Lap shear strength and healing capability of self-healing adhesive containing epoxy/mercaptan microcapsules

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Lap Shear Strength and Healing Capability of Self-Healing Adhesive Containing Epoxy/Mercaptan Microcapsules

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Abstract. The aim of this work is to develop a self-healing polymeric adhesive formulation with epoxy/mercaptan microcapsules. Epoxy/mercaptan microcapsules were dispersed into a commercialize two-part epoxy adhesive for developing self-healing epoxy adhesive. The influence of different content of microcapsules on the shear strength and healing capability of epoxy adhesive were investigated using single-lap-joints with average thickness of adhesive layer of about 180 μm. This self-healing adhesive was used in bonding of 5000 series aluminum alloys adherents after mechanical and alkaline cleaning surface treatment. The adhesion strength was measured and presented as function of microcapsules loading. The results indicated that the virgin lap shear strength was increased by about 26% with addition of 3 wt% of self-healing microcapsules. 12% to 28% recovery of the shear strength is achieved after self-healing depending on the microcapsules content. Scanning electron microscopy was used to study fracture surface of the joints. The self-healing adhesives exhibit recovery of both cohesion and adhesion properties with room temperature healing.

Keywords: Polymeric Adhesive, Self-Healing, Epoxy, Lap Shear Strength

INTRODUCTION

The concept of self-healing of materials with encapsulated healing agents composed of both healing resin and curing catalyst was proposed more than half a century ago. However, it did not evolve into a viable method because of a very limited "no-curing" lifetime, until recently when researchers developed techniques to encapsulate or graft the healing resin and curing catalyst independently. In the early 2000s researchers from University of Illinois at Urbana-Champaign USA developed a bio-inspired material with the ability to automatically heal cracks, which can be seen as an engineering solution to address engineering materials failures [1]. This material was design with the idea of repairing damage autonomously whenever it happens and the material subsequently recovers its load bearing ability [2, 3]. Over the past years, many studies on self-healing polymers with different self-healing mechanisms had been reported [4-6], but very little have addressed its application and performance as adhesives [7, 8].

Two-part epoxy adhesives have been widely used in engineering applications due to their superior properties such as high modulus and strength. Though, despite these advantages, pure epoxy resins when crosslinked are fairly brittle which make them susceptible to crack initiation and propagation.

Jin et al. [8] discussed the possibility of embedding microcapsules containing microencapsulated dicyclopentadiene (DCPD) monomer, into epoxy adhesives. When micro cracking happens, the microcapsules break to release its core content that polymerizes with the catalyst, this subsequently seals the crack and arrest crack propagation. Measurement of mode-I fracture toughness using width-tapered double cantilever beam (WTDCB) was done to quantify fracture toughness and fatigue of the adhesive. It was observed that at room temperature healing of the adhesive can restore more than a half of its fracture toughness.

Single lap shear joint (SLSJ) is very simple to prepare, cost-effective and practical and it is commonly used in automotive and aerospace industry [9, 10]. Despite the fact that self-healing has been successfully obtained for bulk polymers, very little work data has been published on self-healing of polymeric adhesive. Therefore, it is interesting to study the joints involving these materials to further its application as adhesive.

In the present work, we demonstrated self-healing in thin layer epoxy adhesive when incorporated with epoxy/mercaptan microcapsules. The effect of microcapsules loading on the lap shear strength and the recovery of the lap shear strength of the adhesive was studied at room temperature after complete fracture.

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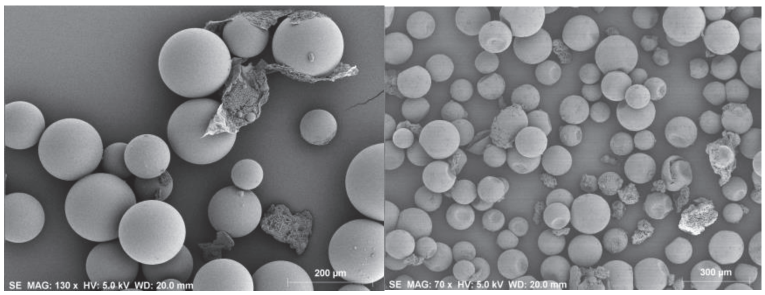
EXPERIMENTAL

Microencapsulation of two-component self-healing system

For a two-component self-healing system used in this study, a diglycidyl ether of Bisphenol A (Araldite-F (Ciba-Geigy, Australia)) epoxy resin was employed as a polymerizable component of the healing agent. Pentaerythritol tetrakis(3-mercaptopropionate) obtained from Sigma Aldrich was used as a hardener for the epoxy for curing at room temperature. Both epoxy and its hardener were encapsulated independently in melamine-formaldehyde according to a method describe elsewhere [11, 12]. The average diameter is 110 µm for epoxy-loaded microcapsules whilst 120 µm for mercaptan-loaded microcapsules. Geometry and surface feature of the shell for both microcapsules are shown in Figure 1.



(a) (b)

FIGURE 1. Geometry and size of microcapsules (a) epoxy-loaded microcapsules, (b) hardener-loaded microcapsules

Preparation of Self-Healing Adhesive

The adhesive used in this study is a commercially available epoxy adhesive supply by Sulley DuluxGroup (Australia). This adhesive cures at a room temperature and consists of two parts (A and B) with chemical entity and composition listed in Table 1. Epoxy/Mercaptan microcapsules and Part A (epoxy resin) of the adhesive were mixed in a glass flask. Since the epoxy resin is very viscous at room temperature, it was heated to 60°C to ensure better miscibility with the microcapsules. In order to disperse microcapsules in the epoxy resin, the mixture was sonicated for 13 min at 60°C in an ultrasonic bath at 35 kHz. After ultrasonication, the mixture was placed in a vacuum chamber to remove bubbles trapped in the mixture. Finally, part B of the adhesive with mixing ratio 1:1 was added to the mixture with stirring to ensure homogeneity. After curing, the adhesive was maintained at room temperature for at least 48 h before testing. Scanning electron microscopy was used to analyze the fracture surface of the adhesive.

Lap Shear Strength Test

Aluminum plate 5000 series adherents were cut and used in all joints tested. Adherents' surface were manually abraded with emery paper (320 grade), cleaned and degreased with acetone. The adherents will then undergoes alkaline cleaning by immersion in 100 g/l NaOH solution, at 60 °C for 1 min, and rinsed in tap water [13].

After surface treatment, aluminum pieces were assembled into single-lap shear joints according to ASTM D 1002, as shown in Figure 2(a), with the recommended length of overlap of 12.70 ± 0.25 mm (as shown in Figure 2b). The applied contact pressure was controlled, which allows obtaining adhesive joints with the same uniform adhesive thickness. The thickness was measured with help of optical microscopy as shown in Figure 2(c). Single lap shear tests were performed at room temperature using the universal tensile machine Instron 3366 with a 10kN load cell. The crosshead speed was 1.3 mm/min. At least 5 samples were tested as a function of microcapsules content in the adhesive. Load and displacement data were recorded and the peak load at failure was recorded, and the apparent shear rupture strength was calculated by dividing the peak load by the ovelapping area. The fracture surfaces were analysed visually to determine the percentage of cohesive failure. For self-healing, the broken specimens were reattached using metal clamp and kept at room temperature. After 24 hours of healing time, the specimens were retested following to the same conditions mentioned above for the original specimens.

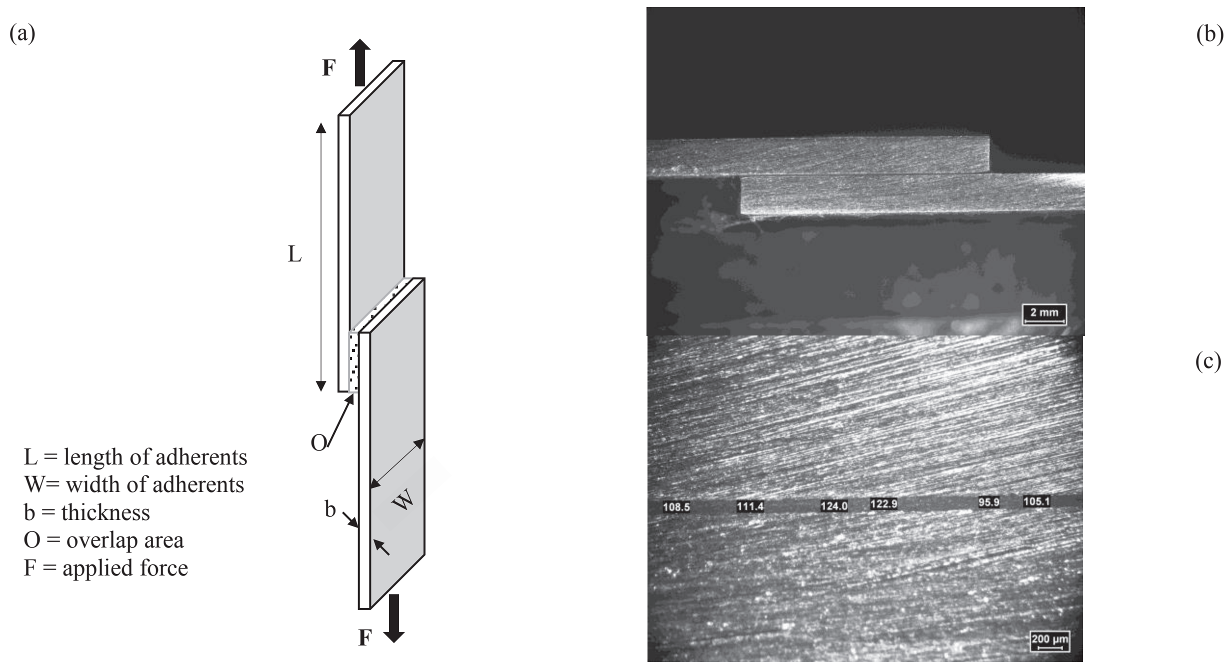


FIGURE 2. (a) Geometry and dimension of lap shear joints (b) adherents with overlap of 12.70 mm and (c) optical microscopy images showing adhesive thickness

TABLE 1. Composition of two-part epoxy adhesive

Part A	Proportion
Bisphenol A-Epichlorhydrin reaction product	>60%
Bisphenol F epoxy resin	10-30%
Ingredient determined to be non-hazardous	Balance
Part B	
Dimethylaminopropyl-1, 3-propylenediamine	1-10%
Triethylenetetramine	1-10%
Ingredient determined to be non-hazardous	Balance

RESULTS AND DISCUSSION

Original Lap Shear Strength of Self-Healing Adhesive

The typical curves of load vs. displacement of the tensile lap shear tests of the adhesive joints with the neat adhesive (0%) as well as the adhesives containing 3 wt%, 5 wt% and 10wt% of self-healing microcapsules are shown in Fig. 3 (a). The tensile lap shear strength of these adhesives with respect to microcapsules content is shown in Fig. 3 (b) with scattering bars defined by the standard deviation. The lap shear strength of the neat epoxy adhesive is 11.31 MPa. Addition of microcapsules into the adhesive shows an increment of the lap shear strength. However it is noticeable that the adhesive with 3 wt% of microcapsules content shows the maximum lap shear strength of about 14.26 MPa, which is about 26% higher than that of the neat adhesive. The shear strength of the adhesives containing 5% and 10% microcapsules is lower than that with 3% microcapsules. The similar trend is observed for the failure strain values, suggesting that the further increase of microcapsules content did not increase the lap shear strength much though the average strength values are still higher than the neat adhesive.

This result showed that the lap-shear strength depended on the content of microcapsules in adhesive. This tendency was often seen on epoxy adhesives with either nano- or microphase soft inclusions such as rubber particles that increase the ductility of the adhesive [14, 15]. Brittleness in general decreases mechanical properties of materials, including lap shear strength. The addition of microcapsules produces a ductile adhesive promoting matrix deformation, which is better in absorbing energy than a brittle matrix [15, 16]. Figure 4 shows the fracture surface of the self-healing adhesive after the lap shear strength test. In contrast to smooth clean fracture of neat epoxy adhesive, the self-healing adhesive fracture reveals side cracks, increasing the resistance to main crack propagation, which gives the reason for better shear strength.

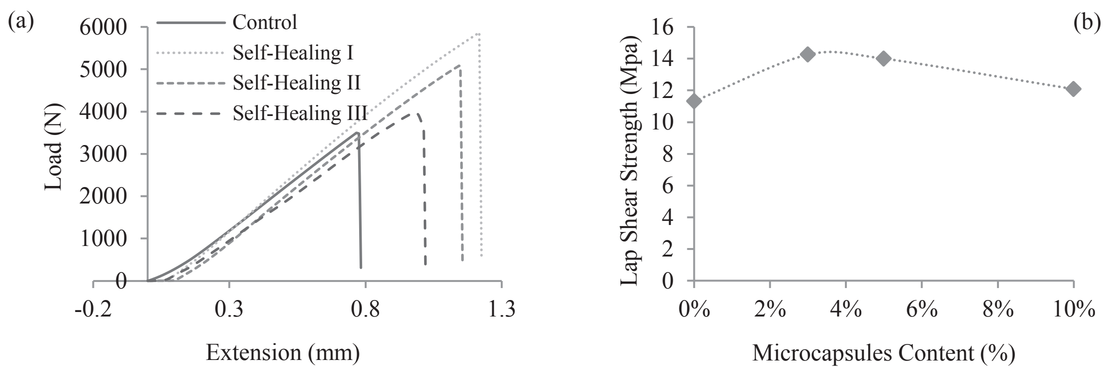


FIGURE 3. (a) Typical stress vs. displacement curves of single lap shear joint of neat epoxy and epoxy adhesive containing self-healing microcapsules (b) Lap shear strength of self-healing adhesives with respect to microcapsules content

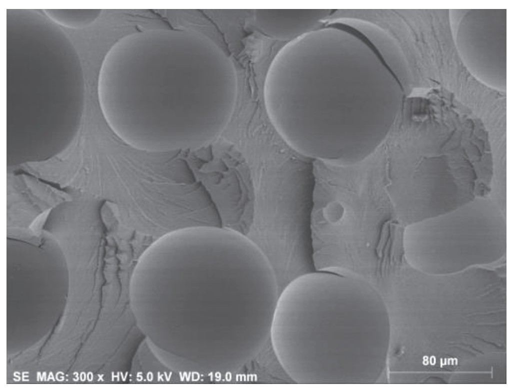


FIGURE 4: Fracture plane of adhesive containing microcapsules

TABLE 2. Healing ability of adhesive

Sample Type	No. Of Specimen	Microcapsules wt fraction (%)	Average original Shear Strength (MPa)	Average Healed Shear Strength	Percent Shear Strength Recovered (%)	Healing Condition
Control	5	0	11.32 (0.91)	-	-	
Self-Healing I	7	3	14.25 (2.15)	1.63 (0.88)	11.60 (6.03)	24 hours at room temperature
Self-Healing II	7	5	14.00 (1.95)	2.82 (0.69)	20.37 (5.08)	
Self-Healing III	5	10	12.08 (1.69)	3.35 (1.12)	28.12 (9.48)	

Self-Healing Capability of Epoxy Adhesive

Self-healing capability of the adhesives in this study was quantified by recovery of its shear strength. Table 2 shows the summary of the self-healing ability of the adhesives with different amount of healing capsules. The self-healing adhesive containing 10% microcapsules shows the highest healing ability with an average value of 28.12%, which is directly related to the amount of healant contained in the adhesive. From the results it can be concluded that the healing ability of the adhesive is strongly influence by the amount of healant embedded into the adhesive with the lowest healing ability obtained for the adhesive containing the smallest amount of microcapsules.

CONCLUSIONS

The self-healing adhesive containing two-component healing capsules with epoxy and mercaptan as its hardener has been developed. The effect of microcapsule content on the lap shear strength and healing ability has been studied. Several conclusions can be drawn from the finding:

1. Incorporation of microcapsules into the epoxy adhesive has increased its original lap shear strength with 3% microcapsules content showing the optimum result with an increment of 26% as compared to that of neat epoxy adhesive.
2. Incorporation of epoxy/mercaptan microcapsules into the epoxy adhesive shows a recovery as high as 28% of its original lap shear strength after complete fracture.

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REFERENCES

1. S. R. White *et.al*., Nature 409 (6822), 794-797 (2001).
2. E. N. Brown *et. al*, Experimental Mechanics 42 (4), 372-379 (2002).
3. L. Yao *et.al*., Polymer 52 (14), 3137-3145 (2011).
4. X. Luo *et.al*., ACS Applied Materials & Interfaces 1 (3), 612-620 (2009).
5. R. S. Trask *et.al*., Journal of The Royal Society Interface 4 (13), 363-371 (2007).
6. T. Yin *et.al*., Composites Science and Technology 67 (2), 201-212 (2007).
7. H. Jin *et.al*., International Journal of Adhesion and Adhesives 44 (0), 157-165 (2013).
8. H. Jin *et.al*., Polymer 52 (7), 1628-1634 (2011).
9. L. D. R. Grant *et.al*., International Journal of Adhesion and Adhesives 29 (4), 405-413 (2009).
10. K. Naito *et.al*., International Journal of Adhesion and Adhesives 36, 77-85 (2012).
11. Y. C. Yuan *et.al*., Macromolecules 41 (14), 5197-5202 (2008).
12. Y. C. Yuan *et.al*., Polymer 50 (24), 5771-5781 (2009).
13. S. G. Prolongo and A. Ureña, International Journal of Adhesion and Adhesives 29 (1), 23-31 (2009).
14. A. J. Kinloch *et.al*., The Journal of Adhesion 79 (8-9), 867-873 (2003).
15. Q. Meng *et.al*., Journal of Materials Research 29 (05), 665-674 (2014).
16. Y. Kwon and Y. Choe, Molecular Crystals and Liquid Crystals 598 (1), 47-53 (2014).