Characterization of Epoxy Prepreg SPX 8800 System by Isothermal Differential Scanning Calorimetry

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SUMMARY: Isothermal Differential Scanning Calorimetry (DSC) was used to study the curing behavior of epoxy prepreg SPX 8800 system, which contains DGEBA/DICY/Diuron (Diglycidyl ether of bisphenol A/Dicyandiamide/Diuron) reinforced by three layers of glass fibre. The rate curves from the DSC study agreed well with those obtained from the isothermal FT Near Infrared (FTNIR) study and similar activation energy was obtained in the range of 92.6 to 87.7 kJ/mol up to 50% total conversion. Modelling of the whole DSC trace with empirical equation $dx/dt=kx^m(A-x)^n$ gave relatively good fitting of the experimental curves (the error is lower than 15%.) in the whole studied cure temperature range (75-110°C) and no significant difference in cure kinetics was observed for both epoxy prepreg and neat resin.

Introduction

Epoxy prepreg SPX8800 is a commercial one formulation epoxy resin impregnated in glass fibre laminates, which is widely used in making windmill blades and construction of marine vessels. The epoxy resin contains DGEBA, DICY hardener and Diuron accelerator up to 45% by weight. The Diruon accelerator enables a latent and relatively low temperature curing process and the glass fibre reinforcement leads to a low cost product with good mechanical property. Since the cure temperature, time and other factors have large effect on the final properties of the cured sample, it is important to study the cure kinetics as well as the correlation between the degree of cure and the thermal and mechanical properties in order to design the optimum cure conditions. Among the techniques that utilized in the study of the epoxy curing, DSC has been proved to be a very useful tool in studying both the cure kinetics and the thermal properties. [1,2]

Since the heat envolved during the reaction and the glass transition temperature (Tg) can be measured directly from the DSC measurement, the important Tg versus extent of conversion relationship can be obtained. [3,4] In addition, various approaches have been investigated on modelling the cure kinetics. Equation 1 shows a general rate law [1] where x is the extent of cure, k is the Arrhenius rate constant, and f(x) is a function that depends on the reaction mechanism which can be treated in a phenomenlogical manner

 CCC 1022-1360/00/$ 17,50+.50/0

to obtain a useful kinetic model without requiring a thorough understanding of the cure chemistry. Several researchers had studied the DICY cured epoxy resin by assuming the cure following the same reaction mechanism and they found this assumption was valid at low epoxy conversion degree.

$$dx/dt = kf(x) \quad (1)$$

$$dx/dt = (k_1 + k_2x^m)(1-x)^n \quad (2)$$

Equation 2 is a widely used rate law which considers the autocatalytic characteristic of the epoxy curing where initial reaction rate exists. k_1 and k_2 are the rate constants, and m and n are the reaction orders which contribute to the autocatolytic and noncatalytic reactions, respectively. With this rate law, good fittings and predictions on the DSC cure trace were accomplised for different epoxy systems. [8-10] In case of a study on DICY cured epoxy adhesive, [11] however, the rate law could not predict the cure kinetic at low cure temperatures at the later stage of cure. In this study, the isothermal DSC curing of both reinforced epoxy prepreg and neat resin and the curve fitting of DSC traces by the above two rate laws were carried out and compared. A modification of equation 2 by using the final conversion degree A instead of an overall conversion degree 1 was found to be efficient in modelling the whole DSC trace at different temperatures. A comparison of DSC and FTNIR isothermal curing results is also discussed.

Experimental

The epoxy prepreg SPX 8800 is a commercial product from SP System (UK) and used directly as received. The epoxy neat resin with the same resin formulation was made by mixing the SPX7650 resin with SPX7922 hardener (100:21 by weight). Both the later two products were from SP System (UK) also.

FTNIR study on the isothermal cure of epoxy prepreg was performed on the Bomem FTNIR spectrometer with InAs detector. One layer of epoxy prepreg was either cured directly in a glass vial (cure condition 1) or between two pieces of glass plates (cure condition 2) as described in reference. [12]

Isothermal DSC curing of epoxy prepreg was carried out on the Mettler Toledo DSC 822 module equipped with TSO 801RO universal sample robot autosampler. The epoxy prepreg was cut to a sample size of about 15 to 25 mg and put into a volatile 40 µl aluminum pan. In case of epoxy neat resin, 10 to 20 mg sample was used. The weight loss during the cure can be neglected. Samples were cured at different temperatures

from 75 to 120 °C for different time periods. The cured sample was cooled down to room temperature and Tg (1) was measured by scanning from 25 to 230 °C at 10 °C/min. Then the sample was quenched to 25 °C and scanned again from 25 to 300 °C at the same heating rate to get Tg (2). The neat amount of epoxy resin in the prepreg was obtained by decomposing the cured sample at 600 °C for 20 min.

The area under the isothermal DSC curve was integrated by an extrapolated straight line at the end of reaction in the Star software. The total heat of the reaction (Q_{Total}) was determined from the integral area of the DSC curve cured at 120 °C for 2 hours. The DSC curves were normalized to epoxy sample size and based on the assumption that the heat evolved at any time during the cure reaction is proportional to the extent of monomer conversion, the conversion degree is $x = Q_t/Q_{Total}$ and the cure rate is $dx/dt = (1/Q_{Total}) \times (dQ/dt)$, where Q_t is the area (accumulated heat) up to cure time t and dQ/dt was read from the DSC curve.

Results and Discussion

Comparison of the DSC and FTNIR epoxy cure results

Figure 1 shows the conversion degree versus time during the epoxy prepreg cure, which indicates that the conversions at the early stage of reaction at different temperatures are similar detected by DSC and NIR, but the rates decrease faster in DSC curing and lower conversion degree obtained for samples cured at low temperatures from 75 to 90 °C. Comparison of the Tg of cured samples are listed in Table 1 and generally agree with the conversion results, that is, lower epoxy conversion results in lower Tg (1).

The reaction rate from DSC and NIR studies are further compared in Figure 2. The rate value for DSC is obtained directly from the DSC curve and for FTNIR is calculated from the first differential of conversion versus time curve as shown in Figure 1. It can be seen that the shapes of the rate curve are quite similar and the time to reach the peak position also close to each other. It has been found [12] that moisture in the epoxy prepreg could influence the curing kinetics and the final epoxy network due to the different cure conditions. The different final conversion degree obtained under NIR and DSC curing is supposed to be caused by the difference in the water evaporation rate and degree as well as the small sample dimension used in DSC study.

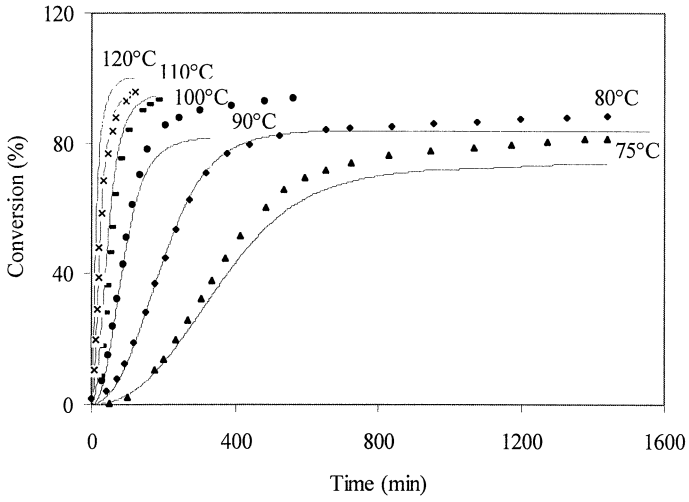

Figure 1. Plot of conversion *vs* time at different cure temperatures obtained from isothermal DSC (line) and NIR (cure condition 1, solid points) study.

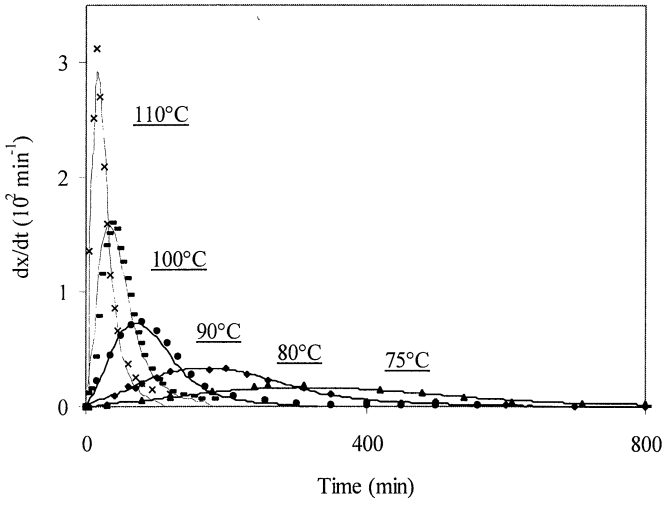

Figure 2. Comparison of rate curves from DSC (line) and NIR (solid points) study.

As described in the introduction part, if the reaction follows the same reaction mechanism, the f(x) fraction in equation (1) will be independent of temperature. The

rate constant k can be expressed through an Arrhenius relationship and the activation energy at different conversion degree can be obtained from the slope of the plot of ln(dx/dt) against temperature T. The activation energy falls in the range 92 – 86 kJ/mol up to 50% conversion, which is consistent with the results from NIR study and other reported values on the DGEBA/DICY/Uron systems. [5,12,13]

Table 1. Comparison of Tg of the samples cured under DSC and NIR conditions.

Cure Temp. (°C)	Cure Condition [a]	Tg (1) [b]	Tg (2) [b]	Conversion (%)
75	NIR (a)	89.5	115.8	81.4
	NIR (b)	92.9	113.0	85.4
	DSC (prepreg)	85.6	111.9	73.7
	DSC (neat resin)	91.7	105.7	77.3
80	NIR (a)	97.5	117.8	88.3
	NIR (b)	98.0	114.0	87.5
	DSC (prepreg)	93.7	112.8	83.6
	DSC (neat resin)	99.5	105.3	83.8
90	NIR (a)	104.5	116.8	94.0
	NIR (b)	105.6	113.4	91.3
	DSC (prepreg)	99.7	110.5	81.4
	DSC (neat resin)	99.6	104.9	85.4
100	NIR (a)	108.0	114.5	93.5
	NIR (b)	108.4	109.8	98.6
	DSC (prepreg)	105.1	112.8	94.4
	DSC (neat resin)	105.0	103.7	90.8
110	NIR (a)	111.2	115.8	95.6
	NIR (b)	110.1	110.4	97.3
	DSC (prepreg)	107.1	111.2	94.5
	DSC (neat resin)	105.8	102.3	97.6

[a] In cure condition NIR (a) the epoxy prepreg was cured directly in a glass vial, in condition NIR (b) the epoxy prepreg was put between two glass plates.
[b] Tg (1) was determined by scanning the cured sample from 25 to 230 °C at 10 °C/min, by quenching the same sample to 25 °C, a second scan at the same heating rate was run to get Tg (2).

Modelling of DSC cure kinetics on epoxy prepreg and neat resin

Equation 3 is used to model the whole DSC curves at different cure temperatures.

$$dx/dt=kx^m(A-x)^n \qquad (3)$$

Equation 3 is derived from equation 2 since zero initial rate were observed from the DSC traces of epoxy prepreg. Second order reaction is assumed as m + n =2, and A is the final conversion degree at cure temperature T. When A is assumed to equal to 1 in all the cure temperature range, a precise fit of the calculated and experimental curves up to 50% conversion is obtained and the activation energy is similar to the above results

by assuming the reaction mechanism is the same. However, the experimental rate decreased markedly afterwards due to reaching the diffusion controlled stage. The diffusion controlled kinetics results in the vitrification of the resin and ultimate conversion degree lower than 100% at low cure temperatures, so final conversion degree A is used in equation 3 instead of 1, and relatively good fittings of the calculated and experimental curves are obtained in the whole DSC trace as shown in Figure 3. The prediction error between the experimental and calculated curves is expressed by the difference in the integrated area under the curve. It is found that the error or difference is lower than 15%. Table 2 lists the different parameters that used in the curve fitting. To ascertain the kinetic parameters, the plots of conversion versus time calculated by the numerical integration of equation 3 through the Runge-Kutta method are compared with experimental values as shown in Figure 4. Very good agreement is observed confirming that the kinetic parameters have been chosen correctly. From Table 2, we can see that the conversion degree at the DSC curve peak position is around 0.3 in spite of cure temperature (75-110°C), which is a typical phenomenon in autocatalytic reaction system with known chemistry. The value of m decreases with increasing temperature. The activation energy is 69,9 kJ/mol as shown in Figure 5.

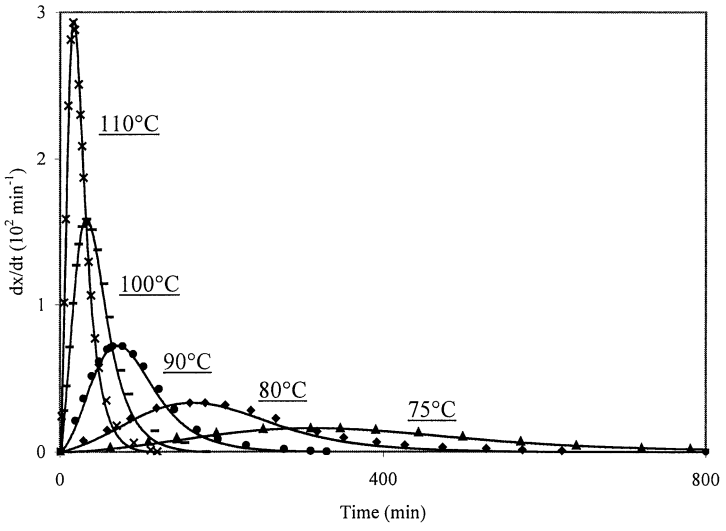

Figure 3. The DSC curing curve obtained experimentally (solid points) and theoretical prediction from equation 3 (line) for the epoxy prepreg.

Table 2. Temperature dependence of cure kinetics parameters in equation 3.

Epoxy type	Cure Temp.(°C)	Cure Time (h)	t_p [a] min	x_P [b]	m[c]	A	K (10^2 min^{-1})
	75	24	322.3	0.31	0.8	0.737	1.13
	80	26	164.7	0.32	0.765	0.836	1.79
Epoxy	90	5	70.7	0.30	0.74	0.814	4.07
prepreg	100	3	32.3	0.30	0.65	0.944	6.29
	110	2	16	0.28	0.6	0.945	11.13
	120	2	6.8	0.24	0.477	1	18.49
	75	24	230	0.31	0.78	0.773	1.59
	80	26	147.3	0.30	0.71	0.838	2.33
Epoxy	90	5	58.5	0.31	0.79	0.854	5.08
neat	100	3	27.8	0.31	0.76	0.908	9.81
resin	110	2	13	0.30	0.65	0.976	16.58
	120	2	6.7	0.30	0.53	1	26.73

[a] t_p is the time to reach the DSC peak position.
[b] x_P is the conversion degree at the DSC peak position.
[c] n=2-m.

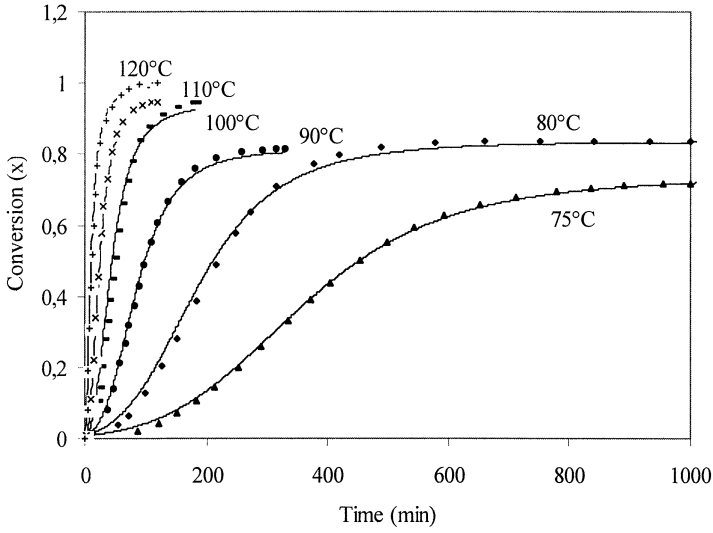

Figure 4. Conversion *vs* time for epoxy prepreg. The solid symbols represent the experimental data and the lines represent the theoretical predictions.

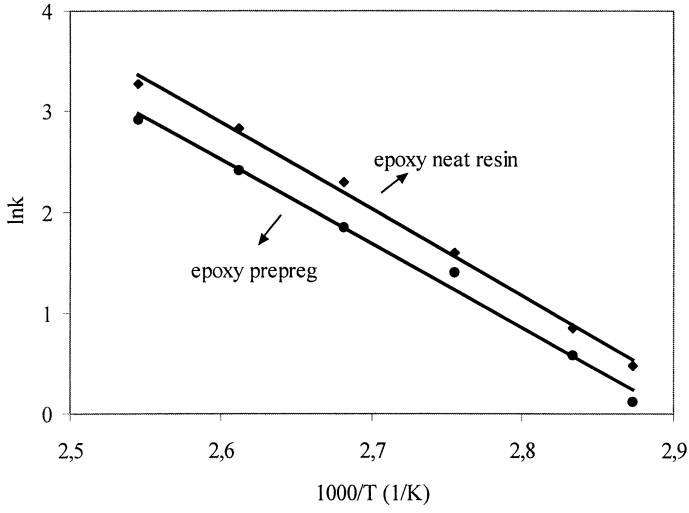

Figure 5. The Arrehnius plot of lnk *vs* 1/T predicted by empirical equation 3 for the neat epoxy resin (♦) and for the epoxy prepreg containing 45% epoxy resin (•).

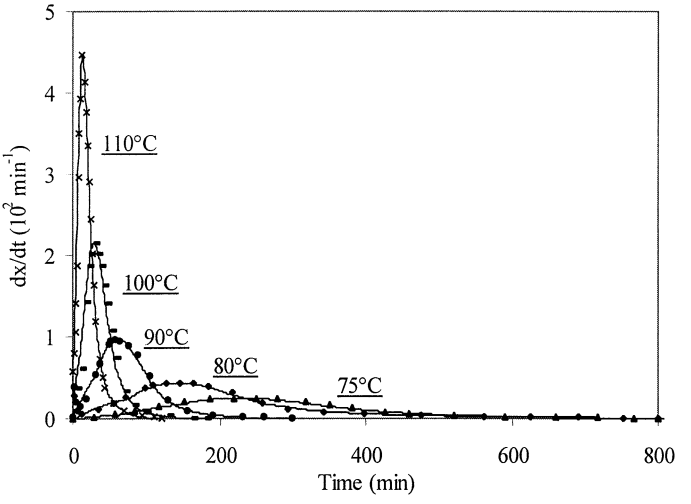

Figure 6. The DSC curing curve obtained experimentally (solid points) and theoretical prediction from equation 3 (line) for the epoxy neat resin.

The experimental DSC traces of the neat epoxy resin showed small peak at the beginning of the reaction due to the decomposition of Diuron to the reactive species, thus contribute to a nonzero initial rate, but the reaction rate decreased afterwards and

the total contribution of the heat envolved by Diuron decomposition is small and can be negelected. The same equation was applied to model the DSC cure trace on the neat epoxy resin. The results are shown in Figure 6 and 7. Very good fitting is obtained again for the whole DSC trace at different temperatures.

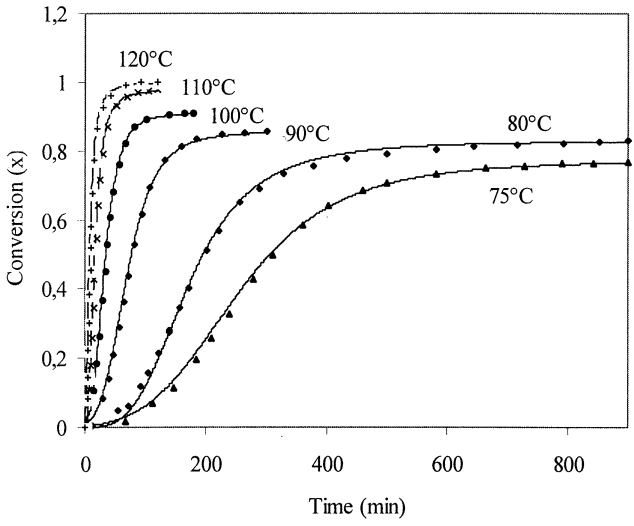

Figure 7. Conversion *vs* time for epoxy neat resin. The solid symbols represent the experimental data and the lines represent the theoretical predictions.

Comparison of the DSC cure on the epoxy prepreg and neat resin

From Table 2 it can be seen that the time to reach the DSC rate peak position for the epoxy neat resin is faster than that of the epoxy prepreg. And the total heat envolved in the neat resin (312.9 J/g) is higher than in the epoxy prepreg (234.3 J/g). However, it is also found that the conversion degree at the DSC peak position for both reinforced and neat resin is around 0.3 independent of cure temperature. The activation energy derived from euqation 3 for the two formulations are also very close. These observations indicate that there is no significant difference in the cure kinetics for the neat and reinforced resin. Similar results have been reported in literature. [14,15] Some authors [14] argued that the presence of fillers reduce the molecular mobility of reactive species and lower reaction rate. However, the difference of heat capacity between glass fibre and epoxy resin can also cause the observed reaction rate lower due to the large amount of glass fibre added (up to 55 wt%). The existence of glass fibre decreases the total reaction rate due to the difference in the heat capacity caused by its large amount (up to

55 wt%). Another significant effect of glass fibre addition is possibily its interaction with the final epoxy network formed in the cured resin. This effect can be obviously seen by comparing the Tg (2) in Table 1 for the neat and reinforced resin. The reinforced resin has higher Tg (2) than that of the neat resin. Further investigation on the interaction between the epoxy resin and the glass fibre at the interface should be done to declare the observed results.

Conclusion

Isothermal DSC curing of epoxy prepreg shows similar cure kinetics as observed from the FTNIR study. Modelling of the DSC curing on the neat and reinforced epoxy resin by modified empirical rate equation give good fittings to the experimental conversions. No significant difference in the cure kinetics observed for both the neat and reinforced epoxy resin. The existence of glass fibre increased the final Tg of the cured resin and other factors, such as water and small difference in the cure conditions could cause big difference in the final material thermal property but relatively less effect on the cure kinetics.

Acknowledgement

The authors would like to thank Vestas A/S for the financial support for this work.

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