Solid State Science and Technology, Vol. 11, No.1 (2003) 95-102

THE EFFECT OF CURING TECHNIQUE ON THERMAL PROPERTIES OF BISMALEIMIDE RESINS

Ismail Zainol
Advanced Materials Research Centre (AMREC), SIRIM Berhad, Lot 34,
Jalan Hi-Tech 2/3, Kulim Hi-Tech Park, 09000 Kulim, Kedah.
Email: ismail@sirim.my

ABSTRACT

Bismaleimide resin was cured using two different techniques i.e conventional and microwave ovens. Thermal properties of the samples cured using both techniques were determined and the results were compared to predict the difference in morphology. The sample was studied using differential scanning calorimetry (DSC) to determine thermal characteristics of the sample and degree of cure. Dynamic mechanical properties such as storage modulus and loss tangent were studied using dynamic mechanical thermal analysis (DMTA). Modulated differential scanning calorimetry (MDSC) was used to determine the glass transition temperature. The DSC results showed that microwave heats samples faster than conventional oven. Thermal properties from DMTA and MDSC results proved that different network structure was formed in both curing techniques where conventionally cured sample showed higher cross-linking density.

INTRODUCTION

Bismaleimide (BMI) resins are presently the best candidates to replace epoxy resins in high performance composites. This is due to their high temperature stability and hot/wet environment resistance [1]. Conventional curing processes of BMI involve heating in an oven, autoclave or compression mould where heat transfers to the material through conduction and/or convection. Like other thermosetting materials, the low thermal conductivity of these resins leads to thermal gradients inside the resin and the curing cycle becomes longer. Research shows that microwave processing of thermosetting materials offers significant advantages over conventional heating such as reduced cure cycle, more uniform cure and an improved physical/mechanical properties [2]. Microwave heating takes place through dipolar interaction between molecules and the alternating electric field rather than thermal conduction and/or convection as in conventional heating. Since conventional ovens and microwaves heat samples in different ways, different network structures are expected and hence resulting in different physical properties. Thermal properties are sensitive to changes in network structure, thus studies on these properties will give an understanding on the difference network morphologies produced between conventional and microwave heating.

In this study, the changes in thermal properties such as glass transition temperature (T_g), cold crystalline temperature (T_c), melting temperature (T_m), polymerisation onset temperature (T_o), exothermic peak temperature (T_{exo}) and dynamic mechanical properties were studied as the curing progressed in both conventional and microwave curing techniques. The results obtained were compared and the differences in network morphologies were predicted.

EXPERIMENTAL PROCEDURES

Material

The bismaleimide resin used in this study was Matrimid 5292A (Ciba Geigy) (M5292A). The chemical structure is shown in Figures 1.

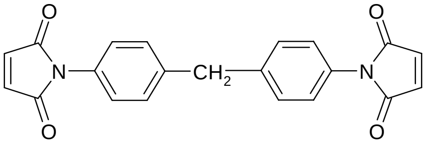


Figure 1. Chemical structure of Matrimid 5292A [3].

Processing

Conventional curing was carried out in an oven (Townson + Mercer, Model 9-300) at 190 °C for different period of time. Microwave processing was done in Moulinex Quickchef 1000QE microwave oven at full power (645 W) for different period of time untill fully cured as determined using DSC technique. The sample, weight 5.0 g was cured in a glass mould, 60 mm diameter and 10 mm high. The temperature of the sample was measured using digital temperature probe.

Characterisation

Differential scanning calorimetry (DSC), model DuPont 900 was used to study the thermal characteristic and to calculate the degree of cure (α) [4]. The DSC cell was first calibrated using high purity indium. Samples with weights in the range 8 - 12 mg, were transferred into aluminium pans and crimped, but not hermetically sealed. Each sample was scanned from 25 °C to 400 °C at a heating rate of 10 °C min^{-1} in an inert atmosphere of nitrogen. The glass transition temperature (T_g) was determined using MDSC model Perkin Elmer, Pyris 1. In MDSC analysis, the temperature was programmed from 80 to 250 °C which consisted of 240 repetitions of short isothermal temperature steps with equilibration time of 50 seconds and heating rate at 2.4 °C min^{-1}. The sample was ground and about 4.0 – 6.0 mg was hermetically sealed in the aluminium pan. Dynamic mechanical properties such as storage modulus and loss tangent were studied using DMTA model Polymer Laboratories. In this analysis the sample was analysed from 10 to 300 °C at a heating rate of 5 °C min^{-1} and frequency of 1.0 Hz. The sample was cut into a rectangular bar (1.3 x 6.2 x 12.0 mm^3) and clamped rigidly at both ends using the medium size clamp with single cantilever.

RESULTS AND DISCUSSION

DSC results of samples cured at 190 °C at different period of time are presented in Figure 2. DSC curve of uncured sample (Figure 2 (a)) showed T_m at 157 °C and no T_g was observed. It was found that sample started to melt after 30 min when heated from 25 °C to 190 °C at a heating rate of 13 °C min^{-1} in a conventional oven. The DSC curve of this sample is shown in Figure 2 (b). From this curve, it is observed that two additional transitions at 50 to 56 °C and 90 to 150 °C appeared compared to uncured sample (Figure 2 (a)). The changes in heat capacity at 50 to 56 °C are characteristic of a glass transition (T_g) and the second transition between 90 to 150 °C, which is an exotherm, is probably due to cold crystallisation. Cold crystallisation is a process where crystalline polymer is formed as a result of rapid cooling. In this study the sample was cooled to room temperature immediately after each curing process. Cold crystallisation was also observed by Wang *et al.* when they studied another semicrystalline polyimide [5]. The temperatures where the cold crystallisation occurred is labelled as T_c. The T_m was observed at 166 °C where it shifted to higher temperature when compared to uncured sample. The appearance of a T_g indicates that the resin had become amorphous after melting.

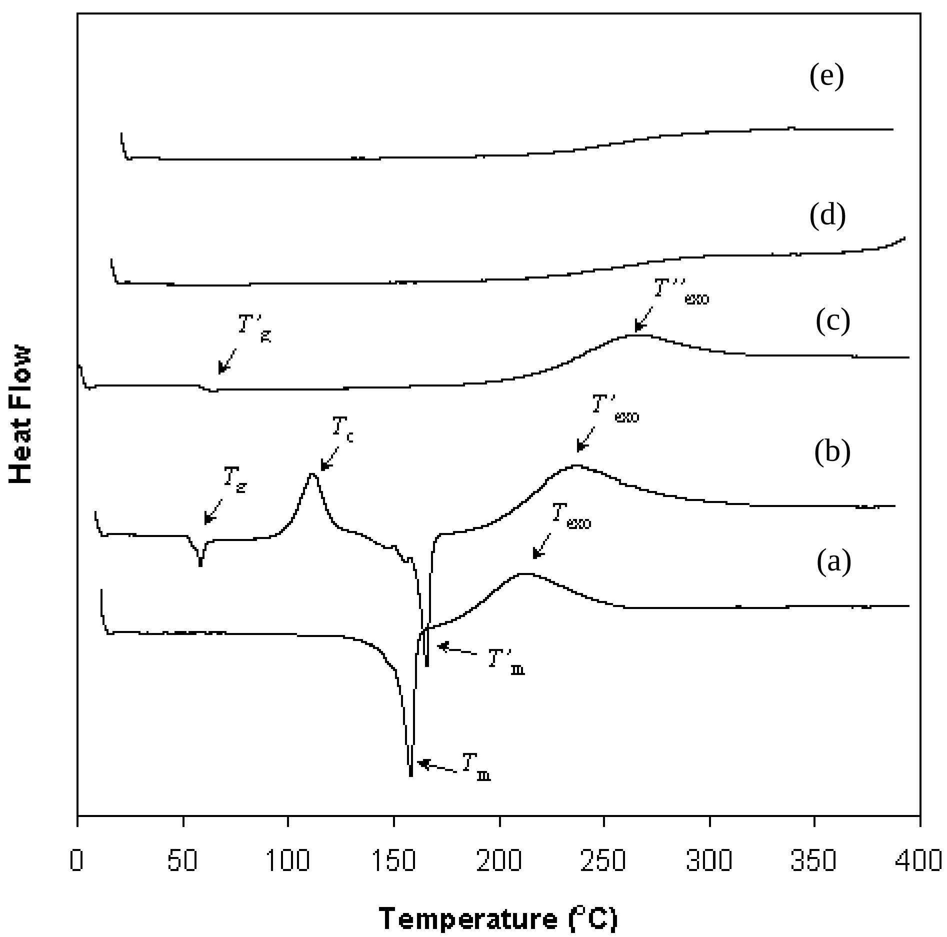


Figure 2. Overlaid DSC curves for 5.0 g sample cured in conventional oven at 190 °C for different period of times; (a) 0 min, (b) 30 min, (c) 90 min, (d) 180 min and (e) 12 hours (manufacturers recommended cure cycle).

Thermal characteristic results for conventionally cured sample are summarised in Table 1. These show that the T_g increased as the cure time increased. After 180 min curing, the

T_g was not observed in the DSC curve. The disappearance of T_g did not indicate the absence of a glass transition, but rather the DSC used was not sensitive enough to detect the transition. The exothermic peak due to cold crystallisation decreased as the curing time increased and disappeared at above 60 min curing time. The T_m was shifted to higher temperature and also disappeared at above 90 min cure. The onset temperature when the polymerisation started, T_o also increased as cure time increased.

Table 1. Thermal characteristics of 5.0 g samples of sample cured in a conventional oven at 190 ^oC of different periods of time. (Note: ND = not detected).

Curing Time (min)	**T_g (^{o}C)**	**T_m (^{o}C)**	**T_c (^{o}C)**	**ΔH_c (Jg^{-1})**	**T_o (^{o}C)**	**T_{exo} (^{o}C)**
0	ND	155	ND	-	174	202
30	57	157	111	50	190	231
45	61	164	115	12	191	243
60	63	166	ND	-	193	265
90	67	ND	ND	-	201	273
180	ND	ND	ND	-	240	290
1440	ND	ND	ND	-	257	300

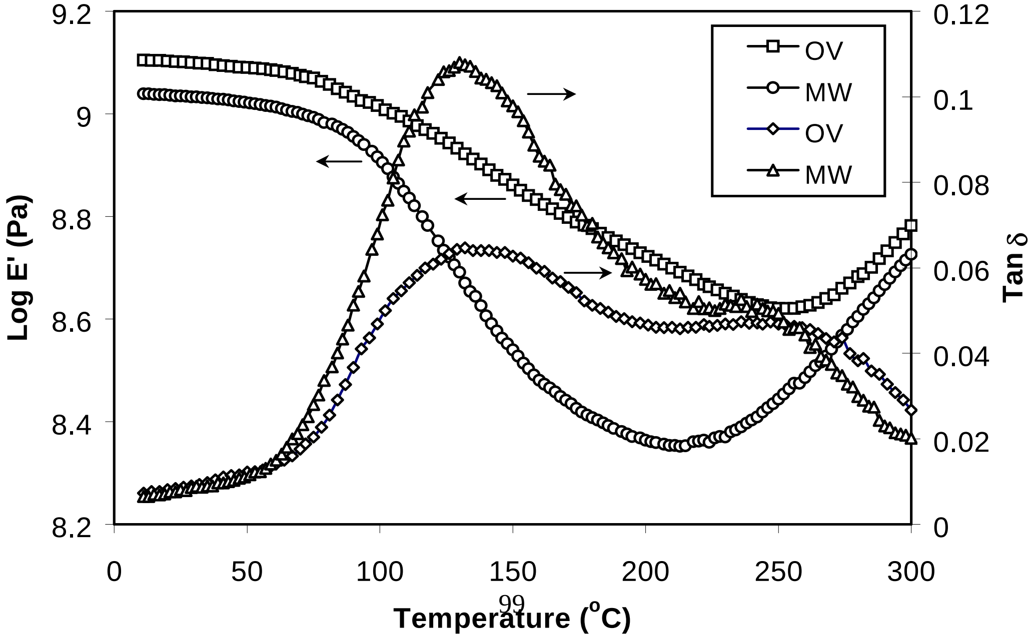
The disappearance of transition temperatures and the shift of other thermal properties to higher temperatures are expected due to the increase in average molecular weight and cross-link density between the molecules as polymerisation proceeds. As the cross-link density increased, further reaction became difficult and can only occur when curing temperature was higher than vitrification temperature.

In microwave curing process with the powered 635 W, the sample started to melt after only 6 min of curing. This show that microwaves can heat samples much faster than using conventional oven. Thermal characteristics of samples cured at different times in a microwave oven are summarised in Table 2. From the results it was observed that all transition temperatures (T_g, $T_{c,}$ and T_m) increased as the curing time increased, a similar observation to conventional curing. However, none of these transitions were observed after 10 min curing, compared to 180 min in a conventional oven. This suggests that the morphology of sample cured 10 min in microwave may be comparable to the morphology of a sample cured for 180 min in conventional oven. The DSC study shows that thermal characteristics of cured sample are similar for both curing techniques. However curing process occurred faster in microwave than in conventional oven.

Table 2. Thermal characteristics of the 5.0 g sample cured in a microwave oven at 635 W for different periods of time. (Note: ND = not detected).

Curing Time (min)	T_g (°C)	T_m(°C)	T_c (°C)	ΔH_c (Jg^{-1})	T_o (°C)	T_{exo} (°C)
0	ND	155	ND	-	174	202
6	47	162	110	18	177	204
7	50	165	120	9	181	215
8	53	ND	ND	-	210	235
10	ND	ND	ND	-	229	256
11	ND	ND	ND	-	219	259

The effect of degree of cure on dynamic mechanical properties such as storage modulus (*E'*) and loss tangent (*tan δ*) of conventionally and microwave cured samples were studied. The results obtained were used to relate the morphology of the cured samples network structure. DMTA data for a conventionally with degree of cure, α = 0.96 and microwave cured sample with α = 0.98 as a function of temperature are shown in Figures 3. The degree of cure of each sample was determined using DSC method. The results revealed that conventionally cured sample exhibits a higher initial storage modulus ($E'_{initial}$) and broadened *tan δ* when compared to the microwave cured sample. The higher $E'_{initial}$ for the conventionally cured sample suggests that it is stiffer than microwave cured sample. This probably due to a higher cross-link density in conventional cured sample than microwave cured sample.



It is observed that the E' decreases to a minimum value of 398 MPa at 256 °C and 224 MPa at 213 °C for conventional and microwave cured samples respectively. Beyond this two temperatures, E' was observed to increase. The increase in E' could be due to post-cure in the sample during the DMTA measurement [6]. This is very likely to happen since the sample used was not fully cured by both curing methods as determined by DSC. The conventionally cured sample showed broader $\tan\delta$ peak compared to microwave cured sample. This indicates that different network structures were present in both cured samples. Nielsen [7] proposed that $\tan\delta$ peak broadening could be due to the cross-linking effect and/or due to the heterogeneity in the cross-link structure. Nielsen points out that the $\tan\delta$ peak would remain sharp if there is no distribution in the length of chains between cross-links.

Glass transition temperature, T_g, is also known to be sensitive to the polymer network structure [8]. The changes in T_g as the curing progressed were used to investigate the network structure produced in both cure methods. Studies shows that conventional DSC could not be used to detect T_g for all of the cured samples especially at high degrees of cure [9]. In this study the ability of modulated DSC (MDSC) to determine T_g was studied. Example of MDSC curve of conventionally cured sample with α_{DSC} of 1.0 shown in Figure 4. The figure shows MDSC was capable of detecting T_g at high degrees of cure.

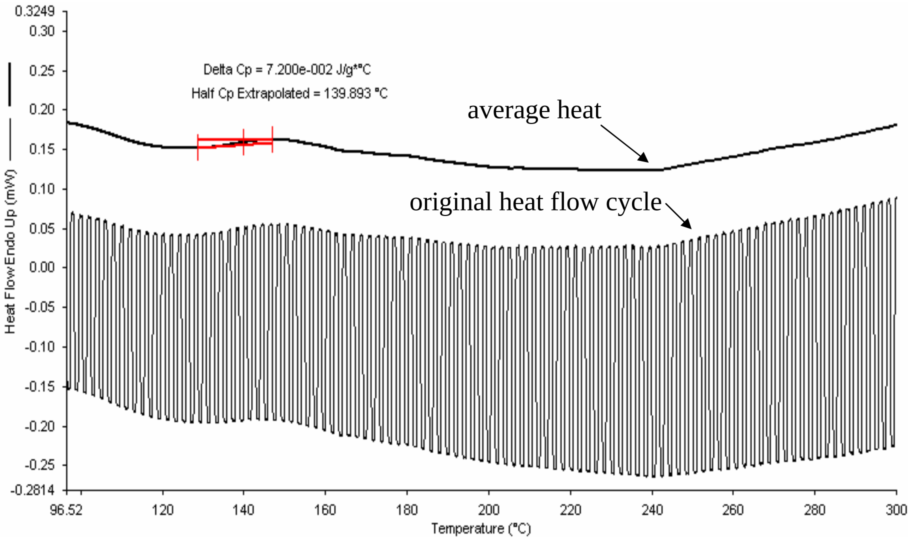


Figure 4. MDSC curves of conventionally cured sample with $\alpha_{DSC} = 1.0$.

Figure 5 shows the gl[illegible]on temperature (T_g) obtained from MDSC as a function of degree of cure for conventionally and microwave cured sample. The T_g showed a similar pattern for both conventional and microwave cured samples with $\alpha < 0.60$. In this region, the T_g increased slightly as the degree of cure increased i.e between 48 to 57 °C. The slight increase in T_g is probably due to low average molecular weight and few cross-links between molecules [7]. The T_g of a polymer is very much influenced by its molecular weight and cross-link density. It increases proportionally with increasing molecular weight and cross-link density [8]. This observation shows that a similar structure was formed in conventional and microwave ovens until $\alpha = 0.60$. It also suggests that similar curing reaction took place in both cases.

For samples with $\alpha > 0.60$ the T_g increased rapidly for both curing methods. The increase in T_g suggests that the molecular weight and cross-link density of polymer became higher

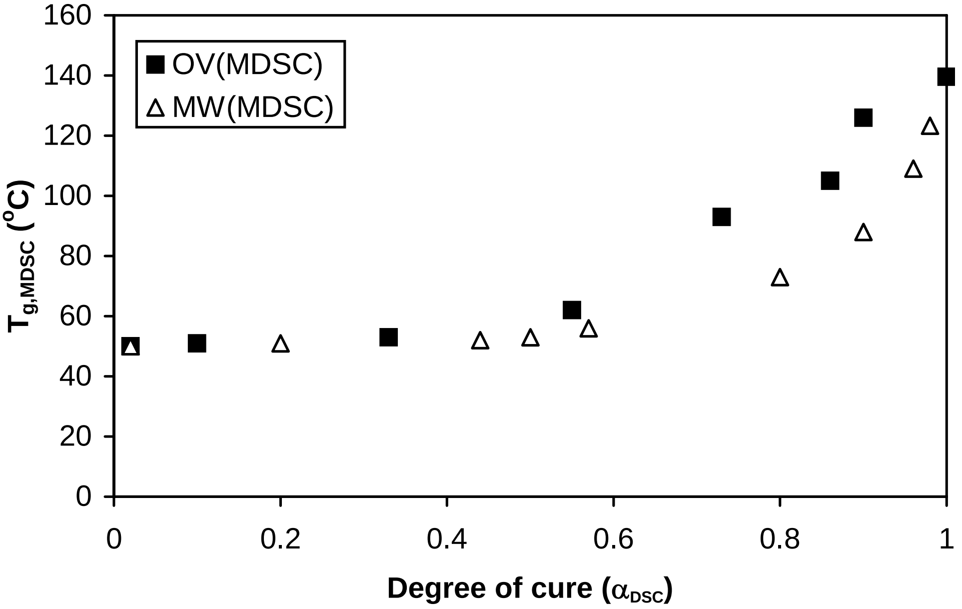


Figure 5. Glass transition temperature from MDSC analysis for conventional and microwave cured sample.

as the curing progressed. As a result the movement between polymer chains became more restricted [10], thus giving a higher T_g. Microwave cured samples, however, show lower

T_g than equivalent conventionally cured samples at degree of cures between 0.6 and 0.9. The difference in T_g may be attributed to the variation in the morphology of cross-linking network produced at higher degrees of cure. The results suggested that conventionally cured samples had a higher cross-link density than microwave cured sample. This was supported by DMTA results where *tan* δ of conventional cured samples was more broadened than that of the microwave cured samples.

CONCLUSION

Bismaleimide resin processed using microwave shows different thermal properties compared to using conventional oven. The difference is believed due to rapid curing in the microwave oven results different cross-linking network structure was formed. Fast curing in microwave probably alters the chemical reaction of the resin. The results show conventional cured samples had a higher cross-link density than microwave cured sample.

ACKNOWLEDGMENT

I would like to thank SIRIM Berhad for funding my work and my supervisor Dr R. J. Day for his guidance in this study.

REFERENCES

[1] Stenzenberger, H.D., Romer, W., Herzog, M., and Konig, P., *33rd International SAMPE Symposium*, 7-10 March 1988, 546-1559.
[2] Mijovic, J, and Wijaya, J., (1990), *Macromolecule*, 23, 2243
[3] K. A. Barrett, M. A Chaudhari and B. H. Lee, 33rd Int. SAMPE Symp, 1988, March 7-9, 398.
[4] A. P. Surrett, R. J. Lauf, F. L. Paulauskas and A. C. Johnson, Mat. Res. Soc. Sym. Proc., 1994, **347,** 691.
[5] Y. D. Wang, M. Cakmak and F.W. Harris, J. App Polym Sci., 1995, **56**, 837.
[6] S. C. Liptak, S. P. Wilkinson, J. C. Ward and J. E. Mc Grath, Am. Chem. Soc., Symp. Series, 1991, **475**, 364.
[7] Nielson LE, J. Macromol. Sci, 1969, **C3**, 69.
[8] T. G. Fox and S. J. Loshaek. Polym. Sci., 1955, **15**, 371.
[9] I. Zanol, PhD Thesis, UMIST UK, 2001, 172.
[10] D. O. Hummel, K. U. Heinen, H. Stenzenberger and H. Siesler, J. Appl. Polym. Sci., 1974, **18**, 2015.