Toughened Polyester Matrices for Advanced Composites

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ABSTRACT: An intercrosslinked network of hybrid bis-maleimide (BMI) modified vinyl ester oligomer–unsaturated polyester matrix systems have been developed. Vinyl ester oligomer (VEO) was used as a toughening agent for unsaturated polyester resin and was added in 2, 4, and 6% (by wt). Benzoyl peroxide was used as curing agent. The VEO-toughened unsaturated polyester matrix systems were further modified with 5, 10, and 15% (by wt) of bismaleimide. Bismaleimides modified vinyl ester–unsaturated polyester matrices were characterized by mechanical (tensile strength, flexural strength, tensile modulus, flexural modulus, and impact strength), thermal [differential scanning calorimetry (DSC), thermogravimetic analysis (TGA), heat deflection temperature analysis (HDT)] and morphological studies [scanning electron microscope (SEM)] and water absorption. Data obtained from mechanical studies indicated that the introduction of VEO into unsaturated polyester resin improves the fracture toughness. The introduction of BMI into VEO incorporated unsaturated polyester resin enhanced both thermal and mechanical behavior. The scanning electron micrographs of fractured surfaces of VEO-modified unsaturated polyester systems and BMI modified vinyl ester–unsaturated polyester matrices illustrate the presence of homogeneous morphology. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 167–177, 2007

Key words: unsaturated polyester; vinyl ester oligomer; N,N'-bismaleimido-4,4' diphenylmethane; tensile strength; thermal stability; water absorption; morphology

INTRODUCTION

Polyester resins form highly crosslinked networks. The high crosslink density results in brittle composites prone to microcracking and failure under impact. Improving the mechanical, electrical, thermal, optical, and processing properties of the polymers with the addition of plastic filler materials while reducing their costs[1] has become a very popular research interest. Improvements are carried out in the impact strength at the expense of stiffness and glass transition temperature. Unsaturated polyester resins have been used in the development of high-performance lightweight fiber reinforced composites, for manufacturing marine crafts, automotive parts,[2] etc., because of their excellent mechanical[3] and lightweight properties. Unsaturated polyester resins exhibits many desirable properties, such as high strength and modulus, excellent chemical, solvent, and salt water resistance, good thermal and electrical properties, outstanding adhesion to various substrates, and easy processability under various conditions. Liquid rubbers have been used with unsaturated polyester resin to increase the impact properties of unsaturated polyester.[4–8] Improvements of fracture toughness and strain to failure of the neat resin have also been with block copolymers of carboxyl and hydroxyl terminated acrylonitrile butadiene copolymer, CTBN, HTBN,[9] low profile additives like poly(methylmethacrylate), poly(vinyl acetate) polypropylene glycol,[10–12] and polyurethanes.[13] Modification with these polymeric materials have enhanced toughness behavior, but failed to enhance thermomechanical properties. Hence, to enhance both toughness and thermomechanical properties, vinyl ester oligomer (VEO) and bismaleimide (BMI) are chosen as the suitable modifiers for unsaturated polyester resin.

In the first approach, VEO, a polymeric intermediate, is used to modify unsaturated polyester resin because of its good tensile strength and chemical resistance of the epoxy resin, but with faster curing times and high volumetric shrinkage on cure associated with the unsaturated polyesters. Vinyl ester resins are normally an epoxy resin backbone grafted with an unsaturated carboxylic acid to permit cure by an addition reaction. Vinyl ester resins are similar to polyesters in their molecular structure, but differ in their reactive sites, which are positioned at the ends of the molecular chains. The whole length of the molecular chain is available to absorb shock loading and makes vinyl ester resins tougher and more resilent than polyesters. Some of the important uses of vinyl ester resins are in the manufacture of chemical plant, pipes, storage tanks, etc., where high chemical resistance is required.

The second approach is to introduce bismaleimide, a reactive component to enhance thermomechanical
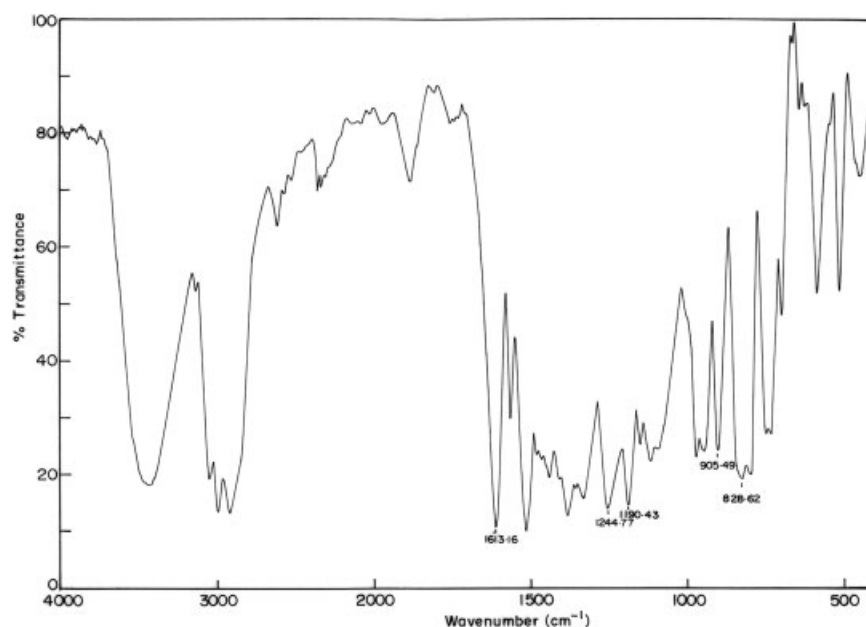
Figure 1 FTIR spectrum of tetraglycidyldiaminodiphenyl methane (TGDDM).

properties of unsaturated polyester resin.[14] Bismale-imides are leading classes of thermosetting polyimides. The introduction of BMI into epoxy,[15,16] siliconized epoxy,[17] unsaturated polyester modified epoxy[18] resin enhanced thermomechanical properties. BMI are thermosetting resins and can be used for high performance structural composites requiring higher temperature (200–230°C) use and increased toughness. Bismaleimide resins can be produced from maleic anhydride and aromatic (or) aliphatic diamine. BMI resins possess superior thermomechanical properties viz. high crosslinking ability, high glass transition temperature, high thermal stability, high char yield, excellent fire resistance, specific strength and specific modulus, and low water absorptions. The major applications for BMI structural composites are in aero engines and military aircraft.

The objective of this work is to obtain an intercrosslinked network of BMI–VEO modified unsaturated polyester with commercially available polyester resin using VEO and bismaleimide having excellent mechanical properties, water resistance, and thermal stability.

EXPERIMENTAL

Materials

Commercially available general purpose unsaturated polyester resin (GP resin manufactured using phthalic acid, maleic anhydride, and propylene glycol with 30% styrene having viscosity of 600 cP), benzoyl peroxide, and acrylic acid (Merck, Darmstadt, Germany) were used as received. Tetraglycidyldiaminodiphenyl

methane (TGDDM), VEO, and BMI were prepared in the laboratory.

Synthesis of TGDDM

576.36 g (6.25 mol) of epichlorohydrin, ECH (distilled under vacuum at 70°C to get pure ECH), was taken in a 1-L three-necked RB flask provided with a mechanical stirrer, N_2 inlet tube, and a water condenser. This was heated to 50°C in a water bath. Then, 93.8 g (0.47 mol) of 4,4′-diaminodiphenylmethane was added and was stirred continuously for 4 h at the tempera-
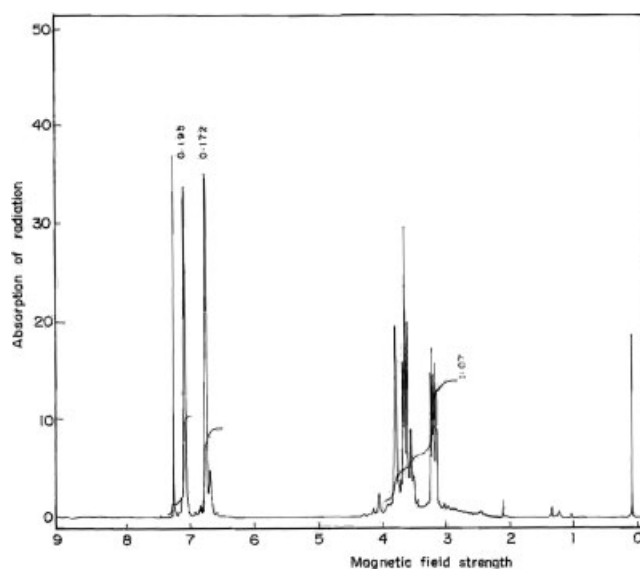

Figure 2 ^{1}H-NMR spectrum of tetraglycidyldiaminodiphenyl methane (TGDDM).
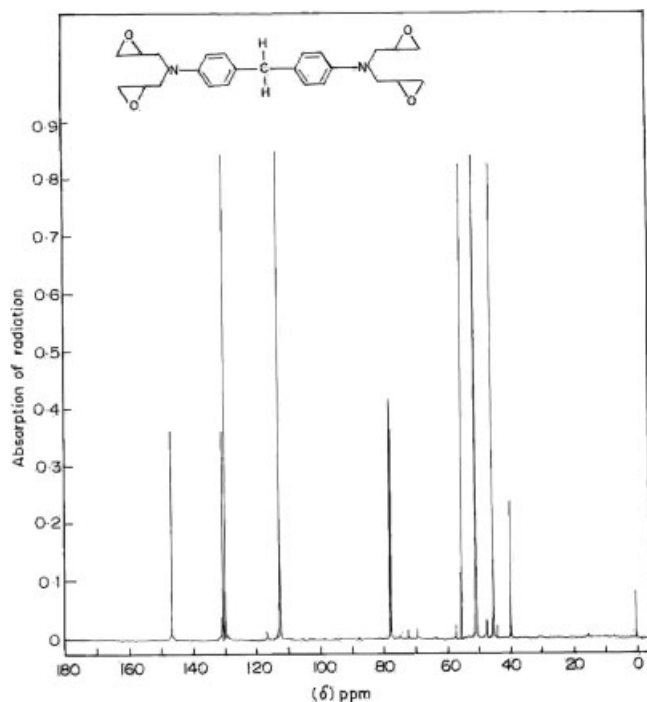
ture range of 50–55°C under N_2 atmosphere. Chloro-hydrin, the intermediate product, was formed and excess ECH used in was distilled off under vacuum. Then, 113.7 g (2.84 mol) of 40% NaOH solution was added dropwise for 1 h at 55°C. Then, the reaction was continued at this temperature for further period of 1 h. Then, 250 mL of benzene was added to the mixture and stirred for 15 min. Two layers were formed. The aqueous layer with NaCl by product was discarded, while the organic layer was purified by washing several times with water. Then benzene was evaporated to get the yellow colored epoxy liquid product. The resultant product was characterized by FTIR and NMR (Figures 1–3). The sequence of reactions involved in the preparation of TGDDM is given in Scheme 1.
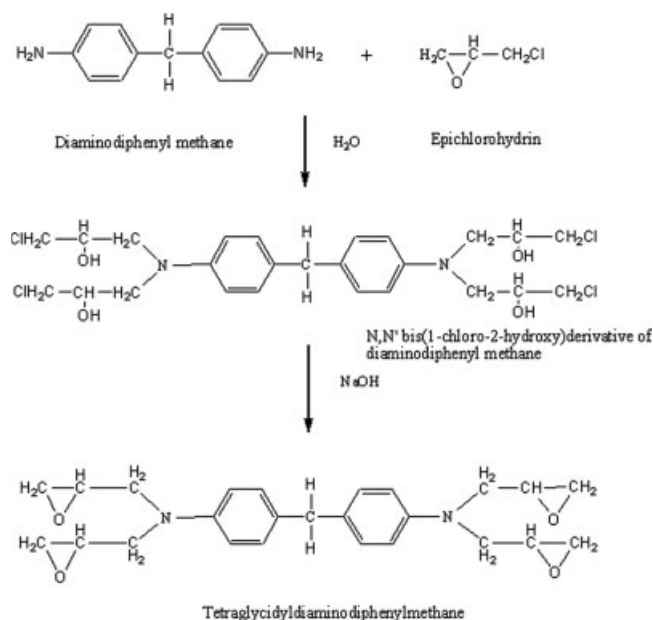
Preparation of VEO

VEO was prepared using TGDDM and acrylic acid. 1 mol of epoxy resin and 4 mol of acrylic acid is mixed in RB flask at 50°C for 2 h with constant stirring to obtain VEO. The sequences of reaction for the preparation of VEO is given in Scheme 2.

Preparation of unsaturated polyester–VEO systems

A known amount of unsaturated polyester resin (100 g) and varying amounts of VEO (2, 4, and 6 g) was taken in a round-bottomed flask and stirred at room temperature 30°C for 1 h. After obtaining homogene-

Scheme 1 Synthesis of tetraglycidyldiaminodiphenylmethane (TGDDM).

ous mixture, benzoyl peroxide (2% by wt) was mixed at 50°C for 10 min with constant stirring. It was then subjected to vacuum to remove the entrapped air without affecting the composition of styrene content and then cast and cured at 60°C for 4 h and 100°C for 2 h. The castings were post cured at 120°C for 2 h and finally removed from the mold and characterized.

Preparation of N,N′-bismaleimido-4,4′diphenyl methane

Bismaleimide was prepared according to the reported procedure.[19] In a 1-L three-necked flask fitted with paddle stirrer, reflux condenser, and nitrogen inlet, 600 mL of acetone, 1.0 mol (98.1 g) of maleic anhy-

Figure 3 ^{13}C-NMR spectrum of tetraglycidyldiaminodiphenyl methane (TGDDM).
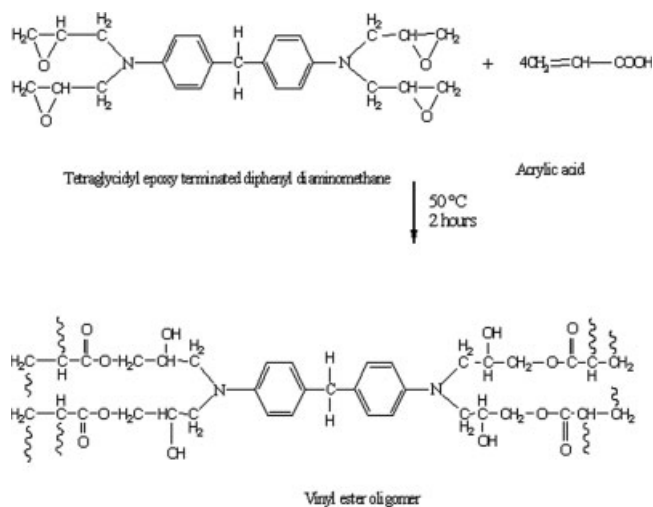
Scheme 2 Synthesis of vinyl ester oligomer.
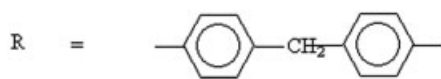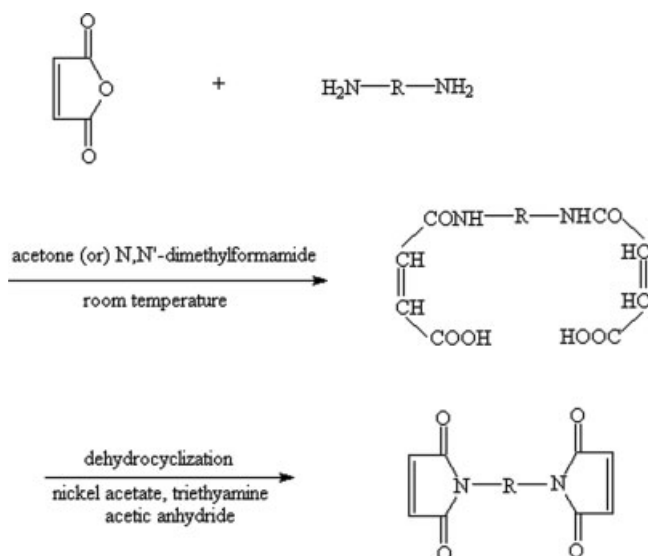
Scheme 3   Synthesis of bismaleimide.

dride, and 0.5 mol (54.1 g) of *N,N*-diamino diphenyl methane was added. Rapid formation of precipitate of bismaleiamic acid occurred on mixing the reactants together, and the mixture was allowed to stand for 30 min to complete the reaction. To the reaction vessel were now added 1 g of nickel acetate and 25 mL of triethylamine and the mixture was refluxed. By means of pressure equalizing funnel 117.9 mL of acetic anhydride was added to the refluxing mixture and heating was continued for an additional 3 h. The mixture was diluted with 500 mL of water and chilled to crystallize
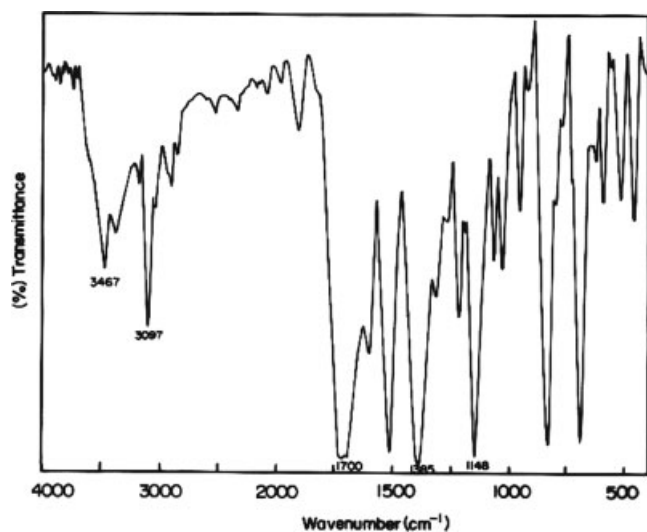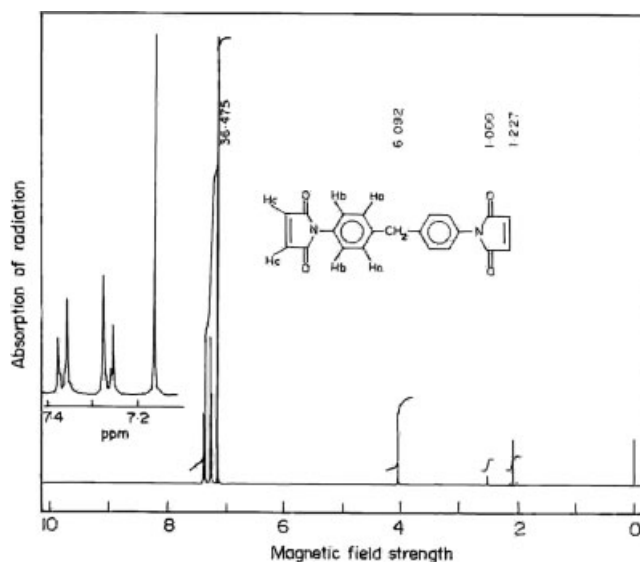

Figure 4   FTIR spectrum of BMI.

Figure 5 ^{1}H-NMR spectrum of BMI.

the bismaleimide. The resulting bismaleimide was filtered and recrystallized from acetone. The reaction for the preparation of bismeleimide *N,N'*-bismaleimido-4,4'diphenyl methane is given in Scheme 3 and characterized by FTIR and NMR (Figures 4–6).

Preparation of BMI–VEO–UP system

A typical BMI–VEO–UP matrix was prepared as follows. A known amount of VEO modified unsaturated polyester is taken in round bottomed flask and varying amounts of *N,N'*-bismaleimido-4, 4'diphenyl methane was dissolved at 100°C under vigorous stirring. The temperature was brought down to 50°C after complete dissolution. Benzoyl peroxide (2% by wt) was added as curing agent. The product was subjected to vacuum to remove entrapped air without
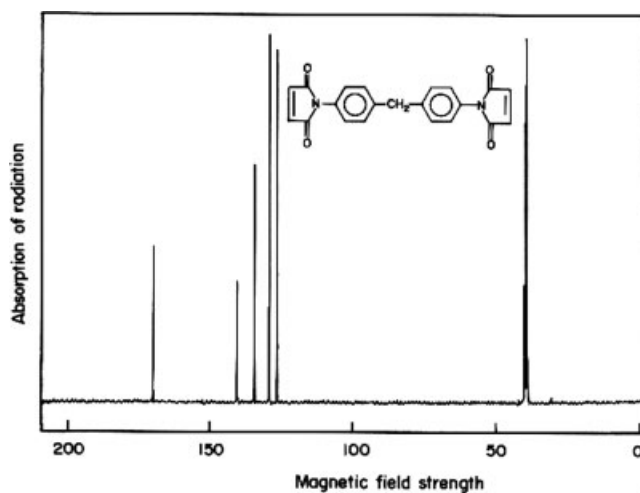

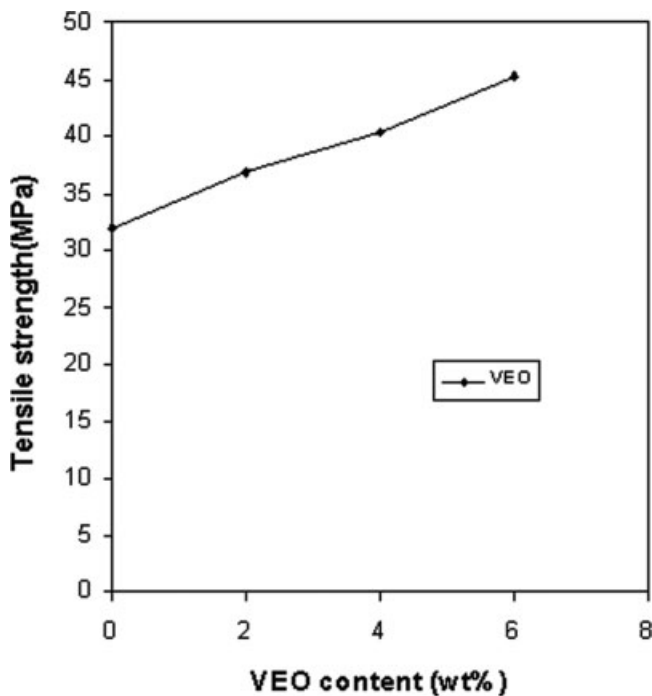**Figure 6** ^{13}C-NMR spectrum of BMI.

Figure 7 Effect of vinyl ester on tensile strength of UP systems.

affecting the composition of styrene content and then cast and cured at 60°C for 4 h and 100°C for 2 h. The castings were post cured at 120°C for 2 h and finally removed from the mold and characterized.

TEST METHODS

Tensile and flexural properties

Tensile properties are studied as per ASTM-D3039 using Instron testing machine (Model 6025 UK) at 2 mm/min crosshead speed, using specimen with a width of 25 mm, length of 150 mm, and thickness of 3 mm. The flexural properties are studied as per ASTM-D790 using specimen with 3 mm in depth, 10 mm in width, and 90 mm in length using Instron testing machine (Model 6025, UK). The five different specimens are made by using Diamond wheel cutter.

Unnotched izod impact Test

The unnotched Izod impact strength is studied as per ASTM D256-88 using specimen width 10 mm, 3.2 thickness, and length 63 mm. The five different specimens are made by using Diamond wheel cutter.

Thermal studies

Differential scanning calorimeter DSC 2910 (TA instruments) was used to determine glass transition temperature (T_g) in the temperature range between 50 and 250°C at a heating rate of 10°C/min in nitrogen atmosphere.

Thermogravimetric analysis (TGA) of the polymer matrices was carried out using a Thermal analyst 2000 (TA instruments) at a heating rate of 10°C/min in an inert atmosphere to determine thermal stability of the matrices. Heat deflection temperature of polymeric material is determined as per ASTM-D648 using specimens of size 120 mm in length, and 13 mm in thickness are kept in oil bath under a load of 1.82 MPa. The temperature was raised at a rate of 2°C/min and the temperature was noted when the specimen deflected by 0.25 mm.

Scanning electron microscope

The fractured surfaces were coated with gold and examined under a scanning electron microscope (SEM) (JEOL, JSM model 6360). Fractured surfaces were obtained from plain strain fracture toughness tested specimens using Instron testing machine (Model 6360, UK) at a crosshead speed of 2 mm/min. Excess material was removed from the other faces of the specimens by razor blade.

Water absorption

Samples were tested according to ASTM D570 using specimens of 60 mm square and 3 mm thickness. Test specimen was immersed in water for 24 h at 30°C and the percentage of water absorbed by the specimen is calculated using the equation given below.

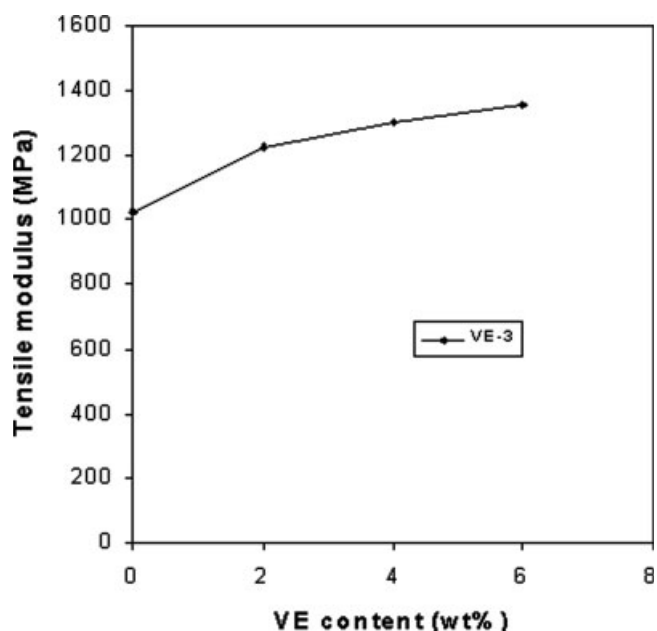$$\% \text{ Increase in weight} = (W_2 - W_1) \times 100/W_1$$

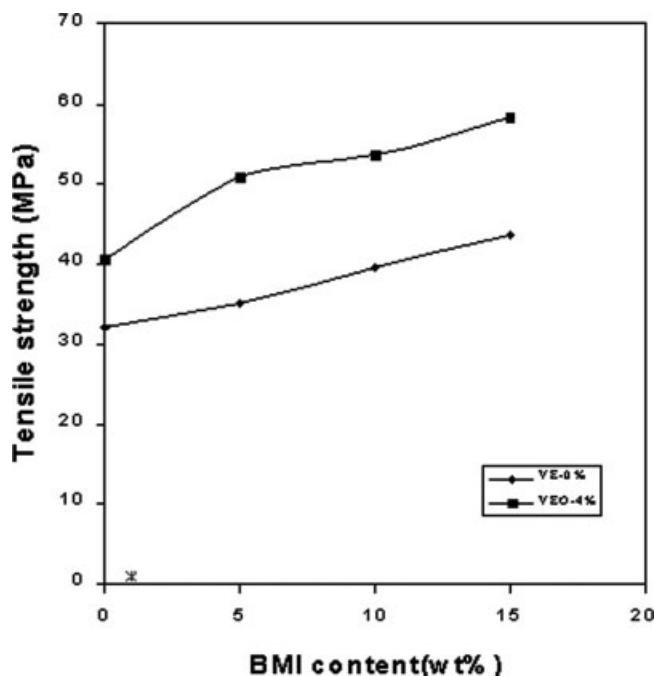**Figure 8** Effect of vinyl ester on tensile modulus of UP system.

Figure 9 Effect of BMI content on tensile strength of UP and UP/VE systems.

where W_1 is the initial weight of the sample, and W_2 is the final weight of the sample after immersed in water for 24 h at 30°C.

RESULTS AND DISCUSSION

Tensile properties

The plots of tensile strength and modulus of unmodified unsaturated polyester, vinyl ester modified unsaturated polyester systems, and BMI modified vinyl ester-unsaturated polyester systems are presented in Figures 7–10. The VEO is used up to 6% for the modification of unsaturated polyester due to the premature curing imparted by tetrafunctional nature of TGDDM.
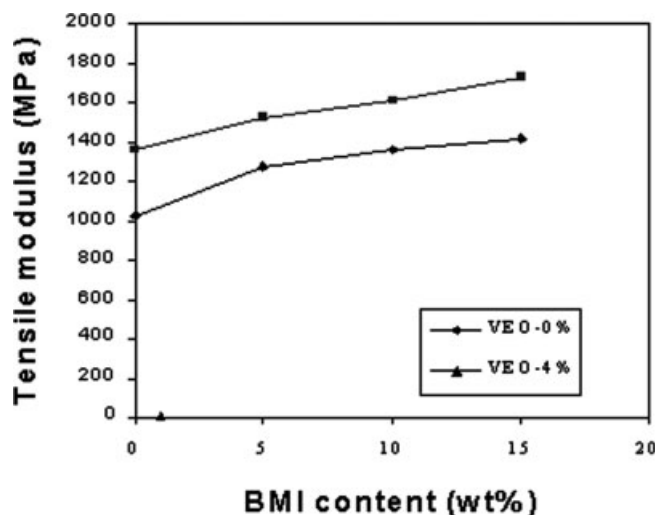

Figure 10 Effect of BMI content on tensile modulus of UP and UP/VEO systems.

The introduction of 2, 4, and 6% (by wt) of VEO into unsaturated polyester increases the tensile strength by 15.3, 26.2, and 41.2% respectively. The may be due to the higher degree of interpenetrating network formed between unsaturated polyester chains and VEO molecules, which in turn enhances the values of tensile strength.[20] The values of tensile modulus exhibit a similar trend as in the case of tensile strength. The introduction of 5, 10, and 15% bismaleimide into unsaturated polyester system increases the value of tensile strength by 9.6, 23.7, and 35.9% respectively. This may be due to the formation of intercrosslinking network between BMI and unsaturated polyester resin. The introduction of both vinyl esters and BMI into unsaturated polyester resin changes the values of tensile strength according to their nature and percentage content. This is due to the formation of intercross linking network between BMI and vinyl ester modified unsaturated polyester systems. The values of tensile modulus exhibit a similar behavior as in the case of tensile strength and are shown in Table I.

TABLE I
Mechanical Properties of BMI Modified Unsaturated Polyester and BMI
Modified VEO Unsaturated Polyester Systems

| Matrix system	UP/VEO/ BMI	Tensile strength (MPa)	Tensile modulus (MPa)	Flexural strength (MPa)	Flexural modulus (MPa)	Unnotched Izod impact strength (J/m)
A	100/00/00	32.0	1023.0	42.1	780.2	23.0
B	100/02/00	36.9	1223.8	44.3	810.3	24.3
C	100/04/00	40.4	1301.1	46.9	880.7	26.7
D	100/06/00	45.2	1353.8	49.8	948.3	28.3
E	100/04/05	50.7	1423.7	55.3	971.6	22.7
F	100/04/10	53.6	1510.8	59.7	1065.4	21.3
G	100/04/15	58.3	1625.3	64.3	1137.3	20.0
H	100/00/05	35.1	1220.1	46.4	905.3	21.0
I	100/00/10	39.6	1298.7	50.7	943.6	19.6
J	100/00/15	43.5	1360.2	56.5	1005.5	17.9
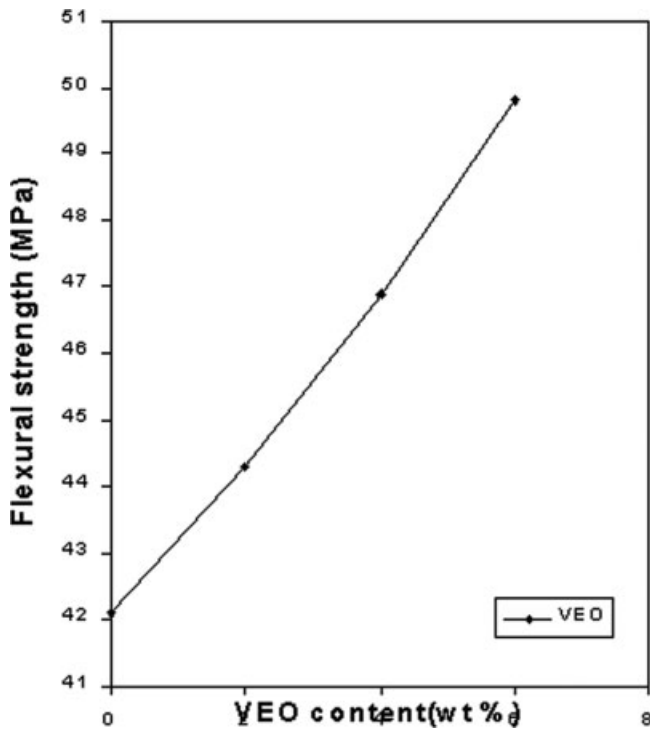
Figure 11 Effect of vinyl ester on flexural strength of VEO modified UP systems.

Flexural properties

The observed values of flexural strength of unmodified unsaturated polyester and unsaturated polyester modified with vinyl ester are plotted and shown in Figures 11–14 and in Table I. The introduction of 2, 4,
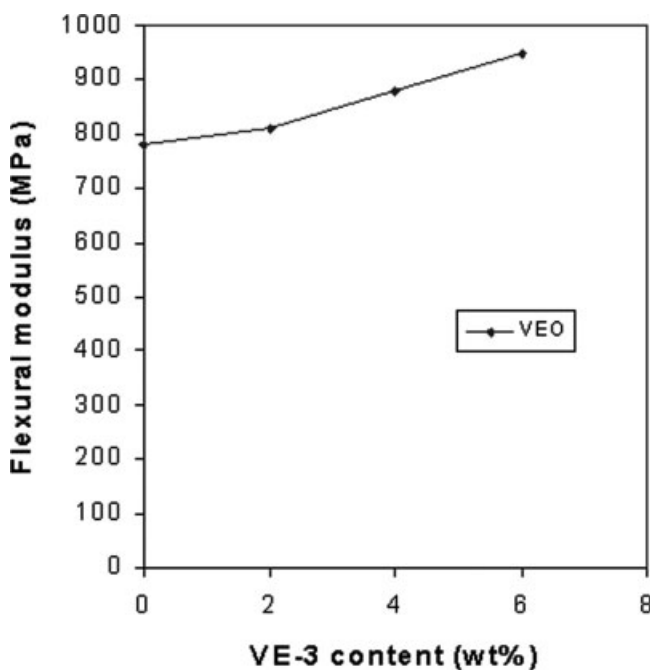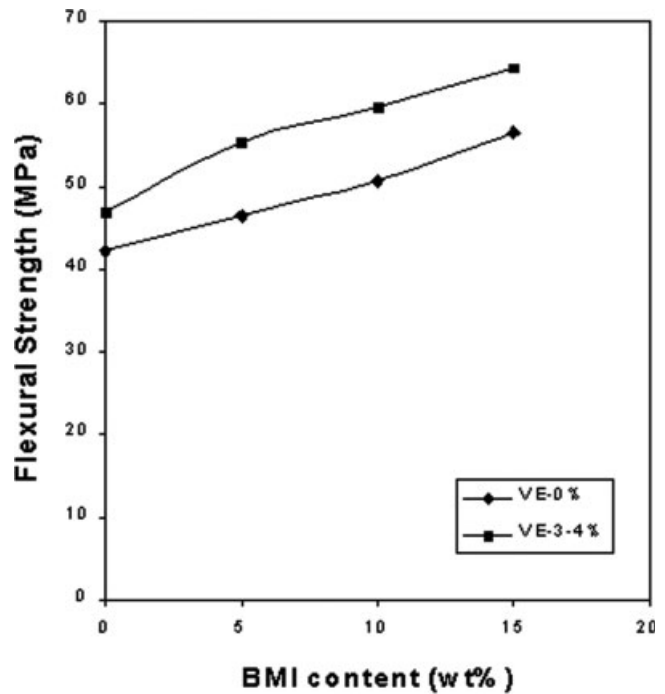

Figure 13 Effect of BMI content on flexural strength of UP and UP/VE systems.

and 6% of vinyl ester (by wt) VEO into unsaturated polyester resin increases the flexural strength by 5.2, 11.4, and 18.3% respectively. The increase in value may be explained due to the formation of chain entanglement between vinyl ester and unsaturated polyester matrix.[20] A similar trend is observed in the case of
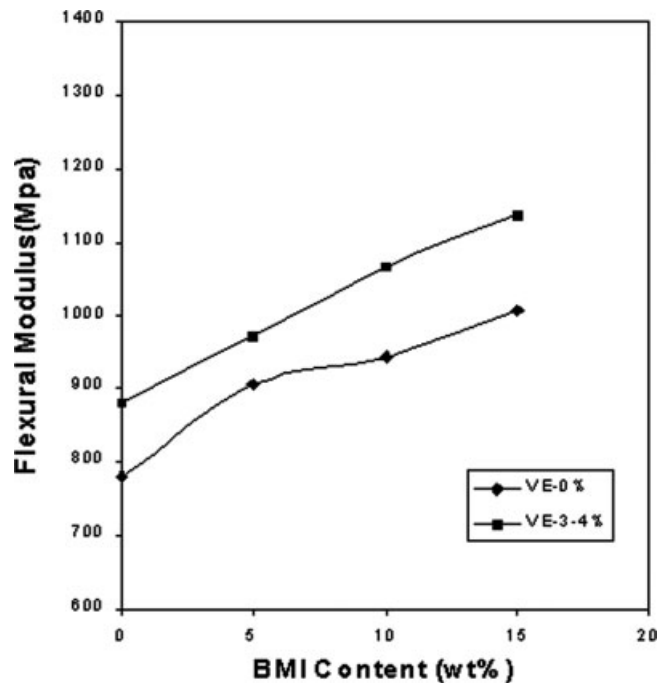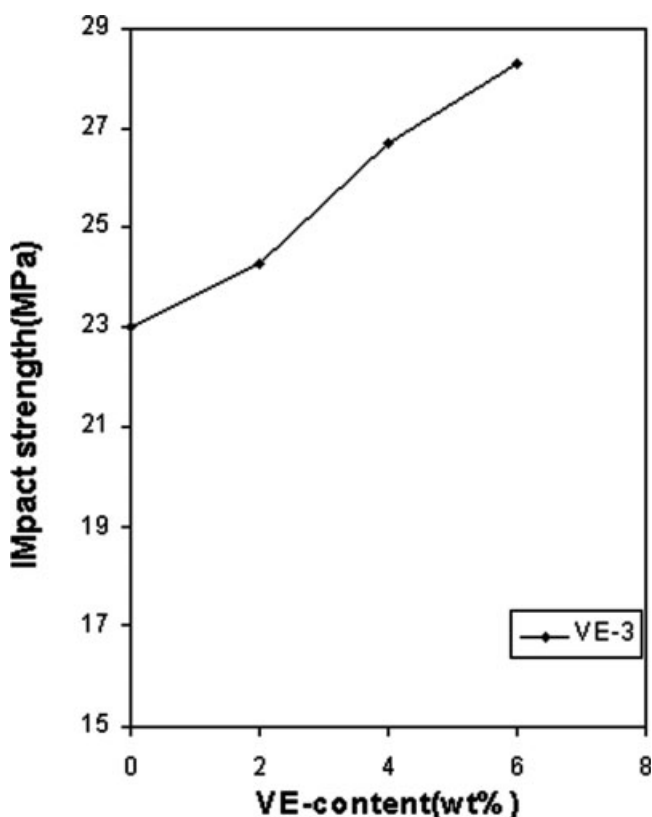

Figure 12 Effect of VEO on flexural modulus of UP system.

Figure 14 Effect of BMI content on flexural modulus of UP and UP/VE systems.
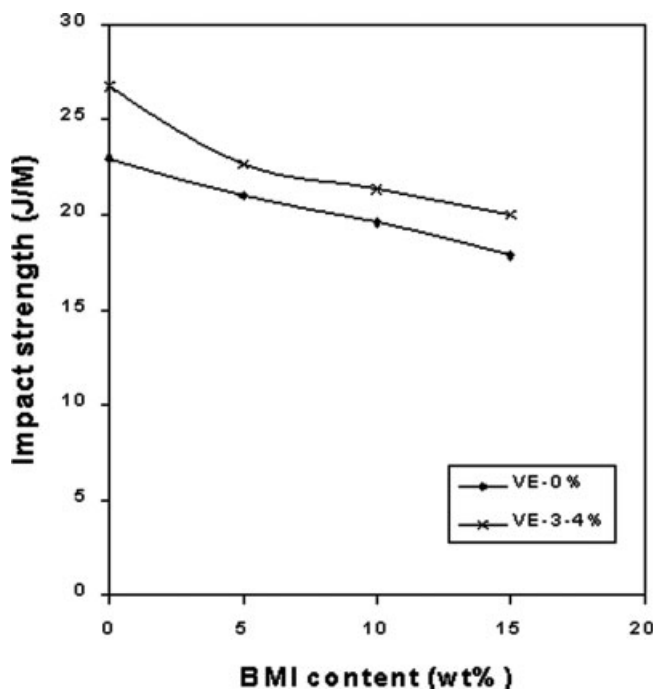
flexural modulus. The incorporation of bismaleimide into the vinyl ester modified unsaturated polyester system indicates an enhancement in the values of flexural strength according to their nature and percentage concentration as observed in the case of tensile strength. The enhancement is influenced by the synergistic effect of toughening and rigidity imparted by vinyl ester and bismaleimide.

Unnotched izod impact strength

The values of impact strength of unsaturated polyester and vinyl ester-unsaturated polyester matrices are plotted and shown in Figures 15 and 16. The incorporation of vinyl ester into unsaturated polyester resin improves the toughness according to the percentage content of vinyl ester and is due to high-energy absorption and the increase in the free volume created by long and bulky molecular chain. The improvement in toughness imparted by 2, 4, and 6% vinyl ester incorporation are 5.6, 16, and 23% respectively. The incorporation of bismaleimide into unmodified unsaturated polyester lowers the values of impact strength. The reduction in the values may be attributed to the restricted chain mobility due to the formation of inter-crosslinking network structure, which in turn enhances the rigidity.

Figure 16 Effect of BMI content on impact strength of UP and UP/VE systems.

Thermal properties

The DSC thermograms of unsaturated polyester, vinyl ester modified unsaturated polyester, and bismaleimide modified vinyl ester-unsaturated polyester are shown in Figures 17 and 18. The glass transition temperature of unsaturated polyester and vinyl ester modified unsaturated polyester systems are presented in Table II. The glass transition temperature obtained for unsaturated polyester system is 133°C. The value

Figure 15 Effect of vinyl ester on impact strength of UP systems.
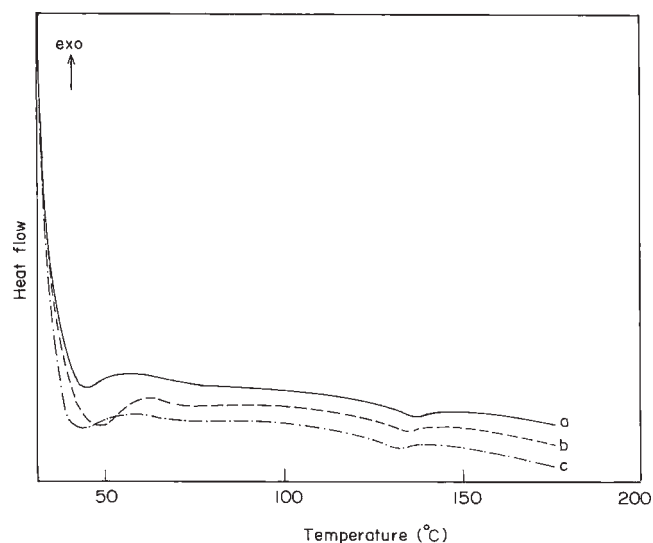
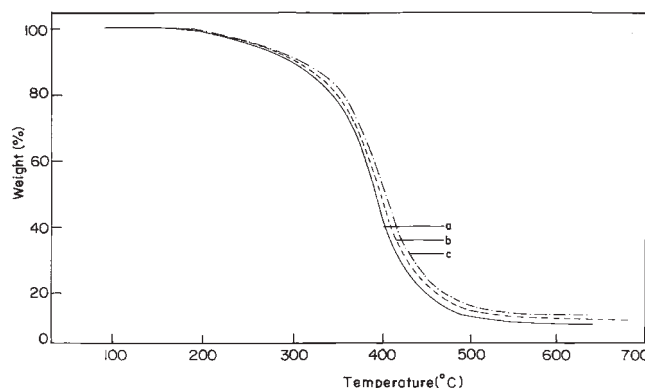**Figure 17** DSC traces of UP and VEO modified UP systems (a) 2% VEO (b) 4% VEO (c) 6% VEO.
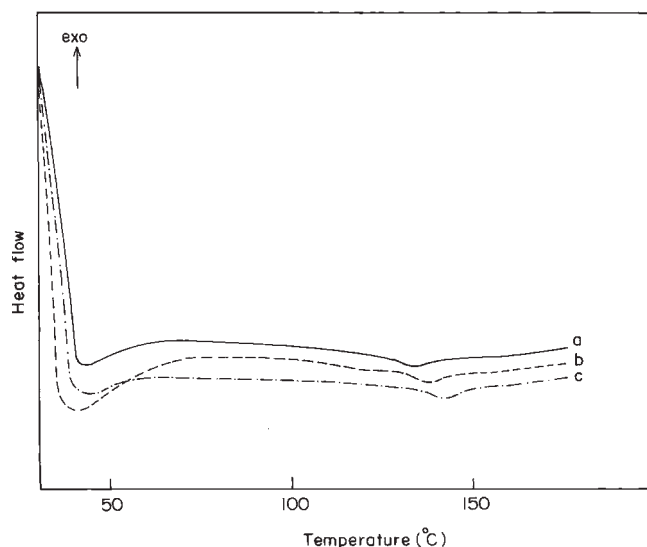
Figure 18 DSC traces of BMI modified UP systems (a) 5% BMI (b) 10% BMI (c) 15% BMI modified UP systems.

Figure 19 TGA curves of VEO modified UP systems (a) 2% VEO (b) 4% VEO (c) 6% VEO.

of T_g decreases with increase in concentration of vinyl ester. For example, the value of T_g for 2, 4, and 6% of vinyl ester modified unsaturated polyester systems are 132, 130, and 128°C respectively, and this may be due to the presence of substituted methylene group of TGDDM, present in the vinyl ester moiety, creates more free volume, thereby making the chain flexible and in turn decreases the value of T_g. The single T_g value obtained for the vinyl ester modified unsaturated polyester system indicates that the vinyl ester is chemically incorporated into the systems. The introduction of bismaleimide into unsaturated polyester and vinyl ester modified polyester systems enhances the higher degree of formation of intercross linking network, which in turn decreases the molecular relaxation and increases the rigidity thereby increases the value of glass transition temperature. The single T_g value obtained for the bismaleimide modified unsatu-

rated polyester systems further confirmed the formation of intercrosslinking network structure and is shown in Table II.

Thermogravimetric analysis is used to assess the thermal stability and utility of polymer matrices for thermal insulating applications. The TGA curves of degradation temperature of unsaturated polyester and vinyl ester modified unsaturated polyester systems showed an increase in the degradation temperature according to its percentage concentration. The presence of vinyl ester skeleton in the unsaturated polyester system delays the degradation process, since higher thermal energy is required to attain the same percentage weight loss than that required for unmodified unsaturated polyester system. The degradation at more high temperature caused by the vinyl ester moiety may be attributed to the presence of stable —C—C— linkages and aromatic rings. For example, the temperature required for 20, 40, and 60% weight loss of unmodified unsaturated polyester systems are 325, 348, and 370°C respectively, whereas the temperature required to attain the same percentages of weight loss for 4% modified unsaturated polyester systems are increased to 351, 376, and 407°C respec-

TABLE II
Heat Distortion Temperature and Glass Transition Temperature of UP, VEO Modified UP, BMI Modified UP, and BMI Modified VEO/UP Systems
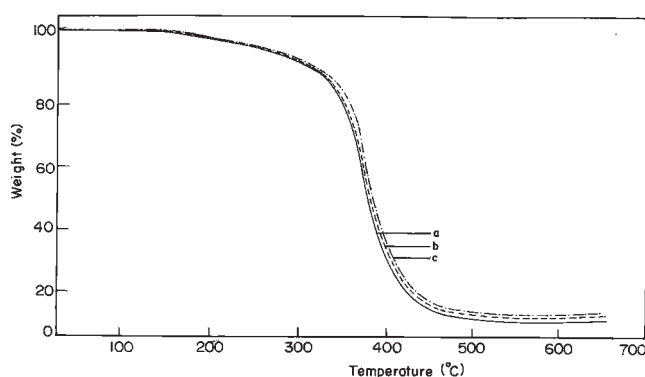
Matrix system	UP/VEO/BMI composition	Heat distortion temperature (°C)	Glass transition temperature (°C)
A	100/00/00	72	133
B	100/02/00	71	132
C	100/04/00	70	130
D	100/06/00	68	128
E	100/04/05	77	134
F	100/04/10	79	138
G	100/04/15	80	143
H	100/00/05	80	138
I	100/00/10	82	143
J	100/00/15	85	150

Figure 20 TGA curves of BMI modified UP systems (a) 5% BMI (b) 10% BMI (c) 15% BMI modified UP systems.
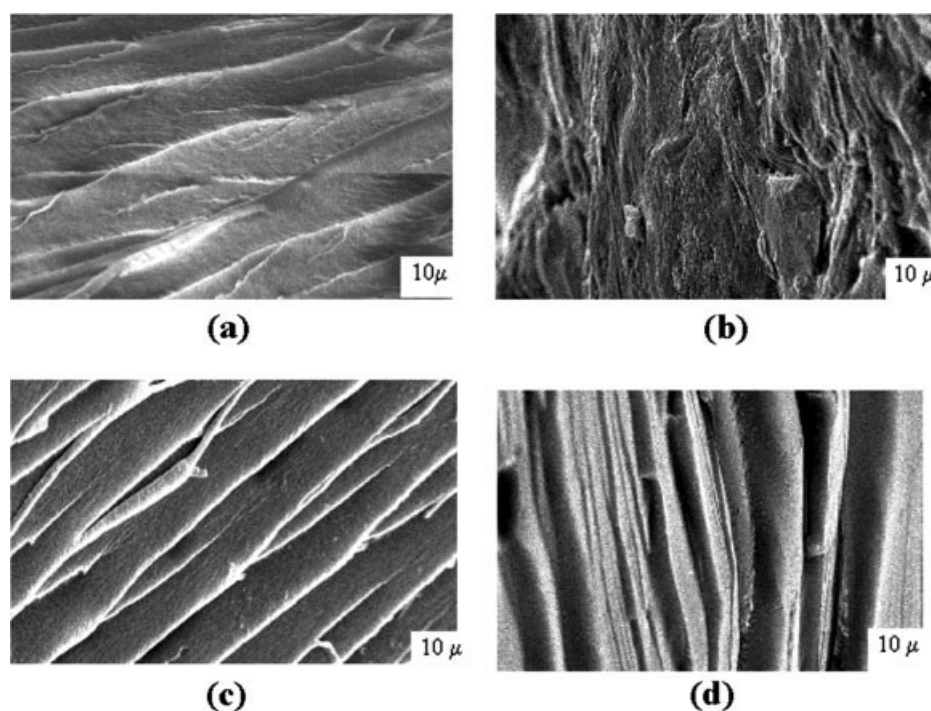
Figure 21 SEM Photographs of (a) unmodified unsaturated polyester, (b) VEO (4%) modified unsaturated polyester systems, (c) BMI modified VEO/UP system, (d) BMI modified/UP system.

tively. The thermal degradation temperatures of bismaleimide modified unsaturated polyester systems are increased with increasing bismaleimide concentration and are shown in Figures 19 and 20. This may be due to the formation of intercrosslinking network between unsaturated polyester and BMI and the presence of thermally stable aromatic rigid structure in the BMI molecule.

Heat distortion temperature (HDT) is determined to assess the thermomechanical behavior of matrix systems. It is observed that the HDT decreases with increasing concentration of vinyl ester into unsaturated polyester. This is due to the extension of chain length and consequent lowering of crosslinking density. The incorporation of BMI into vinyl ester modified unsaturated polyester system, increases the values of HDT with increase in BMI concentration. This may be attributed to high crosslinking density and ri-

gidity imparted by heterocyclic and aromatic rings of BMI. The values are listed in Table II.

Morphology

SEM is used to investigate the morphology of matrix systems (Fig. 21). Scanning electron micrographs of fractured surfaces of unmodified unsaturated polyester, vinyl ester modified unsaturated polyester resin systems indicate smooth, glassy, and homogeneous microstructure. This indicates the presence of homogeneous morphology due to the effective interaction between the vinyl ester and unsaturated polyester resin [Fig. 21(a,b)]. The scanning electron micrograph of the fractured surface of bismaleimide modified unsaturated polyester system is also similar to that of the unmodified unsaturated polyester system. This indicates that there are no phase domains

TABLE III
Water Absorption Behavior of Unsaturated Polyester, Vinyl Ester Modified Unsaturated Polyester, Bismaleimide Modified Unsaturated Polyester, and Bismaleimide Modified Vinyl Ester–Unsaturated Polyester Systems

	Percentage of water absorption			
Percentage of vinyl ester content in UP system	0%	2%	4%	6%
VEO	0.2401	0.2705	0.3065	0.3415
Percentage of BMI content in UP system	0%	5%	10%	15%
BMI	0.2401	0.1689	0.1594	0.1482
Percentage of BMI content in 4% VEO modified UP system	0%	5%	10%	15%
BMI	0.3065	0.3019	0.2956	0.2886

of the two components and it also suggests the formation of homogeneous intercrosslinked network [Fig. 21(c)].

Water absorption

The vinyl ester incorporation into unsaturated polyester system increases the water absorption behavior with increasing its concentration. For example, the percentage water uptake for unmodified unsaturated polyester system is 0.2401, whereas for 2, 4, and 6% vinyl ester, incorporation increases the water uptake percentage 0.2705, 0.3065, and 0.3415 respectively (Table III). The increase in percentage water uptake for vinyl ester incorporated system may be due to the presence of more number of hydrophilic vinyl ester linkages. The introduction of bismaleimide into unsaturated polyester and vinyl ester modified unsaturated polyester systems decreases the percentage water uptake. This may be due to the fact that more effective network formation when increasing BMI concentration, which in turn increases the crosslink density and rigidity.

CONCLUSIONS

Data resulted from mechanical studies infer that the incorporation of vinyl ester and bismaleimide into unsaturated polyester increases the tensile and flexural properties according to their percentage content. In the case of impact behavior when VEO is incorporated into unsaturated polyester an increasing trend is observed, and on the other hand, the introduction of BMI into unsaturated polyester showed a decreased value. Further the incorporation of vinyl ester and BMI into unsaturated polyester exhibited an improvement in thermal stability and better resistance by water absorp-

tion of unsaturated polyester. The scanning electron micrograph indicates that the homogeneous morphology exists in the case of vinyl ester and bismaleimide incorporated unsaturated polyester systems.

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