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Interpenetrating polymer networks of polyurethane and graft vinyl ester resin: polyurethane formed with toluene diisocyanate[☆]

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Abstract

For enhancing the compatibility and/or the interpenetration of the simultaneous interpenetrating networks (SINs) composed of polyurethane (PU) formed with toluene diisocyanates (TDI) and vinyl ester resin (VER) in which there were no chemical bonds between the two networks, a series of well-defined graft VERs consisting of different side chains were synthesized and characterized. The side chains existing in such graft VERs were formed from TDI and butanol (called BO-g-VER) or poly(oxypropylene) with different molecular weights (M_w: 200 and 390, called 200-g-VER and 390-g-VER, respectively). Differential scanning calorimetry measurements and the scanning electron microscopy observation indicated that the morphology of graft VERs had a great effect on the interpenetration and/or the compatibility between the two networks for PU/graft VER SIN systems. The SIN consisting of 200-g-VER exhibits excellent interpenetration between the two networks, as 200-g-VER network is a compatible system. For SIN composed of BO-g-VER, the compatibility between the two phases is greatly improved, since there are more content of urethane groups existing in grafts which should mix well with those in the PU network. Thus, the mechanical properties increase appreciably with the increase of graft VER content for these two SIN specimens. However, the reinforcement effect of 390-g-VER network on PU network is poor, as such a SIN shows a serious phase separation due to the micro-phase separated morphology of 390-g-VER network's own self. © 2000 Elsevier Science Ltd. All rights reserved.

1. Introduction

The interpenetrating polymer networks (IPNs) have been studied extensively as polymer alloys with synergistic physical properties of technological interest. Pernice et al. [1] first reported some simultaneous interpenetrating networks (SINs) composed of polyurethane (PU) and industrial unsaturated polyester resin or epoxy resin for application in reaction injection moulding (RIM) technology. Since then, the interest of using IPNs as RIM materials has increased. Most of these research works were related to the SINs consisting of PU and industrial unsaturated polyester resin [2,3]. However, the hydroxyl and carboxyl groups usually existing in commercial unsaturated polyester resin can easily react

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with isocyanates and it could make the complicated structure and morphology for such SINs, because there should have some chemical bonds between the two networks.

In our laboratory, the vinyl ester resin (VER) has been prepared by reacting epoxy resin with methacrylic acid, and the SIN consisting of this kind of VER and PU has been synthesized and studied for RIM process [4,5]. Since there also have hydroxyl groups in VER, it has been found that the chemical bonds between the two networks have great effect on the kinetics of network formation and the morphology development for these SIN systems [6–8]. Furthermore, if the hydroxyl groups existing in VER were capped with acetyl groups (it was called VERA), the miscibility between the PU and VERA networks was found to be limited, and this rigid VERA network could not well enhance the elastic PU network [9]. It is well known that for the SIN consisting of some grafts, the interpenetration between the two networks as well as the physical properties could be improved appreciably [10], since these side chains existing in one of the networks act as a compatibilizer between the two phases [11]. However, in most cases this kind of graft network is formed in situ by means of the chemical reaction method during the SIN formation. Thus, in such a SIN system, the structure and morphology should be very complicated, as the graft efficiency and the length of grafts are difficult to be controlled [12]. In order to improve the compatibility and/or the interpenetration between the VER and PU networks, a series of well-defined graft VERs have been synthesized and characterized. The morphologies and mechanical properties of SINs composed of PU and graft VER are reported in this article.

2. Experimental

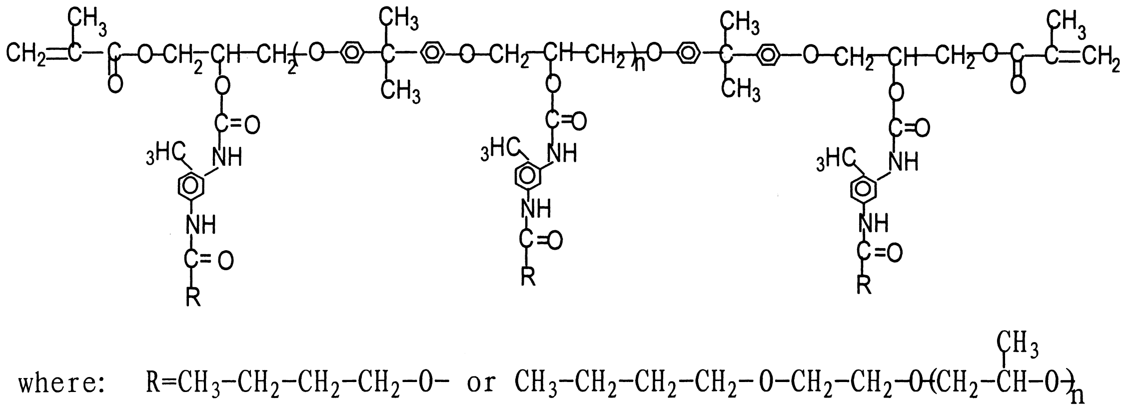
2.1. Material

Tri-functional poly(oxypropylene) polyol capped with ethylene oxide (GEP330N, hydroxyl number: 36 mgKOH/g) was supplied by Gaoqiao No. 3 Chemical Plant. Toluene diisocyanate (TDI, 80/20) and 2,4-TDI were provided by Olin Co. and Sanjing Co., respectively. E-51 epoxy resin (bisphenol A-type, 0.51 epoxide equivalent/100 g resin) was produced by Shanghai Synthetic Resin Plant. Mono-functional poly(oxypropylene) polyols (PPO200, PPO390; hydroxyl number: 280 and 143 mgKOH/g, respectively) were kindly synthesized in Jinling Petro-Chemical. All other chemicals used in this study were standard laboratory reagents obtained from various manufacturers.

The polyols were dried at 100°C under vacuum for 12 h, and treated with 4A molecular sieves for over one week before use. 1,4-butanediol (1,4-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 was washed, dried and distilled under vacuum. The benzoyl peroxide (BPO) was recrystallized and dried for removing the water.

2.2. Synthesis of graft VER

The vinyl ester oligomer (VEO) was prepared by the reaction of epoxy resin and methacrylic acid. All the synthesis and characterization of VEO were described in detail, elsewhere [6,7]. BO, PPO200 or PPO388 was reacted with 2,4-TDI at 50°C to prepare the NCO-terminated products (called as BO-NCO, PPO200-NCO and PPO390-NCO, respectively), till the value of NCO



where: $R=CH_3-CH_2-CH_2-CH_2-O-$ or $CH_3-CH_2-CH_2-CH_2-O-CH_2-CH_2-O(CH_2-\overset{CH_3}{CH}-O)_n$

Fig. 1. The structure formula of graft VEO.

content measured according to ASTM D2572-80 fitted well with the theoretical value. The NCO-terminated products were characterized by using Nicolet 5DXC FTIR spectrometer. It was found that there was no characteristic peak of hydroxyl group at 3500 cm^{-1} on FTIR plot for these products. The graft VERs were synthesized by reacting VEO with BO-NCO, PPO200-NCO and PPO388-NCO, respectively, in the presence of dibutyltin dilaurate (DBTDL, 2×10^{-2} wt% of VEO) as catalyst at 50°C, till the NCO content was lower than 0.02%. Then, the styrene (St) as co-monomer was added to such graft VEOs to prepare the graft VERs (graft VEO/St = 64/36, by wt). For simplicity, the graft VER made from BO-NCO, PPO200-NCO and PPO390-NCO was named as BO-g-VER, 200-g-VER and 390-g-VER, respectively, and the structure formula is shown in Fig. 1. Graft VERs were characterized by means of Nicolet 5DXC FTIR spectrometer and the hydroxyl number measurement.

2.3. Preparation of PU/graft VER SINs

GEP330N, TDI 80/20, 1,4-BDO, DBTDL (2.0×10^{-2} wt% of GEP330N), graft VER and a redox initiator of BPO/dimethylaniline (2.0 and 1.0 wt% of graft VER, respectively) were mixed in a reactor at high speed stirring (1200 rpm) for 30 s at first. Then, it was degassed for 1–2 min and cast onto a dry plate glass mould. Finally, the samples were cured at room temperature for 10 h and 80°C/1 h, 110°C/3 h. The hard segment content of PU network is all at 44.5% (based on total mass of TDI 80/20 and 1,4-BDO).

2.4. Morphology characterization and mechanical property measurement

Differential Scanning Calorimetry (DSC) was measured with a TA Instruments Modulated DSC 2910 Analyzer at a heating rate of 20°C/min under nitrogen atmosphere. For investigating with a scanning electron microscopy (SEM) (Stereoscan 250 MK3, Cambridge), the tensile fracture surface of SIN specimens was etched by dimethylformamide (DMF) for more than one month at room temperature and coated with gold vapor before examining. The specimens for tensile and elastic modulus test 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 at 298 K, and the cross-head rate is at 50 mm/min.

Table 1
Some physical parameters of graft VERs

Samples	Theoretical molecular weight of graft VEO	Concentration of urethane groups ($\times 10^3$ mol/g)	Absorption peak of carbonyl group (cm^{-1})	Hydroxyl number before reaction (mgKOH/g)	Hydroxyl number after reaction (mgKOH/g)	Graft efficiency
BO-g-VER	1100	2.52	1720	72.0	1.7	0.98
200-g-VER	1373	2.02	1725	56.7	2.5	0.96
390-g-VER	1781	1.56	1728	44.3	3.5	0.92

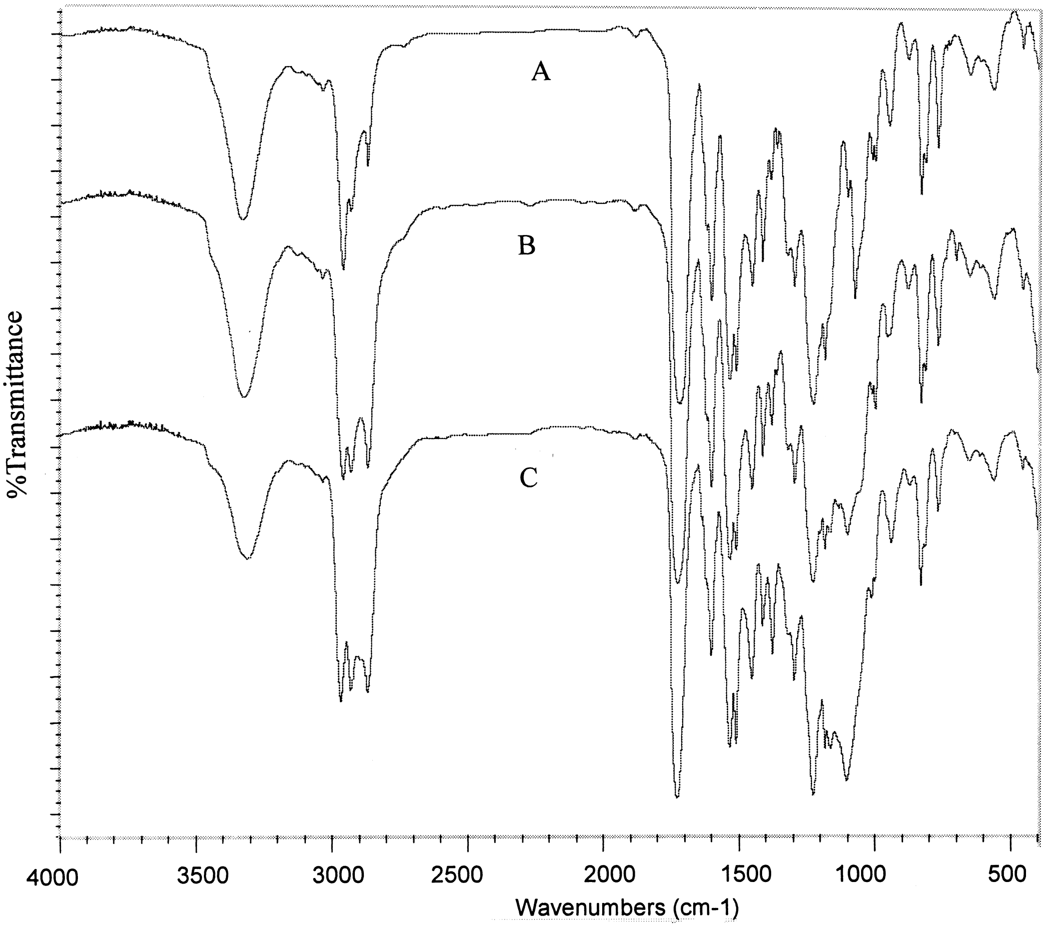


Fig. 2. FTIR spectra of various graft VERs: (A) BO-g-VER, (B) 200-g-VER, (C) 390-g-VER.

3. Results and discussion

3.1. Characterization and morphology of graft VERs

Table 1 shows that the graft efficiency of all graft VERs calculated from hydroxyl number measured before and after reaction is more than 0.90, and it indicates that the graft VERs have been well synthesized. FTIR spectra for graft VERs, i.e., BO-g-VER, 200-g-VER and 390-g-VER, are illustrated in Fig. 2. It is clear that the FTIR absorption peaks of NH group of urethane, hydrogen bonded carbonyl group and C═C group at about 3300, 1730 and 946 cm^{-1} are strong for all graft VERs, while almost no absorption peaks at 3500 and 2270 cm^{-1}, which indicate that the hydroxyl groups existing in graft VERs have been reacted with 2,4-TDI, and the C═C groups are not destroyed. The FTIR observation is consistent with the result of hydroxyl number analysis. It should be pointed out that the situation of absorption peak of graft VERs at around 1730 cm^{-1} is quite different, which may be attributed to the hydrogen bonding between the NH group of urethane and carbonyl group of urethane, ester carbonyl group or ether oxygen in graft VERs [13–15]. With increasing the molecular weight of side chain in graft VERs, the concentration of urethane group decreases and the characteristic absorption peak for 390-g-VER does not shift appreciably resulting from decreasing the hydrogen bonding strength, as listed in Table 1.

Fig. 3 shows the DSC scan plots for the graft VER

Table 2
The results of DSC scan for PU-graft-VER networks

Samples	T_{g_1} (K)	T_{g_2} (K)
BO-g-VER	–	353[a]
200-g-VER	–	364
390-g-VER	270	327

[a] An endothermal peak was observed at 337 K.

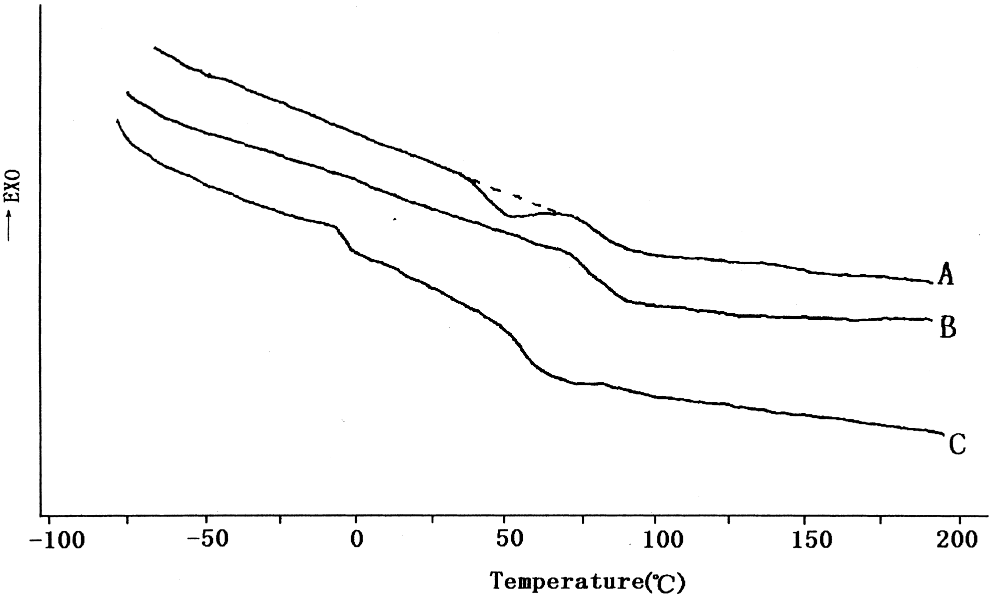


Fig. 3. The DSC scan plots of different graft VER networks: (A) BO-g-VER, (B) 200-g-VER, (C) 390-g-VER.

networks. The DSC scan results are listed in Table 2. For BO-g-VER network, there have a glass transition temperature (T_g) and a small endothermal peak at 337 K. This endothermal peak may be attributed to the disruption of some aggregates with limited short-range order [16,17] due to the strong hydrogen bonding existing in the system. Table 2 also shows that there is only one T_g for 200-g-VER network, indicating that it is a compatible system. However, for 390-g-VER network, there have two T_gs. It is evident that such a network exhibits a micro-phase separated morphology. In the previous papers, we reported that the values of T_g of VER and poly(oxypropylene) polyol are at 392 K [9] and 203 K [18], respectively. Thus, the shift of two T_gs for 390-g-VER network must result from some miscibility between the backbone and side chains existing in the 390-g-VER network. Hua et al. [18] have observed the similar phenomenon for the epoxy resin network grafted with poly(oxypropylene) polyol.

Table 3
DSC scan results for different SINs[a]

Type of SIN	Composition (wt/wt)	T_{g_1} (K)	T_{g_2} (K)
PU/BO-g-VER	70/30	249	303
	50/50	248	302
PU/200-g-VER	70/30	–	350
	50/50	–	312
PU/390-g-VER	70/30	272	319
	50/50	–	303

[a] T_g for pure PU network is at 223 K.

3.2. Morphology of PU/graft VER SINs

Fig. 4 shows the DSC scan results for different PU/graft VER SINs, and the T_gs are given in Table 3. PU network exhibits a T_g of soft segment and an endothermal peak at 383 K due to disruption of domains composed of hard segments with long range order [4]. There have two T_gs for PU/BO-g-VER SIN systems, but compared to pure PU and pure BO-g-VER network, T_{g_1} and T_{g_2} for these SINs shift to higher or lower temperatures considerably. Thus, the shifts in the range of temperatures must result from the compatibility and/or interpenetration between the two networks, since the urethane groups existing in both networks are compatible. Table 3 shows that PU/200-g-VER SINs only exhibits one T_g. It is clear that the urethane groups and polyol segments, existing in the 200-g-VER network, should have good miscibility with the PU network so as to increase the compatibility and/or interpenetration between the two phases appreciably. PU/390-g-VER (70/30) SIN, however, shows two T_gs whose values are very close to those of 390-g-VER network, as listed in Table 3. In this case, it seems that the micro-phase separation of 390-g-VER network has great effect on the morphology of SIN formed. For PU/390-g-VER (50/50) SIN, there is only one T_g and it may be attributed to enhance the extent of interpenetration between the PU network and grafts of 390-g-VER network with increasing the content of graft network in the SIN system.

In order to examine the compatibility and/or interpenetration between the two networks more directly, it is of interest to observe the tensile fracture surfaces of SIN specimen using SEM. Fig. 5 shows SEM photographs of PU/graft VER SINs. Since the specimens were etched by DMF for a long time and the soft segments in PU network on fracture surface were dissolved, Fig. 5(a) clearly exhibits the hard segments with long range order in the PU network, as consistent with the endothermal peak observed on DSC plot. Fig. 5(b) indicates that for PU/200-g-VER (70/30) SIN the ordering structure of hard segments in PU network is obscure and this SIN exhibits a compatible system. The phase separation of PU/BO-g-VER (70/30) SIN is observed on SEM photograph (see Fig. 5(c)), but the size of domains is small whose average diameter is only at around 0.13 μm and the interface between the two phases is not clear indicating the partial phase separated morphology. Fig. 5(d) clearly shows the phase separated morphology for PU/390-g-VER(70/30) SIN, and the appearance of these big domains is very interesting which exhibits a tree-like structure. Furthermore, such a SIN was observed with wide-angle X-ray diffraction analysis, but there is no crystal in the system. Since the morphology of this SIN is mainly controlled by micro-phase separation of graft network existing in the system, as described before, the tree-like structures observed on the SEM photograph may be mainly formed from the aggregates of side chains in 390-g-VER network in which the polyol chains should be easier to be etched by DMF than those existing in PU backbone so as to give rise to form the domains with special shape. All these SEM photographs are consistent well with the DSC scan results.

3.3. Mechanical properties

The mechanical properties for the SINs synthesized have been measured, and the experimental results are

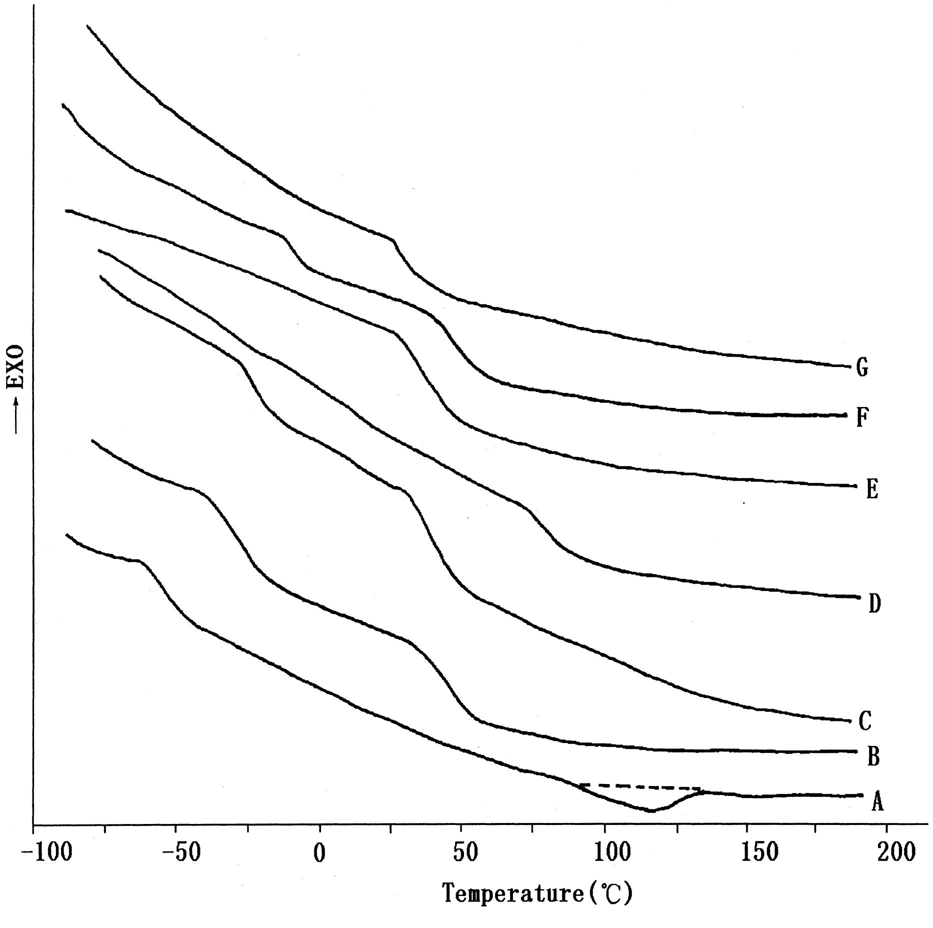


Fig. 4. The DSC scan plots for various PU/graft VER SINs with different compositions: (A) PU, (B) PU/BO-g-VER (70/30) SIN, (C) PU/BO-g-VER (50/50) SIN, (D) PU/200-g-VER (70/30) SIN, (E) PU/200-g-VER (50/50) SIN, (F) PU/390-g-VER (70/30) SIN; (G) PU/390-g-VER (50/50) SIN.

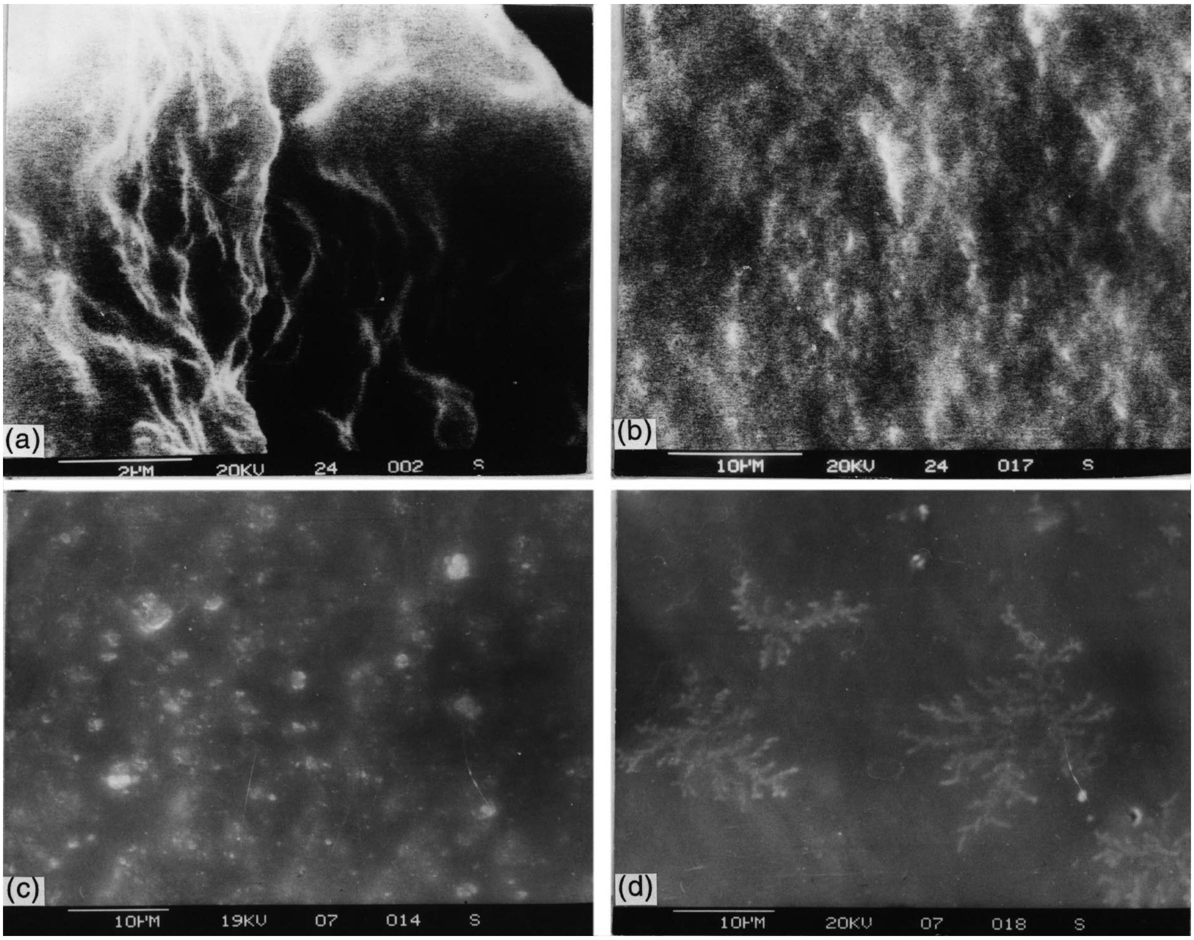


Fig. 5. SEM photographs of different PU/graft VER SINs: (a) PU, (b) PU/200-g-VER (70/30) SIN, (c) PU/BO-g-VER (70/30) SIN, and (d) PU/390-g-VER (70/30) SIN.

listed in Table 4. This table shows that the tensile strength and the elastic modulus over the ranges of PU/BO-g-VER SIN and PU/200-g-VER SIN composition increase with the increase of BO-g-VER or 200-g-VER content, while the elongation at rupture decreases. These phenomena indicate that both BO-g-VER and 200-g-VER phases indeed reinforce the PU phase in SIN systems, as the compatibility and/or the interpenetration between the two networks are enhanced appreciably compared with the similar SINs reported previously [4,8,9]. For PU/390-g-VER SIN, the reinforcement effect of graft VER network on PU

Table 4
Mechanical properties of different SINs

Type of SIN	Composition (wt/wt)	Tensile strength (MPa)	Elongation at break (%)	Elastic modulus (MPa)
PU/BO-g-VER	100/0	9.4	489	12
	70/30	16.2	239	73
	50/50	20.0	68	262
PU/200-g-VER	70/30	15.5	261	55
	50/50	18.5	78	245
PU/390-g-VER	70/30	8.3	282	46
	50/50	9.7	97	97

network is poor. It must result from the micro-phase separation of 390-g-VER network giving rise to complex morphology of SIN systems.

Acknowledgements

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