

Synthesis and characterization of high temperature stable epoxy adhesive

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For the integration of multi-chip module required thermally stable epoxy adhesive, the effects of clay incorporation on the thermal stability of cured epoxy adhesive were investigated. Various epoxy adhesives were prepared as a function of a number of epoxy rings and the amount of hardener. Based on the relationship between the glass transition temperature (T_g) and cross-linking density obtained from the curing mechanism analyzed by FT-IR, the epoxy adhesive with T_g higher than 200°C was synthesized by raising cross-linking density to the maximum. With the incorporation of clay, the curing reaction rate and the degradation of epoxy adhesive can be controlled. The epoxy/clay composite showed the higher height of $\tan\delta$ peak than that of pure epoxy adhesive.

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1. Introduction

With the remarkable advance of electronic industry, most of the electronic systems could be compact with high performance and numerous functions and the materials required in the electronic systems should have good properties available to those systems. Epoxy polymers are widely used in coatings and high performance applications because of their good adhesion to various types of substrates, high mechanical strength and good resistance to chemicals.^{1),2)} They have also been used for adhesive layers of printed circuit boards because they have a good heat resistance at high frequency.

For the applications of various type substrate of system in package (SIP), the inherent brittleness and the glass transition temperature (T_g) of epoxy adhesives should be improved. Many efforts have been made to improve toughness of epoxy thermosets such as the incorporation of elastomers or thermoplastics³⁾ and/or the addition of inorganic materials.⁴⁾

Also, the T_g of epoxy adhesives could be controlled by a number of epoxy ring, the relative amount of hardener to epoxy, and curing conditions of polymer.⁵⁾ The curing conditions determine the physical and mechanical properties of polymers. With the increasing of cross-linking density of polymer, the T_g could be improved,⁵⁾ while the toughness of the polymer backbone should be decreased, which in turn restrict applications.⁶⁾

In this study, the effect of clay incorporation on the thermal stability of cured epoxy adhesives were investigated based on the curing behavior of epoxy adhesives with different cross-linking densities. An attempt was also made to fully cross-linked polymer with various molar ratio of hardener.

2. Experimental

2.1 Sample Preparation

The epoxy prepolymers, a diglycidyl ether of bisphenol A (DGEBA, 99%, Sigma-Aldrich, USA) and a N,N-Diglycidylaniline (DGA, 99%, Sigma-Aldrich, USA) were mixed with a hardener, 3-amino-methyl-3,5, 5-trimethyl cyclohexyl-amine (Isophorone diamine, IPD, 99%, Sigma-Aldrich, USA) in the

molar ratio of epoxy resin to hardener from 1:1 to 1:1.75,⁷⁾ respectively. These mixtures were gently stirred to avoid bubbles in the polymers, and slowly poured in the aluminum mold ($52 \times 5 \times 2 \text{ mm}^3$) and then cured in convection oven at 50 to 150°C for 0.5 to 24hr. The clay/epoxy composites were also prepared to study the effect of clay incorporation on thermal properties of epoxy adhesives. The clay (Cloisite® 30B, Southern Clay Products, USA) was mixed to the epoxy prepolymer with hardener by 1 and 3 mass% based on organic polymer. The curing procedure was the same as that of neat epoxy adhesives described the above.

2.2 Characterizations

A differential scanning calorimeter (DSC V4.313B, Perkin Elmer, NC, USA) was used to monitor the degree of curing after the epoxy/amine resin was thermally heated. The sample was scanned in a DSC pan at a heating rate of 10°C/min with a temperature range from 20°C to 250°C. The optimal curing temperature in convection oven was selected from the interval of 10°C approximately which is defined between 10°C below the onset temperature of cure and the point midway to the maximum of the exothermic peak of DSC scan,⁸⁾ and then fresh samples were analyzed isothermally at the curing temperatures.

Infrared spectra of the samples were obtained from a Fourier Transform Infrared Spectroscopy (430FT-IR, Jasco., USA) over the frequency range from 400 to 4000 cm^{-1} . For each spectrum, 16 runs were collected and be averaged. The FT-IR specimens of the epoxy adhesives were prepared by adding approximately 1% of sample powder to dry KBr powder and pressed into disc. The liquid epoxy and diamine samples were tested by casting a thin film on KBr window.

The dynamic mechanical properties of the epoxy adhesives were obtained from the dynamic mechanical analyzer (DMA2980, TA Instruments, USA). Samples with the dimensions of $40 \times 10 \times 2 \text{ mm}^3$ were prepared for the measurements carried out the single cantilever at 1Hz. Oscillation amplitude of 20mm was employed at a heating rate of 3°C/min. The distribu-

tion of clay layers in epoxy polymer matrix was measured by Wide angle X-ray diffractometer (XPERT-PRO, PANalytical, The Netherlands) at a scan rate of 0.05°/min with CuK α radiation operated at 40KV and 30mA.

3. Results and Discussion

Figure 1 shows FT-IR spectra of samples obtained during curing with different resin and hardener at various reaction temperatures. It was confirmed that there was a ring opening reaction between epoxy ring and primary amine hardener mixture from the amine peak at 3300–3500 cm⁻¹. Secondary amines and –OH were formed as a result of the ring opening reaction. The primary amine peak having two bands at 3300–3500 cm⁻¹ is diminishing and some broad –OH stretching vibration peak appears at about 3200–3500 cm⁻¹ as the reaction proceeds. These results are also agreed well with the previous report⁷⁾ that the curing kinetics of epoxy (DGEBA) with various amine resins (Isophorone diamine, Diethylene triamine, Triethylene tetraamine).

The epoxide group reacted with primary and secondary amines. The amine hardener mixture was confirmed from the amine peak at 3300–3500 cm⁻¹, and then curing mechanisms can be expressed by Eq. (1) for primary amine and Eq. (2) for secondary amine, respectively.⁷⁾

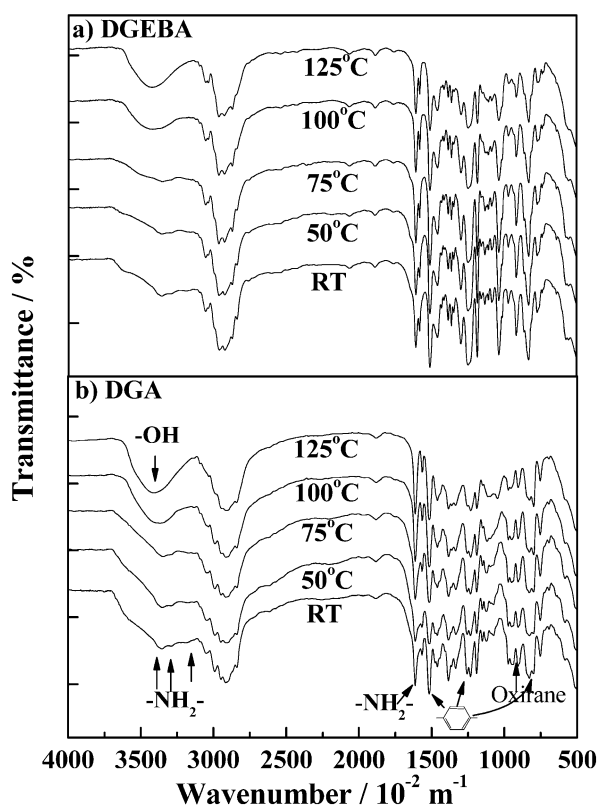
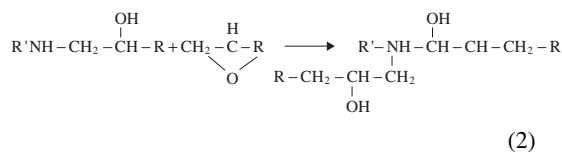
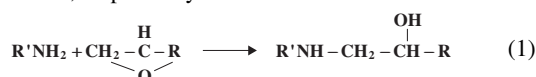


Fig. 1. FT-IR spectra of curing reaction of (a) DGEBA and (b) DGA with Isophorone diamine mixture with a/e molar ratio, 1.1 at various temperature.

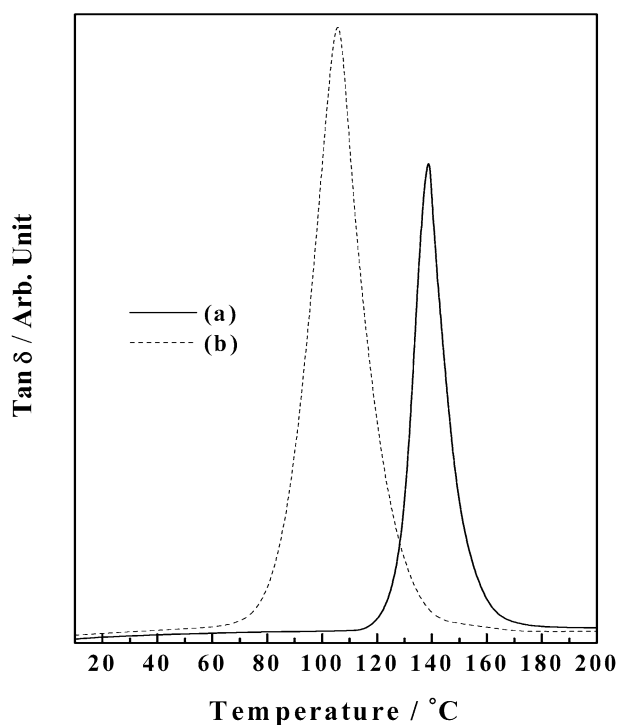


Fig. 2. DMA result of two cured epoxy adhesives (a) DGEBA/hardener (b) DGA/hardener (partially decomposed epoxy polymer) cured at 100°C in oven.

Therefore, the high cross-linking density could be obtained if the epoxy adhesives have two or more epoxy rings and/or the amine hardener with high excess ratio to epoxy adhesives is used for curing.

The dynamic mechanical properties data of **Fig. 2** shows the glass transition temperature (T_g) of DGEBA with two epoxy rings and DGA with four epoxy rings per molecule, respectively. Unexpectedly, T_g of DGA polymer was shown to be much lower than that of DGEBA polymer. It seems that there was partial decomposition of the DGA polymer because too much heat was evolved during the curing reaction. To confirm the decomposition of DGA, two sets of DGA polymer were prepared by a different curing condition. One was prepared by the heating rate of 10°C/min to the 100°C (**Fig. 3(a)**), the other was immediately cured in oven at 100°C (**Fig. 3(b)**) and both samples were cured for an hour. As shown in **Fig. 3**, it is clearly confirmed from FT-IR analysis that stretching vibrations of oxirane group appeared at 850 cm⁻¹, 900 cm⁻¹ and 1250 cm⁻¹⁷⁾ disappeared after decomposition and intensity of C–N peak at 1560 cm⁻¹ reduced possibly due to breakage of C–N bonding.⁷⁾ **Figure 4** shows the reaction heat (ΔH) of epoxy/amine during curing reaction obtained from DSC. The exothermic peak for DGA was much higher than DGEBA which is due to the higher the reaction heat of DGA than that of DGEBA. This was resulted to the trace of burning of DGA sample cured immediately at 100°C. Therefore, T_g of DGA was lower than that of DGEBA in **Fig. 2** which was due to the partial decomposition of DGA.

The curing behavior of epoxy adhesives (DGEBA, DGA) with isophorone diamine (IPD) as hardener, and epoxy/clay composites (epoxy resins, IPD and organo-clay) were investigated by isothermal DSC at 100°C. The curing reaction was considered to be completed when the DSC curve level lowered down to the baseline. The areas of the peak under the isothermal curves at

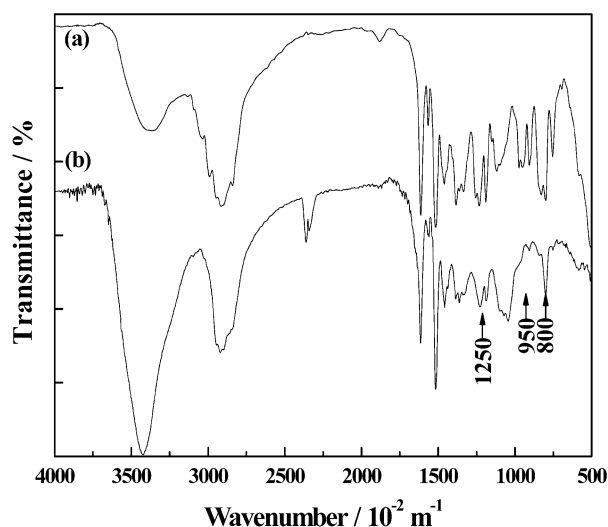


Fig. 3. FT-IR spectra of (a) DGA, (b) decomposed DGA epoxy adhesives (cured at 100°C in the oven).

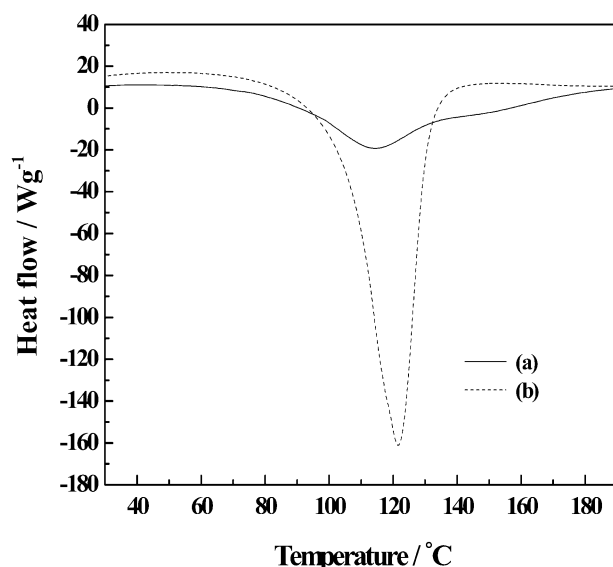


Fig. 4. DSC scans of curing reaction at the heating rate of 10°C/min for the ratio of epoxy adhesive to hardener 1:1.1 (a) DGEBA/IPD ($\Delta H = 565 \text{ W} \cdot \text{s}$), (b) DGA/IPD ($\Delta H = 2590 \text{ W} \cdot \text{s}$).

various times were used to determine the conversion (α) at various times. The chemical conversion (α) at cure time t , was determined from Eq. (3)⁵⁾

$$\alpha = \Delta H_i / \Delta H_T \quad (3)$$

where, ΔH_i and ΔH_T are the isothermal heat and the total heat evolved up to cure time t , respectively.^{5),7)}

To confirm the thermal stability of each epoxy adhesives with various a/e value which is the ratio of the amine hydrogen equivalent weight to the polymer equivalent weight, each epoxy adhesives was cured at 100°C for 3h without decomposition and T_g of epoxy adhesives was obtained from the dynamic mechanical analysis, as shown in Table 1. T_g of DGA was higher than that of DGEBA and the optimum ratio of a/e was 1.25 for both epoxy adhesives types. Figure 5 shows the variation of conversion rate of polymer with time curves obtained by isothermal DSC at 100°C for the different molar ratio of IPD/DGEBA and IPD/

Table 1. Glass Transition Temperature (T_g) of Epoxy Adhesives with Various a/e

Prepolymer	DGEBA				DGA			
a/e	1	1.25	1.5	1.75	1	1.25	1.5	1.75
$T_g/^\circ\text{C}$	148	150	144	136	170	248	165	162

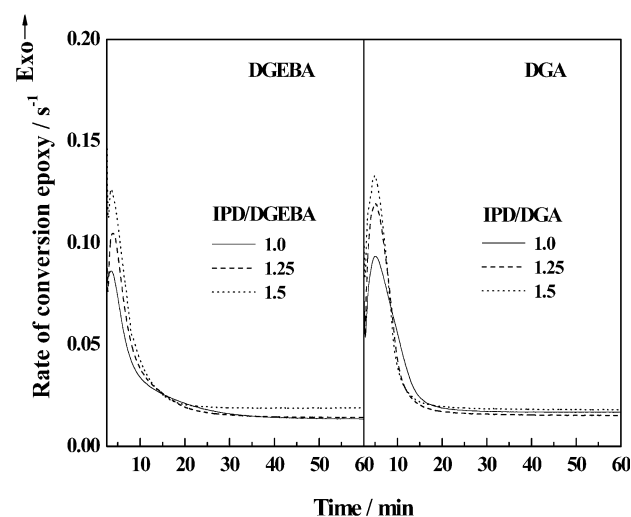


Fig. 5. Rate vs time curves obtained by isothermal DSC at 100°C for IPD/DGEBA and IPD/DGA system at different molar ratios.

DGA, respectively. The reaction rate increased with the amount of hardener for both epoxy adhesives types. According to the data, curing reaction was completed at 10 min. regardless of epoxy adhesives types.

Reaction rate and conversion value for DGA with four epoxy rings are higher than those for DGEBA with two epoxy rings. Therefore, cross-linking density of DGA is expected to be larger than that of the DGEBA, and finally the network structure of the epoxy adhesives with DGA should also be expected to be dense if decomposition of DGA can be reduced.

Figure 6 indicates the relationship between conversion and reaction time of neat epoxy adhesives and epoxy/clay composite. Comparing to the neat epoxy, the conversion and the reaction rate of the composite was decreased, and the composite with 1 mass% clay showed lowest conversion at the same curing time. This indicates that the curing reaction of epoxy adhesives with amine hardener and the mobility of polymer chains were reduced by the clay particles. Therefore, the curing reaction rate of epoxy adhesives can be controlled by a small addition of clay, which in turn, the degradation of the polymer during curing process by high heat generation can be prevented. These results are also agreed with the reports of various type of modified epoxy with liquid rubbers, glass bead and other inorganic materials.⁸⁾⁻¹⁰⁾

Based on the optimum curing conditions of each epoxy adhesive obtained from Fig. 5 and Table 1, the effect of clay on thermal stability of epoxy/clay composites were investigated by the dynamic mechanical analysis and are shown in Fig. 7.

It has been reported¹⁰⁾ that an annealed specimens of polycarbonate/multi-walled carbon nanotube composite showed the broad $\tan\delta$ peak with lower height due to retard of a segmental chain motion of the composite. Also, the $\tan\delta$ peak with higher height indicates more damping characteristics or more flexibility of polymer.¹¹⁾ Comparing with the mobility of polymer chains of

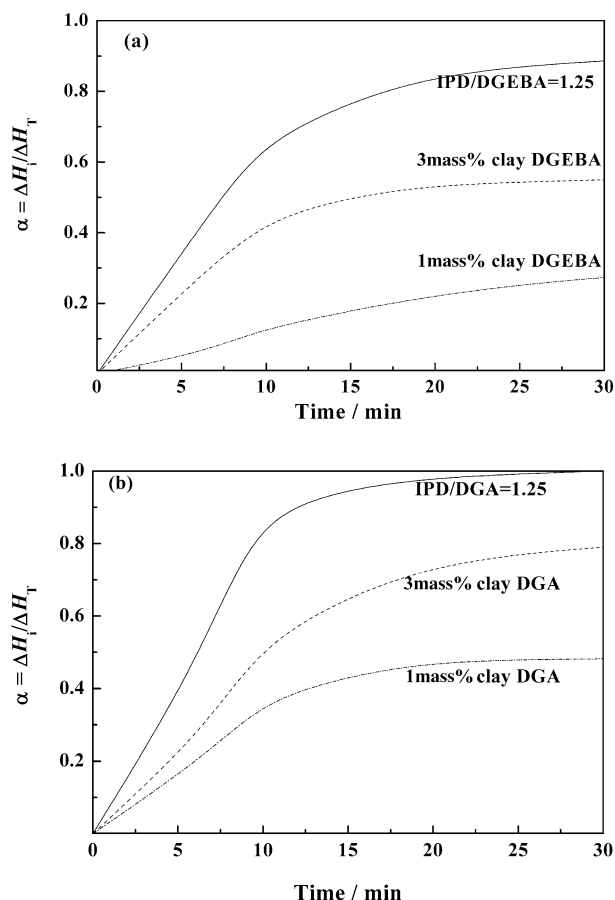


Fig. 6. Isothermal DSC experiments at 100°C: conversion vs time (a) DGEBA epoxy adhesive and DGEBA epoxy adhesive/clay composite (b) DGA epoxy adhesive and DGA epoxy adhesive/clay composite.

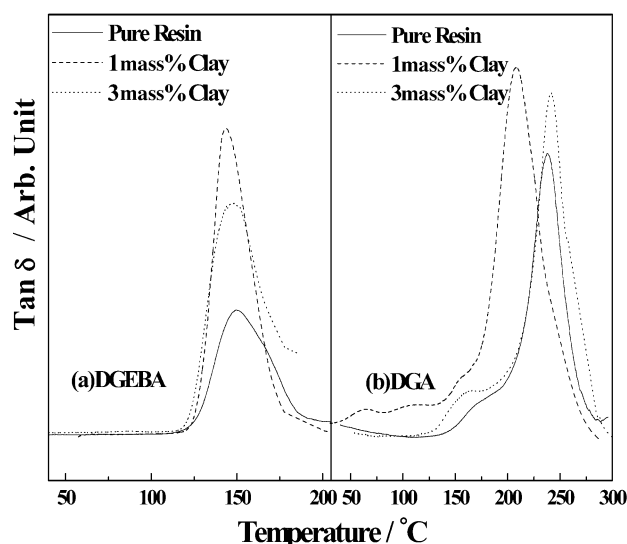


Fig. 7. Tan δ vs temperature/°C for the neat epoxy adhesive and epoxy/clay composites. (a) DGEBA, (b) DGA.

pure epoxy adhesives, the mobility of polymer chains of composites with clay increased, which is corresponded to the increase of flexibility of epoxy adhesives. The reasons why the mobility of polymer chain with 1 mass% clay was larger than that with 3 mass% clay are still under investigated, however, it may

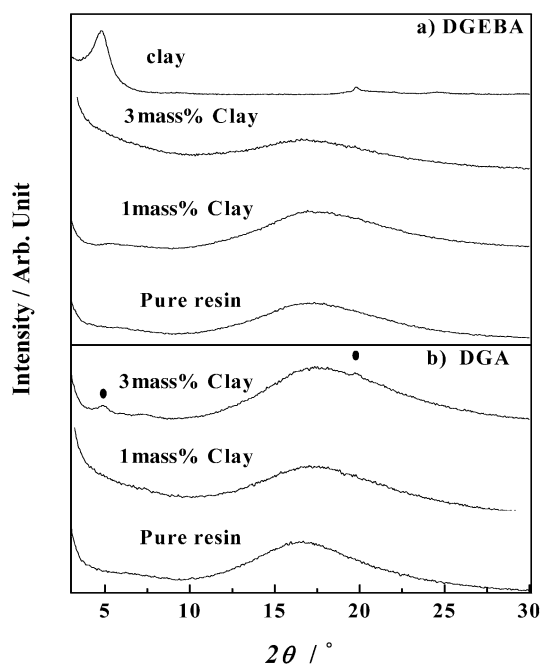


Fig. 8. X-ray diffraction patterns of epoxy adhesives with clay.

be related to the homogeneity of clay particle in epoxy/clay composite.

Thermal stability of epoxy/clay composite for DGEBA was not changed with the addition of clay, while that for DGA was decreased slightly with the addition of clay content. These results could be attributed to uneven distribution of clay for 3 mass% clay addition to DGA, as confirmed in Fig. 8 (b).

Figure 8 shows the X-ray diffraction patterns of clay, epoxy adhesives and epoxy/clay composite. For the neat epoxy adhesives (DGEBA and DGA), the X-ray diffraction patterns show a broad peak corresponding to the amorphous epoxy adhesives. For the epoxy/clay composite, the X-ray diffraction pattern of DGA with 3 mass% clay shows small peaks at $2\theta = 5^\circ, 20^\circ$ which are the peaks appearing for pure clay. Since the peak was not shifted at peak position of pure clay, it seems that the clay was not fully exfoliated or partially agglomerated in the epoxy matrix and it indicated that there was an uneven distribution of clay.

4. Conclusions

Epoxy adhesive with DGA showed the larger degradation than that with DGEBA due to the high heat generation of curing reaction for DGA. With increasing the molar ratio of Isophorone diamine to DGEBA and/or DGA, the conversion rate was increased, and the glass transition temperature (T_g) of epoxy adhesive with DGA was 240–260°C and it was very thermally stable.

The polymer chains of composites with clay showed larger mobility than pure epoxy adhesive, and thermal stability of epoxy/clay composite for DGEBA was not changed with clay content, while that for DGA was decreased slightly.

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References

- 1) K. J. Saunders, Chapman and Hall, "Organic polymer chemistry," 2nd ed., 412–435 (1988).
- 2) S. A. Chambers and T. Gordon, *International Journal of Adhesion & Adhesives*, **27**, 277–287 (2007).
- 3) E. S. Balcerzak, H. Janeczek, B. Kaczmarczyk, H. Bednarski, D. Sek and A. Miniewicz, *Polymer*, **45**, 2483–2493 (2004).
- 4) I. Isik, U. Yilmazer and G. Bayram, *Polymer*, **44**, 6371–6377 (2003).
- 5) C. W. Wise, W. D. Cook and A. A. Goodwin, *Polymer*, **38**, 3251–3261 (1997).
- 6) R. Thomas, S. Durix, C. Sinturel, T. Omonov, S. Goosens, G. Groeninckx, P. Moldenaers and S. Thomas, *Polymer*, **48**, 1695–1710 (2007).
- 7) E. G. Karayannidou, D. S. Achilias and I. D. Sideridou, *European Polymer Journal*, **42**, 3311–3323 (2006).
- 8) Prime RB. Thermosets. In: Turi EA, editor. *Thermal Characterization of Polymer Materials*. New York: Academic Press; 198111.
- 9) M. S. Soto, P. Pages, T. Lacorte, K. Briceno and F. Carasco, *Composites Science and Technology*, **67**, 1974–1985 (2007).
- 10) Y. T. Sung, C. K. Kum, H. S. Lee, N. S. Byon, H. G. Yoon and W. N. Kim, *Polymer*, **46**, 5656–5661 (2005).
- 11) B. Francis, V. L. Rao, G. V. Poel, F. Posada, G. Groeninckx, R. Ramaswamy and S. Thomas, *Polymer*, **47**, 5411–5419 (2006).