

An Assessment of Interfacial Chemistry and Character of Fiber/Polymer Microcomposites

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Abstract

The interfacial chemistry and character of hygrothermally treated E-glass/epoxy microcomposite have been investigated by Fourier transform infrared spectroscopy (FTIR-imaging), temperature-modulated differential scanning calorimeter (TMDSC) and scanning electron microscope (SEM) techniques. The physico-chemical interactions occurring between absorbed water molecules and the network of a tetrafunctional epoxy resin were studied by FTIR-imaging. This is used to study the mechanistic details of epoxy curing on the molecular level. Absorbance peaks of OH stretching bands were focused to study the effects of hygrothermal exposure at the interphase of microcomposite by FTIR-imaging. TMDSC is for studying the glass transformation behavior of glasses and for measuring the glass transition temperature (T_g). Failure modes as swelling stress, brittle fracture of fiber, fiber/matrix interfacial debonding, were obtained in SEM fractographic analysis. Scanning electron microscope (SEM) study helped in revealing the phase contrast which might have been developed by the generation of differential straining at different zones of the resin matrix.

Keywords: Glass/epoxy microcomposites, hygrothermal treatment, FTIR-imaging, TMDSC, SEM

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INTRODUCTION

Severe environmental exposure, long-term loading and temperature can have a direct impact on the durability of polymeric composite materials resulting in the degradation of interfacial adhesion [1, 2]. The contemporary view of adhesion results in an interphase model in which not only the actual chemical and physical interactions between fiber and matrix are considered, but also the structure and the properties of both the fiber and the matrix in the region near the interface [3]. By assuming perfect interfacial chemistry and linear stress-strain relationships for the fiber and matrix, a simple rule of mixtures (RoM) can be applied to predict the composite strength and modulus from known properties of the constituents [4]. If the fiber/matrix interface strength is high, it is often referred to as brittle fracture. If the fiber/matrix interface strength is weak, this leads to broom-like failure [5]. The environmental effect of moisture on the polymer matrix composite (PMC) material is of significant

interest, particularly since mechanical and physical property modifications are generally the manifestations of its presence [6]. Moisture penetrates into composite materials by diffusion through the polymer matrix and a network of microchannels formed along the imperfectly bonded polymer-fiber interface [7]. Moisture absorption in polymer composites leads to changes in the thermophysical, mechanical and chemical characteristics of polymer matrix by plasticization and hydrolysis, often referred to broom-like failure [5, 8]. Silane agents are intended to act as a protective coating for glass fiber surface and as a coupling agent to promote the adhesion with the polymer matrix [8]. In epoxy, aromatic groups are often chosen for improved stiffness, thermal stability and higher glass transition temperature (T_g) [9]. A small amount of water causes the fiber/matrix interfacial degradation (lower value of modulus, brittleness) due to (a) water acting as a plasticizer, decrease of T_g (20 °C for every 1% of water absorbed) and

thus enhancing the structural relaxation; (b) stress generated due to swelling stress; (c) chemical degradation; (d) creation of osmotic cracks [10, 11]. In addition, absorbed water molecules forming double hydrogen bonds will cause an increase of T_g , which has been found in epoxy resins [11]. This strong physical interaction can create a region where a larger area of fiber and matrix participates in adhesion process. A larger contact area allows better transfer of load between fiber and matrix and thus maintaining strength [12]. In many cases, failure occurs in the interface region due to chemical reactions or plasticizing, when impurities, commonly water, are present in the interface [13]. However, the constituent that is most sensitive to moisture is the fiber/matrix interface, and, therefore, moisture promotes damage mechanisms that are controlled by the interfacial performance [14]. The effect of increasing moisture is to deteriorate the ILSS value progressively and reduce the maximum operating temperature of the material [15]. To understand the properties of the interface and its role in controlling fracture, it is essential to know the mechanisms of adhesion at the interface involved. To obtain a clear picture of the moisture diffusion process, various techniques have been employed in this field, such as FTIR-imaging, attenuated total reflection (ATR-FTIR), ultraviolet (UV) reflection, solid-state nuclear magnetic resonance (NMR), electrochemical impedance spectroscopy (EIS) and molecular simulations. Several models have been put forward to address the issue of the state of water molecules in epoxies [11, 16]. In the present study, FTIR-imaging and TMDSC techniques were used to assess the interphase of hygrothermally treated glass/epoxy microcomposites. Since the interphase is buried inside the composite material and is nanoscopic in nature, the characterization is complicated.

MATERIALS AND METHODS

Materials

Araldite LY-556, an unmodified epoxy resin based on Bisphenol-A and hardener (Ciba-Geigy, India) HY-951, aliphatic primary amine were used with E-glass fibers (FGP, RP-10) treated with silane-coupling sizing system (Saint-Gobian Vetrotex)

monofilaments to fabricate the micro-composite.

Sample Preparation

The microcomposite is prepared to be more accurately predictable in assessing fiber-polymer interfaces because of less interfacial area. The impact and implications of neighboring interfaces might be deconvoluted in characterizing the presence of limited fiber/matrix interface. The specimens were fabricated using the conventional hand lay-up method. A plane mold was treated with a silicon-based releasing agent for easy removal of glass/epoxy microcomposites. Some amount of epoxy and hardener mixture was poured on the mold and then the single strand of glass fiber slowly placed uniformly on to it. The microcomposite was left for curing without applying any load on it for 24 h. Then the prepared samples were treated in a microprocessor-controlled Brabender climatic chamber for hygrothermal conditionings. The sample was divided into three lots; they were hygrothermally treated for 10 and 60 h at 60 °C and 95% humidity.

FTIR-imaging analysis was performed in FTIR spectrophotometer interfaced with IR microscope operated in reflectance mode.

The TMDSC measurements were performed on a Mettler-Toledo 821 with intracooler, using STAR software with temperature-modulated DSC module. The temperature calibration and determination of the time constant of the instrument were performed by standards of In and Zr, and the heat flow calibration by In. The underlying heating rate of 10 °C min⁻¹, was used. Standard aluminum pans were used. The experiments were performed in the temperature range 25–150 °C.

RESULTS AND DISCUSSION

Water-uptake Kinetics

The positive shift of O-H stretching spectra in the structure of epoxy resin as a result of hygrothermal process at the fiber/matrix interfacial region was monitored by FTIR-imaging. During the diffusion process, water molecules may form H bond with epoxy resin; consequently, some of the water-water H bonds have to be compromised. This reveals the interaction between water molecules and

the carbonyl oxygen in the epoxy matrix and thus a weakening of the water-water H bonding. Besides that, the polar groups at the inner surface of free volume provide the bonding sites for water molecules, while the limited space of nanopores restricts the formation of water-water H bonding [17].

Chemically specific images of the OH group near the interface region were found. Change in FTIR spectra shows alteration and deviation of stoichiometry. Figure 1 shows that the absorbance of the hydrogen-bonded O-H stretching band (3600 cm^{-1}) increases.

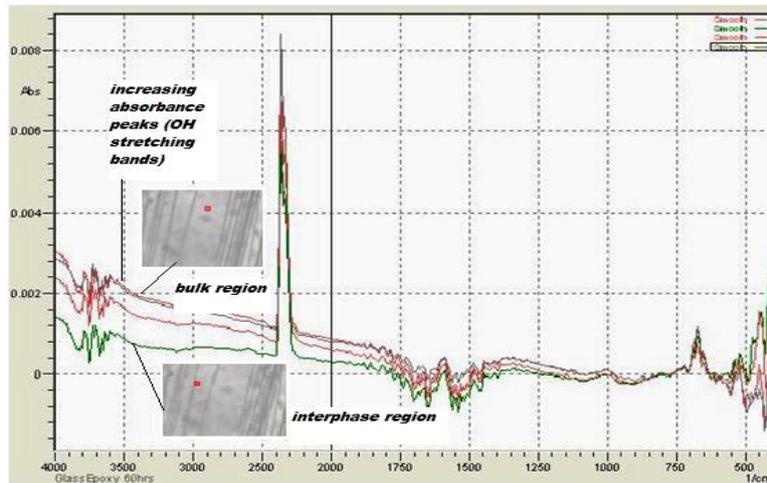


Fig. 1: FTIR-Imaging Spectra of Treated Glass/Epoxy Microcomposite.

The O-H absorption band is broad and strong which shows there is disappearance of the ring of epoxy. This happens from the center of the glass fiber to the bulk of the polymer, where the O-H band increases from interphase region to the bulk region. The rest of the pixels show spatial distribution and contain spectra with similar evolution in their characteristic IR bands.

TMDSC Study

The physical cause of glass transition of polymers is place change of molecular groups. T_g corresponds to a mobility change in a polymer and has a definite free volume associated with it. The glass transition (T_g) value usually decreases with aging, but when the aging time was much less, an increase of T_g comes into the picture which is shown in Figure 2.

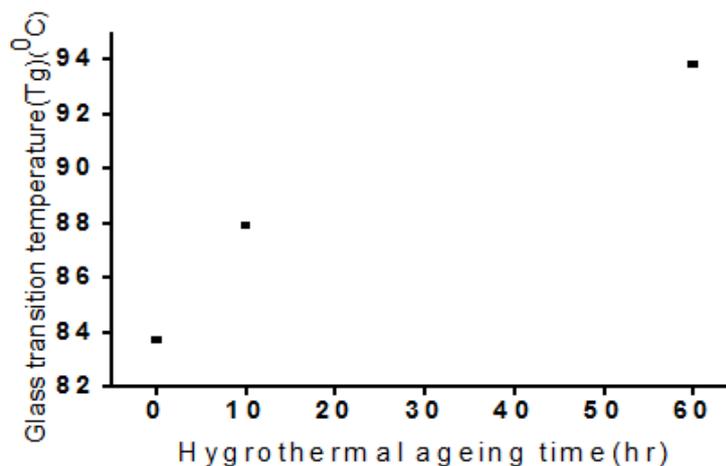


Fig. 2: Change of Glass Transition Temperature with the Hygrothermal Aging Time.

This may be due to increase of cross-link density of matrix which decreases the molecular mobility of the polymer. This may be due to reaction of water molecules with the hydroxyl group of the epoxy matrix resulting in the formation of a strong double H bond by replacing the existing covalent bond with the interface region/maybe due to formation of a crack closure which forms early in the absorption process [18]. In the TMDSC measurement, the structure through the T_g region is in a nearly quasi-equilibrium state [19].

Microscopic Interphase Analysis

It is at the interfacial region where stress concentration develops because of difference in the thermal expansion coefficient between the reinforcement and the matrix phase due to load applied to the structure and the time of curing shrinkage. This nature of stress may weaken the brittle thermoset epoxy resin and/or the interfacial region of the composite. Some degree of debonding at the interface region appears due to moisture absorption [20]. After hygrothermal treatment, this curing stress converts to swelling stress. The swelling stress is related to the differential strain which is created by the expansion force exerted by the liquid while stretching polymeric chains and molecules form disentanglement as shown in Figure 3.

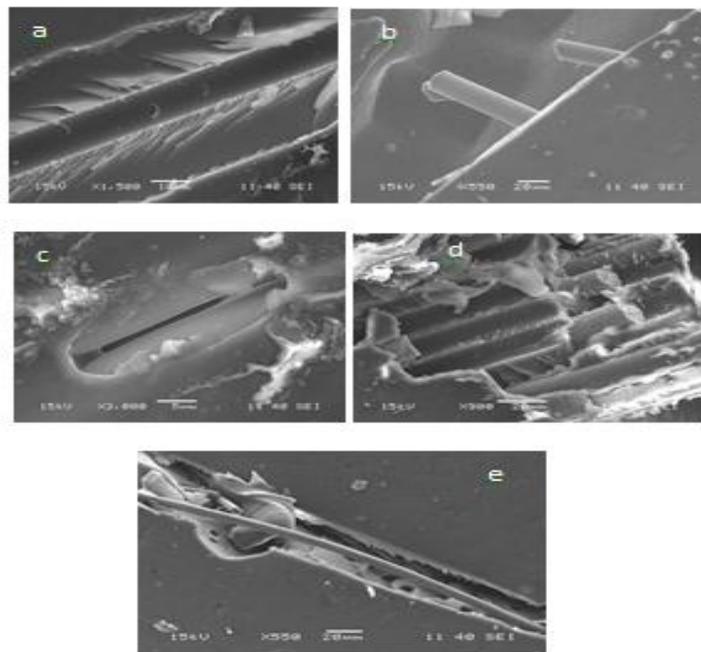


Fig. 3: Formation of (a) Swelling Stress at the Fiber/Matrix Interface Region, (b) Brittle Fracture of the E-Glass Fiber, (c) Fiber-Fiber Debonding, (d) Fiber Fracture, (e) Fiber/Matrix Debonding.

The fracture morphologies associated with fiber-dominated failure are shown in hygrothermal-treated samples. The approach is to present the morphologies associated with fiber and matrix failure modes in environmentally conditioned microcomposites. In glass fiber/epoxy composites, the poor matrix interface strength tends to promote an increased prevalence of longitudinal splitting, leading to fiber separation [14].

CONCLUSIONS

The effect of water ingress in polymeric composites on the variation of T_g value of epoxy matrix has been more closely monitored by TMDSC and FTIR-imaging. Failure modes are clearly observed by SEM during the hygrothermal treatment. The intensity of composite is mostly and critically guided by the small fluctuation in chemistry and character of interphase, which is manifested by adhesion and progressive failure between reinforcement fibers and polymer matrix.

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