Correlations Involving Modulae and Cross-Polarization Time Constants for a Series of Polyurethane Elastomers

J. J. MARCINKO,[1] A. A. PARKER,[2] Y. T. SHIEH,[3] and W. M. RITCHEY*[,4]

[1]Department of Chemistry, The University of Akron, Akron, Ohio 44325, [2]Aluminum Company of America, Alcoa Center, Pennsylvania 15069, [3]Beloit Manhattan Inc., Clarks Summit, Pennsylvania 18411, and [4]Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106

SYNOPSIS

Correlations between the macroscopic bulk polymer properties storage modulus (E') and loss modulus (E'') and the microscopic property of cross-polarization as represented by the time constant T_{CH} have been established for a series of polyurethane elastomers. The dependence of E', E'', and T_{CH} as a function of molecular weight, rigid domain concentration, and temperature are graphically presented as a series of log plots. An experimental relationship is presented that shows that the distribution of motions of the flexible domains appears to be the major factor in the success of these correlations.

INTRODUCTION

In a recent publication, we showed a correlation between the dynamic storage modulus (E') and a mean cross-polarization constant $\langle T_{CH} \rangle$ for a series of morphologically diverse polymers.[1] This preliminary correlation established the relationship between the two physical measurements and demonstrated that these measurements are modulated by similar molecular motions.

In this article, we expand on the previous work by looking at a series of polyurethane elastomers correlating T_{CH} not only with storage modulus but also with the loss modulus (E''). Further, we demonstrate that it is the mobile or flexible components of T_{CH} that govern the relationships derived and allows these types of correlations to be successful.

BACKGROUND

In our earlier correlation, we showed that an initial approximation can be derived using mathematical models that describe the relaxation behavior for cross-polarization (CP) and E'. The reduced expression for T_{CH}, given as a function of a single correlation—time, can be expressed as[2,3]:

$$1/T_{CH} = (\pi^{1/2}/4)(\sin^2\Theta_c \sin^2\Theta_H M_2^{CH})$$
$$\times [\tau_c \exp(-\Delta\omega^2\tau_c^2/4), \quad (1)$$

where T_{CH} is the cross-polarization time constant between the carbon and proton spins, M_2^{CH} is the second moment of the heteronuclear dipolar coupling, Θ_H and Θ_C are the angles corresponding to proton and carbon nuclei in the rotating frame, respectively, in relation to the static field (H_0), $\Delta\omega$ is the angular mismatch of the Hartmann–Hahn condition, and τ_C is a correlation time influenced by near static molecular motion.[4] The carbon-proton second moment can be expressed as a function of motional correlation times, and in the simplest case the effect of the M_2 term in eq. (1) will be parallel to the effect of the τ_c term.

A Maxwell–Wiechert model was used to describe the storage modulus in terms of a single relaxation time constant given as[6,7]:

$$E' \propto \omega^2\tau^2/(1 + \omega^2\tau^2), \quad (2)$$

where ω is the frequency of the mechanical perturbation.

Similarly, the loss modulus can be described as

$$E'' \propto \omega\tau/(1 + \omega^2\tau^2). \quad (3)$$

Previously, we hypothesized a relationship between microscopic and macroscopic behavior by combining eqs. (1) and (2) and by assuming a perfect Hartmann–Hahn match ($\Delta\omega = 0$) as shown in eq. (4):

$$E' \propto \{[\omega^2(1/T_{CH})^2]/[1 + \omega^2(1/T_{CH})^2]\} = \phi. \quad (4)$$

Likewise, if we now consider eqs. (1) and (3) under the condition of a perfect Hartmann–Hahn match, the following expression can be obtained:

$$E'' \propto \{[\omega(1/T_{CH})]/[1 + \omega^2(1/T_{CH})^2]\} = \Psi. \quad (5)$$

Furthermore, double-log plots of E' vs. ϕ and E'' vs. Ψ should yield slopes differing by the ratio of 2 : 1, respectively, and would only apply under conditions of a low-frequency range of motions if these relationships are indeed valid.

Thus, the objective of this article is to expand and test the relationships given by eqs. (4) and (5) through the study of a series of polyurethane elastomers.

EXPERIMENTAL

Nuclear magnetic resonance (NMR) measurements were acquired on a Bruker MSL spectrometer operating at a ^{13}C resonance frequency of 100.627 MHz. The proton dipolar coupling and spin-lock field strengths employed were matched at 57 kHz.

Variable-temperature experiments were performed utilizing a Bruker temperature control unit capable of controlling with a precision of $\pm 3°C$. The subambient temperature experiments were performed using dry nitrogen instead of compressed air for the bearing and drive pressures.

The inversion recovery cross-polarization (IRCP) experiment, illustrated in the pulse sequence in Figure 1, utilizes variable hold times (τ_2) of 0.0–4000 μs. The cross-polarization contact time was held constant at 1.5 ms. The experimental data was analyzed according to the methods previously described.[1,8]

Storage and loss modulae for the polyurethane samples were measured with a Polymer Laboratories' DMTA operating at a frequency of 1 Hz.

The polyurethane samples used were all commercially available materials (PTMEG/TDI pre-
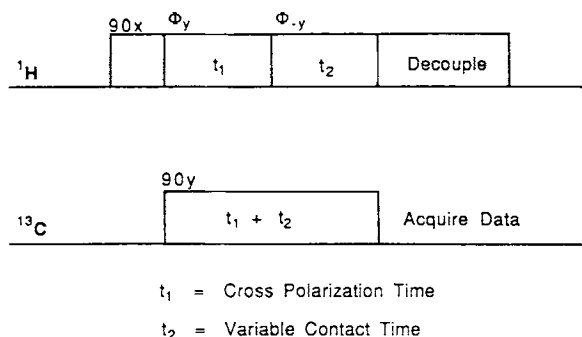

Figure 1 IRCP pulse sequence.

polymers from Uniroyal Chemical Co.). These materials consist of poly(tetramethylene ether glycol) (PTMEG) segments of varying molecular weights difunctionally endcapped with toluene diisocyanate (TDI). The particular prepolymers used bear the trade names Adiprene L-100, L-167, and L-200. The liquid prepolymers were chain extended to form solid polymers using the diamine chain extender 4,4'-methylene-bis-2-chloroaniline (MOCA) at a 90% stoichiometry. The basic structure of these polyurethanes is represented in Figure 2. The M_n values for the PTMEG "flexible" segments are 1000 for these three samples. The "rigid" TDI segment concentrations follow the trend L-200 > L-167 > L-100.

RESULTS AND DISCUSSION

Polyurethane elastomers are two-phase polymer systems that exhibit elastomeric behavior in part as a result of the microdomain phase separation of the rigid and flexible copolymer segments. The mechanical properties these materials exhibit are a result of the interactions of these rigid and flexible segments. Likewise, the NMR relaxation behavior should also exhibit a dependence on the microdomain phase separation.

From the polyurethane data in Table I, the two-phase nature of the polyurethane elastomers can easily be seen. The fractions (X) and ($1 - X$), which result from the data fitting, represent the fractions of T_{CH}^A and T_{CH}^B, respectively. T_{CH}^A is the fast relaxation component of the IRCP process and is usually associated with rigid or crystalline regions of the polymer. T_{CH}^B is the slower relaxation component and is usually associated with the more mobile or amorphous portions of the polymer system.[9]

Upon further examination of the data in Table I, we can see the trends expected for this series of
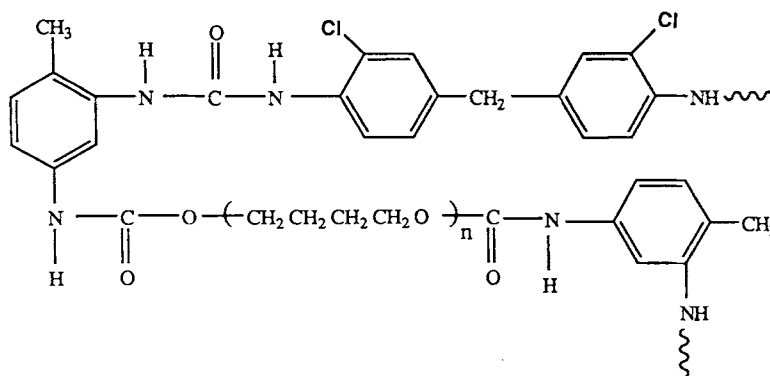
Figure 2 Representative structure of PTMEG/TDI/MOCA polyurethanes.

polyurethane samples. In particular, we point out that the values obtained as T_{CH}^A for the rigid domain carbons (130 ppm) are similar for the three polyurethanes and are also essentially independent of temperature. This is to be expected since the rigid domains of these three samples differ only in their concentration and bulk molecular packing configuration. At room temperature, the data given as T_{CH}^B for these rigid carbons also shows the expected trend of L-100 having a higher mobility resulting in a larger T_{CH}^B value, followed by L-167 and then L-200. Likewise, the T_{CH}^B data obtained for the flexible segments (27 ppm) at room temperature show a similar trend. Much more can be said about this data and its dependence on the domain packing configurations and on the polymers thermal history;

however, it is beyond the scope of this particular article. Thus, we refer the readers to a forthcoming publication involving the use of IRCP in the study of polyurethane morphology.[10]

The resonances 27 and 130 ppm were chosen to represent backbone carbons from each of the two phases of the polyurethane, flexible and rigid, respectively. The 27-ppm resonances arises from the methylene carbons of the PTMEG flexible segments and the 130-ppm resonances are representative of protonated aromatic carbons from the rigid domains. The significance of these particular resonances has no meaning other than that already stated. A number of other resonances from each phase could have been chosen as well, yielding similar information about backbone motion.

Table I   Cross-Polarization Relaxation Constants and Fitting Parameters

Polymer/ppm	(X)	T_{CH}^A (μs)	$(1 - X)$	T_{CH}^B (μs)	X^2
IRCP data (rm. temp.)					
L-100/27	0.35	340	0.65	4400	1.05 E^{-2}
L-100/130	0.40	38	0.60	1100	2.11 E^{-3}
L-167/27	0.27	130	0.73	3850	1.38 E^{-2}
L-167/130	0.43	37	0.57	520	2.09 E^{-2}
L-200/27	0.22	160	0.78	3800	6.91 E^{-3}
L-200/130	0.40	40	0.60	300	1.54 E^{-3}
IRCP data (+75°C)					
L-100/27	0.10	120	0.90	4600	4.75 E^{-2}
L-100/130	0.51	40	0.49	1100	8.48 E^{-3}
L-167/27	0.38	175	0.62	3620	1.60 E^{-2}
L-167/130	0.45	33	0.55	800	5.32 E^{-3}
L-200/27	0.34	220	0.66	2600	2.44 E^{-2}
L-200/130	0.60	43	0.40	1200	2.48 E^{-2}

Table II Polyurethane Phase Structure and Correlation Parameters

Polymer	Temp. (°C)	Phase	Estimated Fraction	$\langle T_{CH} \rangle$	ln (E') (Pa)	ln (E'') (Pa)
L-100	25	Rigid	0.08	2520	18.08	2.90
		Semirigid	0.12			
		Semimobile	0.28			
		Mobile	0.52			
L-100	75	Rigid	0.10	6450	17.04	2.65
		Semirigid	0.10			
		Semimobile	0.08			
		Mobile	0.68			
		Liquid-like	0.04			
L-167	−20	Rigid	0.16	1000	20.50	3.47
		Semirigid	0.14			
		Semimobile	0.40			
		Mobile	0.30			
L-167	25	Rigid	0.13	2085	18.54	3.17
		Semirigid	0.17			
		Semimobile	0.20			
		Mobile	0.50			
L-167	75	Rigid	0.13	3095	17.17	2.89
		Semirigid	0.16			
		Semimobile	0.27			
		Mobile	0.40			
		Liquid-like	0.04			
L-200	25	Rigid	0.16	1870	19.21	3.31
		Semirigid	0.24			
		Semimobile	0.13			
		Mobile	0.47			
L-200	75	Rigid	0.24	2095	18.65	3.15
		Semirigid	0.16			
		Semimobile	0.20			
		Mobile	0.37			
		Liquid-like	0.30			

A weighted average T_{CH} value was obtained via calculations from the two component model using eq. (6)[1]:

$$\langle T_{CH} \rangle = \sum N_i T_{CH} / \sum N_i, \qquad (6)$$

where N_i is the fraction of each relaxation component and T_{CH} is the corresponding cross-polarization time constant. The values calculated as $\langle T_{CH} \rangle$ are given in Table II along with the fractional composition of the various solid phases obtained using the stoichiometric values for the respective rigid and flexible domains. Further explanation of the purpose of using an average T_{CH} and representative backbone carbons along with an explanation of the solid-phase

composition can be obtained from our original correlation study.[1]

Figures 3 and 4 show the correlations of $\langle T_{CH} \rangle$ with E' and E'', respectively. Note that the ratio of the slopes of the two plots is 1.98, which compares well with the value of 2.0 predicted by comparison of eqs. (4) and (5). This is further verification for the hypothesis that macroscopic moduli and T_{CH} measurements are influenced by similar distributions of molecular motions[1] and that near-static motions are the type of motions that predominantly effect T_{CH}.[11] Also, this is further evidence that the correlations are indeed valid.

Both correlations include three polyurethanes of different rigid domain concentrations. The L-100
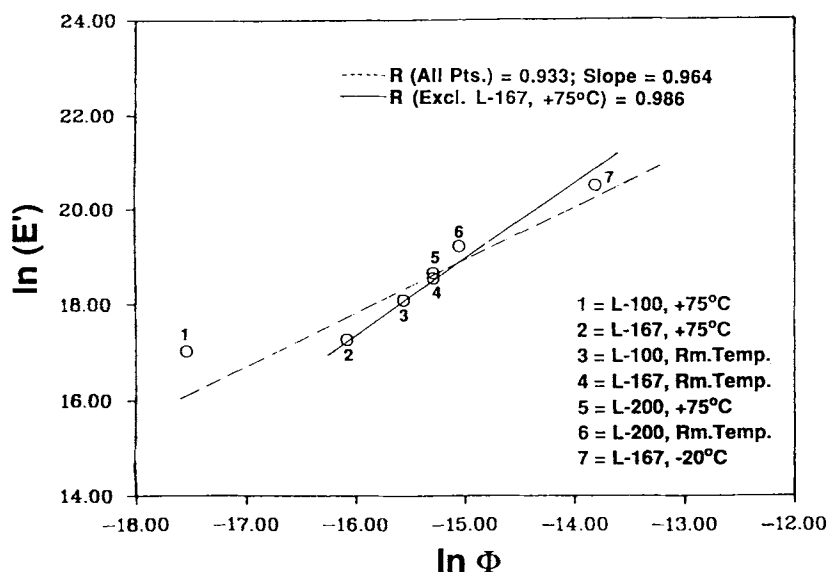
Figure 3 Correlation between E' and T_{CH}.

sample has the lowest rigid domain concentration, L-167 is an intermediate polymer, and L-200 has the highest rigid domain concentration. Experimentally, this equates to L-200 having the highest modulus and L-100 having the lowest modulus at room temperature. Likewise, at room temperature L-200 has the smallest $\langle T_{CH} \rangle$ and L-100 has the largest $\langle T_{CH} \rangle$. The module and $\langle T_{CH} \rangle$ will change as a function of temperature.

L-100, the "softest" of the polyurethanes observed, does not fit the correlation as well as the other data points. Although this could represent limitations of the model, the more likely cause seems to be experimental error. The first problem arises in the mechanical property measurements. As the temperature is increased in the mechanical experiments, this sample expands and becomes soft and flexible. This leads to changes in the mode of de-
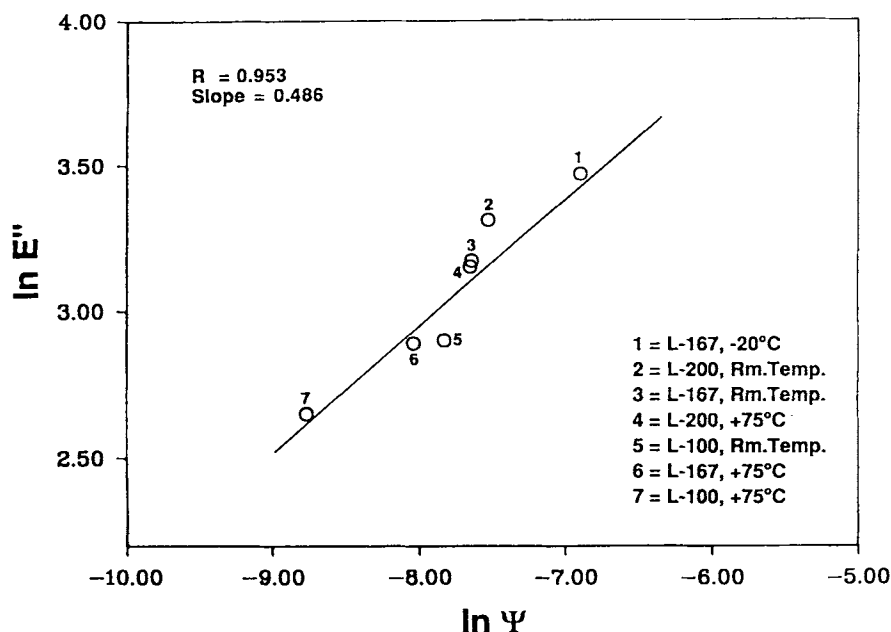

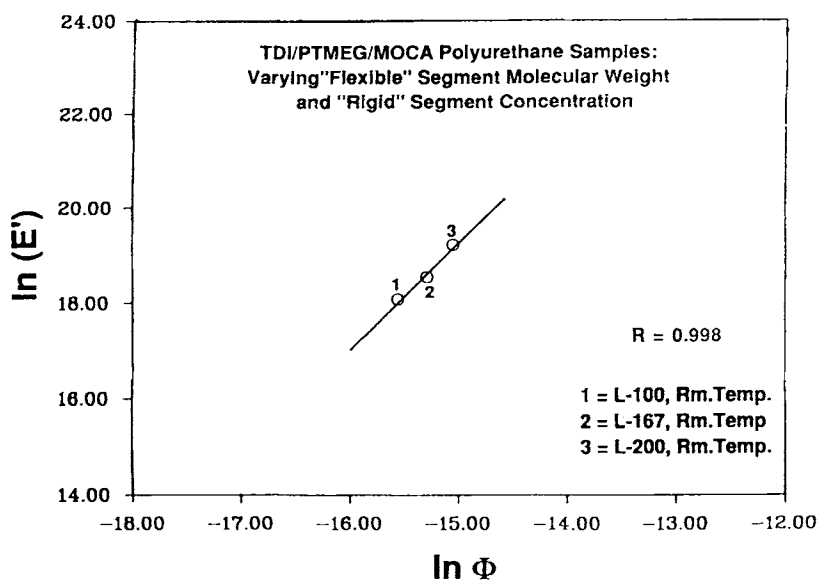**Figure 4** Correlation between E'' and T_{CH}.

Figure 5 Correlation between E' and T_{CH} showing molecular weight trends.

formation for the sample. The operating range of the transducer used for mechanical detection has been exceeded as a result of the changes in the geometry of the sample due to softening, and leads to a larger error in the experimental analysis. Another problem arises with the L-100 sample when measuring T_{CH}. Since this sample has the lowest concentration of rigid domain, the signal from the aromatic region of the NMR spectra is reduced. This lack of sensitivity also results in a larger source of error in the analysis. For these reasons, the corre-

lation of E' vs. $\langle T_{CH} \rangle$ (Fig. 3) has been fit both including and excluding this data point to illustrate the uncertainty involved in the measurements. (Experimentally, the magnitude of the error for both measurements is approximately 20%.)

Looking closer at Figure 3, we see that we can extract various trends out of the overall correlation and narrow the plot down to one polyurethane at various temperatures, Figure 5, or the three polyurethanes at one temperature, Figure 6. These smaller correlations behave well and as expected in
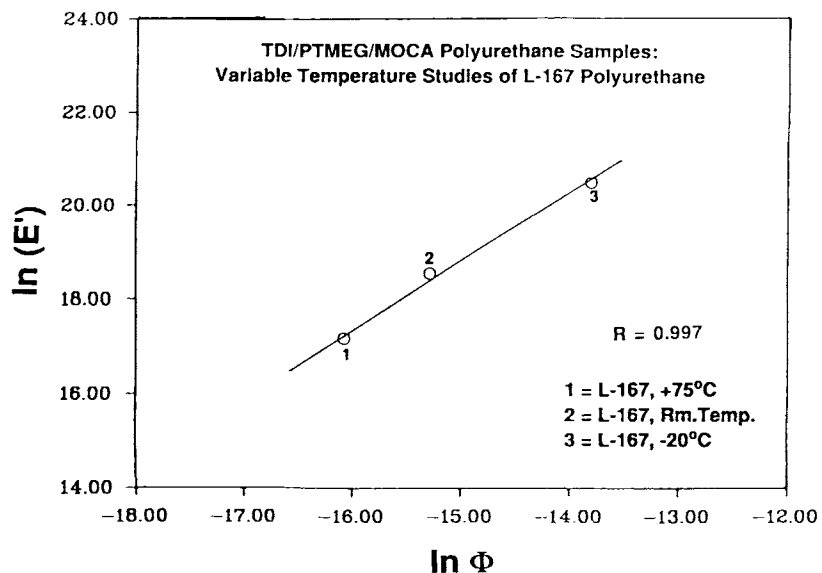

Figure 6 Correlation between E'' and T_{CH} showing temperature dependence.

terms of modulus and $\langle T_{CH} \rangle$. The larger amount of scatter in the overall correlation (Fig. 3) results from the propagation of uncertainties of the individual trends. In particular, the slight changes in slope between Figures 5 and 6 need to be considered further in theory and experimentally. It must be remembered that the Maxwell–Wiechert model, which we use to describe the dynamic modulae, is only a first approximation and is based on a single correlation time. Not only are there a distribution of correlation times present but there may be a change in the characteristics of the correlation time distribution as a function of temperature or molecular weight that needs to be considered. Consequently, the Maxwell–Wiechert model may be too simple a model for such correlations.

As pointed out in our original correlation, despite the use of simple models a reasonable correlation exists between the macroscopic bulk storage modulae and the microscopic NMR relaxation property $\langle T_{CH} \rangle$ for a series of diverse polymers. We further show that this is also true for the series of polyurethanes reported here, indicating that the molecular correlation time distributions for both of these measurements are similar. This is true not only for E' but also for E'', as would be expected (Figs. 3 and 4).

In our original correlation, we pointed out that a correlation of this type is not possible unless all the motional components of the polymer system are considered. This was shown by comparing the E' vs. $\langle T_{CH} \rangle$ and also E' vs. initial slope T_{CH} (where the initial slope T_{CH} is predominantly weighted by rigid components that cross-polarize faster). However, at this time the data does not entirely support the idea that all components need to be considered. Although it seems intuitively better to consider all motional components through a weighted composite average, and indeed a better correlation is obtained vs. an initial slope measurement of T_{CH}, it is the flexible or mobile components of T_{CH} that seem to be dominant in these correlations. This is illustrated by Figures 7 and 8, which show correlations between E' and E'' and a weighted average of only the mobile or flexible components of T_{CH}, $\langle T_{CH} \rangle_{\text{(Mobile)}}$. This suggests that the motion within the flexible domains strongly influences the macroscopic modulae of these polyurethane elastomers.

This finding seems reasonable since the rigid domains have T_{CH} values similar to those of glassy-state polymers, even when the NMR measurements of the polyurethanes are taken at elevated temperatures.[1,4] Thus, the motion within rigid domains would have little influence on bulk tensile behavior other than to serve as physical crosslinks that would limit the mobility of the flexible segments. However, cooperative interphase motion involving the flexible segments in cooperation with rigid domains would be expected to influence macroscopic properties.[5,12] More simply, it is the properties and the motions of
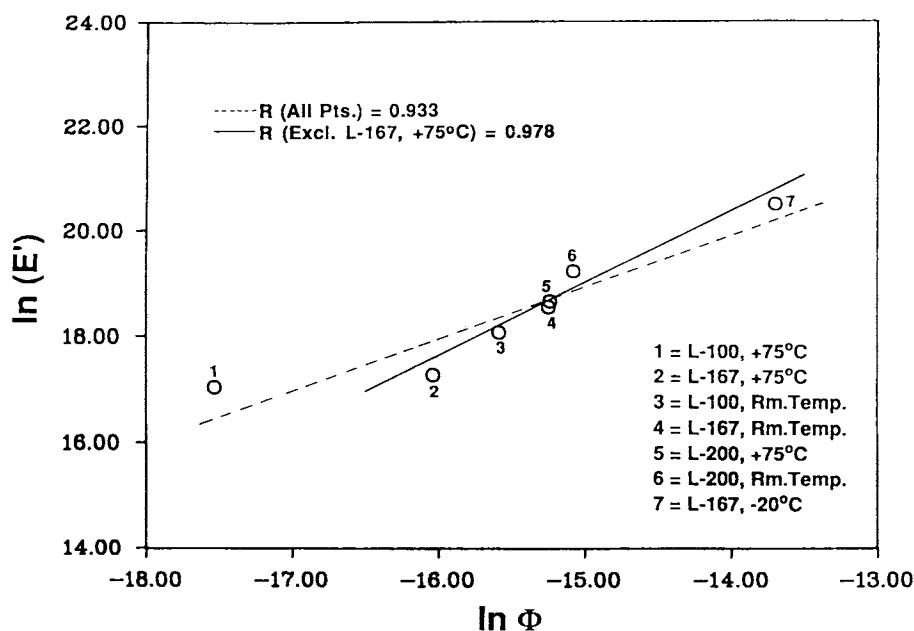

Figure 7   Correlation between E' and mobile components of T_{CH}.
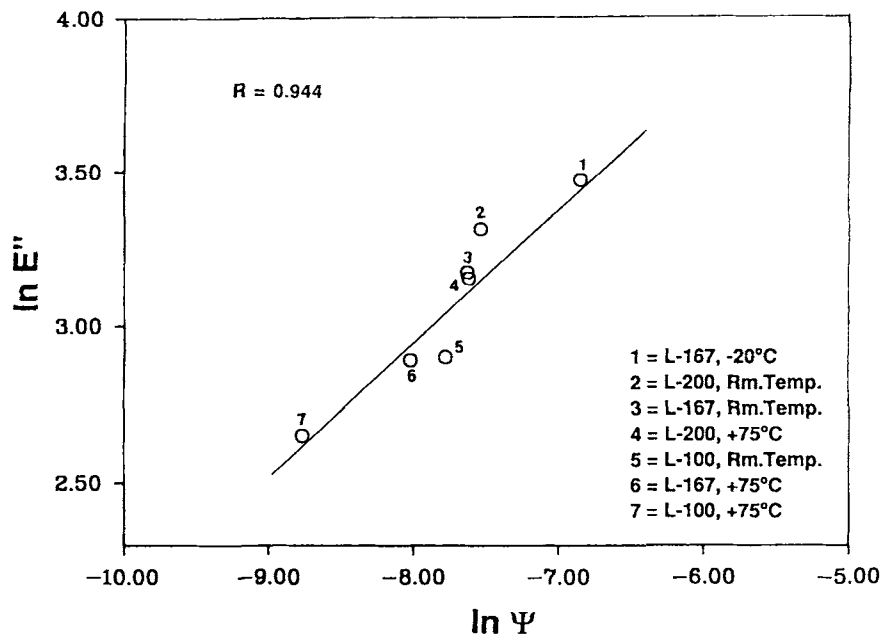
Figure 8 Correlation between E'' and mobile components of T_{CH}.

the flexible domains or the flexible domains associated with the rigid domains, either through phase mixing or interface association, that control modulus.

SUMMARY

A correlation has been established between modulae and T_{CH} for a series of similar polyurethane elastomers. These correlations illustrate that E', E'', and T_{CH} are modulated by similar distributions of molecular motions. Further, it has been demonstrated that the distribution of motions governing the flexible or mobile components appear to be the most important factors in these correlations.

It is important to consider all motional possibilities when attempting to make a connection between microscopic phenomenon and macroscopic properties. Unfortunately, not all experimental techniques have the ability to sample more than one motional regime. IRCP experiments allow us to look at a minimum of two motional components. In systems like the polyurethane samples studied here, which are known to have two-component phase behavior, IRCP allows us to break up these motionally different components further and thus allows for a greater understanding of the microdomain morphology that exists within these systems.

REFERENCES

1. A. A. Parker, J. J. Marcinko, Y. T. Shieh, D. P. Hedrick, and W. M. Ritchey, *J. Appl. Polym. Sci.*, **40**, 1717 (1990).
2. M. Mehring, *Principles of High Resolution NMR in Solids*, 2nd. ed., Springer-Verlag, Berlin, 1983.
3. D. A. McArthur, *Phys. Rev.*, **188**, 609 (1969).
4. J. Schaefer, E. O. Stejskal, and R. Buchdahl, *Macromolecules*, **10**, 384 (1977).
5. M. D. Meadows, C. P. Christenson, W. L. Howard, M. A. Harthcock, R. E. Guerra, and R. B. Turner, *Macromolecules*, **23**, 2440 (1990).
6. A. V. Tobolski and E. Catstiff, *J. Polym. Sci.*, **19**, 111 (1956).
7. I. M. Ward, *Mechanical Properties of Polymers*, 2nd. ed., Wiley, New York, 1979.
8. A. A. Parker, J. J. Marcinko, Y. T. Shieh, C. Shields, D. P. Hedrick, and W. M. Ritchey, *Polym. Bull.*, **21**, 229 (1989).
9. D. G. Cory and W. M. Ritchey, *Macromolecules*, **22**, 1611 (1989).
10. J. J. Marcinko, D. P. Hedrick, and W. M. Ritchey, *Macromolecules*, to appear.
11. A. A. Parker, Y. T. Shieh, and W. M. Ritchey, *Structure, Relaxation, and Physical Aging of Glassy Polymers*, vol. 215, Materials Research Society, 1990.
12. L. M. Leung and J. T. Koberstein, *Macromolecules*, **19**, 706 (1986).