

Cure Studies of Interpenetrating Networks by Microdielectrometry

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Synopsis

Microdielectrometry has been used to follow the cure kinetics of interpenetrating polymer networks (IPNs). The rate of formation of a polyurethane-poly(*n*-butyl acrylate) IPN has been characterized at three temperatures. The dielectric data indicate that the relative homonetwork formation rates dominate the resultant material properties.

INTRODUCTION

Interpenetrating polymer networks¹ consist of two mutually entangled polymer networks that are not chemically bound to each other. Total interpenetration of the polymers would provide a blend of the homopolymer network properties. Since the polymers involved are generally immiscible, the networks are not totally entangled, and the amount of network entanglement is inversely proportional to the degree of phase separation. The amount of entanglement or phase separation is influenced by the order of homonetwork formation (e.g., simultaneous or sequential IPNs). We have found that the amount of phase separation in simultaneous IPNs can be controlled by the relative rates of formation of the two networks.

Dielectrometry can be used to measure changes in the dielectric characteristics, permittivity (ϵ'), and loss factor (ϵ'') of polymeric materials as a function of time and temperature during the cure cycle. Microdielectrometry,^{2,3} a recently developed technique, uses a miniature probe to monitor the temperature and dielectric behavior during the cure of materials.

This technique has been used to investigate the cure characteristics of IPNs. The system studied consisted of polyurethane and poly(*n*-butyl acrylate) networks. Since polyurethanes are formed by step-growth polymerization reactions and poly(*n*-butyl acrylate) is formed by chain-growth polymerization reactions, the two independent reactions should be capable of yielding ideal IPN networks. Three reaction temperatures were chosen in order to change the relative network reaction rates and therefore the amount of phase separation.

EXPERIMENTAL

The polyurethane elastomer used in this study was a commercial, two-part product from Products Research Corporation (Glendale, CA) (PR 1592). The recommended mixing proportions of 53 parts A (polyether polyol compound)

and 100 parts B (polyurethane prepolymer) were used. The second network, based on poly(*n*-butyl acrylate), was made from *n*-butyl acrylate (nBuA) with tetramethylene glycol dimethylacrylate (TMGDM) as a crosslinking agent and azobisisobutyronitrile (AIBN) as the initiator. All materials were mixed, degassed, and cured in air-tight Teflon molds along with a microdielectric sensor. Samples of various compositions of PR 1592 and nBuA were cured at 40, 60, and 90°C for 24 h. The resultant materials were then dried to a constant weight at 90°C in a vacuum oven prior to testing.

The instrument used in these experiments, a microdielectrometer (Micromet Instruments, Inc., Cambridge, MA), uses minisensors which are 15–40 cm long with an active area of 0.25×0.35 cm. The miniature sensor can be used with milligram samples or embedded in full scale parts. The instrument measures dielectric permittivity (ϵ') and dielectric loss factor (ϵ''). The frequency range over which the dielectric measurements can be made is 0.005–10,000 Hz.

Tensile properties were evaluated using ASTM D-638 type IV specimens at 100% elongation/min on an Instron Model 4206.

RESULTS AND DISCUSSION

Dielectric cure monitoring relies on measuring changes in ϵ' and ϵ'' that occur during cure of polymeric materials.⁴ Both ϵ' and ϵ'' result from internal

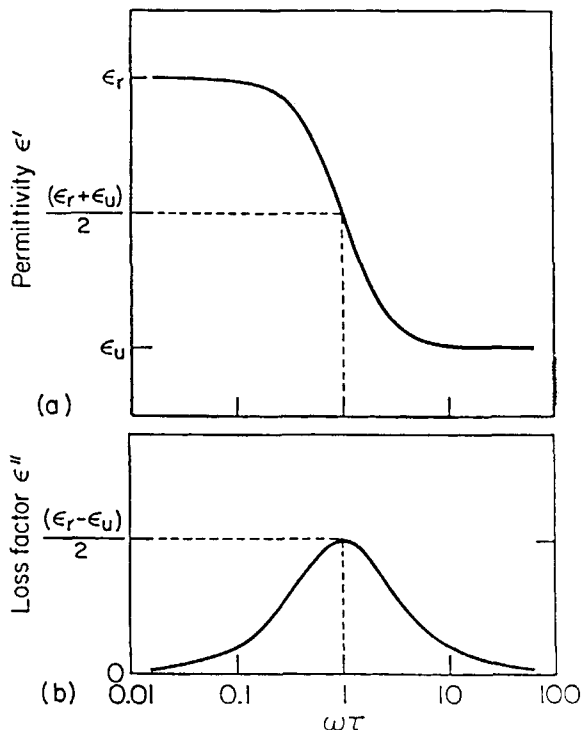


Fig. 1. The Debye single relaxation time model for dipole orientation showing (a) permittivity and (b) loss factor as a function of the product of the angular frequency (ω) and the dipole relaxation time (τ). The relaxed permittivity is ϵ_r and the unrelaxed permittivity is ϵ_u . (Reprinted from Ref. 6 with authors' permission.)

polarization created in the sample by the electric field applied during measurement. The polarization is attributed to orientation of molecular dipoles and to ionic conductivity. Based on the simplest Debye model⁵ which assumes a single relaxation time for all molecular species, the permittivity is expressed as follows:

$$\epsilon' = \epsilon_u + \frac{\epsilon_r - \epsilon_u}{1 + (\omega\tau)^2} \tag{1}$$

The loss factor is

$$\epsilon'' = \frac{\sigma}{\epsilon_0\omega} + \frac{(\epsilon_r - \epsilon_u)(\omega\tau)}{1 + (\omega\tau)^2} \tag{2}$$

where ϵ_u = high frequency permittivity ("unrelaxed" permittivity), ϵ_r = low frequency permittivity ("relaxed" permittivity), ω = applied field frequency, σ = ionic conductivity ($\Omega \text{ cm}^{-1}$), τ = dipole relaxation time, and ϵ_0 = permittivity of free space ($8.85 \times 10^{-14} \text{ F/cm}$). Since the frequency of the applied field determines the time available for the dipoles to orient, the measured values of dielectric properties are frequency dependent.

Figure 1(a) illustrates the frequency dependence of ϵ' for eq. (1). When $\omega\tau = 1$, ϵ' is midway between ϵ_u and ϵ_r . The corresponding plot for ϵ'' is more complex because of the relative contributions of ionic conductivity and dipole effects [eq. (2)]. Figure 1(b) illustrates the simplest case where $\sigma = 0$ and

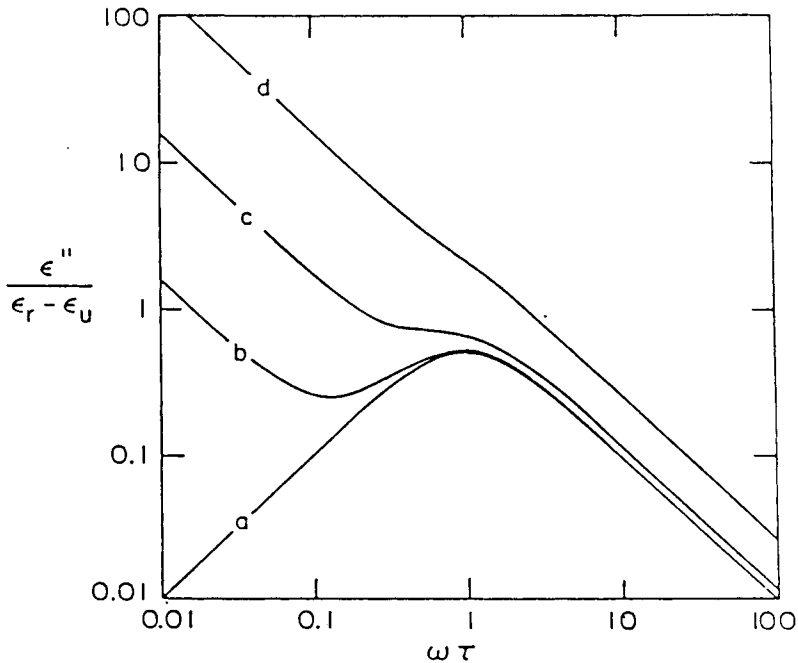


Fig. 2. Illustration of the effect of conductivity (σ) on the frequency dependence of the loss factor. $\sigma/[(\epsilon_r - \epsilon_u)\epsilon_0] = 0, 0.1, 1, \text{ and } 10$ for curves (a)-(d), respectively. (Reprinted from Ref. 6 with authors' permission.)

$\epsilon'' = (\epsilon_r - \epsilon_\infty)/2$ at $\omega\tau = 1$. For nonzero σ , however, the $1/\omega$ dependence of ϵ'' distorts the ideal Debye ϵ'' curve. As σ increases, it becomes increasingly difficult to discern the dipole loss peak (Fig. 2). In general, for σ/ϵ_0 greater than about three times ϵ_r , the observed ϵ'' is entirely dominated by ionic conductivity and the plot of $\log \epsilon''$ vs. time will exhibit parallel plots for the respective frequencies.⁶

At the beginning of the polymerization reaction, the viscosity of the prepolymer mixture is low, so that the dipoles reorient quickly and τ is short. As the polymerization proceeds or as the molecular weight increases, the viscosity increases. Dipoles, which are present in the prepolymers, exhibit a transition from an unhindered to a hindered state as molecular weight increases. Ions, which are usually present as impurities, initially exhibit high mobility (as measured by electrical conductivity), but become slow as polymerization proceeds. During the polymerization reaction in the presence of an alternating electric field, the dipoles and ions move more slowly relative to the frequency of the applied field and, eventually, reach a random condition as the polymer network forms (Fig. 3). The materials studied were far enough

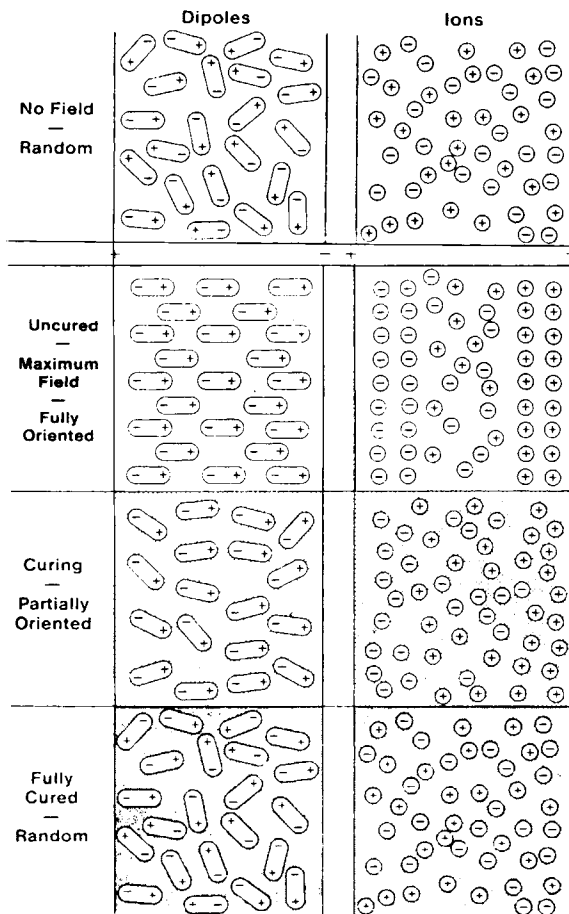


Fig. 3. The behavior of dipoles and ions present in prepolymers before, during, and after cure in the presence of an electric field.

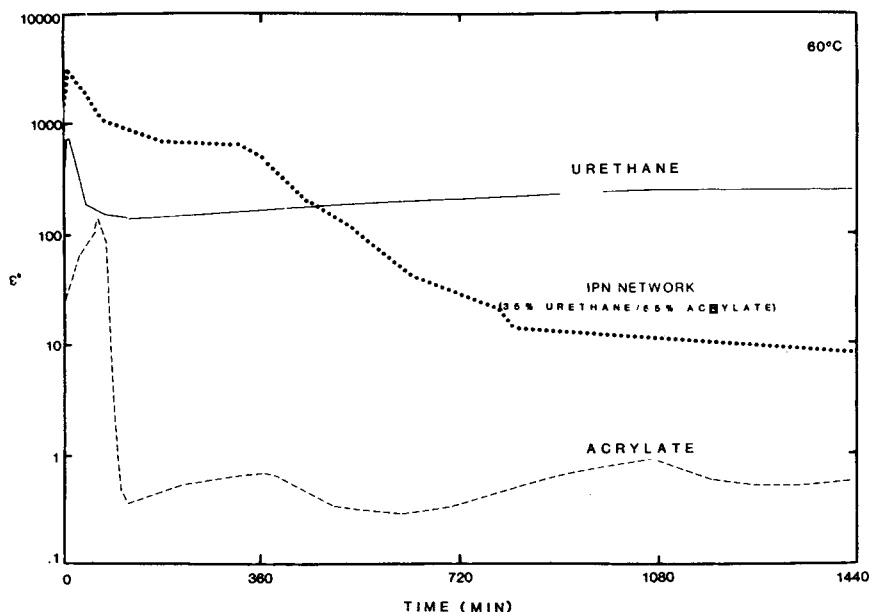


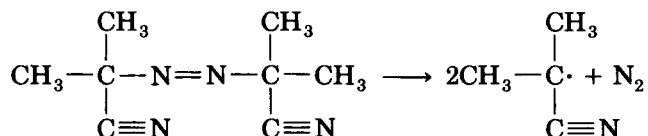
Fig. 4. The loss factor vs. time curves at 100 Hz for the cure at 60°C of the urethane (—), the acrylate (---), and the 35% urethane/65% acrylate IPN network (···).

above their glass transition temperature (100°C) that the measured mobility was not affected.

In most polymerization reactions or cures, the change in permittivity is a factor of 3–5. However, the change in loss factor during a cure is typically 3–5 orders of magnitude. Loss factor, thus, provides large and easily discriminated signals which can be used in studying the formation of polymer networks. In these experiments, the loss factor proved to be more sensitive of the two dielectric properties and was, therefore, chosen as the dielectric characteristic which was monitored in the cure of the IPN networks.

The loss factor vs. time curves for the cure studies at 60°C of the urethane and acrylate networks and the 35% urethane/65% acrylate IPN network are shown in Figure 4. The data taken at 100 Hz are plotted for each network. The urethane cure is a typical elastomer cure for which ϵ'' rises at the beginning due to the drop in the viscosity of the system with the increase in temperature. The data for two other frequencies, 1000 and 10,000 Hz, were parallel to the curve shown, indicating that the changes in loss factor were predominantly ionic conductivity changes in the system (Fig. 5).

The acrylate cure curve shows a very sharp rise at the beginning of the cure cycle. The acrylate cure is also dominated by ionic conductivity rather than dipolar reorientation. At the beginning of the polymerization of the nBuA, the initiator, AIBN, decomposes to generate a molecule of nitrogen plus two nitrile stabilized alkyl radicals:



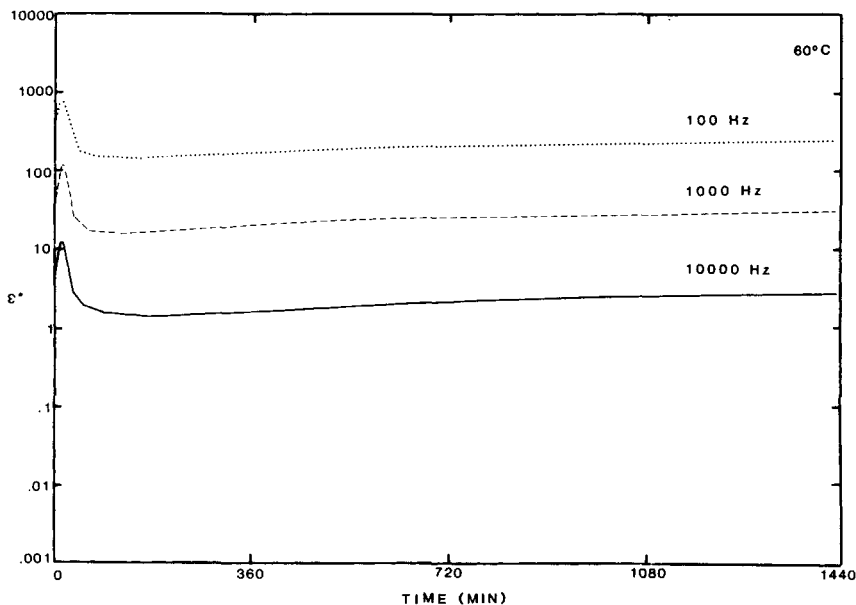


Fig. 5. The loss factor vs. time curves at 100, 1000, and 10,000 Hz for the cure of the urethane at 60°C. There is no evidence of a dipole peak in the three curves.

As the polymerization proceeds, the radicals react with the double bond of the nBuA and the polymer chain propagates until terminated by combination or disproportionation.⁷ We interpret the sharp rise in the ϵ'' vs. time curve (Fig. 4) as arising from the changes in ion concentration as the AIBN decomposes into radicals. As the polymer chain propagates, the loss factor drops to almost a constant value at all frequencies because the chain is not highly conductive and is rather rigid. The small rises in ϵ'' which occur near 360 and 1080 min correspond to acrylate network dynamics which are being investigated further.

The loss factor vs. time curve for the cure of the 35% PRC 1592/65% nBuA IPN network, also shown in Figure 4, begins very much like the urethane cure curve alone and then takes on characteristics of the acrylate system. Calculations were done to determine if the network cure curve resulted from adding the cure curves of the individual polymerizations. Figure 6 shows both the real network and the theoretical network as calculated from the equation below:

$$\epsilon''_{(\text{theoretical network})} = 0.35\epsilon''_{(\text{urethane})} + 0.65\epsilon''_{(\text{acrylate})} \quad (3)$$

If the network cured as two totally independent, noninterpenetrating polymers, the loss factor would be the addition of the weighted loss factors of the two polymers. The fact that the network after 1.5 h establishes its own characteristic values indicates that the polymers must physically or chemically interfere with one another. The decrease in the loss factor of the IPN reflects the decrease in the overall mobility of the network as the cure proceeds.

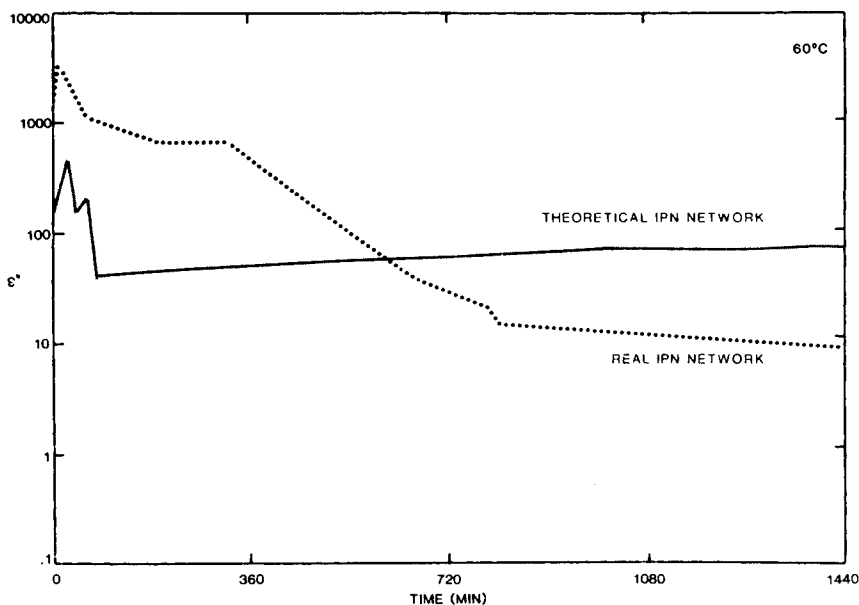


Fig. 6. The loss factor vs. time curves at 100 Hz for the cure at 60°C of the real IPN network (· · ·) and of the theoretical network (- · -). The IPN network was 35% urethane/65% acrylate.

The independent kinetics of the two polymerizations is illustrated in Figure 7 as we follow the isothermal cure at 40°C of a 35% urethane/65% acrylate IPN network for 46 h and then raise the temperature to 90°C for 2 h. For the first 46 h, the urethane system alone was curing at 40°C. The initiator, AIBN, for the nBuA system does not decompose at a significant rate into radicals at 40°C, so the acrylate does not polymerize. When the system was raised to 90°C, the initiator decomposed into radicals as indicated by the sharp rise in ϵ'' and the cure of the acrylate proceeded. This illustrates that when two chemically independent polymerizations are occurring in the same container, the cure temperature can control the rate and/or order of formation of the polymers.

By definition, simultaneous interpenetrating networks are formed if both networks are polymerized such that both monomers, crosslinking agents, and initiators react in the presence of each other by essentially independent routes.⁸ In the experiments at 60°C, the IPNs were formed simultaneously since they formed independently in the presence of one another and, we find, at approximately the same rate. The IPN formation at 40°C and subsequently raised to 90°C more closely resembles a sequential IPN in which one network is formed first (urethane) and the second network (acrylate) is formed when the AIBN rapidly decomposes at 90°C.

In a contrasting experiment, the temperature of the system was immediately ramped to 90°C and held for 10 h (Fig. 8). Both networks cure at higher rates with the acrylate forming faster than the urethane. The IPN cure at 90°C shows the sharp rise for the AIBN decomposition and the initial drop for acrylate propagation, and, then, the urethane cure proceeds. The final loss factor of the IPN network cured at 90°C is nearly the same as that for the

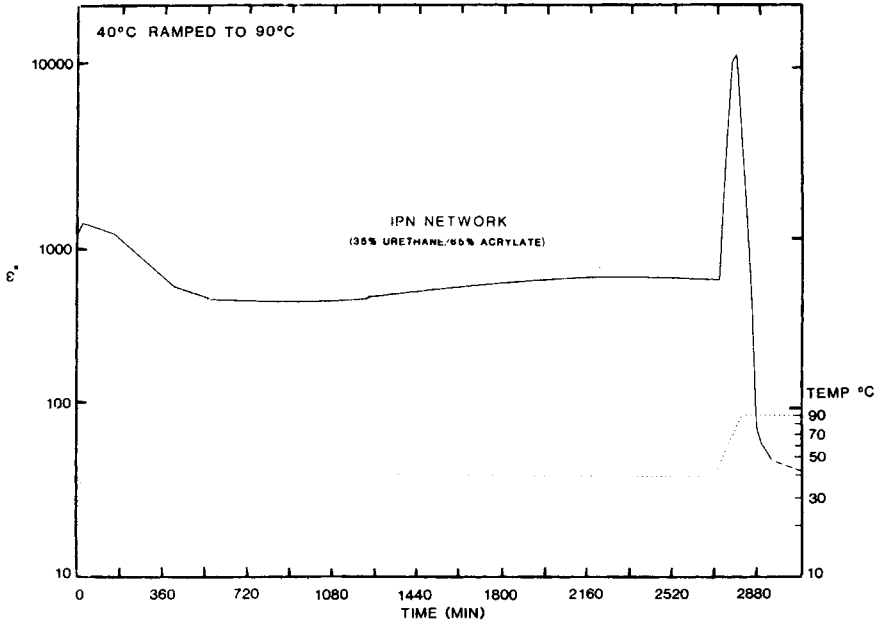


Fig. 7. The loss factor vs. time curve at 100 Hz for the cure of the IPN network at 40°C for 46 h and 90°C for 2 h. The IPN network was 35% urethane/65% acrylate. The temperature ramp is represented by the dotted line.

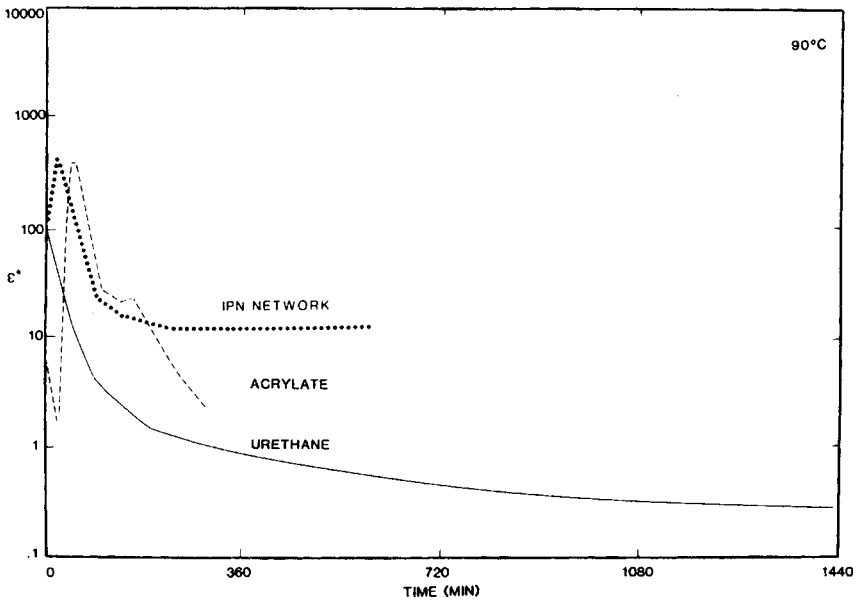


Fig. 8. The loss factor vs. time curves at 100 Hz for the cure at 90°C of the urethane (—), the acrylate (- - -), and the 35% urethane/65% acrylate IPN network (· · ·).

TABLE I
Mechanical Properties of Cured Materials

Urethane (wt %)	Acrylate (wt %)	Temp (°C)	Modulus (MPa)	Break strain (%)
100	0	40	49.6	693
100	0	60	44.0	593
100	0	90	36.6	463
0	100	90	2.18	47
35	65	40	6.83	253
35	65	60	5.13	263
35	65	90	3.08	291

network cured at 40°C with the 90°C ramp. This indicates that the ionic conductivity or the mobility of both networks are similar, though the urethane cured first at 40°C and the acrylate cured first at 90°C. In other words, ionic conductivity is not dependent on which polymer is formed first, though the physical and mechanical properties are.

According to Frisch et al.,⁸ varying degrees of phase separation depend primarily on the respective compatibility of the component polymers. The IPNs which were cured at 40° and 60°C were transparent, while those cured at 90°C were opaque, indicating that the phase separation not only depends on the compatibility of the two polymer systems, but also on the relative rate of formation.

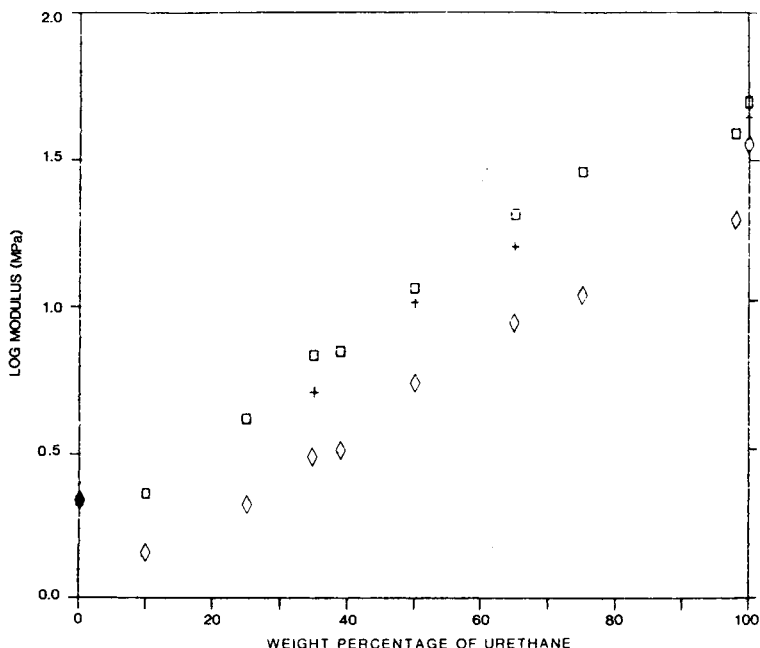


Fig. 9. The log modulus vs. weight percent of urethane in the IPN network for cure temperatures of 40°C (□), 60°C (+), and 90°C (◇).

The mechanical properties of the IPNs are listed in Table I. It is evident from this data how the relative rate of network formation can effect IPN properties at a constant composition. Figure 9 demonstrates the dependence of Young's modulus on composition and cure temperature in these IPNs. The transparent materials (40, 60°C) follow the log rule of mixtures, suggesting some type of cocontinuous dispersion.^{9, 10} The opaque samples (90°C) appear to fit a series arrangement better.

CONCLUSIONS

Microdielectrometry is an effective technique for studying the cure characteristics of interpenetrating networks (IPNs). We can detect the cure of each network independently of one another, yet see the interactions of both networks when they cure at close to the same rate. Microdielectrometry allows us to monitor the cure state of IPNs and determine which phase is forming under the specific reaction conditions. Mechanical tests reflect the different properties which can be achieved by varying reaction conditions in constant composition IPNs. This knowledge about different cure rates can aid in designing processing conditions to optimize the mechanical properties of the IPN systems.

Further experiments are being conducted on the effect of crosslinker in the network formation as well as the effect on the kinetics of IPN formation. Microdielectrometry, because it monitors the *in situ* cure characteristics of IPNs, will prove invaluable in these studies.

We give special thanks to Mr. Fitzroy K. Francis for his assistance with these experiments.

References

1. L. Sperling, *Interpenetrating Polymer Networks and Related Materials*, Plenum, New York, 1981.
2. N. Sheppard, Jr., D. Day, H. Lee, and S. Senturia, *Sensors Activators*, **2**, 262 (1982).
3. S. Senturia, N. Sheppard, Jr., H. Lee, and D. J. Day, *Adhesion*, **15**, 69 (1982).
4. Micromet Instruments, Inc., Cambridge, MA, Technical Supplement No. 1-84, 1984.
5. P. Debye, *Polar Molecules*, Chemical Catalog Co., New York, 1929, Chap. V.
6. S. Senturia and N. Sheppard, Jr., Technical Report No. 4, Office of Naval Research, Contract N00014-84-K-0274, Oct. 7, 1985; S. Senturia, N. Sheppard, Jr., H. Lee, and S. Marshall, *SAMPE J.*, **19**(4), 22 (1983).
7. J. E. McGrath, *J. Chem. Ed.*, **58**, 844 (1981).
8. K. Frisch, D. Sakhpara, and H. Frisch, *J. Polym. Sci., Polym. Symp.*, **72**, 277 (1985).
9. L. E. Nielson, *J. Appl. Polym. Sci.*, **21**, 1579 (1977).
10. D. R. Paul, *Polymer Blends*, Academic, New York, 1978, Chap. 1.

Received April 9, 1987

Accepted June 25, 1987