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Reinforced Vinyl Ester Resin Composites with
Different Co-Monomers**

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ABSTRACT: This article reports the mechanical characterization and sliding wear behavior of glass fiber-reinforced vinyl ester resins of varying acid values, based on epoxy-novaloc in the presence of three different comonomers (styrene, methyl acrylate and butyl acrylate) as reactive diluents. It presents a special account of the optimization of fabrication techniques of glass fiber-reinforced vinyl ester resin composites. It outlines optimum reaction conditions such as temperature, time, monomer type and initiator concentration. The experimental plan consisted of preparation of vinyl ester resin followed by the composite samples. Mechanical characterization was done and a comparison was made between the different samples. It was found that these composites have fairly good tensile and flexural properties. The composites with styrene and butyl acrylate as co-monomers had similar tensile strength which was higher than that of the composite with methyl acrylate. Hardness values of the three composites were almost the same without any significant effect of the comonomer type. Volumetric wear rate was estimated for these samples under various test conditions. A steady wear rate regime after certain amount of sliding was observed all the three cases.

KEY WORDS: phenol formaldehyde resin, sliding wear test, comonomers, glass fiber.

INTRODUCTION

COMPOSITE MATERIALS HAVE replaced metals in various engineering applications owing to their numerous advantages, like high strength-to-weight ratio, low cost, etc. There is always an increasing demand for use of these materials in defense applications like naval ships, warplanes, armored vehicles, and re-entry vehicles. Conventionally, metal-based materials are used in these applications and reports are available in the literature [1,2] that characterizes mostly the structural behavior of these materials.

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In recent times, E-glass and carbon fiber based composites have also found extensive application in naval structures [3–5]. Fiber-reinforced polymer composites offer numerous technical advantages for variety of engineering, aerospace and automotive applications. A composite in the present context is a multiphase material that is artificially made, as opposed to one that occurs or formed naturally. In addition, the constituent phases must be chemically dissimilar and separated by a distinct interface [6]. As with resin development; the pace of fiber development has accelerated since the 1950s with the introduction of E glass, R glass, S glass, and special acid and alkali-resistant glass. Glass fiber has been a major reinforcement for the FRP industry, but the drive for lighter, stronger, and stiffer structures has seen the introduction of carbon and poly-aramid fibers. As the result of introduction of carbon and poly-aramid fibers, weaving with glass fibers has led to the proliferation of ‘hybrid’ composites where the optimum properties of the different fibers can be utilized at optimum cost [7].

Vinyl ester resins were first introduced commercially in early 1960s [8]. Today they are one of the most important thermosetting materials. Vinyl ester resins have been widely recognized as materials with excellent resistance to a wide variety of commonly encountered chemical environments. Vinyl ester resins are used to fabricate a variety of reinforced structures [9–16] including pipes, tanks, scrubber and ducts. They are the prime candidates for use in composite for transportation and/or infrastructure. In addition to these applications, vinyl esters are also being used in coatings, adhesives, molding compounds, structural laminates, electrical applications etc. Vinyl ester resins combine the best properties of epoxies and unsaturated polyesters. They can be easily handled at room temperature and have mechanical properties similar to epoxy resins. They have better chemical resistance than cheaper polyester resins, especially hydrolytic stability and at the same time offer greater control over cure rate and reaction conditions than epoxy resins [8]. Vinyl ester resin based on epoxy novaloc are used for chemical storage tanks, pipes and ducting, fume extraction systems, and gas cleaning units as this resin shows superior chemical resistance at high temperatures. These have high tensile elongation along with better corrosion resistance which makes them promising material for producing lining coating with outstanding adhesion to other types of plastics and conventional materials such as steel and concrete. Vinyl ester resin also finds a variety of application in optical fiber coating, topcoats for containers as well as printed circuit boards.

This article reports the mechanical characterization and sliding wear behavior of glass fiber-reinforced vinyl ester resins of varying acid values, based on epoxy-novalocs in the presence of three different comonomers (styrene, methyl acrylate and butyl acrylate) as reactive diluents. The experimental plan is divided into two sections. The first section consists of preparation of vinyl ester resin followed by the cross-linking of vinyl ester with three different comonomers with benzoyl peroxide as the initiator in all the cases. The second part consists of preparation of composite samples. Mechanical characterization is done and a comparison is made between the different samples.

EXPERIMENTAL DETAILS

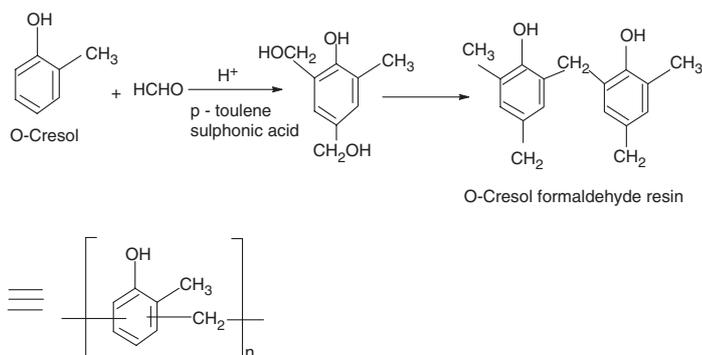
Preparation of Vinyl Ester Resin

Vinyl ester resins (EPN-1138, Ciba-Geigy Ltd., India) are addition products of various epoxide resins and unsaturated monocarboxylic acids, most commonly methacrylic acid [17]. They have terminal reactive double bonds derived from the carboxylic acid used. These

reactive groups can form a cross-linked network with or without the addition of a co-monomer. In many industrial products, vinyl ester resins are comprised of 40–50 wt% styrene. It is common to dilute the vinyl ester oligomers with a low molecular weight co-monomer, such as styrene, vinyl-toluene, or methyl methacrylate, to reduce the room temperature viscosity of the mixture and yield a solution with a typical viscosity in the range of 200–2000 cps. The reaction to form the vinyl ester oligomers is usually catalyzed by tertiary amines, phosphines and alkali salts. Previous research shows that triphenyl phosphine is a more effective catalyst for this reaction as compared to other catalysts [18]. Typical reaction conditions are 120°C for 4–5 h, and hydroquinone is commonly used as the initiator. The conversion of the reaction is 90–95%.

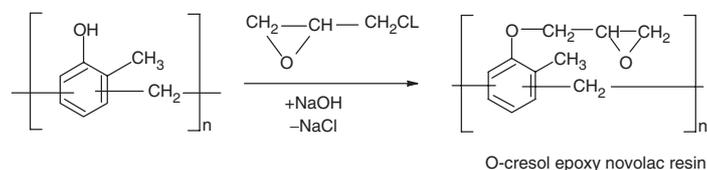
Preparation of O-cresol Formaldehyde Novolac Resin

Preparation of O-cresol formaldehyde novolac resin



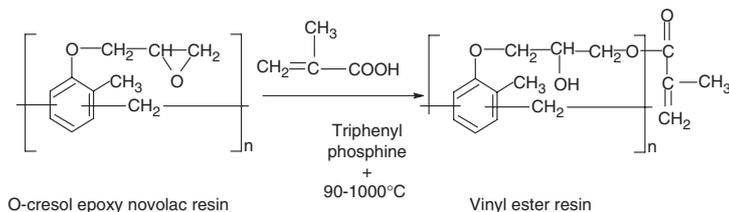
Preparation of O-cresol Epoxy Novolac Resin

Preparation of O-cresol epoxy novolac resin



Preparation of Vinyl Ester Resin Based on O-cresol Novolac Resin

Preparation of vinyl ester resin based on O-cresol novolac resin

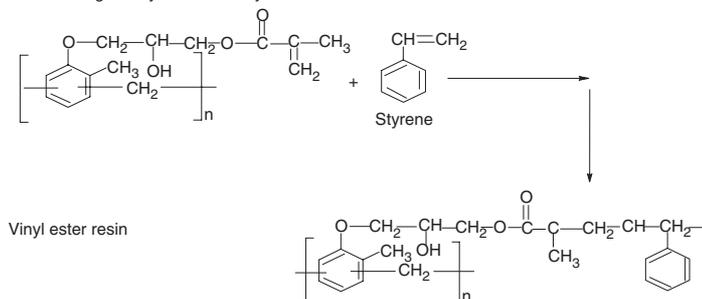


Cross-linking Reaction with Three Different Co-Monomers

Vinyl ester resins are cross-linked by free radical copolymerization of methacrylate end groups with styrene. It is a system of copolymerization of vinyl/divinyl monomers. Gelation occurs when a three-dimensional network or an infinite molecular weight polymer (gel) is formed. A gel molecule cannot be dissolved in any solvent. Experimentally, gel times (the time to reach the onset of gelation at a particular temperature) are measured using solubility experiments. Vinyl ester resins usually contain 30–50 wt% styrene and 50–70 wt% vinyl ester oligomers. Early work on the model phenyl-glycyl-ether methacrylate showed that it reacted more rapidly than styrene in bulk or in solution because of hydrogen bonding between the polymer radical and the methacrylate monomer [19]. Reactivity ratios for this co-polymerization with styrene show that, at least in the early stages of the reaction, the methacrylate content is high relative to styrene and methacrylate's copolymerization. Due to the very high concentration of divinyl monomers, gelation begins at very low conversions. For vinyl ester resins, the onset of gelation is usually rapid-right after the induction period with little or no appreciable increase in viscosity prior to gelation. The time to the onset of gelation is dependent on the concentration of free radical. Increasing the concentration of the initiator and/or accelerators and the use of elevated temperatures will shorten the time to onset of the gel. In this article three different monomers, i.e., styrene, methyl acrylate and butyl acrylate are used for preparing three different samples so as to compare the properties of the three samples. In all the three cases the ratio of resin to comonomer (reactive diluent) is kept 10 : 4 by weight.

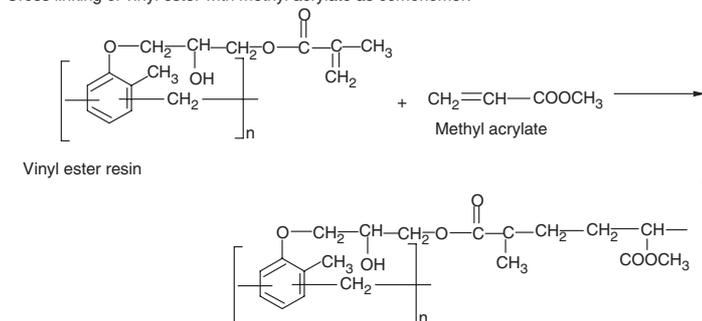
Cross-linking of Vinyl Ester with Styrene as Comonomer

Cross linking of vinyl ester with styrene as comonomer



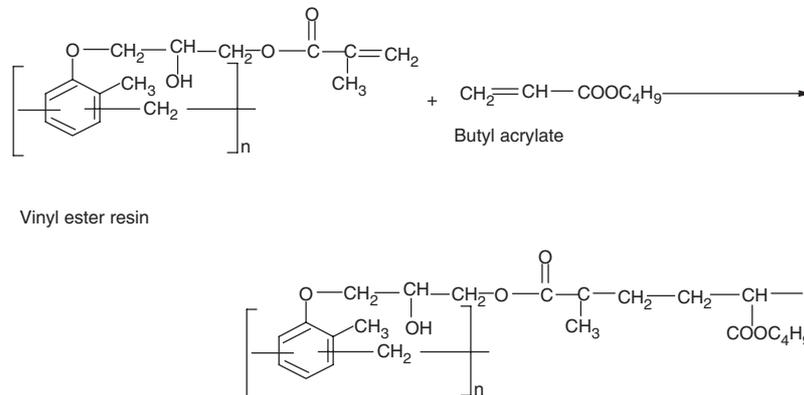
Cross-linking of Vinyl Ester with Methyl Acrylate as Comonomer

Cross linking of vinyl ester with methyl acrylate as comonomer:



Cross-linking of Vinyl Ester with Butyl Acrylate as Comonomer

Cross linking of vinyl ester with butyl acrylate as comonomer



Preparation of Composite Samples

PROCEDURE

Glass fiber-reinforced composites are manufactured in the laboratory by contact molding process. The type of resin used in this work is vinyl ester resin (density 1.42 g/cm^3) supplied by Ciba-Geigy Ltd., India. S-glass fibers (modulus 85.5 GPa , density 2.49 g/cm^3) supplied by Saint Gobian Ltd., is employed as the reinforcing phase. After the mixing of the resin with the comonomer, an initiator benzoyl-peroxide (Central Drug House Ltd. India) is added to the resin in order to have pre-gel formation of the resin. Similar procedure is followed for all the three samples. As thermosetting resins are among the simplest of plastic materials to mix in the activator, pour into a mould, leave to set and then remove from the mould. An exact reproduction of the mould contours is produced, without any need of heat or pressure. The mould can be made from almost any non-porous material such as metal, wood, or plastic, and even from plaster or cardboard if the surface is sealed. Heat speeds up the curing process, produces a more complete cure and allows the use of activators which give a longer pot life. In this study the composite samples are made by hand lay-up technique. Composite slabs of suitable dimension are cut using a diamond cutter for further characterization and wear test.

CURING OF VINYL ESTER RESIN

After preparing the laminates, the samples are air dried for about 4h so that pre-gelation takes place. The curing reaction of vinyl ester resin is a free-radical chain growth cross-linking polymerization between the reactive diluent and the terminal ethylene group of the vinyl ester resin. The vinyl ester monomer provides cross-linking capacity and branch points for the developing network while the styrene monomer provides linear chain extension. Depending on the temperature and other curing conditions, some of the species remain unreacted after the curing in the form of residual monomer and soluble polymer and do not contribute towards the cross-linked network.

Table 1. Curing schedule for the composite samples.

Sl. No.	Temperature (°C) (Curing process)	Pressure (kgf/cm ²)	Time (h)
01	Room temperature	60	12
02	60	60	8
03	90	60	4
	Post curing process		
04	120	60	4

A compression molding machine is used for curing of the samples. The curing schedule followed is detailed in Table 1.

Three different composite samples are manufactured. They are named on the basis of type of comonomer used (sample A – styrene as comonomer, sample B – methyl acrylate as comonomer, and sample C – butyl acrylate as comonomer).

MECHANICAL CHARACTERIZATION

Micro-hardness

Micro-hardness measurement is done using a Leitz micro-hardness tester. A diamond indenter, in the form of a right pyramid with a square base and an angle 136° between opposite faces, is forced into the material under a load F . The two diagonals X and Y of the indentation left on the surface of the material after removal of the load are measured and their arithmetic mean L is calculated. In the present study, the load considered $F=24.54$ N and Vickers hardness number is calculated using the following equation.

$$H_V = 0.1889 \frac{F}{L^2} \quad (1)$$

and $L = X + Y/2$, where F is the applied load (N), L is the diagonal of square impression (mm), X is the horizontal length (mm), and Y is the vertical length (mm).

Tensile Strength

The tensile test is generally performed on flat specimens. The commonly used specimens for tensile test are the dog-bone type and the straight side type with end tabs. During the test a uni-axial load is applied through both ends of the specimen. The ASTM standard test method for tensile properties of fiber resin composites has the designation D 3039-76. The tensile test is performed in the universal testing machine (UTM) Instron 1195 and results are analyzed to calculate the tensile strength of composite samples.

Flexural and Inter-laminar Shear Strength

The short beam shear (SBS) tests are performed on the composite samples at room temperature to evaluate the value of inter-laminar shear strength (ILSS). It is a three-point

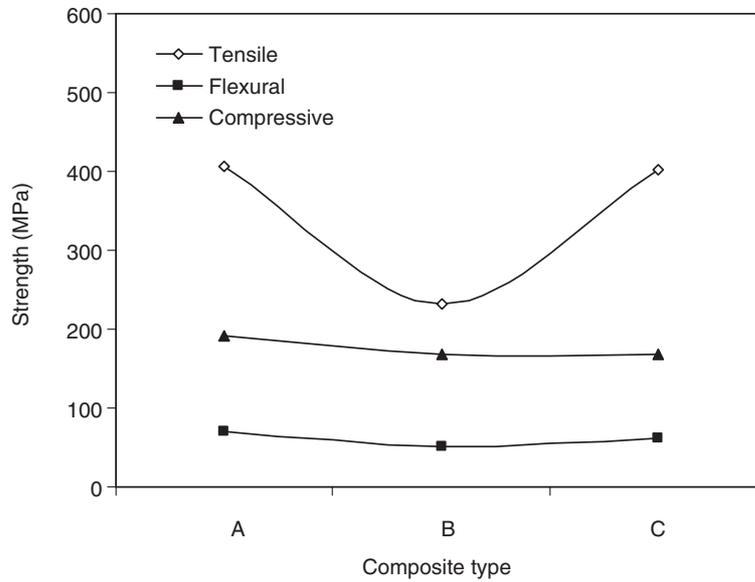


Figure 1. Strength comparison of various composite samples.

bend test, which generally promotes failure by inter-laminar shear. The SBS test is conducted as per ASTM standard (D2344-84) using the same UTM. The loading arrangement is shown in Figure 1. A span length of 40 mm and a cross-head speed of 10 mm/min are maintained. The ILSS values are calculated as:

$$\text{ILSS} = \frac{3P}{4bt} \quad (2)$$

where P is maximum load, b is the width of the specimen, and t is the thickness of the specimen.

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:

$$\text{FS} = \frac{3PL}{2bt^2} \quad (3)$$

where L is the span length of the sample.

Scanning Electron Microscopy

The surfaces of the specimens are examined directly by scanning electron microscope JEOL JSM-6480LV. The composite samples are mounted on stubs with silver paste. To enhance the conductivity of the samples, a thin film of platinum is vacuum-evaporated onto them before the photomicrographs are taken.

Wear Test

To evaluate the performance of these composites under dry sliding condition, wear tests are carried out in a pin-on-disc type friction and wear monitoring test rig (supplied by DUCOM) as per ASTM G 99. The counter body is a disc made of hardened ground steel (EN-32, hardness 72 HRC, surface roughness $0.6 \mu Ra$). The specimen is held stationary and the disc is rotated while a normal force is applied through a lever mechanism. A series of tests are conducted with three sliding velocities of 54, 80, and 110 m/min under two different normal loading of 10 and 15 N. The material loss from the composite surface is measured using a precision electronic balance with accuracy ± 0.1 mg and the volumetric wear rate (mm^3/s) is then expressed on 'volume loss' basis as:

$$W_v = \frac{\Delta m}{\rho t} \quad (4)$$

where Δm is the mass loss in the test duration (g); ρ is the density of the composite (g/mm^3); and t is the test duration (s).

RESULTS AND DISCUSSION

The characterization of the composites reveals that inclusion of any comonomer has strong influence on the physical and mechanical properties of composites as shown in Table 2. In this section results of the various characterization tests are presented and discussed.

SAMPLE DESCRIPTION

Sample A is made by using styrene as the comonomer with the vinyl ester resin. Density of this sample is found to be $1.87 \text{ g}/\text{cm}^3$.

Sample B is made by using methyl acrylate as the comonomer with the vinyl ester resin. Density of this sample is found to be $1.77 \text{ g}/\text{cm}^3$.

Sample C is made by using butyl acrylate as the comonomer with the vinyl ester resin. Density of this sample is found to be $1.82 \text{ g}/\text{cm}^3$.

Fiber weight fraction in all the three samples is taken as 65%.

Tensile, Compressive and Flexural Strength

Figure 1 presents the comparison of tensile, compressive and flexural strength of the three different composites. It is seen that the composites with styrene and butyl acrylate (samples A and C) possess almost the same tensile strength while the one with methyl acrylate exhibits a much lower value. This implies that the type of comonomer in the vinyl ester resin affects the strength of fiber-reinforced composite in tension. It is also clear from this figure that all the three types of composites have more or less equal strength in compression and bending. Another important observation is that these composites are much weaker in bending than in compression and tension.

Micro-hardness

The hardness values on the B scale of the Rockwell hardness test for the three samples A, B and C are recorded as 90HRB, 92HRB, and 89HRB, respectively. It can be seen that

the type of comonomer has marginal effect on the hardness of the composites taken in this investigation.

Sliding Wear Characteristics

The variation of volumetric wear rate of three composites with sliding distance is presented in Figure 2. The sliding velocity is kept constant at 80 m/min and the normal load at 10 N throughout the test duration. It is seen that the wear rate for all the samples increases linearly with sliding distance and after certain duration attains almost a steady value. It is also noted that in the steady region, the wear rates of samples A, B, and C differ only marginally.

It is worth noting that the volumetric wear initially increases with time and sliding distance and this trend is observed in the case of all the three composites. When there is

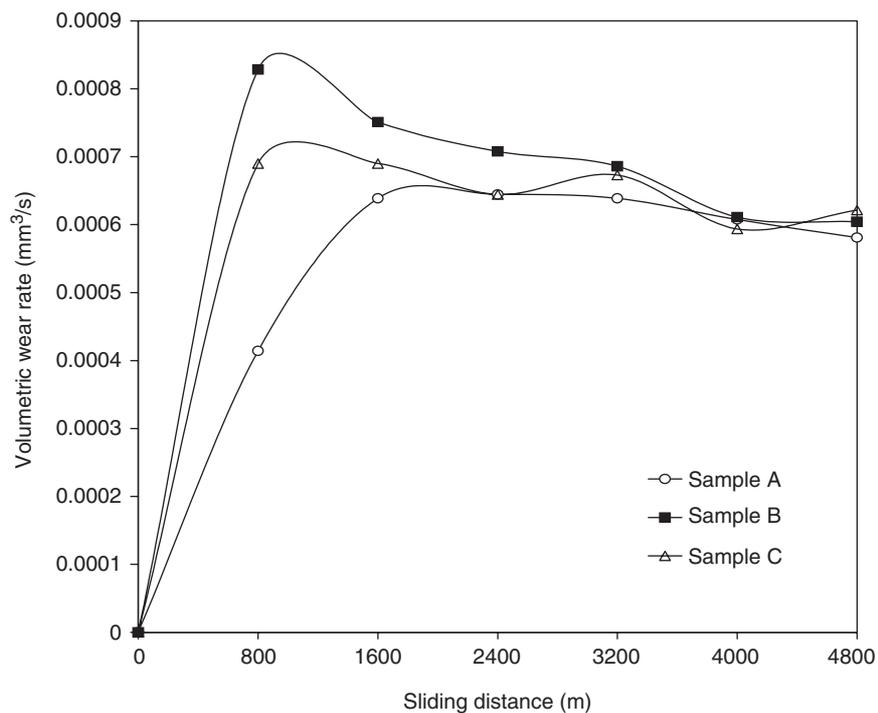


Figure 2. Variation of wear rate with sliding distance.

Table 2. Mechanical properties characterization of three composites.

Sample type	Tensile strength (MPa)	Compressive strength (MPa)	Flexural strength (MPa)	Hardness (HRB)	Density (g/cm ³)
A	405.50	70.83	190.76	90	1.87
B	231.94	50.32	168.63	92	1.77
C	401.82	60.93	168.26	89	1.82

contact between the composite and counter body, the surface is sheared and ploughed. This leads to mass loss at a relatively faster rate. With increase in test duration and sliding distance the asperities on the composite surface gradually disappear and a decline in the rate of material loss is observed.

CONCLUSIONS

The following conclusions are drawn on the basis of results obtained:

1. Fabrication of S-glass fiber-reinforced vinyl ester resin composites with different co-monomers such as styrene, butyl acrylate and methyl acrylate is possible.
2. These composites are found to have fairly good tensile and flexural properties along with low densities. The composites with styrene and butyl acrylate as co-monomers have similar tensile strength which is higher than that of the composite with methyl acrylate.
3. Hardness values of the three composites are almost the same without any significant effect of the co-monomer type.
4. Volumetric wear rate is maximum for Sample A, intermediate for Sample B and least for Sample C under similar test conditions. A steady wear rate regime after a certain amount of sliding is observed in all three cases.

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