Application of NMR Cross-Polarization/Modulus Correlations to a Series of Polyurethane Elastomers

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SYNOPSIS

A structure/property relationship is developed between the dynamic storage modulus, E', and the cross-polarization time constant T_{CH} for a series of polyurethane elastomers. The correlations made are based on the standard linear solids model (SLSM) and on the concept that T_{CH} is modulated by near static molecular motions. The use of the SLSM to describe the main viscoelastic range of these polyurethanes is contrasted to previous models used to develop similar correlations. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

In a series of recent papers, we discussed the relationships between dynamic storage modulus (E'), loss modulus (E''), and the solid-state NMR cross-polarization time constant T_{CH} for a series of diverse polymers and for a series of polyurethane elastomers.[1-3] In these studies, we attempted to correlate average T_{CH} rates $\langle T_{CH} \rangle$ with the moduli of these materials. These correlations have established the concept that E', E'', and T_{CH} are modulated by similar distributions of correlation times.

The earlier correlations were based on simple Maxwell and Maxwell–Weichert models and on the basis that in the cross-polarization process the static component of the dipolar interaction is sensitive to near static, low-frequency motions.[4] Thus, we implied that T_{CH} measurements are weighted by molecular motions having long correlation times and that $1/T_{CH}$ scales with τ_c. Applying this concept, the following relationship was derived for the storage modulus:

$$E' \propto [\omega^2(1/\langle T_{CH} \rangle)^2]/[(1 + \omega^2(1/\langle T_{CH} \rangle)^2] \quad (1)$$

which at a frequency (ω) of 1 Hz and assuming a slow correlation time reduces to

$$E' \propto 1/(\langle T_{CH} \rangle)^2 \quad (2)$$

Furthermore, we established a correlation for loss modulus, E'', using the same rationale, thus giving the relationship

$$E'' \propto [\omega(\langle 1/T_{CH} \rangle)]/[(1 + \omega^2(1/\langle T_{CH} \rangle)^2] \quad (3)$$

which at a frequency of 1 Hz would reduce to

$$E'' \propto (1/\langle T_{CH} \rangle) \quad (4)$$

In an attempt to broaden our understanding of how $\langle T_{CH} \rangle$ and τ_c are related, a standard linear solids model (SLSM) was used in the place of the Maxwell model on 16 polymer data sets with different bulk polymer properties.[3] The SLSM is a simple continuum model used to describe the behavior of polymers in their main viscoelastic range. This model describes the underlying behavior of a mechanical perturbation in terms of a single correlation time, τ_c, and can be written as[5]

$$E' = E_r + E_g\omega^2\tau^2/(1 + \omega^2\tau^2) \quad (5)$$

where ω is the frequency of the mechanical perturbation, and E_r and E_g are the theoretical modulus values for a perfect rubbery and glassy polymer, respectively.

If we make an assumption that τ_c is equal to a constant (c) divided by $\langle T_{CH} \rangle$, then at $\omega = 1$ Hz,

eq. (5) reduces to[3]

$$E' = \{c^2(E_g - E')/(T_{CH})^2\} + E_r \qquad (6)$$

If we then define a term, Ω, as

$$\Omega = (E_g - E')/(T_{CH})^2 \qquad (7)$$

and plot Ω vs. E', such a plot should yield a straight line having a slope of c^2 (which would be the proportionality constant between T_{CH} and τ_c) and an intercept of E_r.

In our previous work with 16 data sets, we showed that a reasonable correlation could be obtained with a general value of $c = 2.95 \times 10^{-5}$ s^2. However, we noted that the SLSM is probably too simplistic for such a diverse set of polymers since it is based on the assumption that E_g and E_r are constants. Given that E_g and E_r can vary from polymer to polymer, we hypothesized that the SLSM would be best suited to the study of a homologus series of polymers that share common values for E_g and E_r. Therefore, in this work, we apply the SLSM to a homologous series of polyurethane elastomers to test the utility of the SLSM correlation.

EXPERIMENTAL

The polyurethanes utilized in these studies were commercially available, polyether-based prepolymers obtained from Uniroyal Chemical Co., Naugatuck, CT, and bearing the trade names Uniroyal Adiprene L-200, L-167, and L-100. These materials contain a poly(tetramethylene oxide) (PTMO) flexible segments, having an M_n of approximately 1000, endcapped with toluene diisocyanate (TDI). The rigid domain concentrations follow the trend L-200 > L-167 > L-100. The prepolymers were chain-extended to solid polymers utilizing 4,4'-methylene-bis-2-chloroaniline (MOCA) at a 90% stoichiometry.

The NMR data were collected on a Bruker MSL-400 operating at a static field strength of 9.4 Tesla. For this instrument, the proton and carbon resonance frequencies observed were 400.130 and 100.627 MHz, respectively. The B_1 and B_2 fields employed were matched to 57 kHz. Variable temperature experiments were performed on this instrument utilizing a Bruker temperature control unit capable of regulating the temperature to $\pm 3°$C. Room-temperature experiments utilized in-house compressed air for the drive and bearing pressures required for spinning. Low-temperature experiments employed high-pressure dry nitrogen for the bearing and drive pressures, run through a series of copper coils submerged in a dry ice/isopropanol bath.

The low-temperature NMR experiments were performed at $-20°$C. The samples were allowed to thermally equilibrate in the spectrometer for approximately 45 min prior to starting the experiments.

Polyurethane samples were cut into discs and stacked into ceramic MAS rotors having Kel-F caps. The spinning rates employed were 4-5 kHz. The spinning rates were adjusted so that the spinning sidebands would not interfere with the resonances of interest.

The 90° pulse widths were determined by finding the 180° and 360° pulse widths via nulling of the signal from adamantane. Typical 90° pulse widths were 4.4 μs, the CP contact times were 1.5 ms, and the recycle delays were 3.0 s. Average cross-polarization time constants, $\langle T_{CH} \rangle$, were calculated as described previously.[1,2,6]

Dynamic mechanical analyses of the polyurethane samples were obtained utilizing a Polymer Laboratories dynamic mechanical thermal analyzer (DMTA) fitted with a low-temperature control unit. The sample sizes were approximately 2 × 5 × 50 mm.

Experiments were performed at a fixed frequency of 1.0 Hz and over a temperature range of -150 to $+150°$C. Samples were allowed to equilibrate for a period of 60 min prior to starting the experiment. All samples were run in a double-cantilever mode in which they were clamped at the ends and perturbed via a drive arm at the center of the sample. Quantitative measurements of storage modulus (E'), loss modulus (E''), and loss tangent (tan δ) were obtained and plotted as a function of temperature and/or frequency.

RESULTS AND DISCUSSION

The relationship between E' and $1/\langle T_{CH} \rangle$ given in our earlier SLS correlation makes use of two assumptions[3]: First, that T_{CH} scales proportionally with τ_c and, second, that all the polymers are characterized by the same glassy and rubbery moduli, E_g and E_r. These assumptions may have been too general to apply to the diverse set of polymer data that was described. However, despite these simplifications, a reasonable correlation was established. In an attempt to further establish the validity of this correlation, we applied the SLSM to the homologous series of polyurethanes discussed in our second cor-

Table I   Average T_{CH}, $\langle T_{CH} \rangle$, Storage Modulus, E', and SLSM Correlation Parameters, Ω, for the Series of Polyurethane Elastomers

| Polyurethane	Temperature (°C)	$\langle T_{CH} \rangle$ (μs)	E' (Pa)	Ω (Pa/s^4)
L-100	25	2520	7.1×10^7	1.6×10^{16}
	75	6450	2.5×10^7	2.4×10^{15}
L-167	−20	1000	7.9×10^8	9.9×10^{16}
	25	2085	1.1×10^8	2.3×10^{16}
	75	3095	6.0×10^7	1.0×10^{16}
L-200	25	1870	2.2×10^8	2.9×10^{16}
	75	2095	1.3×10^8	2.5×10^{16}

relation paper.[2] The assumptions discussed above should be valid for the polyurethanes since their main viscoelastic range should be adequately described by the SLSM and since they have similar values for E_g and E_r.

Applying the SLSM to the polyurethane data in Table I and utilizing an E_g of 1.0×10^{11} Pa, we obtained the data given in the last column of Table I and the resulting correlation as given in Figure 1. From this figure, we observe that the correlation between E' and Ω, for all the polyurethane points, is much better (correlation coefficient = .99) than that obtained utilizing the simplified Maxwell–Weichert model of our previous work.[2] It should be noted that the value given for E_g is unrealistic. However, it is a necessary condition for this corre-

lation since T_{CH} approaches a lower limiting value characteristic of rigid lattice systems. The choice of an alternate model could eliminate the need for such a high E_g value. Despite its limitations, the SLSM seems to adequately represent the relationship between E' and T_{CH} for this homologous series of polyurethanes. The poorer fit of the data in the previous work[2] (Maxwell–Weichert model correlation) could be attributed to the inadequacy of the model used to represent the viscoelastic behavior of the polyurethane systems.

Further evidence for the validity of this SLS correlation is that the value obtained as the intercept E_r in this correlation, 4.02×10^7 or 7.6 log Pa, agrees well with the rubbery moduli obtained from the experimental data.
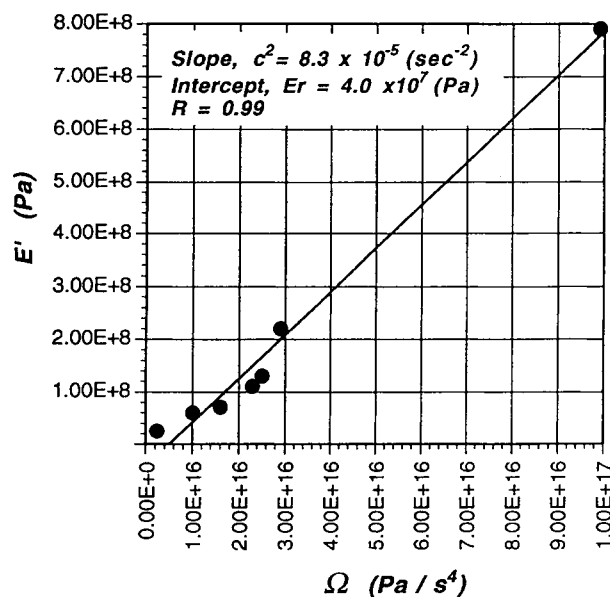
Figure 1   SLSM correlation between E' and T_{CH} for the series of polyurethane elastomers.

CONCLUSIONS

The relationship between an average cross-polarization time constant, $\langle T_{CH} \rangle$, and the dynamic storage modulus, E', has been illustrated for a series of homologous polyurethanes using the standard linear solids model, SLSM. Successful correlations of this type appear to be based on the ability of the model to adequately describe the main viscoelastic range of polymeric behavior.

From these data, it is apparent that T_{CH} can be modulated by near-static molecular motions and that there is indeed linearity between T_{CH} and τ_c for this series of homologous polyurethanes (in the temperature range observed). The utility of the SLSM was further illustrated by its ability to predict the E_r for this series of polyurethanes. The success of correlations of this type extends the possibility of developing other meaningful structure/property relationships within the realm of materials science.

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