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Effect of carbon nano-filler addition on the degradation of epoxy adhesive joints subjected to hygrothermal aging

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ABSTRACT

In this study, the effect of hygrothermal aging on the strength of pure and carbon nano-filler reinforced epoxy adhesive joints is presented. Epoxy adhesives containing three different carbon nano-fillers, namely, multi-walled carbon nanotubes (CNT), graphene nanoplatelets (GNP) and single walled carbon nanohorns (CNH) were prepared by using a high shear rate mixer. Thermogravimetric analysis (TGA) of the nano-filler reinforced epoxy indicated an improvement in the thermal stability compared to pure epoxy. Aging studies were carried out on single lap-shear specimens as per EN ISO 9142:2003 standard (cycle D3). The strength of the joints was found to decrease with hygrothermal aging time. The nano-filler reinforced joints showed less reduction in joint strength with aging compared to pure epoxy joints. The GNP/epoxy joints showed the best resistance to aging followed by CNT and CNH reinforced joints. Fourier Attenuated Total Reflectance Transformation Infrared Spectroscopy (ATR-FTIR) analysis of the hygrothermal aged samples indicated lower degradation in terms of hydrolysis of epoxy groups for nano-filler reinforced epoxy. Gravimetric analysis of samples immersed in water showed lower weight gain for nano-filler reinforced epoxy composites. Fracture surface analysis was carried out to study the change in failure mechanism with aging time.

1. Introduction

Adhesive bonding technology has become popular in recent years due to the capability of joining various types of materials (metals, ceramics, polymers, composites etc.) [1]. Adhesive bonding is an alternative method to conventional methods such as mechanical fastening (bolts, screws, and rivets), welding and soldering [2]. The application of adhesive bonding is mainly in automotive, aerospace [3],and electronic packaging applications [4]due to low specific weight and uniform strength throughout the joint [5]. Epoxy resins are the most widely used adhesives for joining different materials in aerospace and advanced automotive applications due to their excellent adhesionproperty along with a combination of mechanical properties and corrosion resistance [3,6,7]. Many investigations have focused on further improving the properties of the epoxy adhesive by use of nano-filler. It has been shown that the cohesive strength and bond strength of the epoxy systems can be significantly improved by using different nano-filler such as carbon nanotubes (CNT), nano-SiO_2, nano-Al_2O_3, and nano-$CaCO_3$ [8–14]. The large surface area (up to 200 $m^2\ g^{-1}$) and the high elastic modulus (300–1500 GPa) of these nano-filler result in significant increase in the strength of epoxy adhesive joints. However, the bond strength and durability of the adhesively bonded joints has been one of the major concerns due to the poor cohesive strength and poor adhesion of epoxy under humid conditions [15,16]. Long term hygrothermal aging is known to result in irreversible damage of epoxy system due to the vulnerability of the polymer to hydrolysis, oxidation, and change of the effective average cross-linked molecular weight [17,18]. Thus, the absorbed moisture has unfavorable effects on the physical properties of epoxies, which greatly affects the performance of epoxy adhesives [19,20]. It is well known that the glass transition temperature (T_g) is related to the cross-link density; a higher cross-link density leads to higher T_g [21–23]. There are few reports which show that T_g decreases for the epoxy system after hygrothermal aging conditions due to the decrease in cross-link density [17,24,25]. Apicella et al. [26] have proposed that the moisture absorption by polymer produces irreversible damage in the form of microcavities. These

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microcavities would result in loss of cohesive strength of the polymer [27,28]. The effect of moisture on the mechanical properties (tensile strength, elastic modulus, etc.) of the epoxy system under hygrothermal aging has also been reported [29–32]. It is observed that the elastic modulus and the tensile strength were reduced due to the reduced physical properties of epoxy system after hygrothermal aging.

In engineering applications, adhesive joints are subjected to hygrothermal aging under wet conditions or elevated temperatures or both. Such conditions often lead to the reduction in strength of adhesive joints. Hence, an understanding of hygrothermal ageing effects on the degradation of the strength of adhesive joints is important for the design of adhesively bonded structures. Molitor et al. [15]have reported that the adhesive/polymer interface is much more stable than the equivalent polymeric adhesive/metal interface under hot/humid conditions. The absorption of moisture decreases the mechanical properties of adhesives resulting in the reduction of the joint strength [33]. It is found that the joint strength reduces with aging time and becomes constant after some time [34]. Some researchers have reported that the mode of failure of the adhesive joints changed from cohesive to interfacial failure with the increase in moisture content [35,36].

Attempts have been made on reducing the effect of moisture absorption by incorporating different nano-filler into polymers such as nanoclay [37,38], carbon fibre [39], glass fibre [40], etc. Carbon nanomaterials such as carbon nanotubes (CNT), graphene nanoplatelets (GNP), can be regarded as more efficient fillers for improving properties of the polymers due to their outstanding mechanical, electrical and thermal properties and high specific surface area [41–43]. Single-walled carbon nanohorns (CNH) are recently reported novel materials having a typical diameter of 2 nm and a length of 30–50 nm which have not yet been commercialized. The individual CNH have a tendency to couple together and form stable dahlia flower-like particles with a narrow diameter distribution of 80–100 nm [44]. The presence of nano-filler acts as effective barriers against diffusion of water molecules, thereby reducing the water permeability through the polymer [45]. The nano-sized particles also restrict the movement of the molecular chains surrounding them and retarding the relaxation of polymeric chains [37,38]. These two effects can help in improving the durability of epoxy joints by the addition of nano-filler and this is explored in this work.

In our previous work, we have reported the effect of different carbon nano-filler such as CNT, GNP, and CNH on rheological, thermal stability and lap shear strength of the epoxy adhesive joints. A high energy shear mixer (Brabender® Plasti-Corder®) was used for efficient dispersion of the nano-filler. The results showed that at 0.5 wt% of nano-filler reinforcement, the maximum lap shear strength was achieved with GNP [14]. There are no systematic studies available on the water absorption characteristics of carbon nano-filler reinforced epoxy joints and their effects on the lap shear strength. Thus, the objective of present work was to carry out a detailed study of the effect of standard hygrothermal aging treatment on the joint strength and durability of different carbon nano-filler (CNT, GNP and CNH) reinforced epoxy adhesive joints. The variation of the lap shear strength with aging time is presented for both pure and carbon nano-filler reinforced epoxy adhesive joints. The mechanisms of improved durability of the nano-filler reinforced joints have been also discussed.

2. Experimental

2.1. Materials

A commercially available di-glycidyl ether of bisphenol-A (DGEBA) based two-part epoxy adhesive EP-415 epoxy resin, and EH-400 hardener (Roto polymers and chemicals, Chennai, India) was used in the present study. CNT of diameter 10–20 nm and length 10–30 μm were obtained from Cheaptubes Inc. (Texas, USA). GNP having a thickness of 3–10 nm were purchased from Redex Nano (Ghaziabad, India). The CNH were synthesized in-house by using a DC arc discharge technique. The synthesis of CNH was discussed in our previous report [14].

TEM and SEM images of the CNT, GNP and CNH are shown in Fig. 1. From Fig. 1a shows entangled CNT and Fig. 1b shows stacks of GNP. Spherical morphology of CNH aggregates can be observed in Fig. 1c. These CNH have dahlia flower structure as shown in Fig. 1d. These CNH images are similar to that reported by Iijima et al. [46].

2.2. Preparation of carbon nano-filler epoxy adhesive joints

The epoxy resin and carbon nano-filler were taken in required quantities to prepare 0.5 wt% nano-filler/epoxy adhesives. The components were mixed using a Brabender® Plasti-Corder® at 100 rpm for 15 min. The hardener was then added in the requisite weight ratio (10:4 by weight) and mixed manually for 10 min using a Teflon rod. AA6061 substrates measuring 100 mm × 25.4 mm × 1.1 mm were used to prepare standard lap shear specimens. The surface was prepared by grit blasting using a grit blasting machine (Sandstorm, SB-9090, Bangalore, India) with F400 aluminum oxide grit under a pressure of 4–5 bar to obtain rough surface and higher surface energy. After grit blasting, the substrates were ultrasonically cleaned for 15 min in acetone followed by drying. The lap shear joints were prepared as per the ASTM D1002 standard with 25.4 mm × 12.5 mm bond area. A bond line thickness of 0.2 mm was maintained using a spacer. After preparation of the single lap joints, samples were cured at 60 °C for 2 h.

2.3. Thermogravimetric analysis (TGA)

The thermal stability of the cured pure and carbon nano-filler reinforced epoxy composites were studied using a thermogravimetric analyzer (TGA, SDT Q600). The composites were heated to 800 °C at a heating rate of 10 °C/min under nitrogen atmosphere. The percentage of weight loss as a function of temperature was studied and the onset of degradation temperatures were compared.

2.4. Hygrothermal aging and testing of lap shear adhesive joints

The temperature and humidity cycle for aging studies of adhesive bonded samples was selected as per EN ISO 9142:2003 standard and vary as shown in Fig. 2. Each cycle has a duration of 24 h. A controlled climate test chamber (Memmert CTC 256, Germany) was used for carrying out the aging treatment of adhesive joints. For each type of the joints, five specimens were taken out from the environmental test chamber for the evaluation of lap shear strength after every two weeks of exposure for a total time of 12 weeks. Samples were conditioned at 27 °C for one day to achieve a thermal balance as well as humidity balance before mechanical testing. Lap shear tests were conducted using a tensile testing machine (Instron 3367, 30 kN). The specimens were tested at 1.27 mm/min crosshead displacement as per the ASTM D1002 standard. The epoxy adhesive joints containing 0.5 wt % of CNT, GNP and CNH were named as EP-CNT, EP-GNP and EP-CNH respectively.

2.5. Water absorption studies

Water absorption studies were carried out for both the pure and