α−β Splitting Region in the Dielectric Relaxation Spectrum of PEA-PEMA Sequential IPNs

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ABSTRACT: The dielectric relaxation spectra of poly(ethyl acrylate)-*i*-poly(ethyl methacrylate) sequential interpenetrating polymer networks, IPNs, are presented. In addition, dynamic-mechanical data were used to study the compatibility of the networks as the main relaxation predominates on the secondary relaxation in mechanical spectroscopy. When the IPNs are highly cross-linked, both networks are forced to mix at the molecular level, and as a consequence, a single main dynamic mechanical relaxation appears. By contrast, when the cross-linking density is small, the individual relaxation behavior of the component networks can be observed. The poly(ethyl methacrylate) networks with low cross-linking density show the merging of the secondary β dielectric relaxation and the main α relaxation with the same characteristics as the poly(ethyl methacrylate) chain polymer. This behavior changes, however, in the highly cross-linked network in which the influence of the main relaxation on the overall behavior is smaller, and it was not possible to separate the α and β components in the merging region. The incorporation of the poly(ethyl acrylate) chains to the cooperative motions of the poly(ethyl methacrylate) network shifts the α and β relaxations to a different extent, which induces changes in the shape of the spectrum in the merging zone.

Introduction

One of the most salient features of the dielectric relaxation spectrum of the polymers of the series of polymethacrylates is the merging of the main or α dielectric relaxation with the local β relaxation in the frequency range of the available instrumentation. Already in 1966 Williams[1] stated that the main α relaxation and the secondary β relaxation merge at temperatures above the glass transition temperature T_g into a new αβ relaxation process, which has characteristics different from both the α and β relaxation; that is, it is not a mere superposition of both processes. The crossover region is the frequency−temperature region in which the relaxation times of the α and β processes approach each other. An extensive analysis of the knowledge and different points regarding this question of view can be found in refs 2 and 3.

Garwe et al.[4] described the dielectric relaxation spectrum defining three different zones. Because of the characteristic curvature of the α relaxation in the Ahrrenius plot, which is a consequence of its cooperative character, this relaxation appears at extremely low frequencies for low enough temperatures, in the glassy state, and thus, its influence on the local β relaxation is not significant. Thus, at very low temperatures, in the regime (c), a pure β relaxation can be observed. There is a temperature interval in which the β and the α relaxation merge, that will be called regime (b). The frequency dependence of the complex dielectric permittivity measured at constant temperature can be resolved, in this temperature range, into two relaxation functions, one of them characteristic of the α relaxation and the other one corresponding to the β relaxation. Nevertheless, there is no agreement about the procedure to perform the decomposition of the overall process into the two components. Two different approaches have been proposed. One of them is based on the fit of the experimental isothermal data of the complex dielectric permittivity as a function of frequency using the sum of two Havriliak−Negami[5] equations; the fitting parameters allow the α and β processes to be located in an Ahrrenius diagram and the temperature dependence of the relaxation strength to be calculated.[3,6] The other approach is based on the so-called Williams ansatz, in which the total relaxation function in the time domain is expressed in terms of the α and β relaxation functions.[2,6,7] The relaxation strength of the α process decreases with increasing temperature, and some results indicate that it would vanish at a temperature that is called the α-onset temperature. Nevertheless, this conclusion may depend on the procedure used to decompose an experimental isotherm into the α and β components. The strength of the β relaxation increases with temperature. At higher temperatures, in regime (a), the αβ relaxation is observed. Its strength decreases with increasing temperature.[8,9] In poly(ethyl methacrylate), PEMA, an α-onset temperature of 110 °C has been reported, and the transition from the (c) regime to the (b) regime takes place around 73 °C.[4,6]

One of the key theoretical questions to understand this complex behavior is the degree of cooperativity of the molecular motions that are responsible for the different relaxation processes. The α relaxation, originating in the conformational motions of the polymer chains, is a cooperative process. The concept of a cooperatively rearranging region, CRR, introduced by Adam and Gibbs[10] is useful to analyze the phenomenology of this relaxation. The β relaxation is probably a local process at low temperatures, but the increase in

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the apparent activation energy of this relaxation when going from regime (c) to regime (b) led Garwe et al.[4] to postulate that some coordination between the polymer side chains appears in regime (b). One of the ways to check the cooperativity is to study the influence of a second component on the mobility of the polymer chains.[3] Kahle et al.[8] studied the dielectric relaxation spectrum of poly(*n*-butyl methacrylate-*stat*-styrene) copolymers and found a continuous shift of the onset temperature and frequency of the α relaxation varying the styrene content of the copolymer. Zhang et al.[11] reported a clear shift of the α relaxation of PEMA toward high temperatures when blending with poly(4-vinylphenol) with little change in the β relaxation but a significant increase of the apparent activation energy of the αβ relaxation as the content of PEMA in the blend decreased.

In refs 12 and 13, our group studied the dielectric relaxation spectrum of poly(butyl acrylate)-*i*-poly(butyl methacrylate), PBA-*i*-PBMA, sequential interpenetrated polymer networks. By swelling a polymer network of component A in the monomer of component B and then polymerizing the second network, a sequential IPN is formed. Most IPNs show phase separation. If polymers A and B are immiscible and the cross-linking density of A is small, i.e., the number of monomer units between cross-links is high, then during the polymerization of network B, the growing B chains will push apart the already existing A chains, and a phase separated IPN will be obtained. This was the case of the PBA-*i*-PBMA IPNs when the networks were cross-linked with 0.1 wt % of ethylene glycol dimethacrylate EGDMA.[13] However, if the cross-linking density of A is high, the positions of the A chains will hardly be changeable, and the B network will grow by interpenetrating the existing network A. Thus, a homogeneous IPN can eventually be obtained, achieving a forced compatibilization[14,15] of both polymers, as occurs in the PBA-*i*-PBMA IPNs cross-linked with 10% of EGDMA. A continuous shift of the whole dielectric spectrum toward lower temperatures with increasing acrylate content of the IPN was found, when the cross-linking density of the IPN was high enough to force both components to mix at a molecular level.

The compatibilized IPNs present an extremely broad glass transition. Thus, a poly(methyl acrylate)-*i*-poly(methyl methacrylate) IPN cross-linked with 10% EGDMA shows a single glass transition in DSC covering a temperature interval of around 100°.[16] It was shown that the dependence of the conformational mobility with temperature is monotonic, and it is not representative of a phase separation. This behavior can be explained by the existence of fluctuations of the local composition around the average value (see ref 17 and the references therein).

Experimental Section

Sequential interpenetrating polymer networks, IPNs, were prepared by block polymerization using benzoin as photoinitiator. Two series of IPNs were prepared: one of them with 1 wt % and the other one with 10 wt % of ethyleneglycol dimethacrylate, EGDMA, as cross-linking agent. The same amount of EGDMA was added in the polymerization of the two component networks. The poly(ethyl acrylate) network was polymerized in the first place. A 0.5-mm-thick sheet was obtained. This sheet was immersed in a solution of ethyl methacrylate monomer, EMA, and ethanol containing EGDMA in the same EGDMA/monomer ratio as the PEA network and the photoinitiator. The swollen sample was exposed to ultraviolet light to polymerize the poly(ethyl methacrylate) network. Low molecular weight substances were extracted from the IPN by boiling it in ethanol for 24 h and then drying it in a vacuum to a constant weight.

This procedure allowed us to synthesize a series of IPNs with a content of PEA equal to or below 50 wt % in the series with 10% of EGDMA monomer by varying the ratio of EMA/ethanol in the second stage of the synthesis. Nevertheless, only up to 33% of PEA was obtained in the IPNs of the series polymerized with 1% of EGDMA, because the PEA network polymerized first is able in this case to absorb great amounts of ethyl methacrylate. An IPN containing 29% of PEMA was prepared allowing the PEA network to absorb ethyl methacrylate for a limited time. The sample was isolated to allow a complete diffusion of the monomer, and then, the second network was polymerized. In this work, we will present the results obtained on IPNs cross-linked with 1% EGDMA containing 29, 67, and 80% of PEMA and IPNs cross-linked with 10% EGDMA containing 23, 36, and 50% of PEMA. The pure PEMA networks cross-linked with 1% and 10% EGDMA were also prepared following the same routine as in the case of the PEA networks.

The IPN samples will be named IPNXX-YY; XX indicating the weight % of PEMA network in the IPN and YY is 1 or 10 indicating 1% or 10% of EGDMA as cross-linking agent. PEA-YY and PEMA-YY will be used for the pure PEA and PEMA networks.

Dielectric relaxation spectroscopy, DRS, conducted on the samples of the series with 10% EGDMA was performed in a General Radio 1689M dielectric analyzer in a frequency range between 90 and 10^5 Hz, using a Novocontrol BDS1300 cell thermostatised between −160 and 200 °C within 0.1 °C. In the series with 1% EGDMA, a broader frequency range, 10^{-2}–10^9 Hz, was covered. For the measurements in the 10^{-2}–10^6 Hz frequency range, two different arrangements were used: a Schlumberger frequency response analyzer FRA 1260 with a buffer amplifier of variable gain and a working frequency of 10^{-2}–10^6 Hz and a Hewlett-Packard 4284 A LCR meter in the frequency range between 20 and 10^6 Hz. The sample was sandwiched between nickel-coated stainless steel electrodes in an Ando SE−70 dielectric cell. The temperature of the measurement was controlled to a 0.1 °C between −65 and 200 °C by means of an Ando type TO-19 thermostatic oven. For the measurements in the 10^6–10^9 Hz frequency range, a Hewlett-Packard Impedance/Material Analyzer 4291 A integrated with a Tabai Espec Temperature Chamber SU-240-Y in the temperature range −35 to +130 °C was employed. The sample was sandwiched between gold-coated brass electrodes.

Dynamic-mechanical analysis, DMA, was carried out in a Seiko DMS210 instrument at 1 Hz.

Results

The dielectric relaxation spectrum of PEMA1 network (Figure 1a) shows the same features reported for PEMA in refs 2−4 and 6. At temperatures above 100 °C, in the (a) region, corresponding to the αβ relaxation, the ϵ'' isotherm can be fitted with a single Havriliak−Negami function (Figure 1a shows the 110 °C isotherm as a representative example). The merging or (b) region covers the temperature interval between 60 and 100 °C. Figure 1a shows clearly that in this temperature interval (the isotherms corresponding to 70 and 80 °C are included in the figure) the superposition of two HN relaxation functions is necessary to reproduce the experimental result (the full lines in Figure 1a). The low-frequency peak is ascribed to the appearance of the α relaxation, whereas the main high-frequency peak is due to the β relaxation. At temperatures lower than 60 °C, the relaxation spectrum can be described again by a single HN curve, this region corresponds to the β relaxation or regime (c). Figure 1a shows the 40 °C

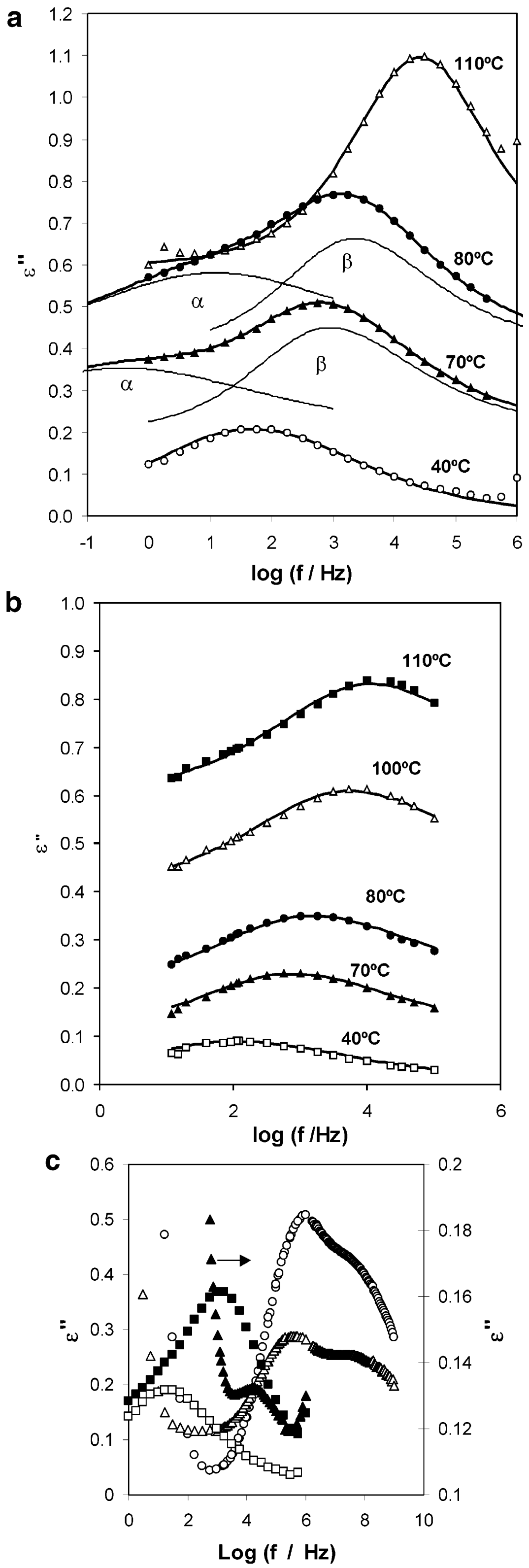

Figure 1. Imaginary component of the dielectric permittivity measured for PEMA-1 (a) and PEMA-10 (b) networks. Several characteristic isotherms, corresponding to the different zones of the relaxation spectrum (see text), have been represented and they have been shifted vertically (by 0.2 with respect to the preceding one) for clarity. The *y*-axis scale corresponds to the 40 °C isotherm. The full lines correspond to the fitting with one or a sum of two HN terms. In (c) the relaxation spectra of PEA-1 (○), IPN29−1 (△), and PEMA-1 (□) are shown, the open symbols correspond to 30 °C and the solid symbols to 80 °C. Note the different scale in the *y* axis of the spectrum corresponding to IPN29-1 at 80 °C.

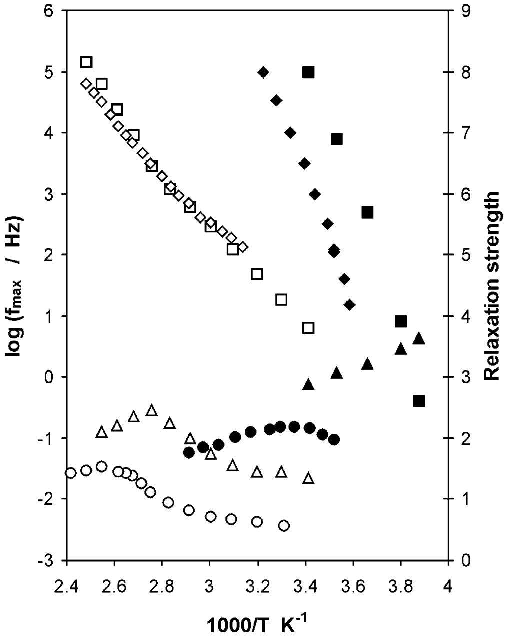

Figure 2. Frequency of the maximum of the ϵ'' isotherms for the network cross-linked with 1% of EGDMA (□) and 10% EGDMA (◇) and the relaxation strength of these networks (△) and (○), respectively, as a function of the reciprocal of temperature. Open symbols correspond to PEMA networks, and full symbols correspond to PEA networks.

isotherm. The apparent activation energy (the Ahrrenius diagrams are represented in Figures 2 and 5a) in this regime is 75 kJ/mol. A value of 77 kJ/mol was reported for PEMA by Ishida and Yamafuji,[18] and 79 kJ/mol was determined in refs 19 and 20 for the β relaxation measured at low temperatures by dielectric experiments in the time domain, and values between 65 and 70 kJ/mol are given in more recent works.[4,6,11] The activation energy in the (a) regime is higher, 114 kJ/mol, close to the value reported in ref 4 for PEMA. In the intermediate (b) regime, the apparent activation energy cannot be determined accurately due to the insufficient number of data points, but it can be said that its value must be quite close to that of the (a) regime around 110 kJ/mol. The relaxation strength increases with increasing temperature for the β relaxation (in the (c) regime) and in the merging zone, goes through a maximum at 90 °C and decreases in the temperature interval of the $\alpha\beta$ relaxation (Figure 2).

The phenomenology in the highly cross-linked PEMA-10 network is significantly different. As shown in Figure 1b, all of the ϵ'' isotherms can be described with a single HN function. The transition from the (a) to the (b) regime is not apparent, nevertheless the transition from the (b) to the (c) regimes can be detected by a change of slope in the Ahrrenius diagram (Figure 2). For the PEMA-10 network, the apparent activation energy of the β relaxation in the (c) regime is 59 kJ/mol and that of the $\alpha\beta$ relaxation is 91 kJ/mol, both significantly smaller than for the same relaxations of PEMA-1 network.

In the frequency interval up to 10^6 Hz, PEA networks show only the main α relaxation in the temperature range of our measurements. The secondary β relaxation appears in this polymer at lower temperatures and well apart from the α relaxation in this range of frequency. A series of experiments were conducted in the network cross-linked with 1% EGDMA in the frequency interval

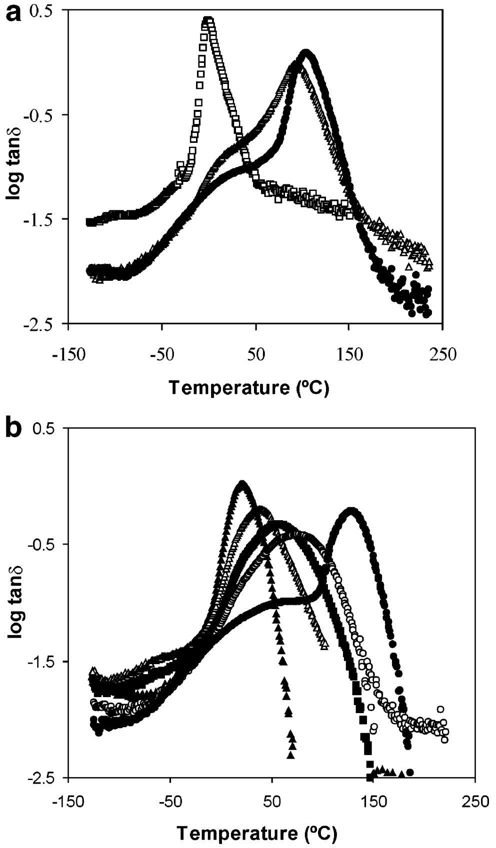

Figure 3. Temperature dependence of the loss tangent measured in a dynamic−mechanical experiment at 1 Hz. (a) PEMA-1 (●), IPN67-1 (△), PEA-1 (□), (b) PEMA-10 (●), IPN50-10 (○), IPN36-10 (■), IPN23-10 (△), PEA-10 (▲).

between 10^6 and 10^9 Hz. Figure 1c shows the spectrum corresponding to 30 °C. A shoulder in the high-frequency side of the main peak should correspond to the secondary relaxation. The frequency interval of the crossover region in this network, at much higher frequencies than in PEMA-1, is consistent with the extrapolation of the classical results reported for poly(ethyl acrylate).[21] A detailed study of the merging of the α and β relaxations in this polymer is out of the scope of this paper. The Ahrrenius diagram of these polymers shows the curvature characteristic of the cooperative main relaxation, and the relaxation strength decreases with increasing temperature with the exception of the two points corresponding to the lowest temperatures in the case of PEA-10 network (Figure 2).

In Figure 1c the spectrum of the PEMA-1 network obtained at 80 °C is also shown. We emphasize the significant difference between the temperature intervals in which each network (PEA and PEMA) exhibits dielectric dispersions in the frequency range of our measurements (10^{-2}−10^9 Hz). This result reflects the difference between the glass transition temperatures of the two networks.

Dynamic-mechanical spectroscopy is useful to understand the behavior of the main relaxation in the IPNs because the α relaxation predominates over the local β relaxation in dynamic-mechanical spectroscopy. Figure 3a shows the temperature dependence of the loss tangent measured at 1 Hz in the PEA-1 and PEMA-1 networks and IPN67-1. The spectrum of the PEMA-1 network shows the main relaxation peak at around 107 °C, and the secondary relaxation appears as a shoulder in the temperature interval between roughly −70 and +50 °C. The PEA-1 network shows the main relaxation peak at 0 °C. The IPN presents the main peak at 97 °C, a temperature which is lower than that of PEMA-1, but the shift toward low temperatures is smaller than it would be if PEA and PEMA segments were mixed at molecular level. The secondary relaxation is also apparent in the relaxation spectrum of the IPN. The temperature range of this relaxation is quite close to that of the main relaxation of PEA and thus some participation of the main relaxation of PEA segments in this relaxation zone cannot be ruled out. In IPN80-1, the main relaxation peak is closer to that of PEMA1 (results not shown).

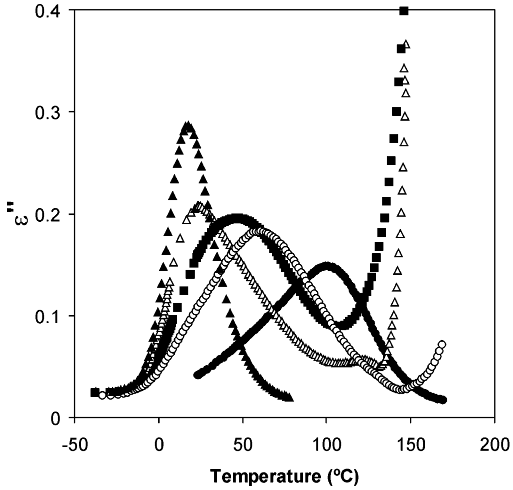

Figure 4. Temperature dependence of the imaginary component of dielectric permittivity measured at 10 kHz. PEMA-10 (●), IPN50-10 (○), IPN36-10 (■), IPN23-10 (△), PEA-10 (▲).

In contrast, the IPNs cross-linked with a 10% EGDMA (Figure 3b) show a single relaxation peak whose temperature (maximum of the loss tangent) changes continuously with composition from that of PEA-10 to that of PEMA-10. The relaxation covers in the IPNs a broader temperature interval than in the pure component networks and is indicative of the forced compatibilization of both networks.

The forced compatibilization can be also seen in the isochronous representation of the dielectric data (Figure 4). The IPNs cross-linked with 10% EGDMA show a single relaxation peak that shifts in the temperature axis as the composition of the IPN changes.

The Arrhenius diagram of the IPNs cross-linked with 1% of EGDMA is shown in Figure 5a. IPN67-1 and IPN80-1 present a behavior analogous to that of PEMA-1. It has been possible to fit the experimental ϵ'' isotherms with a sum of two HN functions in the (b) region. The accuracy in the calculation of the HN parameters is low especially in the case of the α relaxation, but the position of its maximum in the frequency axis can be reasonably determined in this temperature interval to support the fact that the α relaxation clearly shifts toward low temperatures as the content of PEA in the IPN increases. Representative error bounds are drawn in some points of Figure 5a (data of IPN80-1). In the (a) region, the $\alpha\beta$ relaxation also shifts toward lower temperatures with increasing content of PEA, but the shift is smaller than in the case of the α relaxation. IPN29-1 presents two separated relaxation zones that may be due to two separated phases in the material. The two peaks appearing at 30

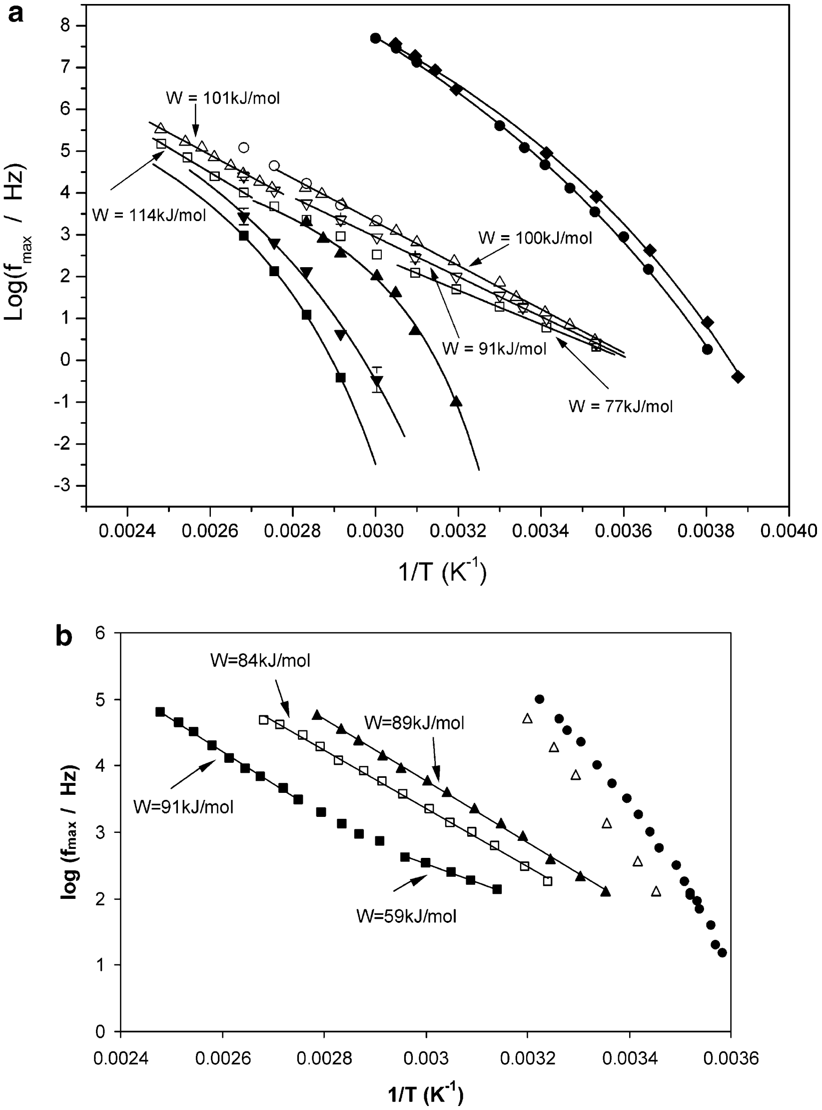

Figure 5. Ahrrenius diagram showing the position of the dielectric relaxations in pure networks and the IPNs. (a) PEMA-1 (■), IPN80-1 (▼), IPN67-1 (▲), IPN29-1 (●), PEA-1 (◆). The open symbols correspond to the β relaxation and the solid ones to the α relaxation. The individual contribution of each relaxation was determined by fitting a sum of two Havriliak−Negami terms to the overall relaxation curve (see text). (b) PEMA-10 (■), IPN50-10 (□), IPN36-10 (▲), IPN23-10 (△), PEA-10 (●).

°C in Figure 1c are analogous to those shown by PEA-1 network at the same temperature. The position of the low-frequency one has been represented in Figure 5a and correspond to the region of the main relaxation of PEA segments. The α relaxation mechanism appears at low temperatures, slightly shifted toward higher temperatures with respect to that of PEA-1 network. This relaxation can be attributed to a PEA-rich phase. The other relaxation mechanism (an example is the peak shown at 80 °C in Figure 1c) appears in the region of the $\alpha\beta$ relaxation of PEMA and may correspond to PEMA-rich regions.

The apparent activation energy in the (a) region of the IPNs cross-linked with 1% EGDMA is $w = 100$ kJ/mol, only slightly lower than in the PEMA-1 network. In the region (c), $w = 91$ kJ/mol for IPN80-1 and $w = 100$kJ/mol for IPN67-1, higher than in PEMA-1 and increasing with the content of PEA in the IPN (the fitting straight lines to the experimental data are shown in Figure 5a).

The points corresponding to the α relaxation in the pure networks and the IPNs cross-linked with 1% EGDMA were fitted to the VFTH equation

$$\log f_{\max} = A - \frac{B}{T - T_0}$$

Figure 5a shows the continuous lines corresponding to the model that were used to calculate the dielectric glass transition temperature, $T_{g,diel}$, defined as the temperature for which the dielectric relaxation time is 100 seconds; that is, the peak frequency 1.6×10^{-3} Hz. The values of the calculated dielectric $T_{g,diel}$ are shown in Table 1.

Despite the remarkable errors of data for α relaxation shown in the Arrhenius diagrams in Figure 5a, the estimated $T_{g,diel}$ values in Table 1 reveal the trend of a decrease of T_g for PEMA-1 component with an increase of PEA-1 content in the IPN.

The IPNs cross-linked with 10% EGDMA show a single relaxation that in IPN50-10 and IPN36-10 present an Ahrrenius behavior as seen in Figure 5b, with an apparent activation energy of 84 and 89 kJ/mol, respectively. The Ahrrenius diagram of IPN23-10 obeys the

Table 1. Parameters of the VFTH Equation for the α Relaxation of IPNs Crosslinked with 1% EGDMA and the Calculated $T_{g,diel}$ Values

	A	B (K)	T_o (K)	$T_{g,diel}$ (K)
PEMA-1	9,0	504	289	332
IPN80-1	10,5	776	263	321
IPN67-1	6,3	218	283	307
IPN29-1	15,7	1165	189	252
PEA-1	14,4	909	196	249

Vogel behavior of a cooperative relaxation as in PEA-10 network, but appearing at temperatures significantly higher than in PEA-10.

Discussion

The increase in the cross-linking density of the networks produces an important decrease of the relaxation strength of the dielectric relaxation of both PEA and PEMA networks. The same result was found in PBA and PBMA networks in reference 12. The α relaxation is clearly shifted toward higher temperatures in PEA network with increasing cross-linking density and the same behavior is expected in the case of PEMA, although in this case it was not possible to separate the α and β components in the (b) region. In fact, the difference of the temperatures of the αβ relaxations of PEMA-1 and PEMA-10 at a given frequency increases with increasing temperature, but this difference is very small in the (b) and (c) regions, as seen in the Ahrrenius diagram of Figure 2. This behavior has to be interpreted in the sense that the motions originating the main and the secondary relaxations of PEMA network are not affected in the same way by the decrease of mobility produced by an increase of the cross-linking density. Because the position and strength of the β and α relaxations change differently, the merging region is affected. It seems that the effect of the α relaxation is not strong enough to appear as a separate relaxation process in the (b) region. Nevertheless, there is a significant difference in the apparent activation energy at low temperatures, in the (c) region, and at high temperatures, in the (a) region, that is a clear indication of the cooperativity characteristic of the αβ relaxation process in the (a) region. The decrease of the apparent activation energy of the αβ relaxation with increasing cross-linking density can be attributed to the participation of a smaller number of groups in the cooperatively rearranging region due to the loss of mobility, which is also responsible for the smaller ability to orient the permanent dipolar moments of the side chains in the direction of the applied electric field. It is interesting to note that in region (c), where a pure β relaxation is seen, the same features appear, a decrease of the apparent activation energy and of the relaxation strength with increasing cross-linking density. More experimental results are needed to further clarify the role of cross-links in the loss of mobility of the side chains of methacrylates. New experiments are currently in progress in a homologous series of networks with varying cross-linking density in a broad interval.

The analysis of the dielectric spectrum of the IPNs permits the study of the participation of the PEA segments in the cooperative motions of PEMA chains. The dielectric spectra shown in Figure 1c and the results shown in Figure 5a prove that in IPN29-1 there exists a phase rich enough in PEA as to present a main α relaxation nearly at the same temperature as pure PEA network. The difference between the glass transition temperatures of the two components of the IPN, PEA, and PEMA makes that at any temperature the length of cooperativity in the main dielectric relaxation is much smaller for PEA segments than for PEMA ones. This phenomenon has been called dynamic heterogeneity[22] and it is due to the fact that the length of cooperativity highly increases as the distance to the glass transition decreases. Thus, it is easier to find domains large enough to produce the main dielectric relaxation as pure PEA network, but there hardly exist domains large enough consisting only of PEMA segments able to produce the relaxation process as pure PEMA network. In fact, this happens in IPN29-1, where some of the PEA segments participate in the cooperative motions of the PEMA chains affecting the mobility in its αβ relaxation. This is also a strong support of the cooperative character of this relaxation process. The temperature shift of the αβ relaxation with respect to pure PEMA-1 network is more than 30° in this IPN. The shift of the αβ relaxation with respect to pure PEMA-1 network means that the size of the largest domains containing only PEMA segments is smaller than the length of cooperativity at its glass transition temperature, i.e., in the order of few nanometers.

The position of the relaxation processes in the (b) and (c) regions of the PEMA-rich phase could not be resolved in this IPN. Figure 5a shows the position of the α and β relaxations in the (b) relaxation region of IPN67-1 and IPN80-1, obtained by fitting the relaxation spectrum to a sum of two HN functions as explained for PEMA-1 network. It seems clear that the α relaxation shifts toward low temperatures as the content of PEA increases, as expected, but also that the temperature of the β relaxation in this region decreases. The influence of the PEA segments on the β relaxation seems to be less important at low temperatures in the (c) region. Thus, cooperativity of β relaxation in the (c) region seems to be very small, if any at all, but some cooperative character is present in the (b) region in agreement with the conclusion of Garwe et al.[4]

The behavior of the highly cross-linked IPNs is quite different. Forced compatibilization hinders phase separation but, as shown by other similar IPNs,[11,12] a broad distribution of local compositions (at the level of the volume of a CRR) must be expected. The peak of the mechanical loss tangent as a function of temperature is much broader in the IPNs than in the pure network components. This is an indication of the presence of a fluctuation in the local glass transition temperatures that is difficult to analyze quantitatively in isochronous plots. The low-temperature side of the peak must overlap with the β relaxation of PEMA segments but its influence in the overall peak is small (in the case of the dynamic-mechanical experiments at 1 Hz no merging of both relaxation is expected because of both the low frequency and low intensity of the β mechanical relaxation with respect to the main α relaxation).

As the content of PEA in the IPN decreases, a change in the shape of the Ahrrenius diagram (Figure 5b) takes place. At high PEA contents, the case of IPN23-10, the diagram is similar to that of pure PEA-10 network, with the characteristic Vogel curvature and a high slope. For lower PEA contents, IPN50-10 and IPN36-10, the behavior is more similar to that of the αβ relaxation of PEMA-10, the curvature is not clear, and the apparent activation energy is very close to that of the αβ relaxation of PEMA-10. It is noteworthy that the change of slope of the diagram from the (c) region to the (a) one is absent in these IPNs. It seems that the transition from the (a) to the (b) regimes does not take place in the IPNs when decreasing temperature. The reason for this may come from the large composition fluctuations mentioned above, that make the α relaxation, as the glass transition, to be distributed over a very large temperature interval. At any temperature, the fraction of polymer segments that contributes to the cooperative conformational motions is small, being the rest of the material distributed in regions which are frozen due to a high local PEMA content or, on the contrary, more mobile than the average due to a local composition richer in PEA. A decrease of the temperature of the transition from the (a) to (b) regime as the PEA content of the IPN increases cannot be ruled out due to a stronger temperature dependence of the α relaxation with the PEA content than that of the β relaxation, as has been described in the case of the IPNs cross-linked with 1% EGDMA. Nevertheless, it seems improbable that this fact would suffice to displace the splitting region out of the experimental frequency window.

Conclusions

The dielectric relaxation spectra of poly(ethyl acrylate)-*i*-poly(ethyl methacrylate) sequential interpenetrating polymer networks, IPNs, are presented. When the IPNs are highly cross-linked, both networks are forced to mix at the molecular level and, as a consequence, a single main dynamic mechanical or dielectric relaxation appears. On the contrary when the cross-linking density is small, the individual relaxation behavior of the component networks can be observed. The poly(ethyl methacrylate) networks with low cross-linking density present the merging of the secondary β dielectric relaxation and the main α relaxation with the same characteristics of PEMA, but this behavior changes in the highly cross-linked network in which the influence of the main relaxation in the overall behavior is smaller. It was not possible to separate the α and β components in the merging region in this network. The incorporation of the poly(ethyl acrylate) chains to the cooperative motions of the poly(ethyl methacrylate) network shifts the α and β relaxations to a different extent, which induces changes in the shape of the spectrum in the merging zone.

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References and Notes

(1) Williams, G. *Trans. Faraday Soc.* **1966**, *62*, 2091.
(2) Willams, G. *Adv. Polym. Sci.* **1979**, *33*, 60.
(3) Beiner, M. *Macromol. Rapid Commun.* **2001**, *22*, 869.
(4) Garwe, F.; Schönhals, A.; Lockwenz, H.; Beiner, M.; Schröter, K.; Donth, E. *Macromolecules* **1996**, *29*, 247.
(5) Havriliak, S.; Negami S. *J. Polym. Sci. Part C: Polym. Symp.* **1966**, *14*, 99.
(6) Schröter, K.; Unger, R.; Reissig, R.; Garve, F.; Kahle, S.; Beiner, M.; Donth, E. *Macromolecules* **1998**, *31*, 8966.
(7) Bergman, R.; Alvarez, F.; Alegría, A.; Colmenero, J. *J. Chem. Phys.* **1998**, *109*, 7546.
(8) Kahle, S.; Korus, J.; Hempel, E.; Unger, R.; Höring, S.; Schröter, K.; Donth, E. *Macromolecules* **1997**, *30*, 7214.
(9) Beiner, M.; Kahle, S.; Hempel, E.; Schröter, K.; Donth, E. *Macromolecules* **1998**, *31*, 8973.
(10) Adam, G.; Gibbs, J. H. *J. Chem. Phys.* **1965**, *43*, 139.
(11) Zhang, S.; Jin, X.; Painter, P. C.; Runt, J. *Macromolecules* **2002**, *35*, 3636.
(12) Meseguer Dueñas, J. M.; Torres Escuriola, D.; Gallego Ferrer, G.; Monleón Pradas, M.; Gómez Ribelles, J. L.; Pissis, P.; Kyritsis, A. *Macromolecules* **2001**, *34*, 5525.
(13) Pissis, P.; Kyritsis, A.; Meseguer Dueñas, J. M.; Monleón Pradas, M.; Torres Escuriola, D.; Gallego Ferrer, G.; Gómez Ribelles, J. L. *Macromol. Symp.* **2001**, *171*, 151.
(14) Li, B. Y.; Bi, X. P.; Zhang, D. H.; Wang, F. S. In *Advances in Interpenetrating Polymer Networks Vol. 1*; Klempner, D., Frisch, K. C., Eds.; Technomic: Lancaster, 1989.
(15) Fradkin, D. G.; Foster, J. N.; Sperling, L. H.; Thomas, D. A. *Polym. Eng. Sci.* **1996**, *26*, 730.
(16) Gómez Ribelles, J. L.; Monleón Pradas, M.; Meseguer Dueñas, J. M.; Torregrosa Cabanilles, C. *J. Non-Cryst. Solids* **2002**, *307*−*310*, 731.
(17) Gómez Ribelles, J. L.; Monleón Pradas, M.; Meseguer Dueñas, J. M.; Torregrosa Cabanilles, C. *J. Phys. Cond. Mater.* **2003**, *15*, S1149.
(18) Ishida, Y.; Yamafuji, K. *Kolloid Z* **1961**, *177*, 97.
(19) Tetsutani, T.; Kakizaki, M.; Hideshima, T. *Polym J.* **1982**, *9*, 305.
(20) Gómez Ribelles, J. L.; Díaz Calleja, R. *J. Polym. Sci. Polym. Phys. Ed.* **1985**, *23*, 1505.
(21) McCrum, N. G.; Read, B. E.; Williams, G. *Anelastic and Dielectric Effects in Polymeric Solids*; Dover Publications, Inc.: New York, 1991.
(22) Kumar, S. K.; Colby, R. H.; Anastasiadis, S. H.; Fytas, G. *J. Chem. Phys.* **1996**, *105*, 3777.

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