Polyurethane–polysiloxane interpenetrating networks: 3. Polyetherurethane–poly(phenylmethylsiloxane) systems

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Room-temperature-cured simultaneous interpenetrating polymer networks (IPNs), comprising poly(phenylmethylsiloxane) (PPMS) and polyurethanes (PU) have been synthesized. Two PU networks were employed, one based on Adiprene L-100, and one prepared from poly(propylene glycol) (PPG) and toluene diisocyanate (TDI). The cured IPNs were examined by dynamic mechanical analysis. By considering solubility parameters, and prepolymer molecular weight, all compositions were predicted to be compatible on initial mixing, but to phase separate at some degree of network cure. The Adiprene L-100 based system comprised phase separated IPNs. Evidence was found, from ^{13}C n.m.r. linewidth measurements, of mutual interpenetration at the phase boundaries. The PPG/TDI based PU system showed compatible (single T_g) IPNs at PU concentrations from 90 to 50%, and phase separation for the 30% PU IPN. The compatibility of the PU-rich IPNs was ascribed to the low $\bar{M}_c$ of the PU network, causing a kinetic opposition to phase separation. For the compatible IPNs, the plot of T_g versus composition could be described by the Gordon–Taylor equation. However, the relationship between modulus and composition for neither system conformed particularly well to empirical mixing equations.

(Keywords: interpenetrating polymer networks; polyurethane; poly(phenylmethylsiloxane); phase separation; dynamic mechanical analysis)

INTRODUCTION

The first paper in this series[1] considered polyurethane (PU)–poly(dimethylsiloxane) (PDMS) interpenetrating polymer networks (IPN). The IPNs showed gross phase separation. In the second paper[2], it was shown that this level of phase separation was not reduced by replacing the pure PDMS with a PU-*co*-PDMS network. In both cases, the prepolymers were immediately immiscible, and the resulting two-phase character was readily apparent in the mechanical behaviour of the cured products. Although, at the molecular level, evidence was obtained from ^{13}C n.m.r. studies for a small degree of mixing at the phase boundaries, the tensile and dynamic mechanical properties of any blend were essentially those of the continuous phase, the dispersed phase being mechanically isolated. The underlying reason for the inherent PU–PDMS incompatibility is the magnitude of the polymer–polymer interaction parameter[3]. An approximate indication of the likely degree of compatibility can be obtained from a comparison of the solubility parameters.

The present study concentrates on PU–PPMS IPNs. PPMS has a solubility parameter of 18.5×10^3, compared with 19.4×10^3 (J m^{-3})$^{1/2}$ for the PU, and so there will be a far greater chance of initial prepolymer miscibility, leading to one-phase IPNs, or compositions showing only limited phase separation. Two PU prepolymers were used in the present work; Adiprene L-100 and a prepolymer based on poly(propylene glycol) (PPG) and toluene diisocyanate (TDI). Both PUs are crosslinked with trimethylolpropane (TMP). The PPG-based prepolymer has a nominal structure of significantly lower molecular weight than Adiprene L-100, and was used to investigate the effect of the crosslink density of the first-formed network on the IPN morphology. The structure and properties of the IPNs were investigated by dynamic mechanical analysis and ^{13}C n.m.r. spectroscopy.

EXPERIMENTAL

Adiprene L-100 (ref. 4) kindly donated by Du Pont (UK) Ltd, is an isocyanate-terminated PU prepolymer based on polytetramethylene ether glycol and TDI. The α,ω-hydroxy-terminated PPMS prepolymer was supplied by Dow Corning Ltd. The siloxane crosslinking agent, tetraethoxysilane (TEOS) was supplied by BDH Laboratory Reagents and the PU crosslinker, TMP, the PPG and 2,4-TDI by Aldrich Chemical Co. Ltd. The catalyst used was tin octoate (stannous 2-ethylhexanoate) (Sigma Chemical Co.). All materials were thoroughly dried using conventional techniques and stored over molecular sieve or in a desiccator.

To obtain the solubility parameters of the homonetworks, approximately 0.2 g pieces were immersed in a number of solvents covering the solubility parameter range from 14.3×10^3 to 29.7×10^3 (J m^{-3})$^{1/2}$.

The dynamic mechanical behaviour of the materials was examined with a Polymer Laboratories dynamic mechanical thermal analyser, at a heating rate of approximately 2°C min^{-1}, and at a frequency of 0.33 Hz.

Proton-decoupled ^{13}C n.m.r. spectra were recorded at 20 MHz on a Varian Associates CFT-20 n.m.r. spectrometer. For the solution-state experiments,

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approximately 25% w/v solutions in CDCl$_3$ or (CD$_3$)$_2$CO were used. For quantitative measurements, standard 'gated' decoupling techniques were employed, and a 5 s delay between pulses was inserted. For the solid-state experiments, the materials were cured inside an 8 mm tube, which was then inserted into a standard 10 mm tube containing sufficient D$_2$O to provide the internal lock signal. The spectra were recorded at ambient temperature and were the result of 2–3 K accumulations, recorded over 2 kHz, pulse width 19 μs (~80°), with an acquisition time of 2 s, with no additional pulse delay. The spectra were sampled using 8 K data points. Linewidth measurements were made for the Adiprene-based formulations only. For the system based on PPG/TDI, most of the materials were below or around the T_g, resulting in spectra dominated by ^{13}C–^{1}H dipolar interactions, such that simple linewidth measurements were not possible.

In the IPN synthesis, the mole ratio of isocyanate to hydroxyl used to prepare the PU networks, and the hydroxyl to ethoxy ratio for the siloxane networks was 1:1. For the Adiprene-based system, the required weight of TMP was dissolved in tetrahydrofuran (10% by weight of total ingredients). The Adiprene and the PPMS were blended with a high speed mixer for 2 min, and then the TMP solution, the TEOS and the catalyst were added, and mixing continued for a further 30 s. The flask was then transferred to a vacuum oven, at room temperature, and the mixture was degassed for approximately 10 min. It was then poured into a Teflon-lined Perspex mould fitted with an aluminium spacer. The mould was then placed in a desiccator at 20°C and left for 24–48 h to ensure complete network cure. The catalyst concentration was 2% by weight for the PPMS homonetwork, and for the IPNs containing up to 70% Adiprene. Above this concentration of PU, the catalyst concentration had to be reduced, otherwise the rapidly obtained advanced state of cure resulted in a material of too high viscosity for the degassing to be completed. A concentration of 0.33% was found to be adequate for the 90% PU IPN and the PU homonetwork. For the PPG/TDI based system, the procedure was identical except that PPG/TDI replaced the Adiprene L-100. No catalyst was required for the PU homonetwork, 0.33% was used for the 90% PU, 0.67% for the 70% PU, 1.0% for 50% PU and 2.0% thereafter. All the cured materials were stored under vacuum at 20°C for at least one week prior to investigation.

RESULTS AND DISCUSSION

Figure 1 shows the ^{13}C n.m.r. spectrum of PPMS. The peaks between 120 and 140 ppm are assigned to the aromatic carbon resonances, and those around 0 ppm to the methyl groups. The ratio of the area of aromatic carbon peaks to the methyl carbon peaks (6:1), together with the observation of only one type of phenyl end-group (136.8 ppm) and methyl end-group (−1.2 ppm), indicates that the prepolymer contains exclusively –(SiMePhO)– repeat units.

Figure 2 shows the ^{13}C n.m.r. spectrum of PPG, recorded over 2 kHz. The tallest peak, at 75.03 ppm, is assigned to the in-chain methine carbon, those at 72.94 and 72.80 ppm to the in-chain methylene carbons, and the peak at 16.85 ppm to the in-chain methyl carbon. These assignments are in agreement with previous ^{13}C n.m.r. studies of this polymer[5–7], and were confirmed by recording the spectrum without proton decoupling, and observing the multiplet patterns. *Figure 3* shows a 100 Hz expansion of the methine and methylene carbon region of the spectrum. The tallest peak (the methine carbon), at 75.03 ppm, can be just discerned as having two shoulders, assigned[5,6] to isotactic (furthest downfield) and syndiotactic triad sequences, the centre being the resonance from the heterotactic triad. The methylene carbon is resolved into two peaks, assigned[5,6] to the meso

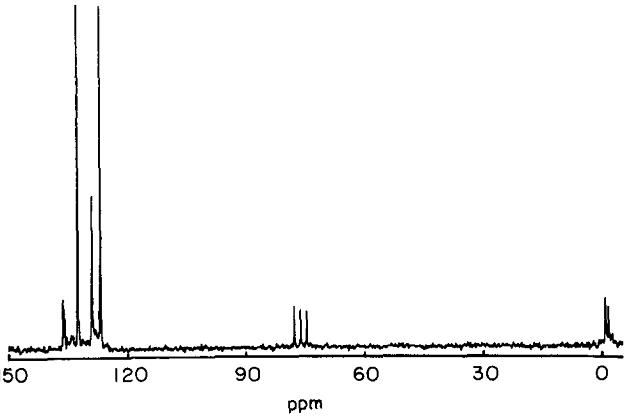

Figure 1 ^{13}C n.m.r. spectrum of PPMS. The triplet centred at 76 ppm is from the solvent, CDCl$_3$

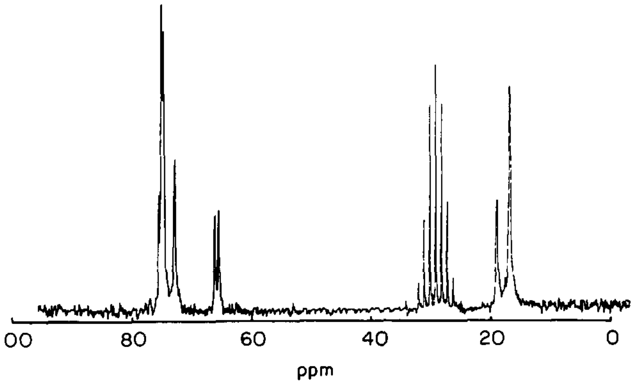

Figure 2 ^{13}C n.m.r. spectrum of PPG. The multiplet centred at 29 ppm is from the solvent, d_6-acetone

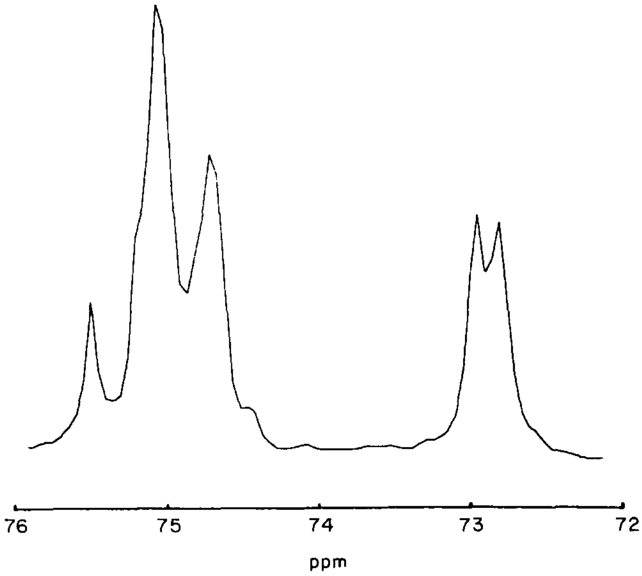

Figure 3 100 Hz expansion of the ^{13}C n.m.r. spectrum of PPG, showing methine and methylene peaks

(downfield) and racemic dyads. That the height of these peaks is approximately equal indicates that the polymer is essentially atactic, having been polymerized from a racemic monomer. The remaining peaks at 75.48 and 74.69 ppm are end-group peaks, arising from the influence of the hydroxyl group. These can, again, be seen in *Figure 2*, together with other end-group peaks at 66.21, 65.55 and 19.07 ppm. The observed chemical shifts of these end-group peaks are in excellent agreement[8] with those calculated for a polymer containing exclusively secondary hydroxyl groups. This is consistent with the PPG having been synthesized by the ring-opening, base-catalysed polymerization of propylene oxide[9].

The number-average molecular weights ($\bar{M}_n$) of the prepolymers were calculated by comparing the areas of the in-chain and end-group carbon resonances. The results are shown in *Table 1*.

The network solubility parameters (δ_p) were obtained from the maximum in the swelling coefficient versus solubility parameter of solvent (δ_s) plots[10]. The number-average molecular weight between network junctions ($\bar{M}_c$) was then calculated from the Flory–Rehner equation[11–15]:

$$\frac{\rho}{M}\phi_r^{2/3} = -\frac{1}{V_s}\left[\frac{\ln(1-V_r)+V_r+\chi V_r^2}{V_r^{1/3}-\dfrac{2V_r}{F}}\right] \qquad (1)$$

In this equation, V_r is the volume fraction of rubber in the swollen gel at equilibrium, V_s is the molar volume of the solvent, ρ the density of the rubber, ϕ_r the volume fraction of polymer present at the time of crosslinking, and F the network functionality. χ is the polymer–solvent interaction parameter, which can be obtained from the following approximate expression[16]:

$$\chi = \beta + \frac{V_s}{RT}(\delta_p - \delta_s)^2 \qquad (2)$$

In equation (2), β is a lattice constant, equal to 0.34 (ref. 17) and R and T have their usual significance. *Table 2* shows the δ_p and the $\bar{M}_c$ results for three homonetworks synthesized in this work.

For the Adiprene L-100/PPMS system, all compositions were compatible on initial mixing of the prepolymers. However, as the materials cured, phase separation occurred. The IPNs were translucent at the compositional extremes, but opaque in the mid-range. For the PPG–TDI/PPMS system, all compositions were miscible on initial mixing. After cure, the 90% PU IPN was transparent, the 70% and 50% PU IPNs were translucent, the 30% IPN was more opaque, and the 10% blend transparent.

Table 1 Prepolymer molecular weight data

Prepolymer	$\bar{M}_n$ (g mol^{-1})
Adiprene L-100	1990[a]
PPG	410[b] 425[c]
PPMS	616[b] 775[c]

[a] See ref. 4
[b] ^{13}C n.m.r. spectroscopy
[c] Suppliers information

Table 2 Homonetwork solubility parameters and crosslink densities

Network	$\delta_p \times 10^{-3}$ (J m^{-3})$^{1/2}$	$\bar{M}_c$ (g mol^{-1})	Swelling agent
Adiprene/TMP	19.4	3000	Chloroform
PPG/TDI/TMP	19.5	1300	Chloroform
PPMS/TEOS	18.5	1000	Tetrahydrofuran

The subject of compatibility in polymer blend systems has been extensively discussed in the literature[3]. A brief outline of the more pertinent points will be given here. For two polymers, mixing without specific interaction, the heat of mixing, ΔH_m, has to be very small, or zero. The polymer–polymer interaction parameter, χ, related to ΔH_m, is given by:

$$\chi = \frac{V_d}{RT}(\delta_1 - \delta_2)^2(1-\phi_d) \qquad (3)$$

Here, V_d is the molar volume of diluent, ϕ_d its volume fraction, and $\delta_{1,2}$ the solubility parameters of the polymers. The critical interaction parameter, χ_{cr}, in such a system is given by[3]:

$$\chi_{cr} = \frac{1}{2}\left[\frac{1}{x_1^{1/2}} + \frac{1}{x_2^{1/2}}\right]^2 \qquad (4)$$

$x_{1,2}$ are proportional to the polymer molecular weights. If $\chi > \chi_{cr}$, then a blend will be incompatible at all or some compositions. For the PU/PDMS systems studied previously[1,2], χ was much greater than χ_{cr}, and so phase separation occurred immediately. However, PPMS has a δ value much closer to that of the PUs, and for these present systems, the combination of a relatively small $(\delta_1 - \delta_2)$ term and the relatively low molecular weights of the prepolymers ($x_{1,2}$) results in the favourable situation where $\chi < \chi_{cr}$. Theoretically then, the polymers will form one phase on mixing, providing much greater opportunity for mutual interpenetration at the molecular level after cure. This initial compatibility is indeed observed. As the cure of each network proceeds, the increase in molecular weight will tend to encourage phase separation. Determination of the point of incompatibility (the spinodal) can be calculated[3] from equation (5), where $\phi_{1,2}$ is the polymer volume fraction.

$$\chi_{sp} = \frac{1}{2}\left[\frac{1}{x_1\phi_1} + \frac{1}{x_2\phi_2}\right] \qquad (5)$$

When $\chi_{sp} \leq \chi$, phase separation will occur at the composition of interest. For the present systems, the situation is simplified by the discrepancy in the rate of cure of each network. With tin octoate as catalyst, the PU networks are substantially cured (x equal to ∞) in a few minutes, whereas the PPMS network takes several hours to cure. Therefore, the expression for χ_{sp} can be modified to:

$$\chi_{sp} \simeq \frac{1}{2}\cdot\frac{1}{x_2\phi_2} \qquad (6)$$

Assuming the PU network cures to very high molecular weight before the PPMS network cure begins, then χ is always less than χ_{sp} at this point. That is, the semi-IPN is predicted to be one-phase. However, as the PPMS network cures, and x_2 increases, a point will be reached where phase separation will be predicted to occur, on purely thermodynamic grounds. *Table 3* gives the critical PPMS molecular weight for each composition. Of course, this theoretical treatment takes no account of the kinetic factors involved in phase separation. The higher the molecular continuity of the PPMS blocks, then the greater will be the extent of inter-network physical entanglements. Therefore, the phase separation will be limited, depending on the restriction on polymer chain mobility brought about by the crosslinking. Except for the blends of high ϕ_2, appreciable permanent inter-polymer chain mixing would be expected. This aspect will be discussed further, in light of the dynamic mechanical behaviour of the IPNs.

The dynamic mechanical behaviour of the Adiprene L-100/TMP network has been discussed in several previous publications[1,4,18], including the first paper in this series[1]. *Figures 4* and *5* show the plots of tan δ, E' and E'' versus temperature for the PPMS/TEOS network. The only feature is the glass transition at −16°C. It is of interest to compare the properties of the PPMS network with those of the PDMS network studied previously[1,2]. For PDMS, the T_g was observed at −97°C, and the material was highly crystalline below −38°C. The differences in behaviour of the two materials can be attributed to chemical structure and degree of crosslinking. The substitution of a methyl group by a comparatively large phenyl group would be expected to raise the T_g on steric grounds[19–21], there being a similar difference between the T_g values of polypropylene (0°C) and polystyrene (100°C), where one can consider that an analogous substitution has been made. The $\bar{M}_c$ of the PPMS network is much less than that of the PDM network, and the associated decrease in free volume also contributes to the higher T_g[21]. The restriction imposed on the mobility of the chains by the tight network would also not favour crystallization. Furthermore, the polymer is most likely to be atactic, which would also inhibit crystallization.

Table 3 Critical PPMS molecular weights for each IPN composition

ϕ_2	$(x_2)_{critical}$	(Molecular weight)$_{critical}$ (g mol^{-1})
0.1	250	20300
0.3	85.3	6800
0.5	50.0	4100
0.7	35.7	2900
0.9	27.8	2300

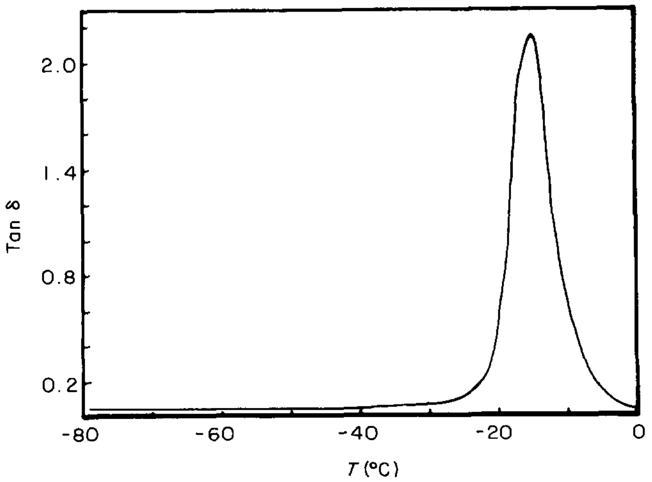

Figure 4 Tan δ versus temperature for the PPMS/TEOS network; 0.33 Hz

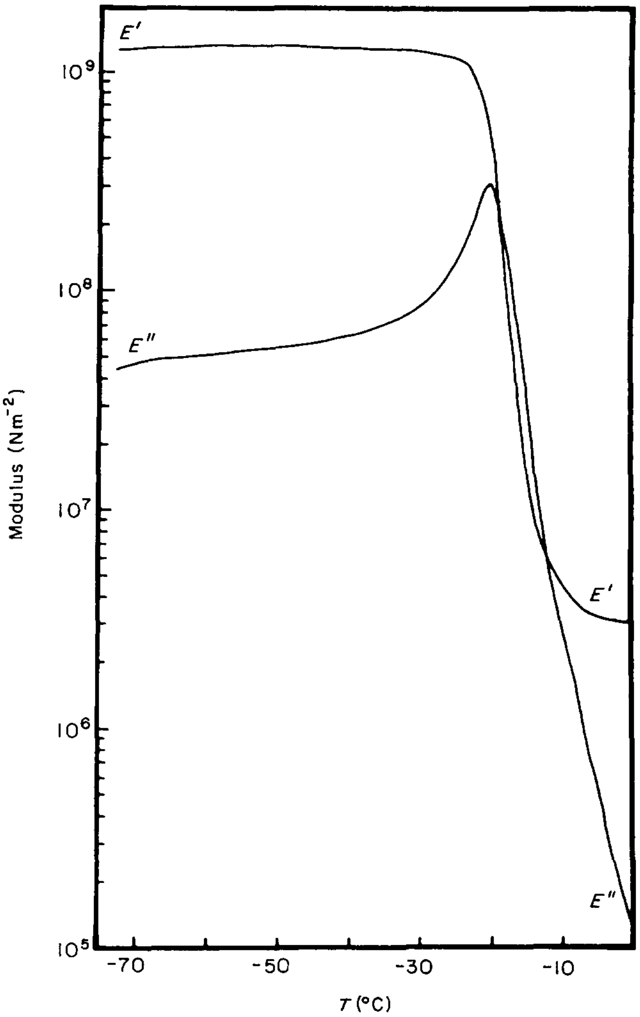

Figure 5 E' and E'' versus temperature for the PPMS/TEOS network; 0.33 Hz

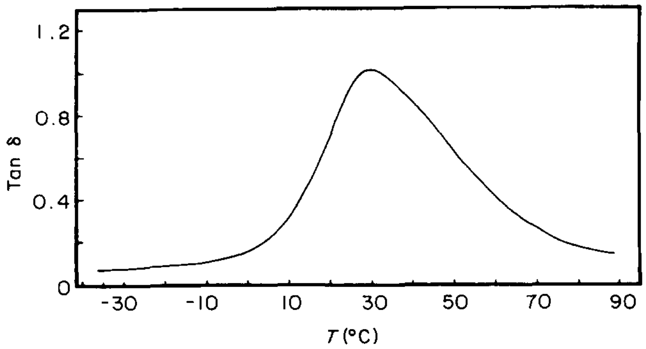

Figure 6 Tan δ versus temperature for the PPG/TDI/TMP network; 0.33 Hz

The dynamic mechanical behaviour of the PPG/TDI/TMP network is shown in *Figures 6* and *7*. Again, the only discernible feature is the T_g, at 30°C in the tan δ versus temperature plot. This is approximately 50°C higher than the Adiprene L-100/TMP network T_g. This can be attributed to the presence of side groups (methyl) in the polyether block, and to the higher extent of

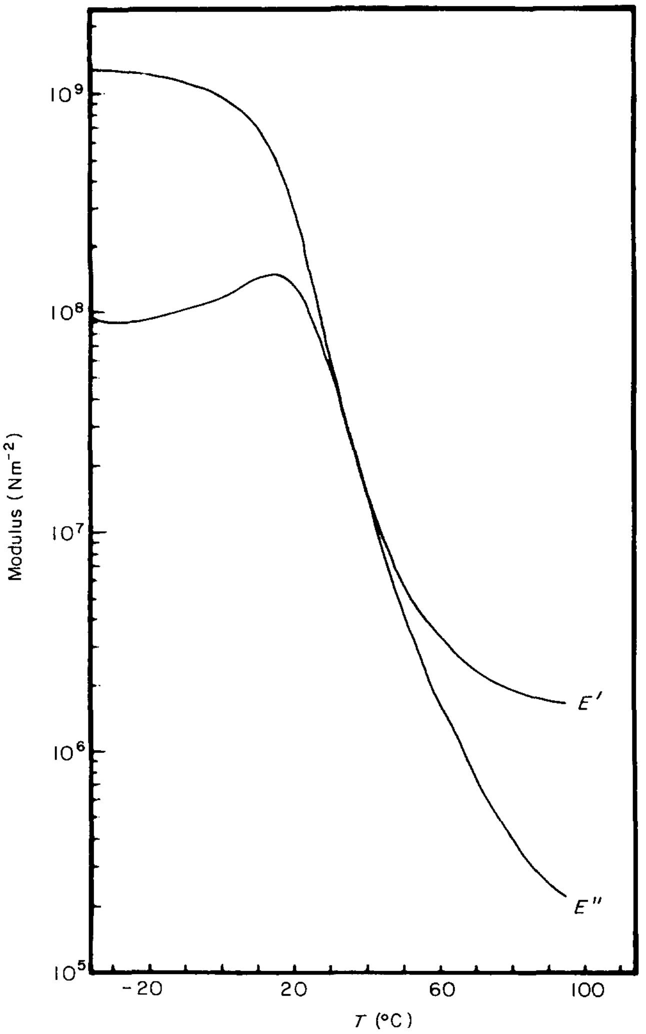

Figure 7 E' and E'' versus temperature for the PPG/TDI/TMP network; 0.33 Hz

crosslinking. The tighter network is also expressed in terms of the half-peak width, which is some 9°C greater than that of the Adiprene L-100/TMP peak.

Figure 8 shows plots of tan δ versus temperature for the Adiprene L-100/PPMS IPNs containing 30, 50 and 70% PU. For each composition, the glass transitions of both networks can be observed, at the homonetwork temperatures. Therefore, the IPNs are phase separated. *Table 4* shows the ^{13}C n.m.r. linewidths (at half-peak height) for the polyether carbons of the PU, in the homonetwork, and in the 50 and 70% PU blends. The rationale behind examining linewidths as a probe of interchain mixing has been discussed in the first paper in this series[1]. For both the 50 and 70% PU blends, the linewidths of both carbons indicate considerable motional narrowing, suggestive of some inter-network chain mixing at the phase boundaries.

Figure 9 shows the tan δ versus temperature plots for the PG/TDI system, for the IPNs containing 90, 70, 50 and 30% PU. At 50% and above of PU, there is essentially only one T_g, the temperature of which increases in proportion to the PU concentration. This suggests a high degree of inter-chain mixing, and a single phase. The narrowness of the glass transition also indicates a high degree of inter-chain mixing (*Table 5*). Closer examination of these single T_g IPNs reveals a slight shoulder around the pure PU T_g. For the 30% PU IPN, two T_g values are in evidence, at the homonetwork temperatures, indicative of phase separation.

The differences between the mechanical properties of these two PPMS-based systems can be attributed to the difference between the crosslink densities of the two polyurethane networks. For the Adiprene L-100-based system, the $\bar{M}_c$ of 3000 g mol^{-1} is, presumably, sufficient to allow phase separation to occur for all compositions, even at 90% PU, where, according to equation (6) and *Table 3*, the PPMS network must cure up to a molecular weight of greater than 20 000 g mol^{-1} before phase separation is predicted. For a high polysiloxane concentration of 90%, the network only has to cure up to 2300 g mol^{-1} before phase separation can occur. Since this is only about two prepolymer blocks, the structure will still be linear, and the phase separation will proceed with little difficulty. Similarly, at 70% polysiloxane a molecular weight of 2900 g mol^{-1} corresponds to only about three blocks, which will be either an entirely linear polymer or a structure with one side-chain, and so there will be little opportunity for inter-chain entanglements. At 50%, though, the point is reached where the advanced

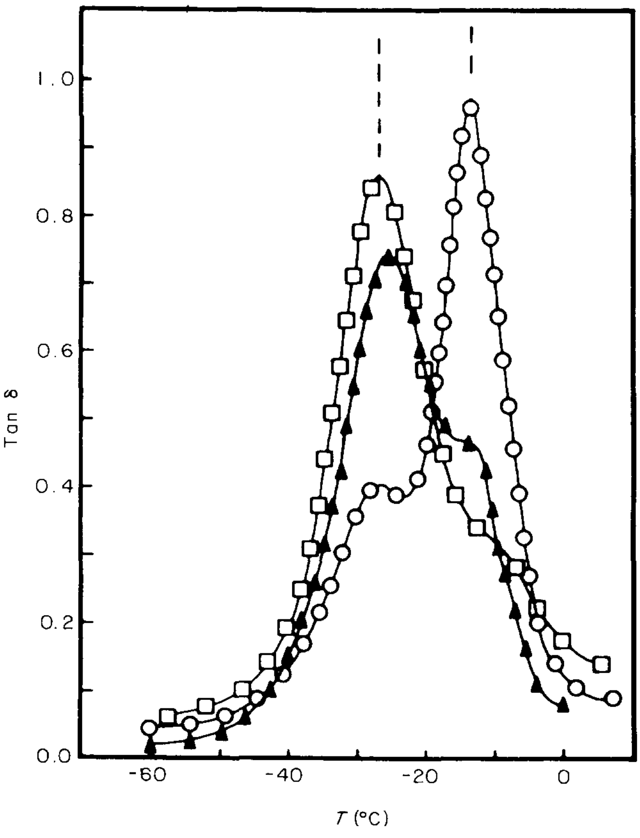

Figure 8 Tan δ versus temperature for PU/PPMS IPNs containing 30 (○), 50 (▲) and 70% (□) PU based on Adiprene L-100/TMP; 0.33 Hz

Table 4 ^{13}C n.m.r. linewidth measurements for Adiprene/PPMS IPNs

Composition (wt% PU)	Linewidth, $(\Delta\nu)_{1/2}$ (Hz)	
	C_1[a]	C_2[a]
50	21.6	17.3
70	24.0	16.9
100	44.0	26.7

[a] C_1 refers to the carbons α to the oxygen, and C_2 to the carbons β to oxygen

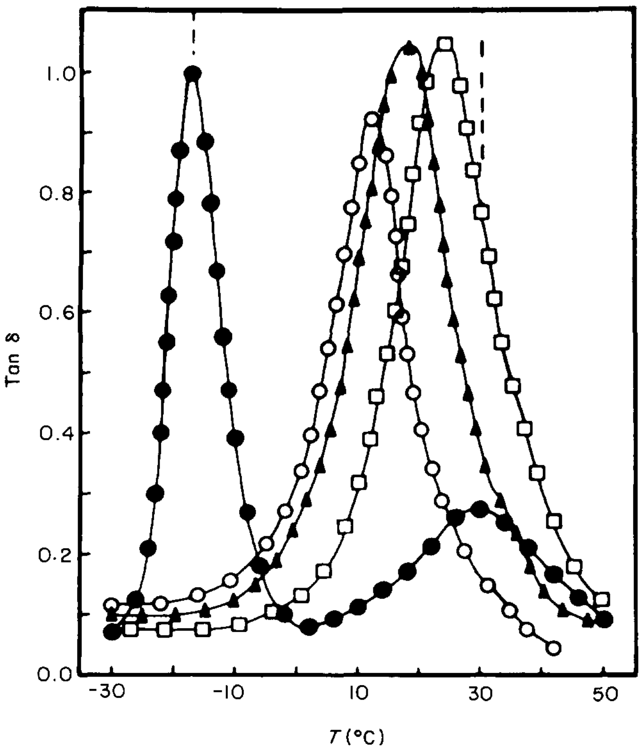

Figure 9 Tan δ versus temperature for PU/PPMS IPNs containing 90 (□), 70 (▲), 50 (○) and 30% (●) PPG/TDI/TMP; 0.33 Hz

Table 5 Glass transition temperatures and half-peak widths for the compatible PPG/TDI-based IPNs

Composition (wt% PU)	T_g (°C)	Half-peak width (°C)
100	30	29
90	24	20
70	18	19
50	13	15
0	−16	7

state of PPMS network polymerization is such that the siloxane polymer cannot disentangle from within the relatively tight PU network, and so a one-phase IPN results.

Figure 10 shows the T_g of the compatible IPNs plotted versus composition. There are several examples in the literature[22] of linear relationships between T_g and composition, as well as positive and negative deviations. For the present compatible compositions, the relationship is either poorly linear, or may have a slight positive deviation. Positive deviations are usually ascribed to specific intermolecular interactions, suggesting that compatibility in these cases is not the result solely of the match between solubility parameters (dispersive interactions), but also the consequence of the exothermic heat of mixing. There are several equations used to relate the blend T_g to those of its constituents. An example is the Gordon–Taylor equation[22]:

$$T_{g_{\mathrm{blend}}} = [W_a T_{g_a} + k(1 - W_a)T_{g_b}]/[W_a + k(1 - W_a)] \quad (7)$$

In equation (7) T_{g_a} and T_{g_b} are the T_g values of the pure components, W_a and W_b their corresponding weight fractions, and k is the ratio of the thermal expansion coefficients between rubber and the glassy states of the component polymers. Certain systems, including PMMA/PVA and poly(styrene-*co*-butadiene)/polybutadiene have been shown to obey the Gordon–Taylor equation[22]. For the present system, a reasonable fit is obtained when k is equal to 1.2, as seen in *Figure 10*.

Turning to the mechanical properties of the IPNs, several theories have been developed to relate the modulus of a multicomponent system to its composition[22]. The Davies equation (8), is claimed to be suited to systems in which both components are continuous.

$$G^{1/5} = V_a G_a^{1/5} + V_b G_b^{1/5} \quad (8)$$

Here, G is the shear modulus and V is the volume fraction. Equation (8) may be regarded as a special application of the Nielson general mixing equation, which often successfully describes certain properties of composites when two continuous phases are present[22].

$$P^n = V_a P_a^n + V_b P_b^n \quad (9)$$

$$\text{wherein } -1 < n < 1$$

In this equation, P is a physical property, such as elastic modulus, and n is some function of the morphology and possibly of the property being measured. In systems where both phase separation and dual phase continuity have been postulated, n is close to 0.2 (i.e. the Davies equation). *Figure 11* shows the experimental plot of E' at 0°C versus composition for the PPG/TDI-based IPNs, together with theoretical curves for various values of n. It is clear that the Davies equation does not fit this data. For the compatible compositions, n between 0.8 and 1.0 gives a reasonable fit. *Figure 12* shows similar plots for the same system at 15°C. Here, at 70% and below of PU, a good fit is obtained with n equal to −0.2, encompassing both the compatible and incompatible compositions. The curve relating to the Davies equation is shown for comparison, and appears to be possibly applicable only for blends of very high PU content.

CONCLUSIONS

Phase separation in PU/polysiloxane systems is considerably reduced by the use of PPMS. The prepolymers were seen to be compatible, consistent with the prediction based upon the Krause method of

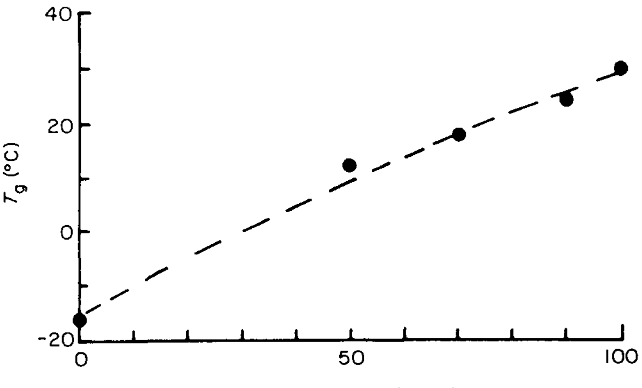

Figure 10 Glass transition temperature (T_g) versus composition for PPG/TDI based PU/PPMS IPNs. The broken line is the Gordon–Taylor equation with k equal to 1.2

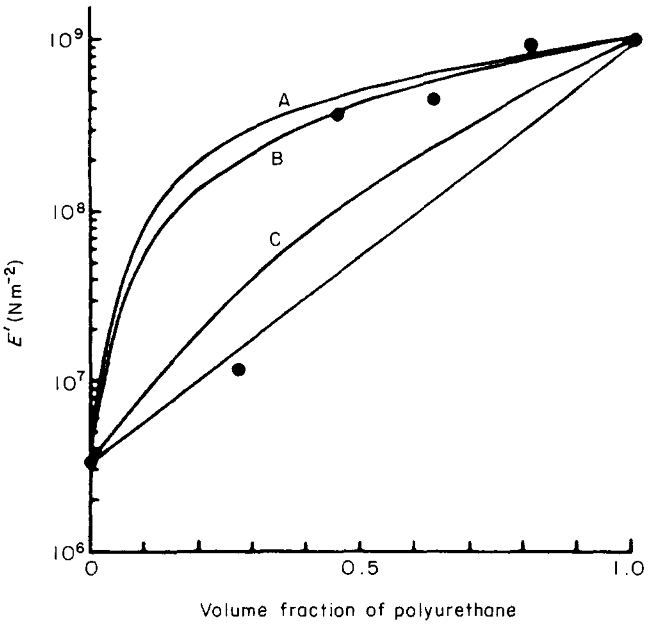

Figure 11 Plots of log E' versus composition for the PPG/TDI system at 0°C. Curves A, B and C are for n equal to 1, 0.8 and 0.2, respectively, in equation (9)

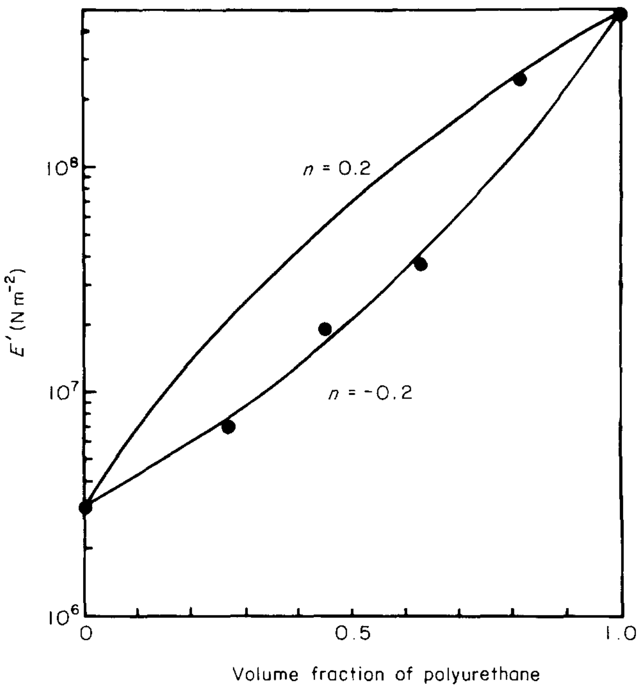

Figure 12 Plots of log E' versus composition for the PPG/TDI system at 15°C with n equal to ±0.2 in equation (9)

comparing solubility parameters. For the system based upon Adiprene L-100, the IPNs were translucent at the compositional extremes, and both T_g values were detected at the homonetwork transition temperatures, in dynamic mechanical experiments, indicating phase separation. In the PPG/TDI-based system, the reduction in $\bar{M}_c$ of the first-formed (PU) network resulted in single T_g IPNs at PU contents of 90 to 50%, inclusive. At 30% PU, phase separation (two homonetwork T_g values) was observed. The compatible/incompatible nature of the IPNs of both systems was seen to be roughly consistent with the thermodynamic predictions.

For the compatible IPNs, the Gordon–Taylor equation provided a good description of the T_g–composition relationship, for k equal to 1.2. However, on examining the relationship between modulus and composition, neither the Davies or Nielsen equations gave adequate fits to the data for either system.

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