DSC STUDY OF THE MISCIBILITY OF POLY(METHYL ACRYLATE)-POLYSTYRENE SEQUENTIAL INTERPENETRATING POLYMER NETWORKS

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Abstract

The phenomenon of forced compatibilization has been studied in poly(methyl acrylate)-polystyrene PMA-i-PS sequential interpenetrating polymer networks, IPNs, using differential scanning calorimetry. Both networks in the IPN were prepared using the same amount of ethylene glycol dimethacrylate, EGDMA, as crosslinking agent. The samples were subjected to thermal treatments which included annealing at different ageing temperatures T_a, for 300 min. From the DSC curves, recorded on heating the enthalpy loss during the isothermal annealing, Δh_a was calculated. The dependence of Δh_a with the annealing temperature was used to define the temperature interval in which the conformational mobility is significant. The comparison of the $\Delta h_a(T_a)$ curves obtained in an IPN and the results obtained with the pure component homo-networks with the same crosslinking density reveal some details of the miscibility of the IPN. In the case of the IPN crosslinked with 10% EGDMA, two peaks are apparent in the $\Delta h_a(T_a)$ curve, but the high-temperature peak is shifted towards lower temperatures compared to that of the polystyrene network while the low-temperature one is nearly at the same temperature than the one of the poly(methyl acrylate) homonetwork. This means that compatibilization is not complete and phase separation still exists even at this high crosslinking density. The different behaviour of the high and low temperature transitions can be explained by the dynamic heterogeneity of the sample, i.e. by the different length of cooperativity of the conformational rearrangements of PMA and PS domains at any temperature.

Keywords: glass transition, interpenetrated polymer networks, miscibility, poly(methyl acrylate), polystyrene, structural relaxation

Introduction

The formation of a sequential interpenetrating polymer network is a two-step process. The polymer network A is first polymerised and swollen in the monomer of the second component. The second network B is then polymerised in presence of the already existing network A. The result is a multicomponent polymer system that can be homogeneous or phase separated. The phase morphology of the sequential IPN depends on the thermodynamic miscibility of the two polymeric components but also on the crosslinking density (mainly that of the first network), the polymerisation sequence and the kinetics of

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polymerisation and phase separation. It has been shown that two polymers which are im-miscible can form homogeneous IPNs if the crosslinking density of the first network is high enough, what has been called forced compatibilisation [1, 2]. This was the case of PMA-i-PMMA sequential IPNs, in which the first network was PMA [3, 4]. When the PMA network was polymerised with 0.1% by mass of ethylene glycol dimethacrylate, EGDMA, as cross-linking agent, the IPN presented phase separation but when polymer-ised with 10% EGDMA the IPN presented a single although extremely broad glass tran-sition or main dynamic-mechanical relaxation. Poly(methyl acrylate) and polystyrene are also immiscible. The study of the viscoelastic properties of sequential PMA-i-PS IPNs, by dynamic-mechanical spectroscopy and thermally stimulated recovery showed that two main relaxation processes appear in the IPN even at high crosslinking densities of the first network [5].

The existence of a single glass transition is a widely applied criterium of misci-bility in a polymeric multicomponent system. The cooperative conformational rear-rangements in a miscible polymer should involve the motion of polymer segments pertaining to the different components of the system. The structural relaxation or physical ageing process is closely related to the glass transition phenomenon [6–8]. Let 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 tempera-ture below the glass transition, the specific volume or entropy are higher than those corresponding to the equilibrium states determined by the extrapolation of the experi-mental 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 specific volume, enthalpy and entropy decrease with time.
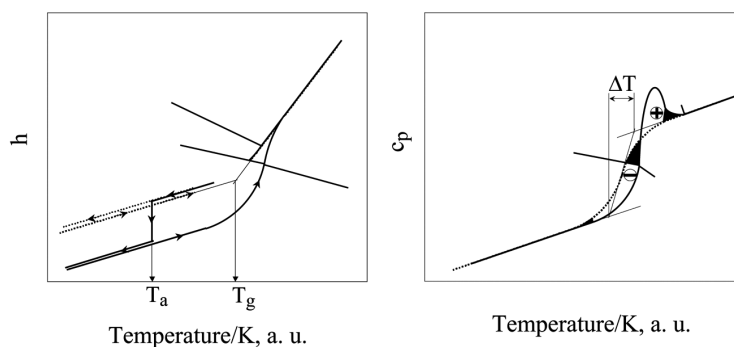

Fig. 1 Sketch of the temperature dependence of the a – enthalpy and b – heat capacity of a polymer sample subjected to a thermal history that includes an annealing at temperature T_a (solid line). The unannealed or reference scan is represented by the dotted line. The shadowed area is the enthalpy loss during the annealing at temperature T_a (see text)

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 range 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 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 enthalpy and specific heat during the whole experiment. DSC curve 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. DSC curve measured after cooling from T_0 to T_1 with no annealing (the reference scan) is also represented in Fig. 1b. It can be shown that the enthalpy increment Δh_a 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, $c_{p,ref}(T)$ [9]. This area is represented in Fig. 1b. 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 study of the kinetics of the structural relaxation process has been useful to reveal the characteristics of the conformational mobility in miscible and also in heterogeneous multicomponent polymer systems [10–14]. The aim of this work is to analyse the miscibility in PMA-i-PS sequential IPNs with varying crosslinking density on the basis of experimental DSC data of the structural relaxation process.

Experimental

Sequential interpenetrating polymer networks, IPNs, were prepared by block polymerisation using 0.2 mass% benzoin as photoinitiator. Monomers from Aldrich, 99% pure, were used without further purification. Poly(methyl acrylate), PMA, network was first polymerised with a 0.1 or a 10 mass% ethyleneglycol dimethacrylate, EGDMA, as cross-linking agent. Those networks will be named PMA01 and PMA10, respectively. Sheets of around half a millimetre thick were obtained. The PMA network sheets were dried in vacuum to constant mass and immersed in a solution of styrene in ethanol, containing EGDMA in the same proportion as in the PMA network and the photoinitiator. The change in the mass ratio ethanol/monomers in the polymerisation of the second network allows to modify the resulting composition of the IPN. The swollen samples were exposed to ultraviolet light to polymerise the polystyrene PS networks. Low molecular mass substances were extracted in boiling ethanol and finally the IPNs were dried in vacuum to constant mass. In this work only two IPN samples are studied, both prepared with similar PMA and PS monomer content and polymerised with 0.1 and 10 mass% EGDMA. These two materials will be named IPN01 and IPN10, respectively (IPN01 contained 48% and IPN10 44% by mass of PS). Two pure polystyrene networks (PS01 and PS10) were prepared following the same procedure described for the preparation of the pure PMA networks.

A Pyris 1 Perkin Elmer calorimeter was used in the DSC experiments. All the thermal treatments were carried out in the calorimeter. The thermal profile of the DSC experiments started at a temperature T_0 higher than the glass transition of the sample (180°C in the case of PS and the IPNs, 90°C in the case of PMA networks).

The sample was then cooled at 40°C min^{-1} until the annealing temperature T_a, kept at this temperature for the period of time t_a and cooled again at 40°C min^{-1} until the temperature T_1 (–40°C in the case of PMA and the IPNs and 20°C in the case of PS). The heating scan, at 10°C min^{-1} followed between T_1 and T_0. The sample was kept at T_0 for 5 min and cooled again at 40°C min^{-1} to T_1. A new heating DSC curve was recorded which 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 DSC curve measured after annealing and the reference scan is

$$(\dot{Q}-\dot{Q}_{ref})/m\dot{T}=c_p-c_{pref}$$

Results

The DSC curves obtained in the homopolymer networks and the IPNs, previously cooled at 40°C min^{-1} from a temperature well above the glass transition, are shown in Fig. 2. The glass transition in the highly crosslinked homopolymers appears at higher temperatures than in the networks polymerised with only a 0.1% of EGDMA, the values of the glass transition temperature defined by the mid-point of the rise of the heat capacity in the transition are included in Table 1. The width of the transition in the temperature axis clearly broadens in both networks with increasing crosslinking density. On the other hand the DSC curves corresponding to the unannealed samples of loosely crosslinked networks shows a small overshoot that disappears in the highly crosslinked networks. Both features are not independent from each other since the amorphous polymers with a narrow glass transition show a sharper endothermic peak that those in which the glass transition covers a broad temperature interval ([15–17], and the references there cited). The width of the relaxation can be characterised by the difference between the onset and the end glass transition temperatures defined by
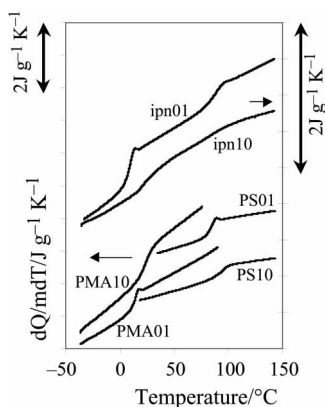

Fig. 2 Normalised DSC curves measured on heating scans on the PMA01, PMA10, PS01, PS10 networks and the interpenetrated polymer networks IPN01 and IPN10 crosslinked with 0.1% EGDMA and 10% EGDMA, respectively

the intersection point of the tangent to the DSC curve in the inflection point of the transition and the lines corresponding to the glassy and the liquid state respectively (Fig. 1). The relevant data are shown in Table 1.

Table 1 Glass transition temperature and the width of the glass transition ΔT_g of the PMA and PS networks and the IPNs. In the latter two temperatures are shown corresponding to the low-T_g and the high-T_g transitions shown in Fig. 2

	T_g/°C	ΔT_g/°C
PMA01	11	5
PMA10	24	16
PS01	84	8
PS10	94	17
IPN01	9.5 – – – 85	8 – – – 16
IPN10	26 – – – ?	33 – – – ?

The IPN01 presents two well separated glass transitions which appear nearly at the same temperatures than in PMA01 and PS01 networks. The highly crosslinked IPN still shows two heat capacity steps in the DSC curve. It is difficult in this case to determine accurately the values of the glass transition temperatures or the width of the transitions (in fact it was impossible to carry out the calculation in the case of the high-temperature transition). It seems that the glass transitions cover broader temperature intervals in the IPN than in the pure component networks but this is few information when trying to reach conclusions about the changes in the segmental conformational mobility in the IPN with respect to the behaviour of the pure PS and PMA network.

The experiments in which the sample is subjected to annealing previously to the heating DSC curve allows to determine the evolution of the enthalpy during the isothermal structural relaxation process. A series of these curves, corresponding to the sample PS01, is represented in Fig. 3. The evolution of the shape of these curves with the annealing temperature and time has been described with great detail in the literature ([6–8] and the references therein). The c_p–c_{pref} traces obtained after annealing at temperatures close but below the mid-point T_g show negative values at low temperatures and then the characteristic peak. This behaviour is due to the fact that in this interval of annealing temperatures the onset of the transition shifts to higher temperatures in the DSC curve measured after annealing than in the reference scan. As the annealing temperature decreases, the absolute values of c_p–c_{pref} in the negative part of the curve decreases and when the annealing temperature is around 30 degrees below T_g the c_p–c_{pref} trace is positive in the complete temperature interval. These curves correspond to DSC curves of the annealed sample in which the peak appears in the low-temperature side of the transition, what can be called the sub-T_g peaks. The values of Δh_a obtained from the experimental DSC curves are shown in Fig. 4. The accuracy in the calculation of Δh_a depends strongly on the definition of the horizontal baseline for the integration. Figure 3 shows the beselines used, the integration was
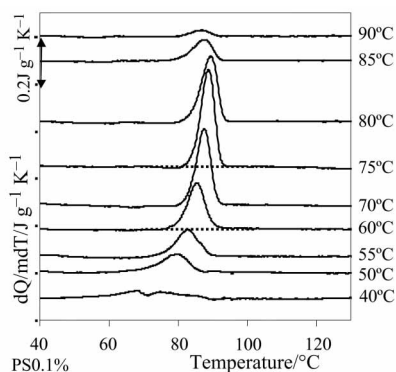
Fig. 3 Temperature dependence of $[c_p - c_{p,ref}]$ calculated in PS01 network from the DSC
curves measured after annealing at different temperatures for 300 min. The
traces have been shifted arbitrarily in the y-axis for the sake of clarity. The an-
nealing temperatures are shown on the graph

conducted in a temperature interval of around 40 degrees centered in the maximum of
the $c_p - c_{pref}$ trace. The uncertainty in this calculation can be roughly estimated in
a 10%. The dependence of Δh_a with T_a presents a maximum. At temperatures around
10 degrees above the mid-point T_g the value of the Δh_a is zero because when the sam-
ple attains the temperature T_a and the annealing starts it is already in equilibrium. As
T_a decreases, on the one side the difference between the enthalpy when the annealing
starts and that corresponding to equilibrium increases, so tending to increase the
value of Δh_a, but on the other side the rate of the structural relaxation process tending
to approach equilibrium decreases. The combination of these opposite effects pro-
duces the peak shown in Fig. 4. This plot can be used to define the temperature inter-
val in which the structural relaxation produces, in the period of 300 min, an enthalpy
loss which is significant enough to be measured by DSC. In other words, in this tem-
perature interval the segmental conformational mobility can be considered signifi-
cant from the point of view of the DSC technique. At higher temperatures
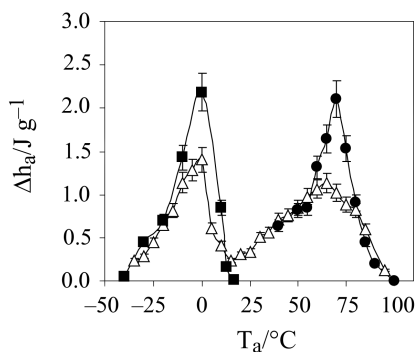

Fig. 4 Enthalpy loss during the isothermal annealing for 300 min against the annealing
temperature in ■ – PMA01, ● – PS01 networks and the △ – IPN01. Lines are
only intended as guide to the eye

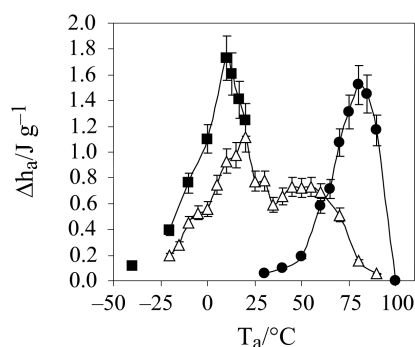**Fig. 5** Enthalpy loss during the isothermal annealing for 300 min against the annealing temperature in ■ – PMA10, ● – PS10 networks and the △ – IPN10. Lines are only intended as guide to the eye

conformational rearrangements takes place in times shorter than the response of the DSC and at lower temperatures they are slow compared with the period of annealing of 300 min. The same experiments were carried out in the case of PMA01, PMA10 and PS10 samples, and the results are summarised in Figs 4 and 5.

In the case of the IPN01, Fig. 6, the c_p–c_{pref} traces, calculated from the DSC curves measured after annealing at different temperatures for 300 min, show a peak for any annealing temperature between –20 and 90°C. The T_a dependence of Δh_a present two maxima which appear in the same temperature intervals than in the pure component networks (Fig. 4). In the case of the IPN10 (c_p–c_{pref} traces shown in Fig. 7) the two peaks of Δh_a appear at different temperatures than in the pure networks (Fig. 4), the low-temperature one is only a few degrees above that of PMA10, but the high temperature peak in IPN10 is around 30 degrees below the temperature of the maximum corresponding to PS10.
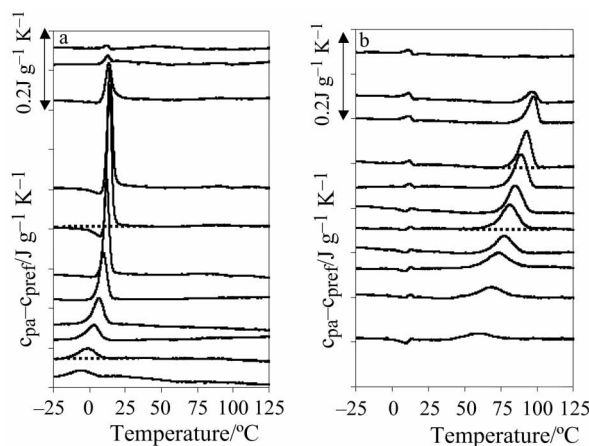

Fig. 6 Temperature dependence of [c_p–$c_{p,ref}$] calculated in the IPN01. The traces have been shifted arbitrarily in the y-axis for the sake of clarity. The annealing temperatures were (from bottom to top) a – –35, –30, –25, –20, –15, –10, –5, 0, 5, 10 and 20°C, b – 30, 40, 45, 50, 55, 60, 65, 70, 80, 85 and 95°C
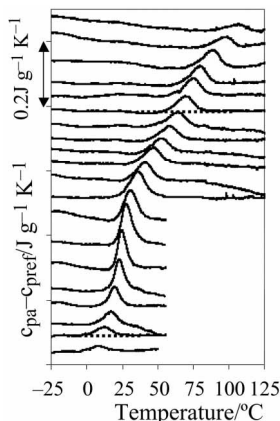
Fig. 7 Temperature dependence of $[c_p - c_{p,ref}]$ calculated in the IPN10. The traces have been shifted arbitrarily in the y-axis for the sake of clarity. The annealing temperatures were (from bottom to top) –20, –15, –10, –5, 0, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 70, 80 and 90°C

Discussion

The average number of monomeric units between crosslinks $\bar{\nu}$ in the PMA network of the IPN can be estimated from the elastomeric plateau modulus, E'_e, using the results of the theory of rubber elasticity. Using the affine network model ([18] and the references therein)

$$\bar{\nu} = \frac{3\rho RT}{M_m E'_e} \tag{1}$$

where ρ is the density, R is the gas constant and M_m the molecular mass of the monomeric unit. The modulus E'_e slightly increases with increasing temperature is due to the same behaviour in the product ρT (results not shown). Equation (1) was applied using the value of the density measured at 25°C, and the value of the elastic modulus at the same temperature obtained by linear extrapolation to 25°C, of the experimental data in the rubber-like region. The values of $\bar{\nu}$, shown in Table 2, can be used to estimate the characteristic size of the region that is available for the growing of the second network. The entanglement spacing for a dry network is [19]

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

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

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

The calculations were performed using a=0.65 nm for PMA [19], and the volume fraction of styrene absorbed in the PMA network was estimated from styrene density and the mass fraction of polystyrene in the IPN. The results are shown in Table 2.

Table 2 Average number of monomeric units between crosslinks in PMA networks, $\bar{v}$, and crosslinking spacing, d_{ES}, in the PMA networks swollen with styrene in the amount needed to form the IPNs

First network in the IPN	$\bar{v}$	d_{ES}/nm
PMA01	142	11.7
PMA10	23	4.7

Due to the immiscibility of polystyrene and poly(methyl acrylate), during the polymerisation of the styrene absorbed in the PMA network the growing polystyrene network push apart the PMA chains trying and form a phase with no presence of PMA segments. The results of Table 2 show the styrene absorbed in the PMA01 network can find spaces to form domains whose size is in the order of 12 nm. This size is greater than the length of cooperativity at the glass transition (which has been estimated in few nanometers in several polymers [19, 20]) and, as a consequence, a glass transition of these domains can be experimentally measured with the characteristics of the pure polystyrene network.

The space allowed for the growth of the PS network from the styrene absorbed in the PMA10 network is significantly smaller, below 5 nm. The thermodynamic equilibrium criterium makes that the PS10 network tends to separate from the PMA polymer segments, but the domains of pure PS network will be small and a part of the PS chains are forced to truly interpenetrate the PMA network. Still two glass transitions can be observed in the IPN10 but the small size of the PS10 domains makes then some PMA chain segments (perhaps pertaining to the interface between PMA and PS-rich domains) participate in any conformational rearrangement produced in the region of the PS10-rich domains. The relaxation time in a conformational rearranging region that contains some PMA segments in addition to PS segments is much shorter than in a region that contains only PS chain segments. Figure 5 shows that the annealing of PMA10 network at temperatures between 80 and 95°C produces a significant enthalpy loss, i.e., conformational rearrangements take place in the time scale compatible with the period of time of 300 min. On the contrary in the case of IPN10, the annealing at these temperatures produces nearly no change in the enthalpy, the sample is in equilibrium at these temperatures. The consequence to be reached is that there exists no region or domain with a size in the order of the length of cooperativity at the glass transition temperature containing only in PS chain segments. This confirms that this length of cooperativity is in the order of 4 nanometers. At low temperatures, in the temperature region of the PMA10 network, the behaviour is quite different. Figure 5 shows small differences in the position of the $\Delta h(T_a,t_a)$ *vs.* T_a plot, although the values of $\Delta h(T_a,t_a)$ are smaller in the IPN than in PMA10 network because the number of polymer segments responsible for the structural relaxation at each tem-

perature in the IPN are smaller than in the pure network. Thus, it can be concluded that there exist rearranging regions containing only PMA segments. The difference between the behaviour of the PS domains and those of the PMA domains can be related to the phenomenon of dynamic heterogeneity [21]. The length of cooperativity decreases as the temperature increases above the glass transition. This means that in the multicomponent material, at any temperature the length of cooperativity of the rearranging regions rich in the low-T_g component, PMA in this case, are much smaller than in regions rich in the high-T_g component. It is easier to find a region with the size of the length of cooperativity of PMA consisting only in PMA segments than to find a rearranging region with the size of the length of cooperativity of PS containing only PS segments. A model that simulates this behaviour has been proposed that explain the temperature modulated DSC results obtained in PMA-i-PMMA IPNs [4].

Conclusions

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

PMA-i-PS IPNs are phase separated even if the PMA network is crosslinked with 10% by mass of EGDMA. Varying the crosslinking density of the PMA network it is possible to change the space available to the formation of domains of pure PS network in the IPN. When the spacing between crosslinks in the PMA network is around 5 nm no domains of pure PS able to undertake conformational rearrangements exists in the IPN. This allows to characterise the length of cooperativity of PS at its glass transition temperature. On the contrary, conformational rearrangements of PMA segments can take place without participation of any PS segment. This feature is connected to the concept of dynamic heterogeneity.

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References

1 B. Y. Li, X. P. Bi, D. H. Zhang and F. S. Wang, in Advances in Interpenetrating Polymer Networks. Vol. 1, D. Klempner and K. C. Frisch Eds, Technomic, Lancaster 1989.
2 D. G. Fradkin, J. N. Foster, L. H. Sperling and D. A. Thomas, Polym. Eng. Sci., 26 (1996) 730.
3 M. Salmerón Sánchez, G. Gallego Ferrer, C. Torregrosa Cabanilles, J. M. Meseguer Dueñas, M. Monleón Pradas and J. L. Gómez Ribelles, Polym. Commun., 42 (2001) 10071.
4 J. L. Gómez Ribelles, M. Monleón Pradas, J. M. Meseguer Dueñas and C. Torregrosa Cabanilles, J. Non-Cryst. Solids, 307–310 (2002) 731.

5 J. M. Cuesta Arenas, J. F. Mano, J. L. Gómez Ribelles, J. Non-Cryst. Solids, 307–310 (2002) 758.

6 W. Scherer, J. Non-Cryst. Solids, 123 (1990) 75.

7 I. M. Hodge, J. Non-Cryst. Solids, 169 (1994) 211.

8 J. M. Hutchinson, Prog. Polym. Sci., 20 (1995) 703.

9 J. L. Gómez Ribelles, A. Ribes Greus and R. Díaz Calleja, Polymer, 31 (1990) 223.

10 J. M. G. Cowie and R. Ferguson, Macromolecules, 22 (1989) 2312.

11 G. ten Brinke and R. Grooten, Colloid Polym. Sci., 267 (1989) 992.

12 T. S. Ellis, Macromolecules, 23 (1990) 1494.

13 A. A. C. M. Oudhuis and G. ten Brinke, Macromolecules, 25 (1992) 698.

14 J. M. G. Cowie, S. Harris, J. L. Gómez Ribelles, J. M. Meseguer Dueñas, F. J. Romero
   Colomer and C. Torregrosa, Macromolecules, 32 (1999) 4430.

15 J. L. Gómez Ribelles and M. Monleón Pradas, Macromolecules, 28 (1995) 5867.

16 J. L. Gómez Ribelles, M. Monleón Pradas, A. Vidaurre, F. Romero, J. Más and
   J. M. Meseguer Dueñas, Macromolecules, 28 (1995) 5878.

17 N. M. Alves, J. F. Mano, E. Balaguer, J. M. Meseguer Dueñas and J. L. Gómez Ribelles,
   Polymer, 43 (2002) 4111.

18 B. Erman and J. E. Mark, Structure and Properties of Rubberlike Networks,
   Oxford University Press, 1997.

19 E. Donth, Relaxation and Thermodynamics in Polymers, Glass Transition, Akademie Verlag,
   Berlin 1992.

20 J. L Gómez Ribelles, A. Vidaurre Garayo, J. M. G. Cowie, R. Ferguson, S. Harris and
   I. J. McEwen, Polymer, 40 (1998) 183.

21 S. K. Kumar, R. H. Colby, S. H. Anastasiadis and G. Fytas, J. Chem. Phys., 105 (1996) 3777.