NSWC/WOL TR 78-195

MEASUREMENT OF THERMOPHYSICAL PROPERTIES OF EPOXY/DIAMINE POLYMERS AND ASSOCIATED ADDITIVE PROPERTIES

BY   GILBERT F. LEE

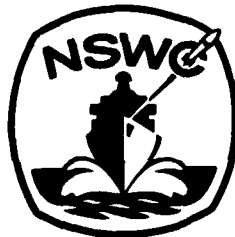RESEARCH AND TECHNOLOGY DEPARTMENT

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Coefficient of Thermal Expansion	Atomic Increments
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The coefficient of linear thermal expansion and specific heat capacity of several epoxy/diamine polymers were determined as a function of temperature (-160 to 190°C). The epoxies in this study are: diglycidyl ether of bisphenol A, resorcinol diglycidyl ether, and butanediol diglycidyl ether. The diamines are: propanediamine, hexanediamine, dodecanediamine, and metaphenylanediamine. The values of the thermal expansion range from a low of 2.51×10^{-5} °C-1 at

20. (Cont.)

$-170^\circ C$ to a high of $21.8 \times 10^{-5} \,^\circ C^{-1}$ at $15^\circ C$. The values of specific heat capacity range from a low of 0.10 cal/g-$^\circ C$ at $-8^\circ C$ to a high of 0.79 cal/g-$^\circ C$ at $190^\circ C$.

The density, coefficient of cubic thermal expansion, and molar heat capacity were predicted using the method of additive parameters at $25^\circ C$. The method predicts the correct structure to property (density and thermal expansion) relationship. Van Krevelen's method predicts lower densities than the measured values (experimental densities were obtained from another study) with a 5 to 10 percent error. Sewell's method predicts densities approximately 1 to 7 percent also lower than the experimental values. The thermal expansion predictions are 16 to 69 percent lower than the measured values. The method of additive parameters has been demonstrated to give a fair estimate of density, coefficient of thermal expansions, and heat capacity of epoxy/diamine polymers.

SUMMARY

This report describes work done on several epoxy/diamine polymers. The goal of this work was to determine the coefficient of thermal expansion, specific heat capacity, and the structure to property relationship. Also the density, coefficient of thermal expansion, and heat capacity were predicted using the method of additive parameters. A comparison between the experimental and predicted properties was made to determine the accuracy of this method.

This work was carried out during FY 78 with funds provided IR funding Task Number 171, Polymer Science.

J. R. DIXON
By direction

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INTRODUCTION

The goal of this work is to determine the structure to property relationships of several epoxy/diamine polymers. In a recent technical report,[1] the dynamic mechanical and ultrasonic properties of these polymers have been investigated. Thus the purpose of this work is to further characterize the epoxy/diamine polymers by determining the coefficient of linear thermal expansion and specific heat capacity.

In the present literature[2-4] the density, coefficient of cubic thermal expansion, molar heat capacity, and many other properties have been determined from the principle of additive parameters associated with the constituent groups of linear polymers. It is the intention of this study to predict the density, coefficient of cubic thermal expansion, and molar heat capacity of the epoxy/ diamine polymers by applying the principle of additive parameters. Then a comparison is made between the measured and calculated properties to determine the accuracy of the method.

EXPERIMENTAL

Material. The following epoxies: 2, 2-bis p-(2, 3-epoxypropoxy) phenyl-propane, commonly known as diglycidyl ether of bisphenol A (DGEBA), m-bis (2, 3-epoxypropoxy) benzene or resorcinol diglycidyl ether (RDGE), and 1, 4-bis (2, 3-epoxypropoxy)- butane or butanediol diglycidyl ether (BDGE) were cured with the following diamines: 1, 3-propanediamine (PDA), 1, 6-hexanediamine (HDA), 1, 12-dodecanediamine (DDA), and m-phenylenediamine (MPDA). The chemical structures of these monomers are listed in Table 1. The preparations and physical properties of the epoxy and diamines monomers including the synthesis of the polymer have already been reported.[5]

1. Lee, G. F., "Torsional Pendulum Study on Several Epoxy/Diamine Polymers," NSWC/WOL TR 77-162, October (1977).

2. Van Krevelan, D. W., Properties of Polymers Correlations with Chemical Structure, American Elsevier Publishing Co. Inc., 1972, p. 41-76.

3. Sewell, J. H. and B. Stagg, "Calculation of the Coefficients of Cubical Expansion of Linear Polymers," Royal Aircraft Establishment TR 7168, August (1971).

4. Sewell J. H., "A Method of Calculating Densities of Polymers," J. Appl, Polym. Sci., 17, 1741 (1973).

5. Booth H. J., "Synthesis of Epoxy Resins for Property-Structure Studies," NOLTR 73-112, July (1973).

Thermal Expansion Apparatus. The linear thermal expansion apparatus is manufactured by E. I. Du Pont De Nemours and Co. (Inc), Instrument Products Division. The apparatus consists of a recorder-temperature controller (990 Thermal Analyzer) and an attachment module (943 Thermomechanical Analyzer). The purpose of the module is to measure the linear diminsional changes L of the test polymer as a function of temperature T and the recorder plots a curve of L versus T. Measurements were made from $-170^{\circ}C$ to the glass transition temperature T_g of the polymer. Liquid nitrogen is used to cool the test polymer to subambient temperatures. The heating rate is $0.5^{\circ}C$ per minute. The dimensions of the test polymers are in the shape of cylinders 0.635 centimeters (diameter) and 1.27 centimeters (length). At temperatures near T_g, the polymer began to creep (decreasing in length) making the expansion measurement inaccurate. The cause for this creep was probably due to the nature of the experimental apparatus. One part of the apparatus, the expansion probe is placed in contact with the polymer. The dimensional changes of the polymer are followed by the probe. Due to this contact a small stress of approximately 790 dynes/cm^2 is exerted by the probe causing the test sample to creep. The dimensional changes due to creep at temperatures below T_g should be small but large near and above T_g. This phenomenon has been observed.[6]

Differential Scanning Calorimeter. The differential scanning calorimeter DSC is also manufactured by E. I. Du Pont De Nemours and Co. (Inc), Instrument Products Division. The apparatus consists of a recorder-temperature controller which is the same used in the thermal expansion measurement but with a different attachment module (990 Cell Base with a Differential Scanning Calorimeter Cell). Measurements were made from $-170^{\circ}C$ to $200^{\circ}C$. Liquid nitrogen is used to cool the test polymer and cell to subambient temperatures. The heating rate is $10^{\circ}C$ per minute. Nitrogen gas is used to purge the cell at a flow rate of 90 ml/min. Approximately 10 to 18 mg of test polymer is used. The apparatus is standarized with sapphire, because the specific heat is known,[7] over the desired temperature range.

THEORY

Thermal Expansion Measurements. The expression for the coefficient of linear thermal expansion β_L is

$$\beta = \frac{1}{L_o} \frac{dL}{dT} \qquad {}^{\circ}C^{-1} \qquad (1)$$

6. Nielsen, L. E., Mechanical Properties of Polymers and Composites, Marcel Dekker, Inc., New York, 1976, vol. 1, p. 87.

7. Ginnings, D. C. and Furukawa, G. T., "Heat Capacity Standards for the Range 14 to 1200°K," J. Am. Chem. Soc., 75, 522 (1953).

where L_o (cm) is the length dimension of the test polymer at temperature T and dL/dT is the slope of the linear dimension versus temperature plot. A method of least squares[8] is used to determine the slope. The coefficient of cubic thermal expansion α is expressed as

$$\alpha = 3\beta \qquad ^oC^{-1} \tag{2}$$

Differential Scanning Calorimeter Measurements. By calibrating the DSC with sapphire it is now possible to determine the specific heat capacity of new materials from the expression

$$C_p = \frac{m'}{m} \frac{D}{D'} \quad C_p' \qquad Cal/g^oC \tag{3}$$

where m (g) is the mass of material, D (cm) is the deflection of the pen from the baseline, and C_p (cal/g^{o}C) is the specific heat capacity. The primed quantities represent sapphire and the unprimed quantities refer to the polymer.

Density Calculations. There are two methods to determine the density from the chemical structure of a polymer. They are describe in Van Krevelen[2] and Sewell.[4] Thus only a brief description of each method is given in this section.

Van Krevelen's method applies the concept of group increment. A group is considered to be a mono-, bi-, tri-, or tetravalent chemical entity with nearest neighbors, for example, a hydroxide group -OH, a bisubstituted methane $-CH_2-$, a trisubstituted methane $-CH-$, and a tetrasubstituted methane$-C-$. There are many other groups which are listed in Van Krevelen. To determine the density of a polymer the following expressions are used. The molar volume V of a polymer repeat unit is determine by applying the expression

$$V = \sum_{j=1}^{n} a_j V_j \qquad cm^3/mol \tag{4}$$

where a_j is the number of group j in the repeat unit and V_j (cm^3/mol) is the molar volume of the group j. Then the density ρ is

$$\rho = MW/V_v \qquad g/cm^3 \tag{5}$$

8. Wylie, Jr., C. R., Advanced Engineering Mathmatics, McGraw-Hill Book Co, 1960, 3rd ed., p. 126-136.

where MW (g/mol) is the molecular weight of the repeat unit. The repeat unit
of the epoxy/diamine polymers is assumed to be a 100 percent or an infinitely
crosslinked polymer. This assumption keeps the repeat unit simple. A schematic
representation of the repeat unit of polymer DGEBA and MPDA is given below:

DGEBA

MPDA   DGEBA   MPDA   DGEBA

DGEBA   Repeat Unit

MPDA
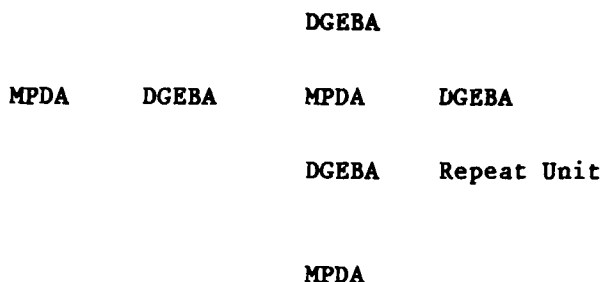
Sewell's method applies the concept of atomic and structural increments.
An atomic increment is for example a carbon atom, a hydrogen atom, or an oxygen
atom. A structural or bond increment is for example a double bond, a six membered
ring, or an ester. Other atomic and structural increments are discussed in Sewell.
To determine the density of a polymer the following expressions are used. The
molar volume V_v of the polymer repeat unit is

$$V_v = 2.966 + \sum_{j=1}^{n} a_j P_j \qquad cm^3/mol) \qquad (6)$$

where a_j is the number of atomic or structural increments and P_j (cm^3/mol)
is parachor contributions of the atomic and structural increments. Values of
P_j are found in Sewell. Thus the density ρ is obtained from equation 5.

The disadvantage of the group increment method is that if a polymer contains
a new group which is not present in Van Krevelen's group list then, for this study,
the new group is considered to be equivalent to an existing group in the list.
For instance, a trisubtituted nitrogen $-\overset{|}{N}-$ is assumed to be equivalent to a bisub-
stituted oxygen $-O-$. But the atomic and structural increment method does not have
this problem therefore this method is applicable to polymers with unusual groups.
However the atomic and structural increment method does not take into account
the effect of nearest neighbors, meaning an atomic increment has a different molar
volume with different nearest neighbors. This effect is discussed in detail in
Van Krevelen and Hoftyzer.[9] These disadvantages may cause errors in predicting
densities of polymers. Sample calculations of Van Krevelen's method are demon-
strated in the Appendix for polymer DGEBA and MPDA.

9. Van Krevelen, D. W. and Hoftyzer, P. J., "Prediction of Polymer Density,"
    J. Appl. Polym. Sci., 13, 871 (1969).

<u>Thermal Expansion Calculation</u>. The method to determine the thermal expansion coefficient is decribed in Sewell.[3] The coefficient of cubic thermal expansion α is expressed as

$$\alpha = \sum_{j=1}^{n} a_j V_j \beta_j \Bigg/ \sum_{j=1}^{n} a_j V_j \qquad {}^{\circ}C^{-1} \tag{7}$$

where β_j is the additive coefficient expansion parameter of group increment j. Two group increments are s not available in the results of Sewell. Thus two assumptions are made. First, a trisubstituted nitrogen group is equivalent to a bisubstituted oxygen group and second, a metasubstituted phenyl group is equivalent to a parasubstituted group. A sample calculation for polymer DGEBA and MPDA is presented in the Appendix.

<u>Heat Capacity Calculations</u>. The method to determine the heat capacity is described in Van Krevelen.[2] The molar heat capacity C_p is expressed as

$$C_p = \sum_{j=1}^{n} a_j C_{pj} \qquad cal/mol-{}^{\circ}C \tag{8}$$

where C_{pj} the molar heat capacity of group increment j. One assumption is made; a metasubstituted phenyl group is equivalent to a parasubstituted phenyl group.

RESULTS AND DISCUSSIONS

<u>Density Results</u>. The densities for the twelve epoxy/diamine polymers at $25^{\circ}C$ are tabulated in Table 2. For polymers of DGEBA the measured or experimental densities range from a low of 1.1255 g/cm^3 to a high of 1.2033 g/cm^3. The density decreases with a decrease in aromaticity of the diamine monomer and an increase in the aliphatic chain length of the diamine monomer. The trend of the measured densities is MPDA > DDA > HDA > DDA. Van Krevelen's method predicts densities in the correct trend but the values are approximately 5 to 6% lower than the measured values. The predicted or calculated densities range from 1.0726 g/cm^3 to 1.1327. Sewell's method also predicts the correct trend but the values are approximately 1 to 3 percent lower than the measured values. The calculated densities range from a 1.1121 g/cm^3 to 1.2151 g/cm^3.

For polymers of RDGE and BDGE the trend of the measured densities is also MPDA > PDA > HDA > DDA. Again Van Krevelen's method predicts densities in the correct trend and lower values than the measured densities, approximately 6 to 8 percent for polymers of RDGE and 5 to 10 percent for polymers of BDGE. Similary, Sewell's method predicts the correct trend and also lower than the measured values, approximately 3 to 7 percent for polymers of RDGE and 1 to 6 percent for polymers of BDGE.

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Overall both methods predicts the correct trend where Van Krevelen's method predicts low densities, with a 5 to 10 percent error, while Sewell's method predicts low densities, with a 1 to 7 percent error.

Thermal Expansion Results. A typical plot of the linear dimensional change versus temperature for polymer RDGE + HDA is presented in Figure 1. The linear dimension of the test sample increases with increasing temperature. Also the slope of the curve is greater at high temperatures than at low temperatures. From this data the coefficient of linear thermal expansion versus temperature is determined and is presented in Figure 2. There is some scatter in the data. One cause is due to the nature of the apparatus. The measuring probe is not only sensitive to the dimensional changes of the test polymer but to the vibrations of the surroundings producing false readings, and nonsystematic errors. Another cause is due to the errors in digitizing the linear dimension versus temperature plot, leading to random errors. The coefficient of linear thermal expansion increases slowly at subambient temperatures, from 2.51×10^{-5} $^{o}C^{-1}$ at $-170^{o}C$ to 5.49×10^{-5} $^{o}C^{-1}$ at $25^{o}C$. Above $25^{o}C$ the thermal expansion increases rapidly to 11.4×10^{-5} $^{o}C^{-1}$ at $60^{o}C$.

The coefficient of linear thermal expansion results are tabulated as a function of temperature in Table 3 for polymers of RDGE, Table 4 for polymers of DGEBA, and Table 5 for polymers of BDGE. The coefficient of thermal expansion varies with the aromaticity and the aliphatic chain length of both the epoxy and diamine monomers. Epoxies cured with the aromatic diamine MPDA have lower coefficient of thermal expansion values than epoxies cured with aliphatic diamines PDA, HDA, and DDA. Epoxies cured with short chain diamines PDA and HDA have similar coefficient of thermal expansion values, except for the polymer of DGEBA and PDA has smaller value than DGEBA and HDA. Diamines reacted with aromatic epoxies RDGE and DGEBA have lower coefficient of thermal expansion values than diamines cured with the aliphatic epoxy BDGE. These results indicate that the coefficient of thermal expansion is dependent on the rigidity of the polymer network. Rigid polymer networks (or polymers with a high crosslinked density) are obtained with aromatic monomers thus leading to low coefficient of thermal expansion.

The method of additive parameters predicts a coefficient of cubic thermal expansion at $25^{o}C$. Thus the measured linear values are converted to cubic values. The experimental and predicted coefficient of cubic thermal expansion are listed in Table 6. For the polymers of DGEBA the measured thermal expansion range from 16.66×10^{-5} $^{o}C^{-1}$ to 23.34×10^{-5} $^{o}C^{-1}$ with a trend of MPDA > PDA > HDA > DDA. The calculated values are in the correct trend but they are approximately 16 to 34 percent smaller than the measured values. The predicted values range from 11.48×10^{-5} $^{o}C^{-1}$ to 19.54×10^{-5} $^{o}C^{-1}$. For the polymers of RDGE the measured thermal expansion values range from 14.4×10^{-5} $^{o}C^{-1}$ to 22.14×10^{-5} $^{o}C^{-1}$. Again the predicted trend is the same as the polymers of DGEBA. The calculated values are in the correct trend but again they are about 13 to 69 percent lower than the measured values. The calculated values range from 4.44×10^{-5} $^{o}C^{-1}$ to 16.99×10^{-5} $^{o}C^{-1}$. The thermal expansion and heat capacity for polymers of BDGE cured with aliphatic diamines can not be predicted since the additive parameter data applies only to glassy polymers and the aliphatic diamine cured BDGE polymers are rubbers at $25^{o}C$. The measured value is 65.4×10^{-5} $^{o}C^{-1}$ for polymer BDGE and MPDA and predicted value is 10.16×10^{-5} $^{o}C^{-1}$ which is about a 84 percent difference.

Heat Capacity Results. The specific heat capacity as function of temperature results for polymers of DGEBA, RDGE, and BDGE are presented in Table 7, 8, and 9, respectively. The specific heat capacity results vary from 0.1 cal/g-$^{\circ}$C at -80°C to 0.84 cal/g-$^{\circ}$C at 190°C. A typical example of a plot of specific heat capacity versus temperature for polymers of DGEBA is presented in Figure 3. The specific heat capacity increases with temperature. The glass transition of a polymer is represented by the midpoint on the curve with the steepest slope. For instance, the glass transition temperature for the polymer of DGEBA and MPDA is approximately 93°C. Table 10 lists the glass transition temperatures for the other polymers.

The method of additive parameters predicts a molar heat capacity at 25°C. Thus, the specific heat capacity divided by the molecular weight of the polymer repeat unit is the molar heat capacity. The measured and calculated molar heat capacity at 25°C are listed in Table 10. For polymers of DGEBA the measured heat capacity results range from 208 to 336 cal/mol-$^{\circ}$C. The trend is PDA > MPDA > HDA > DDA. The heat capacity increases with an increase in the aliphatic chain length of the diamine monomers. The calculated values are in the correct trend but for MPDA and DDA they are approximately 1 to 16 percent larger than the measured values. However, the calculated values for PDA and HDA are approximately 1 to 10 percent smaller than the measured values. For polymers of RDGE the measured heat capacity results range from 112 to 236 cal/mol $^{\circ}$C. The trend is PDA > HDA > MPDA > DDA. However, the calculated values do not follow this trend, for the calculated values of HDA and MPDA are in reversed order. Also they are 7 to 42 percent smaller than the experimental values. The trend of calculated heat capacity results for polymers of RDGE is similar to polymers of DGEBA. For polymers of BDGE the measured values range from 189 to 401 cal/mol-$^{\circ}$C with the following trend MPDA > PDA > HDA > DDA. The predicted values range from 170 to 224 cal/mol-$^{\circ}$C, approximately 9 to 46 percent smaller than the experimental values. The calculated trend is PDA > MPDA > HDA > DDA, where the order of PDA and MPDA is reversed compare to the measured trend.

CONCLUSIONS

The method of additive parameters predicts the correct structure to property (density and thermal expansion) relationship. An epoxy cured with an aromatic diamine has a higher density and thermal expanison than the same epoxy cured with an aliphatic diamine. The same holds true for aromatic and aliphatic epoxies. The method also predicts density and thermal expansion to decrease with an increase in the aliphatic chain length. Van Krevelen's method predicts lower densities than the measured values with a 5 to 10 percent error. Sewell's method predicts densities approximately 1 to 7 percent also lower than the experimental values.

Thermal expansion values are predicted for nine of the twelve polymers, because three of them are rubbers at 25°C. The thermal expansion predictions are 16 to 69 percent lower than the measured values. Molar heat capacity values are also predicted for the nine glassy polymers and of that nine, six calculated values are 1 to 28 percent greater than the measured values and the remaining three are about 2 to 42 percent lower than the measured values.

The measured heat capacity results increase with an increase in aliphatic chain length of the diamine monomers, however, the results are not consistent

in order to ascertain a trend between aromatic and aliphatic diamines. However, the predicted trend is PDA $\geq$ MPDA > HDA > DDA. Whether this trend is true or a manifestation of the method it is not known at this time. A percent error of 1 to 42% exists between the measured and calculated C_p.

The method of additive parameters has been demonstrated to give a fair estimate of density, coefficient of thermal expansion, and heat capacity of epoxy/diamine polymers. The method can be improved by adding new polymers to the polymer list of Van Krevelen and Sewell and then deriving numericals for each new chemical group. In the future the following additive properties will be investigated electrical (dielectric polarization), mechanical (bulk modulus), and thermophysical (glass transition) for these crosslinked polymers.
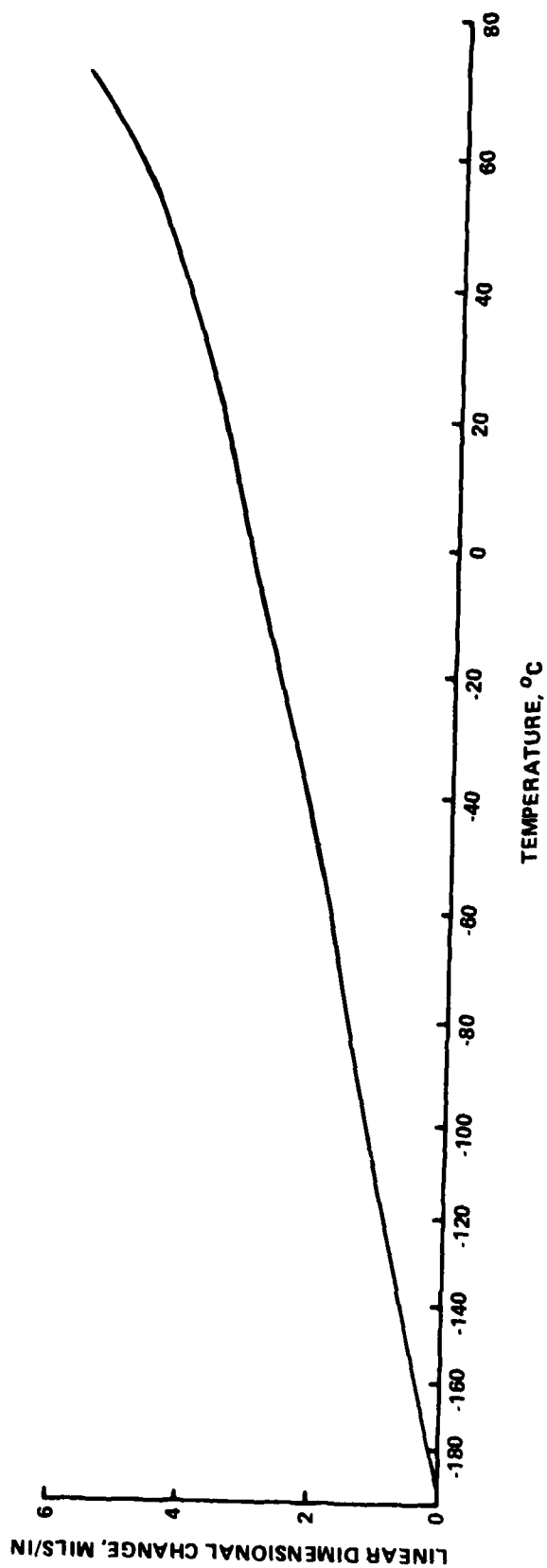
FIGURE 1   LINEAR DIMENSIONAL CHANGES VS TEMPERATURE FOR POLYMER OF RDGE AND HDA

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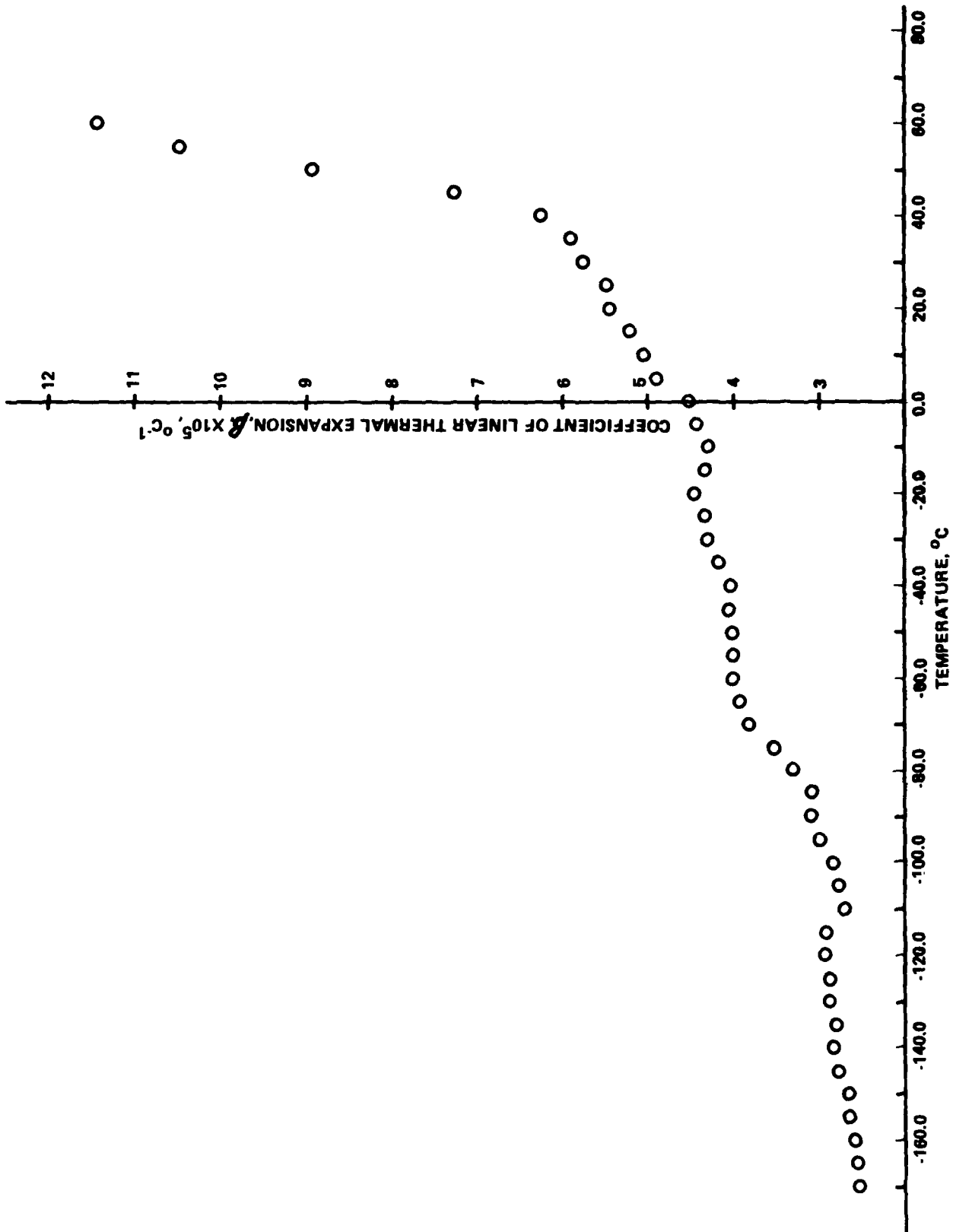
FIGURE 2 COEFFICIENT OF LINEAR THERMAL EXPANSION VS TEMPERATURE FOR POLYMER RDGE AND HDA
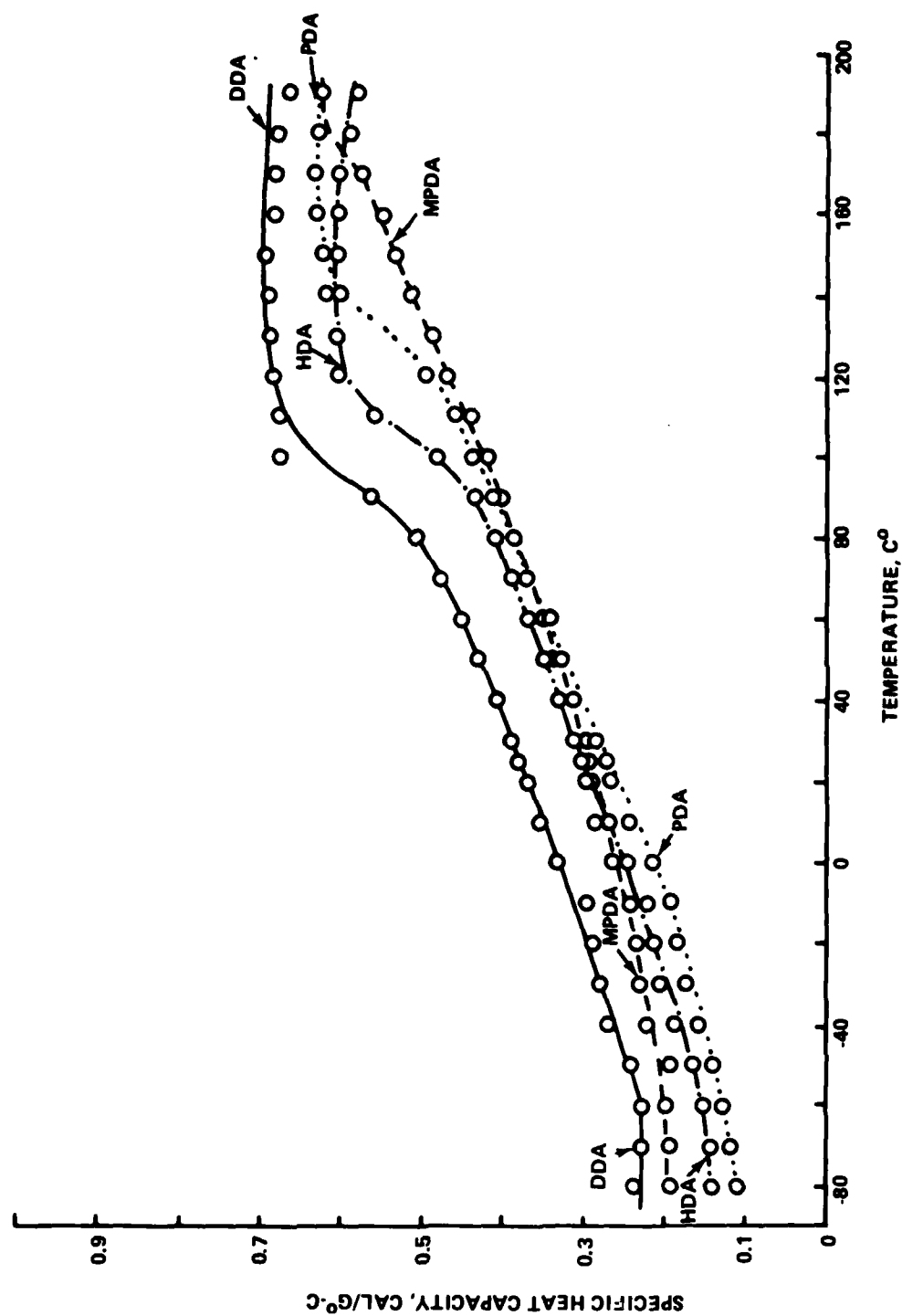
FIGURE 3 SPECIFIC HEAT CAPACITY VS TEMPERATURE FOR POLYMERS OF DGEBA

Table 1

Structures of the Epoxy and Diamine Monomers

Resorcinol Diglycidyl Ether (RDGE)
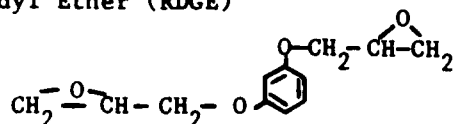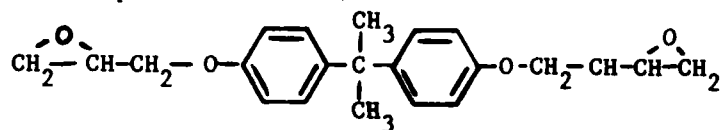
$$CH_2 - O - CH - CH_2 - O \quad O - CH_2 - CH - CH_2 \quad (O)$$

Diglycidyl Ether of Bisphenol A (DGEBA)

$$CH_2 - CH - CH_2 - O \quad C \quad O - CH_2 - CH - CH_2 \quad CH_3 \quad CH_3$$

1,4-Butanediol Diglycidyl Ether (BDGE)

$$CH_2 - CH - CH_2 - O - CH_2 - CH_2 - CH_2 - CH_2 - O - CH_2 - CH - CH_2$$

1,3-Propanediamine (PDA)

$$H_2N - (CH_2)_3 - NH_2$$

1,6 - Hexanediamine (HDA)

$$H_2N - (CH_2)_6 - NH_2$$

1,12 - Dodecanediamine (DDA)

$$H_2N - (CH_2)_{12} - NH_2$$

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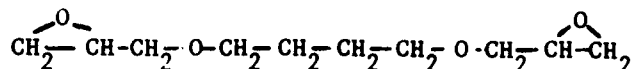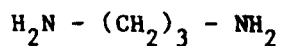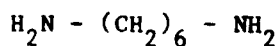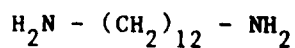
Table 1 (Cont'd)

m-Phenylenediamine (MPDA)
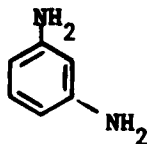
Table 2   Densities of the Epoxy/Diamine Polymers at 25°C

		Measured (g/cm^3) Booth[5]	Calculated (g/cm^3) Van Krevelen[2]	Sewell[4]
DGEBA +	DDA	1.1255	1.0726	1.1121
	HDA	1.1595	1.0975	1.1353
	PDA	1.1844	1.1125	1.1442
	MPDA	1.2033	1.1327	1.1629
RDGE +	DDA	1.1667	1.1016	1.1339
	HDA	1.2299	1.1440	1.1720
	PDA	1.2711	1.1721	1.1970
	MPDA	1.3023	1.2003	1.2151
BDGE +	DDA	1.0942	1.0241	1.0884
	HDA	1.1519	1.0588	1.1187
	PDA	1.1741	1.0821	1.1388
	MPDA	1.2274	1.1235	1.1604

Table 3   Coefficient of Linear Thermal Expansion Versus
Temperature for Polymers of RDGE

COEFFICIENT OF LINEAR THERMAL EXPANSION, $\beta \times 10^5$, $^{\circ}C^{-1}$

Temperature $^{\circ}C$	PDA	HDA	DDA	MPDA
-180.0				
-175.0				
-170.0	2.51			
-165.0	2.55			
-160.0	2.61	2.59	2.99	2.17
-155.0	3.01	2.65	3.42	2.48
-150.0	3.09	2.65	3.66	2.60
-145.0	3.37	2.77	3.74	2.73
-140.0	3.57	2.83	3.73	2.71
-135.0	3.57	2.81	3.85	2.70
-130.0	3.53	2.89	3.81	2.64
-125.0	3.25	2.89	3.77	2.64
-120.0	3.29	2.95	3.89	2.72
-115.0	3.44	2.93	3.97	2.64
-110.0	3.40	2.71	4.25	2.56
-105.0	3.40	2.79	4.24	2.52
-100.0	3.24	2.84	4.40	2.62
-95.0	3.04	3.03	4.48	3.07
-90.0	3.16	3.11	4.36	2.98
-85.0	3.36	3.10	4.52	2.82
-80.0	3.48	3.30	4.91	2.90
-75.0	3.68	3.55	5.07	2.94
-70.0	3.51	3.83	5.03	3.41
-65.0	3.31	3.95	4.91	3.53
-60.0	3.23	4.02	4.98	3.65
-55.0	3.35	4.02	5.22	3.92
-50.0	3.47	4.02	5.34	3.96
-45.0	3.51	4.06	5.45	3.97
-40.0	3.51	4.04	5.73	3.99
-35.0	3.43	4.18	5.96	3.99
-30.0	3.58	4.32	5.92	4.07
-25.0	3.82	4.33	6.12	4.03
-20.0	3.94	4.45	6.35	4.05
-15.0	3.86	4.33	6.54	4.07
-10.0	3.86	4.29	6.70	4.08
-5.0	3.93	4.43	6.57	4.10
-0.0	4.25	4.52	6.93	4.06
5.0	4.81	4.90	7.04	4.26
10.0	4.92	5.04	6.80	4.48
15.0	5.08	5.22	6.79	4.62

Table 3   Coefficient of Linear Thermal Expansion Versus
Temperature for Polymers of RDGE (Cont'd)

Temperature ^oC	COEFFICIENT OF LINEAR THERMAL EXPANSION, $\beta \times 10^5$, $^oC^{-1}$			
	PDA	HDA	DDA	MPDA
20.0	5.51	5.45	6.95	4.76
25.0	5.75	5.49	7.38	4.80
30.0	6.10	5.77	7.72	4.78
35.0	6.18	5.90	7.99	4.70
40.0	6.29	6.26	8.66	4.67
45.0	6.88	7.27		4.73
50.0	7.47	8.93		4.97
55.0	8.33	10.5		5.13
60.0	8.33	11.4		5.13
65.0	8.67			5.35

Table 4   Coefficient of Linear Thermal Expansion Versus
Temperature for Polymers of DGEBA

Temperature °C	COEFFICIENT OF LINEAR THERMAL, EXPANSION, $\beta \times 10^5$, $°C^{-1}$			
	PDA	HDA	DDA	MPDA
-160.0		2.74	3.03	2.88
-155.0		2.98	3.19	2.96
-150.0	2.90	3.06	3.31	3.12
-145.0	2.90	3.18	3.43	3.32
-140.0	2.94	3.18	3.74	3.24
-135.0	2.98	3.14	3.94	3.24
-130.0	3.01	3.18	4.02	3.20
-125.0	2.89	3.38	4.06	3.24
-120.0	2.89	3.45	4.06	3.35
-115.0	2.89	3.13	4.13	3.31
-110.0	2.93	2.85	4.13	3.31
-105.0	3.01	2.93	4.21	3.35
-100.0	2.89	3.17	4.37	3.47
-95.0	3.05	3.53	4.36	3.63
-90.0	3.32	3.85	4.28	3.71
-85.0	3.60	4.05	4.56	3.74
-80.0	3.88	4.25	4.87	3.78
-75.0	3.95	4.36	5.15	3.82
-70.0	3.95	4.40	5.30	3.94
-65.0	3.95	4.60	5.38	4.06
-60.0	3.95	4.96	5.50	4.06
-55.0	3.95	4.92	5.65	4.13
-50.0	3.94	4.95	5.61	4.13
-45.0	4.10	4.91	5.68	4.29
-40.0	4.34	5.03	6.00	4.64
-35.0	4.57	5.23	6.19	4.80
-30.0	4.80	5.26	5.99	4.88
-25.0	4.76	5.34	5.63	4.91
-20.0	4.72	5.57	5.51	5.11
-15.0	4.76	5.81	5.98	5.07
-10.0	4.99	5.97	6.64	5.03
-5.0	5.19	6.20	7.11	4.87
0.0	5.46	6.40	7.42	5.18
5.0	5.49	6.67	7.26	5.93
10.0	5.69	6.51	7.52	6.20
15.0	6.11	6.54	7.42	6.20
20.0	6.19	6.70	7.47	5.68
25.0	6.34	6.69	7.78	5.56
30.0	6.06	6.77	7.97	5.87
35.0	6.10	6.48	8.35	6.18

Table 4   Coefficient of Linear Thermal Expansion Versus
Temperature for Polymers of DGEBA

Temperature °C	COEFFICIENT OF LINEAR THERMAL, EXPANSION, β X 10^5, $°C^{-1}$			
	PDA	HDA	DDA	MPDA
40.0	6.49	6.36	8.31	6.81
45.0	6.83	6.79	8.46	6.80
50.0	7.14	7.77	8.29	6.64
55.0	7.17	8.75	8.68	6.68
60.0	7.13	9.30	8.75	6.71
65.0	7.36	9.41	8.82	7.21
70.0	7.51	8.93	9.27	
75.0	7.70	9.00	10.0	
80.0		9.14	16.6	

Table 5   Coefficient of Linear Thermal Expansion Versus
Temperature for Polymers of BDGE

Temperature °C	COEFFICIENT OF LINEAR THERMAL EXPANSION, β X 10^5, $°C^{-1}$			
	PDA	HDA	DDA	MPDA
-160.0		2.96	3.11	3.02
-155.0		3.27	3.36	3.46
-150.0	3.25	3.23	3.64	3.66
-145.0	3.53	3.31	3.84	3.62
-140.0	3.80	3.42	4.04	3.74
-135.0	4.20	3.50	4.24	3.78
-130.0	3.72	3.61	4.52	3.86
-125.0	3.88	3.57	4.68	3.93
-120.0	4.00	3.57	4.76	3.69
-115.0	4.19	3.65	4.71	3.61
-110.0	4.19	3.34	4.55	3.53
-105.0	4.19	3.26	4.59	3.53
-100.0	3.95	3.34	4.95	3.89
-95.0	3.63	3.61	5.23	4.21
-90.0	3.59	4.15	5.47	4.28
-85.0	3.75	4.49	5.62	4.36
-80.0	4.22	4.76	5.66	4.60
-75.0	4.57	4.99	6.02	4.72
-70.0	4.85	5.14	6.14	4.92
-65.0	5.16	5.49	6.13	4.99
-60.0	5.43	5.64	6.33	5.03
-55.0	5.12	5.72	6.44	5.15
-50.0	5.66	5.83	6.96	5.14
-45.0	6.09	6.06	7.47	4.42
-40.0	6.83	6.86	8.03	4.94
-35.0	7.69	8.05	9.14	5.81
-30.0	8.08	9.54	1.04	6.57
-25.0	9.68	1.11	1.22	7.32
-20.0	11.6	12.9	14.3	6.68
-15.0	13.3	14.8	16.4	6.79
-10.0	15.0	16.4	18.2	7.18
-5.0	16.6	18.1	19.3	7.38
0.0	19.6	19.3	20.1	7.85
5.0	24.4	20.6	20.6	8.71
10.0		21.8	21.3	12.2
15.0				21.8

Table 6   Coefficient of Cubic Thermal Expansion of
the Epoxy/Diamine Polymers at 25°C

Polymer	Measured (X 10^5)	Calculated (X 10^5)
DGEBA + MPDA	16.68	11.48
PDA	19.02	12.51
HDA	20.07	15.16
DDA	23.34	19.54
RDGE + MPDA	14.4	4.44
PDA	17.25	5.69
HDA	16.47	10.15
DDA	22.14	16.99
BDGE + MPDA	65.4	10.16

Table 7   Specific Heat Capacity as a Function
of Temperature for Polymers of RDGE

Temperature °C	Specific Heat Capacity, cal/g°C			
	PDA	HDA	DDA	MPDA
-80	0.101	0.164	0.214	0.227
-70	0.097	0.146	0.217	0.233
-60	0.105	0.158	0.211	0.263
-50	0.117	0.167	0.226	0.286
-40	0.132	0.195	0.251	0.305
-30	0.144	0.213	0.264	0.318
-20	0.152	0.218	0.279	0.322
-10	0.158	0.214	0.290	0.329
0	0.180	0.237	0.309	0.360
10	0.196	0.271	0.335	0.382
20	0.211	0.319	0.357	0.397
25	0.217	0.341	0.366	0.404
30	0.224	0.348	0.397	0.406
40	0.243	0.382	0.408	0.422
50	0.259	0.401	0.440	0.441
60	0.275	0.436	0.539	0.461
70	0.302	0.571	0.722	0.484
80	0.340	0.683	0.714	0.505
90	0.435	0.734	0.712	0.530
100	0.529	0.749	0.707	0.556
110	0.529	0.766	0.702	0.575
120	0.534	0.800	0.700	0.604
130	0.534	0.826	0.696	0.633
140	0.537	0.836	0.694	0.697
150	0.552	0.832	0.696	0.827
160	0.558	0.820	0.686	0.815
170	0.569	0.812	0.693	0.807
180	0.570	0.793	0.691	0.797
190	0.564	0.777	0.691	0.791

Table 8 Specific Heat Capactiy as a Function
of Temperature for Polymers of DGEBA

Temperature °C	Specfic Heat Capacity, cal/g°C			
	PDA	HDA	DDA	MPDA
-80	0.115	0.146	0.243	0.198
-70	0.130	0.148	0.233	0.198
-60	0.138	0.157	0.234	0.193
-50	0.151	0.173	0.248	0.201
-40	0.167	0.194	0.274	0.230
-30	0.181	0.213	0.286	0.238
-20	0.194	0.220	0.295	0.243
-10	0.200	0.227	0.306	0.244
0	0.224	0.255	0.341	0.272
10	0.252	0.281	0.361	0.291
20	0.277	0.301	0.377	0.302
25	0.282	0.313	0.390	0.301
30	0.298	0.319	0.399	0.312
40	0.323	0.342	0.418	0.332
50	0.344	0.354	0.441	0.347
60	0.358	0.373	0.459	0.361
70	0.381	0.397	0.486	0.380
80	0.398	0.416	0.515	0.393
90	0.422	0.443	0.572	0.411
100	0.446	0.492	0.684	0.431
110	0.465	0.570	0.684	0.448
120	0.505	0.611	0.693	0.478
130	0.498	0.614	0.696	0.502
140	0.623	0.615	0.697	0.522
150	0.633	0.619	0.701	0.541
160	0.640	0.613	0.692	0.553
170	0.644	0.610	0.691	0.582
180	0.640	0.599	0.687	0.633
190	0.635	0.589	0.675	0.631

Table 9   Specific Heat Capacity as a Function
of Temperature for Polymers of BDGE

Temperature °C	Specific Heat Capacity, cal/g°C			
	PDA	HDA	DDA	MPDA
-80	0.183	0.162	0.180	0.209
-70	0.185	0.161	0.193	0.202
-60	0.208	0.165	0.208	0.212
-50	0.215	0.180	0.230	0.237
-40	0.238	0.200	0.261	0.254
-30	0.244	0.196	0.287	0.267
-20	0.254	0.244	0.352	0.270
-10	0.268	0.263	0.531	0.279
0	0.298	0.354	0.727	0.299
10	0.527	0.578	0.696	0.340
20	0.652	0.643	0.672	0.355
25	0.659	0.631	0.665	0.369
30	0.672	0.627	0.665	0.381
40	0.662	0.620	0.666	0.435
50	0.655	0.613	0.666	0.536
60	0.646	0.605	0.667	0.687
70	0.655	0.606	0.677	0.687
80	0.653	0.605	0.681	0.688
90	0.660	0.611	0.687	0.694
100	0.660	0.609	0.692	0.698
110	0.655	0.609	0.690	0.696
120	0.661	0.618	0.685	0.708
130	0.667	0.621	0.677	0.707
140	0.665	0.618	0.666	0.705
150	0.682	0.623	0.663	0.707
160	0.674	0.618	0.653	0.700
170	0.668	0.620	0.647	0.696
180	0.662	0.624	0.639	0.689
190	0.672	0.633	0.639	0.679

Table 10   Glass Transition Temperature, Measured and
Calculated Molar Heat Capacities at 25°C of
the Epoxy/Diamine Polymers

Polymer		T_g, °C	Molar Heat Capacity, cal/mol°C	
			Measured	Calculated
DGEBA +	MPDA	178	232	230
	PDA	122	208	229
	HDA	108	243	247
	DDA	93	336	284
RDGE +	MPDA	142	223	160
	PDA	84	112	159
	HDA	70	191	177
	DDA	62	236	213
BDGE +	MPDA	49	189	170
	PDA	12	315	---
	HDA	5	328	---
	DDA	-10	401	---

Appendix A

Sample Calculations. The following steps are used to determine the density, coefficient of cubic thermal expansion, and molar heat capacity:

1. Determine the polymer repeat unit.
2. Determine the number a_j of each group increment in the repeat unit.
3. Find the numerical values of molar volume parameter V_j for a density calculation in reference 2 or 4, expansion paramteter β_j for a thermal expansion calculation in reference 3, or molar heat capacity parameter C_{pj} for a heat capacity calculation in reference 2 for each group increment j.

Sample calculations of polymer DGEBA and MPDA are shown below.

a. Density Calculation at 25°C Using Van Krevelen's Method

j	Group Increment	Number of Group Increment a_j	Molar Volume V_j (cm^3/mol)	Molecular Weight of Group Increment M_j (g/mol)
1	CH$_2$	8	15.85	14
2	CH	4	9.45	13
3	OH	4	9.7	17
4	O	4	10.0	16
5	N	2	10.0	14
6	⬡	4	65.5	76
7	⬡	1	65.5	76
8	C	2	4.6	12
9	CH$_3$	4	23.9	15

then $V = \sum_{j=1}^{9} a_j V_j = 695.7$ cm^3/mol   and

$MW = \sum_{j=1}^{9} mw_j = 788$ g/mol

therefore the density ρ is

ρ = MW/V

ρ = 788/695.7 = 1.1327 g/cm^3

b. Coefficient of Cubic Thermal Expansion Calculation at 25°C

j	Group Increment	a_j	V_j (cm³/mol)	β_j (× 10⁵-°C⁻¹)	$a_j V_j \beta_j$	$a_j V_j$
1	CH₂	8	16.3	54.13	6984.94	129.04
2	CH	4	11.47	-55.47	-2544.96	45.88
3	OH	4	17.26	-49.88	-3443.72	69.04
4	O	4	7.61	-111.67	-3399.23	30.44
5	N	2	7.78	-111.67	-1737.59	15.56
6	⬡	4	69.27	27.75	7688.97	227.08
7	⬡	1	69.27	27.75	117.8	69.27
8	C	2	5.88	-317.54	-3543.75	11.16
9	CH₃	4	22.1	71.53	6323.25	88.4

Number of Molar Volume Expansion Parameter

the $\sum_{j=1}^{9} a_j V_j \beta_j = 8445.5$ cm³/mol-°C and $\sum_{j=1}^{9} a_j V_j = 735.87$ cm³/mol

therefore $\alpha = \sum_{j=1}^{9} a_j V_j \beta_j / \sum_{j=1}^{9} a_j V_j = 11.48 \times 10^{-5}$ °C⁻¹

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c. Molar Heat Capacity Calculation at 25°C

j	Group Increment	Number of Group Increment a_j	Molar Heat Capacity C_{pj} (cal/mol-°C)	$a_j C_{pj}$ (cal/mol-°C)
1	CH₂	8	6.05	4.84
2	CH	4	3.72	14.88
3	OH	4	4.05	16.2
4	O	4	4.02	16.08
5	OH	2	4.08	8.16
6	⊙	4	18.80	75.2
7	⊙	1	18.80	18.8
8	C	2	1.47	29.4
9	CH₃	4	7.38	29.52

then $C_p = \sum_{j=1}^{9} a_j C_{pj} = 256.64$ cal/mol-°C

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