

# Modification of Unsaturated Polyester Resin by Polyurethane Prepolymers

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**ABSTRACT:** Unsaturated polyester resins (UPRs) are extensively used by the fiber-reinforced plastic (FRPs) industry. These resins have the disadvantages of brittleness and poor resistance to crack propagation. In this study, UPRs were chemically modified by reactive blending with polyurethane prepolymers having terminal isocyanate groups. Hybrid networks were formed by copolymerisation of unsaturated polyesters with styrene and simultaneous reaction between terminal hydroxyl groups of unsaturated polyester and isocyanate groups of polyurethane prepolymer. The prepolymers were based on toluene diisocyanate (TDI) and each of hydroxy-terminated natural rubber (HTNR), hy-

droxy-terminated polybutadiene (HTPB), polyethylene glycol (PEG), and castor oil. Properties like tensile strength, toughness, impact resistance, and elongation-at-break of the modified UPRs show considerable improvement by this modification. The thermal stability of the copolymer is also marginally better. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 449–456, 2006

**Key words:** hybrid polymer networks; impact resistance; polyurethane prepolymers; toughness; unsaturated polyester resin

## INTRODUCTION

Unsaturated polyester resins (UPRs) are widely used for the fabrication of glass-reinforced plastics (GRP) and other polymeric composites. The widespread use of these resins is due to their relatively low cost, ease of processing, excellent wetting properties, good overall performance, and the wide variety of grades available. They are generally prepared by the reaction of a saturated diol with a mixture of unsaturated and saturated dibasic acids or their anhydrides. Commercially, the resin is available in the form of solutions containing 60–70 wt % of the condensate in an unsaturated coreactant diluent like styrene. Styrene is commonly used as the comonomer because of its low cost and good compatibility with the resin. Carothers was the first to prepare UPR with well-defined polymeric structures.<sup>1</sup> Typical grades are orthophthalic, isophthalic, and bisphenol A resins.

The general purpose (GP) grade orthophthalic resin is a blend of styrene with the condensation product of 1,2 propylene glycol and a mixture of maleic anhydride and phthalic anhydride. When crosslinking is initiated, with the help of a catalyst and an accelerator, styrene forms polystyrene chains, which crosslink the

polyester chains at the sites of unsaturation.<sup>2</sup> The highly crosslinked three-dimensional molecular structure of the cured resin gives high stiffness, strength, glass-transition temperature, and moderate heat and solvent resistance. However, they suffer from a major drawback. They are brittle and have low impact resistance and poor resistance to crack propagation.<sup>3</sup> Although failure in GRP is often limited to the resin-reinforcement interface,<sup>4</sup> areas with relatively low amount of fibers are prone to damage when the product is in use or during demoulding. The damage usually starts as a micro-fracture of the matrix, which on propagation can result in disintegration of the system.

UPRs are blended with several materials to improve their impact strength and fracture properties. These additives should be miscible in the uncured resin, but phase separation during the curing is essential, as phase separated blends are tougher than homogeneous blends.<sup>5</sup> The miscibility and interfacial properties of the additive and the resin play important roles in the toughening process.<sup>6</sup> The modification of resin, using elastomer additives, leads to a randomly dispersed rubbery phase in the material, and creates high dissipation energy during impact failure. Both solid and liquid rubbers are dispersed in the resin for enhancement of toughness. The toughening effect of an elastomer additive depends on phase separation to provide the final morphology and to control the rubber particle size and volume fraction.<sup>7</sup> But the tough-

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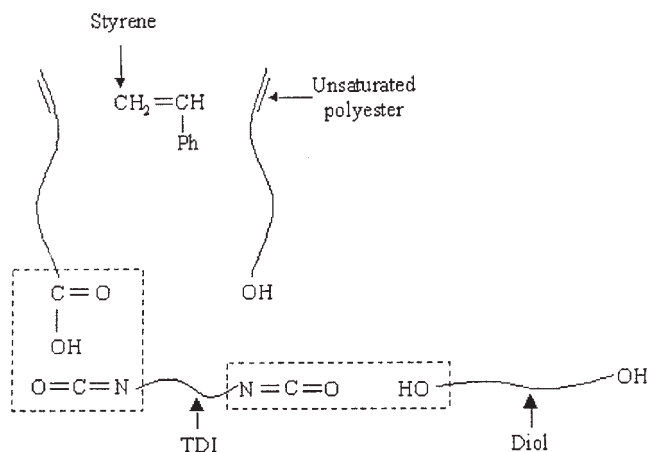
ening effect is often modest because of the poor solubility of the rubber component in the resin and the low chemical reactivity of the rubber towards polyester end groups. Modification by blending with thermoplastic additives<sup>8</sup> is another possibility. The solubilized or finely dispersed thermoplastics are precipitated into the interstitial spaces within the crosslinked network as styrene is depleted from the solution during crosslinking.

Block copolymers of UPR with polyurethanes, polyureas, polysiloxanes, polyimides, polyoxazolines, or polyglycols have also been reported.<sup>6</sup> Another approach is the condensation of hydroxyl or carboxyl-terminated liquid rubbers and the polyester reactants, which result in polyesters containing rubber segments in the main chain.<sup>9</sup> Modification of UPR with dicyclopentadiene,<sup>10</sup> bismaleimide,<sup>11</sup> and poly( $\epsilon$ -caprolactone)-per fluoro polyethers<sup>12</sup> is among other reported recent developments. Reactive blending offers another attractive possibility.

### Reactive blending

Acidic and alcoholic chain ends of the resins are chemically sensitive. Consequently, embrittlement of the fiber-reinforced unsaturated polyester composites occurs when exposed to moisture. Reactive blending with thermoset resins can lead to deactivating the end groups. The mechanical properties of resins and laminates can be improved by this technique. Semi interpenetrating polymer networks (IPNs) and hybrid polymer networks (HPNs) based on UPRs are of current interest. Blending of epoxy resin and polyesters resulting in IPNs<sup>13-15</sup> has been extensively studied. Modification by chemical bonding between elastomer and UPR using methacrylate end-capped carboxy-terminated nitrile rubber<sup>16</sup> or isocyanate end-capped polybutadiene<sup>17</sup> or epoxy-terminated nitrile rubber<sup>18</sup> is a promising development.

Alcoholic and carboxyl end groups of the resin can be blocked by isocyanates that form covalent urethane bonds. Hybrid polymer networks of polyurethane prepolymers and unsaturated polyester are a related development.<sup>19-22</sup> Segmented polyester polyurethanes have been studied by Cooper and coworkers.<sup>23,24</sup> Chou and Lee<sup>20</sup> studied the morphology-kinetics-rheology relationship of polyurethane (PU)-unsaturated polyester interpenetrating polymer networks (IPNs). They found that the PU rich phase formed the dispersed domains in the continuous UP rich phase. The interaction between the two reactive systems may give rise to a synergistic effect on the properties of IPN/HPN. The interactions have been attributed to an increase in crosslink density because of mutual interpenetration of network chains.<sup>25</sup> Other specific interactions like grafting<sup>26</sup> and opposite charged group interactions<sup>27</sup> between the two networks are possible reasons for property enhancement.



**Figure 1** Schematic representation of PU-UPR HPN formation.

In the present study, hybrid networks of polyester and polyurethane prepolymers are investigated. Urethane linkages are formed by reaction between terminal hydroxyl and carboxyl groups of UPR and isocyanate groups of a PU prepolymer. The schematic representation of PU-UPR HPN is shown in Figure 1. The polyols selected were HTNR, HTPB, PEG, and castor oil. HTPB has superior water resistant properties to that of the conventional polyols. HTNR is a hydroxyl-terminated elastomer that can be easily prepared by photo depolymerization. PEG chosen had a molecular weight of 6000. Castor oil is a naturally occurring polyol, which contains the glyceride ester of ricinoleic acid. Among various diisocyanates, TDI has been chosen for this investigation.

## EXPERIMENTAL

### Materials

GP grade UPR (Bakelite Hylam resin HSR 8113M), methyl ethyl ketone peroxide (catalyst), and cobalt naphthenate (accelerator) were supplied by M/s Sharon Engineering Enterprises, Cochin, India. Toluene diisocyanate and polyethylene glycol ( $M_n = 6000$ ) was supplied by E. Merck India Ltd, Bombay, India. HTPB ( $M_n = 2620$ ) was obtained from Vikram Sarabhai Space Centre, Thiruvananthapuram, India. High purity castor oil was procured locally.

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 photo-depolymerization in the presence of  $\text{H}_2\text{O}_2$ .<sup>28</sup> Natural rubber was first masticated for 30 min. A 5 wt % solution of this NR in toluene was mixed with a 30 wt %  $\text{H}_2\text{O}_2$  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

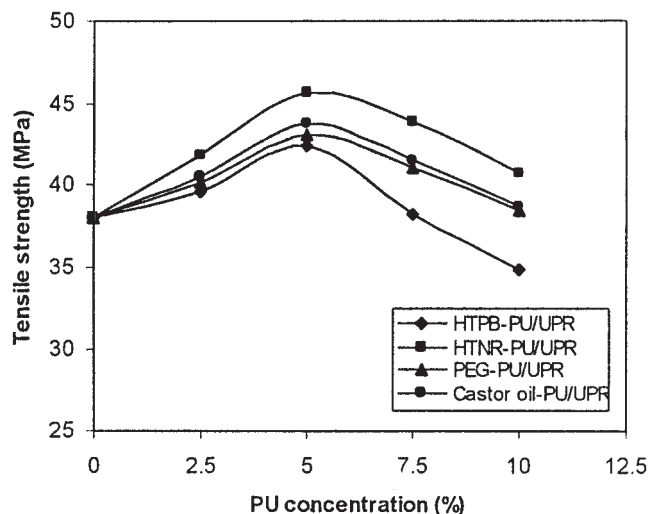


Figure 2 Tensile strength of modified resin versus PU concentration.

depolymerised and hydroxy-terminated NR was recovered by precipitation with methanol and purified by repeated precipitation. Molecular weight was determined by end group analysis and hydroxyl value was estimated by well-known procedures.

**Preparation of polyurethane prepolymers**

Polyurethane prepolymers were prepared via the reaction of TDI and different polyols. The polyols were initially degassed under vacuum for 2 h at 50°C to remove moisture. PU prepolymers were prepared by mixing TDI and each of the polyols in the molar ratio 2.4:1 at room temperature and keeping at 75°C for 4 h. The —OH groups in the polyol as well as —OH and —COOH end groups in the UPR were taken into

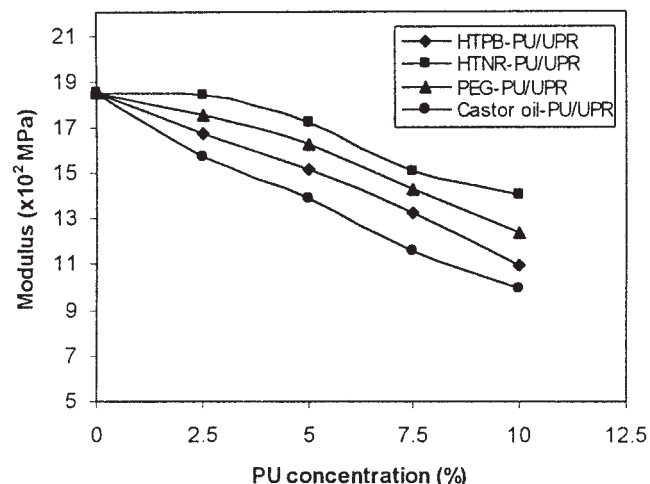


Figure 3 Tensile modulus of modified resin versus PU concentration.

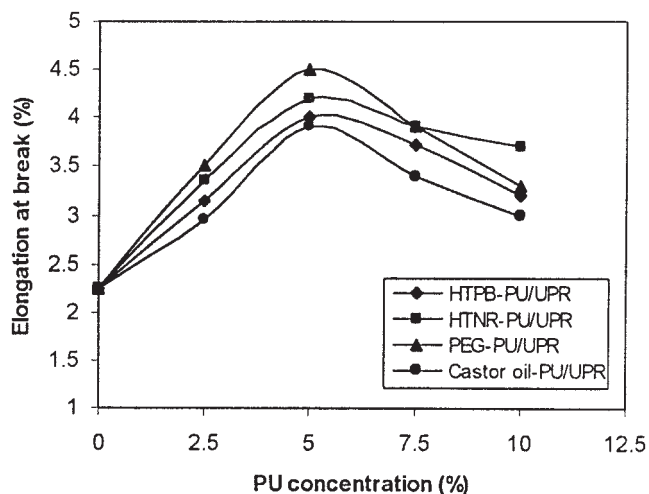


Figure 4 Elongation at break of modified resin versus PU concentration.

account for the calculation of NCO/OH (and COOH) stoichiometry.

**Modification of UPR by polyurethane prepolymers**

Unmodified resin was first cured at room temperature by a catalyst (methyl ethyl ketone peroxide dissolved in dimethyl phthalate containing 60% peroxide) and accelerator (6% solution of cobalt naphthenate in styrene) combination. These were used in concentrations of 1 and 0.5% of the weight of the resin, respectively. The resin was then poured into appropriate molds coated with a releasing agent. Curing was done at room temperature for 24 h, followed by post curing at 80°C for 3 h.

Varying amounts (0–10 wt %) of these PU prepolymers were added to the resin. The mixture was stirred

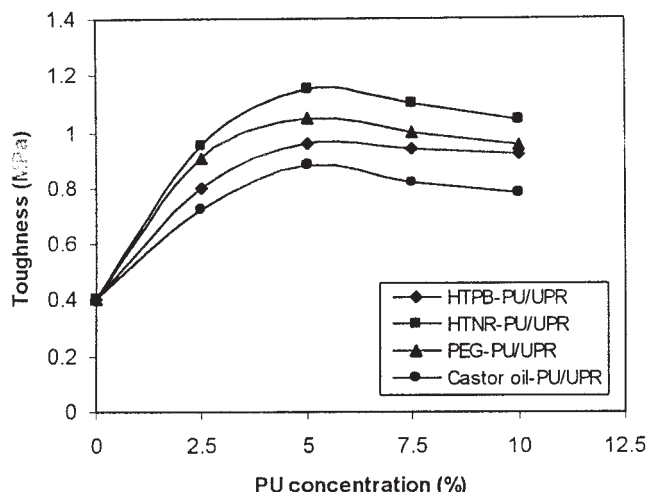
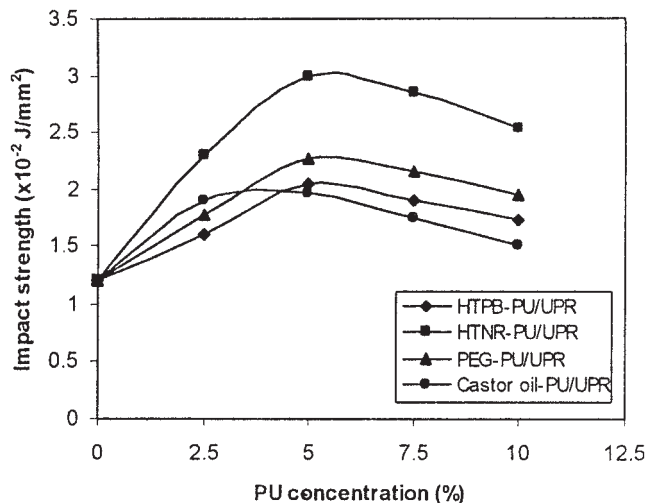
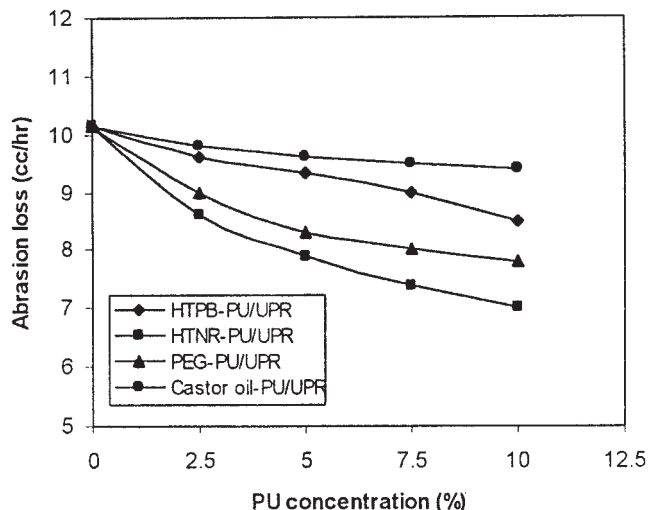


Figure 5 Toughness of modified resin versus PU concentration.



**Figure 6** Impact strength of modified resin versus PU concentration.



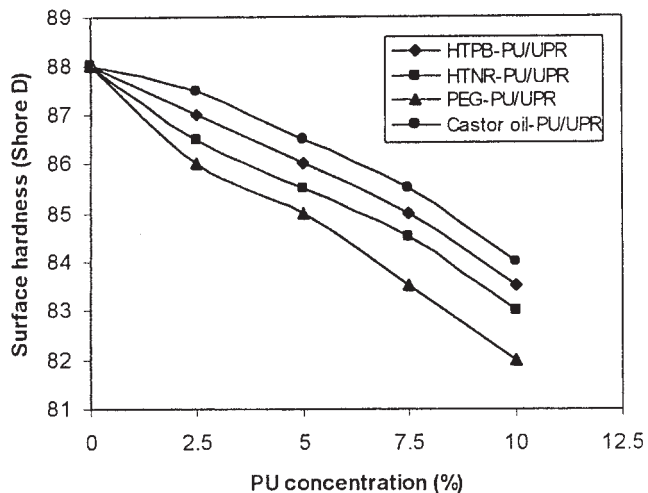
**Figure 8** Abrasion loss of modified resin versus PU concentration.

well for 1 h to get a homogeneous liquid. Curing of the blend was done by the same procedure employed for UPR.

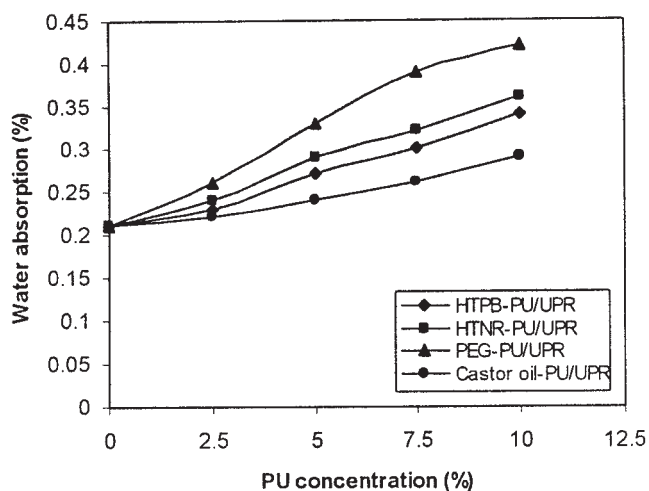
The samples after post curing were tested for tensile strength, modulus, elongation at break, toughness, impact strength, surface hardness, abrasion resistance, and water absorption taking six trials in each case. The tensile properties were tested on a Shimadzu Autograph Universal Testing Machine (ASTM D 638–89), and Izod impact strength was measured on a Zwick impact tester as per ASTM D 256 specifications. A Shore D Durometer was employed for measuring surface hardness (ASTM D 2240–86). Abrasion resistance was tested on a Zwick DL 100 machine as per DIN 55,516. Water absorption was tested as per ASTM D 570. The scanning electron micrographs of fracture

surfaces of unmodified and modified UPR were taken in a Cambridge Instruments S 360 Stereoscanner- Version V02–01. A TA Instruments' TGA Q 50 analyser was used to investigate thermal degradation. TA Instruments DSC Q 100 equipped with an RCS cooling system was used to study thermal transitions in the samples at a rate of heating of 10°C/min. The damping qualities were measured using fixed frequency dynamic analysis techniques. A dynamic analyser model DMA-983 from DuPont, USA, was made of use for this purpose. DMA test was conducted at a constant frequency of 1 Hz. A temperature ramp was run from room temperature to 200°C at 1°C/min to get an overview of the thermo mechanical behavior of modified and unmodified samples.

Soxhlet extraction of cured resin samples using benzene was done to determine the amount of soluble



**Figure 7** Hardness of modified resin versus PU concentration.



**Figure 9** Water absorption of modified resin versus PU concentration.

TABLE I  
Summary of Properties of UPR Modified with 0–10% PU-Prepolymers

Property	Maximum improvement achieved (%)/PU prepolymer concentration (%)				
	UPR	PU-HTPB/UPR	PU-HTNR/UPR	PU-PEG/UPR	PU-castor oil/UPR
Tensile strength (MPa)	38	11.45/5	19.95/5	13.42/5	15.13/5
Modulus (MPa)	1850	-40.81/10	-23.89/10	-46.49/10	-33.19/10
Elongation at break (%)	2.25	77.78/5	86.67/5	100/5	73.33/5
Toughness (MPa)	0.4	140/5	187.5/5	162.5/5	120/5
Impact strength ( $10^{-2}$ J/mm <sup>2</sup> )	1.21	69.42/5	147.93/5	86.78/5	61.98/5
Hardness (shore D)	88	-5.11/10	-5.68/10	-6.81/10	-4.55/10
Abrasion loss (cc/h)	10.15	-16.26/10	-31.03/10	-23.15/10	-7.39/10
Water absorption (%)	0.21	61.9/10	71.43/10	100/10	38.1/10

matter. Samples for spectral studies were prepared by casting films and subsequently extracting them with benzene to remove any unreacted material. The crosslink density was indirectly estimated from the equilibrium swelling data. The volume fraction of polyester ( $V_p$ ) in the swollen samples was calculated.<sup>29</sup>  $V_p$  is linearly related to the crosslink density of the polymer samples.

## RESULTS AND DISCUSSION

### Properties

Two reactions are possible when the PU prepolymer is blended with UPR and cured. The —NCO end groups of the prepolymer react with —OH and —COOH functionalities present at the chain ends of the polyester. This gives rise to new urethane groups and causes chain extension. Secondly, grafting of polystyrene short chains on to sites of unsaturation can take place. The latter reaction can lead to crosslinking between a) polyester chains b) polyester and PU chains, and c) PU prepolymer chains. Crosslinking between polyester chains, however, will be predominant.

### Tensile properties

Referring to Figure 2, tensile strength values obtained by adding HTNR-PU prepolymer are higher than that obtained by adding other prepolymers. Tensile strength values reach a maximum on adding progressively larger amounts of prepolymer, but addition of rubber beyond 5% results in a reduction of tensile strength. It is likely that beyond 5%, there is reduced

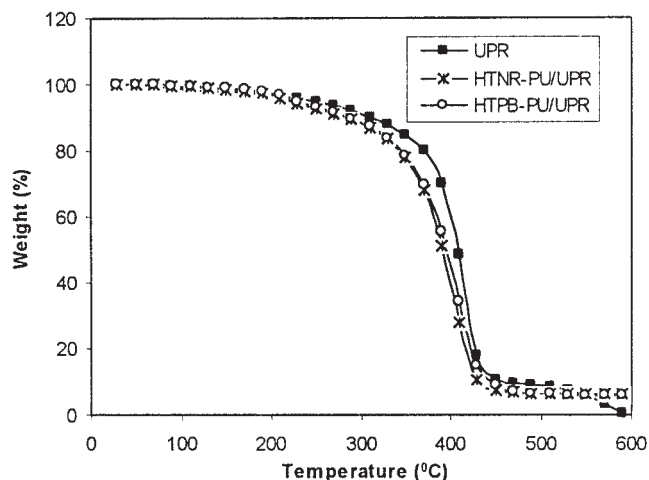
compatibility between the phases. Figure 3 shows the effect of elastomers on tensile modulus. The modulus values fall steadily for all PU prepolymers. This is due to the flexibility of the elastomer chains. The effect of PU addition on the elongation at break is shown in Figure 4. The addition of PEG produced the greatest increase in elongation at break, at 5% PU concentration. At higher percentages, intercomponent grafting reduces the flexibility of the polyester chains, resulting in lower elongation at break.

### Toughness properties

The variation in toughness of the cured resin as the PU content increases is shown in Figure 5. At 5% HTNR concentration, the toughness of the blend is at a maximum (about 288% of the toughness of UPR). Higher molecular weight polyols produce polymer chains with fewer urethane groups. HTNR has greater molecular weight compared with HTPB. The pendent cis methyl groups of HTNR also enhance the flexibility. These soft segments are more flexible than those produced from low molecular weight polyols. Figure 6 shows the variation of impact strength with polyurethane content. The effect is at a maximum for HTNR at 5% rubber concentration. The impact strength reaches a maximum and then drops for higher levels of rubber. The increase in impact strength of HTNR-PU prepolymer results from improved flexibility of NR chains. The rubber phase absorbs the energy of impact and crack propagation is prevented.

TABLE II  
Soxhlet Extraction and Swelling Data—PU Prepolymer (5%)

Property	UPR	PU-HTPB/UPR	PU-HTNR/UPR	PU-PEG/UPR	PU-castor oil/UPR
Soluble matter (%)	9.02	5.2	4.7	5.80	6.70
$V_p$	0.92	0.952	0.96	0.95	0.942



**Figure 10** TGA curves of UPR, 5% HTNR-PU/UPR, and 5% HTPB-PU/UPR.

#### Hardness and abrasion loss

Figure 7 indicates a general lowering of surface hardness on addition of all types of PU elastomers. This is due to the lower surface hardness values of the PU elastomers. This effect is maximum for PEG and minimum for castor oil. There is a decrease in abrasion loss on addition of all polyurethane prepolymers (Fig. 8), the best results being given by HTNR. The stereo specific cis alkyl chain of HTNR provides an elastically more effective network and the surface cannot be easily abraded.

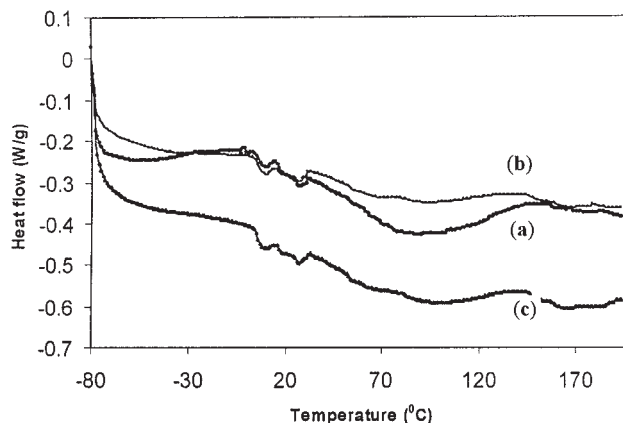
#### Water absorption

Water absorption of polyurethane-modified resins increases with PU concentration (Fig. 9). The hydrogen bonding between water and polar urethane linkages enhances the water absorption of cured resin.

Table I summarizes the overall effect of adding varying amounts of PU elastomers. The maximum improvement achieved in each property and the corresponding PU concentrations are tabulated. It is evident that the performance of HTNR is superior to other PU prepolymers considered.

#### Soxhlet extraction and swelling studies

The Soxhlet extraction data (Table II) show that very little soluble matter could be extracted from PU-mod-



**Figure 11** DSC thermograms of (a) UPR, (b) 5% HTPB-PU/UPR, and (c) 10% HTPB-PU/UPR.

ified UPR compared with unmodified UPR. Graft reactions between PU chain and polyester chains as well as chain extension reactions between the PU prepolymers and UPR end groups are responsible for this.

#### Thermal studies

The TGA curves of UPR and its blends with PU prepolymers are shown in Figure 10. Copolymers of PU-prepolymers and UPR have marginally better thermal stability compared with UPR as shown in Table III.

The DSC curves of UPR and its blends with PU prepolymers are shown in Figure 11. UPR has a  $T_g$  of 93°C. Reactive blending with 5% HTPB PU prepolymers results in a homogeneous HPN with a single  $T_g$  (97.62°C). Addition of 10% PU prepolymers exhibits heterogeneity with two  $T_g$ s at 54 and 101°C. This shows that there is reduced compatibility at higher percentages of the prepolymer.

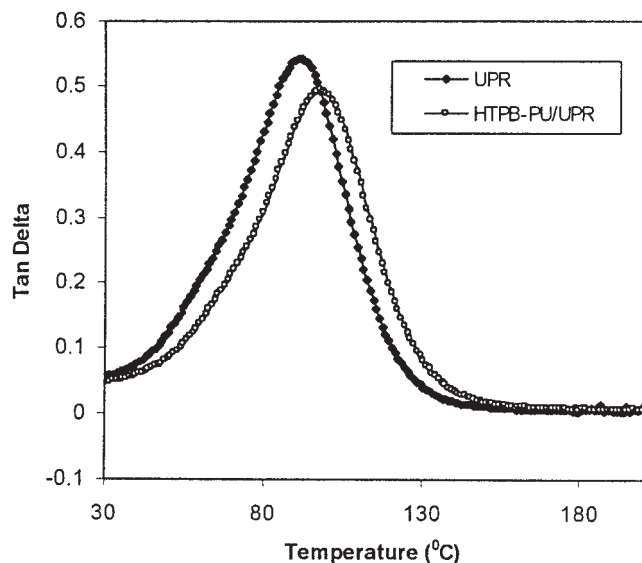
$T_g$  values obtained from DMA-Tan  $\delta$  curves (Fig. 12) for UPR (92°C) and UPR/5% PU-prepolymers (98°C) are in good agreement with  $T_g$  values obtained from DSC curves. The tan  $\delta$  values at 92°C for these polymers are 0.5421 and 0.4569, respectively. The marginal lowering in  $T_g$  may be due to the enhanced flexibility.

#### Spectral studies

Comparing the FTIR spectra of UPR and UPR modified by 5% PU prepolymer of HTPB (Fig. 13),

**TABLE III**  
Thermal Properties of TGA

Resin	Onset temperature (°C)	Temperature of maximum rate (°C)	Temperature of half loss (°C)	Residue (%)
UPR	296.88	412.53	408.98	0.3327
PU-HTNR/UPR	328.28	404.18	391.24	6.17
PU-HTPB/UPR	316.45	410.77	395.90	5.82

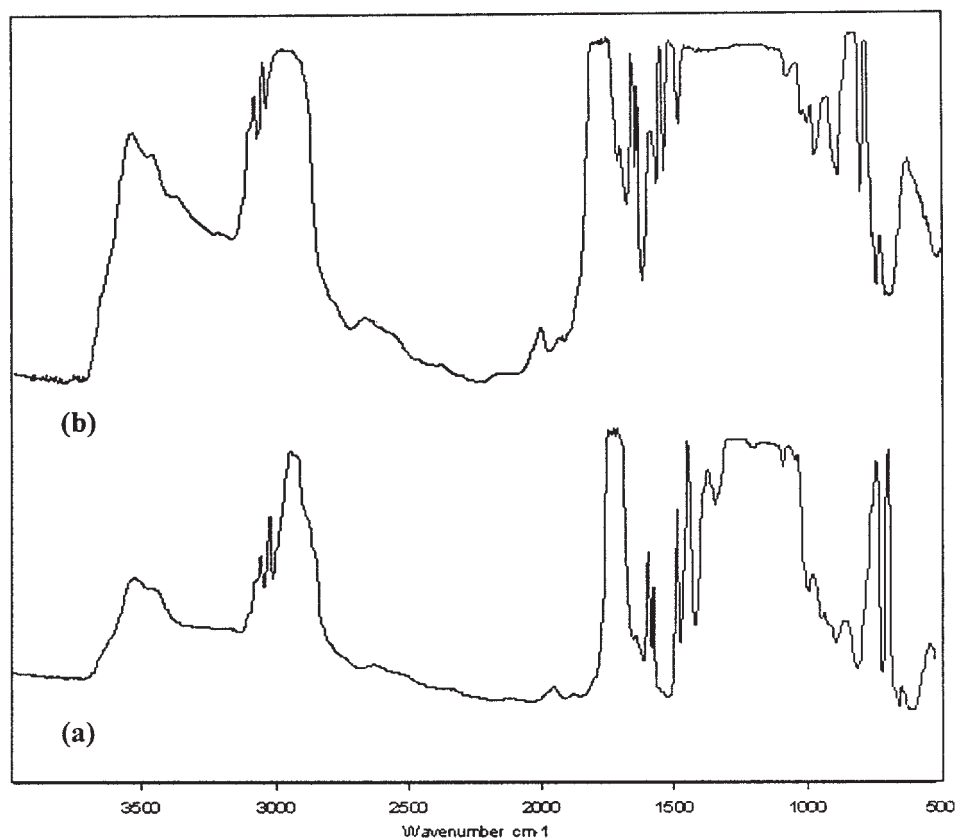


**Figure 12** DMA-Tan  $\delta$  curves: (a) UPR and (b) 5% HTPB-PU/UPR.

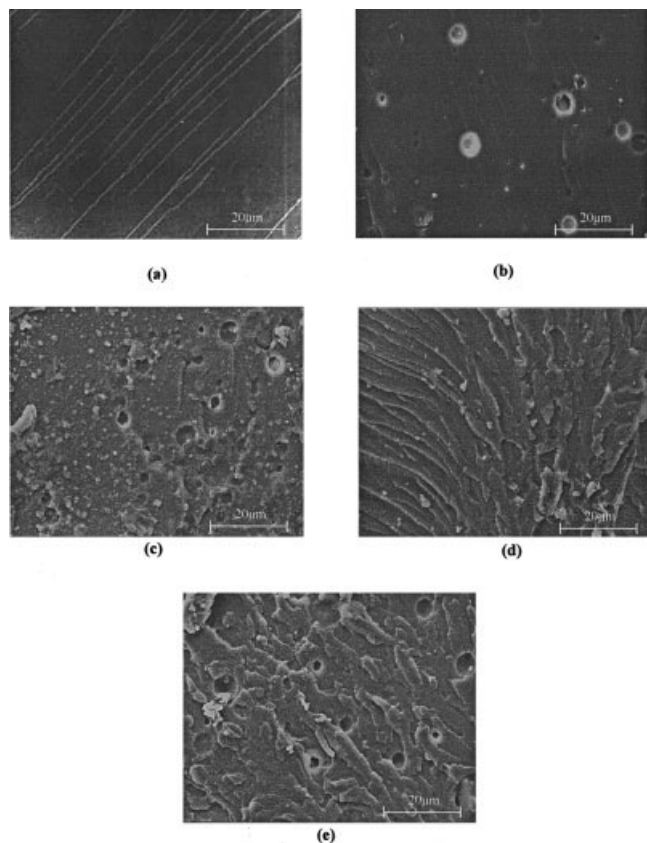
additional peaks in (b) at  $1700\text{ cm}^{-1}$  and  $1528\text{ cm}^{-1}$  are due to N—H stretching and N—H bending vibrations, respectively, of the urethane linkage.

### Morphological studies

Scanning electron micrographs of unmodified and modified UPR fractured at low deformation rate are shown in Figure 14. Referring to the micrograph (a), the fracture path for unmodified resin (UPR) is narrow and continuous, indicating rapid crack propagation along the axis of crack growth. The fracture surface is smooth with low ridges and shallow grooves. But all the fracture surfaces of the blends are characterized by a morphology in which the additive is segregated into spherical-shaped domains. A bimodal distribution of particle size is seen in most cases. Polyurethane with reactive —NCO groups result in grafting, which gives high adhesion. Cavities remain after the rubber particles, have been ejected from the fracture surface. These small PU particles are a result of nucleation and growth type phase transfer. PU-HTNR-modified resin fracture pattern is shown in micrograph (b). The cavitated rubber particles are filled with an internal void in some cases. Phase-separated morphology and good dispersion of rubber particles are indicated. This leads to high-energy absorption. The micrograph of PU-HTPB-modified resin (c) shows enhanced stress whitening. The holes in the stress-whitened regions presumably result from dilation and rupture of elastomer



**Figure 13** FTIR spectra of UPR and 5% HTPB-PU/UPR.



**Figure 14** Scanning electron micrographs of fracture surfaces: (a) UPR, (b) HTNR-PU/UPR, (c) HTPB-PU/UPR, (d) PEG-PU/UPR, and (e) Castor oil-PU/UPR.

particles. Most of the large holes, however, contain round inclusions, which are hard. The initiation and growth of voids in the rubbery particles give rise to stress whitening often observed before crack tip and on the fractured surface. These point to high toughness and load-bearing characteristics. Referring to PU-PEG-modified resin (d), the fracture surface shows furrows and cavitation. The circular depressions represent the sites of PU domains. Micrograph of PU-castor oil-modified resin (e) shows multiple cracks, stress distribution, localization of stress, and cavitation. Increased surface roughness and drawn ridges of polyesters are seen. The cavitated rubber particles are filled with an internal void in some cases.

## CONCLUSIONS

Tensile strength, toughness, impact resistance, and elongation-at-break of UPR have increased on incorporation of PU prepolymers. Unlike rubbers, PU prepolymers are highly miscible with UPR. Polyurethane prepolymers prepared by reacting HTNR and TDI are found to bequeath superior properties to UPR compared with other PU prepolymers considered. In the

case of HTNR-PU prepolymers, the tensile strength of the cured UPR has been found to increase by as much as 20%, simultaneously improving the toughness by about 188%. A single  $T_g$  is observed for PU prepolymer-modified resins, which indicate compatibility and homogeneity. DMA investigations show that the modified samples have lower  $\tan \delta$  values, indicating greater flexibility and toughness. Hence PU prepolymers at low percentages are useful modifiers for UPR.

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