

Polyurethane–polysiloxane interpenetrating polymer networks: 1. A polyether urethane–poly(dimethylsiloxane) system

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The synthesis and properties of a polyether urethane network based on Adiprene L-100, of a poly(dimethylsiloxane) network and of nine interpenetrating polymer networks based on these polymers were investigated. To form the latter materials, the prepolymers were mixed and crosslinked simultaneously, but by separate mechanisms. Comparison of the network solubility parameters suggested marked incompatibility. Optical microscopy, dynamic mechanical analysis and the tensile testing indicated gross phase separation. From 90 to 50% of the polyether urethane component, this network was continuous and the poly(dimethylsiloxane) was present as dispersed phases. From 40 to 10% of the polyether urethane, the situation was reversed. Some degree of interchain mixing at phase boundaries was detected by ^{13}C nuclear magnetic resonance spectroscopy.

(Keywords: polymer blends; interpenetrating polymer networks; poly(dimethylsiloxane); polyurethane; dynamic mechanical analysis; nuclear magnetic resonance spectroscopy)

INTRODUCTION

In recent years, considerable attention has been paid to various aspects of polymer blends^{1–3}. Interpenetrating polymer networks, IPNs, are a class of blend where a polymeric network is synthesized in the presence of another previously or simultaneously established network⁴. Most polymer blends show phase separation³, the degree of which can be largely predicted from thermodynamic considerations. The vast majority of IPNs are also phase separated, but this separation may be restricted to some extent⁵ by the formation of chain entanglements between the constituent polymers, which then become permanent features on crosslinking. However, polymer pairs for which the free energy of mixing is positive and large will exhibit gross phase separation before network formation occurs, resulting in only limited interpenetration at the phase boundaries⁶.

Polymer blends and IPNs containing a polyurethane have been extensively studied, typically with acrylic polymers^{7–9}, polyesters^{5,10} or epoxies⁵ as the other component. Little work, however, has been reported^{11,12} on systems containing silicone polymers.

The subject of this paper is the synthesis and characterization of polyether urethane–poly(dimethylsiloxane) IPNs. From swelling measurements, the solubility parameters of the homopolymer networks were evaluated, and the likelihood of compatibility assessed. The prepolymers were mixed and crosslinked simultaneously by separate, non-interfering mechanisms. The resulting materials were examined by dynamic mechanical analysis, tensile testing, optical microscopy and ^{13}C nuclear magnetic resonance spectroscopy.

EXPERIMENTAL

Adiprene L-100¹⁰, donated by DuPont (UK) Ltd., is an isocyanate-terminated polyurethane prepolymer based on poly(tetramethylene ether glycol) and toluene diisocyanate. The α,ω -hydroxy-terminated poly(dimethylsiloxane) was supplied by Compounding Ingredients Ltd. It bears the trade name Silopren C18. The poly(dimethylsiloxane) crosslinking agent, tetra ethoxysilane, TEOS, and the catalyst, di-n-butyltin dilaurate, were supplied by BDH Laboratory Reagents. The polyurethane crosslinking agent, trimethylolpropane, TMP, was supplied by the Aldrich Chemical Co. Ltd. It is believed that the prepolymers and their corresponding crosslinking agents react virtually exclusively. This topic will be discussed in the next paper in this series. All materials were dried before use and either stored over molecular sieve or in a vacuum desiccator.

Table 1 shows the characterization data for the prepolymers. The mole ratio of isocyanate to hydroxyl used in the polyurethane network preparations and the hydroxy to ethoxy ratio in the poly(dimethylsiloxane) network synthesis were 1:1. The required weight of TMP was dissolved in tetrahydrofuran (10% by weight of total ingredients). The Adiprene L-100 and the Silopren C18 were blended by hand using a spatula. The TEOS and the TMP solution were then added and the mixture was stirred vigorously for 5 min. 0.5% by weight of catalyst was then added and carefully stirred into the mixture. The beaker was then transferred to a vacuum oven and the mixture degassed for approximately 10 min. It was then poured into a mould with an aluminium frame and perspex top and bottom plates which were covered with PTFE sheet to facilitate sample removal. The mould was left in a desiccator at room temperature for 24–48 h. The cured rubber, or IPN, was then removed and stored, at

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Table 1 Characterization data for the prepolymers

Prepolymer	\overline{M}_n (g mol ⁻¹)	$\overline{M}_w/\overline{M}_n$
Adiprene L-100	1 990 ¹	2.0 ¹
Silopren C18	36 000 ²	2.43 ³

¹ See ref. 10

² From membrane osmometry

³ By Gel permeation chromatography

room temperature, under vacuum for at least a week prior to testing.

To obtain the network solubility parameters, approximately 0.2 g pieces of the homopolymer sheets were subjected to equilibrium swelling in a series of solvents covering the solubility parameter range from 14.3×10^3 (J m⁻³)^{1/2} to 29.7×10^3 (J m⁻³)^{1/2}.

The IPN morphologies were examined with a Nikon model L-Ke optical microscope equipped with a microflex model PFM photomicrographic attachment.

For dynamic mechanical analysis, a Polymer Laboratories Dynamic Mechanical Thermal Analyser was used at a frequency of 10 Hz. The sample heating rate was approximately 2°C min⁻¹.

The stress-strain characteristics (20°C) of dumb-bell shaped specimens were measured with a J-J Lloyd model 5002, tensile tester. The extension rate was 15 mm min⁻¹.

Proton-noise decoupled ¹³C n.m.r. spectra were recorded at 20 MHz and at ambient probe temperature (approximately 40°C) on a Varian Associates CFT-20 n.m.r. spectrometer. The materials were cured in an 8 mm tube which was then inserted into a standard 10 mm tube, containing D₂O, so that the resulting sleeve of D₂O provided the internal lock signal. Chemical shifts are quoted relative to TMS at 0 ppm, but were referenced initially to the D₂O lock frequency. Relevant instrument operating parameters were: sweep width, 2000 Hz; pulse width, 19 μs (corresponding to a nuclear tip angle of approximately 80°) and acquisition time, 2 s (with no additional pulse delay). Spectra were sampled using 8K data points and were the result, normally, of 2–3K accumulations.

RESULTS AND DISCUSSION

Plots of swelling coefficient *versus* solubility parameter¹³ gave, in both cases, a Gaussian-type curve. The maximum swelling was taken to correspond to the solubility parameter of the polymer network^{13,14}. The polymer-solvent interaction parameter, χ , was then determined from the following approximate expression¹⁵:

$$\chi = \beta + \frac{V_s}{RT} (\delta_p - \delta_s)^2 \quad (1)$$

V_s is the molar volume of the swelling agent. δ_p and δ_s are the solubility parameters of the polymer and the swelling agent, respectively. β is the lattice constant for which a value of 0.34 was assumed¹⁶. R and T have their usual significance. The number average molecular weight between crosslinks, \overline{M}_c , was evaluated from the modified Flory-Rehner^{17–21} equation.

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

V_r is the volume fraction of rubber in the swollen gel, F is the network functionality, l is the density of the rubber and ϕ_r is the volume fraction of polymer present at the time of crosslinking²¹. Table 2 shows the values of δ_p and \overline{M}_c for the homo-networks.

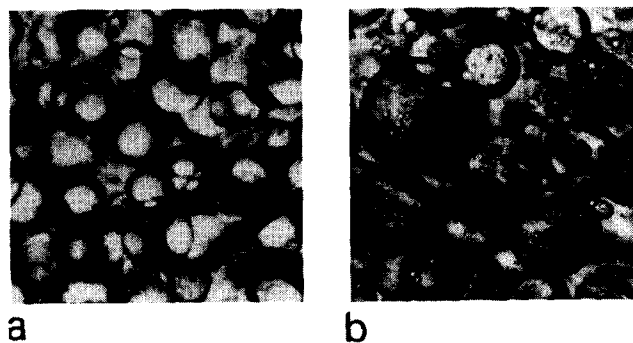
Considering that the solubility parameters of the two components differ by 4.7×10^3 (J m⁻³)^{1/2}, application of the Krause²² method of compatibility prediction leads to the conclusion that the system will be incompatible at all compositions, except those very close to the compositional extremes.

Both the homo-networks produced transparent sheets, while all of the IPNs were white and opaque, indicating macrophase separation. The polyether urethane network was the first formed, being essentially cured after about 10 h at the catalyst concentration used. This compared to a cure time of about 25 h for poly(dimethylsiloxane) network. Using a light microscope, phase structure could be observed for all the IPNs (see Figure 1). Both the 50% and the 70% polyether urethane IPNs show small phases of the continuous phase within the dispersed phases. Figure 2 shows the graph of the average domain diameter *versus* composition. The curve is reasonably symmetrical; the smallest domains, of approximately 9 μm, occur at the extremes of the range, and the maximum domain diameter, of about 80 μm, occurs for the mid-composition blend.

The stress-strain curves for the homo-networks and for the IPNs are shown in Figures 3 and 4. The materials can be clearly divided into two categories; those containing 50% or more by weight of the polyether urethane, which behave in the same manner as the polyether urethane homo-network, and those containing 60% or more by weight of poly(dimethylsiloxane), which take on the characteristics of the poly(dimethylsiloxane) homo-network. At the high polyether urethane concentrations, the inclusion of the poly(dimethylsiloxane) network has an increasingly detrimental effect on the tensile behaviour. A similar effect is apparent at the high poly(dimethyl-

Table 2 Solubility parameters and molecular weights between crosslinks for the homonetworks

Material	Swelling agent	$\delta_p \times 10^{-3}$ (Jm ⁻³) ^{1/2}	\overline{M}_c (g mol ⁻¹)
Polyether urethane	chloroform	19.4	3 000
Poly(dimethylsiloxane)	<i>n</i> -hexane	14.7	14 600


Figure 1 Representative optical micrographs showing IPNs containing (a) 30 and (b) 70% by weight of polyether urethane. 0.75 cm is equivalent to 25 μm

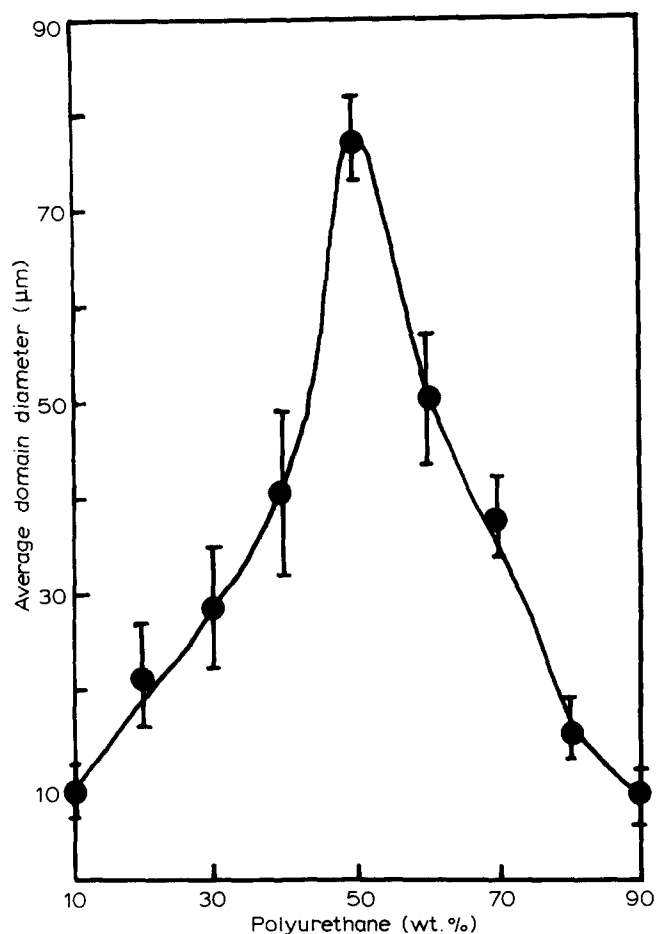


Figure 2 Average domain diameter-composition

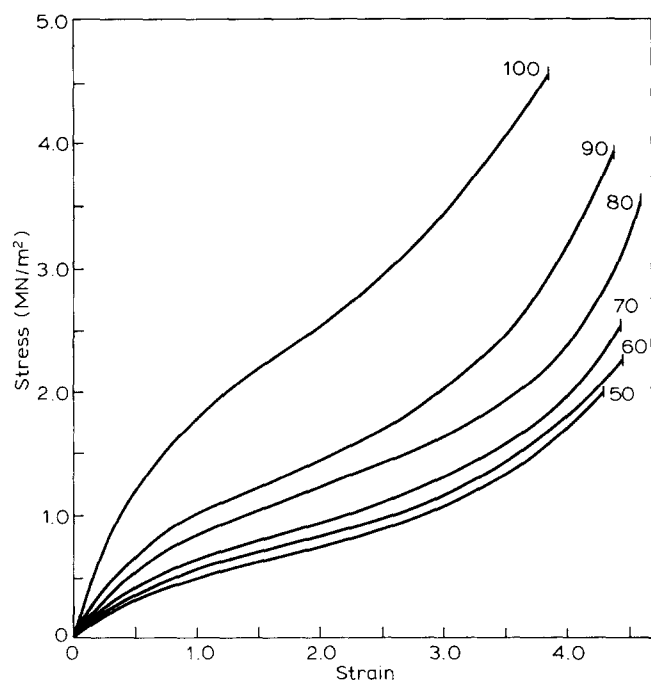


Figure 3 Stress-strain curves (20°C) for the IPNs containing 90, 80, 70, 60 and 50% by weight of polyether urethane and for the polyether urethane network (100)

siloxane) end of the composition range. The addition of 10% polyether urethane leads to an increase in the initial modulus and the IPNs with 10% and with 20% polyether

urethane have superior tensile strengths to the poly(dimethylsiloxane) homo-network.

These tensile observations are consistent with the gross multiphase morphology observable with the light microscope and with the observation that at polyurethane contents of 50% and above this network is continuous, with isolated domains of crosslinked poly(dimethylsiloxane). At poly(dimethylsiloxane) concentrations of 60% or more, the situation is reversed.

Figures 5 and 6 show the $\tan \delta$ -temperature dispersion and the dynamic storage modulus, E' , and the dynamic loss modulus, E'' , versus temperature plots for the polyether urethane homo-network. This network, based on Adiprene L-100 and TMP, has been well characterized^{10,23} previously. The glass transition temperature, T_g , is apparent at -20°C in the $\tan \delta$ -temperature plot. The minor transition at -108°C has been ascribed²³ to motions of methylene units via a Schatski-type mechanism²⁴. A small transition is also discernible in the E'' -

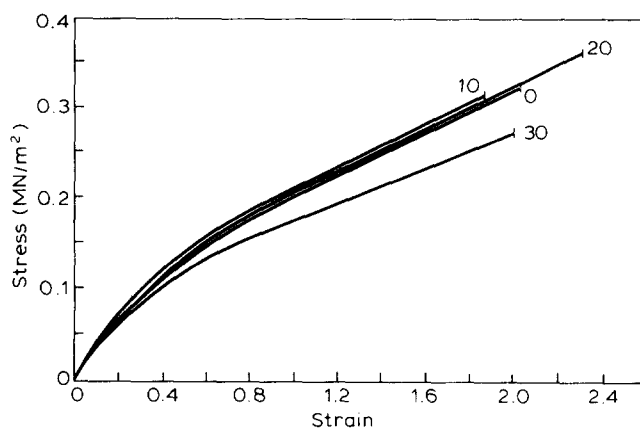


Figure 4 Stress-strain curves (20°C) for the IPNs containing 30, 20 and 10% by weight of polyether urethane and for the poly(dimethylsiloxane) network (0)

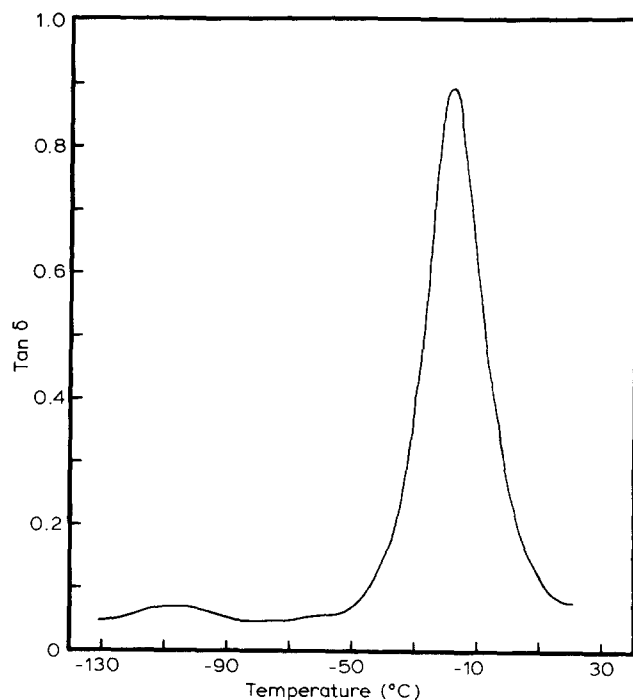


Figure 5 $\tan \delta$ -temperature plot (10Hz) for the polyether urethane network

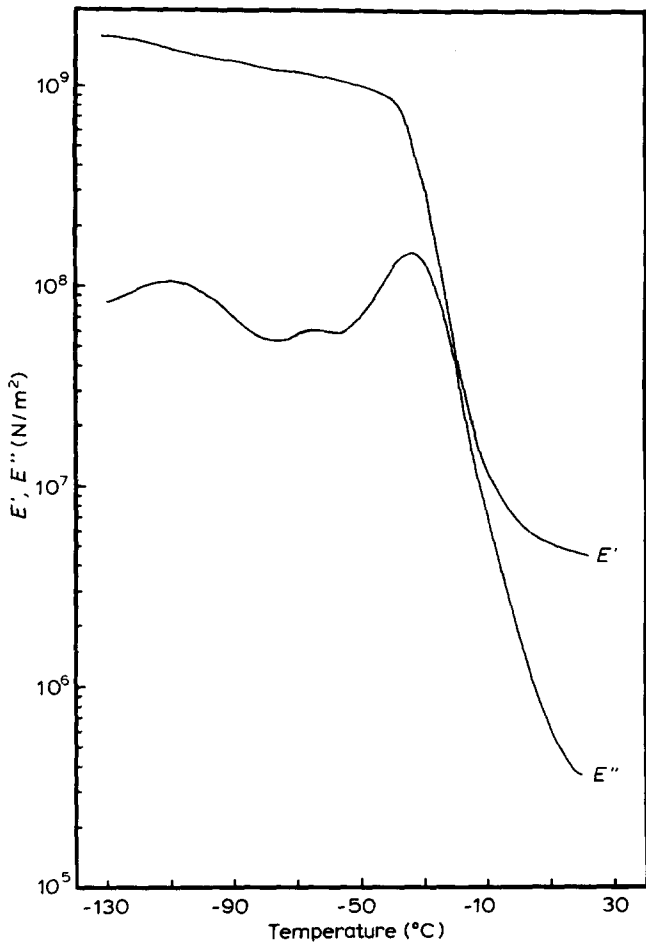


Figure 6 E' and E''-temperature plots (10Hz) for the polyether urethane network

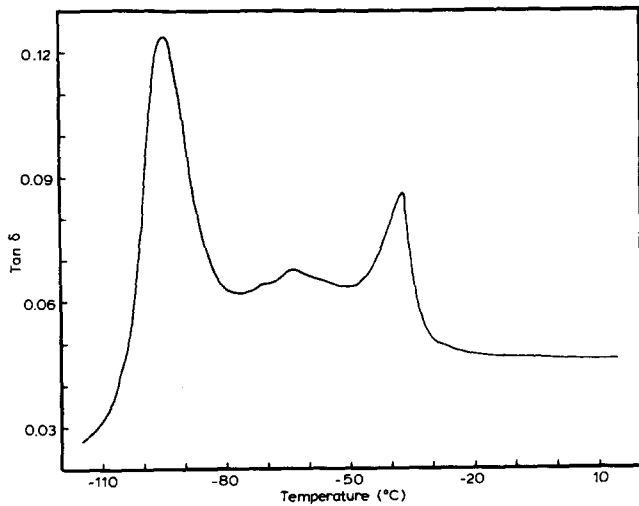


Figure 7 Tan δ-temperature plot (10Hz) for the poly(dimethylsiloxane) network

temperature plot (Figure 6) at -68°C and is most likely associated with adsorbed moisture²³.

For the poly(dimethylsiloxane) network (Figures 7 and 8), three main features are apparent. The transition in $\tan \delta$ at -38°C , corresponding to the catastrophic fall in E' , is associated with crystalline melting²⁵⁻²⁷. The T_g , at -97°C ,²⁵⁻²⁸ shows a low $\tan \delta$ maximum value and a corresponding relatively minor drop in E' of only about a

factor of five, compared with a reduction in this modulus of the best part of two orders of magnitude at the crystalline melting point. This is indicative of a high degree of crystallinity which has been measured, by differential scanning calorimetry²⁹, to be about 74%. There is a small peak in the $\tan \delta$ -temperature plot at -68°C , interpreted as resulting from cold crystallization²⁵.

Figure 9 shows the E'' -temperature curves for the IPNs containing 70, 50, 40 and 20% by weight of polyether urethane. As can be seen, the 70 and 50% polyether urethane IPNs display the features of the polyether urethane homo-networks, whereas the blends containing 40 and 20% polyether urethane have curves similar to that of the pure poly(dimethylsiloxane) network. These results further confirm the incompatible nature of these polymers. The dispersed phase is almost totally discontinuous. Figure 10 shows the $\tan \delta$ -temperature behaviour for the IPNs containing 40 and 50% by weight of polyether urethane. For the 50% IPN, the polyether urethane T_g can be observed at -20°C , together with the minor transition at -100°C . For the 40% polyether urethane IPN, the poly(dimethylsiloxane) T_g is apparent, together with the crystalline melting transition at -38°C . If the polyether urethane network was to any significant extent continuous throughout this latter sample, its T_g should be

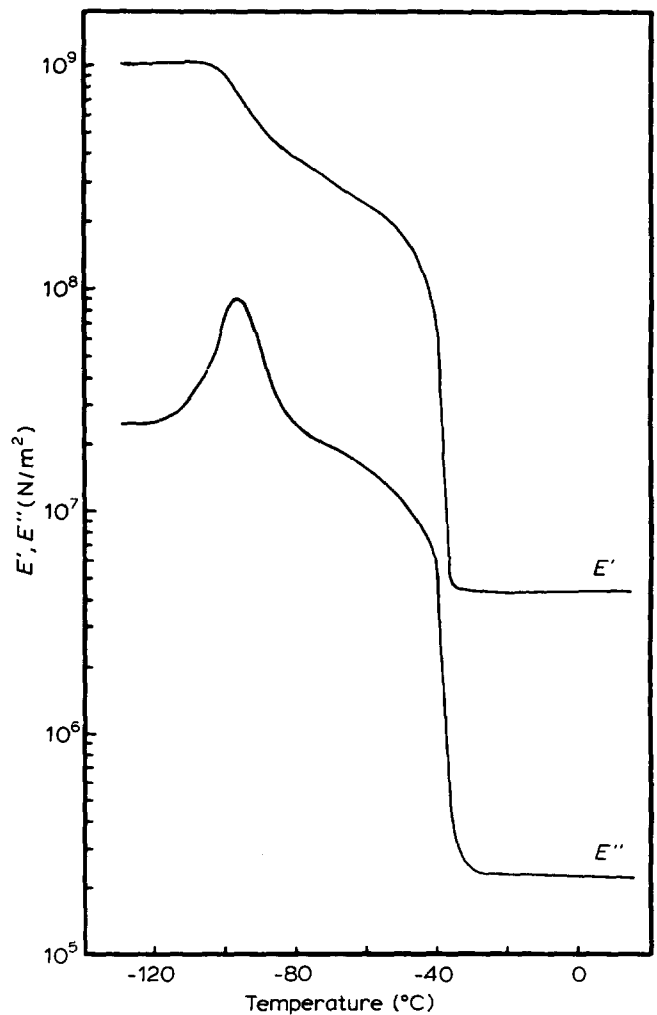


Figure 8 E' and E''-temperature plots (10Hz) for the poly(dimethylsiloxane) network

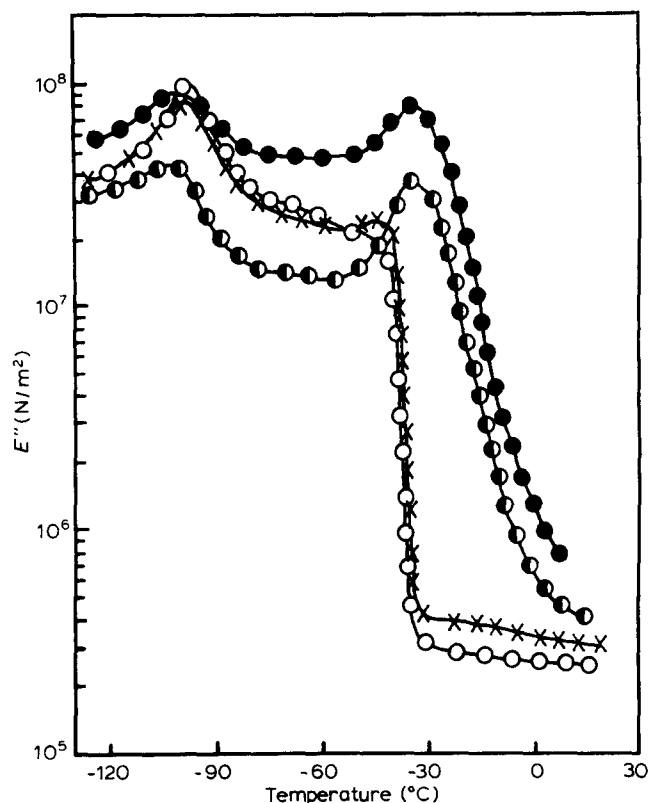


Figure 9 E'' -temperature plots (10Hz) for the IPNs containing 70(●), 50(○), 40(X) and 20(○) percent by weight of polyether urethane

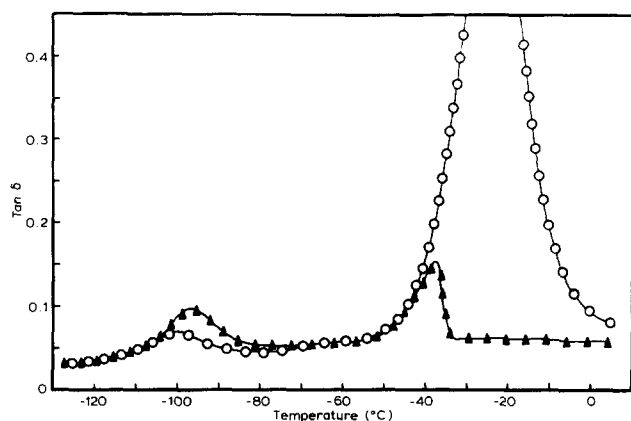


Figure 10 $\text{Tan } \delta$ -temperature plots (10Hz) for the IPNs containing 40(▲) and 50(○)% by weight of polyether urethane

observable at -20°C . However, there is absolutely no evidence of such a transition, supporting the contention that the domains are essentially mechanically isolated.

^{13}C n.m.r. studies of the cured homo-networks and IPNs were undertaken to gain an insight into the degree of inter-chain mixing at the phase boundaries. For proton-decoupled ^{13}C n.m.r. spectra, the individual peaks can give information about the dynamics of individual carbon atoms in the polymer chain³⁰. For solid, glassy polymers below T_g , the strong carbon-proton dipolar interactions, and the chemical shift anisotropies, lead to very broad lines, typically of several kHz width; high resolution spectra can only be obtained on such solids by the use of 'magic angle' sample spinning and high power decoupl-

ing³¹. However, for polymers above T_g , the chain mobility is often sufficient to produce considerable motional narrowing of the peaks, and a reasonably resolved spectrum can often be obtained under the instrumental conditions more usually used for acquiring solution spectra. For solid polymers, the frequency of segmental motion is usually much lower than that for the motions of small molecules in solution, and the spin-spin relaxation time, T_2 , is less than the spin-lattice relaxation time, T_1 , and continues to decrease as the isotropic correlation time, τ , describing the segmental motion becomes longer³². The relation between the peak width at half height, $(\Delta\nu)_{1/2}$, and T_2 is given by equation (3)

$$(\Delta\nu)_{1/2} = 1/\pi T_2 \quad (3)$$

Consequently, the more rapid the motion of a particular carbon atom in the chain, the narrower will be the peak arising from that carbon in the spectrum. If a chain segment is associated with rigid domains, then the linewidths will be greater than if the chain is in a softer, rubbery environment. In the case of polymer blends and IPNs, the linewidths should give information about the extent of interfacial mixing. For a compatible one phase blend, chemically identical carbons will have identical relaxation characteristics. For an incompatible blend, with some degree of interfacial mixing, the different mobilities of different regions of the polymer chains will be describable in terms of a distribution of relaxation times^{33,34} among otherwise identical carbons. Therefore, a peak in a spectrum of an incompatible blend can be regarded as a superposition of several peaks of varying width. A ^{13}C spectrum of a polyether urethane-poly(dimethylsiloxane) blend consists essentially of three peaks, two from the in-chain methylene ether and methylene carbons of the polyether (1 and 2 below) and one from the in-chain methyl carbon of the poly(dimethylsiloxane) (3 below).

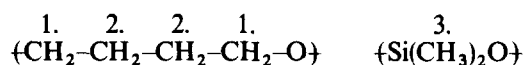


Table 3 shows the chemical shifts of these carbons, and their linewidths, in the solid homo-networks and the IPNs. Figure 11 gives the linewidths as a function of the blend composition. For the polyether urethane network, C-2 is consistently narrower than C-1. This feature has been observed also in ^{13}C n.m.r. studies of HytreI³⁵ which

Table 3 Linewidths and chemical shifts for solid polyether urethane, poly(dimethylsiloxane) homo-networks and for selected IPNs.

Polyether urethane (wt. %)	Linewidth $(\Delta\nu)_{1/2}$ (Hz)*		
	C-1	C-2	C-3
0	—	—	2.7
20	20.1	12.0	3.1
40	25.8	17.0	4.1
50	32.7	20.4	5.7
70	32.1	18.9	2.8
100	44.0	26.7	—
Chemical shift (ppm)	72.0	28.2	0.7

* ± 0.2 Hz

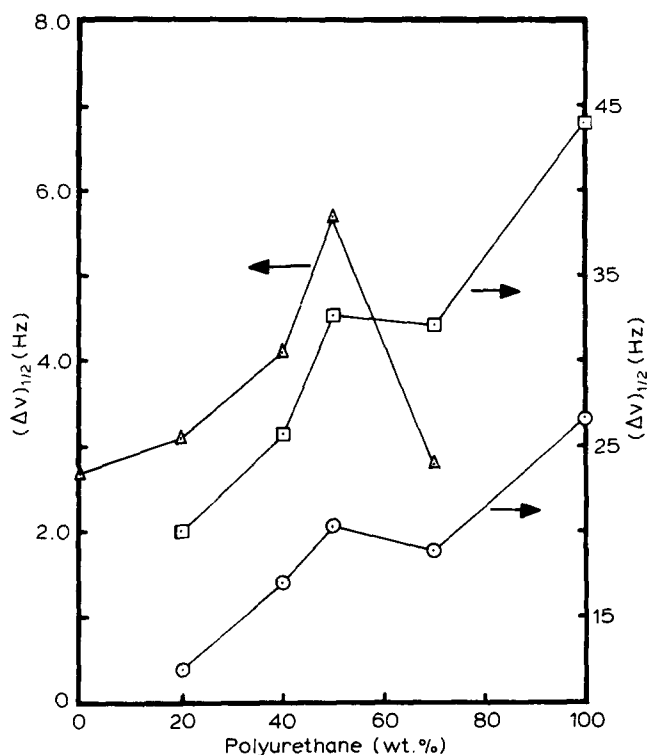


Figure 11 $(\Delta\nu)_{1/2}$ - composition plots. Symbols have the following significance. □ - carbon 1; ○ - carbon 2; Δ - carbon 3

contains the same polyether repeat unit. The authors in that case suggested that the difference in linewidths may be due to additional modes of low frequency being available to the central carbons (that are not available to the carbons directly bonded to oxygen) or, alternatively, that the chemical shift anisotropies for the two types of carbon may be different. C-3 is very narrow and the linewidth approaches the value obtained in solution. This is consistent with the considerable flexibility of the siloxane backbone and indicates, furthermore, that the crosslink density is sufficiently low that the crosslink sites do not restrict reorientation. Both C-1 and C-2 linewidths are narrowed by the addition of poly(dimethylsiloxane). This suggests that, at the phase boundaries, polyether chain segments penetrate, to some extent, the poly(dimethylsiloxane) phase and are consequently associated with a more mobile environment. At a polyether urethane concentration of 20%, the domains are relatively small ($\sim 10 \mu\text{m}$ radius) and, furthermore, the polyether urethane is the dispersed phase. The surface area (SA): volume (V) ratio of the polyether urethane phase is therefore high, and a substantial proportion of the polyether urethane chains are in contact with the interface, providing maximum opportunity for mixing. At 40% polyether urethane, the domain radius is higher ($\sim 21 \mu\text{m}$), the $SA:V$ ratio is correspondingly lower, a smaller fraction of polyether urethane chains is at the interface and so the C-1 and C-2 peak widths increase, since they now reflect largely the relatively immobile carbons situated well within the polyether urethane domains. At 50 and 70% polyether urethane, the polyether urethane is the continuous phase and so the contributions to linewidths from carbons at the interface are very much less. The linewidths of all three carbons at 50% polyether urethane undergo a pronounced increase. However, at this composition, the two polymers are highly incom-

patible and the uncured mixture is very viscous and difficult to cure in an n.m.r. tube without the introduction of voids. The large $\Delta V^{1/2}$ values are, therefore, believed to be the consequence of this sample inhomogeneity rather than of any phenomenon at the molecular level. Except for the 50% polyether urethane IPN, the peak width of C-3 is essentially constant at 3–4 Hz, suggesting that the local effect of polyether urethane chains on the mobility of poly(dimethylsiloxane) chains (probably predominantly methyl group rotation) is very slight.

CONCLUSIONS

This polyether urethane and poly(dimethylsiloxane) are incompatible as predicted from solubility parameter considerations. At 50% polyether urethane and above, the polyether urethane phase is continuous, and at 40% polyether urethane and below, it is dispersed. The dynamic mechanical data illustrate the extent of the incompatibility. Most incompatible polymer pairs display two T_g s, identical in temperature and width to the homopolymers³⁶. This system is sufficiently phase separated so that the domains of the dispersed phase are mechanically isolated and so are not detected by this technique. However, the ¹³C n.m.r. experiments can highlight a certain degree of interfacial mixing, not observed by either stress-strain (except for the IPNs containing 10 and 20% polyether urethane) or dynamic mechanical testing, suggesting that this technique may be a sensitive probe of blend morphology.

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