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Studies on effect of acrylates diluents on the properties of glass vinyl ester resin composite

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ABSTRACT

The article describes preparation of vinyl ester resin & diluents effect on the mechanical properties of glass fiber-reinforced composites. Resin is prepared by reacting epoxy LY-556 with methacrylic acid in presence of catalyst & thermal polymerization inhibitor. Progress of reaction was monitored by measuring the acid valve of the reaction. VM and VB resin mixture were prepared by mixing the vinyl ester resin with butyl methacrylate and methyl methacrylate in 10: 4 molar ratios respectively using benzoyl peroxide as a initiator (4phr) at 30^{0}C till mixture become homogenous. With the use of these resin mixtures two laminate sheets were fabricated using a glass fiber in compression molding machine. Resin content and degradation temperature of the both laminates were studied using TGA. Mechanical, thermal test were performed on both composite laminate to study the effect of diluents on the properties of composite laminates followed by the morphological study of tensile fractured surface of samples by using scanning electron microscopy. A significant increase in the number of methylene groups and polar nature of groups in the diluents present in vinyl ester resin (i.e., increasing the bridge length) did not show any major significant effect on flexural strength & inter laminar shear strength but tensile strength, increased.

Key word: VER, Methacrylic acid, diluents, glass fiber, DSC, TGA, SEM.

INTRODUCTION

Metals can be replaced by composite materials due to their numerous advantages like high strength-to-weight ratio, low cost, high corrosion resistance, etc. Such characteristics fulfill the materials requirements in several industrial sectors such as building and construction, oil and gas, naval, aerospace, among others that are gradually introducing composite materials into their main products and processes. In present, carbon and glass fiber based composites have found application in naval structure [1, 2]. A composite is an artificially made multiphase material in which the constituent phase must be dissimilar and separated by a macroscopic distinct phase [3]. Glass fiber is used as a major reinforcement in FRP industry. Now a day's glass fiber in combination with carbon and poly-aramid fiber have led to the development of hybrid composites in its present versatile applications in which the optimum properties of different fiber can be utilized at optimum cost and performance [4]. When selecting a polymeric resin for use in a structural composite several factors must be considered, like ease of application such as desirable viscosity, strength, stiffness, toughness, adhesion with the fibers and durability. In the stage of selection, information regarding the service environment including temperature, manufacturing method, cure conditions and properties required are also important [5]. S.Chauhan et al. [6] reported the mechanical and sliding wear characteristics of glass fiber reinforced vinyl ester resins based on epoxy – novalocs resin using styrene and acrylates as reactive diluents. The effect of structure on properties of glass fiber reinforced vinyl ester (based on cycloaliphatic epoxy resin) resins composites reported recently. [7]

VERs are important classes of thermosetting polymer used for obtaining high performance composites with military, commercial as well as medical application and also find multiple applications in optical fiber coating, UV curing ink, and in printed circuit board due to their ability to form cross link [8]. Vinyl ester resins are used to fabricate a variety of reinforced structures [9-10] including pipes, tanks and ducts. VERs have superior properties compared with other thermosetting polymers such as unsaturated polyester resins, are less expensive and easier to process than epoxy polymers. Most of the studied related to synthesis, modification, curing and effect of diluents carried out on VERs, based on diglycidyl ether of bisphenol –A, reported elsewhere [11-15]. Efforts are being made to develop VE resin with better toughness, lower viscosity and reduced shrinkage during cure but no studies have been reported on VE resin based on a Araldite LY556 (epoxy resin based on diglycidyl ether of bisphenol-A) and methacrylic acid therefore it interested the authors to investigate vinyl ester resin based Araldite LY556 as matrix resin in glass fiber reinforced composite and effect of diluents on the mechanical properties such as tensile strength, flexural strength, and ILSS.

A typical vinyl ester resin composite contains styrene as reactive diluents and is one of the major source of air pollutants due to emission of volatile organic compounds during the mixing of diluents with resin. A significant loss is also observed during the mixing as well as during the molding, so, it can dramatically affect the performance and service life of composites. Replacing the diluents is one of the direct ways to solve the problem.

In the present article the approach has been to replace the conventional styrene diluents with methyl methacrylate and butyl methacrylate having the less volatility as compared to styrene. The main aim of study is to see the effect of these diluents on mechanical properties of composite.

Experimental plan consists of preparation of vinyl ester resins cross-linking with co-monomers/reactive diluents with benzoyl peroxide as initiator in both cases followed by preparation of glass fabric laminates. Mechanical and thermal characterization was also done. Furthermore morphology of fractured surface has been studied by using SEM.

EXPERIMENTAL SECTION

2.1 Materials

VERs prepared in our laboratory by using methacrylic acid , triethylamine, toluene, sodium bicarbonate (Merck Chemical Company), acetone, phenolphthalein (Samir chemicals) and diglycidyl ether of bisphenol-A epoxy resin(Araldite LY556), benzoyl peroxide(fluka) were used as received.

2.2 Synthesis of VERs

VERs was synthesized from methacrylic acid and diglycidyl ether of bisphenol-A type of epoxy resin. Thus, to a three necked 2 liter flask fitted with condenser, thermometer and mechanical stirrer were added with epoxy resin and methacrylic acid in molar ratio 0.3 to 0.5 followed by addition of triethylamine(1 per cent of total weight of resin) as a catalyst and hydroquinone(0.03 per cent of total weight of resin). Typical reaction conditions are 90^0C-110^0C for 5-6 hours and the progress of the reaction can be monitored by measuring the acid value until the resin with desired acid valve (4-5 mg NaOH /g solid) was obtained.

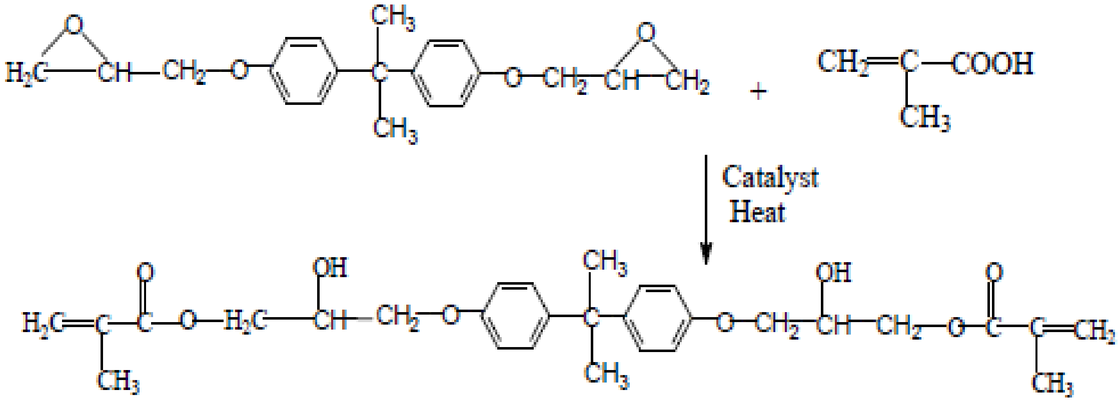

Figure 1 synthesis of vinyl ester resin by the reaction of epoxy resin and methacrylic acid

The synthesized resin was purified by dissolution in toluene. The obtained solution was washed with sodium bicarbonate (30wt%aqueous solution) in order to remove the traces of untreated acid .It was then dried in anhydrous calcium chloride solution and distilled under vacuum. The final crude product was dried in the oven at 50^0C for duration of 72 hours. Vinyl ester, in the form of a straw yellow colored liquid resin was formed, which was soluble in acetone, methyl ethyl ketone, toluene, ether, chloroform, carbon tetrachloride, and benzene.

2.3 Characterization of Resin

2.3.1 Acid number titration

The acid number tests were performed during the course of reaction in accordance with ASTM D 1980-87. Approximately 1 gram of the vinyl ester resin taken from reaction mixture was dissolve in 5 gram of acetone. Three drop of 0.1wt% phenolphthalein in ethanol was added to mixture to determine the neutralization point. The solution was titrated with 0.5 mole / L sodium hydroxide until the solution remained slightly pink in color for 30 second. The acid number of VER mixture was than calculated;

$$\text{Acid number} = \frac{\text{mg of NaOH}}{\text{g of VE}}$$

Where V is the volume in ml of NaOH solution used, N is the normality of NaOH solution and m is the weight of VE in gram.

2.3.2 IR Analysis

IR Spectra was recorded on a Perkin Elmer model-521 spectrophotometer in a 400-4000 cm^{-1} region. Sample was prepared in KBr disc. Calibration of the frequency readings was made by polystyrene.

2.3.3 NMR analysis

Proton NMR of the vinyl ester resin was recorded on a Brucker av 400 MHz spectrometer in $CDCl_3$ at room temperature using tetramethyl silane as internal standard with 1.36 acquisition time and 2 sec. pulse delay.

2.3.4 Curing behavior of resin

Curing behavior of vinyl ester resin mixed with diluents was studied using Q20 as a basic DSC instrument. The resin mixtures were prepared just before the taking DSC scan. DSC scans were obtained under dynamic conditions at the program rate of 10^0C/minute up to temperature on which exothermic reaction completed.

2.4 Preparation of composite

Resin mixed with diluents followed by addition of initiator benzoyl-peroxide added to 4 phr with some amount of suitable solvent to decrease the viscosity of resin to $\approx$ 500cps. When a pre gel formation of resin started, composite laminates were made using 18 ply of glass fibers in each laminate by hand layup technique. Samples were air dried for 4 hours and than compression molding machine was used for curing the sample.

Curing schedule was set according to DSC analysis. Samples of suitable dimension are cut with the help of diamond cutter for further characterization. Prepared composite samples are named as VM (Vinyl ester-methyl methacrylate) and VB (Vinyl ester -butyl methacrylate).

2.5 Mechanical characterization

2.5.1 Tensile strength

Test is performed on flat specimens having the dog bone type shape and the straight side type with end tabs. During the test a uni-axial load is applied through both ends of specimen according to ASTM D 3039-76, a standard test method for tensile properties of fiber resin composites. Test is performed in universal testing machine (UTM) Instron 3382 and results are analyzed to calculate the tensile strength of composite samples.

2.5.2 Flexural and inter-laminar shear strength

It is a three-point bend test that promotes the failure by inter-laminar shear. The test is conducted as per ASTM D-2344-84 using the same UTM. A span length of 40 mm and a cross-head speed of 10 mm/minute were maintained. The data recorded during the test used to evaluate the flexural strength using the equation-

$$\mathrm{ILSS} = \frac{3P}{4bt}$$

Where P is the maximum load, b is the width of the specimen, t is the thickness of specimen, and L is the span length of sample.

The data recorded during the three-point bend test is also used to evaluate the flexural strength. The flexural strength (FS) of any composite specimen is determined using the equation:

$$\mathrm{FS} = \frac{3PL}{2bt^2}$$

2.5.3 Dynamic mechanical Analysis

Dynamical behaviors of samples were studied with the help of DMA instruments of Q-800 series controlled stress with a combined motor and transducer. DMA instrument mechanically deforms a sample and measure the sample response. The response of the deformation was monitored as a function of temperature. Energy dissipation by the sample causes the actual sample strain out of the phase with the driver signal. The instrument detects this time shift as a phase angle and the calculation are made to determine the storage modulus E', a measure of material stiffness and the loss modulus E، a measure of material’s viscosity. The ratio of these two properties, E’/E, is designated tan delta (δ) which is useful in determining the extent of mechanical cure.

2.5.4 Thermal gravimetric analysis

Q-500 series TGA instrument was used to determine the composition of laminate (i.e. ratio of fiber –to-resin) and to predict the thermal stability of both composite laminate up to 1000^0C. Technique was also used to predict the weight loss in composite laminates.

2.5.5 Scanning electron microscopy

Surface of the fractured specimen of sample was observed using scanning electron microscope JEOL-JSM-6480LV. SEM used to study the dispersion behavior and the fractured surface topography. Tensile fractured composite sample were coated with a thin platinum layer and cross section of composite samples were analyzed using SEM.

RESULTS AND DISCUSSION

3.1 IR of vinyl ester resin

An FTIR spectrum of synthesized vinyl ester resin is shown in Figure 2. The preparation of resin was confirmed with the IR spectrum study. Band at 1722 cm^{-1} in vinyl ester spectrum is due to the carbonyl group of the ester and at 1636 cm^{-1} due to the acryloyl double bond which confirms the formation of vinyl ester. Furthermore, lack of ether bond adsorption band at 1120 cm^{-1} and absence of absorption band at 1700 cm^{-1} (attributed to the carboxyl group in methacrylic acid in the vinyl ester resin) also confirms the completion of acid epoxy esterification reaction.

3.2 NMR spectrum

NMR spectra of vinyl ester resin (Figure 3) shows the chemical shift of aromatic protons at 7.15and 6.80 ppm respectively. Methylene group of ethoxylated proton shows the signal at 3.06 and 2.69 ppm. There was an also small doublet at 4.2 ppm due to ethoxylated bis phenol-A-glycidyldimethacrylate. The sharp resonance signal at 1.7 ppm was due to backbone of methyl group of BPA.

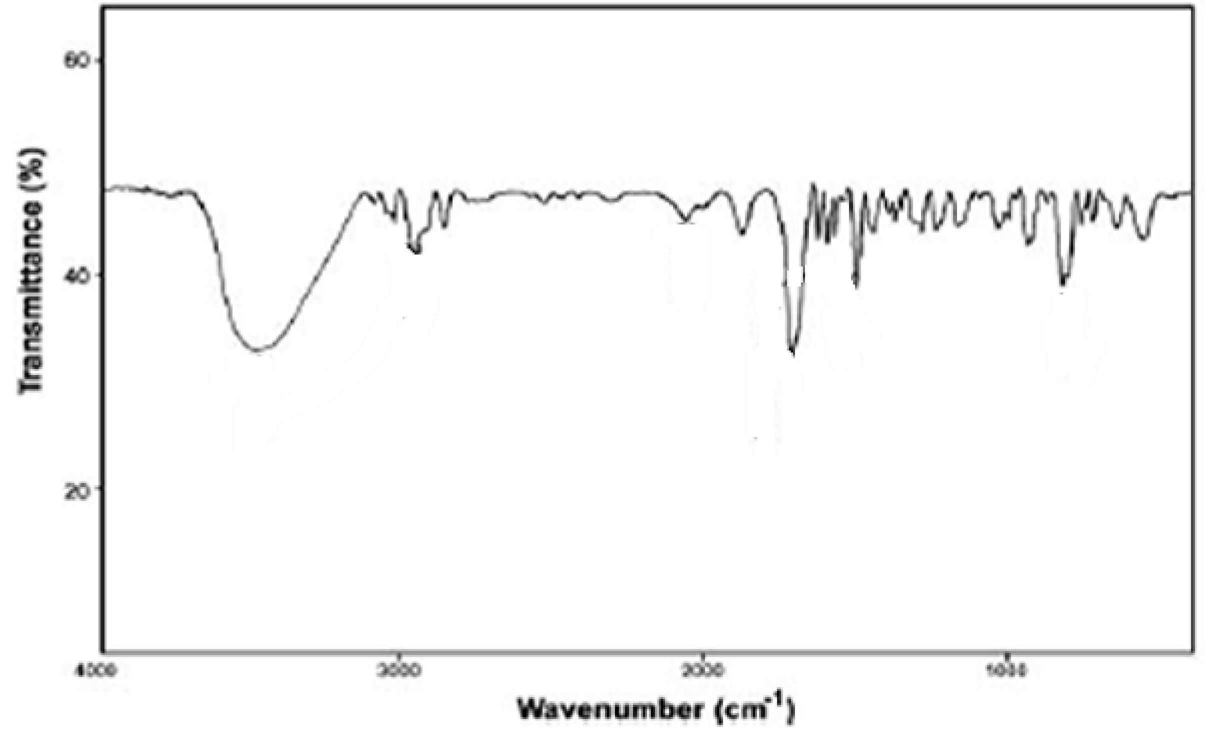

Figure 2—IR spectra of vinyl ester resin

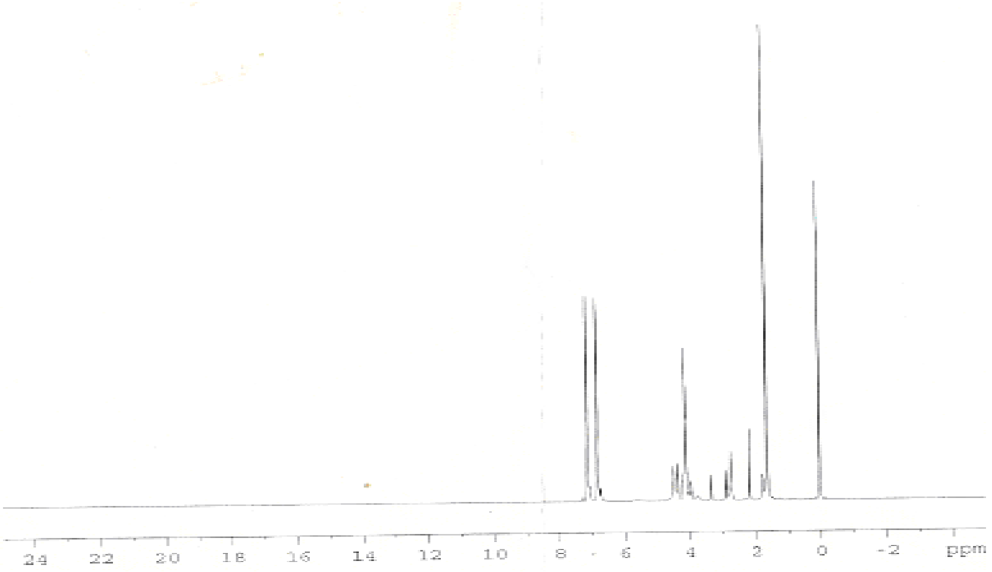

Figure 3 NMR spectrum of vinyl ester resin

3.3 Curing studies of resin

Typical dynamic scans for curing of sample at the program rate of 10^0C/minute are shown in Figure 4. The exothermic curve are in the temperature range 85-110^0C .The thermograph of vinyl ester methyl methacrylate based composite (VM) shows rate of curing become sluggish in the later stage of reaction and is comparatively faster in the early stage where as thermograph of vinyl ester butyl methacrylate based composite (VB) shows the different behavior. The difference in the nature of exotherm containing methyl methacrylate and butyl methacrylate is due to difference in their polar characteristics. In the presence of methyl methacrylate, the reactivity of benzoyl peroxide enhanced more than butyl methacrylate and is act as chain transfer agent. This is the may be the reason for delayed curing with vinyl ester resin in early stage but its effect is not possible in latter stage of the reaction.

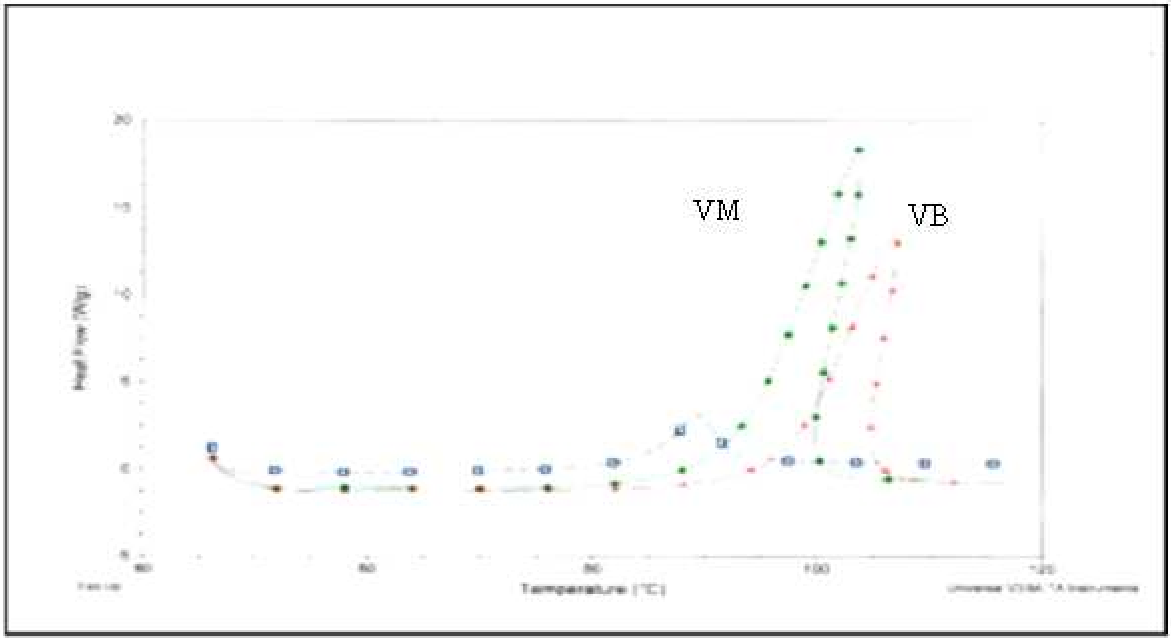

Figure 4 DSC scans at heating rate 10^{0}C/min. of vinyl ester resin with butyl methacrylate & methyl methacrylate in presence of benzoyl peroxide

3.4 Mechanical characterization

Results obtained from mechanical properties characterization of composite is given in table 1. Study shows that inclusion of acrylate diluents has strong influence on the properties of composites. These composite are weaker in bending than in compression and tension.

Table 1 Testing Result (average out of five samples)

S.N.	Laminate code	Tensile strength MPa	Flexural strength Mpa	ILSS MPa
1	**VM**	**342.32**	**188.4**	**33.30**
2	**VB**	**461.74**	**187.78**	**38.11**

The Table 1 indicates the variation of tensile strength by changing the diluents in vinyl ester resin. The higher strength attributed to the presence of polar group in the resin and the silicate and other oxide present in the glass, increasing the interaction due to electrically polarities between the fiber and the matrix. Result shows that laminate VB that is prepared using the butyl methacrylate as diluents in vinyl ester resin shows the higher strength than VM that is from methyl methacrylate. The diluents affect the strength of laminate only in tension having the approximately same value of flexural, ILSS. The type of co-monomer showed marginal effect on the flexural strength and inter laminar shear strength.

3.5 Dynamic mechanical characterization of laminates

Storage modulus, loss modulus, and tan delta curves of the two samples are shown in Figure 6, at different temperature. Typically a sample made of vinyl ester butyl methacrylate /glass (VBD) shows higher initial modulus at room temperature as comparative to vinyl ester methyl methacrylate / glass (VMD) composite. VBD composite shows higher stiffness as VMD can do. At this temperature composite behaves as a tough material because at this it is highly cross link. Above it material goes progressive change in their structure. On increasing the temperature the modulus value of both samples is decrease due to breaking of chain length, loss of moisture.

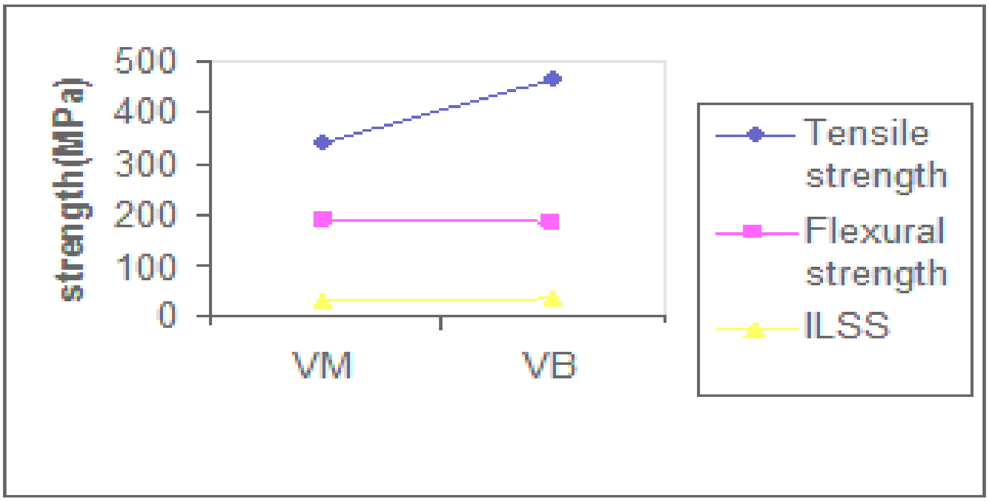

Figure 5 Mechanical characterizations of glass/vinyl ester composite laminates

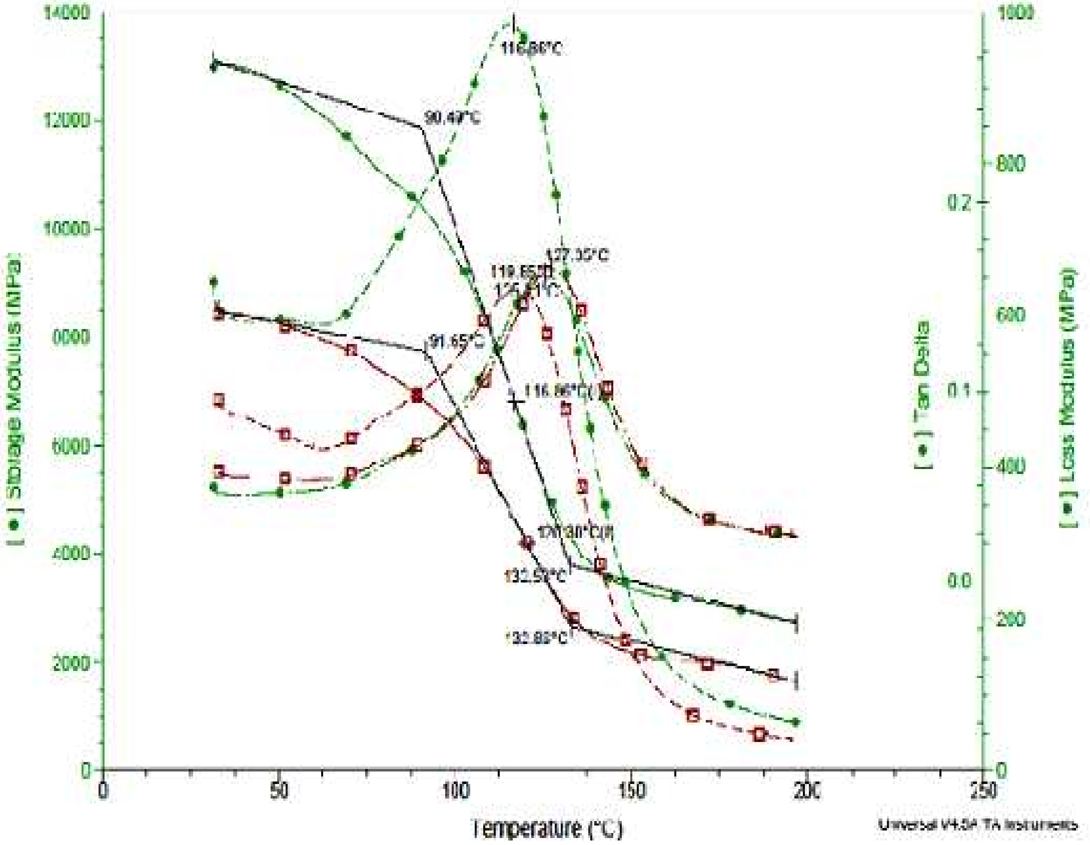

Figure 6 DMA of composite samples

There is rapid decrease in value is observed at 90^0C this may be due to volatile content of acrylate present in the sample and almost constant value of storage modulus is obtained above 120^0C. Loss modulus curve of these two samples at different temperature are indicating that VBD having the higher loss modulus than VMD. Both samples have higher loss modulus at temperature ≈$118\text{-}119^0$C than sharp decrease occurs. Maximum amount of energy is lost as a heat and the loss of vibrational energy is maximum at 118 ^{0}C. High tan delta value of VBD is indicative that it has a non elastics strain component and the low value of VMD indicates that this one is more elastics as comparative to VBD.

3.6 Thermo gravimetric analysis

Composite scrap was analyzed and tested according to ASTM D3418 using heating rate 10^0C/ minute. A graph was plotted between residual weight and temperature. The thermograph of the vinyl ester glass composite using butyl methacrylate is shown in Figure 7. It is clearly shows from Figure 7 that the onset temperature of degradation is about to 375^0C having very less weight loss but suddenly reaching to this temperature, degradation takes place more rapidly due to emission of diluents and resin content leading to a stable mass at about 458^0C. Similar pattern (Figure 8) is obtained with another glass composite having methyl methacrylate as a diluents. The thermograph of this composite show that slight degradation is started is about 387^0C and constant mass is obtained at 446^0C.The experiment results revels that in both composite fiber resin ratio is kept almost 60-65%. Charring in both composite started when the temperature is raised up to 445^0C. Thermal stability of these composites increases in presence of diluents which resulted change in their decomposition behavior due to cross linking. The thermal stability of VMG is slightly higher than VBG.

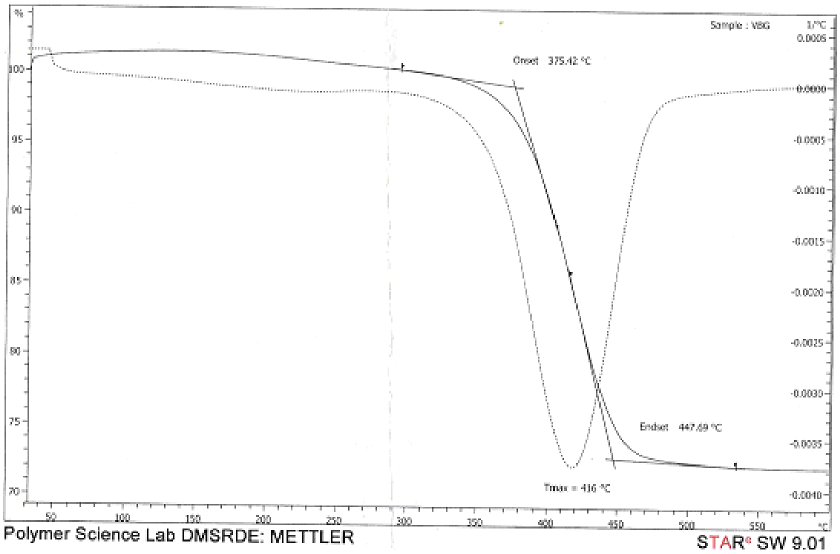

Figure 7 The thermograph of the vinyl ester glass composite using butyl methacrylate

The morphology of the fractured surface (Figure 9, 10) suggested the formation of networks with different microstructure. A slight phase separation is observed in composite made using butyl methacrylate because of least polar character which is due to increased in chain length as well as high molecular weight of butyl methacrylate than methyl methacrylate. In fact, the tendency of phase separation increases with increase in molecular weight.

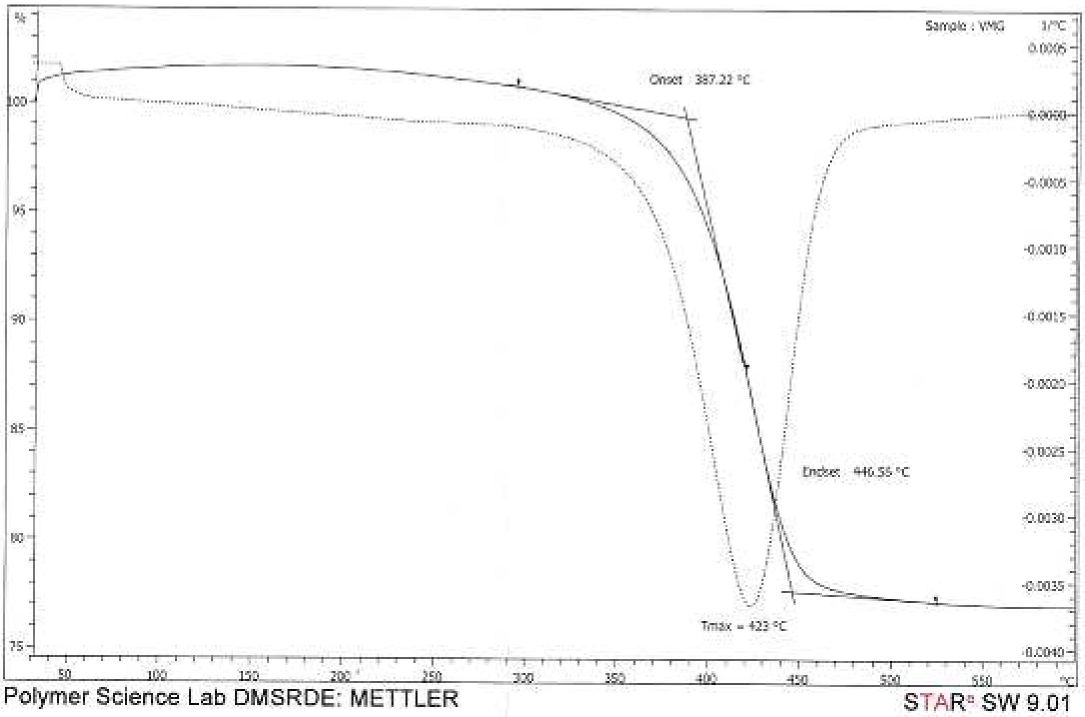

Figure 8 The thermograph of the vinyl ester glass composite using methyl methacrylate

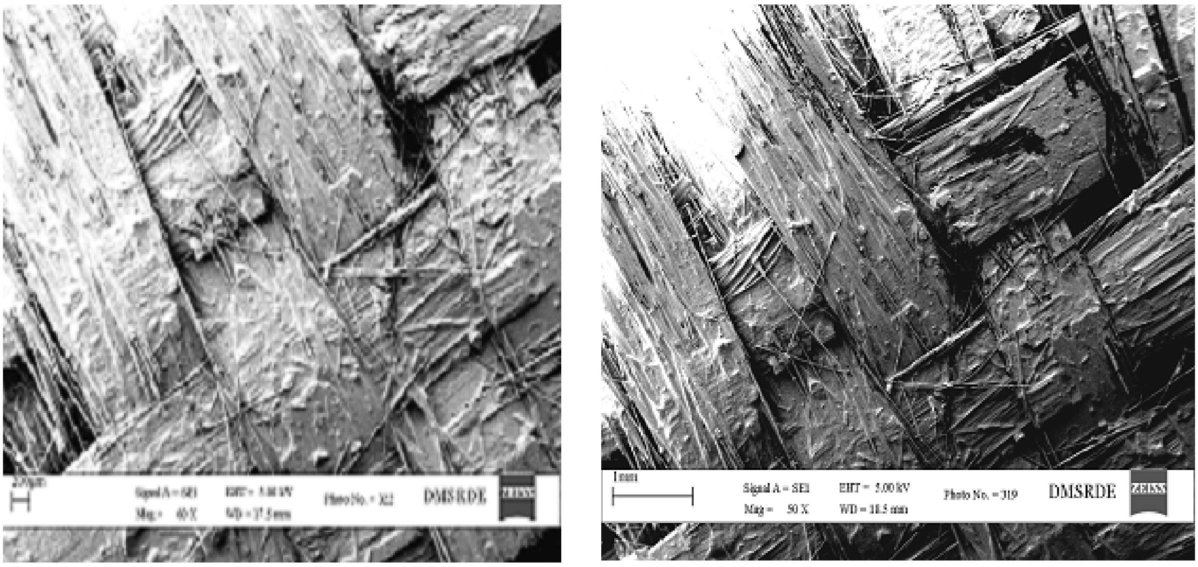

Figure 9 SEM image of failed tensile specimen of glass /vinyl ester composite (VMT) used for conventional tensile test at different magnification

Tensile fractured specimens showed that initially there had been matrix cracking and debonding but fiber were not damaged sufficiently. Slight propagation in crack has been observed in the form of debonding and delamination and then reaches up to maximum valve indicating that complete load transfer from matrix to the fiber has taken place of loading and this failure mode covers maximum percentage followed by the fiber pull out and break due to tensile stress corresponding to a normal tensile test. Fiber bundle fracture is an indicative of the fact that tensile stress failure has occurred.

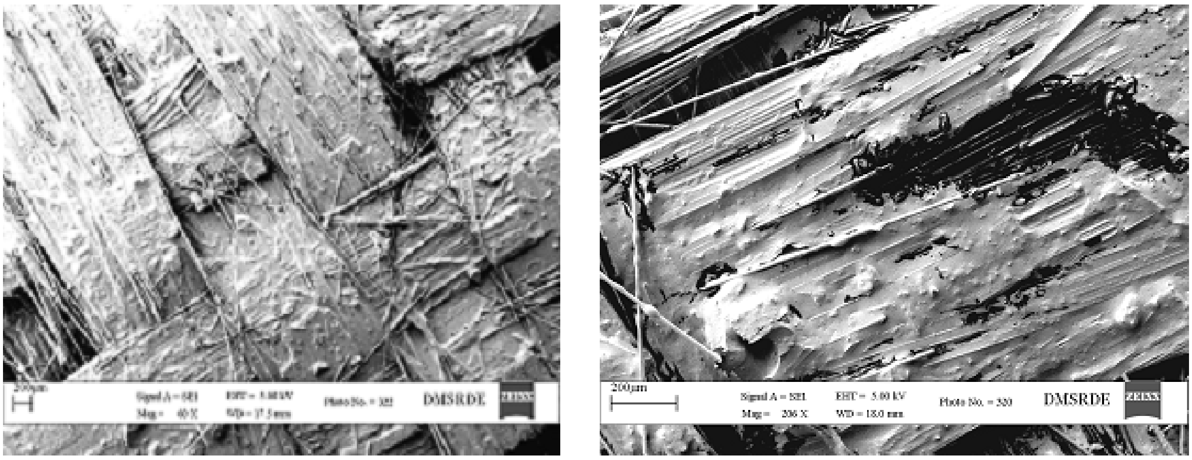

Figure 10 SEM image of failed tensile specimen of glass /vinyl ester composite (VBT) used for conventional tensile test at different magnification

CONCLUSION

Following conclusion can be drawn from this work-

Vinyl ester resin was synthesized from epoxy resin and methacrylic acid using triethylamine as catalyst. IR and NMR spectra confirm the formation of vinyl ester resin. Curing exotherm of this resin with diluents in presence of peroxide was investigated using DSC analysis. The nature of reactive diluents affects the cure isotherm of resin.

Secondly by comparing the tensile, flexural, inter laminar shear strength, we have shown that composite with using butyl methacrylate show higher tensile strength than with methyl methacrylate. Diluents show strong effect on tensile strength but marginal effect on the flexural and inter laminar shear strength. This happens due to increase in the chain length that decrease the chain mobility and hence increase the tensile strength. Increase in chain interaction due to hydrogen bonding and polar attraction tends to fix the individual chain more strongly in position and resists deformation and matrix breakup and therefore produces higher strength.

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