# Cure and Glass Transition Temperature of the Bisphenol S Epoxy Resin with 4,4′-Diaminodiphenylmethane

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**ABSTRACT:** The curing reaction of bisphenol S epoxy resin (BPSER) with 4,4′-diaminodiphenylmethane (DDM) was studied by means of torsional braid analysis (TBA) in the temperature range of 393–433 K. The glass transition temperature ($T_g$) of the BPSER/DDM system is determined, and the results show that the reaction rate increases with increasing the $T_g$ in terms of the rate constant, but decreases with increasing conversion.[1] The $T_g$ of BPSER/DDM is about 40 K higher than BPAER/DDM. The gelation and vitrification time were assigned by the isothermal TBA under 373 K; in addition, an FTIR spectrum was carried out to describe the change of the molecular structure. The thermal degradation kinetics of this system was investigated by thermogravimetric analysis (TGA). It illustrated that the thermal degradation of the BPSER/DDM has $n$-order reaction kinetics.[2] © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 78: 794–799, 2000

**Key words:** bisphenol S epoxy resin; 4,4′-diaminodiphenylmethane; glass transition temperature; thermal degradation kinetics

## INTRODUCTION

Bisphenol A epoxy resin (BPAER) is widely employed as polymeric materials, as polymer matrices for composite material, and as adhesives. The improved epoxy resin based on bisphenol S (BPSER) is considered worthy of further study in terms of its good thermal stability, chemical resistance, mechanical properties, and modification because of the introduction of sulfonyl groups into the backbone of the resins.[3,4] The cure process and thermal properties of this thermosetting material affect its macroscopic properties, which govern its end-use performance. This resin has been synthesized, and the formation kinetics have been studied.[5–7] However, the description of thermal property and degradation kinetics about the BPSER/DDM system has been lacking until now.

The glass transition temperature ($T_g$) can be used effectively to illustrate the curing reaction process.[1] In this article, torsional braid analysis (TBA), used to determine the $T_g$ of the BPSER/DDM system, is a particularly convenient index for relating cure to properties. Moreover, the $T_g$s were measured for BPSER/DDM cured isothermally at different temperatures for various periods. The effect of the BPSER/BPAER ratio on $T_g$ was investigated. Structure changes of BPSER/DDM during the curing process were investigated by Fourier transition infrared analysis (FTIR). The mechanism and kinetics of thermal degradation were studied by means of thermogravimetric analysis (TGA).

## EXPERIMENTAL

### Material

Bisphenol S (BPS) was recrystallized from the toluene, and a crystal with a melting point of

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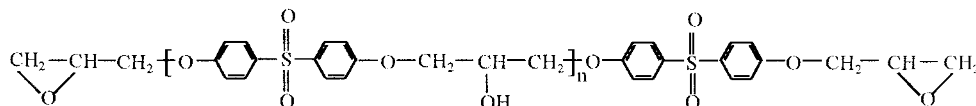
240°C was obtained. Epoxy resin based on bisphenol S was synthesized according to the literature,[8] and its molecular structure has the following approximate form:



where $n$ = 0–1. The epoxy value, determined according to the literature,[9] was 0.31 mol/100 g. Bisphenol A epoxy resin E44 was available commercially. Epichlorohydrin, NaOH, KOH, acetone, ethylalcohol, hydrochloric acid, and DDM were all analytically pure grade, and were supplied by the Beijing Chemical Reagent Co.

### IR Measurements

The BPSER/DDM samples were prepared with a stoichiometric ratio of one epoxy group with one amine hydrogen, and they were mixed uniformly. During the isothermal curing, an FTS-40 IR spectrophotometer was used for the investigation of the structure changes of the curing system. The sample was dissolved in trichloromethane, then coated into a thin film on a potassium bromide plate. When the solvent in the film was completely evaporated in vacuum, the potassium bromide plate was first scanned by the IR instrument. Thereafter, the plate was placed in a heated oven with a fixed temperature of 358 K. During the curing reaction at this temperature the plate was repeatedly withdrawn at regular time intervals for analysis.

### Torsional Braid Analysis (TBA)

Specimens, prepared by dipping heat-cleaned glass fiber braid in the solution of the BPSER/DDM system, which was mixed at an equivalent ratio of 1 : 1, were completely evaporated in vacuum.

1. One was inserted into the GDP-3 TBA analyzer, which had been preset at the fixed cure temperature, $T_c$, 373 K for 325 min.
2. The air oven was first heated up to a desired temperature and kept for a certain period of time until the system reached the equilibrium state. Specimens were quickly set into the thermostatic baths at a $T_c$ between 393 and 433 K. After curing 5, 10, 15, 20, 25, 30, 60, and 120 min, respectively, they were taken out and cooled them to room temperature, then their $T_g$s were determined with a heating rate of 2 K/min.
3. The thermomechanical properties were determined with TBA by changing the ratio of BPSER and BPAER. But the ratio of the epoxy group and the amine hydrogen remained 1 : 1 after being cured at 343 K for 2 h, 403 K for 2 h, and 433 K for 2 h. The TBA measurement was to be carried out.

### TGA Measurements

BPSER were used as received, and mixed with the hardener DDM at a ratio of 1 : 1.1. After curing at 413 K for 6 h, thermal analysis was carried out on a Shimadzu DT-40 thermogravimetric analysis (TGA). About 3 mg of the sample, which had been completely cured and grounded to fine powders, was put into a platinum cell and placed on the detector plate, then the furnace was heated at a heating rate of 10 K/min in nitrogen atmosphere from 25 to 500°C.

## RESULTS AND DISCUSSION

### Isothermal Curing

The FTIR spectrums of the BPSER/DDM system were investigated. The most significant feature is the appearance of the epoxide group absorption at 914 $cm^{-1}$. It is observed that this absorption gradually decreases with increasing time, and finally becomes a tiny peak when the curing time increases to 6 h at a $T_c$ equal to 373 K. The main change of the structure for the epoxy resin curing system can be reflected.

The dynamic mechanical spectrum of the epoxy system during the isothermal cure at 373 K is shown in Figure 1. From the maxima in the logarithmic decrement vs. the curing time plot the times to gelation and vitrification were conveniently assigned. The first transition is assigned to macroscopic gelation: $t_{gel}$ = 5.2 min. The second transition is assigned to vitrification, which oc-

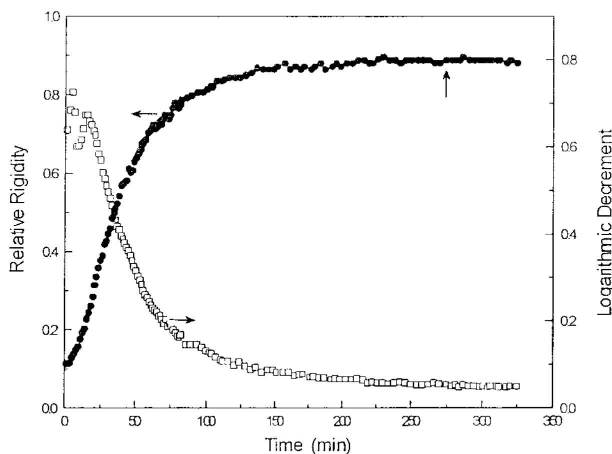



**Figure 1** The dynamic mechanical spectrum of the BPSER/DDM system during the isothermal cure at 373 K for 325 min.

curs when the glass transition temperature rises to the cure temperature: $t_{\text{vit}} = 15.7$ min. Cure proceeds beyond the assigned time to vitrification to eventually form a glassy state, and the relative rigidity at each $T_c$ reaches a plateau. As seen from Figure 1, the time of complete curing or to a glassy state is beyond 270 min under this cure temperature, $T_c = 373$ K, which is identical with the FTIR analysis we have already discussed.

## $T_g$ Value and the Curing Process

$T_g$ has been used directly as a parameter for conversion in analysis of reaction kinetic models,[10,11] and there is a one-to-one relationship between the $T_g$ and the degree of cure. It is a sensitive parameter because of the ease of measurement of $T_g$ by TBA, and is particularly useful at high conversion and after vitrification because of the nonlinearity of $T_g$ vs. conversion reaction.[12,13] The $T_g$ values are measured for the BPSER/DDM specimen cured isothermally at different temperatures for various periods. $T_g$s obtained from TBA measurement plotted vs. cure time under different $T_c$s is shown in Figure 2. As seen from Figure 2, different glass transition behaviors occurred for the samples with different degrees of cure. The initial $T_g$ of this system, that is to say, the $T_g$ of the uncured system, was determined to be 275.6 K.

At the beginning of the curing reaction process, only primary amines are contained in the system, so primary amines in DDM first react with epoxide groups in BPSER, and small linear molecular are formed. This process is characterized by a gradual increase in molecular weight. At this stage, the degree of cure is low, and the sample gives a low $T_g$ value. Certainly, this transition behavior is the reflection of the movement of the linear molecular chain in the system. With the molecular weight increasing, the $T_g$ value increases. Because only linear molecular chains exist in this stage, there are many chances for the moleculars to collide, and this results in a high reaction rate. With the reaction of primary amines proceeding, some secondary amines gradually get the chance to react with epoxide groups. As a result, crosslinking has occurred, and the weight-average molecular weight increases. So the mobility of the chains is decreased, and the chances for the molecular to collide with each other are reduced. With the reaction time rising, the crosslinking density further increases, and the unreacted epoxide groups in the linear chain segment gain a chance to react with secondary amines. With a rising curing time, the $T_g$ of the network is enhanced with a decrease in the distance between crosslink points. Correspondingly, the increasing crosslinking density does not allow the intermolecular reaction to proceed any longer. At this time, the sample has been highly cured and the $T_g$ value is get higher.

At low $T_c$s, as observed, $T_g$ increases rapidly during the early stages of cure, then levels off and remains a low temperature value compared with the higher $T_c$s. Even if we prolong the curing time under low $T_c$s, the resin system is difficult to reach high conversion. At the higher curing temperature, $T_g$ reaches the maximum so quickly that a high degree crosslink structure is formed

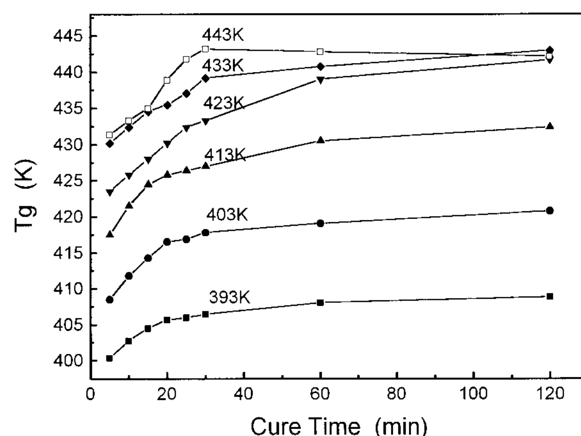



**Figure 2** $T_g$ values of the BPSER/DDM cured isothermally at different temperatures for various periods.

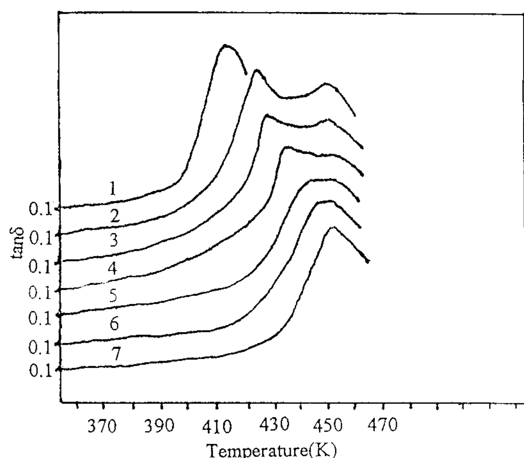



**Figure 3** Mechanical loss spectrum of BPSER/BPAER/DDM BPSER/BPAER: (1) BPAER 100, (2) 1/9, (3) 2/8, (4) 3/7, (5) 5/5, (6) 7/3, and (7) BPSER 100.

after a very short period. The maximum $T_g$ did not increase at $T_c$ = 443 K in comparison with $T_c$ = 433 K, and it is 443 K in the curing system. But the $T_g$ value decreased a little to the contrary at $T_c$ = 443 K when the curing time is prolonged because of the partial degradation of the polymer chain. So, it was better for this curing system to control the $T_c$ under 443 K so that the break of the chain could be prevented. Because the process of vitrification usually drastically lowers the reaction rate, a complete cure usually involves temperatures in the vicinity of the maximum of the glass transition temperature. This is indicative of autocatalytic kinetics in the first stages and diffusion-controlled reaction as the $T_g$ rises.[11] Similar results have been obtained based on our study of the conversion or reaction rate vs. time at different isothermal cure temperatures.[14] Obviously, it is improper to be utilized in industrial production. A technique of three stages—low temperature, moderate temperature, and high temperature—could be better for the practice. To obtain an ideal curing conversion and appropriate curing rate, we should select a suitable $T_c$ such as 343 and 353 K in the first stage. Then we should raise the temperature to 403 and 413 K, and finally to 433 K so that the system can cure completely.

### Curing Process of BPSER/BPAER/DDM

In recent years, the production of the BPAER is larger than any other epoxy resins. There are many references[15,16] describing the BPAER modified by BPSER, but the studies on the cure process have been lacking until now. Also, by monitoring the dynamic mechanical property of the BPSER/BPAER/DDM system, we can determine its cure reaction. Fixing the ratio of the epoxy group and the amine hydrogen of DDM at 1 : 1, the effect of the BPSER/BPAER ratio on mechanical loss was determined, and the result is shown in Figure 3. With increasing the content of BPSER, a double peak of tan δ turned into a single one. The system has two $T_g$s when it has the lower proportion of BPSER. The first $T_g$ of curve 2 is 421 K, and the second one is 449 K when the content of BPSER was 10%. It shows that the phase separation appeared in the system then. The system almost turned into one phase when the proportion of BPSER was 50%. The peak of tan δ gets thinner as the content of BPSER increases.

As seen from $T_g$ values, the first glass transition temperature depended on the content of BPSER, and it is 10–20 K higher than the system of BPAER/DDM. Although the second one stabilized at 451 K, which was the $T_g$ of the completely cured BPSER/DDM system, it is about 40 K higher than that of BPAER/DDM system of 413 K. This is due to the different molecular structure of the BPSER and BPAER. Bisphenol S has an electron-withdrawing group, —$SO_2$—, which effects the epoxide group more than the —$C(CH_3)_2$— group of the bisphenol A. Higher $T_g$

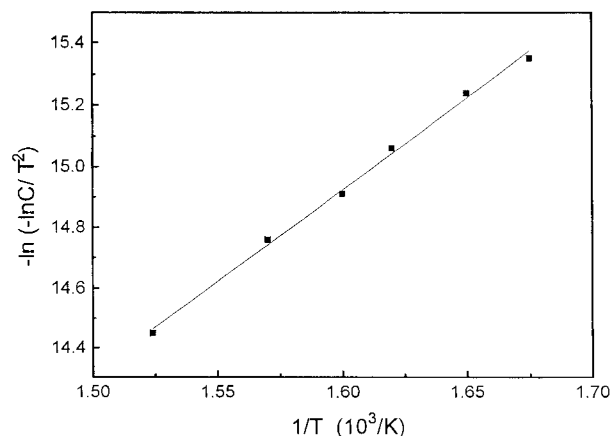



**Figure 4** Weight loss function,

$$-\ln\left(-\frac{\ln C}{T^2}\right)$$

vs. reaction temperature $T$ of the thermal degradation for the BPSER/DDM system.

**Table I Thermal Weight Loss (%) of BPSER/DDM at Different Temperatures**

| T (K) | 576 | 596 | 616 | 636 | 656 | 676 | 696 | 706 |
|---|---|---|---|---|---|---|---|---|
| C (%) | 5.51 | 7.51 | 10.37 | 14.21 | 21.00 | 25.68 | 27.61 | 28.45 |

values were found at polymers with a higher polar group —$SO_2$— in comparison with the —$C(CH_3)_2$— group. We can say that the —$SO_2$— group in the resin raises the $T_g$ of the cured material. Furthermore, there is no a long-pair electron in the hardener, DDM, which corresponds to the ring opening of the epoxy groups during the reaction. Thus, investigation of molecular structure–macroscopic property relations is the principal theme of polymer material science. When BPAER was the main body, BPSER partly came into the BPAER phase and was crosslinked. So the separated phase of the BPSER resin remained in the system. BPSER can disperse into the BPAER phase while the content of BPSER is above 50%. The BPSER is the main body; it has better compatibility, and results a wider single peak in the tan $\delta$ curve.

### Thermal Stability

When thermogravimetric analysis was carried out, the weight loss fractions of BPSER/DDM were calculated, and the weight loss rates were shown as a function of temperatures in Figure 4 and Table I. The following kinetic equation was assumed to hold for the thermal degradated reaction.[2] When the reaction order $n = 1$, it follows as:

$$\ln\left(-\frac{\ln C}{T^2}\right) = \ln\left[\frac{AR}{\varphi E}\left(1 - \frac{2RT}{E}\right)\right] - \frac{E}{RT}$$

where

$$C = \frac{W}{W_0}$$

$W$ is remaining weight, $W_0$ is the total weight loss, $E$ is the activation energy, $A$ is the frequency factor, $\varphi$ is the heating rate, and $R$ is ideal gas constant. According to this equation, a plot of

$$\ln\left(-\frac{\ln C}{T^2}\right)$$

against $1/T$ is shown in Figure 6. It is observed that the activation energy of thermal degradation for the BPSER/DDM system is 50.025 kJ/mol, and the linear correlation coefficient is 0.998.

## CONCLUSIONS

1. TBA can be used effectively to study the curing process of epoxy resins and determine the $T_g$.
2. The BPAER/DDM system has a 5.2-min time to gelation, and a 15.7-min time to vitrification; the complete curing time is about 270 min at 373 K. The conversion of the curing reaction and $T_g$ depend on the curing temperature. For this system, we can obtain an ideal curing conversion and appropriate curing rate at 413 or 403 K.
3. The BPSER/DDM has a $T_g$ of 451 K, which is about 40 K higher than BPAER/DDM. The BPSER/BPAER/DDM system has two $T_g$s when it has a lower content of BPSER. The system almost turned into one phase when the proportion of BPSER was 50%. The peak of tan $\delta$ got thinner as the content of BPSER increased.
4. The thermal degradation kinetics of this system investigated by thermogravimetric analysis illustrates that the thermal degradation of the BPSER/DDM has $n$-order reaction kinetics. The activation energy of this system is 50.025 kJ/mol and $n = 1$.

## REFERENCES


1. Pang, K. P.; Gillham, J. K. J Appl Polym Sci 1990, 39, 909.
2. Liu, Z. H. Thermoanalysis Introduction: Chemical Industry Publishing Co.: Beijing, 1991.
3. Liaw, D. J.; Shen, W. C. Angew Makromol Chem 1992, 199, 171.
4. Bansal, R. K.; Agarwal, R.; Keshav, K. Angew Makromol Chem 1979, 79, 125.
5. Masters, J. E. U.S. Pat. 2,767,157 (1956).

6. Gao, J. G.; Liu, Y. H.; Wang, F. L.; Shi, L. Q. Technol Adhes Sealing 1986, 7, 5.
7. Gao, J. G. J Appl Polym Sci 1993, 48, 237.
8. Rainer, E.; Udo, G.; Heinrich, H. W.; Eruin, B. Ger. Pat. DD 228,279 (1985).
9. Jay, R. R. Anal Chem 1964, 36, 665.
10. Simon, S. L.; Gillham, J. K. J Appl Polym Sci 1993, 47, 461.
11. Wisanrakkit, G.; Gillham, J. K. J Appl Polym Sci 1990, 41, 2885.
12. Wisanrakkit, G.; Gillham, J. K.; Enns, J. B. J Appl Polym Sci 1990, 41, 1895.
13. Venditti, R. A.; Gillham, J. K. J Appl Polym Sci 1997, 64, 3.
14. Li, Y. F.; Shen, S. G.; Liu, Y. F.; Gao, J. G. J Appl Polym Sci 1999, 73, 1799.
15. Gao, J. G.; Wang, F. L. Chem. J. Chin Univ, 1987, 8, 572.
16. Masuo, M.; Satoru, O.; Sumitomo Baketite Co. Ltd. Jpn. Pat. 91,143,980 (1991).