

STUDY THE EFFECT OF HYGROTHERMAL AGEING ON GLASS/EPOXY MICRO-COMPOSITES BY FTIR-IMAGING AND ALTERNATING DSC TECHNIQUES

Neeti Sharma, Surendra Kumar M and B. C. Ray*

Department of Metallurgical and Materials Engineering,
National Institute of Technology, Rourkela 769008, India

*Author for correspondence:

Email: drbcray@gmail.com (B C Ray) Fax: +91-661-2472926

ABSTRACT

An effort was made to study the effect of hygrothermal ageing at varying interval of time on the interphase of the fiber reinforced polymer composites. Silane-coated glass fibres and epoxy as matrix were used to fabricate the micro-composite. Absorbance peaks of OH stretching bands were focused to study the curing mechanism of epoxy matrix and effect of hygrothermal exposure at the interphase of the micro-composite by FTIR imaging. The DSC was carried out to monitor the glass transition temperature of hygrothermally aged samples after each interval. The FTIR results shows existence of gradient in degree of curing from the interphase to the bulk matrix and with the increase in aging time the water absorption increases at the interphase leading to improvement in the adhesion initially, as it is reflected in the results obtained with DSC analysis i.e increases in glass transition temperature with the aging time was reported. Obtained improved results may be attributed to moisture induced additional ring opening polymerization of epoxide molecule and/or formation of strong hydrogen double bonds with the epoxy matrix by water molecule. Microstructural analysis was done for hygrothermally treated samples by Scanning Electron Microscope.

Keywords: glass/epoxy micro-composite, hygrothermal ageing, FTIR-imaging, epoxy curing, glass transition temperature

INTRODUCTION

Polymeric composites are used in many applications such as aircraft, supersonic jet, automotive materials due to its high specific strength, high stiffness and tailor able properties [1-3]. But in many applications they have the disadvantage of moisture absorption because of the large amount of hydroxyl groups in the structure which are susceptible to the polar water molecules which causes degradation in there mechanical, thermal and dielectric properties [4, 5]. Moisture diffuses into the matrix of the composites and attacks the area near the interface due to its heterogeneous nature [6]. The coefficient of thermal expansion of glass fiber and epoxy are different so the moisture absorption causes differential volumetric expansion which leads to localized stresses and strain at the interface [7]. Moisture penetrates into the polymeric composites to lower the internal stresses and sometimes hygro-elastic swelling of the polymer occurs to as the constituent macromolecules rearrange to relieve the osmotic pressure generated by the water molecules [8]. Moisture penetration is explained by many techniques in polymer composites. There are two main mechanisms involved first one is moisture diffusion into matrix and second mechanism is water diffusion along the fiber-matrix interface by capillary flow [9, 10]. Water may be present in the polymeric composite material in dual phase i.e. either in the free molecules or/and clustered group [11]. It has been shown that absorption of moisture causes degradation of matrix dominating properties such as interlaminar shear strength, in-plane shear strength, compressive modulus and fracture strength [12]. However in some cases, during initial sorption period the longitudinal strength increases, this may be due to reduced flaw size in the matrix as a result of plasticization [13]. Chemical degradation includes matrix hydrolysis, interface hydrolysis and fiber degradation in some cases while physical degradation involves plasticization and swelling of the matrix [14]. These effects are generally reversible when water is removed but high temperature exposure can produce irreversible effects which cause chemical degradation of the matrix and attack on the fiber-matrix interface [15]. Further there may be increase in internal voids, chain expansion and the micro-crack formation into the matrix. However in many cases in the initial sorption period glass transition temperature increases, this may be due to formation of strong double hydrogen bond in the epoxy matrix or at the interface [11]. This shows that moisture absorption is matrix

dominating property in fibrous composites [16]. The structure near the interface is different from the bulk matrix so this leads to composite absorbing different amount of water per unit mass of resin than the bulk polymer [17]. The amount of water absorbed at the interface also depends upon nature of the glass surface, lower the functionality of the silane is higher the cross-link density at the interface and lesser will be the amount of moisture absorbed [18]. Moisture penetration at the interface contributes free volume of mesoscopic origin in addition with the one existing in the bulk of the matrix phase [19]. The performance of fiber-reinforced polymer composite is controlled by the adhesion chemistry at the fiber-matrix interface [20]. Low temperature conditioning causes strengthening phenomenon due to mechanical keying at the fiber-matrix interface and high temperature act as a softening agent [21]. It was also reported that water at the interface causes replacement of covalent bonds between the siloxane backbones of the sizing material on the glass surface with strong hydrogen bonds between the glass surface, water molecules and the network of silane coupling agents [22]. This strong physical interaction can create region where larger area of fiber and matrix participate in adhesion process. Larger contact area allows better transfer of load between fiber and matrix and thus maintaining the strength.

In the present work, FTIR-imaging and DSC techniques were used to assess the interphase of hygrothermally treated glass/epoxy composites. Since the interphase is buried inside the composite material and they are nanoscopic in nature there characterization is complicated. So there are many difficulties encountered in physio-chemical analysis of interphases [23, 24]. FTIR-imaging technique can be used for the distinct characterization in particular region such as interphase of nano-dimensions. Till now this technique was used by many researchers for determining the structural gradient at the interphase in epoxy curing at a glass fiber/ epoxy matrix. DSC technique was used to monitor the effect of hygrothermal treatment on the glass transition temperature.

EXPERIMENTAL

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 fibres treated with silane-coupling sizing system (Saint-Gobian Vetrotex) monofilaments to fabricate the micro-composite.

Sample preparation

The specimens were fabricated using the conventional hand lay-up method. A plane mould was treated with silicon based releasing agent for easy removal of glass/epoxy micro-composites. A single strand of glass fiber was placed on the mould and the layer of catalyzed epoxy was poured on to it uniformly. Very light rolling was then carried out to remove any gas pockets if present and to uniformly distribute the epoxy resin through out the composite. The micro-composites prepared were then cured at room temperature for 24 hours. Then the samples were treated in microprocessor controlled climatic chamber for hygrothermal conditioning. The samples were divided into six batches, they were hygrothermally treated for 10, 20, 30, 40 and 50 hours in 95% RH and one batch remain untreated.

Fourier Infrared Spectroscopy Analysis (FTIR)

FTIR analysis was performed in FTIR spectrophotometer interfaced with IR microscope operated in reflectance mode. The microscope was equipped with a video camera, a liquid nitrogen-cooled mercury cadmium telluride (MCT) detector and a computer controlled translation stage, programmable in the x and y directions.

The spectra were collected in the 2500 cm^{-1} to 4000 cm^{-1} region with 8 cm^{-1} resolution, 60 scans and beam spot size of $10\mu\text{m}$ - $100\mu\text{m}$. The spectral point-by-point mapping of the interphase of the epoxy cured composites was performed in a grid pattern with the use of computer controlled microscope stage. Since the surface of the film was not perfectly smooth and its thickness was not uniform so the care was taken to mount the sample such

that a major portion of the plane was in the same focal plane. The FTIR imaging was performed in AIM-800 Automatic Infra red Microscope.

Differential Scanning Calorimetry Analysis (DSC)

The DSC measurements were performed on a Mettler-Toledo 821 with intra-cooler, using the STAR software with Alternating DSC (ADSC) module. The temperature calibration and the determination of the time constant of the instrument were performed by standards of In and Zn, and the heat flow calibration by In. The underlying heating rate of $10^{\circ}\text{Cmin}^{-1}$ was used. In order to calibrate the heat flow signal, a blank run with an empty pan on the reference side and an empty pan plus a lid at the sample side was performed before the sample measurements. Standard aluminum pans were used. The experiments were performed in the temperature range from 40°C to 100°C .

There are certain limitations of refraction and reflection at the fiber surface in the spectroscopy that will finally affect the FTIR spectra of glass/epoxy composites. Due to this only a small percent of light reaches the detector. It is difficult to separate these optical effects from the samples. However these optical effects can be minimized by taking FTIR spectra over the same region of the micro-composites.

RESULTS AND REMARKS

FTIR measurements

Peiyi Wu et.al [24] investigated water diffusion process in epoxy resin by 2D ATR-FTIR spectroscopy and focused their observation on the $3900\text{-}2800\text{ cm}^{-1}$ spectral region to study OH stretching bands. They reported that the major difference in absorption of water occurs at about 3450 cm^{-1} . With the increase of ageing treatment the intensity at 3450 cm^{-1} increased and peaks got broaden. They differentiated the OH band in IR spectra into three bands, 3610 cm^{-1} (water hydrogen bonded with epoxy resin), 3450 cm^{-1} (weak hydrogen bonded with epoxy resin and partially dissolved) and 3240 cm^{-1} (strong water-water hydrogen bonded or cluster of water).

Figure 1 represents the spectra of untreated glass/epoxy micro-composites at different region from the interphase to the bulk matrix. The grey line shows the spectral region

near the interphase of the micro-composites and the blue is the spectral region away from interphase. Finally the green line represents the spectral region in the bulk of the micro-composites. To study the water diffusion we will only consider OH stretching bands ($3900\text{-}2800\text{ cm}^{-1}$). From the figure 1 we note that the absorbance of the peaks OH stretching bands continuously increases with the distance from the interphase region to the bulk. This shows the gradient of curing reaction i.e the degree of crosslinking in the epoxy matrix is not uniform. Epoxy resins are characterized by the presence of three-membered ring containing two carbons and an oxygen (epoxy group or epoxide). The curing of epoxy resins is associated with a change in state from a low molecular weight liquid mixture to a highly cross-linked network. The molecular mobility in the system decreases as the cure proceeds due to cross-linking of several chains into network of infinite molecular weight. Hence, the epoxy hardens on curing due to large cross-linking networks. Here the primary amines are used as curing agent. With primary amines, the reaction consists in the epoxy ring opening by the amine reactive group generating secondary amines and hydroxyl groups. As the secondary amines are generated they can react with the epoxy rings at the same time as primary amines to yield tertiary amines and hydroxyl groups. Therefore, as the curing reaction proceeds the OH concentration must increase in proportion to the disappearance of the epoxy groups and the concentration of primary amines will continuously decrease. J. Gonzalez-Benito [17] studied the curing characteristics of epoxy by FTIR imaging and reported increases in OH concentration and disappearance of primary amines with the curing time of the epoxy resin.

The gradient in the degree of curing on going away from the interphase which is reflected from the spectra obtained for the OH absorbance may be attributing to gradient in the active amine/epoxy ratio from the glass fiber surface to the bulk matrix and smaller molecular size of ethylenediamine (EDA) than epoxy [17]. The glass fibres were treated with silane coupling agents to improve durability and mechanical strength of the fibre/matrix bond by increasing the wettability of fibres. These silane based coupling agents have general chemical formula R-Si-X_3 which reacts at one end with the surface of glass and at the other end with polymer phase. The silane is hydrolysed to silanol in the aqueous solution to which the glass fibres are exposed. The hydroxyl groups of the silanes and those of the glass fiber surface react (condensation reaction) with each other

through siloxane bonding or hydrogen bonding and form a water resistant polysiloxane layer bonded to glass surface [16]. The lower concentration of amine at interphase is due to more favorable interaction of amines with the uncondensed silanol groups through hydrogen bonding present on the fibre surface. These interactions are more severe due to smaller size of EDA so that diffusion is easier through the polysiloxane layer [17]. Therefore the concentration of amine decreases at the interphase results in lower degree of crosslinking by epoxide ring opening mechanism and increases with the distance from the interphase to the bulk where high degree of crosslinking results due to the presence of sufficient concentration of amine.

Figure 2 shows the FTIR spectra taken at the interphase for untreated and hygrothermally treated micro-composites at different time intervals of aging for 10hours, 20 hours, 30hours, 40 hours and 50 hours. From the spectra obtained we note that the absorbance of the peaks of OH stretching bands ($3900-2800\text{ cm}^{-1}$) increases with the aging time of hygrothermal exposure. The micro-voids may be formed during curing or stresses generated due difference in thermal expansion coefficient between the glass fiber and the epoxy matrix at the interphase enhancing the moisture absorption. As with the above discussion due to the unavailability of amines at the interphase region the concentration of epoxide remains almost unaltered i.e. Ring opening of the epoxy molecules didn't carried out completely. Thus, the distribution of the epoxide species is not uniform from the interphase region to the bulk. These results in less amount of cross-linking networks at the interphase region which makes it to have poor adhesion between fibre and matrix. Hence, during the initial stages of hygrothermal treatment the moisture adsorbed at the interphase will start the polymerization of remaining unopened epoxide molecules by additional ring opening polymerisation mechanism [26]. This moisture induced additional ring opening polymerisation will increases the amount of cross-linking at the interphase region which helps in completion of the left curing. The effect of additional cross-linking at the interphase after hygrothermal treatment is reflected in the DSC measurements where an increases in the glass transition temperature results with the aging time.

DSC Study

Figure 3 shows the effect of hygrothermal ageing on the glass transition temperature of glass/epoxy micro-composites. The measurement of glass transition temperature (T_g) is very important because it determines the critical service temperature of the polymer composites and finally their engineering application [27]. But when the polymeric composites are exposed to hygrothermal environment, the glass transition temperature usually decreases with the aging time. In the present investigation since the ageing time was very less, an increase in glass transition temperature was observed. This may be attributed to decrease in molecular mobility due to additional ring opening polymerization of epoxide molecules by moisture at the interphase and/or may be due to reaction of moisture water molecule with the hydroxyl group of the epoxy matrix results in the formation of a strong double hydrogen bonds by replacing the covalent bonds with the silane coupling agent. But after long exposure moisture absorption may lead to debonding, delamination at the interphase and plasticization which may decrease the glass transition temperature. This is still not clear that after what time plasticization effect come into picture. The increases in the glass transition temperature may reflect improved mechanical properties like interlaminar shear strength and fatigue strength [17].

Microscopic interphase analysis

It was experimentally shown that if the moisture uptake is less the polymeric composites follow Fickian behavior. As the moisture content increases the non-Fickian behavior becomes more and more obvious [28]. However a 2-phase model of Carter and Kibler referred moisture diffusion as Langmuir-type [29]. The Figure 4 shows scanning micrographs of hygrothermally aged glass/epoxy micro-composites. The curing stresses generated at the interphase can be relieved by the moisture absorption which may results into swelling stresses at the interphase (Fig. 4a, 4b). The kinetics of moisture diffusion is a complex phenomenon. It is different for glass fiber and epoxy matrix and also depends upon their relative volume fraction, direction and type. Moisture penetration can cause matrix crazing (Fig. 4c) and since the hygrothermal ageing time was less it can only increase the interfacial adhesion (Fig. 4d) by moisture induced additional ring opening mechanism and/or by formation of strong double hydrogen bonds and this may increase

the load transfer from matrix to the fiber other through interphase region. This may further increase the mechanical properties of composites.

CONCLUSIONS

In the present work, hygrothermal ageing effect on bisphenol-A based epoxy resin reinforced with glass fibres (micro-composite) was monitored. FTIR analysis shows variation in the degree of curing from the interphase to the bulk epoxy matrix which may be due to incomplete ring opening polymerization of epoxide molecules at the interphase. This lower degree of curing may be attributed to insufficient concentration of amine at the interphase. After hygrothermal conditioning FTIR results shows increase in absorbance peaks of OH stretching bands at the interphase. This may be due to moisture absorption into the micro-voids formed during curing and stresses generated by differential coefficient of expansion of matrix and fibre. There may be possibility that the left curing will be completed by moisture induced additional ring opening polymerization reaction which results increase in degree of crosslinking enhancing the immobility of molecules at the interphase. This is reflected in DSC results where we marked increase in glass transition temperature. This increase may also be attributed to the formation of strong double hydrogen bonds with the epoxy resin by water molecules or due to reduced flaw size by plasticization. This suggests that FTIR-imaging and DSC techniques can solve the problem of physio-chemical analysis of interphase of composites.

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FIGURE CAPTIONS

Figure 1 The FTIR spectra for untreated glass/epoxy micro-composites at different regions and 2D micrographs taken by FTIR spectrophotometer.

Figure 2 The FTIR spectra at the interphase for untreated and hygrothermally treated micro-composites at different time intervals.

Figure 3 Graph showing variation in glass transition temperature (T_g) of glass/epoxy micro-composite with hygrothermal aging time.

Figure 4 Scanning electron micrographs showing (a) stress field, (b) stress relaxation or swelling stresses generated, (c) matrix crazing and (d) adhesion status at the interface in hygrothermally aged glass/epoxy micro-composites.

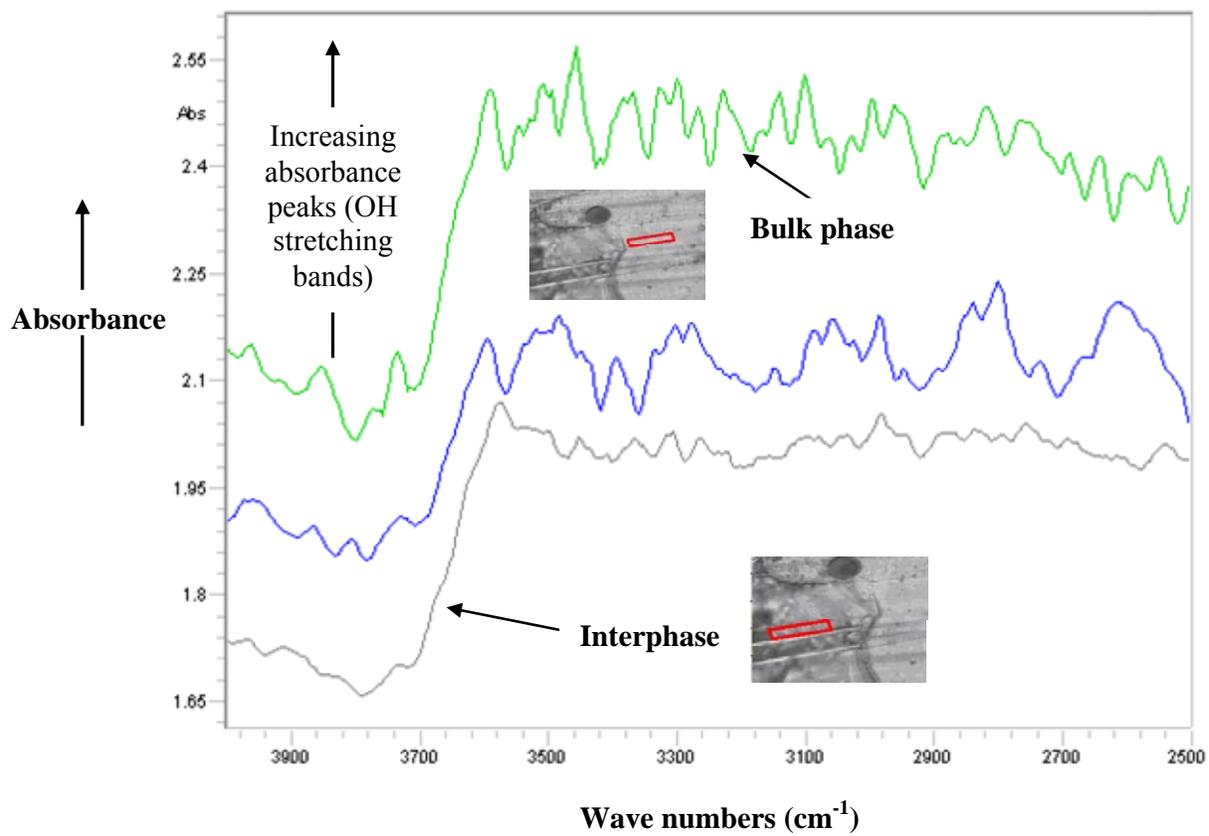


Figure 1

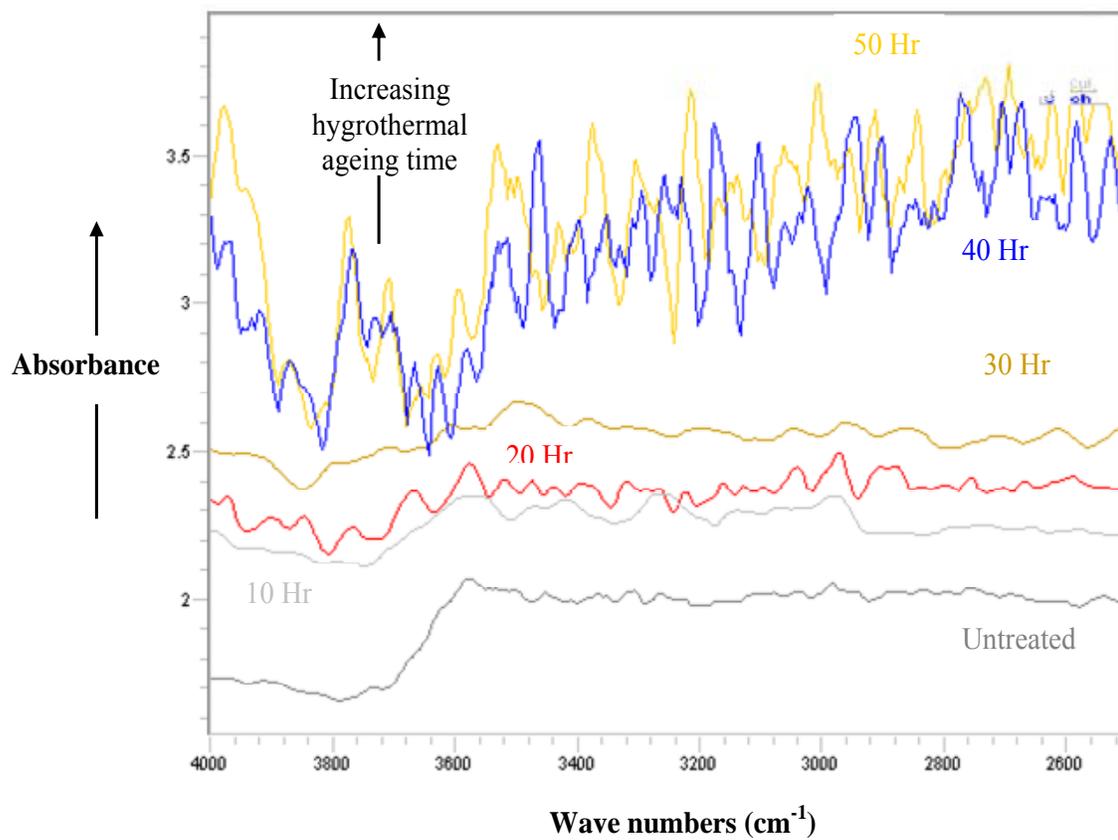


Figure 2

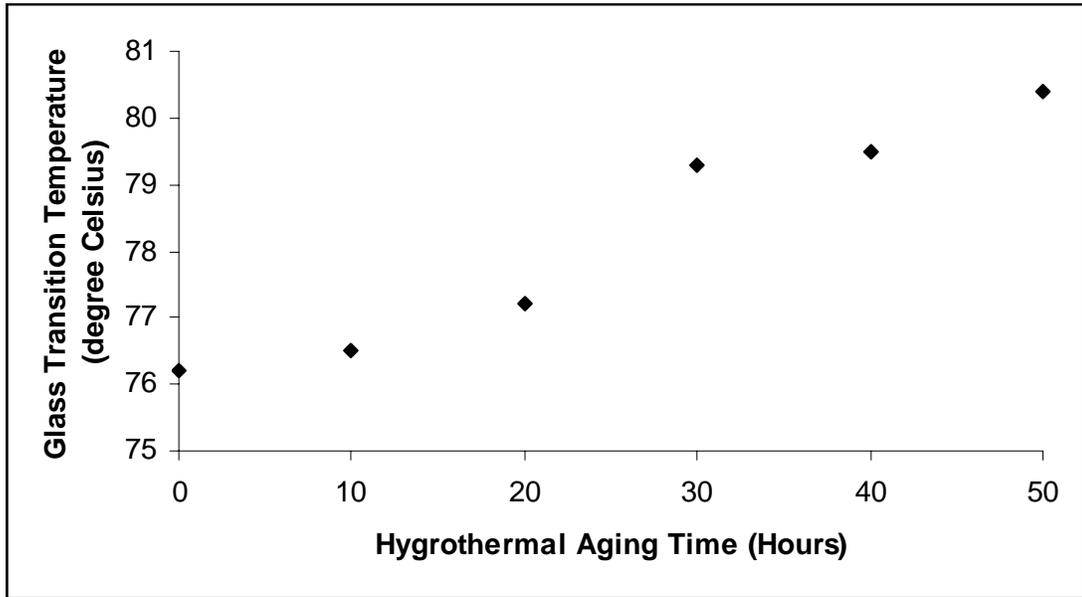
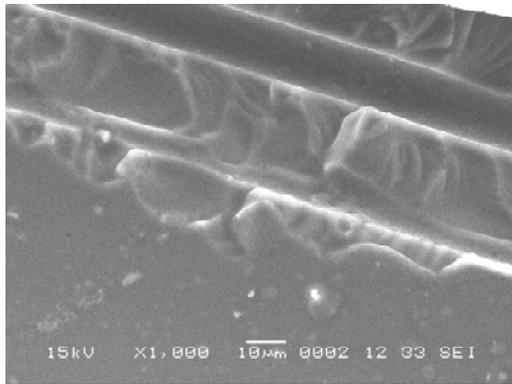
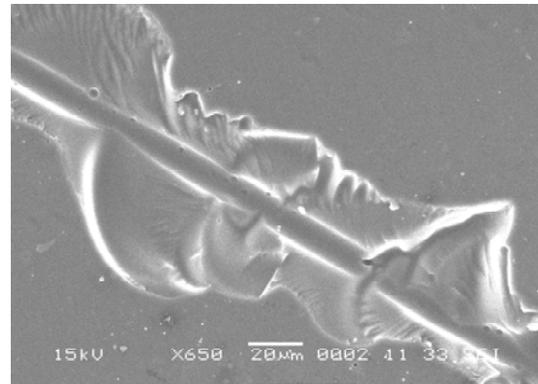


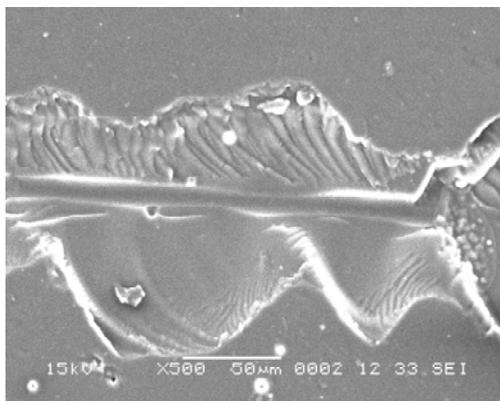
Figure 3



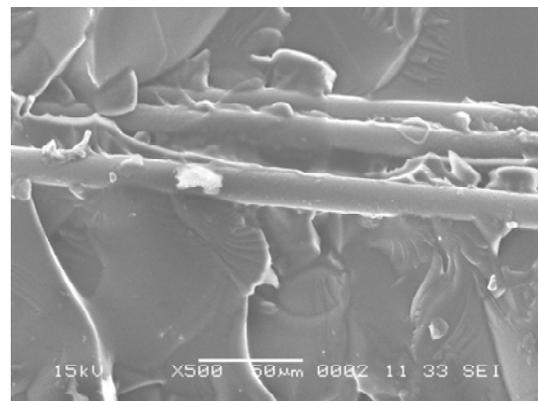
(a)



(b)



(c)



(d)

Figure 4