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DSC and DMTA characterization of ternary blends

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Abstract

The phase behavior of ternary blends made of poly(epichlorohydrin) (PECH), poly(vinyl acetate) (PVAc) and poly(methyl methacrylate) (PMMA) has been investigated by differential scanning calorimetry (DSC) and dynamic mechanical thermal analysis (DMTA). DMTA measurements have been shown to be more sensitive than DSC for the detection of a second phase, for the determination of the composition of each phase, and the distribution of PECH in each of them. About 70% PECH was required to obtain a single narrow T_g in the ternary system, which suggests a single homogeneous phase in the limit of sensitivity of DMTA. This study also emphasizes the importance of the composition of the immiscible polymer pair (i.e. the PVAc/PMMA pair in the PECH/PVAc/PMMA system), in addition to the thermodynamic interaction parameters, for controling the phase behavior of ternary systems. © 2002 Published by Elsevier Science Ltd.

Keywords: Ternary polymer blends; Miscibility; Poly(methyl methacrylate)

1. Introduction

Polymer blends are miscible if their components form a single homogeneous phase at the molecular scale, or immiscible if they exhibit several distinct phases. Most polymer blends are immiscible owing to the negligibly small entropy of mixing between polymers, but it is sometimes possible to add a third component, homopolymer A, which is miscible with each of the polymers B and C, to compatibilize the immiscible binary pair made by B and C [1–7].

In several previous papers, we have shown that the interaction parameter between polymer pairs plays a major role in governing the distribution of compatibilizer in each phase of a ternary immiscible system [4,6,8]. For example, in a system made of poly(vinyl chloride) (PVC), poly(propyl methacrylate) (PPMA) and poly(amyl methacrylate) (PAMA), it was shown that the PVC goes preferentially in the PPMA phase in a proportion of 2 to 1 at the expense of the PVC/PAMA phase [8]. In another system made of PVC, chlorinated polyethylene (CPE48) and dioctyl phthalate (DOP), it was shown that the observation of a single T_g by differential scanning calorimetry (DSC) does not necessarily correspond to the occurrence of a single-phase system due to the lack of resolution of this method [4]. In ternary systems, it has always been difficult to determine the real composition of each of the phases involved, and how this composition evolves with the amount of compatibilizer added. It is one of the purposes of this study to answer this question better using the poly(epichlorohydrin) (PECH)/poly(vinyl acetate) (PVAc)/poly(methyl methacrylate) (PMMA) ternary system.

This ternary system has already been studied by Champagne [9], and its binary miscible pairs, PECH/PVAc and PECH/PMMA, by Pinoit [10]. It exhibits a single-phase region when it contains 53% or more PECH and a two-phase region at other compositions [9]. However, in that previous work, the miscibility was established by means of DSC measurements and we will show here that the phase resolution obtained by dynamic mechanical thermal analysis (DMTA) is better for this kind of blends.

2. Experimental

The polymers used in this study and their main characteristics are listed in Table 1. PECH and PVAc were supplied by Aldrich Chemicals and PMMA by Fischer Scientific.

In this study, the blends are designated by the percentage by weight of their components in this order: PECH, PVAc and PMMA. For example, a binary blend containing 25 wt% PECH and 75 wt% PMMA takes the abbreviation 25/75 and, similarly, 19/61/20 corresponds to a ternary blend containing 19 wt% PECH, 61 wt% PVAc and 20 wt% PMMA. Binary and ternary blends were prepared using a MiniMax molder from Custom Scientific. The polymers, for

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Table 1
Main characteristics of polymers used

Polymers	Acronym	T_g (K)	M_w (kg/mol)	M_w/M_n
Poly(epichlorohydrin)	PECH	240	1010	1.7
Poly(vinyl acetate)	PVAc	311	260	2.6
Poly(methyl methacrylate)	PMMA	363	571	1.7

a total amount of 1 g, were fed into the mixing chamber of the molder and mixed at 150–180 °C for 20 min at 150 rpm. Then, the samples were coarsely molded in a Carver press at 150 °C for 20 min. Samples were further dried under vacuum at 110 °C for 1 week. The blend samples for DMTA analysis were finally molded at 150 °C with dimensions of $1.5 \times 6 \times 60$ mm^3 while the blend samples for microscopy were prepared in the same manner but in a disk mold having a diameter of 20 mm and a thickness of 0.5 mm.

Calorimetric measurements were made with a Perkin Elmer DSC-7 in a dry nitrogen atmosphere. The DSC was calibrated with ultrapure indium, which has a melting temperature of 429.75 K and an enthalpy of fusion of 28.5 J/g. The samples were first heated at T_{gh} +40 K for 90 s and quenched at T_{gl} −30 K at a cooling rate of 200 K/min. T_{gh} and T_{gl} correspond, respectively, to the highest and the lowest T_g of the pure polymers involved in the blend. Two heating cycles between T_{gl} and T_{gh} were performed in order to verify the reproducibility of the results. The T_g values reported in this paper are the average of two scans, with an accuracy of ±2 °C. In addition, the onset and the end of the transition (T_o and T_c) have been recorded as judged from the first deviation from and the return to the baseline, respectively. These two temperatures were used to assess the transition breadth (ΔT_g). DMTA measurements were recorded with a dynamic mechanical thermal analyzer (Model RSAII) from Rheometrics Scientific. Data were acquired at 10 Hz, by steps of 1 °C, and at the strain of 0.05% only to ensure that the sample was in the linear viscoelastic region. The morphology of the blends was observed with a scanning electron microscope (SEM JEOL 840) operating at 10 kV. For these measurements, blends were fractured in liquid nitrogen and coated with a blend of gold–paladium.

3. Results

3.1. Binary PVAc/PMMA blends

Fig. 1 shows the heat capacity as a function of temperature for PVAc/PMMA blends containing 25, 50 and 75 wt% PVAc. Unlike the previous PECH/PMMA and PECH/PVAc systems, each curve exhibits two steps in heat capacity at about the T_g of the pure polymers and, therefore, indicate immiscible blends. The width of the first glass transition zone (T_{gl}) is 27 °C, which is close to that of PVAc (29 °C). However, it was difficult to measure exactly ΔT_g in the higher temperature zone (T_{gh}) because the onset of the heat capacity jump (T_o) is ill defined. The uncertainty on T_o is about 15 °C, so that the width of this transition zone is of the order of 33 ± 7 °C (the transition breadth for PMMA is 25 °C). The composition dependence of T_{gh} and T_{gl} is shown in the insert, which emphasizes their very small deviation from the corresponding values for pure PMMA and PVAc.

These measurements have been confirmed by DMTA and the results are shown in Fig. 2 where E' and E'' are plotted as a function of temperature for blends containing 25, 50 and 75 wt% PVAc. The loss modulus curves have been chosen for determining T_g because the maximum of E'' relates much better to T_g measured by DSC than tan δ (strickly speaking, the DMTA T_g should be referred to as T_α since one observes by DMTA the α relaxation peak; however, for simplicity, T_g will be used in this article). A similar observation was reported in the literature by Linares and Acosta [11], and Felisberti et al. [12]. The widths of the transitions were also measured from the loss curves, although many examples in the literature have been reported where ΔT_g is measured from the loss tangent curves without, however, any difference in interpretation between the two sets of results.

Two peaks are generally apparent in these examples, for both E' (Fig. 2(a)) and E'' (Fig. 2(b)), except for the blend with a 75 wt% PVAc content. The maximum of the first peak, seen in the three cases, varies between 41 and 46 °C with composition, in the range of that of pure PVAc (44 °C). For the second peak at higher temperatures, for the 25/75 and 50/50 blends, the maximum is located at 87 and 82 °C, respectively, suggesting that this peak corresponds to a pure PMMA phase, whose maximum in E'' is equal to 85 °C. The DMTA measurements, like the DSC results, infer immiscible PVAc/PMMA blends in all proportions.

Therefore, both DSC and DMTA measurements indicate a phase separation; the size of the phases must be larger than 150 Å since this is the limit of resolution of the two

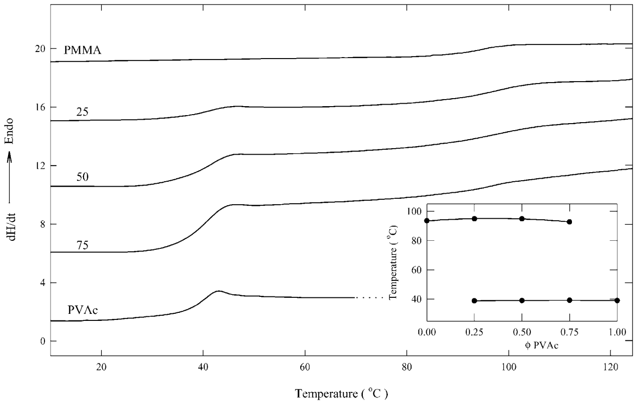

Fig. 1. DSC curves of PVAc/PMMA blends of various compositions (in wt% PVAc). The insert shows the glass transition temperatures of PVAc/PMMA blends as a function of the weight fraction of PVAc. The lines are only a guide for the eye.

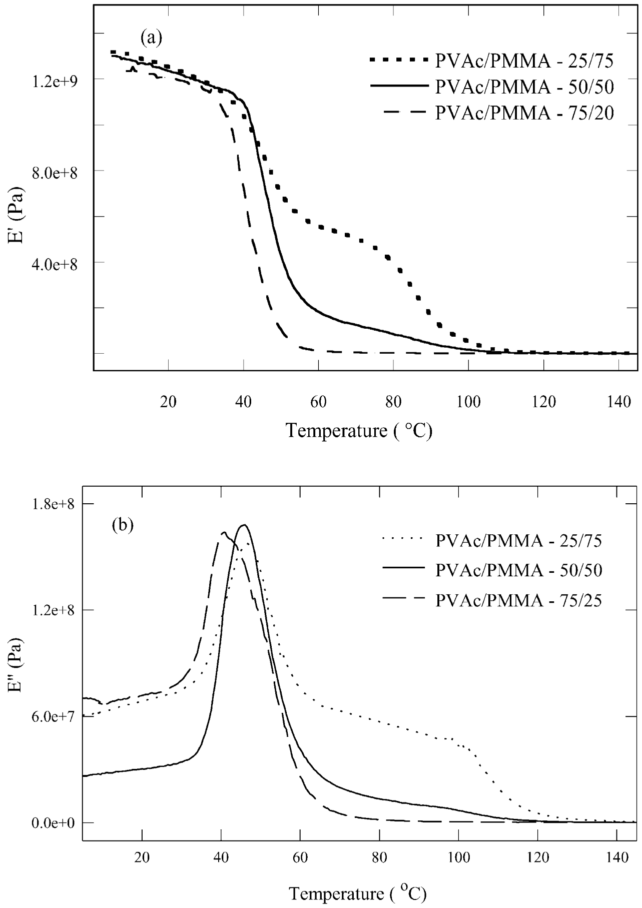

Fig. 2. Isochrones at 10 Hz of (a) E' and (b) E'' of PVAc/PMMA blends.

techniques used [13,14]. However, several studies have shown that the morphology of immiscible blends depends on many factors and, in particular, on the ratio of the viscosity of the dispersed phase and of the matrix [15,16]. When the dispersed phase has a lower viscosity, it forms long fibers in the matrix whereas, with a higher viscosity, the dispersed phase is in the form of droplets. SEM micrographs obtained on PVAc/PMMA blends [10] (not shown here) are in agreement with this trend since PMMA forms droplets in the PVAc matrix while the PVAc dispersed phase takes the form of filaments as the melt viscosity of PVAc is smaller than the melt viscosity of PMMA.

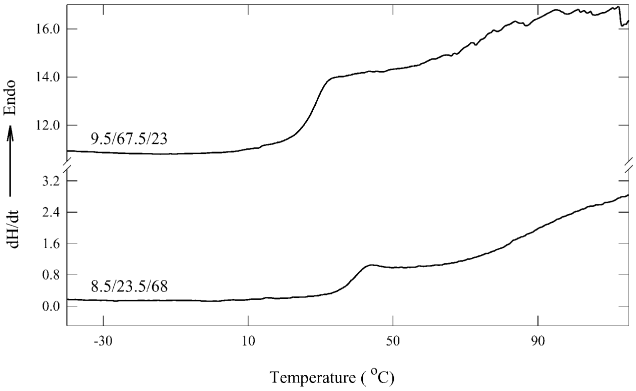

Fig. 3. DSC curves of PECH/PVAc/PMMA ternary blends.

3.2. DSC analysis of the ternary PECH/PVAC/PMMA system

The addition to the PVAc/PMMA blend of a third polymer, PECH, which is miscible with both components when taken separately, is expected, when the amount of PECH is large enough, to give a single-phase system, as previously reported by Champagne [9]. In that work, DSC measurements exhibited a symmetrical two-T_g's zone for blends with a PECH content smaller than 53%; but a single T_g was observed at larger PECH concentrations. However, binary and ternary blends were prepared by casting films from butanone-2 whereas, in this report, blends are prepared by melt mixing. This procedure leads to a different behavior as shown in the following paragraphs.

PVAc/PMMA binary blends were kept in 1/3, 1/1 and 3/1 ratios and the PECH concentration was varied between 9 and 84 wt% in a procedure where the three components were mixed altogether at the same time. The DSC thermograms of these samples show a clear glass transition, called T_{gl}, located at temperatures lower or equal than that of pure PVAc (39 °C). It varies from −5 to 40 °C as a function of blend composition. However, it was difficult or impossible to detect a glass transition at higher temperatures, between the T_gs of pure PVAc and PMMA. In other words, even at low PECH compositions where a two-phase system is expected, only T_{gl} was detected. This is illustrated by the DSC curves of 8.5/23.5/68 or 9.5/67.5/23 blends shown in Fig. 3 where T_{gl} is 39 and 28 °C, respectively. T_g values of all ternary blends investigated by DSC are listed in Table 2. Moreover, the amplitude of the heat capacity jump at T_{gl} (ΔC_p) is about half for the 8.5/23.5/68 blend as compared to the value recorded for the 9.5/67/23 system. Assuming that T_{gl} is related to a PECH/PVAc phase, the decrease of the PVAc content in the former blend should decrease the amplitude of ΔC_p.

The results of Table 2 show that, for PECH concentrations of 19 wt% and higher, PECH does not mix uniquely with PVAc or uniquely with PMMA because this situation

Table 2
Glass transition temperatures for PECH/PVAc/PMMA ternary blends obtained by DSC

$\phi_{\mathrm{PVAc}}/\phi_{\mathrm{PMMA}}$ ratio: 3/1			$\phi_{\mathrm{PVAc}}/\phi_{\mathrm{PMMA}}$ ratio: 1/3		
Blend	T_{gl} (°C)	T_{gh}	Blend	T_{gl} (°C)	T_{gh}
9.5/67.5/23	28		8.5/23.5/68	39	–[a]
19/61/20	31	–[a]			
28.5/53.5/18	25	–[a]	28.5/18/53.5	33	–[a]
37/46/17	16		36/17/47	30	–[a]
56.5/32/11.5	− 2		47/13.5/39.5	4	

[a] Second T_g is probably present.

would generate values of T_g lower than those measured. For example, for the 19/61/20 blend, if PECH was mixed only with PVAc, the corresponding T_g should be equal to 19 °C, in disagreement with the experimental observation. In addition, for blends with a ratio of 1/3, if PECH was assumed to form a blend with only PMMA, T_{gl} should be constant and equal to the T_g of pure PVAc (39 °C), which is not seen in Table 2. Therefore, when ternary blends contain a sufficient PECH concentration, the mixing conditions used (time, temperature and rate of rotation) are sufficient to achieve a distribution of PECH in the two polymers. However, it was not possible to calculate the exact distribution of PECH in each phase because of the limited number of measurements of T_{gh}. This difficulty is the consequence of the weak intensity in the C_p of PMMA (about 0.17 J/g °C) as compared to the C_p of PVAC and PECH (0.45 and 0.46 J/g °C, respectively). If PMMA is involved in this second transition and owing to the small amount of PMMA in the ternary blends, the heat capacity jump of the PECH/PMMA phase becomes difficult to detect and outside the limits of sensitivity of the DSC method.

For the 8.5/23.5/68 blend, T_{gl} is located at 39 °C and is equal to the T_g of pure PVAc suggesting that all the PECH is mixed with PMMA. Considering the T_gs of pure PECH and PMMA, a second transition should be observed at 74 °C corresponding to the PECH/PMMA phase. However, for the reasons aforementioned, this transition cannot be detected by DSC. Conversely, for the 9.5/67.5/23 blend, T_{gl} is found at 28 °C, which implies that the full amount of PECH is mixed with PVAc. Therefore, the DSC results suggest, in first approximation, that PECH associates with the component of higher proportion. Considering this assumption, the distribution of PECH should be mainly a function of the $\phi_{\mathrm{PVAc}}/\phi_{\mathrm{PMMA}}$ ratio. Thus, blends with ratios equal to 1/3 should lead to a distribution where 75% PECH mix with PMMA and the rest with PVAc.

3.3. DMTA results and nature of the phases in the ternary system

For the ternary system investigated, DSC measurements were limited by the difficulties to observe the high temperature transition. However, the DSC observations can be complemented by DMTA measurements. Isochronal loss curves at a frequency of 10 Hz are shown in Fig. 4 for blends with a $\phi_{\mathrm{PVAc}}/\phi_{\mathrm{PMMA}}$ ratio of 1/3. For the 28.5/18/53.5 blend, the curve exhibits clearly two maxima which are located at 20 and 40.5 °C (the meaning of these values will be discussed in the next part). For the 36/17/47 and 47/13.5/39.5 blends, a double-peak is not detected but the single peak appears broader for the 36/17/47 blend than for the 47/13.5/39.5 blend (their widths are 43 and 31 °C, respectively). The broad transition in the 36/17/47 blend, along with the previous DSC results, suggests a two-phase system but with compositions that are close, whereas the narrower transition in the 47/13.5/39.5 blend suggests that PECH can homogenize this blend. The same behavior is observed for blends with a $\phi_{\mathrm{PVAc}}/\phi_{\mathrm{PMMA}}$ ratio of 3/1, as shown in Fig. 5. The 19/61/20 blend also displays two peaks with maxima located at 26 and 44 °C, whereas the 28.5/53.5/18 and 37/46/17 blends show a single broad peak ($\Delta T = 35$ and 33.5 °C, respectively). On the other hand, the peak for the 56.5/32/11.5 blend is narrower than those of the other blends

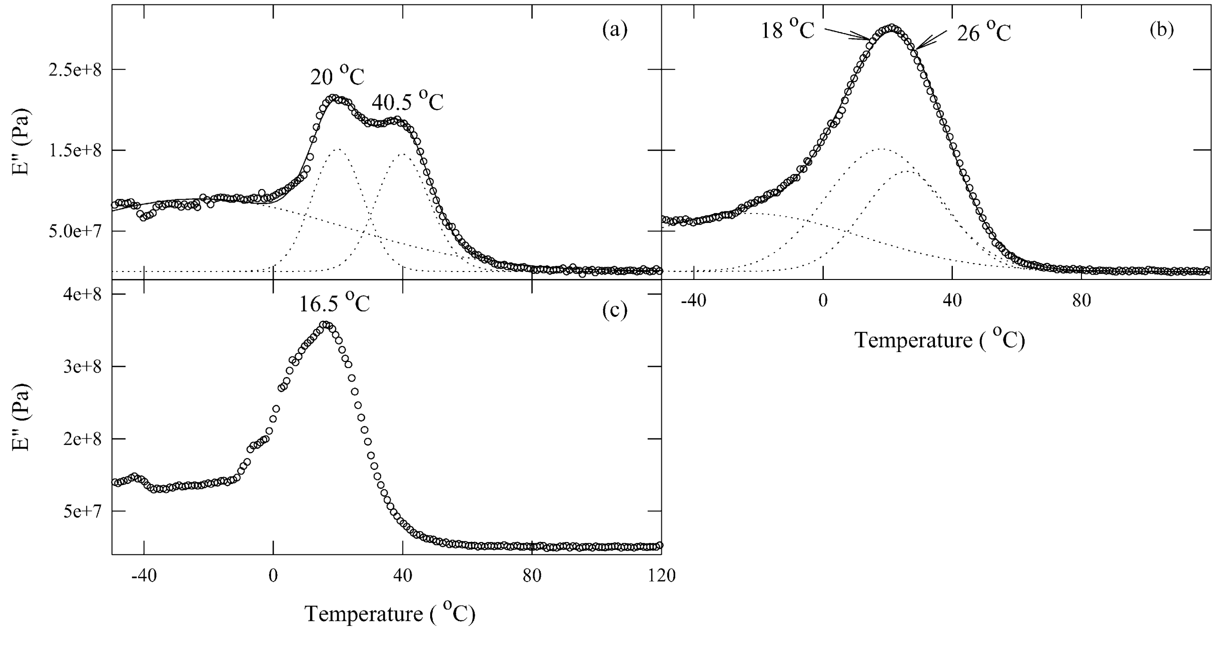

Fig. 4. Isochronal loss modulus curves at 10 Hz of PECH/PVAc/PMMA ternary blends; (a) 28.5/18/53.5, (b) 36/17/47 and (c) 47/13.5/39.5. The solid and dashed lines represent the fitting curves (see text).

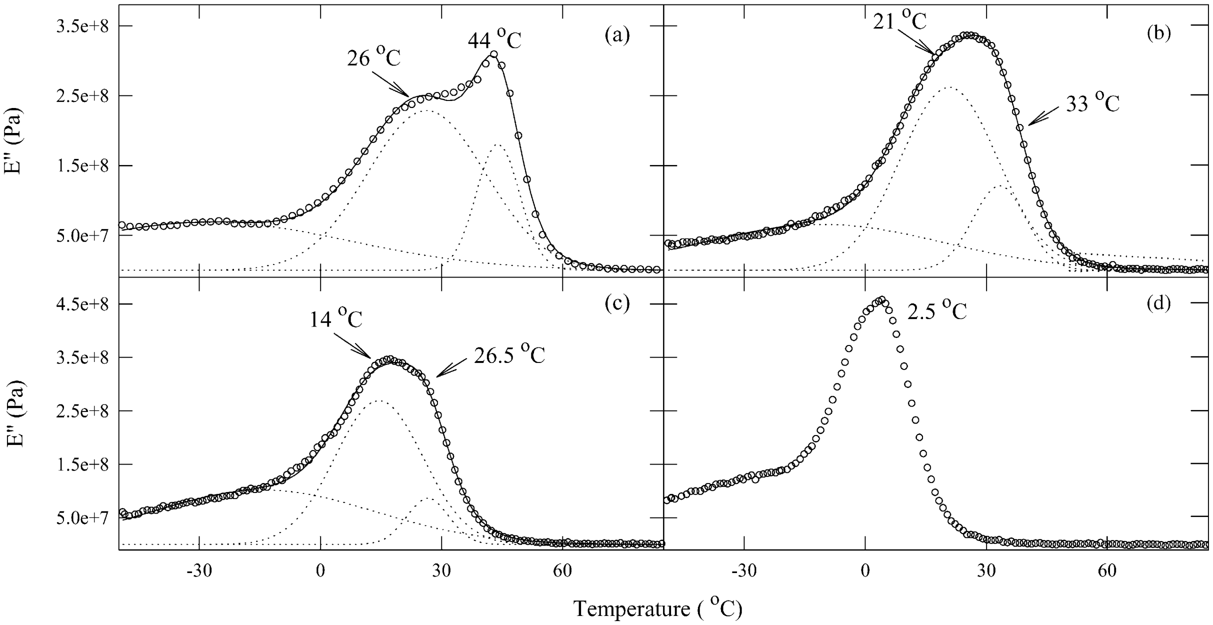

Fig. 5. Isochronal loss modulus curves at 10 Hz of PECH/PVAc/PMMA ternary blends. (a) 19/61/20, (b) 28.5/53.5/18, (c) 37/46/17 and (d) 56.5/32/11.5. The solid and dashed lines represent the fitting curves (see text).

($\Delta T = 23$ °C). At this point, it is important to note that our interpretation differs for 47/13.5/39.5, 28.5/53.5/18 and 37/46/17 blends, even if these blends have a similar ΔT. In fact, the 47/13.5/39.5 blend is assumed to be homogeneous whereas the 28.5/53.5/18 and 37/46/17 blends are two-phase systems keeping in mind that the transition width for PMMA (21 °C) is larger than that of PVAc or PECH (14 and 7 °C, respectively). Thus, it is logical to measure a broad transition in blends with a $\phi_{\mathrm{PVAc}}/\phi_{\mathrm{PMMA}}$ ratio of 1/3, i.e. 47/13.5/39.5, but the same width in blends with a $\phi_{\mathrm{PVAc}}/\phi_{\mathrm{PMMA}}$ ratio of 3/1, i.e. 28.5/53.5/18 and 37/46/17, bears a different meaning.

DMTA measurements were also carried out on blends with equal proportions of PVAc and PMMA, i.e. 38/31/31, 45.5/27/27.5, 70/15/15 and 84/8/8. The results are shown in Fig. 6. As in previous blends, a broadening is observed for 38/31/31 and 45.5/27/27.5 blends with a shoulder at high temperatures in the former case. This shoulder is not observed in the second system but it is likely that the broad single peak consists of two overlapping peaks. On the other hand, there is a narrowing of the transition of the other blends (70/15/15 and 84/8/8) since ΔT equals 17 and 14 °C, respectively, suggesting a homogenization for these blends.

All these results illustrate that DMTA is more sensitive than DSC to the blend morphology. As pointed out by Stoelting et al. [17], the molecular process responsible for the jump in heat capacity observed by DSC may involve longer range motions than the segmental brownian micromotions accountable for the dynamic mechanical peak, such that DSC measurements are less sensitive to small-scale structures than DMTA.

4. Discussion

From these loss modulus curves, it is instructive to undertake a quantitative analysis of the data in terms of the components present in each specific phase. If T_g is taken as the peak maximum in the blends, the apparent weight fraction of PECH in the PECH/PVAc and PECH/PMMA phases can be calculated using the curves describing the dependence of T_g on composition in binary PECH/PVAc and PECH/PMMA blends (as reported in Ref. [10]). When the loss curves exhibited only one broad peak, the fit was achieved by decomposition into two functions; a third function was added in order to fit the β relaxation process at lower temperatures. For that purpose, we used Peakfit (Jandel Scientific). An exponentially modified Gaussian (EMG) function was used to fit the α relaxation peak which results from the convolution of a Gaussian with an exponential. This equation has four independent parameters: the peak area, the intensity, the width and the distortion to characterize slightly distorted asymmetric peaks. A Gaussian function was used to fit the β relaxation peak.

The results of such a procedure are summarized in Table 3. Considering T_{gh} and T_{gl}, the distribution of PECH in each phase can be calculated. We assumed that the maximum of the peak at high temperatures corresponds to T_{gh} and is associated with the PECH/PMMA phase, whereas the maximum of the peak at low temperatures corresponds to T_{gl} and is associated with the PECH/PVAc phase. Ideally, the sum of the two phases should be equal to 100%. Indeed, the values listed in Table 3 are close to the expectations, considering the experimental error involved, since we never have a deviation of more than 6–7%, as found for the

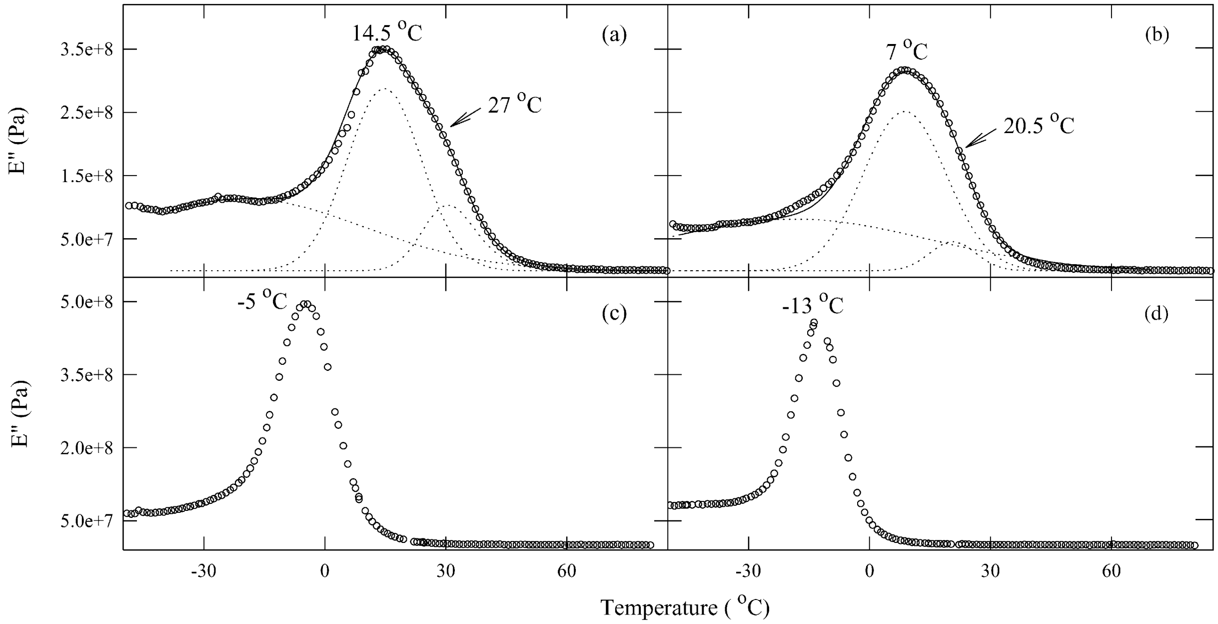

Fig. 6. Isochronal loss modulus curves at 10 Hz of PECH/PVAc/PMMA ternary blends. (a) 38/31/31, (b) 45.5/27/27.5, (c) 70/15/15 and (d) 84/8/8. The solid and dashed lines represent the fitting curves (see text).

28.5/53.5/18, 28.5/18/53.5 and 38/31/31 blends. These results are consistent with the assumption of the coexistence of two PECH/PMMA and PECH/PVAc phases in the ternary blends containing 50% or less PECH.

However, in Table 3, the blends 8.5/23.5/68 and 9.5/67.5/23 are not listed. The DMTA loss curves for these two blends have two maxima and, in addition, they exhibit a shoulder at high temperature, as shown in Fig. 7. This behavior indicates a complex morphology with three transitions, suggesting the presence of three phases in the blend, and not two phases as in previous blends. Using the previous procedure, it is possible to identify these three phases but with a large uncertainty. For example, the analysis of the 8.5/23.5/68 blend resulted into two possibilities [12]: either a blend of PECH/PVAc, PECH/PMMA and pure PMMA, either a blend of PECH/PMMA with pure PVAc and pure PMMA phases. In fact, the amount of PECH in these two blends appears to be insufficient to constitute a regular blend with PVAc and PMMA. This behavior was not detected by DSC due to the very low heat capacity of PMMA.

Nevertheless, for blends containing higher amounts of PECH, DSC and DMTA results are in agreement. PECH is shared between PVAc and PMMA, but is not randomly distributed since about 75% of the PECH mixes with PVAc at a 3/1 $\phi_{\mathrm{PVAc}}/\phi_{\mathrm{PMMA}}$ ratio and, conversely, when the $\phi_{\mathrm{PVAc}}/\phi_{\mathrm{PMMA}}$ ratio equals to 1/3, 75% of the PECH mixes with PMMA. Similarly, for blends with an equal proportion of PVAc and PMMA ($\phi_{\mathrm{PVAc}}/\phi_{\mathrm{PMMA}} = 1/1$), the amount of PECH that mixes with PVAc and PMMA is alike (see Table 3). These results are in agreement with our basic assumption and prove that the proportion of PVAC and PMMA involved in the blends is an essential parameter, which governs the distribution of PECH in this ternary system.

The previous DMTA measurements then reveal a two-phase system in the ternary blend at PECH contents smaller than 50 wt%. However, the presence at higher PECH contents of a true homogeneous ternary phase, or of two immiscible binary phases, which cannot be resolved by the closeness of their T_g, needs to be demonstrated. Indeed, let us take as an example the 47/13.5/39.5 and 56.5/32/11.5 blends. In Figs. 4 and 5, only one peak is observed but its width is narrower than that of previous blends (31 °C for the 47/13.5/39.5 blend and 23 °C for the 56.5/32/11.5 blend). Moreover, the fit of the curves by the aforementioned procedure gives a very good agreement using only one EMG function, which implies only one glass transition and the presence of one phase. However, we cannot dismiss the possibility of having two transitions that would remain undetected by the fitting procedure.

To answer this question, the experimental T_gs of PECH/

Table 3
Glass transition temperatures and distribution of PECH in each phase, for the ternary blends in the biphasic region

Blend	T_{gl} (°C)	T_{gh} (°C)	% of PECH in the PECH/PVAc phase	% of PECH in the PECH/PMMA phase
19/61/20	26	44	68	35
28.5/53.5/18	21	33	63	31
37/46/17	14	27	70	29
28.5/18/53.5	20	40.5	22	71
36/17/47	18	26	20	83
38/31/31	15	27	43	50
45.5/27/27.5	7	21	52	47

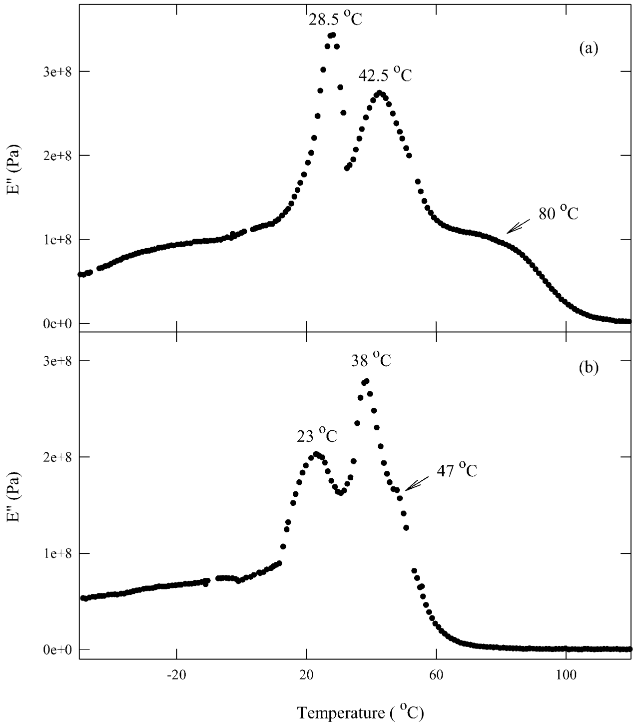

Fig. 7. Isochronal loss modulus curves at 10 Hz of PECH/PVAc/PMMA ternary blends. (a) 8.5/23.5/68 and (b) 9.5/67.5/23.

PVAc and PECH/PMMA binary blends were drawn in Fig. 8 and compared with the evolution of the glass transition temperature of ternary blends. For the ternary blends with a two-phase structure, it is seen that the two T_gs follow the binary lines, suggesting that the mixtures are made of PECH/PVAc or PECH/PMMA phases. For the 47/13.5/39.5 blend, the single T_g observed is on the binary curve of the PECH/PMMA blend and, for the 56.5/32/11.5 blend, the T_g is very close to the binary curve of the PECH/PVAc blend. If these two blends were made of a true ternary phase, the observed T_g should lie in between the two binary lines but not on one of them. Therefore, for the 47/13.5/39.5 and 56.5/32/11.5 blends, we conclude that we still have a two-phase system, but with very close T_gs. Actually, it is interesting to note that, for these compositions in PECH, the difference between the two binary lines is about 10 °C, at the limit of resolution of DMTA, and this is the reason for not observing two peaks by DMTA. The T_g of the 47/13.5/39.5 blend corresponds mainly to the PECH/PMMA phase and the T_g of the 56.5/32/11.5 blend to the PECH/PVAc phase. A simple calculation of the distribution of PECH in each phase shows that 70 wt% of PECH is mixed with PVAc in the 56.5/32/11.5 blend, and 77 wt% with PMMA in the 47/13.5/39.5 blend. The same tendency is then observed as with the previous blends.

At higher PECH contents (for example, 70–80 wt%), it is impossible to tell if there is really a true ternary phase. The experimental loss curves for the 70/15/15 and 84/8/8 blends can be fitted assuming there is one phase only in these ternary blends. Moreover, the experimental T_g lies in between the two binary curves, which is consistent with the assumption of a homogeneous blend. However, the binary curves at these PECH proportions are very close, such that the observation of a single T_g does not necessarily correspond to the presence of a single-phase. This problem is illustrated with the 84/8/8 blend where the discrepancy between the two lines is only 1.5 °C, certainly within the experimental error of the DMTA response (about 2 °C).

It has been demonstrated in Section 3.3 that the ternary PECH/PVAc/PMMA system contains two phases, corresponding to PECH/PVAC and PECH/PMMA phases, with a PECH content up to 60 wt%. At higher contents in PECH, it is possible to obtain a single-phase with an intimate mixing of the three components, but with the limitations mentioned earlier concerning the sensitivity of the DMTA technique. It appears from these results that the immiscible zone is larger than that observed for the same system by Champagne [9]. However, Champagne used DSC data only and considered that a sample was homogeneous if a single T_g was detected but DSC is less sensitive at small scales than DMTA and, therefore, the resolution of the glass transitions that it gives is inferior to that obtained by DMTA. This difference explains the discrepancies observed and, particularly, the more extensive heterogeneous zone found herein. Moreover, Champagne prepared his blends by casting from butanone-2 solutions and this factor also affects the miscibility of blends.

We have also shown in the previous sections that the distribution of PECH in the ternary PECH/PVAc/PMMA system is a strong function of the ϕ_{PVAc}/ϕ_{PMMA} ratio. Indeed, for a ϕ_{PVAc}/ϕ_{PMMA} ratio of 1/3, about 75% of the PECH mixes with PMMA and the remaining with PVAc; conversely, for a ϕ_{PVAc}/ϕ_{PMMA} ratio of 3/1, 75% of the

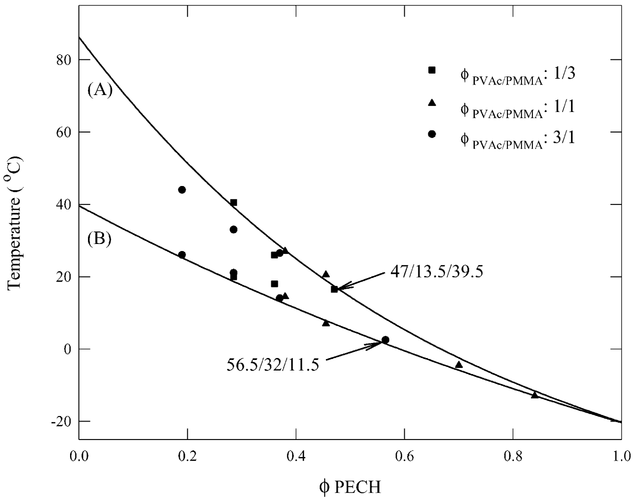

Fig. 8. Glass transition temperature of PECH/PVAc/PMMA ternary blends as a function of the weight fraction of PECH for various ϕ_{PVAc}/ϕ_{PMMA} ratios. The solid lines represent the experimental curves for binary blends: (a) PECH/PMMA and (b) PECH/PVAc.

PECH mixes with PVAc. Similarly, for a $\phi_{\mathrm{PVAc}}/\phi_{\mathrm{PMMA}}$ ratio of 1/1, equal amounts of PECH are shared in each phase of PECH/PVAC and PECH/PMMA. Table 3 illustrates this behavior since, for a $\phi_{\mathrm{PVAc}}/\phi_{\mathrm{PMMA}}$ ratio of 3/1, the amount of PECH mixed with PVAc varies between 63 and 70% whereas, for a $\phi_{\mathrm{PVAc}}/\phi_{\mathrm{PMMA}}$ ratio of 1/3, this amount varies between 29 and 17% (slightly less than 1/3). These values reveal the major role of the binary immiscible blend composition in controlling the distribution of PECH in the ternary system. This is possible if the interaction parameters $\chi_{\mathrm{PECH/PVAc}}$ and $\chi_{\mathrm{PECH/PMMA}}$ are alike, i.e. if PECH is shared between PVAc and PMMA without preference. The distribution then simply depends on the amounts available of each polymer.

Previous papers in this area dealt mainly with the determination of the nature of the phases of ternary blends, and their evolution with the amount of compatibilizer added, without giving the composition of each phase. In some cases, it could be calculated from the curves reported but this procedure implies several errors and has not been pursued here. Nevertheless, a study by Perrin et al. [8] on ternary (PVC/PPMA/PAMA) and PVC/poly(butyl methacrylate) PBMA/PAMA blends contains sufficient data to be compared with the PECH/PVAc/PMMA system.

For these two last systems, PVC acts as a compatibilizer and their ternary phase diagram show an immiscible zone corresponding to the coexistence of two phases made of PVC/PPMA and PVC/PAMA in the first case, and of two phases made of PVC/PBMA and PVC/PAMA in the second one. Perrin et al. calculated the distribution of PVC in each phase and found that, for the PVC/PPMA/PAMA system where $\chi_{\mathrm{PVC/PPMA}}/\chi_{\mathrm{PVC/PAMA}} \cong 1.7$, PVC mixes preferentially with PPMA; for the PVC/PBMA/PAMA system where $\chi_{\mathrm{PVC/PBMA}}/\chi_{\mathrm{PVC/PAMA}} \cong 1.2$, the PVC content of the phase depends on its PBMA/PAMA composition, i.e. on the $\phi_{\mathrm{PBMA}}/\phi_{\mathrm{PAMA}}$ ratio, as observed here for the PECH/PVAc/PMMA system. Therefore, it appears that the distribution of the compatibilizing agent depends, first, on the interaction parameter ratio involved and, second, when the two interaction parameters are equal, on the composition ratio of the two immiscible polymers.

In conclusion, this study has emphasized several factors affecting the behavior of ternary systems consisting of one immiscible polymer pair A/B and a compatibilizer C. In particular, the distribution of compatibilizer between the two immiscible phases, in the immiscible region, is not only determined by the difference between the thermodynamic interaction parameters of the two A/C and B/C pairs but it also depends on the composition of the immiscible polymer pair A/B (taken as the ϕ_A/ϕ_B ratio). Hence, when there are similar thermodynamic interaction parameters between the immiscible pairs A/C and B/C, the quantitative distribution of the compatibilizer follows the ϕ_A/ϕ_B proportion.

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