



Nanofilled epoxy adhesive for structural aeronautic materials



U. Vietri^{a,*}, L. Guadagno^a, M. Raimondo^a, L. Vertuccio^a, K. Lafdi^b

^a Department of Industrial Engineering – DIIN, University of Salerno, Via Giovanni Paolo II, 132, 84084 Fisciano, SA, Italy

^b University of Dayton, 300 College Park Dayton, OH 45440, USA

ARTICLE INFO

Article history:

Received 24 June 2013

Received in revised form 16 January 2014

Accepted 20 January 2014

Available online 27 January 2014

Keywords:

Polymer-matrix composites

A. Thermosetting resins

B. Adhesion

B. Mechanical properties

ABSTRACT

The aim of this work was to develop new adhesive formulations based on epoxy/nanostructured carbon forms. Different types of nanofillers were dispersed into an epoxy matrix for developing toughened epoxy paste aeronautic adhesives. The reinforced adhesives were used for bonding carbon nanofilled/epoxy composite adherents. Data were also compared to the results obtained both for the unfilled adhesive and/or adherents. Tensile butt joint, and single lap joint samples were prepared to measure mechanical strength and adhesion properties of the different joint configurations. The inclusion of carbon nanofillers inside the epoxy adhesive caused a significant improvement in the bond strength of the joints, changing the failure mode of joints in single lap joint shear tests. Significant change of the bonding performance was observed as the weight fraction of carbon nano-fillers increased from 1.37 to 5 wt/wt%. Adhesion between nano-reinforcements and adherents substrate was studied by means of Scanning Electron Microscopy.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

Adhesively bonded joints are increasing alternatives to mechanical joints in engineering applications and provide many advantages over conventional mechanical seal. To join such composite parts, polymer adhesives such as epoxies are commonly used. Using adhesive bonding for joining composite parts provides many advantages such as low cost, high strength to weight ratio, low stress concentration, fewer processing requirements and superior fatigue resistance and environmental resistance [1].

Adhesion between the polymer (composite) surface of adherents and polymeric adhesive substrate is suitably controlled by the chemical groups at or near the interface which lead to a better performance of bonded joint in their application [2]. Several papers have been published on the inclusion of nanostructured carbon forms inside epoxy adhesives in order to enhance the mechanical strength and toughness of the bonded joints [1,3–5]. Yu et al. (2009) studied the mechanical behavior and durability in humid environments of the aluminum joints bonded with an epoxy adhesive reinforced with multi-walled carbon nanotubes (MWCNTs) [3]. Likewise, Hsiao et al. (2003) studied the mechanical strength of epoxy/MWCNT reinforced adhesive to join carbon graphite fiber/epoxy composite adherents [1], while other researcher studied the adhesive properties of nanoreinforced epoxy adhesive

using dissimilar joints composed of carbon fiber/epoxy laminate and aluminum alloy [4]. In any case, the presence of uniformly dispersed CNTs inside the adhesive paste was found to be able to increase bonding strength, Young's modulus as well as ultimate tensile strength of the adhesive. An improvement of CNT's reinforcement on fracture strength for adhesive joints was also observed between steel-composite interfaces and composite-composite interfaces [5]. MWCNTs embedded in the adhesive at a percentage of 1 wt% enhanced fracture toughness for both steel-composite and composite-composite adhesive joints. Adhesive performance of epoxy-based materials was investigated also considering the effects of inorganic nanoparticle inclusions on the adhesive strength of a hybrid sol-gel epoxy system used to joint, either aluminum substrate, and mild steel substrate [6]. The mechanical performance of different formulations was characterized by shear and tensile tests to define the influence of nanofillers on adhesive strength performance of the modified epoxy/hybrid sol-gel. The incorporation of a selected ratio of inorganic nanoparticles in the epoxy/sol-gel adhesive improves the adhesion performance between substrate surfaces. At the same time, it is well known in literature that one of the main predicted advantages related to the inclusion of conductive nanoparticles into epoxy resin is the improvement of its electrical behavior [7–11]. In fact, different types of carbon nanofillers are electrical conductor materials, which well dispersed in the matrix, can drastically increase electrical properties of epoxy based adhesives also using a very low percentage of nanofiller. This property is of special

* Corresponding author. Tel.: +39 089964019; fax: +39 089964057.

E-mail address: uvietri@unisa.it (U. Vietri).

relevance in the joint of electrical conductive substrates and makes adhesive epoxy/nanostructured carbon forms to become a promising new frontier in nanoreinforced adhesive for structural applications. The development of conductive epoxy adhesive to be used in the aeronautic field to join parts of primary structure is a current need with a view to optimizing efficiency of joints while preserving the conductivity of lightweight materials able to provide also in the joints good lightning protection [10,12,13]. The enhancement in different properties of epoxy-based materials and or/adhesives depend on numerous parameters, such as the chemical nature of nanofiller, adhesive and adherents, the applied surface treatment or the tested properties [14–16]. In the present study, we used as fillers heat-treated carbon nanofibers (CNFs) and exfoliated graphite. Heat-treated CNFs (at 2500 °C and 3000 °C) were chosen because they can impart higher conductivity than un-treated CNFs to the epoxy matrix. In particular, different papers dealing with the study on the effect of heat-treatment on CNFs report the beneficial effect on the electrical properties [16–18]; it is also possible to choose the best combination for improving electrical conductivity without to cause a decrease in the mechanical parameters of nanofilled resins [17,19]. In particular, for CNFs heat-treated at 2500 °C, the optimization of these properties were found [17]. The increase in the electrical conductivity consisting in a lower electrical percolation threshold (EPT) and a higher electrical conductivity beyond the EPT, with respect to the resin filled with untreated CNFs, was ascribed to the changes in morphology due to heat treatment (narrowing in the CNF diameter, increase in the length of the CNFs, less tendency to bend, absence of functional groups and then insulating layer on the CNF walls) [19]. Considering that this work is aimed at studying the properties of nanofilled adhesives for aeronautic materials able to hinder the insulating properties of epoxy resins, amount of nanofiller beyond EPT was chosen for all the analyzed nanofillers. In the case of the exfoliated graphite, a higher EPT was found than other nanofillers, then the lower concentration chosen in this paper was 3.7%. In addition, in this work, for the epoxy matrix of unfilled and nanofilled adhesives, a mixture of a tetrafunctional epoxy precursor with a reactive diluent (BDE) was used to facilitate the dispersion step of nanofilled adhesive. This is not a trivial problem especially when a nanofiller must be embedded in a specific resin for industrial applications. In fact, in the choice of the epoxy mixture it is necessary to consider that the structure of the resin strongly governs its chemical and some of the relevant physical properties. The number of reactive sites in the epoxy precursors controls the functionality directly acting on the cross-linking density and this, combined with the nature of hardener agent, the functionality, the stoichiometry and the curing cycle determines the final mechanical and thermal properties. In this case, we used a tetrafunctional epoxy precursor in combination with BDE. While the epoxy precursor is an already established reference material for aeronautic applications, its viscosity may hinder its usage for nanofilled adhesives. This mixture with BDE has never been used before as epoxy matrix for adhesive in aeronautic field.

An interesting aspect of this study is the different approach in preparing adhesive and adherents. In particular, adhesive and adherents were epoxy mixture and or nanofilled epoxy mixture with the same chemical composition in such a way as to obtain chemical interactions inside bonded joints and adherents of the same nature. In addition, a comparison between data detected for unfilled and filled epoxy formulations provided information on the effect of nanofiller into the adhesive formulations. A very relevant result of this work is the role of CNFs heat-treated at 2500 °C in the adhesive properties of the nanofilled formulations. In particular, epoxy formulations at loading rate of 1.3 wt/wt% have shown the best adhesive performance.

2. Experimental procedure

2.1. Materials and preparation

2.1.1. Epoxy resin

The epoxy matrix composite was prepared by mixing an epoxy precursor, tetraglycidyl methylene dianiline (TGMDA) (Epoxy equivalent weight 117–133 g/eq), with an epoxy reactive monomer 1,4-Butandiol diglycidylether (BDE) that acts as reactive diluent.

Epoxy precursor and reactive diluent, both containing an epoxy, were obtained by Sigma–Aldrich. The curing agent investigated for this study is 4,4'-diaminodiphenyl sulfone (DDS). This product was used at stoichiometric concentration with respect to oxirane rings.

2.1.2. Carbon nanofillers

Vapor-grown carbon nanofibers (CNFs) used in this study were produced at Applied Sciences Inc. and were from the Pyrograf III family. The CNFs used in this study are respectively labeled as PR25XTPS2500 and PR24XTHHT where XT indicates the debulked form of the both PR25 and PR24 family, PS indicates the grade produced by pyrolytically stripping the as-produced fiber to remove polyaromatic hydrocarbons from the fiber surface, 2500 is the temperature of the heat-treatment and HHT indicates the grade produced by heat-treating the as-produced carbon nanofiber to 3000 °C.

Exfoliated graphite (EG) is obtained by rapid heating of a graphite intercalation compound (GIC). Exfoliated graphite nanoparticles are composed of stacks of nanosheets that may vary from 4 to 40 nm as resulted from X-ray and SEM investigations.

2.1.3. Curing cycles

Adhesive formulations were cured by a two stage curing cycle: an initial step at moderate temperature (125 °C for 1 h) and the second one at higher temperature (180 °C for 3 h).

2.1.4. Preparation of adherents and adhesive

Tests were carried out on eight series of samples, each one characterized by different combination between adherents and adhesive formulations. The combinations are shown in Table 1. Two different nanofiller percentages were used in preparing the nanofilled formulations (1.3, 3.7 and 5 wt/wt%). These percentages were chosen to significantly improve mechanical behavior, and at same time, electrical conductivity. All the nanofilled adhesives, reached or were just beyond the EPT [9,13].

Epoxy blend (TGMDA and BDE) and DDS were mixed at 120 °C until complete hardener solubilization and then the mixture was cooled to 90 °C. CNFs (samples PR25XTPS2500 and HHT24) and EG (exfoliated graphite) were added and incorporated into the matrix at 90 °C by using an ultrasonication for 20 min. An ultrasonic device, Hielscher model UP200S (200 W, 24 kHz) was used. Such an incorporation method was chosen among other different techniques since it has proven to be very effective for other carbon nanostructured forms leading to the nanofilled resins characterized by the best mechanical and electrical properties [20].

Materials (unfilled and nanofilled epoxy mixture) were cured in two different mold geometry configurations made of Teflon (PTFE). The molds were designed by referring to existing international standard practice in the design of the specimens, in particular ASTM D 2094 and ASTM D 1002 were considered (Fig. 1a and b). In this way, a suitable configuration of specimens for tensile butt joint (referred to ASTM D 2095), and single lap joint (referred to ASTM D 3163) were respectively obtained to measure mechanical strength and adhesion properties in the different joint configurations.

Download English Version:

<https://daneshyari.com/en/article/817699>

Download Persian Version:

<https://daneshyari.com/article/817699>

[Daneshyari.com](https://daneshyari.com)