

# Glass Transition Temperature Predictions in Some Epoxy Polymers

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## Synopsis

The glass transition temperature as an additive property was studied on a series of epoxy/amine crosslinked polymers. Various methods from the literature of analyzing the glass transition temperature in terms of components are presented and then judged to determine which of these methods gives the best agreement between calculated and measured glass transition temperature. It was found that predictions agree on the average with the measurements to within the accuracy of the measurements, approximately 3%.

## INTRODUCTION

The assumption of additive properties has been shown to be valid for many properties of linear polymers.<sup>1</sup> Recently we have applied this assumption to a series of crosslinked polyepoxides. This paper is the fourth in a series that has considered different aspects of the assumption: thermodynamic properties at room temperature,<sup>2</sup> specific heat capacity as a function of temperature,<sup>3</sup> and elastic constants as a function of temperature.<sup>4</sup> In this paper we will examine the glass transition temperature  $T_g$ . Not only is  $T_g$  a crucial polymer property in general but also in our study of heat capacity,<sup>3</sup> it was desirable to consider heat capacity as a function of  $T - T_g$  rather than temperature  $T$  by itself. Thus, it is of interest to predict  $T_g$  rather than requiring supplemental measurements.

There have been a number of studies of  $T_g$  as an additive property of the component groups making up the polymer, at least for linear polymers. The equations used can be broken down into three general categories: (1)  $T_g$  is a linear combination of the component  $T_g$  values, (2) the reciprocal of  $T_g$  is a linear combination of the reciprocals of the component values, and (3) the log of  $T_g$  is a linear combination of the log of the component values. All three of these approaches, which are typically empirical in nature, will be considered here.

The prediction of  $T_g$  for polymers from component values is a problem of considerable interest in the form of copolymer  $T_g$  predictions from homopolymer  $T_g$  values. A considerable body of literature is devoted to this topic. The same form of the equations mentioned above are also used for copolymer predictions, though the significance of the constants in the equations is not the same. While the results are typically presented in terms of two components, the generalization to an arbitrary number of components is usually obvious.

It is the purpose of this paper to apply each of the three types of equations for predicting  $T_g$  to the set of epoxies used in our earlier studies. An attempt will be made to judge which of these approaches gives the best agreement with experimental measurements of  $T_g$ . In addition, some measurements taken from

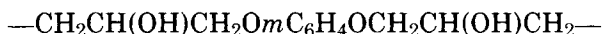
the literature will also be considered as a means of determining values for more components than are included in the original set.

### EXPERIMENTAL

The basic polymer set used in this work was a well-characterized series of epoxy/diamines that were carefully purified and prepared especially for this study. The idealized repeat unit of each polymer is a combination of two bivalent epoxy groups and one tetravalent 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



or resorcinol diglycidyl ether (R) with a group structure



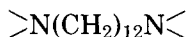
Four diamine curing agents were used: propanediamine (P) with an amine group structure in the polymerized state



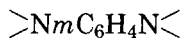
hexanediamine (H), with a group structure



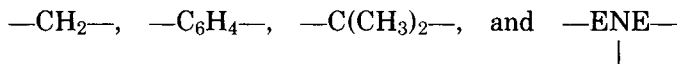
dodecanediamine (D), with a group structure



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



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. Further details of the structure and curing conditions for these polymers have already been published.<sup>2</sup> As shown before, these eight polymers can be expressed in terms of four components:

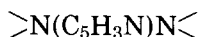


where E stands for the glycol ether group  $-\text{OCH}_2\text{CH}(\text{OH})\text{CH}_2-$ . (Note that there are not enough polymers in this series to distinguish between meta- and paraphenylene.) Finally, a group of eight other epoxies were taken from the literature.<sup>5</sup> These polymers were synthesized from resorcinol diglycidyl ether (R), similar to the one used in this work, and diglycidyl ether of hydroquinone (dH) with a structure given by

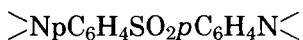


Four amine curing agents were used:

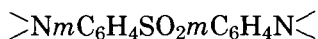
2,6-diaminopyridine (dP)



4,4'-diaminodiphenylsulfone (dpS)



3,3'-diaminodiphenylsulfone (dmS)



and 4,4'-diaminodiphenylmethane (dM)



With the addition of these polymers, new components can be determined, namely  $\text{—SO}_2\text{—}$ ,  $\text{—C}_5\text{H}_3\text{N—}$ , and the distinction between  $\text{—mC}_6\text{H}_4\text{—}$  and  $\text{—pC}_6\text{H}_4\text{—}$ . Thus a total of seven components can be determined.

For the eight polymers synthesized for this work, the glass transition temperatures were determined using a differential scanning calorimeter (DuPont 990 Thermal Analyzer with a sapphire standard). All measurements were made in nitrogen at a heating rate of  $20^\circ\text{C}/\text{min}$  on samples about 2 mm thick and 4 mm diameter, weighing about 20 mg. Based on repeated measurements on the same specimen and different specimens cut from the same block, the precision of these measurements is  $\pm 3^\circ\text{C}$ . These transition temperatures have already been published.<sup>2,3</sup>

For the eight epoxies taken from the literature,<sup>5</sup> glass transition temperatures were determined using volume dilatometry, at a temperature rate of  $1^\circ\text{C}/\text{min}$ .

Experimental values of glass transition temperature for all of the above polymers are given in Table III, which is discussed below.

## METHODS OF ANALYSIS

In this section, various methods of analyzing the glass transition temperature in terms of component properties will be briefly presented. Equations for copolymers will be presented that have the same form as the component equations but the significance of the constants is different.

### Linear Combination

The general form of the linear combination equation is

$$T_g = \sum_i w_i T_{gi} \quad (1)$$

where  $T_{gi}$  is the glass transition temperature for component  $i$ ,  $w_i$  is the weighting function for component  $i$ , and the summation extends over all the components that constitute the repeat unit. Various authors have chosen  $w_i$  in different ways. Van Krevelen<sup>1,6</sup> used the number of component atoms in the main chain,  $s_i$ , divided by the total number of main chain atoms in the repeat unit,  $\sum_i s_i$ , so that

$$T_g = \sum_i s_i T_{gi} / \sum_i s_i \quad (2)$$

Lee<sup>7</sup> did a study for the case when the weighting function was the molecular weight fraction of each component,  $M_i / \sum_i M_i$ , so that

$$T_g = \sum_i m_i T_{gi} / \sum_i m_i \quad (3)$$

Hayes<sup>8</sup> related  $w_i$  to molar cohesive energy which led to the result

$$T_g = \sum_i n_i T_{gi} / \sum_i n_i \quad (4)$$

where  $n_i$  is a number analogous to the degrees of freedom and is related to the rotational properties of the polymer. Becker<sup>9</sup> specifically considered the effect of crosslinking on the  $T_g$  of polymers using a modification of eq. (1),

$$T_g = \frac{\sum_i s_i T_{gi} + KP}{\sum_i s_i} \quad (5)$$

where  $P$  is the number of network points and  $K$  is a constant, equals 890°K, irrespective of its chemical nature. Ponomareva et al.<sup>5</sup> have applied eq. (5) to a series of amine cured epoxides. They define  $s_i$  as  $a_i n_i$ , where  $a_i$  is the concentration of the epoxide and amine monomers and  $n_i$  is the number of atoms introduced into the main chain. Kreibich and Batzer<sup>10</sup> also considered amine cured polyepoxides using eq. (2).

In a study of copolymer transitions, Gordon and Taylor<sup>11</sup> compared properties at the transition temperature (as we did with heat capacity) and started with the assumption of additive properties to the volume of the components. They further assumed that the transition occurs at a temperature determined by the differences between the thermal expansion coefficients in the glassy and rubbery states and that  $A$  and  $B$  are the differences in expansion coefficients:

$$T_g = AT_{g1} + BT_{g2} \quad (6)$$

Equation (6) is obviously a special case of eq. (1). We also see the difference in significance of the equations. For additive properties, the coefficients of the expansion are specified by the structure in some determined fashion while the  $T_{gi}$ 's are found by fitting the equations to experimental data. For copolymer transitions, the coefficients are related theoretically to some transition theory while the  $T_{gi}$ 's are found by independent homopolymer measurements.

### Reciprocal Combination

The general form of the reciprocal combination equation is

$$\frac{1}{T_g} = \sum_i \frac{w_i}{T_{gi}} \quad (7)$$

Lee<sup>7</sup> had used molecular weight fraction as the weighting function to obtain

$$\frac{1}{T_g} = \sum_i \frac{M_i}{T_{gi}} / \sum_i M_i \quad (8)$$

For copolymers, Wood<sup>12</sup> assumed that the transition occurs when the free volume reaches a critical value and obtained

$$\frac{1}{T_g} = \frac{a}{T_{g1}} + \frac{b}{T_{g2}} \quad (9)$$

where  $a$  and  $b$  are related to free volume.

**Logarithmic Combination**

The general form of the logarithmic combination equation is

$$\ln T_g = \sum_i w_i \ln T_{gi} \tag{10}$$

Askadskii<sup>13-15</sup> has extensively considered (empirically) this equation in terms of molecular weight fraction

$$\ln T_g = \sum_i M_i \ln T_{gi} / \sum_i M_i \tag{11}$$

For compatible polymer mixtures, Couchman<sup>16-18</sup> has developed a similar equation based on entropy considerations in the form

$$\ln T_g = \alpha \ln T_{g1} + \beta \ln T_{g2}$$

where  $\alpha$  and  $\beta$  are related to heat capacities. He has also pointed out that the logarithmic form reduces to the linear or reciprocal form depending on the values of the coefficients.

**RESULTS**

In this section, we apply the various equations above to crosslinked polyepoxides to determine which approach gives the best results. Specifically, we will consider linear equations (2), (3), (4), and (5), reciprocal equation (8), and logarithmic equation (11).

The first calculations are for the eight D and R series polymers. There are then eight equations in terms of the four unknown component values. The coefficients are known from the polymer structure and the measured  $T_g$  values were taken from our earlier work.<sup>2</sup> These equations are then solved for the "best" values of  $T_g$ , which are then used to calculate  $T_g$  values. Calculated values of  $T_g$  are compared with the measured values in Table I. At the bottom of this table, the average percent differences between calculated and measured values are given for the eight polymers. As can be seen the agreement is generally good in all cases. It is perhaps significant that most of the average difference comes

TABLE I  
Glass Transition Temperature Calculations

Polymer	Measured $T_g$ (K)	Calculated $T_g$ (K)					
		Eq. (2)	Eq. (3)	Eq. (4)	Eq. (5)	Eq. (8)	Eq. (11)
DM	451	433	430	444	435	435	432
DD	366	366	368	364	366	365	366
DH	381	384	385	384	384	385	385
DP	395	395	395	398	395	396	395
RM	415	416	415	416	417	415	416
RD	334	334	333	334	334	334	334
RH	352	352	352	351	352	352	352
RP	364	364	364	364	364	364	364
Average difference (%)		0.6	0.8	0.6	0.6	0.6	0.7

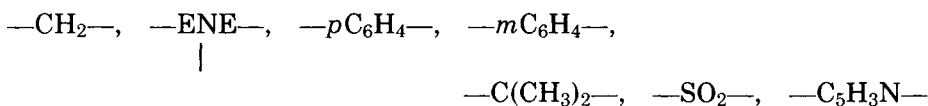
TABLE II  
 Component Values Using Various Methods

Components	$T_g$ (K)					
	Eq. (2)	Eq. (3)	Eq. (4)	Eq. (5)	Eq. (8)	Eq. (11)
—CH <sub>2</sub> —	238	204	265	238	250	233
—ENE— 	254	251	299	151	293	276
—C <sub>6</sub> H <sub>4</sub> —	657	649	1475	667	1019	744
—C(CH <sub>3</sub> ) <sub>2</sub> —	-196	125	224	-232	253	204

from only one polymer, DM. Other than the one polymer, all of the equations predict values within the experimental accuracy of the measurements.

The calculated  $T_g$  values in Table I were obtained from the component values  $T_g$ , listed in Table II. For eqs. (2) and (5) the propyl component, —C(CH<sub>3</sub>)<sub>2</sub>—, is seen to have a negative value. This unphysical result is an example of the fact that the mathematical machinery of the method of additive properties can sometimes give fairly accurate predictions, even though the component values are not physically correct. This type of behavior has been observed before and means among other things that eqs. (2) and (5) are not valid in this case.

The data base of eight epoxies was then expanded by including eight other epoxies from Ponomareva.<sup>5</sup> As mentioned above this allows us to calculate the properties of a total of seven components:



Measured and predicted values of  $T_g$  are given in Table III. The average percent difference is higher than before, 1.9% compared with 0.6%, and once again polymer DM is the biggest problem. There may be an experimental problem with this polymer. Component values calculated from the sixteen polymer are given in Table IV. In this case the component values are positive. As can be

 TABLE III  
 Glass Transition Temperature Calculations

Polymer	Measured $T_g$ (K)	Calculated $T_g$ (K)					
		Eq. (2)	Eq. (3)	Eq. (4)	Eq. (5)	Eq. (8)	Eq. (11)
DM	451	415	412	431	415	419	415
DD	366	366	366	366	366	366	366
DH	381	385	384	389	385	385	384
DP	395	397	395	404	397	397	395
RM	415	394	394	393	394	394	392
RD	334	334	334	334	334	334	333
RH	352	354	355	352	354	352	351
RP	364	368	368	365	368	364	364
RdpS	429	426	426	426	426	426	426
RdmS	418	421	421	419	421	421	421
RdM	396	402	403	402	402	404	403
RdP	413	350	365	349	350	413	335
dHdpS	435	430	431	434	430	430	431
dHdmS	423	426	426	426	426	426	426
dHdM	408	408	408	408	408	408	408
dHdP	418	418	418	418	418	418	418
Average difference (%)		2.3	2.1	2.1	2.3	1.2	1.6

TABLE IV  
 Component Values Using Various Methods

Components	T <sub>g<sub>i</sub></sub> (K)					
	Eq. (2)	Eq. (3)	Eq. (4)	Eq. (5)	Eq. (8)	Eq. (11)
—CH <sub>2</sub> —	233	193	261	233	249	231
—ENE— 	356	349	355	258	338	336
—pC <sub>6</sub> H <sub>4</sub> —	477	481	799	477	544	515
—mC <sub>6</sub> H <sub>4</sub> —	468	458	552	468	514	490
—C(CH <sub>3</sub> ) <sub>2</sub> —	358	363	465	358	391	370
—SO <sub>2</sub> —	1009	612	765	1009	691	650
—C <sub>5</sub> H <sub>3</sub> N—	630	585	1440	630	906	694

seen from the comparison of component values of —CH<sub>2</sub>— in Table II and Table IV, the values are fairly consistent, which may indicate that we can determine the glass transition temperature contribution of —CH<sub>2</sub>— more accurately than, for instance, —ENE— or —C(CH<sub>3</sub>)<sub>2</sub>—, where the component values are not as consistent. Also a comparison is made between four components values of linear and crosslinked polymer in Table V. Component values for the linear polymers are taken from Van Krevelen.<sup>1</sup> Component values for the crosslinked polymers are taken from Table IV and tabulated in Table V as arithmetic averages. The comparison indicates that the component values for the crosslinked polymers are generally larger than for the corresponding linear polymers.

 TABLE V  
 Component Values for Linear and Crosslinked Polymers

Component	T <sub>g<sub>i</sub></sub> (K)	
	Linear	Crosslinked
—CH <sub>2</sub> —	270	233
—pC <sub>6</sub> H <sub>4</sub> —	463	549
—mC <sub>6</sub> H <sub>4</sub> —	500	492
—C(CH <sub>3</sub> ) <sub>2</sub> —	226	384

## CONCLUSIONS

The assumption of additive properties was applied to some crosslinked epoxies. Various forms of this assumption were investigated from the point of view as which method gives the best results. Based on these calculations, the following conclusions have been reached:

(1) The glass transition temperature of crosslinked epoxies is an additive property.

(2) The best equations to use are eqs. (8) (reciprocal) and (11) (logarithmic).

(3) Overall, the predictions agree on the average with the measurements to within the accuracy of the measurements.

(4) These results cannot distinguish between energy theories of the glass transition and entropy theories.

(5) Compared to the same components in linear polymers, the component values in crosslinked polymers are larger than in linear polymers.

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