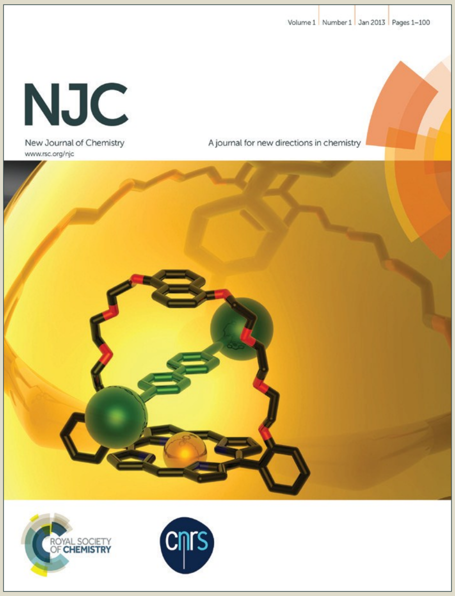

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ARTICLE TYPE

Characterisation of the thermal self-healing of a high crosslink density epoxy thermoset

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A new self-healing thermosetting epoxy polymer with high cross-linked density was prepared using diamine cross-linker with two Diels-Alder (DA) units and tri-functional triglycidyl *p*-amino phenol (TGAP). The curing and self-healing conditions of the TGAP-based epoxy polymer were examined. Using the suitable condition, the self-healing properties of the highly cross-linked polymer were studied via DMA and swelling tests. The different properties of TGAP-based self-healing epoxy polymer were compared to previously-reported lower crosslink density self-healing epoxy polymers and the influence of the crosslink density is discussed.

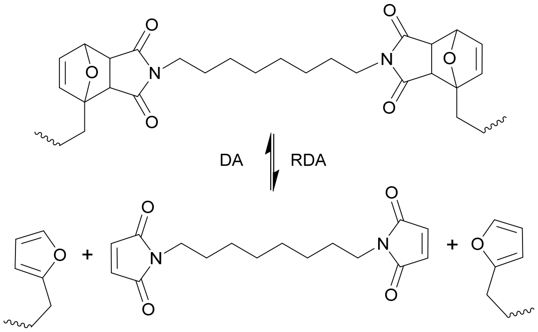
Introduction

The crosslink density of the epoxy polymer influences physical and mechanical properties, such as the glass transition temperature (T_g), modulus, fracture strength and toughness.[1] Therefore, different crosslink density epoxy polymers have different industrial applications.[2-4]

In recent years, increasing research has focused on self-healing polymers, especially cross-linked polymers which have good physical and mechanical properties and yet have limited healing ability if scratched, for example, because of the molecular immobility imposed by the crosslinks.[5, 6] Using different strategies, such as storing healing agents inside capsules within the polymer matrix or by incorporating reversible chemical structures in the molecules of the polymers, cross-linked polymers have been shown to be able to have the ability heal to varying degrees.[7-9]

Several research groups tried to investigate the self-healing polymers with different crosslink density. Wudl's group was the first to develop materials which were formed from multi-functional groups of furan and maleimide to synthesised highly cross-linked polymers using the DA reaction.[10, 11] The resultant polymer with high crosslink density demonstrated a healing efficiency of 57 % using 150 °C as thermal treatment temperature, while the polymer with low crosslink density showed an average recovery of 80 % after being heated at 115 °C for 30 minutes and 40 °C for 6 hours. Tian *et al.* synthesised two new epoxy resins which both contained a furan group, and used them to form two healable epoxy polymers with bis-maleimide and curing agent of anhydride.[12, 13] One of their cured polymer with lower crosslink density demonstrated greater cleavage reversibility using Plaisted and Nemat-Nasser's DCDC test method[14]. After being heated at 110 °C for 20 minutes to open the DA adducts, and then 80 °C for 72 hours to close the DA adducts, the healed sample of cured polymer showed an average self-healing efficiency of 96 %.

In our previous work, a new type of diamine cross-linker with two DA units was synthesised.[15] Unlike DA units in the epoxy monomers[12, 13, 16], which limited the modification of the self-healing polymers, this new diamine with DA units can be used to cure different kinds of commercial epoxy monomers to produce different, resultant self-healing epoxy polymers. With the Retro-Diels-Alder (RDA) reaction to scission the DA units at high temperature and the DA reaction to reform them at low temperature, the damaged cross-linked epoxy polymers could heal and recover to the original state (Scheme 1). A common used di-functional epoxy resin, diglycidyl ether of bisphenol A (DGEBA), was used to react with the synthesised diamine cross-linker to prepare a new self-healing polymer.[17] The thermal self-healing behaviours of this polymer were clearly showed during the experiments, including changes in T_g at different stages of healing, recovery of the swelling properties upon healing and the healing of a scratch on the surface of the sample. The mechanism of this thermal self-healing was also investigated and the healing process was concluded in three steps.



Scheme 1 RDA and DA reactions in the self-healing epoxy system

In this work, tri-functional triglycidyl *p*-amino phenol (TGAP) was used to prepare self-healing polymer with high crosslink density, cured by diamine cross-linker with two DA units. The necessary curing condition was investigated and the self-healing condition of the cured polymer was studied. With the suitable healing conditions, the self-healing behaviour of the high cross-linked epoxy polymer was researched. The physical and mechanical properties of the DGEBA-based and TGAP-based self-healing epoxy polymers were listed and compared to demonstrate the influence of the crosslink density.

Experimental

Materials

Diamine cross-linker with two DA adducts (shown in Scheme 2) was synthesised using the method in the previous work and the purity was more than 95 %.[15] TGAP was purchased from Sigma-Aldrich, with a molecular weight of 277.32 g/mol and the epoxide equivalent weight (EEW) of 92.44 g/eq. All other reactants and reagents were purchased from Merck.

Preparation of the new self-healing epoxy polymer

Diamine cross-linker with two DA adducts (1.5 g, 3 mmol) and TGAP (1.11 g, 4 mmol) were mixed without the use of any solvents and degassed under vacuum (0.5 mm Hg) at room temperature for 3 hours. The uncured mixture was then heated at 60 °C for 24 hours to produce the cross-linked, epoxy polymer. FTIR ν (cm^{-1}) 3436, 2927, 2856, 1687, 1510, 1402, 1228, 1035, 816, 748.

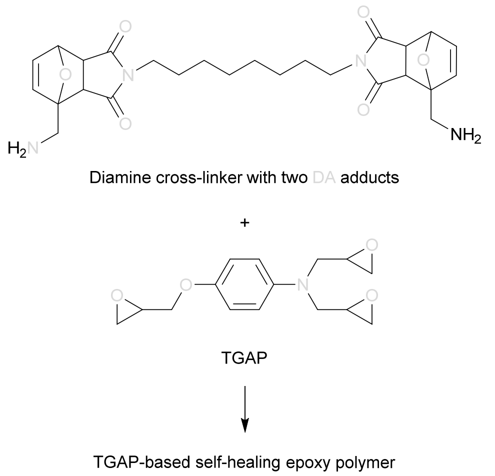
Characterisation

Fourier transform infrared (FTIR) spectra were recorded with a Bruker EQUINOX 55 FTIR fitted with an MCT detector. The ATR sampler is a Specac 'Golden Gate' single bounce diamond ATR. The operation condition was 50 scans at a resolution of 4 cm^{-1}. The sample was cut from thin film samples and the thickness was 0.5 mm. Near infrared (NIR) spectra were obtained from samples of about 0.8 mm thickness using a Bruker EQUINOX 55 FTIR spectrometer with 32 scans at resolution of 8 cm^{-1} in the region 9000-4000 cm^{-1}. Differential scanning calorimetry (DSC) experiments were performed with a Perkin-Elmer DSC-7 using Nitrogen purge (20 ml/min) and aluminium pans. The weight of each sample was about 10 mg. The glass transition temperature (T_g) was obtained with a Perkin Elmer Dynamic Mechanical Analyzer DMA7 using penetration mode and Helium gas (35 cm^3/min). The static force was 800 mN, the dynamic force was 500 mN and the frequency was 1 Hz. The sample was prepared in a cylindrical silicon mould of diameter 5 mm and height was 2 mm. Samples which were exposed to solvents for swelling test were in the form of thin films of 0.5 mm. The sample for the dissolution test was prepared in a smaller cylindrical silicon mould. The diameter was 3 mm and the height was 2 mm. Molecular weights of the dissolved polymers were measured by gel permeation chromatography (GPC) with a Tosoh Ecosec HLC-8320 GPC using Tosoh alpha 4000 and 2500 columns. Dimethylformamide (DMF) containing LiBr (10 mmol/L) was used as the solvent and two detecter (refractive index and UV, λ = 280 nm) were employed. Calibration curves were obtained with polystyrene standards. The healing process of the scratched sample was recorded using an Olympus BX60 microscope with 20X magnification and a Canon Legria HFS20 camera. The sample was put on a piece of glass and the thickness of the sample was about 0.4 mm. The scratch on the sample surface was some 50 μm in width and 5 μm in depth. A Linkam THMS600 hot stage was used to heat the sample under the microscope at a heating rate of 80°C/min. The thermal stability of the polymer was tested by thermogravimetric analysis (TGA) with an EXSTAR TG/DTA6300 at a heating rate of 10 °C/min under Argon atmosphere.

Result and Discussion

Curing condition of the TGAP-based self-healing epoxy polymer

The diamine cross-linker with two DA units was used to cure and cross-link TGAP, which has high functionality with three epoxide groups, to achieve epoxy polymer with high cross-linked density. The curing process was investigated using the same methods, NIR and DSC, as for DGEBA and the cross-linker[17]. TGAP was blended with the diamine cross-linker at room temperature to avoid the occurrence of any curing before testing (Scheme 2). A 1:1 molar ratio of epoxide groups and NH groups equated to a 4:3 molar ratio of TGAP and the cross-linker.



Scheme 2 Curing reaction of the diamine cross-linker with two DA adducts and the TGAP epoxy monomer

The NIR spectra of TGAP and diamine cross-linker are shown in Figure 1. Based on the literature[1], the strong peak at 4524 cm^{-1} reflects the epoxide group and the two peaks at 4628 cm^{-1} and 4682 cm^{-1} are due to the phenyl group in the TGAP spectrum. The two peaks at 4952 cm^{-1} and 6532 cm^{-1} in the diamine cross-linker spectrum reflect the amine groups. No peak appeared at 4524 cm^{-1} in the diamine spectrum. Therefore, in the spectrum of the mixture of TGAP and diamine cross-linker, this peak relates only to the epoxide group.

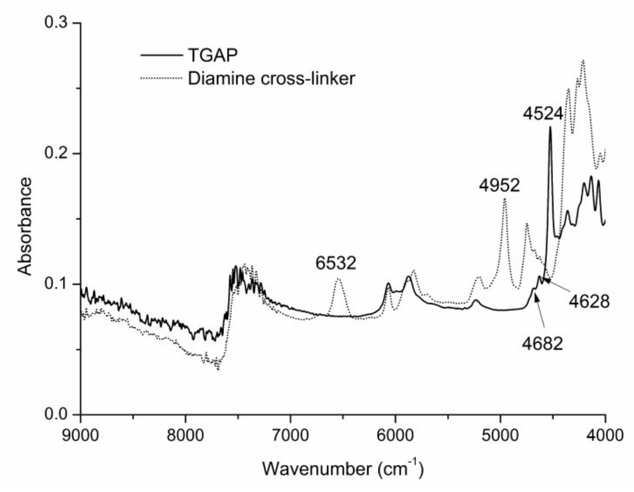


Figure 1 The NIR spectra of the TGAP and diamine cross-linker

The NIR spectra of the mixture of TGAP and diamine cross-linker before and after curing at 60 °C for 12 hours are shown in Figure 2. The figure shows that the epoxide group peak at 4524 cm^{-1} is reduced and likewise the two amine peaks at 4952 cm^{-1} and 6532 cm^{-1} become much weaker than those in the spectrum of the uncured mixture. The appearance of the hydroxyl group peak at 6981 cm^{-1} provides evidence of the TGAP curing reaction. The phenyl group peaks at 4628 cm^{-1} and 4682 cm^{-1} do not change during the curing reaction between TGAP and diamine cross-linker. Either could be used as an internal standard, although the more prominent one at 4628 cm^{-1} was used for this purpose, in this work.

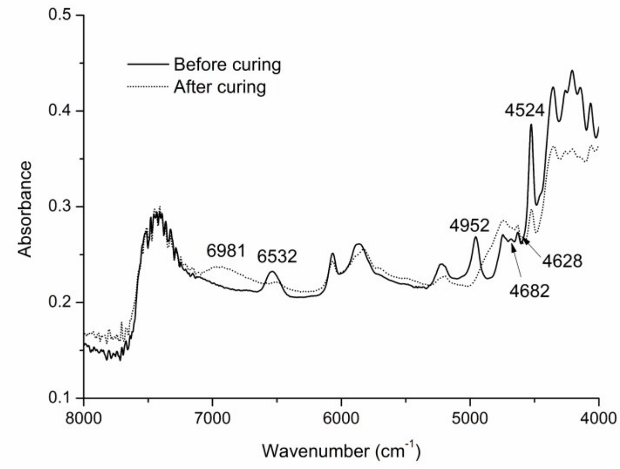


Figure 2 The NIR spectra of the mixture of TGAP monomer and diamine cross-linker before and after curing at 60 °C for 12 hours

The spectral range from 4400 cm^{-1} to 4800 cm^{-1} was used to observe the change of the epoxide group peak during curing in the NIR testing experiments. In Figure 3, the epoxide group peak at 4524 cm^{-1} became weaker after longer curing times at 60 °C.

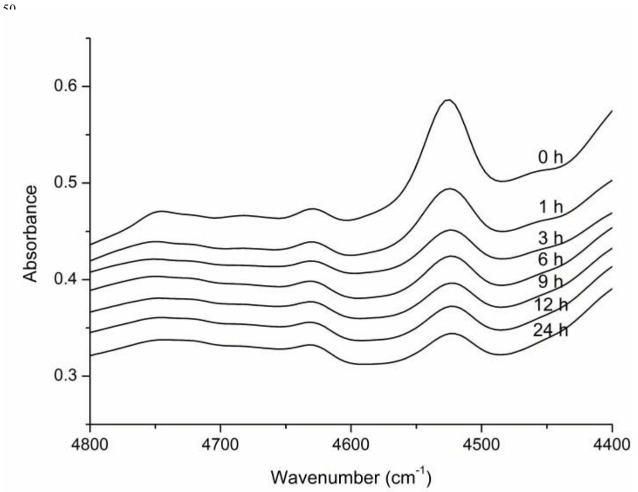


Figure 3 The NIR spectra of the mixture of TGAP and diamine cross-linker, after being heated at 60 °C for different lengths of time

Based on the NIR data, the degree of cure was calculated using the follow equation, which has been mentioned in the previous work^{17}.

$$\alpha = 1 - \frac{[EP]_t / [IS]_t}{[EP]_0 / [IS]_0} \qquad (1)$$

where $[EP]_0$ and $[EP]_t$ are the peak height of epoxide group peak at 4524 cm^{-1} at time t = 0 and t, respectively; $[IS]_0$ and $[IS]_t$ are the peak height of internal standard at time t = 0 and t, respectively. The peak heights of the epoxide group peak at 4524 cm^{-1} and the internal standard peak at 4628 cm^{-1} employed in the calculation were obtained from curve fitting using Igor Pro 6.2.

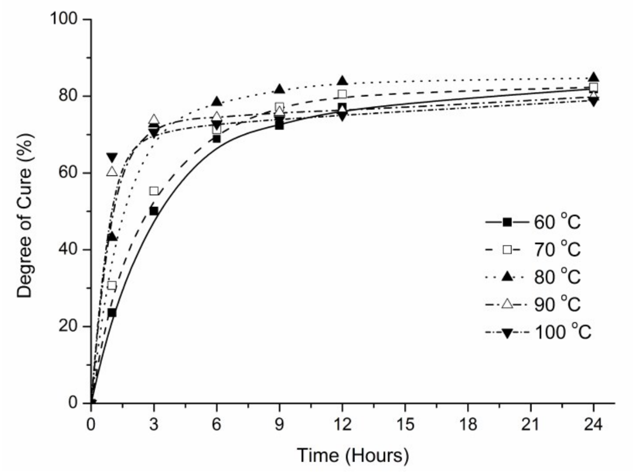


Figure 4 The degree of cure of the uncured mixture of TGAP and diamine cross-linker heated at different temperatures for different lengths of time

The uncured mixture of TGAP and diamine cross-linker was cured at different temperatures from 60 °C to 100 °C, as a function of curing time. In Figure 4, it can be seen that in the early part of the reaction, the degree of cure at higher temperatures increased faster than that at lower temperatures.

With the increasing curing time, the rate of cure at higher temperatures significantly reduced compared to that at the beginning of the cure process. The degree of cure at lower temperatures was similar to that at higher temperatures after 12 hours, and became greater for longer reaction times. The highest degree of cure was about 85 % after curing at 80 °C for 24 hours.

This trend was quite similar to that observed for the DGEBA-based epoxy[17], and can be explained by the competition between the amine-epoxy addition reaction and the Michael addition reaction[18]. At the beginning of the cure process, the reaction between epoxide groups and amine groups dominate for all cure temperatures. After about 1 hour of reaction, the RDA process commences when the temperature is above 80 °C, and the DA adducts of furan and maleimide groups begin to cleave and maleimide moieties appear. With an increase in curing time, the concentration of maleimide groups increases, resulting in the possibility of Michael addition between the maleimide group and the unreacted amine groups[19]. This causes the concentration of amine groups to decrease and unreacted epoxide groups remain, and the cure rate decreases as a result. For cure temperatures above 80 °C, the final degree of cure was lower.

Figure 5 shows the result of competition between the amine-epoxy addition reaction and the Michael addition reaction. The uncured sample was heated at different temperatures for 24 hours. With the variation in curing temperature from 60 °C to 80 °C, the degree of cure increased. When the cure temperature was greater than 80 °C, the ultimate (long time) degree of conversion is reduced. The higher the cure temperature, the lower degree of cure achieved. This result was similar to that of DGEBA-based epoxy polymer[17] and clearly demonstrated that the RDA and Michael addition reactions influence the final degree of cure for high cure temperatures.

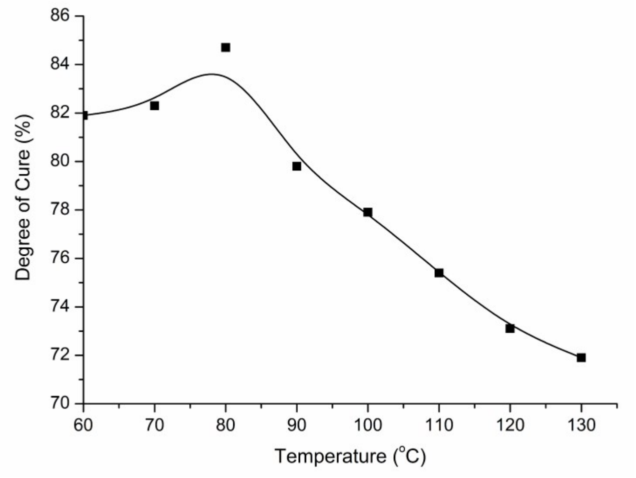


Figure 5 The degree of reaction at different temperatures after 24 hours cure temperatures determined from FTIR data

Due to the possible occurrence of the Michael addition reaction, the choice of the curing temperature was crucial. It should not be so high as to allow the RDA reaction and Michael addition reaction to both occur and damage the self-healing system, nor be too low to make the time of cure of TGAP and diamine cross-linker too long, or to achieve a too low an ultimate degree of cure. Figure 4 and Figure 5 indicate that the influence of the RDA reaction and the Michael addition reaction was moderate when the temperature of treatment was less than 80 °C. The highest degree of cure, about 85 %, was obtained by the curing condition of 80 °C for 24 hours. However, the degree of cure obtained from treatment at 60 °C for 24 hours was only 3 % lower than the highest cure achieved shown in Figure 5. Therefore, the degree of cure for samples cured at the lower 60 °C temperature for 24 hours was acceptable. The cure temperature of 60 °C is optimal, both sufficiently far away from the RDA reaction temperature of 120 °C and is lower than the problematic Michael addition reaction temperature of 70 °C[19].

DSC was used to investigate the curing process of TGAP and diamine cross-linker. Figure 6 shows the results of uncured mixtures treated at 60 °C for different lengths of time. Curve (a) of a temperature scan of the uncured mixture shows a huge exothermic peak at a temperature range from 50 °C to 170 °C, which was a result of the influence of the epoxy curing reaction and RDA reaction, both occurring in the same temperature range. As shown previously[17], since the reaction enthalpy of the epoxy/amine curing reaction is more than twice that of the RDA reaction, the RDA reaction peak is not visible in this thermogram. With a greater length of time of curing at 60 °C, the endothermic peak of the RDA reaction appears after 3 hours in Curve (c), becoming more obvious as the curing reaction process diminishes in comparison. The T_g is first visible in Curve (d) and increases from 51 °C to 72 °C for extended curing times. The DSC results show that no more curing at 60 °C is visible after 24 hours.

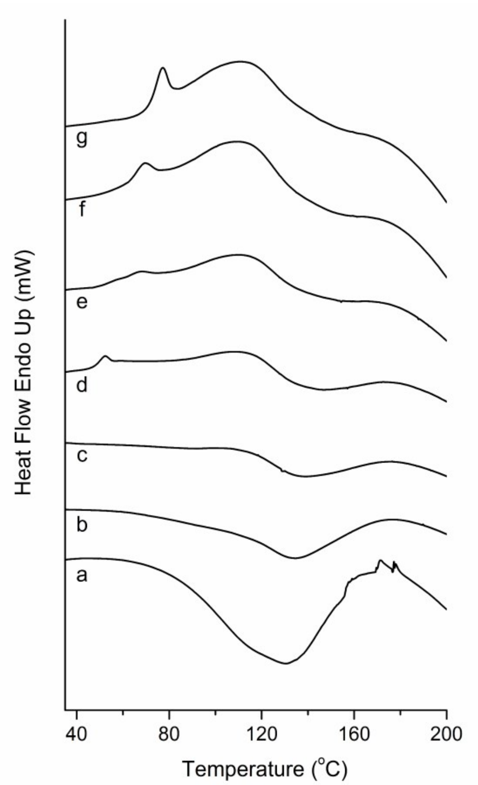


Figure 6 DSC thermograms of samples cured at 60 °C for (a) 0 hour, (b) 1 hour, (c) 3 hours, (d) 6 hours, (e) 9 hours, (f) 12 hours, and (g) 24 hours. The heating scan rate is 5 °C/min.

From the results of NIR and DSC experiments, the suitable condition for curing of the epoxy polymer based on TGAP was 60 °C for 24 hours.

The conditions of DA and RDA reactions in the TGAP-based epoxy polymer

As mentioned in the previous research[17], the healing process of the DA-based self-healing epoxy polymer includes three steps: the cross-link moieties cleave at high temperature via RDA reaction; the mobile, non-cross-linked polymer fragments flow to fill the crack; the cross-linked units reform at low temperature via DA reaction.

The conditions of the healing process are important in this study and Fourier transform infrared (FTIR) was used to investigate DA and RDA reactions. FTIR results of cured samples are shown in Figure 7. The peak at 694 cm^{-1} is due to the free maleimide ring and the peak at 1687 cm^{-1} for the maleimide carbonyl group was again used as an internal standard.[20] The 694 cm^{-1} peak was relatively weak in the spectrum of a cured sample (Figure 7a), which proved that most of the maleimide groups were in the form of DA adducts and there was little free maleimide in the cured sample. After the polymer sample was treated at 150 °C for 10 minutes and quenched quickly to room temperature, the height of the peak (Figure 7b) increased by a factor of three, compared with that of the sample before such treatment (Figure 7a), indicating that more maleimide groups appeared in the sample because the DA units were cleaved by the RDA reaction. After the sample was treated at 60 °C for 5 hours and cooled to room temperature, the height of the peak (Figure 7c) decreased to the level found in the original sample (Figure 7a), which showed that the DA reaction occurred and the DA units reformed in the TGAP system, as was observed in the DGEBA-based epoxy network[17].

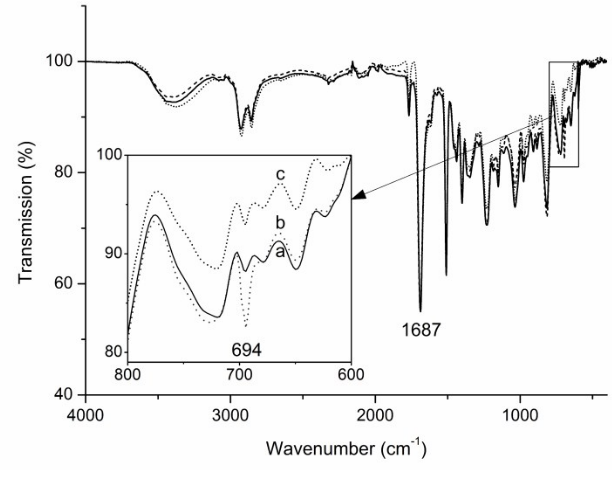


Figure 7 FTIR spectra of (a) the sample of cured TGAP-based epoxy polymer; (b) the sample heated at 150 °C for 10 minutes and quenched quickly to room temperature; (c) following (b), the sample was treated at 60 °C for 5 hours and cooled to room temperature.

The optimal conditions to induce the DA and RDA reactions in the TGAP-based epoxy polymer were then determined. The change in height of the peak at 694 cm^{-1} was followed during the experiment and the maleimide carbonyl group peak at 1687 cm^{-1} was employed as an internal standard to compare different spectra. The change of the peak height [*CPH*] was calculated using the follow equation:

$$[CPH]=\frac{[MM]_t \big/ [IS]_t}{[MM]_o \big/ [IS]_o} \qquad (2)$$

where $[MM]_o$ and $[MM]_t$ are the peak height of maleimide group peak at 694 cm^{-1} at original state of the cured sample and time t, respectively; $[IS]_o$ and $[IS]_t$ are the peak height of internal standard at original state of the cured sample and time t, respectively. For the RDA reaction process, a greater numerical value of [*CPH*] is indicative of more maleimide in the system, which means the degree of RDA reaction is greater. For the DA reaction process, a smaller numerical value of [*CPH*] represents less maleimide content in the system, which means the degree of DA reaction is much higher.

The height change of the maleimide peak, after the cured sample was heated at different temperatures for different lengths of time, is shown in Figure 8. The value of [*CPH*] obtained at a temperature less than 120 °C was low. With the temperature held above 120 °C, the rate of the RDA reaction increased, resulting in the production of more maleimide groups and a greater value of [*CPH*]. For the TGAP-based epoxy polymer, three conditions (130 °C for 30 minutes, 140 °C for 20 minutes and 150 °C for 10 minutes) all demonstrated the ability to bring about high values of [*CPH*] compared with other conditions. Due to the occurrence of side reactions of maleimide groups, such as polymerisation of the maleimide[21, 22] which can occur if the sample is held at high temperatures for an extended time, the shortest annealing time was considered to be the best condition to prevent such side reactions from occurring. The annealing condition of 150 °C for 10 minutes was selected as the most suitable condition for the RDA reaction in the TGAP-based epoxy polymer.

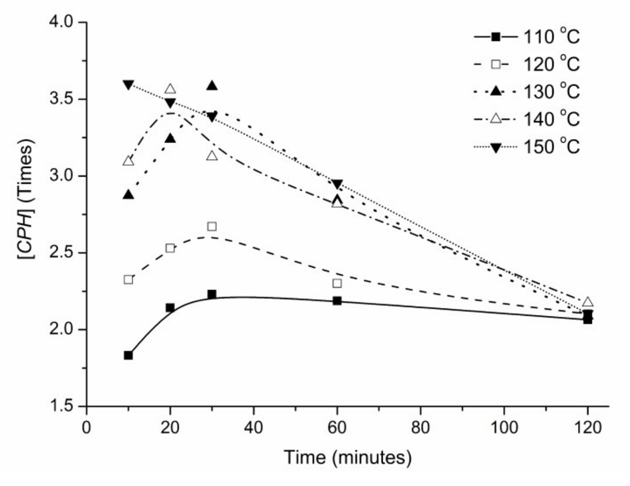


Figure 8 The change in infrared peak height at 694 cm^{-1} as a function of annealing time for different temperatures, for the TGAP-based epoxy polymer.

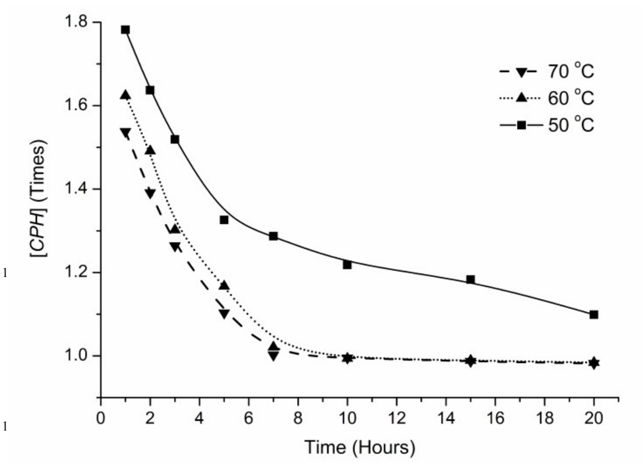


Figure 9 Peak height change at 694 cm^{-1} of the sample of TGAP-based epoxy polymer heated at 150 °C for 10 minutes compared with the original sample, as a function of heating time at different temperatures, as characterised using FTIR.

To find the most suitable condition for the DA reaction, the cured sample of TGAP-based epoxy polymer was heated at 150 °C for 10 minutes and quenched rapidly to room temperature to generate a sample with substantial cleavage of the DA unit in the cross-link unit. The sample was then heated at different temperatures for different lengths of time. The results are shown in Figure 9. It was found that both 60 °C and 70 °C could cause the values of [*CPH*] to be reduced to 1, which meant that the concentration of maleimide groups had returned to the value found in the original cured sample. This showed that the sample was fully recovered in terms of scissioning and reformation. With the lower temperature, the condition of 60 °C for 7 hours was selected as the most suitable condition for the DA reaction to reform the crosslink component of the epoxy cross-linked network.

From the results of the two series of experiments described above, the conditions of 150 °C for 10 minutes and 60 °C for 7 hours were finally confirmed for the RDA and DA reactions in the cured sample of TGAP-based epoxy polymer.

The self-healing properties of the TGAP-based epoxy polymer

The self-healing properties of the highly cross-linked epoxy polymer system based on the tri-functional TGAP monomer were studied using the series of experiments.

Dynamic Mechanical Analyser (DMA) was used to observe the T_g change under the heating conditions above, which indicates the change in the crosslink density. The tan δ traces of the TGAP-based epoxy polymer samples treated under different thermal conditions are shown in Figure 10. The samples were heated and then quenched quickly to room temperature and tested. The T_g of the original cured sample was 92.4 °C. After the cured sample was treated at 150 °C for 10 minutes, the T_g decreased to 81.9 °C due to the cleavage of some DA units in the crosslinks by the RDA reaction, the cross-linked sample becoming more flexible and the molecular units more mobile. The scissioned sample was then heated at 60 °C for different lengths of time. The DA reaction reformed the DA units and the T_g was found to increase to 84.6 °C after 1 hour. As the time of heating increased, the T_g also increased, with greater extent of DA reaction occurring. The T_g was 88.1 °C after 3 hours, 90.5 °C after 5 hours and finally 93.2 °C after 7 hours. The final T_g was, within experimental error, the same as that of the original sample, being some 92.4 °C. As with the DGEBA-based system previously described[17], this indicated that the sample was able to recover to the same state as the original cured sample.

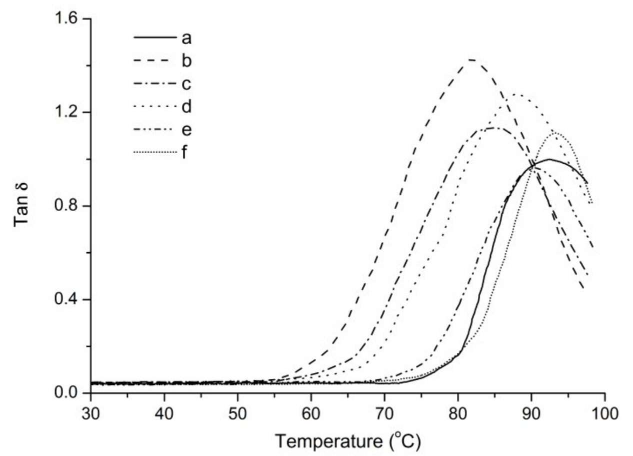


Figure 10 The tan δ traces of (a) cured TGAP-based epoxy polymer, (b) sample heated at 150 °C for 10 minutes, (c) sample heated at 150 °C for 10 minutes and then heated at 60 °C for 1 hour, (d) sample heated at 150 °C for 10 minutes and then heated at 60 °C for 3 hours, (e) sample heated at 150 °C for 10 minutes and then heated at 60 °C for 5 hours, (f) sample heated at 150 °C for 10 minutes and then heated at 60 °C for 7 hours, from DMA. The heating rate of the DMA scan is 2 °C/min and the measuring frequency is 1 Hz.

The swelling tests undertaken for DGEBA system were used to understand the microstructure of the TGAP-based epoxy polymer during the healing process. The equation used to calculate the weight increment of the sample in the previous work[17] was employed again as follows:

$$[WI] = \frac{(W_t - W_0)}{W_0} \times 100\% \qquad (3)$$

where W_0 and W_t are the weight of sample before and after the swelling test, respectively.

From the results of the DGEBA-based epoxy polymer, it was known that the sample would lose weight after the swelling test, because the uncured monomers or the decoupled oligomers arising from scissioning could be dissolved into the solvent.[17] The first parameter measured was the weight decrement after the swelling test. In this case, the samples were dried at 50 °C overnight *in vacuo* after the swelling test, and their weights were measured. The weight decrement of the samples is shown in Figure 11. For the TGAP-based epoxy polymer, the percentage of the weight loss was 5.4 %, which was lower than that of the DGEBA-based epoxy polymer (10.4 %)[17] due to the higher crosslink density of the TGAP system. The sample treated at 150 °C for 10 minutes lost 24.6 % in weight, which was four times more than that of the cured sample, because the RDA reaction enabled the DA units to scission, and thus more small, soluble branched polymers or oligomers were subsequently dissolved. After the sample was held at 60 °C for several hours, the percentage decrease of the sample weight reduced. Finally, after 7 hours, the weight decrement returned to the original level. This showed that the DA units were gradually reformed, and the structure of the sample recovered to be similar to that of the original sample.

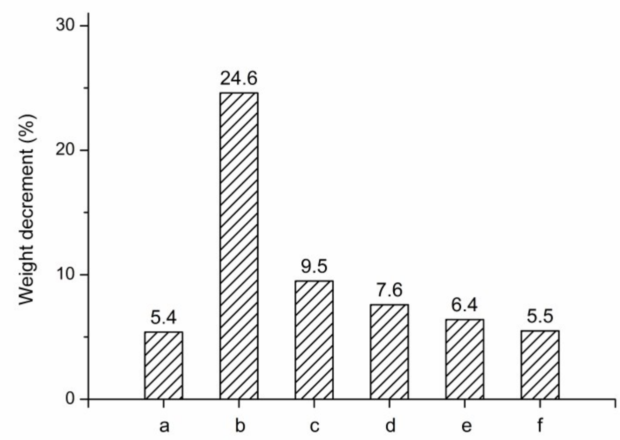


Figure 11 The change in weight of (a) TGAP-based epoxy polymer, (b) sample heated at 150 °C for 10 minutes, (c) sample heated at 150 °C for 10 minutes and then heated at 60 °C for 1 hour, (d) sample heated at 150 °C for 10 minutes and then heated at 60 °C for 3 hours, (e) sample heated at 150 °C for 10 minutes and then heated at 60 °C for 5 hours, (f) sample heated at 150 °C for 10 minutes and then heated at 60 °C for 7 hours, after being placed into acetone for 7 days, dried. All of these were compared with the weight of the original sample.

Based on the dried weight of the samples, the results of the swelling test are shown in Figure 12, with the data calculated using Equation (3). The weight increment of the original cured sample was 24.8 %. After the sample was heated at 150 °C for 10 minutes, the weight increment increased to 32 %, because the scission of the DA units occurred during treatment and the crosslink density reduced, leaving more free volume for ingress of the solvent. When the sample with the lower crosslink density structure was heated at 60 °C, the swelling ability of the sample decreased and reduced to 24.9 % after 7 hours, the same as that of the original cured sample. These results demonstrate that the swelling ability of the sample can be restored once the structure of the original sample was recovered.

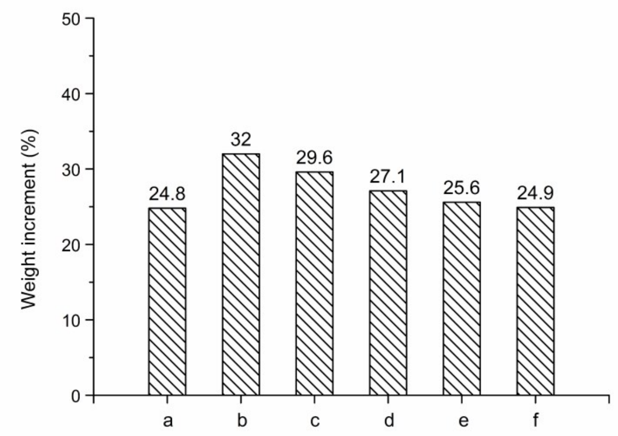


Figure 12 Swelling test results of the sample described in Figure 11, based on the final dried sample weight.

The solubility of the cured sample of TGAP-based epoxy polymer at high temperatures was also investigated. The cured sample was placed into DMF solvent at 140 °C. After 4 minutes, it was fully dissolved, which demonstrated that the DA units in the crosslink were fully scissioned and that the cross-linked polymer was reduced to branched small polymers or oligomers at the temperature above the RDA reaction temperature of 120 °C.

Other cured samples were placed in DMF for the same time (4 minutes) at different temperatures of 130 °C, 120 °C and 110 °C. After 4 minutes the solution was filtered and the residue was dried at 100 °C overnight *in vacuo*. Figure 13 demonstrates the residue weight. Some 10 % of the original weight remained when the temperature was reduced to 130 °C. For treatments at 120 °C, more than 60 % of material remained undissolved. This value increased to over 90 %, when the temperature reduced to 110 °C, showing that the rate of the RDA reaction decreased rapidly when the temperature was lowered. Compared with the results for the DGEBA-based sample[17], higher temperatures and/or greater lengths of time were required to effectively scission the DA units and decouple the architecture of the cross-linked sample based on TGAP because of the more complicated polymer structure.

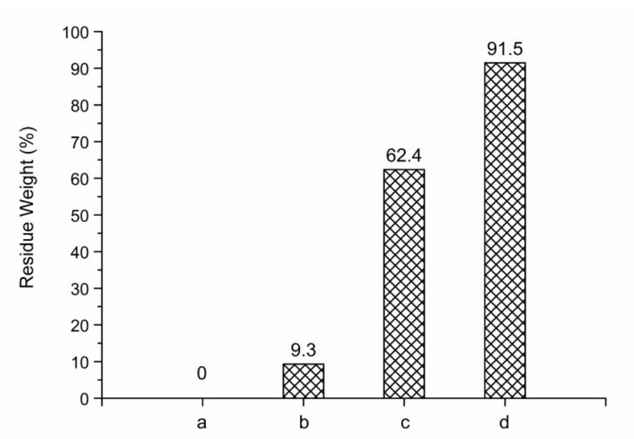


Figure 13 The residual weight of cured sample of TGAP-based epoxy polymer after being placed in DMF at (a) 140 °C, (b) 130 °C, (c) 120 °C and (d) 110 °C, all for 4 minutes.

Gel permeation chromatography (GPC) was used to analyse the dissolved component in the solutions obtained and the resultant GPC chromatograms are shown in Figure 14. Three large peaks overlapped in the range from 13 minutes to 17 minutes and the shapes of the curves were similar for the different temperatures. For the second and third peak, the M_w in each chromatogram are similar, being about 1500 g/mol with M_w/M_n of 1.1 and about 570 g/mol with M_w/M_n of 1.0. These two peaks thus appear to represent small molecular fragments separated from the polymer by the RDA reaction. The M_w of the first peak in each curve is different, from 6 800 g/mol to 31 000 g/mol, along with the decrease of the solvent temperature from 140 °C to 110 °C (Table 1). This demonstrates that fewer DA units were cleaved and thus larger branched polymers or oligomers remained in samples when the temperature was reduced. Although the molecular weight is more than ten thousand, the epoxy network was clearly broken down by the RDA reaction, and small oligomeric species were the result.

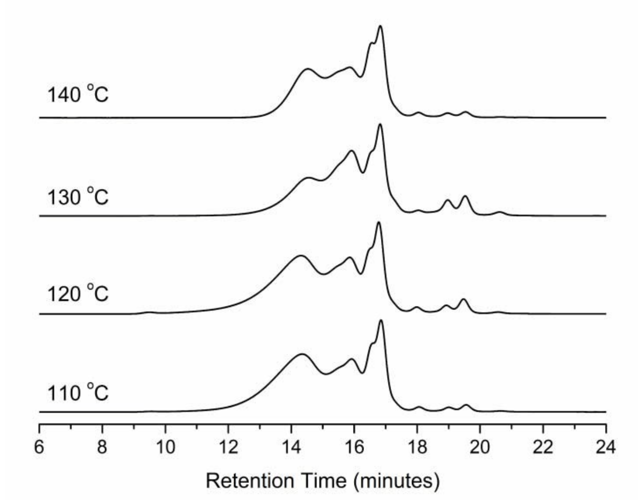


Figure 14 GPC chromatograms (obtained at room temperature) of dissolved components of scissioned TGAP-based epoxy polymer in DMF, undertaken at different temperatures

Table 1 M_w and M_w/M_n of the first peak in each GPC chromatogram in Figure 14

Temperature (°C)	M_w (g/mol)	M_w/M_n
140	6 800	1.35
130	12 000	2.12
120	27 000	3.65
110	31 000	4.37

The above experiments again proved that the DA units in the crosslink were scissioned to deconstruct the cross-linked epoxy polymer by the RDA reaction, but that they could reform to recover the cross-linked polymer structure through the DA reaction.

Self-healing behaviour on the surface of polymer

The self-healing property of the TGAP-based cross-linked epoxy polymer with DA units was clearly demonstrated using optical microscopy. The result for the temperature at 130 °C is shown in Figure 15. The scratch on the sample was some 40 µm in width and 5 µm in depth (Figure 15a). After being heated at 130 °C for 0.16 minutes, the scratch changed to some 10 µm in width (Figure 15b). There was only a faint scratch visible after 1.66 minutes (Figure 15c) and it was not apparent after 5.73 minutes exposure (Figure 15d), which meant it completely healed. The scratch on the sample used for tests at different annealing temperatures was similar in width and depth. Although the healing processes at temperatures of 140 °C and 150 °C were similar to that described above, the times for healing to occur were reduced because the DA unit could readily cleave and the oligomeric materials readily flow at the higher temperatures. Table 2 shows the required healing times for the different temperatures.

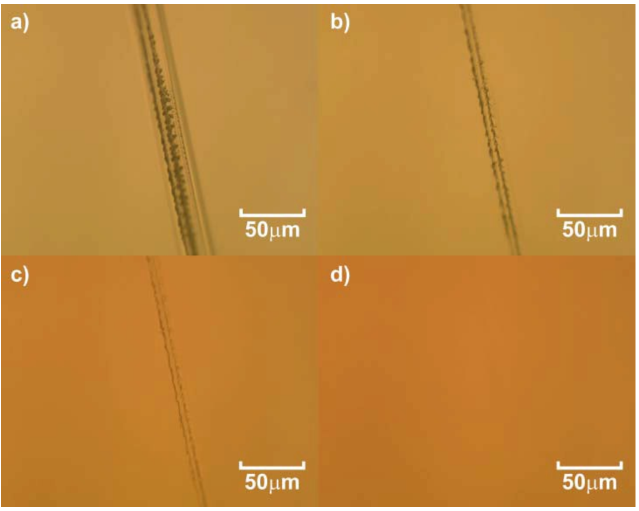


Figure 15 Micrographs of a scratch in the TGAP-based epoxy polymer sample heated at 130 °C for (a) 0 minute, (b) 0.16 minutes, (c) 1.66 minutes and (d) 5.73 minutes.

Table 2 Healing times at different temperatures for the TGAP-based epoxy polymer. The scratch was ca. 40 µm in width and 5 µm in depth.

Temperature (°C)	Healing time (minutes)
130	5.73
140	1.15
150	0.16

The data in Table 2 can be used to calculate the activation energy of flow of the de-cross-linked material obtained from the degradation of the TGAP-based epoxy polymer sample, using the Arrhenius equation as follows.

$$\ln\left(\frac{1}{t}\right) = -\frac{E_a}{RT} + \ln\left(\frac{A}{B}\right) \qquad (4)^{17}$$

Figure 16 shows ln(1/*t*) against 1/*T*. After linear fitting, the result is as follows:

$$y = -30128x + 68.852 \qquad (5)$$

From (4) and (5), the activation energy of flow is calculated as follows:

$$E_a = 30128 \times R = 30128 \times 8.31441\ J/mol = 250\ kJ/mol$$

The flow activation energy of the decomposed epoxy polymer based on TGAP was higher than that of other oligomers from the literature[23, 24] which are lower than 150 kJ/mol. The oligomer from TGAP-based epoxy polymer via RDA reaction is likely highly branched, so that it possesses a greater energy of flow activation to heal the sample surface scratch.

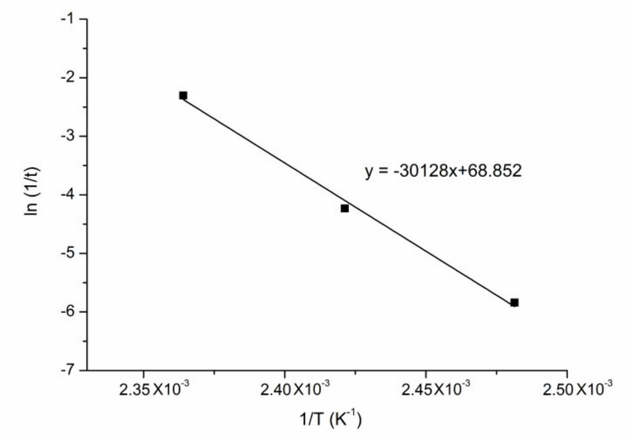


Figure 16 Arrhenius plots of 1/t (rate of healing) as a function of 1/T for the TGAP-based epoxy polymer

The comparison of the two self-healing epoxy polymers

The physical, mechanical and self-healing properties of the TGAP-based self-healing epoxy polymer were clearly shown upon the results of the experiments above. Compared with these properties of the DGEBA-based self-healing epoxy polymer obtained previously[17], the influence of the different functionalities of the epoxy monomers and the crosslink densities of the polymers was shown in Table 3.

Table 3 The comparison of the DGEBA-based and TGAP-based self-healing epoxy polymers.

Properties	DGEBA-based polymer[a]	TGAP-based polymer
Curing condition	60 °C for 12 hours	60 °C for 24 hours
T_g from DSC	61 °C	72 °C
Healing condition	150 °C for 10 minutes and 60 °C for 5 hours	150 °C for 10 minutes and 60 °C for 7 hours
T_g from DMA	81 °C	92 °C
Swelling weight increase	40.7 %	24.8 %
Time to be dissolved in DMSO at 140 °C	2 minutes	4 minutes
M_w of the component from GPC after sample heated at 110 °C in DMF for 4 minutes	12 000 g/mol	31 000 g/mol
Self-healing conditions on surface	130 °C for 10 seconds	150 °C for 10 seconds
Flow activation energy	210 kJ/mol	250 kJ/mol

[a] adopted from reference 17

Although the curing temperature is the same, because of its higher functionality, the curing time of the TGAP-based polymer is longer than that of DGEBA-based polymer. The resultant TGAP-based polymer also has the higher crosslink density, so its T_g is greater than that of DGEBA-based polymer. For the same reason, the recovery time of the TGAP-based polymer (7 hours) was necessarily longer than that used for the DGEBA-based epoxy polymer (5 hours) in the healing process, while other healing conditions remain the same. As regards the swelling behaviour, the internal free volume is lower in the TGAP-based polymer due to lower molecular weight monomer and reduced chain length between two crosslinks, so that fewer solvents can infiltrate the polymer than can the DGEBA-based polymer. The dissolution time of the TGAP-based polymer in DMSO at 140 °C was twice as long as that of the DGEBA-based polymer due to the greater number of DA units in the TGAP-based sample, as well as the higher crosslink density. For the surface healing, the healing temperature of the TGAP-based polymer was higher than that of DGEBA-based polymer to produce the same healing time, because of a greater concentration of DA units and more highly cross-linked system. The activation energy of flow of the TGAP-based polymer was also greater than for DGEBA, likely due to the fact that the resultant oligomer was likely highly branched than that of components cleaved from the DGEBA-based polymer. The GPC results also clearly show that the molecular weight of the oligomer from TGAP-based polymer was greater than that from DGEBA-based polymers, as well as being more branched. Thus, higher healing temperatures are required to provide more energy for the oligomers and fragments from the TGAP-based polymer to flow and complete the healing of the surface scratch.

From the T_g results, it can be seen that the TGAP-based polymer has a higher glass transition than the DGEBA-based polymer, which means it can provide greater protection when used as coating material. The thermal stability of the DGEBA-based and TGAP-based epoxy polymers can be measured by TGA, and the results were shown in Figure 17. The weight loss of the cross-linked epoxy polymer largely commenced at 130 °C, reducing to 93 % by 270 °C. The RDA reaction occurred at 130 °C to break the DA units in the crosslink component of the epoxy polymer, which resulted in the rapid decrease in crosslink density of the polymer. Since the degree of cure of the TGAP-based polymer sample was 82 %, 18 % of unreacted or partly reacted epoxy monomer remained in the system. Due to the scissioning of the epoxy polymer structure by the RDA reaction, this material was free to move. Some proportion reacted with the free amine remaining in the system and continued to cure, while some proportion were thermally released, which led to the 7 % weight loss. For temperatures above 270 °C, the weight was reduced sharply, which meant that the main chain of the TGAP-based epoxy polymer became unstable and started to decompose at that temperature. Compared with the TGA trace of DGEBA-based epoxy polymer, the scissioning temperature of the TGAP-based polymer (270 °C) was lower than that of the DGEBA-based epoxy polymer (300 °C). However, due to its higher crosslink density, the breakdown rate of the TGAP-based polymer was lower than that of the DGEBA-based epoxy polymer, as can be seen in Figure 17. This result is consistent with the research of Petal.[25]

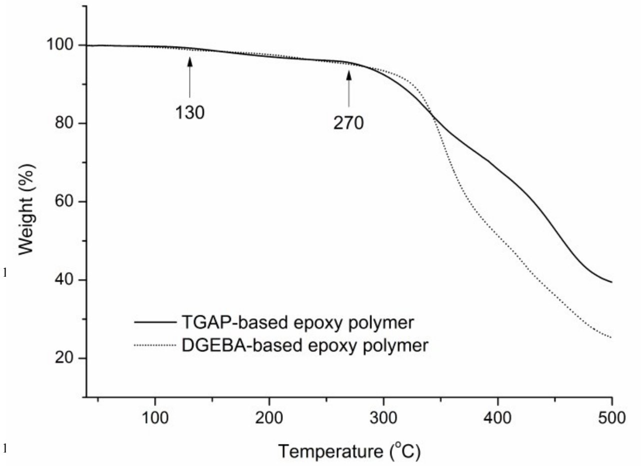


Figure 17 TGA results of the cured TGAP-based cross-linked epoxy polymer and of the cured DGEBA-based cross-linked epoxy polymer

Conclusions

A new self-healing epoxy polymer based on triglycidyl *p*-amino phenol (TGAP) with high functionality was prepared. The curing condition and thermal self-healing properties were investigated using the same methods for the polymer based on diglycidyl ether of bisphenol A (DGEBA). Near infrared and differential scanning calorimetry were used to find the suitable curing condition of 60 ^{o}C for 24 hours for the new polymer with the degree of cure of 82 %. The healing condition was research using Fourier transform infrared and the suitable condition was 150 ^{o}C for 10 minutes and 60 ^{o}C for 7 hours. The self-healing properties were studied via the tests of the samples at different stages using dynamic mechanical analyser and swelling tests. After the healing process, the sample recovered and showed the same glass transition temperature (T_g) and swelling property as that of the original sample. The recovery of the scratch on the surface of the sample was studied and the flow activation energy was obtained, which showed the self-healing behaviour of the TGAP-based polymer. Compared with the DGEBA-based epoxy polymer, the TGAP has higher functionality and the resultant polymer has a higher crosslink density and more Diels-Alder units. This means this epoxy system requires more time to cure and heal. The more highly cross-linked TGAP-based polymer also showed improved mechanical properties with a higher T_g than that of the DGEBA-based materials. The thermal stability was also improved for the higher crosslink density epoxy.

Notes and references

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Table of content

Different properties of a new self-healing TGAP-based epoxy polymer were studied and the influence of the crosslink density is demonstrated.