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Simultaneous full-interpenetrating polymer networks of blocked polyurethane and vinyl ester

Part I. Synthesis, swelling ratio, thermal properties and morphology

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Abstract

This paper presents the synthesis of full-interpenetrating polymer networks (full-IPNs) based on blocked polyurethane (PU)/vinyl ester (VE). The IPNs were prepared from a blocked NCO-terminated PU prepolymer with a chain extender and a VE prepolymer with an initiator using simultaneous polymerization (SINs) method. From IR spectrum analysis, it was found that the major reactions in the blocked PU/VE IPNs system are the self-polymerization of the blocked PU/chain extender and the self-polymerization of the VE/initiator. The swelling ratio of the IPNs increased with an increasing blocked PU content, and decreased with an increasing filler and VE initiator content. The density decreased with an increasing blocked PU content, and increased with an increasing filler and VE initiator content. The weight loss by thermogravimetric analysis decreased with an increasing VE and filler content. It was confirmed from scanning electron micrography that the system was heterogeneous and more than one phase existed in the IPNs. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Interpenetrating polymer networks; Blocked polyurethane; Vinyl ester

1. Introduction

Interpenetrating polymer networks (IPNs) are a special class of polymer blends in which the polymers are crosslinked [1,2]. These materials are characterized by the presence of two networks strongly entangled ideally only by topological constraints [3,4]. Two types of IPNs may be formed, depending on whether the polymer components are crosslinked or not it can mainly be classified into full-IPNs and semi-IPNs [5–9].The full-IPNs are characterized by the presence of crosslinks in both network polymers, as shown in Fig. 1(a); the semi-IPNs exists when one of the components is crosslinked and the other is linear, as shown in Fig. 1(b).

The various techniques for preparing IPNs are sequential polymerization (SIPNs) [5,10–12], latex blending (LIPNs) [5,10,13] and simultaneous polymerization (SINs) [5,14,15]. SIPNs are obtained by swelling a polymer network I with a monomer mixture II, which is polymerized in situ. SINs polymerization is obtained by mixing all monomers or prepolymers and the curing agents together before either polymer is formed. Among the three modes of synthesis, the SINs is generally the best one to have a high degree of intermixing when compared with the other processes due to the compatibility of the monomeric mixture which is much higher than that of a polymeric mixture [16].

The blocked polyurethane (PU)/vinyl ester (VE) system in this study serves as an excellent model SINs system and full-IPNs for the cross-PU/cross-VE while giving good properties. The morphology of the IPNs is particularly complicated and has been subject to many studies [17–19]. During polymerization, two competing processes take place simultaneously. Phase separation of the forming polymer chains proceeds by diffusion through an increasingly viscous medium to form phase domains. The formation of crosslinks restricts diffusion, and at gelation, then the present situation is frozen in Ref. [17]. With highly incompatible polymers, the phase separation is so serious that the gross phase separation occurs before gelation. The SINs process can demonstrate very fine micro-heterogeneous morphology. The other especially important and fundamental properties of polymer networks are their swelling ratio and thermal behavior. The swelling ratio shows the degree of hard or soft segment components in the IPNs. The thermal properties reveal the heat resistance of various different IPN components.

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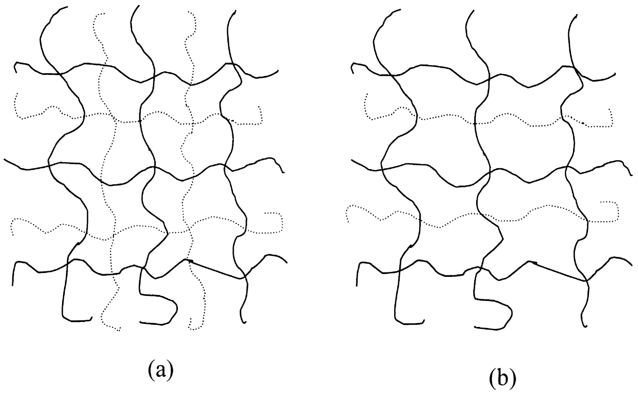


Fig. 1. A schematic of: (a) full-IPNs; (b) semi-IPNs.

In this study, the simultaneous polymerization (SINs) method was used to synthesize PU/VE full-IPNs. The blocked NCO-terminated PU prepolymer with a chain extender and the VE prepolymer with an initiator mixed simultaneously at room temperature, and the interpenetrated reaction at an elevated temperature. The paper is focused on the synthesized method, the swelling ratio, the thermal properties and the morphology of the blocked PU/VE full-IPNs system.

2. Experimental

2.1. Materials

The materials used in this study are listed in Table 1, including the blocked NCO-terminated PU prepolymer, the chain extender of PU, the VE prepolymer, the initiator for vinyl ester polymerization and the filler. Since the blocked NCO-terminated PU prepolymer might contain moisture and reacts with isocyanate at high temperature to generate CO_2 gas bubbles, the blocked NCO-terminated PU prepolymer was stored under vacuum at 60°C for 4 h.

2.2. Preparation of blocked PU/VE IPN samples

The blocked NCO-terminated PU/VE IPN samples was prepared in four stages as follows:

1. One equivalent of the blocked NCO-terminated PU prepolymer was heated to 50°C and then mixed with one equivalent of an aromatic diamine (ACR H-3486) homogeneously. The vinyl ester prepolymer was heated to 50°C and then mixed with 1.5 phr (parts per hundred

Table 1
Raw materials

Material	Specification	Supplier
VE-prepolymer	Vinyl ester (VE) Bisphenol A type Viscosity = 240 mPa s at 25°C	Swancor Co., Taiwan, ROC
Initiator	C-type curing agent (high temperature type) (blend of 80% cumene hydroperoxide and 20% plasticizer) Viscosity = 500 mPa s at 25°C	Swancor Co., Taiwan, ROC
PU-prepolymer	Blocked NCO-terminated PU Prepolymer Viscosity = 31 000 mPa s $M_w = 4230$ Equivalent weight = 1410	Bayer, Germany
Chain extender	Aromatic diamine (ACR H-3486) (blend of 60%, 4,4-methylene diamine and 40% *m*-phenylene diamine) Molecular weight = 266 Viscosity = 20 000 mPa s at 25°C Specific gravity = 1.11 at 25°C	Shell Chemical Co., USA
Filler	Kaolin Specific gravity = 2.7 Particle size = 325 mesh	Yin Chin Co., Taiwan, ROC

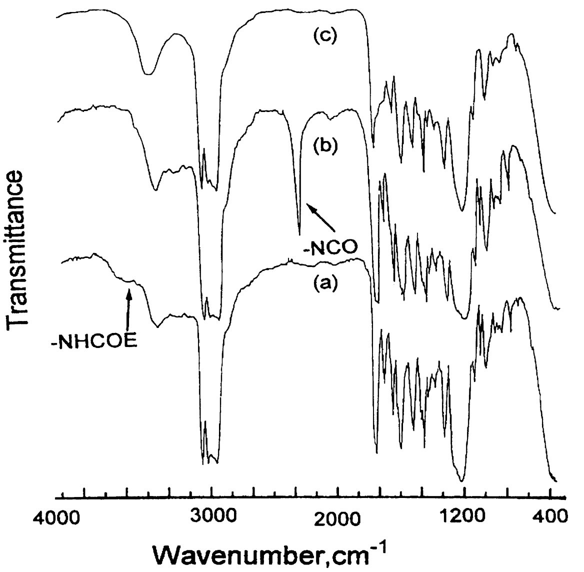


Fig. 2. The IR spectra of the blocked NCO-terminated PU with the chain extender (aromatic diamine) at reaction times of: (a) 0; (b) 3 min; (c) 2 h and at a temperature of 145°C.

parts of resin) of the initiator homogeneously. Then, the two mixtures were blended in various weight ratios at 50°C and mixed completely using a high torque stirrer.

2. The mixture was molded in an ASTM standard stainless steel mold, the surface of which was treated by chrome plating.
3. The mixture of mold was cured in an oven for 3 h and the temperature was maintained at 140°C.
4. Finally, the samples were removed from the mold and kept in a desiccator where the relative humidity was maintained at 50% for at least two days before they were tested.

2.3. Equipment and measurement

1. Infrared (IR) measurements were carried out with a Perkin–Elmer Model IR-983 (Perkin–Elmer Co., USA). The sample was directly dabbed into a KBr pellet or a manufactured film for IR tests.
2. The viscosity of the prepolymer was measured with a Brookfield RVF model viscometer (Brookfield Co., USA).
3. The swelling ratio (q) was determined using the following equation:

$$q = \frac{V}{V_0} = 1 + \frac{(W - W_0) \times \rho_0}{W_0 \times \rho_s} \tag{1}$$

where V_0 is the sample volume before swelling, V the sample volume after swelling by immersing in acetone for 72 h, W_0 the sample weight before swelling, W the sample weight after swelling by immersing in acetone for 72 h, ρ_0 the sample density before swelling, ρ_s the density of acetone.

4. The density was determined using the following equation according to ASTM D792:

$$D = \frac{a \times D_L}{(a - b)} \tag{2}$$

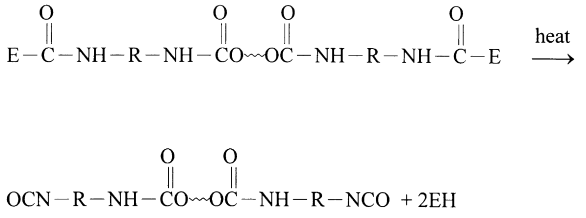
where D is the sample density, D_L the density of using liquid; a the sample weight in air, b the sample weight in liquid.

5. The weight loss of thermogravimetric analysis (TGA) was measured on a TG/DTA 300 (SEIKO Co., USA).
6. The differential scanning calorimeter (DSC) used was a Model 910 (Dupont Co., USA).
7. The SEM photographs were obtained on a S-570 Hitachi scanning electron microscope (Hitachi Co., Japan). The microphotographs were taken on the surface obtained by fracturing the specimen in liquid nitrogen and then coating it with gold powder.

3. Results and discussion

3.1. Synthesis of blocked PU/VE IPNs

The reaction mechanism can be described by IR analysis. The IR spectroscopy analysis is based on the peak change of functional groups during the reaction period. Fig. 2 shows the IR spectra of the blocked NCO-terminated PU with the chain extender (aromatic diamine) at various reaction times and at a temperature of 145°C. The spectrum of Fig. 2(a) shows no absorption peak at 2270 cm^{-1} corresponding to the isocyanate (NCO) when the reaction started, owing to the NCO-terminated PU prepolymer blocked by a blocking agent (ϵ-caprolactam). After reacting for 3 min at 145°C as shown in Fig. 2(b), the absorption peak intensity of NCO at 2270 cm^{-1} appeared clearly, and the absorption peak of –NHCOE– at 3550–3650 cm^{-1} disappeared. From the spectrum in Fig. 2(c), one can observe that the absorption peak intensity at 2270 cm^{-1} (NCO) disappeared clearly after reaction for 2 h at 145°C. The resulting absorption spectra indicated that the majority of the free isocyanate (NCO) groups were generated at elevated temperature, and then, the free NCO groups could easily react with the chain extender (aromatic diamine). Therefore, the reaction process is almost complete in the second hour. The deblocking reaction process of the blocked PU is described by the following equation [20]:



$$\mathrm{E{-}\overset{O}{\overset{\|}{C}}{-}NH{-}R{-}NH{-}\overset{O}{\overset{\|}{C}}O{\sim\sim}O\overset{O}{\overset{\|}{C}}{-}NH{-}R{-}NH{-}\overset{O}{\overset{\|}{C}}{-}E} \xrightarrow{\text{heat}} \mathrm{OCN{-}R{-}NH{-}\overset{O}{\overset{\|}{C}}O{\sim\sim}O\overset{O}{\overset{\|}{C}}{-}NH{-}R{-}NCO} + 2\mathrm{EH} \tag{3}$$

where the blocking agent (EH) is ϵ-caprolactam. The free

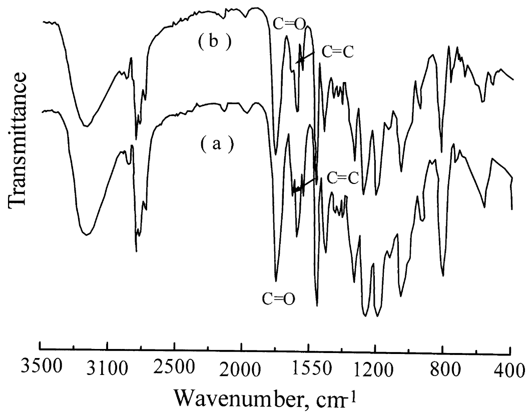
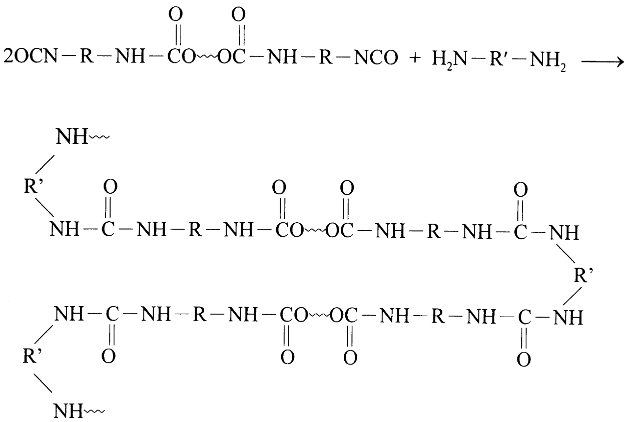


Fig. 3. The IR spectra of (a) the VE prepolymer and (b) the VE polymer reacted at a temperature of 145°C for 2 h.

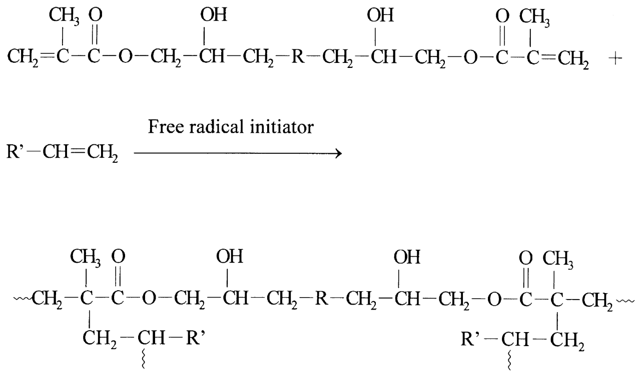
NCO groups can easily react with the chain extender (aromatic diamine). The reaction process is described by the following equation [20]:



$$2\mathrm{OCN{-}R{-}NH{-}\overset{\overset{O}{\|}}{C}O}\sim\mathrm{O\overset{\overset{O}{\|}}{C}{-}NH{-}R{-}NCO} + \mathrm{H_2N{-}R'{-}NH_2} \longrightarrow$$

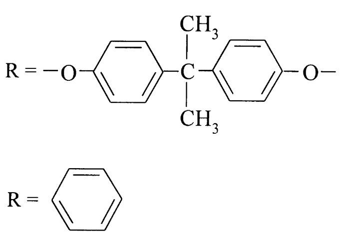
$$\begin{array}{l} \mathrm{NH}\sim \\ \;/ \\ \mathrm{R'} \\ \;\backslash \\ \mathrm{NH{-}\overset{\overset{O}{\|}}{C}{-}NH{-}R{-}NH{-}\overset{\overset{O}{\|}}{C}O}\sim\mathrm{O\overset{\overset{O}{\|}}{C}{-}NH{-}R{-}NH{-}\overset{\overset{O}{\|}}{C}{-}NH} \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad\backslash \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\mathrm{R'} \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad/ \\ \mathrm{NH{-}\underset{\underset{O}{\|}}{C}{-}NH{-}R{-}NH{-}\underset{\underset{O}{\|}}{C}O}\sim\mathrm{O\underset{\underset{O}{\|}}{C}{-}NH{-}R{-}NH{-}\underset{\underset{O}{\|}}{C}{-}NH} \\ \;/ \\ \mathrm{R'} \\ \;\backslash \\ \mathrm{NH}\sim \end{array} \qquad (4)$$

Fig. 3 illustrates that the IR spectra of (a) the VE prepolymer and (b) the VE polymer. In this study, the VE prepolymer is polymerized at 145°C for 2 h. From Fig. 3, one can observe that the absorption peak intensity of C=C at 1630 cm^{-1} of the VE polymer decreases when compared with the corresponding peak of the VE prepolymer during the reaction. Therefore, the reaction process is almost complete (about 95% were reacted) in 2 h at 145°C. The polymerization of vinyl ester is represented by the following equation [21]:



$$\mathrm{CH_2{=}\underset{}{\overset{\overset{CH_3}{|}}{C}}{-}\overset{\overset{O}{\|}}{C}{-}O{-}CH_2{-}\overset{\overset{OH}{|}}{CH}{-}CH_2{-}R{-}CH_2{-}\overset{\overset{OH}{|}}{CH}{-}CH_2{-}O{-}\overset{\overset{O}{\|}}{C}{-}\overset{\overset{CH_3}{|}}{C}{=}CH_2} + \mathrm{R'{-}CH{=}CH_2} \xrightarrow{\text{Free radical initiator}}$$

$$\sim\mathrm{CH_2{-}\underset{\underset{CH_2-CH-R'}{|}}{\overset{\overset{CH_3}{|}}{C}}{-}\overset{\overset{O}{\|}}{C}{-}O{-}CH_2{-}\overset{\overset{OH}{|}}{CH}{-}CH_2{-}R{-}CH_2{-}\overset{\overset{OH}{|}}{CH}{-}CH_2{-}O{-}\overset{\overset{O}{\|}}{C}{-}\underset{\underset{R'-CH-CH_2}{|}}{\overset{\overset{CH_3}{|}}{C}}{-}CH_2}\sim \qquad (5)$$



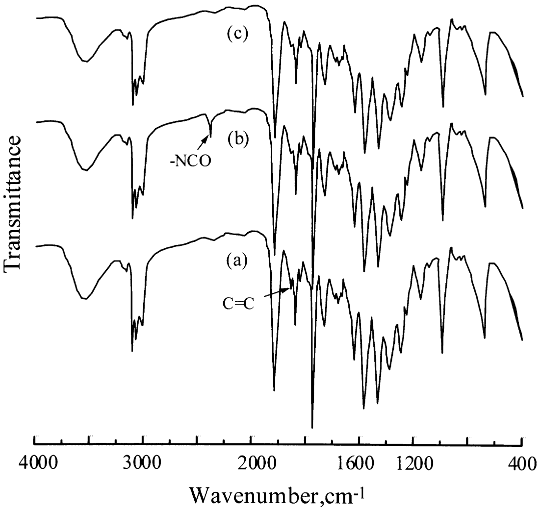


Fig. 4. The IR spectra of the blocked PU and VE at reaction times of (a) 0; (b) 3 min; (c) 2 h and at a temperature of 145°C.

Fig. 4 shows the IR spectra of the reaction system of the blocked PU and VE at various reaction times of 145°C. The figure shows that there was no absorption peak intensity of NCO at 2270 cm^{-1} but had an absorption peak intensity of C=C at 1630 cm^{-1} when the reaction started. After heating at 145°C for 3 min, the absorption peak of NCO at 2270 cm^{-1} appeared, meanwhile, the absorption peak of C=C at 1630 cm^{-1} disappeared. After heating at 145°C for 2 h, about 95% of the absorption peak of NCO at 2270 cm^{-1} and C=C at 1630 cm^{-1} disappeared at the same time. From the above IR spectrum analysis, it was found that the major reactions in the blocked PU/VE system are the self-polymerization of the blocked PU/chain extender and the self-polymerization of the VE/initiator.

3.2. The swelling ratio

In order to understand that the IPN structures were influenced by component segments, the important swelling properties of the IPNs must be discussed. In general, the higher the component soft segments existing in the IPNs, the greater is the swelling ratio of the IPNs. Fig. 5 shows the swelling ratio versus the blocked PU content of the blocked PU/VE IPNs. It was found that the swelling ratio of the IPNs increased with the increasing blocked PU content. As the

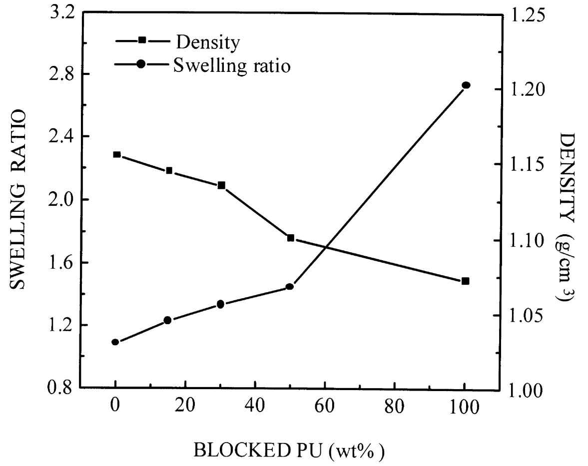


Fig. 5. The swelling ratio and the density versus the blocked PU content for the blocked PU/VE IPNs.

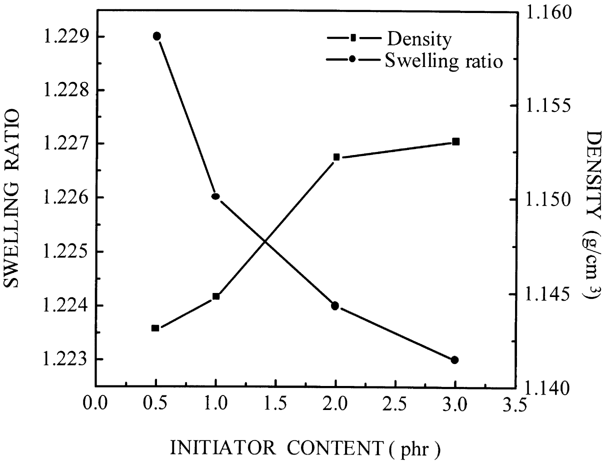


Fig. 7. The swelling ratio and the density versus the initiator content of VE for the blocked PU (15 wt%)/VE (85 wt%) IPNs.

structures of the blocked PU and VE are the soft and hard segments, respectively, the higher the blocked PU content, the greater is the swelling ratio.

The swelling ratio versus the filler (kaolin) content for the blocked PU (15 wt%)/VE (85 wt%) IPNs is shown in Fig. 6. It is observed that the swelling ratio decreased with the increasing filler content; as a result the higher the filler content the higher is the hard segment contents in the IPNs. Fig. 7 illustrates the swelling ratio versus the initiator content of VE for the blocked PU (15 wt%)/VE (85 wt%) IPNs. From the figure, one can observe that the swelling ratio decreased with the increasing initiator content. As a result of the higher initiator content, the higher the degree of VE polymerization (cross-linking) the greater is the hard segment contents existing in the IPNs.

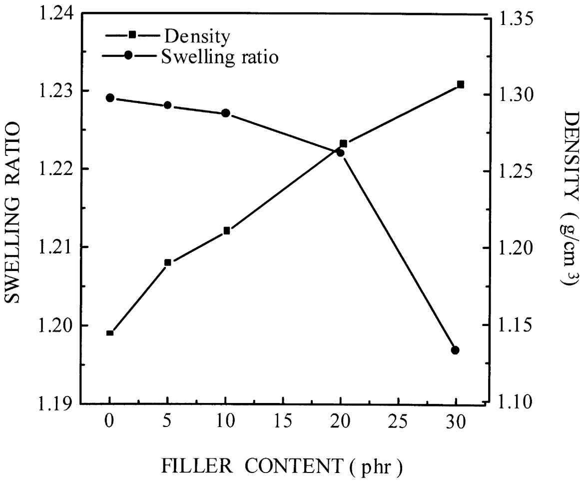


Fig. 6. The swelling ratio and the density versus the filler (kaolin) content for the blocked PU (15 wt%)/VE (85 wt%) IPNs.

3.3. The density properties

Fig. 5 illustrates the density versus the blocked PU content of blocked PU/VE IPNs. It is evident that the density of the IPNs decreased with the increasing blocked PU content. As shown in Fig. 6, the greater the filler content, the higher is the density of the IPNs. As shown in Fig. 7, the density of the IPNs increased as the initiator content of VE increased.

3.4. The thermal properties

The thermal resistance of the IPNs was measured by TGA. The behavior of weight loss by TGA over a range of temperature for various blocked PU/VE IPN compositions and for the individual polymer components is shown in Fig. 8. From this figure, it can be seen that the weight loss

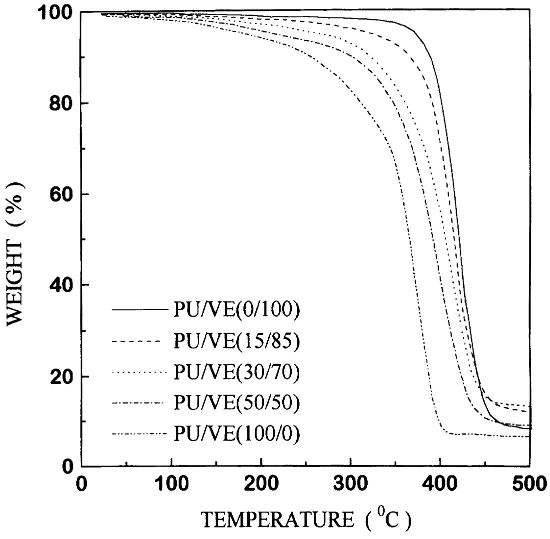


Fig. 8. Weight loss by thermogravimetric analysis versus temperature for various blocked PU/VE IPN compositions.

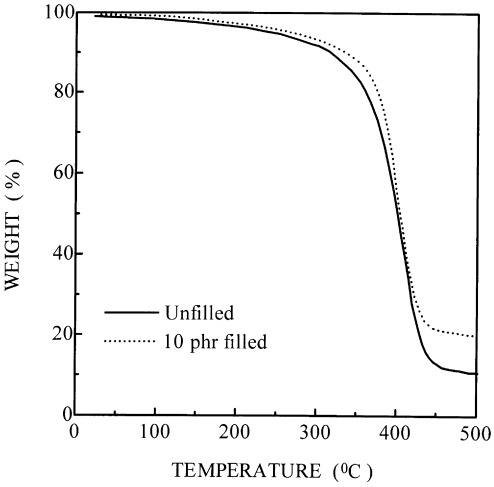
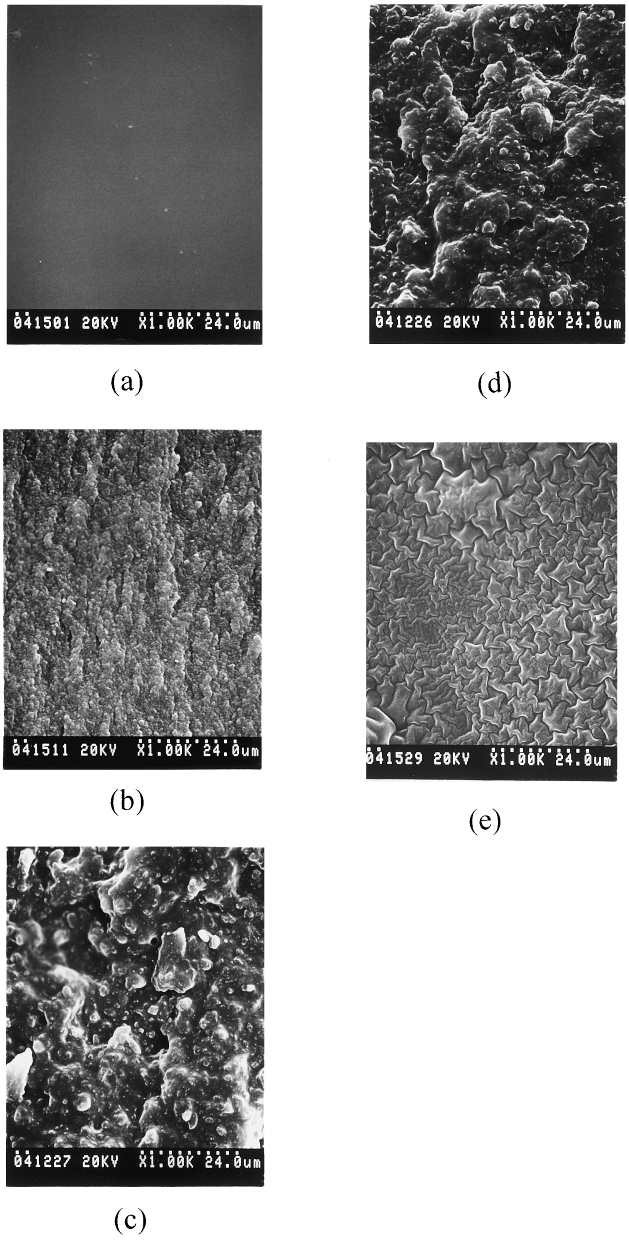


Fig. 9. Weight loss by thermogravimetric analysis versus temperature for unfilled (—) and 10 phr filled (kaolin) (···) of the blocked PU (40 wt%)/VE (60 wt%) IPNs.

increases with the increasing blocked PU content and temperature. When the blocked PU/VE compositions were set at 0/100, 15/85, 30/70, 50/50 and 100/0, the thermal degraded temperatures of the IPNs were 418, 406, 394, 387 and 365°C, respectively. Fig. 9 shows the weight loss by TGA over a range of temperatures for unfilled and 10 phr filled (kaolin parts per hundred parts of resin) of blocked PU (40 wt%)/VE (60 wt%) IPNs. From the figure, one can observe that the weight loss of the IPNs decreased with the increasing filler content. This means that the thermal resistance of the IPNs with the filler is better than that of without the filler.

3.5. Morphology

Fig. 10 showed the scanning electron micrographs of the fracture surface of the blocked PU/VE IPNs at various blocked PU contents. From Fig. 10(a), the pure VE expressed the smooth and glossy microstructure because it was a brittle material. From Fig. 10(e), the blocked PU exhibited a rough microstructure because it was a flexible material. From Fig. 10(b)–(d), when the blocked PU content increased, the microstructure of the IPNs became rougher. As the blocked PU content was above 50 wt%, the microstructure of the blocked PU/VE IPNs was dominated by the PU network. It was clearly found that when the blocked PU network and the VE network penetrated each other, there is an interpenetrating effect existing in the blocked PU/VE IPNs. The morphology study showed that the IPNs system was heterogeneous and more than one phase existed in the networks.



(a) (d) (b) (e) (c)

Fig. 10. The scanning electron micrographs of fracture surface of the blocked PU/VE IPNs of: (a) 0/100; (b) 30/70; (c) 50/50; (d) 65/35; (e) 100/0.

4. Conclusions

In this study, full blocked PU/VE IPNs were synthesized from the blends of the blocked NCO-terminated PU prepolymer with a chain extender and the VE prepolymer with an initiator using the SINs method. The conclusions of this study include the following subjects:

1. From the IR spectrum analysis, it was found that the major reactions in the blocked PU/VE IPNs system are the self-polymerization of the blocked PU/chain extender and the self-polymerization of the VE/initiator.
2. The swelling ratio of the blocked PU/VE IPNs increased with the increasing block PU content, and decreased with the increasing filler and initiator content of VE.

3. The density of the blocked PU/VE IPNs decreased with the increasing blocked PU content, and increased with the increasing filler and initiator content of VE.
4. The weight loss by TGA of the blocked PU/VE IPNs decreased with the increasing VE and filler content.
5. There is an interpenetrating effect existing in the blocked PU/VE IPNs. The morphology study showed that the IPNs system was heterogeneous and more than one phase existed in the networks.

Acknowledgements

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