Study of the crystallization behavior of polyethylene oxide in compatibilized and uncompatibilized polypropylene/polyethylene oxide blends

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STUDY OF THE CRYSTALLIZATION BEHAVIOR OF POLYETHYLENE OXIDE IN COMPATIBILIZED AND UNCOMPATIBILIZED POLYPROPYLENE/POLYETHYLENE OXIDE BLENDS

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A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Material Science and Engineering

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Study of The Crystallization Behavior of Polyethylene oxide in Compatibilized and Uncompatibilized Polypropylene/Polyethylene Oxide Blends.

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Abstract

Compatibilization of incompatible isotactic polypropylene (iPP)/polyethylene oxide (PEO) is studied with an emphasis on the crystallization behavior of polyethylene oxide. An attempt is made to correlate the crystallization data for PEO obtained from optical microscopy, differential scanning calorimetry, x-ray diffraction, infrared spectroscopy and dynamic mechanical analysis.

PEO and iPP are incompatible in the temperature range -50°C to 200°C. iPP was used as the matrix while PEO was used as the dispersed phase. Experimental observations demonstrated that PEO underwent fractionated crystallization in the blends in the temperature region from -10°C to 40°C when cooled at a rate of 10°C/min. PEO domains nucleated homogeneously as well as heterogeneously in these blends. Larger domains (30-100 microns) crystallized at higher temperatures (heterogeneous nucleation), while smaller domains (10-60 microns) crystallized at lower temperatures (homogeneous nucleation). Heterogeneous nucleation occurred both thermally, and athermally. The graft copolymer, polypropylene-graft-maleic anhydride-graft-polyethylene glycol was used to increase compatibility between iPP and PEO. Three blends systems were studied; iPP and PEO, polypropylene-graft-maleic anhydride and PEO and polypropylene-graft-maleic anhydride-graft-polyethylene oxide and PEO. An increase in the concentration of PEO in the blends increased its crystallinity. However there was a decrease in the crystallinity of PEO, as the blends were made more compatible. This behavior of PEO was observed both by optical microscopy differential scanning calorimetry. Results from x-ray diffraction, however, showed an increase in the crystallinity of PEO relative to iPP as compatibility between the blends increased. The
compatibilizer reduced the size of the dispersed phase thus increasing compatibility between iPP and PEO. There was clustering of small PEO domains in the compatibilized blends. Heterogeneous nucleation can be seen only for the 30% PEO concentration of the uncompatibilized blends. The melting point of PEO in the blends was depressed, while that of iPP was the same as the pure polymer. PEO domains existed as spherical droplets in the melt. The crystallization temperatures for PEO were higher when seen through optical microscopy as compared to differential scanning calorimetry. Results from infrared spectroscopy revealed a change in the nature of the spectra for iPP and PEO in the blends as compared to the pure spectra. The infrared spectra of the blends are distinctly different from the coadded spectra of iPP and PEO. Spectroscopy also revealed a change in the composition or structure of PEO in the blends from the targeted compositions. Mechanical analysis revealed a change in the nature of the graph of the loss modulus versus temperature, as the blends are made compatible. Crystal rearrangement of both iPP and PEO is seen as the blends were heated in the temperature range from -50°C to 100°C.
This work is dedicated to
my mother V.S. Ananthalakshmi.
To all the friends and teachers who supported me
Thank You
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Chapter 1

INTRODUCTION

1.1. REVIEW:

In 1994, Tao Tang and Baotong Huang\textsuperscript{1} investigated the compatibilization of incompatible isotactic polypropylene/polyethylene oxide blends and the crystallization behavior of these blends. The experimental results showed that the graft copolymer [(PP-MA)-g-PEO] of maleated PP (PP-MA) and mono-hydroxyl PEO (PEO-OH) was a good compatibilizer for the PP/PEO blends. PP-MA also had some compatibilization in these blends. The crystallization of the blends was affected by the compatibility between PP and PEO. The interfacial behavior of the compatibilizers had an important effect on the crystallization behavior of the PP/PEO blends. PEO exhibited fractionated crystallization in the PP/PEO blends. This behavior was studied from the viewpoint of the theory of fractionated crystallization.

The compatibilization mechanism of (PP-MA)-g-PEO was explained as follows: the PP segment cocrystallizes with the bulk PP; the PEO segment has two kinds of interactions with the bulk of PEO — cocrystallization between the PEO segments and the bulk PEO, and charge transfer between MA and PEO. On this basis it was inferred that the PP-MA also had some compatibilization in the PP/PEO blends. The improvements in the compatibility between PP and PEO mutually increased their nucleation, and consequently, the crystallization rate of the two respective components. PEO underwent fractionated crystallization in the PP/PEO blends.

In October 1995, T. Kowalewski and E. Martuscelli\textsuperscript{2} investigated the stable two-stage system of iPP and PEO in which the polyethylene oxide fraction could be either in
molten or in the crystallized states within the temperature range from 273 K to 327 K. The behavior of the blends system was interpreted on the basis of fractionated crystallization.

The results of these studies indicated that the crystallization behavior of PEO dispersed in the iPP matrix depends mainly on the concentration of the dispersed phase. The polypropylene matrix did not exhibit nucleating activity towards PEO and it was regarded inert with respect to crystallization of PEO.

In the above mentioned study it was found that at small PEO concentrations (PP/PEO, 9:1), the size of the PEO domains was small enough to suppress heterogeneously nucleated crystallization. Under these circumstances, crystallization of PEO was possible only through a homogeneous mechanism at high degrees of supercooling (about 70°C). With increasing concentration of PEO in the blend, PEO particles underwent strong coalescence, which led to an increase in the PEO domain size. At this point heterogeneous nucleation became effective in initiating crystallization and a large fraction of PEO crystallized close to room temperature. Since heterogeneous nucleation could be suppressed, blends with a fine dispersion of PEO were considered suitable as a stable two stage opaque-transparent system in which the PEO could either be in molten or the crystallized form in the temperature range 273 K to 327 K. The transition from transparency to opacity is initiated from the molten state of PEO by cooling it down to 273 K. The melting of the crystallites at 333 K leads to an opaque-transparent transition.
1.2. CRYSTALLIZATION OF iPP:

Since isotactic polypropylene became commercially available in 1958, the crystalline architecture and crystallization of iPP from melt and solution have been topics of interest. Because of the presence of the pendant methyl group, PP exhibits tacticity. In addition to iPP there has been renewed interest in syndiotactic polypropylene. The crystal structure and the crystallization behavior of iPP are dependent on the molecular weight and the tacticity of the polymer chain.

Each iPP chain molecule possesses a chain conformation with a 2x3/1 helix. Since the presence of asymmetrically substituted methyl groups causes the rotation around the backbone bonds to be direction dependent, both right-handed and left-handed helices with stereoisomer configurations of d and l are possible. Combination of these possibilities leads to 4 distinguishable chain conformations. The intramolecular interaction energies of all four types of helices are identical. Their intermolecular interaction however, depends upon crystal packing and geometry. The best packing is achieved when the nearest neighbors of right-handed helices are the enantiomorph left-handed helices and vice versa. Different packing geometries lead to 4 distinct crystal structures: the monoclinic (α form), the hexagonal (β form), the triclinic (γ form) and a quenched form. Some reports have also proposed the existence of a δ form. Among these structures the monoclinic (α) form is the most common, being formed in the typical melt-crystallized and solution crystallized iPP samples. iPP is unique in adopting only the two enantiomeric chain conformations; the right and left handed three-fold helices to form 4 different crystal geometries.
1.2.1. Monoclinic lattice of α-iPP:

Von Falkai and Stuart\(^4\) obtained the first consistent data on the primary nucleation of α-iPP. The nucleation in their experiments was found to be heterogeneous and instantaneous with a calculated Avrami exponent close to 3. The change from instantaneous to sporadic nucleation has been reported in the literature for samples heated to 200°C and above. Under such conditions, polarized light microscopy examination revealed an initial constant nucleation rate, decreasing for longer crystallization time. The Avrami type of fit to the integral exponent was not satisfactory in this case.

The course of primary nucleation in isotactic polypropylene down to 70°C was first demonstrated by Burns and Turnbull and by Koutsky, Walton and Baer, employing the droplet technique originally developed by Vonnegut for tin and water droplets. Four distinct regions can be recognized in the nucleation of molten isotactic polypropylene.

- Immediately below the DSC determined melting point there is a gap in which the crystal nucleation hardly occurs. Neither heterogeneities nor nucleating agents can accelerate the nucleation in this region.

- Most spherulites (birefringent entities made up of several crystallites) are nucleated in the temperature range below 150°C and above 115°C. This is the extended region of activity of heterogeneous (instantaneous) nucleation. Here, the number of nuclei is limited during crystallization.

- Some heterogeneous nuclei become active at even lower temperature, which follows from their smaller size or lower perfection. These nuclei are also limited in number.
Finally, around 80°C and below there is a region of homogeneous (sporadic) nucleation. The number of nuclei in this region increases rapidly with decreasing temperature.

Except for very thin specimens, it is difficult to reach beyond the upper range of activity of heterogeneous nucleation in polymers. This is because of the low thermal diffusivity of polymers, their intense nucleation and fast spherulite growth at lower temperatures. In addition, the latent heat of fusion liberated by the rapid crystallization during quenching tends to maintain the temperature during the crystallization in the upper range of activity of heterogeneous crystallization. This and the instantaneous character of most heterogeneous nucleation events mean that the homogeneous nucleation range is very rarely reached, and many polymeric objects in technological applications result from only heterogeneous nuclei.

The crystal lattice parameters\(^5\) for α-iPP are reported to be:

\[
\begin{align*}
a &= 0.6666 \text{ nm} \\
b &= 2.078 \text{ nm} \\
c &= 0.6495 \text{ nm} \\
\alpha &= \gamma = 90^\circ \\
\beta &= 99.62^\circ
\end{align*}
\]

α-iPP exhibits a monoclinic lattice with 12 repeat units in each unit cell and has a crystallographic density of 0.946 g/cc.

Under the processing conditions used in our laboratory to make the samples, it was found that iPP crystallized into the α-form.

**1.2.2. Hexagonal lattice of β-iPP:**

Early wide-angle x-ray diffraction (WAXD) studies determined that two reflections at d spacings of 0.553 nm and 0.417 nm were exhibited by the β-form of iPP.
These two peaks were believed to fit into a hexagonal lattice structure with \( a = 1.908 \) nm, 
\( c = 0.649 \) nm, \( \gamma = 120^\circ \), and \( \alpha = \beta = 90^\circ \), similar to the case of the \( \alpha \)-form. Samuels and Yee\(^5\) confirmed this. The crystallographic density was found to be 0.921 g/cc\(^6\).

It is however difficult to determine the crystal unit cell of the \( \beta \)-form because it is less thermodynamically stable than the \( \alpha \)-form under normal crystallization conditions. In most cases, the \( \beta \)-form can only be partially formed in samples, mixed with other crystal forms. The preparation of a phase rich in the \( \beta \)-form has been reported through rapid quenching, zone solidification, crystallization in a temperature gradient, or through the use of nucleating agents. It was also found that during drawing, the \( \beta \)-form could be transformed into the \( \alpha \)-form at high temperatures, close to the melting temperature of the bulk sample\(^7\). The transformation of the \( \beta \)-form into the \( \alpha \)-form can also be carried out by melt recrystallization at elevated temperatures close to the melting temperature of the bulk samples.

### 1.2.3. Triclinic lattice of \( \gamma \)-iPP:

The crystal structure and the unit cell geometry of the \( \gamma \)-form of iPP are known only approximately, but bear a strong resemblance to those of the \( \alpha \)-form. The proposed triclinic unit cell parameters are\(^8\) \( a = 0.654 \) nm, \( b = 2.14 \) nm, \( c = 0.650 \) nm, \( \alpha = 89^\circ \), \( \beta = 99.6^\circ \), and \( \gamma = 99^\circ \). The crystallographic density was reported to be 0.954 g/cc. This unit cell appears to result from the monoclinic \( \alpha \)-form by a simple shear along the \( a \) axis. The chain arrangement in the two forms is probably analogous.
The γ-form can be observed in low molecular weight iPP or crystallization of iPP at elevated pressure, above 200 MPa. However, in most cases one may find the coexistence of the α and γ-forms in the crystals. The γ-form is known to nucleate the crystals of the α-form, but the crystallographic relationship between these two forms is still not fully understood. The γ-form crystals display screw dislocations. The γ-form crystal overgrowth reflects the mirror symmetry that exists at the molecular level in the α-form crystals. Since the γ-form crystals have their lamellar surface inclined to the chain axis, while for the α-form crystals it is perpendicular to it, γ-form crystals grown on α-form crystals appear to branch. However, branching results only from the difference in crystal morphology, and it does not result for the different orientation of the α and the γ-form. The thermodynamic properties of this form have not been well studied.

1.2.4. Quenched form of iPP:

The crystals grown during the quenching of iPP are the least understood. Rapid quenching of iPP fails to produce totally amorphous samples even when the cooling rate is as high as 10000°C/min. Natta and Corradini\(^9\) described this structure as smectic and suggested that it is composed of parallel 2 x 3/1, helices but that disorder exists in the packing of the chains perpendicular to their axes. The local correlations between chains are probably closer to those in the α-form than to those in the β-form. Because of the metastability of this form, no equilibrium thermodynamic properties have been reported.
1.3. CRYSTALLIZATION OF POLYETHYLENE OXIDE:

The thermal properties, crystalline morphology and crystallization kinetics of polyethylene oxide have commanded much attention in the past three decades. It has been one of the most extensively studied crystalline polymers. In particular, the melt crystallization of PEO fractions in its low molecular mass range has been of interest\(^{10}\).

A significant portion of the crystallization temperature range of PEO is experimentally accessible. At low to intermediate supercooling, crystallization from the melt yields large distinct spherulites that are easily observed in thin films using polarized light microscopy (PLM). As a result, the crystallization kinetics and morphology of PEO spherulites have been examined in the pure state as well as in numerous blends with other polymers. Yet there remain fundamental questions regarding the crystallization and the melting behavior of this polymer.

PEO has a monoclinic crystal structure with the following crystal parameters\(^{11}\):

\[
\begin{align*}
a &= 8.05 \text{ nm} & \beta &= 125.4^\circ \\
b &= 13.04 \text{ nm} \\
c &= 19.48 \text{ nm}
\end{align*}
\]

It has a crystal density of 1.229 g/cc.

In 1982, R. C. Allen and L. Mandelkern\(^{12}\) studied the morphology of PEO for different molecular weights ranging from \(6 \times 10^3\) to \(1 \times 10^7\) g/mol. Their studies indicate that spherulites are formed at high molecular weight and high supercooling. The morphological character gradually changes to hedrites (polyhedral structures consisting of several lamellae stacked together) at low molecular weights and low undercoolings via an intermediate state for which no precise morphological assignment can be made. They
also found that at very high molecular weights (> 100000 g/mol) and at very high supercoolings (below 0°C) no discernible structure could be seen. The following diagram, taken from the same reference, shows the morphological map for PEO. The dashed line indicates the limit of isothermal crystallization.

Figure 1.1: Complete morphological map of PEO containing both nonisothermal and isothermal crystallization conditions. The regions of different supermolecular structures are indicated.
1.4: OBJECTIVE:

My thesis deals with the investigation of crystallization behavior of PEO in compatibilized and uncompatibilized iPP/PEO blends. Optical microscopy (OM), differential scanning calorimetry (DSC), wide-angle x-ray diffraction (WAXD), infrared spectroscopy (IR) and dynamic mechanical analysis (DMA) will be used to characterize these blends. An attempt is made to correlate the crystallization data for PEO obtained from these characterization techniques.

Previous work included the study of iPP/PEO systems without compatibilizer and using compatibilizer in small percentages (5%). The goal of my thesis was to prepare and use the compatibilizer as one of the blend components. The objective was to reduce the size of PEO domains to suppress the heterogeneous nucleation of PEO at higher mass fractions of PEO than previously reported. With the help of optical microscopy and differential scanning calorimetry we hope to gain insight into the relationship between the domains size and the crystallization behavior of PEO. Infrared spectroscopy was used to determine the composition of the blends and to compare the crystallinity of PEO for different blends. Since dynamic mechanical analysis is more sensitive to transitions in polymers, it was used to obtain information about the secondary transitions in these blend systems.
Chapter 2

THEORY OF CRYSTALLIZATION

2.1. GENERAL NUCLEATION AND GROWTH CONCEPTS

The reason for supercooling and the need for nucleation can be found by analyzing the crystallization process. Any crystal must have its beginning as a small crystal with a large specific surface area. The specific surface free energies are positive for all temperatures of interest to crystallization. Owing to their large size and diverse structure, polymers are subject to different types of nucleation and crystal growth processes. Nucleation processes are often categorized as primary, secondary and tertiary nucleation. These are discussed below.

2.1.1. Primary Nucleation:

The initial process leading from an amorphous state to a growing crystal state of a polymer is known as primary nucleation. Before a thermodynamically stable crystal of sufficient size can be grown, a primary nucleus must be formed with a positive Gibbs free energy. The maximum in $\Delta G$ corresponds to the critical size nuclei. The free enthalpy barrier to crystallization can only be overcome by local, random structure fluctuations. The larger the required size of the nuclei, the longer will be the time required for the nucleation process.

Primary nucleation is called homogeneous nucleation if no preformed nuclei or foreign surfaces are present. A foreign surface frequently reduces the nucleus size needed for crystal growth since the creation of the interface between the polymer crystal and the substrate may require less activation energy than the creation of the corresponding free
polymer crystal surface. The resulting enhanced nucleation process is called heterogeneous nucleation. Heterogeneous nucleation involves a two dimensional growth of the nuclei on a substrate (different from the polymer surface). A special type of primary nucleation is called self-nucleation. This term describes primary nucleation caused by polymeric crystals, which are chemically identical to the crystallizing polymer, but have survived a prior dissolution or melting step.

Primary nucleation can give rise to crystals of equal or varying sizes. The former indicates that all the crystals started growing at the same time (i.e. athermal or instantaneous nucleation); the latter indicates that new crystals are nucleated throughout the time period required for crystallization. This is referred to as thermal or sporadic nucleation. Heterogeneous nucleation may be either athermal or thermal. Since the number of nuclei are limited, however, thermal nucleation of heterogeneous origin must level off after all nuclei are exhausted. Usually self-nucleation appears to be athermal. Any sample may be subject to multiple nucleation processes. However, identification of the process on the basis of the observation of athermal and thermal nucleation is not possible. Only if a more detailed morphology is visible, can additional conclusions can be drawn about homogeneous or self-nucleation on one hand and heterogeneous nucleation on the other hand.

Self-nucleation is used as a general term in describing nucleation of a macromolecular melt or solution by its own previously grown crystals. Macromolecules are particularly well suited for self-nucleation because of the large temperature range over which the crystals melt, yet the nucleated melts do not crystallize. This behavior of macromolecules is explained on the basis of molecular nucleation phenomenon. Crystals
for self-nucleation can also be created on deformation, which shifts the melting point of macromolecules to higher temperatures, due to rubber elasticity effects. Finally it was proposed that crystal fragments grown in small cracks of a foreign surface may have an elevated melting point and thus survive the initial dissolution or melting of the bulk of the polymer, serving as nuclei on subsequent cooling.

![Diagram of crystal nuclei](image)

Figure 2.1: Types of crystal nuclei\(^\text{13}\).
(a) Primary Nucleus, (b) Secondary Nucleus, (c) Tertiary Nucleus

2.1.2. Secondary and Tertiary Nucleation:

There is direct morphological evidence that secondary nucleation is of importance for macromolecular crystal growth\(^\text{13}\). In addition, crystallization rates of macromolecular melts exhibit the temperature dependence predicted by theory. In its simplest form, the theory of secondary nucleation treats growth from both dilute solution and the melt as the adjacent, sequential addition of strands or stems, across an otherwise molecularly flat growth surface. Secondary nucleation is the growth of a polymer crystal on preexisting polymeric surface. It is also assumed that the entire molecular layer is laid down before the next layer commences. It is shown, however, that molecular nucleation has the same temperature dependence and may be the crystallization rate determining step. The tertiary
nucleation concept is of little importance for small molecules. It can be defined as the creation of crystals by addition of the crystallizing unit to a smooth ledge. Its formalism has found application in the description of simplified models of chain folded crystallization. Figure 2.1 (b), and (c) represent secondary and tertiary nucleation concept.

2.2. CRYSTALLIZATION THEORIES:\[^{14}\]

Depending on the origin of the nucleus there are two types of crystallization. These are homogeneous and heterogeneous crystallization. Primary homogeneous nucleation causes homogeneous crystallization in polymers, while primary heterogeneous nucleation causes heterogeneous crystallization. The crystal fraction in a polymer is a function of both the nucleation rate and the growth rate of the spherulite in the sample.

Heterogeneous crystallization occurs in the presence of impurities. It involves two-dimensional growth of a nucleus on an already existing substrate. The Avrami equation for the crystal fraction for a spontaneous heterogeneous crystallization is given by the expression

\[
x_c = 1 - \exp\left(-4\pi(Gt)^{3/2}N/3\right)
\]

where, \( G \) is the growth rate of the spherulite.

\( N \) is the nucleation site density.

\( x_c \) is the crystal fraction.

\( t \) is the time since the nucleation event.
In the case of homogeneous crystallization a surface must be formed by the development of a cylindrical bundle from the quiescent melt. The crystal fraction in the case of homogeneous crystallization, under isothermal conditions is given by,

$$x_c = 1 - \exp \left(-\frac{\pi \eta}{3} \frac{t}{T_m}\right)$$

where, $\eta$ is the nucleation rate per unit volume for making 3 dimensional nuclei.

Three basic regimes of crystallization have been proposed based on both experimental and theoretical grounds\textsuperscript{15}. These three regimes are proposed for heterogeneous crystallization. Fundamentally, a regime transition occurs when the relationship between the growth rate and the surface nucleation rate undergoes a change. In the highest temperature regime (labeled regime I), the observable growth rate,

![Figure 2.2: Plot showing regime behavior in Polyethylene oxide of Molecular weight $= \bullet$, 23000, $\Delta$, 56300, $\bullet$, 105000 g/mol$^9$.](image-url)
G varies as i, the surface nucleation rate. Here one surface nucleus causes completion of a layer of length L on the surface. In the next lower temperature regime, called regime II, multiple nucleation occurs on the substrate and the growth rate varies as the nucleation rate ‘i’, raised to the power half (G \approx i^{1/2}). This leads to the downward break in the growth rate as one passes through a regime I \rightarrow regime II transition when the isothermal crystallization temperature has been lowered. *Figure 2.2* represents the different regimes for polyethylene oxide for three different molecular weights. At still lower temperatures, the mean separation of the nuclei on the substrate approaches the width of the molecular stems, and here regime III is entered; in this regime again G \propto i, so that at the regime II \rightarrow regime III transition an upward break in the growth rate curve is observed.

The radial growth rate, G, of lamellar polymer spherulites or axialites is dependent on the difference between the crystallization temperature and equilibrium melting temperature appropriate to the chain length under consideration, this difference being denoted as \Delta T. The growth rate of polymers during crystallization is then described within a given regime by the equation

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

where, \(G_0\) is the preexponential factor combining quantities not strongly dependent on temperature, yet dependent on the molecular weight,

- \(K_g\) is the nucleation constant, and is dependent on the growth regime,
- \(U^*\) is the energy required for molecular reptation.
- \(T_\infty\) is the temperature, at which chain reptation requires infinite time,
- \(\Delta T = T_m - T\), \(T_m\) being the melting temperature of the polymer, and
- \(T\) is the crystallization temperature of the polymer.
The nucleation rate ‘i’ and the reptation rate ‘r’ (minimum chain length of the polymer which repeats itself in a crystal) is a continuous function of the temperature in all the three regimes and is controlled by an expression which is of the form, \( G \propto i \propto \exp[-U^*/R(T-T_m)] \exp[-K_s/T\Delta T] \). The quantity \( i \) increases rapidly with increasing undercooling \( \Delta T \) at growth temperatures near the melting point as given by the second exponential factor. The distinction between the three regimes in polymer crystallization is a function of the degree of undercooling and depends on the basic relationship between the nucleation rate \( i \) and the overall growth rate \( G \) at various temperatures.

### 2.3. COCRYSTALLIZATION\(^{16} \):

The term cocrystallization refers to crystallization of two crystalline polymers in the same lamellar crystal. For this process to occur, polymers must exhibit a measure of melt miscibility, their repeat unit chemistry must be similar and their crystalline unit cells must have similar lattice parameters. As a result of these restrictive criteria, true cocrystallization is a very rare phenomenon. Cocrystallization has been relatively well established in only a small number of polymer blends. The more rapid the solidification, the greater the probability of cocrystallization. In melt miscible blends, it is inevitable that one of the components of the blend crystallizes first and tends to nucleate the other component. In phase-separated blends, the most plausible explanation for enhancement in crystallization is that crystals on the phase boundaries serve as nucleation sites for the other component.

In 1996, Balijepalli S. and Schultz J. M.\(^{17} \) carried out crystallization studies on blends of high and low molecular weight polyethylene oxide to characterize phase
behavior and morphology. At low crystallization temperatures, it was found that both components cocrystallized into a common crystal lattice. The thickness of the cocrystal was found to vary with the blend composition. At high fractions of the low molecular weight polymer, the cocrystals were thin, suggesting a folding of the long-chain polymer into the lattice of the low molecular weight chain. At lower fractions of the low molecular weight polymer, the cocrystals were thicker, resembling those of the higher molecular weight polymer. At higher crystallization temperatures, the components formed a defective cocrystal, which dynamically phase split into its components. The crystal transformation in the blend occurred by thinning of the low molecular weight chain lamellae and thickening of high molecular weight chain lamellae. The formation of crystal templates of both components eventually resulted in phase-segregated growth. A time-resolved small-angle X-ray scattering study along with complementary calorimetry and optical microscopy results confirmed the mechanism of cocrystallization and dynamic phase separation in these PEO blends.
3.1. MATERIALS:

Isotactic Polypropylene (i-PP) \( (M_w = 190000 \text{ g/mol}, \ M_n = 50000 \text{ g/mol}) \) and Polypropylene-graft-maleic anhydride (PP-g-MA) \( (0.6\% \text{ by weight maleic anhydride}) \) were obtained from Aldrich Chemicals. Polyethylene oxide (PEO) \( (\text{Molecular weight } M_w = 35000 \text{ g/mol}, \ M_w/M_n = 1.8) \) and Polyethylene glycol \( (\text{Molecular weight } = 600 \text{ g/mol}) \) was obtained from Polysciences. Poly(ethylene glycol) bis-(3 aminopropyl) terminated and fluorescein were also obtained from Aldrich Chemicals. Xylene and hexane (reagent grades) were used as the solvent and non-solvents respectively and were obtained from Bayer Chemicals and Fischer Chemicals, respectively. Acetone was obtained from Aldrich Chemicals.

\[
\begin{align*}
\text{CH}_3 \\
\big(\text{CH}_2\text{-CH-CH-}\big)_n \\
\text{Isotactic Polypropylene}
\end{align*}
\]

\[
\big(\text{CH}_2\text{-CH}_2\text{-O}\big)_n \\
\text{Polyethylene oxide}
\]

Polypropylene-graft-maleic anhydride was used as one of the components of a blend, as well as to make a compatibilizer for the iPP/PEO system. The anhydride linkage in PP-g-MA was susceptible to condensation in the presence of a catalyst and was used to chemically link a low molecular weight polyethylene glycol \( (\text{Mol. wt. } = 600 \text{ g/mol}) \) to the main chain (by way of an ester linkage, leaving a carboxylic acid). This was done to increase the compatibility between PP and the PEO and to achieve better dispersion of PEO in the iPP matrix.
The reaction was carried out by dissolving 5 gms PP-g-MA in 100 ml xylene at 80°C with a 10 weight % excess of PEG (on the basis of maleic anhydride groups), for 45 minutes. AlCl₃ (0.1 wt%) was used to drive the reaction. This solution was precipitated with excess acetone to remove the excess polyethylene glycol and to precipitate the polymer. Results from the DSC illustrated that there were no residual traces of polyethylene glycol in the sample. This was then used as one of the components in the blend. The completion of the reaction was confirmed by infrared spectroscopy (Appendix Figure A.I). The graft copolymer has the following structure:

![Polypropylene-graft-maleic anhydride (PP-g-MA)](image)

Polypropylene-graft-maleic anhydride-graft-polyethylene glycol (PP-g-MA600)

All the blends were prepared by dissolving the polymers in hot xylene (5 gm blend/50mls xylene) at 80°C for 45 minutes and precipitating in cold hexane (3:1 hexane:xylene ratio). The powdered precipitate was then filtered and kept in a vacuum
oven at 60°C for 24 hours, to evaporate the solvent completely. These samples were then analyzed by different characterization techniques.

The following blends were prepared:

<table>
<thead>
<tr>
<th>BLEND COMPOSITION</th>
<th>RATIO (WT %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP/PEO</td>
<td>90:10</td>
</tr>
<tr>
<td>PP/PEO</td>
<td>80:20</td>
</tr>
<tr>
<td>PP/PEO</td>
<td>70:30</td>
</tr>
<tr>
<td>PP-g-MA/PEO</td>
<td>90:10</td>
</tr>
<tr>
<td>PP-g-MA/PEO</td>
<td>80:20</td>
</tr>
<tr>
<td>PP-g-MA/PEO</td>
<td>70:30</td>
</tr>
<tr>
<td>PP-g-MA600/PEO</td>
<td>90:10</td>
</tr>
<tr>
<td>PP-g-MA600/PEO</td>
<td>80:20</td>
</tr>
<tr>
<td>PP-g-MA600/PEO</td>
<td>70:30</td>
</tr>
</tbody>
</table>

Table 3.1: List of blends of compatibilized and uncompatibilized PP/PEO blends prepared and used for sample analysis.

To confirm the ratio of the polymers in the blend, PP and PEO were individually dissolved in xylene at 80°C for 45 minutes and crashed out in cold hexane. The percent yields of the precipitate were found to be 97.6% for PEO and 98% for i-PP. From these experiments it was concluded that the blends made in the lab were very close to the target compositions listed above.

In order to observe the melt miscibility, the PEO phases in the blends were stained with fluorescein. The amine terminated PEG (1 gm) was reacted with a 3 weight
% excess of fluorescein, in the presence of AlCl$_3$ catalyst, in n-butanol at 40°C for 30 minutes. This labeled PEO was used in solution form. A small amount of this solution was added to the 80:20 compatibilized and uncompatibilized blends of PP/PEO, while in hot xylene.

3.2. CHARACTERIZATION TECHNIQUES:

3.2.1. Optical Microscopy:

Optical microscopy was used to determine the melt miscibility of the blends and to observe the relationship between the domain size and the mode of nucleation of the dispersed phase. The Nikon E600 POL with an Instec hot-stage and liquid nitrogen attachment was used to analyze the blends.

Samples for the optical microscope were made by smearing a small amount of the powdered blends onto a microscope slide at 200°C and placing a cover slip over the samples. All samples were quenched in a liquid nitrogen bath to inhibit crystallization of the continuous phase. This was done so that the crystallization of the dispersed phase (PEO) could be easily seen under the microscope in transmission mode under cross-polarized light.

To observe the crystallization behavior of PEO in the blends, the slides were heated on the hot stage of the microscope to 90°C for 5 minutes and then cooled at a rate of 10°C/min.
3.2.2. Differential Scanning Calorimetry:

Differential scanning calorimetry (DSC) is a characterization technique used to obtain melting and crystallization data for polymers. The DSC measures the difference in power required to maintain a sample and reference pan at the same temperature. This difference in power directly relates to the transition enthalpies of the polymer. It can also be used to determine the percentage crystallinity of polymers by comparing the enthalpy for melting to that of a pure crystalline polymer. The DSC2010 with a liquid nitrogen cooling system by TA Instruments was used to analyze the blends.

The samples for the DSC were prepared by the following method. About 5-10 mg of the powdered blends were added to a hermetic aluminum pan. The pan was sealed with an aluminum cover. This was the sample pan. A reference pan was made with the aluminum pan without any sample in the pan. These two were then placed into the furnace in the DSC and the furnace was closed. A steady nitrogen flow of 50 ml/min. was maintained in the DSC chamber. The DSC runs were carried out at three different cooling rates: 5°C/min, 10°C/min and 20°C/min. A constant heating rate of 10°C/min. was used to run the samples. The blends were analyzed in the temperature range between -60°C - 200°C. All the blends were run in a heat-cool-heat cycle to see the effect of different cooling rates on the subsequent melting behavior of the blends.

3.2.3. X-ray Diffraction:

X-ray crystallography has been widely used to determine crystal structures in polymers and to observe the purity of crystals. If a polymer is polymorphic, x-ray diffraction may be used to show which crystal phases are present. I am grateful to Dr.
Gupta (Department of Mechanical Engineering, RIT) for allowing me to use the Rigaku Geigerflex x-ray diffractometer in his Materials Testing Lab.

Samples for x-ray analysis were prepared by coating a thin layer of the finely powdered blend onto a microscope slide with adhesive. This was then placed in the slot provided in the instrument and used for analysis. Copper K-alpha ($\lambda = 1.54 \text{ Å}$) was used as the source.

3.2.4. Infrared Spectroscopy:

Infrared spectroscopy is a characterization technique widely used for polymers. It was used to determine the blend composition and the crystal quality in the iPP/PEO blends. It was also used to determine the percentage crystallinity in the samples. The Biorad Excalibur Series FTS 3000 was used to analyze the blends.

Samples for IR spectroscopy were made by solution casting blend films from xylene on KBr salt plates. A background was run of the salt plates. The salt plates with the cast films were then mounted in the instrument and transmission IR was run on these samples in the wavenumber range 7000-350 cm$^{-1}$. The resolution was set at 4 cm$^{-1}$ and the number of scans for each run was selected to be 64.

To determine the concentration of the components in the blend, standard blends of PP: PEO were made in the compositions listed below:

<table>
<thead>
<tr>
<th>Polypropylene (wt%)</th>
<th>65</th>
<th>70</th>
<th>75</th>
<th>80</th>
<th>85</th>
<th>90</th>
<th>95</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyethylene oxide (wt%)</td>
<td>35</td>
<td>30</td>
<td>25</td>
<td>20</td>
<td>15</td>
<td>10</td>
<td>5</td>
</tr>
</tbody>
</table>

Table 3.2: Standards of Polypropylene and Polyethylene oxide made for IR analysis.
The solution for casting films was prepared by dissolving 0.1 gm of the polymer in 10 ml of xylene. The solution was heated to 80°C to dissolve the polymer and was then cast on the salt plates while hot. The solvent was allowed to evaporate before running the samples (IR spectra of the blends did not reveal the presence of any xylene in the sample). The blend samples were run twice; once by cooling down the samples to room temperature and the second time by freezing the samples. The samples were frozen to allow crystallization of small PEO domains.

3.2.5. Dynamic Mechanical Analysis:

Dynamic mechanical analysis is used to determine thermal and mechanical transitions in polymers as a function of a change in frequency of vibration or a change in temperature. The DMA200 by Seiko Instruments with a liquid nitrogen system was used to analyze the blends.

Pellets of the powdered blends were prepared by compressing 0.75 gm of the blends into a cylindrical mold with a vacuum attachment. These pellets were then sandwiched between chemwipes, and, in turn between Teflon coated aluminum sheets. This assembly was heated on a hot plate at 200°C and a load of 5 kgs was applied. The pellets were allowed to melt and form composite sheets. The laminates were cooled to room temperature and then samples for the DMA were cut out from these laminates. Samples of 20mm x 5mm x 0.7mm, were cut out from the laminates and used for testing.

The samples were then run on the DMA in the temperature range from -50°C to 100°C at various frequencies ranging from 0.01 Hz to 50 Hz. The experiments were carried out in 30 isothermal steps in the temperature range specified.
Chapter 4

RESULTS AND DISCUSSION

4.1. OPTICAL MICROSCOPY:

From optical microscopy studies, it was apparent that the dispersed PEO phase crystallized in two temperature ranges; one around 35°C and another one around 10°C. It was observed that the crystallization at 35°C diminished as the concentration of PEO in the blends was decreased. The same effect was also observed, as the blends were compatibilized with iPP. Results from the study showed that larger regions tended to nucleate at higher temperatures while the smaller PEO domains tended to nucleate at lower temperatures. The domain size of the dispersed phase was found to vary from 10 microns to 100 microns depending on the concentration of PEO in the blends and the presence or absence of a compatibilizer.

According to Turnbull and Cech\(^\text{18}\), the equilibrium melting temperature of any polymer is linked to the homogeneous crystallization temperature by the approximation;

\[
T_c^{(0)} - T_{h0} = \frac{T_c}{5}
\]

Where, \(T_c^{(0)}\) is the melt/crystal equilibrium temperature,

\(T_c\) is the actual melting temperature of the polymer, and

\(T_{h0}\) is the temperature for homogeneous crystallization of the polymer.

Using values of \(T_c^{(0)}\) 349 K\(^\text{19}\) and \(T_c\) of 343 K, \(T_{h0}\) is found to be 279.5 K (6.5°C). Therefore any crystallization that occurs below 6.5°C is expected to proceed by homogeneous nucleation.

It was also observed that the crystallization around 35°C occurred sporadically (thermally) i.e., the nuclei were initiated at different times. The crystallization of smaller
domains at lower temperatures was found to be rapid and there was a critical temperature at which most spherulites were nucleated. At low PEO concentrations (10%), crystallization was negligible and it was difficult to pick up the crystallization in the PEO domains as observed under the microscope.

Figure 4.1 is a micrograph of a 70:30 PP/PEO blend observed at 100x magnification. The images were taken at different temperatures using a cooling rate of 10°C/min. It can be seen that at 65°C, the micrograph does not contain any crystalline structure (seen as bright spots). As the sample is cooled, there are bright spots that appear on the micrograph. As the temperature is lowered it is seen that the number of bright spots on the screen increases. There is a large increase in the intensity between the two micrographs at 16°C and 12°C. This led to the conclusion that the majority of the crystallization occurs in this temperature range. According to Turnbull\textsuperscript{19}, any crystallization occurring above 6.5°C is heterogeneous crystallization of PEO. Since the screen was completely filled with bright spots at 12°C, any homogeneous crystallization below this temperature, if present was difficult to observe under the microscope. It was also observed that nucleation of PEO in the heterogeneous region did not occur at the same time. It can therefore be concluded that the crystallization in the temperature range from 12°C to 40°C was not pure athermal nucleation, but rather a combination of thermal heterogeneous nucleation, athermal heterogeneous nucleation, and potentially self nucleation\textsuperscript{13}. It was also determined from repeated runs that within each domain there was no particular point from which the spherulite growth was initiated. Each domain nucleated at different points during successive runs. Sometimes nucleation took place outside the domains and crystallization proceeded into the PEO domains. Hence it was
Figure 4.1: Stages during the crystallization of a 70:30 PP/PEO blend as seen through an optical microscope at a magnification of 100x under cross polarizers.
difficult to measure the growth rate of PEO in these domains. The growth rate of smaller domains could not be measured because of their small size and because of the rapid growth of the spherulites.

The 70:30 PP/PEO blend was also observed under the optical microscopy at a heating rate of 3°C/min. to monitor the melt transition of PEO. It was seen that the first spherulites that melt are the ones in the smaller domains. The smaller PEO domains begin to melt around 51°C. This indicates that there is a significant decrease in the melting point in these domains. Using this value for the equilibrium temperature in the Turnbull\textsuperscript{19} equation, the homogeneous crystallization temperature for the small domains increases to 10.2°C. The decrease in the melting temperature of PEO domains could be explained in terms of the concentration of impurities in the smaller PEO domains. The smaller PEO domains are engulfed by both amorphous and crystalline PP. These domains contain PP chain ends, which have been rejected during crystallization. These act as impurities and reduce the melting temperature of the small PEO domains.

Figure 4.2 shows a series of images taken at different temperatures during a cooling run at 10°C/min for a 70:30 PP-g-MA/PEO blend. In this case it is seen that there are some crystals even at 65°C. These must be attributed to be those of iPP, crystallized during the quenching of the samples. It can also be said that since in the previous case, no iPP spherulites were seen, PP-g-MA must have crystallized at a faster rate than pure iPP.

The images show that the number of large PEO domains is drastically reduced as compared to the uncompatibilized blend system (Figure 4.1). In addition, the domain size of PEO is seen to be more uniform and smaller as compared to the uncompatibilized
Figure 4.2: Stages during the crystallization of a 70:30 PP-g-MA/PEO blend as seen through an optical microscope at a magnification of 100x under cross polarizers.
blend. This indicates an increased compatibility between iPP and PEO in the blend. There is some evidence of heterogeneous nucleation of PEO in the blends although the domain sizes are small and the number of spherulites is greatly reduced. Most spherulite growth occurs in the temperature range 3.5°C to 6°C. Therefore, contrary to the uncompatibilized blend, it was easy to pick up homogeneous nucleation in this blend. From the micrograph it can also be seen that the intensity of the spherulites formed in this case was much lower than in the case of the uncompatibilized blend. This could be attributed to the reduced crystallinity of the dispersed phase.

*Figure 4.3* shows a series of micrographs taken during the cooling run of 10°C/min. of a 70:30 PP-g-MA600/PEO blend. The micrographs demonstrate the presence of iPP crystals as in the previous case. This compatibilized blend exhibited no evidence of crystallization of PEO around 35°C. It can be inferred that crystallization of PEO in this blend was significantly depressed. PEO starts crystallizing at 16°C. It is also observed that the relative amount of homogeneous crystallization has decreased in this blend as compared to the previous blend. This suggests a decrease in the crystallinity of PEO, as the blends were made compatible.

The study of the three blends also revealed that intermediate domain sizes between 30-60 microns revealed the presence of both homogeneous and heterogeneous crystallization.
Figure 4.3: Stages during the crystallization of a 70:30 PP-g-MA600/PEO blend as seen through an optical microscope at a magnification of 100x under cross polarizers.
Figure 4.4: Stages during the crystallization of an 80:20 PP/PEO blend as seen through an optical microscope at a magnification of 100x under cross polarizers.

Figure 4.4 shows a series of micrographs taken for an 80:20 blend of PP/PEO. From the micrographs it can be seen that there is no evidence of heterogeneous nucleation of PEO in these blends from the fact that there is no increase in the intensity of the micrographs between 65°C and 21°C. The PEO phase only nucleates homogeneously at around 7°C as seen in the last micrograph.

In order to study the melt miscibility of the blends, the dispersed phase in the 80:20 blends were stained with a fluorescing dye. The blend was then studied under the microscope. Figure 4.5 shows the nature of the dispersed phase in an 80:20 PP/PEO blend system observed at 200°C. The micrograph shows that there is immiscibility
between the phases even in the melt state. The PEO domains are dispersed as spherical droplets in the PP melt, due to surface tension effects between the phases. The domains are uniformly distributed in the melt suggesting that the blending was uniform throughout the mixture. The PEO domains had a tendency to move in the melt and coalesce to form larger domains. During cooling of the melt it was found that as PP spherulites were being formed, the PEO domains were forced into vacant areas or trapped between the growth fronts of impinging PP spherulites.

Figure 4.6 is an optical micrograph of an 80:20 PP-g-MA/PEO blend observed at 200°C under the microscope. There are several black spots on this micrograph, which are
a combination of air pockets and PEO domains stained with fluorescein. It is evident that there is better dispersion of PEO in this blend as compared to the uncompatibilized blend. A similar behavior was also observed with PP-g-MA600/PEO blend. This demonstrates that PP-g-MA and PP-g-MA600 helped increase the compatibilization of PP/PEO blends by reducing the domain size of the dispersed phase.

Figure 4.16: Optical micrograph of an 80:20 PP-g-MA/PEO blend taken at 200°C at a magnification of 100x. The micrograph shows the reduction of domain size due to compatibilization.
4.2. DIFFERENTIAL SCANNING CALORIMETRY:

Differential Scanning Calorimetry was used to analyze the melting behavior of the blends and to study the effect of different cooling rates on the crystallization and melting behavior of the blend components.

Figure 4.7: DSC thermogram of iPP cooled at a cooling rate of 10°C/min and subsequently heated at 10°C/min.

Figure 4.7 represents the DSC thermogram for iPP run at a cooling rate of 10°C/min. and a heating rate of 10°C/min. The melt temperature of iPP is 169°C and it has a crystallization temperature of 123°C. The heat of fusion was 87.85J/gm. 100% crystalline polypropylene has a heat of fusion of 9.92 KJ/mol (236 J/gm.). This analysis indicates that the polymer sample is about 37% crystalline.
Figure 4.8: DSC curve for PEO (Mol. wt. = 35000 gm/mol) cooled at 10°C/min and subsequently heated at 10°C/min.

Figure 4.8 shows the DSC thermogram of a 35000 g/mol PEO sample run at a cooling rate of 10°C/min and a heating rate of 10°C/min. It has a crystallization temperature of 40°C, a melting temperature of 70°C and a heat of fusion of 180.1 J/gm. 100% crystalline PEO has a heat of fusion of 9.5 KJ/mol. (216 J/gm). Our PEO sample was found to be 83% crystalline based on the DSC results.
Figure 4.9: DSC cooling curves taken at various cooling rates for a 70:30 PP/PEO blend.

Figure 4.9 and Figure 4.10 are thermograms for a 70:30 blend of PP/PEO taken at different cooling rates and a constant heating rate of 10°C/min., respectively. It can be seen that as the rate of cooling is increased there is a lowering of the crystallization temperatures for both PP and PEO. Therefore, a higher degree of supercooling was required to reach the maximum crystallization rate for both PP and PEO. The crystallization temperatures for both components of the blend were lower than those of the pure polymers. It was seen that the crystallization temperature for PP has been reduced from 122°C for the pure sample to about 114°C in the blends. This reduction in the crystallization temperature may be caused by the PEO chains, which hinder the crystallization of i-PP. There are two crystallization peaks for PEO, one around 35°C and
the other one around 10°C. From this we can conclude that PEO undergoes fractionated crystallization in the blends.

The results for the homogeneous crystallization of PEO obtained from the optical microscope do not agree with these DSC curves. The homogeneous crystallization temperatures observed from the optical micrograph are slightly higher than those obtained from DSC. The samples in the DSC were heated up to 200°C, whereas the samples on the microscope were heated only to 90°C. Some residual nuclei may have been left in the PEO domains at the milder heating conditions. Other factors affecting the crystallization temperature are the amount of sample, stresses on the sample and the processing conditions.

![DSC heating curves taken after various cooling rates for a 70:30 PP/PEO blend.](image)

*Figure 4.10: DSC heating curves taken after various cooling rates for a 70:30 PP/PEO blend.*
It was also seen that different cooling rates did not affect the melting temperatures of either components of the blends. The melting temperature of both the components of the blend was the same irrespective of the cooling rates. The melting point of PEO was depressed from 70°C to 65°C, while the melt temperature of PP remained at 169°C.

All the other blend systems under investigation exhibited a similar reduction in the crystallization temperature as the rate of cooling was increased (Appendix Figures A.2 – A.7).

Figure 4.11: DSC cooling curves for 70:30 compositions of compatibilized and uncompatibilized PP/PEO blends cooled at 10°C/min.

Figure 4.11 represents the cooling curves of 70:30 compositions of compatibilized and uncompatibilized blends of PP and PEO for the same cooling rate of 10°C/min. The curve on the bottom is that of a 70:30 PP/PEO blend. The peak at 114°C is the crystallization peak for polypropylene. The peaks on the left of the thermogram correspond to the crystallization of PEO. There are two crystallization peaks at 35°C and
12°C for PEO. It can be seen that the tail of the lower temperature peak levels off only around 0°C. According to Turnbull and Cech\textsuperscript{19}, the higher temperature peak must therefore correspond to the heterogeneous crystallization of PEO while the lower temperature peak is a combination of heterogeneous and homogeneous crystallization. There are a number of small peaks in between the two main ones. Optical microscopy revealed that these peaks corresponded to the crystallization of PEO in different size domains.

The curve in the middle of the thermogram is that of a 70:30 PP-g-MA/PEO blend. As seen from the thermogram the heterogeneous peak for PEO has been considerably reduced in height whereas the height of the homogeneous peak has increased relative to the corresponding uncompatibilized system. This indicates that there is better compatibility between PEO and iPP in the former blend.

The thermogram on the top is that of a 70:30 blend of PP-g-MA-g-PEO/PEO. It can be seen from the graph that there is almost no heterogeneous crystallization for PEO as seen by the DSC. This means that the PEO domains are small enough in size and uniformly distributed so that only homogeneous crystallization takes place in these domains. These results were also confirmed from optical microscopy studies.

Only two blend systems (70:30 iPP/PEO and 70:30 PP-g-MA/PEO) gave rise to a crystallization peak around 40°C, which is close to the crystallization temperature of pure PEO. However, all the samples had a crystallization peak between –4°C and 15°C. These peaks are thought to correspond to the homogeneous crystallization peak of PEO. Optical micrographs indicate that these peaks result from the crystallization of the smaller domains, which were evenly distributed in the blends. A distribution of domain sizes can
explain the difference in the crystallization temperatures and the presence of both a heterogeneous peak and a homogeneous peak.

For all the other blend compositions it was seen that homogeneous crystallization was the only mode of crystallization for PEO in the blends (Appendix Figures A.2 – A.7). This could be attributed to a more uniform distribution of the PEO domains in the PP matrix in these samples.

![DSC heating curves](image)

**Figure 4.12:** DSC heating curves for 70:30 compositions of compatibilized and uncompatibilized blends of PP and PEO heated at 10°C/min after crystallization.

The melting temperature of PP in the blends was insensitive to the concentration of PP in the blends and was also independent of the presence or absence of the compatibilizer. The melting temperature of PEO was found to decrease at lower compositions of PEO. For 80:20 and 90:10 compositions, the melting temperature of PEO was relatively constant for all blends, with and without the compatibilizer. For the
70:30 compositions, however, the melting temperature of PEO increased, as the blend was made more compatible.

Table 4.1 summarizes the melting and crystallization temperatures for PP and PEO for all the compositions used in this study.

<table>
<thead>
<tr>
<th>BLEND</th>
<th>POLYPROPYLENE</th>
<th>POLYETHYLENE OXIDE</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T_m , ^\circ\text{C}$</td>
<td>$T_c , ^\circ\text{C}$</td>
</tr>
<tr>
<td>Pure $i$-PP</td>
<td>169.3</td>
<td>122.9</td>
</tr>
<tr>
<td>Pure PEO</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>70:30 PP/PEO</td>
<td>169.0</td>
<td>114.4</td>
</tr>
<tr>
<td>80:20 PP/PEO</td>
<td>168.8</td>
<td>113.8</td>
</tr>
<tr>
<td>90:10 PP/PEO</td>
<td>169.1</td>
<td>114.9</td>
</tr>
<tr>
<td>70:30 PP-g-MA/PEO</td>
<td>167.3</td>
<td>114.9</td>
</tr>
<tr>
<td>80:20 PP-g-MA/PEO</td>
<td>167.4</td>
<td>115.3</td>
</tr>
<tr>
<td>90:10 PP-g-MA/PEO</td>
<td>167.1</td>
<td>116.4</td>
</tr>
<tr>
<td>70:30 PP-g-MA600/PEO</td>
<td>168.5</td>
<td>112.7</td>
</tr>
<tr>
<td>80:20 PP-g-MA600/PEO</td>
<td>169.0</td>
<td>112.7</td>
</tr>
<tr>
<td>90:10 PP-g-MA600/PEO</td>
<td>167.8</td>
<td>114.5</td>
</tr>
</tbody>
</table>

Table 4.1: Melting temperatures and crystallization temperatures for PP and PEO in various blend compositions. (10°C/min. heating and cooling rate)

The DSC was also used to determine the heats of fusion of the components of the blend systems. It was seen that as the concentration of PEO in the blends increased, the crystallinity of PP decreased whereas the crystallinity of the PEO phase increased. As the blends were made more compatible, the crystallinity of both the components of the blends decreases. One might expect that the grafting of PEO onto the PP-g-MA increases the interfacial area between the two polymer phases, which consequently reduces the
crystallinity of both the phases. Table 4.2 summarizes the heat of fusion and crystallinities of the various blend systems investigated.

<table>
<thead>
<tr>
<th>BLEND</th>
<th>POLYPROPYLENE</th>
<th>POLYETHYLENE OXIDE</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Heat of fusion</td>
<td>% Crystallinity</td>
</tr>
<tr>
<td></td>
<td>J/gm</td>
<td></td>
</tr>
<tr>
<td>100% crystalline i-PP</td>
<td>236.0</td>
<td>100</td>
</tr>
<tr>
<td>100% crystalline PEO</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Pure i-PP</td>
<td>87.9</td>
<td>37.2</td>
</tr>
<tr>
<td>Pure PEO</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>70:30 PP/PEO</td>
<td>81.6</td>
<td>34.6</td>
</tr>
<tr>
<td>80:20 PP/PEO</td>
<td>85.0</td>
<td>36.0</td>
</tr>
<tr>
<td>90:10 PP/PEO</td>
<td>85.2</td>
<td>36.1</td>
</tr>
<tr>
<td>70:30 PP-g-MA/PEO</td>
<td>79.7</td>
<td>33.8</td>
</tr>
<tr>
<td>80:20 PP-g-MA/PEO</td>
<td>82.4</td>
<td>34.9</td>
</tr>
<tr>
<td>90:10 PP-g-MA/PEO</td>
<td>79.0</td>
<td>33.5</td>
</tr>
<tr>
<td>70:30 PP-g-MA600/PEO</td>
<td>72.8</td>
<td>30.8</td>
</tr>
<tr>
<td>80:20 PP-g-MA600/PEO</td>
<td>71.1</td>
<td>30.1</td>
</tr>
<tr>
<td>90:10 PP-g-MA600/PEO</td>
<td>73.6</td>
<td>31.2</td>
</tr>
</tbody>
</table>

Table 4.2: Values for heat of fusion and % crystallinities of the blend systems investigated.

Taking the heat of fusion values obtained from the DSC and dividing them by the concentration of the polymer in the blend gives the heat of fusion values listed in Table 4.2. For example for PP in a 70:30 PP/PEO blend, the value obtained from the DSC for PP was 57.21 J/gm. This value divided by 0.7 yields 81.61 J/gm as the heat of fusion of PP.
In a separate experiment, all the 70:30 blends were run in the DSC under the following conditions. The samples were equilibrated at 55°C, 59°C and 63°C. The samples were then cooled at 10°C/min followed by a 10°C/min heating run to 90°C. It was found that homogeneous crystallization could still be observed under these conditions.

Figure 4.13: DSC cooling curves of the 70:30 PP/PEO blend equilibrated at various temperatures.

The thermograms show that even though the temperature is held constant well below the melting point of pure PEO, it was sufficient to melt the small PEO domains in the blends. Samples held at 55°C showed the presence of homogeneous nucleation. The region of homogeneous crystallization increased, as the blends were made more compatible. There is a significant depression in the melting point of PEO. Optical microscopy revealed that the smaller domains melted at a lower temperature, which crystallize homogeneously in these blends. The thermograms also indicated the presence
of heterogeneous crystallization in all the 3 blends. While heterogeneous crystallization was totally suppressed in compatibilized blends heated to 200°C, the above thermograms show the presence of heterogeneous crystallization even for the PP-g-MA600/PEO blend. It was concluded that there were several residual nuclei left in PEO domains, which led to the heterogeneous crystallization in these domains.

![DSC cooling curves of the 70:30 PP-g-MA/PEO blend equilibrated at various temperatures.](image)

**Figure 4.14:** DSC cooling curves of the 70:30 PP-g-MA/PEO blend equilibrated at various temperatures.

This effect can be explained by the following mechanism; in the 70:30 PP/PEO blend, the dispersed PEO phase is separated from iPP by a thin well-defined interface. As the blend is made more compatible, the interface thickens and interferes with the crystallization of PEO, particularly in the small domains. The heterogeneous nucleation of PEO was suppressed due to reduction in the domain size and also due to the large amount of impurities present at the interface. The presence of large amounts of impurities
also causes a significant reduction in the melting point, which allows for the recrystallization behavior observed for PEO.

Figure 4.15: DSC cooling curves of the 70:30 PP-g-MA600/PEO blend equilibrated at various temperatures.
4.3. **X-RAY DIFFRACTION:**

Results from the DSC demonstrated that there was an increase in the melting point for the 70:30 compatibilized blend as compared to the uncompatibilized blend. It was suspected that the better quality PEO crystals were produced due to compatibilization. X-ray diffraction was used to confirm this by comparing the breadth of the diffraction peaks, which is indicative of the crystal quality of the polymer. X-ray diffraction was also used to confirm the relative crystallinity of the PEO in these blends.

![X-ray diffraction pattern of PEO powder.](image)

*Figure 4.16: X-ray diffraction pattern of PEO powder.*

*Figure 4.16 and Figure 4.17 are X-ray diffraction patterns for pure PEO and iPP samples. From the diffraction pattern it is seen that the α-form of iPP is present in the blends. The methyl group in iPP can be isoclined (methyl group is up relative to the left glide plane) and anticlined (the methyl group is down relative to the right glide plane).*
This introduces a considerable degree of disorder in i-PP crystals. Mencik therefore proposed that 45% disorder with respect to the isoclined and anticlined helices must exist to explain the experimentally obtained diffraction pattern\(^3\).

![X-ray diffraction pattern of i-PP powder.](image)

*Figure 4.17: X-ray diffraction pattern of i-PP powder.*

Since the peak at 19° was common to both PP and PEO the ratio of the peaks at 14° and 23° were taken to get an estimate of the relative crystallinity of PEO.
Figure 4.18: X-ray diffraction pattern of 70:30 PP/PEO blend.

Figure 4.19: X-ray diffraction pattern of 70:30 PP-g-MA/PEO blend.

Figure 4.20: X-ray diffraction pattern of 70:30 PP-g-MA600/PEO blend.
Figure 4.18, Figure 4.19, and Figure 4.20 represent the x-ray diffraction patterns for a 70:30 PP/PEO blend, 70:30 PP-g-MA/PEO blend and 70:30 PP-g-MA600/PEO blend. In order to compare the crystal quality, the width of the peaks had to be compared. This however could not be done, as there was some overlap between the diffraction peak for iPP at 22° and the diffraction peak for PEO at 23. It was however seen that upon increasing the compatibility between PP and PEO, there was a considerable increase in the peak height at 23° relative to 14°. Table 4.3 shows the ratio of the peak heights of PEO:PP for the 3 blends.

<table>
<thead>
<tr>
<th></th>
<th>PP (14°) Intensity</th>
<th>PEO (23°) Intensity</th>
<th>RATIO (PEO/PP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>70:30 PP/PEO</td>
<td>815</td>
<td>650</td>
<td>0.79</td>
</tr>
<tr>
<td>70:30 PP-g-MA/PEO</td>
<td>255</td>
<td>240</td>
<td>0.94</td>
</tr>
<tr>
<td>70:30 PP-g-MA600/PEO</td>
<td>500</td>
<td>475</td>
<td>0.95</td>
</tr>
</tbody>
</table>

Table 4.3: XRD peak ratios for 70:30 compositions of compatibilized and uncompatibilized PP/PEO blends.

The results from the x-ray diffraction indicate that there in an increase in the crystallinity of PEO relative to iPP, as the blends are made compatible. These results were contradictory to the results obtained from the DSC and optical microscopy. Optical microscopy and differential scanning calorimetry indicate that there is a decrease in the crystallinity of PEO as the blends are compatibilized. It was therefore concluded that the increase in peak height for PEO at 23° might have been influenced by other factors, such as loss of randomness in the sample, or alignment of PEO crystals in the direction of scattering. Further investigation is needed to determine this.
4.4. INFRARED SPECTROSCOPY:

In June 1998, Eunsook John\textsuperscript{20} et al from the Korean Advanced Institute of Science and Technology reported on Fourier transform infrared and calorimetric studies of the influence of tacticity of polymethyl methacrylate on its compatibility with polyethylene oxide. Their studies indicate that the bands at 843, 948, 964, 1115, 1343, and 1360 cm\textsuperscript{-1} are unique to PEO. The bands near 1340-1360 cm\textsuperscript{-1} correspond to CH\textsubscript{2} wagging modes, while the bands near 800-1000 cm\textsuperscript{-1} correspond to coupled C-O stretching, CH\textsubscript{2} rocking and C-C stretching modes. They showed that at higher percentages of PEO (80\%), there was incompatibility in the blends based on the IR results. The results showed that the co-added spectrum of the 2 components was almost identical to the synthesized spectrum (by weighted digital addition of pure spectra). It was further found that at lower percentages of PEO (20\%) the bands at 843, 948, 1115, 1343, and 1360 cm\textsuperscript{-1} were not matched in the blend and the synthesized spectrum. From this it was concluded that the 20/80 PEO/s-PMMA was a compatible blend.

Using the above mentioned as a guide, we attempted to study the effect of blending on the structure of PEO chains in crystalline domains. The results did not agree with the paper presented by Eunsook John.
Figure 4.21: 2\textsuperscript{nd} derivative Infrared spectra of isotactic polypropylene and polyethylene oxide.

Figure 4.21 represents the second derivative spectra of pure polyethylene oxide and isotactic polypropylene. As seen from the graph, there are several unique peaks for i-PP and PEO. We decided to focus our attention on the peaks for PEO at 948, 964, and 1343 cm\textsuperscript{-1}, to compare the results with the previous study. The peak at 1368 overlapped with that of i-PP and therefore was excluded from our study. Although the peaks for both the polymers can be distinguished clearly, blending of the two components gave spectra, which were quite different from the peaks predicted by digital coaddition of pure component spectra.
In order to determine the composition of the blends prepared in the lab, the standard blends were run on the IR. Figure 4.22 shows a comparison between the standard and an actual 70:30 PP/PEO blend. In order to compare the IR spectra of the blends, the spectra were normalized to the peak heights for PP at 961, 978, 1368, 1436 and 1450 cm\(^{-1}\). It can be seen that there is some disagreement between the two spectra indicating that there was a deviation from the 70:30 composition prepared in the laboratory. In particular the peak heights at 964, 1058, 1115, 1150, and 1343 cm\(^{-1}\) for the standard is larger than the corresponding peaks in the blend. This shows that there could be a slight deviation in the composition of the blend prepared in the laboratory from the predicted values.
Figure 4.23: Comparison of the IR spectrum of a 70:30 PP/PEO model and a standard 70:30 PP/PEO blend.

Figure 4.23 shows the results of a 70:30 PP/PEO standard blend cast in the form of a film in comparison to a 70:30 PP/PEO blend obtained by coadding the spectra of pure iPP and PEO. This was obtained by the weighted addition of the spectra of pure PP and pure PEO. It is clear that the experimental spectrum of the blend is different than the synthesized spectrum. It is seen that some of the peaks (972, 997, and 1375 cm\(^{-1}\)) for the blend are slightly shifted from that of the coadded spectrum. It is also apparent that the peak heights for corresponding peaks in the two spectra are different. According to the previous study this would mean that the two components of the blend are compatible. But it is well known that PP and PEO are incompatible under all conditions. Therefore these spectral shifts in the blend are due to effects other than compatibility. This could be due
to the lowered crystallinity in the sample or due to stresses that are built up in the PEO phase during the crystallization of PP.

![Graph showing IR spectra comparison](image)

Figure 4.24: Comparison of IR spectra of pure PP with that of a 70:30 PP/PEO blend digitally subtracted from PEO.

In Figure 4.24, the IR of pure PP is compared to that of a spectrum obtained by digitally subtracting pure PEO from a 70:30 PP/PEO blend. It can be seen that the two spectra do not match each other and there are several peaks in the subtracted spectra, which are absent in the pure PP spectra. The cause of these changes in the IR peaks needs further investigation.
IR spectra can also be used to compare the crystallinity of different samples by comparing the nature of the peaks in the fingerprint region. In general, an increase in the peak height and narrowing of the peak width is indicative of increased crystallinity of the sample. Figure 4.25 represents PEO peaks for various compatibilized and uncompatibilized blends of 70:30 PP/PEO. The IR spectra have been normalized to the PP signal. The peak at 1115 cm\(^{-1}\) is unique to PEO and is seen to become broader and smaller as the blends are made compatible. It can be clearly seen from the spectra that as the blends are made more compatible, there is significant loss of crystallinity in the PEO phase. In addition, it is observed that the 70:30 PP-g-MA600/PEO blend when cooled exhibits a higher peak at 1115 cm\(^{-1}\). This is caused by the increased crystallinity of the
sample due to the homogeneous crystallization in PEO domains. Comparison of the peak at 1115 cm\(^{-1}\) between the standard and the blend reveals that it is broader in the blend, which again indicates the lower crystallinity in the sample. When the solution cast films were observed under the microscope, the IR sample did not show the presence of any birefringent crystalline regions. This may be caused by the reduced thickness in the sample and/or the low concentration (0.1 g/ml) of the sample in the casting solution.
4.5. DYNAMIC MECHANICAL ANALYSIS:

Dynamic mechanical analysis was used to determine the effect of blending on the mechanical properties of the blend and to acquire information about the interface between the two polymers. This was done by carrying out tensile tests on the prepared laminates. However, it was seen that the information from the DMA was not conclusive and a better analysis and better instrument is required to carry out the analysis.

In dynamic mechanical analysis, an oscillatory strain is applied to a sample and the resulting stress is measured\(^2\). If the material is viscoelastic and a sinusoidal strain is applied, it will exhibit a sinusoidal stress response. This can be separated into two components, the in-phase (0°) and the out-of-phase component (90°). The in-phase component describes the elastic response of the polymer and is an indication of the elastic modulus \(E'\) while the out-of-phase component is proportional to the viscous response and is represented as the loss modulus \(E''\) of the material. The ratio of the viscous to the elastic component, \(E''/E'\), is called the tan\(\delta\). High tan\(\delta\) values indicate a viscous material and low tan delta indicates an elastic material. In most of our cases, the curves for \(E', E''\), and tan\(\delta\) were not satisfactory in showing transitions unique to each polymer in the blend samples.

To accent the effect of temperature and frequency on the mechanical properties the graphs to be presented are plotted as the second derivative of \(E''\) versus the temperature.
Figure 4.26 shows the transitions in pure isotactic polypropylene during a heating run. The experiment was carried out in the temperature range from -50°C to 100°C in 30 isothermal steps. It can be observed that there are a number of transitions in the sample which can be observed as peaks in the loss modulus. The large transition around 0°C corresponds to the glass transition of iPP. The transitions in the range from 40°C - 100°C can be attributed to recrystallization of iPP. This process is expected to lead to lossy mechanical behavior. It can also be seen that there is a shift in the glass transition of iPP as the frequency increases. In particular an increase in the frequency leads to an increase in the glass transition. At lower frequencies, the polymer chains have more time to react to the applied stress, which lowers the observed glass transition of iPP.

Figure 4.27, Figure 4.28 and Figure 4.29 are the DMA cooling curves for E', E'' and tanδ, respectively for a 70:30 PP/PEO blend. Only cooling runs are presented in this.
study to exhibit the effect of crystallization of PEO on the mechanical response of the polymer.

![DMA curve of E' for a 70:30 PP/PEO blend.](image)

*Figure 4.27: DMA curve of E’ for a 70:30 PP/PEO blend.*

The curve for E’ shows a broad transition over the entire temperature range of the measurement. However, there is a sudden increase in the modulus around 50°C. This is indicative of the heterogeneous crystallization of PEO. Since E’ is related to the elastic properties of the polymer it does not give any direct information about the viscous response of the system to the applied stress.

The curve for E” shows a prominent transition around 0°C. This transition can be assigned to the glass transition of iPP described earlier. The crystallization of PEO can be picked out on the graph as a small shoulder around 40°C. However this transition is broad and cannot be easily observed because of overlap with the glass transition of PP.
Figure 4.28: DMA curve of $E''$ for a 70:30 PP/PEO blend.

Figure 4.29: DMA curve of $\tan\delta$ for a 70:30 PP/PEO blend.
The peak in loss modulus is associated with the partial loosening of the polymer structure so that groups and small chain segments can move. This occurs near $T_g$ at low frequencies. The tan$\delta$ peak at a frequency of 1 Hz generally lies at a temperature 15 to 20$^\circ$C above the glass transition temperature as measured by differential thermal analysis. The temperature for maximum damping is not $T_g$, although it is often taken to be so. The temperature of $(\tan\delta)_{\text{max}}$ is more sensitive to parameters such as crosslink density, filler content, or blend morphology than the $T_g$ itself. The maximum in the loss modulus $E''$ at low frequencies is very close to the $T_g$.

![Figure 4.30: $E''$ versus temperature for various 70:30 PP/PEO blends.](image-url)
Figure 4.30 represents the E'' versus Temperature curves for compatibilized and uncompatibilized blends of 70:30 PP/PEO during a cooling run. In order to accent the differences between the compatibilized and the uncompatibilized blends, these graphs were plotted as separate second derivatives of E'' versus the temperature (See Figures 4.31-4.36).

![Figure 4.31: DMA cooling curves for E'' of a 70:30 PP/PEO blend.](image)

Figure 4.31 shows the results of a DMA run for a sample of 70:30 PP/PEO blend. It can be seen that there are transitions, which were clearly seen in the regions corresponding to PEO crystallization. The transition around -40°C most likely corresponds to the glass transition of polyethylene oxide. It can also be seen that there are clear transitions in the region from 40°C - 60°C. The causes of these transitions are difficult to determine since there are transition observed for both iPP and PEO in the
same temperature range. However, there is an increase in the intensity of these peaks compared to pure iPP. This demonstrates that there is crystallization of PEO in this region. The graph also indicates that these transitions are frequency dependent. The peak for homogeneous crystallization could not be seen at all because of the overlap with the glass transition region of iPP.

![Figure 4.32: DMA heating curves for E'' of a 70:30 PP/PEO blend.](image)

*Figure 4.32* represents the result of a DMA heating run on a 70:30 PP/PEO blend sample that was rapidly cooled and equilibrated at -50°C before the isothermal heating steps. The glass transition of the two polymers can be clearly seen. The peaks at 37°C and 55°C are independent of frequency. This indicates that there is a first order transition in this region such as reorganization/recrystallization of PP or PEO at 37°C followed by melting of PEO at 55°C.
Figure 4.33: DMA cooling curves for $E''$ of a 70:30 PP-g-MA/PEO blend.

There was a marked difference in the responses of the compatibilized and the uncompatibilized blend systems. As can be seen from Figure 4.33, the homogeneous crystallization peak for PEO can be observed up around 0°C. This transition is independent of the frequency. An increased stress in the PEO domains may have caused these transitions to occur at the same temperature. However, these results varied from sample to sample. There is almost no crystallization of PEO around 40°C. This did not agree with the results from the DSC, which exhibited heterogeneous crystallization of PEO at 35°C. This can be attributed to the different sample preparation technique and different processing conditions.
Figure 4.34: DMA heating curves for E'' of a 70:30 PP-g-MA/PEO blends.

**Figure 4.34** represents the heating curves for a 70:30 PP-g-MA/PEO blend. In comparison to the uncompatibilized blend, the melting transition for PEO is much sharper. It is also seen that there is very little or no rearrangement prior to the melting of PEO. This could be caused by an increased crystal quality of the dispersed phase in the compatibilized blends, which explains the increase in the melting temperature of PEO in the compatibilized blend obtained by DSC.

Shown below in **Figure 4.35** and **Figure 4.36** are the DMA cooling and heating curves for a 70:30 PP-g-MA600/PEO blend, respectively. It is seen that there is an overall broadening of the peaks in the temperature region from -40°C to 40°C. The heating run shows some rearrangement before the melting of PEO.
Figure 4.35: DMA cooling curves for $E''$ of a 70:30 PP-g-MA600/PEO blend.

Figure 4.36: DMA heating curves for $E''$ of a 70:30 PP-g-MA600/PEO blend.
Figure 4.37: $E''$ versus Temperature of an 80:20 PP-g-MA600/PEO cooling run.

Figure 4.37 is the result of a cooling run of an 80:20 PP-g-MA600/PEO. As seen from the graph, there are abrupt changes in the loss modulus values at some frequencies. Similar behavior was observed in other blend systems investigated. This could be caused by the heterogeneity in the sample or by stresses in the sample. Further investigation is required to confirm this.
CHAPTER 5

CONCLUSIONS

Polypropylene/polyethylene oxide blends are incompatible in the temperature range -60°C to 200°C. The presence of maleic anhydride increases the compatibility of PEO with iPP. The presence of even very small amounts of maleic anhydride linked to PP (0.06%) caused a significant modification of the crystallization behavior of PEO. Polypropylene-graft-maleic anhydride-graft PEO is a good compatibilizer for PP/PEO blend systems. The grafting of PEO onto PP-g-MA totally suppressed the heterogeneous nucleation of PEO up to 30 weight%. PP-g-MA-g-PEO increases the compatibility by reducing the size of the dispersed phase and by increasing the interfacial area between PP and PEO. There was a reduction in size of the PEO domains in the compatibilized blends as compared to those in the uncompatibilized blends. Although there was clustering of domains in the compatibilized blends, the crystallization temperature of PEO in these domains was around 0°C, indicating that heterogeneous crystallization was totally suppressed. Infrared spectra of PP/PEO blends do not match with the digitally coadded spectra. Factors such as stresses on the PEO domains, amount of sample and the substrate affect the infrared properties and the crystallization behavior of PEO. Dynamic mechanical analysis of these blends demonstrated a change in behavior of the viscous response of the compatibilized blends in comparison to the uncompatibilized blends. DMA heating curves also indicate rearrangement/recrystallization in PEO as well as iPP in these blends.

Further research can be done to devise better techniques for making DMA samples to determine transitions in the PEO phase during heating and cooling cycles. A
much better correlation between the techniques can be made if the same sample preparation technique can be used for all the characterization techniques. The infrared spectra of the polymers need to be better scrutinized in order to determine the effect of blending and compatibilization on the spectroscopic properties of PP and PEO. Similar experiments can also be performed using syndiotactic polypropylene instead of isotactic polypropylene to study the effect of tacticity on the crystallization behavior of polyethylene oxide.
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    Kevin P. Menard.

22. *Mechanical Properties of Polymer and Composites.*


Figure A.1: Infrared spectrum of PP-g-MA and PP-g-MA600

Figure A.2: DSC thermogram of an 80:20 PP/PEO blend at different cooling rates and subsequently heated at 10°C/min.
Figure A.3: DSC thermogram of an 80:20 PP-g-MA/PEO blend at different cooling rates and subsequently heated at 10°C/min.

Figure A.4: DSC thermogram of an 80:20 PP-g-MA600/PEO blend at different cooling rates and subsequently heated at 10°C/min.
Figure A.5: DSC thermogram of a 90:10 PP/PEO blend at different cooling rates and subsequently heated at 10°C/min.

Figure A.6: DSC thermogram of a 90:10 PP-g-MA/PEO blend at different cooling rates and subsequently heated at 10°C/min.
Figure A.7: DSC thermogram of a 90:10 PP-g-MA600/PEO at different cooling rates and subsequently heated at 10°C/min.