

Viscoelastic Behavior of Interpenetrating Networks of Polyurethane and Polyurethane Acrylate

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Synopsis

The temperature dependence of the dynamic viscoelastic behavior of interpenetrating networks (IPN) of polyurethane (PU) prepared from poly(oxypropylenediol) (POP) and toluylene diisocyanate (TDI), and of polyurethane diacrylate (PUA) prepared from POP and TDI by reacting isocyanate groups of the prepolymer with 2-hydroxyethyl acrylate, was measured in the main transition region. The photoelastic behavior of IPN swollen in dimethylformamide (DMF) and methyl ethyl ketone (MEK) was examined in the rubbery region. The temperature dependences of the dynamic Young modulus E^* of IPN in the concentration range of PUA ≥ 50 vol.% indicate a pronounced two-phase behavior. The effect of the composition of IPN on the temperature dependence of the modulus E^* was quantitatively described by Takayanagi's two-phase model with the conclusion that the PU network is the continuous phase of IPN at $\leq 90\%$ PUA. While in the range of high concentrations of PUA ($\geq 50\%$) the contributions of phases to E^* are additive within the whole range of temperatures, the thermomechanical behavior at low PUA concentrations ($\leq 40\%$) is more complex. This finding is interpreted by the existence of an interfacial layer which leads to the loss of the distinct two-phase character of IPN. The higher number of elastically active network chains (EANC) of the PUA network compared with the PU network corresponds to different molecular weights of POP used in the preparation of both components. The nonadditive dependence both of the concentration of EANC and of the stress-optical coefficient on composition confirms the heterogeneous character of the IPN structure.

INTRODUCTION

The study of the physicochemical properties of interpenetrating polymer networks (IPN) has been reported in many papers.¹⁻¹² A special interest was aroused by the problem of mutual miscibility of the individual components in IPN and by the existence of phase boundaries, which may considerably affect the resulting physicochemical properties of IPN. Both inversion gas chromatography⁶ and broad-line NMR spectrometry have demonstrated that in the IPN of polyurethane with a copolymer of styrene and divinylbenzene, an important role is played by the interfacial layer. In some cases^{2,4} the behavior of IPN was interpreted as the effect of filler (network with a higher T_g) on the properties of the polymeric matrix (network with a lower T_g). On the other hand, however, calorimetric studies^{5,13} of IPN based on polyurethane of the polyether or polyester type combined with polyacrylate, epoxide, or unsaturated polyesters showed that in these systems, there was only a single though rather wide T_g transition. Such a result indicates mutual compatibility of the components of IPN and calls for a deeper insight into their viscoelastic properties, particularly with a view to their industrial applications as sound-insulating materials.¹²

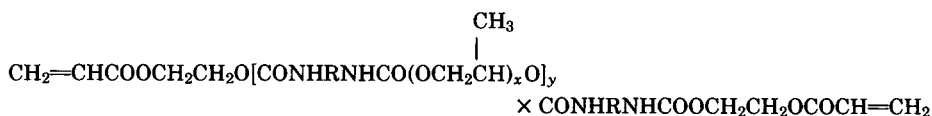
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This paper reports an investigation of the viscoelastic behavior of IPN composed of polyether polyurethane and poly(urethane diacrylate) networks in the main transition and rubbery region as a function of composition of the system; the same IPNs have been examined earlier by IR spectroscopy and NMR.¹⁴ The resulting viscoelastic behavior of IPN is compared with the prediction provided by the two-phase mechanical model for composites. The effects of the interfacial layer on the parameters of the model are discussed.

EXPERIMENTAL

Network Preparation

Polyurethane diacrylate (PUA),



was prepared from polyoxypropylene glycol (POP, number-average molecular weight $M_n = 700$) which was reacted in the first stage with tolylene diisocyanate (molar ratio NCO:OH = 2:1). Acrylate groups were introduced into the product by a reaction with 2-hydroxyethyl acrylate in excess.¹⁵

Samples of IPN were prepared as follows:^{14,15} polyurethane diacrylate with the initiator azobisisobutyronitrile was mixed with polyoxypropylene glycol ($M_n = 2000$), tolylene diisocyanate, and trimethylolpropane in a common solvent—methylene chloride. The mixture was used to cast plates on a Teflon surface which were subsequently dried at room temperature and reduced pressure until the solvent was removed. After 4 hr, the temperature was raised and kept at 75°C for 48 hr. The mechanism of formation of IPN suggests that the PUA network was formed earlier than the PU network. The composition of samples is given in Table I.

Methods of Measurement

The temperature dependence of the dynamic Young modulus of elasticity, $E^* = E' + iE''$ (E' and E'' being the real and imaginary components, respectively), was measured with a RheoVibron DDV II (Toyo Measuring Instruments Co.) at a frequency 110 Hz between -100 and +150°C. The measurements were performed on dry samples 0.05 × 0.2 × 4 cm in size.

The photoelastic measurements were carried out with samples swollen in dimethylformamide (DMF) and methyl ethyl ketone (MEK) at 25°C. The experiments were performed using an apparatus described earlier,^{16,17} in which the birefringence relaxation $\Delta n(t)$ can be recorded simultaneously with the stress relaxation $\sigma(t)$. The sample was deformed to constant elongation $\Lambda = l/l_0$ (l and l_0 respectively being the deformed and initial length of the sample). After relaxation for 2 min, the force f (or stress $\sigma = f/S$, where $S = S_0\Lambda^{-1}$ is the instantaneous cross section of the sample and S_0 is the initial cross section) and birefringence Δn were determined. The sample was deformed to a new value Λ , and the whole procedure was repeated. At least 10 values of Λ in the range $1 < \Lambda \leq 1.1$ were measured. From the values of σ , Δn , and Λ the shear modulus G , the

TABLE I
Mechanical and Optical Characteristics of Networks in the Rubbery Region

Sample No.	V _{PU}	V _{PUA}	ρ , g/cm ³	G, MPa		$\nu_d \times 10^4$, mole/cm ³		ν_2		$C_e \times 10^4$, (MPa) ⁻¹		
				Dry 150°C	DMF 25°C	MEK 25°C	Dry 150°C	DMF 25°C	MEK 25°C	DMF 25°C	MEK 25°C	
1	1.0	0.0	1.094	1.56	0.73	0.72	4.4	4.3	0.328	0.384	15.4	16.0
2	0.0	1.0	1.184	4.39	2.01	5.26	12.5	10.4	0.500	0.755	10.9	9.8
3	0.9	0.1	1.098	—	0.60	0.60	—	3.5	0.334	0.375	15.4	16.6
4	0.8	0.2	1.072	1.71	0.66	0.59	4.9	3.9	0.349	0.398	15.2	16.5
5	0.6	0.4	1.131	1.49	0.92	0.63	4.2	5.2	0.374	0.427	11.1	12.5
6	0.5	0.5	1.127	1.92	0.66	0.92	5.4	3.9	0.343	0.470	9.6	13.1
7	0.1	0.9	1.174	4.1	—	—	11.7	—	—	—	—	—

deformational-optical function A , and the stress-optical coefficient $C = A/G$ were obtained from $\sigma = G(\Lambda^2 - \Lambda^{-1})$ and $\Delta n = A(\Lambda^2 - \Lambda^{-1})$. The samples used in the experiments were $0.1 \times 1.5 \times 5$ cm.

The degree of swelling of IPN, characterized by the volume fraction of the polymer in the swollen state, ν_2 , was determined from the weight of the dry and swollen sample, assuming additivity of the volumes of polymer and solvent. The sample density was determined by the method of double weighing in air and in water in which the samples do not swell.

RESULTS AND DISCUSSION

Dynamic Behavior in the Main Transition Region

Figures 1 and 2 show the temperature dependences of components of the dynamic Young modulus of the individual networks (curves 1 and 2) together with

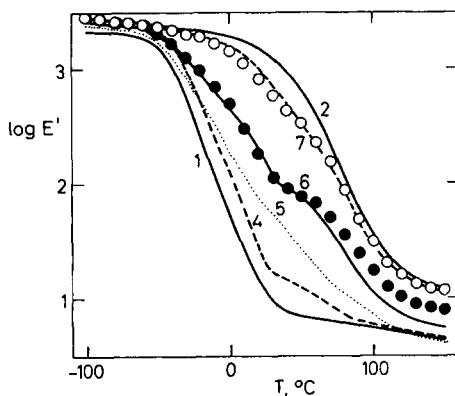


Fig. 1. Dependence of the real component of the Young modulus E' (MPa) on temperature T ($^{\circ}\text{C}$). Curves denoted similarly to samples in Table I; values determined by eq. (2) for $\phi = 1$: (●) sample 6; (○) sample 7.

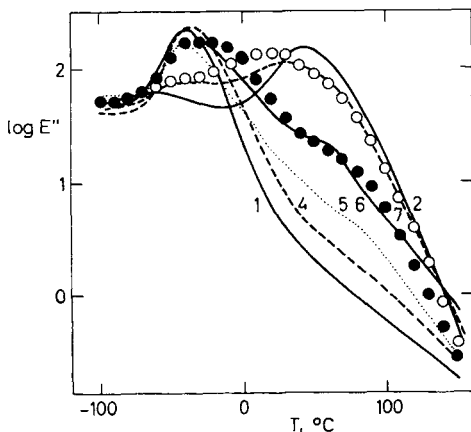


Fig. 2. Dependence of the imaginary component of the Young modulus E'' (MPa) on temperature T ($^{\circ}\text{C}$). Curves denoted as samples in Table I; values determined by eq. (2) for $\phi = 1$: (●) sample 6; (○) sample 7.

four samples of IPN. While the PU network has a maximum E''_{\max} at $\sim -40^\circ\text{C}$, for the PUA network E''_{\max} lies at $\sim 50^\circ\text{C}$. The shift of the transition region of the PUA network toward higher temperatures is caused by a higher concentration of the urethane groups¹⁷ and by the polyacrylate chains formed by chain polymerization. For incompatible networks, two maxima should appear on the dependence of E'' on T , corresponding to the transition temperatures T_g of the individual components. This is observed with sample 7 and to some extent with sample 6; the other IPNs exhibit only one broader transition corresponding to the PU network. The broadening of the transition is usually observed if filler has been introduced into the network; it is interpreted as a decrease in mobility in the polymer-filler boundary regions.⁴

It can be seen that E''_{\max} corresponding to the PUA component of sample 7 is shifted by some 15 K toward lower temperatures compared with the PUA network alone. On the other hand, E''_{\max} corresponding to the PU network is situated at the same temperature for all IPNs. These findings, along with calculations of mechanical models presented below, fit in with the assumed kinetics of the formation of IPN (i.e., that the PUA chains were formed first and segregated owing to their partial solubility in the mixture PU + PUA). The polar character of both networks may lead to the formation of diffuse transition zones, which may affect the mechanical behavior of IPN. The two-phase model is used later on in the description of the viscoelastic behavior of IPN. An attempt will also be made to use the three-phase model, where the third phase formally corresponds to the interphase layer (diffuse transition zone).

Mechanical Models

It is possible to find several theoretical approaches predicting the mechanical behavior of a composite if the mechanical characteristics of the components are known.¹⁸⁻²³ Hashin and Shtrikman²¹ showed that only the upper and lower bounds of the modulus of the composite could be determined from the volume fractions and moduli of components. Our results have been quantitatively described using Takayanagi's models²³ I and II (Fig. 3). The equivalence of the two models was proved earlier.²⁴ Model I predicts for the modulus of elasticity of the composite, E^* , that

$$E^* = (1 - \lambda)E_A^* + \lambda[(1 - \phi)/E_A^* + \phi/E_B^*]^{-1} \quad (1)$$

where E_A^* and E_B^* , respectively, are the moduli of the respective phases A and B, V_B is the volume fraction of the phase B, and λ and ϕ are parameters of the model with $\lambda\phi = V_B$. Equation (1) gives for the real and imaginary components of the modulus of the composite, E' and E'' , the following relationships:

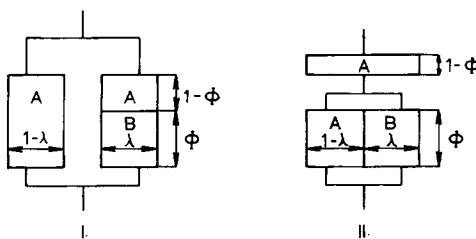


Fig. 3. Takayanagi's models of a two-phase composite.

$$\begin{aligned}
 E' &= (1 - \lambda)E'_A + \lambda X/(X^2 + Y^2) \\
 E'' &= (1 - \lambda)E''_A + \lambda Y/(X^2 + Y^2)
 \end{aligned}
 \tag{2}$$

where

$$X = (1 - \phi)E''_A/(E''_A + E''_A) + [\phi E'_B/(E''_B + E''_B)]$$

and

$$Y = (1 - \phi)E''_A/(E''_A + E''_A) + [\phi E''_B/(E''_B + E''_B)]$$

The temperature dependence of the parameter ϕ (Fig. 4) was determined from eqs. (2) assuming that the continuous phase A (matrix) consists of the PU network (V_B determines the volume fraction of the network PUA). The value of ϕ was determined as a mean from two ϕ values obtained from the real component E' as well as from the imaginary component E'' . Applying eqs. (2), a reasonable value $\phi \leq 1$ could be observed only if one assumed that the PU network formed a continuous phase up to 90 vol.% of the PUA network ($V_B = 0.9$). Thus, model calculations corroborate the view that in our IPN the continuous phase in the range $0 < V_B \leq 0.9$ consists of the PU network. Such a conclusion is not at variance with results obtained by electron microscopy²⁵ which estimates the phase inversion to occur at $V_{PUA} = 0.5-0.9$.

For samples 6 and 7 the temperature dependence of the parameter ϕ is small, and $\phi \rightarrow 1$, which points to additive contributions of the respective phases. The theoretical temperature dependences of E' and E'' of samples 6 and 7 (calculated assuming $\phi = 1$) are given in detail in Figures 1 and 2. One can see that good agreement has been obtained, particularly for the dependence of E' on T . With samples 4 and 5, no constant ϕ can be found in order to describe the temperature dependences of the moduli E^* . The fact that with increasing V_{PU} the $\phi(T)$ dependence increasingly deviates from unity (Fig. 4) means that the behavior of IPN increasingly deviates from additivity. One also observes a pronounced maximum on the temperature dependence of the relative E'/E'_{PU} or E''/E''_{PU} near 20°C.

It can be supposed that difficulties involved in attempts at an adequate description of the mechanical behavior of IPN by means of a two-phase model may be related to the existence of interfacial layers, which render the two-phase model

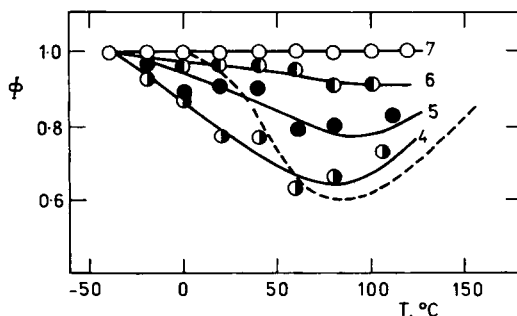


Fig. 4. Dependence of parameter ϕ of Takayanagi's model on temperature T (°C). Curves denoted as samples in Table I; (---) dependence determined by eq. (2) for model data E' of a homogeneous mixture with the composition $V_{PU}:V_{PUA} = 1:1$ [$E' = 2(E_{PU} + E_{PUA})$] assuming that PU is the continuous phase.

inadequate. The results obtained with samples 4 and 5 (Fig. 4) may then be interpreted as an increase in the effect of the interphase on the mechanical behavior of IPN. This conclusion is supported by the results of electron microscopy and small-angle x-ray scattering,²⁵ according to which the number of the PUA regions in IPN increases with increasing V_{PUA} at $V_{PUA} \leq 0.4$. For $V_{PUA} > 0.5$, it is mainly the size of the PUA regions that goes on increasing, while the volume fraction of the interfacial layer (having a thickness²⁵ of 20–40 Å) decreases. Thus, the effect of the transition layer on the mechanical behavior of the two-phase PUA–PU IPN is relatively larger for low concentrations of PUA.

The modulus of the composite, E^* , of a three-phase model analogous to that of the Takayanagi model, Figure 5(a), is given by [cf. eq. (1)]

$$E^* = (1 - \lambda)E_A^* + \lambda[(1 - \phi)/E_c^* + \phi/E_B^*] \tag{3}$$

The volume fractions of phases $V_A = 1 - \lambda$, $V_B = \lambda\phi$, and $V_C = \lambda(1 - \phi)$ determine the values of the parameters λ and ϕ ($\lambda = 1 - V_A + (V_C/2)$; $\phi = V_B - (V_C/2)$; $V_A + V_B + V_C = 1$). For the E^* vs. T dependence, eq. (3), it was assumed that the third phase (phase C) had the character of a homogeneous mixture with the composition $V_{PU}:V_{PUA} = 1:1$ [$E_C^* = (E_A^* + E_B^*)/2$] and that V_C might assume values in the range $0 < V_C \leq 2(V_{PU} \text{ or } V_{PUA})$; in this case the lower of the two values of V_{PU} or V_{PUA} was taken. The calculated curves adequately described experimental data on samples 6 and 7 at constant $V_C = 0.04$ (sample 7) and $V_C = 0.15$ (sample 6), but the results on samples 4 and 5 could not be adequately described using constant V_C . The same assumptions of the interface layer led to a good agreement between the theoretical and experimental dependences of E^* on T with constant values of V_C also for the model given in Figure 5(b) (additivity of moduli). On the other hand, no suitable V_C values could be found for samples 4 and 5 in this case either. The possibility to fit samples 6 and 7 both by two- and three-phase models is due to a low value of V_C (sample 7) or $\phi \rightarrow 1$ (sample 6).

The temperature dependence of the parameter ϕ of the Takayanagi model was also calculated, eq. (2), for a hypothetical homogeneous mixture (1:1) which would have the modulus $E^* = (E_{PU}^* + E_{PUA}^*)/2$. Figure 4 shows that the observed dependences of ϕ on T for samples 4 and 5 resemble the assumed shape calculated for a homogeneous mixture. Hence, the temperature dependence of ϕ for samples 4 and 5 may be due to the reduction of the two-phase character and a closer resemblance to the behavior of homogeneous systems. Such conclusion is supported also by additional calculations for the Takayanagi model, for which it was assumed that the phase A is the PU network and the phase B is the homogeneous mixture ($V_{PU}:V_{PUA} = 0.8:0.2$; modulus $E_B^* = 0.8E_{PU}^* + 0.2E_{PUA}^*$). Application of eq. (2) to the E vs. T dependence for sample 4 (assuming $\phi = 1$)

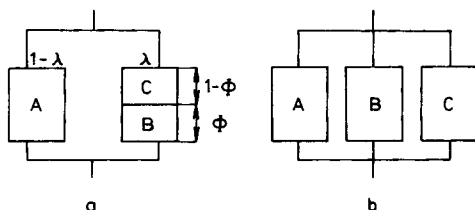


Fig. 5. Three-parameter models of a composite.

led to the temperature-dependent value $V_B \sim 0.7-0.85$, which also indicates a considerable homogeneity of the sample.

Therefore, in the concentration range $V_{PUA} \geq 0.5$, the mechanical behavior of IPN has a pronounced two-phase character, with the effect of the interface layer being small (cf. V_C values of the three-phase model, or $\phi \rightarrow 1$). In the range $V_{PUA} \leq 0.4$, contributions of the interfacial layer are distinctly operative, and experimental results cannot be adequately described by any of the above models.

Rubbery Region

As can be seen in Figure 1, at 150°C all samples are in the rubbery state, and E'_{150} is virtually independent of temperature. Table I gives values of the shear modulus $G = E'_{150}/3$ for dry samples together with the respective moduli of samples swollen in dimethylformamide (DMF) and methyl ethyl ketone (MEK). The higher G values of dry samples compared with the swollen ones are due both to the absence of solvent and to the higher temperature of measurement, because the concentration of elastically active network chains (EANC) related to the dry state, $\nu_d = G\nu_2^{-1/3}/RT$ (R is the gas constant), is already independent of experimental conditions (Fig. 6). Consequently, physical bonds in the dry state have only a small influence on the modulus. The high ν_d value of the PUA network swollen in MEK at 25°C (low degree of swelling) may be explained by the fact that the measurement extends into the main transition region. An important time dependence of force and optical retardation has also been observed with this sample. The values of the stress-optical coefficient C_e are also virtually independent of the type of diluent used. As expected, ν_d of the PU network is

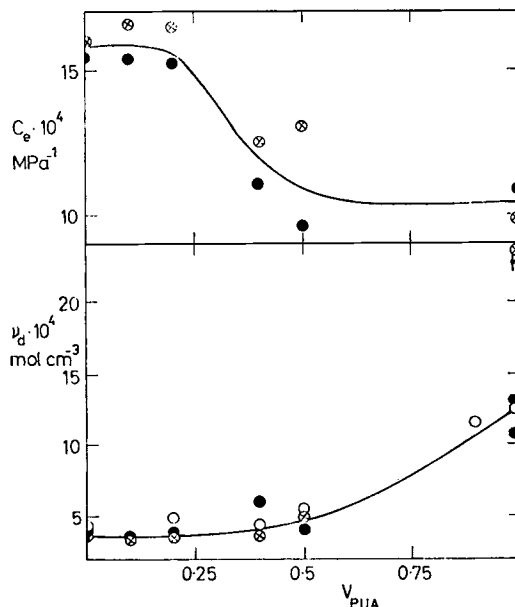


Fig. 6. Dependence of the stress-optical coefficient C_e (MPa^{-1}) or ν_d (moles/ cm^3) on the volume fraction of the PUA phase, V_{PUA} (O) dry state, $T = 150^\circ\text{C}$; (\otimes) swollen MEK, $T = 25^\circ\text{C}$; (\bullet) swollen DMF, $T = 25^\circ\text{C}$.

lower than that of the PUA network, which is mainly due to the higher molecular weight of POP in the PU network (2000 compared with 700). A simple calculation of the theoretical value of EANC in the absence of cyclization, entanglements, and effects of rigid units on the modulus at 100% conversion gives $\nu_d \sim 10^{-3}$ mole/cm³ for PUA and $\nu_d \sim 5 \cdot 10^{-4}$ mole/cm³ for the PU network. These values are in a fairly good agreement with those determined experimentally (Fig. 6). Even though the concentration of urethane groups of the PUA network is higher than that of the PU network and the optical anisotropy of the statistical segment increases with the concentration of urethane groups, the stress-optical coefficient C_e of the PUA network is lower than C_e of the PU network. This may be explained by a possible orientation of the acrylate segments perpendicularly to the polyurethane elastically active chains due to steric reasons.

Figure 6 allows to infer that ν_d remains virtually constant and the stress-optical coefficient decreases up to a 50% PUA content in IPN. The nonadditive dependence of both ν_d and C_e on the composition of IPN is in agreement with the conception of heterogeneous structure of PU-PUA interpenetrating networks.

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