

Block Copolymers of Unsaturated Polyesters and Functional Elastomers

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ABSTRACT: Block copolymers of unsaturated polyester were prepared by condensation polymerization of hydroxyl or carboxyl terminated liquid rubbers with maleic anhydride, phthalic anhydride, and propylene glycol. The condensate obtained was mixed with styrene monomer to get an unsaturated polyester resin formulation. In this study, copolymers of unsaturated polyesters with hydroxy terminated polybutadiene, carboxy terminated nitrile rubber, and hydroxy terminated natural rubber were prepared. Mechanical properties such as tensile strength, tensile modulus, elongation at break, toughness, impact strength, surface

hardness, abrasion resistance, and water absorption were evaluated after the resin was cured in appropriate molds for comparison with the control resin. The fracture toughness and impact resistance of CTBN-modified unsaturated polyester show substantial improvement by this copolymerization without seriously affecting any other property. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 1956–1964, 2004

Key words: unsaturated polyester resin; block copolymers; functional elastomers; toughness; impact resistance

INTRODUCTION

Polyesters

Unsaturated polyester (UP) resins are a class of thermosets that is widely used in the fiber-reinforced plastic (FRP) industry. The widespread use of these resins is due to their low cost, ease of processing, ease of combination with reinforcements, rapid cure without any volatile products, excellent dimensional stability, and wide variety of grades available. UP resins are prepared by blending the polycondensate of unsaturated and saturated dicarboxylic acids with diols and an unsaturated coreactant diluent like styrene. Carothers was the first to prepare polyester with well-defined polymeric structures.¹ The general purpose grade UP resins (UPR) are blends of styrene with the condensation product of 1,2 propylene glycol (PG) and a mixture of maleic anhydride (MA) and phthalic anhydride (PA). When crosslinking is initiated with the help of a catalyst and an accelerator, styrene facilitates crosslinking at the sites of unsaturation in the polyester chains.²

Need for modification

The cured UP resins have high glass transition temperature values and are too brittle for many engineering applications in the absence of reinforcements.³ These polymers usually craze on their free surface and the crazed areas are converted into cracks, which propagate with relatively brittle energy absorption, resulting in fracture. Although failure in FRP is often limited to the resin–reinforcement interface,⁴ areas with a relatively low number of fibers are prone to damage when the product is in use or during demoulding. The damage usually starts as a microfracture of the matrix, which on propagation can result in disintegration of the system. The modification of resin, using elastomers, improves the toughness and impact resistance of the resin-rich locations considerably. Incorporation of elastomers also causes significant reduction in mold shrinkage.

Toughening methods

The toughness and impact resistance of UP resin (UPR) are improved by the incorporation of an elastomeric phase into the polymer matrix.⁵ The elastomers can be incorporated into the resin by physical and chemical methods. In physical modification, solid and liquid rubbers are dispersed in the resin. These rubbers should be miscible in the uncured resin and phase separation during the curing is essential, be-

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cause phase separated blends are generally tougher than homogeneous blends.⁶ The presence of elastomeric domains increases the absorption and dissipation of mechanical energy.⁷ The various mechanisms proposed for toughening by elastomers are energy absorption by rubber particles,⁸ debonding of rubber matrix interphase,⁹ shear yielding,¹⁰ matrix crazing,¹¹ and a combination of shear yielding and matrix crazing.¹² The solid rubbers reportedly used to modify UPR are styrene-butadiene rubbers, 1,2-polybutadiene, 1,4-polybutadiene, butadiene-acrylonitrile rubbers with amine end groups, natural rubber, halogenated butyl rubbers, chlorosulfonated polyolefins, and plasticized polyvinyl chloride.¹³ Modification of UPR with dicyclopentadiene¹⁴ and bismaleimide¹⁵ was also reported recently.

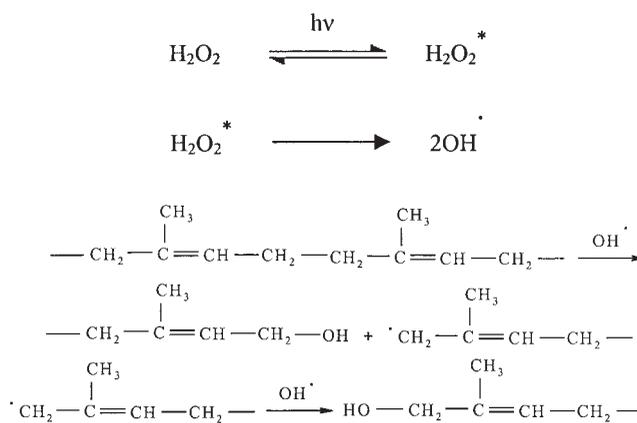
Chemical modification

Chemical modification can be achieved using either long-chain glycols (e.g., diethylene, dipropylene, or triethylene glycol) or long-chain saturated dibasic acids (e.g., adipic acid or sebacic acid) for the resin synthesis. Another approach is the addition of carboxyl or hydroxyl terminated liquid rubbers to the polyester reaction mixture and the cocondensation between terminal acidic or alcoholic groups, which results in UPR containing rubber segments in the main chain.¹⁶ Common liquid rubbers used are liquid polybutadiene and liquid butadiene-acrylonitrile with reactive end-groups.¹⁷ Block copolymers of UPR containing polyethylene glycol segments on the polymer main chain were reported by Schmidt and co-workers.¹⁸ The incorporation of flexible polyorganosiloxane segments in the UPR network enhances its flexibility.¹⁹ Recently, block copolymers that contain UPR with polyurethanes, polyureas, polysiloxanes, polyimides, polyoxazolines, or polyglycols were reported.²⁰

In this study, the liquid rubbers used are carboxy terminated nitrile rubber (CTBN) hydroxy terminated natural rubber (HTNR) and hydroxy terminated polybutadiene (HTPB). A two-stage process is used for the synthesis of polyesters. This results in segmental structures containing alternating rigid crosslinked segments and linear soft segments displaced regularly in the polymer chain. Segmental polyesters show exceptional mechanical properties superior to those of polymers having network structure with random crosslinking.²¹ The first step involves the polyesterification of PA with PG at about 220°C. After being cooled to 160°C, MA and the reactive liquid rubber are added and the temperature is kept at about 190–200°C.²²

HTNR is prepared in the laboratory by photochemical degradation of natural rubber as reported by Ravindran et al.²³ Initial degradation of NR into

shorter chain segments with hydroxyl end groups is carried out in the presence of hydrogen peroxide. HTNR with any range of molecular weight can be prepared by a suitable choice of the composition of reaction mixture and exposure time. The hydroxyl functionality remains slightly less than 2. The following mechanism was suggested for depolymerization and hydroxylation of NR.



EXPERIMENTAL

Materials

Styrene, methyl ethyl ketone peroxide (catalyst), and cobalt naphthenate (accelerator) were supplied by Sharon Engineering Enterprises (Cochin, India). 1,2-Propylene glycol, maleic anhydride, phthalic anhydride, xylene, and hydroquinone were supplied by E. Merck India Ltd. (Bombay, India). HTPB ($M_n = 2620$) and CTBN ($M_n = 3500$, ACN content = 18%) were obtained from Vikram Sarabhai Space Centre (Thiruvananthapuram, India).

HTNR ($M_n = 3000$ and hydroxyl value = 36.35 mg of KOH/g) was prepared from ISNR-5 grade natural rubber dissolved in toluene by photodepolymerization in the presence of H_2O_2 .²⁴ Initially, NR was masticated for 30 min at 40°C. A 5 wt % solution of this NR in toluene was mixed with a 30 wt % H_2O_2 solution and methanol in the volume ratio 20:1:3, respectively. Irradiation using sunlight was carried out in a closed glass vessel for 50 h with constant stirring. The depolymerized NR was recovered by precipitation with methanol and purified by repeated precipitation. Molecular weights were determined by end-group analysis and the hydroxyl value was estimated by reported procedures.²⁵

Synthesis of UP resin

The UP resin was prepared by a two-stage process. PG, MA, and PA were taken in the molar ratio 1.1:0.40:0.60. A slight excess of PG (10%) was provided to allow for evaporation losses. PG and PA were taken in

a 1-L three-neck RB flask equipped with a mechanical stirrer, CO₂ inlet, and reflux condenser. The reaction mixture was heated to 220°C in a temperature-controlled heating mantle. The reaction was carried out in an inert atmosphere of CO₂ to get good color and to prevent premature gelation. Xylene was used to remove water of condensation by azeotropic distillation. The extent of reaction was estimated by measuring the acid number as per ASTM D 4662–87. On reaching an acid value of 50, MA was added and the reaction was continued at a temperature of about 190–200°C. When the acid value became 40, a vacuum was applied to remove excess PG and xylene. At an acid value of about 30, the heater was switched off. When the reaction mixture cooled to 100°C, 0.02 wt % hydroquinone,²⁶ 0.25 wt % paraffin wax,²⁷ and 35 wt % styrene were added and mixed thoroughly.

Synthesis of chemically modified UP resin

UP resin was prepared by condensation polymerization of PG, MA, and PA in the presence of CTBN, HTPB, or HTNR in a two-stage process. PG, MA, and PA were taken in the molar ratio 1.1:0.40:0.60. The synthesis was done according to the procedure employed for unmodified UP resin. PA and PG were added in the first stage. When the acid number became 50, MA and 0–10 wt % of reactive liquid rubber were introduced into the reaction mixture and the reaction was continued to completion.

Curing

Unmodified and modified resins were first cured at room temperature by the addition of catalyst (methyl ethyl ketone peroxide dissolved in dimethyl phthalate containing 60% peroxide) and the accelerator (cobalt naphthenate dissolved in styrene having a cobalt concentration of 1%). These were used in concentrations of 0.5 and 1% of the weight of the resin, respectively. The resin was then poured into the tensile mold with dumbbell-shape cavities coated with a releasing agent. Samples for impact test, abrasion resistance, and water absorption were cast separately in appropriate molds. Curing was done at room temperature for 24 h followed by post curing at 80°C for 3 h.

Testing

Soxhlet extraction of uncured solid polyester samples was done with *n*-hexane for 48 h to determine the amount of unreacted liquid rubber, if any. The polyester samples were further purified from chloroform solution by precipitation with light petroleum ether (bp 60–70°C). The ¹H-NMR and ¹³C-NMR spectra of unmodified and modified UP resin were taken from a

solution in CDCl₃ using a Bruker Avance dpx 300 FTNMR spectrometer, operating at a proton resonance frequency of 300 MHz, to confirm chemical modification. The scanning electron micrographs of fracture surfaces of unmodified and modified UPR were taken in a Cambridge Instruments S 360 Stereoscanner.

The cast samples, after postcuring, were tested for tensile strength, toughness, elongation at break, modulus, impact strength, water absorption, and hardness taking six trials in each case. The tensile properties were tested on a Shimadzu Autograph universal testing machine (ASTM D 638–89) and Izod impact strength was measured on a Zwick/Materialprüfung impact tester as per ASTM D 256 specifications. Abrasion resistance was tested on a Zwick DL 100 machine as per DIN 55,516. A Shore D durometer was employed for measuring surface hardness (ASTM D 2240–86). Water absorption was tested as per ASTM D 570.

RESULTS AND DISCUSSION

The Soxhlet extraction data show that very little soluble matter could be extracted from modified UP resin compared to unmodified UP resin. This suggests almost complete copolymerization reactions between polyester and liquid rubber. The spectral studies also confirm this.

A comparison of the ¹H-NMR spectral patterns of UPR and UPR-*co*-HTPB (Fig. 1) leads to the following observations. There is no change in the patterns of –CH₃ groups as there is no additional –CH₃ group in the modifier. In the –CH₂ region of UPR and UPR-*co*-HTPB (3.5–4.5 ppm) additional peaks are observed. These are due to additional –CH₂ groups present in HTPB, which are chemically and magnetically different from the –CH₂ of UPR. In the –CH region (5–5.8 ppm) there is no change in the spectral pattern, but there is an increase in the intensity of the –CH groups of the copolymer. These results indicate the introduction of HTNR into the UPR chain. Comparing the ¹³C-NMR spectra of UPR and UPR-*co*-HTPB (Fig. 2) there is a sharp increase in the –CH₂ peak intensity, which is a direct consequence of chemical modification. However, there is no change in the splitting patterns. No change in spectral pattern is observed for –CH₂ or –CH or even the aromatic region.

Comparing the ¹H-NMR spectral patterns of UPR and UPR-*co*-HTNR (Fig. 1), it is seen that an alteration of chemical structure has taken place. There is no change in the patterns of the aromatic range, as there are no additional aromatic groups in the HTNR additive. A clear increase in the intensity of the peaks due to –CH₃ (1–1.4 ppm) and –CH₂ (3.5–4.5 ppm) groups is noticed. This is due to the introduction of these groups from HTNR. There is a change in the splitting

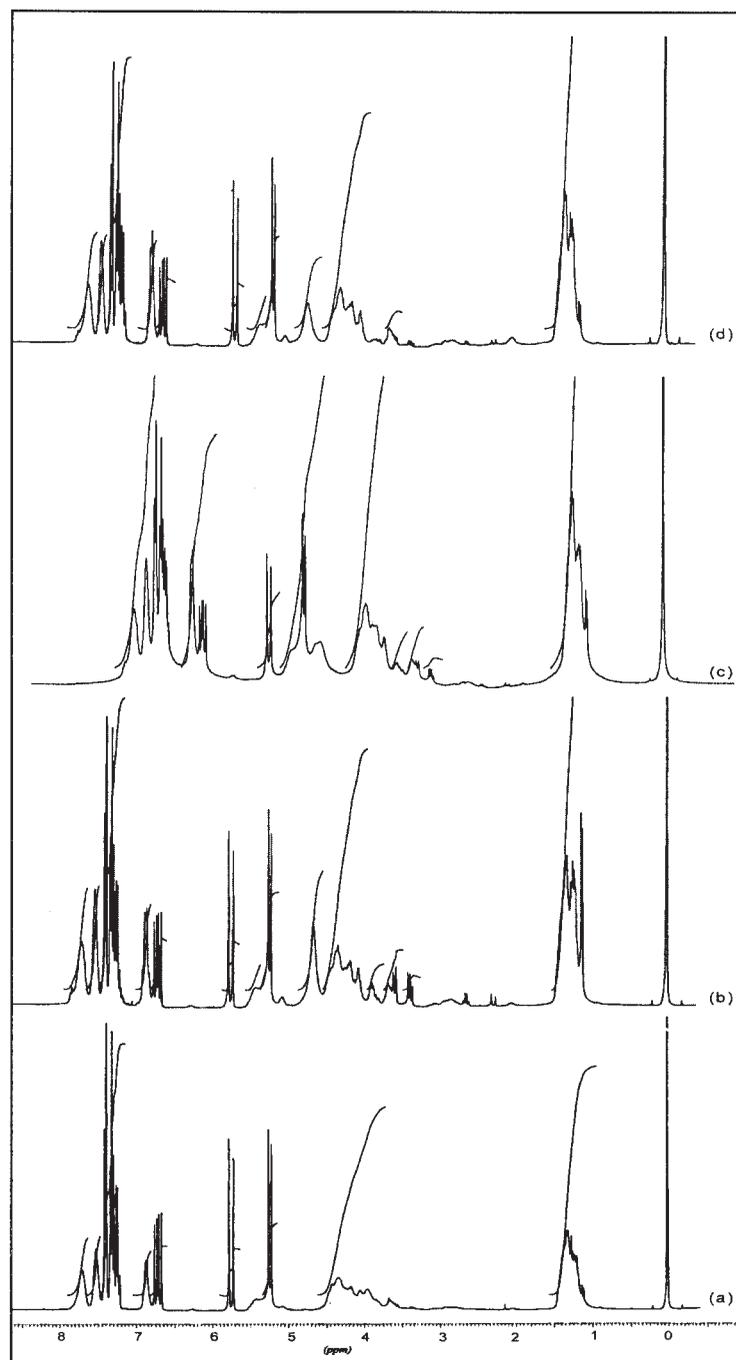


Figure 1 ^1H -NMR spectrum: (a) UPR, (b) UPR-co-HTPB, (c) UPR-co-HTNR, (d) UPR-co-CTBN.

patterns of these groups also. From a comparison of the ^{13}C -NMR spectral patterns of UPR and UPR-co-HTNR (Fig. 2), an increase in intensity of the peaks due to $-\text{CH}_3$ (20 ppm) and $-\text{CH}_2$ (65–75 ppm) groups is observed, which again indicates the introduction of HTNR into the UPR chain.

Comparing the ^1H -NMR spectral patterns of UPR-co-CTBN with those of UPR (Fig. 1) the following observations can be made. There is no change in the

$-\text{CH}_3$ peak pattern as there are no additional $-\text{CH}_3$ groups in the modifier. A total change in the peak positions and intensity of different $-\text{CH}_2$ groups (3.5–4.8) in the copolymer suggests effective modification of UPR with CTBN. There is an increase in the spectral intensity for $-\text{CH}$ regions, which further confirms modification of UPR with CTBN. The appearance of additional peaks in the $-\text{CH}_2$ region in the ^{13}C -NMR also supports chemical modification (Fig. 2).

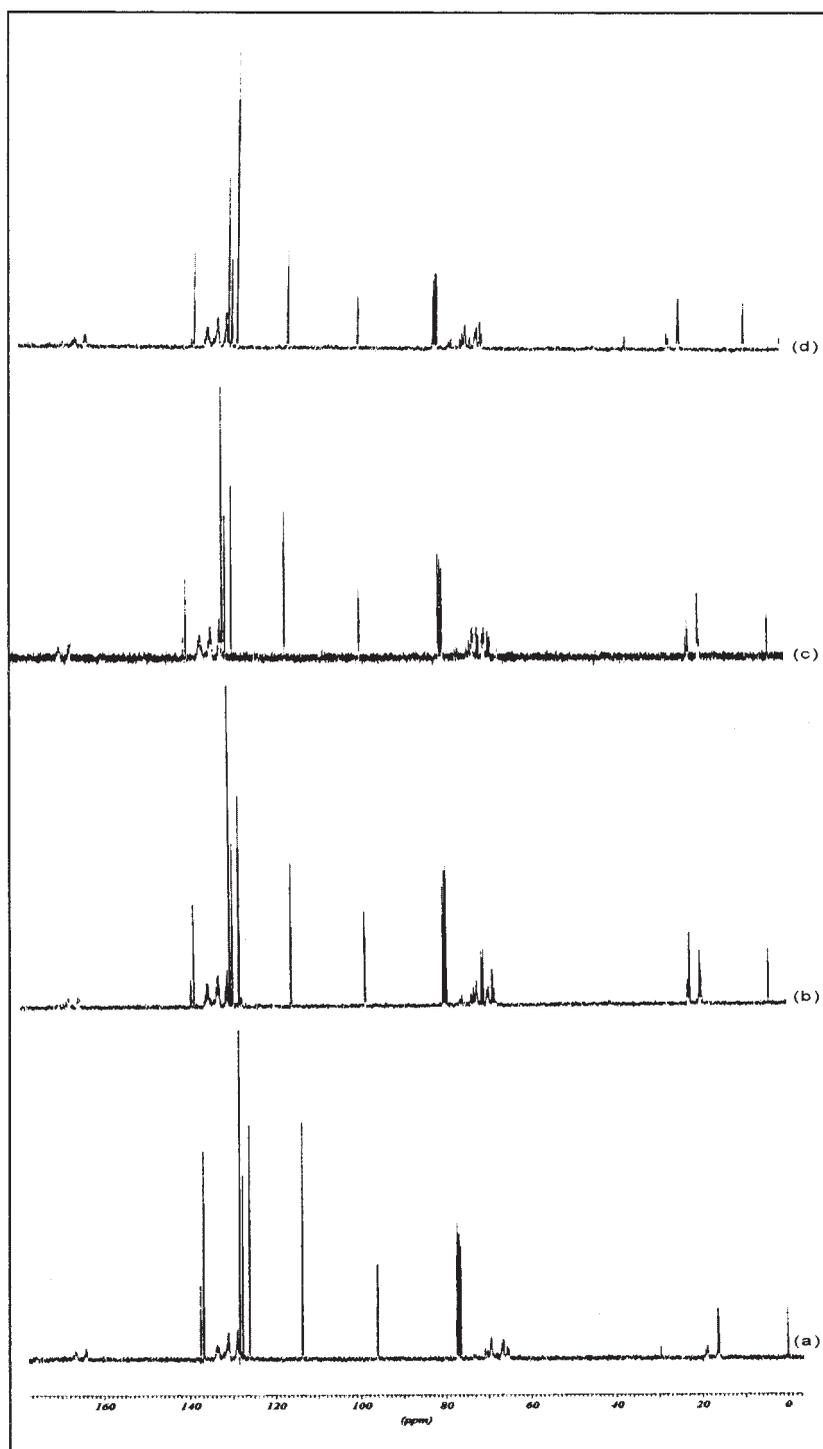


Figure 2 ^{13}C -NMR spectrum: (a) UPR, (b) UPR-co-HTPB, (c) UPR-co-HTNR, (d) UPR-co-CTBN.

The scanning electron micrographs of fracture surfaces of unmodified and modified UPR are shown in Figure 3. Referring to the micrograph in Figure 3a, the fracture path for unmodified resin is narrow and continuous, indicating rapid crack propagation. The micrograph of HTPB modified resin in Figure 3b shows

a profusion of cracks far broader and discontinuous than for Figure 3a. Cracks propagate from the surface across the cross-sectional area and the abrupt fracture propagation along a wide front suggests better load-bearing characteristics for the resin. Referring to HTNR modified resin (Fig. 3c), the fracture paths are

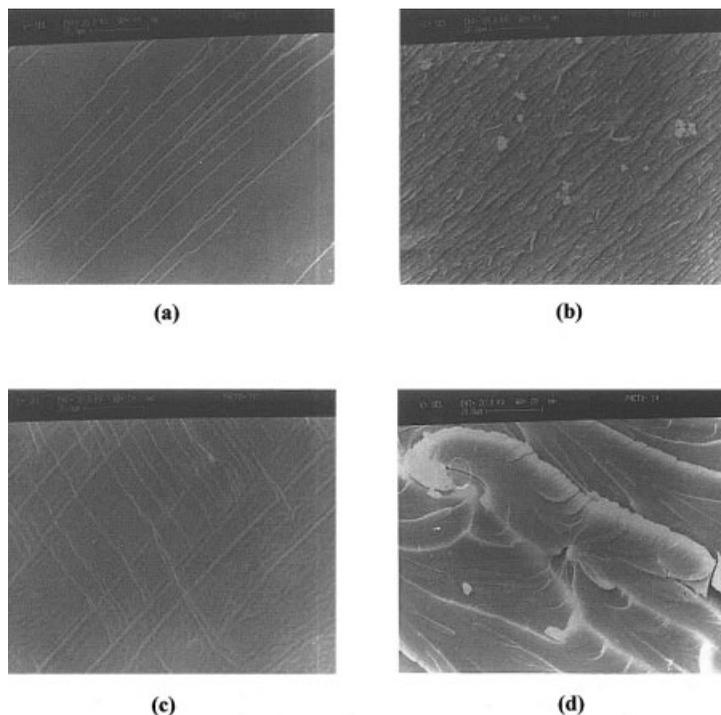


Figure 3 Scanning electron micrographs of fracture surfaces: (a) UPR, (b) UPR-co-HTPB, (c) UPR-co-HTNR, (d) UPR-co-CTBN.

broader and less continuous. This leads to high energy absorption and toughness. CTBN-modified resin shows the best results, as can be seen from the micrograph in Figure 3d. The fracture paths have a feathery texture with large breadth. They are also discontinuous and convoluted. The fracture spreads from the bottom upward. These point to high toughness and load-bearing characteristics.

Mechanical properties of modified UP resin

Tensile properties

The effect of the addition of various reactive liquid rubbers on the tensile properties is shown in Figures 4-6, which indicate the variation in tensile strength, modulus, and elongation at break, respectively. In Figure 4, tensile strength values decrease steadily upon adding progressively larger amounts of rubber. In this case failure can occur in the weak rubber segments. The fall in tensile strength can also be due to the decrease in interchain attractions by the presence of rubber segments. The tensile strength obtained by adding CTBN is slightly higher than that obtained by adding the other rubbers. Interchain attractive forces could be more pronounced in CTBN-modified UPR. Interchain attractive forces are weak in the case of HTNR and this could be the basis for lower tensile strength. However, in a physical modification study of

UPR by functional elastomers reported by our group earlier,²⁸ there is an increase in tensile strength over that of modified resin for these elastomers, especially CTBN. This is due to possible intercomponent grafting of elastomers and polyester chains in the blends.

Figure 5 shows the effect of the addition of elastomers on tensile modulus. Modulus values are lower than the base resin values at all concentrations. This is

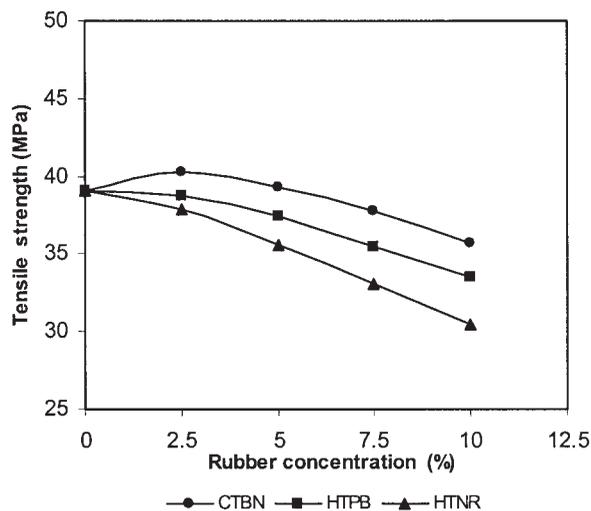


Figure 4 Tensile strength of rubber modified resin versus rubber concentration.

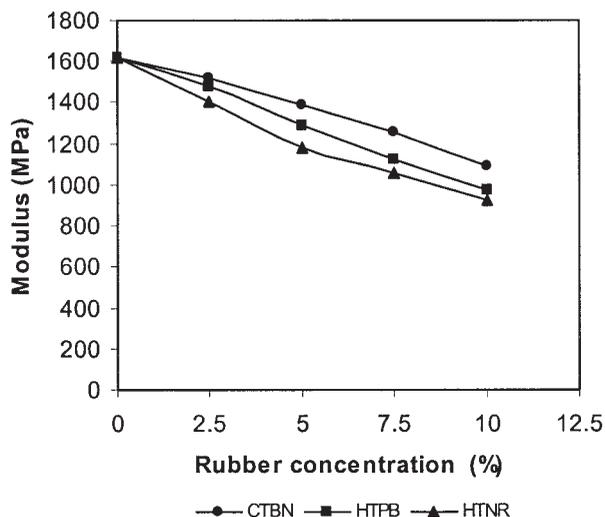


Figure 5 Modulus of rubber modified resin versus rubber concentration.

due to the greater elongation undergone by rubber segments. The effect of elastomer addition on the elongation-at-break (EB) is shown in Figure 6. The EB % values increase due to the incorporation of rubber segments. The addition of HTNR produces the greatest increase in EB at 10% rubber concentration. This can be attributed to the presence of pendant methyl groups and the greater amount of coiling possible in NR chains.

Toughness properties

The variation in toughness of the cured resin with the rubber content is shown in Figure 7. These values are

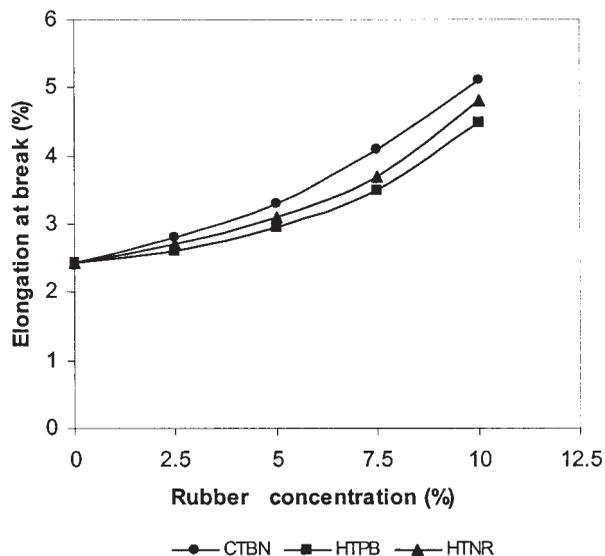


Figure 6 Elongation at break of rubber-modified resin versus rubber concentration.

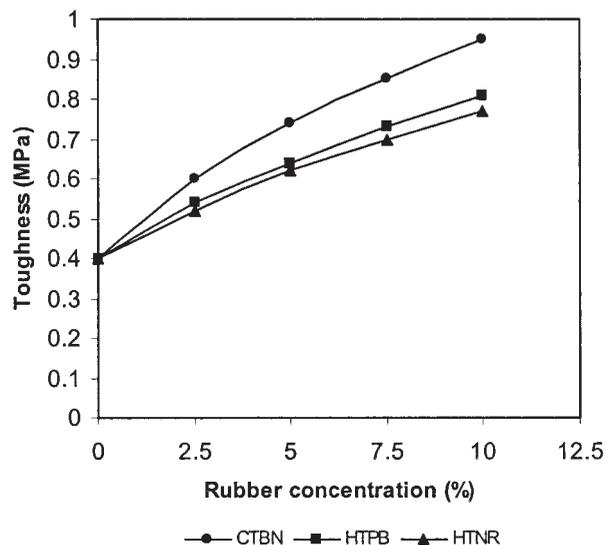


Figure 7 Toughness of rubber-modified resin versus rubber concentration.

computed from the area under the stress-strain curve. All the elastomers are seen to increase in toughness to varying extents upon the addition of progressively larger amounts of rubber. CTBN gives the best result in this respect. This can be attributed to better compatibility of the rubber phase with the continuous polyester phase.²⁹ The toughness of the copolymer at 10% CTBN concentration is about 240% of the toughness of UPR. The enhancement of toughness due to HTNR and HTPB is less remarkable.

Comparing the tensile strength and toughness graphs (Figs. 4 and 7), tensile strength falls in all cases upon addition of the rubber while the toughness increases. The reduction in tensile strength is the least in the case of CTBN. In this case, at 10 wt %, the tensile strength is less than that of the unmodified resin by only 8.7%, whereas the toughness shows a substantial increase of 140%. This retention of tensile strength upon progressive addition of rubber is much less for the other two cases.

Figure 8 shows the variation in impact strength with rubber concentration. In this respect also CTBN shows improvement, again at a concentration of 10%. Both HTPB and HTNR show almost identical behavior. The increase in impact strength is again due to better flexibility of the rubber phase. The rubber segments absorb the energy of impact and prevent crack propagation.

Hardness and abrasion loss

Figure 9 indicates a general lowering of surface hardness on addition of all types of elastomers. This can be due to the lower surface hardness values of the elas-

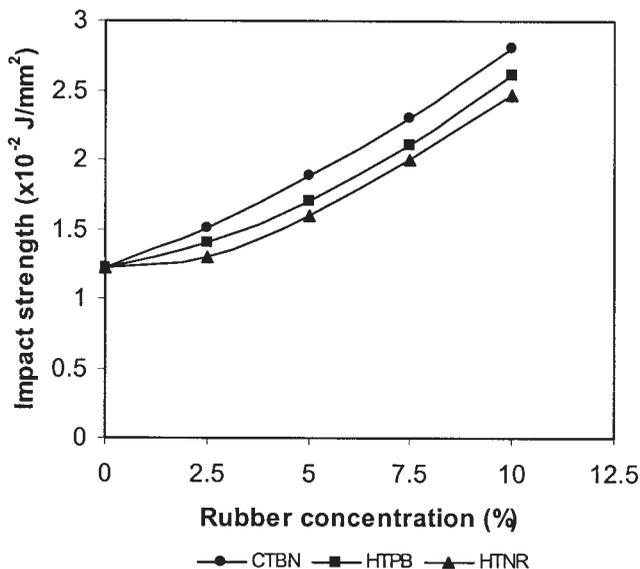


Figure 8 Impact strength of rubber-modified resin versus rubber concentration.

tomers. This effect is maximum for HTNR and minimum for CTBN.

There is a decrease in abrasion loss with an increase in rubber concentration for all rubbers ((Fig. 10). Abrasion loss decreases steadily in the case of HTNR and HTPB. But the abrasion loss of CTBN is still lower. This may be due to the better compatibility between the resin and CTBN and to possible interchain attractions leading to a relatively homogeneous material structure.

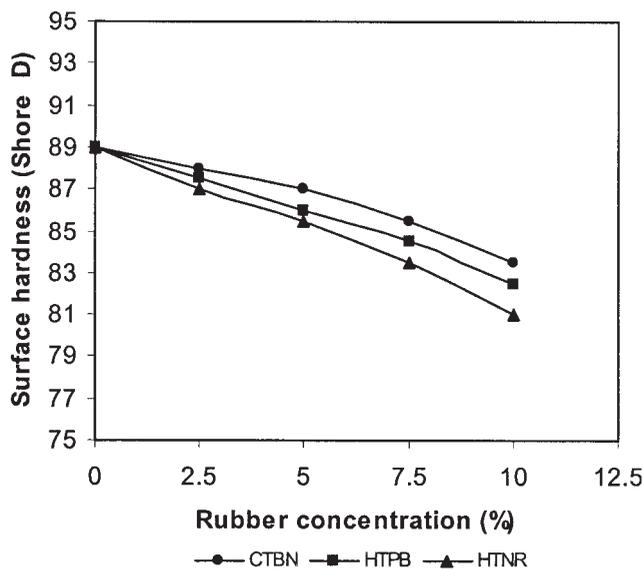


Figure 9 Surface hardness of rubber-modified resin versus rubber concentration.

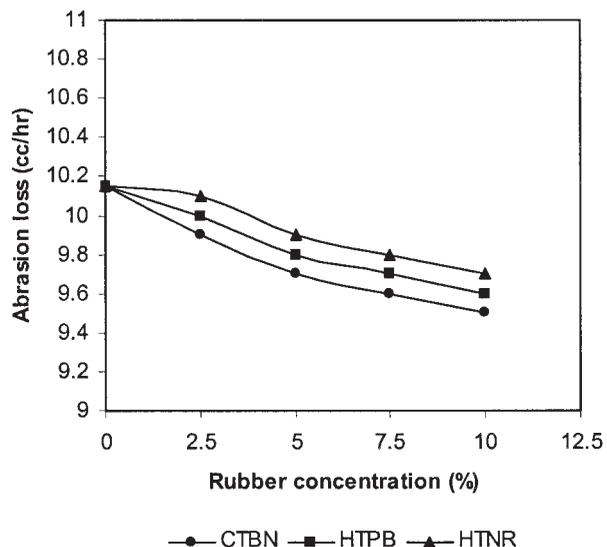


Figure 10 Abrasion resistance of rubber-modified resin versus rubber concentration.

Water absorption

Water absorption of various modified resins is shown in Fig. 11. HTNR is far inferior to other elastomers, especially CTBN and HTPB, due to lower interchain attractive forces and the presence of small quantities of nonrubber constituents occurring in NR latex.

Table I summarizes the effect of adding varying amounts of different elastomers to UPR. The maximum improvement acquired in each property and the corresponding elastomer concentrations are tabulated. It is evident that CTBN enjoys a clear superiority over other elastomers.

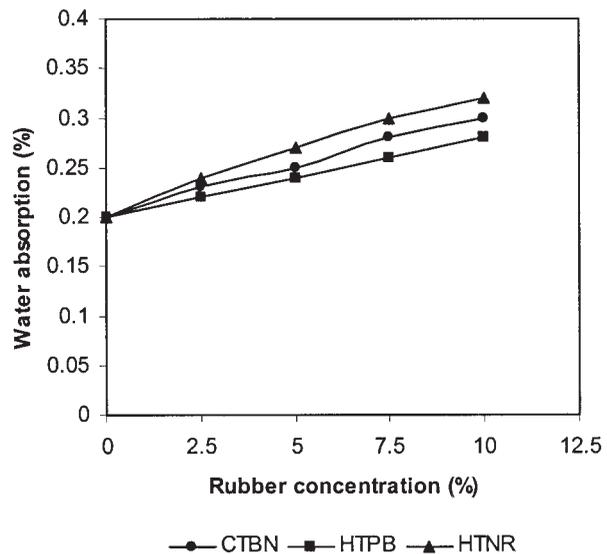


Figure 11 Water absorption of rubber-modified resin versus rubber concentration

TABLE I
Summary of Properties of UPR Modified with 0 to 10% Elastomers

Property	UPR	Maximum improvement achieved (%) / elastomer concentration (%)		
		CTBN	HTNR	HTPB
Tensile strength (MPa)	39.1	3.06/2.5	0	0
Modulus ($\times 10^2$ MPa)	16.2	0	0	0
Elongation at break (%)	2.43	109.9/10	97.5/10	85.18/10
Toughness (MPa)	0.40	137.5/10	102.5/10	112.5/10
Impact strength ($\times 10^{-2}$ J/mm ²)	1.22	129.5/10	113.9/10	122.1/10
Hardness (shore D)	89	0	0	0
Abrasion loss (cc/h)	10.15	0	0	0
Water absorption (%)	0.20	40/10	50/10	60/10

CONCLUSION

Carboxy and hydroxy terminated liquid rubbers can be used to modify UPR by a synthetic route similar to that of the unmodified resin. Toughness shows steady improvement upon increasing the rubber concentration in all three cases studied, viz. CTBN, HTPB, and HTNR. CTBN is far superior in this respect to HTPB and HTNR. Incorporation of CTBN into the polymer chain leads to only a marginal decrease in tensile strength while improving the toughness and impact strength substantially.

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