Calculation of Relaxation Time in Polyurethanes Using Additive Group Contributions

BRUCE HARTMANN,* GILBERT F. LEE, JOHN D. LEE, JEFFRY J. FEDDERLY, and ALAN E. BERGER

Naval Surface Warfare Center, Silver Spring, Maryland 20903-5640

SYNOPSIS

The method of additive properties was used to calculate the dynamic mechanical relaxation time for a series of polyurethanes. Calculations were also made of density and glass transition temperature. Group contributions for nine component groups were determined. With these group values, the densities of the 12 polymers used to determine the groups were calculated and found to agree with measured values within an average of 0.2%. Calculated glass transition temperatures also agreed with measured values within 0.2%. The relaxation time, defined as a parameter in the Havriliak–Negami equation, was shown to be correlated with the glass transition temperature, allowing relaxation time to also be expressed as an additive property. Calculated logarithms of relaxation times agree with measured values to within 7% over a range of relaxation times covering many decades. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The method of additive properties has proven to be a useful approach for many polymer properties. The method has been described in detail by van Krevelen.[1] This approach of calculating polymer properties from component group contributions can give reliable results for many, but not all, polymer properties. The additive function that is valid for one property may not be valid for other properties. The function may involve a linear sum, a sum of reciprocals, or the sum of logarithmic terms. To be useful, one must establish the form of the additive function and determine the values for a variety of groups. Once this has been done, these groups can be used to make predictions for polymers for which data are not available. Trends in data, such as molecular weight dependence of properties, can be easily determined.

As an example of the use of additive properties, it is assumed that the molar volume of a polymer is the sum of the volumes of the individual components making up the polymer and that these component values are the same in every polymer. Thus,

$$V = \sum N_i V_i \qquad (1)$$

where N_i is the number of ith groups in the repeat unit and V_i is the molar volume of the ith group.

Because the molar mass of the polymer can be expressed as

$$M = \sum N_i M_i \qquad (2)$$

where M_i is the molar mass of the ith group, it follows from eqs. (1) and (2) that the density of a polymer can be calculated from

$$\rho = \left(\sum N_i M_i \right) / \left(\sum N_i V_i \right) \qquad (3)$$

Equation (3) is an illustration that not all additive functions have the simple form of eqs. (1) and (2).

Another additive property, which is central to this work, is the glass transition temperature, T_g. There have been a number of empirical forms assumed for this property.[2] The one used here is given by

$$T_g^{-1} = \sum (N_i M_i / M) T_{gi}^{-1} \qquad (4)$$

where T_{gi} is the contribution of the ith group to the glass transition temperature of a polymer containing

that group. The form of eq. (4) is an extension of the relation commonly used for the T_g of a copolymer in terms of homopolymer values. Equation (4) is another example of the fact that not all additive properties are simple linear sums. One must determine the analytical form of the additive function, if it exists.

Equations (3) and (4) can be used to make predictions of the density and glass transition temperature for any polymer that can be expressed in terms of known group values. The general technique for determining group values is to synthesize a series of polymers that contains the desired groups and measure the properties of these polymers. Each polymer represents an equation in terms of the unknown group values. For m polymers and n groups, the system can be expressed as m simultaneous equations in n unknowns with $m > n$. The least-square solution of such a system of equations is well known. Details of the mathematical analysis procedure have already been published.[3,4]

The purpose of this paper is to establish that the dynamic mechanical relaxation time is an additive property; determine the analytical form of the additive function; and determine the group contributions to molar volume, glass transition temperature, and relaxation time for a series of polyurethanes for which all of these properties have been measured on the same samples.

POLYURETHANE GROUP ANALYSIS

The polymers considered here are polyurethanes. They are copolymers consisting of hard and soft segments that can be either phase mixed or phase separated. The group properties can be different in the two cases, and this study is restricted to phase-mixed systems only.

In simplest terms, the polymers of interest are formed by the reaction of a high-molecular-weight diol with a diisocyanate and a low-molecular-weight diol chain extender to form a urethane. As a specific example, when 1 mol of high-molecular-weight diol is reacted with 3 mol of diisocyanate and 2 mol of chain extender, the resulting polyurethane has the idealized structure shown below.

$$1 \ HO-R_n-OH + 3 \ OCN-R'-NCO$$
$$+ \ 2 \ HO-R''-OH \rightarrow$$
$$-R'-U-R_n-U-R'-U-R''$$
$$-U-R'-U-R''-U-$$
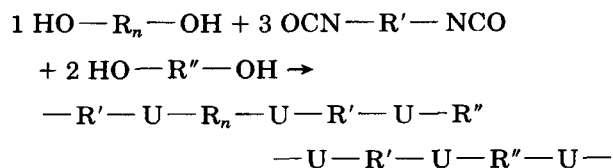
where $U = -OCONH-$ is the urethane group and R, R', and R" are the residues for the high-molecular-weight diol, diisocyanate, and chain extender, respectively. (There is a subscript n on the residue R because the high-molecular-weight diol is made up of a simple group repeated n times.)

Most polyurethanes considered here were taken from our earlier work on hindered diol chain extenders.[5] The high-molecular-weight diol in all the polymers was poly(tetramethylene ether) glycol (PTMG). Two nominal molecular weights were used: either 1000 or 2000. The diisocyanate was 4,4'-diphenylmethane diisocyanate (MDI). Various mole ratios of MDI to PTMG were synthesized. Five chain extenders were used: four hindered diols and 1,3-butanediol. The hindered diols were 2,2-dimethyl-1,3-propanediol, 2,2-diethyl-1,3-propanediol, 2-ethyl-2-methyl-1,3-propanediol, and 2-butyl-2-ethyl-1,3-propanediol. There were 10 polymers in all. They are the first 10 listed in Table I.

For this work, two other diisocyanates were investigated, one aliphatic and the other aromatic. The aliphatic diisocyanate was 1,6-diisocyanato hexane and the aromatic diisocyanate was 1,3-phenylene diisocyanate. Thus, there were two additional polymers added to Table I, for a total of 12 polymers.

Considering only independent bivalent groups, the polymer set given in Table I can be broken down into the nine independent groups listed in the first column of Table II. The groups include a tetramethylene ether group from the high-molecular-weight diol, three groups from the diisocyanates, and five groups from the chain extenders. Molar masses of the groups are listed in the second column of Table II.

Before examining the results obtained using these groups, it is worthwhile to summarize the approximations made in their determination. First, idealized molecular structures are assumed. Second, all polymers are assumed to be in the high-molecular-weight plateau where molecular weight need not be considered. Third, the polymers here were synthesized using a 5% excess isocyanate to produce a small amount of cross-linking. This cross-linking is ignored and the polymers are treated as linear systems. Fourth, one extra oxygen atom is added to the end of the 1000 or 2000 molecular weight tetramethylene ether group to account for the one that goes into the urethane group. To eliminate the approximations would require a significant number of new polymers to be synthesized, and experience has shown that these approximations produce insignificant errors.

Table I Polymer Properties

No.	Description	Density (g/cm³)		T_g (K)		ln τ (s)	
		Meas.	Calc.	Meas.	Calc.	Meas.	Calc.
1	1 PTMG2000/3 MDI/2 DMPD	1.074	1.074	233	235	−15.6	−16.1
2	1 PTMG2000/4 MDI/3 DMPD	1.092	1.088	252	250	−13.4	−12.3
3	1 PTMG2000/6 MDI/5 DMPD	1.108	1.109	275	276	−6.3	−6.7
4	1 PTMG1000/3 MDI/2 DMPD	1.123	1.129	279	278	−7.1	−6.3
5	1 PTMG2000/3 MDI/2 DEPD	1.072	1.072	234	234	−15.7	−16.3
6	1 PTMG1000/3 MDI/2 1,3BDO	1.116	1.116	273	273	−8.8	−7.3
7	1 PTMG1000/3 MDI/2 EMPD	1.119	1.112	282	283	−5.8	−5.4
8	1 PTMG2000/3 MDI/2 EMPD	1.060	1.064	238	237	−16.2	−15.5
9	1 PTMG1000/3 MDI/2 BEPD	1.106	1.108	284	284	−5.8	−5.2
10	1 PTMG2000/3 MDI/2 BEPD	1.064	1.063	239	239	−15.0	−15.0
11	1 PTMG1000/3 HDI/2 BEPD	1.044	1.044	225	225	—	−18.8
12	1 PTMG1000/3 PDI/2 BEPD	1.120	1.120	281	281	—	−5.7

Numbers preceding each chemical are the mole ratios used in the synthesis. PTMG, poly(tetramethylene ether) glycol (The trailing number is the nominal molecular weight.); MDI, 4,4'-diphenylmethane diisocyanate; DMPD, 2,2-dimethyl-1,3-propanediol; DEPD, 2,2-diethyl-1,3-propanediol; 1,3BDO, 1,3-butanediol; EMPD, 2-ethyl-2-methyl-1,3-propanediol; BEPD, 2-butyl-2-ethyl-1,3-propanediol; HDI, 1,6-diisocyanato hexane; PDI, 1,3-phenylene diisocyanate. Taken from reference 5 except Nos. 11 and 12, which are reported here for the first time.

DENSITY

The first application of the above groups is to density predictions. Densities of the 12 polymers were measured using a liquid displacement technique at room temperature. The values are listed in Table I.

The measured values were used in a set of 12 simultaneous equations, of the form of eq. (1), with nine unknown V_i values and known coefficients N_i. Group values were then calculated using a least-square technique.[3]

It is important to know the accuracy of the group values obtained in this manner. The accuracy of the group values depends on the accuracy of the density measurements, assumed to be ±0.5% at

the 95% confidence level (standard deviation $= 0.0025\rho_{\text{measured}}$), and the matrix of coefficients of the simultaneous equations for the 12 polymers. Estimates for the variance (square of the standard deviation) of the component volumes were obtained using the theorem from statistics that states that the variance of the errors in the measured polymer volumes is a linear combination of the variances of the component volume errors with coefficients determined by the N_i values. This analysis assumes that the errors are independently normally distributed. Using this technique, the upper and lower confidence limits (at the 95% confidence level) were determined. In this case, the upper and lower confidence limits are symmetrical. The least-square

Table II Group Values

Group	M_i (g/mol)	V_i (cm³/mol)	T_{gi} (K)	ln τ_i (s)
—(CH₂)₄O—	72.10	73.1 ± 0.8	183 + 2 − 2	−34.00
—U—C₆H₄—CH₂—C₆H₄—U—	284.29	178 ± 24	590 + 106 − 95	21.80
—U—(CH₂)₆—U—	202.24	137 ± 24	269 + 31 − 29	−8.16
—U—C₆H₄—U—	194.15	91 ± 24	1035 + 576 − 396	32.57
—CH₂C(CH₃)₂CH₂—	70.15	111 ± 28	429 + 446 − 218	12.40
—CH₂C(C₂H₅)₂CH₂—	98.21	140 ± 32	319 + 159 − 113	0.57
—CH₂C(C₂H₅)(CH₃)CH₂—	84.14	137 ± 33	531 + 770 − 298	19.05
—CH₂C(C₄H₉)(C₂H₅)CH₂—	126.27	178 ± 33	436 + 222 − 157	12.96
—CH₂CH₂CH(CH₃)—	56.12	108 ± 34	312 + 344 − 162	−0.52

values and their confidence limits are listed in the third column of Table II.

As expected, the PTMG residue is obtained with the smallest confidence range, whereas the other components have an order of magnitude larger range. These components are not known accurately because they are present in much smaller amount than the PTMG residue and for the same reason it is not necessary to know them accurately to make predictions about polymers of this general type.

The group volumes in Table II are all reasonable in comparison with the values given by van Krevelen. The most accurately known group is the PTMG residue. Van Krevelen finds 74 cm^3/mol in excellent agreement with the present 73.1 cm^3/mol. The other components agree with the van Krevelen values within the accuracy of their determination.

Using the group values in Table II, the densities of all the polymers that were used in the determination of the group values were calculated using eq. (3) and are listed in Table I. The results are plotted as calculated versus measured density in Figure 1. The average agreement between calculated and measured is 0.2%. Because the accuracy of the density measurements is 0.5%, the calculations are, on average, as reliable as the measurements.

GLASS TRANSITION TEMPERATURE

The second property considered is the glass transition temperature. Glass transition temperatures of the 12 polymers were determined using a differential scanning calorimeter (DSC) module on a DuPont 9900 Thermal Analyzer at a scan rate of 10°C/min in an inert atmosphere. The midpoint of the transition was taken as the glass transition temperature. The measured values are listed in Table I.

The measured T_g values were used in the 12 simultaneous equations, of the form of eq. (4), for nine unknown T_{gi} values with known coefficients N_i. The polymers and groups were the same as used for density. Group values were then calculated using the same least-square technique used for volume.

Obtaining an estimate of the accuracy of the T_{gi} values is more complicated than for the volume components because the T_{gi} values appear as reciprocals rather than linearly. The following procedure was used. Random errors were added to each of the 12 T_g measurements and the set of resulting T_{gi} values was computed. This calculation was done repeatedly and the smallest interval I_i containing 90%
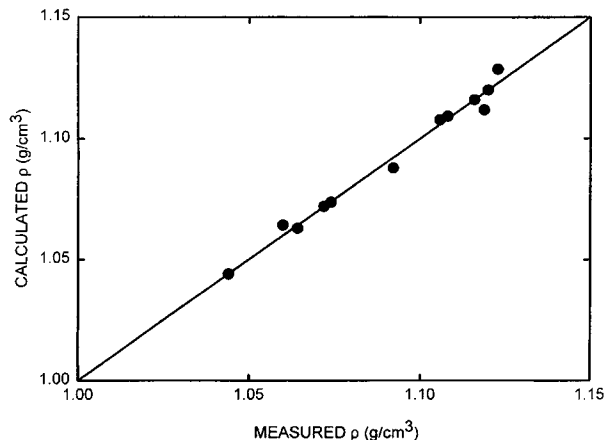

Figure 1   Calculated versus measured density at room temperature.

of the T_{gi} values was determined. A detailed description of the procedure is presented in the Appendix. The least-square group values T_{gi} and their confidence limits are listed in Table II, in the format $T_{gi} + \Delta_+ - \Delta_-$, where $I_i = [T_{gi} - \Delta_-, T_{gi} + \Delta_+]$. As expected, the PTMG residue is determined with the highest accuracy, whereas the other components have an order of magnitude or more higher uncertainty. Note that except for the PTMG residue, $\Delta_- \neq \Delta_+$. This is a result of the nonlinear nature of the glass transition temperature additive equation.

The T_{gi} values in Table II are qualitatively reasonable. The PTMG residue is not only aliphatic but contains an oxygen swivel. It would therefore be expected to have the lowest group value and it does. The two groups that have aromaticity would be expected to have the highest group values and they do. The other groups are intermediate.

Taking group values from Table II, the glass transition temperatures of all polymers used in the determination of the group values were calculated using eq. (4) and are listed in Table I. The results are plotted as calculated versus measured T_g in Figure 2. The average agreement between calculated and measured temperature is 0.2%. Because the assumed accuracy of the DSC measurements is ±2° (about 0.8%), the calculations are, on average, as reliable as the measurements.

The sensitivity of the T_{gi} values determined from the least-square fit to measurement errors in T_g depends on the entries of the matrix $(A^TA)^{-1}A^T$, where A is the matrix of coefficients in the right hand side of eq. (4) (here A was a 12 × 9 matrix and A^T denotes the transpose of A). With the incorporation of this information into a computer program, it is possible
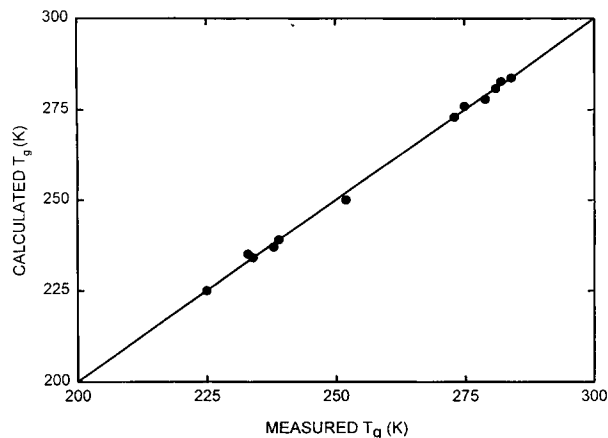
Figure 2 Calculated versus measured glass transition temperature.

to test the sensitivity of T_{gi} values for various polymer sets before actually synthesizing the samples. This methodology provides a means of producing sample sets that exhibit a balanced representation of the component groups. From this, an accurate prediction of the component values should result.

RELAXATION TIME

Polymers exhibit a dynamic mechanical relaxation at their glass transition. Typical shear modulus and loss factor behavior is shown in Figure 3. This relaxation can be located anywhere over a wide frequency range, depending on molecular structure. The frequency at which the transition loss factor peak is located is given approximately by the reciprocal of the relaxation time τ. To proceed with the additive property analysis, this qualitative definition of relaxation time will be made specific and the experimental technique for measuring it described. The next step involves the determination of the analytical form of the additive function. This step involves a correlation between relaxation time and glass transition temperature. Having completed these preliminaries, the group values for relaxation time are determined and used to compare calculated and measured values.

Resonance Apparatus

Dynamic mechanical properties were measured using a resonance apparatus.[6] A schematic of this apparatus is shown in Figure 4. In this device, a sample in the shape of a bar, 10–15 cm long with square

lateral dimensions of 0.635 cm, is driven by an electromagnetic shaker. The shaker is excited by a random noise source. The frequency dependence of the amplitude and phase of the acceleration difference between the driven end of the sample and the free end is determined using a fast Fourier transform. At a resonance, the amplitude has a local maximum, and the phase is a multiple of 90°. At a given temperature, four or five resonant peaks can be determined in a nominal range of two decades, from 100 Hz to 10 kHz. At these frequencies, the wave equation yields two coupled transcendental equations that can be solved numerically for shear modulus and loss factor.

The measurements are repeated as a function of temperature from −60 to 70°C, and the resulting data are shifted to form a master curve over a wide frequency range at one reference temperature using the time-temperature superposition principle.[7] The following procedure is used: log modulus curves at different temperatures are shifted along the log frequency axis until they partially overlap to obtain a best fit, minimizing the sum of the squares of a second-order equation (in log modulus) between two sets of modulus data at different temperatures. The original data, which spanned only two decades of frequency but covered a range of temperatures, has now been shifted to cover a very wide range of frequency at a single reference temperature. As a matter of convenience, all data here were shifted to a reference temperature of 25°C. Typical data are shown in Figure 3.

Havriliak–Negami Model

The most successful description of the dynamic mechanical properties of polymers at the glass transi-
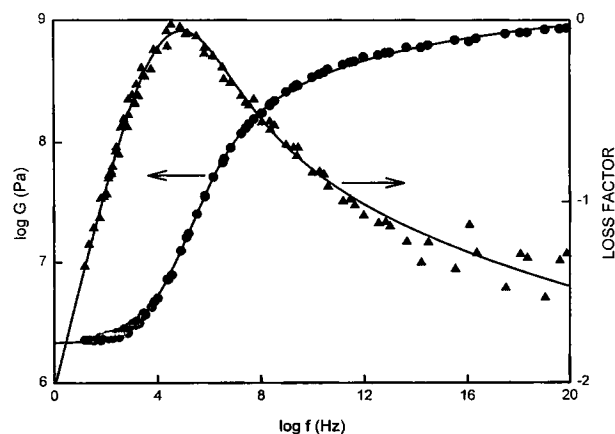

Figure 3 Typical dynamic mechanical properties (polymer no. 1 at 25°C).
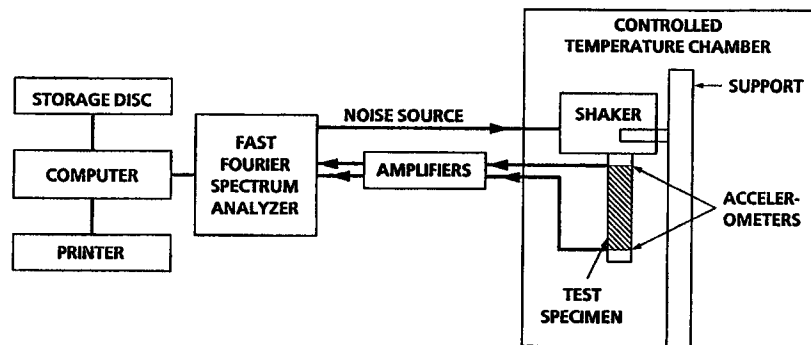
Figure 4 Schematic resonance apparatus.

tion is the Havriliak–Negami (HN) model.[8] In this model, the frequency dependence of the complex shear modulus G^* is given by

$$(G^* - G_\infty)/(G_\infty - G_0) = [1 + (i\omega\tau)^\alpha]^{-\beta} \quad (5)$$

where G_∞ is the limiting high frequency modulus, G_0 is the limiting low frequency modulus, ω is the angular frequency, τ is the relaxation time, α is the transition width parameter, and β is the transition asymmetry parameter. The parameter τ is the relaxation time considered in this work. It can be viewed qualitatively as the reciprocal of the location of the glass transition loss factor peak along the frequency axis. It can be shown that it represents an average value of the distribution of single relaxation times corresponding to the HN equation.

The data in Figure 3 were fitted to eq. (5) using a nonlinear least-square algorithm from the International Mathematical and Statistical Libraries, Inc. The fit is shown in Figure 3 as solid lines. In general, the fit is about as good as the experimental accuracy of the measurements, which is 2% on modulus and 5% on loss factor.

Measured values of $\ln \tau$ are listed in Table I. The accuracy of the relaxation time measurement is difficult to assess, but based on the precision of the measurements, the variability from sample to sample, and the variability from one experimental technique to another, a reasonable estimate is ±1 decade of frequency.

Correlation of τ and T_g

The next step in the program outlined here is to demonstrate a correlation between τ and T_g. This demonstration proceeds with the usual assumption that the frequency f of the loss factor peak shifts with temperature following an Arrhenius behavior of the form

$$\tau = \tau_0 e^{E/RT} \quad (6)$$

where $\tau = 1(2\pi f)$ is the relaxation time for the peak, E is activation energy, τ_0 is a constant, R is the gas constant, and T is absolute temperature. This assumption is almost universally made when considering dynamic measurements, both mechanical and dielectric, and has proven useful for numerous polymers.[9] Note that the assumption of Arrhenius behavior applies only to one point on the loss factor curve, the peak value. The assumption is that the molecular motion corresponding to the peak has an Arrhenius behavior with a certain activation energy. Other motions may have different activation energies. Thus, the shift factor curve may follow the Williams–Landel–Ferry (WLF) equation,[7] which is equivalent to a particular distribution of activation energies, whereas the loss factor peak value follows an Arrhenius equation.

Taking logarithms of both sides of eq. (6) yields

$$\ln \tau = \ln \tau_0 + E/RT \quad (7)$$

This relation holds at any temperature. Evaluating at the glass transition temperature yields

$$\ln \tau_g = \ln \tau_0 + E/RT_g \quad (8)$$

where τ_g is the value of the relaxation time at the glass transition temperature. Subtracting eq. (8) from eq. (7) gives

$$\ln \tau - \ln \tau_g = E/R(1/T - 1/T_g) \quad (9)$$

eliminating the unknown constant τ_0. Rearranging eq. (9) yields

$$\ln \tau = (\ln \tau_g + E/RT) - E/RT_g \quad (10)$$

The derivation thus far has considered a generic polymer. If we now assume that E and τ_g are about the same for all the urethane polymers considered here, it follows that $\ln \tau$ is a linearly decreasing function of $1/T_g$, when all the τ values are evaluated at the same reference temperature. The slope of this line allows a determination of the activation energy for the polymers. The intercept of the line represents the extrapolated maximum relaxation time at the maximum glass transition temperature, infinity.

To see whether the above assumptions are valid, data for more than 20 polyurethanes were analyzed.[10] All data were obtained in our laboratory using polymers of known structure, and they were all analyzed in the same manner, using the resonance apparatus and fitting the data to the HN equation. A plot of the results is shown in Figure 5. The agreement is satisfactory with a correlation coefficient of 0.96, giving a useful tool for predicting relaxation time from glass transition temperature measurements. Recall that the relaxation time was determined from resonance measurements, whereas T_g was determined independently from DSC measurements.

From the slope of the line in Figure 5 fitted to eq. (10), $E = 120$ kJ/mol. In comparing this value with others in the literature, Boyer[11] showed a plot of activation energy as a function of glass transition temperature. For the range of T_g values observed here, 233–284 K, he shows activation energies from 100 to 150 kJ/mol. The value obtained here is in excellent agreement with this range.

From the intercept of the line in Figure 5, $\tau_g = 65$ ms. Thus, for these polymers, one could define the glass transition temperature as the temperature at which the relaxation time is 65 ms.

Analytical Form for Additive τ

It was shown earlier that T_g is an additive property and it was also shown that τ is correlated with T_g. It then follows that τ is also an additive property. The analysis proceeds as follows. As noted earlier, T_g is an additive property given by the relation

$$T_g^{-1} = \sum (N_i M_i / M) T_{gi}^{-1} \qquad (11)$$

In eq. (10), the term in parenthesis is the value of $\ln \tau$ when T_g is infinite so that eq. (10) can be written as
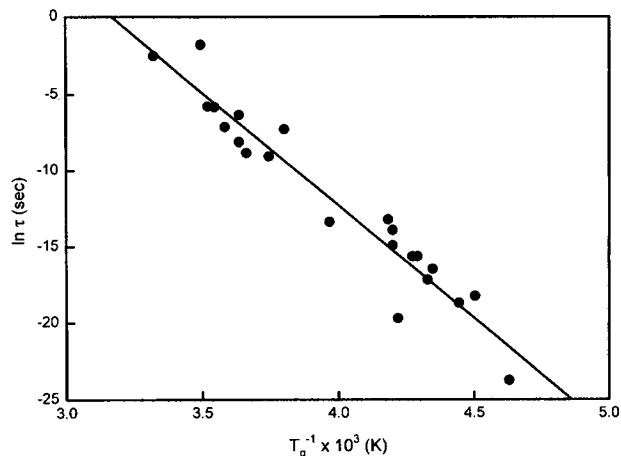

Figure 5 Arrhenius plot of $\ln \tau$ (at room temperature) versus $1/T_g$.

$$\ln \tau = \ln \tau_\infty - E/RT_g \qquad (12)$$

where τ_∞ is the limiting relaxation time for infinite glass transition temperature. Assuming that each component group has the same relaxation time dependence on glass transition temperature as does the overall polymer, it follows from eq. (12) that

$$\ln \tau_i = \ln \tau_\infty - E/RT_{gi} \qquad (13)$$

Substituting eq. (11) in eq. (12) and then solving eq. (13) for T_{gi}^{-1} to substitute in the resulting equation, it follows that

$$\ln \tau = \sum (N_i M_i / M) \ln \tau_i \qquad (14)$$

which is the desired additive functional form.

$\ln \tau_i$ Group Values

Relaxation time group values were calculated from eq. (13) using the known values of T_{gi} from Table II. The results are listed in the last column of Table II. Because the relaxation time group values were calculated directly from the glass transition temperature group values, the qualitative behavior of the relaxation time group values mirror the glass transition temperature group values. Specifically, $-(CH_2)_4O-$ has the shortest relaxation time because it has the lowest T_{gi} value and $-U-C_6H_4-U-$ has the longest relaxation time because it has the highest T_{gi}.

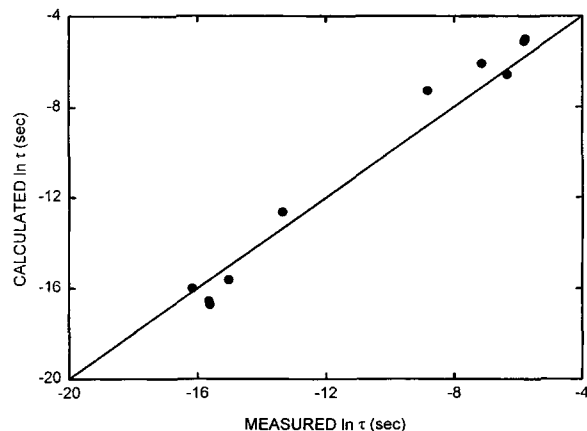Using the group values of $\ln \tau_i$ in Table II, polymer relaxation times were calculated for all those

Figure 6   Calculated versus measured ln τ at room temperature.

systems for which experimental data were available and are listed in Table I. The results are plotted as calculated versus measured ln τ in Figure 6. The average agreement between measured and calculated ln τ is 7%. Especially considering the wide variation in this property, this agreement is sufficient to allow useful predictions to be made.

CONCLUSIONS

Group values of molar volume, glass transition temperature, and dynamic mechanical relaxation time were determined for nine groups that can be used to analytically synthesize a wide range of polyurethanes. The component values were determined from a set of 12 polyurethanes that, with two exceptions, were taken from our earlier work. In this way, all data were obtained in the same manner for all the polymers. A disadvantage of using this particular set is that one group, the PTMG residue, is present in every polymer in much greater concentration than any other group. Thus, this group is known with much greater accuracy than any other group.

The additive property analysis for relaxation time, defined as a parameter in the HN equation, was based on a relation between relaxation time and glass transition temperature.

Using the group values obtained from measurements on the 12 polymers to calculate density, T_g, and τ, it is found that density can be predicted to within 0.2%, T_g within 0.2%, and ln τ within 7%.

APPENDIX. TECHNIQUE FOR ESTIMATING GLASS TRANSITION COMPONENT ACCURACY

A Monte Carlo procedure was used to estimate the accuracy of the glass transition component values. Independent identically distributed random error values e_j were added to each of the 12 measured T_g values in eq. (4), and the nine T_{gi} values resulting from this new T_g set were computed as before. This was repeated N times and for each i, $i = 1, \ldots, 9$, the smallest interval I_i containing 90% of the N calculated T_{gi} values was determined. For each of the N simulations, a vector V of 24 independent normally distributed values with mean $= 0$ and a specified standard deviation σ was calculated. The first 12 entries of V lying within $[-2\sigma, 2\sigma]$ were used for the 12 e_j values. If there were less than 12 such values, a new vector V was computed. The probability density function $f(x)$ for each e_j thus equals $n(x; 0, \sigma)/0.9545$ for $|x| \leq 2\sigma$, and $f(x) = 0$ for $|x| > 2\sigma$, where n denotes the probability density function of the normal distribution with mean 0 and standard deviation σ (0.9545 is the area under n between $x = -2\sigma$ and $x = 2\sigma$). The vector V of normal random numbers was generated using the modified Box-Muller method of Marsaglia and Bray.[12] Only the first number of each pair generated by this method was used in V. The uniform [in (0, 1)] random numbers x_k required by the modified Box-Muller method were generated using the multiplicative linear congruential algorithm (MLCA) $s_{k+1} = as_k \bmod m$ with $a = 16807$ and $m = 2147483647$ (the initial seed s_0 is to be an integer in $[1, m-1]$, and x_k in $(0, 1) = s_k/m$).[13] The value 876366394 was taken for the initial seed s_0. Results of this simulation with $N = 600000$ and $\sigma = 1.0$ are given in Table II, where the value of T_{gi} was calculated from the least-squares fit using the measured data for T_g (Table I) and the upper and lower confidence limits were obtained with the Monte Carlo simulation. The values of Δ_+ and Δ_- (see earlier text for notation) given in Table II did not change by more than 3% when the simulation was rerun, reversing the order of the entries in each vector V; or using initial seed values of 1894012152 or 844624270 (roughly $\frac{1}{3}$ and $\frac{2}{3}$ of the way through the $m - 1$ integers generated by the MLCA starting with 876366394); or with $N = 100000$.

REFERENCES

1. D. W. van Krevelen, *Properties of Polymers*, 3rd ed., Elsevier, Amsterdam, 1990.
2. G. Lee and B. Hartmann, *J. Appl. Polym. Sci.*, **28**, 823 (1983).
3. B. Hartmann and G. F. Lee, *J. Appl. Phys.*, **51**, 5140 (1980).
4. B. Hartmann and G. F. Lee, *Acustica*, **76**, 241 (1992).
5. J. V. Duffy, G. F. Lee, J. D. Lee, and B. Hartmann, in *Sound and Vibration Damping with Polymers*, R. D. Corsaro and L. H. Sperling, Eds., ACS Symposium Series 424, Washington, DC, 1990, Chap. 15, p. 281.
6. W. M. Madigosky and G. F. Lee, *J. Acoust. Soc. Am.*, **73**, 1374 (1983).
7. J. D. Ferry, *Viscoelastic Properties of Polymers*, 3rd ed., Wiley, New York, 1980.
8. S. Havriliak and S. Negami, *J. Polym. Sci. Part C*, **14**, 99 (1966).
9. N. G. McCrum, B. E. Read, and G. Williams, *Anelastic and Dielectric Effects in Polymeric Solids*, Wiley, New York, 1967.
10. B. Hartmann, G. F. Lee, and J. D. Lee, Proceedings 14th International Congress on Acoustics, Vol. 1, paper A8-4, Beijing, China, 1992.
11. R. F. Boyer, *Rubber Chem. Tech.*, **XXXVI**, 1303 (1963).
12. G. Marsaglia and T. A. Bray, *SIAM Rev.*, **6**, 260 (1964).
13. S. K. Park and K. W. Miller, *Comm. ACM*, **31**, 1192 (1988).