

Interface Assessment in Composite Materials

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Abstract:

The state of fiber matrix interface is believed to influence the nature of diffusion modes. A significant weakening often appears at the interface during the hygrothermal ageing. It affects the moisture uptake kinetics and also the reduction of mechanical properties. Absorbance peaks of OH stretching bands were emphasized to study the curing mechanism of epoxy matrix of the micro-composite by FTIR-imaging and ADSC techniques.

1.Introduction:

Advances in composite materials and processing technology are of key importance to aircraft, space industries, defense and automotive materials as well as transportation field.[1]. This is due to their high specific strength, high stiffness and tailorable properties.[2]. The most advanced composites are fiber reinforced polymeric composites. These composites consist of a polymer matrix reinforced with high performance thin-diameter fibers. The drawbacks of FRP composites are low operating temperature,high coefficient of thermal and moisture expansion and low elastic properties in transverse direction.[3]. Fiber-matrix adhesion is a variable to optimized in order to get the best properties and performance in composite materials[4]..An interface is the region of significantly changed chemical composition that constitutes the bond between matrix and reinforcement. The properties of composite materials are strongly influenced by the type of adhesion between the reinforcement and the matrix. The properties depend on the ability of the interface region due to chemical reactions or plasticizing when water intrude the interface.[4]. Proper characterization of composite interfaces, whether it is for chemical, physical or mechanical properties, is extremely difficult because interfaces are buried inside the material [5]. 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 . The structural integrity of polymeric composite materials is strongly influenced by fiber/polymer interfacial region [5]. 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.[6]. 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 .Moisture penetration at the interface contributes free volume of mesoscopic origin in addition with the one existing in the bulk of the matrix phase.[7]. Low temperature conditioning causes strengthening phenomenon due to mechanical keying at the fiber-matrix interface and high temperature act as a softening agent . 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 [8]. 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. The coefficient of thermal expansion of glass fibre and epoxy are different so the moisture absorption causes differential volumetric expansion which leads to localized stresses and strain at the interface [4]. Moisture penetrates into the polymeric composites to lower the internal stresses and sometimes hydroelastic swelling of the polymer occurs to as the constituent macromolecules rearrange to relieve the osmotic pressure generated by the water molecules [6]. Moisture penetration is explained by many techniques in polymer composites.

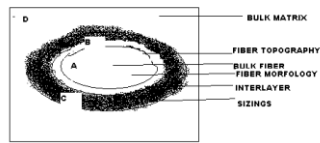


FIG-1 FIBER-MATRIX INTERPHASE(INTERFACE)

FIG-1.Fiber-matrix interphase/interface.

Interphase is a region of chemical inhomogeneity; it is often more susceptible to thermal or chemical degradation than either bulk phase. For this reason, the interphase may provide an easy path into the composite for aggressive agents, notably water. The interphase region is up to few nanometers and the short range forces exist between the monomer segments and the solid surface. These interactions may range from weak dispersion (Van der Waals) forces to chemical attachments [9]. 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. 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. A larger contact area allows for better transfer of load between fiber and matrix and thus maintaining strength. In the present work, Fourier Transform Infrared Spectroscopy (FTIR-imaging) and Alternating Differential Scanning Calorimetry (ADSC) techniques were used to assess the interphase of hygrothermally treated glass/epoxy composite. An FTIR-imaging can be used for the distinct characterization in a particular region whereas ADSC was used to monitor the effect of hygrothermal treatment on the glass transition temperature. A moist environment, coupled with high /low temperature conditions is extremely detrimental for composites. A scientific approach to determine the role of interface in influencing the composite properties. Here work aims at the characterization of the FRP'S by DSC & FTIR imaging techniques with special emphasis on the interface.

2.Experimental Procedure.

Materials

Araldite LY-556 an unmodified epoxy resin based on bisphenol-A and hardener (Ciba-Geigy ,India)HY - 951, aliphatic 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 hygrothermally treated for 100 hours in 95% RH.

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 μm -100 μm . 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, 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. (SHIMADZU). There are certain limitation 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. 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 micro-composite.

Alternating Differential Scanning Calorimetry Analysis (ADSC)

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 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.

3.Results and Discussions

FTIR Measurement

Moisture penetration at the interface contributes free volume of mesoscopic origin in addition with the existing in the bulk of the matrix phase . The OH stretching in polymeric materials occur in the range of 3400-3200 cm⁻¹. Peiyi Wu et al reported that the major difference in absorption of water occurs at about 3450 cm⁻¹ with the increase of aging treatment the intensity of 3450 cm⁻¹ increased and peaks got broader. OH band in IR spectra can be differentiated into three bands, 3610(water hydrogen bonded with epoxy resin), 3450(weak hydrogen bonded with epoxy resin and partially dissolved) and 3240 cm⁻¹(strong water- water hydrogen bonded of cluster of water).

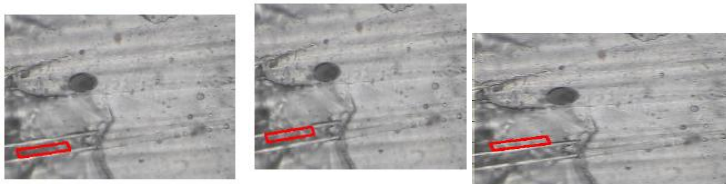


Fig-2 (A) ,(B) ,(C)

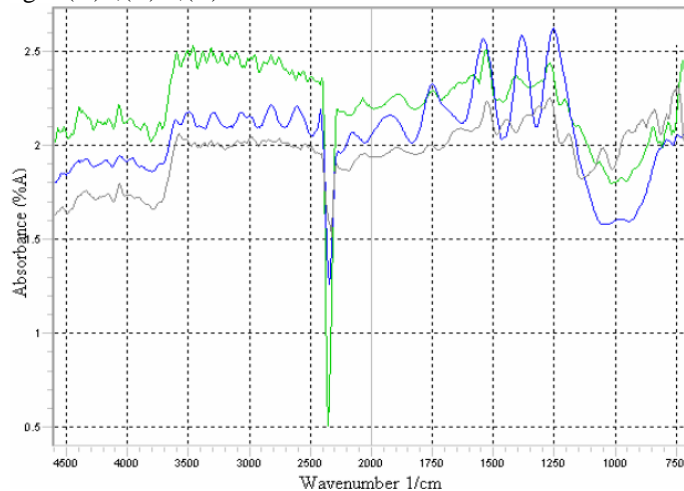


FIG -2(D) The superimposed peaks for untreated glass/epoxy micro-composites from interface to bulk of the epoxy.

Fig.2(A) to 2(C) represents 2D micrographs taken by FTIR spectrophotometer and Fig.2(D) spectra of these micrographs of untreated glass/epoxy micro-composites at different region. In this there is chemical gradient of absorbance from the glass fibre to the bulk of the epoxy resin. The grey line shows the spectral region near the interface of the micro-composites and the blue line is the spectral region away from interface. Finally the green line represents the spectral region in the bulk of the micro composites. During curing the epoxide groups are opened by the amine groups and this may lead to generation of hydroxyl group. Figure 2 represents the superimposed peaks from interface to the bulk phase. The OH absorbance in the bulk region is more than the interface region; this may be due to the varying degree of curing in the bulk region and at the interface. The difference in the curing rate is due to the gradient in the active amine/epoxy ratio from the glass fibre surface to the bulk of the epoxy matrix. The explanation may be that some of the amine group must be reacted with the OH groups of the fibre at the interface and another reason is that the hardener i.e. ethylenediamine used is smaller in diameter than the DGEBA so it is expected to diffuse faster in silane coupling agent at the fibre surface rapidly.

ADSC STUDY: Fig-3 shows the effect of hygrothermal ageing on glass transition temperature(T_g) of glass/epoxy micro-composite. The measurement of T_g is important because it determines the critical service temperature of polymer composite. When polymeric composite are exposed to hygrothermal environment the T_g value decreases. But if ageing time is less then the value of T_g will increases this is due to formation of double hydrogen bond by replacing covalent bond with the silane coupling agent. The formation of hydrogen bond can increase the moisture absorption, which is exothermic in nature. If T_g value increases the mechanical properties of composite increases.

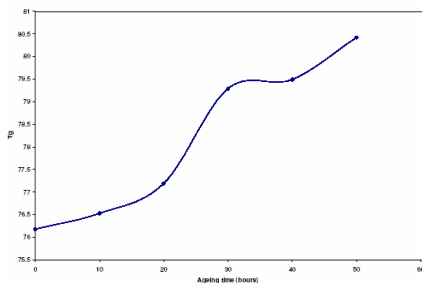


Fig 3-Glass transition temperature at varying hygrothermal conditioning time.

If ageing time is increases the plasticization takes place and T_g will decreases. But for the requirement of time for this is still under research.

4. Conclusion:

In the present work, hygrothermal treatment of bisphenol-A based epoxy resin reinforced with glass fiber (micro-composite) were monitored. The curing process of an epoxy system at the interface formed with a silane coated glass fiber was studied by FTIR imaging. The results of FTIR-imaging and DSC suggest that there is a variation in the chemical behavior after hygrothermal conditioning. The increase of OH absorbance intensity in the FTIR spectra shows that curing is fast in the bulk region in comparison to fibre/matrix interface. Chemically specific images for OH and H-N-H with the system were obtained. The moisture sorption at the interface by the matrix phase is a very complex phenomenon due to different absorption at the interface i.e. water molecule forms strong hydrogen bond with the epoxy resin and polyester resin or less strongly bonded hydrogen bond. If the structure near the interface changes the stress transfer from the matrix to the fibre will change and ultimately the overall performance of FRP composite will be change. 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. 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 may solve the problem of physio-chemical analysis of interface of composites.

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References:

1. [Jang B Z, Advanced Polymer Composites: Principle and Applications, ASM International, Materials Park, OH, 1994.]
- 2.[B.C Ray, "Temp effect during humid aging on interfaces of glass and carbon fiber reinforcing epoxy composite." J .Colloid and interface science ,**298**,111(2006).]
3. [Kim J K, Mai Y W. Engineered Interfaces in Fiber Reinforced Composites. New York: Elsevier, 1998.]
4. [Lee S M. Handbook of Composite Materials. New York: VCH Publishers, 1993.]
- 5.[Neeti Sharma, M.Surendra Kumar, B.C.Ray, "Study the Effect of Hygrothermal Ageing on Glass/Epoxy Micro-composites by FTIR Imaging and Alternating DSC Techniques" , Journal of Reinforced Plastics and Composites, **27**, 1625(2008).]
6. [J.Gonzalez Benito, "The nature of the structural gradient in epoxy curing at a glass fiber/epoxy matrix interface using FTIR imaging", J . Colloid and interface science -267, 326(2003).]
- 7.[Ling Li,Shu Yong Zhang,M.Liu, Y.Ding,X.W.Luo,Z.Pu,W,Zhou,and S.Li, "water transportation in Epoxy Resin". J.chemistry of material ,**17**,839(2005).]
- 8.[Callister W D. Materials Science and Engineering-An Introduction. Asia: John Wiley and Sons, 2001.]
- 9 [Sylvain .p, corinne .R ,C.S Gaillet, "Free/bound water absorption in epoxy adhesive polymer ," J polymer , **46**,10733(2005)].
10. [Wu P, Siesler H.W, "Water diffusion into epoxy resin" ,J chemical physics letters, **374**,74(2005)]
11. [Poljansci I, Krajnc ,"ADSC, isothermal curing of the epoxy resin" J . Acta chimica Slovenica, **50**,461(2005)]
12. [Tsenoglou C J ,Pavlidou S,Papaspyrides C D ,"Evaluation of interfacial relaxation due to water absorption in fiber-polymer composites" J ,composite science and technology, 66, 2855(2006)].
- 13.[Hull D, Clyne T W. An Introduction to Composite Materials. Cambridge, UK: Cambridge Univ. Press, 1996"].
- 14[T.S Ellis & F.E Karasz, "Interaction of epoxy resins with water: the depression of Tg. J Polymer, **25**, 664(1983)]
- 15.[D.Tonchev,S.O Kasap ," Effect of aging on glass transition measurements by temperature modulated DSC" ,J Material science and engg. ,**A-328**,62(2001)].