Crystallization Kinetics of Poly(ethylene terephthalate) in Compositions Containing Naturally Functionalized Triglyceride Oil

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SYNOPSIS

The crystallization of poly(ethylene terephthalate) (PET) in blends with naturally functionalized triglyceride oils and their networks has been investigated. Crystallization kinetics of PET in the presence of small amounts of castor oil is improved, both in cooling from the melt state, and in heating from the glassy state. In conjunction with the nucleating agent sodium benzoate, either chemically bonded to castor oil or as a simple mixture, even greater enhancements of crystallization are observed. The PET crystallinity in semi-IPNs and blends of low to intermediate castor oil–HMDI polyurethane content are higher than that of neat PET (on a per gram of PET basis). Crystallinity in compositions with a high triglyceride oil network content is greatly affected by the presence of the network, with large melting point depressions, and loss in overall crystallinity. In cases where the triglyceride oil network is completely formed in a miscible melt with PET, the PET is unable to crystallize on cooling, resulting in amorphous semi-IPNs. Plasticization due to the oil, nucleation from added agents, bond interchange reactions between the oil and the PET, overall chemical composition, and the presence of a triglyceride oil network are found to have a controlling influence over the type and extent of PET crystallinity in the compositions. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Interpenetrating polymer network (IPN) research involving naturally functionalized triglyceride oils has been a topic of interest at Lehigh University.[1–8] These oils are prepared by nature with multiple chemical functionality, and are thus a renewable resource, providing an alternative to petroleum as a chemical feedstock. The oils may be crosslinked by step-growth reactions, which has prompted their use in IPNs along with chain-growth polymerized plastics. The typical triglyceride oil network is, by itself, a soft elastomer, suitable to be used as a toughening agent in brittle plastics. Castor oil in particular has received much attention in this regard, primarily because of its status as a large-scale commercial product.[1,2] Other functionalized triglyceride oils are numerous, but none are produced in the same quantities as castor oil. Vernonia oil in particular is promising for the future, due to its high purity and functionality and the ability to cultivate its precursor oil-seed plant in arid climates at economical yields.[9,10]

The present work involves use of the naturally functionalized triglyceride oils, castor oil (naturally hydroxylated), and vernonia oil (naturally epoxidized) in conjunction with poly(ethylene terephthalate) (PET). Most prior IPN research has concentrated on amorphous compositions, but PET is a semicrystalline thermoplastic. The use of castor and other triglyceride oils with thermoplastic polymers has mostly been limited to that of a plasticizer

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or stabilizer.[10–14] Semicrystalline PET has outstanding material properties required for an engineering plastic, however, its crystallization rate is slow, forcing long cycle times in injection molding applications. Crystalline PET injection molding grades tend to have lower molecular weight, which increases the crystallization rate and improves melt flow, but the resulting material can be brittle and is nearly always sold as a composite with up to 40 vol % chopped glass fiber for increased toughness.[15] To address these drawbacks of PET, it was thought that by making semi-IPNs and/or blends with functionalized triglyceride oils, toughness, as well as the crystallization rate, could be improved. In earlier research, the properties of semi-IPNs made from PET and castor oil,[16,17] or PET and vernonia oil,[18] were discussed. Because PET is semicrystalline, the morphology of the semi-IPN formed becomes more complicated, introducing crystallinity as a factor to be considered. The present article investigates the crystallization behavior of PET in castor and vernonia oil blends and semi-IPNs.

PET/Triglyceride Oil Semi-IPNs

IPNs may, in general, be formed by two methods.[19] In the sequential method, a polymer network of the first component is formed, then is swelled with the monomer and crosslinker of the second component and polymerized in situ to create the interpenetrating network. If the two components polymerize by noninterfering routes, then the IPN may be formed by the simultaneous method, where monomers and crosslinkers of both components may be mixed and polymerized together simultaneously. Prior triglyceride oil IPN research has proceeded by polymerizing both components from their monomeric state. In this way, the components are initially miscible, either as monomers (simultaneous method), or as a swollen network (sequential method), and they phase separate as polymerization and crosslinking proceeds. It is the relationship between crosslinking and phase separation kinetics that controls the final IPN morphology.[20]

In the present research, fully-polymerized PET is the starting material, which puts some constraints on the IPN formation process. PET may be considered as the condensation product of terephthalic acid and ethylene glycol. Because the castor oil would polymerize with terephthalic acid in competition with ethylene glycol, simultaneous semi-IPN formation from monomers is not possible, since noninterfering polymerization routes are required for this method of IPN synthesis. Although PET and

castor oil polyester network are both polyesters, PET is aromatic and castor oil is aliphatic, and the two are immiscible. Thus, castor oil will not dissolve in PET, nor will polymerized PET swell a castor oil network, making sequential IPN formation impossible. In order to control the IPN morphology of the PET and castor oil network, the two components must first be well mixed or miscible, then must be allowed to phase separate as the castor oil crosslinking occurs.

It was discovered that continued heating of castor oil and PET results in a miscible mixture, a consequence of bond interchange reactions that form a compatibilizing copolymer.[16,17,21] The reactions involve PET ester groups and castor oil ester and hydroxyl groups.[21] The resulting semi-IPN will be a hybrid structure, in which the crosslinked and/or uncrosslinked materials may be copolymers and not pure components. Thus, the extent to which the bond interchange reactions take place will affect many aspects of the resulting semi-IPN. The method of bond interchange copolymer formation is potentially applicable to many other systems to make interesting new IPNs and semi-IPNs.

Crystallization of Poly(ethylene terephthalate)

Poly(ethylene terephthalate) is a widely utilized polymer, due primarily to its high strength, thermal stability, good barrier properties, low price, and good solvent resistance. PET has established itself as a primary material in bottles, textiles, recording tape, and packaging film. Injection molding is, however, one area in which, until recently, PET has not been extensively utilized, due to its slow crystallization rate, which results in poor dimensional stability of molded parts. The crystallization rate of PET upon cooling from the melt to the glass is considerably slower than that of poly(butylene terephthalate) (PBT), due to a great degree to the difficulty in forming chain folds.[22] Its maximum crystallization rate occurs at about 180°C, roughly halfway between its glass transition temperature (approximately 70°C) and its equilibrium melting temperature of about 285°C. At 90°C, a typical injection mold temperature for polyesters, the rate of crystallization for PET is virtually zero. Although one method of improving the moldability of PET has been to raise the temperature of the mold, at temperatures much greater than 110°C it is no longer possible to use water to heat the mold, so that oil must be utilized instead. Since most molders do not wish to switch to oil heating when molding PET, nucleation agents and mobility enhancers have been developed that allow mold temperatures of 100°C or lower. Thus,

much of the prior developments in the area of PET molding concerns nucleating agents, which are effective in inducing rapid PET crystallization at high temperatures when cooling from the melt temperature to the mold temperature.[23]

Developments in the 1970s and early 1980s in PET nucleation[24-27] involved the use of aliphatic and aromatic sodium carboxylates to nucleate reinforced PET. Unlike the traditional inert solid physical nucleation agents, such as talc, which work by an epitaxial mechanism, these chemical nucleation agents work by dissolving in and reacting with PET. Extensive nucleation technology has been developed for PET involving the use of low molecular weight alkali metal carboxylates,[28-34] as well as with polymeric nucleants containing pendant alkali metal carboxylates.[35-37] Technology, developed by Deyrup,[25] describes the combined use of a nucleant as, "a sodium or potassium salt of a hydrocarbon acid containing between about 7 and 25 carbon atoms, or with the sodium or potassium salt of an organic polymer which contains pendant carboxyl groups . . ." and second, he describes it as a mobility enhancer, a molecular weight organic plasticizer (e.g., ketones, esters, or sulfones). A filler is also added for the purpose of reinforcement of the resin. The presence of a chopped glass fiber in injection moldable PETs markedly increased both the tensile strength and modulus of the PET, resulting in improved toughness. The use of carbonyl-containing plasticizers, such as esters and ketones, in reinforced PET in conjunction with selected sodium or potassium carboxylates enhances the rate of crystallization when the molded part has nearly cooled to the mold temperature.[25,36] Additional mobility enhancers that have been developed include mixtures of oligoethers and oligoether segments employed jointly to increase synergistically the mobility of the PET.[38,39] The addition of small amounts of polyolefins, for example, polyethylene, is also observed to enhance the mobility of PET in the melt, as well as to improve its toughness.[40,41]

Research by Biebuyck et al.[42] details the nucleation of PET by a variety of different basic salts of the alkali metals, including carboxylic, phenolic, phosphonic, phosphinic, sulfonic, etc. This study describes the use of a range of ionizable metal salts, which are able to activate the PET chain end and thus are useful in the nucleation of PET. The alkali metal salts of various metal oxides also function to nucleate PET.[43] The mechanism by which alkali metal salts function to nucleate PET was best addressed by the spectroscopic study undertaken by Dekoninck et al.[44] They were able to demonstrate

by FTIR that a basic sodium salt reacts with the ester to cleave the PET chain and to form a sodium carboxylate chain end. The sodium salt on the end of the PET chain then facilitates crystallization by precipitating from the melt, forming sites for nucleation. If the PET is annealed in the melt for extended periods of time, the salt gradually looses its nucleating ability, which occurs by the reaction of two neighboring sodium carboxylate chain ends to form disodium terephthalate, a poor nucleating agent for PET.

Most group-I carboxylates are effective as nucleants for PET along with many other group-I salts. Two examples of group-I carboxylates, which were found to be totally ineffective as PET nucleants, are disodium terephthalate and sodium parahydroxybenzoate. The precise reason that some salts are more effective than others is not understood, but it is believed to depend, at least in part, on the ability of the salt to react with PET and transfer the group-I metal to the chain end. This could involve such factors as solubility of the salt in molten PET, the heat of fusion of the salt crystal, and the relative basicity of the salt. Finally, the method of chemical nucleation with ionic groups on chain ends is transferable to polymers other than PET. Legras et al.[45,46] have shown how polycarbonate and polyetheretherketone (PEEK) can be nucleated by the presence of ionic groups on the chain end.

In this study of the crystallization properties of triglyceride oil/poly(ethylene terephthalate) compositions, the crystallization kinetics of triglyceride oil-containing PET is compared to nucleated PET. Castor oil and vernonia oil have been mixed with PET, and are shown to enhance the crystallization rate. The addition of the sodium benzoate nucleation agent also enhances the crystallization rate, but by a different mechanism. When the sodium benzoate functionality is chemically bonded to the triglyceride oil, and mixed with PET, the two different mechanisms combine synergistically to improve further the crystallization kinetics in a manner different than that obtained by simply mixing the sodium benzoate and the oil with PET.

In the PET semi-IPN systems, the formation of the triglyceride oil network can greatly affect the PET crystallization. Bond interchange reactions, which form the PET/oil copolymer, have an effect on the PET crystallinity, and must also be considered. These crystallinity considerations are in addition to the other factors influencing semi-IPN morphology, providing more possibility for control over the material microstructure, but at the same time making the system more complicated.

EXPERIMENTAL

Poly(ethylene terephthalate) was supplied by EniChem America, Inc., with an intrinsic viscosity of 0.60 dL/g, as measured in 60/40 by weight tetrachloroethane/phenol, corresponding to the viscosity average mol wt of 12,700 g/mole.[47] The PET was dried at 120°C in a vacuum oven for at least 48 h prior to use. Castor oil was supplied by CasChem, Inc., and contained triglycerides with acid residues composed of approximately 90 wt % ricinoleic acid.[48] These hydroxyl-functionalized acid residues were placed nearly randomly on the glycerol backbone, with only 6 wt % of triglycerides being completely nonfunctional.[49] A castor oil network thus contained a small amount of nonfunctional triglyceride oil as plasticizer; however, in PET compositions, the nonfunctional oil can become part of the network structure through bond interchange reactions.[21] Refined vernonia oil was supplied by the Performance Resins & Coatings Division of Rhone–Poulenc, Inc., with an epoxide equivalent weight of 411 g/eq. Vernonia oil contained about 80% epoxy-bearing vernolic acid residues, but fully nonfunctional triglycerides amounted to only 3 wt %.[10] For crosslinking castor oil to form polyurethane, 2,4-tolylene diisocyanate (TDI) was purchased from Aldrich, and hydrogenated methylene diphenyldiisocyanate (HMDI), or 1,1'-methylenebis(4-isocyanatocyclohexane), was the commercial product Desmodur-W, supplied by Mobay Corp. The sebacic acid used in forming the vernonia oil polyester network was obtained from Aldrich, as were other reactants.

Monosodium terephthalic acid (MSTA) was prepared by dissolving terephthalic acid in dimethylsulfoxide (DMSO), and stirring in the presence of insoluble sodium hydroxide pellets at room temperature. In this heterogeneous reaction, when a sodium hydroxide molecule was able to neutralize one of the carboxylic acids on terephthalic acid, the monosodium terephthalic acid precipitated from DMSO. Monosodium terephthalic acid was insoluble in both DMSO and water, and was therefore easily purified from the water soluble sodium hydroxide, and terephthalic acid, which is soluble in DMSO but not in water. Elemental analysis of the resulting MSTA composition, performed by Galbraith Laboratories, Inc. of Knoxville, Tennessee, yielded 50.7 wt % carbon, 4.0 wt % hydrogen, 29.9 wt % oxygen, 3.6 wt % sulfur, and, by difference, 11.8 wt % sodium; calculated values for pure MSTA were 51.1 wt % carbon, 2.7 wt % hydrogen, 34.0 wt % oxygen, and 12.2 wt % sodium. The sulfur detected in the MSTA was apparently due to incomplete separation from the DMSO solvent.

Castor oil monosodium terephthalate (COMSTA) was prepared by direct esterification, by heating castor oil with MSTA at 180°C for 10 h. The reaction scheme is shown below:

$$\text{(1)}$$
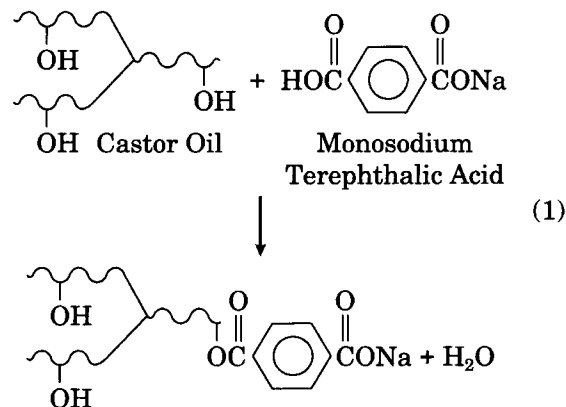
The reaction was not carried to completion, the product being filtered from the remaining MSTA. Fourier transform infrared spectroscopy of the COMSTA showed new absorbance peaks at 1100 and 1240 cm^{-1}, where the benzoate functionality absorbs strongly. Elemental analysis yielded 73.1 wt % carbon, 9.8 wt % hydrogen, 15.2 wt % oxygen, and 1.0 wt % sodium; calculated values were 70.8 wt % carbon, 9.7 wt % hydrogen, 17.4 wt % oxygen, and 2.1 wt % sodium. Based on the sodium analysis, the mixture as used contained about 50 wt % COMSTA, the remainder being unreacted castor oil.

Blends of PET with the triglyceride oil and other ingredients were made at 290°C in a 50cc Brabender Plasticorder torque rheometer batch mixer equipped with sigma blades. The PET was first added and allowed to melt, after which the oil was added by syringe. The compositions made by this method all contained 90 wt % PET, and 10 wt % triglyceride oil product, or 1 wt % nucleating agent (99 wt % PET), or both. The mixing was carried out for a maximum of 8 min with nitrogen purging. Samples of the material were removed from the mixer at specific times and quenched in ice water, but the bulk of the PET compositions were allowed to cool slowly at room temperature, resulting in highly crystalline materials. Samples removed after five minutes mixing were used for analysis. Semi-IPNs were also made in the Brabender mixer, first by melting the PET and then by adding the premixed castor oil and TDI prepolymer. The isocyanate-hydroxyl reaction took place almost instantly at the mixing temperature, forming the castor oil network in the presence of PET. Due to the viscosity mismatch be-

tween molten PET and castor oil, blends containing more than 10 wt % oil were made by a different method, to be described next.

A wide range of semi-IPN compositions were made by a second method, utilizing a flask and magnetic stirring. First, the requisite amount of PET was melted in castor oil in a flask at about 280°C, under nitrogen atmosphere and with stirring, then the temperature was raised to 300°C. With continued stirring at 300°C, the initially immiscible mixture becomes miscible, as is evident by its clarity.[16-18,21] At this point, the synthesis procedure differs, depending upon whether castor or vernonia oil is used. For castor oil mixtures, the source of heat is removed, and the miscible mixture is allowed to cool to 240°C (cooling below this point results in crystallization and precipitation of the PET from solution). The required amount of diisocyanate crosslinker (HMDI) is then rapidly added by syringe, the solution is quickly mixed, and is poured into molds. The hydroxyl-isocyanate reaction occurs very rapidly at 240°C, so that the mixture must be poured into the mold within less than 1 min, before the castor oil gel point has been reached. After pouring, the castor oil semi-IPN molds are placed in an air oven at 100°C for 18 h to complete the network formation. For vernonia oil mixtures, the bond interchange reactions are allowed to continue at 300°C for another 10 min, then the required amount of sebacic acid is added to the flask, which cools the mixture to about 250°C. The mixture is held at 250°C for another 5 min, during which time the vernonia network begins to form, but does not reach the gelation stage. Finally, the vernonia/PET mixture is poured to a mold and placed in a vacuum oven at 160°C for 18 h, where the crosslinking reactions are brought to completion. Alternatively, the mixture may be maintained at 250°C and the network formed at this temperature, where PET and vernonia oil are miscible, and PET remains molten during the network synthesis.

Crystallization characterization used differential scanning calorimetry (DSC), on a Mettler TA-3000 in both scanning (20°C/min) and isothermal modes. Sample size was kept close to 15 mg. Quenched samples were first melted in the DSC for 3 min at 300°C, then were quickly taken out and submerged in liquid nitrogen. The samples were then reheated at 20°C/min to measure the glass transition, crystallization, and melting temperatures. Crystallization from the melt was also measured by simply cooling the sample at 20°C/min from 300°C down to room temperature. The crystallization temperatures reported are from the peak in the DSC exotherm. The DSC was also used isothermally to measure crystallization from either the quenched glassy state at 110°C, or from the melt at 220°C. In these experiments, the sample was rapidly cooled or heated to the isothermal temperature of interest, and heat flow was recorded vs time after the isothermal temperature was reached. In either case, dynamic or isothermal, exothermal crystallization peaks may be integrated and converted to the extent of crystallization, alpha (α), through the relation:

$$\alpha = \frac{X_t}{X_\infty} \tag{2}$$

where X_t is the amount of crystallization at time t, or integrated area of the exothermal peak up to time t, and X_∞ is the ultimate amount of crystallization, or total integrated peak area. Thus, α is a fraction that develops from zero to unity as crystallization proceeds in time, or during a temperature scan.

RESULTS

PET/Triglyceride Oil Blends

PET blends were made containing 10 wt % of castor oil, vernonia oil, and castor oil polyurethane network, and 1 wt % of the nucleating agents sodium benzoate and calcium acetate. The extent of crystallization vs temperature of these blends, as recorded in 20°C/min scanning temperature DSC experiments, are compared in Figure 1, in which the crystallization kinetics are compared both during cooling from the melt and during heating from the quenched glassy state. In crystallization from the melt, 1 wt % of the chemical nucleating agent sodium benzoate is effective at improving the onset and peak crystallization temperature of PET, however, castor oil is close behind, and is in fact better than 1 wt % of the physical nucleation agent, calcium acetate. Although similar in structure to castor oil, the vernonia oil blend actually crystallizes slower than neat PET, and the blend containing the castor oil network crystallizes last of all. In crystallization from the glass, 10 wt % castor oil is significantly better than 1 wt % sodium benzoate, which in this case is no more effective than calcium acetate. The PET/vernonia oil and PET/castor network blends have also improved their ranking, with the castor network blend actually crystallizing before the nucleated materials.

Combinations of sodium benzoate and castor oil were investigated next. The castor oil and sodium benzoate may simply be mixed together with PET,
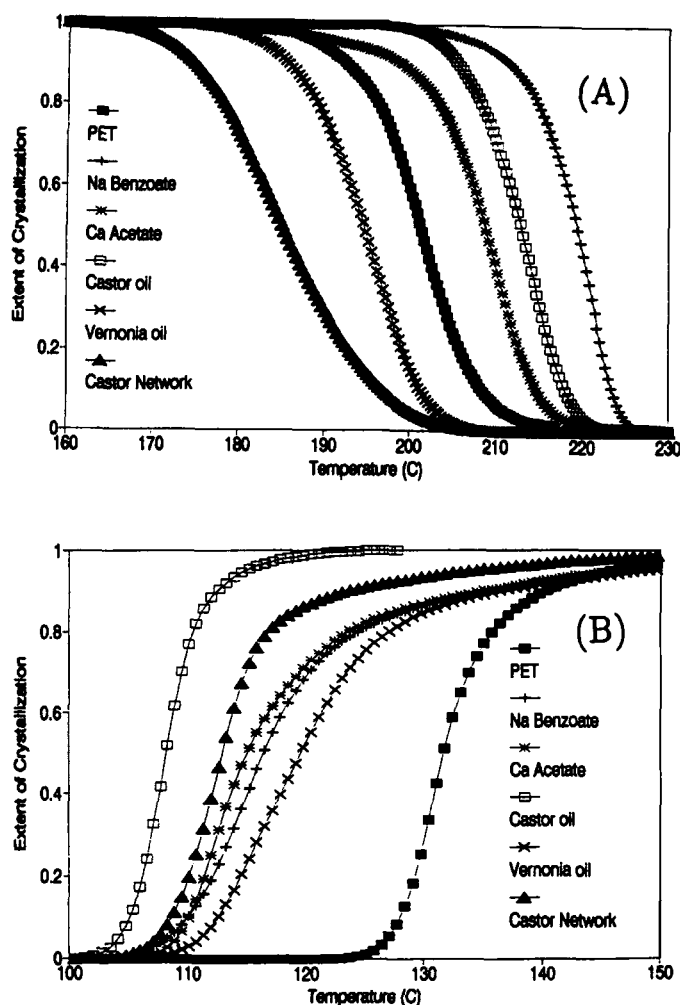
Figure 1 Extent of crystallization vs. temperature during DSC scans taken at 20°C/ min (A) from the melt state and (B) from the quenched glassy state, for various PET compositions.

or else a single molecule can be created, in which the sodium benzoate functionality is bonded to a castor oil molecule. The reaction scheme used to form such a hybrid molecule, castor oil monosodium terephthalate (COMSTA), was shown above in eq. (1). In Figure 2, DSC crystallization scans of PET compositions containing 10 wt % COMSTA are compared with similar compositions, wherein the castor oil and sodium benzoate are simply mixed. In crystallization from the melt, although the simple mixture has a higher onset and peak crystallization temperature, the COMSTA composition has a much sharper crystallization peak. In Table I is presented some of the crystallization data for these compositions. The COMSTA composition has a greater heat of fusion (ΔH) than the simple mixture in cooling, and neat PET has a greater heat of fusion in both heating from the glass and cooling from the melt.

In crystallization from the glass, the simply mixed castor/sodium benzoate composition could not be adequately quenched to yield comparable data, due to rapid crystallization during cooling, and so it is not included. While the COMSTA composition could be quenched in liquid nitrogen, its crystallization temperature is 8°C lower than the castor oil composition, the crystallization temperature of which is about 20°C lower than PET.

The Avrami equation, shown below, has been used extensively to analyze the isothermal crystallization of PET[51-53]:

$$\alpha = X_t/X_\infty = 1 - \exp[-Kt^n] \qquad (3)$$

Where X_t/X_∞ represents the fraction of material crystallized at time, t [see eq. (2)]; and K and n are the Avrami growth and nucleation constants, re-
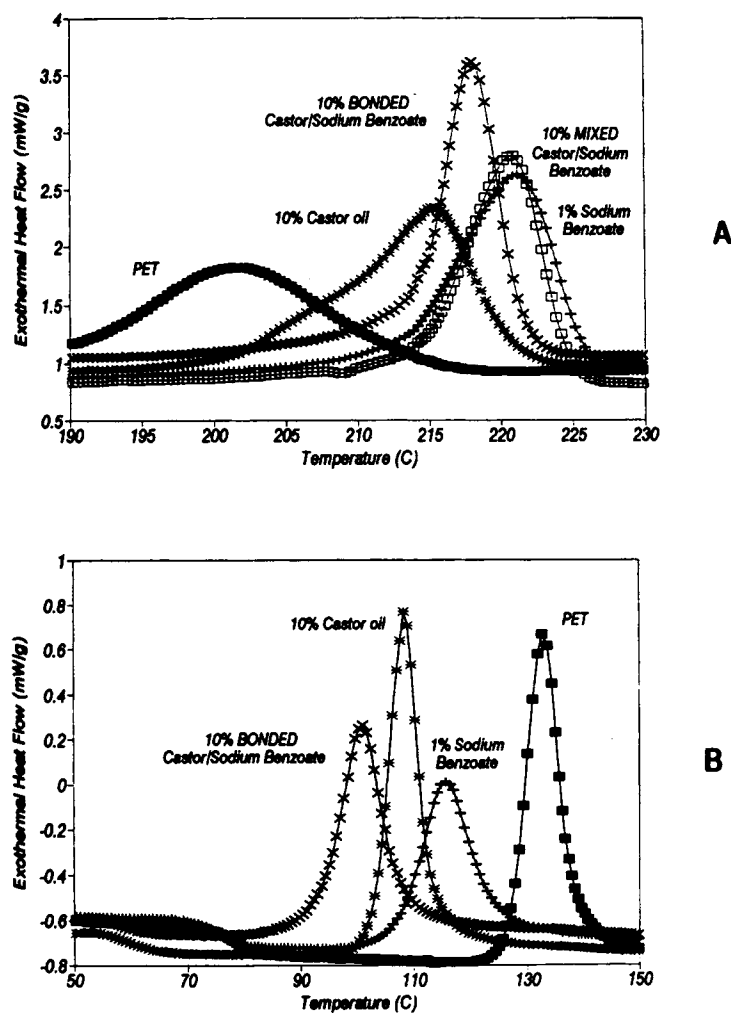
Figure 2   DSC heating scans showing crystallization from the melt (A), and glass transition and crystallization from the glassy state (B), for PET and compositions containing castor oil and/or sodium benzoate.

spectively. Rearranging the equation to form a linear expression, the following is obtained:

$$\log\{-ln[1 - \alpha]\} = n \log t + \log K \qquad (4)$$

By plotting $\log\{-ln[1 - \alpha]\}$ vs. $\log t$, a straight line should be obtained, when a single crystallization mechanism is operative, with the slope of n, and the intercept of $\log K$. The growth constant, K, may also be calculated from the time of peak crystallization rate (t_{max}), as determined from the peak in the DSC crystallization exotherm,[52] allowing the calculation of K from any single data point. During the crystallization of PET, two growth regions have been found, in which the slope of the Avrami plot, or the nucleation constant, goes through a transition. In previous reports, the two regimes have been la-

belled as primary and secondary growth, and they were assigned precise transition points.[52,53] In the primary regime, the nucleation constant, n, is roughly equal to 3, corresponding to spherical growth, while in the secondary regime, the same constant changes to about 1, corresponding to rodlike growth. These types of growth may be rationalized by imagining the crystal nuclei growing outwards as spherulites in three dimensions, until impinging upon one another, whereupon rodlike growth occurs within and between the spherulites. The two mechanisms are observed in crystallization both from the melt and from the glass.

By processing DSC crystallization data on a nearly continuous basis, the distinctiveness of the two regimes disappears, and the PET Avrami plot, often characterized by two intersecting straight

Table I   PET Crystallization Data for Castor Oil and/or Sodium Benzoate Compositions

Composition	Cooling from Melt		Heating from Glass	
	ΔH^{a} (J/g PET)	T_c (°C)	ΔH (J/g PET)	T_c (°C)
PET	45.9	202.2	36.5	133.6
10% Castor oil	58.1	215.0	40.6	109.7
1% Sodium benzoate	52.4	222.5	33.3	117.2
10% Castor + 1% sodium benzoate	49.4	221.8	b	b
10% COMSTA	55.9	219.5	38.7	102.1

[a] The theoretical enthalpy of fusion for 100% crystalline PET is 130 J/g.[50]

[b] These samples could not be quenched effectively enough for comparable data.

lines,[51-53] becomes a continuous curve. In Figure 3, the continuous nature of the transition in mechanisms becomes apparent by plotting the nucleation constant, n, and the growth rate, K, along with the Avrami ordinate log $[-ln(1 - \alpha)]$, for isothermal crystallization of neat PET at 210°C. The change in the nucleation constant, n, vs. time, as the transition from primary ($n \sim 3.5$) to secondary ($n \sim 1.5$) crystallization occurs, is shown to be a gradual process. The growth rate, K, is also observed to increase significantly as the transition from primary to secondary growth occurs, which may be expected if the secondary crystallization is actually space-filling within and between the spherulites. It should be noted that K is a net growth rate, which can increase

either by more rapid movement of individual molecules during crystallization, or by larger numbers of molecules engaging in the crystallization process simultaneously.

In Figure 4, the Avrami ordinate is plotted to compare the isothermal crystallization kinetics of PET in several of the blends at 220°C. The castor oil blend has high curvature in the Avrami plot, indicating a much smoother transition from the primary to secondary crystallization regimes. The sodium benzoate blend displays a distinct change in slope, and thus a rapid transition from primary to secondary crystallization. The data for the blend containing castor oil mixed with sodium benzoate is seen to be different in appearance from the blend
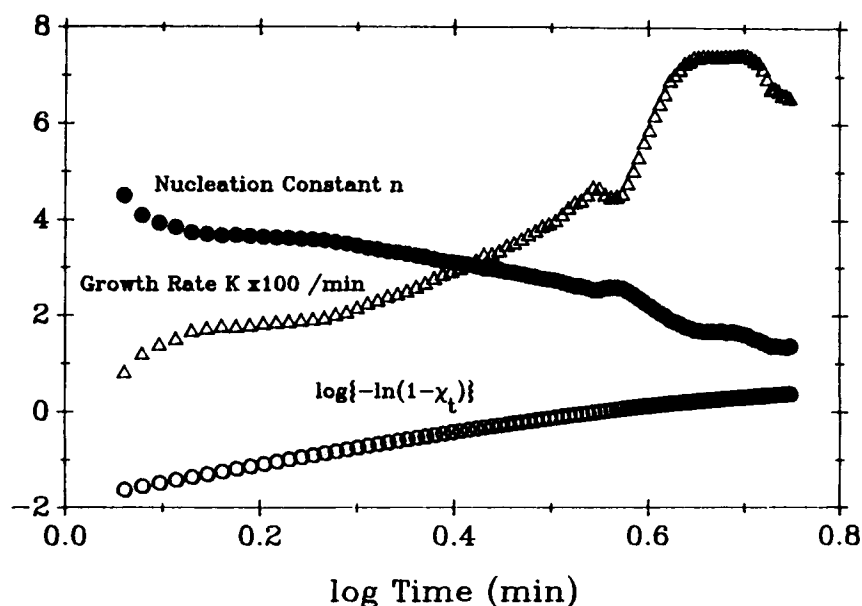

Figure 3   A plot of the Avrami parameters n (nucleation constant), K (growth rate), and the Avrami equation ordinate (log$\{-ln(1 - \alpha)\}$) vs. log time at 210°C for neat PET.
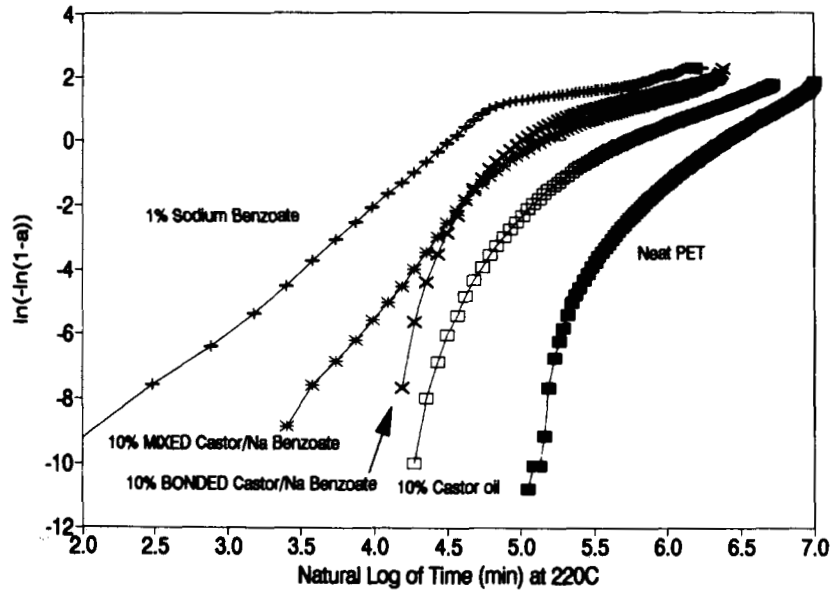
Figure 4 Avrami equation plots for castor oil, sodium benzoate, and related PET compositions during isothermal crystallization from the melt at 220°C.

in which castor oil is bonded to sodium benzoate (COMSTA). The mixture tends to appear more like sodium benzoate, with a rapid transition, while the bonded material has a more gradual transition, resembling castor oil. In Figure 5, the nucleation constant for these same compositions are plotted, which is simply the slope of the curves in Figure 4. Here, the abrupt transition of the sodium benzoate blend

is more obvious, and the continuous change in slope of the other compositions is reflected in their continuously changing nucleation constant. Normally, in studies of crystallization kinetics in which the Avrami equation is utilized, tables showing the nucleation constant are presented, however, from Figure 5 it should be obvious that the nucleation constant is not a constant for the compositions inves-
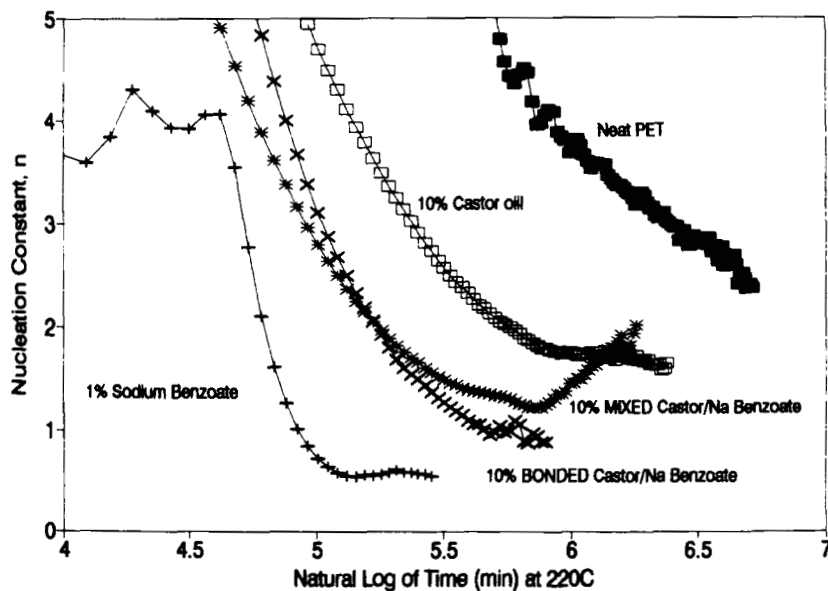

Figure 5 The Avrami nucleation constant, n, vs. crystallization time for various PET compositions during isothermal crystallization at 220°C.

tigated here. It should also be mentioned that, theoretically, in diffusion controlled reactions such as crystallization, the Avrami nucleation constant should not exceed a value of four,[54] however, during the initial stages of crystallization, much larger values are observed.

PET/Triglyceride Oil Semi-IPNs

Using the flask mixture method, the entire range of castor oil–PET compositions were prepared in increments of 10 wt %. In these materials, the PET and triglyceride oil were mixed and heated to the point of miscibility, then the triglyceride oil was crosslinked to form either a polyurethane or polyester network. The resulting semi-IPN materials were yellow-white in appearance, and ranged in properties from elastomeric to plastic, depending on composition.[16–18]

In Figure 6, the crystallization exotherms of several castor oil–HMDI polyurethane network/PET semi-IPN materials, cooled at 20°C/min. from the melt, are shown, comparing the amount of PET in the semi-IPN. As more castor oil is included in the semi-IPN, the melting transition is both depressed and broadened. The calculated peak crystallization and melting temperatures and enthalpies are shown in Table II. While the general trend in the data is that the enthalpy, or total crystallinity, decreases with greater amounts of castor oil network in the

semi-IPN, all of the semi-IPNs with more than 60 wt % PET actually have greater crystallinity (normalized to PET content) than neat PET, although they melt and crystallize at lower temperatures.

The effect of the triglyceride oil network on PET crystallization is another topic of interest. In Figure 7, the DSC heating scan after liquid nitrogen quenching is shown for neat PET, a 50/50 PET/castor oil blend (uncrosslinked), and a 50/50 PET/castor oil–HMDI polyurethane semi-IPN. Crystallization of the neat PET is easily quenched by liquid nitrogen, so that a crystallization peak occurs on heating, with the subsequent melting peak enthalpy equal to that of the crystallization. In the 50/50 PET/castor oil blend, however, no crystallization peak is observed, so that all the crystals, which subsequently melted at around 200°C, were formed during the rapid cooling process, which indicates that crystallization in the blend must be rapid. When the castor oil in the same material is crosslinked to form a semi-IPN, the material may again be completely quenched by cooling in liquid nitrogen. Thus, the presence of the castor oil network slows down the crystallization process considerably.

In the PET/castor oil semi-IPNs, the hydroxyl-isocyanate crosslinking reaction is rapid, and occurs more or less simultaneously with PET crystallization for the semi-IPN materials considered here. With the PET/vernonia semi-IPNs, however, the epoxide–acid crosslinking reaction is much slower, which allows the possibility of forming the network
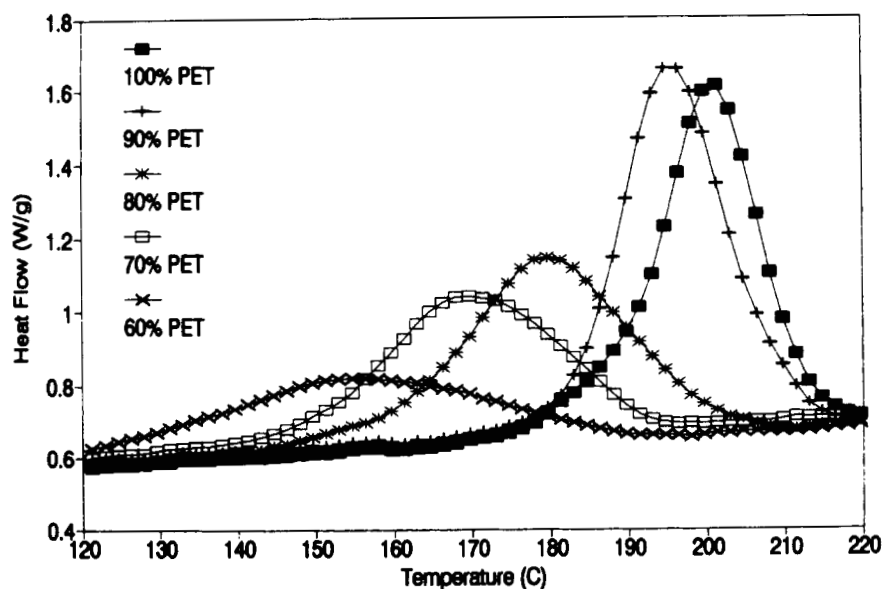

Figure 6 DSC cooling scans from the melt state showing crystallization exotherms for castor/PET semi-IPNs of various PET contents.

Table II   PET Crystallization Data for Castor Oil–HMDI Urethane Semi-IPNs

	First Heating Data		Cooling Data	
% PET	T_m (°C)	ΔH (J/g PET)	T_m (°C)	ΔH (J/g PET)
40	195.3	15.2	149.5	39.5
50	205.6	35.2	153.9	47.7
60	223.3	47.3	157.9	48.2
70	226.8	54.4	171.3	54.7
80	235.5	57.3	180.4	65.1
90	240.6	56.7	196.9	57.1
100	247.4	53.3	202.2	45.9

either before or after the PET has crystallized, depending upon the network synthesis temperature. The melting scans of PET/vernonia oil semi-IPN materials, where the network was synthesized at 250°C and 160°C, are shown in Figure 8. If the network is formed at 250°C, above the crystallization temperature of PET, while the mixture is in a miscible state, a thermally stable, noncrystalline material results. When the network is synthesized at 160°C, after the PET has already crystallized, on the first heating, considerable crystallinity is observed, however, after cooling the sample and heating again, it is observed that most of the crystallinity is easily quenched during cooling and only a small fraction of the crystallization observed in the first heating is recovered.

Bond interchange between the triglyceride oil and PET also affects the crystallization in semi-IPNs. By holding the PET/triglyceride oil mixture for longer periods of time at 300°C before addition of crosslinker, greater extents of bond interchange are reached. These reactions create a block copolymer composed of PET and the triglyceride oil,[21] and if they were left to react indefinitely, the reactions would result in the formation of a statistical copolymer mixture. As more copolymer is formed, the PET and triglyceride oil become more miscible. In Figure 9, the melting endotherms of PET/vernonia oil semi-IPNs, in which the bond interchange reactions were allowed to occur for different periods of time at 300°C, are shown. As greater extents of interchange are reached at longer times held at 300°C, the resulting melting endotherm is broadened, depressed, and diminished.

Finally, it is interesting to look at the melting endotherms of uncrosslinked PET/triglyceride oil blends as a function of bond interchange reaction time at 300°C. In Figure 10, the endotherms of a 50/50 PET/castor oil blend are shown as a function of time held at 300°C. Table III shows the melting and crystallization temperature data for the two triglyceride oils mixed with PET, as a function of bond interchange reaction time. Again, the endotherms are depressed, broadened, and diminished. It is par-
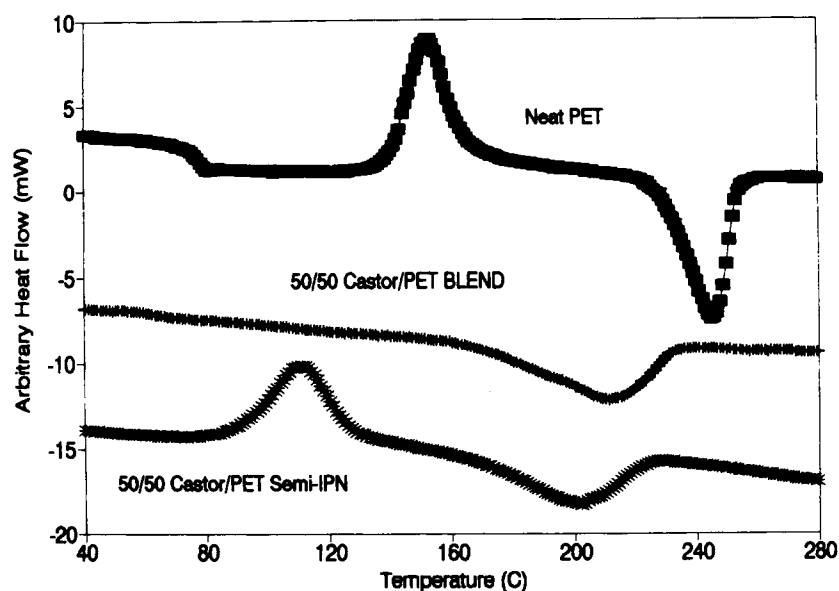

Figure 7   DSC heating scans, taken after quenching from the melt, showing crystallization and/or melting of PET in neat PET, a 50/50 PET/castor oil mixture, and a 50/50 PET/castor oil polyurethane network semi-IPN.
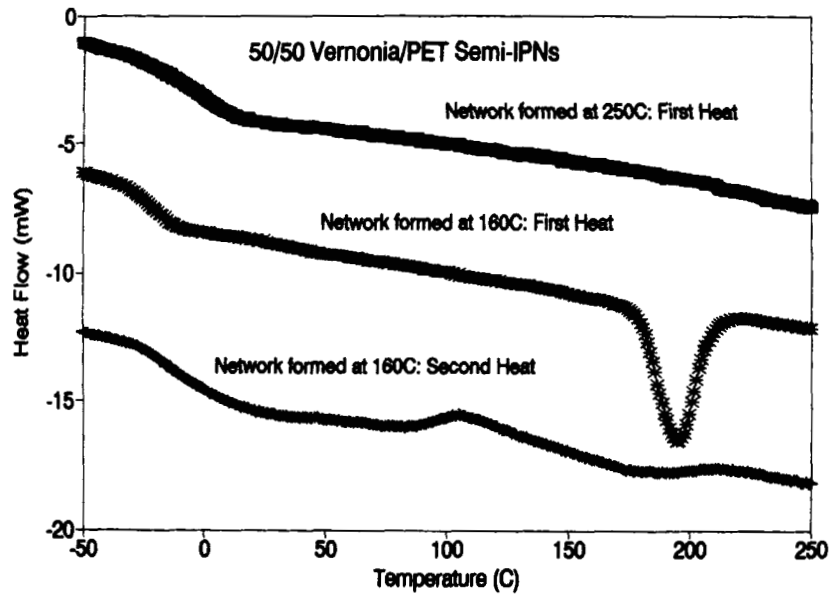
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Figure 8 DSC heating scans, taken after quenching from the melt, showing crystallization and melting, or absence thereof, of PET in 50/50 PET/vernonia oil semi-IPNs, where the vernonia oil network was formed at either 160°C (below the crystallization temperature of PET), or 250°C (above the crystallization temperature of PET).

ticularly interesting to compare Figure 10 with Figure 6. Although one shows crystallization of semi-IPNs with varying composition, and the other melting of 50/50 blends as a function of reaction time at 300°C, the trends are identical. Adding greater amounts of triglyceride oil to the semi-IPN has the same effect as allowing more bond interchange to occur in the uncrosslinked blend.

DISCUSSION

As previously discussed, when injection molding crystalline PET, the molds are typically heated to less than 100°C. In such a cool mold, the PET can become quenched to the amorphous state as it contacts the mold surfaces. This effect can cause poor surface quality of the molded article. To be a useful
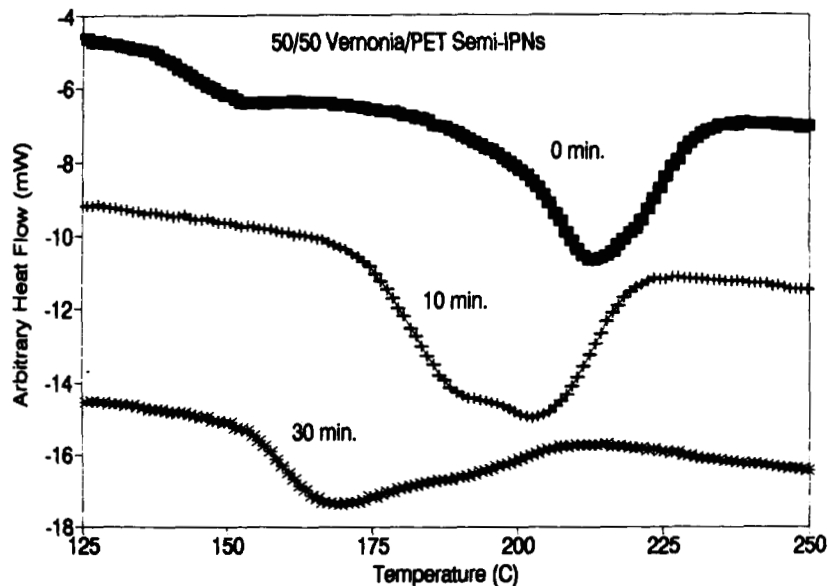

Figure 9 DSC heating scans, taken after quenching from the melt, showing crystallization and melting of 50/50 PET/vernonia oil semi-IPNs, in which different amounts of time at 300°C were used during synthesis, causing the extent of bond interchange to vary.
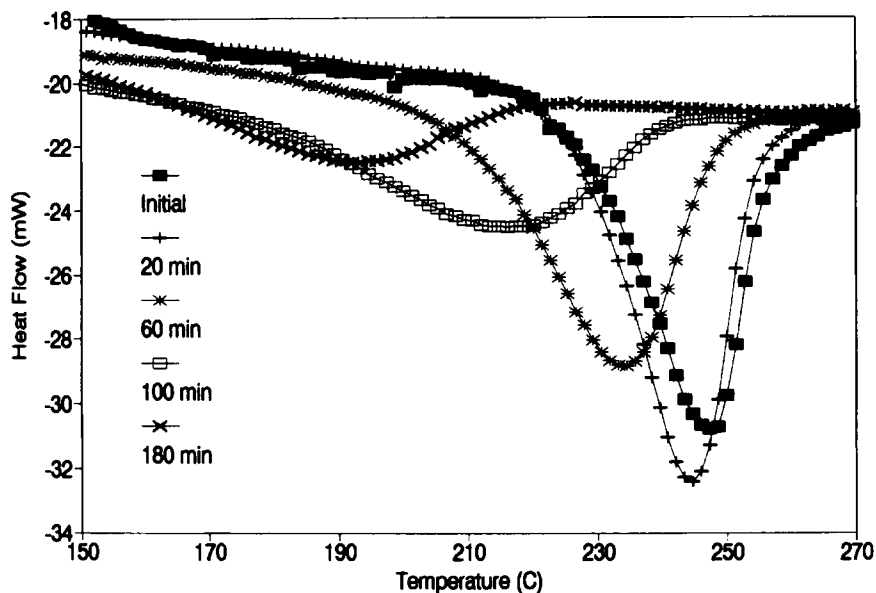
Figure 10   DSC heating scans, taken after quenching from the melt, showing melting endotherms of 50/50 PET/castor blends as a function of time held at 300°C.

engineering plastic material for injection molding applications, PET must have the ability to crystallize rapidly, both as it is cooled from the melt and as it is heated from a quenched amorphous glassy state. Rapid crystallization from the melt allows short cycle times, while rapid crystallization from the glassy state alleviates the quenched mold surface crystallinity problem, by allowing quenched surface material to crystallize as it is heated by transfer of heat from within the molded article. Thus, both a nucleation agent and a mobility enhancer (plasticizer) are required for optimal performance.

Sodium benzoate is effective at creating nucleation sites for crystallization, and so is effective at enhancing crystallization from the melt, where PET mobility is adequate, but nucleation sites are few. On the other hand, in crystallization from the glassy state, mobility is more important than nucleation sites,[55] and this is where castor oil excels since it acts as a plasticizer, and sodium benzoate or calcium acetate are ineffective (Fig. 1). In both the mixed and bonded castor oil/sodium benzoate compositions, a synergism develops between the mobility enhancing castor oil, and the nucleation providing sodium benzoate, which yields a PET material with crystallization enhanced from both the melt and glassy states (Fig. 2). While the reactive nature of both sodium benzoate and castor oil cause reduction in PET mol wt, it is not only the mol wt reduction alone that causes the enhanced crystallization. In Table IV, it may be seen that although a 1 wt % monosodium terephthalic acid (MSTA) composi-

tion had much lower mol wt, the 10 wt % castor oil and 1 wt % sodium benzoate compositions had higher peak crystallization temperatures upon cooling, and took less time to reach the maximum in their endothermic peak during isothermal crystallization at 220°C (t_{max} around 220°C).

Another aspect of castor oil's effectiveness may be found in the Avrami analysis data. The rapid transition from primary to secondary crystallization observed with sodium benzoate indicates a large number of instantaneously formed nuclei, growth of the nuclei, then nearly simultaneous impingement of spherulites, causing an abrupt switch to secondary

Table III   PET Melting Data for 50/50 PET/ Castor Oil and PET/Vernonia Oil Mixtures Held for Various Times at 300°C

	PET/Castor		PET/Vernonia	
Min at 300°C	T_m (°C)	ΔH (J/g PET)	T_m (°C)	ΔH (J/g PET)
0	250	42.0	248	42.0
20	246	45.2	244	48.2
40	236	46.8	241	45.8
60	226	36.2	233	51.0
80	217	39.6	226	45.0
100	206	35.2	216	33.4
120	199	31.4	210	24.2
140	193	31.6	208	18.8
160	188	33.8	197	16.6

Table IV   Molecluar Weights and Crystallization Parameters for PET in Several Compositions

Composition	$[\eta]$ (dL/g)	M_v (g/mol)	T_c (COOL) (°C)	t_{max} at 220°C (min)
Neat PET	0.60	12900	202.2	10.1
Melt processed PET	0.52	10300	205.8	9.7
1% Sodium benzoate	0.42	7400	222.5	1.0
10% Castor	0.44	7900	215.0	3.4
1% MSTA	0.25	3300	210.1	3.8

growth. The castor oil seems to smooth out the transition from primary to secondary crystallization (Figs. 4 and 5). In doing so, it allows the more rapid secondary crystallization to occur sooner in the process, simultaneous with the slower primary crystallization.

It is felt that the copolymer formed through bond interchange aids the crystallization process. In the 10 wt % castor oil mixtures, the castor oil was completely copolymerized with PET during the mixing process; thus the plasticizer responsible for more rapid crystallization was not really castor oil, but was PET/castor oil copolymer. Vernonia oil takes more time to copolymerize completely with PET, displaying a separated phase from the 10 wt % mixture, and much slower crystallization (Fig. 1).

The fact that poly(ethylene terephthalate) may crystallize significantly complicates the morphology of the semi-IPNs made[18] and, conversely, the triglyceride oil network complicates the crystallization of PET. In the present research, three effects on the PET crystallinity have been explored: triglyceride oil composition, network formation, and bond interchange copolymer formation.

In general, as more triglyceride oil is combined with the crystallizing PET phase, either through greater extents of bond interchange reactions (Figs. 9 and 10), or by a greater overall triglyceride oil concentration (Fig. 6), the PET melting temperature is depressed and broadened. This phenomenon is simply the effect of physical interactions between the oil and PET in the amorphous material of the semicrystalline phase, resulting in classical thermodynamic melting point depression. A broadened melting range is indicative of a wider distribution of crystalline morphologies, not surprising for these mixtures, which are composed of varying amounts of random copolymer. The presence of network can make a dramatic difference in the PET crystallinity, as illustrated in Figures 7 and 8. When formed prior to cooling, the network is apparently able to prevent PET chains from the movements required for crys-

tallization. Similarly, even when normal crystallinity is achieved before network synthesis, after these crystals are melted, crystallization on subsequent cooling is considerably impeded by the presence of the network.

CONCLUSIONS

The crystallization of PET in triglyceride oil mixtures is affected by several important factors: plasticization due to the oil, nucleation from added agents, bond interchange reactions, overall composition, and the presence or formation of a crosslinked triglyceride oil network. Crystallization of PET in the presence of small amounts of castor oil is accelerated, both in cooling from the melt state, and heating from the glassy state. From the glassy state, it is the plasticization of PET by the oil that is most likely to improve crystallization, while from the melt state, the copolymer formed through bond interchange reactions may facilitate the process of PET chain-folding. In conjunction with the chemical nucleating agent sodium benzoate, either chemically bonded to castor oil or as a simple mixture, even greater enhancements in crystallization are observed. In this case, the sodium benzoate provides nucleation sites, which synergistically improve crystallization kinetics in conjunction with the mobility-enhancing oil.

Bond interchange reactions lead to lowered PET molecular weight as well as block copolymer, and also increase the PET crystallization rate in triglyceride oil semi-IPNs and blends. In semi-IPN compositions, both the physical presence of the network structure and the sequence of its formation, with respect to crystallization, influence the PET crystallinity. When the triglyceride network is formed in a miscible mixture with PET above its crystallization temperature, the PET is unable to crystallize upon cooling, resulting in amorphous semi-IPNs.

The identification of these factors allows some

control over the microstructure of these and similar blends and semi-IPNs. It is seen that crystallinity of PET may be made to occur more rapidly at higher or lower temperatures or, conversely, crystallinity can be made slower or may be completely eliminated, depending upon how the blend or semi-IPN is processed.

NOMENCLATURE

PET	Poly(ethylene terephthalate)
IPN	Interpenetrating Polymer Network
HMDI	Hydrogenated methylene diphenyldiisocyanate
PBT	Poly(butylene terephthalate)
FTIR	Fourier Transform Infrared
PEEK	Polyetheretherketone
TDI	Tolylene diisocyanate
MSTA	Monosodium terephthalic acid
DMSO	Dimethylsulfoxide
COMSTA	Castor oil monosodium terephthalate
DSC	Differential Scanning Calorimeter
ΔH	Measured enthalpy of fusion
T_c	Peak crystallization temperature
T_m	Peak melting temperature
t	time
α	Extent of crystallization
X_t	Crystallinity at time t
X_∞	Crystallinity at infinite time
K	Avrami growth constant
n	Avrami nucleation constant
t_{max}	Time of peak crystallization rate
$[\eta]$	Intrinsic viscosity
M_v	Viscosity-average mol wt

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