SELF ASSEMBLING HEALING AGENTS FOR MENDABLE EPOXY NETWORKS

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Abstract
This work describes an attempt to demonstrate the benefit of self assembly of healing agents through ionomer formation. In this way the thermal self healing of epoxy resin matrices can be induced while maintaining a low resin blend viscosity for fibre impregnation. A relatively low MW DGEBA molecule was end-capped with 4-amino salicylic acid sodium salt to provide a mechanism for ionomer assembly. Phenoxy polymers also demonstrated the need for linear polymer healing agents of similar molecular structure which remained in solution for diffusional healing.

1.Introduction

Composite materials traditionally employ thermosetting epoxy resins as matrices. Self healing resins are sought to provide structures with in situ repair. Incorporating microcapsules of healing agent (HA) is one technique but providing crosslinked epoxies with mendable characteristics is a longer term option. In previous work, Hayes et al.[1,2,3] used a soluble polymeric HA which diffused to the crack faces where thermal mending occurred. The most effective HA had a average MW of 44000 g/mol but this led to problems with the viscosity of the modified epoxy for impregnation of the fibres in the manufacture of an artefact. Jamil et al.[4,5] used end-capping of low MW epoxies to study the diffusion mechanism for healing. He demonstrated that MW of HA was a critical parameter for healing efficiency and effective healing was significantly by phase separation of the HA.

In this study we explored the self assembly of ionomer end-capped low MW epoxies as a mechanism for dealing with the 'high' viscosity of the healable resin for infiltration. The healability of these cured resins was quantified using the recovery of single-edge notch strength.

2.Experimental

2.1. Matrix Resins

Matrix 1 was a simulated aerospace grade of epoxy. It consisted of 36.9 % w/w TGAP (triglycidylamino phenol-MY 0510), 35.4 % w/w DGEBF (diglycidyl ether of bisphenol F -GY 281 (EEW = 159-172)) and cured with 27.7 % w/w DDS (4,4'-diamino diphenyl sulphone). The resin mixture was degassed at 145°C for 45 mins under vacuum before casting in 'PTFE'

coated metal SENB moulds for curing for 3h at 180°C. The samples were cooled down in the oven over 2 hours at 2°C per min. Matrix 2 was DGEBA (diglycidyl ether of bis-phenol A - DER 331) (Dow,Australia). The hardener was diethyl toluene diamine (DETDA-Ethacure 100) (Chemtura, Australia).The resin blend was degassed in a rotary evaporator at 95°C and cast into silicone moulds for curing at 150°C for 10 hours.

2.2. Healing agents

The control healing agent was DGEBA type polymer with viscosity average molecular weight of 44000 g mol^{-1} without reactive glycidyl end-groups (Sigma-Aldrich). Two analogous commercial Phenoxy polymers without glycidyl end-groups (InChem Corp.USA): PKHP-200 (Mn = 13000, Mw = 52,000 g mol^{-1}) and PKFE (Mn = 16,000, Mw = 60,000 g mol^{-1}) were also used. Two low molecular weight (Mn) diglycidyl bisphenol A-co-epichlorohydrin (DGEBA 4000 and DGEBA 6100)(Sigma -Aldrich) were end-capped by reaction with benzoic acid, 4-amino-salicylic acid sodium salt (Na DGEBA(4000) and (Na DGEBA (6100)/ PolyBis Na)). The latter two were used to establish ionomer characteristics to the HA.
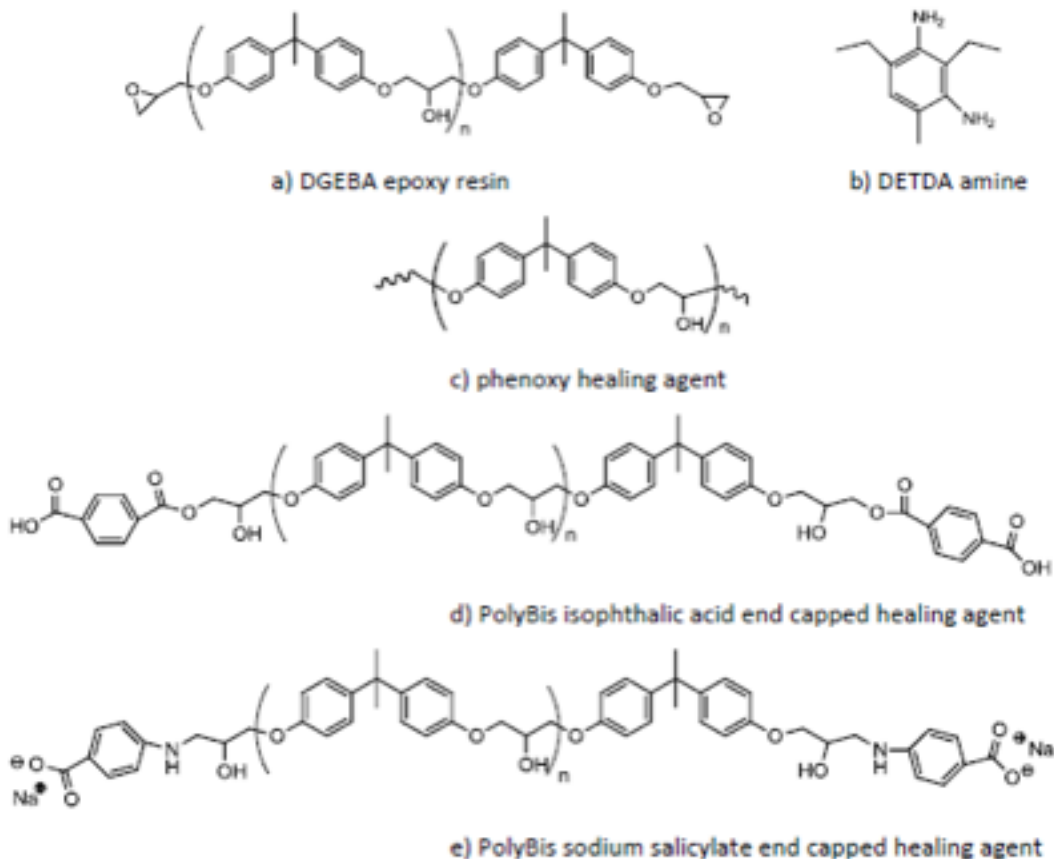

Figure 1.Structures of the components of matrix 2 and healing agents : a) DGEBA Epoxy resin -glycidyl end-capped poly(Bisphenol A-co-epichlorohydrin) where n = ~0.17 b) Matrix 2 hardener-diethyl toluene diamine (DTEDA). Healing agents used are a) glycidyl end-capped poly(bisphenol A- co-epichlorohydrin) with Mn 6100 or 4000 g/mol (DGEBA 6100/ 4000), c) phenoxy polymer d) isophthalic end capped poly(bisphenol A-co-epichlorohydrin) (Mn 6100) and e) sodium salicylate end capped poly(Bisphenol A-co-epichlorohydrin) (Mn 6100 and 4000).

The structures of the epoxy resin and amine hardener for matrix 2 and the commercial linear polymer are shown in Figure 1. The HAs were dissolved in the epoxy resin blends in the absence of the hardener at temperatures up to 130°C. The concentration of HA employed was 7.5% as identified elsewhere [2-4]. The end-capped low Mn DGEBA 4000 and 6100 g mol^{-1} were used at concentrations of 7.0%.

2.3. Healing Assessment

Healing was evaluated using the single end notched beam (SENB) test. Samples were prepared according to ASTM D5045 and a pre-crack was made using a light tap from a hammer with a razor blade in the notch, while the specimen was supported in a jig. A three point bend fixture, with a span of 35 mm was used to measure the failure load. Healing was accomplished by placing the fractured specimen in jig to ensure intimate and aligned contact between the fracture surfaces.

For matrix 1, the heal temperature adopted was equal to the Tg, thus healing took place at 200°C for 3 hours in a preheated oven, with cooling within the oven. The healing efficiency is presented as an average of the percentage recovery of the load to fracture of the virgin coupon. 18 specimens were tested in most cases. Specimens with clear evidence of misalignment after healing were not included in the analysis.

For matrix 2, a Tg of the unmodified resin was 168°C so a healing schedule of 2 hours at 185°C was chosen. Near IR spectroscopy could not detect additional cure during healing [6]. Healing efficiency was determined from the recovery in the load to fracture and no attempt to determine fracture toughness was made because the crack length after healing cannot be determined, as discussed by Brown [7].

3. Results and Discussion

3.1. Matrix 1

Fig.2 shows the efficiency of healing of the various healing agents in Matrix 1. The healing is reported as fraction of the original SENB load to fracture. For each system the results are the average of ≈18 tests. Occasionally misalignment of the crack faces occurred in the jig during healing and these specimens were omitted from the analysis. The most striking result is the healing efficiency of the resin containing the Phenoxy HAs. The PKHP 200 grade enabled the healing efficiency to reach a plateau ≈ 40% after 8 healing events. Taking into account The PKFE grade continued to be healable at a level of ≈ 30%. The HA used in the original research [1] DGEBA 1 and 2 also behaved similarly to Phenoxy PKFE, achieving continual healing capability of approx. 30%. We know from previous research [4,5] that phase separation of the HA is responsible for the reduction in healing efficiency above 7.5% loading so the difference in healing efficiencies of these HAs with nominally identical molecular structure can be attributed to the same effect. Phenoxy PKFE has Mn =16000 and Mw = 60,000 g mol^{-1} while PKHP 200 has Mn and Mw = 1300 and 52,000 g mol^{-1} respectively. As a result, it is more likely that the former will phase separate at a lower concentration than the latter which explains the healing efficacy of the Phenoxy PKFE. The PKHP 200 grade is a powder grade enabling dissolution into the resin blend to be more efficient.
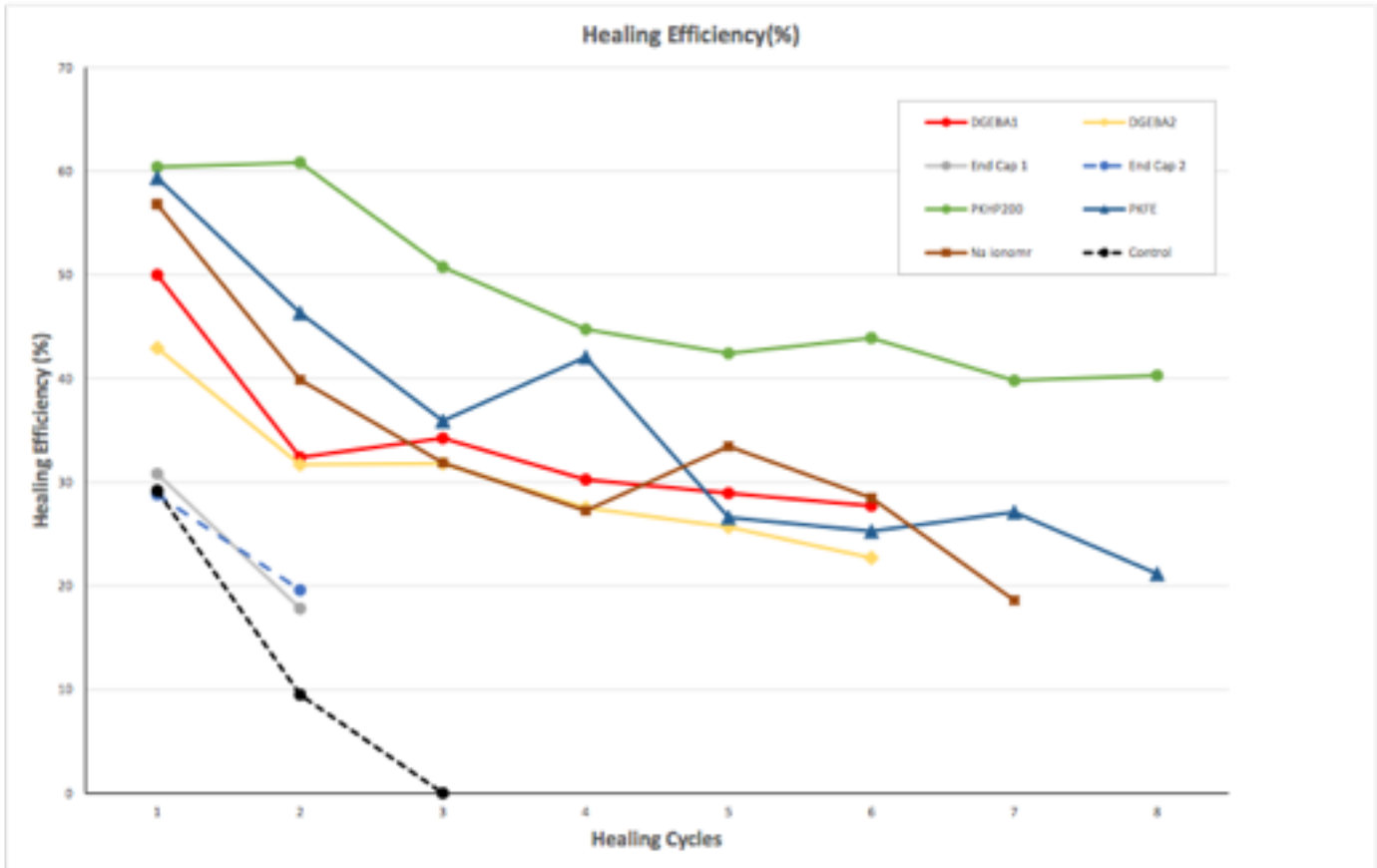
Figure 2. The healing efficiency of a simulated aerospace epoxy resin (Matrix 1) containing 7%w/w of non-reactive end-capped DGEBA 6100 (End Cap 1) and DGEBA 4000 (End Cap 2). 7.5% DGEBA 1and 2 (MW 44,000), PKHP 200, PKFE and Na ionomer (Na DGEBA(4000))

The two benzoate end-capped (to remove reactivity) low Mn (DGEBA 4000 and DGEBA 6100) HAs had similar healing efficiencies to the control, without dissolved HA. Any healing, therefore could be attributed to a post-curing effect. Thus healing during 3rd and higher cycles can be attributed to the diffusion of the soluble, linear polymer molecules to the fracture surfaces. Entanglement theory can explain the need for high molecular weight HAs.

This hypothesis is confirmed by the healing efficiency achieved with the Na ionomer system (Na DGEBA(4000)). By end-capping the DGEBA 4000 with a self assembling group: 4-amino-salicylic acid sodium salt was reacted with glycidyl groups on DGEBA 4000 in the melt, in vacuo, at 130°C for 5 mins, to provide Na^+ carboxylate end-group. It is assumed that the formation of the ionomer occurs in the cured resin. The healing efficiency of the resin containing 7.5 % NaDGEBA(4000) was similar to that of the DGEBA 1 and 2 and PKFE. This can be understood by the hypothesis that self assembly through ionomer formation to provide the HA with a higher molecular weight. It is also possible that the diffusing moiety, during healing cycles, is of 'low' MW and self assembles on cooling. To study this in more detail, further experiments used Matrix 2.

3.2. Matrix 2

Initially the thermal healability of Matrix 2 was examined by examining the efficacy of the Phenoxy PKHP 200 HA. Fig. 3 shows that the recovered load to fracture for a series of healed coupons. In this system and at these concentrations we have not calculated a healing
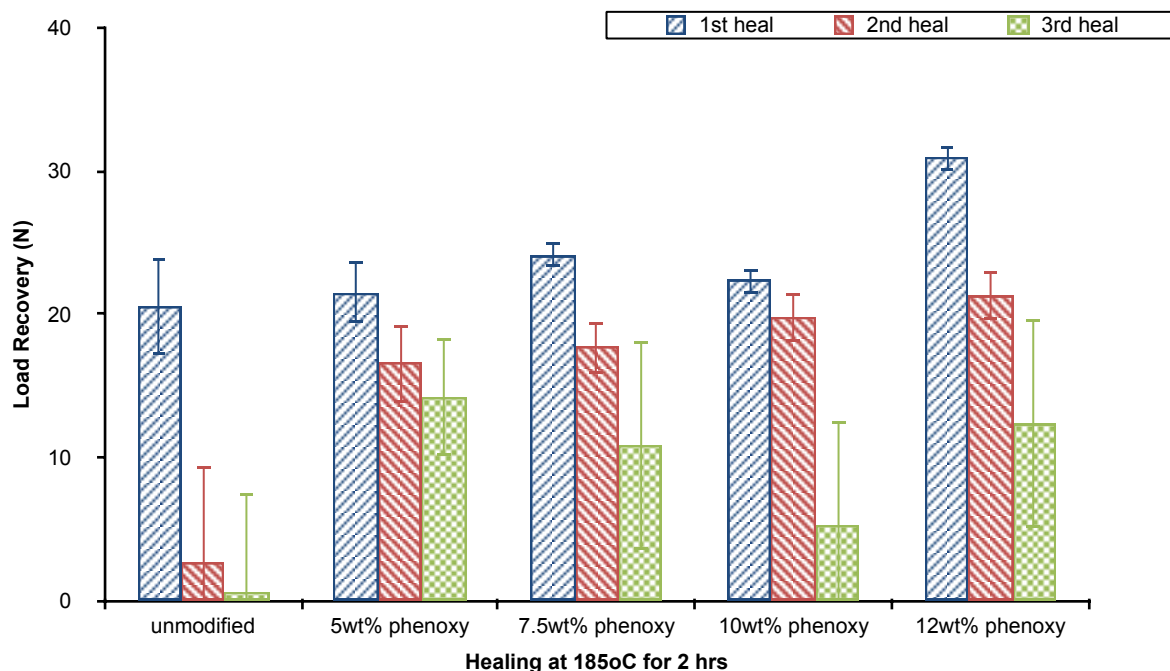

Figure 3. Load recovery after healing as a function of healing event for the Phenoxy PKHP-200 (Mn= 13000, Mw= 52,000 g mol^{-1}) thermoplastic at various concentrations in Matrix 2.

efficiency because of the toughness introduced by the presence of the linear phenoxy polymer complicates the interpretation of the data. For comparison with data for Matrix 1, we estimate that the unmodified coupon exhibited healing efficiency of 13% in cycle 2 and 2% in cycle 3, which compares with the control for Matrix (Fig. 2). With 7.5% HA we see healing efficiencies of 70% and 40% after similar healing cycles. These healing efficiencies compare favourably with those for matrix 1 containing 7.5% HA. Figure 4. shows the efficiency of healing of Matrix 2 with the ionomer HA. After the first healing event, the Na DGEBA(4000) ionomer system exhibited a 40% and 70% increase in healing compared with the unmodified network.

Table 1 shows additional results for isophthalic acid end capped HA. The isophthalic and mixture of sodium and isophthalic end-capped modified DGEBA also exhibited a similar load recovery to the Na DGEBA(4000) modified epoxy network. These latter results also support the mechanism of in-situ self assembly of the modifiers into a linear polymeric healing agent with effective molecular weight . It is suggested that dimerisation of the carboxylic acid

groups via hydrogen bonding may provide a similar self-assembling effect to the ionomer end-capped DGEBA. We can conclude that reversible association of ionomer type healing agents is a mechanism worth further study to improve the healing efficiency of epoxies used for composite matrices.

Table 1. Load recovery (N) after healing as a function of healing event at 185°C for the isophthalic end capped DGEBA 6100 HA and DGEBA4000 Na HA.

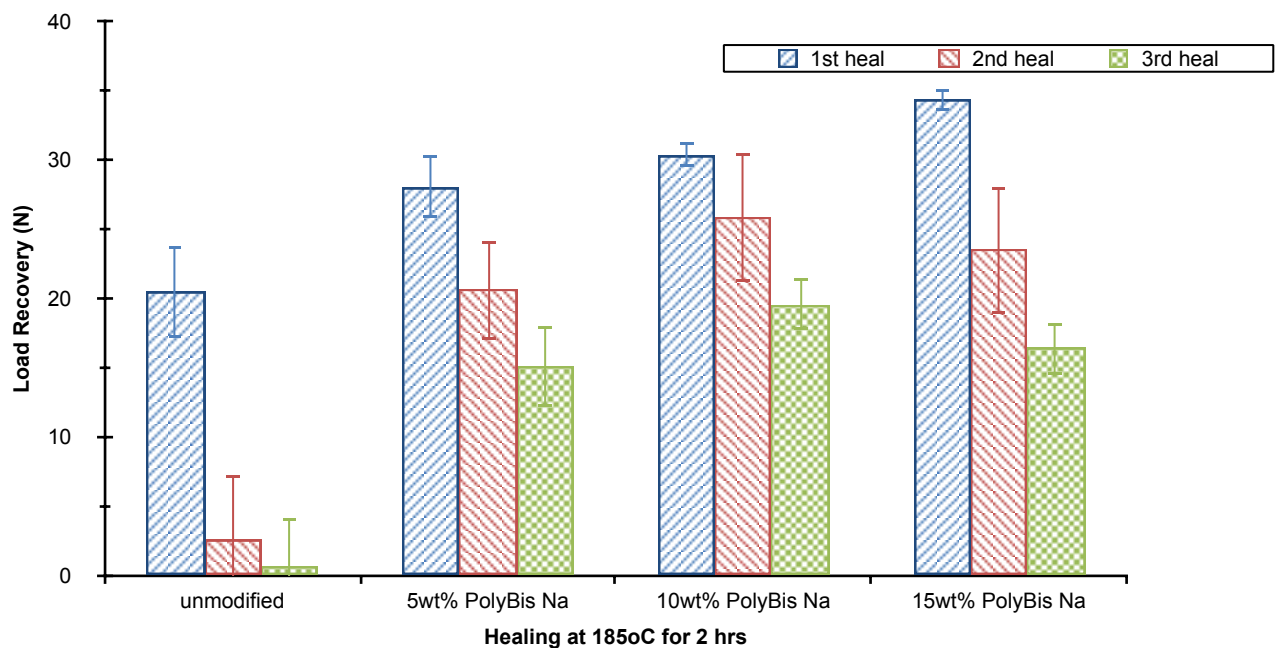| Healing Agent	End Cap	Heal 1 (N)	Heal 2 (N)	Heal 3 (N)
None		20.5 ± 3	2.5 ± 2.	0.6 ± 0.8
DGEBA 6100	Na salicylate	30 ± 3.5	26 ± 3	20 ± 2
DGEBA 6100	Na salicylate/ isophthalic acid	25 ± 6	22±2	17±2
DGEBA 6100	isophthalic acid	30 ± 5	23 ± 3	18.5 ± 2
DGEBA 4000	Na salicylate	28 ± 5	22 ± 5	17 ± 3

Figure 4. Load recovery after healing as a function of healing event for the sodium carboxylate reactively terminated poly(bisphenol A-co-epichlorohydrin) ((Na DGEBA (6100)/ PolyBis Na) at various concentrations.

4.Conclusions

In this study we have shown how thermally mendable solid-state epoxy resin can be synthesised. The polymeric solid state healing agent needs to have an optimum molecular weight yet remain in solution. In order to ensure that the viscosity of the resin can be maintained at a low value suitable for RIM processing, healing agents with low molecular weight which can self assemble in the cured resin when healing is required. Self-assembly of the ionomer end-capped DGEBA into an effective linear polymeric healing agent was demonstrated. Ionomers are known to be thermally reversible so this observation shows that it is now practical to prepare mendable composites by direct impregnation.

5. Acknowledgements

6. References

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