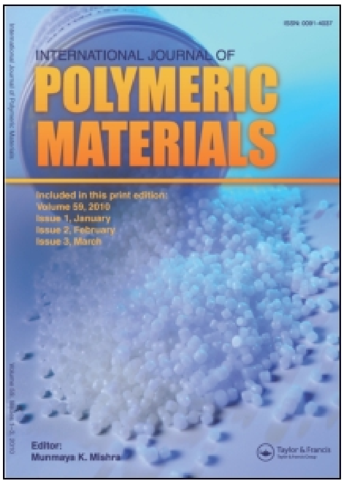

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DEVELOPMENT AND CHARACTERIZATION OF VINYL ESTER OLIGOMER (VEO) MODIFIED UNSATURATED POLYESTER INTERCROSSLINKED MATRICES AND COMPOSITES

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An intercrosslinked network of varying percentage of vinyl ester oligomer (VEO) modified unsaturated polyester matrices has been developed. Vinyl ester oligomer was prepared by reacting commercially available epoxy resins GY 250 (Ciba-Geigy) and acrylic acid and was used as toughening agent for unsaturated polyester (UP) resin. Unsaturated polyesters modified with 10%, 20% and 30% (by wt) of vinyl ester oligomer were made. E-glass reinforced composites were fabricated by hand lay–up technique using VEO-UP matrix systems. VEO modified unsaturated polyesters were characterized using differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and heat deflection temperature (HDT) analysis. The matrices in the form of castings and E-glass reinforced composites were characterized for their mechanical properties, i.e., tensile strength, flexural strength and unnotched-Izod impact test as per ASTM methods. Data obtained from mechanical studies and thermal characterization indicate that the introduction of VEO into unsaturated polyester resin improves the thermo-mechanical properties and negatively affects the moisture resistance according to its percentage concentration.

Keywords: unsaturated polyester resin, vinyl ester oligomer, tensile strength, Izod Impact strength, glass transition temperature, thermal degradation temperature, moisture absorption

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INTRODUCTION

Large amounts of unsaturated polyester resins are used worldwide to fabricate composites employed for engineering and industrial applications. They are mainly used in sheet molding and bulk molding compounds for manufacturing automotive parts [1] and marine crafts and other industrial products because of their light weight, good mechanical properties [2] and excellent processability. However, the use of thermosetting materials is often limited by their toughness properties, which affect the impact property, lifetime and durability of the components, and shrinkage during cure. The shrinkage problems are minimized using additives like poly(methyl methacrylate), poly(vinyl acetate) and polypropylene glycol [3–5]. Improvements in impact strength and strain to failure were achieved by blending with liquid rubbers [6–9]. Block copolymers of carboxyl and hydroxyl terminated acrylonitrile butadiene copolymers (CTBN and HTBN) increase the fracture toughness and strain to failure [10]. Interpenetrating networks of commercial unsaturated polyester and polyurethanes have been used to improve the impact strength [11, 12] and these materials used in reaction injection molding (RIM) technology [13]. Improvements in thermal properties and elastic modulus have been investigated recently by modifying with a co-reactive component bismaleimide [14]. Toughness of unsaturated polyester can also be achieved by the reduction of crosslink density or use of plasticizers. On the other hand, the most effective toughening is achieved by addition of a second phase in the form of particles. In our earlier work, toughness of epoxy matrices was enhanced by the incorporation of siloxane and unsaturated polyester into epoxy resin [15–17]. The thermoset interpenetrating polymer networks (IPNs) have been extensively studied due to their enhanced mechanical properties [18–21].

Vinyl ester resins are similar to polyester resins, however the reactive sites are positioned only at the end of the molecular chains, therefore crosslinking can take place at the chain ends. The whole length of the molecular chain is available to absorb shock loading, making the vinyl ester resin tougher and more resilient than polyesters. Epoxy based vinyl ester resins have exceptionally high physical properties and chemical resistance. Additional attributes include low water absorption rates, high heat distortion temperatures, abrasion resistance combined with light weight and good flexural strength, making these resin products ideal for marine applications as well as applications in extremely challenging environments. Hence, in the present work, an attempt is made to improve both toughness and thermal stability of unsaturated polyester resin by forming hybrid networks with oligomeric vinyl ester.

EXPERIMENTAL

Materials

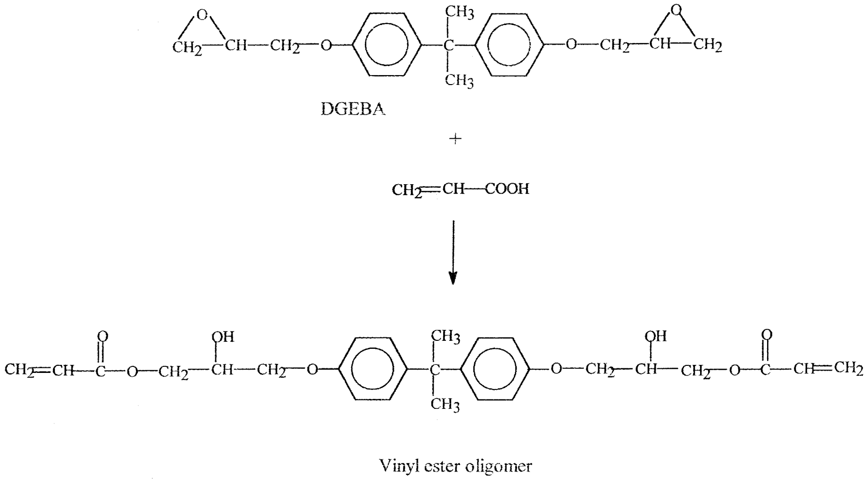
The commercially available unsaturated polyester (UP) resin (manufactured using terephthalic acid, maleic anhydride and propylene glycol with 30% styrene having viscosity of 600 cP), epoxy resin (Diglycidyl ether of bisphenol A (DGEBA) GY 250 having epoxy equivalent of about 180–190, (obtained from Ciba-Geigy Ltd., India), benzoyl peroxide and acrylic acid (E. Merck, Germany) were used as received. VEO was prepared in the laboratory.

Preparation of Vinyl Ester Oligomer

VEO was prepared using acrylic acid and epoxy resin. The synthesis and characterization of VEO were reported in detail elsewhere [22, 23]. The reaction scheme for the preparation of VEO is given in Scheme 1.

Preparation of Unsaturated Polyester-VEO Blends

Fixed amounts of unsaturated polyester resin (100 g) and benzoyl peroxide (2 wt%), and varying amounts of VEO (10, 20 and 30 g) were mixed at 50 °C for 10 minutes with constant stirring. The mixture was degassed to remove entrapped air. It was then transferred into a preheated mold and cured at 60 °C for 4 hours and post cured at 120 °C for 2 hours.



SCHEME 1 Preparation of vinyl ester oligomer.

Fabrication of Composites

Composite material was prepared by hand lay-up technique using 10 mil bi-directional woven E-glass fabric. Fabric pieces of size 20 × 12.5 cm weighing 50 g were heated to 150 °C in a hot air oven for two hours to remove moisture and then cooled to 30 °C. Preweighed mixture of VEO-UP resin with curing agent (benzoyl peroxide) was applied over a fabric sheet using a rubber roller. The prepreg material is laid one over another in the mold and pneumatic pressure of 2 kg cm^{-2} was applied for a period of 30 min at 60 °C for 3.5 hours and post cured at 120 °C for 2 hours.

Test Methods

Tensile and flexural properties

The tensile (stress-strain) properties were determined using dog–bone–shaped specimens according to ASTM-D3039 method using Instron testing machine (Model 6025 UK) at a crosshead speed of 2 mm per minute. For fiber–reinforced composites specimens having dimensions 25 mm width, 200 mm length, and 3 mm thickness were used for tensile testing. The flexural strength was measured as per ASTMD 790.

Unnotched Izod impact test

The unnotched Izod impact strength of each sample was tested as per ASTM D 256–88. All samples were tested unnotched so they would be more sensitive to the transition between ductility and brittleness. Specimens having thickness 3.2 mm with 10 mm cross-section and 64 mm length were clamped in the base of the pendulum testing machine so that they are cantilevered upward. The pendulum is released and the force consumed in breaking each sample is calculated from the height the pendulum reaches on the follow through.

Thermal studies

Glass transition temperature (Tg) of the samples was determined using DSC 2910 (TA Instruments, USA) in the temperature range between 50 °C and 250 °C at a heating rate of 10 °C per minute in nitrogen atmosphere. Thermogravimetric analysis (TGA) was carried out using Thermal Analyst 2000 (TA Instruments, USA) at a heating rate of 10 °C per minute in air atmosphere.

Heat deflection temperature analysis

The heat deflection temperature of the samples was tested as per ASTM D 648–72. The heat deflection temperature measures the temperature at which deformation occurs when the specimen, having dimensions 127 mm in length, 13 mm in thickness and 3 mm in width, [15] placed in an oil bath under a load of 1.82 M Pa and the temperature is raised at a rate of 2 °C per minute. The temperature at which the specimen deflects by 0.25 mm is noted. The deflection is monitored in an linear variable displacement transducer.

Water absorption

The water absorption property of the samples was tested as per ASTM D 570. The cured specimens having dimensions 60 mm in square, 3 mm in thickness, were immersed in distilled water for 24 hours. Specimens were removed, the surface water was removed using a tissue paper, and weighed to an accuracy of 0.001g.

RESULTS AND DISCUSSION

Mechanical Properties

The values of tensile strength of unmodified unsaturated polyester, unsaturated polyester modified with varying percentage of VEO and E-glass reinforced VEO-UP composites are presented in Table 1. From the data, it is observed that the incorporation of 10%, 20% and 30% (by wt) VEO into unsaturated polyester resin increases the tensile strength by 5%, 14% and 25% respectively when compared with unmodified unsaturated polyester system, and this may be due to the formation of network between the unsaturated polyester chains and VEO. Highest tensile value, 46 MPa higher than that of original value 28.4 MPa of unmodified unsaturated polyester, is obtained for the

TABLE 1 Mechanical Properties of Unsaturated Polyester, VEO-UP Matrices, E-glass Reinforced Unsaturated Polyester and VEO-UP Composites

Matrix system	UP/VEO composition	Tensile strength (Mpa)	Tensile modulus (Mpa)	Flexural strength (Mpa)	Flexural modulus (Mpa)	Unnotched Izod impact strength (J/m)
A	100/00	28.2	1001.8	40.1	785.1	20.3
B	100/10	29.4	1051.0	46.2	905.5	21.8
C	100/20	32.2	1144.6	55.9	1039.5	23.4
D	100/30	35.0	1251.2	56.7	1111.7	25.1
		E-glass fiber reinforced composites (40% E-glass)				
E	100/00	84.6	2905.2	201.5	3845.9	198.9
F	100/10	92.3	3153.6	226.3	4344.3	211.4
G	100/20	93.9	3204.8	268.3	4883.7	222.3
H	100/30	105	3503.1	277.4	5002.6	230.8

unsaturated polyester modified with 30% VEO. A three–fold increase in the value of the tensile strength is observed when UP matrix and VEO-UP matrix systems are reinforced with E-glass fiber (Table 1). The E-glass fiber–reinforced composites also exhibit similar trends as that of unreinforced matrices.

Flexural behavior of unmodified unsaturated polyester, unsaturated polyester modified with VEO, are presented in Figures 1 and 2. Introduction of 10%, 20% and 30% (by wt) of VEO into unsaturated polyester resin increases the flexural strength by 14%, 31% and 38%, respectively when compared with an unmodified unsaturated polyester system. This may be attributed to the formation of chain entanglements between unsaturated polyester and VEO matrix which, in turn, enhance the flexural properties. E-glass reinforcement on flexural strength follows the similar trend as observed in the case of tensile strength.

The unnotched Izod impact strength obtained for unmodified unsaturated polyester, modified with VEO, is presented in Table 1. Incorporation of VEO into unsaturated polyester enhances the toughness according to the percentage content due to the excess free volume caused by chain entanglement with high-energy absorption.

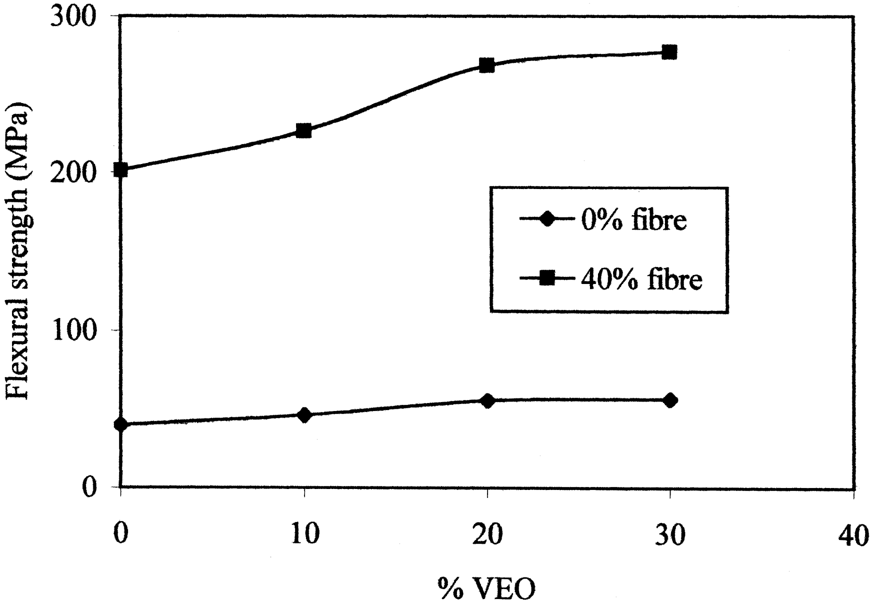


FIGURE 1 Effect of VEO content on flexural strength.

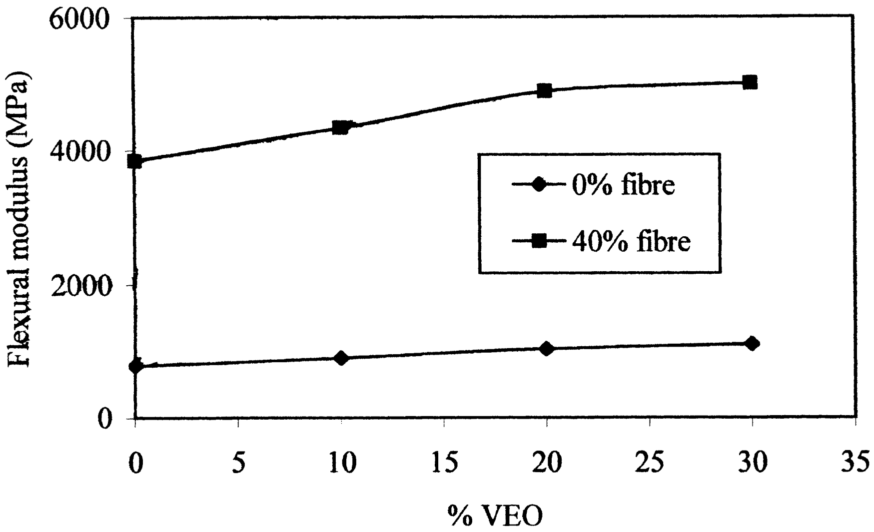


FIGURE 2 Effect of VEO content of flexural modulus.

The influencing effect on toughness by unsaturated polyester varies 7%, 10%, and 23% for the VEO concentration of 10%, 20% and 30% (by wt), respectively. A ten–fold increase in the value of the impact strength is observed when UP matrix and VEO-UP matrix systems are reinforced with E-glass fiber (Table 1).

Thermal Characteristics

The curing behavior of unsaturated polyester resin and VEO modified unsaturated polyester are presented in Table 2. All the modified system show an exothermic peak at higher and broader temperatures

TABLE 2 Glass Transition Temperature and Weight Loss Temperature of UP/VEO Matrices (TGA)

Sample code	UP/VEO composition	Glass transition temperature °C	Weight loss temperature °C	
			10%	20%
A	100/00	75.3	289	321
B	100/10	72.2	300	347
C	100/20	70.5	320	377
D	100/30	68.3	350	392

than the unmodified unsaturated polyester systems. The peak maximum temperature and peak area increase due to the restricted chain mobility of the network with increasing concentration of VEO.

The glass transition temperature of VEO modified unsaturated polyester resin is presented in Table 2. The value of Tg is lowered with respect to increasing VEO concentration due to the reduced crosslink density caused by longer spacing VEO chains.

Thermogravimetric analysis (TGA) of VEO modified unsaturated polyester matrix systems in air was carried out and presented in Table 2. It is observed that the degradation temperature increases with increasing percentage of VEO, which, in turn, implies that the VEO incorporation enhances the thermal stability in addition to the decreases in percentage weight loss. For example, the temperatures required for 10% and 20% weight loss of unmodified unsaturated polyester resin are 289 °C and 321 °C, whereas the temperatures, required to attain the same percentage weight loss for 10% VEO modified unsaturated polyester are increased to 350 °C and 392 °C. This may be explained to the higher thermal stability of epoxy back bone (DGEBA) which, in turn, stabilizers the matrix system against thermal degradation.

Table 3 presents the heat deflection temperature of the unmodified, VEO modified unsaturated polyester matrix systems. The values of HDT were lowered with respect to increased VEO concentration due to reduced crosslink density caused by VEO chains.

Water Absorption

Even though epoxy based vinyl ester resins are known for their low water absorption, the water absorption of VEO modified unsaturated polyester increases. This may be due to the formation of excess free volume caused by chain entanglement and reduced crosslink density (Table 3).

TABLE 3 Heat Deflection Temperature and Water Absorption Properties of UP/VEO Matrices

Sample code	UP/VEO composition	Heat deflection temperature °C	Water absorption(%)
A	100/00	72.3	0.23
B	100/10	70.1	0.27
C	100/20	68.5	0.30
D	100/30	64.2	0.33

CONCLUSIONS

Vinyl ester oligomer (VEO) modified unsaturated polyester hybrid network matrices and composites were developed and characterized for their thermal and mechanical properties. From the data it is concluded that significant improvement in toughness of the unsaturated polyester matrix was obtained by forming interpenetrating network with vinyl ester oligomer. Mechanical studies and thermal characterisation indicate that the introduction of VEO into unsaturated polyester resin improves the toughness and thermal stability due to the presence of epoxy back bone. The E-glass fiber reinforcement in VEO toughened unsaturated polyester further enhances the mechanical properties. In addition, it was observed that the moisture absorption increases with increasing VEO content. It is suggested that the vinyl ester modified unsaturated polyester matrix system can be used to fabricate advanced composite components of improved toughness with better thermo-mechanical behavior for engineering applications.

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