Table I
Experimental and Calculated ϕ_U and ϕ_L (Tensile Modulus at 23 °C)

	Expl		Calcd	
Composition	ϕ_U	ϕ_L	ϕ_U	ϕ_U
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 ϕ_U and ϕ_L are the effective volume fractions for a given ϕ_C relative to $1 - \phi_M'$ and ϕ_M.

$$\phi_U = \frac{\phi_C - (1 - \phi_M')}{\phi_M - (1 - \phi_M')} \tag{13}$$

$$\phi_L = \frac{\phi_M - \phi_C}{\phi_M - (1 - \phi_M')} \tag{14}$$

where ϕ_C is the volume fraction of the rigid phase, ϕ_M is the maximum packing fraction of the rigid inclusions in the elastomeric matrix, and ϕ_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 ϕ_U and ϕ_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",[17] 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,[1a] D. Klempner,[1a] K. C. Frisch,[1a] and H. L. Frisch[1b]

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[2–4] and it was shown that the Kerner model[5] 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[6] predicted the modulus behavior well.[7] Since the mathematical treatment of the modulus and volume resistivity properties of the composite material is the same,[8] it is expected that the volume resistivity behavior of the simultaneous IPN's will follow the Budiansky model or other equivalent models. The modulus and volume resistivity properties in these models are expressed in terms of volume fractions and the component network properties. The phase domain size and the interaction between the phases were not included as a factor in the expression and it could be noted that the effect of interpenetration had little influence on these properties. In this paper, the dc volume resistivity behavior of polyurethane–poly(methyl methacrylate) IPN's is reported.

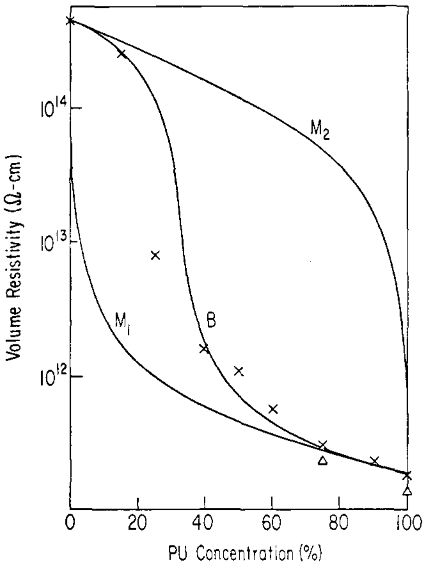

Figure 1. Volume resistivity of polyurethane–poly(methyl methacrylate) IPN's (×) and linear blends (△). Solid lines are the calculated curves based on the Maxwell equation (M_1 assuming the polyurethane as the matrix, M_2 assuming the poly(methyl methacrylate) as the matrix), and on the Böttcher model (B).

Experimental Section

Synthesis. The synthesis of the polyurethane–poly(methyl methacrylate) simultaneous IPN's is reported elsewhere.[9] Briefly, the linear prepolymers were combined in bulk in various proportions, along with their cross-linking agents, and sheets were molded and thermally cross-linked. Pseudo-IPN's (one component linear) and linear blends were prepared in a similar fashion, omitting the appropriate cross-linking agent. The samples were coded for convenience of presentation. 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.

Measurements. The dc volume resistivities of the samples were measured according to ASTM procedures.[10] The samples were dried at 50 °C under 5 mm of Hg for 2 to 3 days and kept in a desiccator prior to testing in order to remove the effect of moisture. A three-terminal guarded-electrode system (Balsbaugh Type ES 100-3T50) with an 0.5-in. diameter measuring electrode was used along with a General Radio Model 1664-A MΩ bridge. The contact between the sample and the electrode was enhanced by applying a load of 100 pounds to the electrodes. The volume resistivity was measured under 500 V dc at room temperature.

Results and Discussion

Maxwell[11,12] assumed that the "average sphere" was surrounded by an annulus of the matrix material and that the composite was composed of many of the equivalent sphere-annulus composites that had the same volume resistivity of the composite. It is expressed as:

$$\frac{K}{K_{\mathrm{m}}} = \frac{2K_{\mathrm{i}} + K_{\mathrm{m}} + V_{\mathrm{i}}(K_{\mathrm{i}} - K_{\mathrm{m}})}{2K_{\mathrm{i}} + K_{\mathrm{m}} + 2V_{\mathrm{i}}(K_{\mathrm{i}} - K_{\mathrm{m}})} \tag{1}$$

where K, K_{m}, and K_{i} are the volume resistivities of the composite, matrix, and inclusion, respectively, and V_{i} is the volume fraction of the inclusion (dispersed phase). By rearranging, we obtain:

$$\frac{K}{K_{\mathrm{m}}} = \frac{(1 - V_{\mathrm{i}})K_{\mathrm{m}} + (2 + V_{\mathrm{i}})K_{\mathrm{i}}}{(1 + 2V_{\mathrm{i}})K_{\mathrm{m}} + 2(1 - V_{\mathrm{i}})K_{\mathrm{i}}} \tag{2}$$

Kerner[5] employed a similar approach for the modulus behavior of the composite materials and his equation is:

$$\frac{G}{G_{\mathrm{m}}} = \frac{(1 - V_{\mathrm{i}})G_{\mathrm{m}} + (\alpha + V_{\mathrm{i}})G_{\mathrm{i}}}{(1 + \alpha V_{\mathrm{i}})G_{\mathrm{m}} + \alpha(1 - V_{\mathrm{i}})G_{\mathrm{i}}} \tag{3}$$

where G, G_{m}, and G_{i} are the shear moduli of the composite, matrix, and inclusion, respectively, V_{i} is the volume fraction of the inclusion, and α is a constant expressed as:

$$\alpha = 2(4 - 5\nu_{\mathrm{m}})/(7 - 5\nu_{\mathrm{m}}) \tag{4}$$

where ν_{m} is the Poisson's ratio of the matrix. Equations 2 and 3 are in exactly the same form. Budiansky[6] assumed that each average sphere of the inclusion is imbedded directly into the effective medium (composite). He obtained:

$$\frac{V_1}{1 + \delta(G_1/G - 1)} + \frac{V_2}{1 + \delta(G_2/G - 1)} = 1 \tag{5}$$

where

$$\delta = \frac{2(4 - 5\nu)}{15(1 - \nu)} \tag{6}$$

G, G_1, and G_2 are the shear moduli of the composite, components 1 and 2, respectively, V_1 and V_2 are the volume fractions of the components 1 and 2, and ν is the Poisson's ratio of the composite. The α in the Kerner equation and the δ in the Budiansky equation are related as follows:

$$\delta = \frac{\alpha}{1 + \alpha} \tag{7}$$

if we assume that ν_{m} and ν are the same. Böttcher[13] attempted to interpolate between the lower and upper bounds of the Maxwell equation.[12] He employed the same approach as Budiansky and obtained exactly the same form as Budiansky for the electrical property behavior of a composite material. If we use the relations of α and δ in eq 7, the Budiansky or Böttcher equation corresponding to the Maxwell equation can be expressed as:

$$\frac{V_1}{1 + \frac{2}{3}(K_1/K - 1)} + \frac{V_2}{1 + \frac{2}{3}(K_2/K - 1)} = 1 \tag{8}$$

where K, K_1, and K_2 are the volume resistivities of the composite, components 1 and 2, respectively.

It was suggested that the Budiansky or Böttcher approach would predict the composite property behavior well when the composite system undergoes a phase inversion and the matrix and inclusion (dispersed) phases were not well defined.[4]

Studies of the morphology of the polyurethane–poly(methyl methacrylate) IPN's showed that a phase inversion occurred in the intermediate compositions and that the phases were locally interconnected.[9] The modulus behavior of the IPN's was predicted quite well by the Budiansky model.[7] Thus it is expected that the volume resistivity behavior of the IPN's will also follow the Böttcher model.

The experimentally measured dc volume resistivities of the IPN's (k_{E}) are shown in Figure 1. The calculated volume resistivities based on the Maxwell equation (k_{M1}, assuming polyurethane phase as the matrix, and k_{M2}, assuming the poly(methyl methacrylate) phase as the matrix) and the volume resistivities based on the Böttcher model (k_{B}) are also shown in the figure. In the figure it can be seen that the theoretical equation of the Böttcher model fits the experimental data quite well. This is in line with the mechanical modulus behavior where the Budiansky equation fit the experimental results well.[7] Another noteworthy factor in Figure 1 is that the volume resistivity data of the high percentage polyurethane IPN's (75 and 85% polyurethane concentration) fit well with the model. The modulus behavior of these IPN's did not follow this model and it was explained as being due to reduced crystallinity in the polyurethane phase, due to interpenetration. This supports this explanation since the effect of crystallinity is much smaller here than in the mechanical modulus (as evidenced by comparing UC 100 and UC75MC25 with the linear counterpart UL100, UL75ML25 in Figure 1).

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this grant. We also wish to acknowledge National Science Foundation Grants No. ENG 740 1954 and ENG 76-10066 for partial support of this study.

References and Notes

(1) (a) University of Detroit; (b) State University of New York.

(2) (a) V. Huelck, L. H. Sperling, and D. A. Thomas, *Macromolecules*, **5**, 348 (1972); (b) D. Klempner, K. C. Frisch, and H. L. Frisch, *J. Elastoplast.*, **3**, 2 (1971).

(3) D. W. Friedman and L. H. Sperling, *J. Polym. Sci., Part A-2*, **7**, 425 (1969).

(4) G. Allen, M. J. Bowden, S. M. Todd, D. J. Blundell, G. M. Jeffs, and W. E. A. Davies, *Polymer*, **15**, 28 (1974).

(5) E. H. Kerner, *Proc. Phys. Soc., London, Sect. B*, **69**, 808 (1956).

(6) B. Budiansky, *J. Mech. Phys. Solids*, **13**, 223 (1965).

(7) S. C. Kim, D. Klempner, K. C. Frisch, and H. L. Frisch, *J. Polym. Sci.*, in press.

(8) Z. Hashin, *J. Compos. Mater.*, **2**, 284 (1968).

(9) S. C. Kim, D. Klempner, K. C. Frisch, W. Radigan, and H. L. Frisch, *Macromolecules*, **9**, 258 (1976).

(10) 1974 Annual Book of ASTM Standards, Part 35, ASTM D 257-66, American Society for Testing and Materials, Philadelphia, Pa., 1974.

(11) W. E. A. Davies, *J. Phys. D*, **4**, 318 (1971).

(12) J. C. Maxwell, "Treatise on Electricity and Magnetism", 3rd ed, Vol. I, Oxford University Press, London, 1904.

(13) C. J. F. Böttcher, "Theory of Electric Polarization", Elsevier, Houston, 1952.

Fluorescence Studies of the Microviscosity of Polymer Solutions. 1. Microviscosity of Polymerizing Media

R. D. M. Neilson, I. Soutar,* and W. Steedman

Heriot-Watt University, Riccarton, Currie, Edinburgh EH14 4AS.

Received March 18, 1977

ABSTRACT: Changes in microviscosity during polymerization of vinyltoluene have been studied using fluorescence polarization and intensity measurements. A variety of fluorescence probes were employed. "The" microviscosity of the polymerizing medium experienced by a fluorescent probe is dependent upon the size of the kinetic unit responsible for the variation in observed emission characteristic. No stepwise increments in microviscosity upon conversion to polymer were recorded in any of the systems studied.

The sensitivity of the photophysics of a molecule to changes in its microenvironment has prompted the use of fluorescence techniques in the investigation of such phenomena as energy migration, segmental relaxation, and microviscosity effects in polymers in bulk or solution. The attraction of the use of fluorescent probes in macromolecular systems derives from the fact that minimal perturbation of the sample is necessary due to the low concentrations of fluor involved and the absence of any externally applied constraints on the system. The study of microviscosities of polymer solutions by fluorescence methods can involve either (a) the use of the polarization characteristics of the emitted radiation or (b) the observation of changes in fluorescence intensity of suitable molecules, as discussed below.

(a) The degree of polarization, p, of fluorescence emitted by a molecule following excitation with polarized radiation reflects the extent to which the transition axes of the photoselected species can randomize by rotation during the time interval between absorption and emission of radiation. For spherical molecules, Perrin[1] has shown that

$$\left(\frac{1}{p}-\frac{1}{3}\right)=\left(\frac{1}{p_0}-\frac{1}{3}\right)\left(1+\frac{3\tau}{\rho}\right) \qquad (1)$$

where p_0 is the intrinsic polarization (i.e., that observed in the absence of all external depolarizing factors), τ is the lifetime of the excited state, and ρ is the rotational relaxation time. If ρ may be approximated by

$$\rho = 3\eta V/RT \qquad (2)$$

where η is the viscosity experienced by the molecule and V is the molar volume, the Perrin equation becomes

$$\left(\frac{1}{p}-\frac{1}{3}\right)=\left(\frac{1}{p_0}-\frac{1}{3}\right)\left(1+\frac{RT\tau}{\eta V}\right) \qquad (3)$$

Hence the degree of polarization can be used to monitor changes in the microviscosity of the medium in which the probe is dispersed.

(b) The use of fluorescence intensity measurements in the study of phenomena involving microviscosity effects involves the dependence of quenching mechanisms upon the viscosity of the medium. In general external quenchers may be employed. However, certain molecules, notably flexible molecules capable of internal rotation, exhibit radiationless deactivation processes which are viscosity dependent.[2,3] A Stern–Volmer type treatment of internal quenching due to torsional deactivation leads to a relationship of the form[2,4]

$$\phi_f^0/\phi_f = 1 + A(\tau^0/\rho_i) \qquad (4)$$

where ϕ_f and ϕ_f^0 are the fluorescence quantum yields in the presence and absence of internal quenching, respectively, A is a constant, τ^0 is the fluorescence lifetime in the absence of internal rotation, and ρ_i is the relaxation time characteristic of the rotation. If ρ_i is approximated by a Stokes–Einstein relationship as in eq 2, the fluorescence intensity, I_f, may be related to that at infinite viscosity, I_f^0, by eq 5[2,4]