

Assessment of small interactions and structural gradient at the interface of glass and carbon fibers epoxy micro-composites by FTIR-imaging and DSC techniques

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ABSTRACT

Many complex reactions occur at the interface due to moisture absorption and temperature and very little information is available regarding the chemical deviation near the interface due to moisture absorption. The present work uses FTIR-imaging and modulated temperature DSC to assess the structural gradient at the interface due to hygrothermal ageing of glass/epoxy and carbon/epoxy composite materials. The specimens were conditioned at 50°C in hydrothermal chamber with 90% humidity for the duration of 50 hours. The samples were studied before and after the hydrothermal aging near the interface i.e. in the interphase region to evaluate the chemical changes from the bulk of the matrix phase by FTIR-imaging. Alternating DSC was also done to study the deviation in the glass transition temperature of FRP composites. Mechanical properties of composite materials are dependent on the properties of the interphase region and even small chemical deviation effect the overall performance of composite materials. It was observed that hygrothermal treatment leads to change in chemical spectra and glass transition temperature near the interface which ultimately leads to change in interface dominating properties.

Keywords: FTIR-imaging, ADSC (Alternating Differential Scanning Calorimetry), interface/interphase, hygrothermal ageing.

INTRODUCTION

Composites are considered to be material of tomorrow; though the issue of understanding the composition and properties of interfaces in FRP composite materials are evolving still they are in great number of applications because of its diversified properties such as light weight, high specific strength, high specific stiffness and a key feature of FRP composites that make them promising engineering material is the opportunity to tailor the properties through the control of fiber and matrix combinations and the selection of processing techniques [1]. Earlier it was believed that the mechanical behavior of interphase controls the properties of FRP composites than after sometime it was said that physical nature of interphase controls the properties of FRP composites, physical nature was further replaced by physico-chemical nature. But now it is believed that chemical nature of interphase controls the properties of FRP composites. It is a region through which fiber and matrix phase are physically combined and give combination of properties without losing there original properties and maintains the bond in between for the transfer of load [2]. Proper characterization of composite interfaces, whether it is for chemical, physical or mechanical properties, is extremely difficult because interfaces are buried inside the material [3]. Further nanoscopic nature of interfaces in advanced composite requires the characterization and measurement techniques to be of ultra-high magnification and resolution for sensible and accurate solutions. There are many difficulties encountered in physico-chemical and chemical analysis of interfaces [3]. The structural integrity of polymeric composite materials is strongly influenced by fiber/polymer interfacial region [4].

Polymers matrix composites are relevant materials for structural applications such as aerospace, future supersonic, automotive materials because of its tremendous properties [5, 6]. In these cases they are exposed to environments involving both temperature and

humidity. Interface is more susceptible to the moisture absorption due to its heterogeneous nature. Over the past few years a great deal of experimental work has been done to study humid ageing and which finally affects the composite performance [6]. Moisture absorption may be due to capillary action between the fibers [7]. Water may be present in the composite either in the free molecules or clustered group. This shows the dual moisture sorption in the matrix phase at the interface region [8]. The CTE of fiber and matrix phase are different so the moisture absorbed causes differential volumetric expansion which leads to localized stress and strain [9]. Another important mechanism is hygroelastic swelling of the polymer as the constituent macromolecules rearrange to relieve the osmotic pressure generated by the water molecules [7]. It has been observed that absorption of moisture causes degradation of matrix- dominating properties such as interlaminar shear strength and in-plane shear strength, and compressive modulus and strength [10]. The longitudinal strength has actually been shown to increase slightly with initial moisture sorption and this may reflect for instance reduced flaw sensitivity in the matrix as a result of plasticization or improved ability to transfer stress efficiently in the region of a fiber break [9].

Epoxy resins are commonly used as adhesives, coatings and in composites materials. They have good combination of chemical, thermal, electrical and mechanical properties but in many applications they have the disadvantage of absorption of water because of the large amount of polar OH groups in the structure which is susceptible to the polar water molecules [11]. Moisture sorption leads to failure may be due to plasticization, formation of double bond which act as a physical link or hydrolysis reaction i.e. scission of polymer chains [8]. This effect is usually reversible when water is removed but exposure to high temperature can produce irreversible effects, which is attributed to the chemical degradation of the matrix and attack on the fiber/matrix interface [12]. This causes

increase of internal voids of the entangling polymer chain, promoting chain expansion and the micro-cracks formation into the polymer matrix. However in many epoxy polymers moisture absorption showed increase in T_g in the initial stages may be due to formation of double hydrogen bond at the interface [8]. But it is not evident that after how long period of sorption water molecule can form double hydrogen bonds. On the contrary it has been found that in the initial stage of sorption experiments, water molecules with double hydrogen bonds were generally observed in different epoxy systems. When composites are exposed to hygrothermal environment for longer period, the T_g usually decreases and therefore, the service temperature of the material changes. Moisture sorption is a matrix dominating property in fiber reinforced polymer composites. High temperature ageing not only increases the moisture uptake rate but it may modify the local stress that is required for delamination nucleation [13]. The fiber plays a role as much as the interface region between the fiber and the matrix may be of different network structure to that of the bulk matrix away from the fiber. This leads to the composite absorbing different amount of penetrant (i.e. water) per unit mass of resin than the bulk polymer [14].

To obtain a clear picture of diffusion process, various techniques have been employed in this field, such as near-infrared Fourier transform infrared spectroscopy (NIR-FTIR), attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR), ultraviolet (UV) reflection, solid state nuclear magnetic resonance (NMR), dielectric relaxation measurements, positron annihilation lifetime spectroscopy (PALS), electrochemical impedance spectroscopy (EIS), fluorescence and molecular simulations. In this case FTIR imaging in mid-infrared range is used because of its ultra high magnification power which is helpful in study of nanoscopic interphase region [15, 16].

In the initial stages of thermal and cryogenic conditioning shear strength improves and high temperature conditioning contributes more strengthening effect and better adhesion at the interface. High temperature ageing not only increases the moisture uptake rate but it may modify the local stress that is required for delamination nucleation [4, 9, 17].

EXPERIMENTAL

An unmodified epoxy resin based on Bisphenol-A and aliphatic primary amine hardener (Ciba-Geigy, India, LY-556 Araldite, HY-951 hardener) was used with E-glass treated with a siliane-based sizing system and carbon fiber woven roving to fabricate the laminated composites. 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 FRP composites. A single strand of glass and carbon 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 half of the micro-composite samples were exposed to moisture in humidity chamber for 50 hours at temperature of 50 degree Celsius and half of it was kept as such at room temperature.

FTIR analysis was performed in FTIR spectrophotometer interfaced with IR microscope operated in reflectance mode. The microscope is 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 650 cm^{-1} to 4000 cm^{-1} region with 8 cm^{-1} resolution, 60 scans and beam spot size of $50\mu\text{m}$ - $50\mu\text{m}$. The spectral point-by-point mapping of the interface 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 care should be 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.

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 modulation conditions used were amplitude of and the period of 1 min. with underlying heating rate of 1°min^{-1} 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 .

RESULTS AND DISCUSSION

There are certain limitations of the spectroscopy of fibers that will finally affect the FTIR spectra of glass/epoxy and carbon/epoxy composites. The limitations are generally light refraction and reflection at fiber surfaces. Because of the refraction on the fibers only a small percent of light reaches the detector. It is difficult to separate these optical effects from the samples. The optical effect can be minimized by taking FTIR spectra over the same region of the micro-composites. Any spectral changes are due to the molecular changes in the composites [18].

The OH vibration modes lead to very complicated spectrum by both intermolecular and intramolecular hydrogen bonding. The fundamental stretching vibration and the in-plane

bending vibration occur within the 3900-2800 cm^{-1} region and at around 1640 cm^{-1} . Our discussion will focus on the 3900-2800 cm^{-1} spectral region, where the peaks are more intense [22]. The OH stretching band occurs in this range [19].

The FTIR spectra of cured glass/epoxy micro-composites are at different positions is shown in Fig. 1. The micro-composites are positioned at the interface i.e. in the interphase region and in the bulk region and their intensities centered in the 3800-3000- cm^{-1} region were compared. The green spectra represent the bulk region whose intensity is less than the other spectra in the Fig. 1. The graph is in transmittance mode i.e. if the transmission is more absorbance is less. The baseline of the epoxide band indicates the degree of cure of the resin; the higher the intensity the lesser the cure [18]. The presence of the amine group associated with the silane coupling agents may change the local concentration. This may change the kinetic of epoxy reaction that is faster in the bulk region than the filler/matrix interface [20]. Due to the heterogeneous nature of the interface the reaction is not uniform.

Spectrum of hydrothermally treated glass/epoxy composite is shown in Fig. 2. The major difference that is noted in the spectra as a result of hydrothermal treatment is increase in intensity of the spectra centered on 3450 cm^{-1} . The wide range of vibration band in the spectral region 3800-2900 cm^{-1} is due to different types of absorption at the interface by the epoxy resin. The moisture diffusion by the epoxy resin is in situ in nature i.e. absorption from the strongly hydrogen-bonded and less strongly hydrogen-bonded [19]. The kinetic absorption increases in Fickian and non-Fickian mode with more conditioning time in glass/epoxy micro-composites [21]. The epoxy resin swells due to moisture absorption. This may lead to crazing of the matrix and microvoids or cracks at the interface.

The FTIR spectra of cured carbon/epoxy micro-composites showed in Fig. 3 and hydrothermally treated samples showed in Fig. 4 same type of results. However due to

the larger interface area in carbon/epoxy micro-composites the amount of moisture absorbed by the composite is less. This shows the better adhesion of the carbon fiber with the epoxy resin.

Alternating differential scanning calorimetry (ADSC) or modulated temperature (MTDSC) was performed of glass/epoxy and carbon/epoxy composites. MTDSC is thermoanalytical technique which involves superimposition of a modulation on the conventional linear heating, cooling or isothermal temperature program. The advantage of ADSC over conventional DSC is that enhancement of both sensitivity and resolution in the same experiment, analysis of complex overlapping transitions, direct measurement of the heat capacity and detection of weak glass transitions [22].

The ADSC of untreated and hygrothermally treated glass/epoxy and carbon/epoxy are shown in Fig.6 and Fig.7. The hygrothermal treatment was only for 50 hours which shows that in the initial conditioning period glass transition temperature increases. This may be due to the formation of double hydrogen bonds in the initial stages or reduced flaw sensitivity in the matrix as a result of plasticization or improved ability to transfer stress efficiently in the region of a fiber break. The change of T_g depends upon both the double bond formation and plasticization of matrix. Many works represented that interlaminar shear strength also increases in the initial stages of hygrothermal treatment this may be one of the reason.

CONCLUSION

In the present work, hygrothermal treatment of bisphenol-A based epoxy resin reinforced with glass and carbon were monitored. The results FTIR-imaging and ADSC suggest that there is a variation in the chemical behavior after hygrothermal treatment. The decrease of intensity in the FTIR spectra shows that curing is fast in the bulk region in comparison

to fiber/matrix interface. The moisture sorption at the interface by the epoxy resin is a very complex phenomenon due to different absorption at the interface i.e. water molecule forms strong hydrogen bond with the epoxy resin or less strongly bonded hydrogen bond. Due to moisture absorption peaks get widen and intensity increases. This shows that it that hygrothermal treatment leads to change in the structure at the interface and bulk, but the interface is more affected due to its heterogeneous nature. If the structure near the interface changes the stress transfer from the matrix to the fiber will change and ultimately the overall properties of FRP composite will be change. T_g also increases in the initial stages of hygrothermal treatment. This may be due to the double bond formation in the matrix or reduced flaw size due to plasticization.

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FIGURE CAPTIONS

Figure1 The FTIR spectra of untreated glass/epoxy micro-composites. The green line represents the spectra of bulk region and sky blue, grey and blue represents the region near the interface i.e. in the interphase region. Two-dimensional view of one of the sample is also shown.

Figure2 The FTIR spectra of hygrothermally treated glass/epoxy micro-composites. The red line represents the spectra of bulk region and blue, black and yellow represents the region near the interface i.e. in the interphase region. Two-dimensional view of one of the sample is also shown.

Figure3 The FTIR spectra of untreated carbon/epoxy micro-composites. The green line represents the spectra of bulk region and blue and red represents the region near the interface i.e. in the interphase region. Two-dimensional view of one of the sample is also shown.

Figure4 The FTIR spectra of hygrothermally treated carbon/epoxy micro-composites. The yellow line represents the spectra of bulk region and purple, grey and blue represents the region near the interface i.e. in the interphase region. Two-dimensional view of one of the sample is also shown.

Figure5 The ADSC of untreated and hygrothermally treated glass/epoxy micro-composites. The purple line represents the untreated sample and green treated sample.

Figure6 The ADSC of untreated and hygrothermally treated carbon/epoxy micro-composites. The green line represents the untreated sample and purple treated sample.

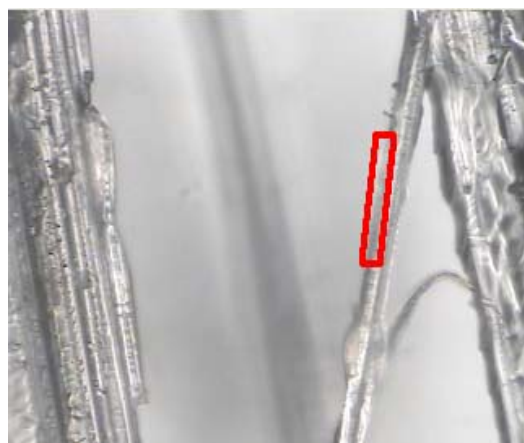
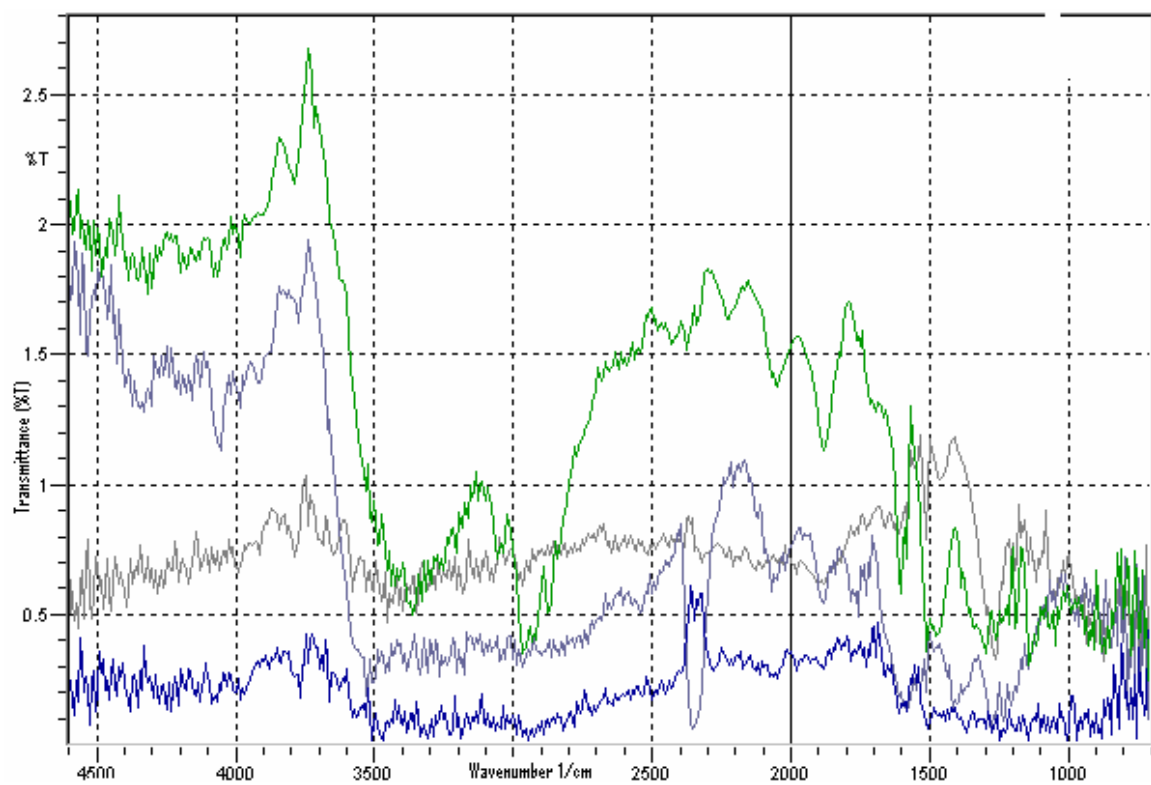


Figure 1

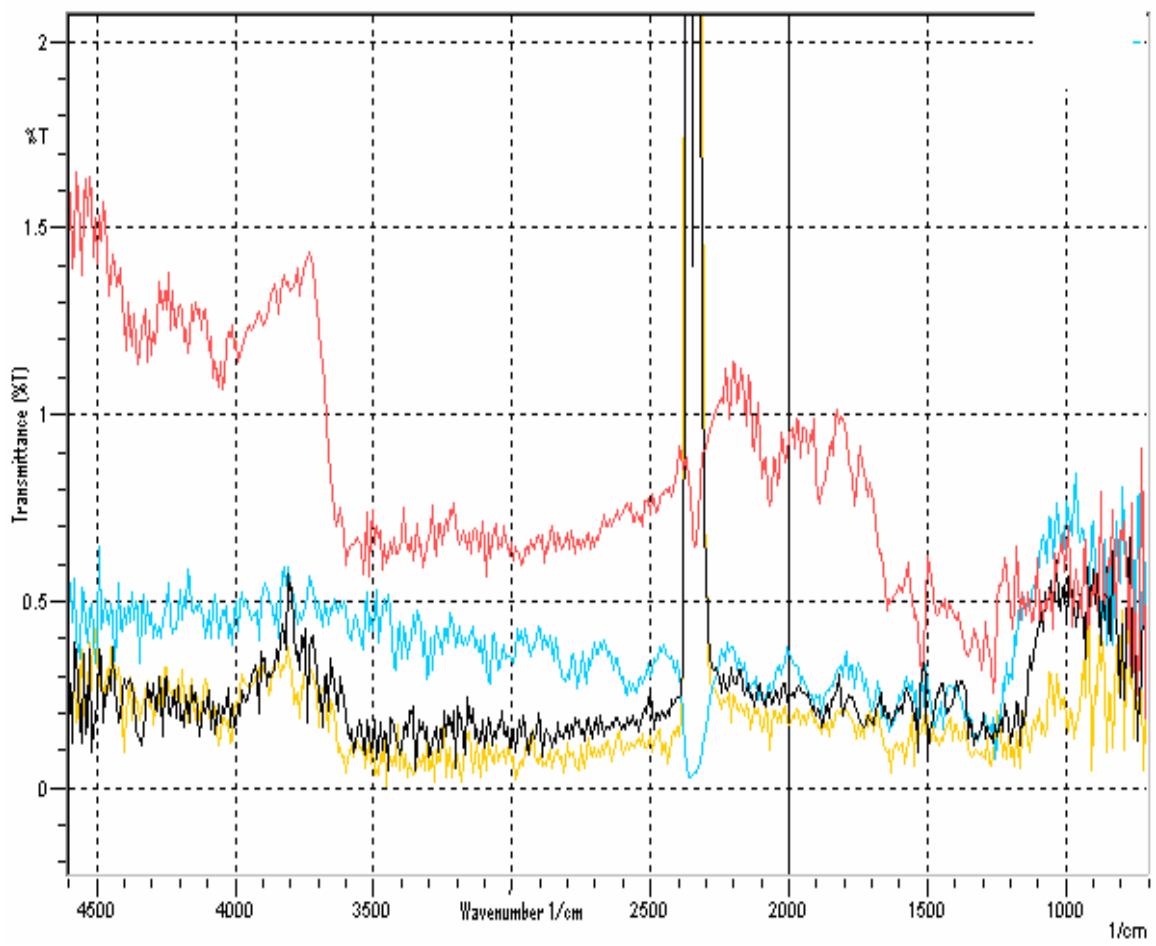


Figure 2

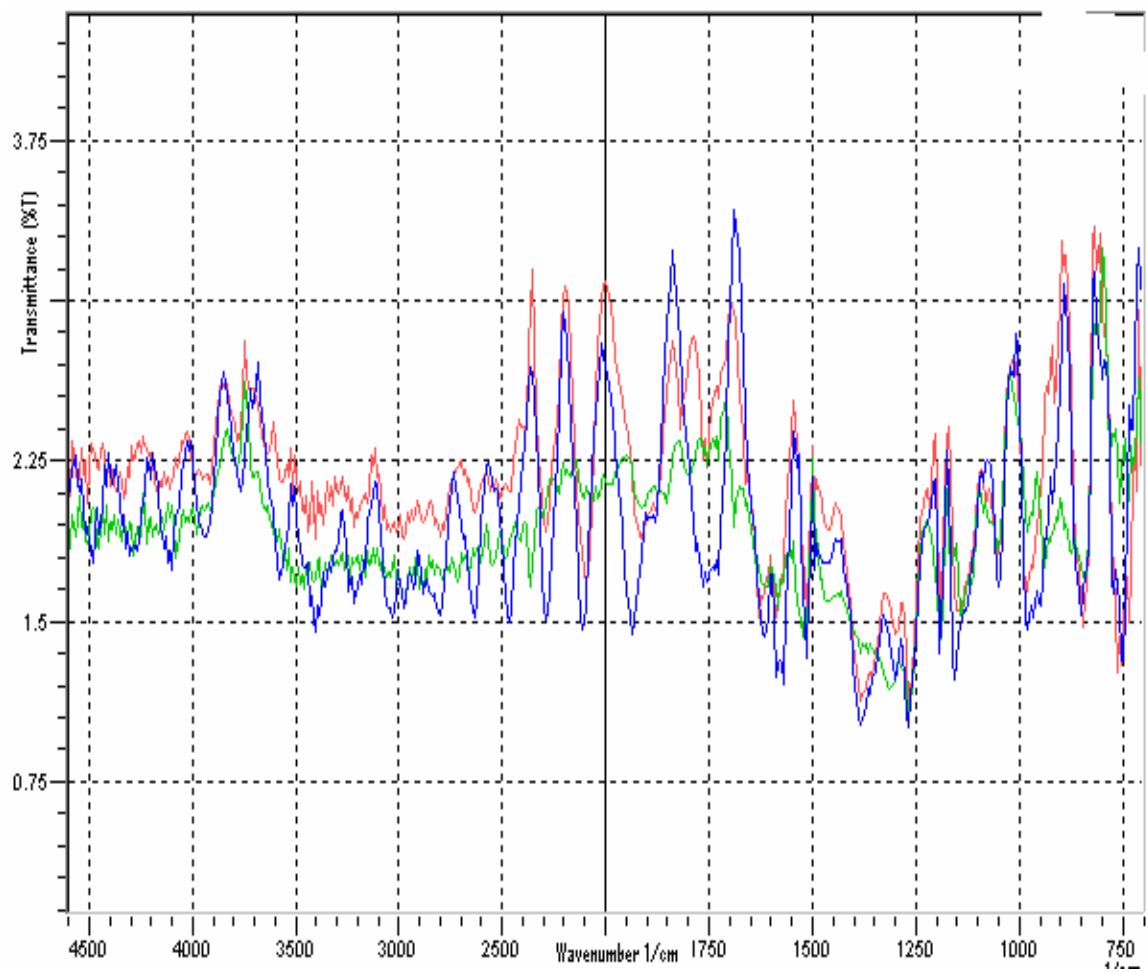


Figure 3

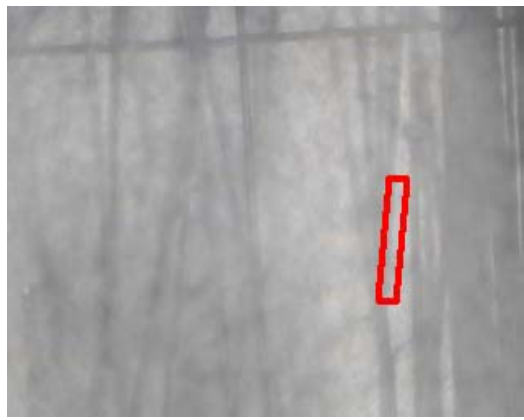
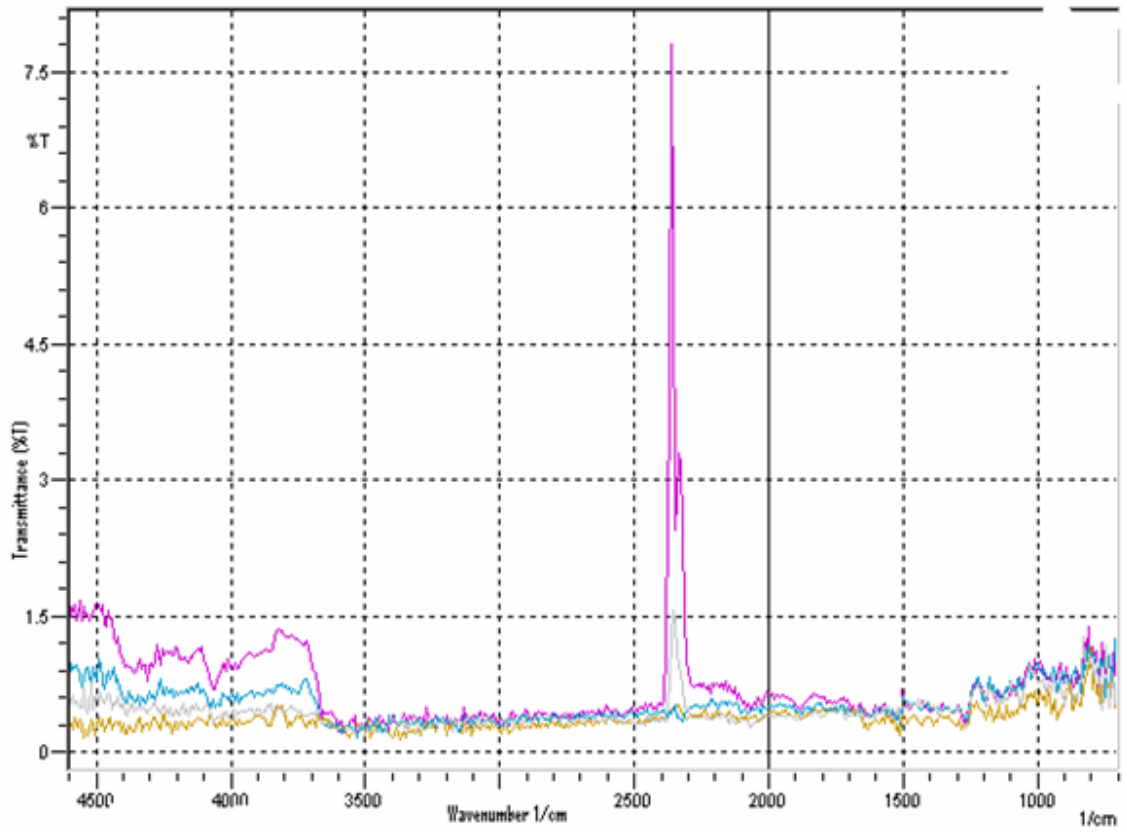


Figure 4

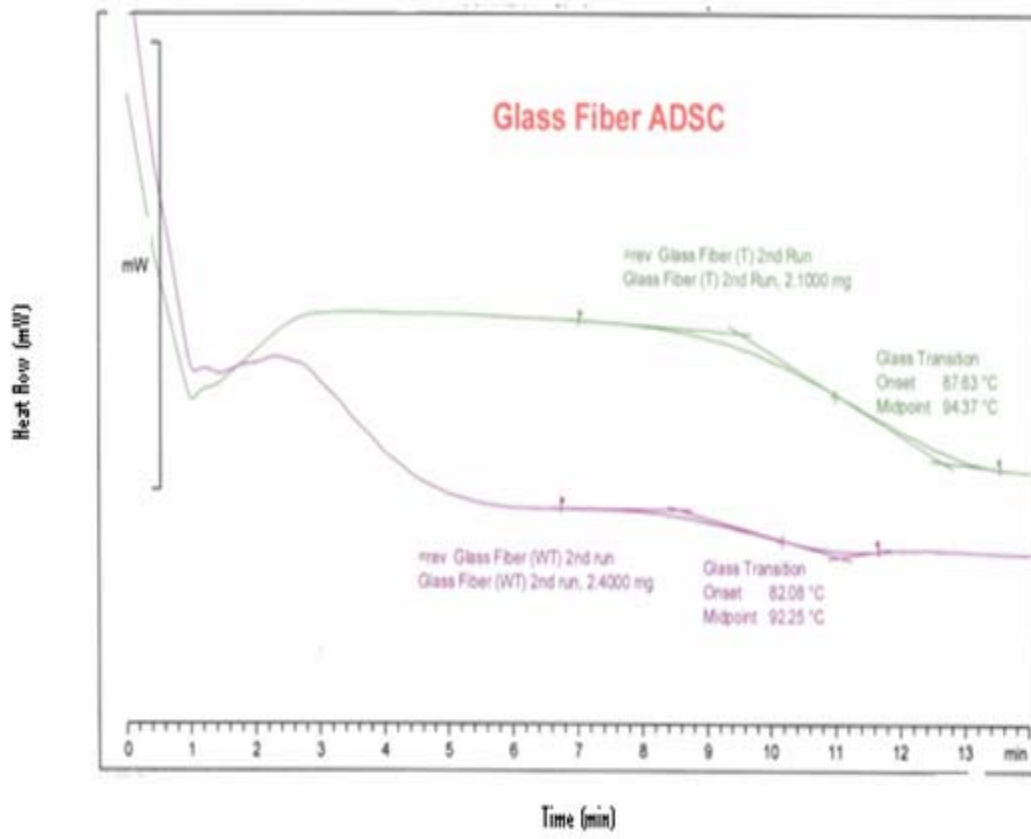


Figure 5

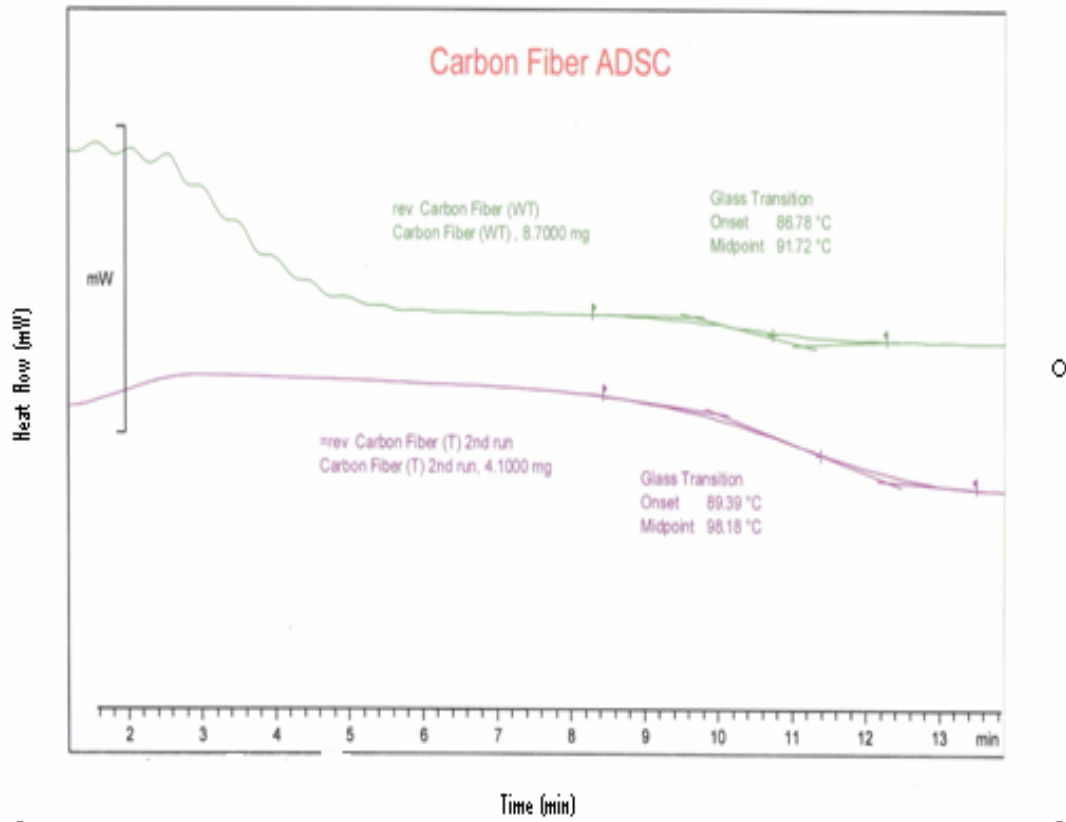


Figure 6

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