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Effect of epoxy resin and hardener containing microcapsules on healing efficiency of epoxy adhesive based metal joints

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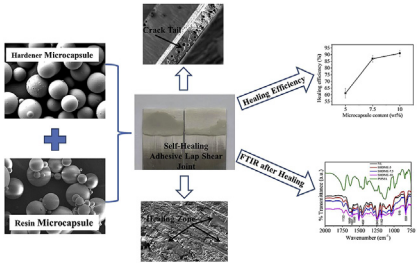
HIGHLIGHTS

- High SDS concentration was used to control the dual component microcapsules shell wall thickness.
- Self-healing performance of dual component microcapsules reinforced epoxy adhesive based single lap joints was studied.
- 90.93% of the damage healing was achieved for self-healing adhesive based single lap joints.
- Increase in concentration of microcapsules reduces the lap shear properties of the self-healing joints.

GRAPHICAL ABSTRACT



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ABSTRACT

Dual component microcapsules of epoxy resin and polyamine hardener with polymethyl methacrylate (PMMA) shell were synthesized using a water-oil-water emulsion solvent evaporation method. The high concentration of sodium dodecyl sulfate (SDS) was used to reduce the thickness of shell wall of dual component microcapsules. The dual microcapsules of 1:1 weight ratio were introduced in the epoxy adhesive to study the healing effect. The morphology, chemical structure and thermal characteristics of the microcapsules were characterized by scanning electron microscopy (SEM), Fourier-transform infrared spectroscopy (FTIR) and thermogravimetric analysis (TGA), respectively. The insertion of dual component microcapsules in epoxy matrix reduced the lap shear strength of adhesive joints, which may be attributed to the generation of stress concentration cites because of micron sized capsules. However, the extension and absorbed failure energy of adhesive joints under uniaxial loading increased with the increase of concentration of dual microcapsules. The viscoelastic nature of the dual microcapsules may be responsible for this enhancement. Significant enhancement in the healing efficiency (90.93%) of the joints was achieved for 10 wt% of dual microcapsules. The crack pinning and crack blunting mechanisms at the vicinity of the crack path adjacent to the microcapsules were found responsible for significant enhancement in the healing efficiency of the adhesive joints.

1. Introduction

The use of epoxy adhesives is a field of interest because of its high performance industrial applications such as aerospace and automobile in place of traditional joining processes like

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fasteners, welding, riveting etc. This is primarily due to its capability of joining dissimilar materials and having high strength to low weight ratio, low shrinkage during curing, better stress distribution and low creep ability, high modulus, tensile strength and ease of processing, These features raises the interest of worldwide researchers to scrutinize further use of epoxy adhesives in primary load bearing applications [1–4]. Moreover, the superior damping and noise absorption ability and the corrosion resistant property are the remarkable advantages of adhesive joints [2]. Though, there are lots of advantages of epoxy adhesives but some of major disadvantages are low toughness and poor resistant to crack propagation and thereby, limits its use in various advance applications [1,5,6]. Poor resistance towards crack propagation subsequently leads to the premature failure. Therefore, large efforts have been made to enhance the crack resistance property and toughness of the adhesive lap shear joints by reinforcing it by micron/nano size inorganic or organic and rubber fillers [7–11]. Khoramishad (2014) et al. [8] tried to increase the adhesive toughness by introducing metal particles and fibers. They found diameter and uniform distribution of metal fiber in the matrix were major key challenges to improve the toughness of adhesive lap shear joints. Ameli (2011) et al. [12] studied the crack growth behaviour of two different heat-cured rubber-toughened structural epoxy adhesives. They found that there was a significant relationship amongst the average crack depth, the fracture surface roughness and the fracture surface angle with the critical strain energy release rate. From the literature, it was observed that not a single attempt has been made to increase the toughness and crack resisting properties of the adhesive lap joint by introducing self-healing concept of the crack generated in the epoxy adhesive lap joint. The improvement of self-healing polymeric composite is new paradigm due to their self-healing capability of the internal or externally generated crack. The most important parameter for these composites is the process of encapsulation and type of healing agent filled in microcapsules. Worldwide research is pursued for improving the encapsulation process of several self-healing agents such as dicyclopentadiene, latent curing agent, polydimethylsiloxane, hardener and epoxy system etc. by in-situ polymerization method [13–17]. Brown (2003) et al. [13] prepared self-healing microcapsules containing dicyclopentadiene as core material and poly-(ureaformaldheyde) as shell materials by in-situ polymerization method. They prepared microcapsules with wide size distribution (10–1000 μm) by selecting agitation speed in the range of 200–2000 rpm. However, the number of literature on solvent evaporation technique for the preparation of microcapsules containing self-healing agent is very less. Li (2013) et al. [18,19] synthesized the hardener containing microcapsules with polyvinyl alcohol (PVA) as the emulsifier and epoxy containing microcapsules with sodium dodecyl sulfate (SDS) as the emulsifier.

In this study, epoxy resin and hardener encapsulated dual microcapsules were synthesized by solvent evaporation technique [20] by utilizing high concentration of SDS. A comprehensive characterization of the synthesized dual microcapsules has been carried out to evaluate its chemical and physical nature. The synthesized SDS emulsified dual microcapsules were introduced into the epoxy adhesive for the first time to develop adhesive based self-healing joints. The lap shear strength and toughness of single lap joints were determined. The healing ability of the composite adhesive reinforced with self-healing dual microcapsules was determined from the fracture load of the healed and virgin specimens. The mechanisms responsible for healing of adhesive joints were studied subsequently.

2. Experimental procedure

2.1. Materials

Diglycidyl ether of bisphenol A (Lapox L12) based epoxy resin (density: 1.20 g/cc) and Triethylenetetramine, (TETA, K6) based hardener (density: 0.95 g/cc) supplied from Atul India Ltd were used as the healing agents. The shell material of microcapsule was Poly (methyl methacrylate) (PMMA), supplied from Sigma–Aldrich, USA. Other ingredients for preparing the microcapsules such as dichloromethane (DCM) and sodium dodecyl sulfate (SDS) were obtained from Sigma–Aldrich, Germany. An epoxy adhesive system, Araldite AW 106 resin/Hardener HV 953U, provided by Huntsman (Los Angeles, California, USA) was used as the base material in this work. Extruded commercial aluminium (ASTM specification SB-209 Grade 1100) sheet provided by Bharat Metal Industries (Mumbai, India) were used for preparation of adhesive based single lap joints.

2.2. Synthesis of hardener and epoxy microcapsules

Synthesis of hardener encapsulated microcapsules (HMC) was performed in two steps. The process is schematically illustrated in Fig. 1. In the first step, a solution containing 4 g TETA and 1 g PMMA in a dispersed phase (dichloromethane) was prepared. In the second step, the resulting solution was added drop-wise to a continuous phase holding 50 ml of 3 wt% of aqueous SDS solution. Then, the mixture was agitated at a speed of 500 rpm with the help of a mechanical stirrer for 30 min under ambient conditions in order to obtain an oil/water emulsion. Consequently, the resultant mixture was poured into 150 ml of an aqueous SDS solution under continues agitation. The dispersed phase was evaporated at 40 °C to obtain hardener encapsulated PMMA microcapsules. The HMC were washed several times by double distilled water and dried at room temperature for 24 h. Similar procedure was adopted for the synthesis of epoxy resin encapsulated microcapsules (RMC) initially by taking 2 g epoxy resin and 1 g PMMA. The continuous phase in this case was 50 ml of 6 wt% of aqueous SDS solution. The oil water emulsion was prepared by pouring the mixture of DGEBA, PMMA and SDS solution into a 150 ml solution of aqueous SDS under constant agitation speed of 500 rpm. However, previously reported results of others showed the formation of non-agglomerated microcapsules at lower concentration of SDS [12]. But in this study, the high concentration of SDS is found very effective for synthesis of non-agglomerated resin encapsulated microcapsules. The RMC were also washed several times by double distilled water and dried at room temperature for 24 h.

2.3. Preparation of self-healing epoxy adhesives

For the preparation of dual component microcapsules induced epoxy (DME) adhesives, the HMC and RMC were mixed in accordance with the stoichiometric ratio of 1:1 by weight. Li (2013) et al. [18] showed the optimized HMC and RMC weight ratio for maximum healing efficiency for self-healing composites. The resulting mixture of HMC and RCM was added at varying concentration of 5, 7.5 and 10 wt% respectively to the epoxy adhesive followed by mechanical stirring for 10 min at 1200 rpm to achieve homogeneous distribution of microcapsules into the epoxy resin. Then, a stoichiometric amount of hardener (80% by weight of epoxy resin) was added to the self-healing dual microcapsule containing epoxy resin followed by mechanical stirring for 5 min at 1200 rpm. Afterward, the entire mixture was kept under high vacuum at ambient temperature for 30 min to remove the entrapped air bubbles. After degassing, some portion of the mixture was poured