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Modulated-temperature differential scanning calorimetry: 15. Crosslinking in polyurethane–poly(ethyl methacrylate) interpenetrating polymer networks

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Abstract

The glass transition behaviour and morphology of 70 : 30 polyurethane–poly(ethyl methacrylate) (PU–PEMA) interpenetrating polymer networks (IPNs) in which the crosslink density in both networks was systematically varied were investigated by means of modulated-temperature differential scanning calorimetry (M-TDSC) and dynamic mechanical thermal analysis (DMTA). The observed influence on the glass transition temperature, T_g, was similar for both the M-TDSC and DMTA studies, but some substantial differences also existed. M-TDSC was more sensitive to phase separation than DMTA. On increasing the crosslink density in the first-formed PU network, the weight fraction of the interphase component increased. Higher crosslinking levels in the PEMA network had relatively little influence.

Keywords: Interpenetrating polymer networks; Modulated DSC; Glass transition

1. Introduction

It is widely accepted that most polymer pairs are immiscible. One possibility to reduce the degree of phase separation in such circumstances is by forming interpenetrating polymer networks (IPNs) [1,2]. In recent decades, a wide variety of IPNs have been synthesized (sequential, simultaneous, latex, gradient, thermoplastic, and semi) and their physical properties and structure have been extensively studied by differential scanning calorimetry (DSC), dynamic mechanical thermal analysis (DMTA), electron microscopy, and scattering methods [3–7]. From these investigations, it is known that IPNs do not interpenetrate, except possibly in very exceptional circumstances, on a repeat unit scale, but have a rather nebulous micro-heterogeneous morphology with regions enriched by segments of one of the components and interfacial zones, where substantial amounts of network interpenetration occurs. There is a clear need for techniques that provide information about this complex morphology. Recently, the differential of reversing heat capacity versus temperature, dC_p/dT, signal from modulated-temperature differential scanning calorimetry (M-TDSC) [8] has been applied to elucidate the morphology of multi-component polymer materials [9-11].

The special properties of IPNs are brought about by the permanent physical interlocking (cocatanation) [1] of network rings. Transmission electron microscopy and other studies [12] have revealed that high levels of crosslinking in the first-formed network restricts the phase domain size of the second network. Thus, the crosslink densities in the polymer networks greatly influence the mechanical properties and the damping characteristics [7]. In this paper, the influence of the crosslink density of both networks in a polyurethane–poly(ethyl methacrylate) (PU–PEMA) IPN is investigated. The 70 : 30 PU–PEMA IPN composition (by weight) was selected for these studies because of its exceptionally broad loss factor transition [13]. These IPNs exhibited values for the loss factor ($\tan\delta$) of ≥ 0.3 spanning a temperature range of more than 120°C.

2. Experimental

2.1. Chemicals

The polyurethane component was prepared from

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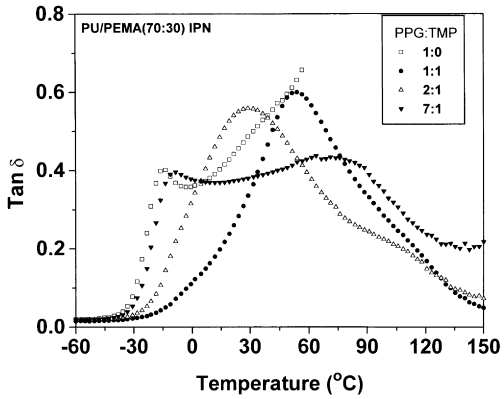

Fig. 1. Loss factor versus temperature data for the 70 : 30 PU/PEMA IPNs with different PU network crosslink levels (PPG : TMP). The PEMA networks were crosslinked with 5 mol% TEGDM.

1,1,3,3-tetramethylxylene diisocyanate (m-TMXDI, kindly donated by Cytec Industries), a polyoxypropylene glycol with a molar mass of 1025 (PPG1025, BDH) and the crosslinker, trimethylol propane (TMP, Aldrich). Stannous octoate (SnOc, Sigma) was used as the polyurethane catalyst. The monomer for the second network was ethyl methacrylate (EMA, Aldrich). The PEMA was crosslinked with tetraethyleneglycol dimethacrylate (TEGDM, Fluka). The free radical polymerization of EMA was initiated with azoisobutyronitrile (AIBN, Aldrich).

2.2. PU–PEMA IPNs

The free radical initiator, AIBN, was dissolved in the monomer, EMA, and the crosslinker, TEGDM. In a separate vessel, TMP was dissolved at 60°C in the PPG1025. Both of these mixtures were combined at room temperature and the SnOc and m-TMXDI added. After vigorously stirring for 5 min, the mixture was degassed for 1 min to remove any entrapped air. The mixture was carefully poured into a spring-loaded O-ring mould and the latter placed in an air oven. The curing cycle comprised three stages each of 24 h at 60°C, 80°C and 90°C, respectively.

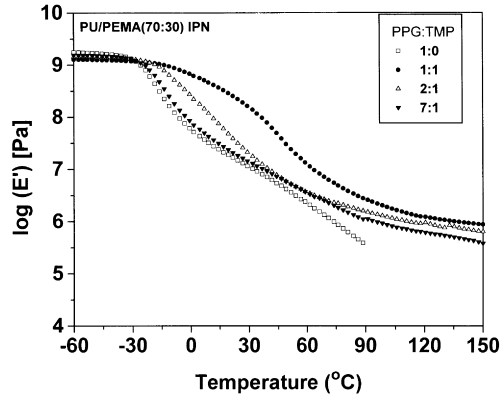

Fig. 2. Storage modulus versus temperature data for the 70 : 30 PU/PEMA IPNs with different PU network crosslink levels (PPG : TMP). The PEMA networks were crosslinked with 5 mol% TEGDM.

2.3. M-TDSC measurements

A TA Instruments M-TDSC 2900 calorimeter was used. An oscillation amplitude of 1°C, an oscillation period of 60 s and a heating rate of 3°C/min were used. The calorimeter was calibrated with a standard indium sample.

2.4. DMTA

The samples were measured in the bending mode (single cantilever) with a Polymer Laboratories MKII dynamic mechanical thermal analyser. The temperature programme was run from − 60°C to 200°C using a heating ramp of 3°C/min at a fixed frequency of 10 Hz.

3. Results and discussion

3.1. The glass transition behaviour

Figs. 1 and 2 show, respectively, the loss factor and the storage modulus versus temperature data for the 70 : 30 PU–PEMA IPNs with a fixed PEMA crosslink level of 5 mol% TEGDM and various PPG1025/TMP ratios. The loss factor data showed, as expected, that with increasing triol content, the PU transition moved to increasingly higher temperatures. The PU–PEMA IPN which was synthesized by leaving out the triol in the PU (a semi-1 IPN results) had the lowest glass transition temperature, T_g, with a value of − 16°C (Fig. 1).

The loss factor peak height of the PU in the semi-1 IPN (0.4) was four times lower than that in the PU homonetwork [15]. This could indicate that the linear PU in the semi-1 IPN exhibited only limited phase continuity. No loss factor transition peak was obtained by DMTA for the PEMA network in this semi-1 IPN because of extensive softening at temperatures above 50°C. As already indicated, with increasing triol content, the PU T_g shifted to higher temperatures. At a PPG1025/TMP ratio of 7 : 1, the PU transition shifted to − 9°C. A very broad transition plateau was obtained which made the determination of the PEMA transition difficult to locate precisely. The loss factor values were greater than 0.3 from − 20°C to 100°C, thus, making this IPN an excellent damping material. The IPN crosslinked at a PPG1025/TMP ratio of 3 : 1 (not shown in Fig. 1) showed an equally broad high damping transition at a slightly higher temperature range. The loss factor values were greater than 0.3 for a temperature range of 120°C from 0°C to 120°C. These two IPNs had PU and PEMA loss factor peaks of roughly equal heights which suggested dual-phase continuity in these materials.

However, this changed at a PPG1025/TMP ratio of 2 : 1. The PU transition continued to shift to higher temperature

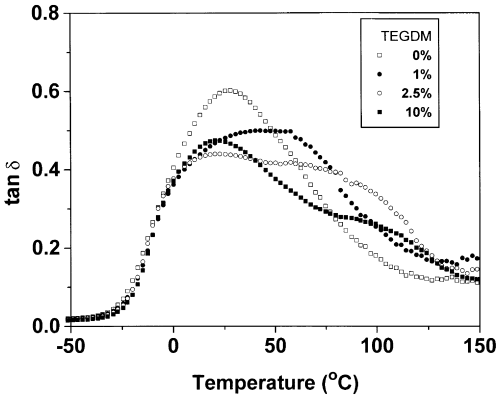

Fig. 3. Loss factor versus temperature data for the 70 : 30 PU/PEMA IPNs with different PEMA network crosslink levels. The PU network was crosslinked with a PPG1025/TMP ratio of 3 : 1.

(29°C) and the loss factor peak had a value of 0.55. For the PEMA transition, only a high-temperature shoulder was observed. This trend continued for the IPN crosslinked at a PPG1025/TMP ratio of 1 : 1. The T_g, 54°C, and the highest loss peak, 0.60, coincided with the lowest value for the half-peak width, 72°C. The fact that only a very small shoulder for the PEMA transition remained confirmed that the highest degree of network mixing was obtained at the highest PU crosslink density based on these DMTA observations.

The crosslink density in the PEMA component of the IPN was also varied. While varying the PEMA crosslinking levels, the PPG1025/TMP ratio was fixed at 3 : 1. The loss factor and storage modulus versus temperature data for these 70 : 30 PU–PEMA IPNs are shown, respectively, in Figs. 3 and 4. Increasing the crosslinker level moved part of the IPN transition to higher temperatures. The transition split into two parts, with the PU part shifting to slightly lower temperatures, whereas the PEMA shifted strongly to higher temperatures. Thus, as opposed to higher crosslinking in the PU network, higher crosslinking in the PEMA network generally resulted in a broadening of the IPN transition. The storage modulus–temperature plots (Fig. 4) shows this transition broadening and the expected increased rubbery modulus as the PEMA networks became more crosslinked.

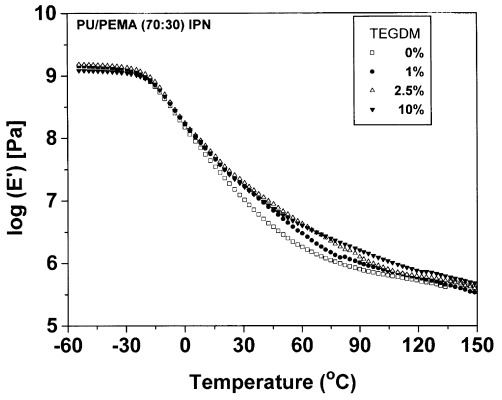

Fig. 4. Storage modulus versus temperature data for the 70 : 30 PU/PEMA IPNs with different PEMA network crosslink levels. The PU network was crosslinked with a PPG1025/TMP ratio of 3 : 1.

The T_g behaviour of these 70 : 30 PU–PEMA IPNs with varying crosslink densities in both networks was also investigated by M-TDSC. Figs. 5 and 6 show, respectively, the reversing heat capacity and the differential of the reversing heat capacity, dC_p/dT, versus temperature data for the 70 : 30 PU–PEMA IPNs with a fixed PEMA crosslink level (5 mol% TEGDM), but with various PPG1025/TMP ratios. Figs. 7 and 8 show, respectively, the equivalent reversing heat capacity and dC_p/dT versus temperature data for the 70 : 30 PU–PEMA IPNs with a fixed PPG1025/TMP ratio but with varying PEMA crosslinking levels. The general trend of the T_g behaviour is similar from both the M-TDSC and DMTA studies, but some substantial differences also existed. From the dC_p/dT versus temperature signal, with the exception of the IPN crosslinked at a PPG1025/TMP ratio of 1 : 1, two M-TDSC T_g transitions were resolved for all compositions. The dC_p/dT versus temperature signal of M-TDSC thus seems to be somewhat more sensitive to phase separation than DMTA.

Similar to the DMTA data, increasing the crosslink density in the PU network resulted in a steady increase in the PU M-TDSC T_g. The magnitude of the T_g increase, however, was very different. The PU T_g of the semi-1 70 : 30 PU–PEMA IPN was -16°C and -41°C for the DMTA and M-TDSC studies, respectively. When changing the crosslink density in the IPN PU component from a PPG1025/IMP ratio of 1 : 0 to 1 : 1, the T_g shifted to 54°C (DMTA) [15] and to -22°C (M-TDSC). From DMTA data, a T_g increase of 70°C was obtained [14], while only 19°C was observed with M-TDSC. The more than three-fold lower T_g shift in the M-TDSC data showed that the different measurement principles of these techniques strongly influence the T_g results. Thus, in addition to a difference in sensitivity to phase-separated structures, also the observed transition magnitudes and the T_g shifts with increasing crosslinking were different. Consequently, M-TDSC measurements may be sensitive to a difference in heat capacity and polymer weight fraction whereas DMTA may to a much greater extent be influenced by phase continuity.

It can be seen from Fig. 6 that, with increasing the crosslink density in the first-formed PU network, the transition (dC_p/dT versus temperature signal) became broader. The height of peak associated with the glass transition of PU-rich phase decreased. The area under the peak is relative to the weight fraction of this PU-rich phase. The decrease in area of the peak means that the PU-rich phase decreases. This indicated that the increase in crosslink density of the first-formed PU network obstructs phase separation and increases component mixing. Compared with Fig. 6, Fig. 8 indicates that higher crosslinking levels in the PEMA network had little influence.

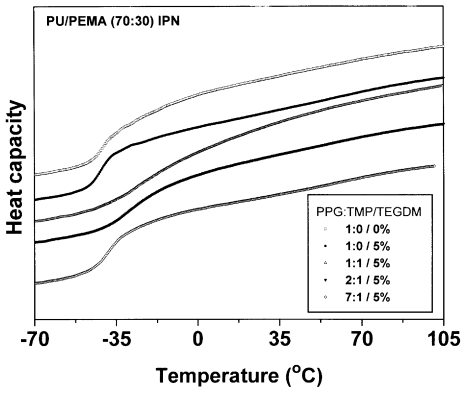

Fig. 5. Heat capacity versus temperature data for the 70 : 30 PU/PEMA IPNs with different PU network crosslink levels (PPG : TMP). The PEMA networks were crosslinked with 5 mol% TEGDM.

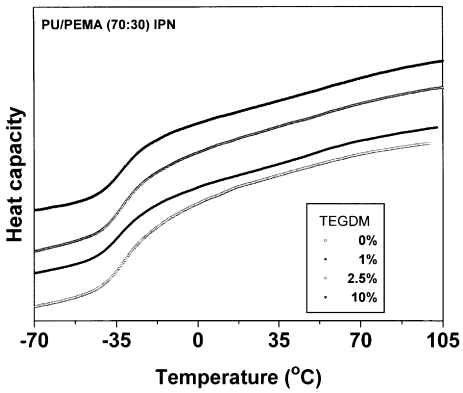

Fig. 7. Heat capacity versus temperature data for the 70 : 30 PU/PEMA IPNs with different PEMA network crosslink levels. The PU network was crosslinked with a PPG1025/TMP ratio of 3 : 1.

3.2. Analysis of the IPN morphology

The real part of the heat capacity for polymers may be expressed as follows:

$$C_p = A + BT + F(T) \tag{1}$$

where A and B are constants and $F(T)$ is a function of temperature. Assume outside the transition region that $F(T)$ is zero. Thus,

$$dC_p/dT = B + dF(T)/dT = B + \phi(T). \tag{2}$$

Previous work [15] has shown for a pure polymer that the dC_p/dT versus temperature signal can be described by the following Gaussian function, G, where T is temperature, ΔC_p is the change in heat capacity and ω_d is the half-width of the glass transition peak (from dC_p/dT versus temperature).

$$G = \Delta C_p/[\omega_d(\pi/2)^{1/2}]\exp[-2(T - T_g)^2/\omega_d^2]. \tag{3}$$

For the transition region of a heterogeneous IPN, it is possible to consider G as a multiple Gaussian function [15].

$$G = \sum G_i(T, T_{gi}, \omega_{di}, \Delta C_{pi}) = \Delta C_{p1}/[\omega_{d1}(\pi/2)^{1/2}] \times \exp[-2(T - T_{g1})^2/\omega_{d1}^2] + \Delta C_{p2}/[\omega_{d2}(\pi/2)^{1/2}] \times \exp[-2(T - T_{g2})^2/\omega_{d2}^2] + \Delta C_{p3}/[\omega_{d3}(\pi/2)^{1/2}] \times \exp[-2(T - T_{g3})^2/\omega_{d3}^2] + \ldots \tag{4}$$

where $G_i(T, T_{gi}, \omega_{di}, \Delta C_{pi})$ is related to ith phase of the multi-phase system. For a multi-phase IPN, the total ΔC_p is the sum of ΔC_{pi} of each phase.

$$\Delta C_p = \sum \Delta C_{pi}. \tag{5}$$

The parameters, ω_d, ΔC_{pi} and T_{gi} can be obtained [15] by a peak resolution technique.

The morphology of these partially compatible PU–PEMA IPNs may be modelled as follows. The dC_p/dT versus temperature signals for the IPNs may be divided into several parts by this peak resolution method [15]. These parts are related to a PU-rich phase, to a PEMA-rich phase and an interfacial phase. The phase which has

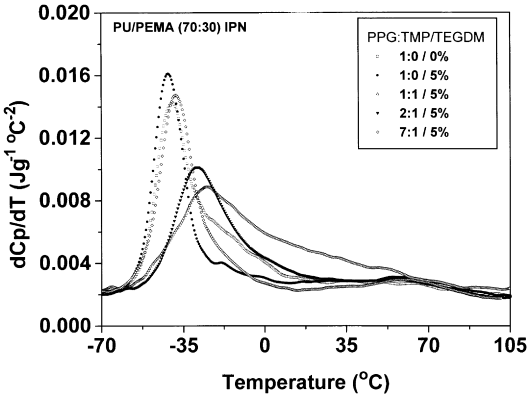

Fig. 6. dC_p/dT versus temperature signal for the 70 : 30 PU/PEMA IPNs crosslinked with different PU network crosslink levels (PPG:TMP). The PEMA networks were crosslinked with 5 mol% TEGDM.

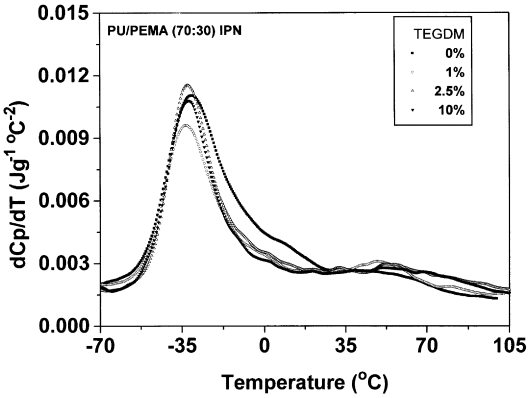

Fig. 8. dC_p/dT versus temperature signal for the 70 : 30 PU/PEMA IPNs with different PEMA network crosslink levels. The PU network was crosslinked with a PPG1025/TMP ratio of 3 : 1.

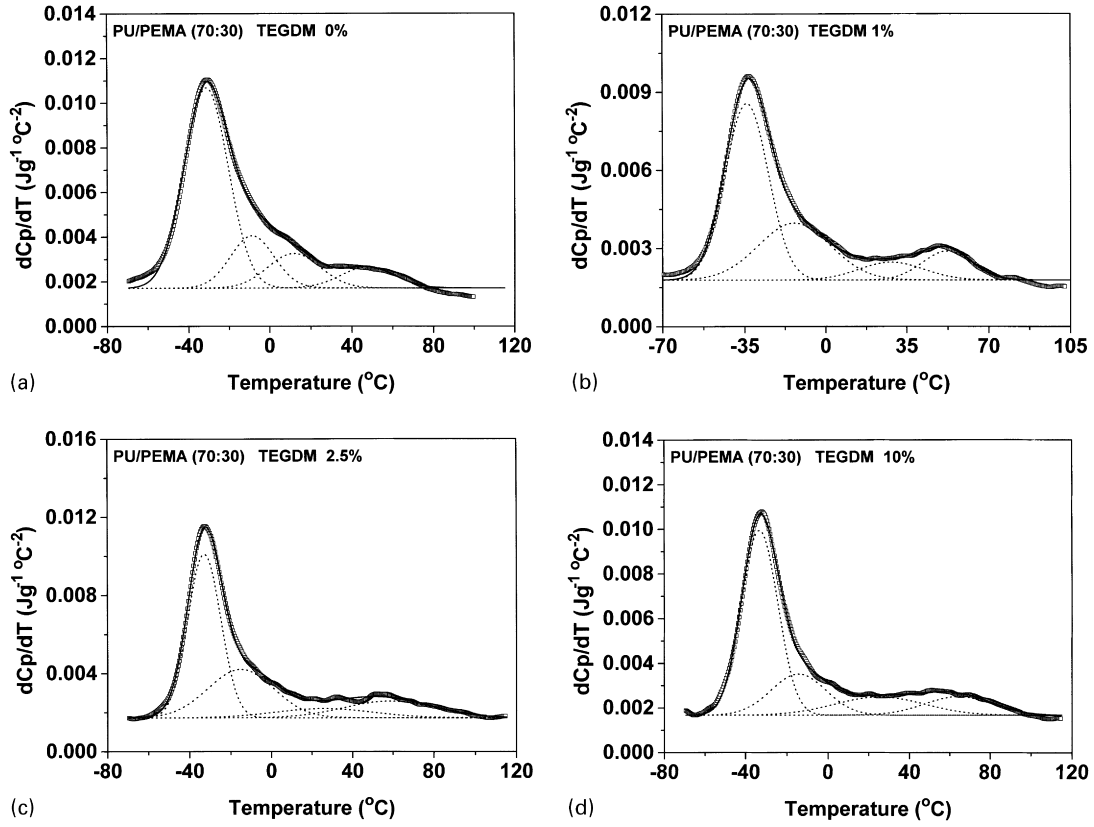

Fig. 9. Peak resolution results for the 70 : 30 PU/PEMA IPNs with a PPG1025/TMP ratio of 3 : 1 and different PEMA network crosslink levels. Dashed lines are peak resolution results.

the lowest T_g is the PU-rich one and the phase with the highest T_g is the PEMA-rich phase. Other phases located between the PU-rich and the PEMA-rich phases are considered as interfacial phases.

Fig. 9 shows the results of peak resolution based on Eq. (4) for the 70 : 30 PU–PEMA IPNs at a fixed PPG1025/TMP ratio, but with varying PEMA crosslink levels. A four-phase morphology gave a satisfactory fit between prediction and experiment. These correspond to a PU-rich phase, a PEMA-rich phase, and other two are considered as interphases. The weight fractions versus TEGDM content is shown in Fig. 10 for the PU-rich phase, the PEMA-rich phase and the interphases. These weight fractions changed little with TEGDM content. The results indicate that the increase of crosslink level in the PEMA network does little to change the morphology dramatically although higher crosslinking did result in a broadening of the DMTA transitions (see Fig. 3).

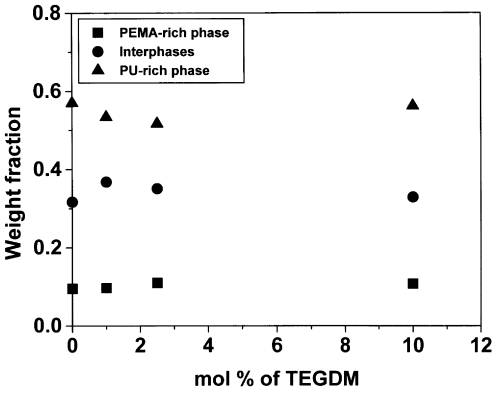

Fig. 10. Weight fraction versus TEGDM content for the 70: 30 PU/PEMA IPNs with a PPG1025/TMP ratio of 3 : 1 and different PEMA network crosslink levels.

Although there was no big overall effect of the TEGDM content on the three weight fractions, some substantial differences exist for the individual interphases. Table 1 gives some information about this aspect. Comparing 0% TEGDM and 10% TEGDM samples, it was found that they have the same individual and total interphase weight fractions. However, they have different interphase glass transition temperatures. The difference between two interphase T_gs for the 0% TEGDM sample was about 20°C and the difference for the 10% TEGDM one was about 39°C. The difference may reflect the different DMTA tan δ curves. Comparison of the 1% and 2.5% TEGDM samples, however, show that although they have the same interphase weight fractions and T_gs, their DMTA tan δ curves are different. From this, it can be concluded that DMTA tan δ curves are influenced by two considerations: composition (weight fraction and T_g) and phase continuity.

Table 1
Weight fraction and T_g values for the interphases in the 70 : 30 PEMA IPNs with fixed PPG1025/TMP ratio but varying PEMA crosslink levels

Sample	Interphase weight fraction (%)		T_g (°C)	
	w_2	w_3	T_{g2}	T_{g3}
0% TEGDM	14	17	11	− 9
1%	8	28	28	− 14
2.5%	7	28	26	− 15
10%	14	19	25	− 14

Table 2
Weight fractions ω_d and T_g values for PU-rich (w_4, T_{g4}), PEMA-rich (w_1,T_{g1}) and for the interphases (w_2, T_{g2}, w_3, T_{g3}) for the 70 : 30 PU–PEMA IPNs at a fixed PEMA crosslink level (5 mol% TEGDM) and various PPG1025/TMP ratios

Sample	w_1	T_{g1}	w_2	T_{g2}	w_3	T_{g3}	w_4	T_{g4}
1 : 0	15	61	8	21	29	− 28	47	− 41
7 : 1	10	60	13	30	28	− 30	48	− 39
2 : 1	11	60	13	17	32	− 11	42	− 30
1 : 1	10	57	14	28	37	− 3	36	− 22

The peak resolution results for the 70 : 30 PU–PEMA IPNs with the PEMA networks at a fixed crosslink level (5 mol% TEGDM) but with varying PPG1025/TMP ratios are shown in Fig. 11. The weight fraction and T_g data from peak resolution are shown in Table 2. Increasing crosslink density in the PU networks results in an increase of the T_g of PU-rich phase (T_{g4}). The highest degree of network mixing (highest total interphase weight fraction) was obtained at the highest PU crosslink density. With increasing the crosslink density in the PU network, the weight fraction of the interphases ($w_2 - w_3$) increased. However, the weight fraction of PEMA-rich phase (w_1) changed only slightly. Higher degrees of crosslinking in the first-formed PU network increased the extent of mixing and the PEMA network domains were restricted in size [15].

4. Conclusions

Increasing the crosslink density in the PU networks resulted in a steady increase in PU (M-TDSC) T_g and the PEMA T_g remained unchanged. Also, the weight fraction of the interphases increased. Higher crosslinking of the PEMA network had little influence on the already formed PU network.

Some differences between the M-TDSC and the DMTA data were in evidence. While from the DMTA data similar loss factor peak heights were observed for most of the 70 : 30 PU–PEMA IPNs, the PU transition was clearly dominant in the M-TDSC traces. M-TDSC measurements are sensitive to differences in heat capacity and polymer

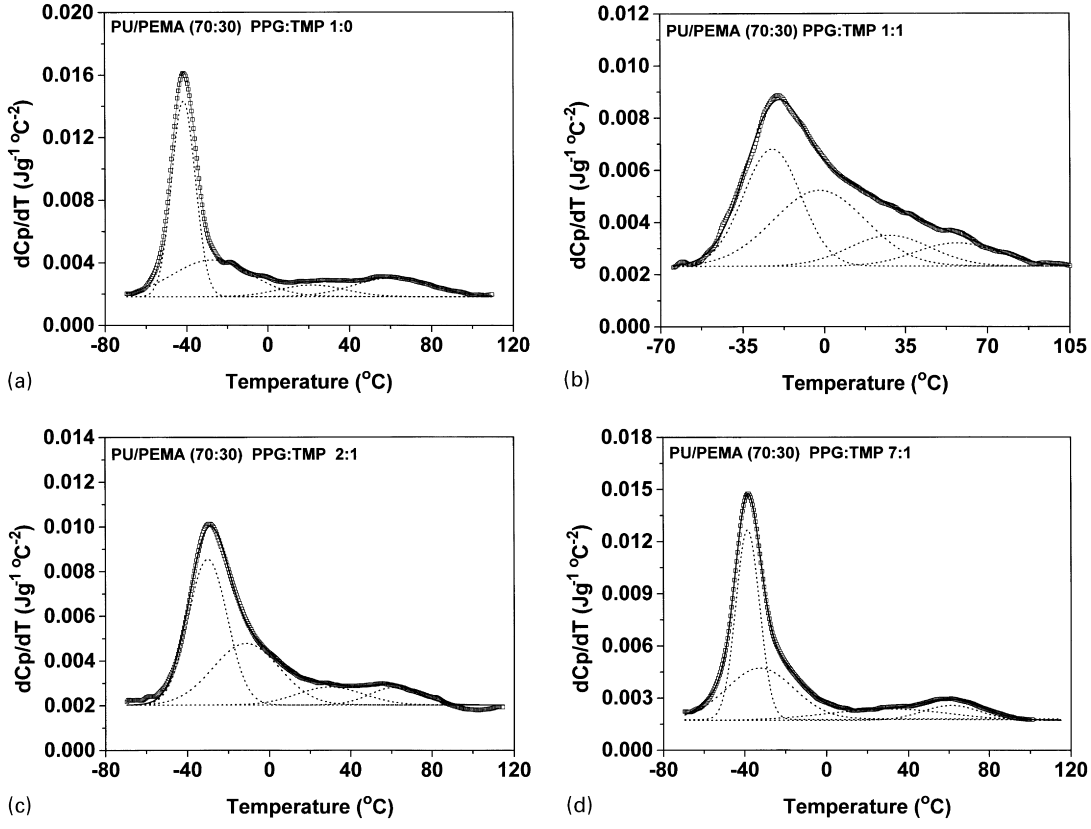

Fig. 11. Peak resolution results for the 70 : 30 PU/PEMA IPNs crosslinked with 5 mol% TEGDM and different PU network crosslink levels. Dashed lines are peak resolution results.

weight fraction, whereas DMTA will be significantly influenced by phase continuity.

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