

Semi- and Fully Interpenetrating Polymer Networks Based on Polyurethane-Polyacrylate Systems. IX. Properties of an Isomerically Related Interpenetrating Network

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Synopsis

Two polyurethane-poly(vinyl acetate) interpenetrating polymer networks of differing composition were synthesized and certain physical properties investigated. The results are compared with semi-1-interpenetrating polymer networks of the same system as well as with, where appropriate, polyurethane-poly(methyl acrylate) interpenetrating polymer networks. Dynamic mechanical analysis clearly indicated phase separation for both compositions. The poly(vinyl acetate) glass transition showed a shift to lower temperatures accompanied by a shift to higher temperatures of the polyurethane transition. Such shifts indicate a certain extent of mixing. Electron microscopy confirmed phase separation and for a material with 20% by weight of polyurethane indicated that both components are continuous. This latter material also had a higher tensile strength and elongation at break than the corresponding poly(vinyl acetate) homopolymer. At 60% by weight of polyurethane the stress-strain characteristics are those of a reinforced rubber. Certain modulus-composition theories, and, also, sonic velocity measurements were consistent with these morphological conclusions.

INTRODUCTION

An interpenetrating polymer network (IPN) comprises two polymeric networks, of which at least one must have been synthesized and/or crosslinked in the presence of the other. If only one of the polymers is crosslinked the material is called a semi-1- or a semi-2-IPN, depending on whether the first or second formed polymer is the network.

IPNs are almost invariably two phase systems,¹⁻³ and, consequently, their properties are a function of the attendant morphology.² The morphology in turn is affected by the method of synthesis,¹ the degree of crosslinking,⁴⁻⁶ and the relative concentrations of the two polymers.^{1,7,8} A number of reviews have been published on IPNs.^{1-3,9,10}

This paper is one of a series^{5-7,11-15} on polyurethane-polyacrylate IPNs. It deals with polyurethane (PU)-poly(vinyl acetate) (PVA) IPNs. Earlier work⁷ investigated PU-PVA semi-1-IPNs as well as PU-poly(methyl acrylate) full IPNs.¹⁶

EXPERIMENTAL

Materials

The diisocyanate used was Adiprene L-100 which was kindly donated by DuPont (U.K.) Ltd. This commercial prepolymer¹⁶ had a number average molecular weight of 1850 g mol⁻¹ and a weight average molecular weight of 3500 g mol⁻¹. Trimethylol propane was supplied by Aldrich Chemicals. Butane-1,4-diol, used as a chain extender, and di-*n*-butyl tin dilaurate, the urethane catalyst, were supplied by BDH Chemicals Ltd. The vinyl acetate (BDH Chemicals Ltd.) was crosslinked with 1% (w/w) divinylbenzene (Cambrian Chemicals) using 0.1% (w/w) azobisisobutyronitrile (Aldrich Chemicals) as initiator.

Synthesis

The IPNs were prepared by dissolving all the reactants in the vinyl acetate. Di-*n*-butyl tin dilaurate was added, the solution was degassed, and then poured into moulds as described previously.¹¹ The temperature was held at 20°C for 24 h to allow the PU network to form, before raising to 65°C for 18 h followed by 6 h at 90°C to establish the PVA network. The NCO:OH ratio was kept constant at 1:1. For the 60 wt % UP IPN butane-1,4-diol was added as a chain extender^{11,17} to maintain a constant value of \bar{M}_c for the PU network. The PU homopolymer used for comparison was prepared in inhibited vinyl acetate which was subsequently slowly removed.

Characterization

Electron micrographs were obtained with a Hitachi HU-11B transmission electron microscope. The sample was hardened and stained with osmium tetroxide vapor prior to microtoming. The PU phases are preferentially stained.^{3,18,19} Dynamic mechanical data were obtained using a Model DDV-IIB Rheovibron Dynamic Viscoelastometer. All data were recorded at a frequency of 35 Hz and a heating rate of approximately 1°C min⁻¹. Stress-strain properties were measured on a Howden tensometer at a temperature of 20°C ± 2°C and at a strain rate of 2.5 cm min⁻¹. A Morgan Pulse Propagation Meter (Model PPM-5R) was used to measure the longitudinal sonic velocities of the samples.

RESULTS AND DISCUSSION

The PU-PVA IPNs prepared for this study contained 20 and 60 wt % of PU. Figure 1 is an electron micrograph of the 20 PU-80 PVA IPN. The darker regions are the polyurethane component.^{3,18,19} The micrograph shows a two-phase structure in which a continuous PU network constitutes cell walls which contain approximately spherical PVA domains. The PVA domains appear to coalesce in a number of regions, indicating a partially open cell structure. Thus, it is probable that the PVA component is also continuous.

Figure 2 shows the tan δ -temperature plots of both IPNs as well as that of the PU network. It is apparent that the IPNs show two transitions,

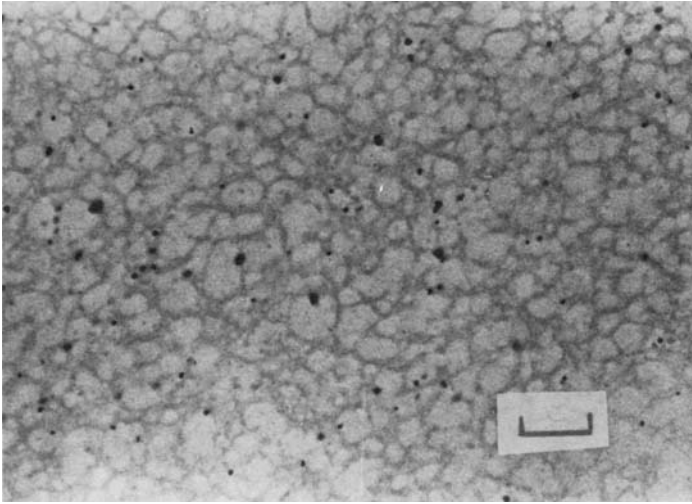


Fig. 1. Electron micrograph of a 20% polyurethane-80% poly(vinyl acetate) IPN. Scale mark represents 500 nm.

proving incompatibility. However, a noticeable feature is the significant shift of the PVA relaxation to lower temperatures as the PU content increases. There is a 10°C difference in the positions of the transition maxima. This shift to lower temperatures indicates increasing levels of mixing. The 60 PU-40 PVA IPN also displays a significant increase in damping in the temperature region between the two glass transitions. This is in marked contrast to the analogous semi-1-IPN(7) where the PVA transition does not shift.

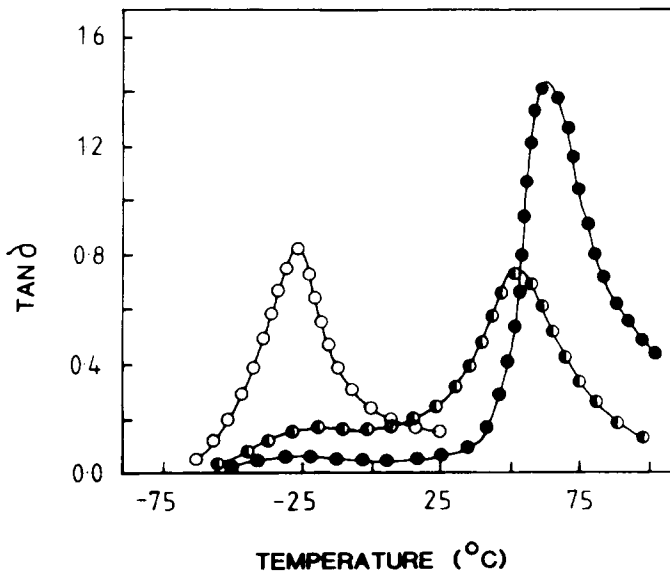


Fig. 2. $\text{Tan } \delta$ -temperature plots (35 Hz) of polyurethane (O) and the IPNs containing 20 (●) and 60 (○) wt % polyurethane.

As in the case¹⁶ of PU-poly(methyl acrylate) IPNs, the magnitude of the PU relaxations are considerably reduced. This may be attributed to the fact that the PVA component is glassy at the temperature of relaxation of the PU component. The PU transitions are also reduced as compared to the analogous PU-PVA semi-1-IPNs.⁷ The presence of crosslinking in the PVA component may affect its continuity, and hence occasion the further suppression of the PU glass transition. The PU relaxations are broader than in the case of the semi-1-IPNs, indicating a greater degree of mixing between the components.

Figures 3 and 4 show the storage (E') and loss (E'') moduli data. Both transitions are clearly resolved in these plots as are the shifts discussed with respect to the $\tan \delta$ -temperature data. The breadth of the transitions in Figure 4 especially is indicative of a significant level of forced mixing. Figure 5 shows E' vs. composition data and the trends predicted by the Kerner²⁰ and Davies²¹ equations and from the logarithmic rule of mixing.²² A value (15°C) of 1.8×10^9 Pa was taken⁷ as the storage modulus of PVA.

Equations of the general form shown below indicate dual phase continuity where n generally lies between zero²² and $1/5$ ²¹:

$$E = E_A^n V_A + E_B^n V_B \quad (1)$$

where E is the modulus, V is the volume fraction, and A and B indicate the two components.

The Kerner equation²⁰ is slightly more complex and holds well for a dispersed phase in a continuous matrix. It generally gives higher values of E than eq. (1) when V_A is less than 0.5 and lower values when V_A is greater than 0.5.²² Obviously more samples would be required in order to fit accurately the data to one of these curves, but it is evident that both points

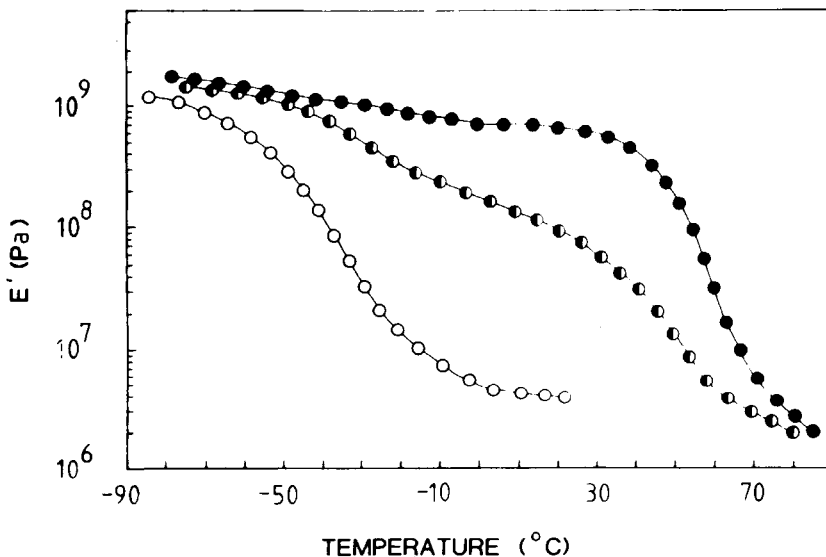


Fig. 3. E' -temperature plots (35 Hz) of polyurethane (○) and IPNs containing 20 (●) and 60 (○) wt % polyurethane.

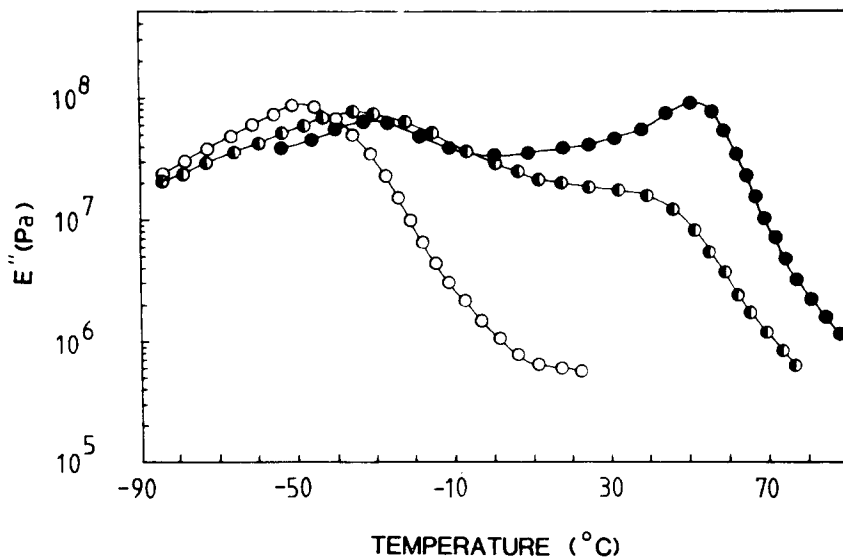


Fig. 4. E'' -temperature plots (35 Hz) of polyurethane (○) and the IPNs containing 20 (●) and 60 (○) wt % polyurethane.

do not fit the same curve. Since electron microscopy has shown the 20 PU-80 PVA IPN to most likely have both components continuous, it should fit eq. (1), which it does if n is taken as 0.01. The storage modulus of the 60 PU-40 PVA IPN is higher than the value predicted by eq. (1), possibly indicating a dispersed PVA phase.

Figure 6 shows the stress-strain curves for these systems and Table I summarizes the principal details. It is apparent that the 20 PU-80 PVA

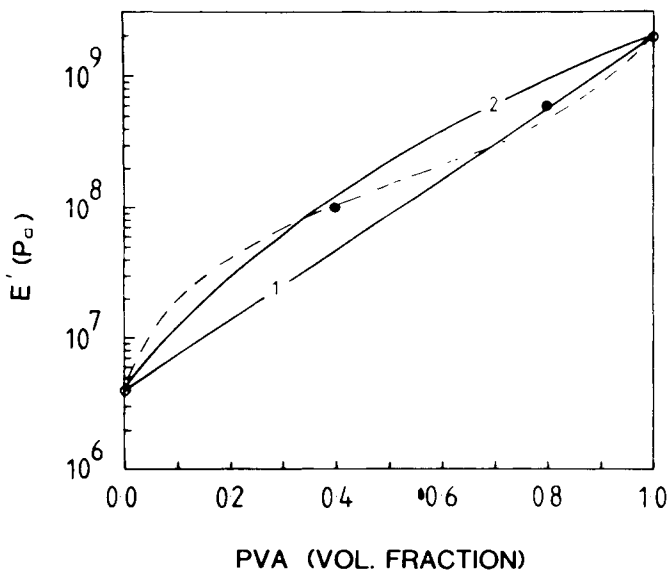


Fig. 5. E' -composition data for the IPNs (●) and the constituent polymers (○). Theoretical curves show the logarithmic rule of mixing (1), the Davies equation (2), and the Kerner equation (---) ($A = 40$; $\psi = 1$). See Ref. 22.

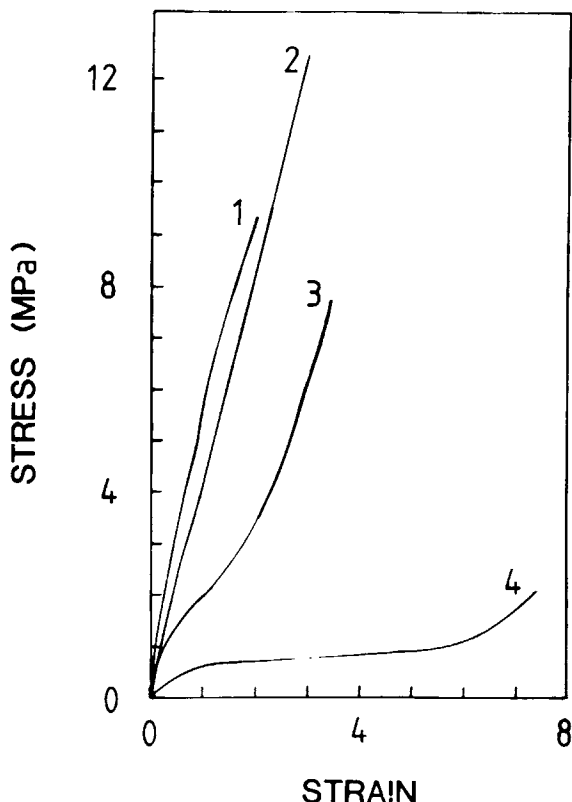


Fig. 6. Stress-strain curves for poly(vinyl acetate) (1), polyurethane (4), and the IPNs containing 20 (2), and 60 (3) wt % polyurethane.

IPN shows higher tensile strength and elongation at break than expected purely on compositional grounds. This synergism is probably as a result of both components being continuous. The 60 PU-40 PVA IPN has stress-strain characteristics intermediate between the two homopolymers, indicating that the minor component is dispersed in the PU matrix. Both IPNs exhibit increased toughness as compared to the homopolymers. This is in line with the results⁷ for semi-1-IPNs of the same system where the PVA component became discontinuous below a concentration of about 60%. For PU-poly(methyl acrylate) IPNs cocontinuity of phases results from 80% down to possibly 40% poly(methyl acrylate).¹⁶

Figure 7 shows the longitudinal sonic velocities (V_L) as a function of

TABLE I
Stress-Strain Data of the Constituent Polymers and of the IPNs

Composition (w/w)	Tensile strength (MPa)	Elongation at break (%)	100% modulus (MPa)
PVA	9.4	200	5.5
20 PU-80 PVA	12.5	300	4.0
60 PU-40 PVA	7.8	350	1.9
PU	2.1	745	0.6

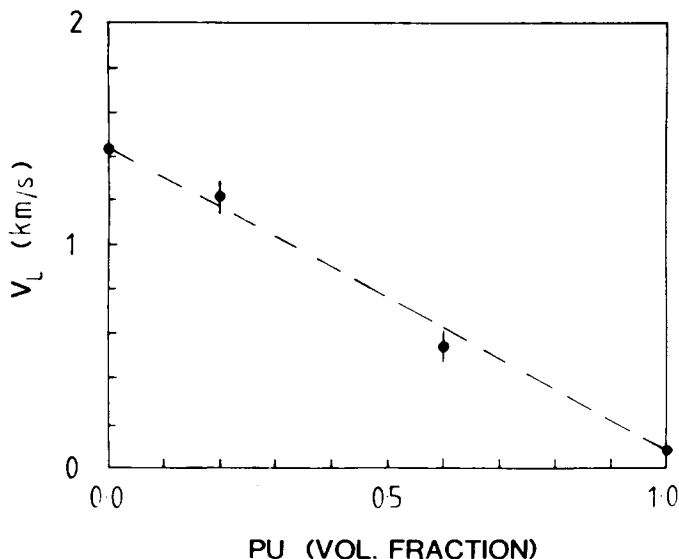


Fig. 7. V_L -composition data for polyurethane-poly(vinyl acetate) IPNs and for the constituent polymers.

composition for the IPNs and the homopolymers. The 20 PU-80 PVA IPN has a V_L value slightly higher than would be expected from simple composition considerations, while the 60 PU-40 PVA IPN has a V_L value closer to that of the PU homonetwork than expected from its composition. These observations suggest that in the 60 PU-40 PVA IPN, the PU forms the more continuous phase, while in the 20 PU-80 PVA IPN the PVA is the more continuous phase. Electron microscopy has shown the 20 PU-80 PVA IPN likely to have both components continuous which is not surprising since PU is the first formed network and as such would be expected to be continuous even at low volume fractions. The PVA component, on the other hand, is formed after completion of the PU network and could quite readily form a dispersed phase if the volume fraction is small and the rate of polymerization is slow enough.

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