Crystallization of Poly(ethylene oxide) in i-Polypropylene–Poly(ethylene oxide) Blends

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ABSTRACT: A two-stage stable system of isotactic polypropylene–poly(ethylene oxide) blend, in which poly(ethylene oxide) can be permanent either in molten or in crystallized states in the temperature range from 280 to 327 K, was described. The behavior of that blend was explained in terms of fractionated crystallization. A fine dispersion of poly(ethylene oxide) inclusions is required for efficient suppression of crystallization initiated by heterogeneous nuclei. The application of a thin film of polypropylene–poly(ethylene oxide) 9 : 1 blend obtained by quenching for multiuse erasable and rewritable carriers for visible information has been demonstrated. The same sample exhibits different dynamic mechanical properties when poly(ethylene oxide) inclusions are molten or crystallized. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **66:** 2047–2057, 1997

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INTRODUCTION

The blends of immiscible or partially miscible polymers, i.e., the blends in which one of the components is dispersed in the matrix of the second polymer, have received wide attention for both fundamental and practical reasons. Under favorable conditions, the presence of the dispersed phase may lead to the substantial improvement of the mechanical properties (e.g., toughness) in comparison with the pure polymer. Toughening due to the incorporation of dispersed particles of the second polymer has been observed both for glassy (e.g., polystyrene) and semicrystalline polymer matrices [e.g., polyamide, i-polypropylene, and poly(methylene oxide)][1,2] and is now widely used in preparation of high-performance polymeric materials. In the second case, the main difficulty in explaining the properties of blends in terms of the properties of their components is associated with their complex crystallization behavior.

It has been shown that due to the mutual influence of the components on primary nucleation, the size and the shape of the spherulites of the polymer matrix are strongly affected by the presence of the second component.[3] The dispersed particles of the second component may also affect the shape of the interspherulitic boundaries (if they are rejected by the growing spherulites), or give rise to the formation of new boundary lines if they are occluded by the growing spherulites.[4] Thus, by changing one parameter (using another component with different mechanical properties), one inevitably affects the morphological parameters influencing the mechanical properties of the matrix.

The studies of the influence of the dispersed particles on the properties of a blend could be simplified if the properties of the dispersed phase are altered within the system, e.g., by changing its phase state, without affecting the properties of the matrix. Establishing such a model system, the conditions of its formation and investigation of its crystallization behavior were the aims of the present work.

Choice of a Polymer Pair Constituting the Model System

It is well known that the undercooling needed for bulk crystallization of the polymer melt relies on the presence of impurities. The dispersion of a polymer into fine droplets[5-7] causes the crystallization of those droplets that contain impurities and prevents from the crystallization those particles that do not contain impurities. At various degrees of undercooling, the droplets containing impurities are solidified, while those not containing impurities are crystallized at a large degree of undercooling when a true homogeneous critical primary nucleation process is undergone. If a polymer is relatively free from nucleating impurities, only a small fraction of droplets undergoes crystallization at a temperature above the intense homogeneous primary nucleation. For a polymer with an intense heterogeneous nucleation for sufficiently fine dispersion, the two modes of crystallization, heterogeneous and homogeneous, can be observed. This is possible when the number of droplets is larger than the number of heterogeneities able to induce the nucleation of crystallization.

Similar effects in phase-separated polymer blends were also reported in the literature.[8-12] For sufficiently fine dispersion of crystallizable polymer in a polymer matrix, two modes of primary nucleation of the dispersed component can be observed. Hence, the effect of segregation of droplets according to the nucleation capability of crystallization is called fractionated crystallization. Also, for polymer blends, for very fine dispersion of a polymer containing only a few nucleating impurities, only a small fraction of droplets undergoes crystallization above the temperature of critical homogeneous primary nucleation. The majority of droplets are not able to crystallize until the temperature would be decreased to the region of intense homogeneous primary nucleation. The detailed discussion of the phenomenon of fractionated crystallization

in polymer blends, including the estimation of the number of nuclei and energetic consideration, was given by Frensch and Jungnickel.[13] Thus, the blend in which the droplets of the dispersed phase might exist at ambient temperature at the same time either in a metastable undercooled molten state or in a solidified state (after quenching below the temperature of strong homogeneous nucleation and warming up to the ambient temperature) should fulfill the conditions of the model system.

The above stated requirements impose the following conditions upon the habits of melting and crystallization of blend components.

- Both polymers should be immiscible.
- Polymer matrix should remain crystallized above the melting temperature of the dispersed phase ($T_{mM} > T_{mD}$), and the dispersed component should exhibit the melting temperature T_{mD} above the ambient temperature.
- The dispersed phase should exhibit low heterogeneous nucleation density; the strong homogeneous nucleation of the dispersed phase should appear at as low as possible temperature (most desirably, well below room temperature).
- The polymer matrix should not exhibit nucleating activity towards the dispersed phase.
- The achievable degree of dispersion of the second component should permit obtaining a sufficiently large number of particles in order to obtain a large fraction of particles free of heterogeneous nuclei.

Isotactic poly(butene-1)(i-PB-1) and poly(ethylene oxide)(PEO) might be chosen for the dispersed phase because, on the basis of fractionated crystallization, they are reported to show homogeneous nucleation at the temperature below 273 K.[6,7,14] From these two polymers, PEO seems to be most suitable as its melting temperature is much lower (342 K),[15] in comparison with 403–411 K for the case of i-PB-1, depending on crystal modification.[16]

The requirement for the high melting temperature of the polymer matrix ($T_{mM} > T_{mD}$; see above) suggests the use of polyamide ($T_m = 543$ K for PA-6; $T_m = 553$ K for PA 6,6), polypropylene ($T_m = 460$ K), poly(methylene oxide)($T_m = 457$–467 K), or polyethylene (HDPE) ($T_m = 413$ K) (see Wunderlich[15]). The choice of PEO as a dis-

persed phase imposes, however, additional conditions connected with its relatively low thermal stability, due to the presence of oxygen in the main chain. As the T_m of polyamides highly exceeds the thermal stability range of PEO (up to 470 K; see van Krevelen[16]), they were rejected. In the choice between poly(methylene oxide) and polyolefins, a more pronounced chemical difference of polyolefins with respect to PEO suggests the use of one of these polymers. Finally, blends of polyolefins with PEO show a remarkable importance because of recent progress in developing degradable polymer blends with the use of PEO.[17–20]

EXPERIMENTAL

Blend Preparation

Isotactic polypropylene (iPP) Moplen C-30-G (melt flow rate according to ISO-1133 is 6 g/10 min), supplied by Montepolimeri (Montepolimeri, Italy), and poly(ethylene oxide) (M_w = 100,000), supplied by Polysciences Inc. (Warrington, PA), were used throughout these studies. The blends were prepared in a laboratory batch mixer (Rheocord E.C. of Haake Inc.) by melt-mixing of the components at 463 K, with a mixing time of 10 min and at a rotor speed of 32 rpm. The following blends were prepared: 90 wt % of iPP to 10 wt % of PEO, 80 wt % of iPP to 20 wt % of PEO, and 70 wt % of iPP to 30 wt % of PEO. The reference samples of plain PEO and plain iPP used in crystallization behavior studies were processed in the batch mixer under the same conditions, in order to avoid differences caused by the different thermomechanical histories of the samples. Before mixing, the components were vacuum-dried in order to avoid the effects connected with high hygroscopicity of PEO. Due to the same reasons, the samples were stored under vacuum between the subsequent experimental steps.

The obtained blends were compression molded in the hot press (463 K, 20 MPa) into 0.5 mm thick (for differential scanning calorimetry studies) and 0.2 mm thick films (for light transparency studies) which, after keeping for 5 min in the press, were quenched to room temperature.

Experimental Techniques

Morphology

Microtomed surfaces of the samples were examined by means of a Phillips 501 scanning electron microscope (SEM), after coating them with a layer of gold–palladium alloy. Some of the blends were also etched in water at 323 K for 1 h in order to dissolve the dispersed phase and were then prepared for SEM examination.

Crystallization Studies

The studies of crystallization behavior of PEO in the blends were carried out by means of the differential scanning calorimetry (DSC) technique (Mettler TA 30000 apparatus), using approximately 20 mg samples taken from the compression-molded films. The DSC experiments were performed in three stages, as follows.

1. Melting and annealing of the components (heating at a rate of 10 K min from room temperature to T_a = 463 K; 5 min annealing time).
2. Fast, nonisothermal crystallization of the polymer matrix (cooling at the rate of 50 K/min to the temperature T_i = 353 K, annealing at T_i for 5 min in order to complete the crystallization of polypropylene).
3. Nonisothermal crystallization of PEO (cooling at a rate of 10 K/min from T_i = 353 K to T_i = 223 K).

The crystallization conditions for the polymer matrix (T_a = 463 K; cooling rate 50 K/min; T_i = 353 K) were chosen in order to obtain a fine structure of polypropylene. Such structure is most desirable for high transparency of polypropylene film and for its high toughness.[21–25] The intermediate temperature T_i was close to the critical temperature of polypropylene solidification determined in the fractionated crystallization experiments[6] and was still 10 K above the melting temperature of PEO. The DSC traces recorded in the third stage (crystallization of PEO) were normalized to the mass of PEO in the samples.

Dynamic Mechanical Properties

Samples of blends in the form of 3 cm long strips with the cross section of 0.4 × 5.0 mm were tested in bending in Rheometrics DMTA III apparatus at the frequency of 1 Hz in the temperature range from 273 to 393 K.

RESULTS

The Phase Structure of the Blends

SEM micrographs of the microtomed surfaces of the blends, arranged at an increasing amount

of PEO, are shown in Figure 1(a)–(c) and in Figure 2(a)–(c) (water-etched surfaces). As can be seen, the blends exhibit a typical morphology of incompatible components. The dispersed phase is segregated in almost spherically shaped domains, the dimensions of which increase with an increasing amount of PEO. This effect is illustrated quantitatively in Figure 3, containing the histograms of the size distributions of PEO particles, obtained on the basis of series of micrographs. The size distributions of particles were obtained by recalculating the size
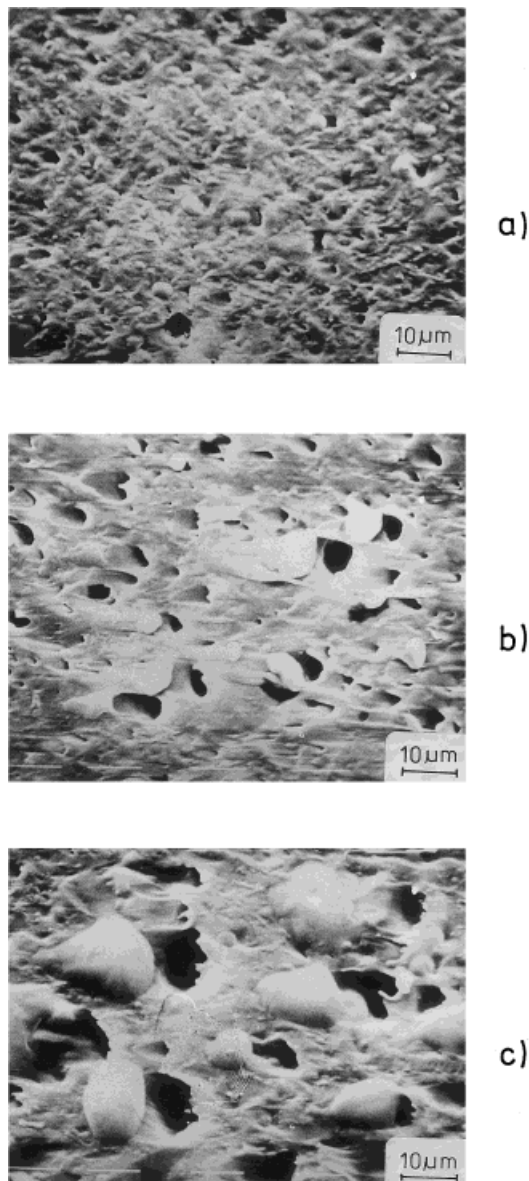

Figure 1 SEM micrographs of the microtomed surfaces of the blends: (a) PP + PEO 9 : 1, (b) PP + PEO 8 : 2, (c) PP + PEO 7 : 3.
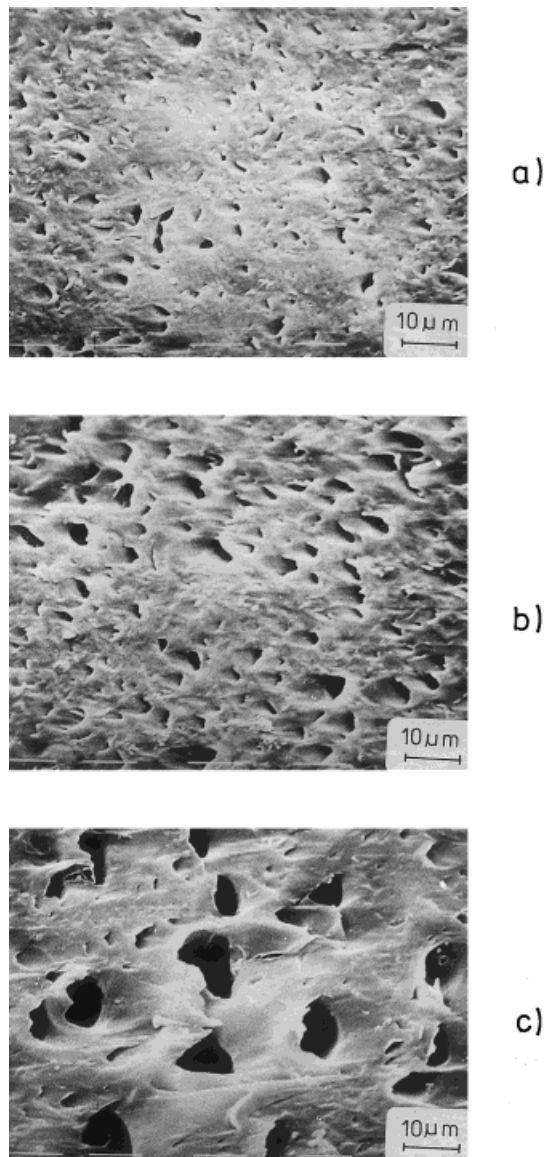

Figure 2 SEM micrographs of the microtomed and water-etched surfaces of the blends: (a) PP + PEO 9 : 1, (b) PP + PEO 8 : 2, (c) PP + PEO 7 : 3.

distributions of circles seen on microtomed surfaces under the assumptions that the spherical inclusions were cut at random in a microtome section.[26] Note that due to the large differences in particle volumes, logarithmic scale was used, in which the width of the histogram bars corresponds to the particle volume (v) intervals (v, $5v$). As can be seen, the maxima of histograms shift about two orders of magnitude towards higher volumes, passing from PP + PEO 9 : 1 to PP + PEO 7 : 3 (from about 10^{-17} to 10^{-15} m^3, respectively). The size distributions of PEO particles are very broad; and, in all cases, they
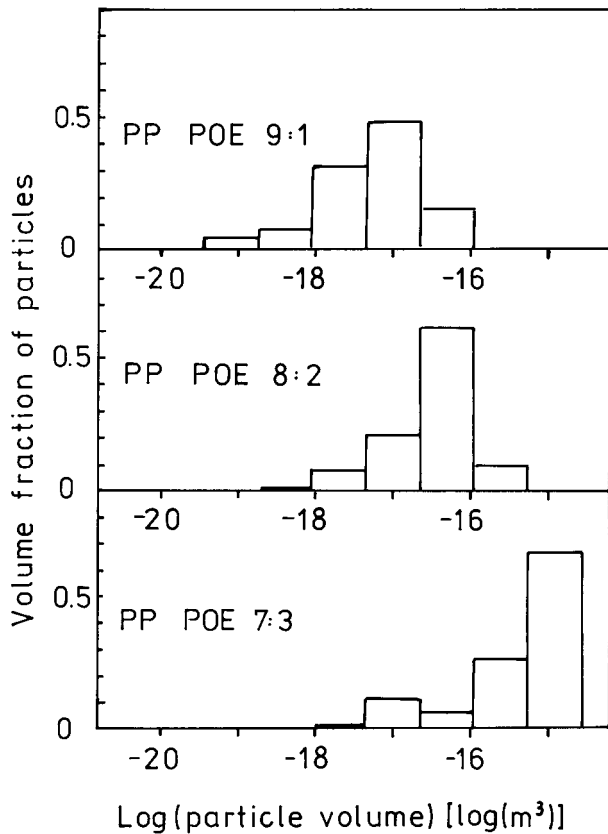
Figure 3 The histograms of the size distributions of PEO particles in PP–PEO blends. The width of the histogram bars corresponds to the particle volume (v) intervals (v, $5v$).

cover the range of at least three orders of magnitude. All the samples contain a significant fraction of particles belonging to the same volume interval (for example, from 10^{-17} to 10^{-16} m^3). The above observations may be explained as a consequence of dispersion and coalescence of PEO inclusions during mixing, with the dispersion mechanism depending on particle size and with coalescence occurring with increasing intensity with the increase of contents of the dispersed phase in the blends. For the reduction of the dispersed phase, the viscosities must be low and similar for both components and the interfacial interaction high, with the surface tension low and shear, or compressive forces strong and acting for long time. If the interfacial interaction is low, i.e., surface tension high, as in the case of immiscible PP–PEO blends, sufficiently large forces are not transferred to inclusions for their small sizes. This effect implements a limiting size of inclusions in a given mixer, independent of the mixing time. There is another mechanism which limits the average particle size, which is coalescence. The average particle size is thus given also by the density of the particles in a unit volume of a blend. The larger the surface tension, the easier it would be for particles to combine on contact. Large surface tension will also make the connection of particles more probable. Hence, the resulting average particle size is a compromise between the two opposing processes, and equilibrium average size is quickly reached, with a large size distribution. Although there are successful attempts to describe the phenomena on the microscale,[27–32] this brief picture cannot be easily quantified for the macroscale given the lack of systematic data and adequate theories, which would utilize measurable parameters. The behavior of PP–PEO blends conforms to the above envisioned processes: there is a limiting particle size that cannot be substantially lowered by prolonged mixing in the same equipment, the distribution of particle sizes is broad, and the average particle size is larger for higher concentration of the dispersed component.

Crystallization Behavior of PEO

The normalized DSC thermograms recorded during crystallization of plain PEO and of PEO in the blends are shown in Figure 4. Numerical data concerning nonisothermal crystallization, obtained on the basis of these thermograms, are collected and described in Table I.

The crystallization exotherms of PEO in the blends differ significantly from the crystallization exotherm of pure polymer. With increasing PEO content, the dispersed phase exhibits the increasing tendency for multiple crystallization behavior. The main (more pronounced) crystallization peak of PEO in all blends occurs in the temperature range indicated; it is associated with the crystallization initiated by the homogeneous primary nucleation. With an increase in PEO concentration, a new, higher temperature peak is developed. The onset of this peak correlates with the position of the DSC peak observed during crystallization of the plain PEO. The peak itself, however, is about 10 K below T_{max} of pure polymer. In view of the above results, the fraction of the heat effect associated with the lower temperature DSC peak, X, should be close to the fraction of PEO particles requiring homogeneous nucleation for initiation of crys-
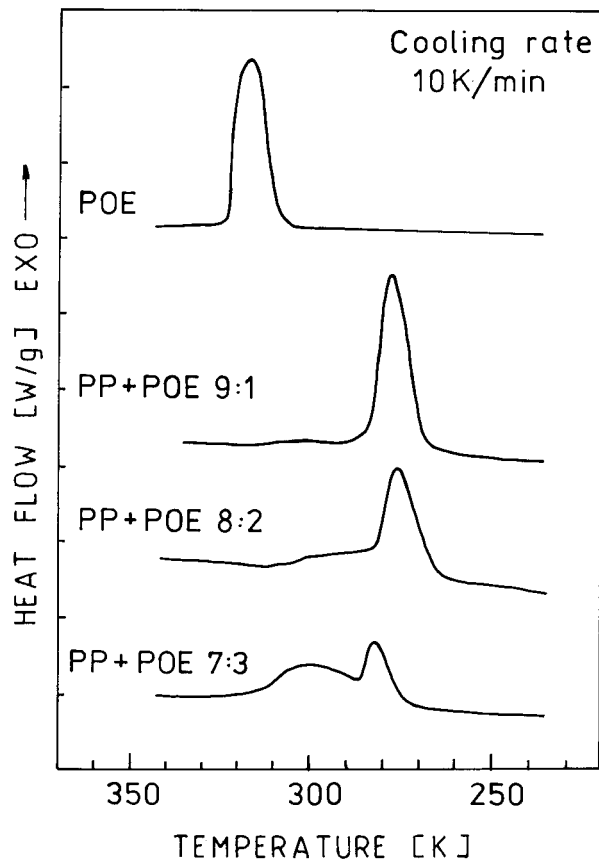
Figure 4 The normalized DSC thermograms recorded during crystallization of plain PEO and of PEO dispersed in iPP matrix.

tallization at the applied cooling rate. As can be seen from the data presented in the latent heat of fusion (in J/g of PEO) of plain PEO and that of PEO in the blends are similar and range from 105 to 128 J/g.

Comparison of these values with the value of heat of fusion of PEO single crystals (196.6 J/g, Klemmer and Jungnickel[11]) yields the values of crystallinity degrees of PEO ranging from 0.53 to 0.65. The observed differences may be explained as a result of fractionated crystallization of PEO occurring at different temperature ranges for heterogeneous and homogeneous modes. The somewhat arbitrary character of the baseline determination (see note to end Table I) and nonuniformities of blend composition in the samples studied may also slightly contribute to the differences in crystallinity degree. The values of X, calculated after applying a procedure for peak separation, are listed in the last column of Table I. As can be seen, the fraction of PEO particles crystallizing due to homogeneous

nucleation decreases from about 1.0 (PP + PEO 9 : 1) to about 0.6 (PP+ PEO 7 : 3) with the increase of contents of the dispersed phase in the blends.

The above effect makes the blends with fine dispersion of PEO suitable as a two-stage stable system in which PEO can be permanently in molten or in crystallized states in the temperature range from 280 to 327 K. The transition between those states is performed from the molten state by cooling down to 273 K while from the crystallized state by heating up above 333 K. The switching characteristics are illustrated in Figure 5 where the DSC thermograms of iPP–PEO 9 : 1 blend recorded during heating and cooling are depicted. The sample in the form of 0.2 mm thick film was prepared from pellets of the iPP–PEO 9 : 1 blend by compression molding, followed by quenching in iced water. The polypropylene matrix remained highly transparent due to rapid solidification during quenching, mostly in the smectic form,[21-23] as

Table I   Summary of DSC Crystallization Data of Plain PEO and PEO Dispersed in Polypropylene Matrix

Sample	T_o[a] (K)	T_{max} (K)	T_f (K)	ΔH (J/g)	X
PEO	325	316	302	120	—
PP + PEO 9 : 1	305	—	276	257	128	0.98
PP + PEO 8 : 2	310	292	275	258	113	0.76
PP + PEO 7 : 3	320	300	281	267	105	0.58

[a] Symbols represent the following: T_o, temperature of crystallization onset; T_{max}, temperature(s) of crystallization peak(s); T_f, temperature of crystallization completion; ΔH, total heat effect associated with PEO crystallization (peak integration performed assuming straight baseline drawn from T_o to T_f); and X, fraction of heat effect associated with lower temperature DSC peak.

it can be identified from the X-ray diffraction (XRD) from the iPP–PEO blend with molten PEO inclusions, while PEO inclusions became opaque due to their rather slow crystallization at 280 K. In this way, the film is highly opaque in the temperature range below 333 K. The light transmittance of the film measured at the wavelength of 500 nm in UV–VIS Specord Spectrometer is equal to 18%. Now, if the film is heated slightly above 333 K, the PEO inclusions melt and the film becomes transparent; the transmittance increases to 67%. The transparency is preserved during cooling to approximately 280 K. The crystallization of PEO inclusions begins slowly again below 280 K. Within the temperature range from 280 to 327 K, two stable forms of the film can exist simultaneously: transparent and opaque. The difference in the sample transparency is distinguished well if the PP–PEO film is examined against a black background.

The possibility of using an opaque iPP–PEO film as a writing thermosensitive paper is demonstrated by placing a black background on a film and writing on it by a hot point pen. Dark permanent inscriptions appear on the film. The inscriptions remained clearly visible with no apparent change in contrast (one and a half years was the longest tested period). The inscriptions can be erased either by cooling down to 273 K when the whole film becomes opaque or by heating up above 333 K when the whole film becomes transparent. The film can be rewritten and erased many times without noticeable change in its characteristics.

Dynamic mechanical properties versus temper-

ature for heating with the rate of 2 K/min of the 0.5 mm thick 5 mm wide strips of iPP–PEO blends show differences for samples with crystallized PEO inclusions as compared to those with molten PEO inclusions. The temperature range of the DMTA measurements for samples with molten PEO inclusions was limited to the range from 280 to 393 K because at the temperature below 280 K, PEO inclusions undergo crystallization from homogeneous seeds; while above 393 K, quenched polypropylene matrix recrystallizes intensively. A typical example is depicted in Figure 6(a) and (b), where the real and imaginary modulae are presented for the sample of iPP–PEO 9 : 1 blend and for pure iPP. It is seen that for the sample, the blend with crystallized PEO inclusions, the modulus E' is higher than the corresponding value for the same sample with molten PEO inclusions in the temperature range from 273 K to the melting temperature of PEO. For higher temperature range, both dependencies show similar values of E'. The corresponding curve for the sample of pure iPP, not shown in Figure 6(a) for the clarity, is very similar to the curve for the sample of the blend with molten inclusions, however, always having slightly higher value of the modulus E'.
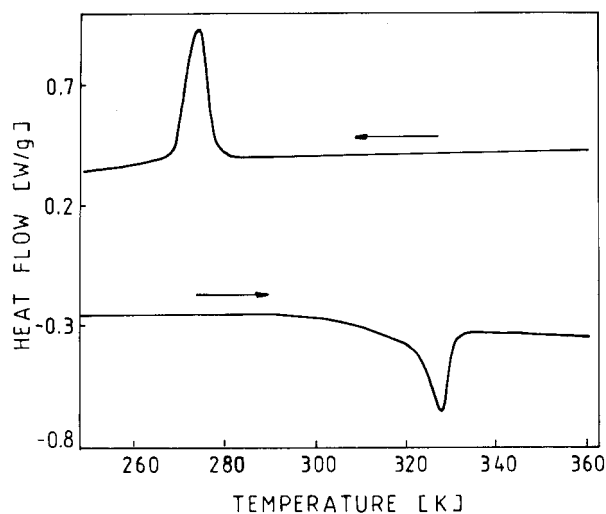
The imaginary modulus E'' for the sample of

Figure 5 Illustration of bistable reversible switching characteristics of the iPP–PEO 9 : 1 blend. Transition from the transparent to opaque state occurs by cooling down to 273 K, while from the opaque to transparent by heating up above 333 K. Both transparent and opaque forms are stable within the temperature range from 280 to 327 K.

pure iPP [see Fig. 6(b)] reveals a well developed peak at 278 K and descending characteristics as the temperature increases. A similar peak in the sample of the blend with crystallized PEO inclusions is shifted towards a higher temperature by 6 K. The corresponding curve for the same sample with molten PEO inclusions shows the descending feature, and no peak at the temperature around 273–283 K can be seen because points below 280 K are inaccessible due to crystallization of PEO inclusions. Above the melting temperature of PEO inclusions, both curves for the blend merge. Within the temperature range of 310–333 K, the blend with crystallized PEO inclusions and also the same sample with molten PEO inclusions exhibit a broad flat peak. The sample of pure iPP does not show such peak in that temperature range.

DISCUSSION

Comparison of the crystallization behavior of PEO in the studied blends with the results concerning their phase structure indicates that the observed effects should be explained as a result of differences in size distributions of PEO domains. On the basis of the obtained results, one may conclude that the size of PEO particles in PP + PEO 9 : 1 ($v < 10^{-16}$ m^3) is small enough to make the heterogeneous nucleation ineffective in crystallization initiation. As can be seen from the data shown in Figure 3, the significant volume fraction of PEO particles, the volume of which is smaller than 10^{-16} m^3, is still present in the blends with higher contents of the dispersed phase (PP + PEO 8 : 2 and PP + PEO 7 : 3). Moreover, this fraction is roughly close to the volume fraction of PEO particles crystallizing with the help of homogeneous nucleation X (see Table I). Thus, taking into account the time intervals associated with the lower temperature peaks (peak widths of approximately 10 K, i.e., at a cooling rate 10 K/min; see Fig. 4), one may roughly estimate that the homogeneous nucleation rate of PEO in the considered case ranges from 10^{16} to 1.4×10^{16} nuclei m^3 min. The obtained value is in good agreement with the values reported for the crystallization of finely dispersed droplets of the polymer (about 10^{16} nuclei m^3 min; see, for example, Ghijsels et al.)[10]

The higher temperature DSC peaks observed during crystallization of PEO in PP + PEO 8 : 2

and in PP + PEO 7 : 3 may be interpreted as the heat effect associated with the crystallization of the PEO particles, the volume of which exceeds 10^{-16} m^3 (see Fig. 3) and is high enough to permit the frequent occurrence of the heterogeneous nuclei inside the particles. The intensity of this peak increases with the increase of the volume fraction of PEO particles from the above-stated volume range. It should be noted, however, that the temperature positions of the higher temperature, heterogeneous nucleation DSC peaks in the studied blends, are about 20 K lower and wider than in the case of plain PEO. The above results indicate that the heterogeneous nuclei responsible for crystallization initiation are thermally activated. At an undercooling at which crystallization of pure polymer proceeds effectively, the heterogeneous nucleation density is too small to assure the effective crystallization of PEO domains, the size of which is lower than about 10^{-15} m^3 (see Fig. 3).

The lack of significant exothermal heat effect at the temperature at which the crystallization of plain PEO is observed indicates that the polypropylene matrix does not exhibit nucleating activity towards PEO. Thus, it may be concluded that the interfacial free energy between solidified PP and PEO crystals is not lower than the interfacial free energy between PEO crystals and PEO melt. The reason for this relationship may be explained in terms of the different contributions of polar and dispersive forces into molecular interactions in PP and PEO resulting from the difference in the chemical structure of chains of both polymers. Thus, one may expect that the interfacial free energy of PEO inclusions in the PP melt should also be reasonably high. Such observations explain well the strong coalescence of PEO particles, which leads to the broad size distribution of PEO domains and causes them to shift towards higher volumes with the increase of PEO contents in the blends.

Within the temperature range from 280 to 327 K, the same sample of the iPP–PEO blend can exist either in the form with molten PEO inclusions, or in the form with crystallized PEO inclusions. It gives the possibility of studying the influence of the mechanical properties of the dispersed phase on the mechanical properties of the blend for the same sample with identical properties of the iPP matrix and identical dispersion of PEO. It seems that solidified PEO inclusions embrittles the iPP matrix by a shift of the E'' peak from 273 to 280 K. Molten PEO inclusions
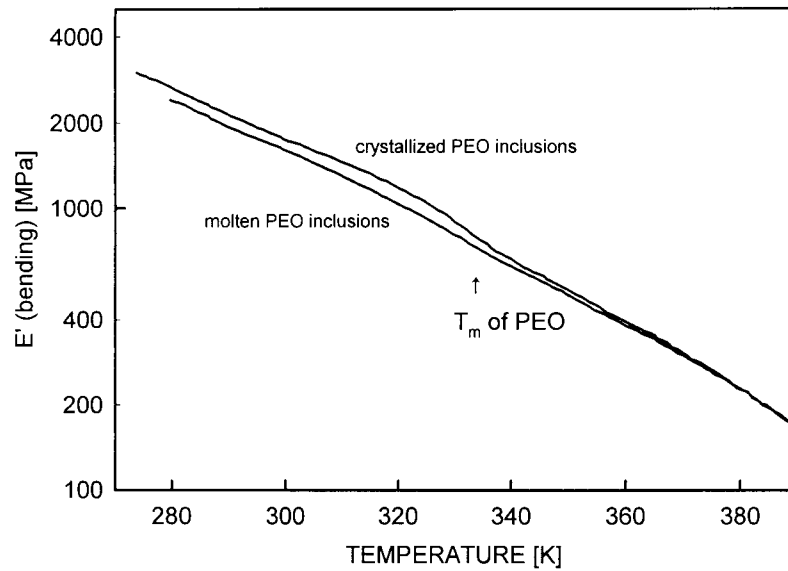
(A)
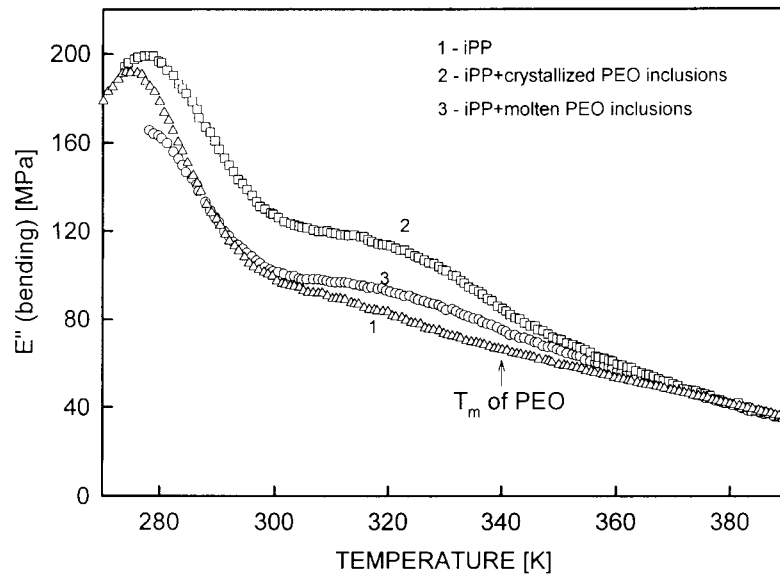
(B)

Figure 6 Dynamic mechanical properties of the iPP–PEO 9 : 1 blend at 1 Hz in bending: (a) real modulus E'; (b) imaginary modulus E''; the respective curve for a pure iPP sample is also plotted.

toughen the sample of the blend by decreasing E'' and shifting the 280 K peak towards lower temperature (only a high-temperature slop of that peak can be recorded for molten PEO inclusions).

It seems that the broad low peak superimposed on the descending slope in the temperature range from 310 to 333 K is characteristic for the particu-

lar dispersion pattern rather than for the properties of the dispersed component.

Light scattering from molten dispersed PEO inclusions connected with the optical density difference between iPP and molten PEO and light scattering from iPP matrix results in the transmittance of as high as 67%. Now, when PEO inclusions are crystallized, the transmittance de-

creases to 18%, and that is due to the stronger scattering from a larger optical density difference between iPP and crystalline PEO and additional strong scattering connected with the birefringence of crystalline PEO inclusions.

CONCLUSIONS

The results of the present studies indicate that the crystallization behavior of PEO dispersed in iPP matrix depends mainly on the concentration of the dispersed phase. Polypropylene matrix does not exhibit nucleating activity towards PEO and thus may be regarded as inert with respect to PEO crystallization.

At low PEO contents (PP + PEO 9 : 1), the size of PEO domains is small enough to make heterogeneous nucleation ineffective in crystallization initiation. Under these circumstances, the crystallization of PEO becomes possible only if the undercooling assures high rate of homogeneous nucleation (i.e., at the temperature of about 273 K). Thus, such a blend satisfies the earlier formulated conditions necessary for the model system, in which the dispersed phase may exist either in a metastable undercooled state or (after cooling below homogeneous nucleation temperature and heating back to ambient temperature) in a stable semicrystalline state.

With increasing concentration of PEO in the blend, PEO particles undergo strong coalescence, which leads to the increase of the PEO domains size. Heterogeneous nucleation becomes then effective in crystallization initiation, and the significant volume fraction of PEO particles crystallizes fast at the temperature close to room temperature. The above effect makes the blends with fine dispersion of PEO suitable as a two-stage stable opaque–transparent system in which PEO can be permanently in molten or in crystallized states in the temperature range from 280 to 327 K. The transition from transparency to opacity is performed from the molten state of PEO by cooling down to 273 K, while from opacity to transparency from the crystallized state of PEO by heating above 333 K.

Having the same sample in two different stages gives a unique possibility of studying the influence of the mechanical properties of the dispersed phase and also of the particular state of dispersion on the overall properties of the blend.

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