Nanoheterogeneities in PEO/PMMA Blends: A Modulated Differential Scanning Calorimetry Approach

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ABSTRACT: Modulated differential scanning calorimetry has been carried out on melt-mixed blends of poly(ethylene oxide)/atactic-poly(methyl methacrylate) (PEO/PMMA). Two PEO molecular weights have been used to prepare blends in the concentration range 10 to 80 wt % of PEO. Two glass transitions temperatures were observed for the fully amorphous blends, in the 10 to 30 wt % PEO range, using the differential of heat capacity with respect to temperature $[dC_p/dT]$ signal. The semicrystalline blends, 40, 60, and 80 wt % PEO, exhibited melting of PEO crystallites and the PEO-rich phase glass transition at -30 to $-50°C$. A second glass transition around $30°C$ was detected for the 40 wt % PEO blend when a cooling run was carried out, because PEO crystallization was avoided under these conditions. Therefore, heterogeneous amorphous phases were observed not only for fully amorphous blends, but also for semicrystalline ones. Further analysis of the dC_p/dT signal, obtained from the MTDSC experiments by fitting with Gaussian curves, showed that there is an interphase that varies in amount between 10 to 50 wt %. Correlation of the MTDSC observations with NMR spectroscopy and SAXS/SANS literature results are discussed. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 77: 2034–2043, 2000

Key words: blend; modulated differential scanning calorimetry; interphase, poly-(ethylene oxide); poly(methyl methacrylate)

INTRODUCTION

PEO/PMMA blends have been considered interesting materials to study because the semicrystalline nature of PEO, the weak interactions between these two polymers, and their large T_g difference provide a complex system for investigation. Conflicting reports concerning DSC results and miscibility conclusions for this blend are frequent in the literature.[1–4] Numerous approaches have been applied including small-angle X-ray and neutron scattering[3,5–7] and NMR relaxation time studies.[8–11]

PEO/PMMA blends are miscible in the melt[12] and are reported[4,13,14] to form "marginally" miscible blends in the solid state, when prepared by casting from solvents. It has been pointed out[5,6] that the interaction parameter is negative, but very low, effectively zero, and that the interaction parameter is also concentration and temperature dependent.

Crystalline PEO is obviously separated from the amorphous phase in blends with high PEO content, when cooled from the melt state. In general, compositions with more than 30 wt % PEO exhibit a crystalline phase. The existence of homogeneity at the molecular level in the amor-

phous phase in fully amorphous blends or in semicrystalline ones is the question remaining.

Conventional DSC studies have frequently reported[2,3] that one T_g, which obeys the Fox equation, is observed for this blend. However, numerous difficulties have been pointed out[4,9,14] by other authors. First of all, the PEO crystallization masks the T_g behavior, and precludes its easy observation for compositions with higher than 30 wt % PEO.[3] This is not only because the T_g is located near the melting region, but is also a consequence of the low sensitivity of conventional DSC measurements to detect T_gs. For the fully amorphous composition range, Liberman and Gomes[2] observed only one T_g. However, the DSC thermograms in their work start at 7°C, far from the PEO T_g, which is around −60°C. On the other hand, Li and Hsu[1] have shown a clear T_g at −36°C for samples with less than 50 wt % PEO. These samples were allowed to crystallize for up to one month. These authors also reported the existence of a second T_g masked by the melting endotherm.

Silvestre et al.[3] have reported that different PMMA tacticities influence the miscibility behavior. Atactic and syndiotactic PMMA are supposed to form a homogeneous amorphous phase, while isotactic PMMA produces phase-separated amorphous phases. Their SAXS results[3] for semicrystalline blends with a-PMMA indicated that the PEO crystalline lamellae are separated by amorphous and interphase regions containing PEO and PMMA. The interlamellar amorphous thickness was estimated to be around 20 nm for a blend with 40 wt % PEO. For this same blend, the parameter associated with interphase thickness yielded a value of 4 nm.

Russell et al.[7] showed with SAXS and SANS studies that, for higher than 70 wt % PEO blends, the average thickness of the amorphous phase was between 10 to 25 nm and the interphase (referred as the diffuse phase boundary) was about 2 nm, when measured by SAXS, but only 0.5 nm when obtained by SANS. This 1.5-nm difference was attributed to the existence of a region on the PEO crystal surface in which the PMMA is excluded.

Recent NMR results for PEO/a-PMMA blends have all agreed that no large-scale heterogeneities occur in the samples prepared by casting[9,11] or by melt-mixing.[8,10] Straka et al.[8] have shown for fully amorphous and semicrystalline blends that T_1^H relaxation data indicated homogeneity on a scale of 20–70 nm. From $T_{1\rho}^H$ relaxation mea-

surements they observed that at least part of the a-PMMA and PEO chains were intimately mixed in the amorphous phase, with the upper limit for the average dimensions of the pure rigid PMMA domains being approximately 6 nm. A similar estimation of the maximum size of the PEO domains was not made because of the two-component-like behavior of the PEO relaxation. Thus, the authors affirm that the presence of PEO-rich amorphous domains cannot be excluded.

Similarly, Schantz[10] demonstrated the homogeneity of amorphous PEO/PMMA blends down to a scale of at least 50 nm, studying samples prepared by melt mixing. Below this limit, the existence of heterogeneities, with average sizes higher than 2 nm, was proved. Amorphous nanoheterogeneities were also observed in semicrystalline blends. Schantz[10] discussed the status of an amorphous nanoheterogeneous structure in PEO/PMMA, and it should be mentioned that in his work the samples were allowed to crystallize at room temperature for 2 months.

The difficulties of using conventional DSC to investigate T_g in PEO/PMMA blends has already been discussed. Moreover, the domains sizes in PEO/PMMA blends observed by NMR techniques in melt-mixed samples were larger than 2–6 nm, but probably smaller than 50 nm in the amorphous. According to Kammer et al.[15] the typical sensitivity of conventional DSC to heterogeneities in polymer blends is approximately for domains larger than 50 nm; therefore, for the PEO/PMMA blends, this could bring some limitations. Another major difficult in using conventional DSC is the occurrence of physical relaxation over the glass transition. To overcome these kinds of difficulties in the DSC method, modulation of the temperature was introduced. MTDSC is a new and powerful tool that can be employed[16] in the study of polymer blends. The modulation permits, for example, the extraction of the C_p signal unperturbed by the physical relaxation at T_g.[16] The purpose of this work is to apply the MTDSC method to study the phase behavior of PEO/PMMA blends prepared by melt mixing using PEO of two different molecular weights and atactic PMMA. The PEO molecular weights were chosen so that one was in the same range as the PMMA molecular weight and the other was much higher. Thus, the influence of PEO molecular weight on miscibility could also be investigated.

MTDSC, first introduced by Reading,[16,17] has proved to be able to measure the glass transition temperature independent of the thermal his-
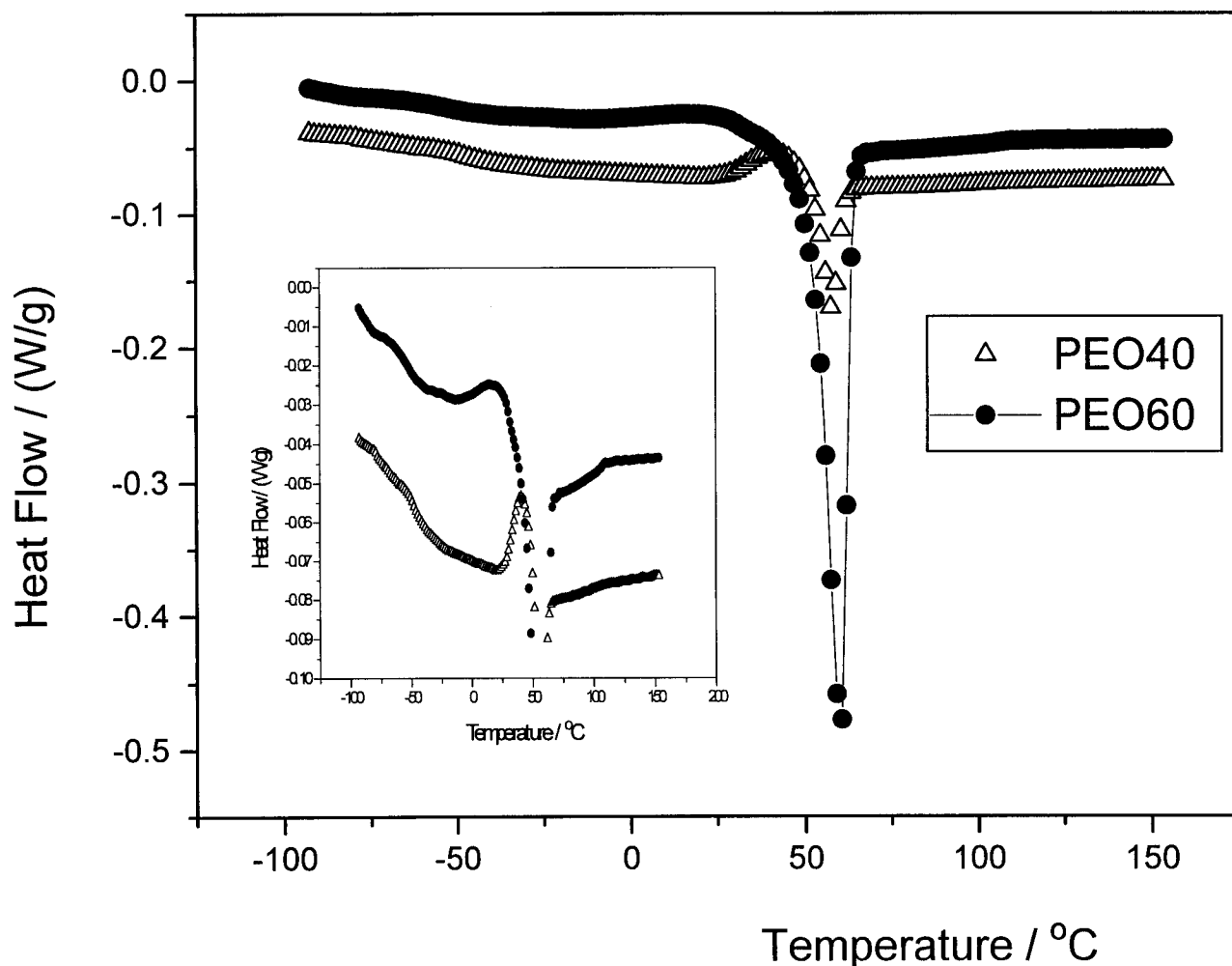
Figure 1   DSC curves (heat flow signal) for the high molecular weight PEO/PMMA blends at 40 and 60 wt % PEO.

tory.[18] The maximum of the differential of heat capacity signal with respect to the temperature has been used by Song et al.[19] to overcome the difficulties of overlapping glass transitions. The behavior of multicomponent polymer materials have been quite extensively studied by this group,[19–22] and the modulation has proven to afford a higher resolution in the detection of heterogeneities. They have introduced an approach that permits the calculation of the weight fraction of each polymer in an interphase. Such an approach will be developed further with these PEO/PMMA blends.

EXPERIMENTAL

Atactic PMMA (Aldrich), with a nominal molecular weight of 120,000, showed a GPC weight-av-

erage molecular weight M_w of 100,000, and a polydispersity index of 2.5. PEO, also from Aldrich, with a nominal M_v value of 4,000,000 was characterized by GPC to have and M_w value of 1,400,000. However, difficulties in dissolving and filtering this polymer indicated the presence of insoluble high molecular weight material. It is known, however, that this sample is completely soluble in toluene, given time. The second PEO sample quoted as having an M_v of 100,000 yielded an M_w (GPC) value of 150,000 with a polydispersity index of 6.4. A Polymer Laboratories GPC-210 with Plgel 2x mixed bed-B columns and DMF at 80°C, plus a refractive index detector was used to carry on these determinations.

Melt mixing was performed using a Haake Rheocord 90 at 180 and 170°C for high and low molecular weight PEO samples, respectively, over a 10-min period and at 40 rpm. The compositions
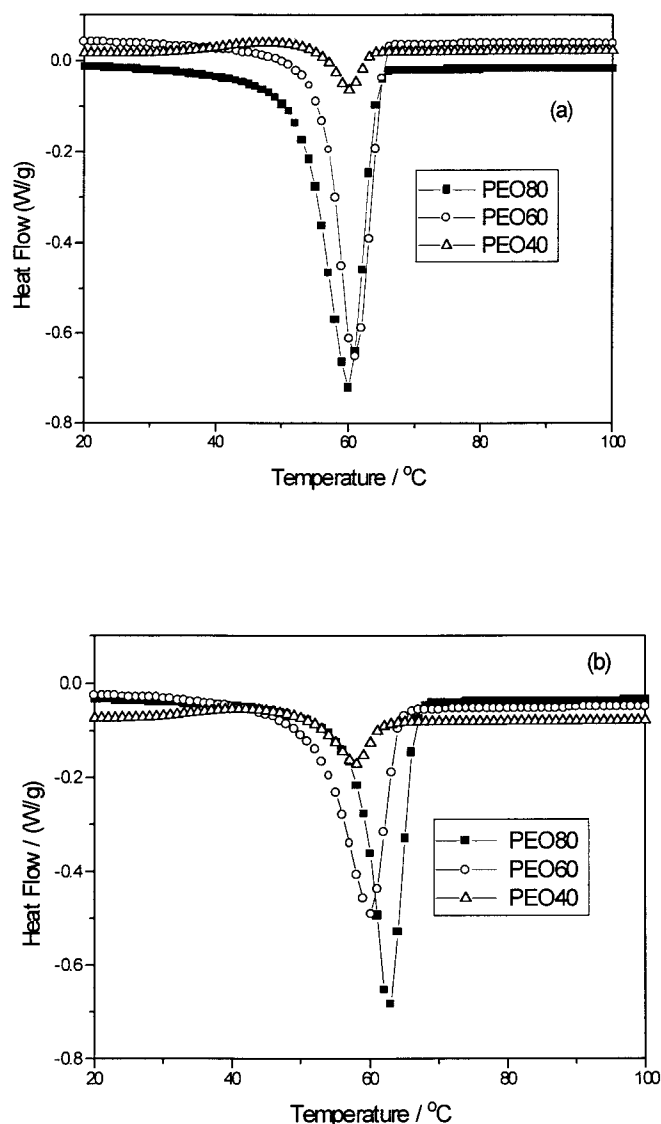
Figure 2 DSC curves (heat flow signal) for the low and high molecular weight PEO/PMMA blends at 40, 60, and 80 wt % PEO.

prepared were 10, 20, 30, 40, 60, and 80 wt % of PEO.

MTDSC experiments were performed using a TA Instruments model 2920 calorimeter. Samples of approximately 10 mg were sealed in aluminium crucibles and placed in the furnace under a flux of nitrogen (70 mL/min). The MTDSC procedure consisted of first annealing the sample at 160°C for 5 min, followed by quenching (40°C/min) in the DSC pan and heating at 3°C/min, with a modulation amplitude of 0.5°C and a period of 60 s. This procedure seeks to avoid different thermal histories between the melt-mixed and pressed materials. PEO crystallization of compositions with more than 30 wt % of PEO was observed during cooling, and also recrystallization during heating was observed, but only for the 40 wt % PEO. The above-mentioned procedure was designed to favor the study of the amorphous phases, even when they were in the presence of crystalline phases. Quenched samples have lower degrees of crystallization. The principal interest in fully amorphous samples is also expressed by two choices: first the amorphous range of concentration is explored in more detail with compositions at 10, 20, and 30 wt % PEO. On the other hand, the semicrystalline samples with 40 and 60 wt % of PEO were followed during a cooling scan in an attempt to detect the T_g transition before PEO crystallization. The pure homopolymers were also analyzed under the same conditions as those for the blends, and the results for 0 and 100 wt % PEO will be reported.

The difficulty in observing, with the total heat flow signal, the T_g behaviors of the samples is demonstrated in Figure 1, in which amplified curves are also shown. Not only does melting mask the second T_g, as could be seen by the difference in ΔC_p after and before melting, but also the first T_g is difficult to observe without very high amplification. As demonstrated pre-

Table I   Melting Data for PEO/PMMA Blends

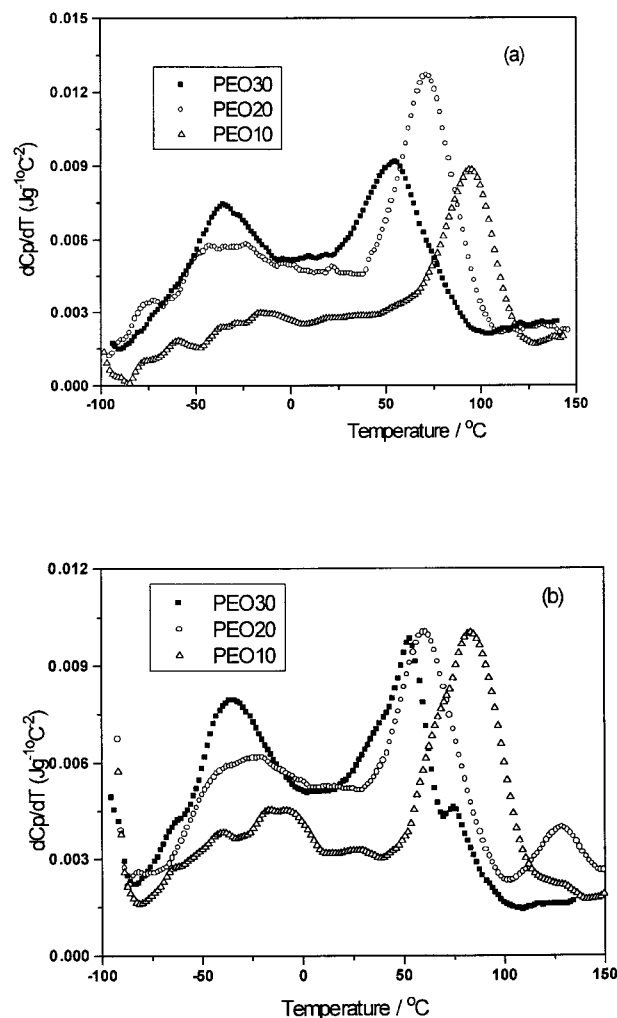| wt % PEO	PEO $M_w = 1.5 \times 10^5$				PEO $M_w = 1.4 \times 10^6$			
	T_m °C	ΔH_f J/g	Blend Cryst. %	PEO Cryst. %	T_m °C	ΔH_f J/g	Blend Cryst. %	PEO Cryst. %
100	60	138	—	70	68	138	—	70
80	60	103	52	65	63	85	43	54
60	61	92	47	78	60	72	37	61
40	60	8	4	10	58	8	4	10

Figure 3 dC_p/dT vs. temperature curves for the low and high molecular weight PEO/PMMA blends containing 10, 20, and 30 wt % PEO (fully amorphous).

viously,[19–21] the MTDSC differential of heat capacity vs. temperature signal permits the observation of glass transitions with better accurancy and helps overcome possible transition overlap. The principal results of this study will be presented using this signal. Moreover, the dC_p/dT signal will be further analyzed by a peak resolution technique using Gaussian curves to fit the data. The main goal of this will be the extraction of apparent heat capacities associated with each main phase in the system, which permits the subsequent evaluation of the polymer content of the interphase regions.

RESULTS AND DISCUSSION

To analyze the results presented below, the two ranges of concentration will be shown separately:

the semicrystalline samples (40, 60, and 80 wt % PEO) and the fully amorphous blends (10, 20, and 30 wt % PEO). The two different sets of blends prepared with the 150,000 and 1,400,000 PEO are presented together for ease of comparison.

Figure 2 shows the heat flow signals for the melting endotherms of the semicrystalline blends. In Table I are presented the data obtained for the three semicrystalline blends and for pure PEO. The two pure PEOs exhibit the same degree of crystallization after quenching. The blends with low molecular weight PEO exhibit a constant T_m at 60°C (±1°C), as opposed to the high molecular weights PEO blends that show a melting depression and a lower degree of crystallinity (in the cases of 80 and 60 wt %). This behavior can be related to the greater difficulty for chain organization to occur (entanglement) in the case of high molecular weight PEO when forming a blend.
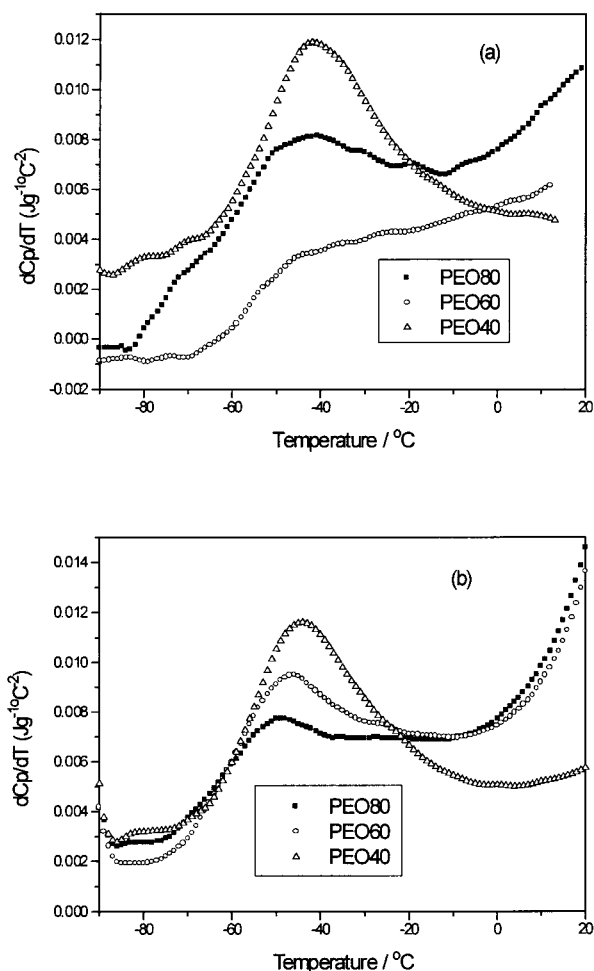

Figure 4 dC_p/dT vs. temperature curves for low and high molecular weight PEO/PMMA blends containing 40, 60, and 80 wt % PEO (semicrystalline).
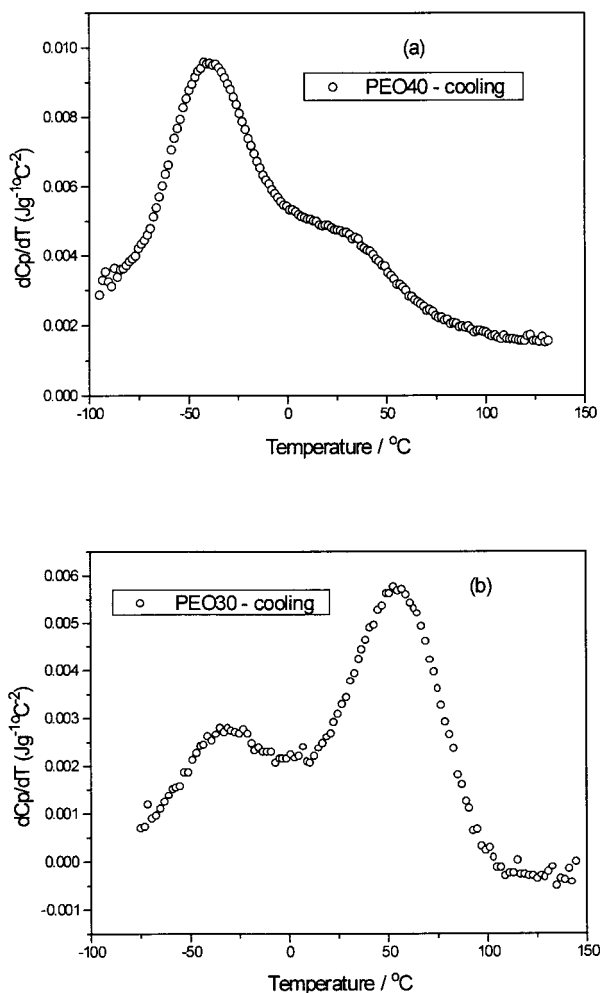
Figure 5 dC_p/dT vs. temperature curves on cooling for low molecular weight PEO/PMMA blends 30 and 40 wt % PEO.

Glass Transition Determinations from the dC_p/dT Signal

Figure 3 shows the differential of heat capacity signal over the entire temperature range studied for the fully amorphous concentrations. The two peaks are attributed to the glass transition of a PEO-rich phase (T_g^1) and a PMMA-rich phase (T_g^2). In these curves, it should be noted that T_g^2 shows a pronounced decrease over the composition range as well as in relation to PMMA (T_g was 121°C for these experimental conditions). The T_g^1 values are less influenced by the composition remaining between −30 and −50°C for these fully amorphous blends. However, no high accuracy is possible for the 10 wt % PEO, because the signal-to-noise ratio is no longer negligible.

Also, using the differential of heat capacity signal, the MTDSC curves for the semicrystalline

blends were inspected for T_g values. Figure 4 shows the low temperature range for the semicrystalline blends in which T_g^1 was observed. The low mol wt 60 wt % PEO blend exhibited a profile in which a peak was not clearly defined. It should be noted that this sample had the highest degree of crystallinity (see Table I). Therefore, this high level of crystallinity is responsible for the difficulty in observing T_g^1. For the high molecular weight PEO blends the signal evolution permitted easy detection of T_g^1. Therefore, the investigation of the differential heat capacity signal allowed the determination of T_g^1 values, associated with PEO-rich phase, for all blends prepared, with limitations in accurancy in a few cases.

The high temperature T_g^2 was not detected in the differential heat capacity curves on heating for the semicrystalline blends. The region is completely masked by the recrystallization/melting of PEO. To try to have access to T_g^2 in this range of PEO concentration, a modulated cooling experiment was performed, and Figure 5(a) presents the curve for the low mol wt PEO 40 wt % blend. For comparison, the cooling run for the fully amorphous 30 wt % PEO blend is shown in Figure 5(b). The same T_g values were found in cooling and heating for fully amorphous blends, such as 30 wt % PEO, which allowed determination of the T_g^2 value from the cooling run. The determination of T_g^2 in the cooling experiment, shown in Figure 5(a), was performed by using the Gaussian fitting procedure already mentioned.[19−21] One Gaussian was centered at −40°C, which corresponds to the T_g^1 value obtained in heating, and the other was

Table II T_g **Data for the PEO/PMMA Blends**

wt % PEO	T_g by Fox eq. °C[a]	PEO $M_w = 1.5 \times 10^5$		PEO $M_w = 1.4 \times 10^6$	
		T_g^{1b} °C	T_g^2 °C	T_g^1 °C	T_g^2 °C
100	−57	−57	—	−57	—
80	−36	−47	—	−52	—
60	−9	−41	—	−49	—
40	24	−40	33[c]	−46	36[c]
30	43	−33	54	−37	51
20	65	−39	72	−31	60
10	91	—[d]	94	—[d]	84
0	121	—	121	—	121

[a] Calculated from total concentration of the components.
[b] Accuracy was ± 2°C.
[c] Obtained from a MTDSC cooling run.
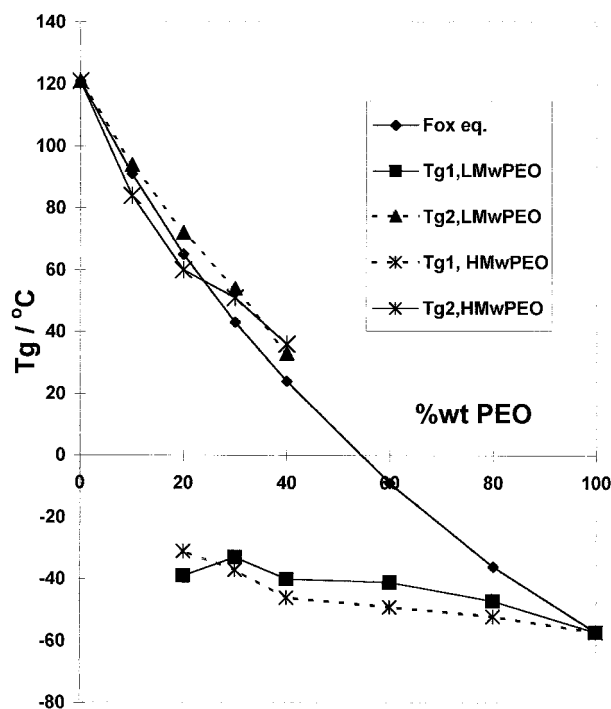[d] Lack of accuracy prevented determination.

Figure 6 T_g results from DSC to low and high molecular weight PEO/PMMA blends ($T_g{}^1$ and $T_g{}^2$) and calculated by Fox equation.

centred at 33°C, which is attributed to T_g^2. The same procedure was used for the high molecular weigth PEO 40 wt % blend.

The values of T_g^1 and T_g^2 obtained from the differential of heat capacity signal and analysed by the TA software, as well as the T_g calculated from the Fox equation,[23] using the total concentration of the components, are shown in Table II and also in the Figure 6.

T_g^1 exhibits a very small increase between -30 and -50°C in a large range of blend compositions. Li and Hsu[1] have already observed the stability of a low temperature T_g, at -36°C. This result can be understood in the light of the SANS/SAXS results of Russell et al.[7] These authors showed the existence of an interfacial zone, when PEO crystallites are present, that is comprised of an essentially amorphous PEO region. Moreover, they observed the PMMA-rich phase to be located between the crystalline lamellae. Therefore, the MTDSC T_g^1 and T_g^2 results and the interfacial SAXS/SANS results[7] point to the existence of two amorphous phases, one of them with a very low PMMA content (related to T_g^1) and the other similar to what can be expected from a typical miscible blend which follows the Fox equation (related to T_g^2). The new information emerging from the

MTDSC data is that this highly rich PEO phase, observed[7] as a narrow boundary around lamellae in semicrystalline samples, is actually also present at a substantial concentration in fully
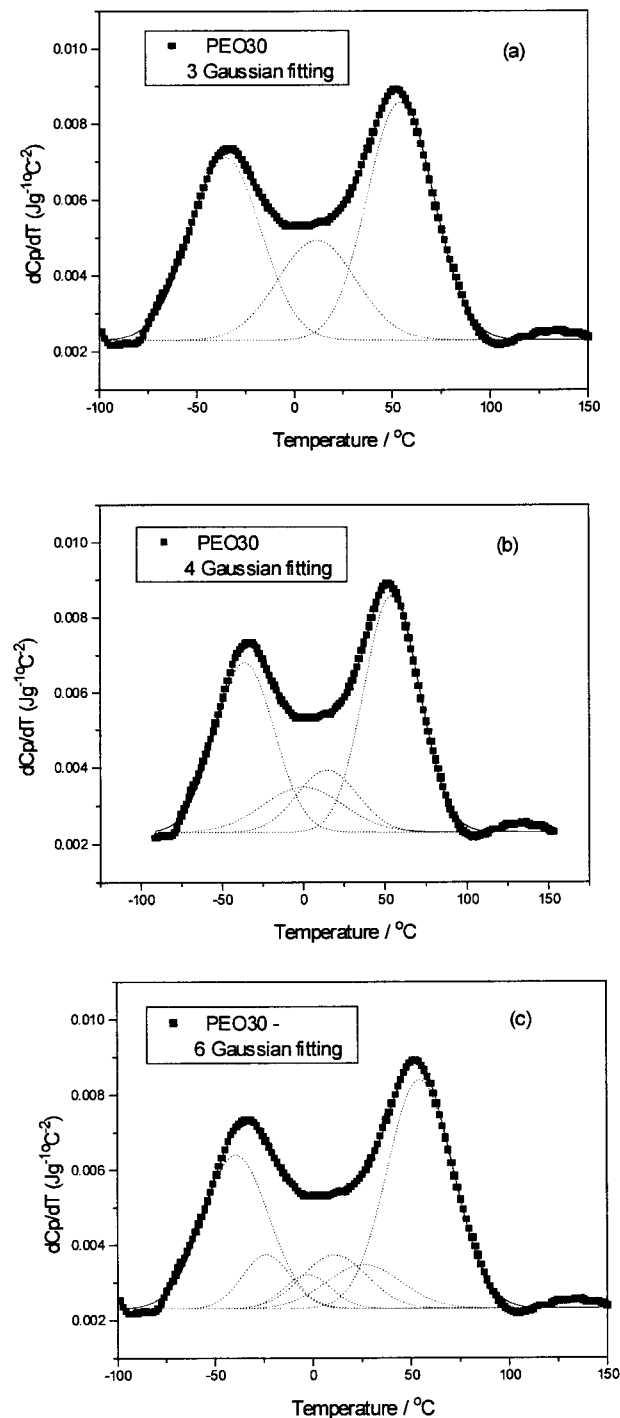

Figure 7 Gaussian fitting (three, four, and six lines) to low molecular weight PEO/PMMA blend 30 wt % PEO.

Table III   Gaussian Fitting Results for Low Mol Wt PEO 30 wt % Blend

No. of Gaussian Curves	T_g^1			T_g^2		
	Center °C	Half Width °C	ΔC_p^1 (J/g °C)	Center °C	Half Width °C	ΔC_p^2 (J/g °C)
3	−35	36	0.22	54	34	0.26
4	−37	35	0.19	55	33	0.24
6	−36	30	0.18	53	34	0.28

amorphous blends. Thus, it seems that not only has PEO a great tendency to arrange itself in a crystalline structure, but also has a tendency to form an amorphous phase, almost excluding PMMA. This structural tendency competes with the interactions[13] that promote the mixing in the PEO/PMMA blends.

The observation of two T_gs in the fully amorphous samples and at least for the 40 wt % PEO semicrystalline sample indicates that the amorphous phase in the PEO/PMMA blend is composed of a PEO-rich phase and a PMMA-rich phase as well as a significant amount of interphase, as indicated by the profile of the differential of heat capacity vs. temperature curves in Figure 3. This is an important information obtained from the MTDSC experiment that is not produced in a conventional DSC study, and the quantitative approach that permit calculation of the amount of material in interphase[20] will be applied to the PEO/PMMA blends below.

Interphase Content

Between the two peaks, the signal does not return to the same base line as at the extremities beyond the glass transition regions. Such a profile between the peaks in Figure 3 indicates that as the concentration of PEO increases, a higher amount of material is located in an interphase with T_g values between T_g^1 and T_g^2. The experimental points were fitted with an increasing number of Gaussian curves ranging from 3 to 6 or 7. The best fit was chosen in accordance with a phenomenological criterion, in which the half width of the two principal Gaussian peaks (associated with the T_g^1 and T_g^2 peaks positions) were minimized. Figure 7 shows an example of the fitting procedure, with an increasing number of Gaussian curves applied to the low molecular weight PEO 30 wt % blend. In Table III, the results of the three fittings in Figure 7 are shown indicating

through the half width value that the best fit to T_g^1, is obtained with six Gaussian curves. The best results obtained from the peak resolution technique for all the PEO/PMMA blends are shown in Table IV. A good agreement was attained between the center of the two mainly Gaussian lines and the T_g^1 and T_g^2 extracted from TA analysis software, when the peak is clearly defined, as can be seen by comparing Table II and Table IV data.

The final purpose of the fitting treatment is to evaluate the content of components in the interphases. In this calculation the apparent heat capacity value obtained for the T_g^1 and T_g^2 transitions is related to the heat capacity expected for the transition at this temperature, considering

Table IV   Gaussian Best Fit Results

wt % PEO	PEO			
	Center °C	ΔC_p^1 (J/g °C)	Center °C	ΔC_p^2 (J/g °C)
		$M_w = 1.5 \times 10^5$		
100	−57	0.35	—	—
80	−47	0.06	—	—
60	−41	0.09	—	—
40	−41	0.18	33	0.13
30	−37	0.19	55	0.24
20	−44	0.14	72	0.32
10[a]	—	—	—	—
0	—	—	119	0.29
		$M_w = 1.4 \times 10^6$		
100	−57	0.26	—	—
80	−52	0.06	—	—
60	−50	0.10	—	—
40	−45	0.18	34	0.10
30	−35	0.22	52	0.20
20	−36	0.14	61	0.27
10[a]	—	—	—	—
0	—	—	119	0.29

[a] Lack of accurancy prevented determination.

Table V   Weight Percent of Components at Interphase

wt % PEO	PEO $M_w = 1.5 \times 10^5$			PEO $M_w = 1.4 \times 10^6$		
	PEOi %	PMMAi %	Total %	PEOi %	PMMAi %	Total %
20	3	7	10	2	20	22
30	6	21	27	2	30	32
40	18 (8)[a]	37	55 (45)[a]	18 (8)[a]	42	60 (50)[a]

[a] 10 wt % of PEO forms crystalline phase.

the composition and the pure amorphous polymers heat capacities. Therefore, the following relation can be applied.[20]

$$\delta_i = w_{i0} - [\Delta Cp^i/\Delta Cp_{i0}] \qquad (1)$$

in which δ_i is the weight fraction in the interfacial region of polymer i, w_{i0} are the weight fractions of the polymers in the blend, ΔC_p^i is the increment of apparent heat capacity in the T_g region, and ΔC_{i0}^p *is the increment of heat capacity in the T_g region before mixing.*

Table V presents the wt % results of PEO and PMMA in the interphases for the 20 and 30 wt % fully amorphous samples and the 40 wt % semicrystalline sample, in which T_g^2 was determined during cooling. The other semicrystalline samples did not permit this kind of analysis, because it was not possible to observe T_g^2, and the T_g^1 value is related only to the PEO content in the amorphous phase. It should be noted that the 40 wt % PEO sample was observed to be 10% crystalline (Table I). Therefore, 10 wt % of PEO is not included in the PEO-rich phase (at T_g^1) as it is actually forming PEO crystals.

A high content of material in the interphase, varying between 10 to 50 wt % (Table V), is observed for these PEO/PMMA blends. The interphase is characterized by mixtures of PMMA and PEO with intermediate T_g between T_g^1 and T_g^2. The main phases and the interphase, or in other words, the heterogeneities of this blend, are probably distributed in a nanoscale with dimensions lower than 50 nm, as has been observed by NMR studies.[8,10]

Between the two sets of blends, with different PEO molecular weight, the high one exhibited a large content of material at interphase (Table V). This result indicates a high distribution of heterogeneities for the high molecular weight PEO, which can be understood if one considers the PMMA-rich phase, represented by T_g^2, as the expression of the "marginally miscible" phase that obeys the Fox equation. Any other phases detected are representative of heterogeneities and if they are more concentrated, the greater is the blend heterogeneity. The high content of interphase obtained with the high molecular weight PEO is probably related to reduced miscibility with increased molecular weight.[15]

CONCLUSIONS

The experimental conditions used for this MTDSC study, i.e., quenching from the melt state, avoiding long times for crystallization, are the best conditions to maximize miscibility observed in PEO/PMMA solid blends. However, the MTDSC approach, with the use of the reversing heat capacity signal, clearly pointed out the heterogeneous nature of the amorphous blends and the amorphous phase in the semicrystalline blends. The differential heat capacity permits not only the observation of two T_gs but the analysis of the interphase between the PEO and PMMA-rich phases as well. This technique represents a new contribution to the study of polymer blends that cannot be obtained from conventional DSC.

A nanostructure heterogeneous picture now emerges from the correlation of the MTDSC data with the SANS/SAXS[7] and NMR[8,10] results recently published. As mentioned before, Schantz[10] and Straka[8] have suggested the existence of heterogeneity in PEO/PMMA blends with dimensions lower than at least 50 nm. Russell et al.[7] have shown the presence of a PEO-rich region. The MTDSC data agreed with this PEO-rich region with a glass transition temperature (T_g^1) detected in the overall range of blend compositions. On the other hand, a PMMA-rich phase with a T_g^2 that nearly follows the Fox equation was observed. The status

of a partially miscible system was demonstrated by MTDSC, and the weight fraction at the interphase was obtained. The content of material in the interphase varied between 10 to 50 wt %, which indicates a high distribution of the PEO and PMMA between the two main phases and the interphase connecting them.

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