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An assessment of interfacial chemistry and character of fiber/polymer micro-composites

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An assessment of interfacial chemistry and character of fiber/polymer micro-composites

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Abstract:

The interfacial chemistry and character of hygrothermally treated E-glass/epoxy micro-composite have been investigated by FTIR-Imaging and TMDSC techniques. The physical 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 micro-composite by FTIR Imaging. Temperature Modulated Differential scanning calorimetry (TMDSC) is for studying the glass transformation behavior of glasses and for measuring the glass transition temperature Tg. SEM study help in revealing the phase contrast which might have been developed by the generation of differential straining at different zones of the resin matrix.

Key words: Glass/epoxy micro-composites, Hygrothermal treatment, FTIR-Imaging, TMDSC

1: Introduction

Severe environmental exposure, long term loading and temperature can have a direct impact on the durability of polymeric composite materials resulting in an degradation of interfacial adhesion [1-2]. The contemporary view of adhesion results on an interphase model in which not only the actual chemical and physical interactions between fiber and the matrix are considered but also the structure and the properties of both the fiber and the matrix in the region near the interface [3]. An interaction reaction may result in various morphological modifications to polymer matrix microstructure in proximity to the fiber surface [4]. If the fiber/matrix interface strength is high, this often referred to as brittle fracture. If the fiber/matrix interface strength is weak, this leads to broomlike failure [5]. The environmental effect of moisture on the PMC material is of significant interest, particularly since mechanical and physical property modifications are generally manifestations of its presence [6]. Moisture penetrates in composite materials by diffusion through the polymer matrix and a network of micro-channels 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 broomlike 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 often chosen for improved stiffness, thermal stability and higher glass transition temperature (Tg) [9]. A small amount of water causes the fiber/matrix interfacial degradation (lower value of modulus, brittleness) due to a) water act as a plasticizer, decrease of Tg (20^0C for every 1% of water absorbed) and thus enhancing the structural relaxation b) stress generate due to swelling stress. c) Chemical degradation [10]. In addition, absorbed water molecules forming double hydrogen bonds will cause an increase of Tg, which has been found in epoxy resins [11]. This strong

physical interaction can create a region where a larger area of fiber and matrix participate in adhesion process. A larger contact area allows for better transfer of load between fiber and matrix and thus maintaining strength [12]. In many cases failures occurs in the interface region due to chemical reactions or plasticizing when impurities commonly water 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 deteriorated the ILSS value progressively of the material and reduce the maximum operating temperature [15]. Thus there has been a pressing need is required to quantify the degree of environmental degradation on the deviation of mechanical properties of fiber/polymer composites. To obtain a clear picture of the moisture diffusion process, various techniques have been employed in this field, such as Fourier Transform Infrared Spectroscopy (FTIR-Imaging), Attenuated Total Reflection (ATR-FTIR), Ultraviolet (UV) reflection, Solid state nuclear magnetic resonance (NMR), electrochemical impendence 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 micro-composites. Since, the interphases is buried inside the composite material and are nanoscopic in nature, the characterization is complicated.

2: Materials and Methods:

2.1 Sample Preparation

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 micro-composites. Some amount of epoxy and hardener mixture was poured on mold and then slowly placed the single strand of glass fiber uniformly on to it. The micro-composite was left for curing without applied any load in it for 24 hrs. Then the prepared samples were treated in a microprocessor controlled climatic chamber for hygrothermal treatment. The sample was divided into 3 batches; they were htgrothermally treated for 10 hrs and 60 hrs at 60^0 C and 95% humidity. And the rest batch for ambient temperature.

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 intra cooler, using the STAR software with Temperature Modulated DSC module. The temperature calibration and the 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 10^0 C min^{-1}, was used. Standard aluminum pans were used. The experiments were performed in the temperature range 25-150^0 C.

3: Results and Discussion

3.1 Water-uptake kinetics

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. 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. This reveals that, 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 restrict 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 alternation and deviation of stoichiometry. Fig.1: shows the absorbance of the hydrogen-bonded O-H stretching band ($3600cm^{-1}$) increases. The O-H absorption band is broad and strong this shows there is disappearance of the ring of epoxy. This happens from the centre 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 shows the spatial distribution and contain spectra with similar evolution in their characteristic IR bands.

3.2 TMDSC Study

The physical cause of glass transition of polymers is place change of molecular groups. Tg corresponds to a mobility change in a polymer and has a definite free volume associated with it. The glass transition (Tg) value usually decreases with ageing, but when the aging time was much less, an increase of Tg was comes in picture which shown in Fig. 2. This is may be 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/ may be due to formation of crack closure which form early in the absorption process [18]. In the TMDSC measurement, the structure through the Tg region is nearly in the quasi-equilibrium state [19].

3.3 Microscopic Interphase Analysis

It is at the interfacial region where stress concentration develop because of difference in the thermal expansion coefficient between the reinforcement and the matrix phase due to loads applied to the structure and the time of curing shrinkage. Some degree of debonding at the interface region appears due to moisture absorption [20]. After hygrothermal treatment this curing stress converts to swelling stress. This swelling stress is related to the differential strain which created by the expansion force exerted by the liquid while stretching polymeric chains and molecules form disentanglement shown in Fig. 3.

4: Conclusion:

The current method of water uptake kinetics in glass/epoxy micro-composite have been monitored.TMDSC is proved to be an useful tool in where there is a marked increase in Tg value, because of formation of double H bond with the epoxy system by water molecules. Hygrothermal treatment causes increase in absorbance peaks of OH stretching bands at the interphase was found in FTIR-Imaging. The discrepancy in the conclusions from this work, with regard to the nature of absorbed water in epoxy resins, relative to the findings from FTIR-Imaging and TMDSC experiments can be partly attributed to the different time scales of the two spectroscopic techniques.

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Figure captions:

1: Fig 1: FTIR-Imaging spectra of treated glass/epoxy micro-composite.

2: Fig 2: Change of glass transition temperature with the hygrothermal aging time.

3: Fig 3: Formation of swelling stress at the fiber/matrix interface region.

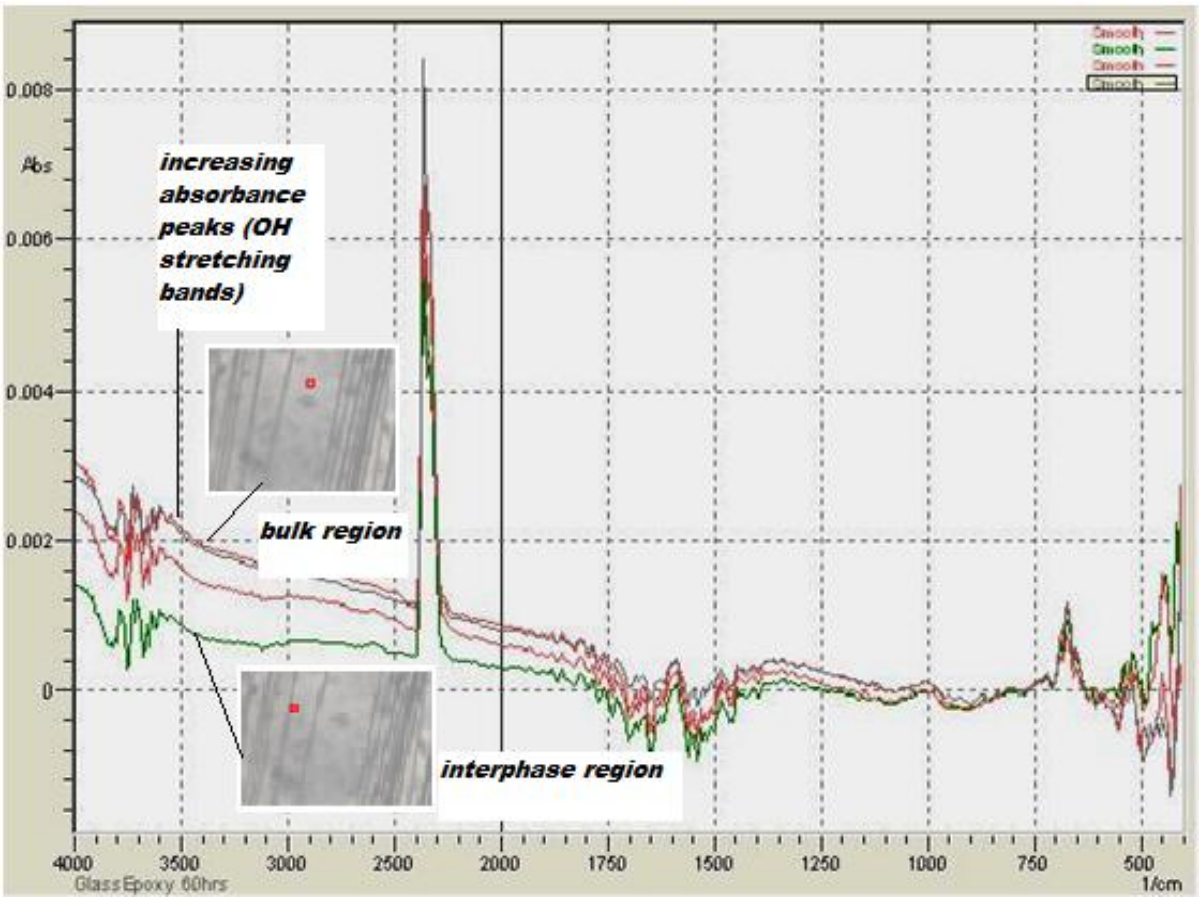
0.008
Abs
0.006
0.004
0.002
0
increasing absorbance peaks (OH stretching bands)
bulk region
interphase region
4000
3500
3000
2500
2000
1750
1500
1250
1000
750
500
1/cm
Glass Epoxy 60hrs

Fig 1.

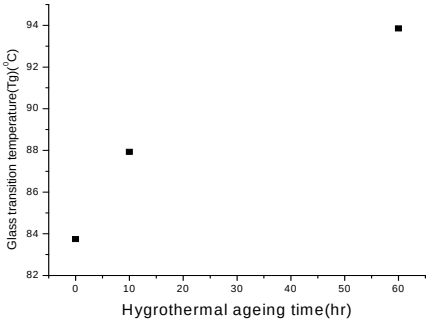
Glass transition temperature(Tg)(°C)
94
92
90
88
86
84
82
0
10
20
30
40
50
60
Hygrothermal ageing time(hr)

Fig 2

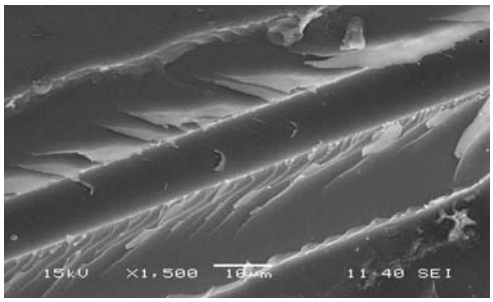

Fig 3