2008
Interface Assessment of FRP by Alternating DSC and FTIR Imaging Techniques

A THESIS SUBMITTED IN PARTIAL FULFILLMENT
OF THE REQUIREMENT FOR THE DEGREE OF

Bachelor of Technology
in
Metallurgical and Materials Engineering

By
KUNTAL DAS
&
ASHUTOSH A. PRIYADARSHI

Under the Guidance of

Prof. B.C.RAY

Department of Metallurgical and Materials Engineering
National Institute of Technology
Rourkela

Rourkela

2008

National Institute of Technology

Rourkela

CERTIFICATE

This is to certify that the thesis entitled, "**Interface Assessment of FRP by Alternating DSC and FTIR Imaging Techniques**" submitted by KUNTAL DAS and ASHUTOSH A. PRIYADARSHI in partial fulfillment of the requirements for the award of Bachelor of Technology Degree in Metallurgical and Materials Engineering at the National Institute of Technology, Rourkela (Deemed University) is an authentic work carried out by them under my supervision and guidance.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University / Institute for the any Degree or Diploma.

Date:

Prof. B.C.RAY
Dept. of Metallurgical and Materials Engineering
National Institute of Technology
Rourkela-769008

ACKNOWLEDGEMENT

We record our sincere gratitude to Prof. B.C.RAY, Dept. of Metallurgical and Materials Engineering for assigning us the project “Interface Assessment of FRP by Alternating DSC and FTIR Techniques”. It is not possible to acknowledge sufficiently his important contribution of talent and time given unselfishly in proceeding with this work. His overall constructive criticism has helped us to present our work in the present form.

We wish to record our gratitude to our project coordinator Prof. A.K.Panda for helping us at each and every step in bringing out this report.

We are also thankful to Prof. U.K.Mohanty, Dept. of Metallurgical and Materials Engineering for permitting us to access the SEM. We would also like to thank

Mr. Sameer Pradhan and Mr. Rajesh Pattnaik of Metallurgical and Materials Engineering Dept. for helping us in DSC measurements, three point bend test and SEM of our samples.

Last but not the least, we would like to thank all our friends who have been a constant source of help to us.

Kuntal Das

Ashutosh A. Priyadarshi

B.Tech

Metallurgical & Materials Engineering

CONTENTS

Abstract…….....i

List of Figures…….ii

Chapter 1 INTRODUCTION……1-9

Chapter 2 WHY WE HAVE TAKEN THIS WORK…….10-11

Chapter 3 LITERATURE REVIEW……..12-20

3.1. **Fiber Reinforced Composite……...13**

3.1.1. **Glass Fibers…….14**

3.1.2. **Epoxy……16**

3.2. **Hygrothermal Diffusion…….....17**

3.3. **Differential Scanning Calorimetry…….18**

3.4. **FTIR-Imaging……..19**

Chapter 4 EXPERIMENTAL WORK……21-23

4.1. **Materials……..22**

4.2. **Experimental Method…….22**

Chapter 5 RESULTS, DISCUSSION & INTERPITATION……24-41

5.1. **DSC measurements…….25**

5.1.1**. Microwave heating……..26**

5.1.2. **UV heating ……...27**

5.1.3. **Hygrothermal treatment…….29**

5.2. **FTIR measurements……....30**

Chapter 6 CONCLUSION……42-43

Chapter 7 SCOPE FOR FUTURE WORK……44-45

REFERENCES……..46-50

ABSTRACT

The quality of the interface of any fiber reinforced polymer (FRP) composite material is critical for its structural and functional integrity. The present work gives an assessment of the degradation in glass fiber-reinforced epoxy matrix composite under thermal and humid conditions. Micro-composites have been employed for this study in order to get a better picture of the physical and chemical changes taking place at the interface. UV and microwave heating techniques were used for the curing process. The samples were exposed to a relative humidity of 95% for 10 hours at a temperature of 60ºC. The DSC (Differential Scanning Calorimetry) curves manifested an increase in glass transition temperature (T_g), of the composite material, due to curing process and hygrothermal exposure. The FTIR (Fourier Transform Infrared Spectroscopy) images further supported the assumption that increase in T_g may be attributed to formation of hydrogen double bonds. Some SEM photographs were also taken to depict the physical changes occurring in the composite, especially in the resin.

Keywords: Glass/epoxy composites, UV and Microwave curing, FTIR, DSC.

LIST OF FIGURES

Fig.1.1 Interface and Interphase……..**10**

Fig.1.2. Step/ramp curing diagram…….**12**

Fig.1.3.Compression residual forces on glass fibers…….1**3**

Fig.1.4. FTIR spectra of epoxy-amine mixture as a function of wavenumber…….**14**

Fig.1.5. Image showing OH absorbance gradient along the interface. OH concentration increases in the direction away from fiber…….**15**

Fig.1.6. AFM images showing topography changes in AS4/VRM34 (carbon/epoxy) composite exposed to 100% RH for different periods of time……**15**

Fig.3.1. Polyhedra network structure of glass fiber……..**23**

Fig.3.2 Structure of DGEBA…….**24**

Fig.3.3.Heat flux DSC……**26**

Fig.3.4. Power compensated DSC……..**26**

Fig.3.5. FTIR-Imaging Principle……**27**

Fig.4.1. (a) Mettler-Toledo 821 with intra cooler for DSC measurements and (b) reference-sample chamber…….**30**

Fig.4.2. (a) FTIR spectrophotometer, (b)-(c) AIM-800 Automatic Infra red Microscope, (d) 2-D view taken by the microscope equipped video camera…….**30**

Fig.5.1. DSC curves for original, cured and hygrothermally treated samples……**32**

Fig5.2(a). DSC curve for original sample…….**34**

Fig.5.2(b). DSC curve for Microwave cured sample……**34**

Fig.5.2(c). DSC curve for UV cured sample…….**35**

Fig.5.2(d). DSC curve for UV cured hygrothermally treated sample……..**37**

Fig.5.2(e). DSC curve for Microwave cured hygrothermally treated sample……..**37**

Fig.5.3(a)-(c). 2D micrographs of original samples at different positions, (d)-(f)corresponding FTIR spectra…….**38**

Fig.5.4.(a)-(c) 2D micrographs of UV samples at different positions, (d)-(f) corresponding FTIR spectra……..**40**

Fig.5.5.(a)-(f) 2D micrographs of microwave cured samples at different positions and corresponding FTIR spectra……**43**

Fig.5.6.(a)-(d) 2D micrographs of UV cured hygrothermally treated cured samples at different positions and corresponding FTIR spectra……...**44**

Fig.5.7.(a)-(f) 2D micrographs of microwave cured hygrothermally treated cured samples at different positions and corresponding FTIR spectra……..**45**

Fig. 5.8.1. SEM electron micrograph of the hygrothermally treated sample……**47**

Fig.5.8.2. SEM micrograph showing matrix crazing……**48**

Fig.5.8.3. SEM micrograph showing well-developed crack in the matrix……**48**

Chapter 1

INTRODUCTION

1. INTRODUCTION

The degree of environmental degradation in FRP composites is closely related with percentage moisture absorption [**1**]. The fibrous composites are increasingly being used in various applications owing to their excellent properties like high specific strength and modulus, high specific strength and controlled anisotropy. But unfortunately polymeric composites are susceptible to heat and moisture when operating in changing environmental conditions [**2**]. It is necessary to understand the damage and failure mechanisms of these materials under severe conditions such as high temperature and high humidity before they can be put into application confidently [**3**]. The properties of the composite depend upon the ability of the interface to transfer stress from matrix to the reinforcement [**4**]. Stress concentrations develop at the interface due to the differences in thermal expansion coefficient between the resin and the fiber phases [**5**], cure shrinkages(in thermosetting matrices) and crystallization(in some thermoplastics) [**6**]. Composite properties are also affected by the presence of structural defects such as voids, impurities and microcracks which tend to concentrate at the interface region [**7**].

Moisture may penetrate into the polymeric composite material principally by diffusion [**2**, **3**]. In addition to this there are other possible mechanisms: capillarity along the fibers, the interface and transport by microcracks [**8**]. Moisture absorption leads to plasticization and interfacial degradation [**9-10**]. Thermal ageing also leads to several chemical and physical changes like oxidation, crosslinking and viscoelastic effects [**11**]. It has been observed that thermal ageing of organic matrix composites in air leads to their superficial oxidation leading to “spontaneous” cracking without the application of external loading [**12,13**].

The growing number of uses for FRPs in many engineering application has made the issue of interface (or more properly termed, interphase [**14**]), a major focus of interest in the design and manufacture of composite. A classic definition [**15**] of the *interface* in fiber reinforced in the fiber reinforced polymers is a surface formed by a common boundary of reinforcing fiber and the matrix that is in contact with and maintains the bond in between for the transfer of loads. In contrast, the *interphase* is the geometrical surface of the classic fiber-matrix contact as well as the region of finite volume extending there from, wherein the chemical, physical and mechanical properties vary either continuously or in a stepwise manner between those of the bulk fiber and matrix material. Usually, it is accepted that the interphase region has a thickness of 100 to 500 nm [**16**]. The polymer structure near the interface is different from that in the bulk matrix [**17**].

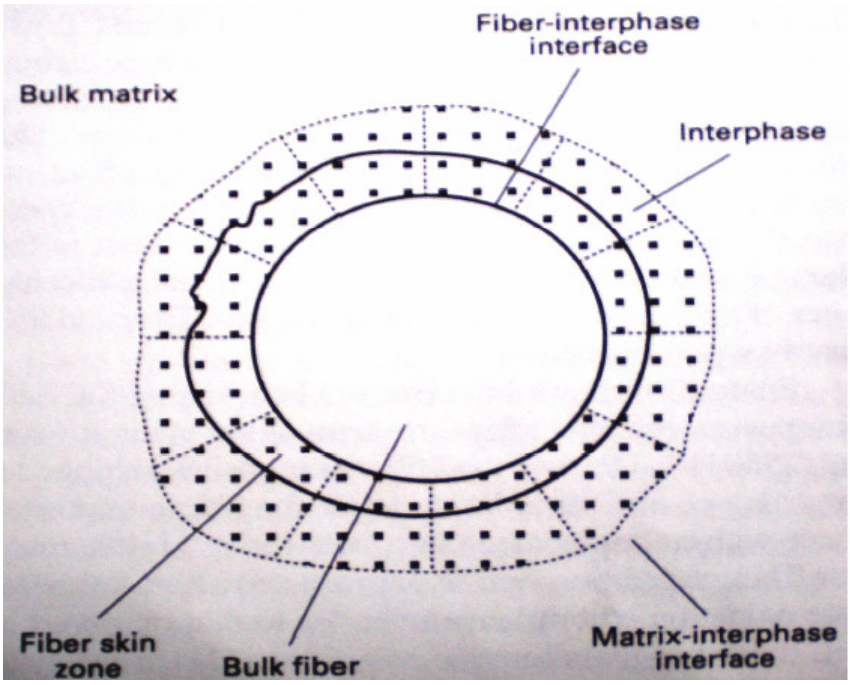


Fig.1.1 Interface and Interphase[18]

The water molecules can be present in the epoxy network either in free form or bound form [**19**]. With NIR-FTIR (near infrared FTIR) spectra water molecules with non-hydrogen bond (free water), single hydrogen bond (single bound water) and double hydrogen bonds (double bound water) can be observed [**20**]. The water vibration bands ranges from 3200-3600 cm-1 in the FTIR images. These are split into two separate bands, indicating two separate states; one confined to relatively free water(at high wavenumbers) and the other could be attributed to bound water(at low wavenumbers) [**21,22**]. The equilibrium water content depends not only on the free volume in the matrix (free water) but also on the number of hydrogen bonds formed between the water and epoxy network polar groups (bound water). For the formation of hydrogen bond there must be molecular rearrangement in epoxy network, to bring the hydrophilic polar groups in association with water molecules [**23, 24**]. This may result in decrease of free volume and also the number of free water molecules, which reside in this free volume. Rearrangement of polymer chains is endothermic, while forming hydrogen bonds which can facilitate the water sorption, is exothermic. The energy required for water sorption is provided by the hydrogen bond formation [**19**]. A tentatively proposed mechanism, by Zhang et al., for diffusion of water in the epoxy network is described below.

H-O-H + P1 (polar group 1) → H-O-H · · · P1 (· · · represents hydrogen bond)

- Open a new polar group P2
- Diffusion of water from P1 to P2.

P1· · ·H-O-H· · ·P2 (Water molecule with double hydrogen bonds)

H-O-H + P2 → H-O-H· · ·P2

Currently, there are three basic types of isobaric curing processes for epoxy matrix composites, room temperature curing, isothermal high temperature curing, and step/ramp curing. A sample which is cured at room temperature without any heating and cooling thermal history is called a room temperature cured sample. In isothermal high temperature curing, the sample and the mold are rapidly heated up to a desired temperature level and held there until the sample is considered to be sufficiently cured. It is then cooled to ambient. The step/ramp curing method does not isothermally cure the sample at only one chosen temperature, unlike room and isothermal high temperature curing. Instead, in this method, the sample is heated up progressively to different temperatures from lower levels to higher levels, and held at each temperature level for a determined period of time, as shown in Figure 1.2. When the number of the steps becomes large, the step curing approximates to a ramp curing process [**25**].

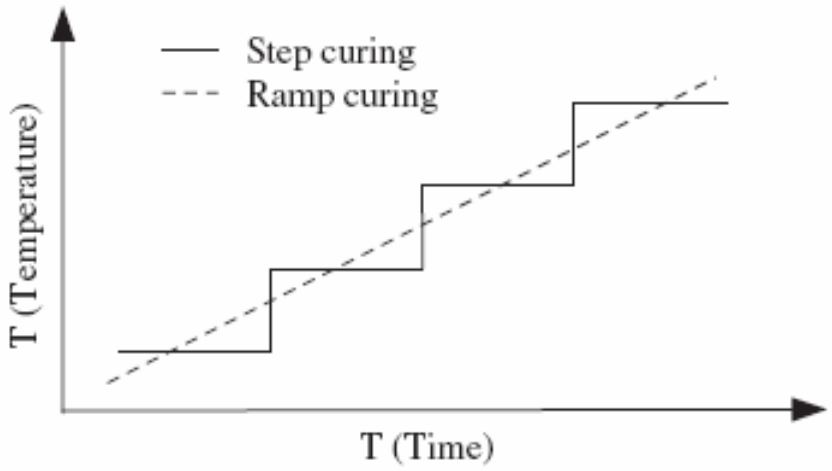
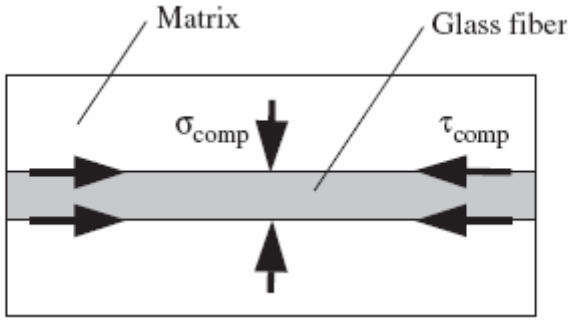


Fig.1.2. Step/ramp curing diagram [25]

In addition, the conversion (cross-linking) extent/rate (the ratio of cross-linked volume to the volume of the whole sample) of the room temperature curing process is much lower than that of the high temperature curing process. As known, a higher conversion

rate/extent results in better properties, thus making the use of high temperature curing a beneficial choice.

During the curing process, liquid to solid state transformation leads to matrix shrinkage. This induces residual stresses in the composite structure owing to the geometrical constraints from the fiber [**26-28**]. Epoxy shrinks to a greater extent as compared to glass fiber, owing to its higher coefficient of thermal expansion. This generates both longitudinal and radial compressive residual stresses on the fiber as shown in figure 1.3. The radial component (σ_{comp}) acts as a clamping stress at the fiber-matrix interface and increases the frictional force at the fiber-matrix boundary during fiber pull-out. Since fiber pull-out is the major failure mechanism, higher pull-out resistance results in better mechanical properties of composites during tensile, flexural, shear and impact tests.



.

Fig.1.3. Compression residual forces on glass fibers [25]

Unlike the radial residual force, the longitudinal component (τ_{comp}) weakens the fiber-matrix bonding. Therefore, an optimal combination of mechanical properties of the composite can be attained by an optimal residual force level.

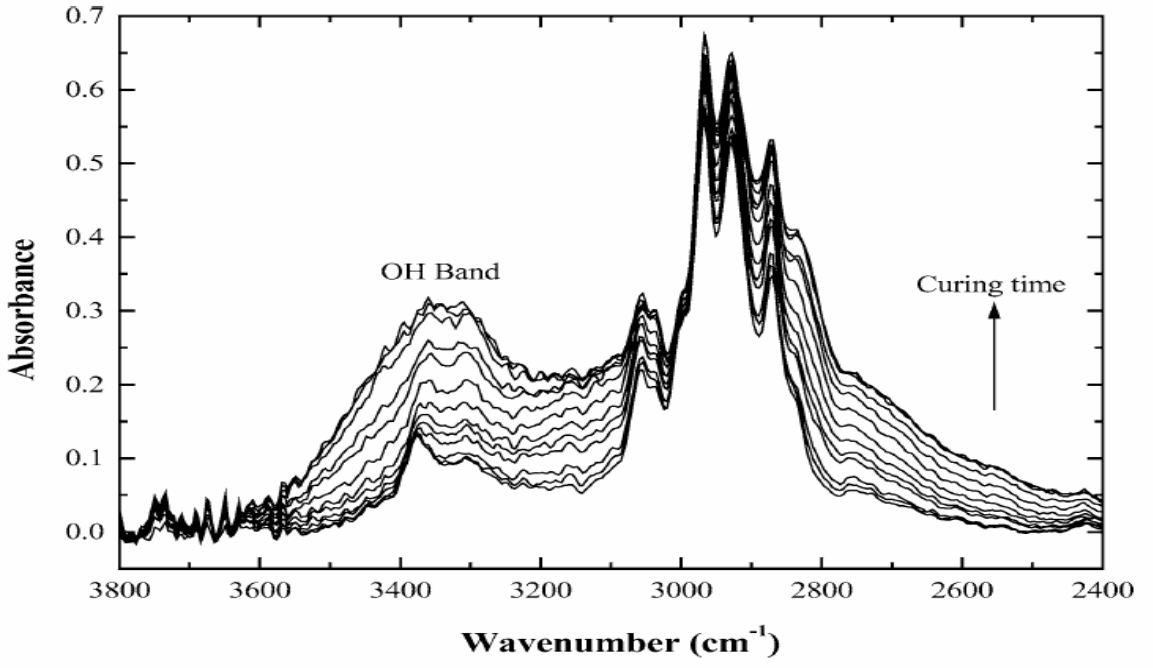


Fig.1.4. FTIR spectra of epoxy-amine mixture as a function of wavenumber [6]

Fig.1.4. shows three distinct regions [**6**] in the FTIR spectra of the epoxy-amine mixture as the curing proceeds. These are: (1) C-H stretching bands(3100-2700 cm-1) which doesn't show great changes, as should happen if there is no change in different groups with the C-H bonds, (2) H-N-H stretching band(centered at 3375 cm-1) which decreases continuously. This happens because during curing the epoxy ring opens up by the reactive amine group generating secondary amines and hydroxyl groups. These secondary amines further react with epoxy rings simultaneously with primary amines generating tertiary amines and hydroxyl groups. So the concentration of OH increases gradually, and (3) OH stretching band (3300 cm-1) continuously increases, as already discussed. The OH absorbance shows a typical gradient along the glass-epoxy interphase as shown in the fig1.5.

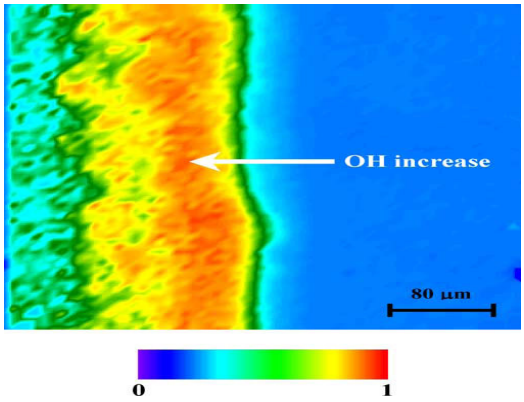


Fig.1.5. Image showing OH absorbance gradient along the interface. OH concentration increases in the direction away from fiber[6]

OH absorbance is higher in the region near the glass fiber in the initial stages. However, as the curing proceeds there is an increase in OH concentration at the polymer. This suggests that curing rate increases with distance from the fiber. In the interphase region there is a gradient in the structure of epoxy matrix from surface to the fiber.

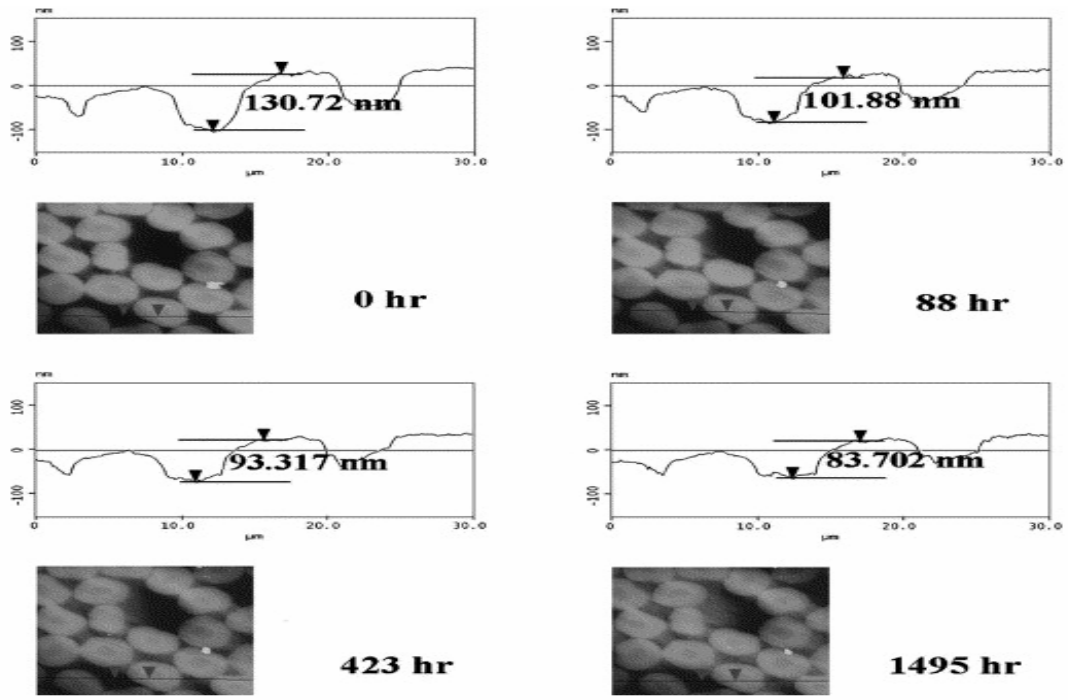


Fig.1.6. AFM images showing topography changes in AS4/VRM34 (carbon/epoxy) composite exposed to 100% RH for different periods of time [3].

Fig.1.6 shows AFM (Atomic Force Microscope) images indicating moisture absorbance in the resin. The difference between the fiber and the matrix got decreased with increase in exposure time. This is due to the swelling of resin due to moisture absorption [3]. Fiber tilting can also be observed due to slipping of fibers relative to epoxy. This indicates weak bonding between fiber and matrix.

Chapter 2

WHY WE TOOK UP THIS WORK?

2. WHY WE TOOK THIS PROJECT ?

The basic reason for working on such a topic arises from the fact that composites are vulnerable to environmental degradation. A moist environment, coupled with high or low temperature conditions is extremely detrimental for composites. The main focus of this work was to apply a scientific approach to determine the role of interface in influencing the composite properties.

There have been many efforts by the researchers in the last few decades to assess the interface in glass fiber reinforced epoxy composites. Many works have also targeted the correlation between the mechanical properties of the material and the moist environment or similar hygrothermal conditions, subjected to thermal shocks, spikes, ambient & sub-ambient temperatures.

But most research has been on the mechanical aspects rather than the physical & chemical interface and how this brings in change in the internal mechanical properties and affects a variety of other morphological changes.

The focus of our research has been to understand the physical changes that take place at the bonding interface between the fibres and the matrix, as it is of prime importance due to its link to the stress transfer, distribution of load, and it also governs the damage accumulation & propagation. The effect of UV and microwave curing on the glass transition temperature (T_g) has also been studied in the present work.

A better assessment of this interface can ensure better analysis of the fracture mechanics of the composites and thus improve their structural reliability. Thus our project work aims at the characterization of the FRP'S by DSC and FTIR Imaging techniques with special emphasis on the interface.

Chapter 3

LITERATURE REVIEW

3. LITERATURE REVIEW

3.1. Fiber Reinforced Composite

A fiber-reinforced composite is not simply a mass of fibers embedded within a polymer, metal or ceramic matrix. A composite consists of fibers embedded in or bonded to a matrix with distinct interfaces (or interphase) between the two constituent phases. The fibers are usually of higher strength and modulus and serve as the principal load carrying members. The matrix must keep the fibers in a desired location and orientation, separating fibers from each other to avoid mutual abrasion during periodic straining of composite. The matrix acts as a load transfer medium between the fibers, and in less ideal cases where loads are complex, the matrix may even have to bear loads transverse to the fiber axis. Since the matrix is generally more ductile than the fibers, it is the source of composite toughness. The matrix also serves to protect the fibers from environmental damage before, during, and after composite processing. In a composite, both fibers and the matrix retain their identities and yet result in many properties that cannot be achieved with either of the composites acting alone.

A variety of fibers are available for use in composites. The most commonly used fibers in polymer matrices include carbon, glass, and aramind (e.g. Kevlar®) fibers. Boron fibers are expensive and are currently used in military and aerospace applications. Also in still limited use are alumina, silicon carbide, mullite, silicon nitride and other ceramic fibers and metal wires. The key features of low fiber density and high strength and moduli give rise to high specific strength(strength/density) and specific stiffness(stiffness/density) properties of composites.

The matrix material may thermoplastic or thermoset polymer. The thermosetting polymers used include unsaturated polyesters, vinyl ester, epoxides, phenolics, polyimides and modified versions of these resins such as interpenetrating networks. Thermoplastic resins include poly(phenyl sulfide) (PPS), poly(ether ether ketone) (PEEK), and poly(ether ketone ketone) (PEKK).

Fibers

1. Glass fibers
2. Carbon fibers
3. Aramid fibers

3.1.1. Glass Fibers

The most common reinforcement for the polymer matrix composites is a glass fiber. Most of the fibers are based on silica (SiO_2), with addition of oxides of Ca, B, Na, Fe, and Al. The glass fibers are divided into three classes -- E-glass, S-glass and C-glass. The E-glass is designated for electrical use and the S-glass for high strength. The C-glass is for high corrosion resistance, and it is uncommon for civil engineering application. Of the three fibers, the E-glass is the most common reinforcement material used in civil structures. It is produced from lime-alumina-borosilicate which can be easily obtained from abundance of raw materials like sand. The glass fiber strength and modulus can degrade with increasing temperature. Although the glass material creeps under a sustained load, it can be designed to perform satisfactorily. The fiber itself is regarded as an isotropic material and has a lower thermal expansion coefficient than that of steel.

1**. E-glass (electrical)**

Family of glassed with a calcium aluminum borosilicate composition and a maximum alkali composition of 2%. These are used when strength and high electrical resistivity are required.

2. **S-glass (tensile strength)**

Fibers have a magnesium aluminosilicate composition, which demonstrates high strength and used in application where very high tensile strength required.

3. **C-glass (chemical)**

It has a soda lime borosilicate composition that is used for its chemical stability in corrosive environment. It is often used on composites that contain or contact acidic materials.

Composition of E-Glass

Constituent	Weight percentage
SiO2	54
Al203	14
CaO+MgO	12
B2O3	10
Na2O+K2O	Less than 2
Impurities	Traces

TABLE 3.1: COMPOSITION OF E-GLASS

Comparison of properties of Glass Fiber

Typical Properties	E-Glass	S-Glass
Density (g/cm^3)	2.60	2.50
Young's Modulus (GPa)	72	87
Tensile Strength (GPa)	1.72	2.53
Tensile Elongation (%)	2.4	2.9

TABLE 3.2: COMPARISON OF PROPERTIES OF GLASS FIBERS

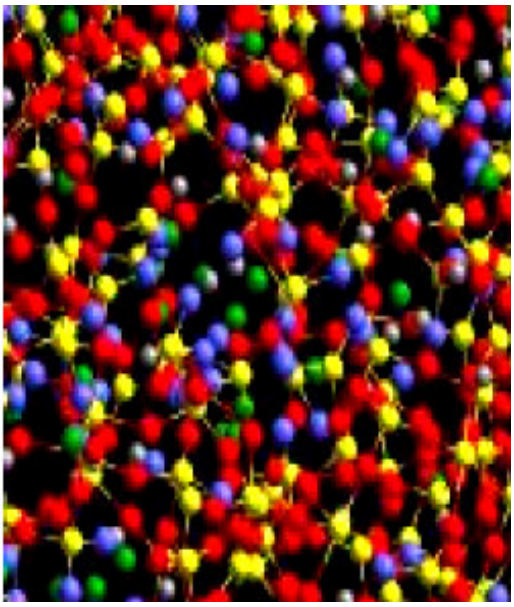


Fig.3.1. Polyhedra network structure of glass fiber

3.1.2 Epoxy

Epoxy resins are relatively low molecular weight pre-polymers capable of being processed under a variety of conditions. Two important advantages of these resins are overunsaturated polyester resins are: first, they can be partially cured and stored in that state, and second they exhibit low shrinkage during cure. However, the viscosity of conventional epoxy resins is higher and they are more expensive compared to polyester resins. The cured resins have high chemical, corrosion resistance, good mechanical and thermal properties, outstanding adhesion to a variety of substrates, and good and electrical properties. Approximately 45% of the total amount of epoxy resins produced is used in protective coatings while the remaining is used in structural applications such as laminates and composites, tooling, moulding, casting, construction, adhesives, etc.

Epoxy resins are characterized by the presence of a three-membered ring containing two carbons and an oxygen (epoxy group or epoxide or oxirane ring). Epoxy is the first liquid reaction product of bisphenol-A with excess of epichlorohidrin and this resin is known as

diglycidylether of bisphenol A (DGEBA). DGEBA is used extensively in industry due to its high fluidity, processing ease, and good physical properties of the cured of resin.

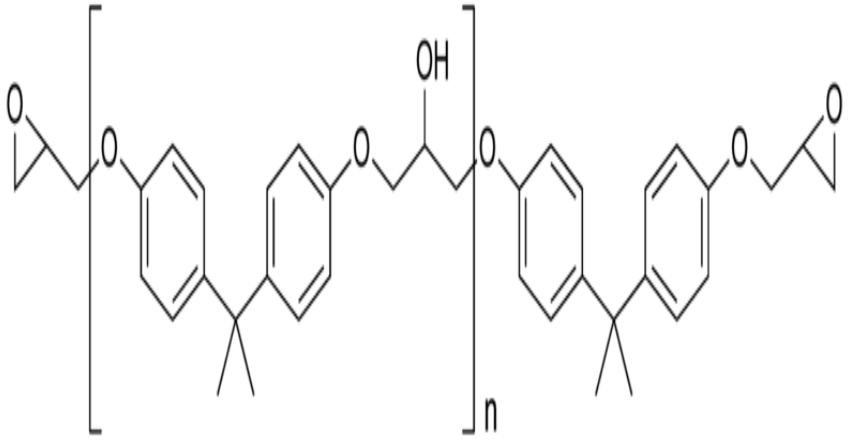


Fig.3.2 Structure of DGEBA

3.2. Hygrothermal Diffusion

Hygrothermal Diffusion usually takes place in presence of thermal and moisture gradients. In many cases water absorption obeys Fick's Law and diffusion is driven by the moisture concentration gradient between the environment and material producing continuous absorption until saturation is reached. The atoms migrate from region of higher concentration to that of lower concentration. The rate of diffusion increases rapidly with the rise in temperature. The concentration gradient of moisture is developed due to the non-uniform distribution of moisture. The presence of imperfections and internal stresses also accelerates the process of diffusion. Epoxy resin absorbs water from the atmosphere from the surface layer reaching equilibrium with the surrounding environment very quickly followed by diffusion of water into all the material. The water absorbed is not usually in liquid form but consists of molecules or group of molecules.

linked by hydrogen bonds to the polymer. In addition water can be absorbed by capillary action along any crack which may be present or along the fiber-matrix interface.

The Fickian diffusion process is influenced mainly by two factors:

(a) The internal (fiber volume fraction and its orientation)

(b) The external (relative humidity and temperature).

Non-Fickian behavior:

Fickian behavior is observed in the rubbery state of polymers but often fails to diffusion behavior in glassy polymers. The deviation from Fickian behavior occurs when:-

(a) Cracks or delamination develops.

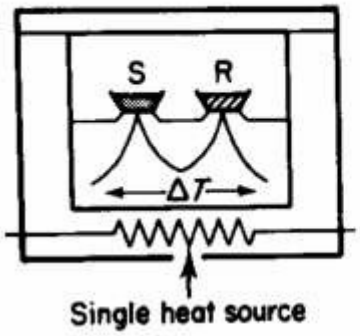
(b) Moisture diffusion takes place along the fiber matrix interface.

(c) Presence of voids in the matrix.

3.3. Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) is a technique for measuring the energy necessary to establish a nearly zero temperature difference between a substance and an inert reference material, as the two specimens are subjected to identical temperature regimes in an environment heated or cooled at a controlled rate. There are two types of DSC systems in common use. In power-compensation DSC (Fig. 3.3) the temperatures of the sample and reference are controlled independently using separate, identical furnaces. The temperatures of the sample and reference are made identical by varying the power input to the two furnaces. In heat-flux DSC (Fig 3.4), the sample and reference are connected by a low-resistance heat-flow path (a metal disc). The assembly is enclosed in a single furnace. Enthalpy or heat capacity changes in the sample cause a difference in its temperature relative to the reference; the resulting heat flow is small compared with that

in differential thermal analysis (DTA) because the sample and reference are in good thermal contact. The temperature difference is recorded and related to enthalpy change in the sample using calibration experiments.



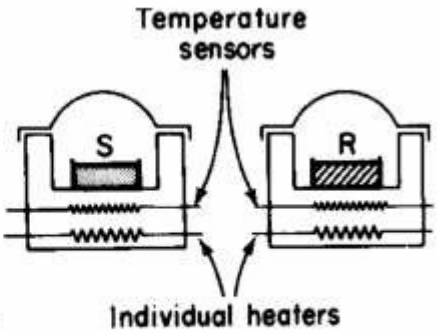


Fig.3.3.Heat flux DSC. **Fig.3.4. Power compensated DSC.**

3.4. FTIR-Imaging

The FTIR measuring principle is a measurement with IR light. Contrary to NDIR with a narrow wave length area by means of an optical filter, the scan area of the IR wave length by use of the FTIR measuring principle is large. The principle of FTIR is that the gas to be analyzed is led through a cuvette with an IR light source at one end that is sending out scattered IR light, and a modulator that "cuts" the infra red light into different wave lengths. At the other end of the cuvette a detector is measuring the amount of IR light to pass through the cuvette. Like the NDIR measuring principle it is the absorption of light at different wave lengths that is an expression of the concentration of gasses to be analyzed. By data processing, Fourier Transformation mathematics is used to turn the measured absorption values into gas concentrations for the analyzed gasses. As the light, when using the FTIR measuring principle, is modulated into many different wave

lengths, it is possible to analyze many different gasses in the same instrument; such as CO, H_2O, SO_2, NO, NO_2, HCl, HF, NH_3.

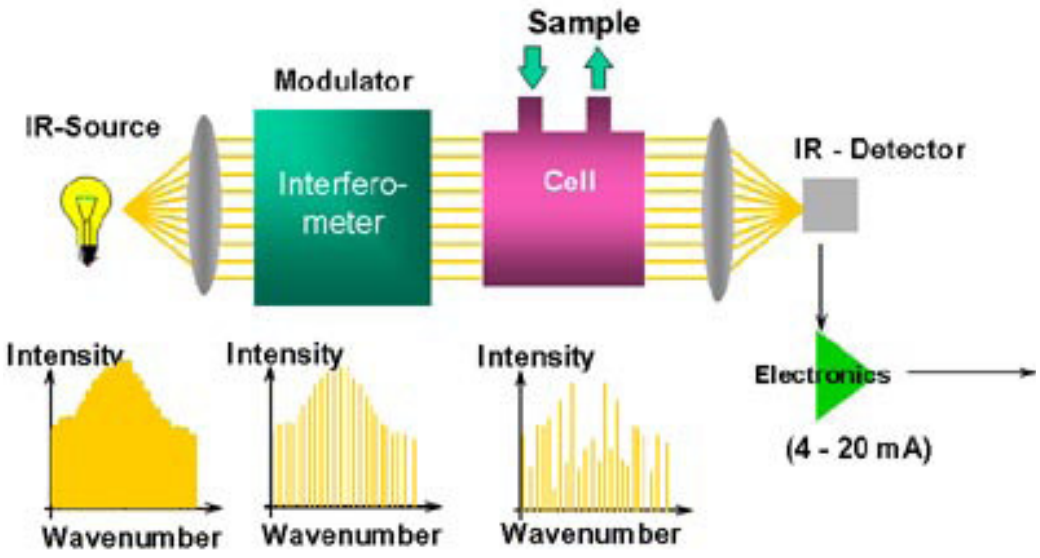


Fig.3.5. FTIR-Imaging Principle

Chapter 4

EXPERIMENTAL PROCEDURE

4. EXPERIMENTAL PROCEDURE

4.1. Materials

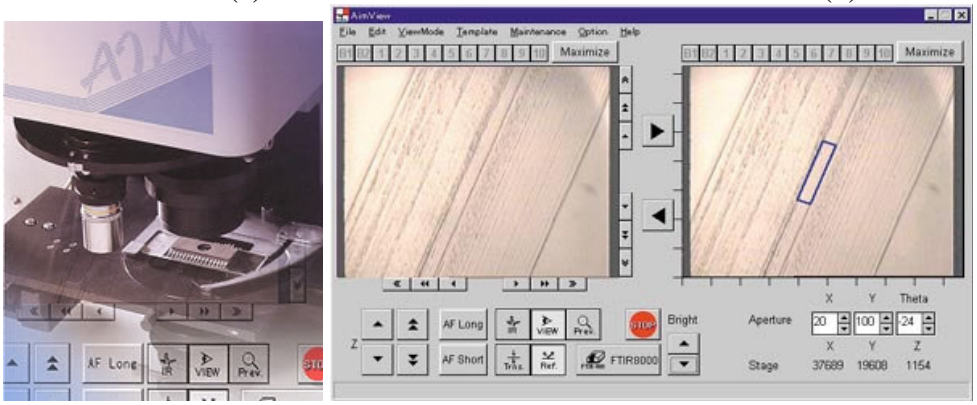
Microcomposite samples were prepared from woven-roving E-glass fibers (Saint Gobain) and epoxy resin (Ciba-Geigy, araldite LY-556 and hardener HY-951). There was no sizing treatment given to the fibers. The weight fraction of fiber was kept 0.60. The composite samples were prepared by hand lay-up method.

4.2. Experimental Method

The samples were cured using UV and microwave techniques. All the samples were divided into two lots- one to be cured using UV radiation (wavelength 384 nm) for about 100 hours, and another lot was treated with microwave for 40 seconds. Some of the cured samples were hygrothermally treated in a Brabender climatic chamber, maintaining a relative humidity of 95% at a temperature of 60 ºC for 10 hours. A comparative study was carried with the original and treated samples using alternating DSC 822^{e} (Mettler Toledo), using the STAR software Alternating DSC (ADSC) module and FTIR-imaging (AIM-800 Automatic Infra red Microscope (SHIMADZU)) techniques. The glass transition temperature (T_g) was the criterion used for comparison, which was very well detected by the DSC curves for each sample. The FTIR imaging revealed the chemistry behind degradation process.

Fig.4.1. (a) Mettler-Toledo 821 with intra cooler for DSC measurements and (b) reference-sample chamber.

(a) (b)



(b) (d)

Fig.4.2. (a) FTIR spectrophotometer, (b)-(c) AIM-800 Automatic Infra red Microscope, (d) 2-D view taken by the microscope equipped video camera.

Chapter 5

RESULTS, DISCUSSION & INTERPRETATION

5. RESULT & DISCUSSION

5.1. DSC measurements

Figure.5.1 clearly shows the DSC curves for original, cured and hygrothermally treated samples. There is an increase in glass transition temperature values, 54.19 ºC for original, 55.48 ºC for only UV cured, 56.49 ºC for microwave cured only, 89.38 ºC for UV cured and hygrothermally treated and 88.36 ºC for microwave cured and hygrothermally treated samples. The sample weights are different because the same sample was not subjected to different treatments. The curing process basically comprises of two mechanisms. Firstly, there is irreversible gelation transforming liquid resin into a gel, which involves three-dimensional cross-linking and subsequent increase in viscosity. Secondly there is reversible devitrification step where the gelled resin transforms into a rubber or glassy phase. Subsequent heating increases the degree of cross-linking, which raises the T_g [**29**].

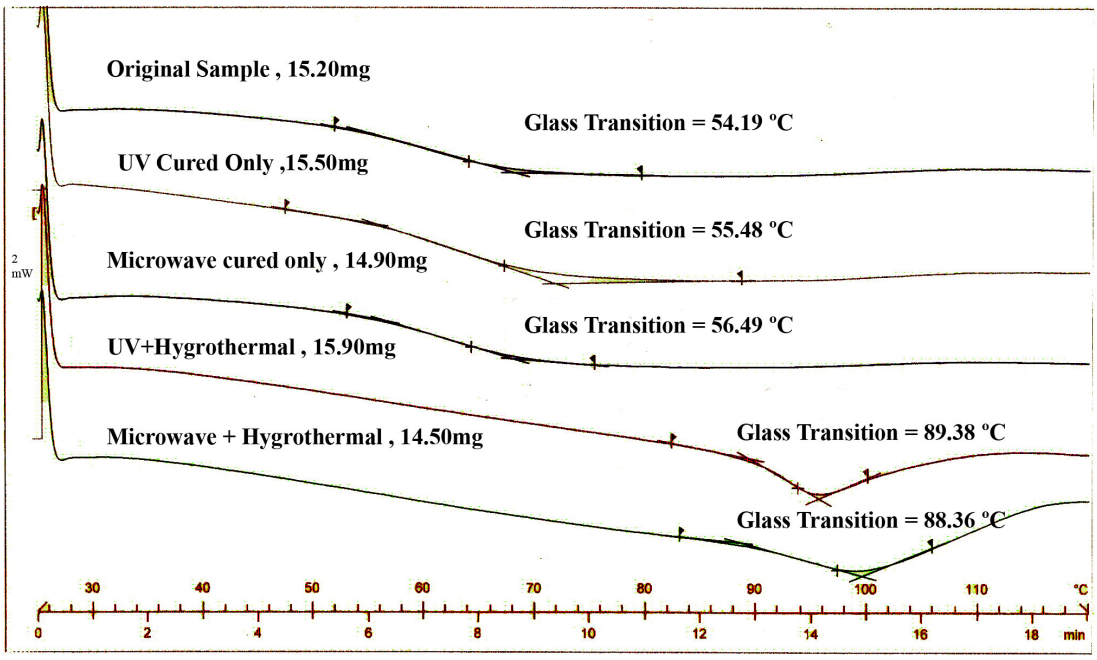


Fig.5.1. DSC curves for original, cured and hygrothermally treated samples.

5.1.1. Microwave Heating

The main advantage of microwave curing is the reduction in curing time [**30,31,32**] as it provides a very fast rate of heating. One of the major problems in microwave curing is the presence of voids in the cured samples, which depend on the curing temperature and pressure as well as the nature of material treated [**30**]. A faster rate of curing with low applied pressure results in entrapment of voids in the composite structure. This can lead to significant degradation of macromechanical properties [**33**]. For maximum and consistent strength in a material the void content should be less than 5% [**34**].

Increasing the pressure during curing can reduce the voids significantly. The use of high pressure of up to 7000 kPa by means of an isostatic press, without vacuum application, can effectively reduce the void levels to below 3% [**35**]. In microwave heating, for E-glass fiber/epoxy matrix composites, the epoxy gets heated first and then the heat gets transferred to the glass fiber through the interface. So there is a thermal gradient across the interface [**30**]. Microwave curing can increase the interlaminar shear strength. In a work by Yue and Looi [**32**] that microwave curing doubled the interfacial strength. Since the composite strength is mainly dependent on the interfacial strength [**36**], the microwave curing technique can result in composites with higher strength and stiffness. The microwave cured sample had a T_g value 2.3ºC greater than the original sample. This is due to the higher degree of cross-linking. The two major parameters affecting processing of thermosetting resins, irrespective of the curing technique, are void content and Tg. The higher value of Tg indicates ability to be used at higher service temperatures. A higher void content can reduce the interfacial strength significantly. So an optimal combination of both these parameters is essential.

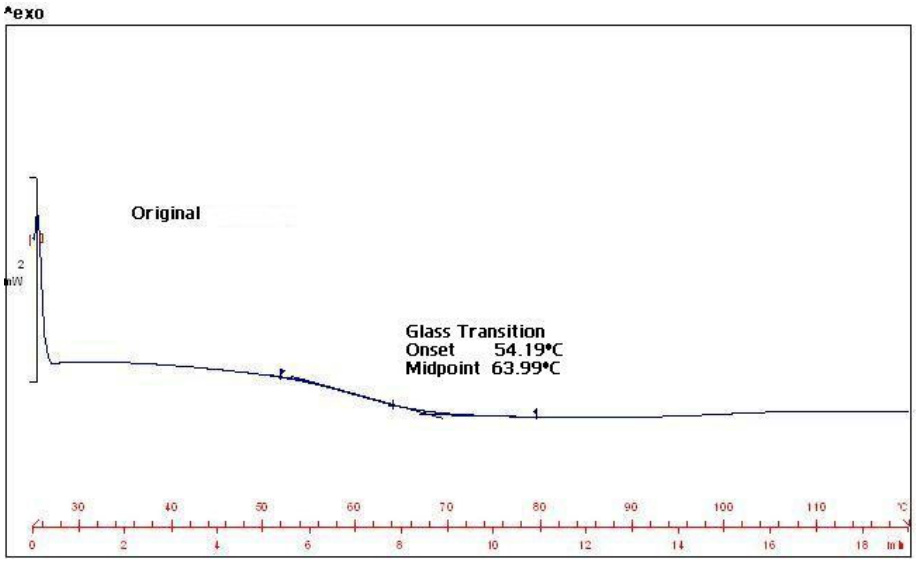


Fig5.2(a). DSC curve for original sample

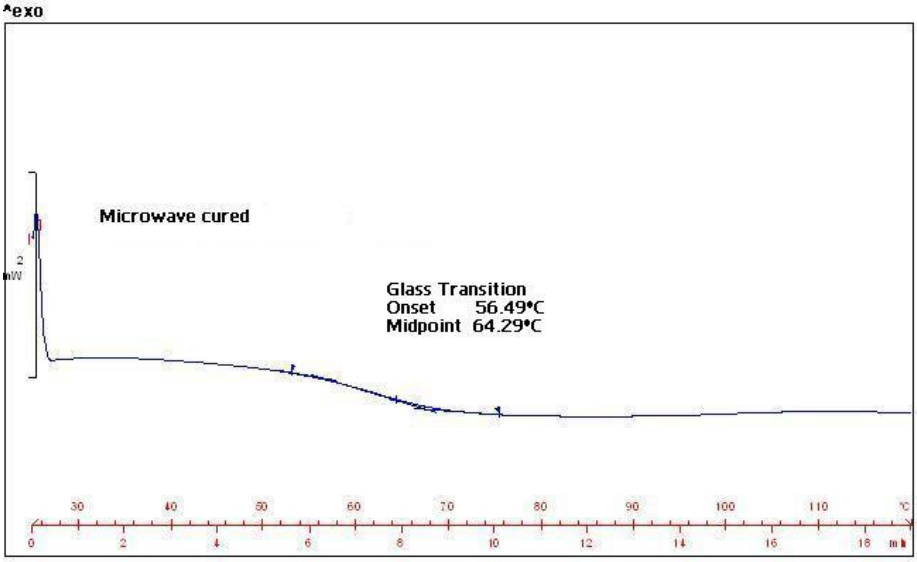


Fig.5.2(b). DSC curve for Microwave cured sample

5.1.2. UV Heating

The main interest of using UV light to induce the polymerization reaction lies in the high polymerization rates, which can be reached under intense illumination, together with the advantage of a solvent-free formulation curable at ambient temperature[**37**]. Optimization

of UV curing resins depends on several factors such as the intensity of UV light used, presence of oxygen in the atmosphere and concentration of photoinitiators[**38**].The effect of these factors were observed by Harris et.al [**39**]. The dynamic modulus of elasticity of two composite materials cured by light intensities 180 mW/cm2, 350 mW/cm2 and 700 mW/cm2 were investigated at 37C and 60C . The specimens exposed to light of intensity180mW/cm2 were found to be weak. Higher intensities resulted in better curing. But one composite material registered higher modulus for higher intensities while the other registered no significant increase. This shows that curing also depends on the monomer and activator/initiator concentrations. Our study used a source of UV light having wavelength 384 nm. A rise of 1.29 C in Tg was observed in the UV cured samples as compared to the original ones. This can be attributed to higher degree of cross-linking in the epoxy chains due to the photoinitiated polymerization.

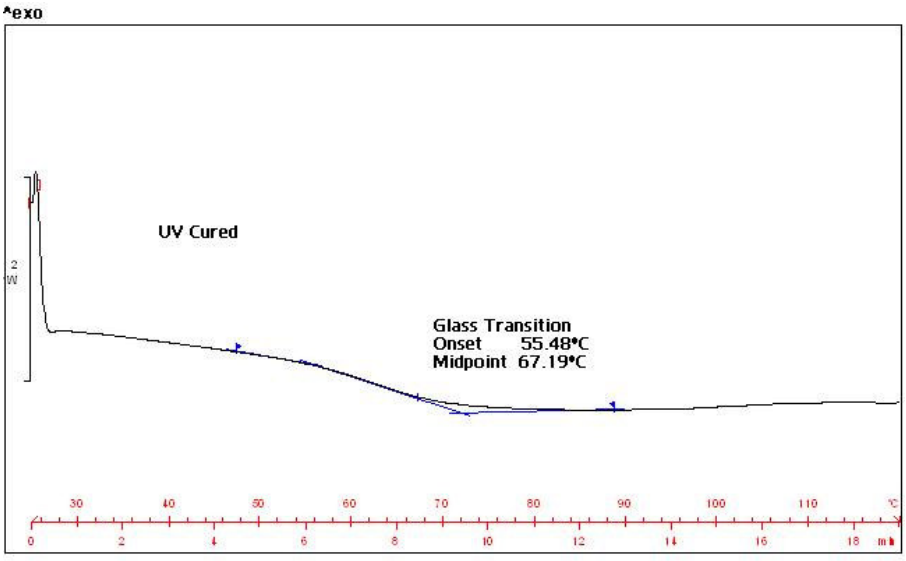


Fig.5.2(c). DSC curve for UV cured sample

There is build-up of hydroxyl groups on UV curing of epoxide. This has been confirmed by IR spectroscopy. Moreover an increase in the relative humidity leads to increase in

epoxy consumption and hydroxyl (OH) group formation. It should be emphasized that generation of hydroxyl groups is rather detrimental to composite properties. The polymer cured by UV in humid atmosphere is softer and less resistant to solvents as compared to those cured in dry atmosphere [**37**].

5.1.3. Hygrothermal Treatment

The exposure of composites to moist environment for a long of time leads to matrix plasticization and swelling. Plasticization results in a decrease of glass transition temperature (Tg) value. Swelling is associated with differential strain created by liquid while stretching polymeric chains [**2**]. However in our case a hygrothermally treated samples registered a rise in the Tg values. An increase of 35.17C and 34.2C was observed in UV cured hygrothermally treated samples and microwave cured hygrothermally treated samples, respectively. This is due to the short period of exposure which resulted in hydrogen double bond formation in the epoxy matrix or at the interface. Thus, moisture absorption is a matrix dominating property in fibrous composites. Moisture interaction with the metal oxides in E-glass leads to corrosion induced damage and thus results in reduced mechanical strength [**40**]. Impurities like water lead to failure at the interfacial region due to chemical reaction and/or plasticization [**41**]. The hygrothermal and residual forces in the composite material may be large enough to cause failure in the laminated composites and should not be neglected in the modern design analysis and lifetime analysis.

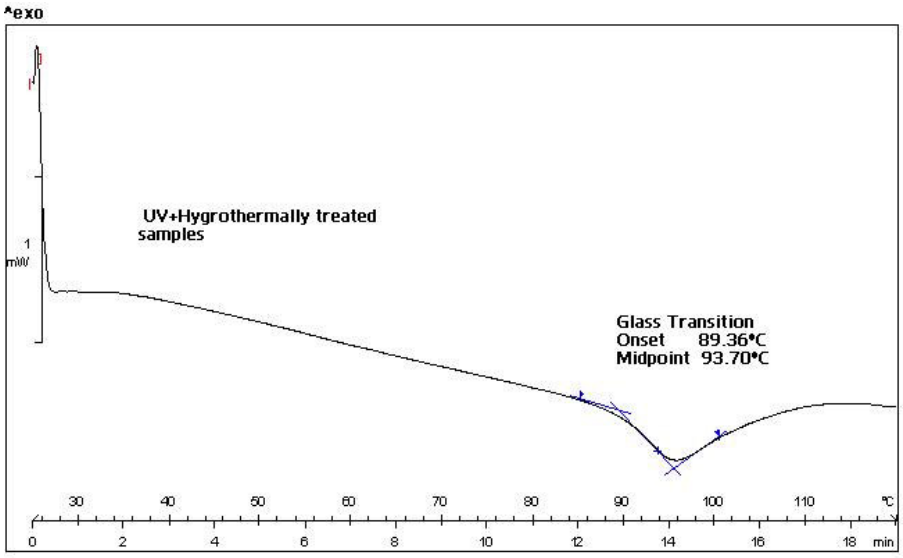


Fig.5.2(d). DSC curve for UV cured hygrothermally treated sample

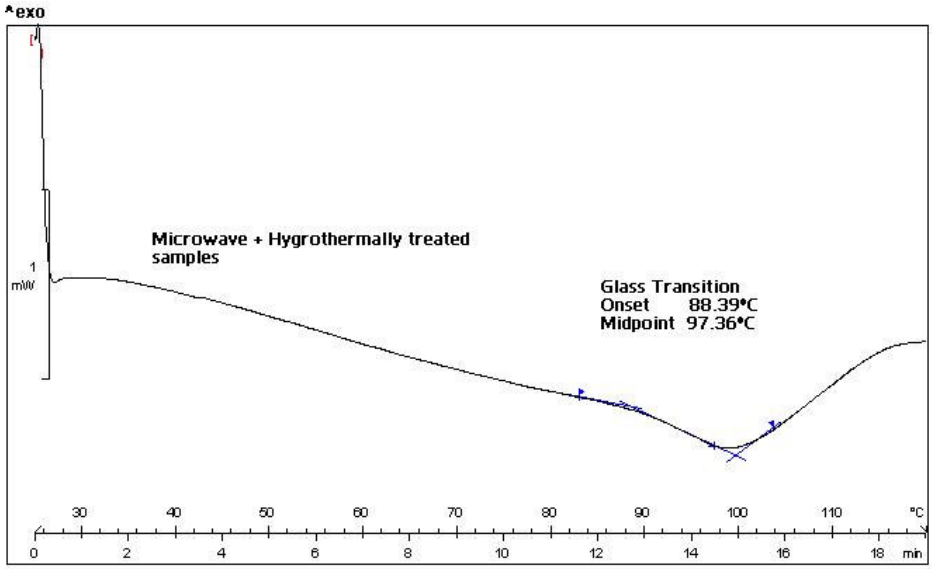
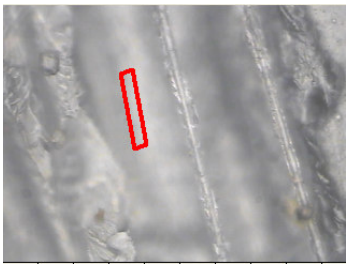


Fig.5.2(e). DSC curve for Microwave cured hygrothermally treated sample

5.2. FTIR measurements

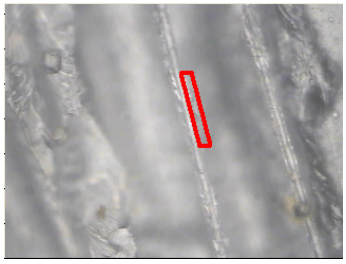
In the present work, FTIR-imaging was also used to assess the interface of various samples. The characterization of interface region is difficult since they are nanoscopic and deeply buried inside the composite material [**42**]. FTIR imaging is used for determination of structural gradient across the interface. The OH absorbance peaks are observed at a wave number of around 3300-3600 cm^{-1}. The peaks obtained at around 2500 cm-1 represent the COOH debonding region.

Fig. 5.3(a) to (c) represent the 2D micrographs of original samples taken by FTIR spectrophotometer and fig 5.3(d) to (f) spectra of these micrographs of untreated glass/epoxy micro-composites at different region. In this there is chemical gradient of absorbance from the glass fiber to the bulk of the epoxy resin. Fig 5.3(d) represents the spectral region in the bulk of the microcomposites. Fig 5.3(e) represents the spectral region away from interface and fig 5.3(f) shows spectral region near the interface of the micro-composites. There is a slight gradient in moisture absorption across the interface.

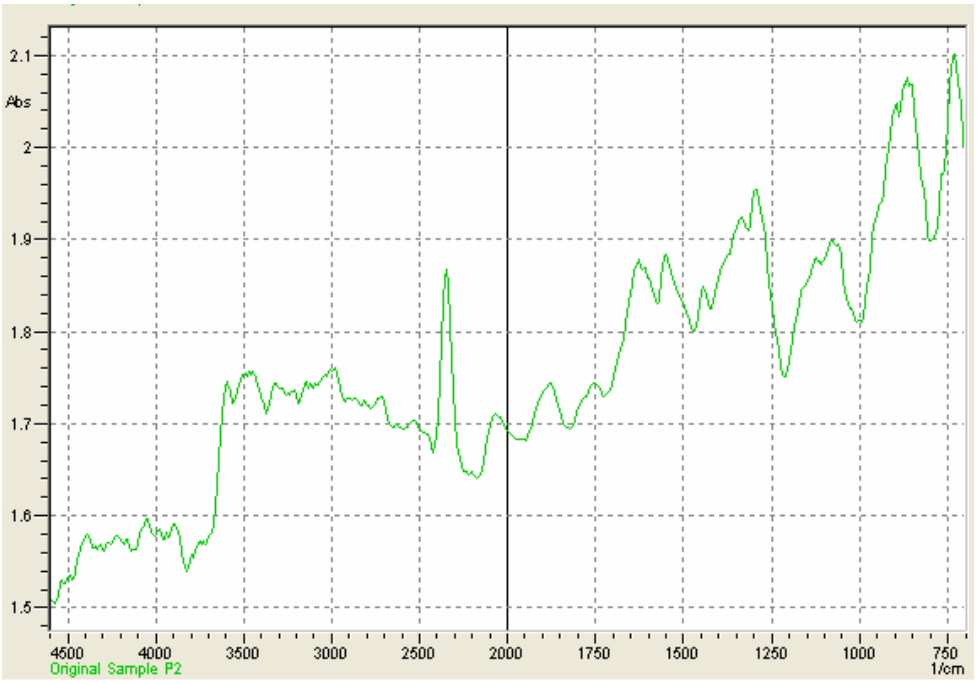


5.3.(a)

5.3(b)

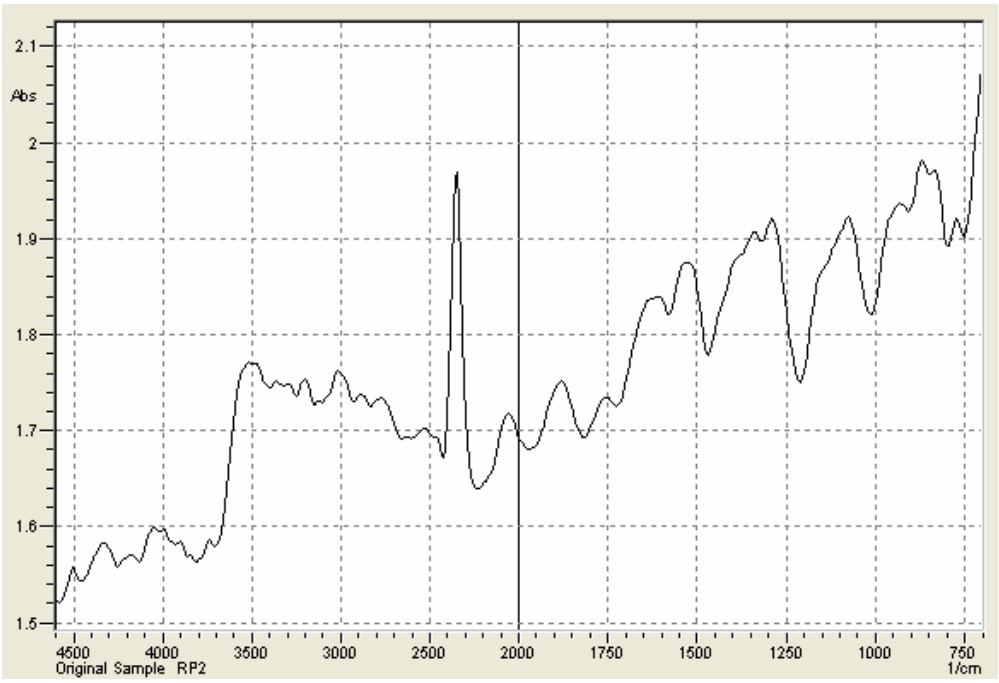


5.3(c)

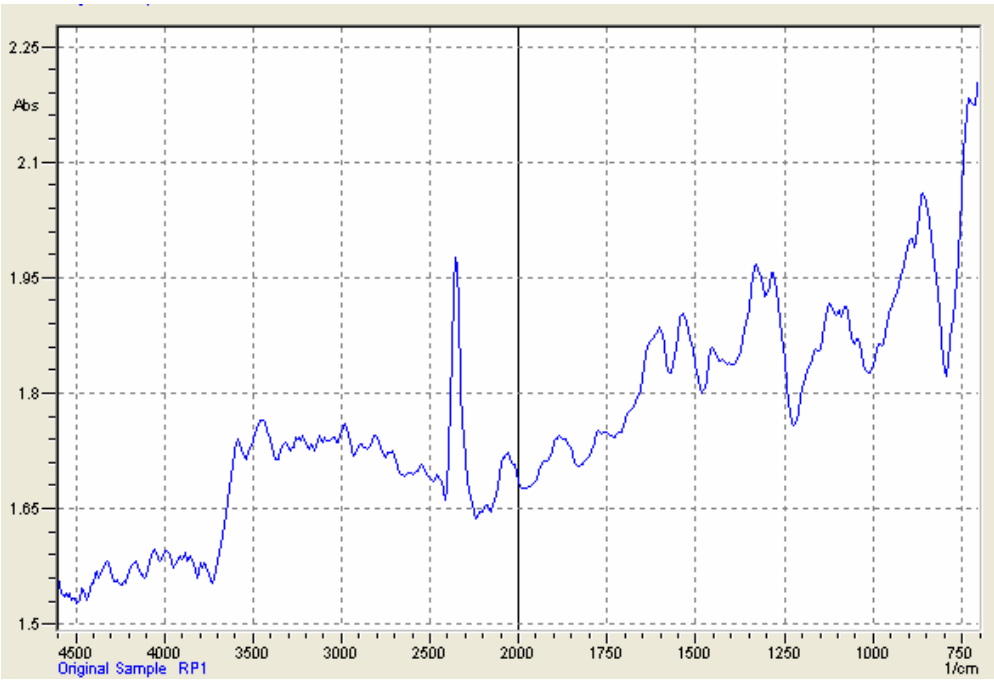

Abs
2.1
2
1.9
1.8
1.7
1.6
1.5
4500
4000
3500
3000
2500
2000
1750
1500
1250
1000
750
1/cm
Original Sample P2

5.3(d)

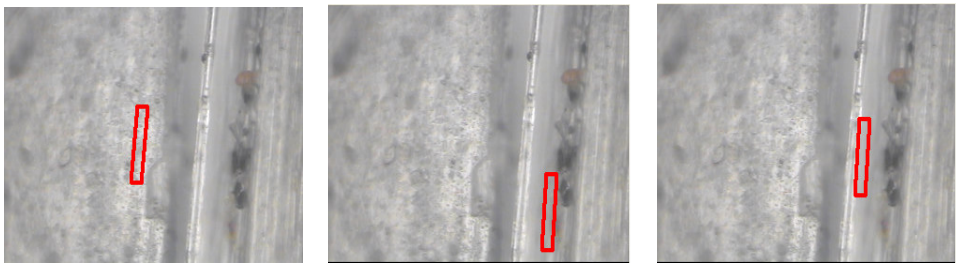
.


Abs
2.1
2
1.9
1.8
1.7
1.6
1.5
4500
4000
3500
3000
2500
2000
1750
1500
1250
1000
750
1/cm
Original Sample RP2

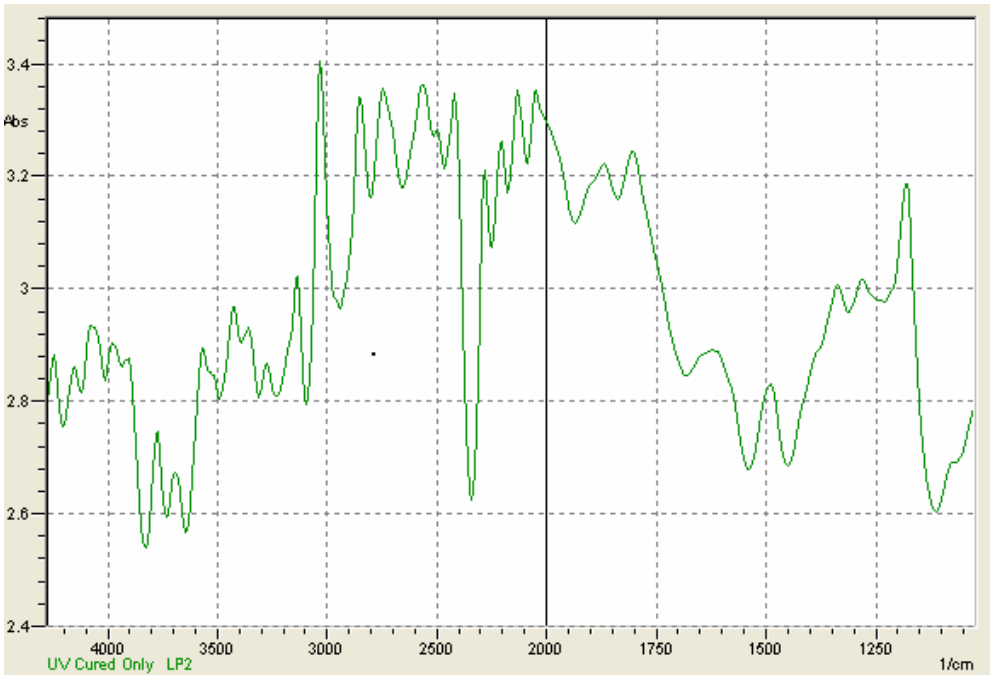
5.3(e)



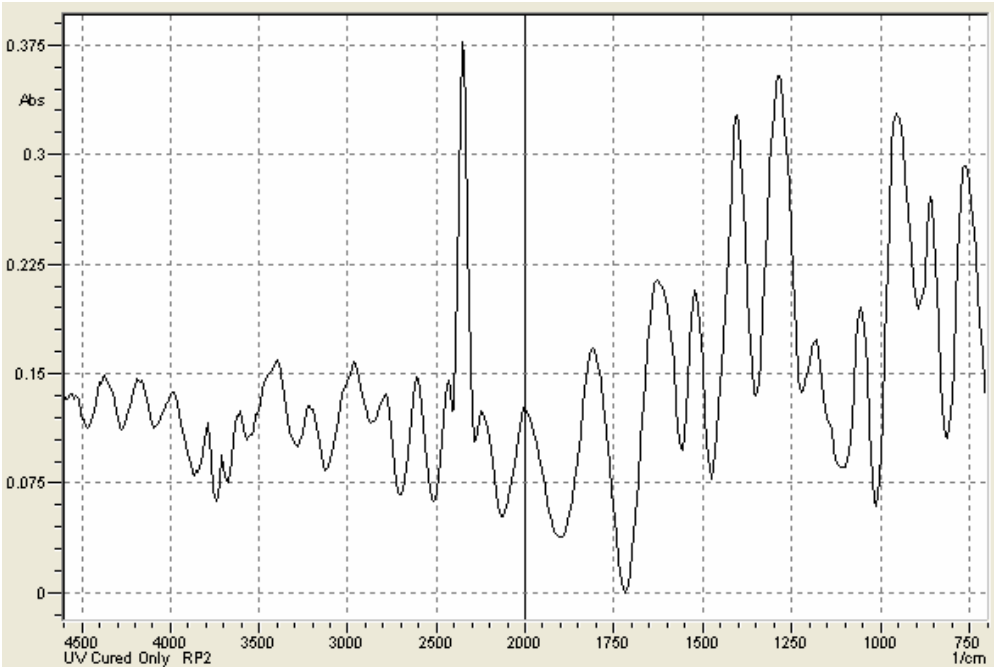
5.3(f)



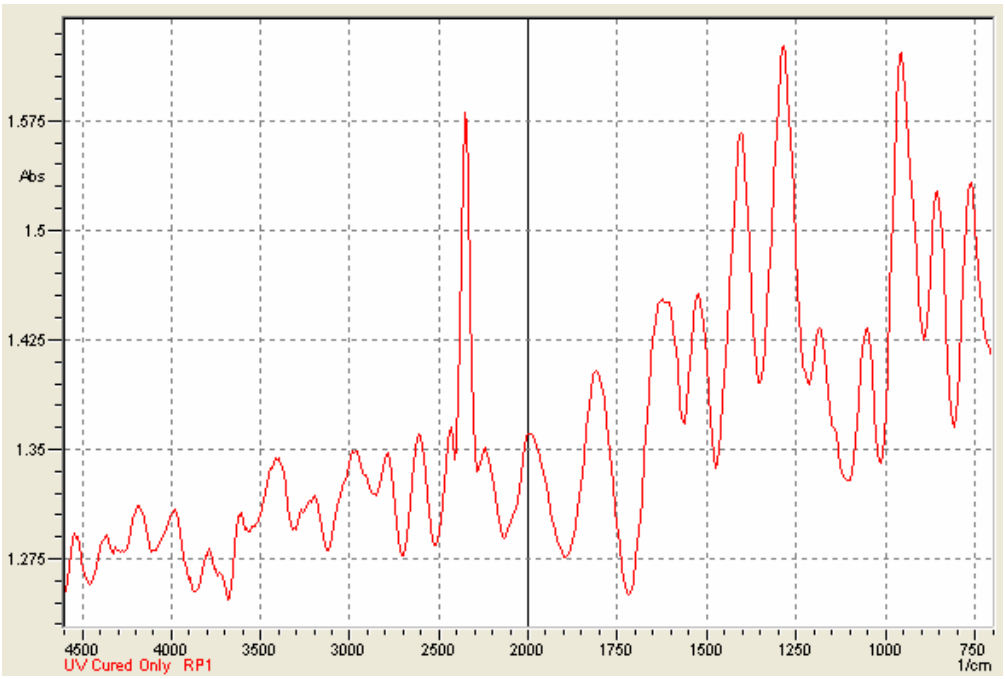
5.4(a) **5.4(b)** **5.4(c)**


3.4
Abs
3.2
3
2.8
2.6
2.4
4000
3500
3000
2500
2000
1750
1500
1250
1/cm
UV Cured Only LP2

5.4(d)


0.375
Abs
0.3
0.225
0.15
0.075
0
4500
4000
3500
3000
2500
2000
1750
1500
1250
1000
750
1/cm
UV Cured Only RP2

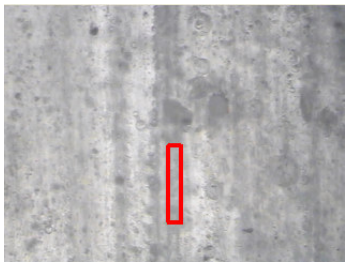
5.4(e)



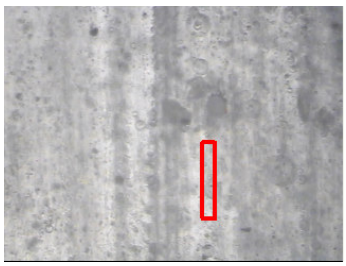
5.4(f)

Fig. 5.4(a) to (c) represent the 2D micrographs of UV cured samples taken by FTIR spectrophotometer at different region. In this there is chemical gradient of absorbance from the glass fiber to the bulk of the epoxy resin. Fig 5.4(d) represents the spectral region in the bulk of the microcomposites. Fig 5.4(e) represents the spectral region away from interface and fig 5.4(f) shows spectral region near the interface of the micro-composites. The FTIR images clearly show large absorbance of OH in the resin. The OH absorbance values decrease as we move from resin towards fiber.

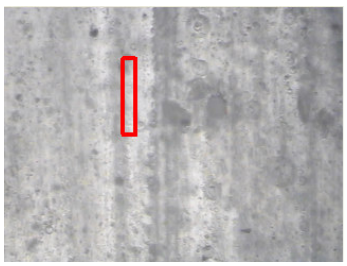
Similar results were obtained for microwave cured samples. Fig.5.5(a) to (f) represent the 2D micrographs and corresponding spectra at different positions for microwave cured samples.



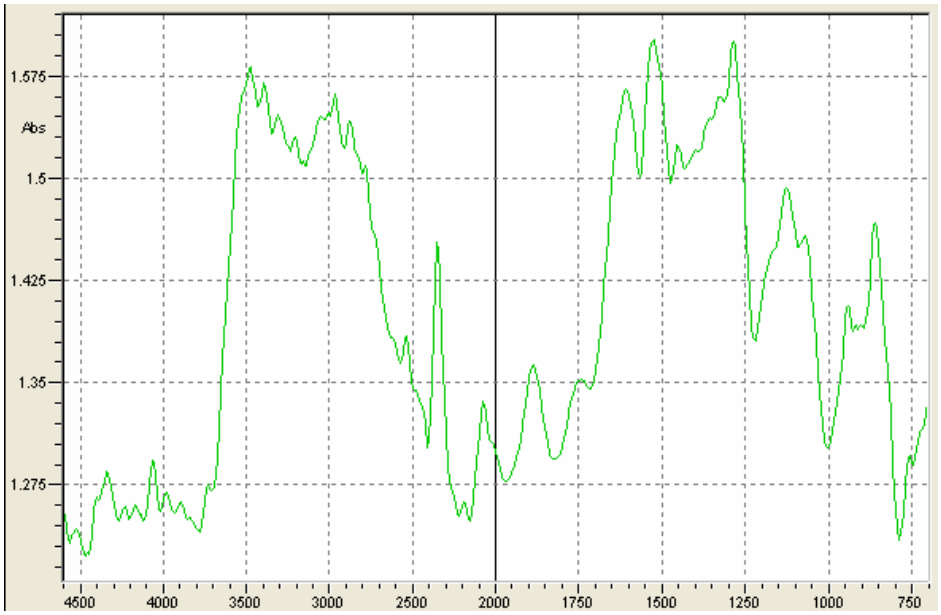
5.5(a)



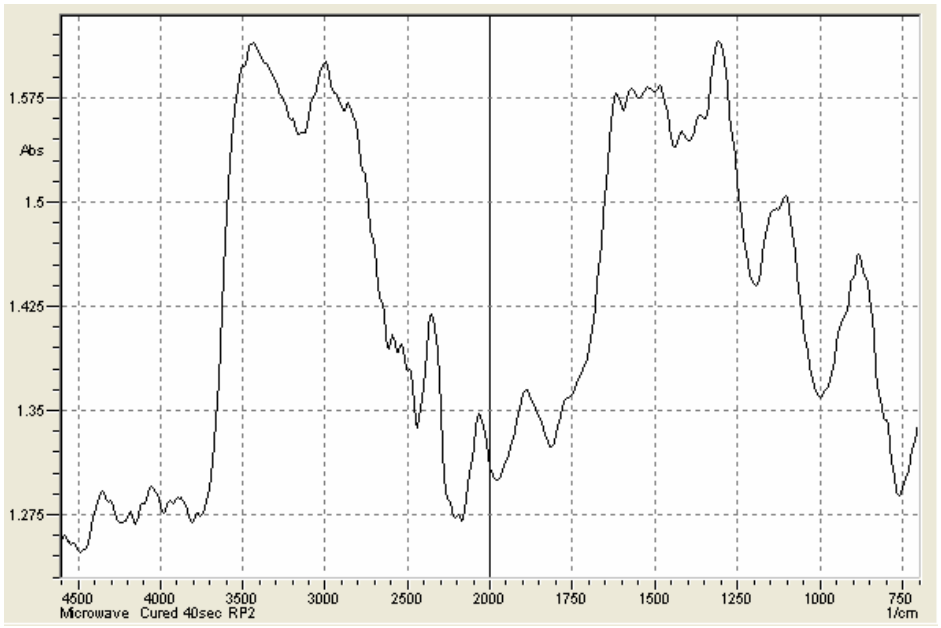
5.5(b)



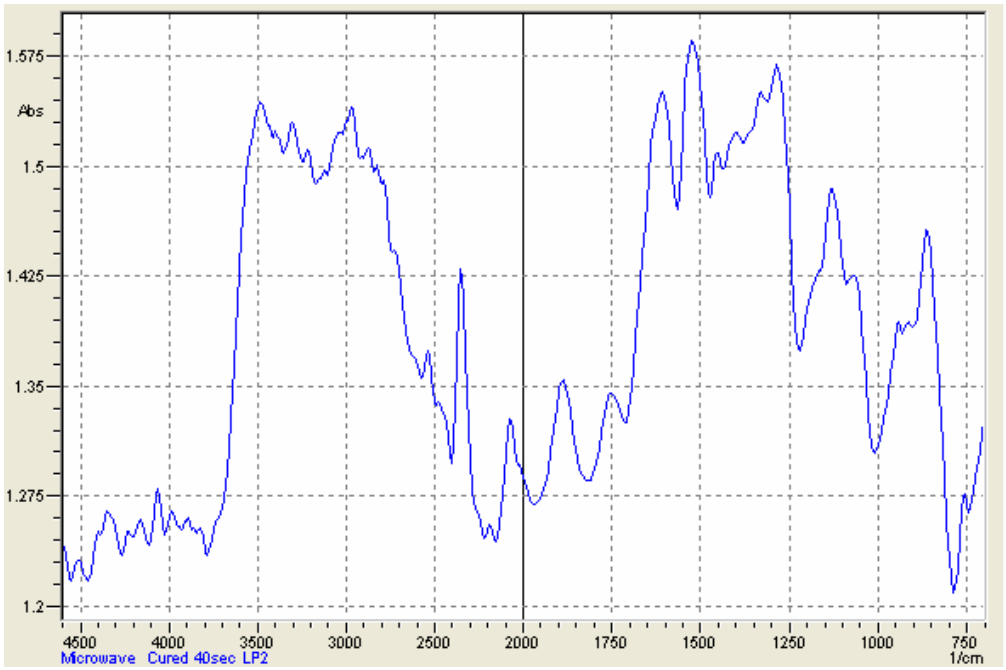
5.5(c)



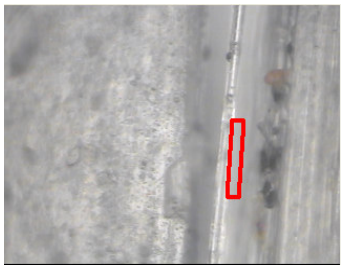
5.5(d)



5.5(e)

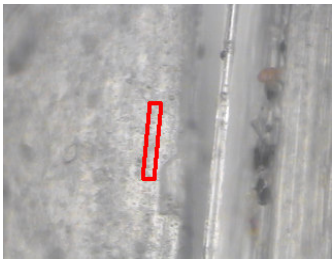


5.5(f)

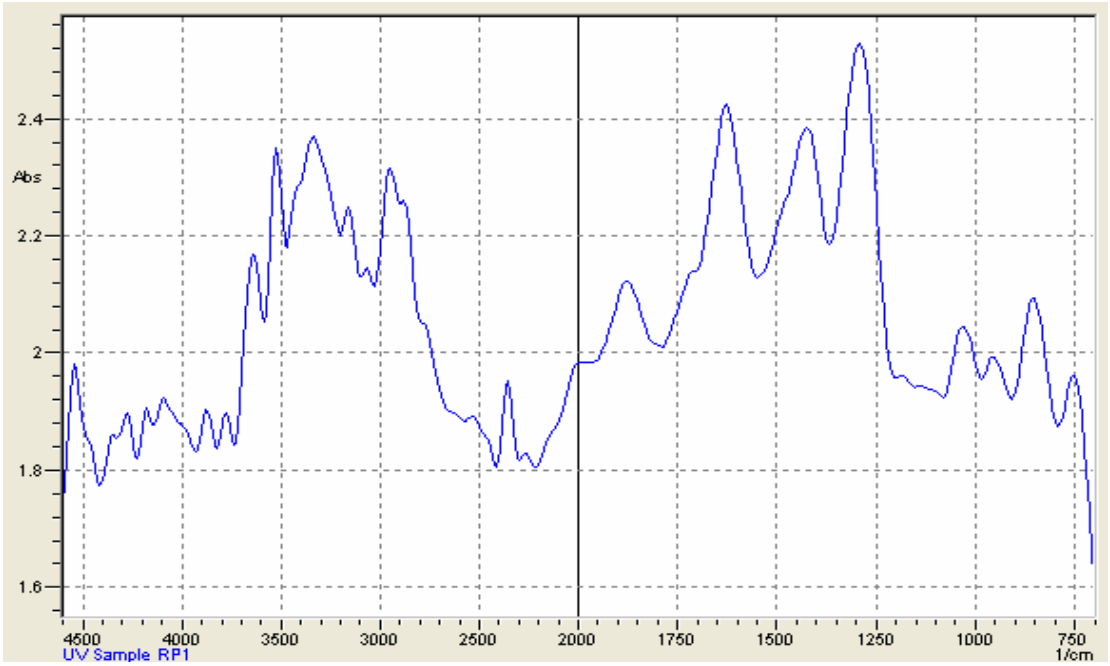


5.6(a)

5.6(b)

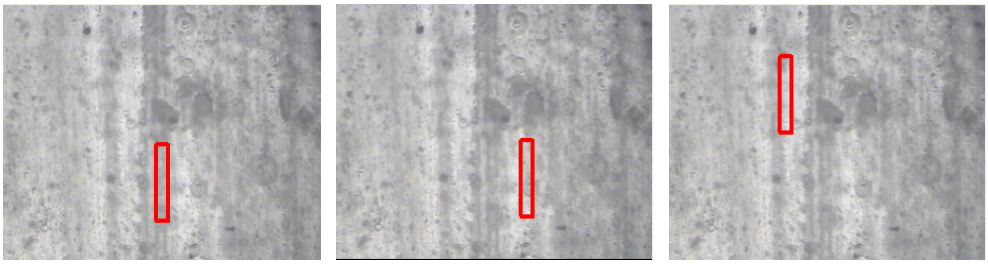


5.6(c)

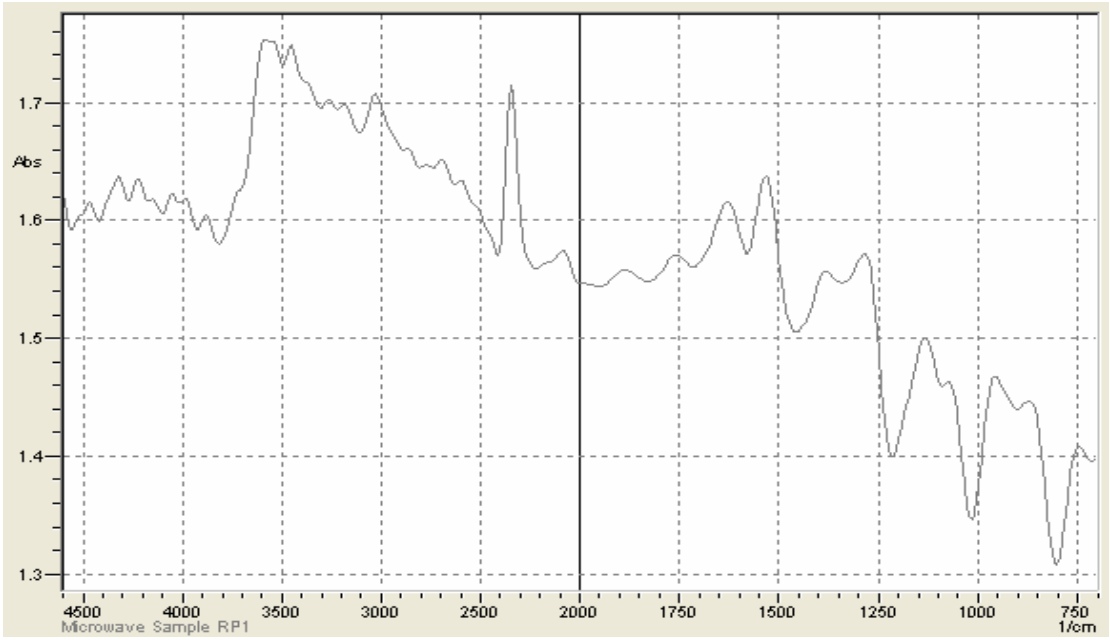


5.6(d)

The figures 5.6(a) to (c) represent the 2D micrographs taken by FTIR spectrophotometer of the UV cured hygrothermally treated microcomposite samples. Fig 5.6(d) shows spectral region near the interface of the sample. The hygrothermally treated samples show much higher absorbance values than the untreated ones. Similar results are obtained for microwave cured hygrothermally treated samples as can be seen in fig 5.7(a) to (f).



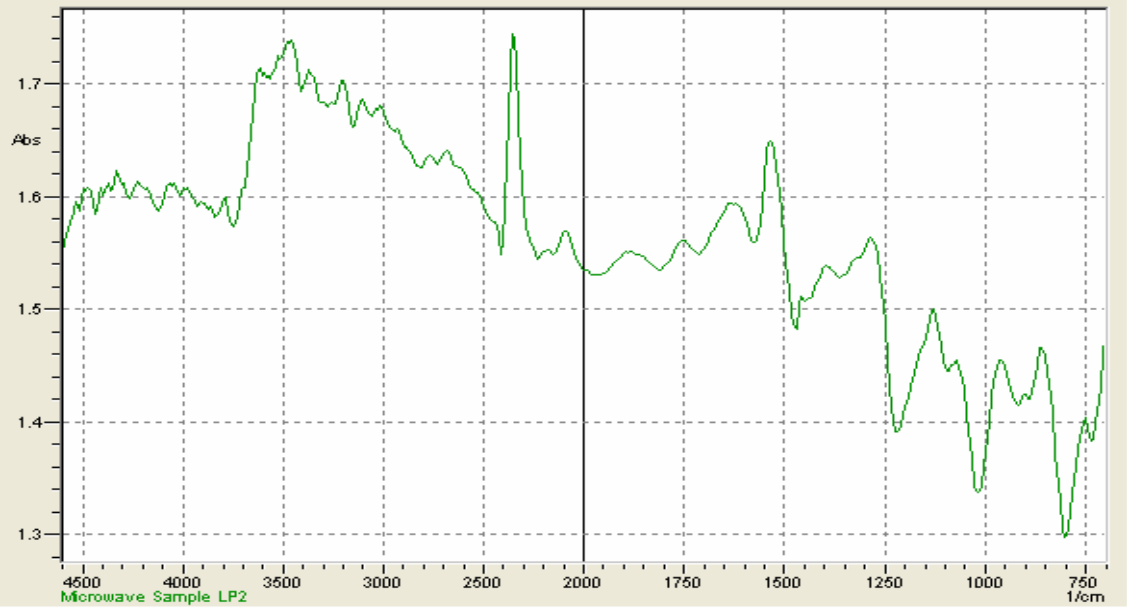
5.7.(a) **5.7(b)** **5.7(c)**


Abs
1.7
1.6
1.5
1.4
1.3
4500
4000
3500
3000
2500
2000
1750
1500
1250
1000
750
1/cm
Microwave Sample RP1

5.7(d)

Abs
1.7
1.6
1.5
1.4
1.3
4500
4000
3500
3000
2500
2000
1750
1500
1250
1000
750
1/cm
Microwave Sample RP2

5.7(e)



5.7(f)

Some SEM micrographs of the samples were also taken to observe the interfacial region and matrix cracking.

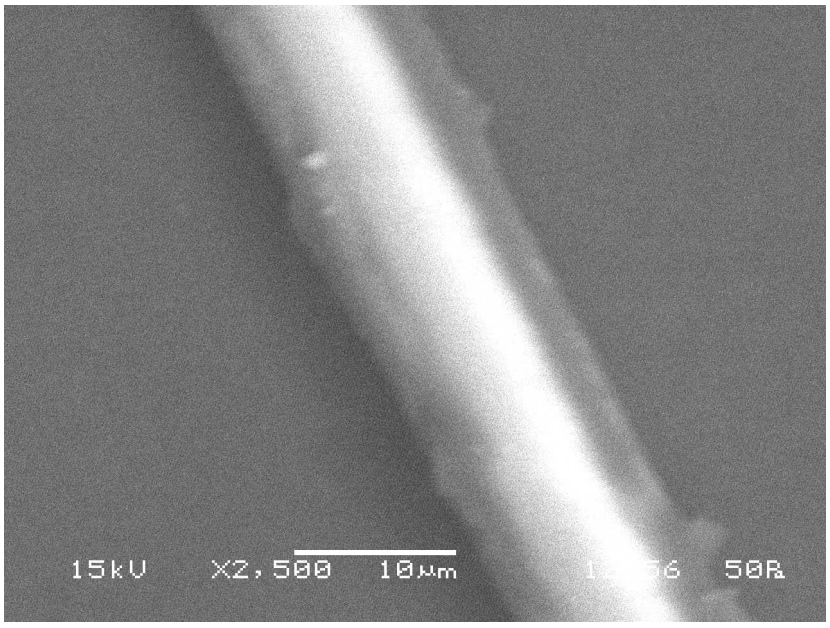


Fig. 5.8.1. SEM electron micrograph of the hygrothermally treated sample.

The above figure clearly shows a faint region in the near vicinity of the glass fiber. This represents the interfacial region, exposing the moisture absorption gradient from the fiber to the resin.

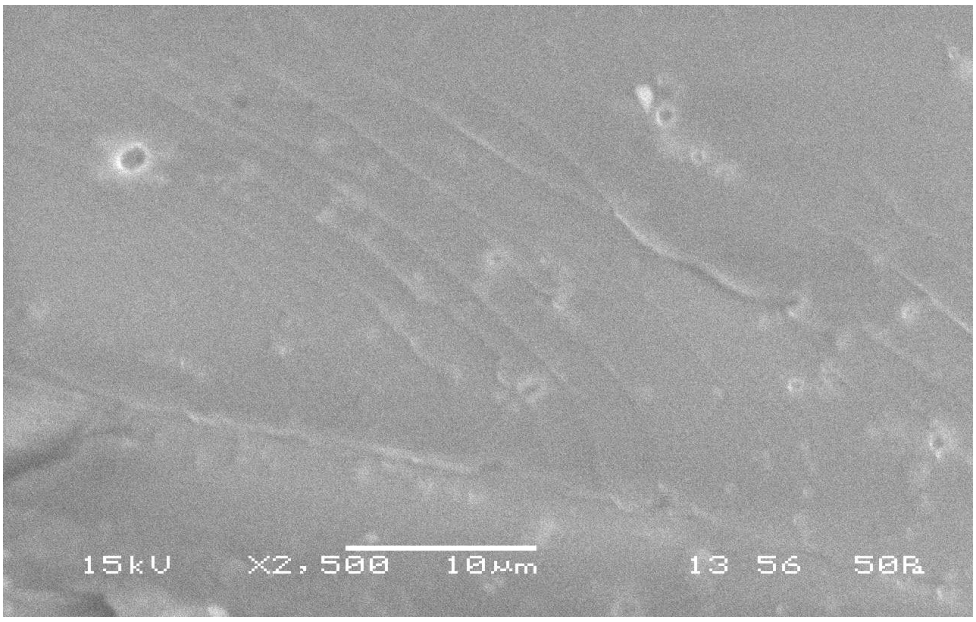


Fig.5.8.2. SEM micrograph showing matrix crazing.

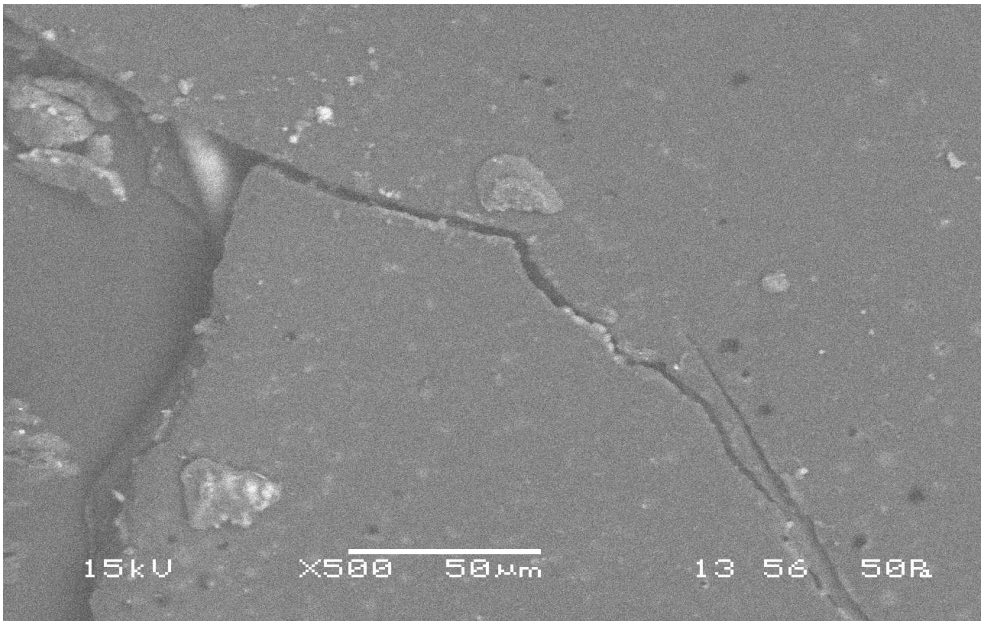


Fig.5.8.3. SEM micrograph showing well-developed crack in the matrix.

Chapter 6

CONCLUSION

6. CONCLUSION

In the present work, we have applied a scientific approach to determine the technological aspects of interface for structural and functional integrity of composites. The use of microcomposites enabled us to have a better and clear picture of the micromechanics of the glass-epoxy composite structure. The increase of glass transition temperature(T_g) value on UV and microwave curing demonstrate the higher degree of cross-linking in the epoxy resin. Also, the short period of hygrothemal treatment given to the cured samples resulted in much higher values of the composite samples as compared to the original sample. This is attributed to the fact that at initial stages of moisture absorption, there is formation of hydrogen double bond in the polar groups of epoxy resin. The OH absorbance in epoxy resin was well demonstrated by FTIR images, which clearly show a decrease in OH absorbance from bulk resin phase towards the fiber. The SEM micrographs illustrate the matrix crazing and subsequent cracking. One of the SEM micrographs showed a faint region near the fiber, which supported the fact that the moisture absorbance varies along the interface. The change in T_g of the composite structure is determining factor for its application in different service conditions. Moreover, in most of the cases the microscopic interfacial region plays a significant role in affecting the composite macroscopic properties like tensile strength, toughness and resistance to environmental degradation. A better assessment of this interface can ensure better analysis of the fracture mechanics of the composites and thus improve their structural reliability.

Chapter 7

Scope for Future Work

7. Scope for Future Work

The present work leaves a wide scope for future investigators to explore many other aspects of physio-chemical analysis of interface of FRP composites. Study of complex moisture diffusion mechanism into the epoxy and polyester resin may help in the evaluation of interface of FRP composites. The moisture present in the matrix is in the free form or/and combined form and which phase come first is still a matter of discussion, this may be evaluated by spectral shift by FTIR-imaging and DSC techniques. A small work has been done here to identify this behaviour up to some extent.

Reference:

[1] **Collings, T.A.,** in: I.H.Marshall (Ed.), Composite Structures, vol.5, Elsevier, London, 1989, p.213.

[2] **Ray, B.C**. *"Temperature effect during humid ageing on interfaces of glass and carbon fibers reinforced epoxy composites"*. J. Colloidal and Interface Sci. 2006; 298:111-117.

[3] **Wang, Y. and Hahn, T.H**. "*AFM characterization of the interfacial properties of carbon fiber reinforced polymer composites subjected to hygrothermal treatments*." Compos Sci. and Tech. 2007; 67: 92-101.

[4] **Hamada, H., Ikuta, N., Nishida, N., and Maekawa, Z**. Composites 1994; 25:512

[5] **Ray, B.C.** *"Adhesion of glass/epoxy composites influenced by thermal and cryogenic environments"*. J. Applied Polymer Sci. 2006; 102(2): 1943-1949

[6] **Benito, J. González**. *"The nature of the structural gradient in epoxy curing at a glass fiber/epoxy matrix interface using FTIR imaging"*. Journal of Colloid and Interface Science 2003;267: 326–332

[7] **Yuan JJ, Kennedy JM, Edie DD**. "*Modeling the dynamic response of the fiber/matrix interphase in continuous fiber composite materials*." In: Spragg CJ,Drzal LT, editors. Fiber, matrix, and interface properties AFTMSTP, 1290. American Society for Testing and Materials; 1996. p. 67–83.

[8] **Loos AC, Springer GS, Sanders BA, Tung RW**. *"Moisture absorption of polyester-E glass composites"*. In: Springer GS, editor. Environmental effects on composite materials. New York: Technomic Publishing Company; 1981.

[9] **Shen CH, Springer GS**. *"Effects of moisture and temperature on the tensile strength of composite materials"*. In: Springer GS, editor. Environmental effects on composite materials. Technomic Publishing;1981. p. 79–93.

[10] **Weitsman Y**. *"Moisture in composites: sorption and damage"*. In: Reifsnider KL, editor. Composite materials series – 4: fatigue of composites. New York: Elsevier; 1990. p. 385–429.

[11] **Naruse T, Hattori T, Miura H, Takahashi K**. *"Evaluation of thermal degradation of unidirectional CFRP rings"*. Composite Structures 2001;52:533–8.

[12] **Colin X, Verdu J.** *"Strategy for studying thermal oxidation of organic matrix composites"*. Comp Sci Tech 2005;65(3–4):411–419.

[13] **Bowles KJ, Jayne D, Leonhardt TA, Bors D**. *"Thermal-stability relationships between PMR-15 resin and its composites"*. J Adv Mater 1994;26(1):23–32.

[14] **Drazal, L.T., Rich, M.J., and Llyod, P.F**. *"Adhesion of graphite fibers to epoxy matrices. part **I**"*. The role of fiber surface treatment. *J.Adhesion* 1983;16, 1-30

[15] **Kim, Jang-Kyo and Mai, Yiu-Wing**. Engineered Interfaces in Fiber Reinforced Composites. Elsevier Science Ltd. 1st edition(1998), printed in The Netherlands. p.1

[16] **Lenhart, J.L., Zanten, J.H., Dunkers, J.P., Zimba, C.G., James, C.A., Pollack, S.K., Parnas, R.S**. J. Colloid Interface Sci. 2000; 221: 75.

[17] **Almousawi, H., Drown, E.K., Drzal, L.T.** Polym. Comp.1993;14:195.

[18] **Jang, Bor.Z**. Advanced Polymer Composite:Principles and Applications. First Edition(1994). ASM International, Materials Park, OH 44073-0002, USA.

[19] **Li, L., Zhang, S.Y., Chen, Y.H., Liu, M.J., Ding, Y.F., Luo, X.W., Pu, Z., Zhou, W.F. and Li, S**. "Water transportation in Epoxy resin". Chem.. Mater. 2005; 17: 839-845.

[20] **Musto, P., Ragosta, G., Masia, L**. Chem.. Mater 2000; 12: 1331.

[21] **Shen, Y, Wu, P**. J.Phys. Chem. B. 2003 ; 107 : 4224

[22] **Peng, Y, Wu, P**. Siesler, H.W. Biomacromolecules 2003 ; 4 : 1041.

[23] **Scoles, C.L., Chang, F.T., Gidley, D.W., Yee, A.F**. J. Polymer Sci, Part B: Polymer Phys. 1998; 36: 3035.

[24] **Scoles, C.L and Yee, A.F.** J. Polymer Sci, Part B: Polymer Phys. 2000 ; 38 :792

[25] **Cao, Y. and Cameron, J**. *The Effect of Curing Conditions on the Properties of Silica Modified Glass Fiber Reinforced Epoxy Composite*. Journal of Reinforced Plastics and Composites 2007; 26; 41

[26] **Lange, J., Toll, S., Manson, J. E. and Hult, A.** *Residual Stress Build-up in Thermoset Films Cured above Their Ultimate Glass Transition Temperature*, Polymer, 1995;36(16): 3135–3141.

[27] **Lange, J., Toll, S., Manson, J. E. and Hult, A.** *Residual Stress Build-up in Thermoset Films Cured below their Ultimate Glass Transition Temperature,* Polymer, 1997**;**38(4): 809–815

[28] **Ochi, M., Yamashita, K. and Shimbo, M.** *The Mechanism for Occurrence of Internal Stress during Curing Epoxide Resins,* Journal of Applied Polymer Science, 1991;43: 2013–2019.

[29] **Boey, F., Gosling, I. and Lye, S.W.** *"High-pressure microwave curing process for an epoxy-matrix/glass-fibre composite"*. Journal of Materials Processing Technology, 1992; 29:311-319.

[30] **Bai, S.L. and Djafari, V.** *"Interfacial properties of microwave cured composites"* . Composites 1995; 26:645-651

[31] **Pera, J., Ambroise, J. and Oriol, M.** *"Microwave Processing of Glass-Fiber Reinforced Composites Modification of the Microstructure"*. Advanced Cement Based Materials 1997;6:116--122

[32] **Yue, C. Y, and Looi, H. C. "***Influence of thermal and microwave processing on the mechanical and interfacial properties of a glass/epoxy composite"*. Composites 1995; 26: 767-773

[33] **Bowles, K. J. and Frimpong, S**. *"Void Effects on the Interlaminar Shear Strength of Unidirectional Graphite-Fiber-Reinforced Composites"*. J. Compos. Mater.1992;26: 1487-1509

[34] **Boey, F., Lee, T. H. & Sullivan-Lee, P**. *"High pressure autoclave curing of composites: effect of high pressure on glass transition temperature"* . J. Mater.Sci., 1994;29

[35] **Boey, F.Y.C. and Lye, S.W**. *"Void reduction in autoclave processing of thermoset composites. I: High pressure effects on void reduction"*. Composites 1992;23:265

[36] **Boey, F. Y. C.** *"Humidity and Autoclave Pressure Effect on the Interfacial Shear Strength of a Microwave Cured Epoxy-Glass Fibre Composite"*. Polymer Testing 1995; 14: 471 477

[37] **Decker, C., Viet, T. N.T., Decker, D., Weber-Koehl, E.** *"UV-radiation curing of acrylate/epoxide systems"*. Polymer 2001; 42:5531-5541

[38] **Peck, J.A., Jones, R.A., Pang, S.S., Li, G., Smith, B.H**. *"UV-cured FRP joint thickness effect on coupled composite pipes"*. Composite Structures 2007; 80:290–297

[39] **Harris, J.S, Jacobsen, P.H, O'Doherty, D.M**. *"The effect of curing light intensity and test temperature on the dynamic mechanical properties of two polymer composites"*. J. Oral Rehab 1999;26(8):635

[40] **Brown, E.N., Davis, A.K., Jonnalagadda, K.D., Sottos**, **N.R.** Compos. Sci. Technol. 2005; 65:129.

[41] **Iglesias, J.G., Gonzalez-Benito, J., Anzar, A.J., Bravo, J., Baselga, J**. J. ColloidInterface Sci. 2002; 250:251.

[42] **Wu, P., Siesler, H.W**. *"Water diffusion into epoxy resin: a 2D correlation ATR-FTIR investigation."* Chemical Physics Letters. 2003; 374: 74-78.