Miscibility in Blends of Model Polyolefins and Corresponding Diblock Copolymers: Thermal Analysis Studies

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ABSTRACT: The miscibility of polymers that are models for polyolefins was examined by thermal analysis in this work. Analogs of ethylene–propylene copolymer (PEP) were made by the hydrogenation of polyisoprenes; similarly, atactic polypropylene models (APP) were produced from poly(2-methyl-1,3-pentadiene)s. PEP–APP diblocks were made from the corresponding polydiene block polymers. Blends of the homopolymers and blocks were made over a broad enough range of molecular weights so that the low molecular weight varieties were single phase and the higher ones showed two phases. From the Flory–Huggins–Staverman theory of blends and Leibler's model of block polymers a value of 3.52×10^{-3} for χ could be found for these polymers. Also, the addition of a single-phase APP–PEP diblock, to a two-phase APP/PEP blend was shown to greatly alter the thermal behavior of the blend and even to convert it into a one-phase system at high enough concentrations.

Introduction

Polymer blends have become important items of commerce in recent years, and the thermodynamics of their mixing has become the subject of intense research.[1] The most widely used expression for the free energy of mixing is that first proposed by Flory,[2] Huggins,[3] and Staverman[4] (FHS) 50 years ago:

$$\frac{\Delta G_m}{VRT} = \frac{\phi_1}{\nu_1 N_1}\ln \phi_1 + \frac{\phi_2}{\nu_2 N_2}\ln \phi_2 + \phi_1\phi_2\frac{\chi}{\nu} \qquad (1)$$

Here V is the total volume of the sample, R is the gas constant, T is the absolute temperature, N_i is the degree of polymerization of component i (=1 or 2), ϕ_i is the volume fraction of that component, ν_i is its molar volume, ν is a reference volume (usually equal to $(\nu_1\nu_2)^{1/2}$), and χ is the interaction parameter reflecting the interactions between the repeat units of the two polymers. For high molecular weight polymers (N_1 and $N_2 \geq 1000$), the first two terms on the right-hand side of eq 1 are negligible, so most of the interest has centered around measuring and understanding χ. One particular result of eq 1 is that the critical value of χ greater than which the blend is phase separated is given by

$$\chi_c = \frac{\nu}{2}\left\{\frac{1}{(\nu_1 N_1)^{1/2}} + \frac{1}{(\nu_2 N_2)^{1/2}}\right\}^2 \qquad (2)$$

If $N_1 = N_2 = N$ and $\nu_1 = \nu_2 = \nu$, then $\chi_c N = 2$.

The thermodynamics of block copolymers have also been studied extensively.[5] The main subject of interest has been the transition from a disordered state to an ordered, microphase-separated one. This order–disorder transition (ODT) is also controlled by the interactions between repeat units of the blocks, and for a symmetric diblock the value of χ at the ODT is given by $\chi_{\mathrm{ODT}}N = 10.5$,[6] where N is the overall degree of polymerization of the block copolymer. A second area of study has been the use of block polymers as modifiers to improve the compatibility of blends.[7] The block polymers act as interfacial agents to reduce the domain sizes in immiscible blends, which generally improves their properties. The effectiveness of such compatibilizers is also a function of the mixing thermodynamics.

Thus χ can be determined by finding the transition temperatures of either blends or block polymers or both. This has been done experimentally for several pairs of polymers. Cohen and Wilfong have examined blends and block copolymers of polybutadiene and polyisoprene and compared the values of the interaction parameter found from both systems.[8] Gardlund has compared the miscibility of blends and blocks of polycarbonate and poly(methyl methacrylate) as determined by differential scanning calorimetry (DSC).[9,10] Both of these studies have confirmed that in certain molecular weight ranges blends will be immiscible while diblocks are disordered. In this paper we report on a similar study using polymers that are good models for polypropylene (PP) and ethylene–propylene copolymers (EP). Not only do we report on the critical molecular weights for phase separation in the blends and those for the ODT for the diblock copolymers, but we also show how addition of a diblock changes the phase behavior of a blend.

Experimental Section

Polymers. The details of the synthesis of these polymers have been reported elsewhere.[11,12] The model of the ethylene–propylene copolymer (PEP) is made by hydrogenating an anionically polymerized polyisoprene. Starting with 2-methyl-1,3-pentadiene as the monomer and using the same steps of anionic polymerization and hydrogenation, one obtains a model of polypropylene which is atactic (APP). The PEP–APP diblocks (DAP) are made by sequentially polymerizing isoprene followed by the methylpentadiene and again hydrogenating the polymer to produce a fully saturated block polymer. Molecular weights were determined by light scattering in THF. The molecular characteristics of the polymers used in these studies are given in Tables I–III.

Blending. All of the blends were made in solution. The components were dissolved in hexane, mixed for 1–2 h, and then precipitated by the addition of methanol. For the binary blends, the APP and PEP components were chosen to have degrees of polymerization as close as possible. A series of ternary blends were made by the addition of varying amounts of APP–PEP diblock DAP174 to a 50/50 blend of APP377 and PEP316.

Thermal Analysis. The majority of the thermal analysis results reported here were obtained by dynamic thermal analysis

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Table I. Hydrogenated Polyisoprenes

sample	M_w (×10³)[a]	N	M_w/M_n	T_g (°C) DSC	T_g (°C) DMTA
PEP5	4.81	68.7	1.09	−64	−49
PEP33	33.0	471	1.02	−62	
PEP58	58.0	829	1.03	−57	
PEP95	95.0	1357	1.03	−59	
PEP316	316	4514	1.08		−44

[a] By light scattering in THF.

Table II. Hydrogenated Poly(2-methyl-1,3-pentadiene)s

sample	M_w (×10³)[a]	N	M_w/M_n	T_g (°C) DSC	T_g (°C) DMTA
APP4	4.17	49.6	1.06	-11	-7
APP45	44.5	530	1.07	-4	6
APP59	58.7	699	1.07	-2	11
APP125	125	1488	1.09	0	
APP377	377	4488	1.10	-3	10

[a] By light scattering in THF.

Table III. Hydrogenated Poly(isoprene-*block*-2-methyl-1,3-pentadiene)s

sample	M_w (×10³)[a]	M_w/M_n	wt % PEP	N_{PEP}	N_{APP}	N_{tot}
DAP25	25.2	1.07	60	216	120	336
DAP101	101	1.04	50	721	601	1322
DAP142	142	1.05	50	1014	845	1859
DAP174	174	1.13	59	1467	849	2316
DAP250	250	1.08	61	2179	1161	3340
DAP268	268	1.08	50	1914	1595	3509
DAP477	477	1.12	70	4770	1704	6474

[a] By light scattering in THF.

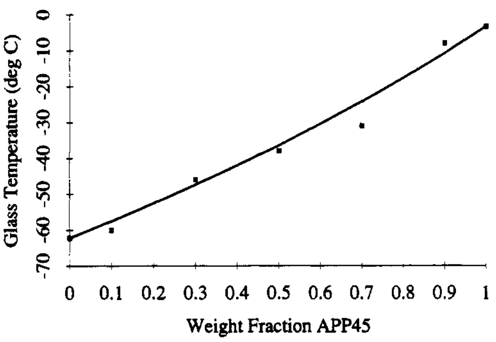

Figure 1. DSC-measured glass temperature versus composition for the APP45/PEP33 blends. The squares (■) are the data, and the line is the prediction from the Fox equation.[13]

(DMTA) using an apparatus from Polymer Labs. Samples of dimension 1 cm × 3 cm × 1 mm were compression molded and tested in a three-point bending mode. The samples were cooled rapidly to −100 °C and then heated at 2 K/min up to around 75 °C. The storage and loss moduli were measured at a frequency of 3 Hz, and the glass transition temperature, T_g, was taken as that at which there was a maximum in tan δ, the ratio of the loss to storage modulus. Glass transition data were also measured using a Perkin-Elmer 7 differential scanning calorimeter (DSC). The samples were quenched to −100 °C and then heated at 20 K/min up to 100 °C. The T_g's reported here are the temperatures at the midpoint of the transitions. The glass transition temperatures as measured by DSC were generally 10 °C lower than those from DMTA (see tables), but there was always agreement in the number of T_g's present in a sample from the two methods.

Results and Discussion

Blends. Glass transition data for several PEP/APP blends are given in Table IV and are also shown in Figures 1 and 2. For the blend of APP45 and PEP33 a single T_g was found at all compositions, and the measured values agree well with the Fox equation.[13] The APP59/PEP58 blend exhibits two T_g's at intermediate compositions. The presence of a single T_g is taken as evidence of miscibility, since the chains of the two components must be mixed intimately on a scale less than 2 nm, while two T_g's are a signature of an immiscible blend. In general all of the low molecular weight blends were miscible at all compositions, and the high molecular weight blends showed some range of immiscibility which was broader the higher the molecular weight. Also given in Table IV for each blend is χ_t, the value of χ which marks the transition between one- and two-phase behavior for a blend of this composition and degrees of polymerization as calculated from FHS theory.[2-4] When the actual value of χ is larger than χ_t, the blend should be phase separated at equilibrium, and single phase when it is smaller. The T_g data in the table thus imply that the value of χ is somewhere between 2.78×10^{-3} and 3.60×10^{-3}. Another reading on this can be found from looking at the order–disorder transitions of the diblocks.

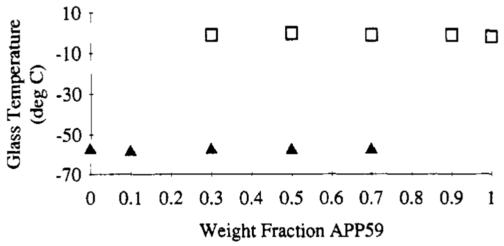

Figure 2. DSC-measured glass temperature versus composition for the APP59/PEP58 blends. The squares (□) are the higher T_g measured at each composition and the triangles (▲) the lower.

Table IV. Glass Transition Temperatures of Blends

component 1	component 2	ϕ_1 (wt frac)	χ_t (×10⁻³)	DSC T_g (°C)
PEP5	APP4	0.5	34.3	−43
PEP33	APP45	0.1	6.24	−8
PEP33	APP45	0.3	4.53	−31
PEP33	APP45	0.5	4.00	−38
PEP33	APP45	0.7	4.04	−46
PEP33	APP45	0.9	4.85	−60
PEP58	APP59	0.1	3.62	−1
PEP58	APP59	0.3	2.78	−57/−1
PEP58	APP59	0.5	2.63	−57/0
PEP58	APP59	0.7	2.78	−57/−1
PEP58	APP59	0.9	3.60	−58
PEP95	APP125	0.1	2.17	−63/1
PEP95	APP125	0.3	1.57	−61/2
PEP95	APP125	0.5	1.40	−61/1
PEP95	APP125	0.7	1.41	−60/0
PEP95	APP125	0.9	1.63	−60/0
PEP316	APP377	0.5	0.446	−59/−2

Table V. Glass Transition Temperatures of Diblocks

diblock	χ_t (×10⁻³)	T_g (°C) DSC	T_g (°C) DMTA
DAP25	33.7	-37	-25
DAP101	7.98	-37	-15
DAP142	5.67	-35	-12
DAP174	4.85	-41	-21
DAP250	3.45	-58/13	-46/12
DAP268	3.00	-52/-9	-32/0
DAP477	2.31	-57/13	-47/10

Block Copolymers. The T_g's of the block polymers are given in Table V. Again the pattern of one T_g at low molecular weights and two at high was seen. The molecular weight at which this transition occurred is clearly higher than that for the transition in the blends. Also given in Table V is the appropriate value of χ_t for these diblocks as calculated from the model of Leibler.[6] These data indicate a value of χ between 3.45×10^{-3} and 4.85×10^{-3}.

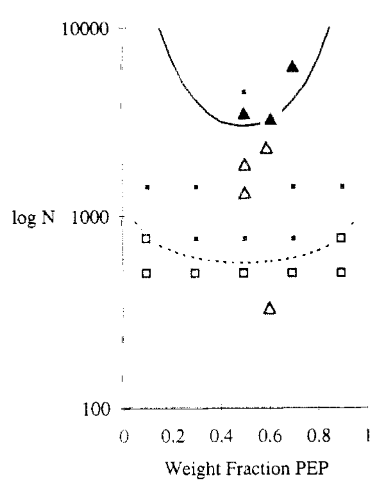

Figure 3. Miscibility of the APP/PEP blends and DAP block copolymers as a function of the degree of polymerization and composition. The open triangles (Δ) represent the disordered, single-phase diblocks and the filled triangles (▲) the ordered, microphase-separated ones. The open squares (□) represent the blends with a single T_g and the filled squares (■) those with two. The solid line is the boundary between ordered and disordered diblocks according to the model of Leibler[6] and a value of $\chi = 3.52 \times 10^{-3}$. The dotted line is the boundary between miscible and immiscible blends from FHS theory[2-4] and the same value of χ. Note that N here is the total degree of polymerization for the diblocks, and it is the geometric mean of those of the two components for the blends.

Thus, taking the two sets of data together leads to the conclusion that χ is $(3.52 \pm 0.08) \times 10^{-3}$.

All of these data are collected into one diagram in Figure 3, which is a plot of composition versus degree of polymerization. (Note that N refers to the geometric mean of the degrees of polymerization of the two components for the blends but is the total degree of polymerization for the diblocks.) Here the blends that showed a single T_g (miscible) are shown as open squares and those with two (immiscible) as filled squares; similarly the diblocks are represented by open and filled triangles for the disordered and ordered states, respectively. The lower line in Figure 3 is the boundary between miscible and immiscible blends based on eq 1 and a value of $\chi = 3.52 \times 10^{-3}$. The upper line in Figure 3 is calculated for the separation between the ordered and disordered regions for the diblocks from the Leibler model. Note that the lines do separate the miscible cases from the immiscible ones. Since the molecular weights of the polymers in the blends were fairly close near this boundary, values of χ that are much different from this will not fit the data. This is presumably the value of the interaction parameter at room temperature, since the samples were "annealed" there for several days before they were measured. This is equivalent to a value for $B \equiv (\chi RT)/\nu$ of 0.0981 MPa. (The reference volume, ν, in this formulation is the geometric mean of the molar volumes of the repeat units of APP and PEP. If one used ν based on ethylene and propylene repeat units, then $\chi = 1.57 \times 10^{-3}$.)

Ternary Mixtures. The diblock DAP174 was added to a 50/50 blend of APP377 and PEP316 to study a possible case of compatibilization. The blend was immiscible with two T_g's, while DAP174 had only a single T_g at -21 °C (as measured by DMTA). The effect of adding various levels of DAP174 to the blend is shown in Figure 4. Notice that the addition of as little as 1% of DAP174 noticeably altered the shape of the tan δ peaks and started to bring the two T_g's of the blend together. This trend continued with a 10% addition, and at 25% the two peaks had begun to merge. At a level of 50% DAP174, only a single T_g was found, although the peak was broader than for the pure diblock.

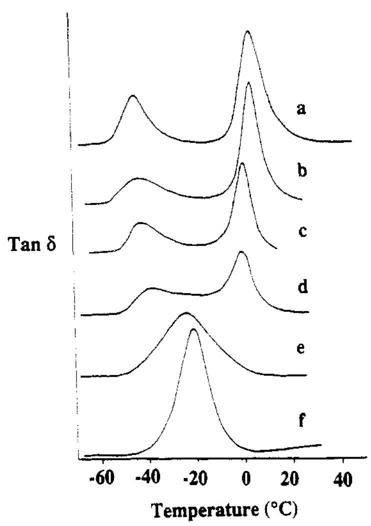

Figure 4. tan δ versus temperature as measured by DMTA for DAP174, a 50/50 APP377/PEP316 blend, and mixtures of all three. The traces have been displaced vertically for clarity. The six curves are for a 50/50 (w/w) blend of APP377 and PEP316 with the following weight percentages of DAP174 added: (a) 0%; (b) 1%; (c) 10%; (d) 25%; (e) 50%; (f) 100% (pure DAP174).

The diblock seems to have gone beyond just compatibilizing the blend (decreasing phase sizes) to the point of "miscibilizing" it, that is, turning it into a single-phase system. This has been predictd by Leibler[14] and demonstrated by Cohen and co-workers for the case of unsaturated polydiene systems.[15-18] The breadth of the tan δ peaks may be a reflection of the degree of mixing in the phases and in the interfacial region between them. For instance, the blend with 50% DAP174 may have greater fluctuations in composition than does the pure diblock, resulting in the broader tan δ peak. However, it is hard to quantify this from the kind of thermal analysis data given here.

Conclusions

Information on the mixing thermodynamics of model polyolefins has been obtained by thermal analysis of blends and diblock copolymers. We find that for these mixtures of models of polypropylene and ethylene-propylene copolymer the χ parameter can be given a value of 3.52×10^{-3} with a fair degree of precision. This is presumably the value at room temperature. We plan to confirm and extend this work by measuring χ at several temperatures by small-angle neutron scattering. We have also shown that the addition of a disordered, single-phase diblock of these polymers at a high enough level can convert a two-phase blend into a single-phase one.

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