A Preliminary Correlation between Macroscopic and Microscopic Polymer Properties: Dynamic Storage Modulus vs. CPMAS NMR Cross Polarization Rates

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Synopsis

A correlation has been established between the dynamic storage modulus (E') and the mean cross polarization time constants $\langle T_{CH} \rangle$ for a set of five morphologically diverse polymers, including one at two temperatures and one at two plasticizer concentrations. The correlation is only possible when the T_{CH} values for all of the motional environments within the polymers are considered. An inversion recovery cross polarization (IRCP) NMR technique is used to obtain motional and morphological information from the main chain carbons of each polymer. After comparing simplified correlation functions for the two parameters, an experimental relationship between them is established that suggests that T_{CH} and E' are both modulated by a similar distribution of molecular motions.

INTRODUCTION

Correlations between macroscopic physical properties of polymers and solid-state NMR relaxation parameters have been slow to develop despite ongoing efforts. Schaefer and co-workers[1] were previously successful at making a general correlation between the impact resistance and CP/MAS relaxation constants of several glassy polymers. However, to the best of our knowledge, no one has attempted a correlation based on a simple comparison of the motional models that describe either the macroscopic properties of interest (such as E') or microscopic relaxation constants (such as T_{CH}).

Correlations of this type could potentially be valuable to scientists that are interested in studying polymer structure–property relationships. Here we attempted to establish a correlation between dynamic storage modulus (E') and the average cross polarization constant $\langle T_{CH} \rangle$ with this purpose in mind.

BACKGROUND

The morphological and motional features of polymer systems can be quite diverse. Thus, it is difficult to describe the macroscopic properties of polymers

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from microscopic properties without accounting for motional and morphological heterogeneities. This problem becomes difficult when the microscopic measurements are influenced by motions that are highly localized as in the case of T_1 spin lattice relaxation.[2] Thus, it may be advantageous to first consider microscopic parameters that are sensitive to long-range cooperative processes. Such processes would implicitly encompass contributions from a variety of localized processes.

It has been previously shown that inversion recovery cross polarization (IRCP) NMR can be used to study the motional and morphological heterogeneities in solid polymers.[3-6] Unlike bulk macroscopic techniques (like thermal mechanical analysis), the IRCP technique allows one to deconvolute different components within a polymer by virtue of their different rates of cross polarization.

Mehring[7] and others[8-10] have established that the efficiency of the cross polarization process between proton and ^{13}C reservoirs depends on the precision of the Hartmann–Hahn match, on the internuclear separation between the cross polarizing nuclei (a $1/r^6$ dependence), and on the extent of the modulation of these factors by molecular motion. This overall dependence can be approximated by

$$1/T_{CH} = \tfrac{1}{2}(\sin^2\Theta_C)(\sin^2\Theta_H)(M_2^{CH})[J(\Delta\omega)] \quad (1)$$

where T_{CH} is the cross polarization time constant between carbon and proton nuclei, M_2^{CH} is the second moment of the heteronuclear dipolar coupling interaction, Θ_H and Θ_C are the angles between the external field H_0, and the rotating frame fields of the respective nuclei (which depend on the efficiency of the Hartmann–Hahn condition), and J is a spectral density function that describes the modulation of the effective cross polarization process by the degree of Hartmann–Hahn mismatch and by molecular motion. The spectral density function for a cross polarization process to a first approximation is weighted by an exponential gaussian-type distribution[7,8] and leads to a reduced expression for T_{CH} (as a function of a single correlation time) given as

$$1/T_{CH} = \Pi^{1/2}/4(\sin^2\Theta_C\sin^2\Theta_H M_2^{CH})[\tau_C\exp(-\Delta\omega^2\tau_c^2/4)] \quad (2)$$

where τ_c corresponds to the mean molecular reorientation time, and $\Delta\omega$ is the angular mismatch of the Hartmann–Hahn condition.

These models of the CP process imply that the T_{CH} values are weighted by motional components with long correlation times ($1/T_{CH} \propto \tau$, assuming $\Delta\omega = 0$) unlike their $T_{1\rho}$ and T_1 counterparts, which are well known to be sensitive to mid kHz and MHz frequency motions, respectively (assuming negligible spin–spin interactions, which is a reasonable assumption in a mobile, amorphous polymer system).[1]

Our current understanding of the interrelationships between the multiple motions that occur in a polymer system make it impossible to calculate J exactly.[4,7] However, it is still possible to qualitatively associate T_{CH} with the rigidity of a system. In fact, it should be possible to correlate some average of the T_{CH} values for the multiple motional components of a polymer with dynamic storage

modulus since both parameters share similar functional dependencies on motional correlation times.[11]

As an initial approximation, we can see how T_{CH} and E' may be related by first considering that a simplified Maxwell–Wiechert model is often used to describe dynamic storage modulus in terms of a single correlation time as shown in Eq. (3).[11,12]

$$E' \propto \omega^2\tau^2/(1 + \omega^2\tau^2) \tag{3}$$

By direct comparison with Eq. 2, assuming a perfect Hartmann–Hahn match ($\Delta\omega = 0$), we can then consider a relationship given as

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

Despite its derivation from simple motional models, it should be possible to apply this equation for the purpose of studying the relationship between E' and T_{CH}. This will be the focus of our present work.

EXPERIMENTAL

The ^{13}C NMR data was acquired on a Bruker MSL-400 spectrometer operating at 100.627 MHz with proton decoupling and spin lock field strengths at approximately 57 kHz. The magic angle sample spinner was a cylinder type made of Al_2O_3 and was spun at 3 kHz for most measurements at the magic angle of 54.7°.

The temperature for the experiments was controlled with a Bruker temperature control unit accurate to ±3°C. All samples were run at 23°C with the exception of one sample that was also run at −20°C. Room temperature experiments were performed with the use of in-house compressed air for spinning. During subambient runs, dry nitrogen from a high-pressure tank was used to obtain the appropriate bearing and drive pressure for spinning. This was done to help prevent moisture condensation and freezing of water on the ceramic spinner and cap. The dry N_2 was run through copper coils submerged within a dry ice/isopropanol bath before entering the probe. All samples were allowed to equilibrate to temperature for 30 min prior to data collection.

IRCP experiments were run using the pulse sequence shown in Figure 1. The cross polarization (CP) contact time (t_1) was held at 1.5 ms for each experiment. The variable contact time (t_2) was varied from 0.0 to 1000.0 μs. The intensity of ^{13}C peaks as a function of t_2 [$M(t)$] was fit to a two-component model[6] given as Eq. (5).

$$M(t) = M_0\exp(-t/T_{1\rho}H)\{(X)[2\exp(-t/T_{CH1}) - 1] + (1 - X)(2\exp[-t/T_{CH2}) - 1]\} \tag{5}$$

where the prefactors (X) and ($1 - X$) correspond to the fractions of rigid and mobile domains having CP time constants T_{CH1} and T_{CH2}, respectively. The

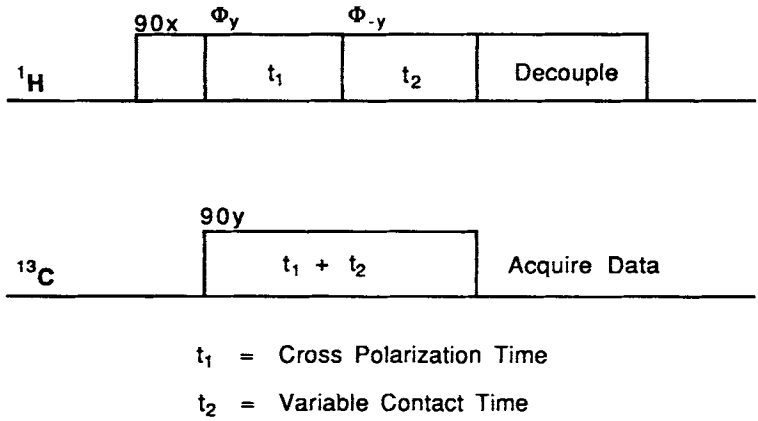

Fig. 1. Inversion recovery cross polarization (IRCP) pulse sequence.

apparent $T_{1\rho}H$ values for this model were obtained from separate experiments using a standard CP pulse sequence with a variable CP contact time.[13]

Most of the analyses were focused on the backbone carbons for each polymer since these carbons are the best representatives of main chain motions.[1,14] The IRCP data for a sample of Dow low-density polyethylene (LDPE) was generated from backbone methylene resonances at 33 and 31 ppm (crystalline and amorphous peaks, respectively).

Poly(vinyl butyral) (PVB) plasticized with 32 phr dihexyladipate (DHA) was obtained from Monsanto Co. as the commercial product Saflex (M_n approximately 100,000). The neat PVB for these studies was obtained by extracting the DHA with n-hexane using a sohxlet extraction procedure. The butyral ring carbon (methine carbon 1 of the six-membered dioxane ring) at 102 ppm was taken as a representative of backbone behavior.[15]

An atactic sample of polystyrene (PS) (M_n approximately 150,000) was obtained and studied as received from Dow as the commercial product Styron. The methylene resonance at 41 ppm was taken as a representative of backbone motion as was done previously.[1]

The polyurethane sample (PU) was made from commercially available PTMEG/TDI pre-polymers cured to solid by the diamine 4,4′-methylene-bis-2-chloroaniline (MOCA). This particular sample was a Uniroyal Adaprene L-167. The aromatic resonance at 136 ppm was taken as a representative of the TDI hard segment behavior while the 27-ppm resonance was taken as a representative of PTMEG soft segment behavior.

Similar data was obtained for a neat poly(phenylene oxide) (PPO) sample from Aldrich Chemical. The 117-ppm protonated aromatic carbon was taken as a representative of backbone motion.

T_{CH} parameters were then analyzed for the purpose of establishing the correlation given previously as Eq. (4). The correlation was made by using T_{CH} values from the method of the initial slope (first 40 μs)[1] and by using the mean $\langle T_{CH} \rangle$ calculated from the parameters of our two component model by using

$$\langle T_{CH} \rangle = \sum N_i T_{CHi} / \sum N_i \tag{6}$$

where N_i and T_{CHi} represent the fractional contribution of each phase to relaxation and the cross polarization constant, respectively.

Dynamic storage modulus values were obtained in some cases from the literature and when possible from direct measurement with a Du Pont 983 Dynamic Mechanical Analyzer (DMA) at 1 Hz as a function of temperature.

RESULTS

Table I shows the fitting parameters and χ^2 values for the fitting of the two component model [Eq. (5)] to the IRCP data. The low χ^2 indicate a good fit in all cases. As the temperature is lowered to −20°C for the case of plasticized PVB, more material cross polarizes as was apparent from higher CP intensities at the same t_2 contact times. The fraction of rigid and mobile phases also changes since material that was too mobile to cross polarize at room temperature is now rigid enough to cross polarize.

Table II shows a refined view of the fraction of each phase in the polymers along with respective $\langle T_{CH} \rangle$ values, T_{CH} values from the initial slope method, and E' values. The refined fractions for LDPE are based on X-ray scattering results[4] that showed that the total amorphous content is 40% while the crystalline content is 60%. The PVB/DHA phase fractions are also refined to account for a component that does not cross polarize at room temperature (30%).[15] The $\langle T_{CH} \rangle$ for the PU sample is calculated by averaging four relaxing components, where the fractions of each are calculated from the prefactors and from the actual fraction of hard and soft segments (30 : 70 from stoichiometric calculations).

Figure 2 shows the correlation between E' and $\langle T_{CH} \rangle$ values, and also between E' and T_{CH} values taken from the initial slopes of the CP curves. The results indicate that the $\langle T_{CH} \rangle$ values from our two-component model provide a better correlation ($R = 0.97$) than the other technique ($R = 0.84$).

TABLE I
Cross Polarization Relaxation Constants and Fitting Parameters for the Two-Phase Model [Eq. (5)]

Polymer	ppm	X	T_{CH1} (μs)	$(1 - X)$	T_{CH2} (μs)	$T_{1\rho}H$ (ms)	χ^2
PVB/NEAT	102	0.61	37	0.39	440	3.5	0.17
PVB/DHA	102	0.64	43	0.36	660	1.4	0.21
PVB/DHA[a]	102	0.42	31	0.58	380	2.5	0.16
PU	27	0.36	63	0.64	4150	8.0	0.02
PU	136	0.33	110	0.67	1420	8.0	0.003
LDPE	33	0.75	33	0.25	550	30.0	0.27
LDPE	31	0.60	70	0.40	3400	30.0	0.03
PS	41	0.68	38	0.32	490	1.3	0.22
PPO	117	0.64	35	0.36	2230	49.0	0.23

[a]Measured at −20°C.

TABLE II
Modified Phase Structure and Correlation Parameters

Polymer	Phase[a]	Estimated fraction	$\langle T_{CH} \rangle$[b] (μs)	T_{CH}[c] (μs)	E'[d] (Pa)
PVB/NEAT	Rigid	0.61	190	49	1.86×10^9
	Mobile	0.39			
PVB/DHA	Rigid	0.45	1080	54	3.98×10^8
	Mobile	0.25			
	"Liquid"	0.30[e]			
PVB/DHA[f]	Rigid	0.42	230	61	1.41×10^9
	Mobile	0.58			
PU	Rigid	0.10	2180	98	7.08×10^7
	Interfacial	0.20			
	Semirigid	0.25			
	Mobile	0.45			
LDPE	Crystalline	0.45	660	54	6.31×10^8[g]
	Interfacial	0.15			
	Semicryst.	0.24			
	Amorphous	0.16			
PS	Rigid	0.68	180	44	2.51×10^9[g]
	Mobile	0.32			
PPO	Rigid	0.64	830	49	5.28×10^8
	Mobile	0.36			

[a] Description of phase assignments based on motional discrimination by NMR data.
[b] Number average $\langle T_{CH} \rangle$ from Eq. (6).
[c] T_{CH} from initial slope method.
[d] Dynamic modulus measured at 1 Hz at temperature of T_{CH} measurement.
[e] Estimated T_{CH} = 3000 μs.
[f] Measured at −20°C.
[g] Dynamic modulae 1 Hz, from Ref. 16.

DISCUSSION

The polymers studied in this article represent a few of the many polymers that are currently classified as homogeneous or heterogeneous systems. Because polymers such as these possess a distribution of motional environments, it has been traditionally difficult to correlate single microscopic CP/MAS relaxation times with the bulk macroscopic properties that arise from the cooperativity of these units.

Despite the use of simplified motional models, it appears that we have discovered a method that adequately relates a microscopic parameter with a macroscopic property. Figure 2 shows that the mean $\langle T_{CH} \rangle$ correlates with E' better than the initial slope T_{CH}. Since these parameters are physical measurements that both implicitly encompass distributions of correlation times, it follows that no explicit mathematical descriptions of these distributions are necessary for establishing a correlation as long as both parameters are modulated by similar motional distributions. Thus, the fact that a good correlation exists between the right- and left-hand sides of Eq. (4) seems to indicate that the complete correlation time distributions may be similar for the two parameters, T_{CH} and E'.

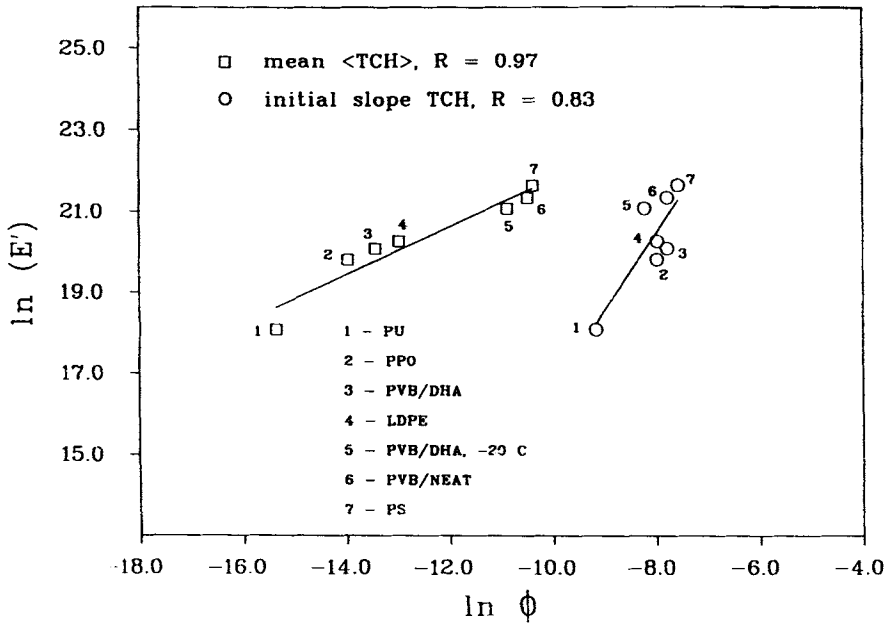

Fig. 2. Correlation between E' and T_{CH}.

This is the first time to our knowledge that such a correlation has been attempted; and although its success is limited thus far to the systems studied here, there are several important points that can be drawn from this relationship. First, this correlation provides evidence to support the hypothesis that T_{CH} is sensitive to near-static motions.[1] Given the dynamic storage modulus measured at low frequencies is determined by the near-static mobility of its molecular components[12] and given the correlation that we have established in Figure 2, we can say that the type of motion affecting these two parameters is similar and that near-static motion must be the type of motion that dominates T_{CH}.

Second, no correlation of this type is possible unless all of the motional components of a polymer are considered. This is reasonable simply by virtue of the fact that macroscopic properties cannot be modeled by simple Maxwell or Voight models but must instead be modeled by some linear combination of these elements.[12] Thus, the method of using the initial slope of the CP curve to determine T_{CH} does not provide an adequate parameter for the motional comparison of polymers. This is because the T_{CH} value from the initial slope ignores the importance of the mobile phases.

In cases where cross polarization is not complete due either to short $T_{1\rho}H$ processes, or due to the existence of highly mobile phases, an erroneous estimation of the rigidity of the system will result. This is true for plasticized PVB since its $T_{1\rho}H$ value is short and since all of its components do not cross polarize at room temperature. This was previously established by Schaefer[15] and is further verified here by the increase in CP intensity at lower temperatures. For this reason, plasticized PVB does not fit our correlation at room temperature unless an arbitrary T_{CH} value is assigned to the highly mobile phase of the

material. This is done by assuming that the T_{CH} of the highly mobile phase is slightly longer than the $T_{1\rho}$ for the material. After taking the fraction of this mobile phase to be 30%,[15] the rigid phase fraction can be reestimated to comprise 40% of the material (see Table II). This reestimated distribution is in agreement with low-temperature results that show 40% of the polymer to be rigid in character, with the remainder being more mobile.

It must also be realized that we have limited our discussion to include only the backbone carbons for each polymer. Polymers such as PVB contain side chains that exhibit entirely different motional behavior from the backbone carbons. Carbons of this type do not fit into our correlation since their motional characteristics are typically independent of the types of main chain processes that most likely control the bulk response of polymers to low-frequency stresses.[14] However, a truly quantitative understanding of structure–property relationships may ultimately depend on our ability to understand the contribution of all functional groups, main chain and side chain, to microscopic and macroscopic properties.

Finally, the use of the mean $\langle T_{CH} \rangle$ for this correlation is a first approximation that seems to work with these limited examples. We suspect that, eventually, as more data becomes available, more sophisticated methods of comparison will be developed. For example, a weighted average of T_{CH} values may be more suitable since separate phases may not contribute equally in a given frequency range. Nevertheless, a simple mean $\langle T_{CH} \rangle$ seems adequate in principle since it shows that T_{CH} can potentially be used as a tool for studying structure–property relationships.

CONCLUSIONS

This preliminary study deals only with establishing a relationship between two measurements: E' and $\langle T_{CH} \rangle$. Obviously, the door is open for future studies that may involve other macroscopic mechanical and microscopic NMR measurements. However, the common element that will eventually link all of these studies is the relationship between physical measurements and molecular motions.

In this work we have shown for a limited number of polymer samples, although representing a considerable array of morphologies, that the microscopic cross polarization rates for main chain carbons can be related to dynamic modulus when motional heterogeneity is taken into account. Since this relationship provides further experimental evidence that indicates that T_{CH} and E' are modulated by similar correlation functions, it therefore follows that T_{CH} must be dominated by near-static motions.

References

1. J. Schaefer, E. O. Stejskal, and R. Buchdahl, *Macromolecules*, **10**, 384–405 (1977).
2. H. T. Edzes and W. S. Veeman, *Polym. Bull.*, **5**, 255 (1981).
3. D. G. Cory, Applications of Cross Polarization Spin Dynamics in Solids, Thesis, Case Western Reserve University, Cleveland, Ohio, 1987.
4. Y. T. Shieh, Polymer Structure and Molecular Dynamics Studied by Solid State NMR, Thesis, Case Western Reserve University, Cleveland, Ohio, 1988.

5. D. G. Cory and W. M. Ritchey, *Macromolecules,* **22,** 1611–1615 (1989).
6. A. A. Parker, J. J. Marcinko, Y. T. Shieh, C. Shields, D. P. Hedrick, and W. M. Ritchey, *Polym. Bull.,* **21,** 229–234 (1989).
7. M. Mehring, *Principles of High Resolution NMR in Solids,* 2nd ed., Springer-Verlag, Berlin, 1983.
8. D. A. McArthur, *Phys. Rev.,* **188,** 609 (1969).
9. L. B. Alemany and D. M. Grant, *J. Am. Chem. Soc.,* **105,** 2133–2141 (1983).
10. O. E. Stejskal and J. Schaefer, *Faraday Symp. Chem. Soc.,* **13,** 56–62 (1978).
11. A. V. Tobolsky and E. Catsiff, *J. Polym. Sci.,* **19,** 111–121 (1956).
12. I. M. Ward, *Mechanical Properties of Solid Polymers,* 2nd ed., Wiley, New York, 1979.
13. E. O. Stejskal and J. Schaefer, *Macromolecules,* **14,** 275–279 (1981).
14. R. F. Boyer, *Polym. Eng. Sci.,* **8,** 161–185 (1968).
15. J. Schaefer and J. R. Garbow, *Macromolecules,* **20,** 1271–1278 (1987).
16. T. C. Ward, *Physical Concepts of Polymer Science,* American Chemical Society, Short Course Series, Blacksburg, VA, 1987.

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