

# Synthesis and Properties of Unsaturated Polyester Diol–Polyurethane Hybrid Polymer Network

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## SYNOPSIS

This article deals with the synthesis and properties of poly[(propylene glycol maleate)-*co*-(propylene glycol phthalate)]diol (PGMPD)/polyester–urethane or polyether–urethane hybrid polymer networks (HPNs). The polyurethane type and the molar ratio of NCO/OH have an effect on their properties. The structure–property relationship is discussed as well. © 1994 John Wiley & Sons, Inc.

## INTRODUCTION

A hybrid polymer network (HPN) is composed of a bone polymer containing two types of reactive groups that can take part in cross-linking reactions via different mechanisms. Thermosetting resins will be modified effectively in this way, because the compatibility of components is improved through the composite cross-link. A powder coating (Dai Nippon Ink Co.) is commercially available. The coating of polyacrylate–polyester–polyurethane is composed of a polyester containing glycidyl and hydroxyl groups, where glycidyl groups can react with hydroxyl groups of a polyacrylate, whereas hydroxyl groups are capable of reacting with a blocked polyurethane prepolymer. The coating developed is characterized by its excellent mechanical properties and weathering resistance.<sup>1</sup>

For the purpose of improving the mechanical properties of general unsaturated resin, the work on the structure–property relationship of an unsaturated polyester/polyurethane (UP/PU) HPN was carried out.

This article is concerned with HPNs composed of an unsaturated polyester/polyester–urethane or polyether–urethane prepolymer. The study focused on the influences of the HPN composition and

structure on the properties. The aim was to investigate a UP/PU HPN that is compromise of several factors.

## EXPERIMENTAL

### Materials

Propylene glycol (PG), maleic anhydride (MA), phthalic anhydride (PA), benzyl peroxide (BPO), and *N,N*-dimethylaniline (DMA) were commercially available products, whereas styrene and stannous octoate were of a chemical pure grade.

Poly(propylene oxide)glycol (PPOG-10) with an  $\bar{M}_n = 1000$  and hydroxyl value of 112 was obtained from Jin Lin Petroleum Chemical Co. and poly(diethylene glycol adipate)diol (PDEGAD) with an  $\bar{M}_n = 1188$  and hydroxyl value of 94.3 was from Tianjin Elastomer Product Co. Toluene diisocyanate (TDI) was used as received.

### Hydroxyl-terminated Unsaturated Polyester (UP)

The titled polyester based on PG, MA, and PA at a molar ratio of 2.4, 1, and 1 was synthesized at 190°C under a nitrogen atmosphere. The poly[(propylene glycol maleate)-*co*-(propylene glycol phthalate)]diol (PGMPD) UP obtained had an  $\bar{M}_n = 940$ , hydroxyl value of 119.4, and acid number of 9.0. The UP was diluted with styrene to form component A.

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### Preparation of Unsaturated Polyester/ Polyurethane (UP/PU) HPNs

The HPNs were prepared by coreactions of hydroxyl-terminated UP-styrene (component A) with a PU prepolymer with a terminated isocyanate group (component B). The prepolymer was prepared via a polyaddition reaction of TDI and dried PDEGAD at molar ratio of 2.4 : 1 in the presence of stannous octoate at 75°C for 4 h. The chain extension of the prepolymer with UP diol was performed in 40% styrene solution for 1 h at 60°C. The UP/PU HPN obtained was casted in a glass model for testing specimens.

### Characteristics of the UP/PU HPN

The infrared (IR) spectra were recorded on a Nicolet 170SX FTIR spectrophotometer using the KBr coating technique. Glass transition temperatures ( $T_g$ ) of the polymer were measured by a Perkin-Elmer DSC-2C differential scanning calorimeter at a heating rate of 20°C/min. Thermogravimetric analyses (TGA) were carried out in air using a Mettler TA 3000 system (Switzerland) at a heating rate of 20°C/min.

Hardness was estimated with a Shore A Tester. Flexural strength was determined on a Dynstat Tester (VEB), whereas tensile strength measurements were carried out with a LJ-500A tensile testing machine at the speed of 70 mm/min.

## RESULTS AND DISCUSSION

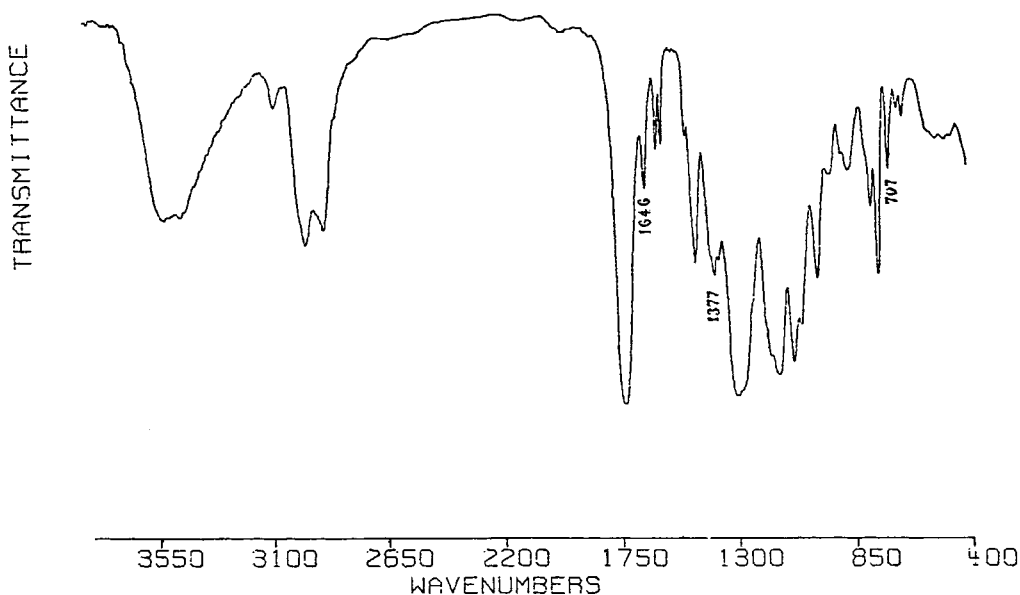
### Hydroxyl-terminated UP

The IR spectrum of the hydroxyl-terminated UP resin with styrene is characterized by 1650, 1400, 865, and 700  $\text{cm}^{-1}$  for the *cis*-vinyl group and by 695  $\text{cm}^{-1}$  for the *trans*-vinyl group<sup>2</sup> (Fig. 1).

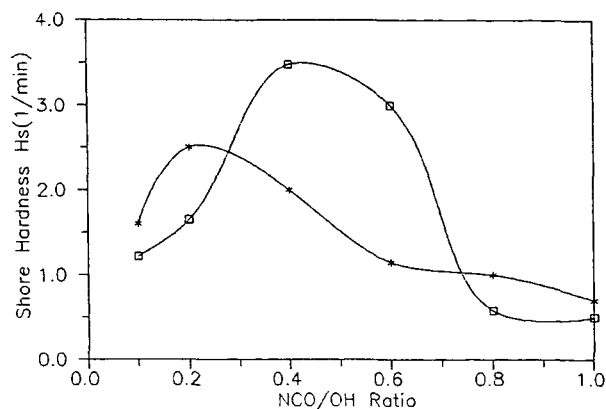
### UP/PU HPN Formation

The HPN is formed through cross-link reactions, i.e., copolymerization of UP with styrene and polyaddition between terminal hydroxyl groups of UP and isocyanate groups of a PU prepolymer.

Because the enhancement in hardness relates to the conversion of the reaction, it is reasonable to use the extrapolated value of the initial hardness enhancement rate in the Shore hardness,  $H_s \text{ min}^{-1}$ , as a relative parameter for studying the correlation of co-instantaneous cross-linking reactions. Data in Figure 2 show that polyester-urethane with poly(diethylene glycol adipate) ( $M_n = 1188$ ) offers a greater contribution to enhancement in Shore A hardness than does polyether-urethane with poly(propylene oxide glycol) ( $M_n = 1000$ ). Moreover, both have maximums at NCO/OH = 0.2 and 0.4, respectively. The latter phenomenon coincides with the monitored result of isocyanate content by FTIR spectroscopy. Polyester-urethane prepolymer and



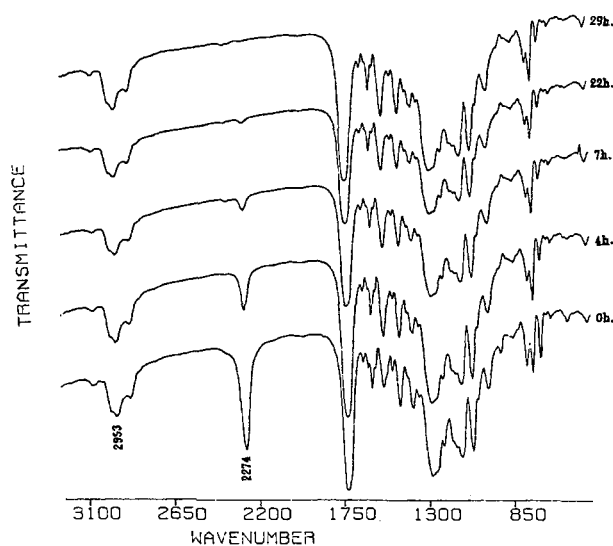
**Figure 1** IR spectrum of poly[(propylene glycol meleate)-*co*-(propylene phthalate)] with 24% styrene.



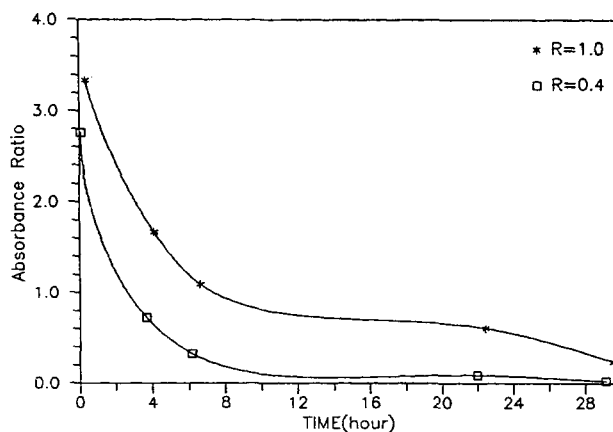
**Figure 2** Hardness enhancing rate of (□) UP/polyester-urethane and (\*) UP/polyether-urethane.

hydroxyl-terminated UP were reacted in the presence of stannous octoate (0.5%) at 60°C, and samples (thin film between KBr plates) of the reaction mixture were analyzed by FTIR spectroscopy at different time intervals (Fig. 3).

The ratio of the height of the peak at 2952  $\text{cm}^{-1}$  (methylene  $-\text{CH}_2-$ ) to that of the peak at 2272  $\text{cm}^{-1}$  ( $-\text{NCO}$ ) was used to monitor the end-capping reaction. Figure 4 shows the ratio reaching a value of 0.2 after 8 h of reaction at 30°C for the HPN with  $R = 0.4$ , which is faster than that for the HPN with  $R = 1.0$ . This result reflects that the diffusive barrier of the viscous PU prepolymer is larger than that of the UP diluted with styrene, because the HPN at



**Figure 3** FTIR spectra of UP/polyester-urethane HPN (NCO/OH = 0.4).



**Figure 4** Absorbance ratio of A-NCO(2272)/A-CH<sub>2</sub>(2952) of IR spectra against time for UP/polyester-urethane HPN.

$R(\text{NCO}/\text{OH}) = 0.4$  content has less PU prepolymer in comparison to the HPN with  $R = 1.0$ .

### Thermal Analysis

The thermal transition of UP and its hybrid polymer network with polyether-urethane ( $R = 0.4$ ) and polyester-urethane ( $R = 0.2, 0.4$ , and  $0.6$ ) were determined by DSC analysis. Table I summarizes the transitions. The cross-linked UP network had a glass transition at 60.59°C. Incorporating a small amount of the PU prepolymer (corresponding  $R = 0.2$ ) into the hydroxyl-terminated UP network will result in a homogeneous HPN with a single  $T_g$  (89.29°C). While increasing the PU prepolymer content to  $R(\text{NCO}/\text{OH}) = 0.4$ , the HPN obtained exhibits heterogeneity with two  $T_g$ 's at 55.75 and 81.43°C for

**Table I** Thermal Transition of Unsaturated Polyester (UP)-based Hybrid Polymer Networks (HPNs)

Materials	Glass Transition Temperature $T_g$ (°C)	
UP	60.57	
UP/polyether-urethane HPN with $R = 0.4$	68.89	106.8
UP/polyester-urethane HPN with $R = 0.2$	89.29	
UP/polyester-urethane HPN with $R = 0.4$	55.75	81.43
UP/polyester-urethane HPN with $R = 0.6$	38.75	53.43

**Table II Thermogravimative Data for Unsaturated Polyester (UP)/Polyurethane (PU) Hybrid Polymer Network (HPN)**

Materials	Weight Loss		
	Onset Temp (°C)	Temp of Maximum Rate (°C)	Temp of Half-loss (°C)
UP	290	380	374
UP/polyether-urethane			
<i>R</i> = 0.4	250	365	359
<i>R</i> = 0.8	250	367	389
UP/polyester-urethane			
<i>R</i> = 0.4	250	380	374
<i>R</i> = 0.8	250	380	385

soft and hard moieties, respectively. Further enhancing *R* to 0.6 leads to decreases in the  $T_g$ 's to 38.75 and 53.43°C, respectively. All the data reveal that HPNs composed of UP and polyester-PU at *R* = 0.4 and 0.6 are characterized by their microphase-separation structure.

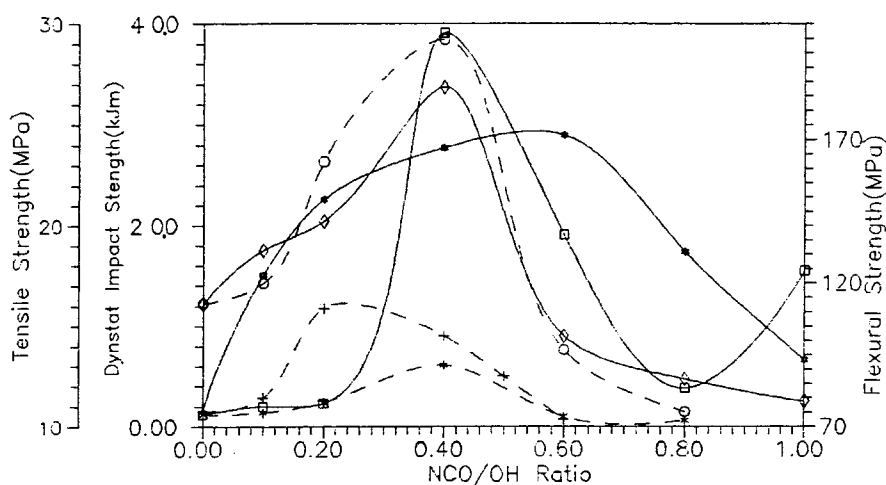
Moreover, the data in Table I indicate that the degree of microphase separation of the HPN at *R* = 0.4 for polyester-urethane is less than that for polyether-urethane with  $T_g$ 's at 68.89 and 106.8°C, respectively. This may be due to their difference in compatibility with UP, because there is greater structural similarity for polyester-urethane in comparison to that for polyether-urethane.

## Mechanical Properties

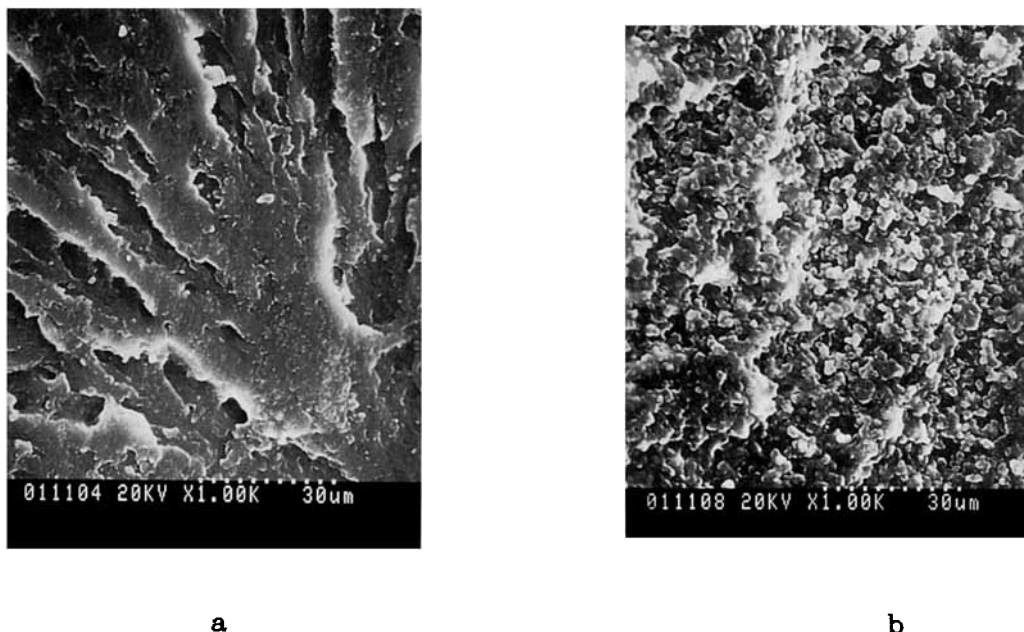
Figure 5 shows the mechanical properties of the HPNs. The maxima in the NCO/OH dependence of mechanical properties reveal the hybrid effect of the component polymers, whereas HPNs of UP/polyester-urethane with *R* = 0.4 exhibits the compromising properties that may be attributed to the optimum phase separation. Moreover, the better compatibility of polyester-urethane and UP results in their HPNs having higher tensile and impact strengths than those of polyether-urethane. This is reflected by the difference in the fractured surface of the impact specimens. From the microphotographs (cf. Fig. 6), one can observe that there is more deformation in the fractured surface for the UP/polyester-urethane HPN specimen than in that of the UP/polyether-urethane HPN sample.

## CONCLUSIONS

A series of unsaturated polyester (UP)/polyester-urethane or polyether-urethane hybrid polymer networks were synthesized. There were hybrid effects in the networks that resulted in optimization of mechanical properties. The UP/polyester-urethane at NCO/OH = 0.4 showed suitable phase separation. This was reflected by the maxima in the mechanical properties and by less difference in the  $T_g$  observed for the UP and that for the diethylene glycol adipate soft segment in the corresponding PU.



**Figure 5** Mechanical properties of UP/polyester-urethane and UP/polyether-urethane. Polyester-urethane: (□) impact strength; (☆) tensile strength; (◇) flexure strength. Polyether-urethane: (\*) impact strength; (+) tensile strength; (○) flexure strength.



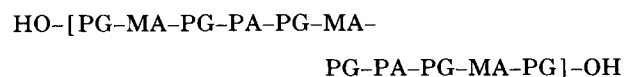
**Figure 6** Microphotographs of fractured-surfaces for (a) UP/polyester-urethane and (b) UP/polyether-urethane HPNs with  $R = 0.4$  specimens for impact.

Finally, the ratio of NCO/OH had influence on the formation of the HPN.

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#### APPENDIX: EXPLANATION OF $\bar{M}_n$ OF POLY[(PROPYLENE GLYCOL MALEATE)-*co*-(PROPYLENE PHTHALATE)]DIOL

Poly[(propylene glycol maleate)-*co*-(propylene glycol phthalate)]diol (PGMPD) was synthesized via polycondensation of propylene glycol (PG) ( $M_w = 76.09$ ), maleic anhydride (MA) ( $M_w = 98$ ), and phthalic anhydride (PA) ( $M_w = 148$ ) at a molar ratio of 2.4 : 1 : 1. The  $\bar{M}_n$  of the unsaturated polyester (UP) obtained was 956, estimated by terminal group analysis. The hydroxyl-terminated UP may be an oligomer, assuming that



Thus,

6	PG	456.64
3	MA	294.00
2	PA	296.00
-5	H <sub>2</sub> O	98
$\epsilon$	=	956.54 ( $\bar{M}_n$ )

Therefore, the calculated value of  $\bar{M}_n$  coincides with the experimental one (940).

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