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Relaxation Studies in PEO/PMMA Blends

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ABSTRACT: To study the influence of PEO on the relaxation process of PMMA, the real and imaginary parts of the permittivity, ϵ' and ϵ'', of PEO/PMMA blends (with PEO contents up to 25 wt %) were measured as a function of frequency and temperature, and the results obtained were compared with those of pure PMMA. It is shown that the presence of PEO broadens the relaxation process of PMMA and increases its relaxation strength. The lower T_g component (PEO) has a plasticizing effect on the relaxation of PMMA, for the blends with 10 and 15% PEO. The splitting of the $\alpha\beta$ process of PMMA seems to be affected by the presence of the second component, being the onset of the α relaxation shifted to lower temperatures with the increase of PEO concentration. The DSC thermograms show a single glass transition temperature, which is displaced to lower temperatures with the increase of PEO content, and no evidence of crystallinity was found. The presence of a singular broad transition in the 20% PEO blend, evidenced in both dielectric and calorimetric experiments, may be associated with the merging of the α and β process and to concentration fluctuations, confirming that this blend lies in the border of the miscibility/immiscibility region.

Introduction

It is well-known that immiscibility is the rule in polymer blends, and finding miscible pairs is still a challenge for those who work with these materials. Yet, even for the miscible blends there are some uncertainties about the miscibility level, depending upon the experimental technique used.

One of the most studied polymer blends is poly(ethylene oxide) (PEO)/poly(methyl methacrylate) (PMMA). A variety of techniques have been employed establishing that PEO and PMMA form a single-phase blend in the melt.[1−4] As PEO is a semicrystalline polymer, the blends with PEO concentrations higher than 20−30% show amorphous (PEO/PMMA) and crystalline (pure PEO) phases. Using vibrational spectroscopy, Ramana Rao et al.[5] came to the conclusion that, upon blending, PEO, originally helical, takes a planar zigzag structure. The morphology of the blends is influenced by the molecular mass of PEO and blend composition. In general, both crystallization rate and degree of crystallinity decrease with the increase of PMMA content.[6] Combined SANS/SAXS experiments performed in blends having more than 50% PEO[7] lead to the conclusion that there exists an interfacial region at the surface of the PEO crystal from which PMMA is excluded. The miscibility is also strongly influenced by the tacticity of PMMA. Atactic and syndioctatic PMMA were found to be incorporated into the amorphous phase between the crystalline PEO lamellae,[3,7] whereas on blends with isotactic PMMA, the structure consists of alternated crystalline and amorphous lamellae of PEO, with the PMMA segregated in interfibrillar regions.[3] That is the reason why atactic and syndiotactic PEO/PMMA molten blends give rise to single-phase blends when quenched directly in differential scanning calorimetry, whereas in isotactic PEO/PMMA blends, two different phases were found.[3,7]

Rao and co-workers[5] have classified the compatibility of this blend as more “physical” than “chemical”. The interactions between the blend constituents are of the van der Waals type,[1,3,5,8,9] and no strong specific interactions are present. The Flory−Huggins interaction parameter was found to be approximately zero within the experimental error.[7,10,11] This is the reason why Colby[1] designates this system as a “marginally miscible blend”, claiming that the miscibility has not been irrefutably proven. Wu[12] calculated the average free volume of different PEO/PMMA blends, covering a large range of compositions; the results indicated a large dilation of free volume on blending, suggesting that the free volumes are largely influenced by segmental conformation and packing rather than specific interactions.

While most of the published studies give particular attention to PEO/PMMA blends where poly(ethylene oxide) is the main component,[3,5,7,13] in this work low PEO content blends will be investigated.

NMR studies performed in blends with 10 and 18% PEO content[14] revealed that the blends are completely homogeneous down to a scale of at least 50 nm. These results are in agreement with IR, WAXS, and NMR studies of 10 and 30% PEO blends that show homogeneity on a scale of 20−70 nm.[15] Below these limits nanoheterogeneities appear. Parizel et al.[16] found slightly different results detecting by NMR a small crystalline content (5 wt %) in 20% PEO blends which was absent in blends containing 5 and 10% of PEO. No evidence of

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these kinds of heterogeneities was found by DSC.[16] Li and Hsu[17] detected by DSC phase separation in blends with PEO contents of 25 and 30%. In a very recent study in low molecular weight PEO/PMMA blends, Baldrian et al.[18] found, by DSC and WAXS, complete miscibility for PEO concentrations up to 20%. Crystallites were detected for concentrations of PEO higher than 30%. So, the complete miscibility and the one-phase behavior seem to occur in compositions less than 20%. Above this value there is some disagreement between different authors.

Infrared spectra show a conformation change in PEO, blended with PMMA, from gauche to trans, in such way that the trans state becomes the dominant component for blends containing low concentrations of PEO (16, 25, 30, and 42%).[17]

There is a general consensus that there is a slowing down of mobility of PEO segments upon blending, while the PMMA backbone mobility is increased. Colby[1] studied the 20.2% PEO blend by oscillatory shear rheometry and came to the conclusion that, for the same $T - T_g$, the PMMA relaxes slower in the blend than in pure PMMA, while PEO relaxes faster in the blend, which represents a new physics not yet explained.

The most common criterion for miscibility is the detection of a single T_g, at a temperature intermediate of that of pure polymers. This is the reason why differential scanning calorimetry (DSC) has been one of the most widely used techniques in determining miscibility. More recently, dielectric relaxation spectroscopy has been claimed to be more sensitive for measuring the degree of miscibility: "a particular blend may be judged compatible by DSC but heterogeneous by dielectric measurements".[19]

In this work we investigate PEO/PMMA blends, with PEO contents up to 25 wt %, by both differential scanning calorimetry and dielectric relaxation spectroscopy. To our knowledge only few studies using dielectric relaxation spectroscopy (DRS) have been published and refer to blends with contents of PEO ≥ 70%.[20,21] It is our purpose, by using DRS, to study the effect of both temperature and frequency on the dynamics of amorphous PEO/PMMA blends, namely, how the PMMA dynamics is affected by the mixing with PEO, contributing to the understanding of this issue.

Experimental Section

Materials and Sample Preparation. The poly(methyl methacrylate) used was an Aldrich product (catalog no. 18, 223-0) with molecular weight of 120 000. The poly(ethylene oxide) was from Polysciences Inc. (catalog no. 06105) with M_w = 300 000. Both polymers were used as received.

Blends of compositions of 10/90, 15/85, 20/80, and 25/75 wt % (PEO/PMMA) were prepared by solution casting in a common solvent (dichloromethane, HPLC, from Aldrich). The films were kept in a vacuum oven at temperatures successively higher: 41, 72, 95, and 105 °C, remaining 1 week at each temperature. This procedure was adopted to ensure the removal of the solvent without producing bubbles in the samples.

The blends were analyzed by polarized light microscopy, at room temperature, and no heterogeneities were found.

Dielectric Relaxation Spectroscopy. The dielectric measurements were performed using a Hewlett-Packard impedance analyzer HP 4282A, covering a frequency range from 20 Hz to 1 MHz. The experiments were performed within a temperature range from −40 to +140 °C. The temperature control was assured by the QUATRO Cryosystem, manufactured by Novocontrol GmbH. The PEO/PMMA samples, with an approximate thickness of 70 μm, were sputtered at both sides with a gold layer to optimize the electrical contact. The films were kept between two gold-plated stainless steel electrodes (diameter 20 mm) of a parallel plate capacitor. This sample cell (BDS 1200) is mounted on a cryostat (BDS 1100) and exposed to a heated gas stream being evaporated from a liquid nitrogen dewar. The temperature in the cryostat is measured by a platinum sensor (PT 100), which is directly connected to the lower electrode. These modules were also supplied by Novocontrol GmbH.

Immediately before the beginning of the experiment the blends and pure PMMA were annealed for 2 h, at 140 and 160 °C, respectively.

The dielectric spectra were obtained in the cooling mode, and a frequency scan was performed every 5 °C. Before each frequency scan, the samples were kept at each temperature step at least 15 min, making sure that the temperature was constant to within ±0.02 °C.

The Havriliak−Negami (HN) model funtion[22] was used for the data analysis. In the frequency domain the HN function reads

$$\epsilon^*(\omega) - \epsilon_\infty = \Delta\epsilon/(1 + (i\omega/\omega_0)^a)^b \tag{1}$$

where $\omega_0 = 2\pi.\ f_0$ is the characteristic HN frequency closely related with f_{max}, the frequency of maximal loss. From this frequency a charateristic relaxation time $\tau = 1/\ (2\pi f_{max})$ can be obtained; ϵ_∞ is the real permittivity for high frequencies compared to f_{max}, i.e., $\epsilon_\infty \cong \epsilon'$ $(f \gg f_{max})$; $\Delta\epsilon$ is the dielectric intensity or relaxation strength, measuring the difference of the real permittivity at low and high frequencies with respect to f_{max}. The curve shape parameters a and b ($0 < a < 1$, $0 < ab < 1$) describe the slopes of the ϵ'' curve below and above the frequency of the peak: $a = \partial \log \epsilon''/\partial \log f$, for $f \ll f_0$, and $ab = -\partial \log \epsilon''/\partial \log f$ for $f \gg f_0$; the a value is related to the broadness of the relaxation while b describes its asymmetry (Debye behavior is given by $a = ab = 1$).

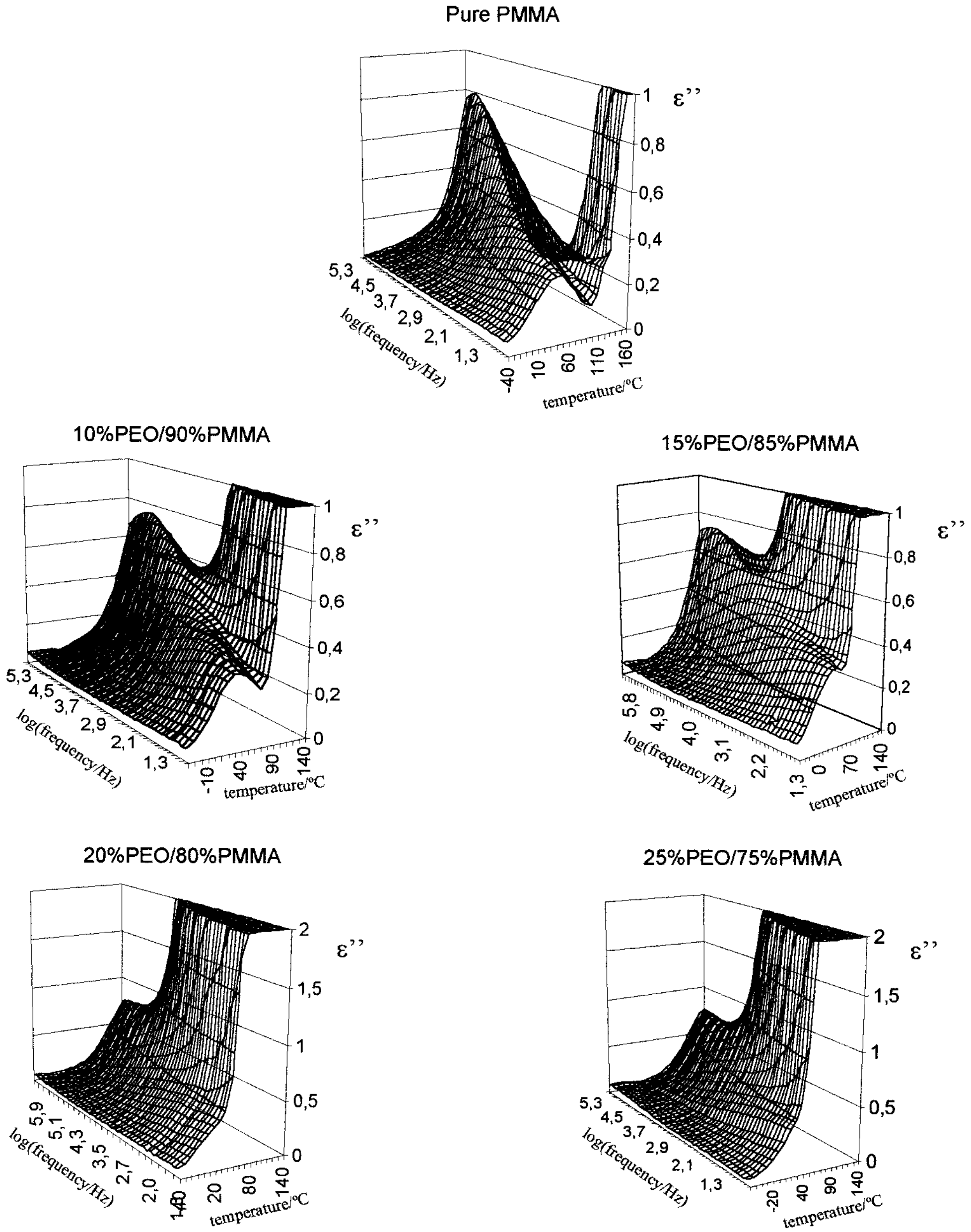
The dielectric data in frequency domain were fitted by eq 1, and the fitting parameters are $\Delta\epsilon$, a, b, and τ. The conductivity contribution for the dielectric loss was described by $\epsilon''(\omega) = \sigma_{dc}/(\epsilon_0\omega^c)$, where σ_{dc} and c are fitting parameters: σ is related to the dc conductivity of the sample, and c describes the broadening of the relaxation time distribution for the dc conductivity.

Differential Scanning Calorimetry. A Setaram differential scanning calorimeter, DSC 121, was used for the thermal analysis of the pure polymer and the blends. Pure PMMA and the blends were annealed, for 15 min, at 160 and 140 °C, respectively, and cooled to −40 °C, at 1 °C/min; this cooling procedure was adopted in order to approximate the experimental conditions used in DRS experiments. Afterward the samples were heated at 20 °C/min, and the thermograms were recorded. The subambient temperatures were achieved using liquid nitrogen, and during the experiments the sample holder was continuously purged with argon.

It must be noted that an annealing period of 15 min was found to be enough in order to obtain reproducible results (≅14 mg samples were used). No differences were observed when longer periods of annealing time were used.

Results

A. Dielectric Relaxation Spectroscopy. 1. Pure PMMA. The dielectric relaxation of pure PMMA has received much attention, and the studies published before 1967 have been reviewed.[23] Below the glass transition temperature the observed relaxation process of PMMA is a β process, whose origin is the partial rotation of the $-COOCH_3$ side groups around the C−C bonds linking these side groups to the main chain. This local process with the increase of temperature becomes "locally coordinative"[24] because the side chain movement implies some coordinated motion with neighboring side chains. At high temperatures, above T_g, this process


Pure PMMA

10%PEO/90%PMMA

15%PEO/85%PMMA

20%PEO/80%PMMA

25%PEO/75%PMMA

Figure 1. Dielectric loss spectra for the pure PMMA and for all the blends: for the pure polymer the temperature range is from −40 to +160 °C and for the blends is from −40 to +140 °C; the frequency range is from 20 Hz to 1 MHz.

merges with the α process (a cooperative process related to the micro-Brownian motions of the main chain backbone), into a complex $\alpha\beta$ process, in which the side group rotation is cooperative with the main chain motion.

The dielectric loss spectra for pure PMMA confirm the previous studies extensively published in the literature (see the top of Figure 1). The peaks shift to higher frequencies, and their height increases with increasing temperature. The shift of the maxima is a consequence of the higher mobility at high temperatures, and the increasing of the peak amplitudes is associated with an increase in the number of relaxed dipoles. Above T_g (T_g = 110 °C) there is a contribution of the movements of the main chain to the relaxation process, and there is a narrowing of the loss curves.[25]

The curves have been fitted by a single HN function. For temperatures above 105 °C, the additional conductivity term was used.

2. PEO/PMMA Blends. The relaxation spectra for the PEO/PMMA blends are presented in Figure 1 (which also contains the spectrum for the pure PMMA).

Independent of the blend composition a single relaxation process is observed, and it is not possible to distinguish any process at low temperatures. The addition of PEO increases largely the conductivity contribution. At low frequencies, this contribution takes large values, even at low temperatures, for the 20 and 25% PEO blends. (Note a different scale in the ϵ'' axis for these two blends, in Figure 1.)

The real part of the complex permittivity is presented in Figure 2 for all the blends. For comparison purposes the spectrum relative to pure PMMA is included in the same figure.

It is clear, from this figure, the increase in the real permittivity, at high temperatures and low frequencies, for the blends containing 20 and 25% of PEO.

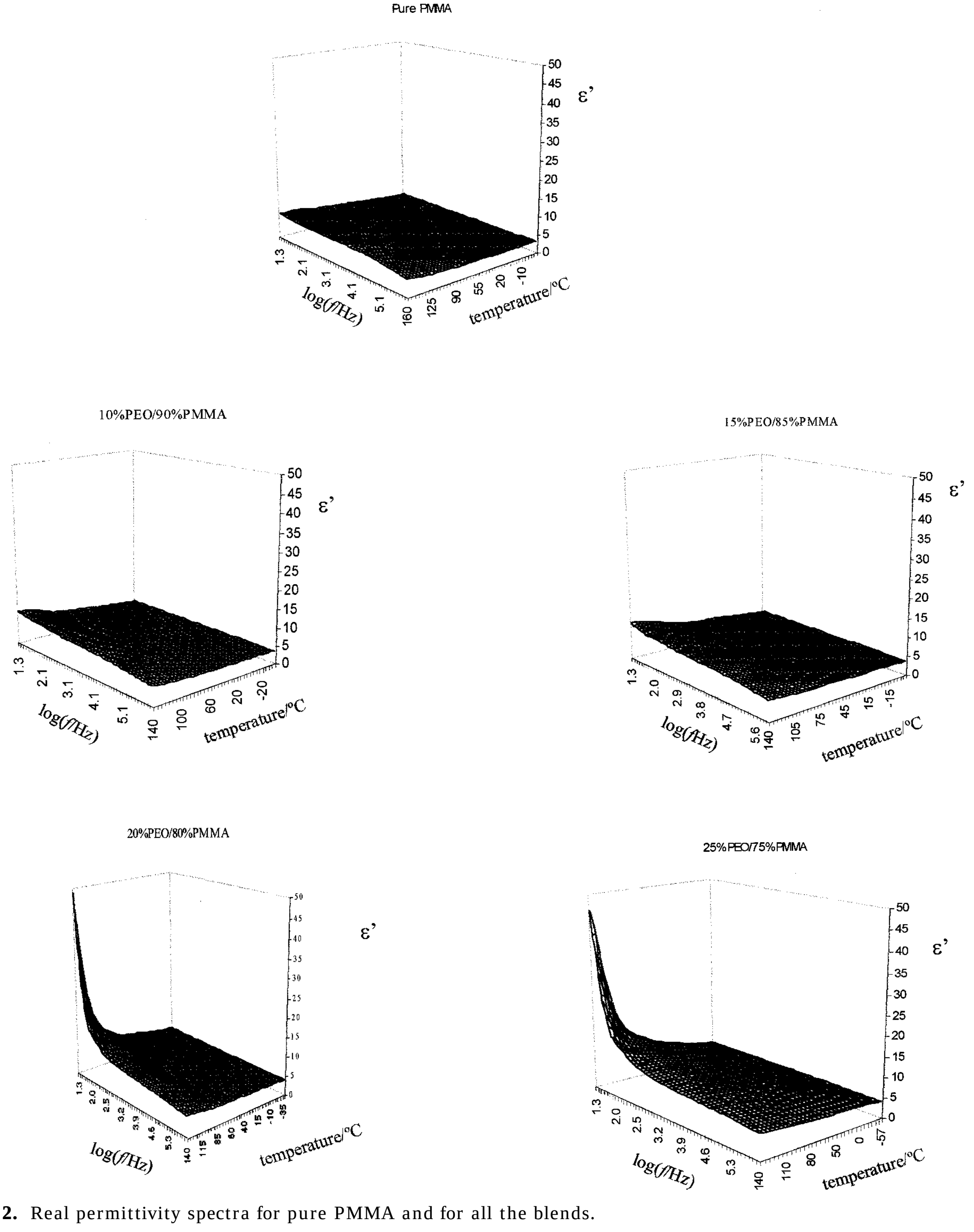


Figure 2. Real permittivity spectra for pure PMMA and for all the blends.

B. Differential Scanning Calorimetry. The thermograms obtained for the pure PMMA and for the blends are presented in Figure 3.

A single T_g is observed, displaced to temperatures successively lower as the concentration of PEO increases.

Discussion

ϵ'' versus Frequency and Temperature. The T_g of the semicrystalline PEO is around −67 °C, and the relaxation related to the glass transition is located, in our frequency range, somewhere between −35 and −16 °C.[26] The relaxation related to the crystalline phase, observed in mechanical studies, cannot be observed in dielectric studies owing to the high conductivities for temperatures higher than −25 °C.[22]

Runt and co-workers found tan δ peaks at 40 kHz, centered at −40 °C for blends having more than 80% PEO.[20] The peaks obtained in their work have the same characteristics, shape and location, as the one found for the pure crystalline component, leading them to the conclusion that the relaxation observed is a pure amorphous PEO phase. In Figure 1, we cannot distinguish, for all the blends, any process at the lower temperatures due to a relaxation process of pure PEO. At a first sight there is no reasons to invoke immiscibil-

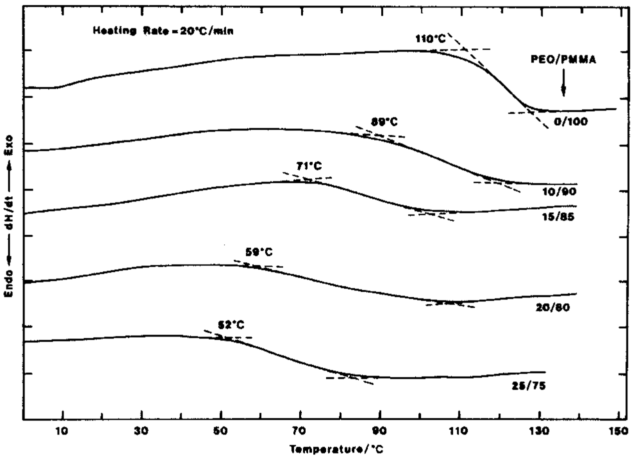


Figure 3. DSC thermograms for pure PMMA and for all the blends.

ity in these blends. The main relaxation process seems to be the PMMA relaxation affected by the addition of PEO.

The dielectric loss curves presented in Figure 1 were fitted with a HN function, with a dc contribution, when necessary. The fitting parameters $\Delta\epsilon$, a, b, and τ were obtained for each blend at each temperature, following the same procedure adopted for pure PMMA. The values of $\Delta\epsilon$ and a together with the product ab are plotted in Figures 4 and 5, respectively. The relaxation times, τ, values will be analyzed later.

It is known that the dielectric intensity, $\Delta\epsilon$, typically increases with increasing temperature for a β relaxation and decreases with increasing temperature for an α relaxation. From the variation of $\Delta\epsilon$ with temperature of the pure polymer, included in Figure 4, it is clear that the main relaxation process at temperatures lower than 125 °C is a β process. Above this temperature there is a merging of the α and β relaxations into an αβ process. For temperatures higher than 145 °C the behavior of $\Delta\epsilon$ with the temperature of this αβ process is in accordance with an α process. With an exception for the 20% PEO blend, the temperature at which $\Delta\epsilon$ ceases to increase decreases with the PEO content (see arrows in Figure 4). This means that the addition of PEO to PMMA displaces the temperature at which the merging with the α process occurs to lower values. For the blend with 20% PEO, $\Delta\epsilon$ does not vary significantly with the temperature.

The similarity of the a and ab values indicates an increase of the symmetry of the relaxation process in a ϵ'' vs log f plot. Once again (see Figure 5), with an exception for the 20% PEO blend, as the PEO content increases, a becomes similar to ab at lower temperatures: the b fitting parameter becomes approximately 1; the HN function becomes equivalent to a Cole−Cole function.[27] For the 20% PEO blend, both a and ab values are identical over almost all the temperature range ($b \cong 1$). The increase in the symmetry of the relaxation process as the PEO content increases may be due to the contribution of the main chain motions which lead to a more homogeneous relaxing environment. The temperature at which this contribution becomes important is, in fact, the onset of the α relaxation which is shifted to lower temperatures with the increase of PEO concentration.

The dielectric relaxation results may be analyzed through the plots of ϵ'' vs log f, at constant temperature. Parts a, b, and c of Figure 6 show these plots at 60, 90, and 110 °C, respectively, for the pure polymer and for the blends, after subtracting the conductivity term. The general effect of the addition of PEO to PMMA seems to be an increase of the intensity of the peak and its deviation to higher frequencies (besides the increase in conductivity mentioned earlier). We will analyze these effects in more detail later in the text.

The addition of PEO also affects the width of the ϵ'' curves. Figure 7 shows the normalized curves for the temperature of 110 °C. With increasing PEO content a broadening of the curves is observed.

The 20% blend is an exception being broader than the 25% PEO blend. This is in accordance with the previous observations relative to the a and ab values in Figure 5, which decrease with the PEO content, except for the 20% PEO blend. This blend presents a lower a value than the 25% PEO blend, indicating a broader relaxation process.

The values obtained for $\Delta\epsilon$ lead to the same conclusion. The area below the $\epsilon''(\log f)$ curves are equal to $\Delta\epsilon$, and the 20% PEO blend presents higher values of $\Delta\epsilon$ (see Figure 6). As $\epsilon''_{\max}$ is higher for the 25% PEO blend, the large values of $\Delta\epsilon$ for the 20% PEO blend can only be explained if the curve is broader.

Let us now observe the τ values ($\tau = 1/(2\pi f_{\max}) = 1/\omega_{\max}$). In Figure 8 the $\log(f_{\max})$ is represented as a function of $1/T$, for pure PMMA and blends. For a better understanding the plots relative to the blends were shifted: one unit was added to each curve relative to the previous one, to avoid superposition. For pure PMMA and for the 10% PEO blend, two regimes can be distinguished, being the slope at low temperatures less pronounced than at high temperatures. These two regimes may be identified with the c and b regimes, respectively, according to the designation of Garwe et al.[24] The low-temperature regime corresponds to the local β process, whereas the b regime corresponds to a locally coordinative process where the side chain cannot move independently from the neighboring side chains: the α and β process are not independent.

The activation energy of the high-temperature process, i.e., using the data obtained for $10^3/T < 2.7$, was calculated according to

$$\ln \omega_{\max} = \ln \omega_0 - E_A/kT \tag{2}$$

The activation energy was found to be 120 ± 8, 121 ± 7, 122 ± 3, 131 ± 8, and 128 ± 8 kJ mol^{-1} for the pure PMMA and for the 10, 15, 20, and 25% PEO blends, respectively. Up to the concentration of 15% PEO, the activation energy remains almost unchanged. However, for the 20 and 25% PEO blends, an increase in E_A of about 10 kJ mol^{-1} was found. The activation energy value of pure PMMA is similar to the one obtained by Garwe and co-workers (112 ± 5 kJ mol^{-1}) for a locally coordinative process,[24] which is the precursor of the αβ process.

The value reported in the literature for the activation energy of the local β process for PMMA is 79 kJ mol^{-1},[28,29] in agreement with the value calculated by Garwe et al., 74 ± 5 kJ mol^{-1}, for the low-temperature region of log $f_{\max}$ vs $1/T$ (c regime).[24] [These authors found a dependency of the activation energy of this regime on the side chain length for the n-alkyl methacrylates, whereas Hideshima and co-workers determined 79 kJ mol^{-1} independently of the size of the n-alkyl group.] These same authors determined for the

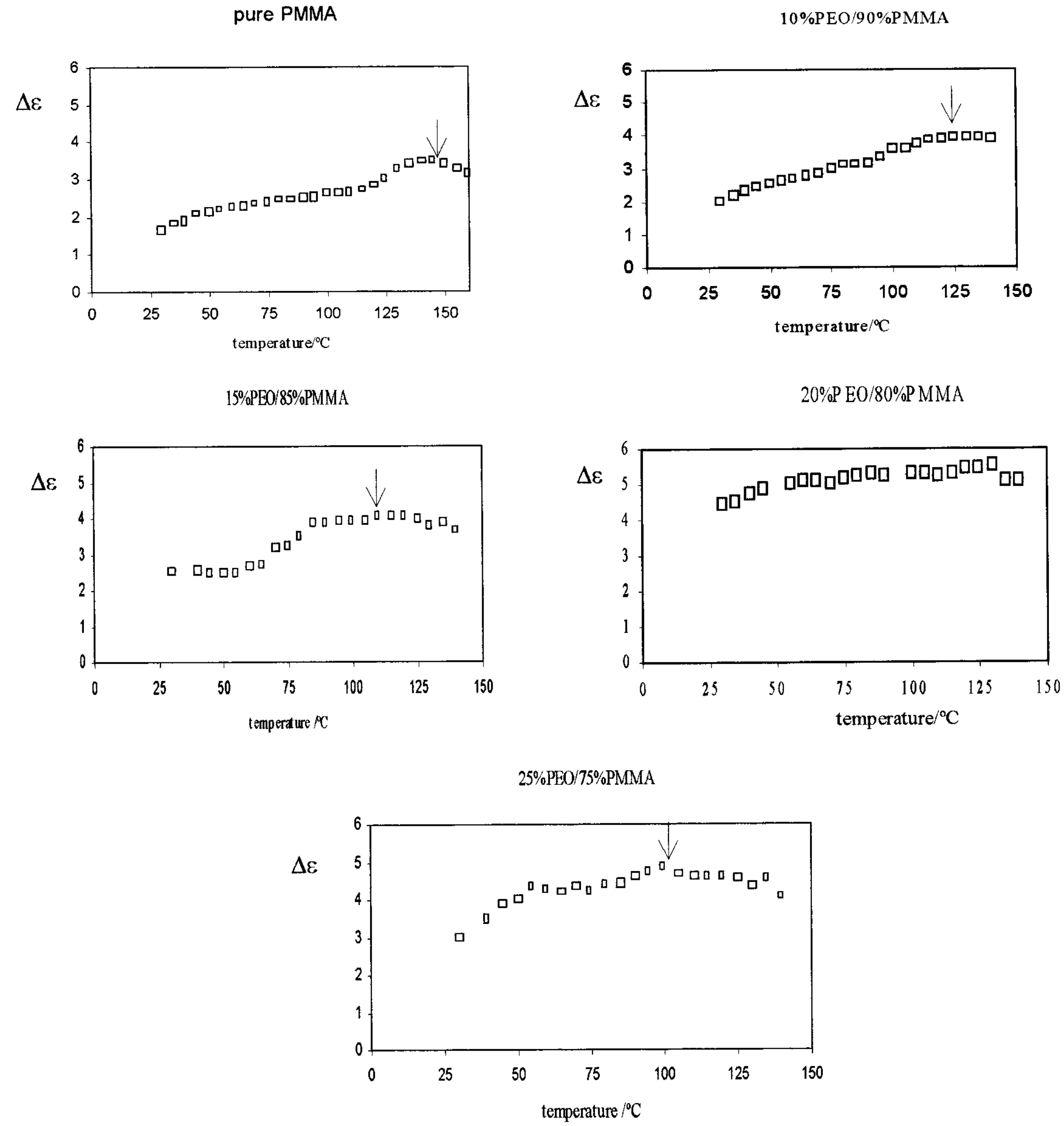


Figure 4. Variation of the dielectric intensity as a function of the temperature for the pure PMMA and the PEO/PMMA blends.

intermediate locally coordinative process an activation energy of 112 ± 5 kJ mol^{-1}. On the other hand, Saito and Nakajima quote an activation energy, for the α relaxation process, of 460 kJ mol^{-1}.[30] These values indicate an increase of the activation energy with the increase of cooperative nature of the relaxation process. The increase of the activation energy for the α process relative to the β process means that the α process is moving faster with the temperature in a frequency window. At high temperatures (and therefore high frequencies), it catches up with and merges with the slower β process to become the $\alpha\beta$ process.

Keeping in mind these observations and in order to interpret the E_A values obtained for the blends, let us reexamine Figure 6, focusing our attention on the behavior of the 20% PEO blend. At 60 °C this blend is retarded relative to the 10 and 15% PEO blends. At 90 °C the 20% PEO blend is more or less at the same position as the 15% blend, and finally, at 110 °C, the curve relative to the 20% PEO blend is shifted to higher frequencies. These results suggest that the PEO for the highest concentrations relaxes cooperatively with the α process of PMMA. At 60 °C, where the relaxation process of pure PMMA is clearly a β process, the α loss peak is still retarded relative to the β process. At 90 °C the α relaxation overlaps the β process into a complex $\alpha\beta$ process. At T = 110 °C, the loss peak of the blend surpasses the slower process of pure PMMA; i.e., while at this temperature the relaxation observed for PMMA is associated with a β process, the relaxation of the blend, at the same temperature, is an $\alpha\beta$ process.

Another way to visualize the variation of the frequency of the maximum of loss peaks with the PEO content is presented in Figure 9.

For the blends with a lower content of PEO (≤15% PEO) $f_{\max}$ increases with the PEO concentration. These results may be interpreted in terms of a plasticizing effect due to the addition of a low-T_g polymer. The increase in free volume leads to an increase of mobility and consequently to the increase of $f_{\max}$. In the case of the 20% PEO blend, and for T < 90 °C, the maximum of the loss peak is retarded relative to the 15% PEO blend. It is only above this temperature that $f_{\max}$ exceeds the maximum of the 15% PEO blend, as we have seen in the analysis of Figure 6. In the 25% PEO blend, the α process is further enhanced, and the curves deviate

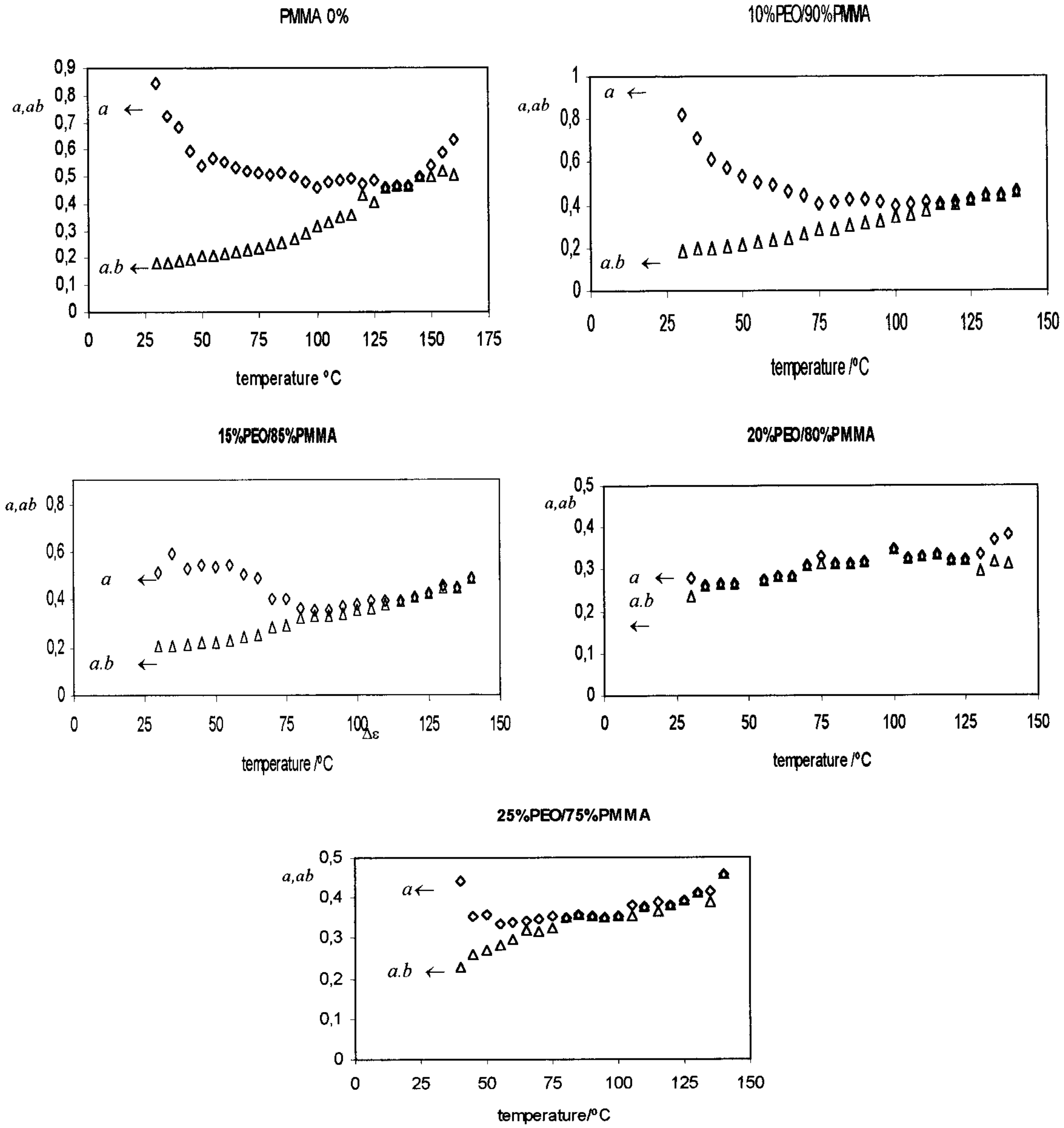


Figure 5. Variation of the HN fitting parameter *a* and the product *ab* as a function of the temperature for the pure PMMA and the PEO/PMMA blends.

even more to higher frequencies and become narrower.

The increase in the activation energy for the 20 and 25% PEO blends is in agreement with the previous arguments, indicating an increase of the cooperative nature of the $\alpha\beta$ process.

The increase in the activation energy found in these blends has a different physical meaning from the one found by Aihara and co-workers in PMMA/PVDF blends.[31] Those authors verified a decrease of $f_{\max}$ for the highest concentrations of PVDF ($\geq$20% PVDF) and for the highest temperatures, due to the restriction of the main chain motion caused by specific interactions.[31] Our results revealed, for the highest concentrations and highest temperatures, an increase of $f_{\max}$. This different behavior suggests the nonexistence of specific interactions in these PEO/PMMA blends, as predicted by the low Flory–Huggins interaction parameter (see Introduction).

Anyway, the enhancement of the α characther of the complex $\alpha\beta$ process is not a new observation: in solid solutions of poly(*n*-alkyl methacrylates) with a low molecular weight solute, *p*-nitroaniline, the $\alpha\beta$ process had some properties that were similar to a pure α process.[32]

ϵ'' versus Temperature at Constant Frequency. In Figure 10 the plots of ϵ'' vs ($T - T_{\max}$) are presented at three different frequencies: 5, 10, and 100 kHz. The temperature of maximum loss at constant frequency, $T_{\max}$, was chosen as the reference temperature.

In this normalized representation the position of the maximum loss remains unchanged for pure PMMA and blends. These results do not confirm the observations of Colby[1] for a blend containing 20.2% of PEO and where PMMA is a mixture of isomers (78% syndiotactic, 21% heteroatactic, and 1% isotactic). This author found that, for the same $T - T_g$, the PMMA relaxes slower in the blend than in pure PMMA. If the relaxation process of pure PMMA was retarded upon blending, the peaks would deviate to high temperatures.

The low-temperature side is not influenced by blending; i.e., the peaks superimpose at the three frequencies shown in the Figure 10. The differences become appar-

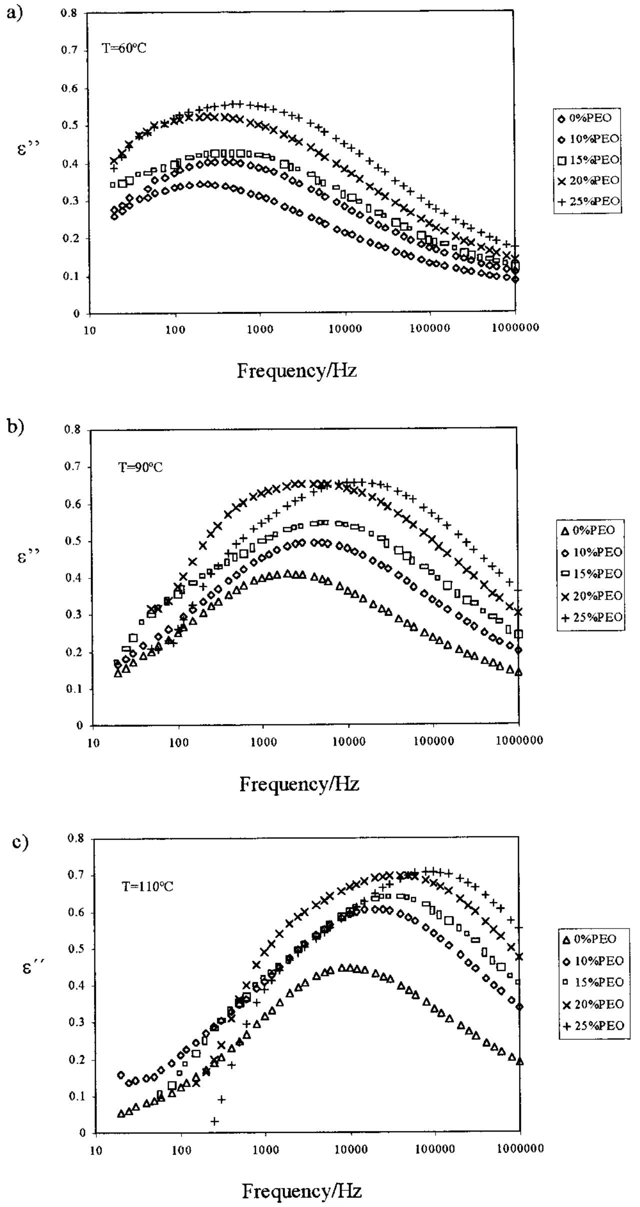


Figure 6. Dielectric loss curves as a function of frequency for the pure PMMA and the four PEO/PMMA blends at (a) 60 °C, (b) 90 °C, and (c) 110 °C.

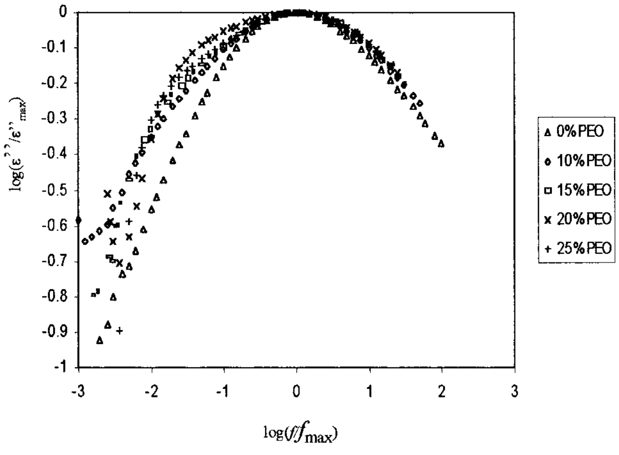


Figure 7. Normalized dielectric loss curves at 110 °C for the pure PMMA and the four PEO/PMMA blends.

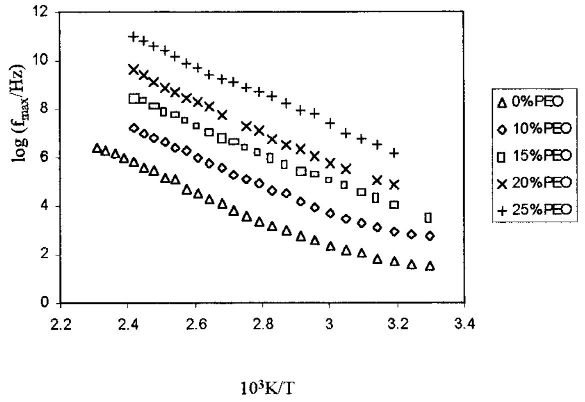


Figure 8. Arrhenius diagram for pure PMMA and blends. The curves were shifted along the vertical direction to avoid overlapping. The values of $\log(f_{\max})$ for the blends with 10, 15, 20, and 25% PEO were increased by one, two, three, and four units, respectively.

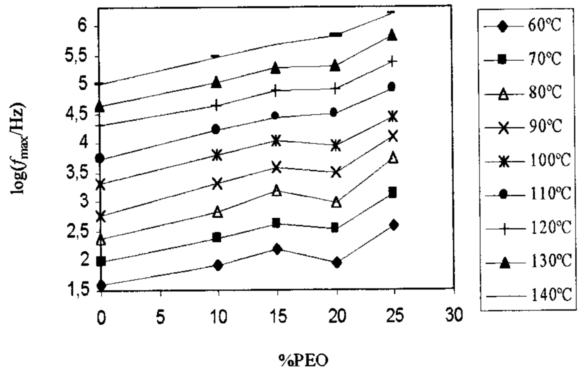


Figure 9. Variation of the frequency of the maximum loss with the PEO content and with temperature, for temperatures between 60 and 140 °C.

ent in the high-temperature side and for the lowest frequencies: 10 and 5 kHz. As the frequency decreases, the peaks become broader and the 20% PEO blend seems to be the broadest curve, as in DSC thermograms (Figure 3). According to Schönhals[33] and Hensel,[34] the low-temperature side (or the high-frequency side) is related with short-mode length molecular motions (short distance fluctuations), while the high-temperature side (low frequency) is related with long mode length molecular motions (long distance fluctuations). The same effect was observed in the frequency domain in the normalized loss curves at 110 °C (Figure 7), where PEO affects mainly the low-frequency side of the loss curves. These arguments confirm that the addition of PEO ($\leq$25%) to PMMA affects essentially the α character of the $\alpha\beta$ relaxation process.

ϵ' versus Temperature and Frequency. The results discussed so far seem to confirm the miscibility of these PEO/PMMA blends. However, the singular behavior of the 20% PEO blend raises some doubts owing to is abnormal broadness revealed by both dielectric and calorimetric techniques. An analysis of the real permittivity behavior with temperature and frequency (see Figure 2) reveals, for the 20 and 25% PEO blends, an increase in ϵ' at high temperatures and low frequencies, which is absent in pure PMMA and in the 10 and 15% blends. This effect may be due to the existence of an electrode and/or interfacial polarization—the Maxwell—Wagner—Sillars (MWS) effect. In Figure 11, where the real permittivity is represented as a function of temperature at 100 Hz, it is clear that this effect is only significant for temperatures higher than 120 °C.

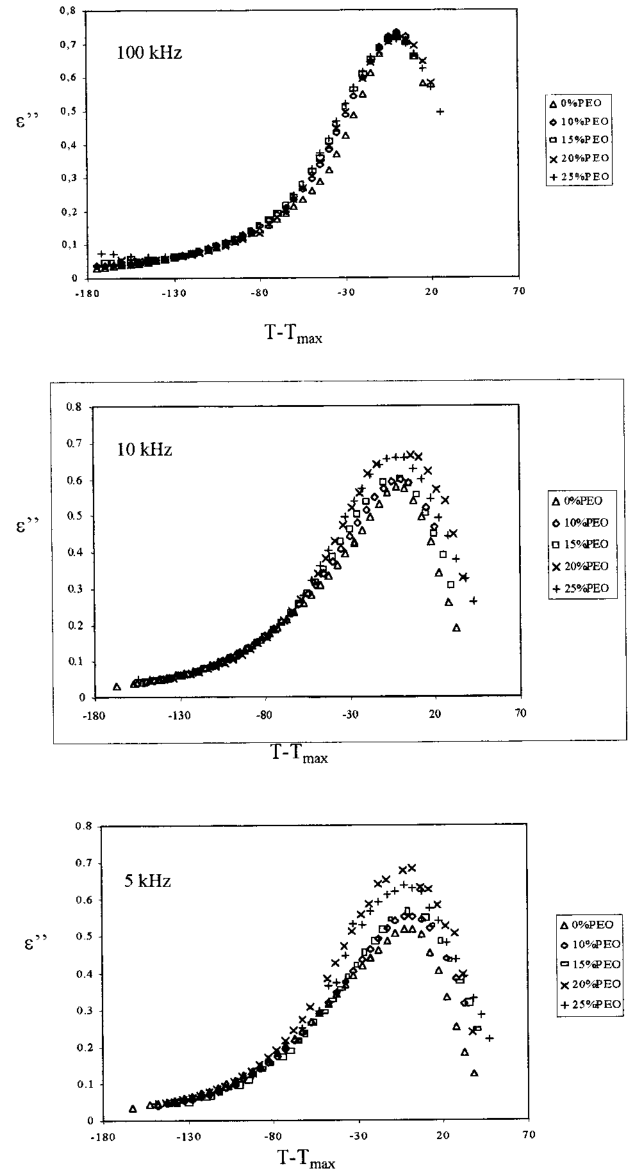


Figure 10. Dielectric loss as a function of the normalized temperature for the pure PMMA and the four PEO/PMMA blends at (a) 100 kHz, (b) 10 kHz, and (c) 5 kHz.

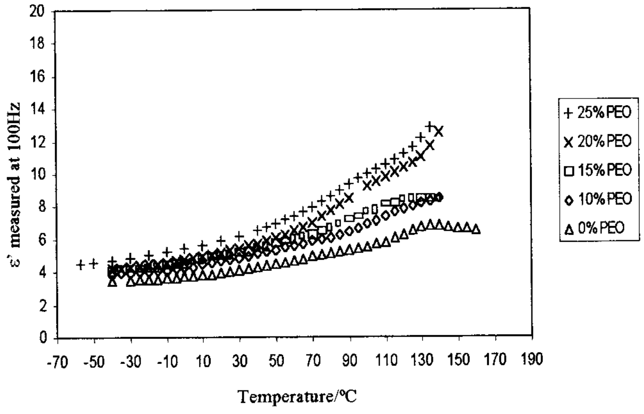


Figure 11. Real permittivity at 100 Hz as a function of temperature for pure PMMA and blends.

The electrode polarization, in general, is attributed to the blocking charge carriers at the electrodes justifying the abnormal increase of the real permittivity at low frequencies and high temperatures.

On the other hand, if an interfacial polarization exists, in what kind of interface does this polarization take place? The existence of crystallinity, absorbed water, and/or the presence of heterogeneities are possible answers.

As referred to in the Introduction, some authors have reported the presence of crystallinity in these types of blends. In this study the MWS effect was detected in the essays performed at high temperatures. Since the melting temperature of PEO is around 67 °C, at 120 °C, for example, it is not possible for crystallinity to exist. Moreover, if it was due to crystallization, the 25% PEO blend should present more crystallinity than the 20% PEO blend, and its relaxation should appear deviated to lower frequencies, due to the restricted motion of the chains in the crystalline regions. Also, the intensity of the peak should decrease significantly, which is not the case. The absence of crystallization peaks in the thermograms obtained by differential scanning calorimetry (Figure 3) confirms that, if an interface exists, it is not due to the presence of a crystalline phase.

It is known that both PMMA and PEO absorb water. Sheiber and Mead[35] found a loss peak due to absorbed water in PMMA, occurring in the region of −20 °C, at 5 kHz, which is absent in the dielectric spectra obtained in this study. As the PMMA content decreases in the 20 and 25% PEO blends, it is probably PEO, instead of PMMA, the polymer responsible for an eventual water absorption. The presence of water, trapped in the structure of the blend or even bonded to PEO, could be in the origin of an interfacial polarization, due to the presence of different dielectric media.

Let us examine the hypothesis of the existence of heterogeneities. The results discussed so far seem to confirm the miscibility of this blend. The real permittivity results confirm this hypothesis, at least for temperatures lower than 120 °C. However, the singular behavior of the 20% PEO blend raises some doubts owing to its abnormal broadness revealed by both dielectric and calorimetric techniques. From the relaxation spectroscopy data this broadness was interpreted as the merging of the α process into a complex $\alpha\beta$ relaxation process. This effect, which is clearly visible at 90 °C, should decrease with the increase in temperature; i.e., the loss curves should become narrower once the $\alpha\beta$ process is established. This narrowing is observed for the 25% PEO blend, but the abnormal broadness is still present, with the increase in temperature, in the 20% PEO blend. This persisting broadness may be due to the presence of concentration fluctuations giving rise to local inhomogeneities.

In conclusion, the increase in ϵ' at high temperatures and low frequencies cannot be attributed to a single factor. Both electrode and interfacial polarizations may be present. The presence of water, even in minor amounts, may be responsible for the interfacial polarization, and in the case of the 20% PEO blend, the presence of heterogeneities is also a possible cause. Owing to the domain size scale of both applied techniques, these heterogeneities should be of the order of a nanolength scale.

Conclusions

Blends of PMMA and PEO with 10, 15, 20, and 25% in PEO were studied by dielectric relaxation spectroscopy and differential scanning calorimetry.

The relaxation of pure PMMA is a β process at temperatures below T_g and, with the merging of the α process above T_g, becomes an $\alpha\beta$ relaxation process. Upon blending with PEO this relaxation behavior is affected, depending on the PEO content in the blends.

The addition of 10 and 15% PEO has mainly a plasticizing effect, shifting $f_{\max}$ to higher frequencies and increasing the dielectric intensity, $\Delta\epsilon$. The detection, by DRS and DSC of a single relaxation associated with the glass transition which is displaced to lower temperatures, leads us to conclude that these blends are miscible in the temperature range studied.

In the blends with a higher PEO content, 20 and 25%, the DRS results suggest that PEO moves cooperatively with the main chain of PMMA, strengthening the α character of the relaxation process in the blend.

The displacement of the glass transition and the onset of the α transition to lower temperatures, with the increase in PEO content, are a further indication of the miscibility of these blends.

The large increase in both real and imaginary parts of the complex permittivity at low frequencies and high temperatures, for both 20 and 25% PEO blends, was attributed to the presence of minor quantities of water causing high conductivities and electrode and/or interfacial polarizations.

Both the loss curves in DRS and the glass transition in DSC become broader with the addition of PEO, being the 20% PEO blend abnormally broad. This fact was explained by the merging of the α transition and by the existence of concentration fluctuations, which also originates an interfacial polarization.

The results presented in this study confirm the results reported by other authors that PEO is miscible with PMMA up to a concentration of 25% PEO in the blend. The singular behavior of the 20% PEO blend confirms that this blend is in the border of the miscibility/immiscibility regions. The dielectric relaxation spectroscopy complemented with DSC measurements was able to give further insight into the mechanisms underlying the mixing process.

One final remark should be made. The behavior of polymer blends and, in particular the degree of miscibility, is strongly dependent on the molecular weight and tacticity of the polymers and on the thermal history previous to the measurements. In consequence, care must be taken when comparing the results presented by different authors.

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