

Interpenetrating Polymer Networks of Polyurethane and Vinyl Ester Resin for Reactive Injection Molding Process

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SYNOPSIS

Three kinds of polyurethane (PU) and vinyl ester resin interpenetrating polymer network (IPN) have been synthesized to study their morphologies and mechanical properties for the potential application in the reinforced reactive injection molding process. For the PU prepared from uretonimine modified pure MDI, the macrophase separation of the IPNs between the rubber and plastic phases was found by DSC measurement and scanning electron microscopy (SEM) observation, whereas the interpenetration between the two networks was also observed on SEM photos at least around the area of interface. However, for the IPN systems including PU prepared from TDI or graft polyol, which was synthesized by using macromer technique, the compatibility between the two phases is excellent. The mechanical properties of these IPNs were measured and could be correlated well enough with their morphologies. The IPN prepared with graft polyol exhibited the best mechanical properties over all IPN specimens studied in this work. © 1992 John Wiley & Sons, Inc.

INTRODUCTION

Interpenetrating polymer network (IPN) as one kind of polymer alloys has been studied extensively. Pernice et al. have first reported that the polyurethane (PU)/epoxy resin IPN and PU-unsaturated polyester resin IPN could be used for reactive injection molding (RIM) systems to form some new reinforced RIM (RRIM) PU materials.¹ In this paper a number of PU-vinyl ester resin simultaneous IPNs prepared from various PUs, which were formed by reacting polyether polyol or graft polyol with isocyanates, is reported. The graft polyol was synthesized by macromer technique. The structures, morphologies, and mechanical properties of these IPNs were examined for developing them as RRIM PU materials.

EXPERIMENTAL

Trifunctional poly(oxypropylene) polyol capped with ethylene oxide (EO capped polyol, hydroxyl value: 30.8 mg KOH/g) and trifunctional poly(oxypropylene) polyol (N-330) were supplied by Zhongshan Chemical Works and Wusi Synthetic Resin Works, respectively. Uretonimine modified pure 4,4'-diphenylmethane diisocyanate (L-MDI, NCO wt % 28.5) and toluene diisocyanate (TDI, 80/20) were provided by Shanxi Research Institute of Chemical Technology and Olin Co., respectively. The vinyl ester resin was prepared from epoxy resin (bisphenol type E-51) with methylacrylic acid in our laboratory. Another chemicals used in this study were standard laboratory chemicals obtained from various suppliers.

The polyol and butandiol (1,4-BDO) were dried at 335 K, 266.6 Pa for 24 h, then treated with 4 Å molecular sieve for one week before use. The vinyl ester resin was dried with anhydrous calcium chlo-

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ride before use, then treated with 4 Å molecular sieve. The benzoyl peroxide (BPO) was recrystallized for removing the water. The styrene was washed, dried, and distilled under vacuum.

A polyol macromer was synthesized from N-330 polyol with maleic anhydride. After finishing this reaction, ethylene glycol was added to form the macromer having hydroxyl groups at all ends of macromolecular chains. A graft polyol prepared from polyol macromer and styrene was synthesized by free radical copolymerization with a redox initiator (BPO and dimethyl aniline). All the synthesis, separation, and characterization for the macromer and graft polyol have been described elsewhere.²

To prepared IPNs, EO capped polyol or graft polyol, L-MDI or TDI, 1,4-BDO, dibutyltindilaurate, vinyl ester resin, and BPO were mixed in a reactor at high-speed stirring (8000 rpm) for 30 s. Plate specimens were formed by casting the mixture in a glass mold and curing them at 353 K for 1 h and 393 K for another 3 h. All these formed IPNs were then treated under vacuum (266.6 Pa) at 333 K for 24 h.

Differential scanning calorimetry (DSC) was measured with a DuPont Instrument 1090 Thermal Analyzer at a heating rate of 10 K/min. For investigating with a scanning electron microscopy (Stereoscan 250 MK3, Cambridge), the surface of the sample was coated by gold vapor before examining. The specimens for tensile and elastic modulus test were made of those IPN plates in accordance with GB1040-70 and kept at 298 K for 24 h before testing. The tensile strength and elastic modulus measurements were conducted on a Shimadzu AG-200A testing machine at 298 K.

RESULTS AND DISCUSSION

Morphology

The results of DSC scan for PU–vinyl ester resin (VER) IPNs, which were prepared from N-330 polyol with L-MDI (for ease, we call it MDI) and various proportions of VER [PU(MDI)/VER IPN], are given in Table I. The low-temperature transitions from 223 to 228 K may be related to the glass transition temperatures (T_g 's) of soft segments in PU network. The transitions over the range of 321 to 335 K and the temperature of endothermal peak at 444 K may be attributed to the disruption of domains, which are composed of hard segments, with limited short-range order and the dissociation of domains containing long-range order in PU network,

respectively.³ However, for the endothermal peak at 444 K the possibility of existing crystallite of the hard segments could not be neglected (it will be discussed later). Table I also shows that there is no T_g of pure VER network (395 K) in all those IPN systems. Furthermore, T_{g1} , T_a , and T_b for those IPNs shift to higher (T_{g1}) or lower (T_a and T_b) temperatures considerably. Thus, greater shifts in the range of temperatures must result from the interpenetration between the two networks, since the forced compatibility between the rubber and plastic phases may increase while the VER content is raised,¹ so as to dissociate those domains, including long-range order, or suppress the formation of crystallites in PU network and lose some T_g 's. On the other hand, since there is some compatibility between the polystyrene segments in VER network (the VER contains 30 wt % styrene as co-monomer for crosslinking) and the hard segments in PU network,⁴ it could make similar shifts for both T_a and T_b .

In order to examine the compatibility between the two networks more directly, it is of interest to observe the tensile fracture surfaces of IPN specimen using scanning electron microscopy (SEM). Figure 1 exhibits the fracture surfaces of PU(MDI)/VER IPN. Since the size of domains in these SEM photos decreases with increasing the content of VER in IPN, these domains should be mainly formed by VER networks, and the PU network exists as matrix in the IPN system. However, the domains formed by hard segments in PU network, which have been mentioned before, may be too small to be detected, so they do not show up in those SEM photos. Thus, we could only discuss the two phases here, i.e., VER phase (domain) and PU phase (matrix). Figure 1(a) clearly indicates that the VER phase existing as domains is well-dispersed through the PU matrix for the system containing less VER (20 wt %). As the VER phase was in a glassy state under the tensile test condition, the deformation of VER networks

Table I Results of DSC Scan for PU(MDI)/VER IPN Systems^a

PU/VER (wt ratio)	T_{g1} (K)	T_a (K)	T_b^b (K)
100/0	217	335	452
80/20	223	333	444
70/30	228	328	
60/40	226	321	
0/100	395		

^a Hard segment content: 41 wt %.

^b The temperature of endothermal peak on DSC plot.

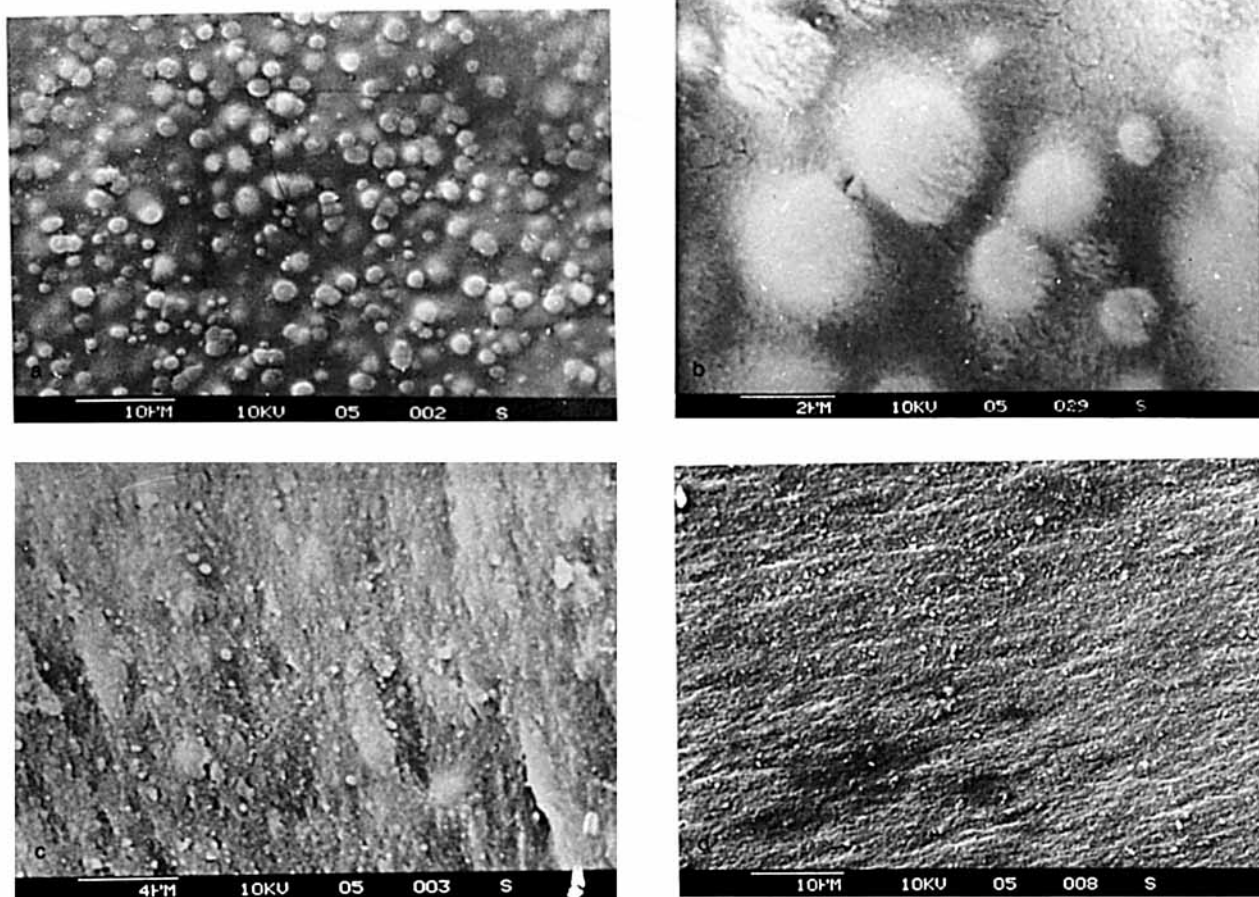


Figure 1 Scanning electron microphotographs of fracture surfaces of PU(MDI)/VER IPN systems. PU/VER weight ratio: (a) and (b) 80/20; (c) 70/30; (d) 50/50.

could be neglected while pull of them from the matrix during the fracture processes left convexes. Thus, the diameter of 0.3–2 μm is estimated for the size of those domains. Figure 1 (b) presents a higher magnification SEM photo for the same system as shown in Figure 1 (a). It exhibits that not only the interface between the two phases is not clear but that there are some black stripes in those domains as well. This behavior may result from the interpenetration between the two networks, at least at the interface. Furthermore, there are some silky stripes in the PU matrix, so they could be attributed to the crystallites of PU. As the size of those domains decreases with increasing the content of VER appreciably and a phase inversion takes place in the ratio of PU/VER around 50/50 [see Figs. 1 (c) and 1 (d)], the compatibility between the PU and VER phases is obviously improved with increasing the concentration of VER in IPN system. These observations from SEM are consistent with the results of DSC presented in Table I.

Table II shows the T_g 's of the IPN prepared with TDI [PU(TDI)/VER IPN]. These IPNs only give rise to one T_g increasing with the increase of VER content in IPN and exhibit quite good compatibility between the two phases. The domain size of these IPNs do decrease so much while comparing with the IPN prepared by using MDI but having the same

Table II Effect of Composition in PU(TDI)/VER IPNs on the Glass Transition Temperatures (by DSC)^a

PU/VER (wt ratio)	$T_{g(\text{DSC})}$ (K)	$T_{g(\text{Fox})}$ (K)	$T_{g(\text{av})}$ (K)	θ
100/0	224			
90/10	229	234	241	0.05
60/40	268	271	292	0.09
0/100	395			

^a Hard segment content: 41 wt %.

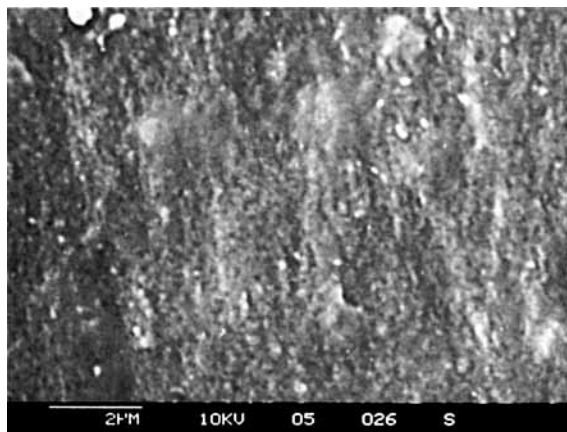


Figure 2 Scanning electron microphotograph of fracture surface of PU(TDI)/VER (70/30) IPN system.

composition, as shown in Figure 2. For those compatible PU(TDI)/VER IPNs, two well-known copolymer equations could be adopted in calculating their T_g 's:

$$\frac{1}{T_{g(\text{Fox})}} = \frac{W_1}{T_{g_1}} + \frac{W_2}{T_{g_2}} \quad (1)$$

$$T_{g(\text{av})} = W_1 T_{g_1} + W_2 T_{g_2} \quad (2)$$

where T_{g_1} and T_{g_2} represent the T_g 's of polymer I and polymer II, respectively, W_1 and W_2 are their weight fractions, and $T_{g(\text{Fox})}$ or $T_{g(\text{av})}$ is the predicted value of T_g for IPN. Both the values of $T_{g(\text{Fox})}$ and $T_{g(\text{av})}$ are listed in Table II. It can be seen that the values of T_g measured from DSC scan are a bit lower than that of $T_{g(\text{Fox})}$, but much lower than that of $T_{g(\text{av})}$. However, Frisch et al.⁵ have pointed out that in the case of a compatible IPN system the mobility of the segment in an IPN could be estimated according to

$$\frac{T_g - T_{g(\text{av})}}{T_{g(\text{av})}} = -\frac{\theta}{\theta + 1} \quad (3)$$

$$\theta = \left(\frac{F_x}{F_m} - 1 \right) Xc' \quad (4)$$

where Xc' ($1 \geq Xc' \geq 0$) represents an increase in physical crosslink density caused by interpenetration in an IPN. F_x/F_m is a ratio of segmental mobilities for interpenetrated and noninterpenetrated network. Values of θ were calculated according to Eq. (3) and found to be more than zero, as shown in Table II. As $\theta > 0$, $F_x > F_m$ could be estimated

from Eq. (4). It seems possible that the mobility of the segments in the IPN is larger than in the non-interpenetrating separated networks. In this case the difference between the $T_{g(\text{DSC})}$ and $T_{g(\text{Fox})}$ or $T_{g(\text{av})}$ could be attributed to the enhancement of mobility for the segments in both networks so as to show the lowering value of $T_{g(\text{DSC})}$ measured.

Table III indicates that there is only one T_g for the PU/VER IPN prepared by using graft polyol and MDI. The compatibility between these two phases is excellent, since its SEM photo exhibits a tough fracture feature and no macrophase separation here, as shown in Figure 3. Thus, these observations may be related to the polystyrene segments that have existed in both networks. However, it should be noticeable that the secondary hydroxyl groups in graft polyol could react with those in VER due to the existence of MDI, so the possibility of forming covalent crosslinks between the two networks in this system should also be considered.

Mechanical Property

The mechanical properties for all these IPNs have been measured. Figures 4 and 5 show that the tensile strength and the elastic modulus over the range of PU(MDI)/VER IPN composition increase with the increase of VER proportion while the elongation at rupture decreases. These phenomena suggest that the VER phase indeed reinforces the PU phase in IPN systems. It can be seen in Figure 4 that the tensile strength curve sharply change at the VER concentration of 20 wt %, and goes through a maximum at about 30 wt %. These experimental results are consistent enough with the observations of SEM (see Fig. 1). In this case the domain size decreases obviously and the compatibility between the two phases is improved while increasing the content of VER from 20 to 30 wt %, so they give rise to better tensile strength. If the concentration of VER in-

Table III Effect of Composition in Graft PU(MDI)/VER IPNs on the Glass Transition Temperatures by (DSC)^a

PU/VER (wt ratio)	T_{g_1} (K)	T_{g_2} (K)
100/0	249	379
70/30	257	
60/40	259	
0/100	395	

^a Hard segment content, 41 wt %.

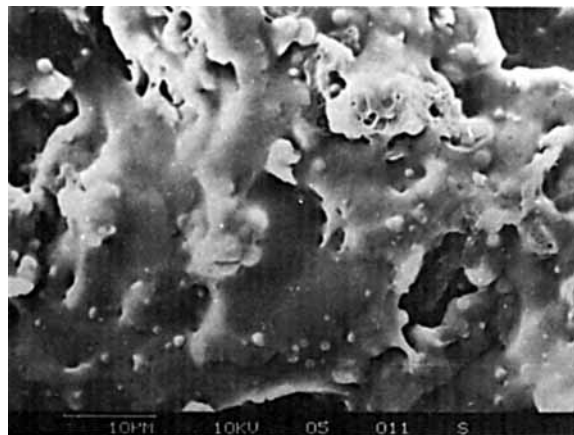


Figure 3 Scanning electron microphotograph of fracture surface of graft PU(MDI)/VER (70/30) IPN system.

creases further, the phase inversion will take place so as to reduce the tensile strength. Similar phenomena have been also observed by Frisch et al. for studying mechanical properties of PU/epoxy resin IPN systems.⁵

Figure 6 illustrates the mechanical properties for the IPN prepared with TDI. As mentioned above, in this system the compatibility between the rubber and plastic phases is greatly improved, so it reveals the maximum of tensile strength at 20 wt % concentration of VER. Finally, it is of interest to show

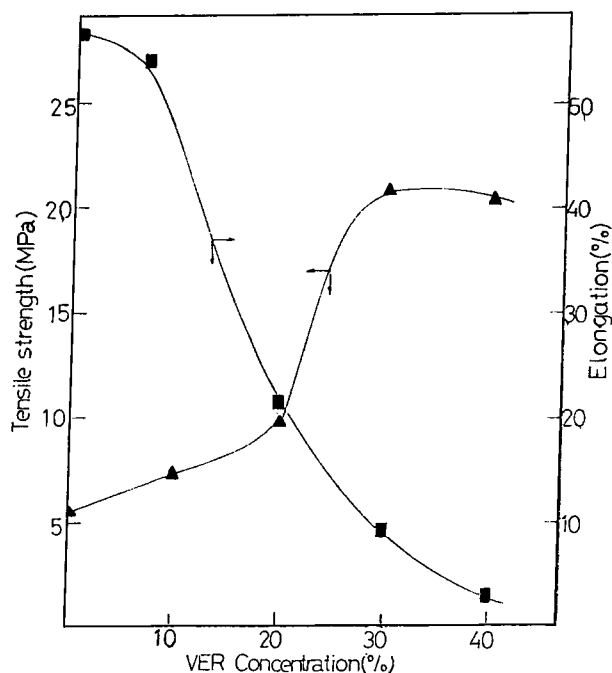


Figure 4 Effect of composition in PU(MDI)/VER IPNs on mechanical properties.

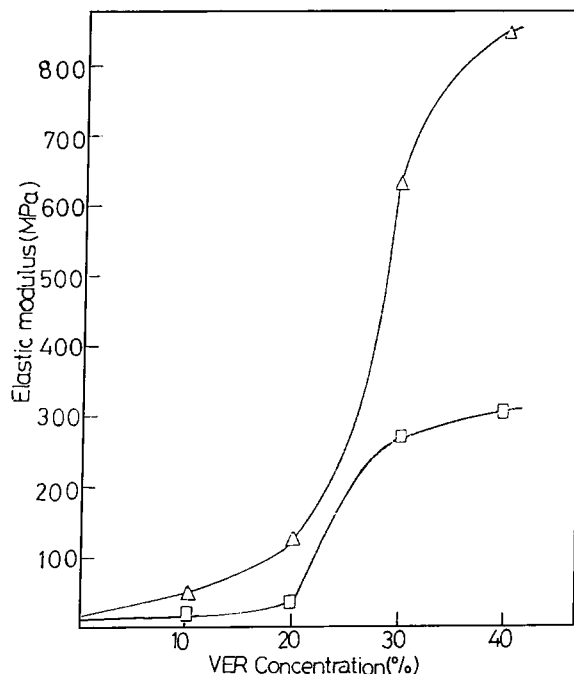


Figure 5 Effect of composition and hard segment content in PU(MDI)/VER IPNs on elastic modulus. Hard segment content (wt %): (□) 29%, (Δ) 41%.

that the IPNs prepared by using graft polyol and MDI [graft PU(MDI)/VER IPN] give rise to the best mechanical properties over all IPN specimens

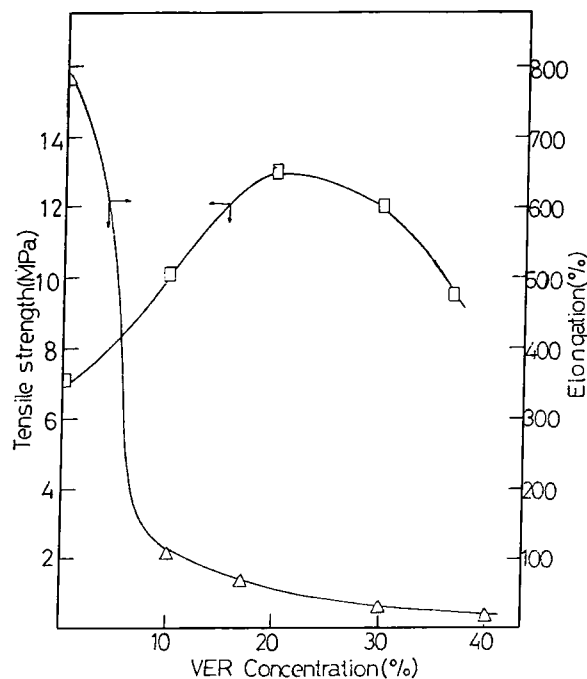


Figure 6 Effect of composition in PU(TDI)/VER IPNs on mechanical properties.

Table IV Mechanical Properties of Three Kinds of IPN

Kind of IPN	Composition of PU and VER (wt ratio)	Tensile Strength (MPa)	Elongation at Rupture (%)
PU(MDI)/VER	80/20	10.0	21.5
PU(TDI)/VER	80/20	12.9	66.0
Graft PU(MDI)/VER	80/20	12.0	23.0
PU(MDI)/VER	70/30	22.1	9.4
PU(TDI)/VER	70/30	12.0	23.0
Graft PU(MDI)/VER	70/30	25.8	19.0

studied here, as presented in Table IV. This observation can be correlated with the SEM photo of tough fracture and will be studied further.

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