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Parameters of Equation of State of Polyurethanes from Acoustic Resonance and Isobaric Expansivity

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ABSTRACT: A series of polyurethanes was synthesized, varying the length of the soft sequences in the chain. Linear isobaric expansitivites, α_L, were measured as a function of temperature, T, from −100 to +100 °C. Volumetric isobaric expansivities, α, and characteristic parameters v^* and T^* in the Hartmann equation of state[23] were computed from α_L values. For these polymers, v^* goes symbatically with the length of the soft segment. T^* decreases at the same time, showing that longer soft segments weaken intersegmental interactions. When the Hartmann equation was used in the opposite way, specific volumes, $v(T)$, were obtained, which agree well with the experimental ones. Dynamic mechanical tests were performed on the same materials by using a resonance method; temperature shift factors, a_T, were obtained from the data. When a formula for a_T in terms of the reduced volume $\tilde{v}$[15,17] and the Hartmann equation again were used, characteristic temperatures, T^*, were obtained also from the resonance data. For each polymer, the T^* value from expansivity is close to the value derived from dynamic mechanical testing. Hence, the Hartmann equation provides reliable results not only for the equation of state data but also for prediction of temperature shift factors via the $a_T(\tilde{v})$ equation.

Introduction

Polyrethanes (PU) have numerous applications in aerospace, automotive, electronics, petrochemical, and other industries,[1] largely due to a wide range of properties they exhibit. The properties are varied by using a number of structural blocks and also by changing relative proportions of hard and shoft segments. PU elastomers are castable, a distinct processing advantage in comparison to rubbers. In a number of cases the hard and soft segments are incompatible.[2–8] Then the hard segments form domains dispersed in a matrix of soft segments; two glass transition temperatures and interesting mechanical properties ensue.

Because of both properties and applications, work on PU proceeds on several fronts including synthesis of new thermoplastic materials.[9] The present work came about from a combination of at least three elements. First, as a continuation of an earlier study,[5] which has shown among other things that dynamic mechanical properties are well correlated with the degree of phase separation and the soft segment glass transition. Second, due to extensive work by Ferry,[10] Holzmüller,[11] Matsuoka,[12] Kubat,[13] Struik,[14] and others, we know how important free volume, v^f, is for the mechanical and rheological properties of polymers. The evidence accumulated by these authors on the role of v^f has led, among other things, to the introduction[15] and applications[16–19] of a concept of chain relaxation capability (CRC). Third, to calculate v^f, we need a reliable equation of state, and various formulas have been proposed, notably by Flory[20,21] and Simha and Somcynsky.[22] By a combination of successful elements of earlier equations, Hartmann[23–26] developed an equation of state that gives good results for polymer solids,[24] melts, and liquids.[25,26]

A series of PUs was synthesized in which the molecular mass M, or more accurately the length of the soft segments in the chain, was varied. For this series, plus for a series developed earlier,[5] the dynamic mechanical responses were measured by a resonance method[27] and the temperature shift factor, a_T, was obtained. In turn, T^* parameters of the Hartmann equation of state were determined via an equation relating a_T and v^f.[15,17] Further, the linear isobaric expansivities, α_L, were measured and the parameters of the Hartmann equation v^* and T^* also obtained from them. Then for each PU the two T^* values obtained by these two vastly different procedures were compared. The results are significant for PU properties, as well as from the point of view of applicability of the equations used.

Key Formulas. Specific volume, v, free volume, v^f, and the reduced volume, $\tilde{v}$, are related by

$$v = v^* + v^f \qquad (1)$$

$$\tilde{v} = v/v^* \qquad (2)$$

where v^* is the characteristic volume for a given equation of state, and each of these quantities can be given in, say, cubic centimeters per gram. Values of $\tilde{v}$ (and hence v^* and v^f) can be calculated from experimental v data; for some equations of state, v values in conjunction with the volumetric expansivities

$$\alpha = v^{-1}(\partial v/\partial T)_{P,\phi} \qquad (3)$$

are needed; ϕ denotes here a constant composition.

The Hartmann equation of state is[23–26]

$$\tilde{P}\tilde{v}^5 = \tilde{T}^{3/2} - \ln \tilde{v} \qquad (4)$$

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where

$$\tilde{P} = \tilde{P}/P^*; \quad \tilde{T} = T/T^* \tag{5}$$

P denotes pressure and T thermodynamic temperature, while P^* and T^* are, similar to v^*, characteristic parameters for a given material dependent on the choice of the equation of state. Since our α and v values pertain to the atmospheric pressure $P \approx 0.1$ J·cm^{-3}, dropping terms negligible in our case from eq 4, we get

$$\ln \tilde{v} = \tilde{T}^{3/2} \tag{6}$$

As derived by one of us,[15,17] a fairly general formula for the temperature shift factor, a_T, based on the Doolittle equation, is

$$\ln a_T = A + B/(\tilde{v} - 1) \tag{7}$$

Specific relations between a_T and temperature can be obtained from eq 7 by inserting a $\tilde{v}/T$ relation. An unusually simple one among these assumptions leads to the well-known Williams–Landel–Ferry equation. Many other choices are possible, and we have taken here the $\tilde{v}$ formula resulting from eq 6. Together eqs 6 and 7 enable the determination of parameters A and B in eq 7 by solving an overdetermined system of $a_T(T)$ equations. Another possibility is to fix B in advance, say, at 2.303, to the first or second power (the latter value results really from a historic mistake, but both were used with success). Then we need only to evaluate A. In other words, a single a_T value, if accurately determined, in conjunction with an equation of state enables prediction of the $a_T(T)$ relationship.

Experimental Section

Synthesis. The synthesis procedures for the polymers used in the present work have been reported,[5,6] but a brief description will be given here. All polymers originated from prepolymers made with poly(tetraethylene ether glycol) (PTMG; Teracol, E. I. du Pont de Nemours and Co., Wilmington, DE) as one reactant and either 2,4-toluenediyl diisocyanate (TDI; Mondur TDS, Mobay Chemical Co.) or 4,4′-methylenebis(phenylisocyanate) (MDI; Isonate 125M, Dow Chemical Co.) as the other reactant. The chemical structures of all the components used in this study are shown in Figure 1. PTMGs with respective molecular masses (M) of 650, 1000, and 2000 were used to prepare the starting prepolymers. It is this flexible PTMG section of the polymer that is referred to as the "soft segment" and the remainder of the structure (isocyanate and chain extender) as the "hard segment". The soft segment is characterized generally by a glass transition temperature below room temperature and crystallinity at molecular masses of 2000 and more. The hard segment seldom has a well-defined glass transition temperature but often has a crystalline phase that melts at higher temperatures. When the prepolymer chain is extended with a diol, the resulting polymer is a polyurethane (PU); when a diamine is the extender, a poly(urethaneurea) (PUU) is formed.

In general, the prepolymers were synthesized as follows: the particular PTMG was added with stirring to the diisocyanate under nitrogen and the addition controlled so that the reaction exotherm was not allowed to exceed 80 °C. The mixture was held at 75 °C for 1–2 h, after which the prepolymer was degassed, cooled, and sealed under nitrogen. The percent free isocyanate (NCO) was determined the following day by using ASTM method D1638. The prepolymers made from TDI and PTMG had a 2:1 molar ratio whereas those made from MDI and PTMG had a 3:1 ratio.

The TDI prepolymers were chain extended with trimethylene glycol bis(p-aminobenzoate) (TMAB, Polacure 740M, Polaroid Corp.), yielding PUUs, while the MDI prepolymers were extended with 2,2-dimethyl-1,3-propanediol (DMPD; Aldrich Chemical Co.), yielding PUs. The stoichiometry of the chain-extension reaction was adjusted so that an excess of isocyanate (105% isocyanate index) was present, which ensured cross-linking through either allophanate (DMPD) or biuret (TMAB) bond formation.

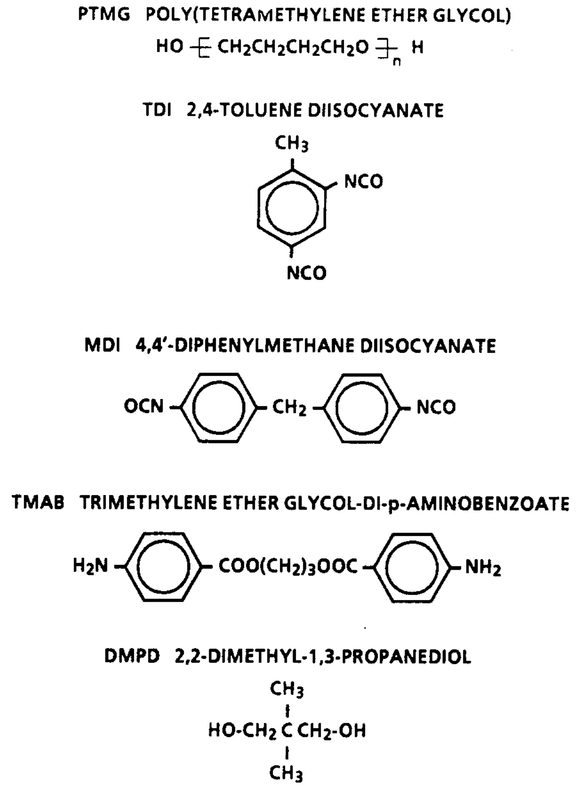

Figure 1. Chemical structures of building blocks for polyurethanes.

The PTMG/TDI/TMAB polymers were cast into molds (0.635 × 0.635 × 20 cm) for resonance specimens and cured at 100 °C for 5 h while the PTMG/MDI/DMPD specimens were cured at 120 °C overnight. The samples were allowed to equilibrate at ambient temperature for a period of at least 1 week prior to performing resonance, differential scanning calorimetry, or expansivity measurements.

Differential Scanning Calorimetry. A 910 differential scanning calorimeter (DSC) was used in conjunction with a 9900 thermal analyzer, both made by the Du Pont Co., Wilmington, DE. Programmed runs 10 °C/min were made from −170 to +250 °C in argon atmosphere. The resulting glass transition temperatures, T_g, of the soft segments are listed in Table I.

Expansivities and Specific Volumes. A 943 thermomechanical analyzer (TMA) connected to a 1090 thermal analyzer was used, both also manufactured by Du Pont. The expansivities of standard samples (Teflon, aluminum) with certificates of the National Bureau of Standards were determined first and found to agree well with already known reference data.

Results and Discussion

For each sample, weighing approximately 0.5 g, we have determined the linear isobaric expansivity

$$\alpha_L = L^{-1}(\partial L/\partial T)_{P,\phi} \tag{8}$$

where L is the specimen length, as a function of the temperature. With a Dewar flask attached and using liquid N_2, we made determinations at temperatures as low as −100 °C. Maximum temperatures were chosen so as to stop before expected glass transition in the samples could occur.

The quantity needed is the volumetric expansivity, α. By assuming that the temperature expansion along each of the Cartesian coordinates is the same, we obtain from

Table I
Temperature Ranges of Experimental Measurements

polymer	T_g, °C	T_m, °C	density, g/cm^3	dilatometer range, °C	dynamic mech range, °C
PTMG650/TDI2/TMAB	21		1.164	25–90	23–75
PTMG1000/TDI2/TMAB	−36		1.113	−34 to +57	−35 to +70
PTMG2000/TDI2/TMAB	−73	6	1.061	−90 to +93	−5 to +70
PTMG650/MDI3/DMPD	32		1.157	38–90	35–70
PTMG1000/MDI3/DMPD	6		1.123	10–85	9–70
PTMG2000/MDI3/DMPD	−40		1.074	−39 to +97	−35 to +70
PTMG650/MDI3/DMPD	32		1.157	−98 to +30	−60 to +30

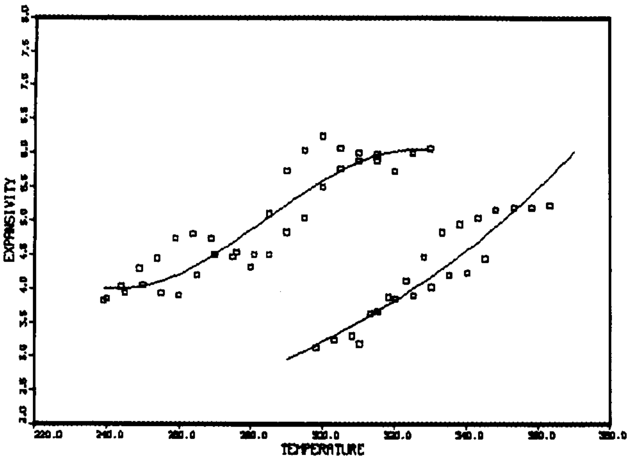

Figure 2. Isobaric expansivities, $\alpha \times 10^4$, as a function of T/K for PTMG1000/TDI2/TMAB (left curve) and PTMG650/TDI2/TMAB (right curve). Squares show experimental points; continuous curves calculated from eq 10.

eqs 3 and 8

$$\alpha = (1 + \alpha_L)^3 - 1 \qquad (9)$$

The experimental values of the three-dimensional expansivity so obtained were fitted to a simple polynomial

$$\alpha = a_0 + a_1 T + a_2 T^2 + a_3 T^3 \qquad (10)$$

Parameters in eq 10 were determined by a least-squares subroutine ZXSSQ from the International Mathematical and Statistical Library (IMSL, Houston, TX).

In general, the TMA technique produces values of limited accuracy; hence, three or four runs were made for each sample. No systematic errors were detected. A couple of curves are shown in Figure 2. There is a scatter of individual points; the average deviations between them and the calculated values are 4.9 and 4.3% for the left and the right curves, respectively. For other materials these deviations ranged between 3.4 and 8.1%. With several dozens of points obtained for each material, the ratios n/c of the number, n, of data points to the number of parameters ($c = 4$ for eq 10) were high in all cases. In other words, the least-squares procedure extracts the maximum amount of information contained in the experimental data set. Since ZXSSQ solves also overdetermined systems of nonlinear equations, it was used again in our subsequent calculations.

Given experimentally determined specific volumes at room temperature, v^{TROM}, typically TROM = 297 K, we have calculated specific volumes in the T range for which α_L were obtained by a simple increment algorithm

$$v(T + 1) = v(T) + \alpha(T) \qquad (11)$$

for $T >$ TROM and subtraction in a similar way for $T <$ TROM.

By using $v(T)$ values so obtained, eqs 6, 2, and 5, and calling the ZXSSQ subroutine again, we obtained v^* and T^* values for each material. These values are listed in Table II. It turned out during the calculations that the v^* and T^* parameters of the Hartmann equation are fairly insensitive to the details of the $\alpha(T)$ curve. In one computation run for PTMG2000/TDI2/TMAB some 16 low-temperature data points were omitted, but $v^* = 0.8412$ cm^3·g^{-1} and $T^* = 1277$ K were obtained, fairly close to the values listed in Table II. Similarly, a small change in v^* and T^* was found for PTMG1000/MDI3/DMPD, when a computation run with only a subset of the existing data points was made.

Subsequently, taking the v^* and T^* values just obtained, we inverted the use of eq 6 so as to compute specific volumes, v. Finally, we compared these computed values with the specific volume data derived from the experiment via eq 11. The average deviations for individual materials varied between 0.038 and 0.064%.

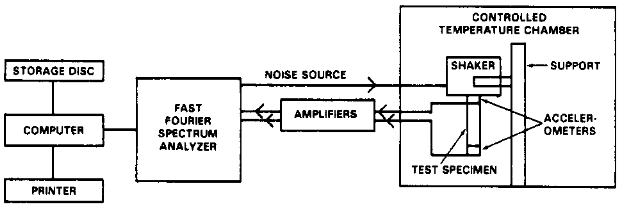

Figure 3. Schematic of the resonance apparatus for the determination of dynamic mechanical data.

Table II
Reducing Parameters for Polyurethanes

	M	v^*, cm^3/g	T^*, K	T^*, K
From the Data in the Rubbery State Only				
PTMG*/TDI2/TMAB	650	0.7829	1461	1383
	1000	0.8024	1265	1417
	2000	0.8474	1330	1092
PTMG*/MDI3/DMPD	650	0.7818	1394	1834
	1000	0.8132	1472	1388
	2000	0.8273	1233	1031
From the Data in the Glassy State Only				
PTMG650/MDI3/DMPD		0.8146	1944	2262

Dynamic Mechanical Testing. The dynamic mechanical apparatus used is based on production of the resonance in a bar specimen.[27] Typical length of a specimen is 10–15 cm with square lateral dimensions of 0.635 cm. In brief, measurements are made over 1 decade of frequency in the kilohertz region from −60 to +70 °C at 5 °C intervals. By applying the time–temperature superposition principle, the raw data are shifted to generate a reduced frequency plot (over as many as 20 decades of frequency) at a constant reference temperature. As shown in Figure 3, an electromagnetic shaker is used to drive a test specimen at one end while the other end is allowed to move freely. Miniature accelerometers are adhesively bonded on each end to measure the driving point acceleration and the acceleration of the free end. The output signals from the accelerometers are amplified and routed to a dual-channel fast Fourier transform spectrum analyzer. The analyzer digitizes and displays the measured signals. The signals (amplitude and phase of the acceleration ratio) can be measured over a frequency range of 3 decades (25–25 000 Hz).

At certain frequencies, the amplitude of the acceleration ratio goes through local resonant peaks. The number of resonant peaks that can be measured is dependent on the loss factor of the material, but, typically, there are three to five peaks. As expected, the resonant peaks appear at higher frequencies in the glassy state than in the rubbery state. From the peak amplitude and frequency of each measured resonant peak, Young's modulus and loss factor are determined at the corresponding frequency and temperature.

When measurements over a temperature range of −60 to +70 °C were made, the following thermal cycle was used: (1) cool the test specimen, which has been mounted in the test apparatus, to −60 °C; (2) allow the specimen to equilibrate at −60 °C for at least 12 h before making a measurement; (3) after each measurement, raise the temperature by 5 K; (4) allow 20 min to elapse between each change in temperature to obtain thermal equilibrium before making the next measurement; (5) measurement is completed at 70 °C.

Modulus and loss factor data were processed into a reduced-frequency plot in the following manner: modulus curves at different temperatures were shifted along the frequency axis until they partially overlapped to obtain a best fit, minimizing the sum of the squares to a second-order equation (in logarithm of the modulus) between two sets of modulus data at different temperatures. This procedure was accomplished by a computer program. A reference temperature was selected near the glass transition, where the modulus is changing rapidly with frequency. The amount of shift for a given set of data at one temperature along the logarithmic frequency axis—so as to overlap with another set of data at a different temperature—is represented by log a_T. The modulus was chosen to be shifted because it is measured more accurately and has less scatter than the loss factor. The final result is a constant-temperature plot or a master curve over a range of frequencies wider than actually measured at any temperature.

When the data are represented by an equation, it is important to be aware of the transitions in these polymers. In particular, dynamic mechanical time–temperature superposition has been found not to be valid when soft-segment crytallinity is present. (Due to the kinetics involved, the results are time dependent.) This fact has limited the molecular mass of the polyurethanes used to no higher than 2000. For molecular mass of 2900, soft-segment crytallinity is observed and dynamic mechanical shifting is not valid. In only one case of PTMG650/MDI3/DMPD was it possible to obtain consistent data above and below T_g; these data were treated as if they came from two different polymers: rubbery state and glassy state.

The range of temperatures covered in the experimental measurements is dependent on the equipment and the polymer. In all cases, the upper limit of the dynamic mechanical measurements is 70 °C, being set by the highest temperature that the shaker can stand. The lowest temperature measurable is −60 °C, being set by the environmental chamber used. In some cases, the usable range of temperatures is less than the total range measured due to the presence of transitions. An effort was made to use expansivity and resonance measurements over approximately the same range of temperature. The ranges used are given in Table I.

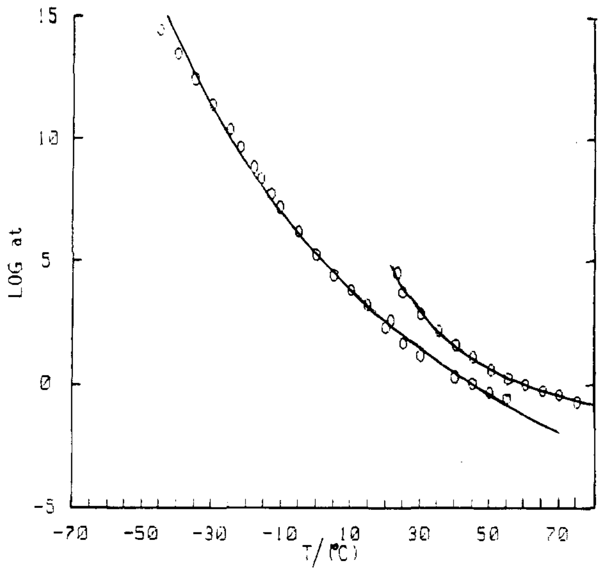

Figure 4. Logarithmic a_T values as a function of T/°C for PTMG1000/TDI2/TMAB (left curve) and PTMG650/TDI2/TMAB (right curve). Circles show experimental points; continuous curves calculated from eq 12.

Substituting eq 6 into eq 7, we obtain

$$\ln a_T = A + B/[\exp((T/T^*)^{3/2}) - 1] \qquad (12)$$

Fixing a value of B in advance, as indicated earlier, namely, $B = \ln 10$, we solved for each material on overdetermined system of eq 12 in two unknowns, A and T^*, using again ZXSSQ. The resulting values of T^*, labeled T^*_f to distinguish them from those from expansivities, are listed in Table II. For a couple of materials (the same as in Figure 2) experimental and calculated values of decadic log a_T as a function of temperature are shown in Figure 4.

Conclusions

Inspection of Table II shows that there is an agreement between T^* and T^*_f, this in spite of so vastly different procedures used to obtain them. We note that the Hartmann equation of state was also used with success when dealing with temperature dependence of electric conductivity of a polymer;[28] the Walden rule provided in this case a connection between v^f and the electric conductivity. The agreement we have found between T^* and T^*_f values means that several things must have happened simultaneously:

(1) The experimental values of linear isobaric expansivity lead via volumetric expansivities to fairly accurate specific volumes.

(2) The experimental acoustic resonance results are fairly accurate, and satisfactory temperature shift factors have been obtained from them.

(3) The Hartmann equation of state, eq 6, provides satisfactory description, as well as prediction capability, of the temperature dependence of specific volumes of polyurethanes.

(4) The relation, eq 7, between the temperature shift factor, a_T, and the reduced volume, $\tilde{v}$, derived by one of us[15,17] produces reliable results.

(5) Equation 12, resulting from simultaneous use of eqs 6 and 7, gives a satisfactory description of $a_T(T)$ results for all polyurethanes studied.

The last conclusion opens interesting possibilities, briefly mentioned above when discussing eq 7. Assume we have at our disposal experimental volumetric data: $v(T)$, or else $\alpha(T)$ plus one value of v. We then solve eq 6 for

v^* and T^*. Moreover, we perform one determination of a_T. With B fixed, we solve eq 12 for one unknown only, that is, A. Then eq 12 enables the computation of a_T for arbitrary temperatures.

We also find in Table II that in each PU series v^* goes symbatically with the molecular weight M or more accurately with the length of the soft segment. That growth is faster for the series of poly(urethaneureas) when the diamine TMAB is the extender and slower for the PU series with the DMPD diol. T^* decreases with increasing M, this at comparable rates in both series. Since T^* represents an average measure of the strength of intersegmental interactions, clearly longer soft segments weaken these interactions. This weakening is reflected also in the glass transition temperatures of the soft-segment regions listed in Table I: an increase in M lowers T_g, with the rate somewhat higher in the TMAB series. These results might be helpful for choosing appropriate soft/hard sequence ratios for polyurethane materials aimed at specific applications.

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Registry No. (PTMG650)(TDI2)(TMAB) (block copolymer), 115218-56-9; (PTMG650)(MDI3)(DMPD) (block copolymer), 121509-72-6.