

Blends of Polymers with Similar Glass Transition Temperatures: A DMTA and DSC Study

D. Bikiaris,¹ J. Prinós,² M. Botev,³ C. Betchev,³ C. Panayiotou²

¹Laboratory of Organic Chemical Technology, Department of Chemistry, Aristotle University of Thessaloniki, 541 24 Thessaloniki, Greece

²Department of Chemical Engineering, Aristotle University of Thessaloniki, 541 24 Thessaloniki, Greece

³Central Scientific and Research Laboratory, University of Chemical Technology and Metallurgy, 8, Kliment Ohridski Blvd., 1756 Sofia, Bulgaria

Received 24 October 2003; accepted 17 December 2003

DOI 10.1002/app.20531

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The miscibility of different polymer blends was studied with dynamic mechanical thermal analysis (DMTA) in conjunction with differential scanning calorimetry (DSC). The blends were prepared by melt mixing polymers having similar glass transitions such as polyglutarimide (PGI), styrene-*co*-maleic anhydride random copolymers (SMA), and polystyrene (PS). In PGI/SMA blends, there is only one glass transition detected with DMTA. In the case of PGI/SMA14 blends, the single glass transition temperature is due to their full miscibility. However, PGI/SMA8 blends are immiscible throughout the whole composition range as was verified by optical observation (opaque appearance), DSC, and scanning electron microscopy. The observation of only one glass transition by DMTA was attributed to weak interactions that take place between the two polymers, lead-

ing to partial mutual solubility and bringing the slightly different T_g temperatures of the pure polymers even closer. In SMA8/SMA14 blends, there are two glass transitions detected with DSC as well as with DMTA, indicating that the two copolymers are immiscible. However, in all compositions, shifts of the glass transitions were observed with DMTA, which is evidence of partial miscibility. The observation of immiscibility was easiest in PS/SMA blends by both techniques, because of the bigger difference in glass transition temperatures of the initial polymers. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 726–735, 2004

Key words: polymer blends; PS; SMA; PGI; miscibility; DMTA; DSC

INTRODUCTION

Polymer blending was recognized in the last few decades as a most promising way to prepare new user-tailored materials. The problem to overcome is the immiscibility and incompatibility of most polymer blends. In immiscible polymer blends, each component retains its own individual properties. Immiscible blends usually show two glass transitions, or melting peaks, in the case of crystalline polymers. This feature may limit the usefulness of the prepared blends. For example, polypropylene (PP)/poly(ethylene terephthalate) blends cannot be used at temperatures higher than 160°C, because PP will melt, while PET will remain at the solid stage. Additionally, the two-phase interface is usually a domain of high energy (interfacial tension) and, therefore, very prone to failing mechanically when stress is applied to the system.

In such multiphase systems, the transitions of each component can be detected by using different techniques. Dynamic thermomechanical analysis (DTMA)

is one of these methods. Due to its high sensitivity, it is appropriate for the detection of very weak molecular motions as those arriving from very small segments or parts of macromolecular chains.¹ For this reason, it was used extensively to study the viscoelastic properties of the polymers. These weak transitions can be recorded with high accuracy in all homopolymers as well as in copolymers, giving much important information. Thus, it has understandably found many applications in the study of polymer blends.^{2–6} It is especially useful for the estimation of the effect of addition of compatibilizers in incompatible blends, to obtain satisfactory mechanical properties.^{7–9} Besides multiphase systems, DMTA can also be used successfully in the study of miscible blends.^{10–12}

In the present work, the application of DMTA and differential scanning calorimetry (DSC) thermoanalytical methods were used to study the miscibility of polymer blends prepared from polymers having very similar glass transition temperatures. Most often, this is a rather difficult task. The polymers that were chosen for blending were polystyrene (PS), styrene-*co*-maleic anhydride (SMA) with different anhydride content, and polyglutanimide (PGI). SMA copolymers have a structure similar to PS and can form miscible

Correspondence to: C. Panayiotou (cpanavio@auth.gr).

blends with many polymers.¹³ In a previous article of ours, we found that SMA copolymer containing 14 wt % maleic anhydride is fully miscible with PGI throughout the whole composition range.¹⁴

The difficulty in studying the above-mentioned polymer blends with DMTA and DSC depends on the sensitivity of the applied method. Usually, it is very difficult to detect the glass transitions of each individual component in a blend by using conventional DSC, if the glass transitions of the initial components do not differ by more than 15–20°C. In this case, special techniques can be applied which include enthalpy relaxation measurements after aging of the blends at temperatures slightly lower than the glass transition temperatures (T_g 's).¹⁵ On the other hand, the sensitivity of DMTA is about 1000 times higher than DSC. However, there are some limitations, which can restrict the conventional application of DMTA technique.¹⁶ Obviously, the field of miscibility studies in polymer blends with thermal techniques such as DMTA and DSC in combination with SEM is still open.

EXPERIMENTAL

Materials

In the present study, two SMA random copolymers were used, supplied by Arco Chemicals (Newtown Square, PA): Dylark 232, containing 8 wt % anhydride groups (SMA8) and $\bar{M}_w = 200,000$; and Dylark 332, with 14 wt % anhydride groups (SMA14) and $\bar{M}_w = 180,000$. PS was commercial grade Styron from Dow Chemicals. Poly(*N*-methyl-glutarimide) (PGI) with trade name HT 510, was supplied from Rohm and Haas Co. It was a random copolymer containing methyl methacrylate and glutarimide units. The degree of imidization was 72%.

Melt-blending

Blends were prepared in a Haake–Buchler Reomixer (model 600) with roller blades and a mixing head with a volumetric capacity of 69 cm³. To avoid any hydrolytic degradation during melt mixing, all polymers were dried by heating in a vacuum oven at 90°C for 12 h. The components were physically premixed before being fed in the reomixer. Melt blending was performed at 220°C and 60 rpm for 15 min. During the mixing period, the melt temperature and torque were continuously recorded in a computer. Five different blends were prepared, namely, SMA14/PGI, SMA8/PGI, SMA8/SMA14, PS/SMA8, and PS/SMA14 at proportions 25/75, 50/50, and 75/25 w/w. Each blend, after preparation, was milled and placed in a tightly sealed vial to prevent any moisture absorption and for further examinations.

Dynamic thermomechanical analysis

The dynamic thermomechanical properties of the blends were measured with a Rheometric Scientific analyzer (model MK III). The bending (dual cantilever) method was used with a frequency of 1 Hz, a strain level of 0.04%, in the temperature range from 20 to 180°C. The heating rate was 3°C/min. The testing was performed by using rectangular bars measuring approximately 30 × 10 × 3 cm. These were prepared in a hydraulic press, at a temperature of 220°C and pressure of 250 bar, for a time period of 5 min. The exact dimensions of each sample were measured before the scan.

DSC measurements

DSC measurements of samples were performed in a Shimadzu DSC-50Q fast quenching differential scanning calorimeter. Samples were placed in sealed aluminum cells, using a fine-milled quantity of about 10 mg for each blend. The samples were initially heated with a rate of 20°C/min up to 180°C and immediately quenched to remove any previous thermal history. They were subsequently rescanned with a heating rate of 20°C/min. From these second thermograms, the glass transition temperatures were determined.

Blend morphology

The morphology of the blends was studied with scanning electron microscopy (SEM), using a JEOL microscope (model JSM-840A). For this purpose, a 6 × 1 × 0.3 cm rectangular strip from each blend was prepared, in a hydraulic press, as described before. These strips were fractured in liquid nitrogen and the surfaces were sputtered with gold.

RESULTS AND DISCUSSION

SMA copolymers/PGI blends

The prepared blends were studied by DMTA in temperatures close to their glass transitions, because this is the area of the most interest. The storage and loss modulus for SMA14/PGI blends are presented in Figure 1. The storage modulus in all cases decreased very sharply above 110–115°C as the studied materials are entering the glass–rubbery transition region. Small parts of macromolecular chains start movements in the free volume and the loss modulus starts increasing. SMA14 has a lower storage modulus than PGI at temperatures up to 110°C. Furthermore, in all prepared blends, the storage modulus is higher than the initial polymers for all the compositions. This is an indication that perhaps there is a synergistic interaction effect between the two polymers and, for this reason, the blends become stiffer. Such a synergistic

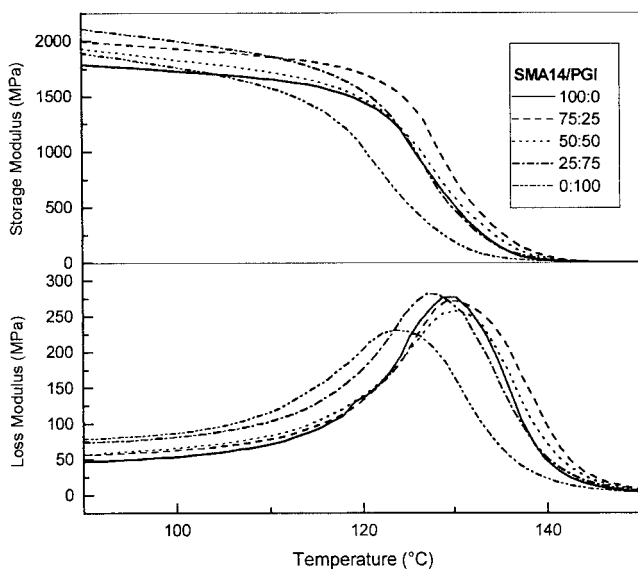


Figure 1 Variation of (a) storage and (b) loss modulus of PGI/SMA14 blends.

effect was also reported for the tensile strength of miscible PS/PPO blends, due to the interactions that take place in the entire composition range.¹⁷ Further evidence for the above conclusion can be drawn from the $\tan \delta$ curves of the blends (Fig. 2).

The maximum of $\tan \delta$ peak, which corresponds to the glass transition, is at about 140°C for SMA14 and at 138°C for PGI. These values are about 5°C higher than the corresponding T_g 's calculated with DSC.¹⁴ Such a difference is very common between the two methods. In DMTA, the exact position of T_g depends mainly on the studied frequency, whereas in DSC T_g depends on the used heating rate. The glass transitions of the initial components are almost identical, making

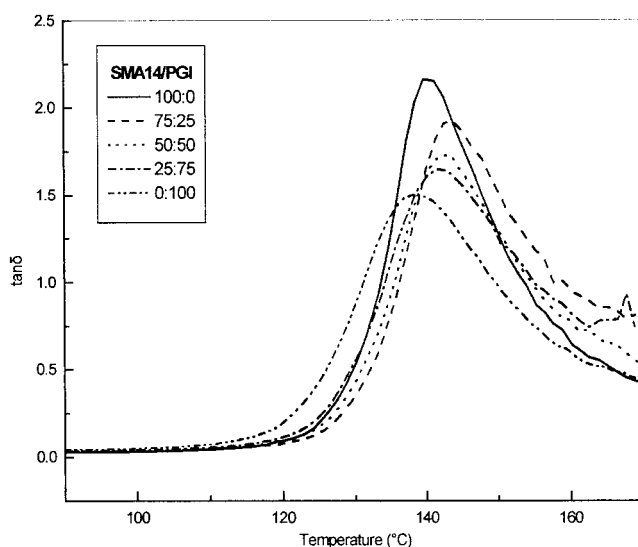


Figure 2 $\tan \delta$ of PGI/SMA14 blends.

TABLE I
Glass Transitions of the Composites in SMA/PGI Blends as Measured with DMTA and DSC Techniques

Blends	Compositions (w/w)	DMTA		DSC	
		T_{g1} (°C)	T_{g2} (°C)	T_{g1} (°C)	T_{g2} (°C)
PGI	100	139 ^a	—	134	—
SMA8	100	127	—	122	—
SMA14	100	140	—	135	—
SMA14/PGI	25/75	142	—	138	—
SMA14/PGI	50/50	143	—	139	—
SMA14/PGI	75/25	144	—	137	—
SMA8/PGI	25/75	137	—	125	133
SMA8/PGI	50/50	134	—	124	132
SMA8/PGI	75/25	132	—	123	132

^a Ref. 14. There is only one glass transition due to the miscibility of the blends in all the compositions.

the estimation of blend miscibility based on the single composition dependent T_g criterion rather ambiguous. Nevertheless, the observation of a single T_g higher than either T_g 's of pure polymers is a very strong indication that some interaction is taking place, which leads to a miscible system. A similar increase in T_g of the blends was also observed in DSC measurements (Table I). The miscibility of the system was also verified by SEM microphotographs, where only one phase is detected.¹⁴

Such an increase in the T_g of polymer blends is very common when strong interactions develop between the components.^{18–21} These interactions result in an increase of the rigidity of the blend. In SMA14/PGI studied blends, this higher stiffness recorded with DMTA can be attributed to the interactions that take place between the polar groups of the two polymers.¹⁴ These interactions induce miscibility in the system and the blends become stiffer because the interactions reduce the mobility of the macromolecular chains. In a previous article of ours, it was found that SMA copolymers, containing 25, 35, and 50 wt % maleic anhydride groups, are miscible with PGI and interactions are very strong in all blends.²²

A single glass transition is also detected in all SMA8/PGI blends as there is only one $\tan \delta$ peak observed in DMTA scans (Fig. 3). SMA8 has a glass transition about 13°C lower than that of PGI. In their blends, the maximum of $\tan \delta$ lies in temperatures between those of T_g 's of pure components and it can be said that it is closer to that of PGI. The appearance of a single glass transition may indicate miscibility of the system. However, because there is not a positive deviation from the linear behavior as was observed in SMA14/PGI blends, the interaction between the groups must be relatively weak. The storage modulus curves verify the above assumption as in all blends the values are between those of the initial polymers. So, it can be concluded that there is no synergistic effect

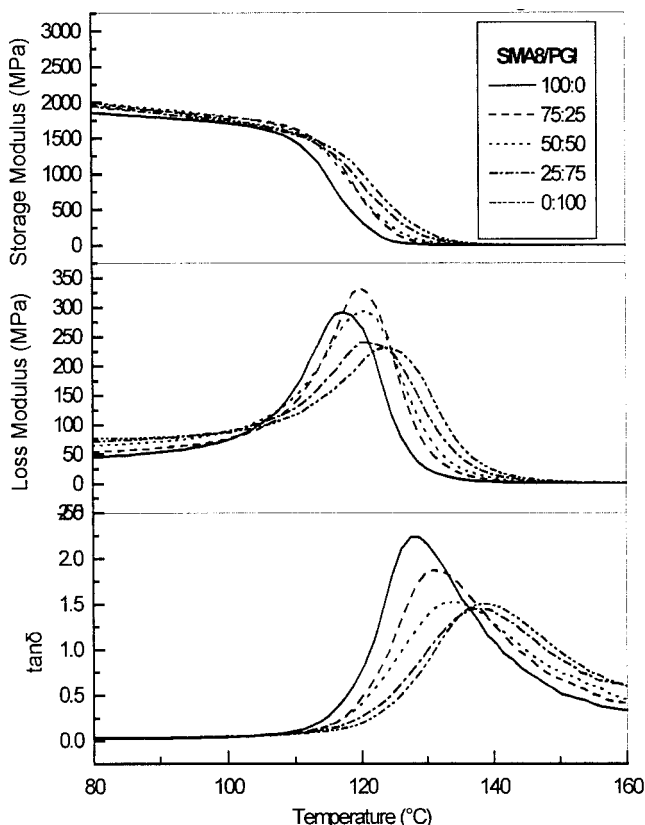


Figure 3 Dynamic mechanical scans of SMA8/PGI blends as function of temperature (a) storage modulus, (b) loss modulus, and (c) $\tan \delta$.

between the two polymers. Furthermore, the loss modulus curves of the blends show single peaks with widths similar to those of pure polymers. This indicates similar relaxation time distributions for all blends.

However, the observation of one T_g is in contradiction with the visual appearance of the blends. All these blends have a white milky appearance and are not transparent. The opaque appearance of the blends suggests that the system is heterogeneous and the two polymers may fractionate in different phases. According to Utraki,²³ the appearance of one T_g is not a proof of miscibility but only a proof of a state of fine dispersion. The presence of a single or dual glass transition could depend on the particle size of dispersed phase in phase-separated blends.²⁴ To verify this assumption, the blends were also studied with DSC. Even from these thermograms, it is very difficult to distinguish between one or two glass transitions, because the glass transitions of the initial components are very close to each other. In this case, the examination of the derivative curve of the transition can be more revealing. The thermogram and the first derivative of the SMA8/PGI 25/75 w/w blend are shown in Figure 4. Two well-separated peaks are observed in the first derivative curve, indicating the existence of two tran-

sitions. These are close to the glass transitions of the initial components. This is also the case for other compositions and is strong evidence that the SMA8/PGI blends are immiscible.

The glass transition of each phase, as measured by DSC, differs compared to that of initial components and varies with composition (Table II). For instance, as the amount of SMA8 increases, the corresponding glass transition attributed to the SMA-rich phase moves to temperatures closer to the glass transition of the initial component, and vice versa. This is an indication that some weak interactions are taking place between the polar groups of the two polymers, leading to a mutual solubility of the polymer with a concurrent change in T_g . These interactions, however, are not strong enough to ensure the miscibility of the system, as was the case for SMA14/PGI blends. A similar observation was reported for SMA/polyacrylates blends, which were immiscible when the amount of maleic anhydride groups was lower than 8 wt %.¹³ Unfortunately, copolymers containing between 8 and 14 wt % maleic anhydride were not available to us to find the exact anhydride content, which leads to miscibility with PGI.

From all the before mentioned facts, the appearance of the single $\tan \delta$ peak seems peculiar, especially taking into account the higher sensitivity of DMTA method compared to that of DSC. However, a possible explanation could be given: The glass transitions of the initial polymers, as they were detected by both methods, differ by 12°C. In SMA8/PGI blends, this difference is reduced to 8–9°C (Table I) and seems to be very small for its definite detection with the DMTA technique. So, the net result of the T_g shifts is that the initially well-separated $\tan \delta$ peaks of SMA8 and PGI

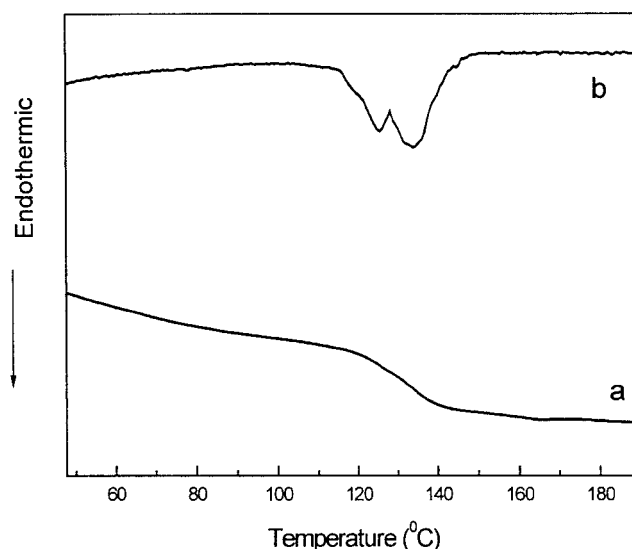


Figure 4 (a) DSC scan of SMA8/PGI 25/75 w/w and (b) first derivative.

TABLE II
Apparent Weight Fraction of SMA8 and PGI in the Rich Phase of Each One Component

Blends	Compositions (w/w)	SMA8-rich phase		PGI-rich phase	
		w_1' (SMA8)	w_2' (PGI)	w_1'' (SMA8)	w_2'' (PGI)
SMA8/PGI	25/75	0.712	0.288	0.077	0.923
SMA8/PGI	50/50	0.819	0.181	0.154	0.846
SMA8/PGI	75/25	0.909	0.091	0.154	0.846

come closer in the blends and finally fuse into an apparently single peak. Hence, it is concluded that the T_g temperatures of polymers are very close and also some interactions take place, the DMTA technique could not be used safely for distinguishing the miscibility of the blends.

The amplitude of the T_g shift in polymer blends is related to the degree of component mixing.²⁵ The apparent weight fraction of SMA8 in SMA8-rich phase and PGI-rich phase, as well as the PGI weight fraction in PGI-rich and SMA8-rich phase, can be estimated by the empirical equation of Wood²⁶

$$T_g = w_1 T_{g1} + w_2 T_{g2} \quad (1)$$

where T_g is the observed T_g of each one polymer in the blend, w_1 is the weight fraction of polymer 1 having T_{g1} , and w_2 is the weight fraction of the second polymer having T_{g2} . This equation can be rearranged as²⁷

$$w_1' = (T_{g1b} - T_{g2}) / (T_{g1} - T_{g2}) \quad (2)$$

where w_1' is the apparent weight fraction of polymer 1 in the polymer-rich phase and T_{g1b} is the observed T_g of polymer 1 in the blend. These apparent weights for each one component in the different rich phases of SMA8/PGI blends are presented in Table II. As can be seen, increasing the amount of one component also increased the apparent weight fraction. Also, the weight fraction of PGI (w_2') dissolved in SMA8-rich phase is higher than the weight fraction of SMA8 (w_1'') that dissolved in the PGI-rich phase. This means that PGI has higher solubility in SMA8 than vice versa.

Scanning electron microscopy microphotographs is the final proof that the system is immiscible at all compositions (Fig. 5). In SMA8/PGI 25/75 w/w blend, there is a homogeneous dispersion of SMA8 spheres in PGI matrix. It was suggested that systems with particles larger than 100 nm should present two glass transitions corresponding to those of initial components.²⁸ In the above blends, particle sizes lie between 0.2 and 0.5 μm . In the blend containing equal amounts of the components, the appearance is quite different. This blend shows a cocontinuous morphology, making the distinction of the matrix and the dispersed phase very difficult. Extraction of one copolymer to detect which one constitutes the dispersed phase was impossible because they are both soluble in the same solvents. In SMA8/PGI 75/25 w/w blend, the dispersed phase is SMA8, because it is the minor component and creates spheres with a radius similar to that of the 25/75 w/w blend.

SMA8/SMA14 blends

As was verified above, SMA14/PGI blends are miscible across the entire concentration range, while SMA8/PGI blends are immiscible, but with the existence of some weak interactions. So it is possible that SMA8/PGI blends become miscible by introducing small amounts of SMA14 in the blends. This requires SMA8 to be miscible with SMA14. For this reason, SMA8/SMA14 blends were prepared by melt mixing and their miscibility was studied with DSC and DMTA. In Figure 6 are presented the storage and loss modulus and $\tan \delta$ of SMA8/SMA14 blends.

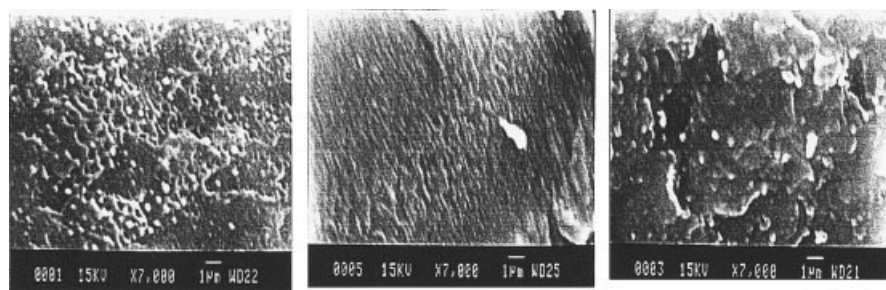


Figure 5 SEM microphotographs of SMA8/PGI blends (a) 25/75, (b) 50/50, and (c) 75/25 w/w.

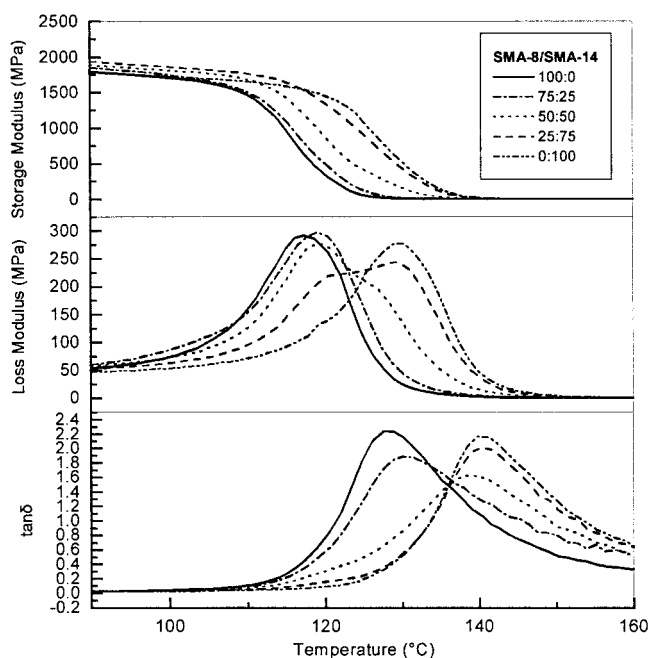


Figure 6 Dynamic mechanical scans of SMA8/SMA14 blends as function of temperature (a) storage modulus, (b) loss modulus, and (c) $\tan \delta$.

Storage modulus of SMA8/SMA14 blends lies between the storage modulus of the initial copolymers, exactly as in the case of SMA8/PGI blends. Also, the reduction in glass transition area is taking place in one step. However, from loss modulus it can be seen that, in blends containing 25 and 50 wt % SMA8, there are two overlapping peaks indicating the existence of two different transitions, each one very close to the other. So, it can be safely concluded that these blends are immiscible. Furthermore, the contribution of each one polymer in the intensity of loss modulus curves of the blends seems to be different. From the magnitude of these peaks, it can be concluded that the first transition, which is attributed to the SMA8 phase, predominates. This becomes more clear by examining these compositions. For 25/75 w/w blends, the two peak areas are almost equal in intensity, while in 50/50 w/w blends, the curve is predominated by SMA8. This copolymer has lower T_g and attains its viscoelastic stage before SMA14.

In the above blends, two peaks are also observed in $\tan \delta$. However, the phenomenon is the opposite from that recorded in loss modulus. The curve attributed to the component with the higher T_g (SMA14) predominates that of the component with the lower T_g (SMA8). The magnitude of the two peaks can be explained from the ratio of loss/storage modulus. For the first peak, the loss modulus is high but also the storage modulus is still very high. For the second peak, the loss modulus remains high too but the storage modulus is very low. For these reasons, the magnitude of

the second peak in $\tan \delta$ predominates and almost hides the first one.

The temperatures of the first peak maximum in the blends containing 25 and 50 wt % SMA8 are shifted toward lower temperature compared to that of pure SMA8. Because the two copolymers differ by only 6 wt % maleic anhydride groups, a mutual solubility of each component would be expected. This shift of T_g values to lower temperatures compared to these of the pure SMA8 copolymer might be evidence for this partial solubility. Only in the blend containing 75 wt % SMA8, the temperature of the $\tan \delta$ peak maximum is higher than that of pure SMA8. Perhaps the two peaks are fused into one and, thus, the $\tan \delta$ peak of SMA14 is not separately observed. However, such differences are not recorded in DSC scans (Fig. 7).

In all SMA8/SMA14 thermograms, two well-separated glass transitions can be seen even without the use of the first derivative, as was the case in SMA8/PGI blends. This is very important because the T_g 's of the initial SMA8 and SMA14 copolymers differ only by 13°C, which is similar to the difference of SMA8/PGI glass transitions (12°C). Examining more carefully the T_g temperatures for each phase as recorded by DSC, it can be seen that they are almost identical to the T_g 's of the pure copolymers and the above difference (13°C) remains stable even in the blends. This is further evidence that the interactions between the two polymers are limited and the glass transitions are more easily detected. However, there is a disagreement with the respective temperatures of SMA8 determined by DMTA, especially in 25/75 and 50/50 w/w blends, which are even smaller than in the pure SMA8 (Table III). From these differences, it can be concluded that when there is a mutual solubility in a blend, DMTA technique can detect such a change more easily than DSC.

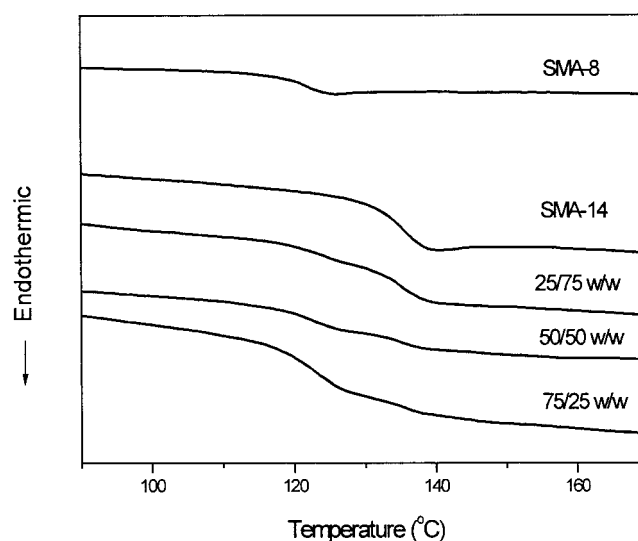


Figure 7 DSC thermograms of SMA8/SMA14 blends.

TABLE III
Glass Transitions of the Composites in SMA8/SMA14 Blends as Measured with DMTA and DSC Techniques

Blends	Compositions (w/w)	DMTA		DSC	
		T_{g1} (°C)	T_{g2} (°C)	T_{g1} (°C)	T_{g2} (°C)
SMA8	100	127	—	122	—
SMA14	100	140	—	135	—
SMA8/SMA14	25/75	120	140	124	134
SMA8/SMA14	50/50	121	138	123	134
SMA8/SMA14	75/25	130	—	123	133

The apparent weight fractions of each copolymer in each phase of SMA8/SMA14 blends are calculated from eq. (2) and are presented in Table IV. The solubilities of the minor component in each phase are very small, verifying the absence of strong interactions between the two components.

PS/SMA copolymers blends

The main question arising from the above measurements is if the detection of solubility in SMA8/SMA14 blends with the DMTA technique is due to the high sensitivity of it, or due to the limitations and peculiarities of the DSC method. To get further experimental information, we decided to prepare blends of PS and SMA copolymers. The differences in the T_g 's of these initial polymers are about 17°C in PS/SMA8 blends and even larger in PS/SMA14 blends (27°C). Also in these blends, we expect a mutual dissolution to take place, as in the case of SMA8/SMA14 blends. The preparation and the study of these blends have a practical interest too. Most of the blends in polymer technology are incompatible, which results in poor mechanical properties and limits their use. To improve their properties, the addition of a compatibilizer is necessary. Reactive compatibilization is perhaps the most useful technique.²⁹ Reactive groups can be either part of the main backbone macromolecular chain, or side chain groups. Copolymers are the most used compatibilizers, while SMA can be used for the reactive compatibilization of PS with other polymers.^{30–33} The dynamic mechanical properties and the morphology of similar blends are particularly interesting.³⁴

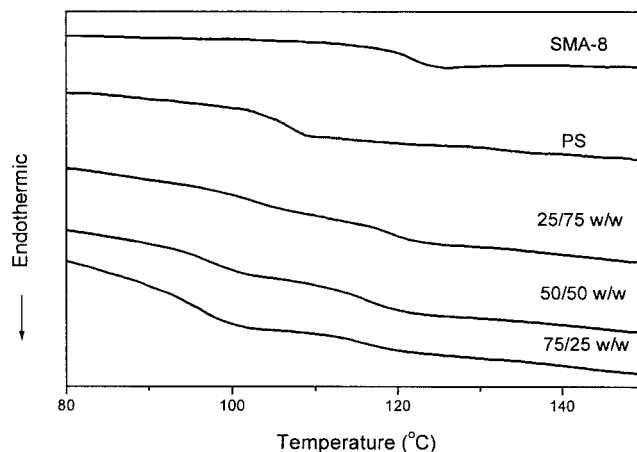


Figure 8 DSC thermograms of PS/SMA8 blends.

The PS/SMA blends are transparent. Such a transparency is a strong indication but not a proof of miscibility. Microphase separated systems can appear transparent when the two components have similar refractive indices. By DSC measurements, two clear glass transitions are detected at all compositions, indicating that the blends are immiscible (Fig. 8 and 9). However, these glass transitions are shifted to lower temperatures than the pure polymers (Table I). In all blends, there is a distinct reduction by about 3–9°C in the T_g of the PS-rich phase, depending only on the blend's composition and not on the kind of the copolymer used (SMA8 or SMA14). As the amount of PS decreases, the reduction is larger.

The same phenomenon also appears in the glass transition of SMA-rich phase. For the SMA8 phase, the glass transition in the blends is about 4–6°C lower than in the pure state, whereas for SMA14, the glass transition is by about 1–4°C lower. Unfortunately, for these blends, it is not possible to calculate the apparent weight fractions of each polymer, because the glass transition of PS shifted to lower temperatures than pure PS. This reduction indicates a mutual solubility between the two polymers as in the case of SMA8/SMA14 blends. By examining the extent of the glass transition reduction, which is larger in PS/SMA8 blends, it can be concluded that this solubility is larger than in PS/SMA14 blends. Based on the above, we can

TABLE IV
Apparent Weight Fraction of SMA8 and SMA14 in the Rich Phase of Each One Component

Blends	Compositions (w/w)	SMA8-rich phase		SMA14-rich phase	
		w_1' (SMA8)	w_2' (SMA14)	w_1'' (SMA8)	w_2'' (SMA14)
SMA8/SMA14	25/75	0.833	0.167	0.077	0.923
SMA8/SMA14	50/50	0.916	0.084	0.077	0.923
SMA8/SMA14	75/25	0.916	0.084	0.154	0.846

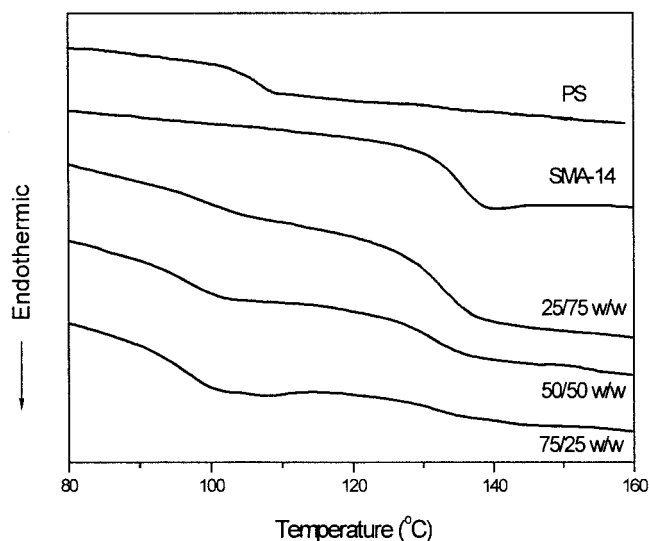


Figure 9 DSC thermograms of PS/SMA14 blends.

conclude that the incorporation of even small amounts of anhydride groups, as in the SMA8 copolymer, is enough to make it immiscible with PS. As the amount of anhydride groups is increasing, the immiscibility with PS becomes greater.

The above conclusion is also verified by the DMTA thermograms (Fig. 10 and 11). The storage modulus of

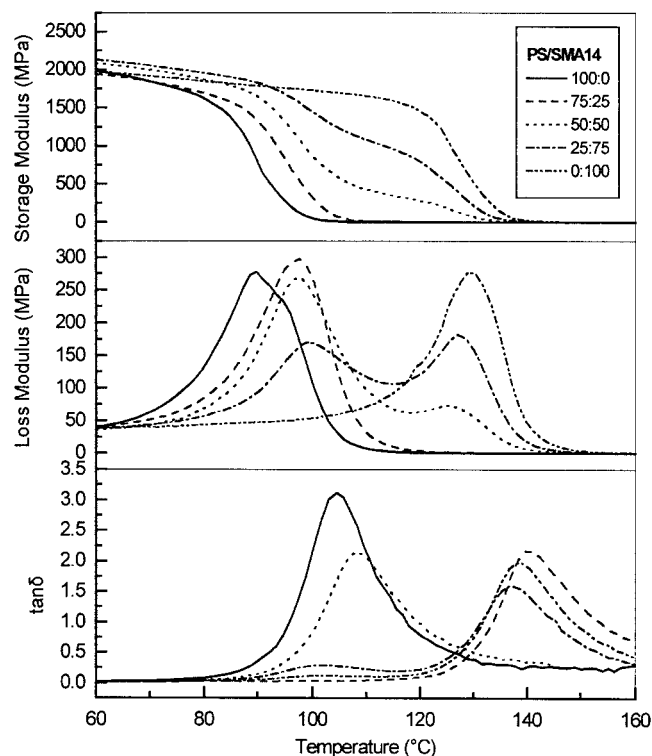


Figure 10 Dynamic mechanical scans of PS/SMA14 blends as a function of temperature (a) storage modulus, (b) loss modulus, and (c) $\tan \delta$.

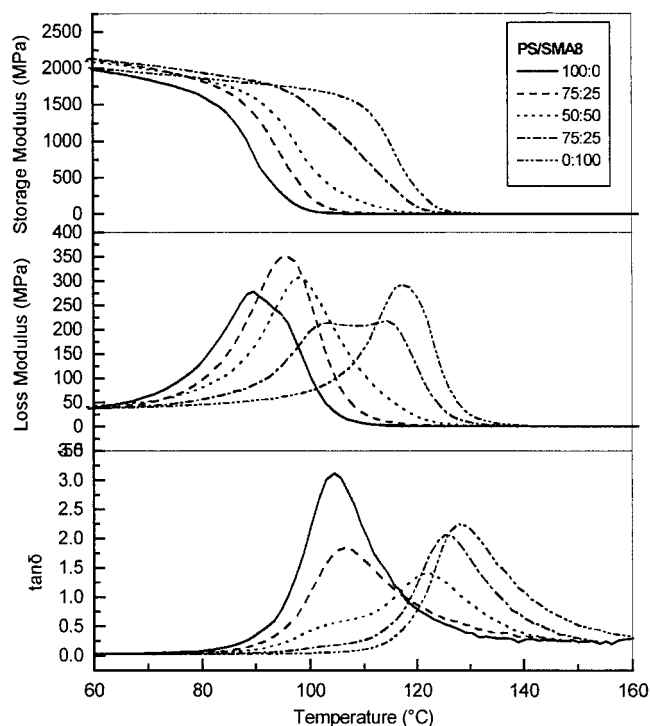


Figure 11 Dynamic mechanical scans of PS/SMA8 blends as a function of temperature (a) storage modulus, (b) loss modulus, and (c) $\tan \delta$.

PS/SMA14 blends in the glass transition area lies between those of pure PS and SMA14. In the 25/75 and 50/50 w/w blends, the reduction of the storage modulus takes place in two well-distinguished steps due to the immiscibility of the blends. However, an analogous reduction was not observed in the 75/25 w/w blend, which is also immiscible as found by DSC. Also in the loss modulus, thermographs, only one single peak appears for this composition, in contrast with the other blends, where two peaks can be observed. This was reflected also in $\tan \delta$, where only one peak was observed at a temperature 4°C higher than the T_g of pure PS.

TABLE V
Glass Transitions of the Composites in PS/SMA Blends as Measured with DMTA and DSC Techniques

Blends	Compositions (w/w)	DMTA		DSC	
		T_{g1} (°C)	T_{g2} (°C)	T_{g1} (°C)	T_{g2} (°C)
SMA8	100	127	—	122	—
SMA14	100	140	—	135	—
PS	100	104	—	105	—
PS/SMA8	25/75	102	126	96	118
PS/SMA8	50/50	103	122	97	117
PS/SMA8	75/25	105	—	102	116
PS/SMA14	25/75	100	139	96	133
PS/SMA14	50/50	102	137	97	131
PS/SMA14	75/25	108	—	100	130

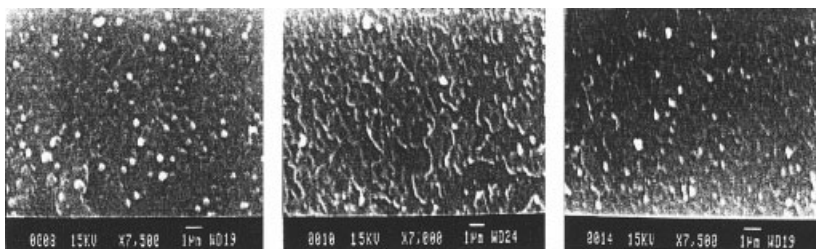


Figure 12 SEM microphotographs of PS/SMA8 blends (a) 27/75, (b) 50/50, and (c) 75/25 w/w.

In the other two blends (27/75 and 50/50 w/w), two peaks were recorded in $\tan \delta$. From these peaks, it can be seen that the glass transition of the SMA14-rich phase is decreasing very distinctly as the amount of PS increases. This is expected because PS has a lower T_g . However, the glass transition attributed to PS was moved to temperatures even lower than the T_g of pure PS. These unexpected results are in good agreement with those observed by DSC. An increase in the glass transition of PS would be expected, because of the addition of SMA14, which has higher T_g than PS. However, in the case of PS, it seems that the incorporation of SMA14 has as a result the softening of PS phase. In many polymer blends and in the absence of any strong intermolecular interactions, the dissolved polymer acts as a plasticizer, thus reducing the T_g of the resulting phase. In this kind of blend, usually negative deviations from the ideal (linear) T_g versus composition behavior occur. Moreover, the incorporation of a second component into the polymer matrix may affect chain packing, leading to low T_g values. Similar observations were also made in the PS/SMA8 blends (Fig. 11).

From the above findings, it can be concluded that for PS/SMA blends both techniques are sensitive for detecting the immiscibility than for PGI/SMA8 blends. One reason for the reduced sensitivity of DSC in the latter blends could be the small size of the dispersed phases, which DMTA could detect. If this is indeed the reason, then in PS/SMA blends the sizes of the dispersed phases are probably larger. To verify the above assumption, the PS/SMA blends were studied by SEM (Fig. 12 and 13).

As can be seen from the microphotographs, in all blends the separate phases are very well distinguished. In the PS/SMA8 25/75 and 75/25 w/w blends, the dispersed phase is in the form of homogeneous spheres with a radius between 0.3 and 0.6 μm , which is a little higher than in PGI/SMA8 blends. In 50/50 w/w composition, there is a small enhancement in the continuities of the phases compared to the corresponding of PGI/SMA8 blend. In the PS/SMA14 blends, the size of the phases is larger at all compositions compared to those of PS/SMA8 blends. Thus, in the 25/75 w/w blends, the dispersed phase is on the order of 0.3–1.1 μm , whereas in the 50/50 w/w blend, the dispersed phase cannot be distinguished. The above observations in PS/SMA blends are in line with the well-detected glass transitions by DMTA and DSC techniques, probably due to the higher phase size compared to that of SMA8/PGI blends.

CONCLUSION

From the above study, it can be concluded that, in phase-separated blends, the results from DMTA study as well as from DSC experiments are not always in good agreement, when the blended polymers present similar glass transition temperatures.

In SMA8/PGI blends, the loss modulus and $\tan \delta$ curves demonstrate a single T_g peak, although parallel studies by DSC and SEM prove the immiscibility of the system. This fact could be explained by either the partial miscibility that could bring closer the T_g 's of pure components and thus makes them invisible for DMTA or the small size of dispersed phases or both.

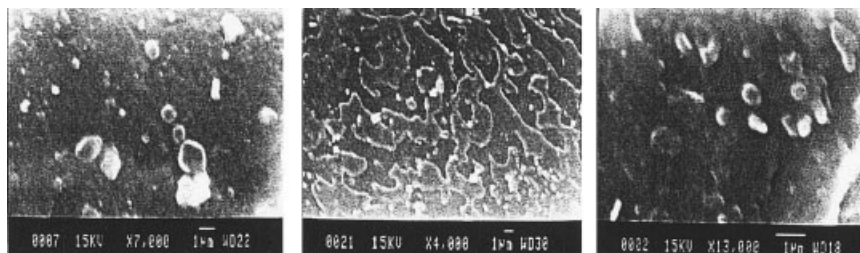


Figure 13 SEM microphotographs of PS/SMA14 blends (a) 27/75 and (b) 50/50 w/w.

Moreover, the difference between the glass transition of the initial components and the interactions between them seems to play the most important role. If these interactions bring the T_g 's of the components closer than 8–9°C, as in SMA8/PGI blends, the immiscibility of the system cannot be detected by DMTA.

In the case that mutual solubility takes place and the glass transitions of the pure polymers are very close, as in SMA8/SMA14 blends, DMTA seems to give more conclusive results from DSC technique. However, when the difference in glass transitions is higher, then both techniques can be used safely. So, the easier observation of glass transition in the PS/SMA8 and PS/SMA14 blends must be attributed to the larger differences between the glass transition of the components.

References

1. Wetton, R. E. in *Developments in Polymer Characterization*; Dawkins, J. V., Ed.; Elsevier Applied Science: London, 1986; p. 179.
2. Cavaille, J. Y.; Jourdan, C.; Perez, J. *Makromol Chem, Macromol Symp* 1988, 16, 341.
3. Nassar, T. R.; Paul, D. R.; Barlow, J. W. *J Appl Polym Sci* 1979, 23, 85.
4. Sjoerdsma, S. D.; Dalmolen, J.; Bleijenberg, A. C. A. M.; Heikens, D. *Polymer* 1980, 21, 1469.
5. Serhatkulu, T.; Erman, B.; Bahar, I.; Fakirov, S.; Evstatiev M.; Sapundjieva, D. *Polymer* 1995, 36, 2371.
6. Flores, R.; Perez, J.; Cassagnau, P.; Michel, A.; Cavaille, J. Y. *J Appl Polym Sci* 1996, 60, 1439.
7. Liang, Z.; Williams, H. L. *J Appl Polym Sci* 1992, 44, 699.
8. Kalfoglou, N. K.; Skafida, D. S.; Kallitsis, J. K.; Lambert, J.-C.; Stappen, L. V. *Polymer* 1995, 36, 4453.
9. George, S.; Neelakantan, N. R.; Varughese, K. T.; Thomas, S. *J Polym Sci, Part B: Polym Phys* 1997, 35, 2309.
10. Natansohn, A.; Murali, R.; Eisenberg, A. *Makromol Chem Macromol Symp* 1988, 16, 175.
11. Goodwin, A. A.; Simon, G. P. *Polymer* 1997, 38, 2363.
12. Robertson, C. G.; Wilkes, G. L. *J Appl Polym Sci, Part B: Polym Phys* 2001, 39, 2118.
13. Brannock, G. R.; Barlow, J. W.; Paul, D. R. *J Polym Sci, Part B: Polym Phys* 1997, 35, 2309.
14. Prinos, J.; Tselios, Ch.; Bikiaris, D.; Panayiotou, C. *Polymer* 1997, 38, 5921.
15. Bosma, M.; TenBrinke, G.; Ellis, T. S. *Macromolecules* 1988, 21, 1465.
16. Cowie, J. M. G. *Polym Eng Sci* 1979, 19, 709.
17. Fekete, E.; Foldes, E.; Damsits, F.; Pukanszky B. *Polym Bull* 2000, 44, 363.
18. Canavate, J.; Pages, P.; Saurina, J.; Colom, X.; Carrasco, F.; *Polym Bull* 2000, 44, 293.
19. Parada, J. M. R.; Percee, V. *Macromolecules* 1986, 19, 55.
20. Lu, X.; Weiss, R. A. *Proc Am Chem Soc PMSE* 1991, 64, 163.
21. Prinos, J.; Dompros, P.; Panayiotou, C. *Polymer* to appear.
22. Prinos, J.; Bikiaris, D.; Panayiotou, C. *Polymer* 1999, 40, 4741.
23. Utraki, L. in *Polymer blends and Alloys*; Hansen: New York, 1989.
24. Privalko, V. P.; Novikov, V. V. *The Science of Heterogeneous Polymers: Structure and Thermophysical Properties*; Wiley & Sons: Chichester, UK, 1995; p. 79.
25. Kim, W. N.; Burns, C. M. *Macromolecules* 1987, 20, 1876.
26. Wood, L. A. *J Polym Sci* 1958, 28, 319.
27. Fox, T. G. *Bull Am Phys Soc* 1956, (2) 1, 123.
28. MacKnight, W. J.; Karasz, F. E.; Fried, J. R. in *Polymer Blends*; Paul, D. R.; Newman, S. By D. R.; Newman, S, Eds.; Academic Press: New York–San Francisco–London, 1978: Vol 1, pp. 219–281.
29. Xanthos, M. *Polym Eng Sci* 1988, 28, 1392.
30. Baker, W. E.; Sallem, M. *J Appl Polym Sci* 1987, 28, 2057.
31. Chen, C. C.; Fontan, E.; Kim, K.; White, J. L. *Polym Eng Sci* 1988, 28, 69.
32. Chang, F.-C.; Hwu, Y.-C. *Polym Eng Sci* 1991, 31, 1509.
33. Tselios, Ch.; Bikiaris, D.; Prinos, J.; Panayiotou, C. *J Appl Polym Sci* 1997, 64, 993.
34. Jarvela, P.; Shuca, L.; Jarvela, P. *J Appl Polym Sci* 1996, 62, 813.