Polyurethane–polysiloxane interpenetrating polymer networks: 2. Morphological and dynamic mechanical studies

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The reaction between an α,ω-hydroxy-terminated poly(ethylene oxide)–poly(dimethylsiloxane)–poly(ethylene oxide) triblock copolymer and toluene diisocyanate was investigated. Network formation was shown to occur through allophanate linkages. Interpenetrating polymer networks based on this triblock copolymer network and on a poly(dimethylsiloxane) network were shown to be substantially phase separated, although ^{13}C n.m.r. linewidth studies suggested some mixing at domain boundaries. A prepolymer containing silylurethane linkages was synthesized from a low molecular weight α,ω-hydroxy terminated poly(dimethylsiloxane) and toluene diisocyanate. A blend of this silyl-urethane prepolymer crosslinked with trimethylol propane and a polyurethane based on Adiprene L-100 and trimethylol propane was also incompatible. The silyurethane linkage was rapidly hydrolysed on exposure to atmospheric moisture.

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

INTRODUCTION

In the first paper in this series[1], it was established that interpenetrating polymer networks (IPN) formed from a polyurethane (PU) based on Adiprene L-100 and trimethylol propane (TMP) and a poly(dimethylsiloxane) network were incompatible and had rather coarse morphologies. This was expected because of the large difference (4.7×10^3 $(J/m^3)^{\frac{1}{2}}$) in solubility parameters of the two networks.

It might be expected that the presence of segments in one of the IPN networks which are chemically identical to structures in the second network might enhance the degree of mixing. One such attempt to investigate this was to use an α,ω-hydroxy terminated poly(ethylene oxide)–poly(dimethylsiloxane)–poly(ethylene oxide) triblock copolymer which forms a network (ESE) on reaction with toluene diisocyanate (TDI). IPNs based on this ESE network and on a poly(dimethylsiloxane) (PDMS) network formed from an α,ω-hydroxy poly(dimethylsiloxane) crosslinked with tetraethoxysilane (TEOS) were investigated.

The formation of a urethane–siloxane prepolymer by the reaction of a low molecular weight, α,ω-hydroxy-terminated PDMS with TDI was also studied. It might be expected that blends of a PU synthesized from Adiprene L-100 and TMP with this prepolymer also crosslinked with TMP, might show a greater extent of inter-network mixing than would an unmodified PDMS.

The reactions involved in the preparation of both the ESE network and the urethane–siloxane prepolymer were investigated using primarily ^{13}C n.m.r. spectroscopy, but also gel permeation chromatography (g.p.c.). The IPN morphologies were studied using dynamic mechanical analysis (DMA) and optical microscopy as well as ^{13}C n.m.r. spectroscopy. For further information on IPNs, see refs. 1 and 2.

EXPERIMENTAL

Materials

Adiprene L-100[3], kindly donated by Du Pont (UK) Ltd., is an isocyanate-terminated polyurethane prepolymer based on poly(tetramethylene ether glycol) and TDI. The PDMS network in the IPNs was formed from Silopren C18 (Compounding Ingredients Ltd.), which is an α,ω-hydroxy poly(dimethylsiloxane). TEOS and di-n-butyltindilaurate (catalyst) were supplied by BDH Laboratory Reagents and TMP and TDI by Aldrich Chemical Co. Ltd.

The poly(ethylene oxide)–poly(dimethylsiloxane)–poly(ethylene oxide) block copolymer was kindly supplied by Dow Corning Ltd. and the low molecular weight α,ω-hydroxy poly(dimethylsiloxane) used in the urethane–siloxane prepolymer synthesis was supplied by J-Sil Silicones Ltd. The characterization data for the prepolymers are given in *Table 1*. All materials were dried before use and stored over molecular sieve or in a vacuum desiccator.

Synthesis of homonetworks and the ESE-PDMS IPNs

The poly(ethylene oxide)–poly(dimethylsiloxane)–poly(ethylene oxide) copolymer and TDI (1:3 moles) were mixed and left over P_2O_5 in a desiccator for 3 h under partial vacuum. THF (10% by wt. of total), α,ω-hydroxy PDMS (15 000 g/mol) and TEOS (hydroxyl:ethoxy ratio was 1) were then carefully blended for 5 min. 2% by wt. of catalyst was then stirred into the mixture which was then

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Table 1 Characterization data for the prepolymers

Material	$\bar{M}_n$ (g mol^{-1})	$\bar{M}_w/\bar{M}_n$
Adiprene L-100	1990	2.0
Silopren C18	15000	2.43
α,ω-Hydroxy poly(dimethylsiloxane)	1000	1.42
Triblock copolymer	2300	–

carefully degassed and poured into an aluminium mould with Perspex top and bottom plates which were backed with PTFE sheet to facilitate sample removal. The mould was left in a desiccator at room temperature for 24–48 h. The cured sheet was then removed and stored in a vacuum oven for at least a week prior to testing. The two homonetworks were synthesized in this was as well as five IPNs, containing 10, 30, 50, 70 and 90% by weight of the ESE network.

Synthesis of the silylurethane prepolymer

1.74 g TDI (0.01 mole) in 14 ml dry THF was brought to reflux, and 5 g (0.005 mole) of the α,ω-hydroxy PDMS (1000 g/mol) was added over a period of 5 min. The mixture was refluxed for 25 h, then allowed to cool. The THF was removed on a rotary evaporator. G.p.c. chromatograms and ^{13}C n.m.r. spectra were obtained for the original α,ω-hydroxy PDMS, for TDI and for the reaction product.

Silylurethane prepolymer–PU blend

The two homonetworks were synthesized, as well as a 1:1 blend. Since both prepolymers had isocyanate end-groups, TMP served as crosslinking agent for both. The required weight of TMP was dissolved in THF (10% w/w). The prepolymers were mixed and the TMP solution added. The mixture was stirred vigorously for five minutes. 0.5% w/w catalyst was added and mixed in, and the blend, or homonetwork, was degassed and cured as before.

Techniques

The solubility parameters, δ, and the average molecular weights between crosslinks, $\bar{M}_c$, were determined, as previously[1], by swelling in a range of organic liquids. The results are shown in *Table 2*.

Optical microscopy. The morphologies of the blends were examined with a Nikon model L-Ke optical microscope equipped with a microflex model PFM photomicrographic attachment.

Dynamic mechanical analysis. A Polymer Laboratories Dynamic Mechanical Thermal Analyser (DMTA) was used at a frequency of 10 Hz. The rate of heating was approximately 2°C min^{-1}.

^{13}C nuclear magnetic resonance spectroscopy. Proton-noise decoupled ^{13}C n.m.r. spectra were recorded at 20 MHz on a Varian Associates CFT-20 spectrometer at ambient probe temperature ($\sim$40°C). Spectra recorded on liquid samples were references to the centre line of CDCl$_3$ added as an internal lock (77 ppm relative to TMS). Solid samples were cured directly in an 8 mm n.m.r. tube which was then inserted into a standard 10 mm tube containing D$_2$O. This 'sleeve' of D$_2$O provided the lock signal and also a reference frequency. Other relevant operating parameters were usually as follows: spectral width, up to 4000 Hz (200 ppm); pulse width, 16–21 μs (nuclear tip angle 70–90°); acquisition time, 1–4 s (depending on spectral width); number of data points, 8K; number of pulses, typically 1–10K.

RESULTS AND DISCUSSION

The ESE network

The reaction between dihydroxy compounds and diisocyanates to form urethane prepolymers is well known[4]. Typically, excess diisocyanate is added to the diol, thereby forming an isocyanate-terminated prepolymer. Adiprene L-100 is a typical example. It would, therefore, appear simple to synthesize the analogous ESE prepolymer from the dihydroxy-ended triblock copolymer and TDI. Accordingly, they were mixed, in bulk, in the mole ratio 1:2. Within 1 h, the mixture had yellowed and become more viscous, and within 30 h, had become an insoluble solid. When a triol, triethanolamine, the dihydroxy-terminated block copolymer and TDI were reacted together in the mole ratio 0.67:1:2, the mixture became more viscous and yellowed, as before, but did not cure, even after several weeks. This apparently paradoxical behaviour has two possible explanations. First, the observations could be accounted for if there were significantly more than two hydroxyl groups per block copolymer molecule. Such an imbalance could lead to a highly branched molecule with too few isocyanate groups to promote cure. No hydroxyl group excess was detected. By assuming two hydroxyl groups per molecule, the molecular weight of the copolymer can be calculated from the ^{13}C n.m.r. spectrum. The result agreed with the molecular weight determined directly by vapour pressure osmometry.

Three uncatalysed mixtures of triblock copolymer and an excess of TDI (mole ratios 2.1, 2.5 and 3.0) reacted to yield solid, dry and insoluble polymer.

When TMP is present, even in catalysed systems, no curing occurs. A greater insight can be obtained by following this reaction spectroscopically. The triblock copolymer and TDI, in the mole ratio 1:3, were mixed, without catalyst, and the ^{13}C n.m.r. spectrum of the reacting mixture was recorded at various times. *Figure 1* shows the methylene carbon region of the spectrum of the unreacted triblock copolymer. The peaks at 61.0, 72.2 and 69.8 ppm arise from the carbons α, β and δ to the hydroxyl end-group, respectively, with the large in-chain methylene resonance at 70.1 ppm[5]. The peaks at 69.5 and 73.6 ppm can be assigned to carbons at the other end of the polyethylene oxide block. As the terminal hydroxyl group reacts with the isocyanate to form a urethane group, the chemical shifts of the end-group carbons will naturally change. The effect of a urethane group on the chemical shifts of neighbouring carbon atoms is known[5], and, therefore, peaks in the spectrum can be assigned to carbon atoms α, β and δ to the urethane linkage. *Figure 2*

Table 2 Network characterization data

Network	$\delta \times 10^{-3}$ (J m^{-3})$^{1/2}$	$\bar{M}_c$ (g mol^{-1})
PDMS	14.7	14600
ESE	18.9	27900

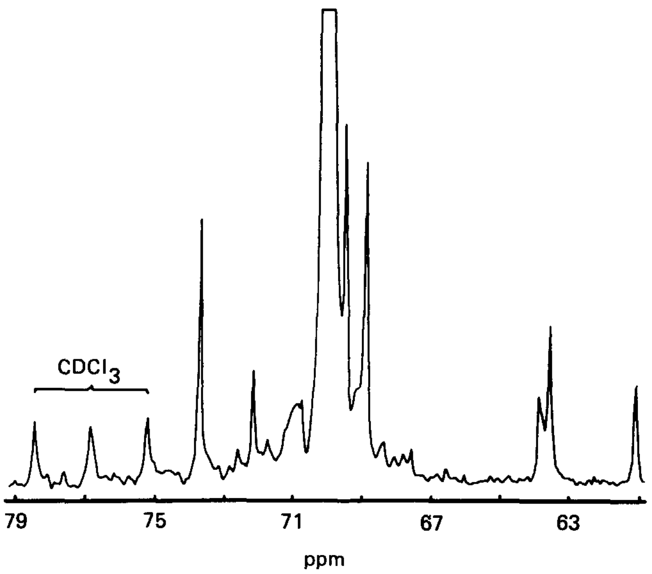


Figure 1 Part of the ^{13}C n.m.r. spectrum of the triblock copolymer

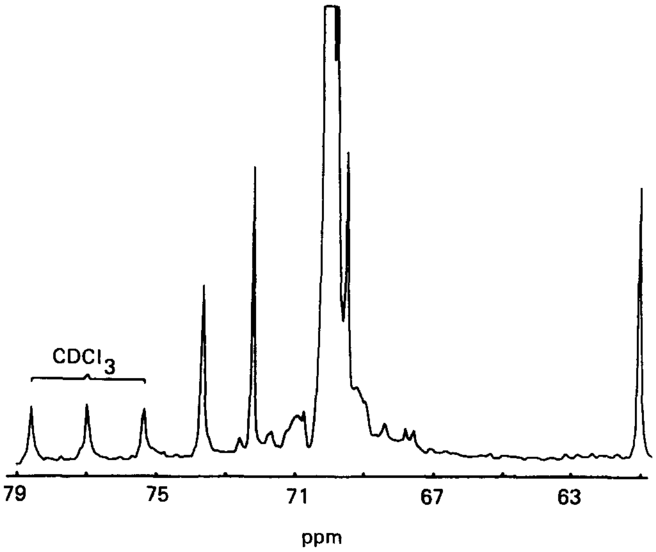
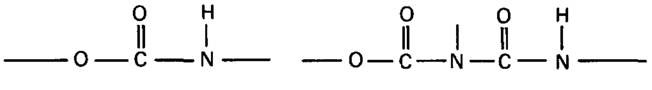


Figure 2 Part of the ^{13}C n.m.r. spectrum of the triblock copolymer/TDI mixture after 45 min reaction

shows the spectrum after 45 min reaction time. The peaks from the carbons α and β to hydroxyl are considerably diminished in intensity, and there can now be observed a peak at 69.0 ppm, arising from the carbons β to the urethane linkage. The carbons α to urethane produce two signals, at 63.0 and 63.7 ppm, since the hydroxyl group can react with an isocyanate group either ortho or para to the methyl group in TDI. After a reaction time of 21 h, the peaks from the carbons α and β to hydroxyl were no longer observable.

The remaining explanation for these observations is that the ESE network cures by allophanate group formation. This reaction between urethane and isocyanate is usually insignificant, except at high temperatures[6], or where the reactivity of the hydroxyl group is low[6,7]. It has been reported[8,9] that polyethylene glycol has a comparatively low reactivity towards isocyanate, accounting for the difficulty in preparing polyurethanes from this precursor. Since the triblock copolymer has polyethylene oxide end blocks, it would seem reasonable to expect that allophanate group formation might be the cause of the network formation.

The carbonyl region of the ^{13}C n.m.r. spectrum is capable of providing evidence in support of this mechanism. If allophanate group formation occurs, three types of carbonyl carbon will be present, as shown below.



$$-\mathrm{O}-\overset{\overset{\displaystyle \mathrm{O}}{\|}}{\underset{1}{\mathrm{C}}}-\overset{\overset{\displaystyle \mathrm{H}}{|}}{\mathrm{N}}- \qquad -\mathrm{O}-\overset{\overset{\displaystyle \mathrm{O}}{\|}}{\underset{2}{\mathrm{C}}}-\overset{|}{\mathrm{N}}-\overset{\overset{\displaystyle \mathrm{O}}{\|}}{\underset{3}{\mathrm{C}}}-\overset{\overset{\displaystyle \mathrm{H}}{|}}{\mathrm{N}}-$$

Urethane　　Allophanate

The chemical shift of Cl is documented[10], and is either 153.7 or 153.0 ppm depending on whether it is derived from the ortho or para isocyanate group of TDI. *Figure 3* shows the carbonyl region of the spectrum of a low molecular weight polyethylene glycol–TDI mixture after three hours reaction. The aromatic peak furthest downfield in polyurethanes derived from TDI is at 138.9 ppm, and arises from the N-substituted carbon[5]. The peaks downfield of this are, therefore, carbonyl signals. The peak between the two urethane carbonyls, at 153.5 ppm, is assigned to C2, since it is similar in structure to a urethane carbonyl, and has directly bonded O and N. The peak at 145.8 ppm is, therefore, assigned to C3. The separation between the two allophanate carbonyls, C2 and C3, of around 7 ppm, is similar to the separation, of approximately 5 ppm, between the two carbonyls of ethyl-α,γ-diphenylallophanate[5], which lends support to the above assignments. It is, therefore, believed that the

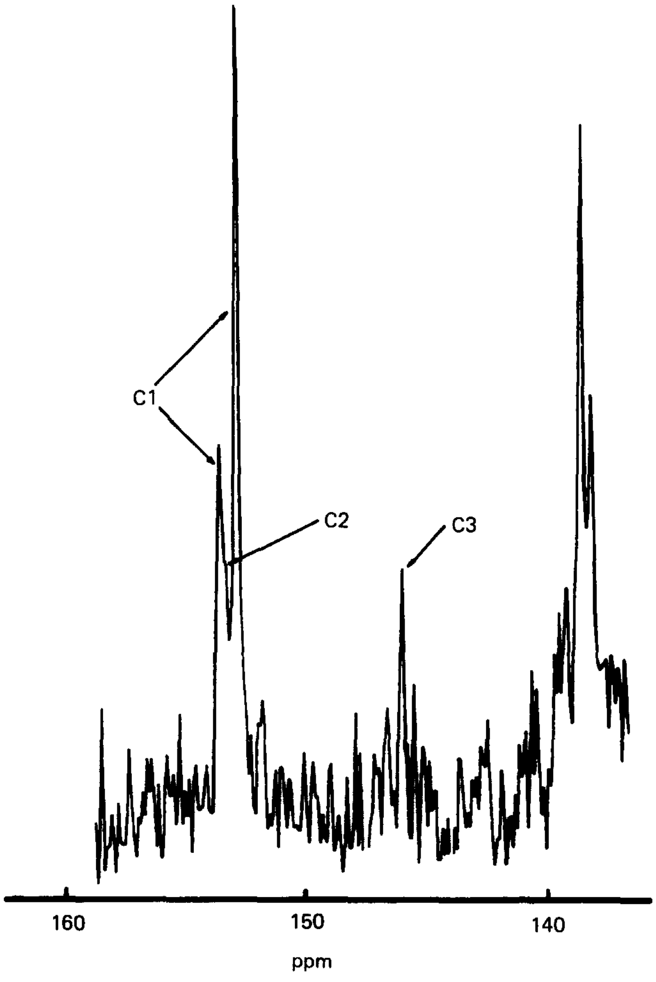


Figure 3 Carbonyl region of the ^{13}C n.m.r. spectrum of a low molecular weight poly(ethylene glycol)/TDI mixture after 3 h reaction

crosslinked network resulting from the reaction between the triblock copolymers and TDI involves the formation of allophanate linkages. It is well known[11] that isocyanates can react with disubstituted ureas to form biuret linkages which can lead to crosslinking. As the reactions were carried out in strictly anhydrous conditions, it is not possible that disubstituted ureas could have been formed to any significant extent. The allophanate group formation is well advanced by three hours, indicating that this reaction takes place at the same time as urethane group formation. Isocyanate groups are being consumed in reactions with both hydroxyl and urethane groups.

Formation of the silylurethane prepolymer

The low molecular weight α,ω-hydroxy-poly(dimethylsiloxane) and TDI were mixed and reacted in a 1:2 mole ratio as described in the Experimental section. There are two likely reaction pathways for such a mixture. The silanol end-groups could condense upon heating, with the elimination of water. TDI would catalyse this reaction[12] by removing the water from the system and lead to the formation of a urea. Alternatively, the TDI could react with the silanol end-groups, with the formation of a silylurethane linkage.

It has been reported[12] that the first reaction is the more favourable, the silylurethane not having been isolated, except in reactions involving monohydroxylsilanes and monoisocyanates[12]. *Figure 4* shows g.p.c. traces (u.v. detector) for the reaction product, TDI and the α,ω-hydroxy-poly(dimethylsiloxane). As can be seen from trace (B), TDI gives a very intense peak, which is to be expected, since the aromatic ring is a strong u.v. absorber. The polysiloxane, trace (C), however, gives only a small peak, even at a forty-fold increase in concentration over that of the TDI. The trace for the reaction product, (A), shows a peak at the same elution volume as the polysiloxane, indicating a polymer of similar molecular weight, but it is a much stronger u.v. absorber, even though diluted by a factor of ten. The indication is that the TDI has reacted with the terminal hydroxyl group of the α,ω-hydroxy-poly(dimethylsiloxane), incorporating the aromatic ring into the molecular structure of the polymer. If the silanol condensation reaction had occurred, there would be a peak at lower elution volume from the higher molecular weight polymer so formed. No such peak was observed.

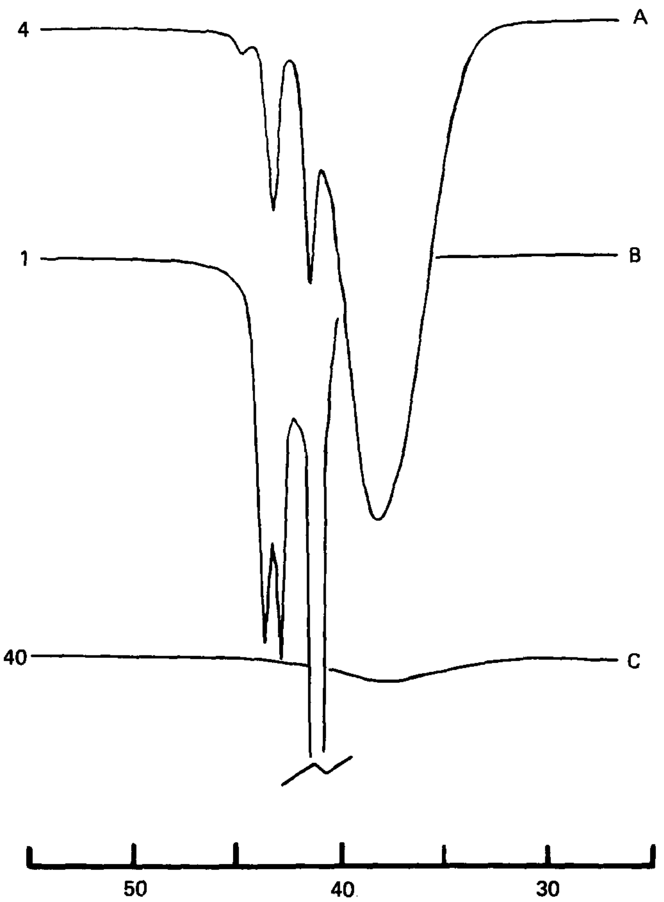


Figure 4 G.p.c. traces of the reaction product (A), TDI (B) and α,ω-hydroxy poly(dimethylsiloxane). The relative concentrations are indicated on the left of the Figure

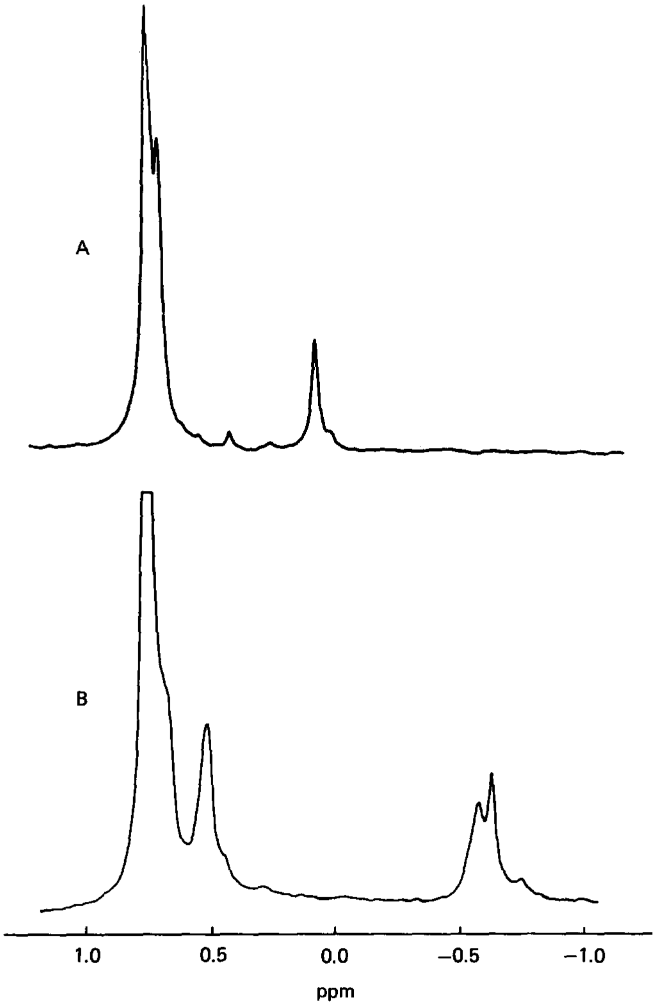
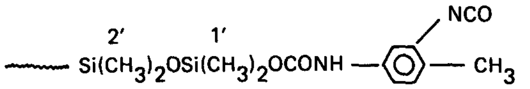


Figure 5 Part of the ^{13}C n.m.r. spectrum for (A) the α,ω-hydroxy poly(dimethylsiloxane) and (B) for the reaction product

The ^{13}C n.m.r. spectra are shown in *Figure 5*. The main region of interest is the high field $SiCH_3$ portion of the spectrum. *Figure 5(A)* is of the hydroxyl-terminated PDMS. The in-chain methyl carbon peak can be seen at 0.73 ppm, with the peaks at 0.11 and 0.69 ppm corresponding to carbons C1 and C2, respectively (see below).

$$—\overset{2}{\mathrm{Si}}(CH_3)_2O\overset{1}{\mathrm{Si}}(CH_3)_2OH$$

Figure 5(B) shows the same region of the spectrum for the reaction product. If the silanol condensation reaction had occurred, precisely the same chemical shifts would be observed, with the end-group peaks diminished because of the higher molecular weight polymer. However, it can be seen that the end-groups peaks have been shifted upfield, as a result of the reaction of the hydroxyl group. There is no peak at 0.11 ppm. Therefore, there is no hydroxy-terminated polysiloxane present. The polymer now has urethane end-groups, as shown below. C1′ appears as two peaks, at −0.58 and −0.63 ppm,



indicating reation with both ortho and para isocyanate groups, whilst C2′ gives rise to the peak at 0.52 ppm. There is also a peak at 151.4 ppm (not shown in *Figure 5*), which does not appear in the spectrum of TDI, or of PDMS. This peak has a chemical shift expected for a urethane carbonyl[10]. The results strongly suggest, then, that a silylurethane has been formed in the silanol–TDI reaction.

ESE–PDMS IPNs

It is clear from the difference in solubility parameters (*Table 2*) that the two networks are likely to be incompatible to a significant extent. Both of the homonetworks produced transparent sheets, whereas all the IPNs were white and opaque. The phases were large enough to be observable by optical microscopy. *Figure 6* shows the graph of domain diameter *versus* composition. As expected, the smallest domains, of about 10–20 μm, are at the compositional extremes, and the maximum domain diameter of about 100 μm occurs for the mid-composition IPN. These results are very similar to those for the previously reported[1] PU–PDMS IPNs. The presence of the polysiloxane block in the ESE network has not led to any reduction in domain size.

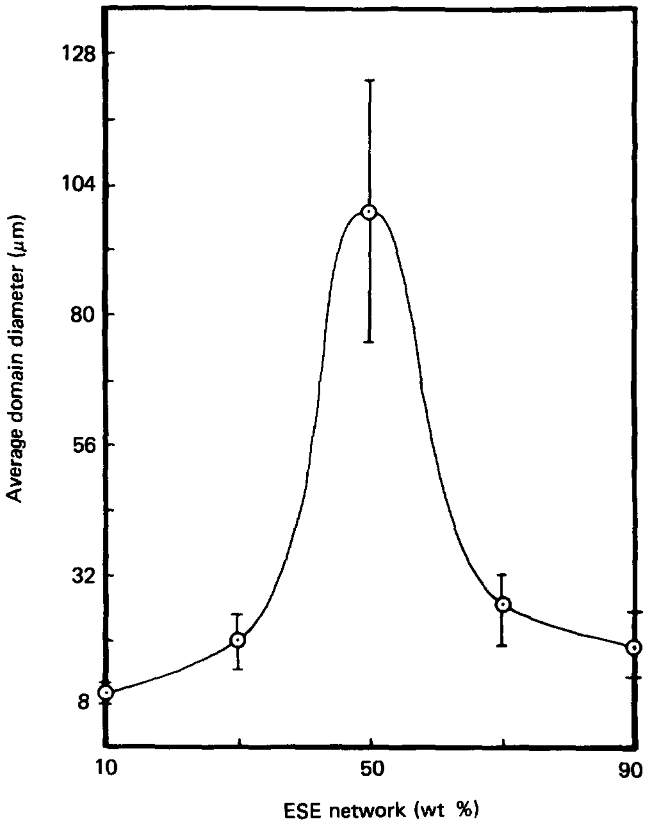


Figure 6 Domain diameter *versus* composition

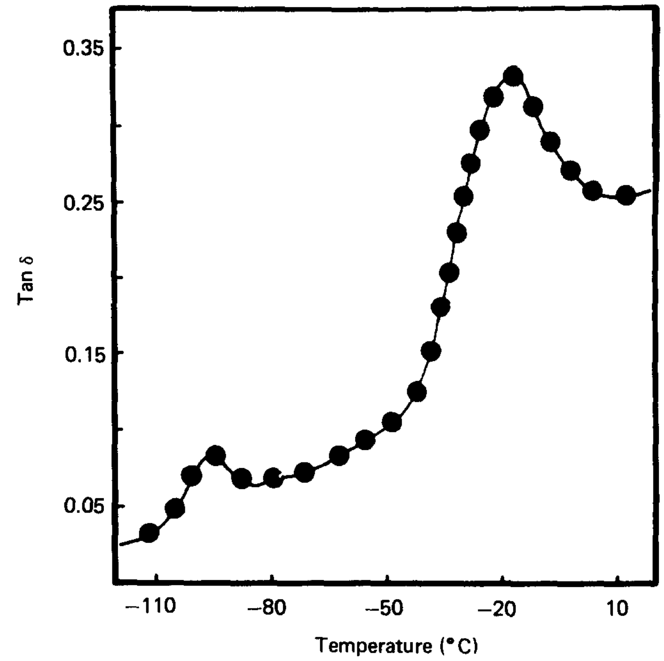


Figure 7 Tan δ *versus* temperature for the ESE network. The frequency was 10 Hz

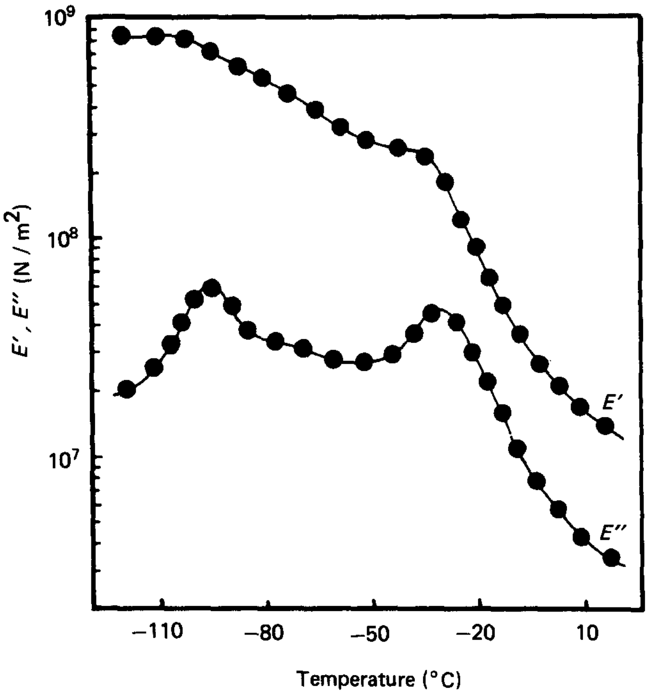


Figure 8 Dynamic storage modulus (E') and dynamic loss modulus (E'') *versus* temperature for the ESE network. The frequency was 10 Hz

Figures 7 and *8* show the plots of tan δ and E' and E'' *versus* temperature for the ESE network. The analogous plots for the PDMS network have been presented[1] in the earlier paper. In *Figure 7*, the maximum in tan δ at −17°C is ascribed to the glass transition temperature, T_g, of the polyether blocks in the network. The T_g is similar (−20°C) to that already reported[1,13] for the polyether urethane network. The transition in E'' at −98°C (*Figure 8*), seen as a small peak in tan δ at −96°C, is interpreted as the glass transition of the polysiloxane blocks, the temperatures being the same as those obtained[1] for the

PDMS network. There is also a very small transition in E''–temperature plot centred around −73°C. This transition is discussed in ref. 1.

Dynamic mechanical data were obtained at 30, 10, 3 and 1 Hz, leading to a value of 222 kJ mol^{-1} for the apparent activation energy[14] for the polyether T_g.

Figure 9 shows the E''–temperature plots for the IPNs containing 70, 50, 30 and 10% by weight of the ESE network. The plots can be separated into two pairs; the 70 and 50% ESE IPNs have mechanical properties similar to the pure ESE network, with two maxima in E'', at −98°C and −32°C. The 90% IPN is also very similar. However, the 30 and 10% IPNs display the features of the pure PDMS network[1], with the PDMS T_g at −98°C, followed by the large drop in modulus, associated with crystalline melting[1,15–17]. *Figure 10* shows the $\tan\delta$–temperature behaviour for the IPNs containing 50 and 30% of the ESE network. Again, for the 50% IPN, the main ESE network T_g can be seen at −17°C, but at 30%, this T_g was not detected, whereas the sharp peak resulting from the crystalline melting of the PDMS network can be observed. The multi-phase morphology of this blend system is, therefore, similar to that of the PU-PDMS IPN system reported previously[1]. At an ESE network concentration of 50% and above, this component is continuous, containing a PDMS dispersed phase. At an ESE network concentration of 30% and below, the situation is reversed, with discontinuous domains of this network in a matrix of PDMS.

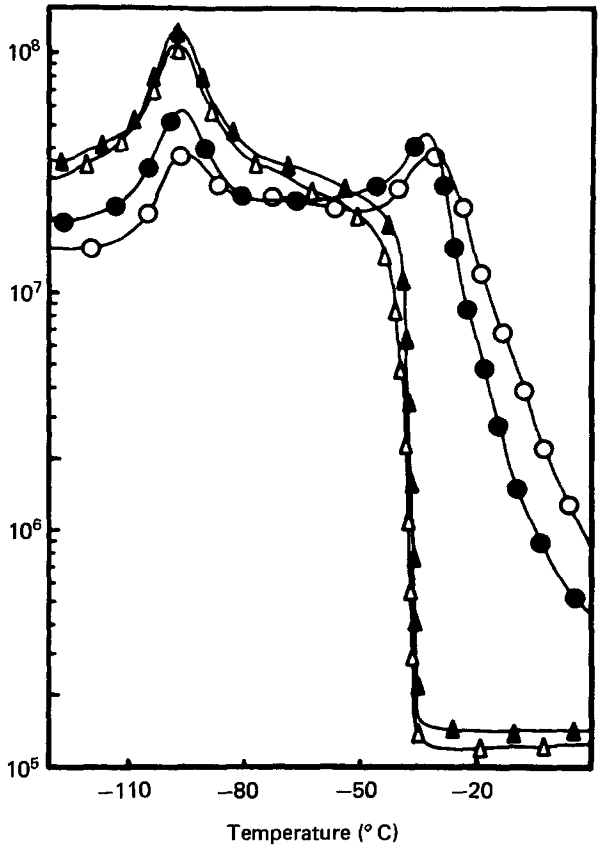


Figure 9 Dynamic loss modulus (E'') *versus* temperature for the IPNs containing 70 (○), 50 (●), 30 (▲) and 10 (△) per cent by weight of the ESE network. The frequency was 10 Hz

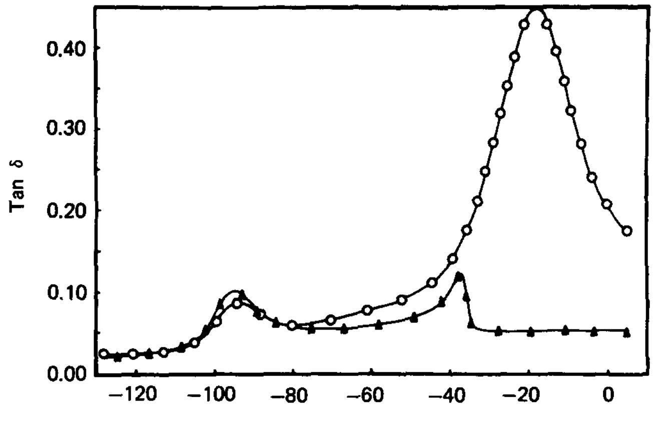


Figure 10 Tan δ *versus* temperature for the IPNs containing 50 (○) and 30 (▲) per cent by weight of the ESE network. The frequency was 10 Hz

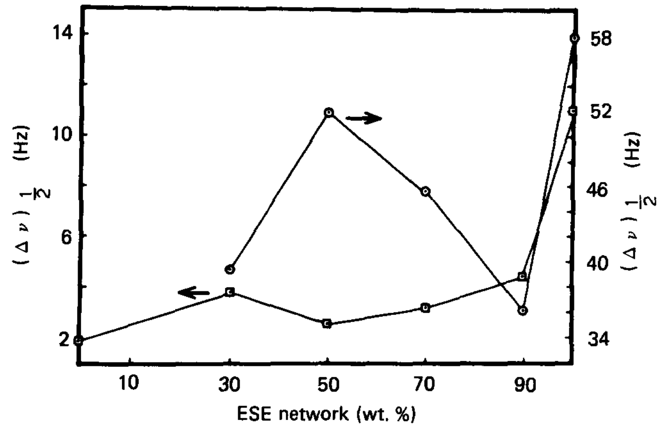


Figure 11 Linewidth $[(\Delta\nu)_{1/2}]$ *versus* composition. (□) methyl carbon. (○) methylene carbon

^{13}C n.m.r. linewidth studies of the cured homonetworks and the IPNs were undertaken to obtain some additional information concerning the degree of mixing at the phase boundaries. Although the optical microscopy and the dynamic mechanical analysis reveal a gross morphology, suggesting little or no chain mixing, n.m.r. spectroscopy may be sensitive enough to detect a very small extent of interpretation, reflected in a variation in the carbon linewidths. This approach was used[1] with some success for studying the PU-PDMS IPN system. Of particular interest in the present case is the degree of association between the polysiloxane blocks of the ESE network and the PDMS network itself. The ESE network give rise to two peaks in the ^{13}C spectrum, one at 70.2 ppm resulting from the in-chain methylene carbons, and one at 0.46 ppm from the in-chain methyl carbons of the polysiloxane block. The PDMS network shows a methyl peak superimposable with the ESE network methyl peak. *Figure 11* shows the linewidths[1] as a function of composition. The 10% ESE IPN was not examined, since the methylene carbon peak was too small for the linewidth to be measured accurately. Of immediate interest is the difference in silicon methyl peak width between the two homonetworks. For the PDMS network, the peak is very narrow. The natural mobility of the in-chain segments is not restricted by the relatively few crosslink sites. In the ESE network, however, the methyl peak is over five times as broad. Here the crosslinking introduces hard segments[18,19] comprising urethane, allophanate and aromatic groups, which will restrict the motion of the polyether, itself a less flexible chain than the polysiloxane. This motional limitation will be transmitted to the central polysiloxane block, and since this comprises[20] only about 15 repeat units, the reorientations of most of the units will be affected, causing a broadening of the methyl carbon peak. The methyl carbon peak in an IPN is, thus, composed of contributions from both the PDMS and the ESE methyl groups. From a knowledge of the molecular weights of both components, the theoretical peak area ratios of the ESE methyl carbon to the PDMS network methyl carbon can be calculated, for any composition *Table 3*). Up to 70% of ESE, the methyl carbon peak is mainly composed of contributions from the more mobile PDMS. At 90% ESE, however, the peak is mainly derived from the ESE network. For the pure ESE network, the methyl carbon linewidth is 11 Hz. At 90% ESE, the ESE methyl carbon makes the bigger contribution, but the peak width is reduced to 4.4 Hz, compared with a theoretical value of 7.1 Hz. It is suggested that this reduction in linewidth may result from a degree of association at the phase boundaries between the polysiloxane blocks of the ESE network and the softer, more mobile PDMS network. Below 70% of ESE the methyl carbon peak is mainly derived from the PDMS network, and, therefore, the linewidth remains virtually constant. Of additional interest is the extent of association between the poly(ethylene oxide) segments and the PDMS network. Knowing, from optical microscopy, the average domain radius for each blend and, from dynamic mechanical studies, which network forms the domains, the effective surface area (*SA*) available for penetration by the polyether chain segments can be approximately estimated. At an ESE network concentration of 30%, the ESE is the dispersed phase, the SA:volume (*V*) ratio is, therefore, high, and so a considerable fraction of the poly(ethylene oxide) blocks could be in contact with the phase boundary providing maximum opportunity for mixing. Poly(ethylene oxide) blocks are postulated to penetrate into the surrounding PDMS network causing a reduction in the methylene carbon peak width compared to that of the pure ESE network. At 50% ESE this network is continuous, the PDMS domains are large and the surface available for mixing is considerably reduced. Consequently, the methylene carbon peak width is similar to that in the homo-network. This correlation between peak width and SA continues at 70% ESE, where the methylene peak width is reduced to a value between that at 30 and 50%. However, at 90% ESE, the peak width is at its lowest value, when the *SA*:*V* calculations indicate that it should be at least as great as at 50%. For this blend, then, the peak width is not controlled by the *SA* available for penetration. A satisfactory explanation for this observation cannot be offered, since both the microscopy and the dynamic mechanical evidence rule out any large scale compatibility between the two networks.

In conclusion, there would appear to be some small-scale mixing between polymer chains which cannot be detected by dynamic mechanical analysis. The extent of this mixing, as revealed by ^{13}C n.m.r., is of the same order as already reported[1] for the PU–PDMS system. Therefore, the presence of the polysiloxane block in the ESE network does not enhance miscibility with the PDMS network. The solubility parameter of the ESE network is 18.9×10^3 $(\mathrm{J\,m^{-3}})^{1/2}$ which is close to the value of 19.4×10^3 $(\mathrm{J\,m^{-3}})^{1/2}$ obtained[1] for the PU network.

Table 3 Theoretical ratio of peak areas of methyl carbon in the ESE network to that of the methyl carbon in the PDMS network

ESE network (wt%)	Theoretical ratio
30	0.06
50	0.15
70	0.35
90	1.34

Polysilylurethane network and the blend with polyurethane

The polysilylurethane network was synthesized by reaction of the silylurethane prepolymer with TMP. A 1:1 blend with PU was also prepared by mixing the two prepolymers and then crosslinking both with TMP. The isocyanate end-groups of both prepolymers are identical, and, therefore, their reactivities towards TMP will be the same. The resulting structure could be that of an AB crosslinked copolymer.

Dynamic mechanical data for the homonetwork are shown in *Figures 12* and *13*. The single T_g can be seen to occur at -70°C in the tan δ–temperature plot. This is about 25°C higher than the T_g of a pure PDMS network[1], and can be attributed to the chain stiffening effect of the rigid urethane and aromatic groups. A significant improvement in physical properties is achieved by incorporation of the urethane linkages. The elastic modulus (20°C) of this network is 113.5MN m^{-2} for the PDMS network[1]. The *E″ versus* temperature data for the blend are shown in *Figure 14*. This curve shows both the PU network T_g at -32°C and the polysilylurethane network T_g at -80°C. There can also be seen a smaller shoulder at -110°C, attributable to the PU γ transition[13]. The tempetatures of the transitions in the blend are identical to those in the homonetworks. Therefore, the two polymers are incompatible and the blend is phase separated[21]. The blend was white and opaque, while both the homonetworks were transparent.

The previously studied[1] PU–PDMS systems showed only one T_g, that of the continuous network. The fact that both T_gs are observable in this blend indicates that the

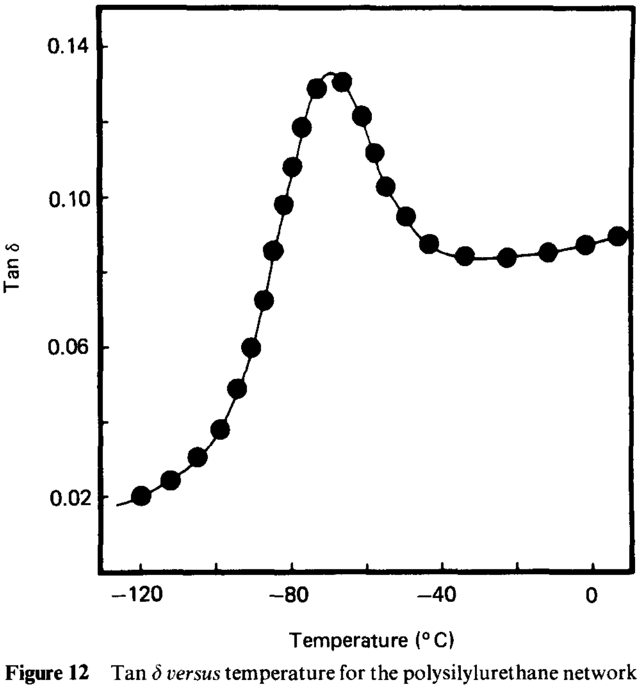


Figure 12 Tan δ *versus* temperature for the polysilylurethane network. The frequency was 10 Hz

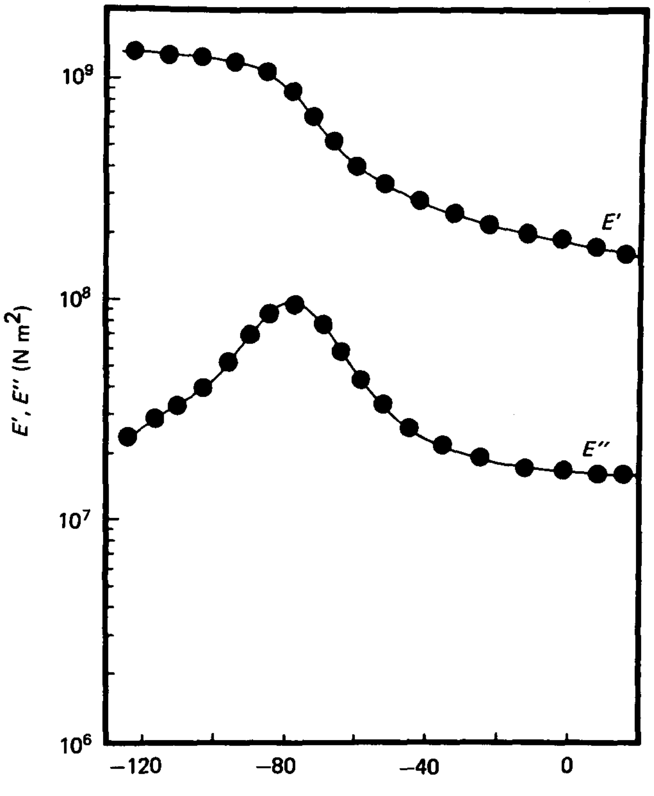


Figure 13 Dynamic storage modulus (E') and dynamic loss modulus (E'') *versus* temperature for the polysilylurethane network. The frequency was 10 Hz

components are more coupled than in the PU–PDMS IPNs[1].

On leaving the homonetwork and the blend exposed to atmospheric moisture for more than 12 h, the surface of the material became moist. This was followed by darkening to yellow, then dark brown, accompanied by a very marked deterioration in the physical properties. After 24 to 36 h, the material had totally disintegrated. This degradation did not occur if the material was kept in a desiccator. The degradation is believed[12] to be the result of the hydrolytic instability of the silylurethane linkage.

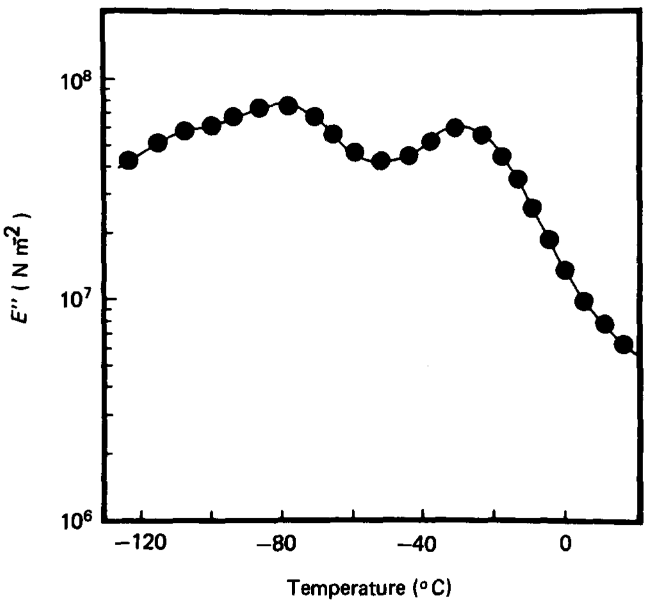


Figure 14 Dynamic loss modulus (E'') *versus* temperature for the polysilylurethane–polyurethane blend (1:1). The frequency was 10 Hz

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