Segmental dynamics in poly(methyl acrylate)–poly(methyl methacrylate) sequential

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Abstract
The miscibility of poly(methyl acrylate)–poly(methyl methacrylate) sequential interpenetrating polymer networks (IPNs) has been studied by probing the conformational mobility of the component polymer chains. These IPNs exhibit the phenomenon of forced compatibilization. In a conventional heating differential scanning calorimetry (DSC) thermogram, the highly cross-linked IPN shows a single glass transition which covers a temperature interval of around 100 °C; in contrast, loosely cross-linked IPNs show two glass transitions. The conformational mobility in these IPNs is studied by subjecting them to isothermal annealings at temperatures in the region of the glass transition and below it. The DSC scans measured after these treatments allow one to determine the temperature interval in which the sample is out of thermodynamic equilibrium but keeps enough conformational mobility to relax during the isothermal annealing in such a way that the enthalpy loss is measurable with the sensitivity of a conventional DSC. The results allow one to reach some conclusions about the compositional distribution of the IPN on the nanometre scale.

1. Introduction

The complex features of the glass transition continue to be among the most difficult unsolved problems in solid-state physics. In the case of glass-forming materials which are non-homogeneous on the nanometric scale, the interplay between the conformational mobility and the vitrification process produces a still more complicated phenomenology, but at the same time allows one to reach conclusions about molecular dynamics from experimental studies of the glass transition process. In this sense, differential scanning calorimetry (DSC) has proved

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to be a very useful technique, being able to characterize the effect of the neighbourhood of the rearranging group on its conformational dynamics (an example is the effect of the nanometric confinement of polymers or low-molecular-weight substances, or the interfacial interaction in heterogeneous multicomponent systems). In this work we show how a detailed experimental DSC study can be used to characterize the heterogeneity of multicomponent polymer systems.

DSC has been widely used in the study of miscibility and phase separation in polymeric multicomponent systems such as polymer blends and interpenetrated polymer networks (IPNs) (see for instance [1–3] and the references cited therein). A blend which presents a single glass transition process is considered miscible. The glass transition is detected as a step in the heat capacity (or simply in the heat flow thermogram) measured in a DSC heating scan. The occurrence of two glass transitions, i.e. two steps in the thermogram of the blend, means the presence of two phases of different composition. The transition from a rubber-like state to the glassy state is produced because of the particular temperature dependence of the relaxation times of the cooperative conformational rearrangements of the polymer segments. The glass transition phenomenon can be explained in terms of Adam and Gibbs' cooperatively rearranging regions (CRR) [4]. A CRR is a region of the polymer in which a conformational rearrangement can take place without disturbing the rest of the material. The size of a CRR is a measure of the length of cooperativity of the conformational motions and is closely related to the relaxation time.

The size of the minimum CRR allowing a rearrangement increases as the temperature decreases and reaches the order of a few nanometres at the glass transition temperature [5, 6]. It can be said that this order of magnitude characterizes the sensitivity of the DSC technique for detecting phase separation in multicomponent polymer systems. If the domains of a component in a phase separated blend are larger than several nanometres, in principle, the glass transition of this component can be detected by DSC, since there are some CRRs that contain polymer segments pertaining solely to this component. Clearly, the amount of this phase in the sample also plays an important role and the technique is not sensitive below a certain mass fraction of a component in the blend.

It has been frequently reported that the temperature interval in which the glass transition takes place is significantly broader in miscible blends than in pure polymer components. This broadening can be explained by composition fluctuations in regions with sizes around that of the CRR [7–13]. Examples of extreme behaviours are the polystyrene–poly(vinyl methyl ether) blends [14], in which the glass transition covers around 70 °C, and certain IPNs such as the one reported in [15] and the one which is the subject of this work. The interpretation of these broad glass transitions is not easy. A single heating DSC thermogram does not contain enough information for one to decide whether there are a significant fraction of domains of the pure components in the blend, i.e., whether there is some degree of phase separation.

The structural relaxation, or physical ageing, process is closely related to the glass transition phenomenon. Let us consider a glass which is formed by a fixed thermal history which starts with the polymer in equilibrium at a temperature above the glass transition. At any temperature below the glass transition, the specific volume and entropy are higher than those corresponding to the equilibrium states determined by the extrapolation of the experimental values measured above the glass transition. Structural relaxation is the process undergone by the glass (at constant environmental temperature and pressure) trying to arrive to the equilibrium state. During this process the specific volume, enthalpy, and entropy decrease with time.

The structural relaxation kinetics is usually studied in DSC by subjecting a sample to a thermal history that starts at a temperature T_0 above the glass transition. The sample is first cooled at a fixed rate to a temperature T_a below, or in the region of, the glass transition, it is annealed at this temperature for a period of time t_a, and then cooled again at fixed cooling rate to
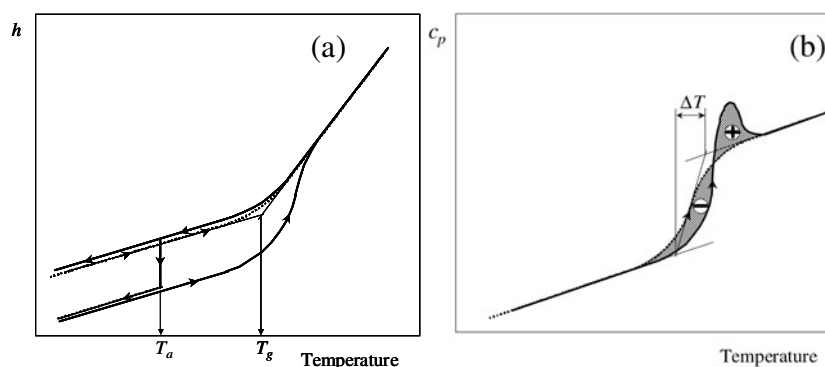
Figure 1. A sketch of the temperature dependence of the enthalpy (a) and heat capacity (b) of a polymer sample subjected to a process which starts at a temperature above T_g, includes an annealing at temperature T_a, and finishes with a heating scan at constant heating rate (solid curve). The unannealed or reference scan is represented by the dotted curve. The shadowed area is the enthalpy loss during the annealing at temperature T_a (see the text).

a low temperature T_1, and the measuring heating scan is then performed from T_1 to T_0. Figure 1 shows a sketch of the evolution of the enthalpy and specific heat during the whole experiment. The thermogram recorded during the heating scan shows the characteristic peak in c_p or in the measured heat flow, whose position and height depends on the annealing temperature and time. The thermogram measured after a cooling from T_0 to T_1 with no annealing (the reference scan) is also represented in figure 1(b). It can be shown that the enthalpy increment suffered by the sample during the isothermal annealing at temperature T_a for a time t_a is equal to the area between the $c_p(T)$ curve measured after this treatment and the curve determined in the reference scan, $c_{p,ref}(T)$ [16]. This area is represented in figure 1(b).

The existence of the structural relaxation process is a proof that conformational motions are possible in the glassy state, although their rates are quite different from those in the rubber-like state.

The kinetics of the structural relaxation process in miscible polymer blends shows significant differences with respect to that of the pure polymer components. Composition fluctuations in the blend can play an important role in the conformational mobility in multicomponent polymer blends [7, 17, 18]. In the case of blends of two polymers with glass transition temperatures close to each other, the isothermal annealing in the glassy state allows one to detect immiscibility even if a reference scan shows a single heat capacity step in the temperature range of the glass transition [19, 20].

Non-cross-linked poly(methyl methacrylate) (PMMA) and poly(methyl acrylate) (PMA) are miscible only if the molecular weight of the components is very small, below $M_n = 5000$. Blends of higher molecular weight PMMA and PMA present two glass transitions, at least in the 50/50 wt% blend [21].

Dynamic mechanical experiments [22] and temperature-modulated differential scanning calorimetry (TMDSC), experiments [23] showed the forced compatibilization phenomenon [24, 25] in PMA–i–PMMA (where 'i' stands for 'interpenetrated') IPNs. If the amount of cross-linking agent in the first network is low, its full swelling in the methyl methacrylate (MMA) monomer allows the formation of PMMA networks in domains large enough to present an independent glass transition process. Since the mass fraction of the PMMA network in the IPN is large and a continuous network of PMA is formed in the first step of the sequential polymerization, the resulting IPN probably consists of two co-continuous phases with a large interfacial surface. The same behaviour was found in poly(butyl acrylate)-

poly(butyl methacrylate), PBA–i–PBMA, sequential IPNs with varying PBA/PBMA ratio. When the first network (PBA) was loosely cross-linked, phase separation occurred in the IPNs at any PBMA content [26].

In contrast, when the amount of cross-linking agent in the first network is large, its expansion when immersed in MMA is quite limited. The final mass fraction of the PMMA network in the IPN is smaller and when the PMMA network grows it has no free space to form a separate domain but is forced to interpenetrate the PMA network at the molecular scale. As a consequence a permanent homogeneous mixture is formed. This is the phenomenon of so-called forced compatibilization.

The aim of this work is to show how the study of the structural relaxation process in multicomponent polymer systems using conventional DSC can provide detailed information about miscibility.

2. Experimental details

Sequential interpenetrating polymer networks, IPNs, were prepared by stepwise polymerization using 0.2 wt% benzoin as the photoinitiator. The PMA network was first polymerized with an amount of ethyleneglycol dimethacrylate (EGDMA) as the cross-linking agent, ranging between 0.1 and 10% by weight. A sheet of around half a millimetre thick was obtained. The rest of the monomer and other low-molecular-weight substances were extracted by boiling for 24 h in ethanol. The sheet was dried *in vacuo* to a constant weight and immersed in MMA monomer containing EGDMA in the same proportion as the PMA network and the photoinitiator. The swollen sample was exposed to ultraviolet light to polymerize the PMMA network. The IPN was again extracted by boiling in ethanol and dried *in vacuo*. Since the degree of swelling of the PMA network in MMA is highly dependent on its cross-linking density, the final composition of the IPN depends on the amount of EGDMA as well. Thus, the weight fraction of PMMA in the IPN was 0.80, 0.71, and 0.49 for the 0.1, 1, and 10% contents in EGDMA, respectively. These three IPNs will be called IPN01, IPN1, and IPN10 respectively. Analogously the pure PMA and PMMA networks will be called PMAXX or PMMAXX, XX being the amount of cross-linking agent used in the polymerization process. All the IPNs were optically transparent.

A Pyris 1 Perkin-Elmer calorimeter was used in the DSC experiments. All the thermal treatments were carried out in the calorimeter. Previous to the heating scan, the sample was subjected to a thermal treatment that started at 180 °C for the IPNs and PMMA samples and at 90 °C in the case of PMA networks. The sample was first cooled at 40 °C min^{-1} to the annealing temperature T_a, annealed at this temperature for 300 min, and cooled again at 40 °C min^{-1} to −40 °C in the case of PMA networks and the IPNs or to 50 °C in the case of PMMA networks. The heating scan followed at the heating rate of 10 °C min^{-1}. The thermogram measured for unannealed samples (cooled at 40 °C min^{-1} from the highest to the lowest temperature of the scan) will be called the reference scan. No absolute values of $c_p(T)$ were calculated; instead, the normalized heat flow $\dot{Q}/m\dot{T}$, which has heat capacity units, was determined. Nevertheless, the difference between the thermogram measured after annealing and the reference scan is equal to the difference between the specific heat capacities after annealing and the reference one, $(\dot{Q} - \dot{Q}_{ref})/m\dot{T} = c_p - c_{pref}$.

3. Results

The reference scan measured for the IPN01 shows two glass transitions (figure 2(a)), one occurring in the same temperature interval as the glass transition of the pure PMA01 network
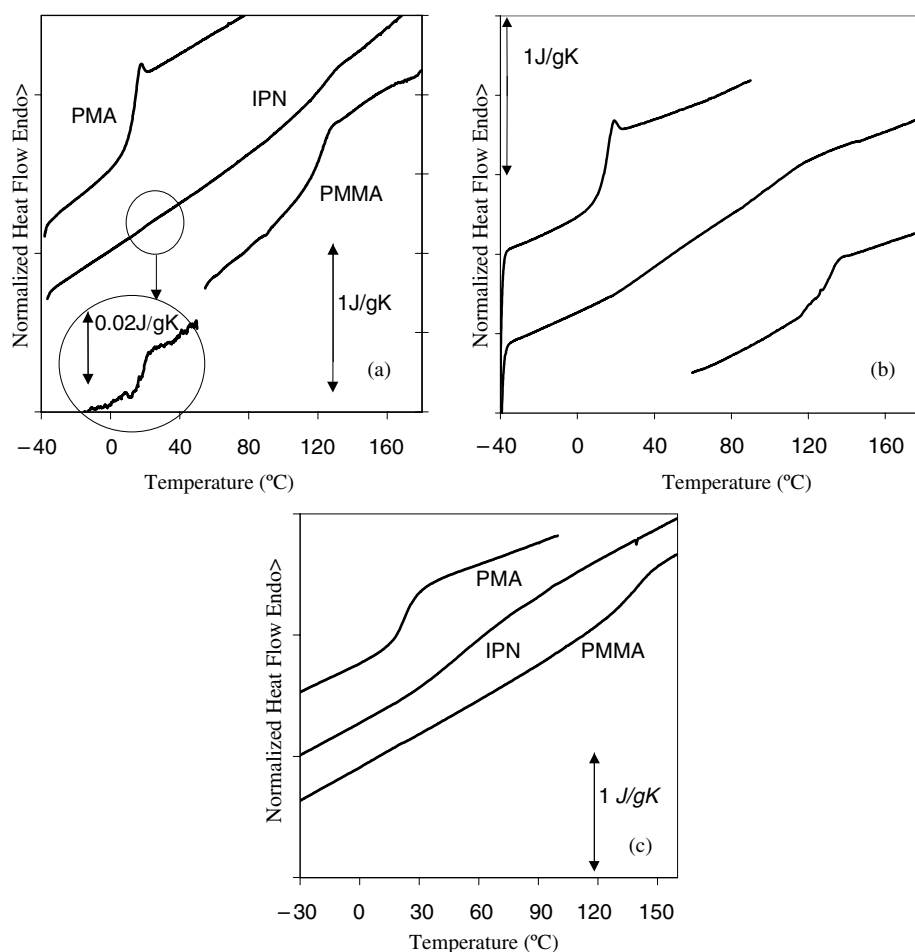
Figure 2. Thermograms measured for heating scans of the networks cross-linked with 0.1% EGDMA (a), 1% EGDMA (b), and 10% EGDMA (c). The samples were previously cooled at 40 °C min^{-1} from a temperature well above the glass transition.

($T_g = 13$ °C for PMA01 and $T_{g1} = 19$ °C for the low-temperature transition of IPN01). The high-temperature glass transition of IPN01 occurs in the same temperature region as in PMMA01 ($T_{g2} = 122$ °C for IPN01 and $T_g = 123$ °C for PMMA01). It is noteworthy that the c_p-increment in the low-temperature glass transition is very small, only 0.01 J g^{-1} K^{-1}, much smaller than what would correspond to the fraction of PMA in IPN01 estimated as the product of the Δc_p for PMA01 and the mass fraction of the PMA network in IPN01, which is 0.09 J g^{-1} K^{-1}.

At the other side of the series, a single, extremely broad glass transition can be seen in the thermogram corresponding to the reference scan of IPN10 (figure 2(c)). This transition covers around 100 °C—nearly the complete temperature interval between the glass transitions of PMA10 and PMMA10 networks.

The results for IPN1, PMA1, and PMMA1 show an intermediate behaviour (figure 2(b)). Two glass transitions can be seen in IPN1, but at temperatures closer to each other than those of the pure component networks. For this IPN it is very difficult to determine the glass transition

temperatures because it is impossible to separate the two specific heat steps from each other. Roughly speaking, it can be said that the low-temperature step is around 40 °C while the higher-temperature one is around 90 °C.

To better understand this behaviour, all the samples were subjected to thermal treatments that included an isothermal annealing for 300 min at different temperatures (every 10 °C) ranging between −20 and 140 °C in the case of the IPNs, between −20 and 30 °C for the PMA networks, and between 50 and 140 °C for the PMMA networks. After each treatment a heating thermogram was recorded and a reference scan followed with no change in the position of the sample and reference pans in the DSC holder. These two thermograms were used to calculate the difference between the heat capacity curves $c_p(T)$ for the two thermal treatments, $[c_p - c_{p,ref}](T)$. As representative examples of the results obtained for pure network and the IPNs, figure 3 shows $[c_p - c_{p,ref}](T)$ obtained for PMA10, IPN01, and IPN10 networks. These curves show the peak characteristic of the structural relaxation process suffered by the material during the annealing previous to the measuring scan.

4. Discussion

The phenomenology of the structural relaxation process is quite complex and has been described in the literature in great detail (see for instance [27–29]). Briefly, it can be said that the peaks appearing in the thermograms of annealed samples are highly dependent both on annealing temperature and time. There are two different situations. When the annealing temperature is low, below the range in which the glass transition takes place, the thermogram measured on heating shows a peak superposed on the low-temperature side of the transition. These peaks can be called sub-T_g peaks. Their main characteristic is that the difference $[c_p - c_{p,ref}](T)$ is positive over the whole temperature range of the measuring scan. This kind of behaviour can be seen for instance in the PMA10 sample annealed at temperatures below or equal to 0 °C (figure 3(a)). When the annealing temperature is close to or even inside the temperature interval in which the glass transition takes place, the onset of the transition in the heating thermogram shifts to higher temperatures as the annealing time increases, as shown in the sketch of figure 1(b). The result is that the difference $[c_p - c_{p,ref}](T)$ takes on negative values at low temperatures and then positive ones in the range where the enthalpy of the sample rapidly approaches the equilibrium values on heating (figure 1(a)). A clear example is the thermogram measured for PMA10 after annealing for 300 min at 10 °C (figure 3(a)).

The presence of the peak in the heating thermogram after annealing at the temperature T_a is a proof that some evolution of the enthalpy to approach equilibrium took place during this isothermal stage. In fact the value of the enthalpy increment during the isothermal period is the area under the curve $[c_p - c_{p,ref}](T)$. Thus, the experimental result detects that at the temperature T_a some conformational rearrangements are possible in the material. Obviously the approach to equilibrium is quicker at a higher temperature, and for a fixed annealing time the peak height rapidly decreases as the temperature goes down below the glass transition. On the other hand, when the temperature is high, within the region of the glass transition, the enthalpy at the beginning of the isothermal annealing is not very different from the value corresponding to the equilibrium state at that temperature. Now the rate of the structural relaxation process is high but the increment of enthalpy produced, Δh_a, is small because the material is close to equilibrium during the whole process. On further increasing the annealing temperature, a value is attained for which the difference between the thermogram measured on the annealed sample and the reference scan disappears, which indicates that at the beginning of the isothermal stage the sample was already in equilibrium.
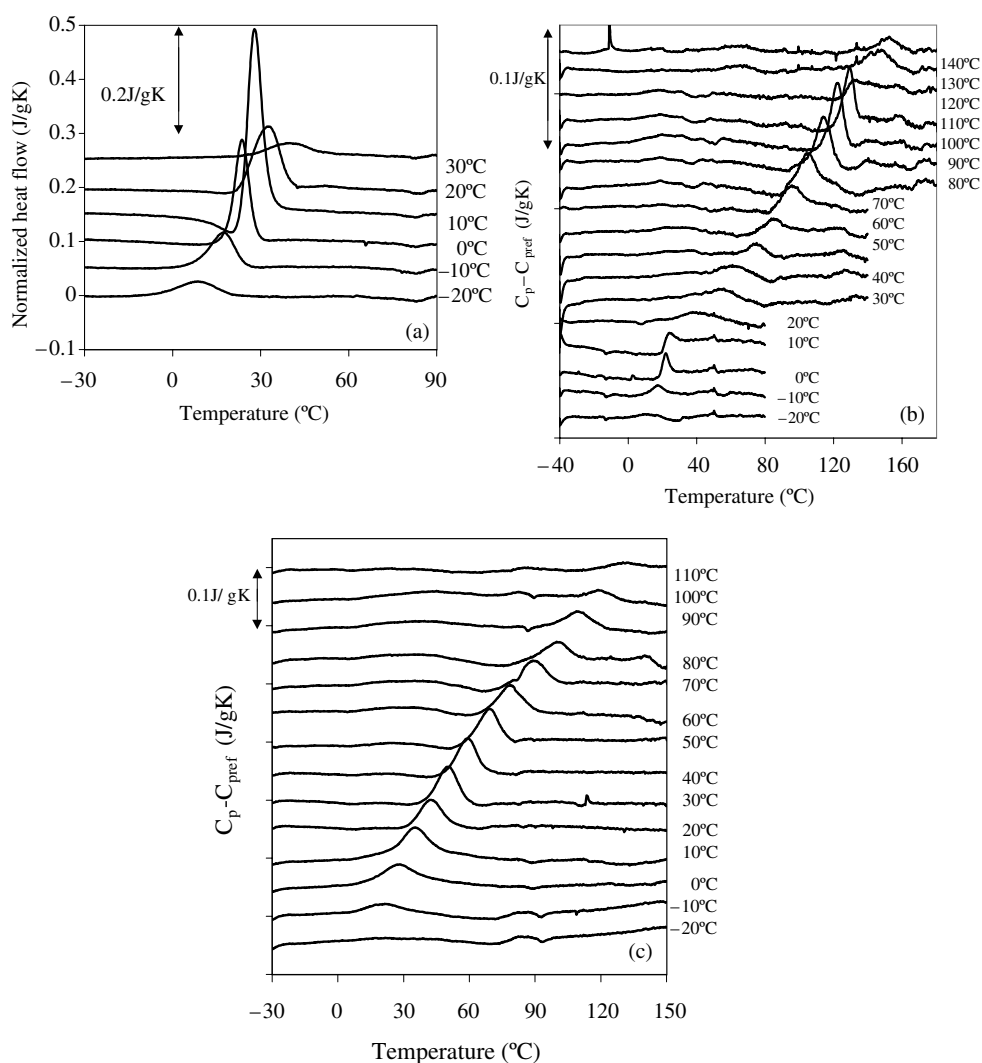
Figure 3. The temperature dependence of $[c_p - c_{p,ref}]$ calculated for PMA10 (a), IPN01 (b), and IPN10 (c) networks from the thermograms measured after annealing for 300 min at the temperature shown on the graph. The curves have been vertically shifted for the sake of clarity. The annealing temperature for each curve is shown in the graph.

Thus, the areas under the peaks of curves $[c_p - c_{p,ref}](T)$ such as those represented in figure 3 allow one to define an interval of temperatures in which the conformational rearrangements take place in the glassy state at an appreciable rate.

Figure 4(a) shows the enthalpy loss during the isothermal annealing of PMA networks as a function of the annealing temperature. It can be observed that the PMA01 network remains in thermodynamical equilibrium during cooling from high temperatures to around 20 °C, as proved by the fact that if the sample is annealed at temperatures T_a above 20 °C, immediately after cooling from equilibrium to T_a, no evolution of the enthalpy is detected. The difference between the thermogram measured after annealing at any temperature immediately below 20 °C and the reference scan is significant, and allows the calculation of the enthalpy decrease
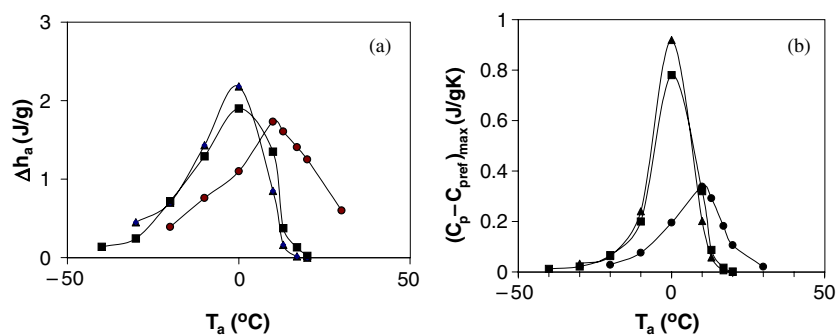
Figure 4. (a) Enthalpy loss and (b) maximum value of the $[c_p - c_{p,ref}](T)$ curve measured during the isothermal annealing for 300 min against the annealing temperature in PMA networks polymerized with 0.1 (▲), 1 (■), and 10 (●) wt% of EGDMA. The curves are only intended as a guide to the eye.

during the isothermal approach to equilibrium. This value of the temperature is the same as that at which the trace of the heating thermogram returns to the equilibrium line after the small overshoot shown on the high-temperature side of the glass transition (figure 2(a)). This means that the structural relaxation process occurs not only at temperatures below T_g but also at any temperature within the whole temperature interval of the transition measured in the heating scan.

The maximum value of Δh_a is found for an annealing temperature around 0 °C, i.e., 13 °C below the enthalpic glass transition temperature. At lower annealing temperatures the value of Δh_a decreases, being measurable until around -40 °C, more than 50 °C below T_g. Below that temperature, conformational rearrangements are probably still possible, but they take place on a timescale larger than that of the experiment.

The plot of figure 4(a) is obviously dependent on the annealing time of the experiments. As the time increases, the measured values of Δh_a increase. This increase should be small for the highest annealing temperatures if the sample arrives at states very close to equilibrium during the annealing period. In this case the value of Δh_a becomes independent of the annealing time. At lower annealing temperatures, in the region of the maximum shown in figure 4, there is a large time interval in which Δh_a depends linearly on the logarithm of time [30]. The slope of Δh_a versus $\log t_a$ is temperature independent in this region and, as a consequence, a change in the annealing time does not modify the temperature of the maximum in figure 4. The T_a-interval in which the structural relaxation is detectable extends on the low-temperature side as the annealing time increases, but due to the sigmoidal form of the Δh_a versus $\log t_a$ curve, no great effects are expected unless the annealing time of the experiment is increased by several decades.

Something very similar happens in the other PMA networks. The increase in the cross-linking density produces a shift of the Δh_a versus T_a curves towards higher temperatures and a broadening of the interval of the structural relaxation, in a manner parallel to the broadening of the glass transition interval measured in the reference scan shown in figure 2. A similar behaviour was found in the PMMA networks.

The accurate determination of Δh_a is difficult when its value is small, as happens in the case of the broad glass transitions shown by the IPNs and polymer blends. But, as shown in figure 4(b), the height of the peak appearing in the $[c_p - c_{p,ref}](T)$ plot (we will call it $[c_p - c_{p,ref}]_{max}(T_a)$) can be used for characterizing the temperature interval in which

the structural relaxation takes place on the timescale of DSC measurements. The annealing temperature at which $[c_p - c_{p,ref}]$ goes through the maximum is not the same as that at which the enthalpy loss does, because for these values of the annealing temperature the negative part of the $[c_p - c_{p,ref}](T)$ curve is quite important. The temperature of the maxima of $[c_p - c_{p,ref}](T)$ is always higher than the annealing temperatures, but the difference between them is a complicated function of the annealing temperature and time. The comparison of the plots in figures 4(a) and (b) allows one to use the latter at least for a qualitative analysis. This is what will be done in the case of the PMA–i–PMMA IPNs.

The results obtained for the highly cross-linked IPN (figure 3(c)) show that conformational rearrangements are possible in the IPN over a very broad temperature interval. The annealing at temperatures ranging between −20 and 100 °C produces in the $[c_p - c_{p,ref}](T)$ trace a peak with a maximum at a temperature around $T_a + 20$ °C, as shown in figure 5(c). The temperature of the maximum in the pure networks tends to be independent of T_a when T_a is high. It is noteworthy that while the glass transition interval measured in the reference scan covers nearly 100 °C, the peaks measured after annealing are relatively narrow, covering a temperature interval of around 20 °C. It is quite apparent that the structural relaxation is significant at very low temperatures, close to those corresponding to the structural relaxation of the PMA10 network, and the maximum shown in the $[c_p - c_{p,ref}]_{max}(T_a)$ is shifted towards the one corresponding to the PMA10 network.

The results shown in figure 5(a) for IPN01 clearly show the presence of two peaks in the representation of T_{max} against the annealing temperature, proving that the IPN consists in two distributions of regions with compositions rich in PMA and in PMMA respectively. Again, it can be seen that the temperature interval of the mobility of PMMA-rich regions shifts towards lower temperatures while the one corresponding to PMA-rich regions appears around 0 °C as in the PMA01 network. Another interesting point is the fact that small but measurable peaks in $[c_p - c_{p,ref}](T)$ appear in IPN01 at temperatures between 30 and 60 °C. This is a temperature interval in which neither PMA01 nor PMMA01 show conformational activity during the annealing, in the case of PMA01 because it is in equilibrium and in the case of PMMA01 because this temperature interval (30–60 °C) is too low. This result shows that although two glass transitions are clearly shown in the reference DSC scan, a significant proportion of each component material is in regions in which the other component is present. This can explain the difference between the increment of the heat capacity in the low-temperature glass transition of IPN01 and what could be expected from the weight fraction of PMA in the sample. This feature has been found in other multicomponent polymeric systems [31, 32], such as polymer blends and semicrystalline polymers. The phenomenology of these materials can be studied with more insight following this methodology.

The behaviour of IPN1 (figure 5(b)) is intermediate between those of IPN01 and IPN10. A region rich in PMMA seems to relax at temperatures close to but below those of the PMMA1 network, but the height of the relaxation peaks continuously increases with T_a between −20 and 80 °C.

The results reported in this work fully agree with those obtained with TMDSC [23] in the same system. In TMDSC, the characterization of the segmental dynamics is based on the measurement of the evolution of the complex heat capacity during a temperature scan across the glass transition. Segmental motions are monitored on the timescale corresponding to the period of modulation, typically 10–100 s. In the case of the structural relaxation experiments performed in this work, the segmental dynamics is probed at longer relaxation times.

In terms of the Adam–Gibbs CRRs, it can be said that a broad interval of the glass transition is produced by a distribution of compositions of the different regions in which the conformational rearrangement takes place. If we accept that the size of these regions is around a
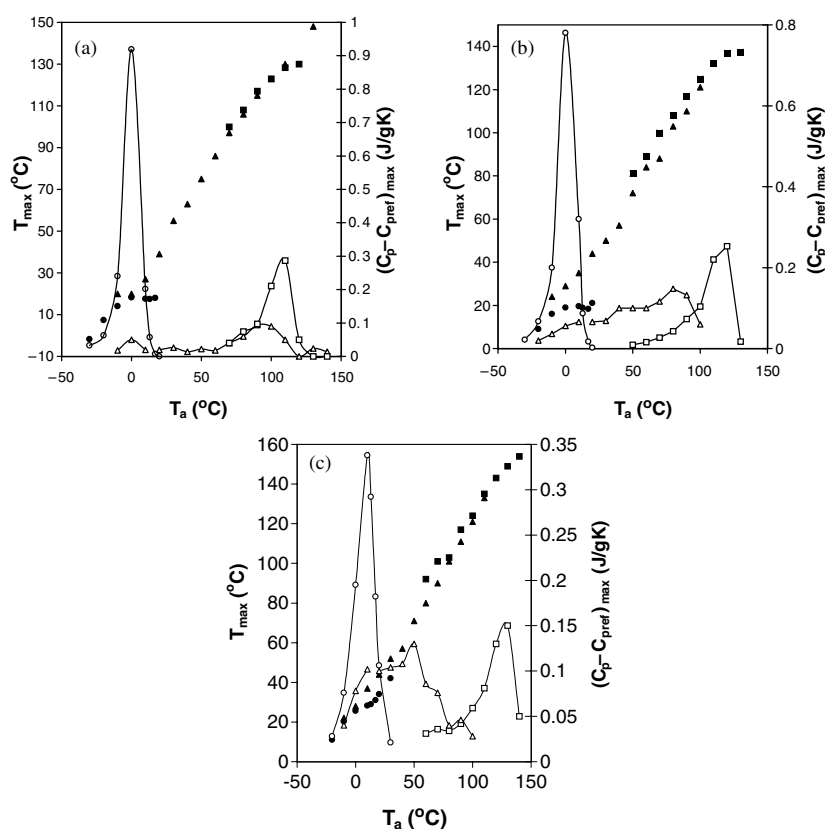
Figure 5. The temperature (solid symbol) and height (open symbols) of the maxima of $[c_p - c_{p,ref}](T)$ for the PMA (●), PMMA (■), and the IPNs (▲) cross-linked with 0.1 (a), 1 (b), and 10 (c) wt% of EGDMA. In the case of the IPNs, the values of $[c_p - c_{p,ref}](T)$ represented have been multiplied by two. Curves are only guides to the eye.

few nanometres, this means that any region with this size contains segments of both component chains, but there is a broad range of compositions within regions of this dimension. When the sample is cooled from equilibrium to the annealing temperature, the PMA-rich regions can rearrange at a higher rate than the PMMA-rich regions. In fact there is a broad range of conformational mobilities. In IPN10, the fact that there is almost no structural relaxation at temperatures above 100 °C means that there are no regions (always with dimensions of the order of the length of cooperativity) containing only PMMA segments. In contrast, there is a significant evolution of the enthalpy on annealing at −20 °C, which means that a number of the CRRs contain only PMA, or, at least, are very rich in this component.

The fact that the PMA network is first polymerized in the IPN can play a role in the spatial distribution of the domains of different composition. The average number of monomeric units between cross-links ν can be estimated from the value of the elastic modulus at temperatures above the glass transition in the rubbery plateau region, E'_e, using the theory of rubber elasticity [33]. The phantom model yields

$$\nu = \frac{3\rho RT}{M_m E'_e}$$

where ρ is the density, R is the gas constant, and M_m is the molecular weight of the monomeric unit. Using Ferry's structure length for PMA as $a = 0.65$ nm [34], the mesh size of the PMA network can be calculated as $d_E = a\nu^{1/2}$. When this network is swollen in MMA to form the second network, the mean distance between cross-links increases to a value d_{ES} given by the equation $d_{ES} = \phi^{1/3}d_E$, where ϕ is the volume fraction of PMA in the swollen network. In the case of the IPNs of this work, d_{ES} was 15, 6, and 2.5 nm for IPN01, IPN1, and IPN10 respectively. This dimension gives a rough estimate of the order of magnitude of the space available for the domains of PMMA in the IPN, and shows that in the case of IPN10 the size of the pure PMMA domains would be anyway of the order of magnitude of the length of cooperativity at the glass transition temperature [5, 6].

In addition to the discussion of the above paragraph, in order to connect the compositional heterogeneity and the distribution of glass transitions one must consider the concept of dynamic heterogeneity proposed by Kumar *et al* [9] in the analysis of the main dielectric relaxation process of a heterogeneous polymer blend. They showed that the isothermal relaxation spectrum of such systems may show the dielectric main relaxation corresponding to the low-T_g component and, in addition, another relaxation process corresponding to the average composition of the blend. The origin of this behaviour is the fact that the length of cooperativity decreases with the difference between the temperature of the experiment and the glass transition temperature, according to the equation proposed by Donth [34]:

$$\xi^3 = d_a^3 \left[\frac{T_\infty(\phi)}{T - T_\infty(\phi)} \right]^2$$

where ξ is the length of cooperativity, $T_\infty(\phi) = T_g - c_2$ (c_2 is the Williams–Landel–Ferry coefficient [35]), ϕ is a measure of the composition of the blend within the CRR, and d_a is a constant. At the temperature of the experiment the length of cooperativity corresponding to the low-T_g component is smaller than that corresponding to the average composition, since the difference $T - T_\infty(\phi)$ is greater in the former. Thus, small aggregates of the more mobile component are able to produce a main relaxation in addition to that of the average composition.

In the case of the glass transition the situation is not the same, since the process is not isothermal. Nevertheless it has been shown, using a very simple model, that something similar may happen [23]. As a rough approximation, we will accept in this discussion that the glass transition of a small domain of the material with composition ϕ takes place during the cooling when the length of cooperativity $\xi(\phi)$ reaches a certain critical value ξ_c. A distribution of T_g comes thus from the composition fluctuation. Think, as a simple model, of a distribution of domains of the pure components A and B with $T_{gA} \gg T_{gB}$ and with a distribution of sizes. The aggregates of the high-T_g component are easily plasticized by the presence of the chains of the low-T_g component at the interfaces; thus only domains of component A with dimensions significantly larger than ξ_c vitrify at the temperature T_{gA}. In contrast, if the mean composition $\tilde{\phi}$ yields a glass transition $T_{g\,average}$, at this temperature the length of cooperativity corresponding to the component B can be much smaller than ξ_c if $T_{g\,average} - T_{gB}$ is large. Thus, the presence of very small domains of component B leads to a significant part of this material being in the liquid state at the temperatures corresponding to the glass transition of the average composition. These aggregates vitrify at lower temperatures, close to T_{gB}.

5. Conclusions

Conformational rearrangements take place in polymeric systems on the timescales of conventional DSC in the temperature range in which the glass transition takes place and in the interval immediately below it, in the glassy state.

DSC experiments conducted on samples subjected to thermal histories that include isothermal annealing at different temperatures can be used to characterize this temperature interval in multicomponent or multiphase polymeric systems such as polymer blends, IPNs, and semicrystalline polymers. This information provides a deep insight into the miscibility of such systems, allowing one to understand the dimensional scales in which segments of the different components participate together in conformational rearrangements.

Forced compatibility can be achieved in PMA–i–PMMA IPNs by means of a high cross-linking density of the first network. In the compatibilized IPNs the glass transition takes place over a broad temperature interval. Structural relaxation takes place at any temperature between -40 and $100\,^\circ$C in this IPN. When comparing this interval with the corresponding ones for the pure polymer network components, it is shown that no conformational rearrangements take place in regions consisting of pure PMMA. A great part of the material relaxes in a temperature region above but not far from the temperatures at which the pure PMA network relaxes. Many of the conformationally rearranging regions contain a significant number of PMA chain segments.

Loosely cross-linked networks present phase separation on the nanometre scale, but even in this case the temperature region in which structural relaxation takes place shows that while some rearranging regions consist of pure PMA, almost no pure PMMA is present even if the overall weight ratio of PMA to PMMA is 20/80. This feature is connected to the concept of dynamic heterogeneity.

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