

Effects of Test Frequency and Cure on Glass Transition Temperature Predictions on Some Epoxy Polymers

INTRODUCTION

One of the uses of the assumption of additive properties is to predict properties from the polymer repeat unit. In this note we will examine the glass transition temperature T_g . To calculate the T_g of polymers, the component contributions must be known. Component contributions are obtained from the measured T_g of known polymers. There are many methods to measure T_g . For the same polymer, different test methods may give different results. For example, the T_g determined by torsional pendulum (TP) is usually 5–15 K higher than by differential scanning calorimetry (DSC). Thus the component contributions will depend on the method of measurement. To investigate this effect, TP measurements of T_g were made on the same series of polymers for which we have already published T_g values¹ determined by using a DSC.

Another complication in predicting the T_g values of polymers from the repeat unit is that T_g is known to depend not only on the idealized polymer structure but also the curing conditions used. As a polymer cures, crosslinking occurs, which has the effect of restricting the molecular motion of chains and increasing the glass transition temperature. To investigate this effect, some epoxies used by Pogany² that have a different cure than the epoxies of this work are included in this study.

The purpose of this note is first to compare the component contributions determined from DSC and TP measurements of the eight polyepoxides previously reported¹ and, second, to use the TP component contributions to calculate the T_g 's of a series of six polyepoxides used by Pogany, and, finally, to determine the TP component contributions for the 14 polyepoxides (i.e., the combination of our eight polymers and the six literature values).

EXPERIMENTAL

The polymer set used in this work was a well-characterized series of epoxy/diamines. The epoxy groups were derived from one of two resins diglycidyl ether of bisphenol A (referred to as D) and resorcinol diglycidyl ether (R). Four diamine curing agents were used: propanediamine (P), hexanediamine (H), dodecanediamine (D), and *m*-phenylene diamine (M). Further details of the structure and curing conditions of these polymers have already been published.³ These eight polymers can be expressed in terms of four components: $-\text{CH}_2-$, $-\text{C}_6\text{H}_4-$, $-\text{C}(\text{CH}_3)_2-$, and $-\text{ENE}-$, where E stands for the glycol ether group $-\text{OCH}_2\text{CH}(\text{OH})\text{CH}_2-$. The six epoxy polymers used by Pogany were synthesized from diglycidyl ether of bisphenol A similar to the one used in this work with six diamine curing agents: ethylenediamine (Et), propanediamine (P), butanediamine (B), pentanediamine (Pt), hexanediamine (H), and diamino diphenyl methane (DDM).

For the eight polymers of this work, the glass transition temperatures were determined using a torsional pendulum. A test specimen was excited in free oscillation at approximately 1 Hz. The logarithmic decrement was determined over a temperature range of 98–473 K. The glass transition temperatures were determined from the peaks of the logarithmic decrement curves. For the same eight polymers, the glass transition temperatures determined by differential scanning calorimetry (DuPont 990 Thermal Analyzer with a sapphire standard) have already been reported.^{1,4} It is expected that the TP T_g 's should be higher than the DSC T_g 's, because of the test frequency dependence of the glass transition temperature.

For the six epoxy polymers used by Pogany, the glass transition temperatures were also determined by using a torsional pendulum. Polymers DP and DH are a part of both sets of epoxies, but the measured T_g 's of this work are lower than Pogany's values. Since the T_g is a measure of the cure state of a polymer, the curing conditions of these two epoxies of this work are not identical to the epoxies of Pogany. It is also suspected that the other epoxies used by Pogany were more completely cured than the epoxies of this work.

Various methods of analyzing the glass transition temperature in terms of component properties

TABLE I
Glass Transition Temperature Measurements and Calculations Using TP Component Contributions

Polymers	Measured T_g (K)		Calculated T_g (K)	
	DSC	TP	a	b
DM	451	461	441	443
DD	366	376	379	380
DH	381	388	392	398
DP	395	409	401	409
RM	415	419	419	419
RD	334	348	348	347
RH	352	365	360	363
RP	364	366	368	375
Average difference (%)			1.3	1.4

^a Calculated from TP component contributions determined from the eight epoxies of this work.

^b Calculated from TP component contributions determined from the eight epoxies of this work and the six epoxies used by Pogany.

have been discussed.¹ For this work, the reciprocal equation was used. The reciprocal equation is

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

where T_{gi} is the component contribution of the glass transition temperature for component i , M_i is the molecular weight of component i , and $\sum_i M_i$ is the molecular weight of the polymer repeat unit. Equation (1) is generally used with linear polymers. We have shown in our previous paper¹ that eq. (1) is also applicable to crosslinked polymers by assuming an idealized polymer structure. However, there is some error in making this assumption. This error appears as scatter in the values of the component contributions.

RESULTS AND DISCUSSION

From the TP measurements, the T_g values are given in Table I, compared with the DSC results previously reported. As expected, the TP values are about 10 K higher than DSC values. Glass transition temperature calculations are also presented in Table I, where at the bottom of the table the average percent differences between the measured and calculated values are shown. Also listed in Table I are the T_g 's calculated from TP component contributions determined from the eight epoxies of this work, where in the last column the T_g 's are calculated from TP component contributions determined from the set of 14 polymers made by combining our eight epoxies and the six epoxies of Pogany. Both columns of calculated values are in very good agreement with the measured TP values, where average percent differences are essentially the same. It has been shown in our previous

TABLE II
Component Contributions Determined from DSC and TP Measurements

Components	T_{gi} (K)		
	DSC	TP ^a	TP ^b
—CH ₂ —	250	286	266
- ENE— ^c	293	280	311
—C ₆ H ₄ —	1019	1425	829
—C(CH ₃) ₂ —	253	230	303

^a Determined from the eight epoxies of this work.

^b Determined from the eight epoxies of this work and the six epoxies of Pogany.

^c Where E stands for the glycol ether group —OCH₂CH(OH)CH₂—.

TABLE III
Glass Transition Temperature Calculations Using DSC and TP Component Contributions on
Polymers from Pogany

Polymers	Measured T_g (K)	Calculated T_g (K)		
	TP	a	b	c
DEt	418	400	404	413
DP	415	396	401	409
DB	405	392	398	405
DPt	403	388	395	401
DH	396	384	392	398
DDm	457	452	464	457
Average difference (%)		3.3	2.2	0.6

^a Calculated from our DSC component contributions.

^b Calculated from TP component contributions determined from the eight epoxies of this work.

^c Calculated from TP component contributions determined from the eight epoxies of this work and the six epoxies of Pogany.

paper¹ that the accuracy of the T_g calculation is dependent on the accuracy of the measurements. The average percent difference for the T_g calculations¹ from DSC contributions is about two times lower, 0.6%, than TP calculations. This is because the TP measurements are not as accurate as the DSC measurements.

The DSC and TP component contributions for the eight epoxy polymers are listed in Table II, columns two and three, respectively. Comparing the DSC contributions of column two and TP contributions of column three, the TP contribution of $-C_6H_4-$ shows a dramatic increase whereas the remaining three component contributions remain unchanged. This increase is expected since the TP T_g 's are larger than the DSC T_g 's. Then the component $-C_6H_4-$ is sensitive to the frequency effect of the two different measuring techniques. Comparing the two sets of TP results, the big change again occurs with $-C_6H_4-$: this time it decreases. This decrease is unexpected since the T_g 's of the epoxides used by Pogany are higher than those of this work, then the expected effect of combining the epoxies is to raise the contributions. It seems that $-C_6H_4-$ is also sensitive to the cure state of the epoxies, but it appears to decrease with increasing curing.

The glass transitions temperature calculations using DSC and the two sets of TP contributions on the six polymers used by Pogany are shown in Table III, with their measured T_g 's. Using DSC contributions the average percent error is the highest, because the effects of test frequency and the cure state of the polymers are not considered by these component contributions. Now using TP contributions determined from the eight epoxies, the agreement between the measured and calculated T_g 's is better than the first calculations as expected, because the comparison is made between TP measurements. Of course, using TP contributions determined from the fourteen epoxies, the agreement is best, because the two effects are considered in these contributions. Also, the accuracy of Pogany's measurements is very good compared to our measurements, because the average percent difference is so low.

CONCLUSIONS

Based on the results presented here, the calculated T_g 's using DSC component contributions of the six epoxies used by Pogany were within 3.3% of the measured TP values. If the frequency effect due to the measuring technique was taken into account, meaning using TP component contributions, the calculated T_g 's were slightly better, where the average difference was 2.2%. Now if both the effects of frequency and curing conditions of six epoxies were considered, then the calculated T_g 's were within 0.6% of the measured values. The component contribution of $-C_6H_4-$ appeared sensitive to both effects.

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