

Crystallization of Crystalline/Crystalline Blends: Polypropylene/Polybutene-1

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Synopsis

The crystallization, from molten blends, of polypropylene (PP) and polybutene-1 (PB), two highly crystallizable polymers, their interaction in the amorphous phase, and the resulting tensile mechanical properties were studied. The crystallization was followed by DSC, showing two separate PP and PB crystallization processes which are affected each by the presence of the other component. The crystallization temperature of PP is significantly affected only in PB rich blends whereas that of PB is affected in the whole composition range. The PP crystalline phase, acting as a nucleating agent, increases the PB crystallization temperature whereas the PP amorphous phase, acting as a high viscosity polymeric diluent, reduces the PB crystallization temperature. The first effect is dominant at low PP content, and the second one becomes increasingly effective with increasing PP content in the blend. The interaction between the two polymers in the amorphous phase was studied by applying dynamic mechanical analysis, in which a single glass transition was observed for the blends and its temperature was found to vary with the blends' composition. Tensile mechanical properties of blends were found to be more sensitive to thermal treatments, such as isothermal crystallization or annealing at elevated temperatures, than single component systems. Such thermal treatments enable better structured blends to be formed, resulting in mechanical properties with no abrupt changes in the whole composition range.

INTRODUCTION

The behavior of polymer blends, whether amorphous or semicrystalline, depends, in general, on the degree of mixing of the components and their mutual interaction as well as on the components individual properties. Most pairs of polymers are not miscible on a molecular level, and, in the majority of cases, the mixing of two polymers results in phase separation. Such systems exhibit poor mechanical properties, which depend on such factors as mode of dispersion and interphase cohesion. The physical state of polyblends comprising of crystallizable components is rather a complex one. The constituents can either co-crystallize or form two separate crystalline phases. Moreover, in the latter they can form a single or multiphase amorphous structure, and, in addition, for each such combination there are several possible morphologies. Another important question which should be raised is the interaction between the various phases. The present work is concerned with such systems.

When a blend of two crystallizable polymers, having different characteristic crystallization temperatures, is cooled from the melt each component could act, if miscible, as a polymeric diluent for the other crystallizing polymer, and in addition the lower melting polymer crystallizes in the presence of an already crystalline phase. The effect of diluents, mainly low-molecular-weight ones, on the crystallization of polymers has been the subject of numerous papers and the main observations of few relevant studies will be summarized here.

Berghmans and Overbergh¹ have studied the crystallization of isotactic polystyrene (IPS) in the presence of poly(2,6-dimethyl phenylene oxide) (PPO) and have observed a strong dependence of the crystallization rate on the degree of mixing prior to crystallization. The rate of overall crystallization and the spherulitic growth rate on heating a blend which had been melt homogenized (annealed above T_m of IPS) were found to be much lower than when a multiphase (freeze-dried) system was similarly heated. The spherulitic growth rate in the former was fivefold smaller (at 175°C) compared with that in pure IPS. Hence, the crystallization rates of IPS decreases with decreasing its concentration and as the viscosity of the melt from which it crystallizes increases; both effects are stronger as mixing increases. Similar reductions in crystallization rates were also reported for other polyblends such as isotactic and atactic polystyrene,^{2,3} poly(ϵ -caprolactone), and poly(vinyl chloride),^{4,5} and isotactic and atactic polypropylene.²

Escala and Stein⁶ have studied the crystallization of blends consisting of two crystallizable polymers namely, poly(ethylene terephthalate) and poly(butylene terephthalate) (PET and PBT). They have shown that these components are compatible in the amorphous phase, exhibiting a single glass transition temperature, which varies with composition. They have also observed that both polymers crystallize separately, according to their own unit cell structure and melt at temperatures slightly shifted compared to T_m of the pure polymers. Studying the overall crystallization behavior of the blends, they have observed a decrease in crystallization rate with increasing the other component content attending a minimum rate at the 85/15 PBT/PET blend. The crystallization kinetics of each component in the blends as studied by IR methods was found to follow the classical nucleation and growth theory, provided that the degree of supercooling with respect to each of the components as well as the actual single T_g of the blends are taken into account. Regarding the morphology of PET/PBT blends, it was observed that the spherulitic structure becomes disordered and the spherulites become larger with the incorporation of small amounts of the second component, whereas larger amounts of the second constituent cause the loss of the spherulitic structure.

In a recent study of polypropylene/polybutene-1 (PP/PB) blends⁷ marked mutual effects, regarding the components crystallization and final structure, were observed, resulting in the following changes in their behavior: the melting temperatures, mainly of PP, were depressed; the total degree of crystallinity has changed more than expected by plain additivity (total degree of crystallinity has been depressed); the PP/PB crystallinity ratio has not changed linearly with composition; and, finally, the blends morphology has changed, with increasing amounts of the other component, from spherulitic, through coarser and fragmented spherulitic to a dispersion of branched crystallites. Furthermore, it appeared at that time that PP starts first to crystallize out from the molten blend, and its crystallization is affected by the presence of still melted PB chains (acting as a high viscosity polymeric diluent), whereas PB crystallizes from a melt consisting of mainly PB, however, in the presence of dispersed PP crystals. Consequently, the crystallographic parameters of the PP phase were not modified, whereas the d -spacings of the PB phase were all shifted to larger values. Moreover, the total degree of crystallinity and overall morphology were more affected by the introduction of PB to PP-rich blends than in the PB-rich ones.

Hence, the incorporation of small amounts of molten PB to a crystallizing PP is more influential than the introduction of small amounts of PP crystals to a crystallizing PB. The quite strong adhesion between these two crystalline phases, resulting in blends having good mechanical properties, has been suggested to stem from a highly compatible amorphous phase (a phase consisting of both constituents).

The presence of one polymer in the other polymer phase and vice-versa is commonly demonstrated by experimental observations of the glass transition of the coexisting phases.⁸ Transition temperatures are somewhat displaced, each in the direction of the second polymer. In the case of one amorphous phase, consisting of two miscible polymers, a single T_g is observed. For example, calorimetric studies⁹ and dielectric relaxation measurements¹⁰ of bulk mixtures of poly(2,6-dimethyl phenylene oxide) (PPO) and atactic polystyrene (PS) reveal a single T_g and a single α relaxation, respectively. However, in dynamic mechanical measurements¹¹ this loss peak is partially resolvable, indicating the coexistence of two distinct phases, one rich in PPO and the other in PS. The authors¹¹ concluded that in PPO/PS blends mixing does not occur at the segmental level; however, mixing is "fine enough so that the T_g 's of the constituents are not seen." In a similar blend of IPS/PPO, the number of T_g 's was found to depend on thermal history.¹ In another system, crystalline/amorphous blends of poly(vinylidene fluoride) and poly(methyl methacrylate), and compatibility in the amorphous phase has been demonstrated by a single transition in the dynamic mechanical behavior, which shifted with composition in the range between the transitions of the pure components. Escala and Stein⁶ have shown a single T_g (as obtained by DSC) for crystalline/crystalline blends of PET and PBT, which also shifted (not linearly) with the blends composition.

In the presently studied system, experimental observations of the glass transition dependence on blends composition are a difficult task, mainly since the two components are rather highly crystalline polymers and their T_g 's are rather close. Calorimetric studies failed in following the glass transition of the blends; however, dynamic mechanical measurements were found to be revealing.

Another important aspect of polyblends is their mechanical properties. They are known to depend on such factors as the properties of the individual constituents as well as degree of compatibility, mode of dispersion, etc. In crystallizable polyblends the mechanical behavior is affected also by degree of crystallinity, ability to cocrystallize, morphology, and compatibility in the amorphous phase. Polyolefin blends such as low and high density polyethylene and polypropylene and polybutene-1, although structurally very similar, exhibit good strain properties; however, at certain composition ranges, high strain properties and impact strength are very poor.^{7,12,13} In the presently studied blends of PP and PB, when prepared by quenching from the molten state,⁷ the modulus was found to change linearly with composition (typical behavior for a system in which the components are compatible through the whole range of composition), and the ultimate tensile strength was found to change gradually with composition (slightly deviating from linear dependence). However, the elongation at break of these blends decreased with increasing the other component content, attaining a minimum at about 40% PB. As in other polyblends, the ultimate elongation is also here the most sensitive tensile property to blends composition and structure.

In blends of homopolymer, at each composition, the mechanical properties

could be altered, perhaps even enhanced, by changing the route of crystallization and thus the blend structure and the interphase adhesion. Structural changes could be brought about by controlling the crystallization process, opposed to most published studies in which blends were prepared by mixing either at elevated temperatures or in solution, followed by quenching or slow solvent evaporation, respectively. Controlled crystallization in blends consisting of two crystallizable polymers can be interesting in the following conditions: isothermal crystallization at such temperatures as $T_{m_2} < T_c < T_{m_1}$ and $T_{m_2} > T_c < T_{m_1}$; preferential nucleation to cause eutectic crystallization; or deep quenching to below the glass transition of both polymers followed by crystallization from the glassy state.

The present work was aimed at the investigation of the effect of thermal history on the behavior of crystalline/crystalline blends, including annealing of quenched blends and isothermally crystallized blends at elevated temperatures. Also, the crystallization process of both components were investigated, and an attempt was made to further study the amorphous phase.

EXPERIMENTAL

Granules of commercial polypropylene (ICI 1608, GWM-101) and polybutene-1 (Witco Chemicals, Witron 0100) were used to form crystalline/crystalline polyblends. The GWM-101 is actually a propylene/ethylene block copolymer containing a small amount of ethylene. Blends of the two polymers were prepared in the molten state using a Brabender Plastograph mixing head (model PL3S) rotating at 30 rpm and heated to 190°C. A blending time of 10 min (after the whole mass has been melted) was used for all compositions. All mixtures, including the pure polymers, were compression molded into 1 mm thick plates in a laboratory Carver press at 190°C, followed by tap water cooling (still under pressure) to ambient temperature. To study the effect of thermal history on the mechanical properties of the blends, two main routes were chosen. The first one included annealing of molded plates in an air circulated oven for 30 min at various temperatures followed by slow cooling at ambient temperature. The annealing temperatures were chosen to be 150°C [$T_m(\text{PB}) < T < T_m(\text{PP})$], 130°C [just below $T_m(\text{PB})$], and 100°C [$T_m(\text{PB}) > T < T_m(\text{PP})$]. The second route included remelting the molded plates at 180°C, isothermal crystallization at various temperatures in an thermostated oil bath, followed by quenching to ambient temperature. The crystallization temperatures were identical to the annealing temperatures. All specimens were aged at room temperature for at least a week to allow complete transformation of the PB crystals to their stable form.

The melting and crystallization of the various blends were studied by thermal analysis using the duPont 990 differential scanning calorimeter. The DSC cell was calibrated at the running conditions using standard materials, which melt in the temperature range of interest. The sample weight was carefully kept in the range of 10 ± 0.5 mg. All samples were heated at a rate of 20°C/min up to 230°C, held at that temperature for 5 min, and cooled back at the same rate to follow the crystallization process.

To study the degree of mixing of the two polymers in the amorphous phase, duPont 981 dynamic mechanical analyzer (DMA) was employed. The DMA was operated at a heating rate of 10°C/min, from -150°C to +150°C, and os-

cillation amplitude of 0.2 mm. The specimens for the DMA were all about $12 \times 12 \times 1$ mm in size.

Tensile properties of the blends were measured at room temperature employing an Instron testing machine. Standard dumbbell-shaped specimens (4 in. long) were cut out from the plates and were drawn at a cross-head speed of 0.5 cm/min. From the stress-strain curves so obtained, the characteristic tensile properties, including tensile modulus, ultimate tensile strength, and elongation at break, were measured. In all cases, the ultimate tensile strength was also the tensile strength at break. All reported results are the average of five measurements.

RESULTS AND DISCUSSION

Thermal Analysis

The melting behavior of the two polymers separately is in agreement with literature. The thermogram (DSC curve) obtained upon the heating of PP includes the main melting endotherm at 172°C as well as a small endotherm at 144°C (appears as a shoulder on the main melting peak), which results probably from the melting of β form PP, and a very small and broad endotherm at 125.5°C, which is due to melting of crystallized polyethylene chains. As mentioned earlier, the PP used in the present study is actually a PP/PE copolymer. The majority of the copolymerized ethylene combines with propylene to form an amorphous E/P rubbery phase, but a small proportion remains as crystalline PE, which melts at 125.5°C. On cooling PP from the melt, two crystallization exotherms are observed. The major one, of PP, at 111°C and a very small one, of PE, at 91°C. The thermogram obtained upon the heating of PB includes a single melting endotherm at 132°C. On cooling PB from the melt, a single crystallization exotherm is observed at 70°C. Upon immediate reheating, the polymer melts sooner at 113°C. This variation in melting temperature results from the different crystalline forms of PB. The lower melting temperature corresponds to an unstable form II, in which the polymer crystallizes when cooled from the melt. The higher melting temperature corresponds to the stable form I. (Form II transforms into form I upon aging at ambient temperatures). Thus, the crystallization at 70°C is of form II PB.¹⁴

The melting behavior of PP/PB blends has been described elsewhere.⁷ In general, the two components melt separately, exhibiting two endotherms; however, their melting temperatures are affected by the presence of the other component. The main shift was observed in the melting phase of the PP phase; it is depressed from 172°C to 164°C in the 1:3 PP/PB blend. Again both DSC and X-ray diffraction⁷ prove the presence of the two polymers as separate crystalline phases, examination of the DSC cooling cycle enables an insight to their crystallization processes, which seem to be mutually affected.

Upon cooling PP/PB blends, the DSC thermograms consist of two exotherms. The higher and lower temperature exotherms result from the crystallization of PP and PB, respectively. (No other exotherms could be observed.) The crystallization peak temperatures of the PP phase (see Fig. 1) are only slightly depressed with increasing PB content, and their peak heights are reasonably consistent with the reduction of PP content. Exceptional is the 1:3 PP/PB blend,

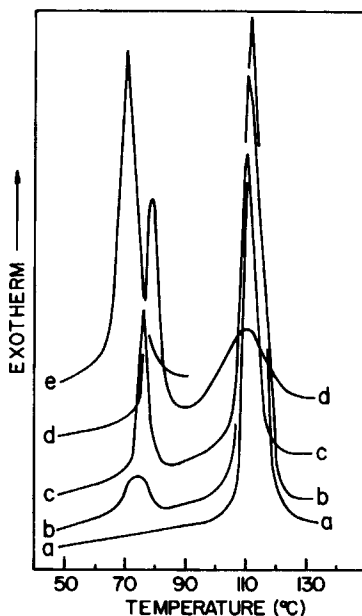


Fig. 1. DSC thermograms of PB/PP blends consisting of (a) 100% PP, (b) 75% PP, (c) 50% PP, (d) 25% PP, and (e) 100% PB (cooling cycles).

for which the peak height has been reduced below the expected one, according to PP content. Hence, the crystallization temperature of PP crystallizing from a PP/PB molten mixture is only slightly disrupted as long as PP is the major component and becomes significantly affected by the presence of PB only when the system consists of mainly PB (probably upon phase inversion). On the other hand, the crystallization exotherms of PB (see Fig. 1) are significantly shifted to higher temperatures with increasing PB content (from 70°C for pure PB to 78°C in the 1:3 PP/PB blend). Moreover, the crystallization exotherms of PB in blends appear sharper than in the pure polymer. Such shifts in crystallization temperatures of PB, resulting from artificial nucleation, were reported also by Foglia.¹⁵ He has observed a much larger shift, from 76°C for pure PB to 94°C for PB consisting 0.5% seeding agent. Thus, upon cooling the PP/PB blends, PB phase is nucleated, probably by the already crystallized PP phase, resulting in lower degrees of supercooling, and higher rates of crystallization.

As illustrated in Figure 2, the incorporation of small amounts of PP result in the high PB crystallization temperatures. However, further addition of PP results in some reduction in this high PB crystallization temperature (but still higher than in homopolymer). Since the PP crystallization exotherms level off at temperatures higher than the onset of the PB crystallization (see Fig. 1), it proves that, at the present experimental cooling rate, PB crystallizes from a melt in which PP is dispersed in two modes namely, crystalline and amorphous. The effect of the crystalline PP, mainly as a nucleating agent, is practically concentration-independent whereas the amorphous PP acts as a highly viscous polymeric diluent (acting at a relative low temperature, about 100°C below its melting) and as such its effect is concentration dependent. Moreover, PP concentration increases during the PB crystallization process and is expected to further slow down the crystal growth rate.¹⁶ Thus, the two PP phases affect the

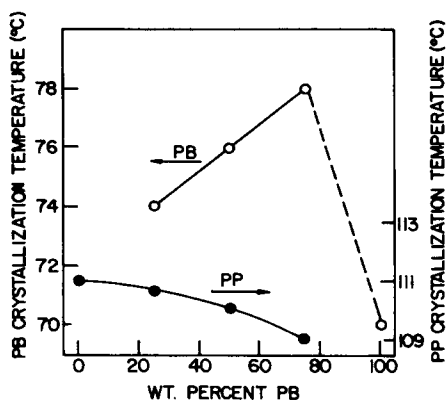


Fig. 2. Variations in crystallization temperatures of PP and PB phases with their blends composition.

PB crystallization in opposite directions: the crystalline phase causes the increase of PB crystallization temperature, and the amorphous phase causes its decrease. Therefore, at low PP content, the nucleating effect is dominant, resulting in the high PB crystallization temperature. However, at high PP content the diluent action becomes more pronounced, resulting in an apparently reduced nucleation effect (e.g., Ref. 5). In either case, the net result is that PB crystallizes out from the blend at higher temperatures than from the homogeneous (100% PB) melt.

These results are complementary to a previous study⁷ and fit well into the description given there to the behavior of PP/PB blend. Previously reported X-ray diffraction study⁷ has revealed that the diffraction pattern of PP is not affected by the presence of PB, except for decreasing relative intensity proportional to the PP content. However, the diffraction pattern of PB is shifted, upon the incorporation of PP, to lower 2θ values; the shift magnitude is independent of PP content. It was then concluded that the lattice dimensions of PP do not change upon crystallization in the presence of PB which is, according to the DSC curves presented above, still in the molten state. However, the lattice dimensions of PB are modified upon crystallization in the presence of PP, already in the crystalline state (PP crystallizes at about 110°C and PB below 80°C). Further, the total degree of crystallinity, as measured by WAXD,⁷ was found to be lower than the linearly added contributions of the components, the largest deviation being observed in PP rich blends. At the same composition also the morphology was observed to be most disrupted.⁷ Hence, although the presence of PB does not significantly affect the crystallization temperature of PP, it is more influential regarding the overall crystallization process and its resulting structure than the presence of PP. In addition, it should be noticed that the whole PB content in the blend acts as a diluent during the PP crystallization, while only the uncrystallizable portion of the PP acts as a diluent during the crystallization of PB. It is an additional cause for the apparent larger effects of small amounts of PP compared to the same content of PB on the behavior of PP/PB blends.

An additional important question regarding the interaction of the two components in PP/PB blends should be raised, namely, the degree of compatibility in the amorphous phase. The two polymers seem to be quite compatible in the melt, resulting in a transparent melt. The two polymers exhibit also a high

degree of mixing and interaction when amorphous PP is dispersed in molten PB, resulting in the depression of the latter crystallization temperature. A similar effect of degree of mixing on the crystallization rate has been reported in blends of IPS and PPO.¹ These observations should indicate a high degree of compatibility also in the amorphous phase. An attempt to clarify this question was made by measuring the damping of PP/PB blends as a function of temperature and by following the characteristic transitions.

Dynamic Mechanical Analysis

DMA is a method which includes the observation of the changes in the materials' natural resonant frequency and dissipation energy (damping) as a function of temperature. (Modulus and $\tan \delta$ can also be obtained.) For the purpose of studying the interactions between PP and PB in the amorphous phase the energy dissipation curves were chosen to look at.

DMA curves of PB (see Fig. 3) include two damping peaks of -136°C and -7°C . The former is thought to be caused by motion in the side groups,¹⁴ and the latter by motion of main chain segments in the amorphous phase and is thus related to the glass transition. This value falls in the rather wide range quoted in literature for the T_g of PB (e.g., Ref. 4). The other component in the present study, PP, shows also two damping peaks at $+6^\circ\text{C}$ and -43°C . The former is related to the glass transition,¹⁷ and the latter, a very broad and shallow, nevertheless pronounced peak is thought to be related to the minor ethylene/propylene rubber phase, which exists in this block copolymer.

DMA curves of the blends (see Fig. 3) exhibit three peaks including the PB low temperature transition, the ethylene/propylene transition and a combined PP/PB glass transition. The two low temperature peaks are too broad to enable the determination of their shift with composition. Nevertheless, they seem to appear at a constant temperature and their height is probably consistent with

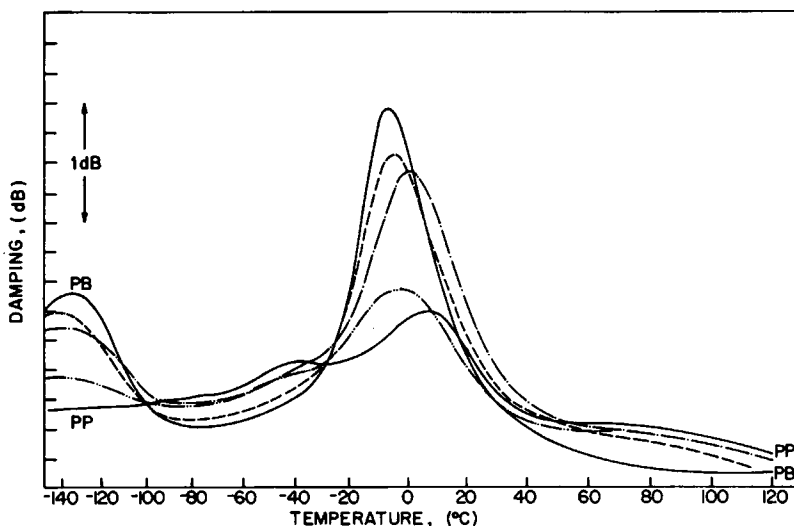


Fig. 3. DMA curves obtained for PP/PB blends of various compositions: (---) 25/75; (- - -) 50/50; (- · · -) 75/25.

TABLE I
DMA Transition Temperatures in PP/PB Blends

Blend composition		PB (°C)	E/P (°C)	PP/PB (°C)
PP (wt %)	PB (wt %)			
100	—	—	-43	+6
75	25	-139	-45	-2.5 (+2.6) ^a
50	50	-138	-43	0 (-0.6) ^a
25	75	-140	-44	-5 (-4.0) ^a
—	100	-136	—	-7

^a Combined calculated values assuming miscibility and PP/PB ratio in the amorphous phase equal to that in the blend.

the blend composition. (DMA transition temperatures are summarized in Table I). The combined peak, at the higher temperature, is either a result of the PP and PB glass transition proximity (being too close to be observed separately) or a result of an averaging effect due to PB/PP interaction in the amorphous phase. A third possibility also exists, in which the two compounds are not fully compatible; however, they affect mutually their glass transitions, causing their shifting and resulting in even closer T_g 's which are practically unresolvable. Nevertheless, the combined transition temperature decreases reasonably with increasing PB content (as expected when a compatible polymer having a lower T_g is added) except for the 75/25 PP/PB blend, which is apparently lower than expected (see Table I). Further information can be deduced from the DMA scans by graphically adding the scans of both pure polymers at various ratios. For example (see Fig. 4), graphical addition of 50% of the pure components scans results in a peak at -0°C , lower than the measured 0°C peak. Hence, PP is probably having a greater effect on the T_g of PB than vice-versa.

The DMA results, regarding the glass transition of PP/PB blends, support the previous assumption⁷ that the good mechanical properties of these blends, in spite of the coexistence of two crystalline phases, result from a highly compatible amorphous phase.

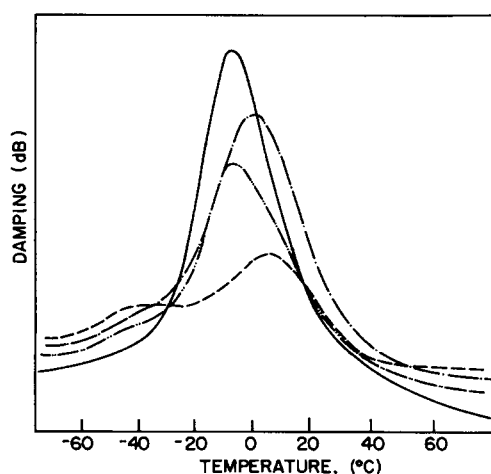


Fig. 4. Comparison of measured (---) and graphically (— · — ·) added DMA curves of 50/50 PP/PB blend, in the glass transition region: (—) 100% PB; (---) 100% PP.

Tensile Properties

The mechanical behavior of PP/PB blends quenched from the molten state were previously reported.⁷ Presently, preliminary tensile properties of these blends, which were either allowed to crystallize isothermally at various elevated temperatures or first quenched and then annealed at these elevated temperatures, are reported. As mentioned above, the quenched blends exhibited tensile moduli linearly dependent on composition, ultimate tensile strengths slightly lower than the linearly interpolated values and elongations at break, which attain a minimum of about 40% PB.

Figure 5 shows the dependence of the tensile modulus on composition and thermal history. For comparison, values obtained previously⁷ for samples, which were water cooled while in the press (quenched), are presented by the dash lines. In general, the moduli of blends which have gone through the various thermal treatments are very similar; however, details of their dependence on blends composition are different. In the annealed systems, the annealing temperature affects the moduli in accordance with expected effects on the degree of crystallinity. For example, PB annealed at 130°C (just below its melting) exhibits the highest modulus; PB annealed at 150°C (above its melting) and quenched to ambient temperature exhibits the lowest modulus whereas PB annealed at 100°C (32°C below melting) exhibits an intermediate modulus. The moduli of the annealed blends are slightly higher than the values expected by linear additivity. On the other hand, in the isothermally crystallized blends a marked deviation from linearity has been observed in the PP rich blends; the moduli consistently attained maximum values at about 75% PP.

Figure 6 shows the dependence of the tensile strength at break, which is in the presently studied systems also the ultimate strength, on composition and thermal history. (The dash lines represent values obtained previously⁷ for samples which were water cooled from the melt, while in the press). In the annealed systems

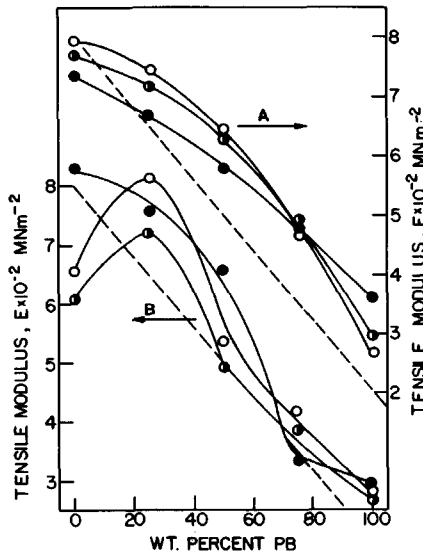


Fig. 5. Tensile modulus dependence on the composition of PP/PB blends; (A) quenched and annealed and (B) isothermally crystallized; both at 150°C (○), 130°C (●), and 100°C (●).

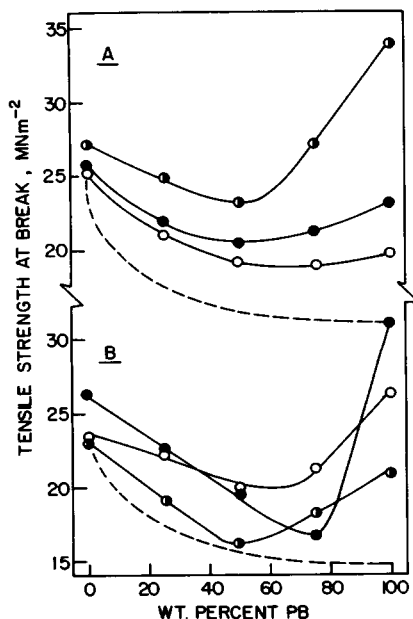


Fig. 6. Composition dependence of tensile strength at break of PP/PB blends; (A) quenched and annealed and (B) isothermally crystallized; both at 150°C (○), 130°C (●), and 100°C (◐).

the tensile strength first decreases with increasing PB content, followed by an increase, the amount of which depends on the annealing temperature. This increase in strength, especially in the PB-rich blends, decreases as the annealing temperature increases from 100°C through 130°C to 150°C. Hence, the annealing temperature affects mainly the PB contribution to the tensile strength. On the other hand, in isothermally crystallized blends, although the general behavior is similar, the lowest tensile strength values were obtained by crystallization at 100°C and the more effective crystallization temperatures, regarding strength, are those which are close in the melting temperature of either components. Moreover, when the blends were crystallized at 150°C [above $T_m(\text{PB})$] the addition of increasing amounts of PB does not result in a significant reduction in the tensile strength. However, when crystallization takes place at 130°C [just below $T_m(\text{PB})$] the incorporation of PB causes the steepest reduction in the tensile strength; only the strength of pure PB remains high, resulting in a minimum strength in blends rich in PB.

Figure 7 shows the dependence of ultimate elongation on composition and thermal history. The large difference between the elongation of PP and PB should be noticed. In general, the ultimate elongation of all blends increases gradually with the incorporation of increasing amounts of PB. However, the stronger effect of PB in the annealed samples compared to the isothermally crystallized blends should be noticed. The large difference between the elongation at break of the presently studied systems and those of blends cooled from the melt while the press⁷ stands out when the latter is presented in the same Figure 7 (dash line). The values in the latter are in general significantly higher, and they exhibit, however, a very deep minimum at 40% PB. This minimum led previously to the conclusion that PP and PB are incompatible and that elongation is the most sensitive tensile property to the degree of compatibility

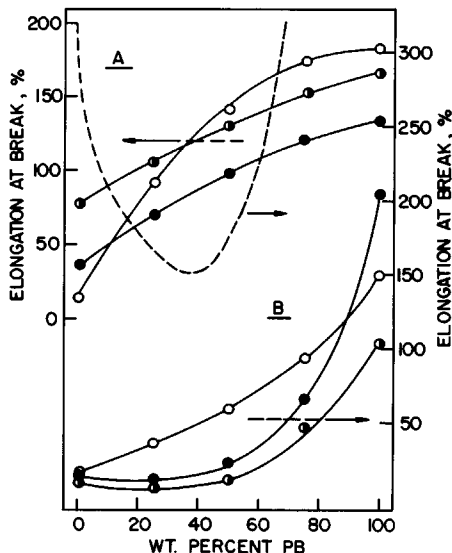


Fig. 7. Composition dependence of elongation at break of PP/PB blends; (A) quenched and annealed and (B) isothermally crystallized; both at 150°C (○), 130°C (●), and 100°C (◐).

in blends. The present work shows that, with the aid of proper thermal history, this drawback in the behavior of PP/PB blends can be overcome. Although the overall elongation in thermally treated blends is lower, its variation with composition, exhibiting no abrupt changes, indicate that the resulting blends are better structured.

SUMMARY

The present study includes the investigation of the mutual influence of two highly crystallizable polymers, namely, PP and PB, regarding their crystallization process from a molten blend, their interaction in the amorphous phase, and the resulting tensile mechanical properties.

When a PP/PB blend is cooled from the melt, a state in which the two polymers are probably highly compatible, the constituents crystallize into two separate crystalline phases, PP being the first to crystallize. It crystallizes from a molten blend, the composition of which affects the PP crystallization temperature only in PB-rich blends. Hence, as long as PB content is lower than about 50%, it acts as a polymeric diluent having probably lower viscosity than PP, at the crystallization temperature, and as such does not exert a significant influence on the PP crystallization temperature. However, as observed previously⁷ it does affect the degree of crystallinity and final morphology. After the PP primary crystallization has been completed, the system includes PP crystalline phase and a molten PP/PB blend from which, upon further cooling, PB crystallizes out. Its crystallization is quite strongly affected by the blend composition; at low PP content the crystallization temperature is the highest, and upon further addition of PP this temperature is reduced approaching that of the pure polymer. Thus, the presence of PP affects the PB crystallization in two modes; the crystalline phase, effective already at low concentration, acts as nucleating agent, resulting in the increase in PB crystallization temperature as well as its crystallographic dimensions,⁷ whereas the amorphous phase, effective at higher concentrations,

acts as a high viscosity polymeric diluent resulting in the reduction in PB crystallization temperature. This latter effect strongly indicates the high interaction between the two polymers in the amorphous state, in which PP strongly affects the mobility of PB chains.

The high degree of compatibility in the amorphous phase is shown also by the DMA measurements. Both the blends and the pure polymers show a single damping transition in the T_g region, but the position of this transition varies with the blends composition. The amount of shift gives additional evidence that the PP has a greater effect on the transition temperature than PB.

The preliminary study of the effect of thermal history on the blends tensile properties shows clearly that, in the case of blends, the effect of thermal history is more pronounced than in one compound systems. In the latter, thermal history affects the properties through such factors as degree of crystallinity and morphology whereas, in blends, thermal history determines also the blends' integrity, which is a dominant factor in controlling the blends' mechanical behavior.

The results presented above are in agreement with and complementary to the previous work⁷ on the structure-property relationships in crystalline/crystalline polymer blends.

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