



Effect of thermal history on the molecular orientation in polystyrene/poly(vinyl methyl ether) blends

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Received 13 November 2002; received in revised form 4 March 2003; accepted 7 March 2003

Abstract

The effect of thermal history on the orientation and relaxation behavior of blends of polystyrene with poly(vinyl methyl ether) (PS/PVME) has been studied using polarization modulation infrared linear dichroism (PM-IRLD) and differential scanning calorimetry (DSC). DSC shows that miscible PS/PVME blends containing 70% of PS can be physically aged at temperatures above their mean glass transition temperature (T_g). PM-IRLD measurements reveal that both components become more oriented upon stretching at 51 °C (8 °C above T_g) if the sample is aged at the deformation temperature prior to stretching. Room-temperature aging can also lead to an increased orientation if the heating time at 51 °C is kept short. Moreover, PS and PVME develop a larger orientation in phase-separated blends than in miscible ones, and their relaxation is hindered. The results have been interpreted considering the morphology of the samples, including the presence of concentration fluctuations in miscible blends, and the effect of the local environment on the rigidity of the chains.

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Keywords: Polystyrene/poly(vinyl methyl ether) blends; Thermal history; Polarization modulation infrared linear dichroism

1. Introduction

The influence of parameters like the draw ratio, stretching temperature, and stretching speed on the deformation and orientation relaxation have been studied in detail for several homopolymers and multicomponent systems [1–14]. In the case of miscible polymer blends, the effect of composition has also been investigated [5–11]. In most cases, a different level of chain orientation has been observed for each component, in spite of the blend's miscibility. On the other hand, the effect of thermal history on the macroscopic deformation of thermoplastic polymers and polymer blends has received much less attention. Several thermally induced phenomena, such as crystallization, physical aging, and phase separation, have a significant impact on the microstructure and physical properties of polymers and could thus influence their orientation following a macroscopic deformation.

The effect of thermal- and stress-induced crystallization

on the deformation of semi-crystalline polymers like poly(ethylene terephthalate) (PET) has been studied in some detail [12–14]. A much larger orientation has been observed in the rigid crystalline domains as compared to the soft amorphous phase. In contrast, physical aging has rarely been considered to influence the deformation of polymers because the deformation is usually performed above the glass transition temperature (T_g) of the polymer, thus erasing the previous thermal history. Nevertheless, studies have dealt with the effect of physical aging on sub- T_g deformations. It has been demonstrated that aged polystyrene (PS) possesses larger elastic modulus and yield stress than quenched samples [15]. Annealing at or below T_g has also been shown to influence the free volume and mechanical deformation of polyimides and polycarbonate [16,17]. Wang et al. have reported that sub- T_g annealing can enhance the orientation obtained following the deformation of poly(methyl methacrylate) [18]. They proposed that it was due to the formation of a stereocomplex that would act as physical cross-links in the sample.

The orientation of blends of PS with poly(vinyl methyl ether) (PS/PVME), phase-separated by heating above their lower critical solution temperature (LCST), has already been reported in the literature. Abtal and Prud'homme have

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shown that PS chains orient more in the phase-separated than in the miscible blends, while PVME remains unoriented [19]. In contrast, Lu et al. have reported a smaller PS orientation in phase-separated 50/50 PS/PVME blends as compared to the miscible ones [20].

We have recently studied the orientation in miscible PS/PVME blends by polarization modulation infrared linear dichroism (PM-IRLD), and measured directly the relaxation curves of both components for the first time [6]. We have also shown by differential scanning calorimetry (DSC) that these blends can be physically aged above their midpoint T_g [21]. In this work, we have used this characteristic of PS/PVME blends to evaluate if physical aging influences the macroscopic deformation of miscible polymer blends above T_g . PM-IRLD and DSC have been used to probe the molecular orientation and physical aging dynamics, respectively. Significant differences in the orientation of samples with different thermal histories have been observed. We have also studied phase-separated PS/PVME blends to achieve a better understanding of the role of morphology on the deformation of polymer blends.

2. Experimental section

Monodisperse atactic PS (Pressure Chemical) with $M_w = 942$ kg/mol and PVME (Polymer Scientific Products) with $M_w = 59$ kg/mol were used. The high- and low-molecular weight fractions of PVME were removed by a series of reprecipitation of benzene solutions of PVME in hexane, a non-solvent. The polydispersity index of PVME was reduced to 1.3, as determined by size exclusion chromatography (Waters Model 590) with a light-scattering detector (Wyatt DAWN DSP) in tetrahydrofuran. Self-supported $0\mu\text{m}$ thick films containing 70% w/w PS were cast on glass plates from 3% benzene solutions, air-dried at room temperature for two days, and then gradually heated under vacuum up to 80°C for 48 h in order to remove the last traces of solvent and residual stresses.

All DSC measurements were performed on samples of 6–8 mg using a Perkin–Elmer DSC-7 calorimeter at a scanning rate of 10 K/min. The temperature and heat of transition were calibrated using an ultra-pure indium reference sample. An empty high-purity aluminum pan was used in the reference furnace in all DSC measurements, and a baseline correction curve determined with empty furnaces was subtracted from all thermograms. For physical aging experiments, the samples were first heated at 80°C for 2 min in order to erase the previous thermal history, and then quenched to the annealing temperature of 51°C . After annealing for a given time, the samples were quenched at -65°C , and two heating scans from -65 to 110°C were performed. The difference between the first (annealed) and second (reference) scans allowed the evaluation of the enthalpic relaxation due to the annealing. The LCST of the 70/30 PS/PVME blend was determined to be 127°C by

optical microscopy at a heating rate of $0.1^\circ\text{C}/\text{min}$, using a Zeiss Axioscop optical microscope equipped with a Toshiba HV-D27 3CCD camera and a Linkam THMS600 heating stage.

For orientation and relaxation measurements, PS/PVME films were cut into strips having 20 mm in length and 6 mm in width, and marked with ink lines to verify the draw ratio. A pyrotape (Aremco Products #546) was used to avoid the slippage of the films during the elongation. PS/PVME films were stretched to a fixed draw ratio of 2, at 51°C ($T_g + 8$), and at a constant draw rate of 10 cm/min. The deformations were made using a custom-built mechanical stretcher fitted with ZnSe windows to allow the in situ recording of PM-IRLD spectra during the orientation and relaxation periods. The temperature was adjusted ($\pm 0.5^\circ\text{C}$) using an Omega temperature controller (CN 7600) and heating cartridges. Some samples (called ‘fresh samples’ in the rest of this paper) were heated at 80°C for 2 min directly in the stretcher using a temperature-controlled heat-gun to erase any previous thermal history. Other samples were aged at room temperature for about 8 weeks prior to stretching. All samples were annealed at the deformation temperature for either 3 or 45 min. The phase-separated samples were prepared by heating at 145°C in a vacuum oven for either 20 or 60 min, and were deformed within the next 8 min in order to avoid any additional aging effect or rehomogenization.

Dichroic difference spectra with a resolution of 8 cm^{-1} were obtained with a Bomem Michelson MB-100 spectrophotometer using the optical setup and the two-channel electronic device previously described [22,23]. A liquid nitrogen-cooled InSb detector (EG&G), a ZnSe photoelastic modulator (Hinds PEM-90 type II/ZS50) operating at 50 kHz, a lock-in amplifier (EG&G 7260 DSP) with a $40\mu\text{s}$ time constant, and two dual-channel electronic filters (Stanford Research Systems SR650) were used to generate the double modulation and to isolate the experimental signals. All experiments were conducted in three consecutive acquisition steps: a first series of 180 spectra of 4 scans, followed by 90 spectra of 30 scans, and by a final series of 80 spectra of 75 scans, for a total measurement time of about an hour. The orientation function, $\langle P_2(\cos \theta) \rangle$, was calculated from the intensity of the dichroic difference ΔA as [23]

$$\langle P_2(\cos \theta) \rangle = \frac{2}{(3 \cos^2 \alpha - 1)} \frac{\Delta A}{3A_0} \sqrt{\lambda} \quad (1)$$

where λ is the draw ratio, A_0 the absorbance of the unstretched isotropic sample, and α the average angle between the transition moment of the vibration considered and the main chain axis. The A_0 values were determined from transmission spectra using Nicolet Magna 560 or 760 spectrophotometers.

3. Results and discussion

3.1. Effect of physical aging

The DSC traces of the pure homopolymers and of the 70/30 PS/PVME blend are shown in Fig. 1 on a relative scale. PS and PVME both exhibit a sharp glass transition with a T_g of 105 and -25 °C, respectively. The 70/30 blend also gives a single T_g of about 43 °C, which is normally considered as proof of blend miscibility at the scale of the DSC measurement [24,25]. However, its glass transition is much broader than that of the two homopolymers. To evaluate the breadth of the T_g zone, the initial (T_{gi}) and final (T_{gf}) temperatures characterizing the transition have been estimated as the intercept of the baseline at low and high temperatures with the tangent of the heat capacity jump, as shown in Fig. 1. For pure PS and PVME, the difference between T_{gf} and T_{gi} is less than 8 °C, while it is about 55 °C for the blend. This transition broadening has a large impact on the aging properties of miscible PS/PVME blends.

When a glassy polymer is annealed a few degrees below T_g , its free volume tends to decrease with time in order to reach its glassy equilibrium value, thus modifying its segmental mobility and several of its viscoelastic properties [26–30]. This phenomenon is known as physical aging or enthalpic relaxation. In principle, no physical aging should occur during the annealing of a polymer or polymer blend above T_g because the system is in thermodynamic equilibrium conditions due to the long range cooperative motions in the rubbery state [26,27]. However, in the case of PS/PVME blends, we have demonstrated that physical aging can occur at temperatures much above T_g , and that the maximum temperature at which an enthalpic relaxation peak can occur is T_{gf} [21].

Fig. 2 shows the DSC enthalpic relaxation peaks of a 70/

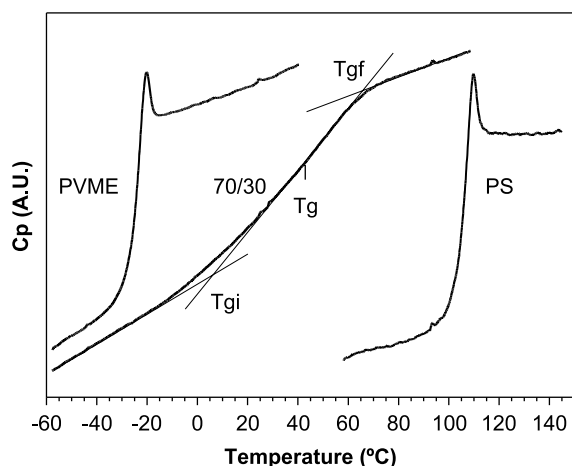


Fig. 1. DSC traces of pure PS and PVME, and of a 70/30 PS/PVME miscible blend. The C_p values (Y scale) are presented in arbitrary units, and the relative intensity of the thermograms has been adjusted to highlight the width difference in the transition between the blend and the homopolymers. The initial and final T_g (T_{gi} and T_{gf}) were determined as shown.

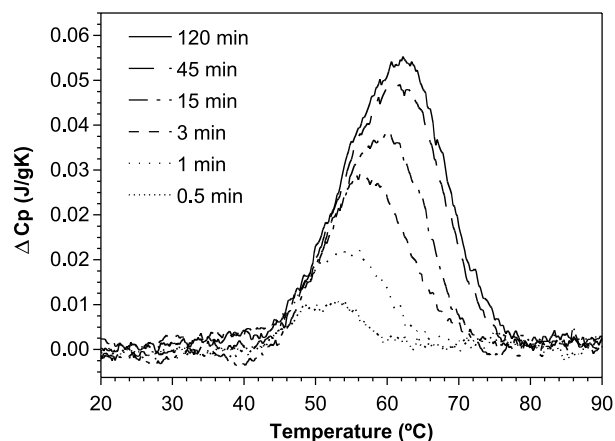


Fig. 2. Physical aging curves determined by DSC following the annealing of fresh 70/30 PS/PVME miscible blends at 51 °C.

30 PS/PVME blend after annealing at 51 °C, which is 8 °C above the mean T_g , but 13 °C below T_{gf} , for times ranging between 0.5 and 120 min. As the annealing time increases, the peak gradually shifts to higher temperatures and becomes broader, but the left-hand side remains the same. The area of the peak, which is directly related to the enthalpic relaxation during the aging, increases rapidly in the first 15 min and more slowly at longer times. After 120 min, the enthalpic relaxation is about 0.91 J/g.

It is considered herein that the broad glass transition in miscible PS/PVME blends is due to the presence of nanodomains possessing a local T_g that depends on their local composition [21,25,31–34]. When the blend is annealed at 51 °C, PS-rich domains with a high local T_g are still below their local T_g , allowing them to age even if the blend is globally in the rubbery state. This can explain the broad relaxation peaks noted in Fig. 2. It can be observed that the ΔC_p values on the low-temperature side of the peaks are very similar for all annealing times, while they continuously increase at higher temperatures. It is well established that the rate of enthalpic relaxation upon annealing below T_g is a temperature-dependant phenomenon: at temperatures much below T_g , the high viscosity of polymers hinders the local motions of the chains and very slow aging occurs, even if the sample is far from its thermodynamic equilibrium conditions. In our case, domains possessing a local T_g only slightly above the annealing temperature could thus reach their equilibrium conditions relatively fast, while those with a local T_g farther above the annealing temperature would relax at a slower rate. Nevertheless, since they are far from their equilibrium conditions, they can eventually relax to a much larger extent, thus producing the higher ΔC_p values observed in Fig. 2 at high temperatures as compared to those observed at lower temperatures after a long annealing time.

Shelby and Wilkes have shown that the rate of enthalpic relaxation of a polymer during an annealing below T_g is modified by the presence of chain orientation in the sample [35]. In the case of a polymer blend with a broad T_g , for

which physical aging is possible above T_g , it is interesting to verify if physical aging can affect the orientation introduced in the sample during a macroscopic deformation. We have thus annealed fresh (see Section 2) PS/PVME samples containing 70% PS for either 3 or 45 min at 51 °C (8 °C above the mean T_g), and then stretched them, and followed their relaxation kinetics at 51 °C using PM-IRLD. As in a previous paper [6], the 2850 cm^{-1} band assigned to the CH_2 symmetric stretching of PS and the 2820 cm^{-1} band related to the methoxy side-chain CH_3 symmetric stretching of PVME have been used to determine the orientation of PS and PVME, respectively. The chain order parameter $\langle P_2(\cos \theta) \rangle$ of both components was determined with Eq. (1) using the dichroic difference intensity of the bands and assuming an α angle of 90°.

Fig. 3 compares the relaxation dynamics of fresh PS/PVME samples that were annealed in the stretcher for 3 or 45 min. Ideally, a completely unannealed sample should have been used, but 3 min appeared to be the minimum time required to stabilize the stretcher temperature at 51 °C following the heating at 80 °C. Fig. 3 reveals that the orientation of both PS and PVME is influenced by the annealing time before stretching. At all relaxation times, the samples annealed for 45 min show a significantly higher level of orientation than those annealed for 3 min. To our knowledge, this is the first observation of the effect of physical aging above T_g on the macroscopic deformation of polymers.

When physical aging occurs, the density of the sample increases, leading to a more rigid and brittle sample. According to the literature, a rigid sample should give rise to a higher orientation upon deformation as compared to a rubbery one. For instance, the rigid crystalline phase of a semi-crystalline polymer is much more oriented than its rubbery amorphous phase [8,12–14]. Rigid segments or conformations have also been shown to lead to a higher orientation in amorphous PET and in blends of poly(vinyl chloride) with poly(α -methyl- α -*n*-propyl- β -propiolactone) [36,37]. In the case of miscible PS/PVME blends, the

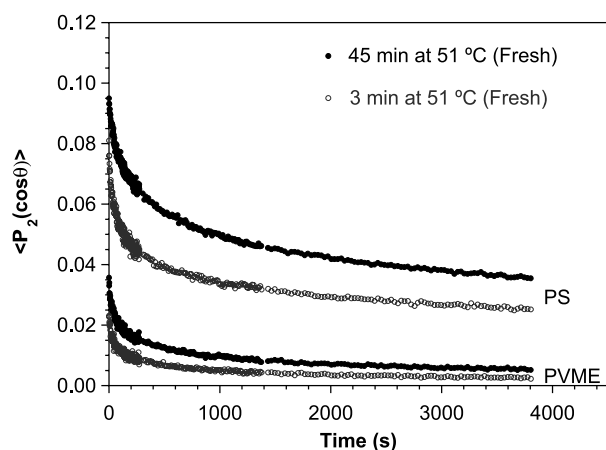


Fig. 3. Relaxation curves of PS and PVME in fresh 70/30 PS/PVME miscible blends annealed at 51 °C for 3 and 45 min.

observations of Fig. 3 can be interpreted by considering the concentration fluctuations hypothesis.

Upon annealing at 51 °C prior to deformation, PS-rich domains with a local T_g above 51 °C were allowed to relax toward their glassy equilibrium state, leading to an increased local density. Considering Fig. 2, this effect should be much more pronounced after 45 than after 3 min of annealing. PS chains should thus be in a globally more rigid environment in these samples, allowing them to acquire a higher orientation during deformation. Of course, PVME chains should be mainly found in the PVME-rich and in the mid-composition domains, which possess a local T_g below 51 °C. For these regions, no annealing effect is expected since the chains should already be in equilibrium. Nevertheless, PVME chains that are present in the PS-rich domains can also experience an environment of increased rigidity following the annealing, which might explain the larger orientation observed for PVME in the blends after 45 min of annealing.

The results of Fig. 3 indicate that, unlike for pure polymers, the time that a polymer blend with a broad glass transition region spends at the stretching temperature prior to its deformation can have a significant effect on its orientation. In our previous experiments, the samples were allowed to equilibrate for 45 min at the stretching temperature, but the previous thermal history was not removed before deformation [6,21]. It is thus interesting to evaluate the combined effect of aging at room temperature during the sample storage with the annealing at the deformation temperature.

Fig. 4 shows the differential DSC curve of a miscible 70/30 PS/PVME blend aged at room temperature for several weeks, along with those of fresh and aged samples annealed for either 3 or 45 min at 51 °C. The sample aged at room temperature shows a large enthalpic relaxation peak with a maximum around 50 °C. This room-temperature aging peak is almost entirely removed by an annealing of only 3 min at 51 °C, but the relaxation peak observed following a 3 min annealing at 51 °C is still larger for the sample that was aged

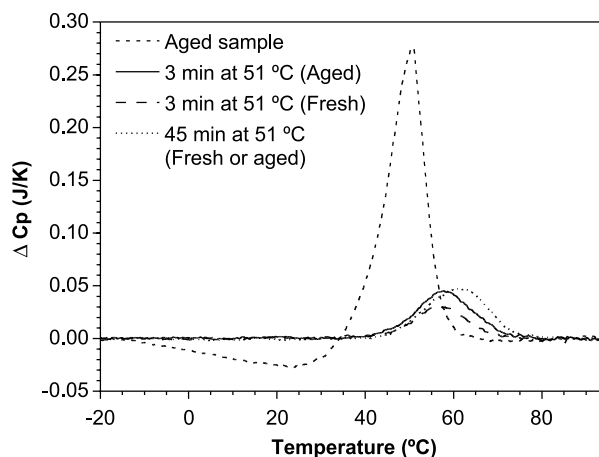


Fig. 4. Physical aging curves determined by DSC of 70/30 PS/PVME miscible blends following various thermal histories.

at room-temperature than for the fresh one. In contrast, aged and fresh samples exhibit the same enthalpic relaxation, about 0.8 J/g, after a 45 min annealing. A long annealing at 51 °C thus removes all the previous room-temperature thermal history of the sample, while a short time (3 min) does not.

According to the correlation established between the enthalpic relaxation peaks and the orientation functions of Figs. 2 and 3, higher $\langle P_2(\cos \theta) \rangle$ values are expected for samples showing greater enthalpy recovery. Indeed, the results of Fig. 5 show that the orientation functions of PS and PVME are larger for the sample aged at room temperature than for the fresh one, in agreement with its larger enthalpic relaxation peak observed in Fig. 4. This implies that the thermal history of the sample during its storage is a significant parameter that must be considered in deformation studies of polymer blends possessing a broad T_g .

These results also seem to confirm the existence of a relation between the enthalpic relaxation, as measured by DSC, and the orientation behavior of the sample as measured by PM-IRLD, suggesting that DSC could be used as a simple and rapid technique to estimate the orientation increase to be expected with regard to the thermal history of the material. In agreement with this proposal, we have verified that the relaxation curves obtained for aged samples annealed for 45 min at 51 °C are superimposable with the curve obtained for a fresh sample, shown in Fig. 3, as suggested from the DSC data of Fig. 4 since their enthalpic relaxation peaks are identical.

It is interesting to note that although the orientation level reached by the samples is significantly dependent upon their thermal history, as observed in Figs. 3 and 5, the relaxation kinetics of PS (and PVME) in the different samples is rather similar. This could be related to a phenomenon called rejuvenation, by which deformation-induced free volume would be created in a polymer upon application of a mechanical stress, thus decreasing the effect of previous physical aging [17,26,27]. In agreement with this hypothesis, smaller enthalpic relaxation peaks have been observed

(not shown) for annealed samples that were stretched just before the DSC measurement as compared to conventionally annealed samples.

3.2. Effect of phase-separation

In order to provide more insight on the influence of morphology on the deformation of PS/PVME blends, phase-separated samples have been prepared and studied under the same stretching conditions as the miscible blends. Fig. 6 shows the DSC thermograms of a miscible blend and of two demixed samples prepared by heating at 145 °C for 20 and 60 min (referred to as D20 and D60 throughout the rest of the text), respectively, followed by two short annealing periods of 5 min at 21 °C and 3 min at 51 °C. These times are representative of the thermal history underwent by the samples between the phase separation and the mechanical deformation.

For both heterogeneous samples, two glass transitions are observed at low and high temperatures. In both cases, the first transition is relatively sharp and is found close to the T_g of pure PVME (−25 °C), at −20.6 and −24.2 °C for samples D20 and D60, respectively, indicating the formation of a phase strongly enriched in PVME. The high-temperature transition is more intense than the low-temperature one (in terms of ΔC_p) and remains broad, especially for the sample annealed for 20 min. This observation indicates the presence of a major PS-rich phase that still contains significant concentration fluctuations. From the ΔC_p and T_g values of the two transitions, it is possible to estimate the composition and relative amount of each phase. After 20 min of demixing, the sample appears to be composed of about 80% of a phase containing 84% of PS, and 20% of a phase containing 20% of PS. Similar relative amounts of both phases are found for sample D60, with 87% of PS in the major phase and only 6% of PS in the minor phase.

A small bump can be observed in Fig. 6 at about 65 °C

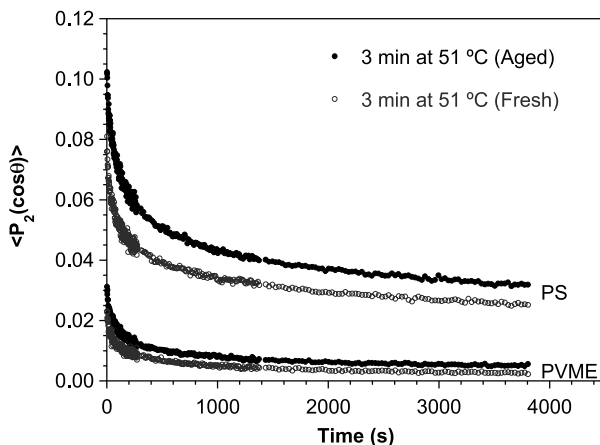


Fig. 5. Relaxation curves of PS and PVME in fresh and aged 70/30 PS/PVME miscible blends annealed at 51 °C for 3 min.

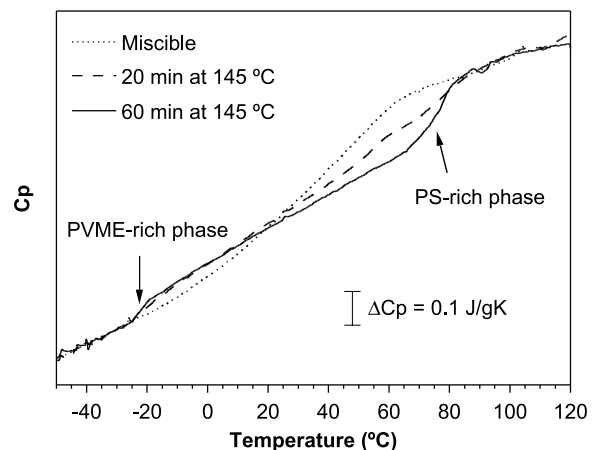


Fig. 6. DSC traces of a miscible 70/30 PS/PVME blend and of blends phase-separated at 145 °C for 20 and 60 min.

due to the enthalpic relaxation occurring during the two short annealings. We have also observed that the intensity of the low-temperature T_g decreases and its position is shifted to a higher temperature on the second DSC scan (not shown), indicating that some rehomogenization has occurred. Okada et al. have observed a similar effect when annealing blends of PS with poly(2-chlorostyrene) a few degrees below their LCST, in the single-phase region of the phase diagram [38]. This phenomenon prevents any storage of the samples at room temperature, so the films were stretched as fast as possible after the phase separation process.

Fig. 7 shows the orientation relaxation curves of PS and PVME for the miscible and phase-separated blends deformed at 51 °C. For PS, significantly larger $\langle P_2(\cos \theta) \rangle$ values are observed with increasing demixing time, and the relaxation dynamics is hindered for D60. The morphology of the phases and the variation of their T_g as compared to that in the miscible blend both play a significant role on the mechanical properties of immiscible polymeric systems [39]. In the early stage of spinodal decomposition, PS/PVME blends are expected to form phases with a strong interface adhesion, allowing an efficient stress transmission and a high orientation [19]. Indeed, optical microscopy measurements (not shown) have revealed the presence of highly interpenetrated domains possessing an average long dimension of about 2 μm for D60.

The difference between the T_g of the phases and the deformation temperature is also an important factor to consider. While 51 °C is 8° above the mean T_g of the miscible blend, it is 20 and 27° below that of the PS-rich phase for D20 and D60, respectively. It is well known that a larger orientation is generated when a polymer is stretched at lower temperatures relative to its T_g [1,3]. Since more than 90% of the PS chains are present in the high- T_g PS-rich phase, it is not surprising to observe a larger orientation and a hindered relaxation for PS in the phase-separated blends as compared to the miscible ones.

As seen in Fig. 7, the orientation of PVME increases for

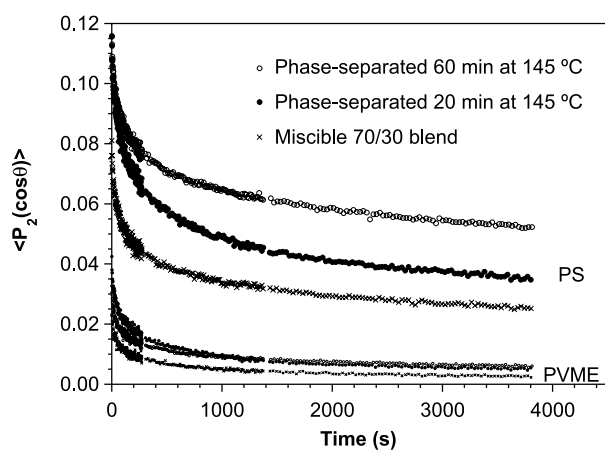


Fig. 7. Relaxation curves of PS and PVME in a miscible 70/30 PS/PVME blend and in blends phase-separated at 145 °C for 20 and 60 min.

sample D20 as compared to that for miscible blends. However, a longer phase separation of 60 min yields slightly smaller initial $\langle P_2(\cos \theta) \rangle$ values, intermediate between those of miscible and D20 samples. Nevertheless, the relaxation kinetics of PVME is slower for D60, and its orientation function eventually crosses that of the D20 after about 1100 s of relaxation. Two opposing contributions can be expected in the case of PVME because a significant amount of chains is found in both the low- T_g PVME-rich and in the high- T_g PS-rich phases. The chains in the PVME-rich phase are deformed well above their T_g , i.e. 71.6 and 75.2 °C above T_g for D20 and D60, respectively. They are thus expected to develop a very low orientation upon drawing, and to relax at a very high rate. On the other hand, PVME chains present in the PS-rich phase are deformed below their T_g and, therefore, they should be more oriented and relax at a slower rate as compared to the chains in the miscible blend.

In both cases, the latter effect appears to be dominant since the orientation of PVME is always larger than that in the miscible blends. The lower orientation level observed for PVME in D60 (as compared to D20) can be explained by the distribution of PVME chains in the different phases. In the first case, the low- T_g phase is almost entirely composed of PVME, leaving only 35% of the total PVME chains in the high- T_g phase, as compared to about 40% in the second case. Since only PVME chains found in the PS-rich phase are believed to orient to any significant level, higher orientation levels can be expected in the D20 sample. On the other hand, the difference between the deformation temperature and the T_g of the PS-rich phase is larger for D60, which could lead to a higher orientation in this sample. In the present case, the influence of the number of chains present in the high- T_g phase is apparently more important, presumably because the T_g difference between the samples demixed for 20 and 60 min is not large enough, only 7 °C. Nevertheless, since the relaxation rate is only influenced by the relative temperature (controlling the rigidity of the chains) and not by the number of chains present in the PS-rich phase, a slower relaxation is observed for PVME in the blend demixed for 60 min.

4. Conclusions

The results obtained on physically aged and phase-separated PS/PVME samples are in qualitative agreement, and clearly demonstrate the impact of thermal history on the orientation and relaxation of polymer blends. In both cases, the orientation developed by PS is larger in more rigid samples. In miscible blends, this effect can be attributed to an increase of the density of PS-rich nanodomains following a physical aging above the mean T_g of the blend (but below T_{gr}), or during the room-temperature storage of the samples while, in phase-separated samples, the larger orientation results from the increase of the T_g of the PS-rich

phase. In addition, phase-separated blends exhibit a hindered relaxation as compared to the miscible ones. The results of this study also indicate that, although the rigidity increase occurs in the PS-rich phase (in the case of demixed samples) and in PS-rich nanodomains (in the case of physical aging), the deformation and relaxation of PVME chains are significantly modified by the thermal treatments, demonstrating a coupling between the chain orientation and relaxation and its environment. To our knowledge, the effect of physical aging above T_g on the orientation of polymer blends has never been considered before. Since most of the previous deformation studies have been performed a few degrees above T_g , this phenomenon might have influenced the results for blends showing a broad glass transition region.

Acknowledgements

This work was supported by NSERC of Canada and FCAR of the Province of Québec. C.P. also expresses his thanks to NSERC and FCAR for post-graduate scholarships, and to V.H. Mareau for his help with the microscopy measurements.

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