

Semi- and Fully Interpenetrating Polymer Networks Based on Polyurethane–Polyacrylate Systems. V. An Isomerically Related Semi-1-Interpenetrating Polymer Network System

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Synopsis

A series of polyurethane–poly(vinyl acetate) semi-1-IPNs were synthesized, and certain physical properties investigated. Electron microscopy showed all the materials to be substantially phase-separated, but evidence from dynamic mechanical analysis indicated that some mixing occurred, because the polyurethane glass transition was shifted in both the $\tan \delta$ - and the E'' -temperature curves. The variation of modulus with composition was found to be reasonably close to the predictions of the Davies equation. When the exponent in that relation was changed to $1/6$, a good fit was obtained. Synergism with respect to tensile strength was observed for two of the semi-1-IPNs. Stress–relaxation measurements, over a fairly narrow temperature range, were made on the semi-1-IPN containing 40% by weight of the polyurethane network. A master curve was constructed. It was noted that the WLF equation was not obeyed by this semi-1-IPN at temperatures above about 50°C.

INTRODUCTION

An interpenetrating polymer network (IPN) is usually defined as a material which consists of a pair of networks, one of which at least has been synthesized and/or crosslinked in the presence of the other. There are several fairly recent reviews^{1–4} of IPNs.

When only one of the polymers is crosslinked, the product is termed a semi-IPN. For a given system, two different semi-IPNs exist. When the first formed material, polymer 1, is crosslinked, a semi-1-IPN results. If, however, polymer 1 is linear and polymer 2 is a network, the material is known as a semi-2-IPN.

Several studies of semi-IPNs have been reported. Klempner et al.⁵ have investigated the morphologies and the properties of both semi-1 and semi-2-IPNs of a polyurethane–polyacrylate system. Allen et al.^{6–10} and Kim et al.¹¹ have reported detailed studies of polyurethane–poly(methyl methacrylate) semi-IPNs. Earlier papers in this series have been concerned with polyurethane–poly(methyl acrylate) semi-1-IPNs,¹² the corresponding semi-2-IPN¹³ and with grafted polyurethane–polyacrylate semi-1-IPNs.¹⁴

In this paper the morphology and properties of polyurethane–poly(vinyl acetate) semi-1-IPNs have been investigated.

EXPERIMENTAL

Synthesis

The synthesis of the polyurethane networks has been described¹⁵ already. They were synthesized for Adiprene L-100,¹⁵ kindly donated by DuPont (U.K.) Ltd., butane-1,4-diol and trimethylol propane. The butane-1,4-diol was added as a chain extender so that the molecular weight between crosslinks, \bar{M}_c of the networks was kept approximately constant^{6,12} at a value of 6400 g/mol. The NCO/OH ratio for all the polyurethanes prepared for this work as 1.1.

To prepare the semi-1-IPNs, all the reactants were dissolved in the required amount of destabilised vinyl acetate. Dibutyl tin dilaurate (2 wt %) was added to promote the polyurethane synthesis. The solutions were degassed and poured into molds¹⁵ and maintained at 20°C for 24 h to allow the polyurethane formation to occur. The temperature was then raised to 60°C for 18 h, followed by a further period of 6 h at 90°C, to polymerize the vinyl acetate, AIBN (0.1% w/w), being used as the initiator.

The polyurethane homopolymer networks were prepared in inhibited vinyl acetate, which was subsequently slowly removed under vacuum. The poly(vinyl acetate) homopolymer (\bar{M}_n was 1.45×10^5 g/mol) was also prepared in the same type of mold and under the same conditions as used for the semi-IPN synthesis.

All materials were placed under vacuum at 20°C for at least 10 days prior to use.

Characterization

The dynamic mechanical data were obtained using a Rheovibron dynamic viscoelastometer (Model DDV-II-B) at a heating rate of approximately 1°C/min. Both the stress-strain data and the stress-relaxation at 100% applied strain data were obtained with a Howden tensometer. In the former case, the strain rate was 2.5 cm/min, and in the latter the desired strain was set at a strain rate of 38 cm/min. The strain in both cases was defined as the change in length divided by the original length.

The longitudinal sonic velocities V_L were determined¹⁶ with a Morgan pulse propagation meter (Model PPM-5R). Densities, at 23°C, were determined using a Davenport density gradient column. A Hitachi HU-11B electron microscope was employed to obtain the transmission electron micrographs. Prior to microtomy the samples were hardened and stained with OsO₄ vapor.

RESULTS AND DISCUSSION

As the crosslink density of the polyurethane component was equal to that of the polyurethane-poly(methyl acrylate) semi-1-IPNs already reported¹², comparison may be made between these two very similar groups of materials.

The semi-1-IPNs prepared for this study contained 20, 40, 50, and 60 wt %, respectively, of the polyurethane. IPNs can exhibit¹⁷ a characteristic cellular morphology where the first crosslinked component constitutes the

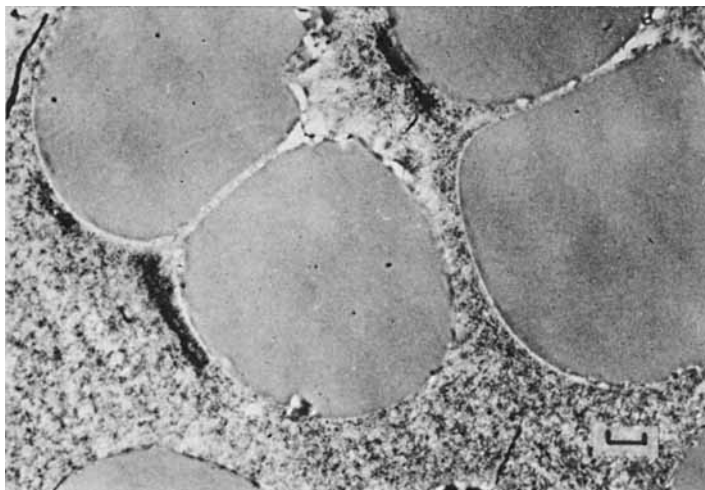


Fig. 1. Electron micrograph of the semi-1-IPN containing 20 wt% of polyurethane. Scale mark represents 3300 nm.

walls of the cells and the second component the contents. The size of the cellular structure depends on the crosslink density¹⁸ and also depends greatly on the compatibility¹⁹ of the two polymers.

Investigators working on polyurethane-poly(methyl methacrylate)-IPNs and semi-IPNs showed^{20,21} that the polyurethane component, without any deliberate addition of double bonds, was preferentially stained by osmium tetroxide. Thus, in the present study the dark areas in the subsequent electron micrographs are polyurethane-rich regions.

Figures 1, 2, and 3 show electron micrographs of the semi-1-IPNs containing 80% and 60% poly(vinyl acetate). Figure 1 shows gross phase separation with very large domains of apparently pure poly(vinyl acetate) averaging about 21 μm in diameter.

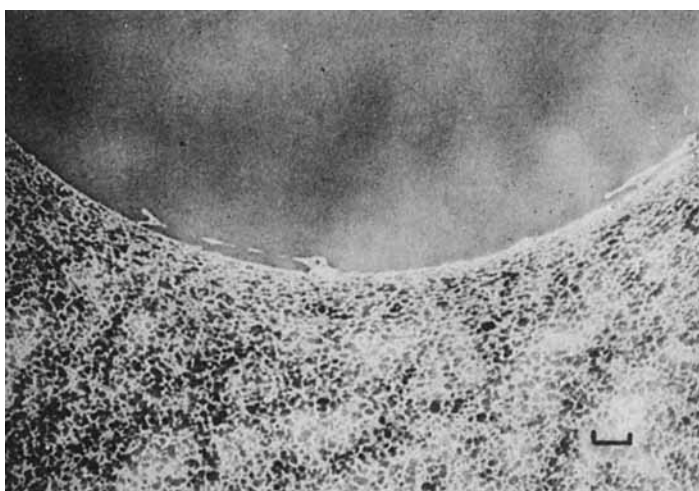


Fig. 2. Electron micrograph of a phase boundary region in the semi-1-IPN containing 20 wt% of polyurethane. Scale mark represents 1000 nm.



Fig. 3. Electron micrograph of the semi-1-IPN containing 40% by weight of polyurethane. Scale mark represents 1000 nm.

However, even when the network component is present at only 20 wt %, it probably still forms a continuous phase as can be seen by looking at Figure 2, which shows, in detail, the boundary region of a poly(vinyl acetate) domain. Here a mixed phase can be seen in which the dark polyurethane-rich regions may well be continuous. When the polyurethane content is raised to 40% (Fig. 3), no large poly(vinyl acetate) phases were observed, but the material is still substantially phase-separated.

Figure 4 shows stress-strain curves for three of the semi-1-IPNs and for the homopolymers. The semi-1-IPNs with 20% and 40% polyurethane show synergism with respect to tensile strength. All other tensile properties (Table I) are intermediate with respect to the homopolymer components. The

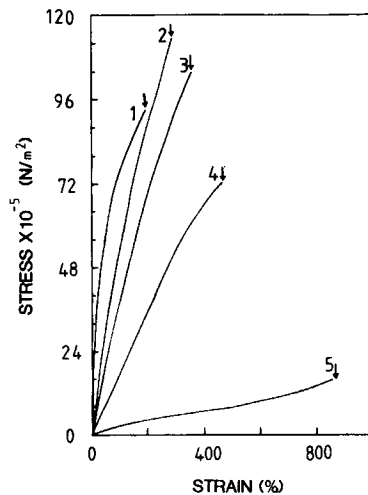


Fig. 4. Stress-strain curves at 20°C for the polyurethane network (5), poly(vinyl acetate) (1), and for the semi-1-IPNs containing 20 (2), 40 (3), and 60 (4) wt% polyurethane. The symbol (1) indicates the breaking point.

TABLE I
 Tensile Data at 20°C

Material	Tensile strength (MN/m ²)	Elongation at break (%)
Polyurethane network	1.55	820
Semi-1-IPN with 60% polyurethane	7.2	420
Semi-1-IPN with 40% polyurethane	10.4	340
Semi-1-IPN with 20% polyurethane	11.6	270
Poly(vinyl acetate)	9.4	200

significant increases in both tensile strength and in elongation at break for the 20% polyurethane semi-1-IPN indicate that it is probable that the minor component is present as a continuous phase.

When V_L is plotted against concentration for polymer blends, there is often¹⁶ a rapid change in slope when phase inversion occurs. This is especially true when the V_L values of the components of the blend system differ significantly. Such is the case (Fig. 5) for polyvinyl acetate and this particular polyurethane. The change in slope at about 60 wt % poly(vinyl acetate) is interpreted as the composition region in which the glassy component forms a continuous phase.

As far as the densities of the semi-1-IPNs are concerned, they are less than predicted by simple additivity considerations (Fig. 6). This was also the case for the polyurethane-poly(methyl acrylate) semi-1-IPNs previously reported.¹² It has been said⁹ that this is general for mixed systems in which a relatively coarse morphology exists.

Dynamic mechanical analysis shows two separate transitions for all the polyurethane-poly(vinyl acetate) semi-1-IPNs, confirming the phase separation shown in the electron micrographs (Figs. 1-3). Figure 7 shows $\tan \delta$ -temperature plots for three of the semi-1-IPNs and for both homopolymers. The large transition located at about 60°C is the glass transition of the poly(vinyl acetate) component. Comparison with the poly(vinyl acetate) homopolymer glass transition (60°C) shows that there is no shift in the poly(vinyl acetate) glass transition in the blends, indicating that there are essentially pure poly(vinyl acetate) phases present. The polyurethane glass

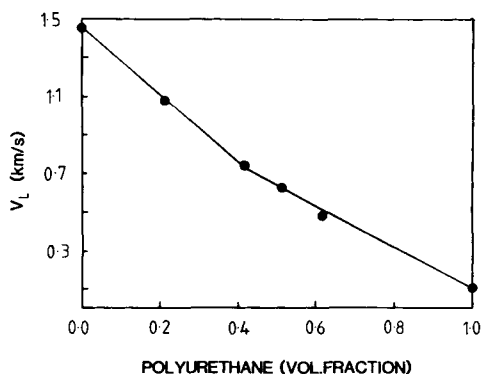


Fig. 5. V_L -composition plot (20°C) of the polyurethane-poly(vinyl acetate) semi-1-IPNs.

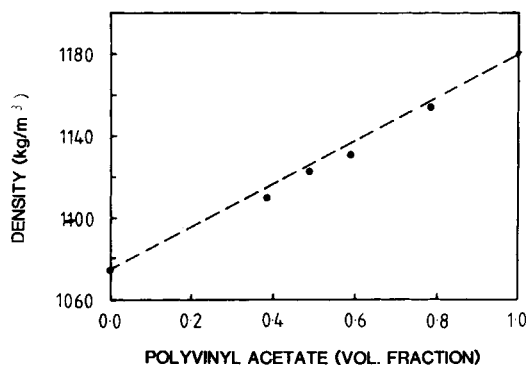


Fig. 6. Density-composition plot (23°C) of the polyurethane-poly(vinyl acetate) semi-1-IPNs.

transitions are significantly shifted to higher temperatures, indicating some molecular mixing between the components. The effect increases as the polyurethane content decreases. This is further evidence of the spatial continuity of the first formed polymer. These shifts are much clearer in Figure 8, which presents plots of the dynamic loss modulus E'' vs. temperature. The poly(vinyl acetate) glass transition is present more as a shoulder than as a resolved peak. This situation is found when systems show a certain amount of mixing. In highly incompatible systems, the E'' -temperature plots show two resolved peaks.

Figure 9 shows the dynamic storage modulus E' vs. temperature plots again for the semi-1-IPNs and the homopolymers. These E' -temperature plots also show the two transitions.

Investigations of the poly(vinyl acetate) glass transition include those of Stratton and Ferry,²² McKinney and Belcher,²³ Thurn and Wolf,²⁴ Williams and Ferry,²⁵ and Schmieder and Wolf.²⁶

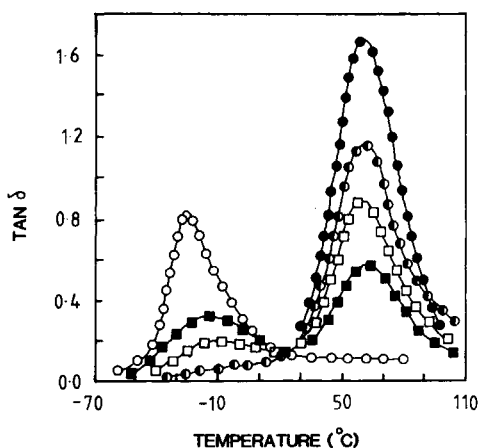


Fig. 7. $\tan \delta$ -temperature plots (11 Hz) of the polyurethane network (○), poly(vinyl acetate) (●), and the semi-1-IPNs containing 20 (●), 40 (□), and 60 (■) wt% polyurethane.

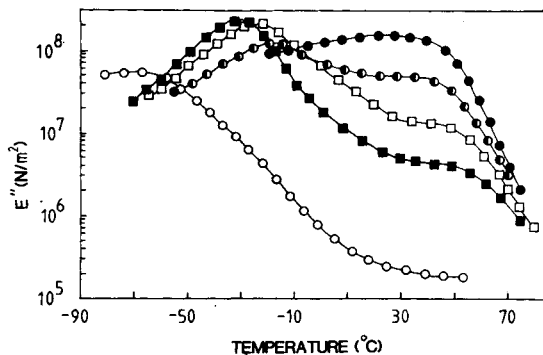


Fig. 8. E'' -temperature plots (11 Hz) of the polyurethane network (○), poly(vinyl acetate) (●), and the semi-1-IPNs containing 20 (◐), 40 (◑), and 60 (■) wt% polyurethane.

Table II compares some of the glass transition properties of poly(vinyl acetate) with those of poly(methyl acrylate).¹²

The shift factor²⁷ for the poly(vinyl acetate) glass transition was found to be 8°C per decade of frequency, yielding an activation energy of 250 kJ/mol. For the poly(methyl acrylate) glass transition it was²⁷ 234 kJ/mol. This corresponds to a peak shift of 7.5°C per decade of frequency.

Numerous relations²⁸ have been proposed to predict how modulus varies with composition in polyblends. Two of the simplest, mathematically, are the logarithmic rule of mixtures,^{28,29}

$$\log E' = \phi_1 \log E'_1 + \phi_2 \log E'_2 \quad (1)$$

the Davies equation,^{30,31}

$$E'^{1/5} = \phi_1 E'^{1/5}_1 + \phi_2 E'^{1/5}_2 \quad (2)$$

ϕ_1 and ϕ_2 are the volume fractions of the two components.

Equation (2) is a specific case of the generalized Nielsen equation³²:

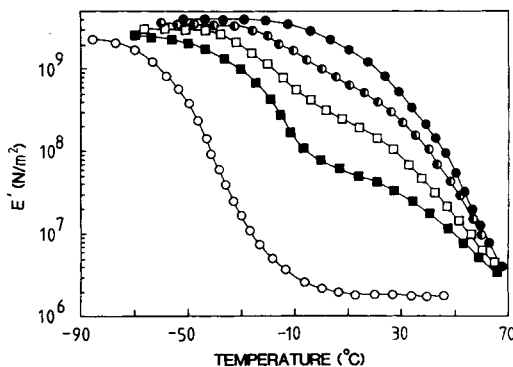


Fig. 9. E' -temperature plots (11 Hz) of the polyurethane network (○), poly(vinyl acetate) (●), and the semi-1-IPNs containing 20 (◐), 40 (◑), and 60 (■) wt% polyurethane.

TABLE II
Some Glass Transition Data (11 Hz) for Poly(vinyl Acetate) and for Poly(methyl Acrylate)

Material	Half-peak width (°C)	Tan δ_{\max}	T_g (°C)
Poly(vinyl acetate)	38	1.65	60
Poly(methyl acrylate)	31	≈ 2	30

$$P^n = \phi_1 P_1^n + \phi_2 P_2^n, \quad -1 < n < 1 \quad (3)$$

P can be any physical property.

E' (20°C) of the polyurethane–poly(vinyl acetate) semi-1-IPNs are plotted against the volume fraction of polyvinyl acetate in Figure 10. Line 1 is the modulus–composition relation according to the Davies equation,^{30,31} and line 2 shows the linear logarithmic rule of mixtures.^{28,29} The experimental points are clearly located between these two lines.

An exact fit by the Davies equation implies²⁹ dual phase continuity. If n in eq. (2) is altered to $\frac{1}{6}$, a good fit is obtained. For the previously reported¹² semi-1-IPNs based on the same polyurethane network, but with polymethyl acrylate as the linear component, the best fit occurred when n was $\frac{1}{10}$. This implies that the current system is more extensively mixed than the polyurethane–poly(methyl acrylate) materials.

Several investigators^{33–35} have studied the stress–relaxation of multicomponent systems such as SBS block copolymers. Isothermal data were shifted³³ to yield master curves.

Shen and Kaelble³³ observed that the shift factor, $\log a_T$, used to construct the relaxation modulus master curves did not obey the WLF equation³³ over the entire range of temperature investigated. The WLF equation is shown below:

$$\log a_T = \frac{-C_1(T - T_r)}{C_2 + (T - T_r)} \quad (4)$$

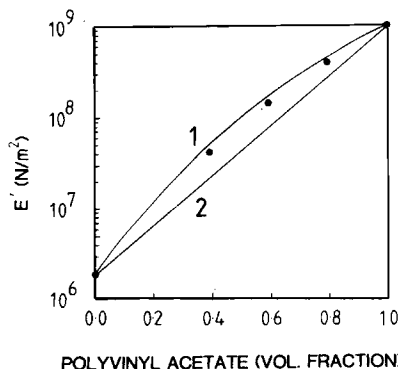


Fig. 10. E' -composition plots for the Davies equation (1) and the logarithmic rule of mixing (2). Experimental data for the semi-1-IPNs and their components are shown by the symbol (●).

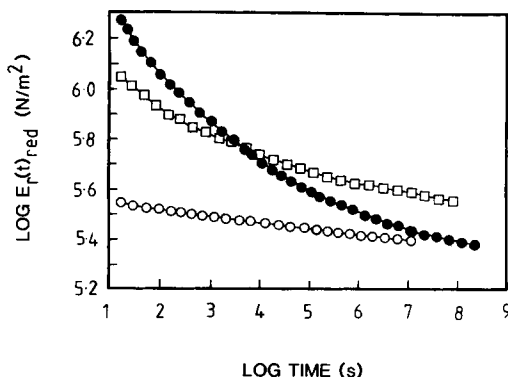


Fig. 11. Log $E_r(t)$ -log time plots (30°C) for a polyurethane-poly(vinyl acetate) semi-1-IPN containing 40 wt% polyurethane (□) and for the polyurethane network (○) and the poly(vinyl acetate) (●) homopolymer.

T_r is a reference temperature, which is often taken to be the glass transition temperature. C_1 and C_2 are empirical constants with so-called "universal" values of 17.44 and 51.6, respectively, but these values, in fact, only apply to a very limited number of polymers.

The stress-relaxation behaviors, at 100% strain, of a semi-1-IPN containing 40 wt % polyurethane and of the homopolymers have been studied. The temperature was varied over only a narrow temperature range from 30°C to 80°C. The relaxation modulus-time master curves (30°C) of this semi-1-IPN and of the homopolymers were constructed³³ and are shown in Figure 11. In constructing the master curves the relaxation moduli $E_r(t)$ were multiplied by the correction factor, T_0/T , to reduce the data. T_0 is the reference temperature, which was 30°C and T is temperature at which the other stress-relaxation curves were obtained. Density changes were ignored. At first the semi-1-IPN relaxes at an intermediate rate, but after about 5250 s its curve crosses that of the poly(vinyl acetate). The WLF constants were determined and are given in Table III. They differ significantly from the universal values.

In Figure 12 the shift factors used to construct the master curves are plotted against temperature. The solid lines show the WLF equation. It was found that the polyurethane and poly(vinyl acetate) homopolymers obeyed this equation extremely well over the entire range of temperature. However, the stress-relaxation behavior of the semi-1-IPN is more complex. It deviates from the WLF equation at temperatures above about 50°C. This stress-relaxation behavior is very similar to that reported earlier¹² for polyure-

TABLE III
WLF Constants for the 40% Polyurethane-60% Poly(vinyl Acetate) Semi-1-IPN and for the Homopolymers

Material	C_1	C_2
Poly(vinyl acetate)	12	105
Polyurethane	15	225
Semi-1-IPN	13.5	149

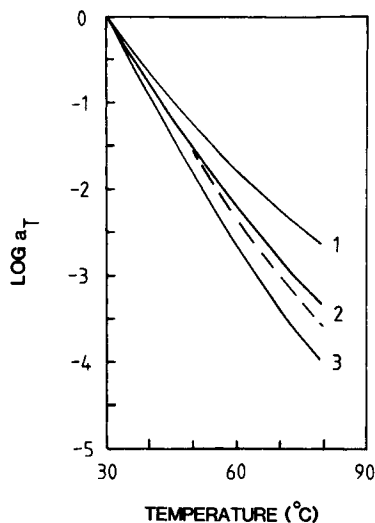


Fig. 12. $\log a_T$ -temperature plots for a polyurethane-poly(vinyl acetate) semi-1-IPN containing 40 wt% polyurethane (2) and for the polyurethane network (1) and the poly(vinyl acetate) (3) homopolymer: solid lines indicate that the data fit the shown WLF curve; for the semi-1-IPN the dashed line shows how the data deviate from the WLF curve.

thane-poly(methyl acrylate) semi-1-IPNs. However, Sperling and Thomas³⁶ have studied the stress-relaxation of poly(ethyl acrylate)-poly(methyl methacrylate) IPNs over a wide range of temperature, and they found that the WLF equation fitted reasonably well.

As the WLF equation was developed for materials showing a single relaxation, it is not surprising that it is not totally applicable to phase-separated polymer blends. The deviation for the semi-1-IPN occurs at a temperature close to the T_g of the linear component and is probably the result of an increased rate of relaxation in this component.

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