Specific Heat Capacities of Some Polyepoxides

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Synopsis

Specific heat capacity measurements were made in a differential scanning calorimeter on a series of eight crosslinked epoxy/diamine polymers over a range of temperatures chosen, for each polymer, to include the glass transition. The tabular data at 5°C intervals was then fitted to a five-parameter empirical equation that represents the data with a deviation less than the experimental uncertainty of the measurements. The measured change in specific heat at the glass transition was an average of 1.9 cal/mol °C for each bead in the polymer repeat unit compared with 2.6 cal/mol °C bead found by Wunderlich for linear polymers. The measurements were then analyzed in terms of the molecular components of the polymers, assuming that the specific heat contribution of each component is independent of its neighbors, i.e., that specific heat is an additive property. In calculating empirical component values as a function of temperature, the polymer specifc heats should be plotted as a function of $T - T_g$ rather than T alone. In this manner, component specific heats as functions of $T - T_g$ were determined over a range from the glassy to the rubbery state.

INTRODUCTION

Specific heat capacity is a fundamental physical property of a polymer and is related to molecular structure and morphology. While there have been extensive measurements of polymer specific heats, most of this work has been done on linear polymers. It is the purpose of this paper to report on specific heat measurements of some crosslinked polymers as a function of temperature. In particular, the polymers are a series of eight well-characterized polyepoxides whose room temperature properties have already been reported.[1] The temperature range of the measurements reported here goes from below the glass transition to above the glass transition for each polymer, a range from 25°C to as high as 250°C.

The polymer specific heats were analyzed in terms of their molecular components, using the assumption that the specific heats of the components are additive. This assumption was used in our earlier, room temperature, paper,[1] and Wunderlich and Gaur[2] have verified this assumption for the specific heat of linear polymers.

There were two major results of the component analysis: (1) the specific heat of crosslinked polymers is an additive property over a significant range of temperture and (2) it is desirable to plot component properties as a function of $T - T_g$ rather than T (where T_g is the glass transition temperature).
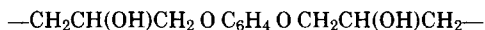
EXPERIMENTAL

The polymers used were a well-characterized series of epoxy/diamines that were carefully purified and prepared for this study. The idealized repeat unit of each polymer is a combination of two bivalent epoxy groups and one tetrava-

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lent amine group.   The epoxy groups were derived from one of two resins: diglycidyl ether of bisphenol A (referred to as D) with an epoxy group structure in the polymerized state given by
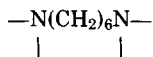
$$-CH_2CH(OH)CH_2 \ O \ C_6H_4 \ C(CH_3)_2C_6H_4 \ O \ CH_2CH(OH)CH_2-$$

or resorcinol diglycidyl ether (R) with a group structure

$$-CH_2CH(OH)CH_2 \ O \ C_6H_4 \ O \ CH_2CH(OH)CH_2-$$

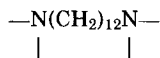Four diamine curing agents were used: propanediamine (P), with an amine group structure in the polymerized state

$$-N(CH_2)_3N-$$
$$| \qquad |$$
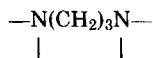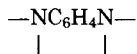
hexanediamine (H), with a group structure

$$-N(CH_2)_6N-$$
$$| \qquad |$$

dodecanediamine (D), with a group structure

$$-N(CH_2)_{12}N-$$
$$| \qquad |$$

and m-phenylene diamine (M), with a group structure

$$-NC_6H_4N-$$
$$| \qquad |$$

All eight possible combinations of these compounds were synthesized and are referred to by two letters: the first for the resin and the second for the curing agent, i.e., DP, DH, etc.   The molecular weights of the repeat units of these polymers are listed in Table I.   Further details on the structure and curing conditions for these polymers have already been published.[1]

Measurements were made using a differential scanning calorimeter (DuPont 990 Thermal Analyzer with a sapphire standard).   All measurements were made in nitrogen at a heating rate of 20°C/min on samples about 2 mm thick and 4 mm diameter, weighing about 20 mg.   Problems were encountered near 0°C due to ice formation.   Therefore, all measurements were made starting at 2°C.   Since there is an unstable initial transient portion of the DSC thermograms, reliable data is only obtained above 25 °C.

In making measurements of this type through the glass transition of a polymer, there is generally a small endothermic peak in the transition region.   To eliminate

TABLE I
Molecular Weight of Polymer Repeat Units

Polymer	Molecular weight (g/mol)
DP	754
DH	796
DD	880
DM	788
RP	518
RH	560
RD	644
RM	552

this peak, all of these specimens were heated up at 20°C/min to about 40°C above the glass transition, then cooled at the same rate to room temperature. Only on heating back up again were measurements made. This procedure not only eliminates the peak but also lowers the overall specific heat by as much as 7%. It was found that further cycling did not change the results.

To improve the accuracy of the measurements, each data point presented here is an average of three replicates. Under the experimental conditions used here, it is expected[3] that the accuracy of the measurements should be ±3%. As a check, measurements were made on a linear polyethylene, Standard Reference Material 1475 from the National Bureau of Standards. The specific heat of this polymer has been determined accurately by Chang and Bestul,[4] using an adiabatic calorimeter. The polymer is supplied in pellet form, and Change and Bestul point out that there is some pellet-to-pellet variation. Their measurements used more than 1000 pellets. Our measurements were made using parts of only three pellets and are therefore expected to show larger variations. In fact, our measurements on the as received polymer are lower than Chang and Bestul by about 5%.

POLYMER PROPERTIES

Graphs of all the data are shown in Figure 1, and tabular results are given in Table II. From Figure 1, it can be seen that the shapes of the graphs are qualitatively similar: two linearly increasing regions separated by the glass transition region. An empirical curve fit was made to the data in terms of the slope above and below (called B and A here) the glass transition temperature, T_g, the specific heat at T_g, given by the symbol C_p^g, and the change in C_p at the glass transition, ΔC_p. These parameters are illustrated in Figure 2. Note that T_g is defined as the temperature for which the measured C_p is halfway between the upper linear extrapolation and the lower one. The following curve fit was found to represent all of the data with a deviation less than the experimental uncertainty:

$$C_p = C_p^g + A(T - T_g) - \Delta C_p(1 - e^x)/2, \quad T < T_g \tag{1}$$

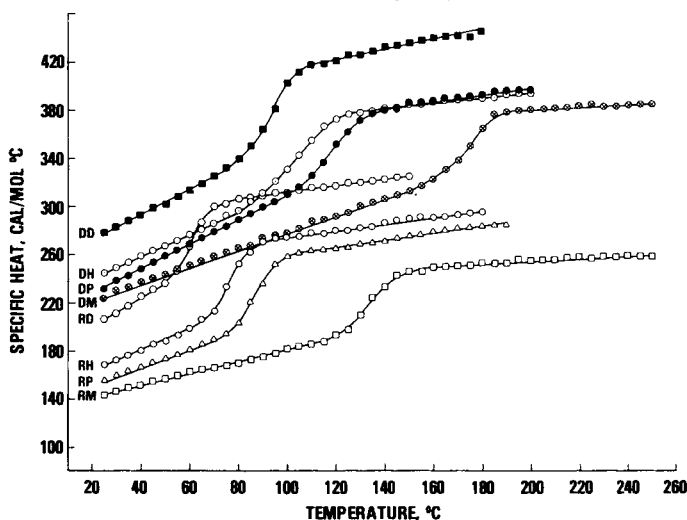$$C_p = C_p^g + B(T - T_g) + \Delta C_p(1 - e^{-x})/2, \quad T > T_g \tag{2}$$

$$x = 70(T - T_g)/T_g \tag{3}$$

Fig. 1. Specific heat vs. temperature for epoxy polymers.

TABLE II
Average Specific Heat of Polyepoxides

			Specific heat, (cal/mol °C)					
T(°C)	RD	RH	RP	RM	DD	DH	DP	DM
25	207	168	156	144	278	245	232	.225
30	212	173	160	147	283	249	239	230
35	218	177	163	150	287	254	242	233
40	225	181	167	152	293	259	248	237
45	231	186	170	155	299	264	254	241
50	236	189	174	157	302	267	259	243
55	248	194	177	160	308	272	264	248
60	267	199	181	163	314	277	269	251
65	287	206	185	164	320	281	275	255
70	300	213	190	166	325	286	279	258
75	303	233	195	169	332	292	284	262
80	307	253	204	171	340	296	289	266
85	309	263	220	174	351	304	295	267
90	309	271	237	176	364	312	299	273
95	312	273	251	178	381	321	304	275
100	312	274	259	182	403	331	311	278
105	314	275	262	184	412	343	317	282
110	316	278	263	186	417	355	326	287
115	316	278	264	188	419	367	337	289
120	318	280	265	194	421	373	352	292
125	320	280	267	199	426	377	362	295
130	320	283	269	210	426	378	372	299
135	322	284	270	224	429	379	377	303
140	323	286	271	234	433	382	379	306
145	324	288	274	242	434	382	382	309
150	325	290	276	245	437	385	386	313
155	—	291	277	247	439	386	387	317
160	—	291	279	248	440	386	387	323
165	—	292	280	250	442	388	390	330
170	—	293	282	250	442	390	389	338
175	—	295	283	251	442	390	391	350
180	—	295	284	253	446	390	393	363
185	—	—	285	252	—	391	396	377
190	—	—	285	253	—	393	396	379
195	—	—	—	254	—	393	397	379
200	—	—	—	255	—	393	397	380
205	—	—	—	255	—	—	—	381
210	—	—	—	256	—	—	—	382
215	—	—	—	256	—	—	—	382
220	—	—	—	257	—	—	—	384
225	—	—	—	257	—	—	—	385
230	—	—	—	258	—	—	—	384
235	—	—	—	258	—	—	—	383
240	—	—	—	259	—	—	—	384
245	—	—	—	259	—	—	—	385
250	—	—	—	259	—	—	—	385

For each polymer all of the data can be represented by giving five parameters: T_g, C_p^g, ΔC_p, A, B. Fit parameters for the eight polymers are given Table III. The solid lines shown in Figure 1 were, in fact, generated using the above curve fit.

The analytic curve fit is very convenient for making calculations. For example,
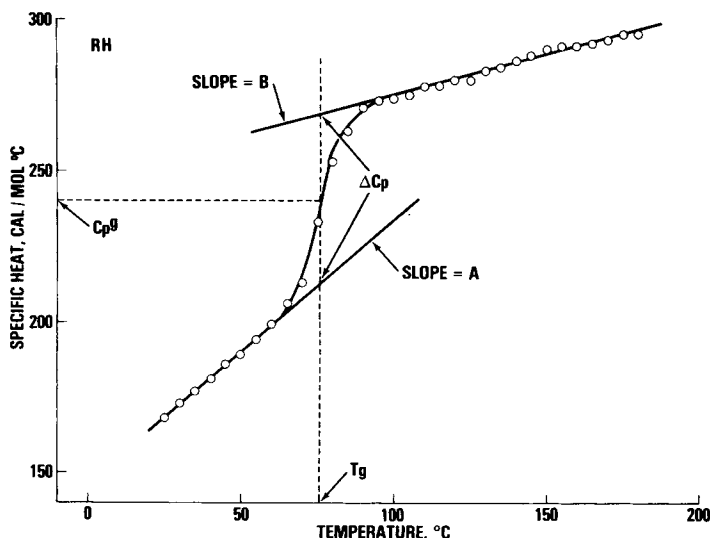
Fig. 2. Illustration of specific heat equation parameters for RD polyepoxide.

we can calculate the width of the glass transition, defined as the temperature interval over which the full analytic curve differs from the linear extrapolation of the curve by more than ±1%. (On any given curve, 1% represents a significant deviation from the straight line compared with the random deviation of the other points about the straight line.) In this manner, we find that the width of the glass transition in these polymers varies from 21°C to 28°C.

There is little specific heat data on similar crosslinked polymers. One exception is the measurements on DM made by Kreahling and Kline.[5] Estimating results for their graphs, we find $T_g = 170$ °C, in fairly good agreement with our value of 177°C. They find a specific heat at T_g of 418 cal/mol °C, somewhat higher than our value of 355 cal/mol °C. One major difference is the fact that they cured their polymer at only 72°C while we cured at 175°C. Considering the variations in starting materials and cure temperature, the overall agreement is considered satisfactory.

One area of theoretical interest is to calculate the specific heat at constant volume, C_v, from these constant pressure measurements since the C_v data can be linked theoretically to the vibrational motion. Wunderlich[6] has shown that the two specific heats are approximately related in the following manner:

$$C_p - C_v = KC_p^2 T \qquad (4)$$

where, for crystalline polyethylene, $K = 6.87 \times 10^{-4}$ g/cal. The constant was evaluated by using the exact thermodynamic relationship

TABLE III
Fit Parameters

	RD	RH	RP	RM	DD	DH	DP	DM
T_g	63	76	87	135	95	107	120	177
C_p^g	278	240	227	224	381	347	352	355
ΔC_p	51	55	55	49	62	53	45	46
A	1.19	0.86	0.73	0.48	1.05	0.93	1.02	0.69
B	0.26	0.28	0.30	0.11	0.40	0.23	0.29	0.10

$$C_p - C_v = \alpha^2 BT/\rho \tag{5}$$

where α is the thermal expansion coefficient, B is the isothermal bulk modulus, T is absolute temperature, and ρ is density. We estimated the value of the right-hand side of eq. (5) using the room temperature data in Ref. 1. (The bulk modulus in Ref. 1 is the adiabatic rather than isothermal value, but this represents a small correction to a correction and will be ignored here.) In this manner, we find $K = 5.35 \times 10^{-4}$g/cal on the average for the eight epoxies. (Individual values vary by as much as $\pm 15\%$ from the average.) Thus, the K value for the epoxies is less than for crystalline polyethylene, namely $K(\text{PE}) = 6.87 \times 10^{-4}$g/cal. For RM, as an example, C_p/C_v is 1.04 at 25°C and rises to 1.07 at 100°C.

The next item of interest is the temperature dependence of the specific heat. It can immediately be seen that the slope of the specific heat curve is less above T_g than it is below T_g. Van Krevelen[7] noted similar behavior for linear polymers and discovered that, on the average, at room temperature $(1/C_p)dC_p/dT = 3 \times 10^{-3}$°C^{-1} for solid polymers while $(1/C_p)dC_p/dT = 1.2 \times 10^{-3}$°C^{-1} for liquid polymers. In the notation of this paper, $(1/C_p)dC_p/dT$ is given by A/C_p^g just below the glass transition and by B/C_p^g just above the glass transition (where A, B, and C_p^g are given in Table III). For the epoxies, $A/C_p^g = 2.9 \times 10^{-3}$°C^{-1} on the average with a mean deviation of $\pm 20\%$ (which is about the same as the experimental uncertainity in our measurements of this quantity) and $B/C_p^g = 0.84 \times 10^{-3}$°C^{-1} on the average with a mean deviation of $\pm 30\%$. Thus our results are very similar to the results for linear polymers. While the constancy of $(1/C_p)dC_p/dT$ is only approximate, to the extent that it is true, it implies that the five variables describing a polymer $(T_g, C_p^g, \Delta C_p, A, B)$ are not independent. Thus, $A/C_p^g = 2.9 \times 10^{-3}$°C^{-1} and $B/C_p^g = 0.84 \times 10^{-3}$°C^{-1} are two relations that reduce the number of variables to three $(T_g, C_p^g, \Delta C_p)$.

The above logarithmic derivative, $(1/C_p)dC_p/dT = d\ln C_p/dT$, is related to the volume dependence of the heat capacity since

$$\frac{d\ln C_p}{d\ln V} = \frac{1}{\alpha}\frac{d\ln C_p}{dT} \tag{6}$$

For the epoxies, the volume derivative of eq. (6), below the glass transition, has an average value of 16 (with individual values of 12–22) compred with an average value of about 10 for linear polymers. We note that the volume derivative $d\ln C_p/d\ln V$ shows somewhat less variation throughout the epoxy series than does the temperature derivative $d\ln C_p/dT$.

Another relationship for these polymers is based on an analysis of ΔC_p. Wunderlich and Jones[8] have pointed out that, for linear polymers, ΔC_p per bead of polymer is a constant. Here a bead is defined as a basic unit of major motion in the liquid state. Some examples of beads are $-CH_2-$, $-CH(OH)-$, $-C(CH_3)_2-$, and $-C_6H_4-$. Applying this approach to crosslinked polymers, we obtain the results shown in Table IV. The average value of the ΔC_p per bead is 1.9 cal/mol °C bead compared with the value of 2.6 cal/mol °C bead found by Wunderlich and Jones for linear polymers. Calculations of ΔC_p from molecular structure reduces the number of variables desribing a polymer to just two: T_g and C_p^g.

While there are some differences in general terms between linear and crosslinked polymers, the overall impression of these specific heat measurements is that the two classes of polymers are more similar than they are dissimilar.

TABLE IV
Change in Specific Heat at the Glass Transition per Bead

Polymer	ΔC_p (cal/mol °C)	Number of beads	$\Delta C_p/N$ (cal/mol °C bead)
RD	51	32	1.6
RH	55	26	2.1
RP	55	23	2.4
RM	49	21	2.3
DD	62	36	1.7
DH	53	30	1.8
DP	45	27	1.7
DM	46	25	1.8
			Average 1.9

COMPONENT PROPERTIES

The major goal of this work is to empirically analyze the polymer specific heats in terms of additive molecular components. The assumption is made that the specific heats of the molecular components are the same in every polymer. This assumption, called the assumption of additive properties, was found to be reasonably accurate for these epoxy polymers at room temperature.[1] In this paper, we wish to extend that approach to component properties as a function of temperature.

Our first intention was to repeat the procedure used in Ref. 1 at a series of temperatures. However, an examination of Figure 1 reveals a problem. At a temperature of, say, 80°C, some of the polymers will be in the glassy state, some in the rubbery state, and some in the transition region. Comparing components at this temperature would then not be comparing similar states of matter, and the assumption of additive properties would not be expected to apply. This observation suggests that polymers should be compared not at the same temperature but at the same distance from their glass transition temperature, i.e., at the same value of $T - T_g$. A replot of the data from Figure 1 in terms of this variable is shown in Figure 3. As can be seen, the somewhat chaotic mass of data from Figure 1 now shows considerably more order. The use of $T - T_g$ as a
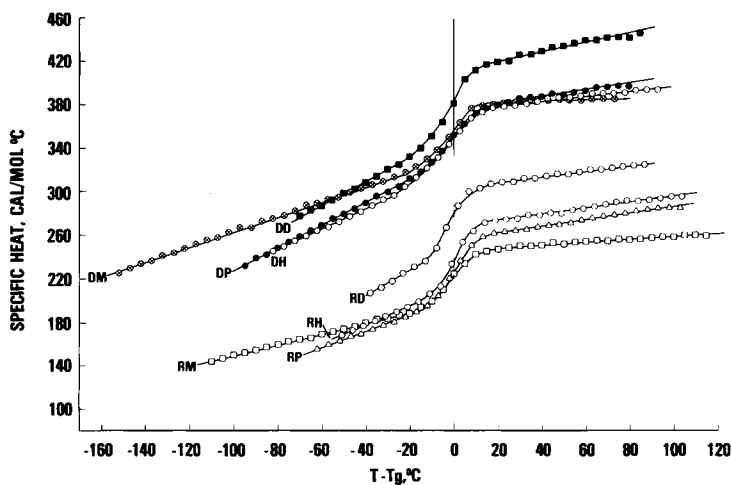

Fig. 3. Specific heat vs. $T - T_g$ for epoxy polymers.

variable instead of T is also suggested by eqs. (1)–(3) since only the combination $T - T_g$ appears, never T by itself.

Using the data shown in Figure 3, the specific heat of the polymer components can be determined for temperature in the range from $T - T_g = -60°C$ to $+60°C$. As shown before,[1] the molecular structures of the eight polymers can be expressed in terms of four components:

$$-CH_2-, \quad -C(CH_3)_2-, \quad -C_6H_4-, \quad \text{and} \quad -ENE-$$
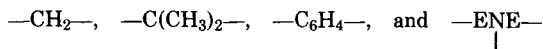
where E stands for the glycol ether group $-OCH_2CH(OH)CH_2-$. Polymer structures can be specified by the number of each of thse four components in the repeat unit. We note that the first three components are bivalent and are also found in linear polymers while the fourth component is trivalent and is responsible for the crosslinking in these polymers. It is interesting that the first three components are also beads as defined by Wunderlich.

Looking at the measured specific heats at a given reduced temperature, the set of polymers used here can be written as eight equations in four unknowns (the component specific heats). In general, such a set of equations cannot be satisfied exactly by any set of component values. The method of least squares is well established for finding the "best" set of values in such cases. In the method of least squares, the criterion for the "best" fit is to minimize the absolute magnitude of the sum of the squares of the differences between measured and calculated specific heats. However, the criterion usually used in judging predictions such as we are making is to minimize the relative magnitude of the difference, i.e., the percent mean deviation. Therefore, a modification of the method of least squares is used.[1]

Carrying out the calculation of the best values to use for component specific heats in this manner we obtain the results shown in Figures 4, 5, 6, and 7. In Figure 4, the component value for $-ENE-$ is shown. This component makes the largest contribution to the specific heat. As expected, the shape of the curve mimics that of the polymer specific heat. We can also see that the component specific heat changes considerably from glassy to rubbery state. Similar results are seen with the $-C(CH_3)_2-$ component in Figure 5. For $-CH_2-$, Figure
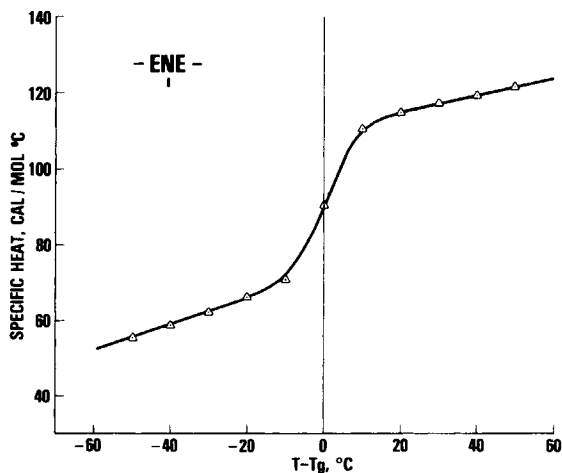

Fig. 4. Specific heat vs. $T - T_g$ for $-ENE-$ component.
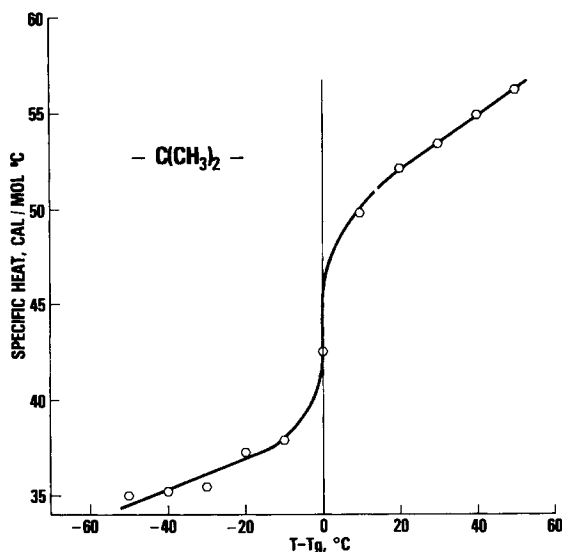
Fig. 5. Specific heat vs. $T - T_g$ for —C(CH$_3$)$_2$— component.

6, the curve is a little different in that there is no significant transition region. For —C$_6$H$_4$—, Figure 7, however, the temperature dependence is opposite that of the other components and also the polymers. The average glassy state value for —C$_6$H$_4$— is, however, in general agreement with the results given by Van Krevelen[7] and also by Wunderlich and Jones.[8]

Before attempting to interpret the negtive temperature dependence of the phenylene group (—C$_6$H$_4$—), an error propagation analysis was performed for the calculation of component specific heat. Preliminary results show that the uncertainty in component specific heat depends on the uncertainty in the measured polymer specific heats and the particular combination of components in the set of polymers analyzed. For the set of polymers used here, the methylene (—CH$_2$—) component specific heat can be determined with the greatest accuracy while the phenylene component is determined with the least accuracy. The uncertainty in the phenylene determination is such that the negative temperature
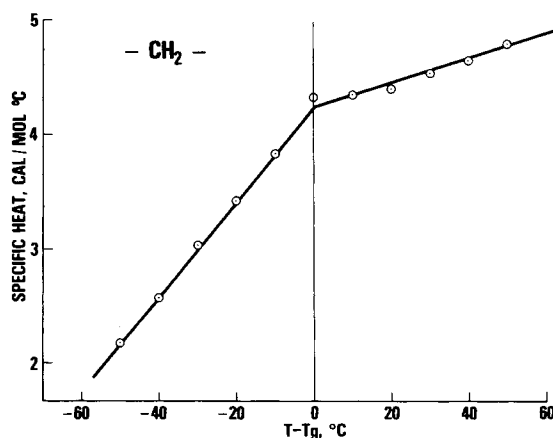

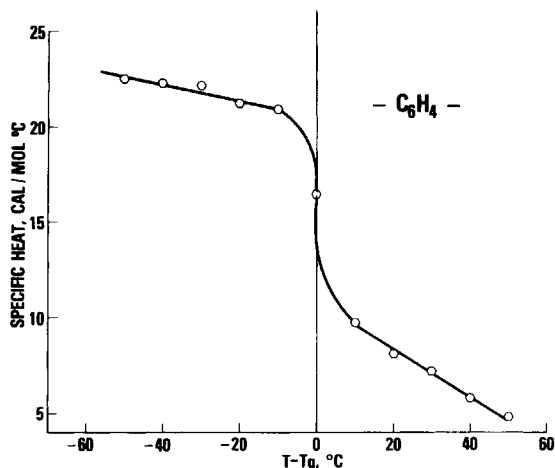Fig. 6. Specific heat vs. $T - T_g$ for —CH$_2$— component.

Fig. 7. Specific heat vs. $T - T_g$ for —C_6H_4 component.

dependence must be considered tentative. Only by making more accurate measurements and/or by using a different polymer set can the temperature dependence be confirmed.

Negative temperature dependence has been reported by Wunderlich and Gaur[2] for the oxygen component in the molten state and also selenium. They speculated that all monatomic components have negative temperature dependence. Based on this observation, it is possible that phenylene is behaving similar to a monatomic component due to its rigid structure, brought about by the double bonds. In this case the internal structural vibrations of the other components are increasing at the expense of the intramolecular skeletal vibrations of the phenylene component. Van Krevelen also concludes that the presence of certain components influences the degrees of freedom of adjacent groups. This interaction provides the mehanism for negative temperature dependence.

Using the component specific heats in Figures 4–7 and the known polymer structures, polymer specific heats were calculated. These results agree with the measured values shown in Figure 3 with an average difference of ±3% for all polymers and all temperatures. This difference is the same as the accuracy of the measurements.

As an illustration of the use of the method of additive properties, predictions were made of the temperature dependence of the specific heat of an epoxy that was not included in the data base used to determine the component properties. The polymer chosen was synthesized from butanediol diglycidyl ether (B) cured with m-phenylenediamine (M). Some synthesis details on this polymer have been reported elsewhere.[9] Its moleular structure is given in the following form:

$$8 \text{ —CH}_2\text{—}, \quad 0 \text{ —C(CH}_3)_2\text{—}, \quad 1 \text{ —C}_6\text{H}_4\text{—}, \quad \text{and} \quad 2 \text{ —ENE—}$$
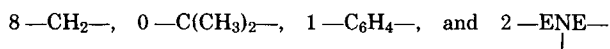
Based solely on this structure, the specific heat of the polymer was predicted using the results shown in Figures 4–7. The resulting prediction is shown in Figure 8. Measurements were then made on this polymer in the same manner as was done for the other polymers. The experimental results are also shown
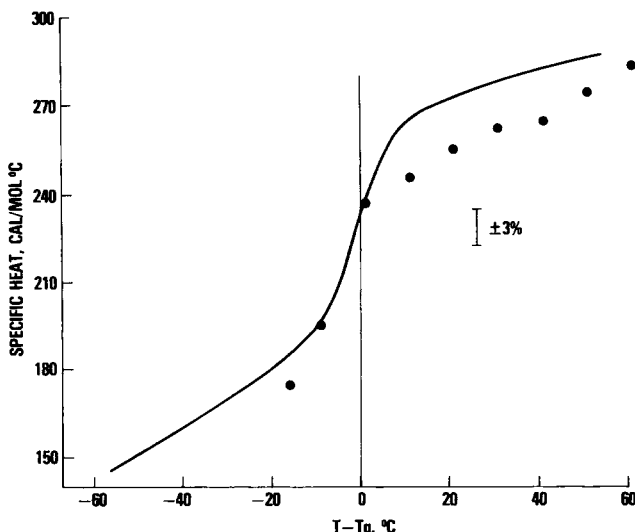
Fig. 8. Specific heat vs. $T - T_g$ for BM polyepoxide.

in Figure 8.   The agreement is within the experimental uncertainty of the measurements, though the experimental results appear to be lower than the predicted values.

The above example also illustrates a limitation of the empirical method of analysis used here: the results are given in terms of $T - T_g$ while we generally would like to know the properties as a function of T.   Fortunately, there is a considerable background in predicting the T_g of polymers in terms of the same additive components that are used here for C_p.   Most of this background is on linear polymers,[7] but some recent work has shown that the same approach can be applied to crosslinked polymers.[10]

CONCLUSIONS

Based on specific heat measurements on a series of eight crosslinked epoxy polymers, we conclude that:

(1) The specific heat of crosslinked polymers is an additive property over a significant range of temperature;

(2) component properties are a function of $T - T_g$, not T alone.

References

1. B. Hartmann and G. F. Lee, *J. Appl. Phys.*, **51**, 5140 (1980).

2. B. Wunderlich and U. Gaur, *Pure Appl. Chem.*, **52**, 445 (1980).

3. A. Mehta, R. C. Bopp, U. Gaur, and B. Wunderlich, *J. Thermal Anal.*, **13**, 197 (1978).

4. S. S. Chang and A. B. Bestul, *J. Res. Natl. Bur. Stds.*, **77A**, 395 (1973).

5. R. P. Kreahling and D. E. Kline, *J. Appl. Polym. Sci.*, **13**, 2411 (1969).

6. B. Wunderlich, J. Chem. Phys., **37**, 1203 (1962).

7. D. W. Van Krevelen, *Properties of Polymers, Correlations with Chemical Structure*, Elsevier, New York, 1972, pp. 69–70.

8. B. Wunderlich and L. D. Jones, *J. Macromol. Sci.*, **B3**, 67 (1969).

9. B. Hartmann, *Polymer*, **22,** 736 (1981).
10. T. I. Ponomareva, V. I. Irzhak, and B. A. Rozenberg, *Polym. Sci. USSR*, **20,** 673 (1978).