

Simultaneous Interpenetrating Networks Consisting of Polyurethane and Graft Vinyl Ester Resin: Effect of Different Radical Initiators

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ABSTRACT: A series of well-defined graft vinyl ester resins (graft VER), composed of butanol side chain (BO) or poly(oxypropylene) side chains with different molecular weights (200 or 390), were synthesized and characterized. The simultaneous interpenetrating networks (SINs) of graft VER and polyurethane (PU) were prepared. The effect of initiators for graft VER on the morphologies and mechanical properties of PU/graft VER SINs was studied through DSC, SEM, and FTIR observations. For PU/graft VER SIN formed with AIBN as initiator, the morphology and structure of these SINs are mainly controlled by the PU network formed first, and the structure of graft VER has almost no influence on the long-range order structure of hard segments in SIN. For PU/graft VER SIN prepared with BPO/DMA as initiator (redox system), the side-chain structure of graft VER greatly affects the morphologies of these SINs, although the PU network and graft VER network formed almost simultaneously. The reinforcement effect of the graft VER network on the PU network is significantly different by using these two different initiators for graft VER, which could be related with the morphologies of SINs and the formation rate of the two networks. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 84: 1629–1636, 2002; DOI 10.1002/app.10502

Key words: polyurethane; graft vinyl ester resin; simultaneous interpenetrating network; formation rate; morphology; mechanical property

INTRODUCTION

Interpenetrating polymer networks (IPNs) have been studied extensively relative to their synergetic physical properties.¹ In our laboratory, the simultaneous interpenetrating network (SIN), consisting of vinyl ester resin (VER) and polyurethane (PU), was studied with respect to the reaction injection molding process.^{2,3} Because VER has hydroxyl groups that easily react with isocyanates and lead to chemical bonds between the two networks, it has been

found that these SINs exhibited complex morphologies.^{4–6} Furthermore, if the hydroxyl groups existing in VER were capped with acetyl groups, referred to as VERA, the rigid VERA network would not enhance the elastic PU network.⁷ To improve the compatibility and/or the interpenetration between the VER and PU networks, a series of well-defined graft VERs, consisting of urethane group and poly(oxypropylene) as side chains, were synthesized and characterized. In previous studies, the SINs composed of PU and such well-defined graft VERs were prepared and studied with benzoyl peroxide/dimethylaniline (redox system) as the initiator.^{8,9} In this study, the morphologies and mechanical properties for such SINs prepared with azodiisobutyronitrile as the initiator are reported, and the effect of the polymerization rate of graft VER

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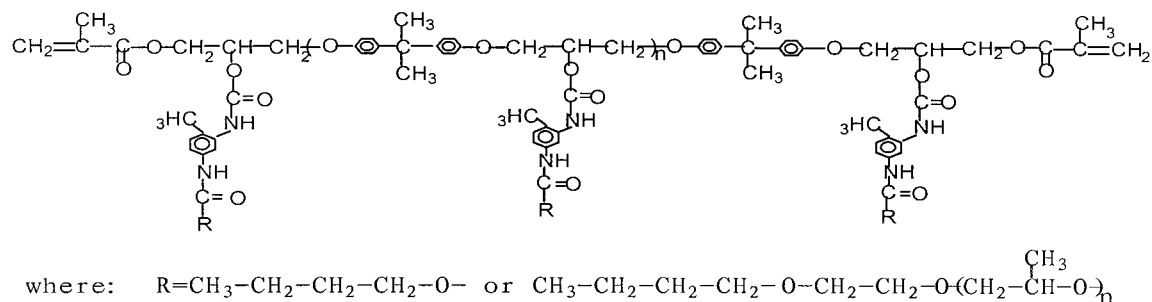


Figure 1 Structural formula of graft VEO.

networks on the morphologies for these SINs is also discussed.

EXPERIMENTAL

Material

Trifunctional poly(oxypropylene)polyol capped with ethylene oxide (GEP330N, hydroxyl number: 36 mg KOH/g) was supplied by Gaoqiao No.3 Chemical Plant. Uretonimine-modified 4,4'-diphenyl methane diisocyanate (L-MDI, NCO content: 28.1%, functionality: 2.13) and 2,4-toluene diisocyanate (2,4-TDI) were provided by Yantai Synthetic Leather General Factory and Sanjing Co., respectively. E-51 epoxy resin (bisphenol A-type, 0.51 epoxide equivalent/100 g resin) was produced by Shanghai Resin Plant. Monofunctional poly(oxypropylene)polyols (PPO200 and PPO390, hydroxyl number: 280 and 143 mg KOH/g, respectively) were kindly synthesized in Jinling Petro-Chemical Co. The products above were all produced in China. All other chemicals used in this study were standard laboratory reagents obtained from various manufacturers in China.

The polyols were dried at 373 K under vacuum for 12 h, and treated with 4-Å molecular sieves for over 1 week before use. 1,4-Butanediol (BDO) was distilled under vacuum in the presence of sodium wire. 1-Butanol (BO) was dried with anhydrous potassium carbonate and distilled before use. Styrene (St) was washed, dried, and distilled under vacuum. The azodiisobutyronitrile (AIBN) was recrystallized and dried to remove residual water.

Synthesis of graft VER

The vinyl ester oligomer (VEO) was prepared by the reaction of E-51 epoxy resin and methacrylic acid. BO, PPO200, or PPO390 was reacted with

2,4-TDI at 323 K to prepare the NCO-terminated products (referred to as BO-NCO, PPO200-NCO, and PPO390-NCO, respectively) until the value of the NCO content was consistent with the theoretical value. The graft VERs were first synthesized by reacting VEO with BO-NCO, PPO200-NCO, or PPO390-NCO at 323 K to form graft VEOs, until the NCO content was lower than 0.02%. Then the styrene as comonomer was added into the graft VEOs to prepare the graft VERs (graft VEO/St = 64/36 w/w). For simplicity, the graft VER made from BO-NCO, PPO200-NCO, or PPO390-NCO was named BO-g-VER, 200-g-VER, or 390-g-VER, respectively, and their structural formulas are shown in Figure 1. Graft efficiency of all graft VERs is greater than 0.90. All the synthesis and characterization processes of VEO and graft VERs were described in detail elsewhere.^{8,9}

Preparation of PU/graft VER SIN

GEP330N, L-MDI, BDO, dibutyltin dilaurate (DBTDL, 4.0×10^{-2} wt % of GEP330N), graft VER, and AIBN (1.0 wt % of graft VER) were mixed in a reactor at high-speed stirring (1200 rpm) for 30 s at 328 K. It was then degassed for about 1 min and cast onto a dry, hot plateglass mold. Finally, the samples were cured at 333 K for 10 h and postcured at 353 K for 3 h and at 383 K for 1 h. The hard segment content of the PU network was 45% (based on the total mass of L-MDI and BDO).

Morphology Characterization and Mechanical Property Measurement

Differential scanning calorimetry (DSC) was used to measure the morphology of PU/graft VER SINs, with a TA Instruments modulated DSC 2910 analyzer (TA Instruments, New Castle, DE), at a heating rate of 20 K/min under nitrogen

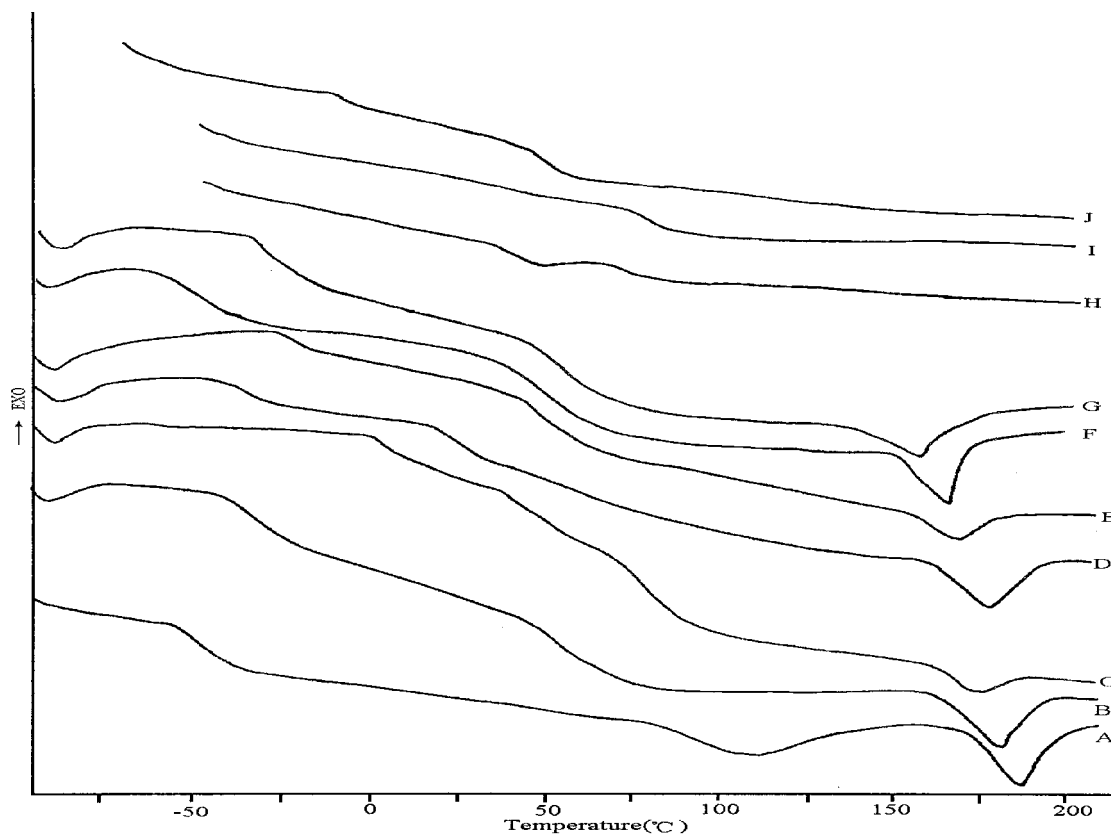


Figure 2 DSC scan plots for PU network and PU/graft VER SINS with different compositions. (A) PU network; (B) PU/BO-*g*-VER 70/30 SIN; (C) PU/BO-*g*-VER 50/50 SIN; (D) PU/200-*g*-VER 70/30 SIN; (E) PU/200-*g*-VER 50/50 SIN; (F) PU/390-*g*-VER 70/30 SIN; (G) PU/390-*g*-VER 50/50 SIN; (H) BO-*g*-VER network; (I) 200-*g*-VER network; (J) 390-*g*-VER network.

atmosphere. For investigating with a scanning electron microscope (SEM, Stereoscan 250 MK3; Cambridge, Rockville, MD), the tensile fracture surface of SIN specimens was etched by dimethylformamide (DMF) for more than 1 month at room temperature and coated with gold vapor before examining. FTIR spectra of SIN samples were recorded by a Nicolet 5DXC FTIR spectrometer (Nicolet Instruments, Madison, WI) at 298 K. The specimens for tensile and elastic modulus tests were made 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-2000A testing machine (Shimadzu, Japan) at 298 K at a cross-head rate of 50 mm/min.

RESULTS AND DISCUSSION

Morphology of PU/graft VER SIN

Figure 2 shows the DSC scan results for the PU network and various PU/graft VER SINS. The

glass-transition temperatures (T_g 's) are given in Table I. The PU network exhibits a T_g of soft segment and two endothermic peaks (T_m) at 383 and 461 K, respectively, which could be attributed to the disruption of domains composed of hard segments with limited short-range order and long-range order, respectively.^{2,10} For the BO-*g*-VER network, there is a T_g and a small endothermic peak at 337 K, which may be related to the disruption of some domains with limited short-range order.^{10,11} There is only one T_g for the 200-*g*-VER network, indicating that it is a compatible system. For the 390-*g*-VER network, there are two T_g 's. It is evident that such a network exhibits a microphase-separated morphology. These experimental results show that the side-chain structure of graft VER had a substantial effect on the morphology of the graft VER network.

Table I also shows there were two T_g 's and one T_m for all PU/graft VER SINS studied. Compared to the T_g of pure networks (PU and graft VER), the value of T_{g1} or T_{g2} for these SINS shifted to

Table I DSC Scan Results for Different SINs

Sample	Composition of SIN (w/w)	T_{g1} (K)	T_{g2} (K)	T_m (K)	ΔH_m (J/g)
PU network	100/0	223	—	461 ^a	9.3
	70/30	235	327	453	4.5
PU/BO- <i>g</i> -VER SIN	50/50	277	340	443	3.1
	0/100	—	353 ^b	—	—
PU/200- <i>g</i> -VER SIN	70/30	236	312	453	5.3
	50/50	255	332	442	3.0
	0/100	—	364	—	—
PU/390- <i>g</i> -VER SIN	70/30	225	326	449	5.0
	50/50	245	336	440	3.0
	0/100	270	327	—	—

^aAnother endothermic peak at 383 K was found on DSC plot.

^bA small endothermic peak at 337 K was found on DSC plot.

higher or lower temperatures resulting from the compatibility and/or interpenetration between the two networks. Furthermore, the values of T_m and ΔH_m of SINs are lower than those of the PU network, indicating that the long-range order structure of hard segments in SINs is somewhat destroyed. It is surprising to find that the values of T_m and ΔH_m for SINs with the same composition are almost identical for different kinds of graft VER/PU SIN. It is clear that the side-chain structure in graft VER had no influence on the long-range order of hard segments in SINs. However, it was reported in a previous investigation⁹ that the values of T_m and ΔH_m for the same SIN are quite different when benzoyl peroxide (BPO)/dimethylaniline (DMA) was used as the initiator.

Thus, the morphologies of these SINs can be changed using different initiators of graft VER. The gel times of the pure PU network and different graft VER networks formed using AIBN at 333 K or BPO/DMA at 293 K were tested to further examine experimental behaviors. Table II shows that the gel time of the PU network is approximate to that of the graft VER network formed with BPO/DMA, although it is appreciably

shorter than that of graft VER formed with AIBN as the initiator. It is clear that when BPO/DMA is used, the PU and graft VER networks were formed at nearly the same time during the synthesis of PU/graft VER SIN, but the PU network was formed first for PU/graft VER SIN prepared with AIBN as the initiator. The different morphologies of this kind of SIN using a different free-radical initiator could thus be attributed to the formation sequence of two networks during the preparation of SINs. This observation is broadly consistent with the observations of other investigators.^{6,12,13} The morphologies of SINs prepared with AIBN as initiator were controlled by the formation of the PU network, leading to the same values of T_m and ΔH_m for different SINs with identical compositions. In this case, there should also exist some independent graft VER networks that formed later in the systems, giving rise to higher values of T_{g2} than those of SINs formed by BPO/DMA.⁹

The ordered structures of hard segments in PU and PU/graft VER SINs can be related to the hydrogen bonding between the urethane linkages,^{14,15} and can be determined using FTIR spectrometer.

Table II Gel Time of graft VER with Different Initiators^a

Initiator	Temperature (K)	Gel Time		
		BO- <i>g</i> -VER	200- <i>g</i> -VER	390- <i>g</i> -VER
BPO/DMA	293	200 s	219 s	572 s
AIBN	333	37 min	42 min	48 min

^aThe gel time of PU at 293 and 333 K is 150 and 61 s, respectively.

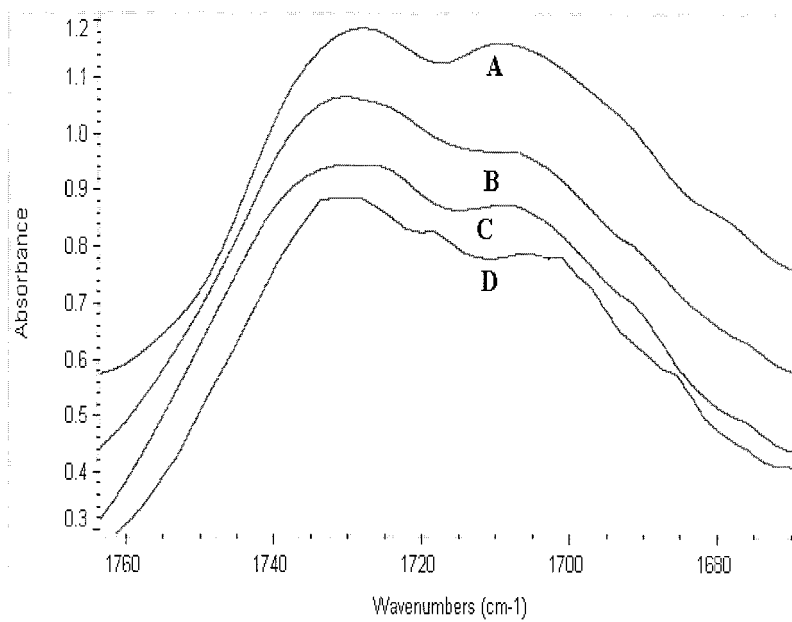


Figure 3 FTIR spectra of PU network and PU/graft VER (70/30) SINS in the carbonyl region at 298 K. (A) PU; (B) PU/BO-*g*-VER SIN; (C) PU/200-*g*-VER SIN; (D) PU/390-*g*-VER SIN.

Figure 3 lists FTIR spectra of the PU network and PU/graft VER (70/30) SINS in the carbonyl region at 298 K, respectively. Multiple bands were observed in these spectra. To separate these peaks, an iteration procedure of damping least squares was used to describe the separated band contour by means of an equation, that is, a Lorentzian and Gaussian combination.¹⁶ Thus, three bands at about 1735, 1711, and 1701 cm^{-1} for the FTIR spectra can be observed. The assignments of the absorption bands are listed in Table III^{10,11} and the least-square curve fitting for the PU network and SINS resulting from the FTIR spectra are shown in Table IV. The degree of hydrogen bonding of urethane groups ($X_{b,UT}$) is defined as follows:

$$X_{b,UT} = \frac{\sum \text{Area}(\text{bonded})}{\text{Area}(1735 \text{ cm}^{-1}) + \sum \text{Area}(\text{bonded})}$$

Table III Assignment of Absorption Band in Carbonyl Region of FTIR Spectra for PU and PU/graft VER (70/30) SINS

Wavenumber (cm^{-1})	Assignment
1735	Free carbonyl stretching
1711	Disordered hydrogen-bonded
1701	Ordered hydrogen-bonded

The calculated values of $X_{b,UT}$ are also listed in Table IV. Table IV shows that the amount of ordered hydrogen-bonded, disordered hydrogen-bonded, and free urethane carbonyl formation as well as the values of $X_{b,UT}$ are almost same for PU/BO-*g*-VER SIN and PU/200-*g*-VER SIN with 70/30 composition, which correlate well with the values of T_m and ΔH_m for the two SINS measured using DSC. Compared to that of the pure PU network, however, the amount of ordered hydrogen-bonded urethane carbonyl formation (1701 cm^{-1}) for both SINS dramatically decreases, giving rise to an enhanced formation of free carbonyl (1735 cm^{-1}) and a decrease in the value of $X_{b,UT}$. These experimental results also indicate that the structure of graft VER network for these SINS had no effect on the long-range order of hard segments in PU, given that their morphologies were controlled by the PU network. For PU/390-*g*-VER (70/30) SIN, the situation is quite complicated. In such SIN systems, although the amount of ordered hydrogen-bonding urethane carbonyl formation (1701 cm^{-1}) is close to that of the pure PU network (which indicates poor compatibility between the 390-*g*-VER network and hard segments of the PU network), the amount of disordered hydrogen bonding is far lower than that of the PU network, yielding a low value of $X_{b,UT}$. However, Table IV exhibits nearly the same val-

Table IV Least-Square Curve-Fitting FTIR Spectra in Carbonyl Region for PU and PU/graft VER (70/30) SINS

Sample	Concentration of Urethane Group ($\times 10^3/\text{mol/g}$)	Peak Area (%)			$X_{b,UT}$ (%)
		1735 (cm^{-1})	1711 (cm^{-1})	1701 (cm^{-1})	
PU	2.42	46.7	15.1	38.2	53.3
PU/BO- <i>g</i> -VER SIN	2.45	56.4	17.5	26.1	43.6
PU/200- <i>g</i> -VER SIN	2.30	54.8	19.2	26.0	45.2
PU/390- <i>g</i> -VER SIN	2.16	56.5	6.2 (1711) 1.7 (1718) ^a	35.6	43.5

^aThe number in bracelet is a real wavenumber of absorption peak measured.

ues of $X_{b,UT}$ for the three kinds of SIN, which is consistent with the observed values of T_m and ΔH_m . It is of interest to note that there was an-

other absorption peak at 1718 cm^{-1} for the PU/390-*g*-VER (70/30) SIN. As mentioned before, the 390-*g*-VER network has long poly(oxypropylene)

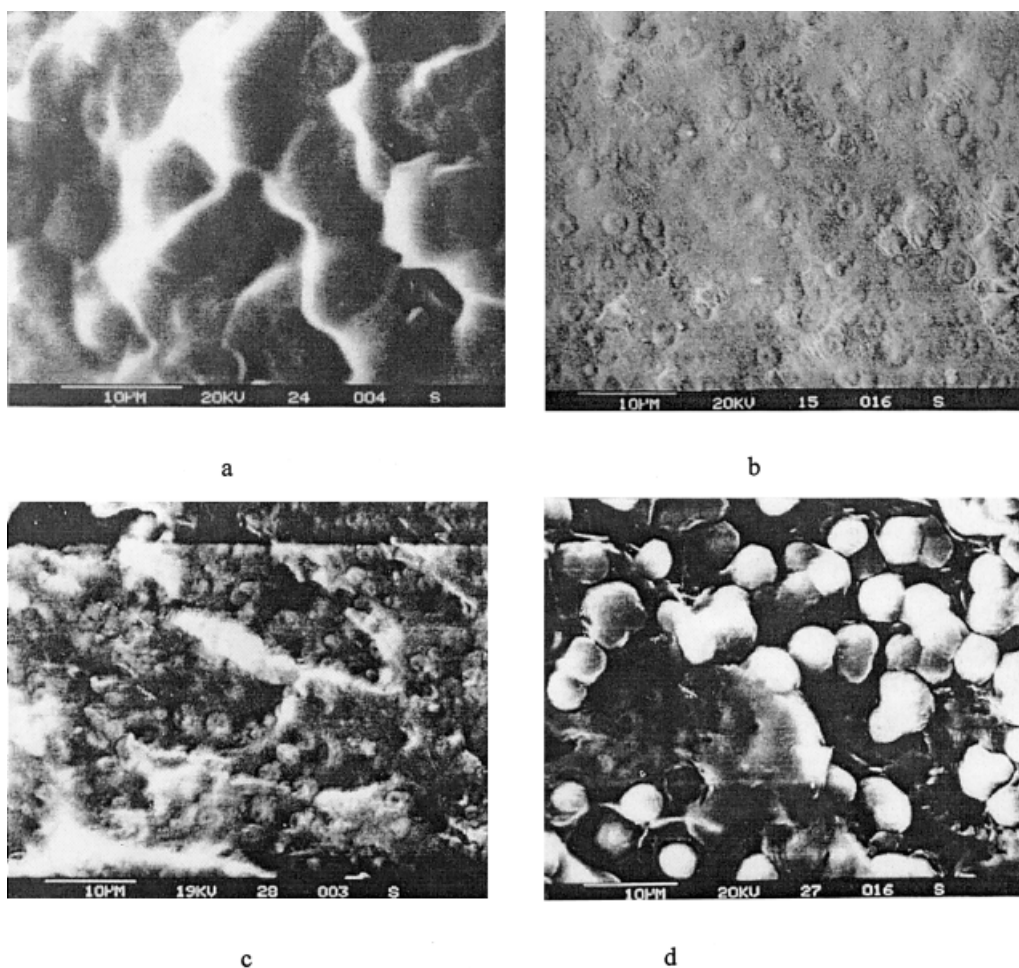


Figure 4 SEM microphotographs of PU and PU/graft VER (70/30) SINS. (a) PU; (b) PU/BO-*g*-VER (70/30) SIN; (c) PU/200-*g*-VER (70/30) SIN; (d) PU/390-*g*-VER (70/30) SIN.

Table V Mechanical Properties of Different SINS

Sample	Initiator of Graft-VER	Composition of SIN (w/w)	Tensile Strength (MPa)	Elastic Module (MPa)	Elongation at Break (%)
PU	—	100/0	10.6	31.3	210.6
PU/BO- <i>g</i> -VER	AIBN	70/30	26.1	136.6	114.5
	BPO/DMA	50/50	31.4	460.0	28.9
PU/200- <i>g</i> -VER	BPO/DMA	70/30	18.2	150.2	97.4
	AIBN	50/50	25.4	513.9	26.6
PU/390- <i>g</i> -VER	AIBN	70/30	20.9	61.4	177.1
		50/50	25.3	240.5	59.2
	BPO/DMA	70/30	17.5	100.4	112.6
PU/390- <i>g</i> -VER		50/50	24.4	355.8	36.8
	AIBN	70/30	17.8	30.9	180.5
		50/50	16.6	111.4	64.9
	BPO/DMA	70/30	12.7	54.0	144.5
		50/50	12.9	188.7	37.2

side chains and microphase-separation structure. The absorption peak at 1718 cm^{-1} is possibly attributable to the hydrogen bonding between the NH group of urethane and ether oxygen in the side chains of the 390-*g*-VER network.

To examine the compatibility and/or the interpenetration between the two networks more directly, the tensile fracture surfaces of SIN specimens were observed using SEM, as shown in Figure 4. Because the specimens were etched by DMF for a long time, the soft segments in the PU network and PPO side chains in the graft VER network on the fracture surface will be significantly dissolved. Figure 4(a) clearly exhibits a white fiberlike structure, which belongs to the long-range order of hard segments in the PU network. Figure 4 shows that there are both fiberlike structures and sphere domains in PU/graft VER (70/30) SINS resulting from the long-range order of hard segments and some independent graft VER networks (sphere domains) dispersed in the PU matrix (black area). For PU/BO-*g*-VER (70/30) SIN [Fig. 4(b)], the fiberlike structures change into spherelike domains (diameter: $\sim 2\ \mu\text{m}$), indicating that the BO-*g*-VER network is mainly compatible with the hard segments of the PU network. From Figure 4(c), it can be seen that the sphere domains are dispersed in the PU matrix (black area) and the interface is obscure, resulting from the compatibility between the two phases. Figure 4(d) exhibits the SEM microphotograph of PU/390-*g*-VER (70/30) SIN. For this SIN system, the contour of the sphere domains (diameter: $\sim 5\ \mu\text{m}$) is very clear, indicating the

limited compatibility and/or the interpenetration between the two networks.

Mechanical Properties

The mechanical properties for all SINS were measured, as listed in Table V. Table V shows that the tensile strength and the elongation at break of SINS formed with AIBN are higher than those of SIN formed with BPO/DMA at identical compositions, although the elastic module is a bit lower. As mentioned before, given that the morphologies of SINS formed with AIBN are mainly controlled by the PU network, the higher elongation at break and lower elastic modulus of these SINS are to be expected. However, the tensile strength of these SINS is much higher than that of SINS made with BPO/DMA, especially for PU/390-*g*-VER SINS. For PU/BO-*g*-VER SIN and PU/200-*g*-VER SIN made with AIBN, where there is compatibility between the two networks and some independent graft VER networks in the SINS, these independent graft networks could act as the reinforced fillers and lead to higher tensile strengths for the SINS. For PU/390-*g*-VER SIN made with AIBN, where there was poor compatibility between the two networks in SIN, there were also independent 390-*g*-VER networks existing in the system that could enhance the tensile strength of this SIN. Thus, the 390-*g*-VER network prepared with AIBN could appreciably reinforce the PU network, although the compatibility between the two phases was limited. These results show that when the PU network in SINS

was made slightly faster, much stronger SIN materials could be prepared. Thus, the reinforcement effect of the graft VER network on the PU network for this kind of graft SIN is quite different and can be controlled by adjusting the reaction rate of the two networks.

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REFERENCES

1. Sperling, H. L. *Interpenetrating Polymer Networks and Related Materials*; Plenum: New York, 1981.
2. Chen, N. P.; Chen, Y. L.; Wang, D. N.; Hu, C. P.; Ying, S. K. *J Appl Polym Sci* 1992, 46, 2075.
3. Fan, L. H.; Hu, C. P.; Pan, Z. Q.; Zhang, Z. P.; Ying, S. K. *Polymer* 1997, 38, 3609.
4. Fan, L. H.; Hu, C. P.; Ying, S. K. *Polymer* 1996, 37, 975.
5. Fan, L. H.; Hu, C. P.; Zhang, Z. P.; Ying, S. K. *J Appl Polym Sci* 1996, 59, 1417.
6. Fan, L. H.; Hu, C. P.; Ying, S. K. *Polym Eng Sci* 1997, 17, 338.
7. Wang, G. Y.; Hu, C. P. *Acta Polym Sinica* 1999, 1, 24 (in Chinese).
8. Wang, G. Y.; Wang, Y. L.; Hu, C. P. *Eur Polym J* 2000, 36, 735.
9. Wang, G. Y.; Zhu, M. Q.; Hu, C. P. *J Polym Sci Part A: Polym Chem* 2000, 38, 136.
10. Seymour, R. W.; Cooper, S. L. *Macromolecules* 1973, 6, 48.
11. Schneider, N. S.; Sung, C. S. P.; Matton, R. W.; Illinger, J. L. *Macromolecules* 1975, 8, 62.
12. Touhsaent, R. E.; Thomas, D. A.; Sperling, L. H. *J Polym Sci* 1974, 46C, 175.
13. Kim, S. C.; Klempner, D.; Frisch, H. L.; Radigan, W.; Frisch, H. L. *Macromolecules* 1976, 9, 258.
14. Bonat, R. *J Macromol Sci* 1968, B2, 115.
15. Clough, S. B.; Schneider, N. S. *J Macromol Sci* 1968, B2, 553.
16. Luo, N.; Wang, D. N.; Ying, S. K. *Polymer* 1996, 37, 3577.