

# Polyurethane Interpenetrating Polymer Networks. 3. Viscoelastic Properties of Polyurethane– Poly(methyl methacrylate) Interpenetrating Polymer Networks

S. C. Kim,<sup>1a</sup> D. Klemmner,\*<sup>1a</sup> K. C. Frisch,<sup>1a</sup> and H. L. Frisch<sup>1b</sup>

*Polymer Institute, University of Detroit, Detroit, Michigan, and The  
Department of Chemistry, State University of New York, Albany, New York.  
Received June 10, 1977*

**ABSTRACT:** The tensile and shear moduli of polyurethane–poly(methyl methacrylate) interpenetrating polymer networks (IPN's) were evaluated. The tensile modulus was obtained on an Instron tensile tester and the shear modulus was measured on a torsion pendulum as a function of temperature and composition. In general, the modulus behavior followed the theoretical models of Budiansky, which predict a phase inversion. The mechanical damping was increased in the IPN's but this increase was not characteristic of interpenetration since it was also found to occur in pseudo-IPN's (only one network cross-linked) and in the linear blends.

The static and dynamic viscoelastic properties of IPN's have been studied by various workers.<sup>2–6</sup> The storage modulus,  $E'$ , showed strong contributions from the continuous phase network. IPN's whose continuous networks are glassy exhibit lower storage moduli than do blends of the same composition using linear polymers. This implies interpenetration of the rubbery network into the glassy network.<sup>5</sup>

The dissipation factor,  $\tan \delta$ , of semicompatible IPN's [e.g., poly(ethyl acrylate)–poly(methyl methacrylate)] was observed to be nearly constant and high ( $\tan \delta$  values of 0.1 to 0.5) over the temperature range of 0–100 °C<sup>2b,4,5</sup> which made the IPN system suitable for noise and vibration damping applications. Similar effects have been noted for semicompatible linear blends and grafts.<sup>7</sup> This phenomenon is a manifestation of the very broad glass-transition behavior.

Several attempts have been made to fit the viscoelastic properties of IPN's with several theoretical models. Frisch et al.<sup>3</sup> found that Takayanagi's series-parallel models<sup>8</sup> fit well with the poly(urethane–urea)–polyacrylate latex IPN data. Sperling et al.<sup>2a</sup> applied the models of Kerner<sup>9</sup> and Hashin<sup>10</sup> to modulus-composition data of polystyrene–poly(ethyl acrylate) sequential IPN's and obtained a fair fit in the regions where the modulus changes slowly.

In this paper, we report the tensile and shear moduli behavior of polyurethane–poly(methyl methacrylate) IPN's.

## Experimental Section

**Synthesis.** The syntheses of the polymers and raw materials employed in this investigation were reported elsewhere.<sup>11</sup> Briefly, IPN's of the simultaneous interpenetrating network (SIN) type were prepared by combining the linear prepolymers in bulk in various proportions, along with their cross-linking agents, placed in sheet molds and simultaneously thermally cross-linked. Pseudo-IPN's (one component linear) and blends of linear polymers were prepared in a similar fashion, omitting the appropriate cross-linking agents. The sample compositions were coded as follows: the first letter denotes the polymer type (U for polyurethane and M for poly(methyl methacrylate)), the second letter denotes the nature of the polymer (L for linear and C for cross-linked), and the third numeral denotes the weight percentage of the polymer component.

**Measurements. Tensile Modulus.** The tensile modulus was computed from the initial linear portion of the stress–strain curve obtained on an Instron Universal Tester Model TTC with a temperature control chamber of Missimiers Environmental Test Chamber Model FTTU 714–100 × 350.

All the samples were dried at 50 °C under 2 mm of Hg for 2 to 3 days and were kept in a desiccator prior to testing. The specimen was cut in a rectangular strip form of 0.5 cm in width, 0.2 cm in thickness, and 5 cm in length. Two millimeters or less on both ends of the specimen were clamped so that the correction to the shape factor for the rectangular strip specimen was negligible (shape factor error less than 2%).

The maximum elongation employed ranged from 5% for elastomeric specimens to 0.02% for rigid specimens. The tensile modulus measurements were carried out at 23 °C with varying crosshead speeds from 0.02 to 20.0 in./min (strain rates ranged from  $4 \times 10^{-4}$  to 4 min<sup>-1</sup>).

**Dynamic Viscoelastic Properties.** Dynamic viscoelastic properties were obtained using a freely oscillating torsion pendulum which was built essentially the same as the one described by Lawson.<sup>12</sup>

The specimens were in the form of rectangular strips with typical dimensions of 5 cm × 1 cm × 0.2 cm. The specimens were dried at 50 °C under vacuum for 2 to 3 days and kept in a desiccator prior to testing in order to remove effects of moisture. The rigid specimens were heated at 120 °C for 10 min and quenched in liquid nitrogen in order to remove residual stress incurred during molding. The linear polyurethane specimens were also heated at 50 °C for 10 min and quenched in liquid nitrogen to prevent crystallization.

The measurements were carried out at intervals of 1 to 2 °C in the transition region and of 5 to 10 °C elsewhere. The temperature control in subambient measurement was within ±0.5 °C; however, the control at higher temperatures (40 to 100 °C) was rather difficult and was within ±5 °C.

A narrow range of frequency variation (from 0.1 to 0.3 Hz) was obtained by varying the moment of inertia when the sample modulus changed with temperature.

The storage and loss moduli,  $G'$  and  $G''$ , were calculated using tabulated correction factors for a rectangular strip specimen.<sup>13,14</sup>

## Results and Discussion

**Young's Modulus.** The strain rate dependence of tensile modulus (Figure 1) is shown to be small since the glass-transition temperature of each component network [–49 °C for the polyurethane and +109 °C for the poly(methyl methacrylate)<sup>15</sup>] is either far above or far below the test temperature (23 °C). Thus each component network lies either in a rubbery or glassy region where there is relatively little time dependence of the modulus.

The modulus–strain rate curves appear to lie in three groups: the two curves for pure polyurethane and 75% polyurethane–25% poly(methyl methacrylate) IPN in the low modulus range; the three curves for 60/40%, 50/50%, 40/60% polyurethane–poly(methyl methacrylate) IPN's in the medium modulus range; and the three curves for 25/75%, 15/85% polyurethane–poly(methyl methacrylate) IPN's and pure poly(methyl methacrylate) in the high modulus range.

The modulus behavior of the three groups relates well with the morphology<sup>11</sup> and the general appearance of the IPN samples. The low modulus group includes elastomeric samples where the polyurethane phase is continuous, the medium modulus group includes leathery samples where the phases are in the inversion process (each phase is locally connected), and the high modulus group includes glassy samples where the poly(methyl methacrylate) phase is continuous.

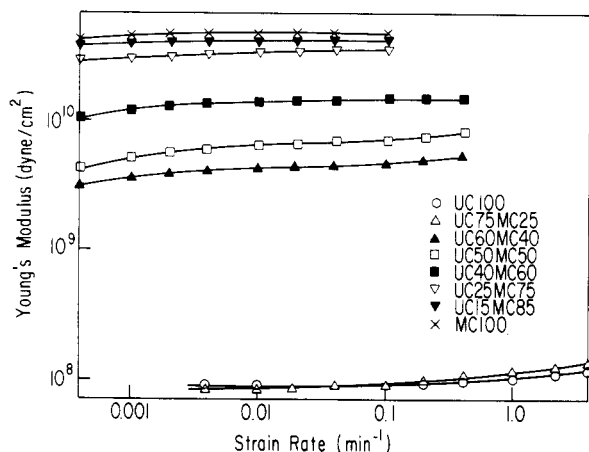


Figure 1. Young's modulus vs. strain rate for the polyurethane-poly(methyl methacrylate) IPN's at 23 °C.

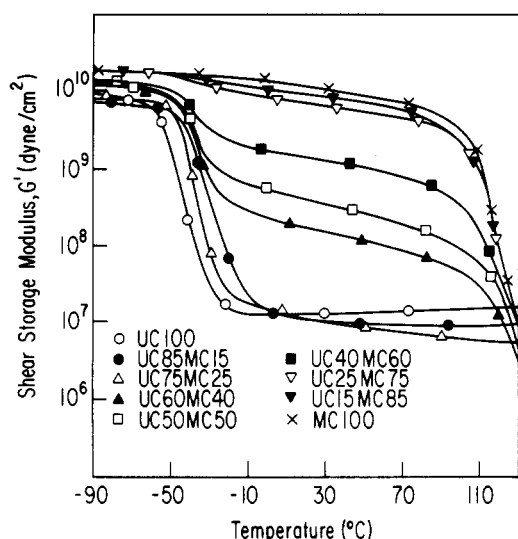


Figure 2. Shear storage modulus,  $G'$ , vs. temperature for the polyurethane-poly(methyl methacrylate) IPN's.

The 75/25% polyurethane-poly(methyl methacrylate) IPN shows little modulus reinforcement over the pure polyurethane samples.

**Shear Modulus.** The shear storage modulus,  $G'$ , vs. temperature plot (Figure 2) for polyurethane-poly(methyl methacrylate) IPN's also reveals three general groups. The 75/25% and 85/15% polyurethane-poly(methyl methacrylate) IPN's show a slightly reduced modulus compared to the pure polyurethane sample at room temperature.

A comparison of the shear storage modulus of the 75/25% polyurethane-poly(methyl methacrylate) IPN with its corresponding pseudo-IPN's as well as the linear blend (Figure 3) shows that the IPN has the lowest modulus at room temperature. This agrees well with the tensile modulus behavior and is probably due to crystallization of the linear polyurethane. The above comparison seems to indicate that the reduction of modulus is related to the interaction and/or interpenetration of the phases. One possible explanation would be that the partial crystallinity in the polyurethane phase (shown earlier<sup>11</sup> to be present, even in the cross-linked polymer) was reduced due to the interpenetration of poly(methyl methacrylate) chains into the polyurethane phase. In the pseudo-IPN's and linear polyblend, the crystallinity of the polyurethane phase was not reduced since there was no interpenetration (interlocking of chains), thus yielding an increased modulus over the pure polyurethane. The increase in

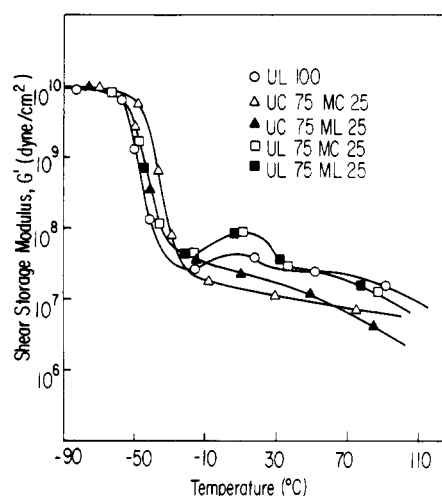


Figure 3. Shear storage modulus,  $G'$ , vs. temperature for the polyurethane-poly(methyl methacrylate) IPN's, pseudo-IPN's, and linear blends.

modulus in the temperature range of -10 to 30 °C is due, most likely, to crystallization of the linear polyurethane caused by the slow heating.

Torsion pendulum measurements for the polyurethane-polystyrene IPN's were reported by Kaplan and Tschoegl.<sup>6</sup> The shear storage modulus also showed little reinforcement of the elastomeric compositions by the embedded hard phase. However, the lack of reinforcement was not as prominent as in the polyurethane-poly(methyl methacrylate) IPN system. This seems to reflect the higher level of mixing and interpenetration in the polyurethane-poly(methyl methacrylate) IPN's.

The shear damping factor,  $\tan \delta$ , vs. temperature plots (Figures 4 and 5) show the glass-transition behavior and were discussed elsewhere.<sup>11</sup> Briefly, the shift in  $T_g$  to higher temperature (most prominent in the full IPN's) also indicates interpenetration.

The shear damping factor,  $\tan \delta$ , vs. temperature plot (Figure 4) of polyurethane-poly(methyl methacrylate) IPN's shows increased damping in the temperature range of -10 to 90 °C at 75/25%, 60/40%, 50/50% and 40/60% polyurethane-poly(methyl methacrylate) compositions. The maximum damping factor in this temperature range is 0.25. The comparison of IPN's, pseudo-IPN's, and linear polyblends (Figure 5) shows that this effect is not related to interpenetration. The increased damping in this case does not seem to be related to the transition behavior (broad glass-transition behavior was one of the contributing factors in the compatible poly(ethyl methacrylate)-poly(*n*-butyl acrylate) IPN's for the increased damping).<sup>16</sup> Rather, it seems to be due to the friction between the glassy-glassy and glassy-rubbery phases<sup>17</sup> and to be dependent on the morphology.

**Composite Models.** The modulus-composition behavior of the polyurethane-poly(methyl methacrylate) IPN's was analyzed with some of the theoretical equations based on mechanical models. Most of these models assumed perfect adhesion between the phases and a spherical inclusion (filler) geometry. They were discussed and reviewed by Nielsen,<sup>17</sup> Dickie,<sup>18-21</sup> and Davies.<sup>22</sup>

Mooney<sup>23</sup> developed relations based on Einstein's theory<sup>24</sup> for elastomers having a Poisson's ratio of 0.5 and filled with rigid spherical fillers:

$$G = G_m \exp \frac{2.5V_i}{1 - V_i/\phi_m} \quad (1)$$

where  $G_m$  is the shear modulus of the elastomer (the matrix),  $V_i$  is the volume fraction of the filler (the inclusion), and  $\phi_m$

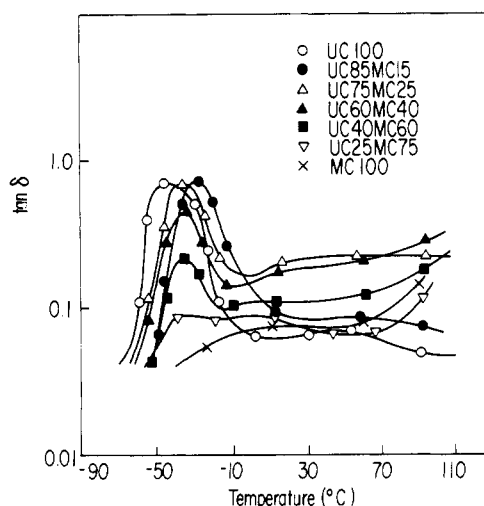


Figure 4. Shear damping factor,  $\tan \delta$ , vs. temperature for the polyurethane-poly(methyl methacrylate) IPN's.

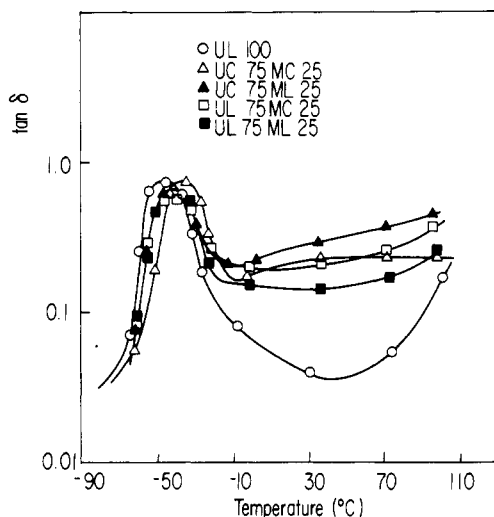


Figure 5. Shear damping factor,  $\tan \delta$ , vs. temperature for the polyurethane-poly(methyl methacrylate) IPN's, pseudo-IPN's, and linear blends.

is the maximum volume fraction that the filler can have due to packing difficulties from particle-particle contact.

Substituting tensile modulus,  $E$ , for  $G$  in the Mooney equation by using the relation  $E = 2(1 + \nu)G$ , it follows that:

$$E = \frac{(1 + \nu)}{(1 + \nu_m)} E_m \exp \frac{2.5 V_i}{1 - V_i/\phi_m} \quad (2)$$

where  $\nu$  and  $\nu_m$  are the Poisson's ratios for the composite and for the elastomer (the matrix), respectively.

Kerner<sup>9</sup> developed relations for the gross bulk and shear modulus of a multicomponent system. For two components, his equation may be written as:

$$\frac{G}{G_m} = \frac{(1 - V_i)G_m + (\alpha + V_i)G_i}{(1 + \alpha V_i)G_m + \alpha(1 - V_i)G_i} \quad (3)$$

where  $G$  is the shear modulus,  $V_i$  is the volume fraction of the inclusions (fillers), subscript  $m$  denotes a matrix property, subscript  $i$  denotes an inclusion property, and  $\alpha$  is a function of  $\nu_m$ , the Poisson's ratio of the matrix:

$$\alpha = 2(4 - 5\nu_m)/(7 - 5\nu_m) \quad (4)$$

In terms of tensile modulus,  $E$ :

$$\frac{E}{E_m} = \frac{\gamma(1 - V_i)E_m + \beta(\alpha + V_i)E_i}{(1 + \alpha V_i)E_m + \alpha\beta(1 - V_i)E_i} \quad (5)$$

where

$$\beta = (1 + \nu_m)/(1 + \nu_i) \quad (6)$$

$$\gamma = (1 + \nu)/(1 + \nu_m) \quad (7)$$

Equivalent equations were also developed by Takayanagi.<sup>11</sup>

Dickie<sup>19</sup> modified eq 5 and introduced an interaction parameter  $\psi$  in the form of a maximum packing fraction  $\phi_m$ :

$$\frac{E}{E_m} = \frac{\gamma(1 - \psi V_i)E_m + \beta(\alpha + \psi V_i)E_i}{(1 + \alpha\psi V_i)E_m + \alpha\beta(1 - \psi V_i)E_i} \quad (8)$$

where

$$\psi = 1 + V_i(1 - \phi_m)/\phi_m^2 \quad (9)$$

The above theories are based on a polymer composite where the matrix and the dispersed phase are well defined, i.e., the matrix and the dispersed phase are both single components of the system. The properties of the matrix material are dominant in determining the composite properties. Theoretically, the equations will represent the composite properties better if the volume fraction of the dispersed phase is small, since they implicitly assume no interaction between the dispersed phase domains.

The distinction between the matrix and the inclusion disappears in the range of intermediate concentrations where the phase inversion occurs. There is also large interaction between the phase domains and one component network does not play a dominant role over the other in determining the composite properties. At these concentrations, the previous theories only give upper and lower bounds of the composite modulus.

In order to account for the interaction between the phase domains, Budiansky<sup>25</sup> used the Kroner's "smearing out" approach<sup>26</sup> and assumed that an isolated spherical inclusion is embedded in an infinite isotropic matrix which itself is a composite material. For two-phase systems, his equation is expressed as:

$$\frac{V_1}{1 + \epsilon(G_1/G - 1)} + \frac{V_2}{1 + \epsilon(G_2/G - 1)} = 1 \quad (10)$$

where

$$\epsilon = \frac{2(4 - 5\nu)}{15(1 - \nu)} \quad (11)$$

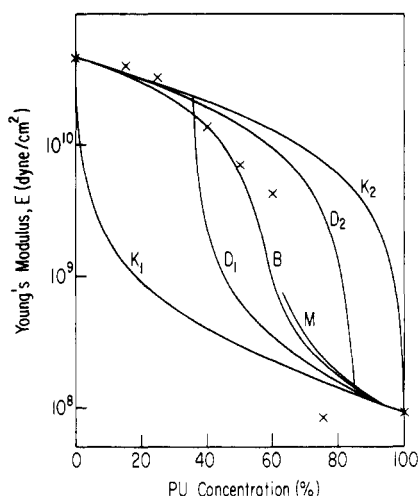
Subscripts 1 and 2 denote component materials and  $\nu$  is the Poisson's ratio of the composite. It is interesting to note that eq 10 is symmetrical and the reversal of geometrical roles of the materials 1 and 2 does not change the composite property in a given concentration. In other words, one does not differentiate materials 1 and 2 as the matrix or the inclusion. The Mooney equation (eq 1 and 2), the Kerner equation (eq 3 and 5), the Dickie equation (eq 8) ( $\gamma = 1$  for shear modulus,  $G$ , in eq 8), and the Budiansky equation (eq 10) were compared with the experimental results at 23 °C. The Poisson's ratio of the polyurethane phase was assumed to be 0.5<sup>9</sup> and that of poly(methyl methacrylate) and polystyrene to be 0.35<sup>9</sup> at 23 °C. The Poisson's ratio of the composite was assumed to be the volume additive of its components:

$$\nu = V_m\nu_m + V_i\nu_i$$

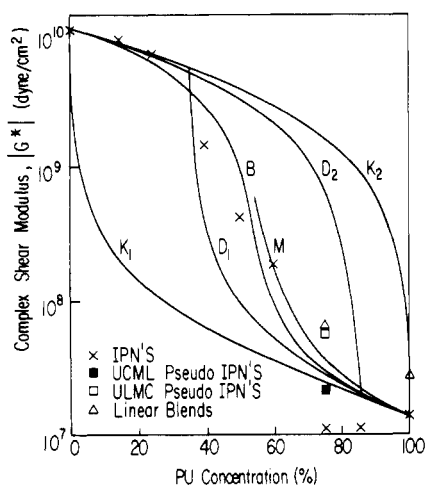
Although this assumption is not theoretically valid, the resulting ratios,

$$\frac{1 + \nu}{1 + \nu_m} \text{ and } \frac{1 + \nu}{1 + \nu_i}$$

in eq 2, 5, and 8, varied at the most  $\pm 5\%$ . The maximum packing fraction,  $\phi_m = 0.64$ , was chosen for rigid inclusions in



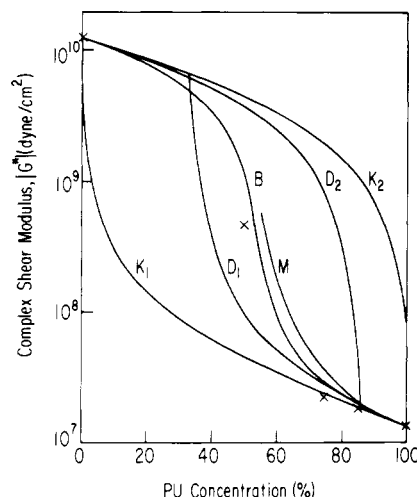
**Figure 6.** Young's modulus vs. polyurethane concentration for the polyurethane-poly(methyl methacrylate) IPN's at 23 °C. Solid lines are based on the theoretical models with  $K_1$ , the Kerner equation, assuming the polyurethane as the continuous phase;  $K_2$ , assuming the poly(methyl methacrylate) as the continuous phase;  $D_1$  and  $D_2$  the respective Dickie equations,  $M$  the Mooney equation; and  $B$ , the Budiansky equation.



**Figure 7.** Complex shear modulus,  $|G^*|$ , vs. polyurethane concentration for the polyurethane-poly(methyl methacrylate) IPN's, pseudo-IPN's, and linear blends at 23 °C. Solid lines are the same as in Figure 6.

an elastomeric matrix, while  $\phi_m = 0.83$  was used for elastomeric inclusions in a rigid matrix.<sup>20,22</sup> The absolute value of the complex shear modulus,  $|G^*|$ , obtained from the torsion pendulum measurement was used for the shear modulus,  $G$ , since they are in principle equivalent. Moreover, Dickie<sup>18</sup> has also shown that  $G/G_m$  and  $G^*/G_m^*$  were equivalent. The results are listed in Figures 6 and 7. The tensile modulus data at 23 °C show that the cross-head speed has relatively little influence on the experimental and calculated values.

The modulus-composition plot at 0.05 in./min cross-head speed (Figure 6) shows a fairly good fit with the Budiansky equation (denoted as  $B$  in the figure). The theoretically predicted modulus values for the high polyurethane concentration with the elastomeric matrix differ little between the Mooney, Kerner, Dickie, and Budiansky equation (denoted as  $M$ ,  $K_1$ ,  $D_1$ , and  $B$ , respectively, in the figure). Also the theoretically predicted modulus values for the low polyurethane concentration with the rigid matrix show little difference between the equations (denoted as  $K_2$ ,  $D_2$ , and  $B$ ). The predicted values differ widely at intermediate polyurethane



**Figure 8.** Complex shear modulus,  $|G^*|$ , vs. polyurethane concentration for the polyurethane-polystyrene IPN's. Solid lines are the same as in Figure 6.

concentrations and the better fit with the Budiansky equation is quite expected since the assumptions made in deriving the equation represent the phase inversion process well. Also, note that the experimental data fall within the upper and lower bounds of the Kerner equations ( $K_1$  and  $K_2$  in the figure) and the Dickie equations ( $D_1$  and  $D_2$  in the figure). The modulus at 75% polyurethane does not fit with any model due to the possible reduction in crystallinity in the polyurethane phase.

The complex shear modulus-composition data at 23 °C (Figure 7) also exhibit a better fit with the Budiansky equation than the other equations. The fit is not as good as the tensile modulus plot. This seems to be due to experimental errors involved in obtaining the complex shear modulus from the free oscillation torsion pendulum measurements.

The experimental complex shear moduli of the pseudo-IPN's and the blends of the linear polymers, along with the linear homopolymers, are also shown in Figure 7. The 75/25% linear polyurethane-linear poly(methyl methacrylate) and the linear polyurethane-cross-linked poly(methyl methacrylate) composite show higher moduli, due to the crystallization in the linear polyurethane phase (the modulus of the linear polyurethane is higher than that of the cross-linked polyurethane). The comparison of the 75/25% IPN with the corresponding cross-linked polyurethane-linear poly(methyl methacrylate) pseudo-IPN is very interesting. The IPN shows a much lower modulus while the pseudo-IPN modulus lies near the range of the theoretically predicted values. This seems to support the previous assumption that the partial crystallinity in the cross-linked polyurethane phase was reduced in IPN's where the degree of mixing of both component networks is increased by interpenetration.

The torsion pendulum results of Kaplan and Tschoegl<sup>6</sup> for the polyurethane-polystyrene IPN's were also analyzed with the theoretical models and plotted in Figure 8. The Budiansky equation again predicted the experimental results well. The crystallinity effect was not observed in this system as would be expected since the degree of mixing in polyurethane-polystyrene IPN's was shown to be lower.<sup>11,27</sup>

In the range of compositions where both phases are partly continuous and where the modulus changes very rapidly with composition, Nielsen<sup>17</sup> observed that the experimental value is close to the logarithmic average of the two theoretical values of  $G$  obtained from his generalized Kerner equation.

$$\log M = \phi_U \log M_U + \phi_L \log M_L \quad (12)$$

**Table I**  
Experimental and Calculated  $\phi_U$  and  $\phi_L$  (Tensile Modulus at 23 °C)

Composition	Expl		Calcd	
	$\phi_U$	$\phi_L$	$\phi_U$	$\phi_L$
UC60MC40	0.75	0.25	0.49	0.51
UC50MC50	0.77	0.23	0.70	0.30
UC40MC60	0.84	0.16	0.91	0.09

where  $M_U$  is the upper modulus assuming rigid matrix and elastomeric inclusion and  $M_L$  is the lower modulus assuming elastomeric matrix and rigid inclusion. The quantities of  $\phi_U$  and  $\phi_L$  are the effective volume fractions for a given  $\phi_C$  relative to  $1 - \phi_{M'}$  and  $\phi_M$ .

$$\phi_U = \frac{\phi_C - (1 - \phi_{M'})}{\phi_M - (1 - \phi_{M'})} \quad (13)$$

$$\phi_L = \frac{\phi_M - \phi_C}{\phi_M - (1 - \phi_{M'})} \quad (14)$$

where  $\phi_C$  is the volume fraction of the rigid phase,  $\phi_M$  is the maximum packing fraction of the rigid inclusions in the elastomeric matrix, and  $\phi_{M'}$  is the maximum packing fraction of the elastomeric inclusions in the rigid matrix.

The tensile modulus data at 23 °C for the leathery polyurethane–poly(methyl methacrylate) IPN's (60/40, 50/50, 40/60% compositions) were evaluated with eq 9. The experimental values of  $E_E$  and the two upper and lower values from the Dickie equation,  $E_{D1}$  and  $E_{D2}$ , were taken to calculate the experimental  $\phi_U$  and  $\phi_L$  values from eq 12. They are compared with the calculated values from eq 13 and 14 in Table I. Overall, the “logarithmic rule of mixtures”,<sup>17</sup> eq 12, is not applicable for this IPN system.

**Acknowledgments.** The torsional pendulum measurements were carried out in Dr. N. W. Tschoegl's laboratory at the California Institute of Technology. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial

support of this research. We also wish to acknowledge National Science Foundation Grant No. ENG7401954 for partial support of this study.

## References and Notes

- (1) (a) University of Detroit; (b) State University of New York.
- (2) (a) L. H. Sperling and D. W. Friedman, *J. Polym. Sci., Part A-2*, **7**, 425 (1969); (b) L. H. Sperling, H. F. George, V. Huelck, and D. A. Thomas, *J. Appl. Polym. Sci.*, **14**, 2815 (1970).
- (3) D. Klempner, H. L. Frisch, and K. C. Frisch, *J. Elastoplast.*, **3**, 2 (1971).
- (4) L. H. Sperling, V. Huelck, and D. A. Thomas, “Polymer Networks: Structural and Mechanical Properties”, Plenum Press, New York, N.Y., 1971, p 435.
- (5) L. H. Sperling, V. Huelck, and D. A. Thomas, *Macromolecules*, **5**, 348 (1972).
- (6) D. Kaplan and N. W. Tschoegl, *Polym. Eng. Sci.*, **15**, 5, 343 (1975).
- (7) H. Oberst et al., U.S. Patents 3 547 755; 3 547 757; 3 547 760 (1970); 3 553 072; 3 554 885 (1971).
- (8) M. Takayanagi, H. Harima, and Y. Iwata, *Mem. Fac. Eng., Kyushu Univ.*, **23**, 1 (1963).
- (9) E. H. Kerner, *Proc. Phys. Soc., London, Sect. B*, **69**, 808 (1956).
- (10) Z. Hashin and S. Shtrikman, *J. Mech. Phys. Solids*, **11**, 127 (1965).
- (11) S. C. Kim, D. Klempner, K. C. Frisch, W. Radigan, and H. L. Frisch, *Macromolecules*, **9**, 258 (1976).
- (12) D. D. Lawson, JPL-NASA SPS Report No. 37-55, Vol. III, Feb. 1969.
- (13) J. D. Ferry, “Viscoelastic Properties of Polymers”, 2nd ed, Wiley, New York, N.Y., 1970, p 158.
- (14) C. J. Nederveen and C. W. VanderWal, *Rheol. Acta*, **6**, 316 (1967).
- (15) S. C. Kim, D. Klempner, K. C. Frisch, and H. L. Frisch, *Macromolecules*, **9**, 263 (1976).
- (16) A. J. Curtius, M. J. Covitch, D. A. Thomas, and L. H. Sperling, *Polym. Eng. Sci.*, **12**, 101 (1972).
- (17) L. E. Nielsen, “Mechanical Properties of Polymers and Composites”, Vol. 2, Marcel Dekker, New York, N.Y., 1974, p 365.
- (18) R. A. Dickie, *J. Appl. Polym. Sci.*, **17**, 45 (1973).
- (19) R. A. Dickie, M. F. Cheung, and S. Newman, *J. Appl. Polym. Sci.*, **17**, 65 (1973).
- (20) R. A. Dickie and M. F. Cheung, *J. Appl. Polym. Sci.*, **17**, 79 (1973).
- (21) R. A. Dickie, *J. Appl. Polym. Sci.*, **17**, 2509 (1973).
- (22) G. Allen, M. J. Bowden, S. M. Todd, D. J. Blundel, G. M. Jeffs, and W. E. A. Davies, *Polymer*, **15**, 28 (1974).
- (23) M. Mooney, *J. Colloid Sci.*, **6**, 162 (1951).
- (24) A. Einstein, *Ann. Phys. (Leipzig)*, **19**, 549 (1905); **19**, 289 (1906); **34**, 591 (1911).
- (25) B. Budiansky, *J. Mech. Phys. Solids*, **13**, 223 (1965).
- (26) E. Kronen, *Z. Phys.*, **151**, 504 (1958).
- (27) S. C. Kim, D. Klempner, K. C. Frisch, H. Ghiradella, and H. L. Frisch, *Polym. Eng. Sci.*, **15**, 5, 339 (1975).

## Polyurethane Interpenetrating Polymer Networks 4. Volume Resistivity Behavior of Polyurethane– Poly(methyl methacrylate) Interpenetrating Polymer Networks

S. C. Kim,<sup>1a</sup> D. Klempner,<sup>1a</sup> K. C. Frisch,<sup>1a</sup> and H. L. Frisch<sup>1b</sup>

Polymer Institute, University of Detroit, Detroit, Michigan 48221, and the  
Department of Chemistry, State University of New York, Albany, New York 12222.  
Received June 10, 1977

**ABSTRACT:** The volume resistivity behavior of interpenetrating polymer networks (IPN's) of polyurethane and poly(methyl methacrylate) was evaluated. The experimental data were analyzed in terms of the theoretical composite models of Maxwell and Böttcher. The assumptions and approaches in the Maxwell model are similar to the Kerner model for the mechanical modulus treatment of a composite material and those of the Böttcher model are similar to the Budiansky model. The Böttcher equation fits the experimental results well. This was in good agreement with the mechanical modulus behavior of the IPN's where the Budiansky model fit the experimental results well.

The electrical properties of interpenetrating polymer networks (IPN's) have not yet been explored and the effect of interpenetration is not known. The mechanical modulus behavior of IPN's, however, has been studied<sup>2–4</sup> and it was shown that the Kerner model<sup>5</sup> predicted the modulus behavior well

for the sequential and latex IPN's. For simultaneous IPN's, where the system usually undergoes a phase inversion, it was shown that the Budiansky model<sup>6</sup> predicted the modulus behavior well.<sup>7</sup> Since the mathematical treatment of the modulus and volume resistivity properties of the composite