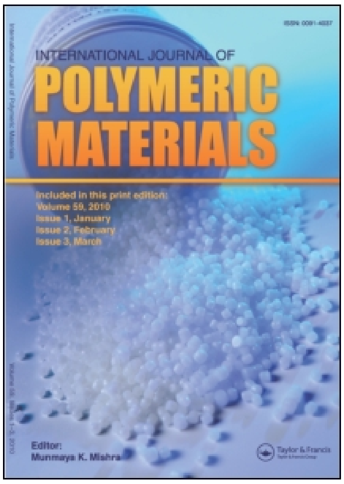

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MECHANICAL PROPERTIES OF BISMALEIMIDE (N,N'-BISMALEIMIDO-4,4'-DIPHENYL METHANE) - VINYL ESTER OLIGOMER (VEO) MODIFIED UNSATURATED POLYESTER INTERCROSSLINKED MATRICES FOR ADVANCED COMPOSITES

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MECHANICAL PROPERTIES OF BISMALEIMIDE (N,N′-BISMALEIMIDO-4,4′-DIPHENYL METHANE) - VINYL ESTER OLIGOMER (VEO) MODIFIED UNSATURATED POLYESTER INTERCROSSLINKED MATRICES FOR ADVANCED COMPOSITES

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An intercrosslinked network of varying percentages of N,N′-bismaleimido-4,4′-disphenyl methane (BMI), vinyl ester oligomer (VEO) modified unsaturated polyester (UP) matrices have been developed. Vinyl ester oligomer was prepared by reacting commercially available epoxy resin GY 250 (Ciba-Geigy) and acrylic acid was used as toughening agent for unsaturated polyester resin. BMI-VEO-UP matrices were characterized for their mechanical properties, viz tensile strength, flexural strength and unntoched Izod impact test as per ASTM standards. The dielectric strength and water absorption measurements were also performed according to ASTM standards. Data obtained from mechanical studies, dielectric strength and water absorption indicate that the introduction of VEO into unsaturated polyester resin improves mechanical properties and affects the moisture resistance according to its percentage concentration. The incorporation of BMI into the VEO modified unsaturated polyester system improves mechanical properties, dielectric strength and resistance to moisture absorption according to its percentage concentration.

Keywords: unsaturated polyester resin, vinyl ester oligomer, bismaleimide, tensile strength, Izod impact strength, dielectric strength, moisture absorption

INTRODUCTION

Among the thermo setting resins, unsaturated polyester resins are most commonly and commercially competitive matrix resins used to fabricate fiber−reinforced polymeric composites. The unsaturated polyester composites are useful in sheet molding and bulk molding compounds for manufacturing automotive parts and marine crafts and

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other industrial products because of their light weight and good mechanical properties [1]. Unsaturated polyester has limited characteristics of impact strength due to its high crosslinking density and shrinkage during cure. The shrinkage of the polyester resin during curing with reactive diluent leads to warpage and cracking, and this can be minimized using low-profile additives like poly(methyl methacrylate), poly(vinyl acetate) and polypropylene glycol [2–4]. Improvements in impact strength and strain to failure were achieved by blending with liquid rubbers [5–8]. Block copolymers of carboxyl and hydroxyl terminated acrylonitrile butadiene copolymers (CTBN and HTBN) increase the fracture toughness and strain to failure [9] IPN's of unsaturated polyester and polyurethanes have been used to improve the impact strength [10]. It has been reported recently that the utility of unsaturated polyester resin can be improved by modifying with a co-reactive component bismaleimide [11]. Improvement in thermo-mechanical properties was observed by the introduction of bismaleimide into epoxy resin [12–13], siliconized epoxy [14] and unsaturated polyester modified epoxy resin [15]. Bismaleimides possess high crosslinking ability, high glass transition temperature, high thermal stability, high char yield, excellent fire resistance, superior specific strength and specific modulus, and low water absorption.

The most common rate employed to toughen the brittle polymer is using a polymer segment capable of absorbing energy and having resilent character [16]. 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 only at the chain ends. The whole length of the molecular chain is available to absorb shock loading, making vinyl ester resin tougher and more resilient than polyesters. Hence, in the present work, an attempt is made to improve toughness, mechanical, and dielectric behavior of unsaturated polyester resin by forming an intercrosslinking network with oligomeric vinyl ester and bismaleimide.

EXPERIMENTAL

Materials

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

N,N′-bismaleimido-4,4′-diphenyl methane and VEO were prepared in the laboratory using reported procedures and characterized.

Preparation of Vinyl Ester Oligomer

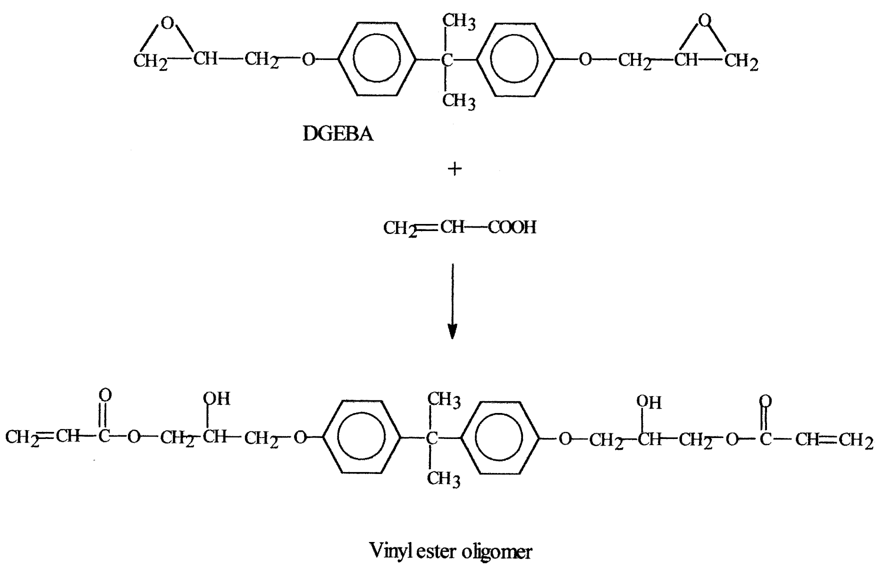
VEO was prepared using acrylic acid and epoxy resin. The synthesis and characterization of VEO were reported in detail elsewhere [17–18]. The reaction scheme for the preparation of VEO is given in Scheme 1.

Preparation of Unsaturated Polyester-VEO Blends

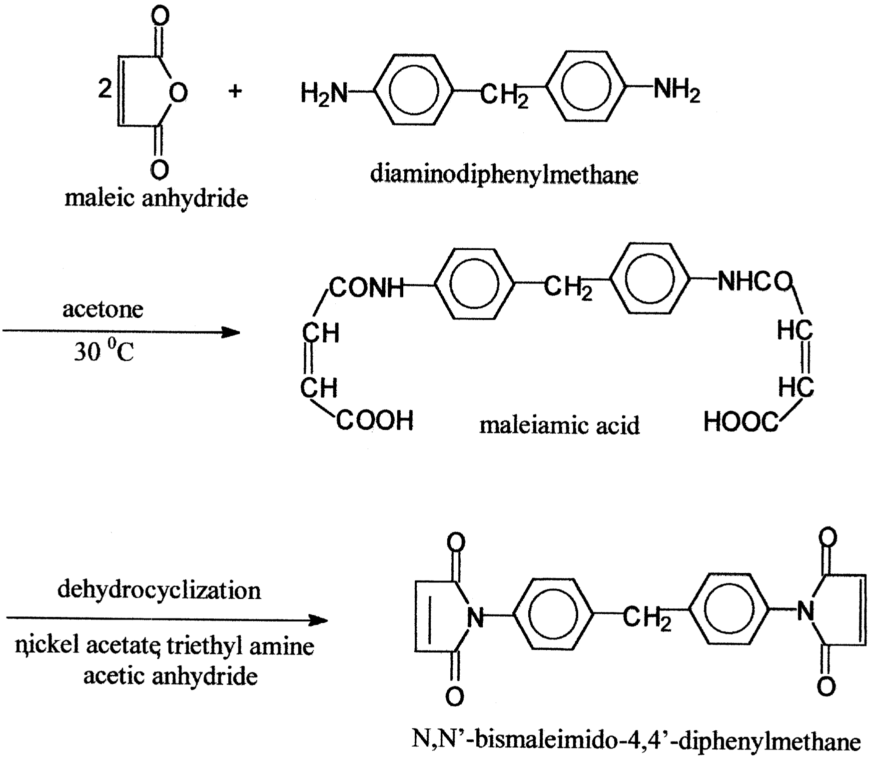
Fixed amount of unsaturated polyester resin (100 g), benzoyl peroxide (2 wt%), and varying amounts of VEO (10, 20 and 30 g) were mixed at 50 °C for 10 minutes with constant stirring. The product was subjected to vacuum to remove the entrapped air and then cast and cured at 60 °C for 4 hours and 100 °C for 2 hours. The castings were post cured at 120 °C for 2 hours and finally removed from the mold and characterized.

Preparation of N,N′-Bismaleimido-4,4′-Diphenylmethane

Bismaleimide was prepared according to the reported procedure [19]. The product was recrystallized from toluene (yield 80%). The reaction scheme for the preparation of bismaleimide is given in Scheme 2.



SCHEME 1 Preparation of vinyl ester oligomer.



SCHEME 2 Synthesis of N,N′-bismaleimido-4,4′-diphenylmethane.

Preparation of BMI-VEO-UP Blend

A typical BMI-VEO modified unsaturated polyester matrix (System E) was prepared as follows. 5 g of N,N′-bismaleimido-4,4′-diphenylmethane was dissolved into VEO (10 g) - unsaturated polyester (100 g) mix at 100 °C under vigorous stirring. After complete dissolution, the temperature was brought down to 50 °C and then benzoyl peroxide (2 wt%) was added. The product was subjected to vacuum to remove the entrapped air and then cast and cured at 60 ° C for 4 hours and 100 °C for 2 hours. The castings were post cured at 120°C for 2 hours and finally removed from the mold and characterized.

TEST METHODS

Tensile and Flexural Properties

The tensile (stress-strain) properties were determined using dog–bone–shaped specimens according to the ASTM-D3039 method using the Instron testing machine (Model 6025 UK) at a crosshead speed of 2 mm per minute. The flexural strength was measured as per ASTM D 790.

Unnotched Izod Impact Test

The unnotched Izod impact strength of samples 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 long were clamped in the base of the pendulum testing machine so that it was cantilevered upward. The pendulum was released and the force consumed in breaking the sample was calculated from the height of the pendulum reaches on the follow-through.

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 and 3 mm in thickness, were immersed in distilled water for 24 hours. Specimens were removed and the surface water was removed using a tissue paper and weighed to an accuracy of 0.001 g.

Dielectric Strength

Dielectric strength of the molded specimens (diameter 100 mm and thickness 3 mm) was measured according to ASTM D 149-87 using Shearing Bridge, Vettiner, France (accuracy 0.08%) at 250 V and 50 Hz.

RESULTS AND DISCUSSION

Tensile Properties

The values of tensile strength of unmodified unsaturated polyester (system A) and unsaturated polyester modified with varying percentages of VEO and bismaleimide (matrix systems B to P) are presented in Table 1. The incorporation of 10%, 20% and 30% (by wt) VEO into unsaturated polyester resin (systems B, C and D) increases the tensile strength by 5%, 14% and 25% respectively when compared with unmodified unsaturated polyester (A) system and this may be explained due to the formation of a network between the unsaturated polyester chains and VEO. Incorporation of bismaleimide into VEO modified unsaturated polyester further enhances the value of tensile

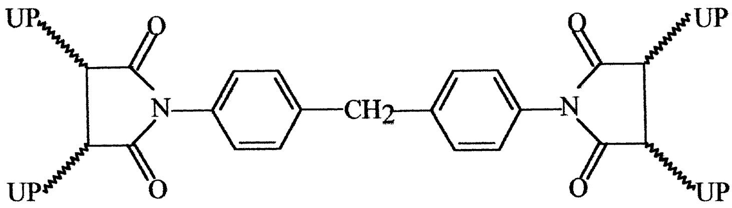
TABLE 1 Mechanical Properties of Unsaturated Polyester, VEO Modified Unsaturated Polyester, BMI Modified VEO-Unsaturated Polyester Systems

Matrix system	UP/VEO/BMI composition	Tensile strength (Mpa)	Tensile modulus (Mpa)	Flexural strength (Mpa)	Flexural modulus (MPa)	Unnotched izod impact strength (J/m)
A	100/00/00	28.2	1001.8	40.1	785.15	20.3
B	100/10/00	29.4	1051.05	46.20	905.55	21.8
C	100/20/00	32.8	1144.62	53.09	1039.50	23.4
D	100/30 /00	35.3	1251.25	56.78	1111.75	25.1
E	100/10/05	31.5	1128.27	49.20	1000.14	21.5
F	100/10/10	33.2	1179.75	54.30	1116.06	20.5
G	100/10/15	37.1	1322.57	59.36	1213.90	19.0
H	100/20/05	34.7	1240.52	56.90	1135.64	22.8
I	100/20/10	38.1	1362.50	62.13	1233.90	22.0
J	100/20/15	42.5	1526.52	66.01	1335.49	21.4
K	100/30/05	36.7	1287.60	61.10	1213.69	24.8
L	100/30/10	39.4	1409.28	67.41	1351.02	24.1
M	100/30/15	46.0	1644.69	72.60	1444.02	23.6

strength according to its concentration due to the increased crosslink density and rigidity imparted by dismaleimide. The schematic representation for the crosslinking of BMI with unsaturated polyester is presented in Scheme 3. The highest tensile value, 46 Mpa higher than that of the original value 28.2 Mpa of an unmodified unsaturated polyester, is obtained for the unsaturated polyester modified with 30% VEO and 15% bismaleimide (System K). Similarly, lowest tensile value 31.5 Mpa is obtained for the (System E) unsaturated polyester system modified with 10% of VEO and 5% bismaleimide. The other systems (F to I) exhibit the tensile behavior between the above two extremes.

Flexural Properties

Flexural behaviors of unmodified unsaturated polyester, unsaturated polyester modified with VEO, VEO and bismaleimide are presented in Table 1. Introduction of 10%, 20% and 30% (by wt) of VEO into unsaturated polyester resin (systems B, C and D) increases the flexural strength by 14%, 31% and 38% respectively when compared with unmodified unsaturated polyester (A). This may be attributed to the formation of chain entanglement between the unsaturated polyester and VEO matrix, which in turn enhances the flexural properties. Similarly, the incorporation of 5%, 10% and 15% bismaleimide into



SCHEME 3 Bismaleimide - Unsaturated polyester networks.

VEO modified unsaturated polyester further improves the value of flexural strength according to its percentage concentration due to the combined effect of toughening and rigidity imparted by VEO and bismaleimide respectively. The highest value of 72.6 Mpa is observed for the matrix system M with 30% (by wt) VEO and 15% (by wt) bismaleimide and lowest value of 49.2 Mpa is observed in the case of matrix system E with 10% (by wt) VEO and 5% (by wt) bismaleimide.

Unnotched Izod Impact Strength

The unnotched Izod impact strength obtained for unmodified unsaturated polyester, modified with VEO, bismaleimide and a combination of both, are presented in Table 1. Incorporation of VEO into the unsaturated polyester enhances the toughness according to its percentage content due to the excess free volume caused by chain entanglement with high-energy absorption. 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. From Table 1, it is evident that the incorporation of 5%, 10% and 15% bismaleimide into VEO modified unsaturated polyester (systems E to M) decreases the toughness behavior due to the formation of an intercrosslinked network and rigid molecular structure (Scheme 3).

Dielectric Strength

Introduction of 10%, 20% and 30% (by wt) of VEO into the unsaturated polyester resin (systems B, C and D) increases the dielectric strength when compared with unmodified unsaturated polyester (A). This may be attributed to the higher dielectric strength of epoxy networks Similarly, the incorporation of 5%, 10% and 15% bismaleimide into VEO modified unsaturated polyester further improves the value of dielectric strength according to its percentage concentration. The aromatic and heterocyclic skeletons of epoxy and bismaleimide, respectively, contributes to the improvement in insulation behavior (Table 2).

TABLE 2 Dielectric Strength Water Absorption Properties of BMI-VEO-UP Matrices

Sample code	UP/VEO/BMI composition	Dielectric strength (V/mil)	Water absorption (%)
A	100/00/00	480	0.23
B	100/10/00	510	0.27
C	100/20/00	545	0.30
D	100/30/00	586	0.33
E	100/10/05	538	0.22
F	100/10/10	555	0.21
G	100/10/15	581	0.20
H	100/20/05	562	0.29
I	100/20/10	587	0.27
J	100/20/15	608	0.26
K	100/30/05	601	0.30
L	100/30/10	626	0.28
M	100/30/15	645	0.27

Water Absorption

Resistance to water absorption character decreases with an increase in VEO content due to the enhanced free volume and reduced crosslink density caused by VEO chains. Introduction of BMI into the VEO modified unsaturated polyester systems shows a lower percentage of water absorption. All BMI modified systems show a good resistance to moisture absorption because of rigid aromatic hydrophobic structure. The moisture resistance property increases with increasing BMI content (Table 2) and it is observed that the BMI incorporation plays an important role in improving resistance to the moisture absorption property of unsaturated polyester systems.

CONCLUSION

The significant improvement in toughness of the unsaturated polyester matrix was made by forming intercrosslinked network with vinyl ester oligomer. The incorporation of bismaleimide into VEO modified unsaturated polyester (systems E to M) decreases the impact character due to formation of rigid intercrosslinked network structure. The incorporation of bismaleimide into VEO toughened unsaturated polyester further enhances the dielectric strength according to its percentage concentration. In addition, it was observed that the moisture resistance decreases with increasing VEO content and increases with increasing BMI content. BMI incorporation plays an important role in resisting moisture absorption property of unsaturated polyester.

Among the different matrix systems studied, matrix system M is considered to be the best combination, and it exhibits higher strength properties associated with improvement in toughness and thermal stability than those of all other systems. This matrix system can be used to fabricate advanced composites components for engineering and aerospace applications for better performance.

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