Synthesis, Thermal Properties, and Morphology of Blocked Polyurethane/Epoxy Full-Interpenetrating Polymer Network

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ABSTRACT: Blocked polyurethane (PU)/epoxy full-interpenetrating polymer network (full-IPN) were synthesized from blocked NCO-terminated PU prepolymer, with 4,4-methylene diamine as a chain extender and epoxy prepolymer, with 4,4-methylene diamine as a curing agent, using simultaneous polymerization (SIN) method. From FTIR spectra analysis it was found that the major reactions in the blocked PU/epoxy IPN system are the self-polymerization of block PU/chain extender and the self-polymerization of epoxy/curing agent. Meanwhile, from reaction mechanisms the copolymerization of IPN may have occurred at the same time. The weight loss by thermogravimetric analysis decreased with increasing epoxy and filler content. It was confirmed from scanning electron micrography (SEM) that when the blocked PU content increased, the microstructure of IPN became rougher. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 323–328, 2006

Key words: interpenetrating polymer network (IPN); blocked polyurethane; epoxy; thermal properties; morphology

INTRODUCTION

The interpenetrating polymer network (IPN) is a unique type of polyblend; it is defined as a mixture of two or more crosslinked polymer networks that have partial or total physical interlocking between them[1–3]. IPNs can be viewed as the crosslinking of one component in the presence of another already crosslinked polymer network. Two types of IPN may be formed, depending on whether the polymer components are crosslinked or not that it can mainly be classified into full-IPN and semi-IPN.[4–7] A full-IPN are characterized by the presence of crosslinks in both network polymers, as shown in Figure 1(a); a semi-IPN exists when one of the components is crosslinked and another is linear, as shown in Figure 1(b). The various techniques for preparing IPN can be distributed into sequential polymerization (SIPN)[8,9] and simultaneous polymerization (SIN).[10–12] SIPN are obtained by swelling a polymer network I with a monomer mixture II, which is polymerized *in situ*. SIN polymerization is obtained by mixing all monomers or prepolymers and the curing agents together before either polymer is formed. Among the two modes of synthesis, the SIN is generally the best one to have a high degree of intermixing compared with the other processes due to the compatibility of the monomeric mixture, which is much higher than that of a polymeric mixture.[13]

The blocked polyurethane (PU)/epoxy system in this study serves as an excellent model SIN system and full-IPN of cross-blocked PU/cross-epoxy while giving good properties. The morphology of IPN is particularly complicated and has been subject to many studies.[14–16] 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, the present situation is frozen in.[14] With highly incompatible polymers, the phase separation is so serious that the gross phase separation occurs before gelation. The SIN process can demonstrate very fine micro-heterogeneous morphology. The other especially important and fundamental properties of polymer network is thermal behavior. The thermal properties reveal the heat resistance of various different IPN components.

In this study, the SIN method was used to synthesize blocked PU/epoxy full interpenetrating polymer network (full-IPN). The blocked NCO-terminated PU prepolymer with chain extender and epoxy prepolymer with curing agent mixed and reacted simultaneously at elevated temperature. The article is focused on the synthesized method, thermal properties, and morphology of blocked PU/epoxy full-IPN system.
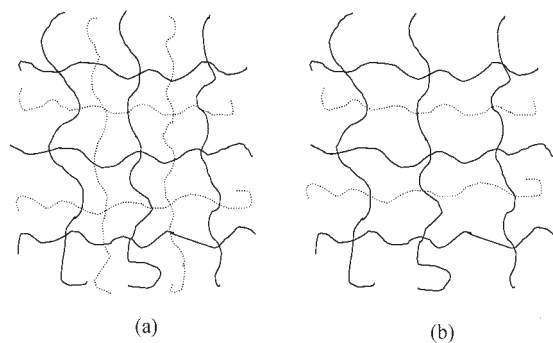
Figure 1 A schematic of (a) full-IPN; (b) semi-IPN.

EXPERIMENTAL

Materials

The materials used in this study are listed in Table I, including blocked NCO-terminated PU prepolymer, chain extender of PU, epoxy prepolymer, curing agent for epoxy polymerization, and 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.

Preparation of blocked PU/epoxy IPN samples

1. One equivalent of blocked NCO-terminated PU prepolymer with ε-caprolactam was heated to 70°C and then mixed with one equivalent of 4,4-methylene diamine homogeneously. The epoxy prepolymer was heated to 70°C and then mixed with one equivalent of 4,4-methylene diamine 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 surfaces of the stainless steel mold have been treated by chrome plating.
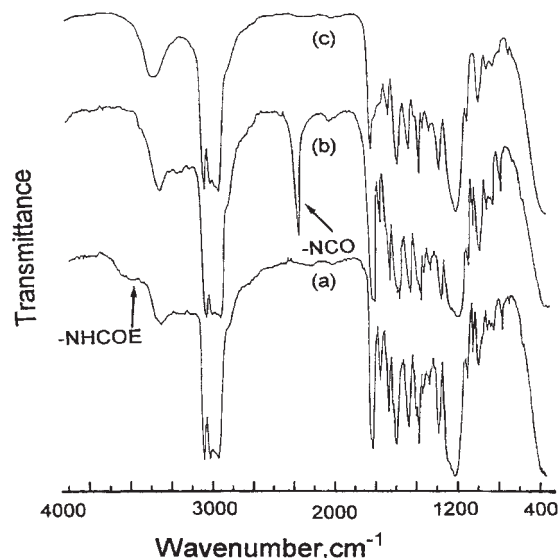

Figure 2 FTIR spectra of blocked PU with chain extender (4,4-methylene diamine) at reaction times of (a) 0; (b) 3 min; (c) 2 h and at a temperature of 145°C.

3. The mixture of mold was cured in an oven for 2 h and the temperature was maintained at 145°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 2 days before they were tested.

Equipment and measurement

1. Fourier Transform Infrared (FTIR) measurements were carried out with a Model FTIR-5300 (Jasco Co., Japan).
2. The weight loss of thermogravimetric analysis (TGA) was measured on a TG/DTA 300 (SEIKO Co., USA).
3. The SEM photographs were obtained on a *S*-570 Hitachi scanning electron microscope (Hitachi Co., Japan). The microphotographs were taken

TABLE I
Raw Materials

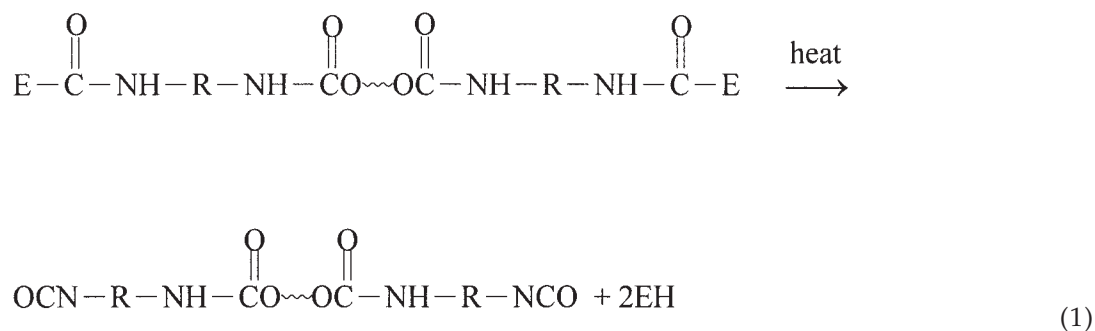| Material	Specification	Supplier
Epoxy prepolymer	BE-188; viscosity, 12 Pa · s at 25°C	Chang Chun Resin Co., Taiwan, ROC
Curing agent	4,4-methylene diamine $C_{13}H_{14}N_2$; melting point, 91.5–92°C; boiling point, 398–399°C	Anchor, UK
PU prepolymer	Blocked NCO-terminated PU Prepolymer; viscosity, 31,000 mPa · s; M_w, 4230; equivalent weight, 1410	Bayer, Germany
Chain extender	4,4-methylene diamine $C_{13}H_{14}N_2$; melting point, 91.5–92°C; boiling point, 398–399°C	Anchor, UK
Filler	$CaCO_3$; specific gravity, 2.7; particle size, 2.02 μm	Yin Chin Co., Taiwan, ROC

on the surface obtained by fracturing the specimen in liquid nitrogen and then coating it with gold powder.

RESULTS AND DISCUSSION

Synthesis of blocked PU/epoxy IPN

The reaction mechanism can be described by FTIR analysis. The FTIR spectroscopy analysis is based on the peak change of functional groups during the reaction period. Figure 2 shows FTIR spectra of blocked NCO-terminated PU with chain extender (4,4-methylene diamine) at various reaction times and at a temperature of 145°C. The spectrum of Figure 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 blocking agent (ε-caprolactam). After reaction for 3 min at 145°C, as shown in Figure 2(b), the absorption peak intensity of NCO at 2270 cm^{-1} appeared obviously, and the absorption peak of -NHCOE- at 3550–3650 cm^{-1} disappeared. From the spectrum in Figure 2(c), one can observe that the absorption peak intensity at 2270 cm^{-1} (NCO) disappeared obviously 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 be reacted with chain extender (4,4-methylene diamine). Therefore, the reaction process is almost completed in the second hour. The deblocking reaction process of blocked PU was described by eq. (1)

$$E-\overset{O}{\underset{\|}{C}}-NH-R-NH\text{--}\overset{O}{\underset{\|}{CO}}\leadsto\overset{O}{\underset{\|}{OC}}-NH-R-NH-\overset{O}{\underset{\|}{C}}-E \quad \xrightarrow{\text{heat}}$$

$$OCN\text{--}R-NH-\overset{O}{\underset{\|}{CO}}\leadsto\overset{O}{\underset{\|}{OC}}-NH-R-NCO\ +2EH \tag{1}$$

Where the blocking agent (EH) is ε-caprolactam. The free NCO groups can easily be reacted with chain extender (4,4-methylene diamine). The reaction process was described by eq. (2)
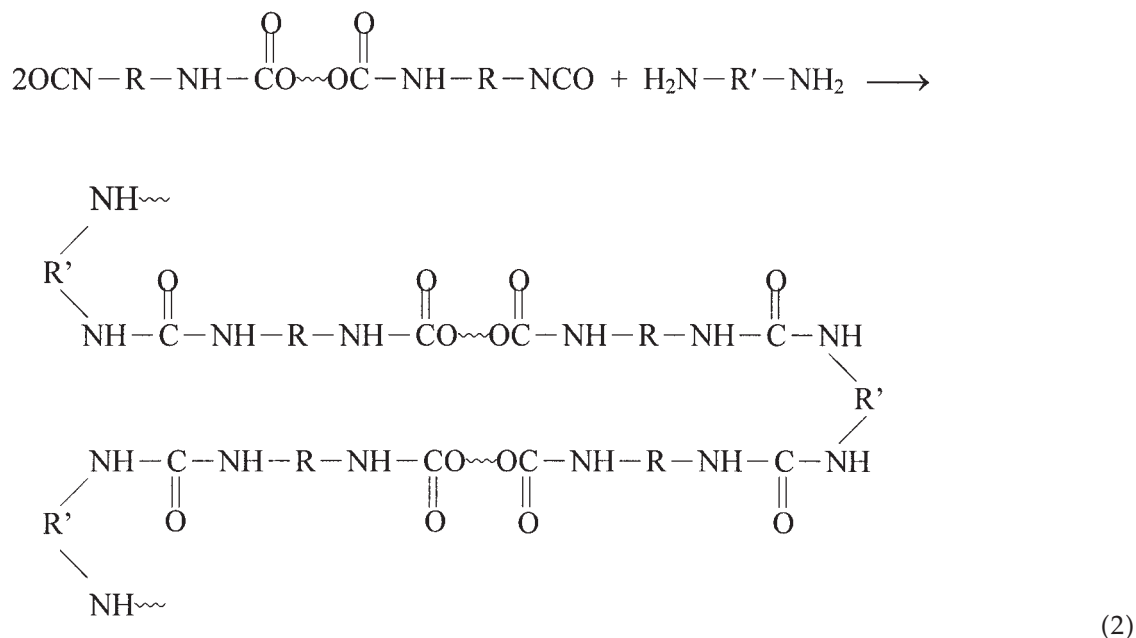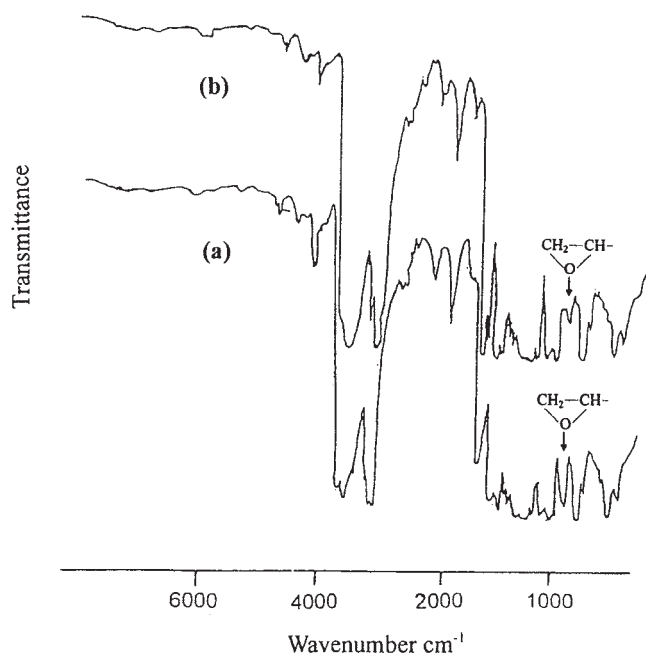
$$2OCN-R-NH-\overset{O}{\underset{\|}{CO}}\leadsto\overset{O}{\underset{\|}{OC}}-NH-R-NCO\ +\ H_2N-R'-NH_2 \longrightarrow$$

$$\begin{array}{c}
NH\leadsto \\
/ \\
R' \\
\backslash \\
NH-\overset{O}{\underset{\|}{C}}-NH-R-NH-\overset{O}{\underset{\|}{CO}}\leadsto\overset{O}{\underset{\|}{OC}}-NH-R-NH-\overset{O}{\underset{\|}{C}}-NH \\
\backslash \\
R' \\
/ \\
NH-\overset{}{C}\text{--}NH\text{--}R-NH-\overset{}{CO}\leadsto\overset{}{OC}-NH-R-NH-\overset{}{C}-NH \\
/ \quad \| \qquad\qquad\quad \| \quad \| \qquad\qquad\qquad \| \\
R' \quad O \qquad\qquad\quad O \quad O \qquad\qquad\qquad O \\
\backslash \\
NH\leadsto
\end{array} \tag{2}$$

Figure 3 illustrates that the FTIR spectra of epoxy mixed with one equivalent of curing agent (4,4-methylene diamine) at (a) $t = 0$; (b) $t = 2$ h and a temperature of 145°C. From Figure 3, one can observe that the

Figure 3 FTIR spectra of epoxy with curing agent (4,4-methylene diamine) at reaction times of (a) 0; (b) 2 h, and at a temperature of 145°C.

absorption peak intensity of $\underset{CH_2{-}CH-}{\overset{O}{\diagup\;\diagdown}}$ at 915 cm^{-1} of epoxy at $t = 2$ h decrease compared with the corresponding peak of the epoxy at $t = 0$ h during the reaction. Therefore, the reaction process is almost complete in 2 h at 145°C. The polymerization of epoxy was represented by eqs. (3)–(5)

$$RNH_2 \;+\; \overset{O}{CH_2{-}CH}\rightsquigarrow \;\rightarrow\; RNH{-}CH_2\underset{OH}{CH}\rightsquigarrow \tag{3}$$

$$RNH{-}CH_2\underset{OH}{CH}\rightsquigarrow \;+\; \overset{O}{CH_2{-}CH}\rightsquigarrow \;\rightarrow\; RN\!\begin{array}{l}\overset{OH}{CH_2{-}CH}\rightsquigarrow\\[4pt] CH_2{-}\underset{OH}{CH}\rightsquigarrow\end{array} \tag{4}$$

$$\rightsquigarrow\underset{OH}{CH}\rightsquigarrow \;+\; \overset{O}{CH_2{-}CH}\rightsquigarrow \;\rightarrow\; \begin{array}{l}\rightsquigarrow CH\rightsquigarrow\\[2pt] OCH_2{-}\underset{OH}{CH}\rightsquigarrow\end{array} \tag{5}$$
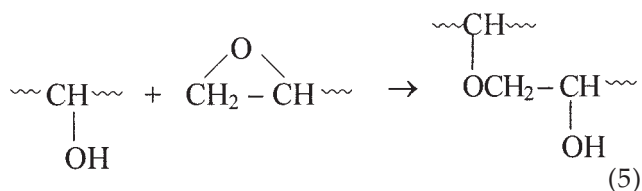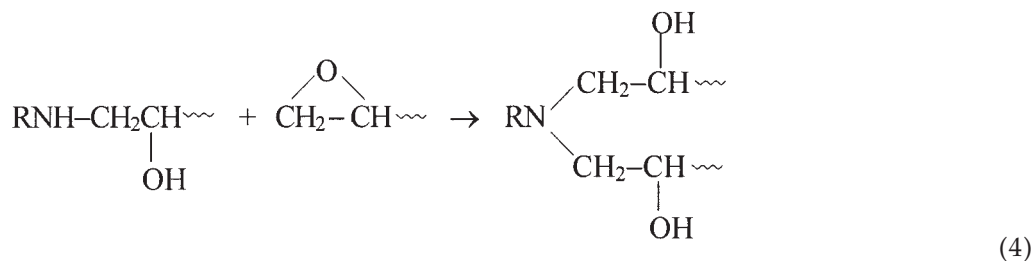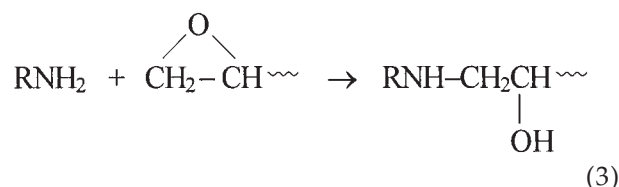
Figure 4 shows the FTIR spectra of the reaction system of blocked PU and epoxy at various reaction times of 145°C. From the figure, there was no absorption peak intensity of NCO at 2270 cm^{-1} and having absorption peak intensity of $\underset{CH_2{-}CH-}{\overset{O}{\diagup\;\diagdown}}$ at 915 cm^{-1} 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 $\underset{CH_2{-}CH-}{\overset{O}{\diagup\;\diagdown}}$ at 915 cm^{-1} disappeared slightly. After heating at 145°C for 2 h, about 90% of the absorption peak of NCO at 2270 cm^{-1} and $\underset{CH_2{-}CH-}{\overset{O}{\diagup\;\diagdown}}$ at 915
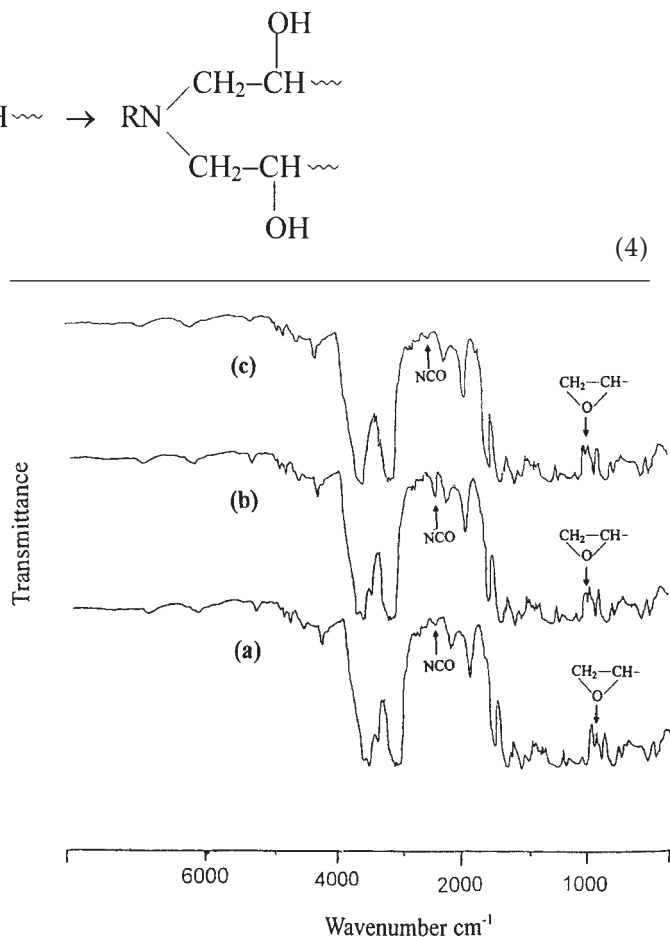

**Figure 4** FTIR spectra of blocked PU and epoxy at reaction times of (a) 0; (b) 3 min; (c) 2 h and at a temperature of 145°C.
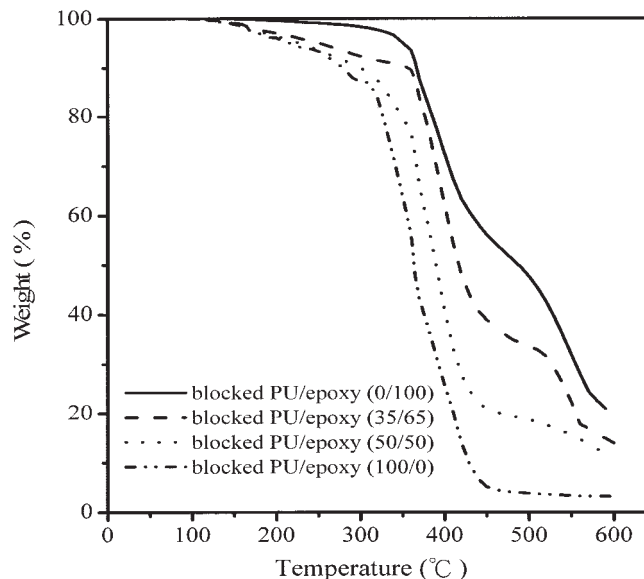
Figure 5 Weight loss by thermogravimetric analysis versus temperature for various blocked PU/epoxy IPN compositions.

cm^{-1} disappeared during the same time. From the earlier mentioned FTIR spectrum analysis, it was found that the major reactions in the blocked PU/epoxy system are the self-polymerization of blocked PU/chain extender and the self-polymerization of epoxy/curing agent. Meanwhile, from reaction (2) and reaction (3) the copolymerization may have occurred at the same time.
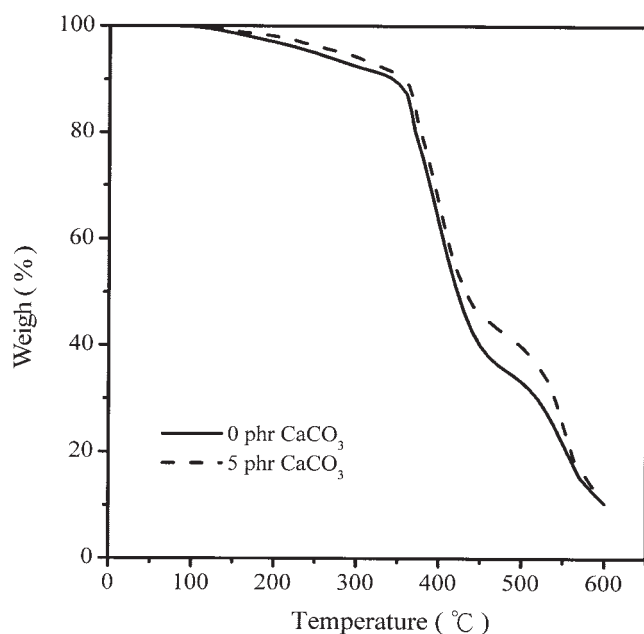
Figure 6 Weight loss by thermogravimetric analysis versus temperature for unfilled and 5 phr filled (CaCO$_3$) of blocked PU (35 wt %)/epoxy(65 wt %) IPN.
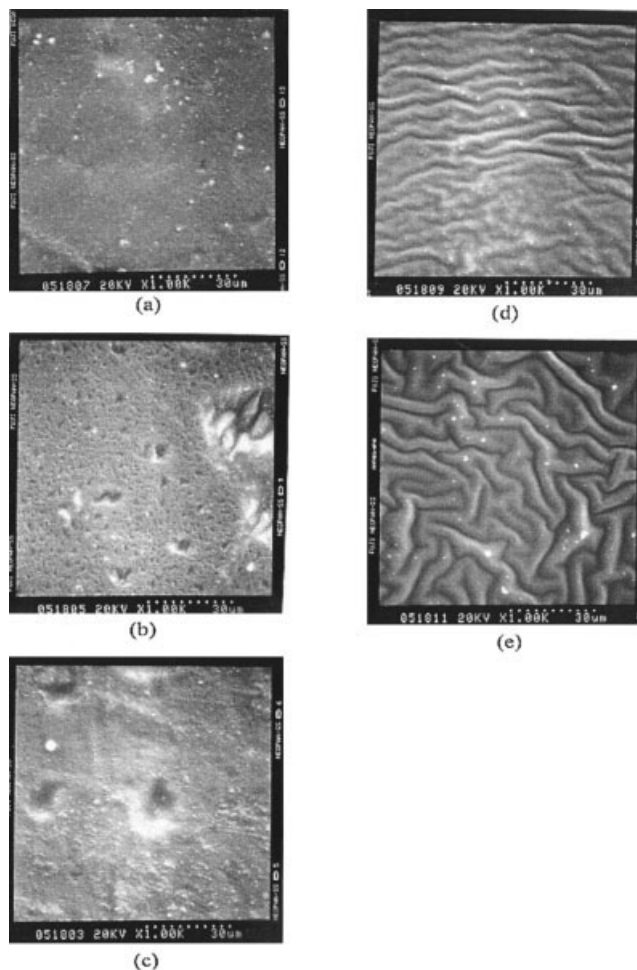
Figure 7 Scanning electron micrographs (SEM) of fracture surface of the blocked PU/epoxy IPN of (a) 0/100; (b) 25/75; (c) 50/50; (d) 75/25; (e) 100/0.

The thermal properties

The thermal resistance of IPN was measured by means of TGA. The behavior of weight loss by TGA over a range of temperature for various blocked PU/epoxy IPN compositions and for the individual polymer components was shown in Figure 5. From this figure, it can be seen that the weight loss increase with increasing blocked PU content and temperature. When the blocked PU/epoxy compositions were set at 0/100, 35/65, 50/50, and 100/0, the thermal degraded temperatures of IPN were 367, 355, 301, and 281°C, respectively. The thermal degraded temperature is defined as that the weight loss of IPN is 10%. Figure 6 shows the weight loss by TGA over a range of temperature for unfilled and 5 phr filled (CaCO$_3$ parts per hundred parts of resin) of blocked PU (35 wt %)/ epoxy (65 wt %) IPN. From the figure, one can observe that the weight loss of IPN decreased with increasing filler. From Figure 6, one can observe that the degraded temperature of IPN is 360°C with 5 phr CaCO$_3$ and is 350°C without CaCO$_3$. This means that the

thermal resistance of IPN with filler is better than that without filler.

Morphology

Figure 7 showed the scanning electron micrographs of fracture surface of the blocked PU/epoxy IPN at various blocked PU contents. From the Figure 7(a), the pure epoxy expressed the smooth and glossy microstructure because they were brittle materials. From the Figure 7(e), the blocked PU exhibited the rough microstructure because they were flexible materials. From the Figures 7(b)–7(d), when the blocked PU content increased, the microstructure of IPN became rougher.

CONCLUSIONS

In this study, full-blocked PU/epoxy IPN were synthesized from the blends of blocked NCO-terminated PU prepolymer with chain extender and epoxy prepolymer with curing agent, using SIN method.

From FTIR spectrum analysis, it was found that the major reactions in the blocked PU/epoxy IPN system are the self-polymerization of blocked PU/chain extender (4,4-methylene diamine) and the self-polymerization of epoxy/curing agent (4,4-methylene diamine). Meanwhile, from reaction mechanisms the copolymerization of IPN may have occurred at the same time. The weight loss by thermogravimetric analysis

of blocked PU/epoxy IPN decreased with increasing epoxy and filler content. There is an interpenetrating effect existing in the blocked PU/epoxy IPN. It was confirmed from SEM that when the blocked PU content increased, the microstructure of IPN became rougher.

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