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## Thermal Properties and Chemical Conversion of a Trifunctional Epoxy Resin Cured with Aromatic Amine

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### ABSTRACT

The thermal properties such as evolution of glass transition temperature,  $T_g$  with curing time and reaction conversion of a triglycidyl *p*-amino phenol (TGpAP) cured with 4, 4'-diaminodiphenyl sulfone (DDS) are difficult to measure. In this study, dynamic mechanical analysis (DMA), differential scanning calorimeter (DSC) and temperature-modulated differential scanning calorimeter (TMDSC) were used to characterize the TGpAP/DDS samples cured at 180°C. The results show that DMA is not sensitive enough to detect the evolution of  $T_g$  with curing time and the peak exotherm of DSC curves overlapped with  $T_g$ . Two different maximum  $T_g$  values were obtained from using two different equipment. DMA results show that the epoxy reached the maximum  $T_g$  after 90 minutes cured at 180°C while the maximum  $T_g$  obtained from TMDSC was 236°C after 150 minutes. The result from TMDSC seems more accurate because the evolution of  $T_g$  and chemical conversion can be followed starting from the beginning of the reaction until vitrification. At the maximum  $T_g$  the chemical conversion attained was 93 %. The  $T_g$  of 236°C, which is higher than the curing temperature,  $T_c$  (180°C) or  $T_g > T_c$  is due to the reactive nature of the TGpAP/DDS system.

**Keywords:** Epoxy, amine, DMA, DSC, TMDSC, conversion, glass transition temperature.

### Introduction

Epoxy resin is one of the most important thermosetting polymers, which is extensively used as the matrix for fiber-reinforced composites, structural adhesives, coatings, and other plastic engineering materials because of its high modulus and thermal stability. (Morgan 1985; Trostyanskaya & Shalin 1995). The degree of formation of epoxy networks during curing process i.e the reaction between epoxy prepolymer and amine compound is important because it determines the state of cure. The state of cure or the degree of conversion,  $p$ , of epoxy resin is one of the factors that determine the physical characteristics of epoxy resin, apart from aromatic content, cross-link density, type of curing agent and cure conditions. (Ellis 1993). The state of cure of an epoxy resin refers to the extent of cross-linking that has advanced throughout the polymer network. The epoxy-amine reaction must be taken to completion in order to achieve maximum cross-link density. Maximum conversion is necessary in order to minimise the presence of unreacted reactive groups, which can cause network defects and consequently introduce structural weaknesses in the cured resin. (Min et al. 1993). In addition, maximum chemical conversion in epoxy resin is desirable in order to produce a maximum glass transition temperature,  $T_{g\%}$ , for the highest application temperature. (Ellis 1993). In this case the maximum glass transition temperature,  $T_{g\%}$  can be taken as a point when the reaction has reached 100% conversion provided that no degradation has occurred during the curing process.

Most of the work on epoxy resin has been concentrated on the reaction of diglycidyl ether of Bisphenol A (DGEBA), a difunctional epoxy prepolymer with amine because the reaction is simpler and not as highly exothermic as TGpAP (Bonnaud *et al.* 2000). TGpAP, a trifunctional epoxy prepolymer is capable of generating materials with high glass transition temperature, which are in demand for high temperature applications. In industrial applications, TGpAP having a dynamic viscosity in the range of 0.55 – 0.8 Pa.s at 25°C is usually added to DGEBA prepolymers of viscosity ranging from 8 - 20 Pa.s at 25°C. The addition of TGpAP reduces the viscosity of the DGEBA prepolymers, which subsequently will improve the wetting of reinforcing particles or fibers. In addition, the presence of TGpAP in the blend will increase the final  $T_g$  of the matrix. In a DGEBA/DDS system, the resin can be cured at 190°C and post cured at 220°C for a specific time in order to obtain maximum conversion necessary for optimum mechanical properties. The reported value of  $T_{g\%}$  of DGEBA/DDS system is 210°C. However, not much work have been reported on the thermal properties of TGpAP cured with amine compound (Bonnaud *et al.* 2000) worked on a TGpAP/MCDEA (4,4'-Methylenebis (3-chloro-2,6-diethylaniline) system and followed the  $T_g$  as a function of reaction time, for partially-reacted sample at 160°C. Other author Varley *et al.* (2001) used DMA to follow the  $T_g$  of partially-reacted TGpAP/DDS system and reported difficulties in determining  $T_g$  from the peak of  $\tan \delta$  (DMA spectrum) for samples reacted above 160 °C. Most of the published reports on TGpAP/DDS (Varley *et al.* 2001; Hourston *et al.* 1997; Kim *et al.* 1995) show that:

- i. mostly DMA has been used to study the glass transition temperature,  $T_g$ ,
- ii. conclusive information on the curing cycle to achieve  $T_{g^*}$  or a fully-reacted state of MD system cannot be obtained,
- iii. the maximum glass transition temperature  $_{\max}T_g$ , from DMA varies from 205 to 265 °C.

Since not much work has been published on the TGpAP/DDS system, this study was conducted in order to elucidate the thermal properties of a trifunctional epoxy resin cured at 180°C and to establish the maximum glass transition temperature,  $T_{g^*}$ . In this study, differential scanning calorimeter, DSC, temperature-modulated differential scanning calorimeter (TMDSC) and dynamic mechanical analysis (DMA) were used to study the thermal properties of partially reacted and fully reacted epoxy resin.

## Materials and Methods

### Materials

The epoxy prepolymer used in this work was a triglycidyl p-amino phenol, (TGpAP), with an epoxy equivalent weight of  $101.8 \pm 1.2 \text{ g mol}^{-1}$ . The curing agent was 4,4'-diaminodiphenyl sulfone (DDS) supplied by Aldrich, which has a molar mass of  $248 \text{ g mol}^{-1}$  and purity > 98 %. The samples were prepared by mixing epoxy with DDS at 110°C using rotary evaporator. The amine/epoxy stoichiometric ratio was held constant at  $r = 1.0$ . After mixing, each mixture was immediately quenched with liquid nitrogen to stop the reaction and was stored at -28°C.

### Dynamic Mechanical Analysis

In this work a Rheometrics Mechanical Spectrometer, RMS-800 with a torsional-rectangular fixture was used to obtain the storage modulus ( $G'$ ), shear modulus ( $G''$ ) and  $\tan \delta$ . The partially and fully-reacted samples were machined to obtain specimens with dimensions of  $50 \times 10 \times 3 \text{ mm}^3$  for DMA measurement. Testing was done at a frequency of 6.28 radians/s (1 Hz) with a strain rate of 0.2 %. The temperature was lowered to -100 °C at the initial temperature sweep and was gradually increased to 330 °C at a rate of  $2 \text{ }^\circ\text{C min}^{-1}$ .

### Differential Scanning Calorimetry, (DSC) and Temperature Modulated Differential Scanning Calorimetry (TMDSC)

Measurements were conducted on a TA Instrument DSC 2920, equipped with a temperature-modulated facilities to allow either for TMDSC or normal DSC modes of analysis. The equipment was calibrated with high purity indium standards and dry nitrogen was used as purge gas. The samples were removed from the freezer and were allowed to warm to room temperature before testing. For comparison purposes, analyses were conducted under normal DSC and TMDSC modes.

The value of heat of complete reaction,  $H_c$ , associated with complete chemical conversion of the reactive groups was calculated from the average of five temperature scan experiments from -80 to 350°C using different heating rates of 2, 5, 10, 15, and  $20 \text{ }^\circ\text{C min}^{-1}$ . The experiments were performed for reaction times ranging from 4 to 480 minutes at 180°C. From these analyses  $T_g$  and  $DH_{\text{res}}$  were obtained at the different reaction times,  $t$ .

Two sets of sample were used for the determination of  $T_g$  and residual heat of reaction,  $DH_{\text{res}}$ . The samples were first reacted under isothermal temperature for a pre-determined time,  $t$ , and then was cooled to -50°C at  $20 \text{ }^\circ\text{C min}^{-1}$ . After the samples have been cooled, they were re-scanned using normal DSC mode ( $10 \text{ }^\circ\text{C min}^{-1}$  to 350°C). For comparison, another set of samples were re-scanned using modulated heating programme (TMDSC mode) at  $5 \text{ }^\circ\text{C min}^{-1}$  to 350°C, at an amplitude of  $2 \text{ }^\circ\text{C}$ , and a period of 60 s. The calorimetric scans were performed with nitrogen gas flow of  $50 \text{ cm}^3 \text{ min}^{-1}$ .

For the determination of  $T_{g^*}$ , the sample was heated at  $10 \text{ }^\circ\text{C min}^{-1}$  to  $30 \text{ }^\circ\text{C}$  above the  $T_{g^*}$ . The sample was maintained at that temperature for approximately 2 min, then it was cooled to  $100 \text{ }^\circ\text{C}$  below the  $T_{g^*}$  at a rate of  $20 \text{ }^\circ\text{C min}^{-1}$  to remove any thermal history. The sample was then re-scanned using a modulated heating programme as described above.

The conversion at time,  $t$  can be defined as

$$\begin{aligned}
 P &= \frac{(\Delta H_c - \Delta H_{\text{res}})}{\Delta H_c} \\
 &= 1 - \left( \frac{\Delta H_{\text{res}}}{\Delta H_c} \right)
 \end{aligned}
 \tag{1}$$

where  $DH_{res}$  is the enthalpy residue after reaction at time  $t$ , and  $DH_c$  is the enthalpy of complete reaction, obtained from temperature-scan mode.

## Results and Discussion

### Reaction Schedule for TGpAP/ DDS Epoxy System

A typical DMA spectrum of TGpAP/ DDS system of storage modulus ( $\log G'$ ) and  $\tan \delta$  versus temperature is shown in Figure 1. From the plot,  $T_g$  was taken as the position of the maximum peak of  $\tan \delta$  against temperature. As can be seen (Figure 1), the sample reacted for 30 minutes displays two  $\tan \delta$  peaks, first at 187 °C and a second peak at 274 °C. The first  $\tan \delta$  peak could be identified as the  $T_g$  of the sample that reacted at time,  $t$ , (partially-reacted sample). The second  $\tan \delta$  peak could correspond to the final  $T_g$  (or  $T_{gy}=274^\circ\text{C}$ ) as the polymerisation progressed during the temperature ramping (at 2 °C  $\text{min}^{-1}$ ) and reached a fully-reacted state. Figure 1 show that only one peak of  $\tan \delta$  was obtained for the sample reacted for 90 minutes, indicating that the sample has already reached a fully-reacted state. Varley *et al.* (2001) using DMA on a similar system found similar results and were able to observe the  $\tan \delta$  peak of the sample up to 30 minutes reacted at 180 °C. They explained this as being due to further reaction of unreacted species during temperature scanning of the sample. Even after partially-reacted in the oven at time  $t$ , the sample continued to react due to the high residual functionality of the epoxy. The appearance of the two peaks of  $\tan \delta$  was due to the segregation of epoxy oligomer and the crosslinked phase. When the reaction time was extended, the oligomer was converted into a crosslinked phase to establish a homogeneous network. From the above results, it can be seen that the use of DMA to determine the reaction schedule may lead to the conclusion that curing at 180 °C for 90 minutes is sufficient to obtain a fully-reacted state for the TGpAP/DDS system.

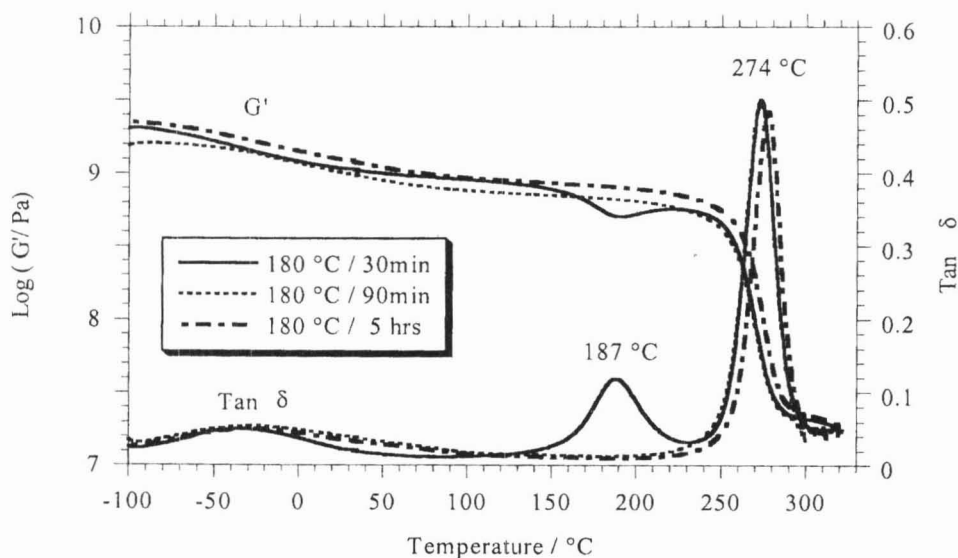


Fig. 1: DMA spectrum of the unmodified TGpAP/DDS system, reacted at 180 °C at various reaction time

Using the same partially-reacted samples, conventional DSC analyses were conducted to obtain  $T_g$  at each reaction time. Figure 2 shows DSC curves for the sample reacted at 180 °C at various reaction times. The results show that the overlapping of  $T_g$  with the peak exotherm renders DSC

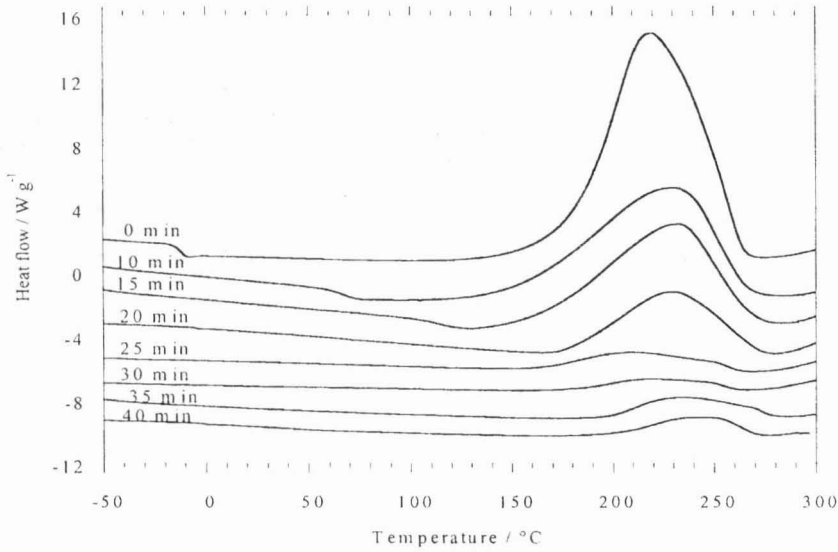


Fig. 2: DSC curves of the epoxy system, reacted at 180°C for the various indicated times.

as an unsuitable technique for measuring  $T_g$  of partially-reacted TGpAP/DDS system, hence no report has been published. As can be seen clearly in Figure 2, after 20 minutes of reaction at 180°C, the  $T_g$  cannot be measured using DSC. This problem can be alleviated by using TMDSC. These two events that occur simultaneously, the  $T_g$  and residual heat of reaction can be separated into reversible heat flow and non-reversible heat flow respectively from a single experiment using TMDSC. (Simon 2001). The experiments were repeated using TMDSC to separate the reversible component for  $T_g$  determination and non-reversible component to yield kinetic information. The results are shown in Figure 3. In the TMDSC curves (Figure 3) two transitions are observed on each curve. For the sample reacted for 30 minutes, the first transition occurred at 162°C and a second transition at 251°C was observed. This second transition is suspected as due to further reaction of the unreacted species as mentioned earlier. For other samples, the second transition that occurred at about 251-256°C could be due to the final  $T_g$  that has been observed previously in the DMA measurement. This seems to indicate that the  $T_{g\gamma}$  is approximately 256°C. Therefore, a similar value of  $T_{g\gamma}$  will be obtained if the samples are post-cured at a high temperature. A summary of the glass transition temperature,  $T_g$  obtained from TMDSC and DMA measurements is given in Table 1.

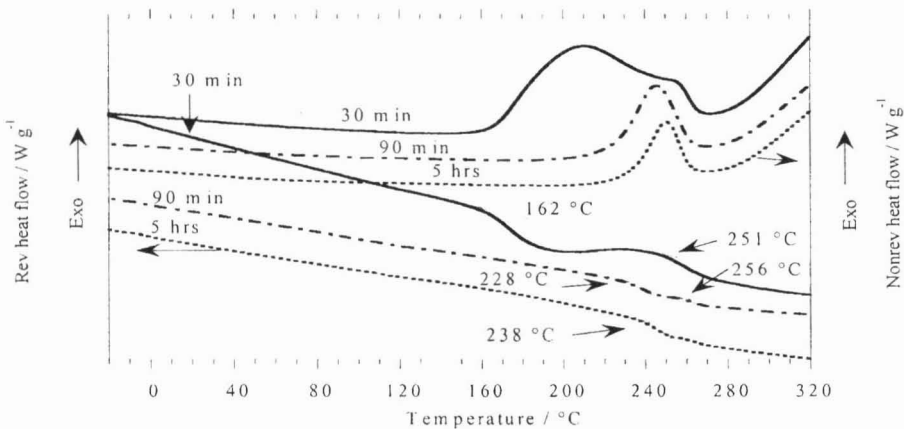


Fig. 3: TMDSC curves of the epoxy system, reacted at 180°C for 30, 90 and 300 minutes. The  $DH_r$  for each reaction time is 204, 43, and 30 J g<sup>-1</sup> respectively

Table 1 : The  $T_g$ , obtained from different techniques of measurement.

Samples / cured at 180 °C at time, $t$	TMDSC	DMA	
	(°C)	(°C)	
	$T_g$	$T_g$	$T_{g\#}$
30 min	162 (251)	187	274
90 min	228 (256)	ND	276
300 min	238 (256)	ND	276

Note:  $T_g$  is the first inflection in the TMDSC curve or the first peak in the DMA spectrum.

From Table 1, DMA recorded two  $T_g$  for the sample reacted for 30 minutes. While only one  $T_g$  was recorded for each of the samples cured for 90 and 300 minutes and both  $T_g$  values are the same. Since these  $T_g$  values are close to the second  $T_g$  of the sample reacted for 30 min, they could be taken as  $T_{g\#}$ . Hence the DMA results seem to indicate that for the TGpAP/DDS system, a fully-reacted state could be reached after 90 minutes of reaction with a  $T_{g\#}$  of 276°C. However, when the results of TMDSC are compared against that of DMA, it can be observed that the sample has not reached fully-reacted state because the  $T_g$  at 90 minutes is lower than the  $T_g$  at 300 minutes. This suggests that a combination of DMA and TMDSC is necessary in order to establish a more accurate thermal properties of the TGpAP/DDS system. The values from TMDSC are always lower than the DMA values. In TMDSC,  $T_g$  is taken from the onset of transition at zero frequency, which results from the change in specific heat capacity ( $C_p$ ) as the polymer changes from glassy to the rubbery states. Whereas in DMA,  $T_g$  is taken at the maximum peak of tan  $\delta$  at the frequency of 1 Hz and not at the beginning of the transition in storage modulus. In DMA,  $T_g$  is affected by frequency and it decreases with frequency. Therefore it is important to recognise the difference between  $T_g$  (DSC) and  $T_g$  (DMA) particularly when  $T_g$  is used as a reference. The results from TMDSC can be used to follow the evolution of  $T_g$  with reaction time and therefore, can be used to obtain the correct reaction schedule for the TGpAP/DDS system.

In order to obtain the  $T_{g\#}$  of the unmodified TGpAP/DDS system (as an index of complete conversion), the sample was reacted at 180°C for 3 hours and post-cured at various temperatures and times in the oven before measuring the  $T_{g\#}$  using TMDSC. The results of the TMDSC analyses are tabulated in Table 2.

Table 2:  $T_g$  values of the TGpAP/DDS system (reacted at 180 °C and post-cured at various temperatures and times) measured using TMDSC.

Reaction Schedule	DH residue / J/g <sup>-1</sup>	$T_g$ / °C	Colour
180 °C / 3 hrs +220 °C / 1 hrs	ND	246 ± 1	brown
180 °C / 3 hrs +220 °C / 2 hrs	ND	246 ± 1	Dark brown
180 °C / 3 hrs +220 °C / 3 hrs	ND	245 ± 1	black
180 °C / 3 hrs +230 °C / 1 hrs	ND	243 ± 1	black
180 °C / 3 hrs +230 °C / 2 hrs	ND	242 ± 1	black
180 °C / 3 hrs +240 °C / 1 hrs	ND	242 ± 1	black
180 °C / 3 hrs +260 °C / 1 hr	ND	231 ± 1	black

The TMDSC results obtained on the samples post-cured at 220°C show that the maximum  $T_g$  is about 246 ± 1°C. Table 2 also shows that post-curing at temperatures higher than 220°C will cause the sample to degrade since the sample colour turned darker and the  $T_g$  value decreased. After taking all of the above analyses into consideration, it was decided that the reaction schedule for the unmodified and modified TGpAP/DDS system is 180°C for 3 hours and post-cure at 220°C for another 1 hours.

The plot of  $T_g$  evolution against reaction time for the epoxy system reacted at 180°C is shown in Figure 3. From this figure,  $T_g$  continues to increase above the reaction temperature,  $T_c$  (180°C) and levels off at about 236°C after 150 minutes of reaction. This finding is in contrast with reported trends for difunctional DGEBA-amine systems, where the  $T_g$  increases with reaction time and reaches the reaction temperature,  $T_c$  or  $T_g = T_c$ . (Ellis 1993; Nunez et al 2001). An extended reaction usually leads to a small increase in both  $T_g$  and conversion. From this phenomena,

most literatures define vitrification as the point when  $T_g$  of the curing resin increases to the current resin temperature,  $T_c$ . However this definition cannot be applied to the TGpAP/DDS system.

For TGpAP-amine system, the difference between the  $T_g$  and the  $T_c$  (curing at 180°C for 150 min) is 56°C. The  $T_c$  at 180°C is indicated by the arrow on the plot. The increase in  $T_g$  such that  $T_g > T_c$  is possibly due to the high functionality of the TGpAP, which produces more reactive sites. These reactive sites exist in close proximity such that the polymerisation can continue into the glassy state. In this study the maximum  $T_g$  achieved for isothermal reaction at 180°C was  $236 \pm 2$  °C and the chemical conversion attained was only  $93 \pm 2$  %. Continued heating at 180°C for 4-5 hours did not increase the  $T_g$  very much.

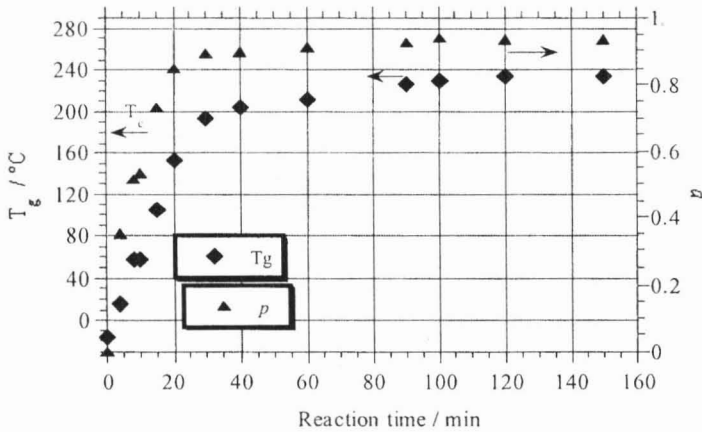


Fig. 4: Plots of  $T_g$  and conversion  $p$  versus reaction time of the epoxy system determined by TMDSC. The reaction temperature,  $T_c$ , is indicated by the arrow on the plot.

## Conclusion

The findings of this study have shown that DMA and DSC are unable to detect the evolution of  $T_g$  with reaction time of TGpAP/DDS system cured at 180°C. The use of only DMA to determine the curing schedule may lead to the conclusion that curing at 180°C for 90 minutes is sufficient to obtain a fully-reacted state. From the DSC analysis,  $T_g$  cannot be determined accurately due to overlapping with the exotherm peak. However, using TMDSC,  $T_g$  can be well separated from the exotherm peak, thus making it the best thermal characterization technique to follow the evolution of  $T_g$  and chemical conversion with curing time. The results from TMDSC show that  $T_g$  continues to increase above the reaction temperature,  $T_c$  (180°C) and levels off at about 236°C after 150 minutes of reaction. For TGpAP/DDS system, the difference between the  $T_g$  and the  $T_c$  (curing at 180°C for 150 min) is 56°C. The increase in  $T_g$  such that  $T_g > T_c$ , is possibly due to an increase in the number of reactive sites, which is affected by the high functionality of the TGpAP. The reactive sites being in close proximity promotes further polymerisation until the glassy state is reached. In this study the maximum  $T_g$  achieved for the isothermal reaction at 180°C was  $236 \pm 2$  °C and the chemical conversion attained was only  $93 \pm 2$  %. The TMDSC results obtained on the sample post-cured at 220°C for 1 hour show the maximum  $T_g$  of  $246 \pm 1$  °C. Extended curing time and post-cured at higher temperature than 220°C caused thermal degradation. Thus, the curing schedule for TGpAP/DDS system obtained from this study is 180°C for 3 hours followed by post-curing at 220°C for another hour.

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## References

- Bonnaud, L. Pascault, J. P. Sautereau, H. (2000). Kinetic of a thermoplastic-modified epoxy-aromatic diamine formulation: modeling and influence of a trifunctional epoxy prepolymer. *Eur. Polym. J.* 36: 1313-1321.
- Ellis, B. (eds.) (1993). *Chemistry and Technology of Epoxy Resins*. Glasgow: Blackie Academic.

- Hourston, D. J. Lane, J. M., Zhang, H. X.. (1997). Toughening of Epoxy Resins with Thermoplastics:3 . An Investigation into the Effectd of Composition on the Properties of Epoxy Resin Blends. *Polym. Int.* 42: 349-355
- Kim, B. S. Chiba, T. Inoue, T. (1995). Morphology development via reaction-induced phase separation in epoxy/poly (ether sulfone)blends: morphology control using poly(ether sulfone) with functional end-groups. *Polymer.* 36: 43-47.
- Min, B. G. Hodgkin, J. H. Stachurski, Z. H. (1993). The Dependence of Fracture Properties on Cure Temperature in DGEBA/DDS Epoxy System. *J Appl. Polym. Sci.*48: 1303-1312
- Morgan R. J. Dusek, K. eds. (1985). Epoxy Resins and Composites I, *Adv. Polym. Sci.*, (72). Berlin: Springer-Verlag.
- Nunez, I. Fraga, F. Castro, A. Nunez, M. R. Villanueva, M. (2001). TTT cure diagram for an epoxy system diglycidyl ether of bisphenol A/1,2 diamine cyclohexane/calcium carbonate filler. *Polymer.* 42: 3581-3587.
- Simon, S. L. (2001). Temperature-modulated differential scanning calorimetry: theory and application. *Thermochim. Acta.* 374: 55-71.
- Trostyanskaya, E. B. Shalin, R. E. eds. (1995). *Polymeric matrices in fiber-reinforced composite materials*. London: Chapman & Hall.
- Varley, R. J. Hodgkin, J. H. Hawthorne, D. G. Simon, G. P. (2001). Toughening of trifunctional epoxy system Part VI. Structure property relationships of thermoplastic toughened system. *Polymer.* 42: 3847-3858.
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