymer. PVDF crystallizes at lower temperatures in the solution blends due to an enhancement of the dilution effect. The higher molecular weight PHB in the solution blend (see section 4.4.2) will entangle more easily with the crystallizable component and will force it to crystallize at lower temperatures where crystallization will proceed at a reasonable rate. Unlike the melt blended samples, the 30/70 solution blended PVDF/PHB exhibits simultaneous crystallization of both blend components (see figure 13).

Simultaneous crystallization is a result of the fact PHB has a lower molecular weight in the melt blend (see section 4.4.2). Because PHB has a lower molecular weight, its equilibrium melting temperature is lower. This is caused by the fact that there will be a greater percentage of chain ends per unit mass, and less perfect crystals, with lower equilibrium melting temperatures, will be formed (see section 2.3.2 of the literature review). Therefore, at a given temperature, the undercooling is lower for PHB in the melt blend than in the solution blend. As a result, PHB will crystallize at a higher temperature in the solution blend than in the melt blend. In addition, PVDF will crystallize at lower temperatures in the solution blend due to a more pronounced dilution effect. These two factors allow their crystallization exotherms to coincide.
Table 2. Temperature of Crystalization at the Fastest Rate of Cooling for Melt and Solution Blended PVDF/PHB (where NA signifies the given polymer doesn't crystallize at this blend composition).

**Melt Blended PVDF/PHB**

<table>
<thead>
<tr>
<th>Weight Fraction of PVDF</th>
<th>PVDF $T_{\text{max}}$ ($^\circ$C)</th>
<th>PHB $T_{\text{max}}$ ($^\circ$C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>139.6</td>
<td>NA</td>
</tr>
<tr>
<td>0.9</td>
<td>137.3</td>
<td>NA</td>
</tr>
<tr>
<td>0.8</td>
<td>135.5</td>
<td>NA</td>
</tr>
<tr>
<td>0.7</td>
<td>133.5</td>
<td>67.8</td>
</tr>
<tr>
<td>0.6</td>
<td>129.6</td>
<td>82.4</td>
</tr>
<tr>
<td>0.5</td>
<td>125.5</td>
<td>87.0</td>
</tr>
<tr>
<td>0.4</td>
<td>122.6</td>
<td>95.2</td>
</tr>
<tr>
<td>0.3</td>
<td>113.7</td>
<td>95.8</td>
</tr>
<tr>
<td>0.2</td>
<td>NA</td>
<td>97.7</td>
</tr>
<tr>
<td>0.1</td>
<td>NA</td>
<td>99.2</td>
</tr>
<tr>
<td>0</td>
<td>NA</td>
<td>110.4</td>
</tr>
</tbody>
</table>

**Solution Blended PVDF/PHB**

<table>
<thead>
<tr>
<th>Weight Fraction of PVDF</th>
<th>PVDF $T_{\text{max}}$ ($^\circ$C)</th>
<th>PHB $T_{\text{max}}$ ($^\circ$C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>139.6</td>
<td>NA</td>
</tr>
<tr>
<td>0.8</td>
<td>133.2</td>
<td>NA</td>
</tr>
<tr>
<td>0.7</td>
<td>128.4</td>
<td>NA</td>
</tr>
<tr>
<td>0.6</td>
<td>122.5</td>
<td>78.1</td>
</tr>
<tr>
<td>0.5</td>
<td>117.1</td>
<td>85.5</td>
</tr>
<tr>
<td>0.4</td>
<td>112.6</td>
<td>100</td>
</tr>
<tr>
<td>0.3</td>
<td>NA</td>
<td>96.7-105</td>
</tr>
<tr>
<td>0.2</td>
<td>NA</td>
<td>95.9</td>
</tr>
<tr>
<td>0.1</td>
<td>NA</td>
<td>101.2</td>
</tr>
<tr>
<td>0</td>
<td>NA</td>
<td>121.7</td>
</tr>
</tbody>
</table>
Figure 12. Crystallization exotherms recorded at a cooling rate of 10°C/minute for melt blended PVDF/PHB
Figure 13. Crystallization exotherms recorded at a cooling rate of 10°C/minute for solution blended PVDF/PHB.
Figure 14. Crystallization temperature at the fastest rate of cooling for PVDF and PHB in (a) melt blended and (b) solution blended PVDF/PHB.
4.2.3 Analysis of the Melting of Isothermally Crystallized Samples

Isothermal crystallization experiments was the third method utilized to study miscibility by thermal analysis. As discussed in the literature review (section 2.4), the equilibrium melting point for the semicrystalline component in a miscible blend will be depressed. The equilibrium melting point is found by extrapolation of the line $T_m$ (the observed melting point at crystallization temperature $T_x$) versus $T_x$, and the line is described by the following equation:

$$
T_m = T_m^0 \left( 1 - \frac{1}{\gamma} \right) + T_x \left( \frac{1}{\gamma} \right)
$$

(see section 2.4 of the literature review).

Dynamic cooling studies revealed PVDF crystallizes first both in the melt and solution blends at PVDF blend contents greater than 30%. The $\alpha$ phase of PVDF was chosen for isothermal crystallization studies since it crystallized first in polarized optical microscopy studies (see section 4.3.2). Furthermore, it has been documented that the $\alpha$ phase is predominant in samples crystallized at high undercoolings, and it has the lowest melting endotherm.

In figure 15, the results of isothermal crystallization of the $\alpha$ phase of PVDF, maintaining 10% crystallinity, are shown. It is assumed that the degree of crystallinity roughly equals the ratio of the observed heat of fusion of the $\alpha$ phase of PVDF to the heat of fusion of an infinitely large and perfect crystal of the $\alpha$ phase (25 cal/g)[55]. The crystallinity was limited to 10% because of PVDF's tendency to anneal or thicken. In this figure, therefore, the $\alpha$ phase of PVDF in the 50/50 and 70/30 PVDF/PHB blends was allowed to crystallize until it reached a heat of fusion of 1.25 and 1.75 cal/g, respectively, and in pure PVDF, until it had a heat of fusion of 2.5 cal/g.
Figure 15. Hoffman-Weeks Plot for PVDF/PHB (a) melt blends and (b) solution blends for 10% of the $\Delta h_f$ of the $\alpha$ phase of PVDF.
The reason behind maintaining the same degree of crystallinity for all blend compositions at all crystallization temperatures is the following. If crystal thickening takes place, as in the case of PVDF, the melting temperature will increase with time or with the degree of crystallinity, and the proportionate increase in $T_m$ will not be the same at each crystallization temperature. Therefore, the slope of the line used to extrapolate to the equilibrium melting temperature will decrease with crystallinity, although the observed melting temperatures increase with the crystallization temperature[117]. As a result, the equilibrium melting temperature will decrease with increasing crystallinity. This has been observed for poly(ethylene) and poly(ethylene oxide) [118, 119].

In these studies, the temperature window in which isothermal crystallization studies could be conducted was narrow as a result of two factors. First, for very low temperatures of crystallization, temperature equilibration prior to crystallization couldn't be reached. Furthermore, the crystallization rate was so large that further crystallization could occur while the polymer was being heated to its melting point. Therefore, the final melting point reflected more perfect crystals grown at temperatures higher than the experimental crystallization temperature. In figure 16, a series of DSC melting endotherms is shown for crystals grown under such conditions. In figure 16a, an asymmetric peak is evident. Longer crystallization times allowed the polymer to crystallize more completely prior to heating leaving less amorphous material available for crystallization upon heating. From figure 16, it is evident that as the crystallization time increased by only a few seconds, the low temperature side of the peak increased, leading to the final lower temperature melting
Figure 16. DSC traces of the 70/30 melt blended PVDF/PHB at 144°C at (a) 1 minute, (b) 1 minute and 15 seconds, (c) 1 minute and 30 seconds, and (d) 2 minutes.
endotherm (see figure 16d). Such behavior was not observed in the intermediate temperature range studied.

The lower end of the temperature range was less restricted in the case of the solution blended PVDF/PHB than in the case of the melt blended samples. At a given crystallization temperature, the lower melt viscosity of the melt blends due to the higher degree of degradation of PHB (see section 4.4.2), gives rise to a higher crystallization rates (for an explanation, see section 2.3.2). Furthermore, when the crystallization temperatures are low enough, crystallization can occur during the heating process, and thermodynamic equilibration will not be achieved. A falsely high melting temperature for the sample will result.

Two events take place to restrict the higher end of the temperature window. First, it is very probable that PHB degradation will occur. Kunioka and workers observed a drop in PHB's $M_n$ from 564 to $170 \times 10^3$ after 20 minutes at 170°C [1]. Therefore, the highest temperature studied for the 50/50 PVDF/PHB melt blend was 152°C, where the time necessary for the $\alpha$ phase of PVDF to crystallize 10% was 50 minutes. At 154°C, it would have taken one hour and forty-five minutes for 10% crystallinity to be achieved, and PHB degradation probably would have occurred in this time period.

Second, at higher temperatures, the appearance of the $\gamma$ and $\varepsilon$ phases make it difficult to accurately determine the heat of fusion of the $\alpha$ phase melting endotherm. The $\gamma$ phase of PVDF begins to crystallize due to the long crystallization times, and the high temperatures provide the energy necessary for the $\alpha$ to $\varepsilon$ phase transformation. This phenomenon is observed for 70/30
PVDF/PHB melt blends at temperatures higher than 156°C where crystallization times necessary to achieve 10% crystallinity are greater than two hours and twenty minutes. After two hours, three peaks are already evident in the melting endotherm. At very high temperatures the γ phase overpowers the α phase. Gianotti and workers state that this is due to the greater temperature dependence of the nucleation rate of the α phase of PVDF. Therefore, even though the growth rates of the α and γ phases have similar temperature dependence, the nucleation rate of the α phase is low at high temperatures and the γ phase is mostly observed[27].

Figure 15, where this procedure is followed, reveals the equilibrium melting temperatures for the blends coincide with that of pure PVDF. This would indicate incompatibility where other techniques indicate compatibility. The observed nonlinearity in the plots may be attributed to possible temperature dependence of the side surface free energy as other workers have reported[79], or it may be due to isothermal thickening at higher temperatures. The different slopes of the lines at different compositions may be due to a composition dependence of the thickening coefficient (see equation 35).

Therefore, another method of performing Hoffman-Weeks analysis was employed. With the belief the degree of thickening was more dependent on time than on the degree of crystallinity, the blends were crystallized for the same period of time as the 50/50 blend at a given crystallization temperature. Furthermore, it was believed the heats of fusion for the 70/30 PVDF/PHB blends and the pure PVDF would remain the same over the range of crystallization temperatures studied. The 50/50 PVDF/PHB blends were crystallized to 10% crystallinity as before which allowed enough time for the α phase of PVDF to
crystallize in all the blends, yet prevented significant isothermal thickening of PVDF.

It was found that the heats of fusion for 70/30 PVDF/PHB and pure PVDF did remain approximately the same over the temperature range studied. At temperatures where it was impossible to conduct studies on the 50/50 PVDF/PHB blend, it was possible to isothermally crystallize the 70/30 PVDF/PHB blend and pure PVDF. This was accomplished by attempting to achieve approximately the same heats of fusion as those obtained at lower temperatures for a particular sample.

The high temperature end in the 70/30 blends and in pure PVDF was restricted, however. It was impossible to achieve the same degree of crystallinity beyond the temperature range indicated in figure 17 because of the slow growth of the α phase of PVDF at these low undercoolings. For example, at 154°C, the heat of fusion of the α phase of PVDF in the pure PVDF sample, remained the same going from a crystallization time of two hours and thirty minutes to six hours. The same type of behavior was observed in the 70/30 PVDF/PHB melt and solution blends. In the blends, the upper temperature range was restricted still more due to lower undercoolings. Furthermore, the necessarily long crystallization times resulted in a substantial amount of the γ and ε phases which made it difficult to accurately determine the heat of fusion for the α phase (see figure 18).

The lower temperature range was restricted for the same reasons cited previously.

The results obtained by this method give an equilibrium melting point depression for the PVDF/PHB melt blends but not for the PVDF/PHB solution
Figure 17. Hoffman-Weeks Plot for the α phase of PVDF in (a) melt blended and (b) solution blended PVDF/PHB for the same crystallization time at a given crystallization temperature.
Figure 18. DSC traces of the 50/50 PVDF/PHB melt blend at 152°C after (a) 2 hours, (b) 2 hours and 30 minutes, (c) 3 hours, and (d) 5 hours and 45 minutes.
blends which instead exhibit a physically meaningless equilibrium melting point elevation.

Hoffman-Weeks analysis may not be valid for the solution blends. PHB crystallizes in the 70/30 PVDF/PHB solution blends at 148°C but not at the same crystallization temperature in the 70/30 melt blends (see section 4.7). Therefore, there is reason to believe that PHB may be crystallizing in the solution blends during the isothermal crystallization studies performed on the DSC. Crystallization of the two polymers in the blend would create a nonequilibrium situation in the melt (see section 2.8 of the literature review).

The second technique allowed for the determination of the equilibrium melting points of the α phase of PVDF in pure PVDF as well as in the 70/30 and 50/50 PVDF/PHB melt blends. These were 180, 179, and 178°C respectively. The equilibrium melting point for pure PVDF is close to values averaging at 179 ± 10°C as reported by other researchers[28, 42, 43]. The variation in the equilibrium melting point is dependent on the percentage of head-to-head defects[28, 29]. Since the equilibrium melting points for the blends and pure PVDF fall in a very narrow temperature range, there is no trend within experimental certainty. Therefore, Hoffman-Weeks analysis (equation 42) cannot be used to find a meaningful χ parameter.
4.3 Polarized Optical Microscopy

4.3.1 Introduction

Polarized Optical Microscopy (POM) was utilized for growth rate and morphological studies. The composition and temperature dependence of the growth rate of the α phase of PVDF in melt and solution blends was determined as a test of miscibility. As a further test of the blends' miscibility, the composition dependence of the morphology of the melt and solution blends was studied.

4.3.2 Growth Rate Studies

Growth rate analysis was the first method used to test the blends' miscibility. If the PVDF/PHB blends are miscible, the radial growth rate of the α phase of PVDF will decrease as the blend weight fraction of PHB increases.

The following equation is used to describe the radial growth rate of a polymer:

\[ G = G_0 \exp\left(-U^*/R(T_x - T_\infty)\right) \exp\left(-K_g/(T_x \Delta T f(T_x))\right) \]

where \( f(T_x) = 2T_x/(T_m^c + T_x) \)

and \( K_g = 2b_0(\sigma \sigma_0)T_m^c/(\Delta h_f)k_B \)

where all terms have been defined previously (see section 2.3.2 of the literature review)[14].

The factors which affect the growth rate of a crystallizable component in a miscible polymer blend have been discussed in section 2.4 of the literature review. After examining the results in tables 3 and 4 and in figures 19a and b, it is clear the melt and solution blended PVDF/PHB exhibit a decrease in the growth rate of the α phase of PVDF as the weight fraction of PHB increases. This is expected since the glass transition temperature and \( U^* \) of the blend increase along with the weight fraction of PHB. Furthermore, the results of the
Table 3. Growth Rates for Melt Blends.

<table>
<thead>
<tr>
<th>Pure PVDF</th>
<th>70/30 PVDF/PHB</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Tx (°C)</strong></td>
<td><strong>Growth Rate (μm/s)</strong></td>
</tr>
<tr>
<td>150.3</td>
<td>1.03E-1 ± 4E-3</td>
</tr>
<tr>
<td>153.3</td>
<td>4.96E-2 ± 6E-4</td>
</tr>
<tr>
<td>155.3</td>
<td>3.37E-2 ± 3.9E-3</td>
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<tr>
<td>157.3</td>
<td>2.21E-2 ± 9E-4</td>
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<td>159.2</td>
<td>9.10E-3 ± 3.3E-4</td>
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<td>163.3</td>
<td>2.25E-3 ± 8E-5</td>
</tr>
<tr>
<td>153.2</td>
<td>1.69E-2 ± 5.7E-3</td>
</tr>
<tr>
<td><strong>50/50 Melt Blend</strong></td>
<td><strong>Growth Rate (μm/s)</strong></td>
</tr>
<tr>
<td><strong>Tx (°C)</strong></td>
<td><strong>Growth Rate (μm/s)</strong></td>
</tr>
<tr>
<td>137.4</td>
<td>9.74E-2 ± 1.27E-2</td>
</tr>
<tr>
<td>139.4</td>
<td>7.41E-2 ± 2.4E-3</td>
</tr>
<tr>
<td>141.3</td>
<td>5.30E-2 ± 3.3E-3</td>
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<tr>
<td>143.3</td>
<td>3.97E-2 ± 1.5E-3</td>
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<tr>
<td>145.3</td>
<td>2.65E-2 ± 1.4E-3</td>
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<td>147.3</td>
<td>2.07E-2 ± 1.3E-3</td>
</tr>
<tr>
<td>149.3</td>
<td>1.50E-2 ± 1.1E-3</td>
</tr>
<tr>
<td>151.3</td>
<td>1.00E-2 ± 8E-4</td>
</tr>
<tr>
<td>153.3</td>
<td>5.45E-3 ± 2.2E-4</td>
</tr>
<tr>
<td>155.3</td>
<td>4.10E-3 ± 2.5E-4</td>
</tr>
</tbody>
</table>
Table 4. Growth Rates for Solution Blends.

<table>
<thead>
<tr>
<th>100/0 PVDF/PHB</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_x$ (°C)</td>
<td>Growth Rate ($\mu$m/s)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>150.3</td>
<td>1.03E-1 ± 4E-3</td>
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</tr>
<tr>
<td>153.3</td>
<td>4.96E-2 ± 6E-4</td>
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<td></td>
</tr>
<tr>
<td>155.3</td>
<td>3.37E-2 ± 3.9E-3</td>
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<tr>
<td>157.3</td>
<td>2.21E-2 ± 9E-4</td>
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</tr>
<tr>
<td>159.2</td>
<td>9.10E-3 ± 3.3E-4</td>
<td></td>
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</tr>
<tr>
<td>163.3</td>
<td>2.25E-3 ± 8E-5</td>
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<table>
<thead>
<tr>
<th>70/30 PVDF/PHB</th>
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<tr>
<td>$T_x$ (°C)</td>
<td>Growth Rate ($\mu$m/s)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>143.0</td>
<td>9.11E-2 ± 3.3E-3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>145.1</td>
<td>5.88E-2 ± 1.4E-3</td>
<td></td>
<td></td>
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<td>4.5E-2 ± 1.8E-3</td>
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<td>2.76E-2 ± 1.9E-3</td>
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<td>2.57E-2 ± 9E-4</td>
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<td>154.9</td>
<td>8.67E-3 ± 6.9E-4</td>
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<table>
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<tr>
<th>50/50 Solution Blend</th>
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<tbody>
<tr>
<td>$T_x$ (°C)</td>
<td>Growth Rate ($\mu$m/s)</td>
<td></td>
<td></td>
</tr>
<tr>
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<td></td>
</tr>
<tr>
<td>131.4</td>
<td>0.108±1.2E-2</td>
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<tr>
<td>133.3</td>
<td>7.58E-2±7.6E-3</td>
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<tr>
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<td>137.4</td>
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<td>143.3</td>
<td>1.71E-2±1.4E-3</td>
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</tr>
<tr>
<td>145.3</td>
<td>1.45E-2±8E-4</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 19. Growth rate versus crystallization temperature for (a) melt and (b) solution blended PVDF/PHB.
Figure 20. log G vs the crystallization temperature for the $\alpha$ phase of PVDF in PVDF/PHB (a) melt and (b) solution blends.
Hoffman-Weeks analysis discussed in section 4.2.3 reveal the melt blends do exhibit an equilibrium melting point depression which will also give rise to a decrease in the growth rate at a given crystallization temperature. Finally, the dilution effect discussed in section 4.2.2 will also lead to a decrease in the growth rate at a given crystallization temperature.

The solution blends exhibit an even larger change in the growth rate (see figure 19b). The T_g difference between the melt and solution blends is within the experimental error of the DSC. Furthermore, there is no detectable melting point depression and the Hoffman-Weeks analysis may even be invalid in this case (see section 4.2.3). The larger decrease in the growth rate may be attributed to a more pronounced dilution effect with a higher molecular weight blend component. The subsequently smaller G_o may result in a dramatic decrease in the growth rate.

The product \( \sigma_u \sigma_e \) can be calculated from the growth rate data by means of the radial growth rate equation. In figure 21, \( \ln G + \frac{U^*}{(R(T_x - T_m))} \) is plotted against \( \frac{1}{(T_x \Delta T f(T_x))} \) (\( U^* = 1500 \text{ cal/mole}, b_o = 4.41 \text{ Å}, \Delta h_f = 1.87 \times 10^8 \text{ J}[24], T_m = 180, 179, \text{ and } 178^\circ \text{C for pure PVDF, and the 70/30 and 50/50 melt blends respectively, and the } T_g \text{'s calculated by the Fox equation are -35, -24.9, and -17.7^\circ \text{C for pure PVDF, and the 70/30 and 50/50 melt blends respectively). Since Hoffman-Weeks analysis is invalid for the solution blends, the product } \sigma_u \sigma_e \text{ can only be computed for the melt blends. The slopes of the lines computed by linear least squares analysis are equal to } -K_g, \text{ and } K_g \text{ is defined as:} \)

\[
K_g = n b_o \sigma_u \sigma_e T_m \Delta h_f k_B
\]
Figure 21. Growth rates analysis of the α phase of PVDF in melt blended PVDF/PHB.
where the \( n \) refers to the regime of crystallization (\( n = 2 \) for regime II for the \( \alpha \) phase of PVDF). The \( \sigma_u \sigma_e \) values derived from the slopes are 470.9, 592.1, and 540.8 erg\(^2/cm^4\) for the pure PVDF, 70/30 and 50/50 melt blends respectively.

The trend in the surface free energies cannot be explained. If an interphase region exists at high PVDF blend content which has been documented in other PVDF systems[71, 72], \( \sigma_u \sigma_e \) would be similar to that for pure PVDF, assuming the end surface free energy is composition independent as demonstrated by other groups[16]. The product, \( \sigma_u \sigma_e \) might be lower for the melt blends than for pure PVDF since specific interactions are likely to exist between PVDF and PHB (see section 2.5.5). This would give rise to a more ordered melt, and a \( \sigma_u \) and \( \sigma_u \sigma_e \) lower than those of PVDF since \( \sigma_e \) is not expected to change significantly on blending. This is not observed, so the trend is not explainable.

This may be due to some assumptions made in equation 31. First, \( U^* \) is thought to be composition independent. However, it is likely \( U^* \) is composition dependent, since the energy needed to transport crystallizable segments from the melt to the crystal face may depend on the melt composition. Second, \( \sigma_u \sigma_e \) was assumed to be temperature independent. This may not be valid in the case of PVDF crystals since thickening plays a large role, and according to Lauritzen and Hoffman:

\[
\sigma_e = \sigma_{e1}(1 + \gamma \Delta T)
\]

[49]

where \( \sigma_{e1} \) is the end surface free energy in the absence of thickening[14]. Third, the equilibrium melting temperatures computed for pure PVDF and the

Chapter 4. Results and Discussion
melt blends may be incorrect for the other reasons cited in section 4.2.3. Finally, equation 43 identifies $v_2$, $T_m^\circ$, and $T_g$ with the blend rather than with the depletion layer, with the assumption that the consequences of compositional changes at the growth fronts are insignificant compared with those of the initial dilution[16].

All these factors may give rise to an unusual trend in the composition dependence of $\sigma_u\sigma_e$ which may not be real but a result of the inadequacy of the growth rate equation.

4.3.3 Morphological Studies

Morphological studies were performed as another test of the miscibility of PVDF/PHB melt and solution blends. If the blend were miscible, the ring spacing of PVDF's $\alpha$ phase would reflect changes in the blend composition, as has been observed in other PVDF blend systems[19]. This is due to a change in the composition of the interlamellar amorphous phase which affects the surface stresses on the lamellae and the degree of twisting.

Furthermore, the morphology of the blends is expected to change with composition. For example, the percentage of the $\beta$ phase increases in PMMA/PVDF blends[80]. Other groups have observed an increase in the $\gamma$ phase content of PVDF in solution blended samples cast from DMF[84]. These morphological changes may result from the strong interaction between PVDF and DMF or PVDF and PMMA. Such systems may favor a more extended chain conformation characteristic of the $\gamma$ phase which would increase the number of contacts between the PVDF and DMF or PMMA. Such an explanation has been given in the case of PMMA and PVDF[80].
The optical micrographs in figures 22 through 25 and the graphs in figure 26 qualitatively and quantitatively indicate the ring spacing of the α phase increases with increasing PHB blend content in both blend systems. Again the temperature window was restricted since PHB degradation may occur at high temperatures and no ring spacings were observed at low temperatures. In spite of this, it is still clear the ring spacing increases along with the PHB blend content. The ring spacing increases because PHB's presence in the interlamellar regions decreases the undercooling at a given crystallization temperature. Therefore, crystallization occurs at a lower rate and a less disordered surface and a lower degree of twisting result (see section 2.3.2).

However, it appears that the difference between the degree of twisting of the α phase in the blends and in pure PVDF is greater in the melt blends than in the solution blends. This may be due in part to the larger equilibrium melting point depression in the melt blends, which would result in a lower undercooling at a given crystallization temperature. This would give rise to the formation of more ordered crystals at a given crystallization temperature and a lower degree of twisting. Furthermore, it was observed late in the project that blends with a high percentage of PHB became somewhat cloudy when heated to high temperatures which would indicate that phase separation may be taking place.

It is possible that PHB is less compatible in the solution blends than in the melt blends as a result of its higher molecular weight. Work by Barron, et. al. [122] has indicated that PVDF blends with strong interactions have less of a crystal/liquid interphase than those with weaker interactions. Perhaps, the weaker interactions in the solution blends give rise to an interphase at the
Figure 23. Optical micrographs of PVDF/PHB melt blends at 140.5°C.
Figure 24. Optical micrographs of PVDF/PHB melt blends at 150.5°C.
Figure 25. Optical micrographs of PVDF/PHB solution blends at 140.5°C.
Figure 26. Optical micrographs of PVDF/PHB solution blends at 150.5°C.
Figure 26. Ring spacing versus $T_x$ for the $\alpha$ phase spherulites of PVDF in PVDF/PHB (a) melt and (b) solution blends.
crystal surface richer in PVDF, and the changes in the surface stresses with blend composition are not as great as in the melt blended systems.

Another explanation is the crystallization of PHB. FT-IR studies have indicated the PHB crystallizes at 148°C in the solution blends but not in the melt blends. Since the morphological studies were conducted in approximately the same temperature range, it is also possible PHB is crystallizing in the solution blends but not in the melt. As PHB crystallizes, the regions adjacent to the crystal surface of the α phase of PVDF may become richer in PVDF, and the end effect would be similar to that produced by an interphase.

The temperature dependence of the ring spacing for the 70/30 PVDF/PHB blends is similar in the solution and melt blends. In the 50/50 solution blends, it is difficult to quantitatively determine the temperature dependence. This stems from the large error associated with the calculated ring spacings, and the narrow temperature window, where the temperature dependence is nonlinear, in which they could be calculated.

The nucleation density appears to be greater in the solution blends than in the melt blends. This may be due to a higher impurity concentration and a greater potential for heterogeneous nucleation in the solution blends. It may also be attributed to a larger γ phase population in the solution blends which don't melt completely at 190°C. The high temperatures necessary to destroy γ phase nuclei would have degraded the PHB further.
4.4 Poly(3-hydroxybutyrate) Characterization

In the above studies, differences in the behavior of the melt and solution blends were observed. Since it had been reported that PHB undergoes thermooxidative degradation by the following mechanism [1]:

\[
\begin{align*}
\text{CH}_3 & \quad \text{O} \quad \text{CH}_3 \\
\text{O} \quad \text{CH}_3 & \quad \text{C} \quad \text{H} \quad \text{C} \quad \text{O} \\
\text{H} & \quad \text{O} \\
\end{align*}
\]

studies were conducted to determine if PHB had undergone degradation during blending. This was accomplished by nuclear magnetic resonance (NMR) spectroscopy and intrinsic viscosity experiments.

4.4.1 Nuclear Magnetic Resonance Experiments

\(^1\text{H}\) and \(^{13}\text{C}\) NMR spectra of as-received PHB and PHB subjected to solution and melt blending conditions were performed to determine if the chemical structure of PHB had changed during the blending process. Figures 27 and 28 do indicate that the chemical structure has remained the same. The peak at 2.3 ppm in figure 27b may be due to an impurity since signals from end
Figure 28. $^1$H NMR Spectra of (a) as-received PHB, and (b) PHB subjected to melt blending conditions.
Figure 29. $^{13}\text{C}$ NMR Spectra of (a) as-received PHB, and (b) PHB subjected to melt blending conditions.
groups of possible degradation products would fall at 1.9, 5.8, and 7 ppm. Otherwise, the spectra are similar to those obtained by other groups\cite{123}.

4.4.2 Intrinsic Viscosity Experiments

Intrinsic viscosity studies were performed on as-received PHB and PHB subjected to "melt" and "solution" blending conditions. The results are in table 5 \((T_{\text{proc.}}\) refers to the blending temperature). The Mark-Houwink constants given in section 3.5.2 were used to calculate the \(M_v\)'s. These studies clearly indicate PHB undergoes a dramatic change in molecular weight upon melt blending and a smaller change upon solution blending.

4.5 Thermogravimetric Analysis

Thermogravimetric Analysis (TGA) studies were performed to determine the effect PVDF had on PHB degradation in the melt and solution blends. The findings in table 6 and in figures 29 and 30 indicate the presence of PVDF dramatically decreases the rate of PHB degradation.

It appears that the melt blended samples experience more degradation than the solution blended samples. This may result from the fact that PHB has already undergone significant degradation during the melt blending process (see section 4.4.2), and in the TGA, less energy is required to form the low molecular weight volatiles which give rise to a significant weight loss. Furthermore, it appears that a smaller amount of PVDF is necessary in the melt blends than in the solution blends to significantly decrease the degree of
Table 5. Intrinsic viscosity results for as-received PHB, and "melt" and "solution" blended PHB.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\eta$ (dL/g)</th>
<th>$M_v$</th>
<th>$T_{\text{proc.}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-received PHB</td>
<td>1.64</td>
<td>205,000</td>
<td>NA</td>
</tr>
<tr>
<td>&quot;Solution blended PHB&quot;</td>
<td>1.23</td>
<td>141,000</td>
<td>120°C</td>
</tr>
<tr>
<td>&quot;Melt Blended PHB&quot;</td>
<td>0.75</td>
<td>75,000</td>
<td>180°C</td>
</tr>
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</table>
Table 6. Thermogravimetric analysis (TGA) results for solution and melt blended PVDF/PHB and as-received, solution, and melt blended PHB.

<table>
<thead>
<tr>
<th>Material</th>
<th>PHB Percent Weight Loss</th>
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<tbody>
<tr>
<td></td>
<td>220°C</td>
</tr>
<tr>
<td>As-received PHB</td>
<td>7.52</td>
</tr>
<tr>
<td>Solution Blended PHB</td>
<td>11.42</td>
</tr>
<tr>
<td>Melt Blended PHB</td>
<td>5.86</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>Melt Blended PHB</td>
<td>5.86</td>
</tr>
<tr>
<td>50/50 PVDF/PHB Melt Blend</td>
<td>4.29</td>
</tr>
<tr>
<td>70/30 PVDF/PHB Melt Blend</td>
<td>2.73</td>
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<tr>
<td>Solution Blended PHB</td>
<td>11.42</td>
</tr>
<tr>
<td>50/50 PVDF/PHB Solution Blend</td>
<td>11.15</td>
</tr>
<tr>
<td>70/30 PVDF/PHB Solution Blend</td>
<td>2.69</td>
</tr>
</tbody>
</table>
Figure 29. Isothermal Degradation of PVDF/PHB Melt Blends at (a) 220°C and (b) 230°C.
Figure 30. Isothermal degradation of PVDF/PHB solution blends at (a) 220°C and (b) 230°C.
degradation. This may result from the fact PHB has already undergone significant degradation in the melt blending process, rendering PVDF less effective. The observed discrepancies for pure PHB (as-received, "melt" and "solution" blended PHB) may be due to experimental error--slightly different sample surface areas and changes in the oxygen flow rate. There may even be uneven degradation, since PHB may undergo more degradation in areas near the sides of the blender which may be hotter than the center.

The solution blended samples require a great deal more PVDF before a significant change in the degradation rate is observed, and the overall degree of degradation is less. Any errors may be attributed to the same sources of experimental error cited in the case of the melt blends. In addition, uneven degradation during the blending process is also possible.

Two explanations have been given for PVDF's affect on the degradation behavior of PHB. First, it may result from an enrichment of PVDF at the surface. If PVDF has a lower surface free energy, it would preferentially migrate to the polymer/air interface. Second, Kwei, et. al. have observed the stabilization of poly(vinyl pyrrolidone) (PVP) by poly(4-hydroxystyrene)[124]. They attribute this to the stabilization of the carbonyl group of PVP by its interaction with groups on poly(4-hydroxystyrene)[124]. It is possible PVDF stabilizes PHB in a similar manner.
4.6 Fourier Transform-Infrared Spectroscopy Results

Fourier transform-infrared (FT-IR) spectroscopy studies were performed to determine if PHB crystallized in the melt and solution blends in the same temperature range as PVDF and if so, at what relative rate.

The spectra in figures 31 and 32 are the PHB and PVDF crystalline and amorphous regions of the spectra taken at the point at which the heat cell reaches 148°C and after 65 minutes at 148°C. The spectra in figures 33 and 34 are 3-D FT-IR spectra where the z axis is the time axis. The spectra begin at the time at which the heat cell reaches 148°C and are taken at one minute intervals. Again, the two regions represented are the PVDF and PHB crystalline regions. The region around 1750 cm\(^{-1}\) is the ester carbonyl stretching mode region[125] which contains both the crystalline and amorphous ester carbonyl stretching modes for PHB, and that from 450 to 560 cm\(^{-1}\) is the crystalline and amorphous region for PVDF[84].

The FT-IR spectra prove that PHB crystallizes in the solution but not in the melt blends. Note in figure 31b that the higher frequency band diminishes while that at a lower frequency begins to grow. This second band is believed to be a crystalline band. It may be at a higher frequency than the amorphous band because the closer proximity of the chains in the crystal lattice may give rise to a greater degree of intramolecular hydrogen bonding. This would result in a shift in frequency, since hydrogen bonding will lengthen the double bond and decrease the amount of energy necessary to stretch it[125].

Furthermore, it appears that in the solution blends, PVDF crystallizes more slowly, and the γ phase content is greater (see figures 32a and b and 34a and b). In the PVDF region of the melt blend spectra, the only bands are at 490
Figure 31. The PHB crystalline and amorphous regions of the FT-IR spectra taken at the time the cell reached 148°C and after 65 minutes for (a) melt and (b) solution blends.
Figure 32. The PVDF crystalline and amorphous regions of the FT-IR spectra taken at the time the cell reached 148°C and after 65 minutes for (a) melt and (b) solution blends.
Figure 32. The 3-D FT-IR spectra of the PHB crystalline and amorphous regions in 70/30 (a) melt and (b) solution blends at 148°C.
Figure 34. The 3-D FT-IR spectra taken at 1 minute intervals of PVDF crystalline and amorphous regions in 70/30 (a) melt and (b) solution blends at 148°C.
cm$^{-1}$ (α phase) and 512 cm$^{-1}$ (γ phase)[51]. Amorphous bands are absent. However, in the solution blend spectra, there is a band midway between these two bands which diminishes in the course of the crystallization process. This behavior indicates it may be an amorphous band. In the solution blends, the γ phase band is larger than that of the α phase whereas in the melt blends, it is smaller. This follows with the observations of an increase in the γ phase content in other PVDF solution blend systems cast from DMF[53].
Chapter 5. Conclusions

The purpose of this project was to blend PVDF and PHB, to determine if the blends were miscible, and to determine how blending affects the crystallization and melting behavior of the two polymers.

The following conclusions can be drawn from the thermal analysis work. Melt and solution blended PVDF/PHB exhibit a single, composition dependent $T_g$. Dynamic cooling experiments reveal a decrease in the crystallization rate of each polymer as the weight fraction of the second polymer increases. In the melt blends, PVDF crystallizes first in blends containing at least 30\% PVDF. In the solution blends, PVDF and PHB crystallize simultaneously in the 30/70 PVDF/PHB blend. Hoffman-Weeks analysis gives an equilibrium melting point depression for melt blended PVDF/PHB. However, this type of analysis may not be valid for solution blended PVDF/PHB because of possible crystallization of PHB in the time scale of the experiment.

The following conclusions can be drawn from the optical microscopy work. The growth rate of the $\alpha$ phase of PVDF decreases in melt and solution
blended PVDF/PHB as the weight fraction of PHB increases. Morphological studies indicate the nucleation density is greater in the solution blends because of a larger impurity concentration and an increase in $\gamma$ phase nucleation, and in both blend systems the ring spacing and coarseness of the $\alpha$ phase spherulites increases with crystallization temperature and with the weight fraction of PHB.

The melt and solution blended samples behave differently in the thermal analysis and optical microscopy work. Therefore, NMR and intrinsic viscosity studies were performed to determine if PHB had undergone thermooxidative degradation as observed by other groups[1]. NMR spectra indicate no chemical composition change in PHB after it was suspected to either melt or solution blending conditions. Intrinsic viscosity results reveal a dramatic decrease in PHB's viscosity average molecular weight after melt blending and a smaller drop after solution blending.

TGA studies were performed to determine if PVDF would hinder or accelerate PHB degradation in the blends. PVDF did hinder PHB degradation in melt and to a greater extent in the solution blends.

Finally, FTIR studies were performed to determine if PHB crystallized in the melt or solution blends in the same temperature range as PVDF. PHB only crystallizes in the solution blends. Furthermore, the PVDF $\gamma$ phase content is greater in the solution blends.

It can be concluded that PVDF and PHB are miscible in the amorphous phase in the melt blended samples, and partially miscible in the solution blended samples which may be due to selective fractionation during precipitation or may be due to PHB's higher molecular weight. PHB undergoes a greater degree of degradation in the melt blending than in the solution.
blending process, and PVDF appears to hinder this degradation in both melt and solution blends. Due to PHB's higher molecular weight in the solution blends, it crystallizes more readily.
Chapter 6. Future Work

Many questions have been answered in this work, but many still remain. This chapter will discuss possible future work.

First, does the solution blended PVDF/PHB have a lower LCST brought on by PHB's higher molecular weight or is the observed partial phase separation brought on by the method by which the blend is precipitated out in the nonsolvent? It would be interesting to utilize neutron scattering[126] to construct a phase diagram for different molecular weights of PHB blended with PVDF. However, this would require deuterated PVDF or PHB and may not be practical or viable. In addition, different nonsolvents could be tested to determine if possible phase separation during the precipitation process could be avoided.

Since the $\alpha$ phase of PVDF thickens to a great extent, small angle x-ray scattering could be utilized to determine how the lamellar thickness varies with the melting temperature and subsequently to find the equilibrium melting temperature (see equation 25 in the literature review)[5].
Is the surface of the blends enriched with PVDF? Surface elemental analysis by X-ray Photoelectron Spectroscopy (XPS) could be performed to quantify the surface compositions in both the melt and solution blends.

It would be interesting to determine if the PVDF/PHB blends have an interphase as observed by other groups with other PVDF blends[69-72], and if it does, to determine if it is affected by the molecular weight of the PHB. Would the interphase be larger in the solution blends due to PVDF and PHB's lower degree of compatibility as observed with other systems by Barron, et. al.[122]? Such studies could be performed on a Dielectric Thermal Analyzer (DETA) with different blend compositions of both melt and solution blends.

Do the blends have good mechanical properties? Mechanical testing by stress-strain analysis could be performed to determine how the modulus and toughness vary with composition, and at which blend composition these mechanical properties are optimized.

Finally, it would be of interest to determine if the piezoelectric and pyroelectric properties of the blends were better or worse than that of pure PVDF. One problem with pure PVDF is its high crystallinity which prevents major changes in the attainable degree of crystallinity. Therefore, the piezoelectric properties can only be altered by orienting the amorphous phase by uniaxial or biaxial drawing[72]. By blending PVDF with another piezoelectric polymer, PHB, the properties of the amorphous phase can be altered more dramatically. If PVDF favors an extended chain conformation in the amorphous phase in order to maximize the number of possible contacts with PHB, the piezoelectricity of the amorphous phase will increase. The pyroelectric
coefficient could be obtained by subjecting the sample to heating and cooling cycles and measuring the resulting current density with the same technique.
Bibliography


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VITA

Sharon Cooper, daughter of Dan and Margaret Edie, was born in Sandusky, Ohio on July 22, 1967. She spent most of her childhood in Clemson, South Carolina. In 1985, she graduated from D. W. Daniel High School, and the following August, she started at the University of Virginia in chemistry. After taking an advanced physical chemistry course from Dr. Schatz at UVa and doing an internship at Hoechst-Celanese in polymers the summer after her third year, she decided to go to graduate school in polymer characterization. In May of 1989, she graduated from UVa with a Bachelor of Science in Chemistry and in August she began her graduate work under the supervision of Dr. Hervé Marand at Virginia Tech. Her graduate research efforts have been focussed on the characterization of blends of poly(vinylidene fluoride)/poly(3-hydroxybutyrate).

Sharon met her husband, Kevin Cooper, at Virginia Tech, they married in June 1991, and moved to Annandale, Virginia in August, 1991. She has accepted a position as a staff chemist at the Merck Sharp & Dohme Research Laboratories in Rahway, New Jersey.

Sharon Edie Cooper