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Forced compatibility in poly(methyl acrylate)/poly(methyl methacrylate) sequential interpenetrating polymer networks

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Abstract

The aim of this work is to study the miscibility of poly(methyl acrylate)/poly(methyl methacrylate), (PMA/PMMA), sequential interpenetrating networks, (IPNs), as a function of the crosslink density using dielectric and dynamic-mechanical techniques. The PMA/PMMA system is immiscible and so, for low crosslink densities, phase separation appears, as detected by the occurrence of two clearly differentiated main dynamic-mechanical relaxation processes corresponding to the two components. If crosslink density is high enough, a homogeneous IPN can be obtained, achieving a forced compatibilization of both networks. The IPN crosslinked with 10% ethyleneglycol dimethacrylate shows a single main dynamic-mechanical relaxation process. Only the α main relaxation process appears in the PMA networks within the temperature range (−60 to 200°C) of the experiments conducted in this work. The dielectric relaxation spectrum of PMMA networks shows the secondary β relaxation followed by a small α relaxation partially overlapped with it. In the IPNs, both the main relaxation processes tend to merge into a single one and the dielectric spectrum shows a single peak that mainly corresponds to the secondary relaxation of the PMMA.

Keywords: Interpenetrating polymer networks; Dielectric relaxation; Dynamic-mechanical relaxation

1. Introduction

Polymer miscibility is determined by the composition dependence of the free energy of the blend due to thermodynamic equilibrium and stability criteria. The same physical laws apply in the case of polymer networks, but here some additional features have to be considered because the constraint imposed by crosslinks play an important role. Swelling a polymer network of component A in the monomer of component B and then polymerizing the second network forms a sequential interpenetrating network (IPN). The phase morphology in sequential IPNs is affected by the miscibility of the polymer components, composition, crosslink density, polymerization sequence (i.e. which polymer network is polymerized first as a pure network and which one is polymerized in presence of the other component) and the kinetics of polymerization and phase separation. It is possible that an IPN prepared with polymers that form a compatible blend presents phase separation and vice versa (all these features are described in Refs. [1,2]).

If polymers A and B are immiscible and the crosslink density of A is small, i.e. the number of monomer units between crosslinks 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. However, if the crosslinking density of A is high, the positions of the A chains will hardly be changed and the B network will grow interpenetrating the existing network A. Thus a homogeneous IPN can eventually be obtained, achieving a forced compatibilization of both the polymers [3,4].

The conformational rearrangements of the polymer chains around and above the glass transition temperature is a co-operative process that involves polymer segments pertaining to different polymer chains which move simultaneously or sequentially. The region in which a co-operative rearrangement takes place without disturbing the rest of the material is called a conformational rearrangement region [5]. The size of this region can be characterized by means of a length of co-operativity, which is around few

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nanometers at the glass transition temperature T_g [6,7] and decreases as the temperature increases above T_g. In the case of a polymer blend or an IPN, the study of the co-operative conformational mobility is an important tool to characterize the miscibility. It can be proved experimentally if the conformational motions involve polymer segments pertaining all of them to the same component or, on the contrary, if in any rearrangement segments of both polymer chains participate. In the former case, the blend contains phases of the individual components and the size of their domains is at least in the order of magnitude of the length of co-operativity. In the latter case, the blend is homogeneous although the presence of concentration fluctuations cannot be discarded.

Conformational mobility can be studied by dynamic-mechanical analysis (DMA), and dielectric relaxation spectroscopy (DRS). The analysis of the main relaxation process (or processes) of the IPN will be used in this work to characterize the miscibility of the system. In comparison with differential scanning calorimetry (DSC), DMA and DRS techniques allow to get information about the mobility at temperatures higher than DSC, and hence at temperatures at which the length of co-operativity is smaller.

The effect of blending on the local motions that originate the secondary relaxation is not well understood. There is some information about the secondary β relaxation of poly(methyl methacrylate), PMMA. This relaxation process appears at lower temperatures and with a lower apparent activation energy in miscible blends of PMMA with bisphenol-A polycarbonate [8]. It is also clearly shifted towards lower temperatures in polyurethane/PMMA IPNs with respect to pure PMMA [9]. Nevertheless, in miscible blends of PMMA with poly(vinylidene fluoride) the β relaxation appears exactly in the same position as in pure PMMA [10].

The aim of this work is to study the phenomenon of forced compatibility in poly(methyl acrylate)/poly(methyl methacrylate), PMA/PMMA, sequential IPNs by dielectric and dynamic-mechanical techniques and its effects on the conformational motions of the polymer chains.

2. Experimental

Sequential interpenetrating polymer networks, IPNs, were prepared by block polymerization using a 0.13 wt% of benzoin (Scharlau 98% pure) as photoinitiator. PMA (monomer from Aldrich 99% pure), network was first polymerized with an amount of ethyleneglycol dimethacrylate, EGDMA (Aldrich 98% pure), as a crosslinking agent, ranging between 0.1 and 10% relative to monomer weight. A sheet of around half-millimeter thick was obtained. This sheet was immersed in a solution of methyl methacrylate monomer, MMA (Aldrich 99% pure), containing EGDMA in the desired proportion and the photoinitiator. The swollen sample was exposed to ultraviolet light to polymerize the PMMA network. Low molecular weight substances were extracted from the IPN by boiling in ethanol for 24 h and then drying it in vacuum to a constant weight.

The degree of swelling of the PMA network is highly dependent on its crosslinking density; as a consequence, the final composition of the IPN depends on the amount of EGDMA as well. Thus, for example, the weight fraction was 0.75, 0.71, 0.61, and 0.49 for the 0.1, 1, 5, and 10% content in EGDMA in both networks forming the IPN.

DRS was conducted in a GENERAL RADIO 1689M dielectric analyzer in the frequency range between 90 and 10^5 Hz, using a Novocontrol BDS 1300 cell thermostatised between 10 and 200°C within 0.1°C.

DMA was carried out at a heating rate of 1°/min in a Seiko DMS210 instrument from −60 to 200°C at frequencies of 0.1, 1 and 10 Hz.

3. Results and discussion

The dynamic-mechanical relaxation spectrum of PMMA networks shows a single maximum, which corresponds to the main relaxation, or α process. The temperature of the maximum in the loss tangent, measured at 1 Hz, henceforth called $T_{\alpha \mathrm{DMA}}$, increases with the content of crosslinking agent, 144, 150, 162°C for PMMA networks containing EGDMA in proportions 1, 5, 10%, respectively. Similar features can be observed in the case of the PMA network, but now the main relaxation process appears at 36, 41 and 45°C for the same EGDMA contents. The DRS shows the same trend for the temperature of the main relaxation, both in the PMA and PMMA networks, with the amount of the crosslinking agent. Nevertheless, the dielectric spectra of the PMMA network shows the secondary β relaxation followed by a small α relaxation partially overlapped with it (Fig. 1). This is a great handicap in the dielectric study of polymethacrylates systems. The position of the β relaxation is independent of the amount of crosslinking agent in the network. This is interpreted in the sense that β relaxation is related to residual mobility, and it depends only on the size of the side group, in this case the easily orientable methyl group. This is clearly seen, for example, in the PMA networks used in this work (results not shown).

Dynamic-mechanical experiments performed on IPNs show that as the amount of the crosslinking agent is raised (Fig. 2), the two main DMA relaxations of PMA and PMMA merge into a main relaxation process at a temperature ranging between those of the pure components networks. This is an indication that the crosslink density has forced both networks to interpenetrate homogeneously. The single peak of the loss tangent has two overlapped components that are easier to identify for low contents of EGDMA. For the IPN containing 5% of crosslinking agent (Fig. 3), the values of $T_{\alpha \mathrm{DMA}}$ corresponding to the regions richer in PMMA is around 30°C below that of the pure PMMA network; on the contrary the $T_{\alpha \mathrm{DMA}}$ of the regions richer in PMA is more than

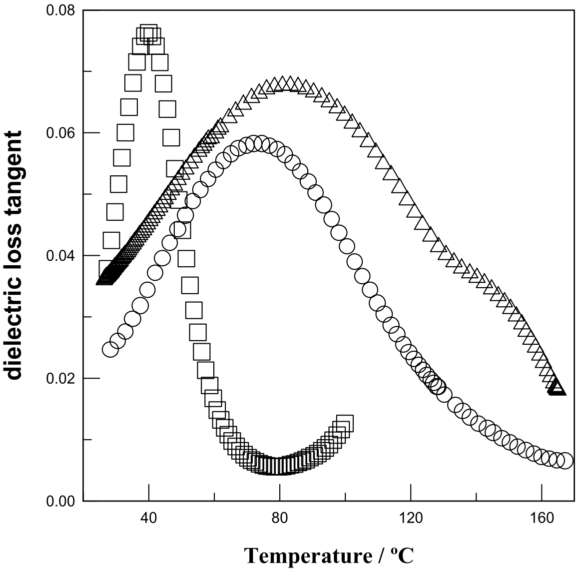

Fig. 1. Temperature dependence of the dielectric loss tangent measured at 1 kHz in the PMA (□) and the PMMA (△) networks crosslinked with 5% of EGDMA and the PMA/PMMA IPN in which both networks are crosslinked with 5% of EGDMA (●).

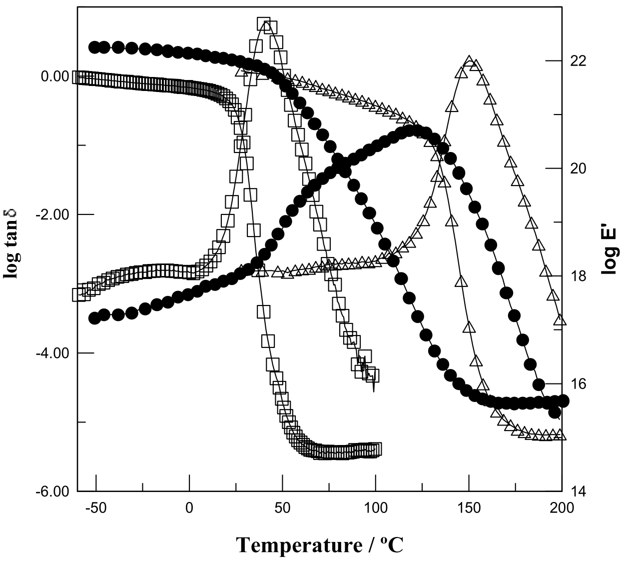

Fig. 3. Dynamic-mechanical relaxation spectra measured at 1 Hz in the PMA(□) and PMMA (△) networks crosslinked with 5% of EGDMA and the PMA/PMMA IPN in which both networks are crosslinked with 5% EGDMA (●).

20°C higher than that of the pure PMA network. These features show that in these regions both components participate in the co-operative conformational motions of the polymer chains. A unique broad peak is appreciated (Fig. 2) in the IPN containing 10% EGDMA. These results allow to conclude that any region with size in the order of nanometers contains both PMA and PMMA chain segments that participate simultaneously in the co-operative conformational motions.

It is known that the forced compatibilization of the IPN mainly depends on the crosslinking density of the network polymerized first [3]. This is clearly seen in the system studied in this work. Fig. 4a shows the mechanical loss tangent in a series of IPNs in which the PMMA network was polymerized with 10% EGDMA while the crosslinking density of PMA network (the one polymerized first) was varied from 0.1 to 10%. Although different crosslinking contents involve different composition of the IPN, thus changing the intensity of the relaxations peaks, it is clearly observed that the more compatibilized IPN is the one in which the PMA network contains the highest content of crosslinking agent. Keeping constant the crosslink density of the PMMA network, the crosslinking content of the network I is the critical factor in the miscibility of both networks (Fig. 4a). Fig. 4b shows how, on the contrary, if the crosslink density of the PMA network is low, even a 10% content of crosslinker in the PMMA network is not able to produce a homogenous system.

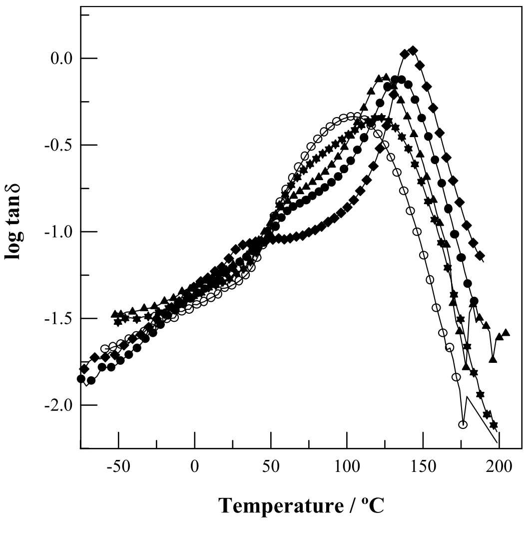

Fig. 2. Temperature dependence of the mechanical loss tangent for PMA/PMMA IPNs with several contents of EGDMA (equal in both networks): 0.1% (◆), 0.5% (●), 1% (▲), 5% (∗), 10% (○).

The dielectric relaxation spectrum of the IPNs shows a single peak that mainly corresponds to the secondary relaxation of the PMMA. This is clearly shown in Fig. 1 for the IPN containing 5% EGDMA. A similar result is also obtained in the IPN with low crosslink content, where a phase-separated system was expected, a single peak is observed (results not shown). Both main relaxations processes (the narrow α process of the PMA network and the small — partially overlapped with the β process — main relaxation of the PMMA network) tend to merge into a single one or at least are shifted in the temperature axis approaching each other. These features only allow to conclude that the two networks are at least partially miscible (the single peak could be the overlap of several peaks) because the α relaxations tend to approach each other. Dielectric miscibility studies of multicomponent systems in which PMMA takes part are difficult, because the strength

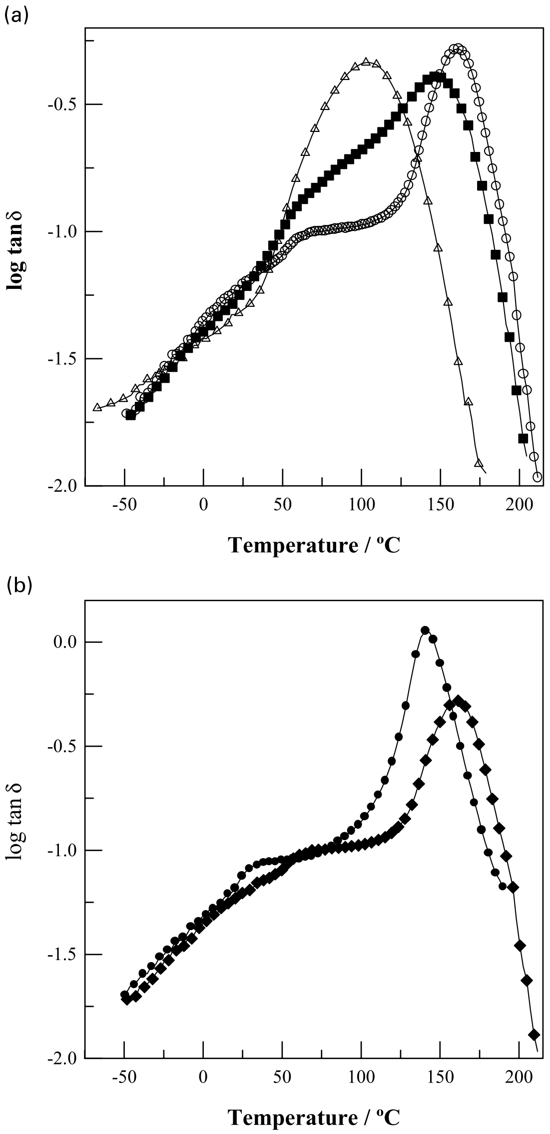

Fig. 4. (a) Temperature dependence of the mechanical loss tangent for three IPNs in which the PMMA network was crosslinked with 10% EGDMA while the PMA network was crosslinked with 0.1% (○), 0.5% (■) and 10% (△). (b) Temperature dependence of the mechanical loss tangent for two IPNs with 0.1% EGDMA in the PMA network and 0.1% (●), and 10% (◆) in the PMMA network The PMA network was always polymerized first.

of its main relaxation is smaller than that of the secondary one.

The number of monomeric units between crosslinks, ν, of the PMA and PMMA networks was calculated both from stoichiometry and from the elastomeric plateau modulus using the results of the theory of rubber elasticity (see Ref. [11] and the references therein), according to this

$$\nu = \frac{\rho}{M_m} \frac{3RTA_\phi}{E'} \tag{1}$$

where ρ is the density, R the constant gas, M_m the molecular weight of the monomeric unit, T the absolute temperature, E' the modulus in the elastomeric region and A_ϕ is a factor that depends on the functionality of the crosslinker. (Functionality is 4 in the case of EGDMA). Results are shown in Table 1. It can be observed that values obtained from stoichiometric considerations are higher than those calculated from the modulus for low contents of the crosslinking agent, what can be explained by the appearance of physical entanglements. However, as the amount of the crosslinker is increased, the situation changes and the number of elastically active chains is lower than what stoichiometric calculus predicts, i.e. the final balance between factors favorable (physical entanglements) and against (for example chains with a free extreme) is won for the last. The calculus of the number of monomeric units between crosslinks allows to determine the characteristic size of the region that is available for the growing of the second network and determine the formation or not of a separated phase. The entanglement spacing for a dry network can be estimated as [5]

Table 1
Monomeric units between crosslink points obtained from the experimental modulus (ν_{exp}) through rubber elasticity and from a stoichiometric calculation (ν_{st}) for PMA and PMMA networks, crosslinking spacing for the PMA network in the IPN (d_{ES}) and rubbery modulus obtained from Eq. (4) (E_{th}) and from experiment (E_{exp}) with different EGDMA contents

% EGDMA	PMMA		PMA			IPN	
	ν_{exp}	ν_{st}	ν_{exp}	ν_{st}	d_{ES} (nm)	E_{th} (Pa)	E_{exp} (Pa)
1	23.5	98	48.9	113.9	8.5	2.9×10^6	3.1×10^6
5	18.6	18.8	25.9	21.9	3.3	4×10^6	6.1×10^6
10	6.8	8.9	15	10.3	2.5	8.4×10^6	11×10^6

$$d_E = a\nu^{1/2} \tag{2}$$

where a is the Ferry's structure length. The swelling in the monomer of the second component will increase the entanglement or crosslinking spacing to a value d_{ES} which depends on the volume fraction of monomer absorbed by the network $(1 - \phi)$ according to approximately

$$d_{ES}^2 \phi \approx d_E^2 \tag{3}$$

The calculations were performed for the IPNs employed in this work using the a value 0.65 nm for PMA (see p. 23 in Ref. [6]) and the results are shown in Table 1. These values clearly show that the size of the region available for the growing of the PMMA network reduces as the EGDMA density increases. It is important to note that all the values are found in the 10 nm scale, which agrees with the mutual displacement of the main relaxations in the IPN in respect to the pure components (even the one with 1% of crosslinking agent). The crosslinking spacing found for the PMA network containing 10% EGDMA, and swollen with methyl methacrylate monomer, (a few nanometers) is similar to the length of co-operativity in the glass transition region, that supports the idea that in the IPN both components participate in the co-operative conformational motions of the polymer chains.

It is interesting to note that the plateau modulus in highly crosslinked IPNs can be higher than in the pure components networks with the same crosslinking density. The experimental values can be compared with the equation proposed by Siegfried et al. [12]

$$E_{\mathrm{IPN}} = \phi_{\mathrm{I}}^{1/3} E_{\mathrm{I}} + \phi_{\mathrm{II}} E_{\mathrm{II}} \quad (4)$$

where E_{I} and E_{II} represent the experimentally obtained rubbery modulus of PMA and PMMA networks, respectively. For calculating ϕ_{I} and ϕ_{II}, the volume fraction of the two networks, a zero excess volume is assumed. In the derivation of Eq. (4), the contribution of mutual physical entanglements between the two networks was not considered. If there are some physical crosslinks arising from internetwork entanglements, the modulus of the IPN is expected to be higher than the theoretical value obtained from Eq. (4). Rubbery modulus values (theory and experiment) for IPNs are listed in Table 1. The experimental values are higher than the theoretical ones which confirms the existence of physical entanglements in the IPN, the more, the higher the crosslink density.

4. Conclusions

While the polymer mixture PMA/PMMA presents phase separation, a sequential IPN of these two components can be compatibilized increasing the crosslinking density. The IPN crosslinked with 10% EGDMA shows a single main dynamic-mechanical relaxation process. Since the length of co-operativity in the glass transition region has been determined to be around few nanometers, this fact suggests that any region of the IPN with this approximate size contains both components. Permanent physical internetwork entanglements are also characteristic of the compatibilization. It has been shown that the key factor controlling the miscibility in the IPN is the crosslinking density of the network polymerized first.

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