

Preparation and Characterization of Bismaleimide (*N,N'*-bismaleimido-4,4'-diphenyl methane)-Vinyl Ester Oligomer-Modified Unsaturated Polyester Interpenetrating Matrices for Advanced Composites

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ABSTRACT: Interpenetrating networks of varying percentages of bismaleimide (BMI) in 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, and used as a toughening agent for unsaturated polyester resin. Unsaturated polyesters modified with 10, 20, and 30 wt % vinyl ester oligomer were made. The VEO toughened unsaturated polyester matrix systems, further modified with 5, 10, and 15 wt % bismaleimide (BMI). BMI-VEO-UP matrices were characterized using differential scanning calorimetry, thermogravimetric

analysis, and heat deflection temperature analysis. The matrices, in the form of castings, were characterized for their mechanical properties according to ASTM methods: tensile strength, flexural strength, and unnotched Izod impact test. Data obtained from mechanical studies and thermal characterization indicate that the introduction of VEO and BMI into unsaturated polyester resin improves thermomechanical properties according to their percentage concentration. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 2502–2508, 2002

Key words: unsaturated polyester resin; matrix; strength; glass transition; thermal properties

INTRODUCTION

Unsaturated polyesters represent some of the most important matrices used to fabricate composites employed for engineering and industrial applications. They are particularly useful in sheet molding and bulk molding compounds for manufacturing automotive parts,¹ marine crafts, and other industrial products because of their light weight and good mechanical properties.² Unsaturated polyester has limited impact strength because of its high crosslinking density and high shrinkage during cure. These problems are minimized using low-profile additives such as poly(methyl methacrylate), poly(vinyl acetate), and polypropylene glycol.^{3–5} Improvements in impact strength and strain to failure have been 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 (IPNs) of unsaturated polyester and polyurethanes have been used to improve their impact

strength.¹¹ It has been reported recently that the utility of unsaturated polyester resin can be improved by modifying with a coreactive component bismaleimide.¹² Improvement in thermomechanical properties was observed by the introduction of bismaleimide into epoxy resin,^{13,14} siliconized epoxy,¹⁵ and unsaturated polyester modified epoxy resin.¹⁶ 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.

Vinyl ester resins are similar to polyester resins; however, the reactive sites are positioned only at the end of the molecular chains, and thus crosslinking can take place only at the chain ends. Because the whole length of the molecular chain is available to absorb shock loading, this makes vinyl ester resin become tougher and more resilient than polyesters. Hence, in the present work, an attempt is made to improve both toughness and thermomechanical behavior of unsaturated polyester resin by forming an IPN with vinyl ester oligomer (VEO) and bismaleimide.

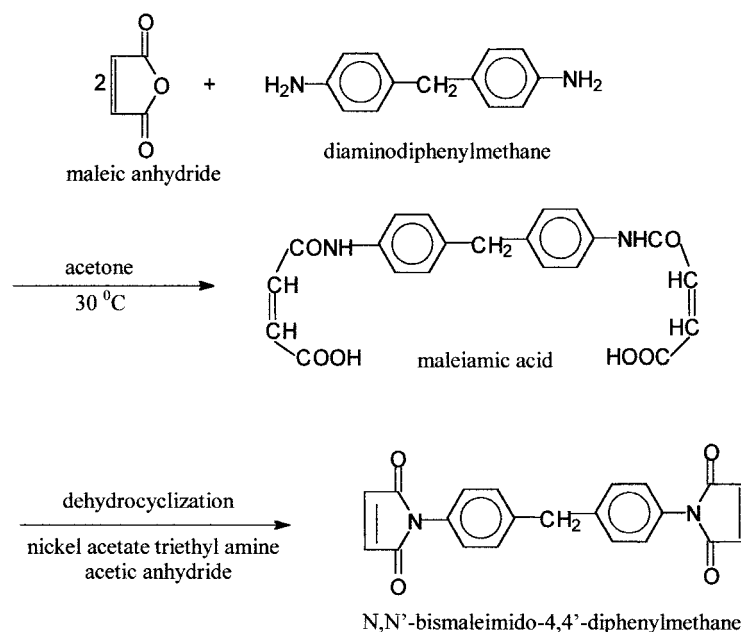
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EXPERIMENTAL

Materials

The commercially available unsaturated polyester resin (manufactured using phthalic acid, maleic anhy-



Scheme 1 Synthesis of *N,N'*-bismaleimido-4,4'-diphenylmethane.

tride, and propylene glycol with 30% styrene having viscosity of 600 cP), benzoyl peroxide, epoxy resin (diglycidyl ether of bisphenol A, DGEBA) GY 250 [epoxy equivalent \sim 180–190; Ciba-Geigy (India)], and acrylic acid (Merck, Darmstadt, Germany) were used as received.

Preparation of vinyl ester oligomer

VEO was prepared using acrylic acid and epoxy resin. The synthesis and characterization of VEO were reported in detail in elsewhere.^{17,18}

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 min with constant stirring. The product was subjected to vacuum to remove the entrapped air and then cast and cured at 60°C for 4 h and 100°C for 2 h. The castings were postcured at 120°C for 2 h 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 structure of the prepared BMI was confirmed by IR and NMR. The reaction for the preparation of bismaleimide is given in Scheme 1.

Preparation of BMI-VEO-UP blend

A typical BMI-VEO-modified unsaturated polyester matrix (system E) was prepared as follows. *N,N'*-Bismaleimido-4,4'-diphenylmethane (5 g) was dissolved into VEO (10 g)-unsaturated polyester (100 g) mix at 100°C under vigorous stirring. After complete dissolution, the temperature was reduced 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 h and 100°C for 2 h. The castings were postcured at 120°C for 2 h and finally removed from the mold and characterized.

Test methods

Tensile and flexural properties

The tensile (stress-strain) properties were determined using dumbbell-shaped specimens according to the ASTM D3039 method using an Instron testing machine (Model 6025 UK), at a crosshead speed of 2 mm/min. The flexural strength was measured according to ASTM D790.

Unnotched Izod impact test

The unnotched Izod impact strength of each sample was tested according to ASTM D256-88. All samples were tested unnotched so that they would be more sensitive to the transition between ductility and brittleness. Specimens (dimensions: 3.2 mm thick, 64 mm long, 10-mm cross section) were clamped in the base

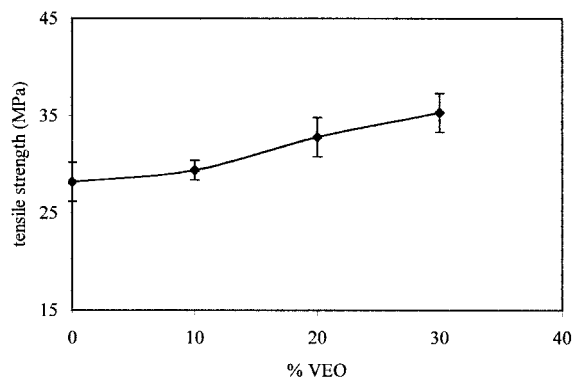


Figure 1 Effect of VEO content on tensile strength.

of the pendulum testing machine so that they cantilevered upward. The pendulum was released and the force consumed in breaking the sample was calculated from the height the pendulum reached on the follow-through.

Thermal studies

The glass-transition temperature (T_g) of the samples was determined using a DSC 2910 (TA Instruments, New Castle, DE) in the temperature range between 50 and 250°C at a heating rate of 10°C/min in nitrogen atmosphere. Thermogravimetric analysis (TGA) was carried out using a Thermal Analyst 2000 (TA Instruments) at a heating rate of 10°C/min in air atmosphere.

Heat deflection temperature analysis

The heat deflection temperature (HDT) of the samples was tested according to ASTM D648-72. The HDT measures the temperature at which deformation occurs when the composite specimens [dimensions: 127 × 13 × 3 mm (length × thickness × width)] were placed in an oil bath under a load of 1.82 MPa and the temperature was raised at a rate of 2°C/min. The temperature at which the specimen deflected by 0.25 mm was noted. The deflection was monitored in an linear variable displacement transducer.

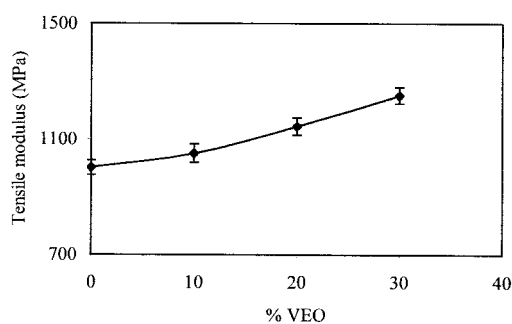


Figure 2 Effect of VEO content on tensile modulus.

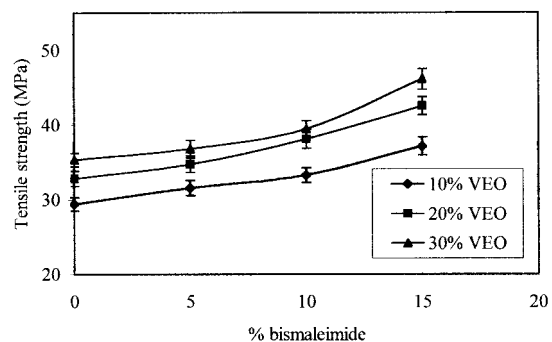


Figure 3 Effect of BMI content on tensile strength.

Water absorption

The water absorption property of the samples was tested according to ASTM D570. The cured specimens (dimensions: 60 mm square, 3 mm thick) were immersed in distilled water for 24 h. Specimens were removed and the surface water was removed using a tissue paper and weighed to an accuracy of 0.001 g.

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–P) are presented in Figures 1–4. From the data, it is observed that the incorporation of 10, 20, and 30 wt % VEO into the unsaturated polyester resin (systems B, C, and D) increases the tensile strength (Fig. 1) by 5, 14, and 25%, respectively, compared with that of unmodified unsaturated polyester (A) system; this may be explained as being attributed to the formation of a network between the unsaturated polyester chains and VEO. Incorporation of bismaleimide into the VEO-modified unsaturated polyester further enhances the value of tensile strength according to its concentration, which is explained as being the result of the increased crosslink density and rigidity imparted by bismaleimide. The

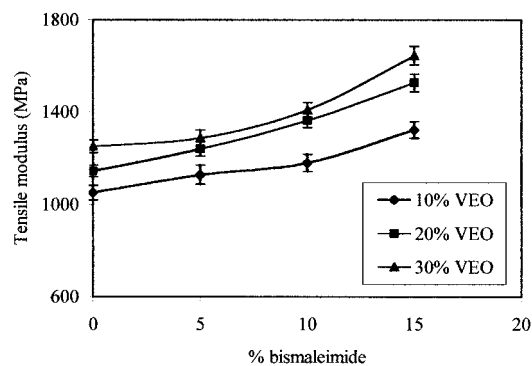


Figure 4 Effect of BMI on tensile modulus.

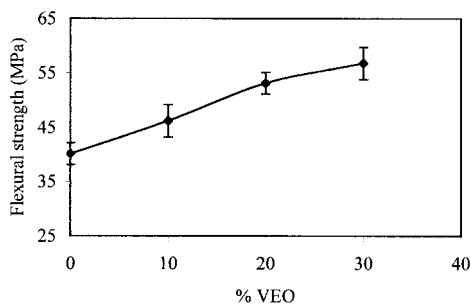


Figure 5 Effect VEO content on flexural strength.

highest tensile value, 46 MPa (higher than the original value of 28.4 MPa for unmodified unsaturated polyester), was obtained for the unsaturated polyester modified with 30% VEO and 15% bismaleimide (system M). Similarly, the lowest tensile value, 31.5 MPa, was obtained for the unsaturated polyester system modified with 10% of VEO and 5% bismaleimide (system E). The other systems (F–L) exhibited tensile behavior between the above two extremes (46 and 31.5 MPa).

Flexural properties

The flexural behaviors of unmodified unsaturated polyester, unsaturated polyester modified with VEO, and VEO and bismaleimide are presented in Figures 5–8. Introduction of 10, 20, and 30 wt % VEO into unsaturated polyester resin (systems B, C, and D) increased the flexural strength (Fig. 5) by 14, 31, and 38%, respectively, compared with that of unmodified unsaturated polyester (A). This may be attributed to the formation of chain entanglements between unsaturated polyester and VEO matrix that, in turn, enhance the flexural properties. Similarly the incorporation of 5, 10, and 15% bismaleimide into VEO-modified unsaturated polyester further enhanced the value of flexural strength according to its percentage concentration, resulting from the combined effect of toughening and rigidity imparted by VEO and bisma-

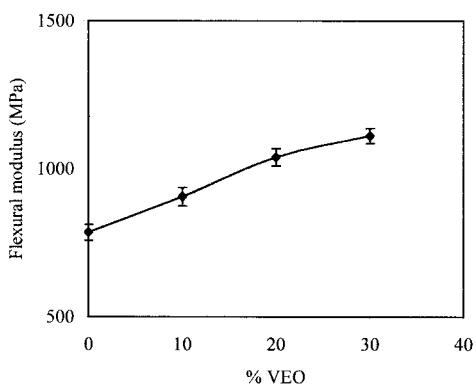


Figure 6 Effect of VEO content on flexural modulus.

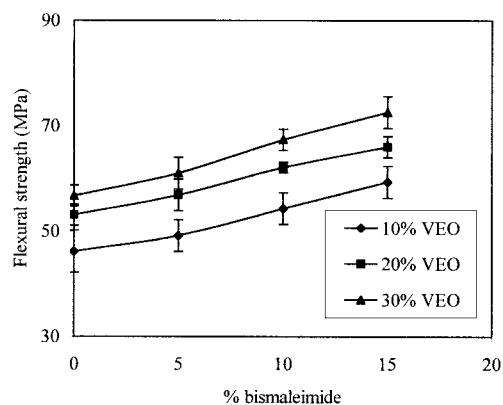


Figure 7 Effect of BMI on flexural strength.

leimide, respectively. The highest value of 72.6 MPa was observed for the matrix system M with 30 wt % VEO and 15 wt % bismaleimide, and the lowest value of 49.2 MPa was observed in the case of matrix system E with 10 wt % VEO and 5 wt % bismaleimide.

Unnotched Izod impact strength

The unnotched Izod impact strengths obtained for unmodified unsaturated polyester, and that modified with VEO, bismaleimide, and combinations of both are presented in Figures 9 and 10. Incorporation of VEO into unsaturated polyester enhanced the toughness according to the percentage content resulting from the excess free volume caused by chain entanglement with high-energy absorption. The influence on toughness of the unsaturated polyester varies by 7, 10, and 23% for the VEO concentrations of 10, 20, and 30 wt %, respectively. A noticeable (steep) increase (Fig. 9) in the values is observed. From Figure 10 it is evident that the incorporation of 5, 10, and 15% bismaleimide into VEO-modified unsaturated polyester (systems E–M) decreased the toughness behavior because of the formation of an intercrosslinked network and the rigid molecular structure; however, the values

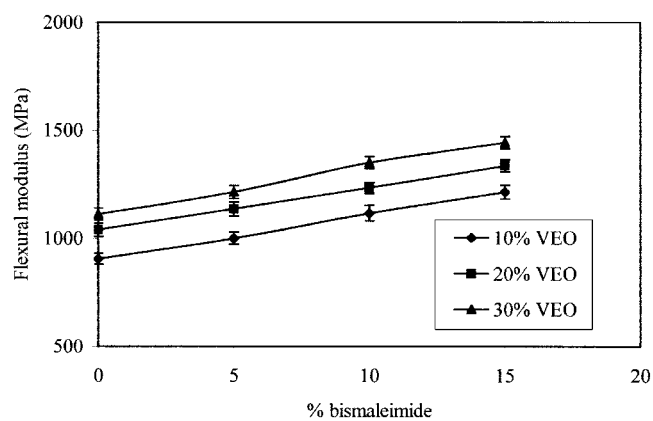


Figure 8 Effect of BMI on flexural modulus.

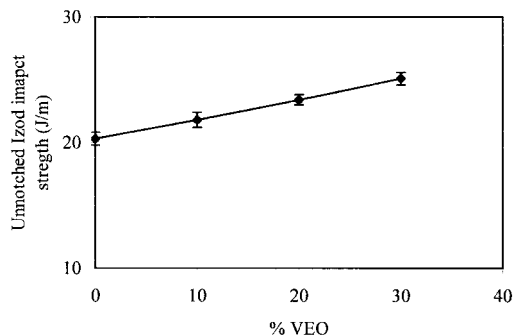


Figure 9 Effect of VEO on Izod impact strength.

are found to be higher than that of the unmodified unsaturated polyester.

Thermal characteristics

The values of glass-transition temperature of VEO-modified unsaturated polyester are presented in Figures 11 and 12. The T_g value is lowered with respect to increasing VEO concentration as a result of the reduced crosslink density caused by longer spacing of VEO chains. T_g values of VEO-modified unsaturated polyester resin increased with increase in bismaleimide content because of the increased crosslink density and rigidity imparted by the tetra-functional bismaleimide.

Thermogravimetric analyses (TGA) of VEO-modified unsaturated polyester and bismaleimide-incorporated VEO-unsaturated polyester matrix systems in air were carried out and the results are presented in Figures 13 and 14. It is observed from Figure 13 that the degradation temperature increased with increasing percentage of VEO, which implies that the VEO incorporation enhances the thermal stability and, in addition, led to the decreased percentage weight loss. The bismaleimide-modified VEO-unsaturated polyester shows two thermal degradation temperatures, one at 600°C and the other at 350°C. From the figures it is concluded that the increase in higher degradation temperature (T_{dh}) with increasing bismaleimide con-

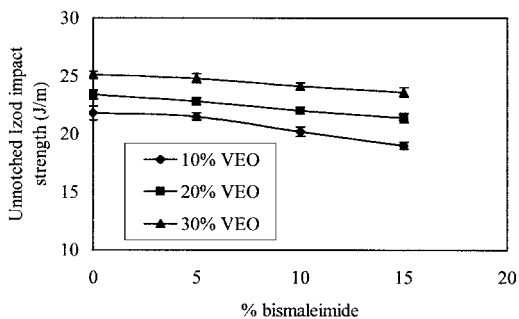


Figure 10 Effect of BMI on Izod impact strength.

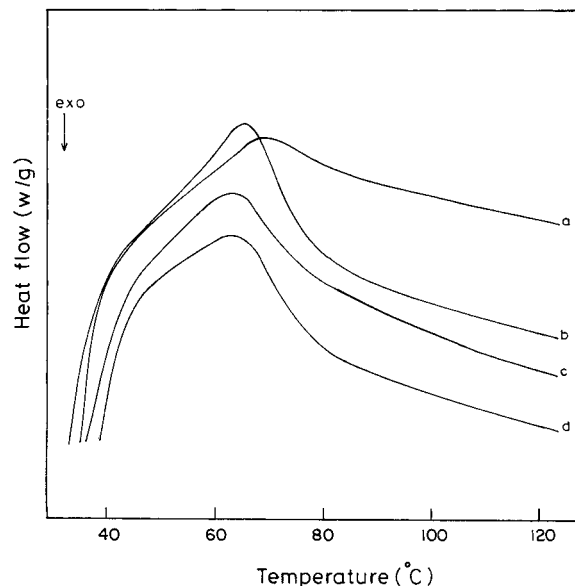


Figure 11 Glass-transition temperature of unsaturated polyester modified with (a) 0% VEO, (b) 10% VEO, (c) 20% VEO, (d) 30% VEO.

centration is the result of its thermally stable heterocyclic aromatic structure.

Heat deflection temperature

Table I presents the HDTs of the unmodified, VEO-modified, and BMI-VEO-modified unsaturated polyester matrix systems. The values of HDT are lowered with increased VEO concentration because of reduced

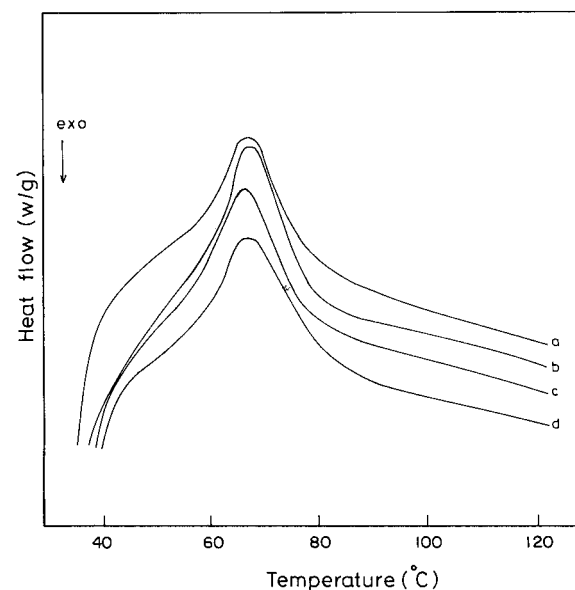


Figure 12 Glass-transition temperature of unsaturated polyester-VEO (10% by wt) with (a) 0% bismaleimide, (b) 5% bismaleimide, (c) 10% bismaleimide, (d) 15% bismaleimide.

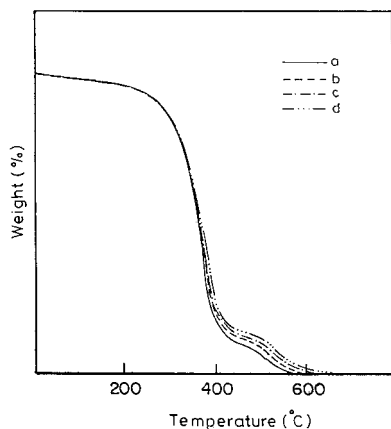


Figure 13 Thermograms of unsaturated polyester modified with (a) 0% VEO, (b) 10% VEO, (c) 20% VEO, (d) 30% VEO.

crosslink density caused by VEO chains. HDT values of VEO-modified unsaturated polyester increased with an increase in bismaleimide content as a result of the increased rigidity of the matrix systems imparted by the highly crosslinked nature of BMI.

Water absorption

Water absorption increased with increase in VEO content as a result of the reduced crosslink density caused by VEO chains. Introduction of BMI into the VEO-modified unsaturated polyester systems caused lower water absorption. All BMI-modified systems showed good resistance to moisture absorption because of the rigid aromatic hydrophobic structure. The moisture resistance property increased with increasing BMI content (Table I) and it was observed that the BMI incorporation plays an important role in improving resistance to moisture absorption of unsaturated polyester systems.

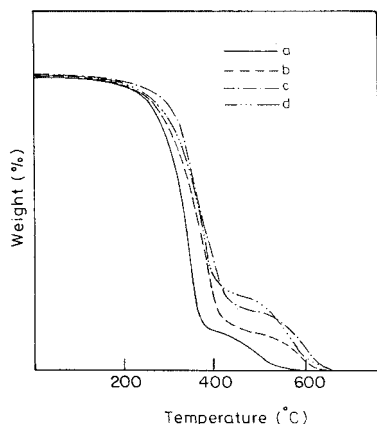


Figure 14 Thermograms of unsaturated polyester-VEO (10% by wt) with (a) 0% bismaleimide, (b) 5% bismaleimide, (c) 10% bismaleimide, (d) 15% bismaleimide.

TABLE I
Heat Deflection Temperature and Water-Absorption Properties of BMI-VEO-UP Matrices

Sample code	UP/VEO/BMI composition	Heat deflection temperature	Water absorption (%)
A	100/00/00	72.3	0.23
B	100/10/00	71.0	0.27
C	100/20/00	68.5	0.30
D	100/30/00	64.2	0.33
E	100/10/05	72.3	0.22
F	100/10/10	74.1	0.21
G	100/10/15	75.6	0.20
H	100/20/05	69.5	0.29
I	100/20/10	70.2	0.27
J	100/20/15	71.4	0.26
K	100/30/05	67.0	0.30
L	100/30/10	71.1	0.28
M	100/30/15	74.0	0.27

CONCLUSIONS

From the data it is concluded that a significant improvement in toughness of the unsaturated polyester matrix was made by forming an interpenetrating network with vinyl ester oligomer. The incorporation of bismaleimide into VEO-modified unsaturated polyester (systems E-M) decreases the impact characteristics as the result of formation of a rigid intercrosslinked network structure. Mechanical studies and thermal characterization indicate that the introduction of VEO into this unsaturated polyester improves toughness and thermal stability because of the higher thermal stability. The incorporation of bismaleimide into VEO-toughened unsaturated polyester further enhances both the mechanical and thermal properties 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 reducing the moisture absorption of this unsaturated polyester.

Among the different matrix systems studied, matrix system M is considered to be the best combination because it exhibits higher strength properties associated with improvement in toughness and better 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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