

# Effects of Reaction and Cure Temperatures on Morphology and Properties of Poly(ester-urethane)

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**ABSTRACT:** Poly(ester-urethane) was synthesized from poly(ethylene glycol adipate) (PEG) and 2,4-toluene diisocyanate (TDI) to study the effects of reaction temperature and cure temperature on the crystallization behavior, morphology, and mechanical properties of the semicrystalline polyurethane (PU). PEG as soft segment was first reacted with TDI as hard segment at 90, 100, and 110°C, respectively, to obtain three kinds of PU prepolymers, coded as PEPU-90, PEPU-100, and PEPU-110. Then the PU prepolymers were crosslinked by 1,1,1-tris (hydroxymethyl) propane (TMP) and were cured at 18, 25, 40, 60, and 80°C. Their structure and properties were characterized by attenuated total reflection Fourier transform infrared, wide-angle X-ray diffraction, scanning electron microscopy, dynamic mechanical analysis, and tensile testing. With an increase of the reaction temperature from 90 to 100°C, the crystallinity degree of soft segment decreased, but interaction between soft and hard

segments enhanced, leading to the increase of the glass transition temperature ( $T_g$ ) of soft domain and tensile strength. When the cure temperature was above 60°C, miscibility between soft and hard segments of the PEPU films was improved, resulting in relatively low crystallinity and elongation at break, but high soft segment  $T_g$  and tensile strength. On the whole, all of the PEPU-90, PEPU-100, and PEPU-110 films cured above 60°C possessed higher tensile strength and elongation at break than that of the films cured at other temperatures. The results revealed that the reaction temperature and cure temperature play an important role in the improvement of the crosslinking structure and mechanical properties of the semicrystalline PU. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 708–714, 2006

**Key words:** poly(ester-urethane); miscibility; crystalline; reaction temperature; cure temperature

## INTRODUCTION

Polyurethanes (PUs) have been constituted as one of the most interesting classes of synthetic copolymers composed of soft and hard segments, which can vary from rubbery materials to glassy thermoplastics and from being linear polymers to being thermosetting plastics.<sup>1,2</sup> As a result of their excellent tensile strength, flexibility, fatigue resistance, and biocompatible nature, PUs are used in a wide variety of products in the medical, automotive, and industrial fields,<sup>3–5</sup> and has been found to be susceptible to biodegradation by microorganisms.<sup>6</sup> It is generally agreed that the unique mechanical properties of PU are predominantly influenced by the phase separation resulting from the incompatibility of the soft and hard segments.<sup>7–9</sup> Factors that control the degree of microphase separation include copolymer composition, block length, crystallization of either segment, the synthesis conditions, and thermal history.<sup>10–14</sup> According

to the different types of polyols as soft segment, which are used to react with isocyanate, PU can be divided into poly(ester-urethane) and poly(ether-urethane),<sup>15</sup> in which the former has better biodegradability.<sup>6</sup> However, the studies on the polyester-based systems have been scarcely published.<sup>16</sup> In the case of polyester-based polyurethane-segmented block copolymers, both ester and urethane carbonyl groups are the potential hydrogen bonding acceptors, leading to the obscure  $\text{—C=O}$  absorption patterns and analysis difficulty of the system.

The economic importance of PU based on 2,4-toluene diisocyanate (TDI) and a polyester macroglycol drives the interest of this particular class of PU elastomers. It has been reported that a two-step method includes the polyol end-capped with excess diisocyanate, followed by chain extension with stoichiometric amount of chain extender.<sup>17</sup> Furthermore, the reaction temperatures 90, 100, and 110°C were chosen because they correspond to the range generally used in most applications.<sup>14</sup> However, the effect of the cure temperatures on the morphology and properties of the final products has not been studied. In the present work, by changing the processing conditions of the poly(ester-urethane), the crystallization behavior, morphology, and mechanical properties of the semicrystalline PU were investigated and discussed.

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## EXPERIMENTAL

### Preparation of poly(ester-urethane) films

The poly(ester-urethane) prepolymer was prepared by the reaction of macrodiol as soft segments with excess of diisocyanate as hard segments. The reaction was carried out in the melt at 90, 100, and 110°C. The value of [NCO]/[OH] was predetermined theoretically to be 1. Poly(ethylene glycol adipate) (PEG; 66.5 g;  $M_n = 2499$ ; Tiangou Polyurethane Factory, Jiangsu, China) was vacuum-dried for 5 h at 110°C before use. Its acid value (mg KOH/g) and OH value (mg KOH/g) were 0.20 and 44.7, respectively. Commercial TDI (11.6 g; Shanghai Chemical Co., Shanghai, China) was redistilled under reduced pressure to be dehydrated before use, and then dropped into the PEG melt at 90, 100, and 110°C for 2 h to obtain the PU prepolymer. Then, 35 g of 2,2-bis(hydroxymethyl) propionic acid (Chengdu Polyurethane Factory, Sichuan, China; vacuum-dried for 2 h at 110°C) was added into the prepolymer to continue the chain-extending reaction at the designed temperature for another 1 h until the NCO groups content reached a given value, determined by dibutylamine back titration.<sup>2</sup> After the mixture was cooled to 40°C, 90 g of THF was added to adjust the solid content of the resulting mixture to 40 wt %. Three kinds of the resultant PU prepolymers were coded as PEPU-90, PEPU-100, and PEPU-110, respectively.

In the presence of curing agent, the curing reaction was carried out for 24 h. 1,1,1-Tris(hydroxymethyl) propane (TMP; Shanghai Chemical Co., Shanghai, China) was dried until the moisture content was less than 0.1 wt %, and was then used as the crosslinker of the PU prepolymer. The amount of TMP was 2.5 wt % of the solid content of PU prepolymer. The mixture solutions of TMP and PU prepolymer were cast on the glass plate and cured at 18, 25, 40, 60, and 80°C for 24 h. To ensure the complete elimination of the solvent, the resultant films were dried at 60°C for 2 h. The films were kept at room temperature for at least 2 weeks before the measurements. The PEPU-90, PEPU-100, and PEPU-110 films were cured at 18, 25, 40, 60, and 80°C, and coded as PEPU-90-18, PEPU-90-25, PEPU-90-40, PEPU-90-60, and PEPU-90-80 for the reaction temperature ( $T_{rea}$ ) of 90°C; PEPU-100-18, PEPU-100-25, PEPU-100-40, PEPU-100-60, and PEPU-100-80 for the  $T_{rea}$  of 100°C; and PEPU-110-18, PEPU-110-25, PEPU-110-40, PEPU-110-60, and PEPU-110-80 for the  $T_{rea}$  of 110°C, respectively.

### Characterization

Attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy was carried out on a spectrometer (Thermo Nicolet 670, Nicolet, USA). Spectra in the wavenumber range of 4000–500  $\text{cm}^{-1}$  were

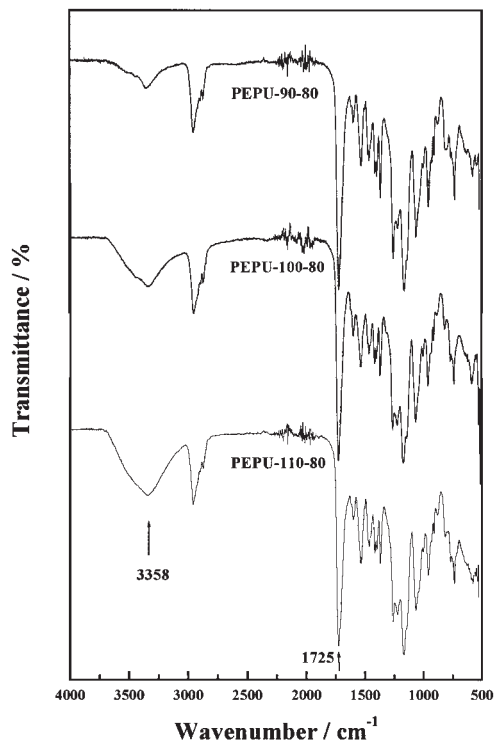
collected over 64 scans with a resolution of 4  $\text{cm}^{-1}$ . The measurements were made at room temperature on a diamond, using a variable-angle ATR unit at a nominal incident angle of 45°. Optical alignment of the unit was set to achieve maximum throughput of the infrared beam to the detector. The samples were taken at random from the flat films. Scanning electron microscopy (SEM) images of the films were taken with a microscope (X-650, Hitachi, Japan). The films were frozen in liquid nitrogen and snapped immediately, and then vacuum-dried. The surface and the cross section of the films were sputtered with gold, and then observed and photographed. Wide-angle X-ray diffraction (WAXD) was recorded on an X-ray diffraction (XRD-6000, Shimadzu, Japan) by using Cu  $K\alpha$  radiation ( $\lambda = 15.405$ ) at 40 kV and 30 mA with a scan rate of 4°/min. The diffraction angle ranged from 5° to 35°.

Dynamic mechanical analysis (DMA) was carried out with a dynamic mechanical thermal analyzer (DMTA-V, Rheometric Scientific Co.) at 1 Hz and at a heating rate of 5°C/min in the temperature range from 25 to 80°C. The specimens with typical size of 10 × 10  $\text{mm}^2$  (length × width) were used here. Tensile strength and elongation at break of the films were measured on a versatile tester (CMT-6503, Shenzhen SANS Test Machine Co. Ltd., Shenzhen, China), according to the ISO6239–1986 standard, with a tensile rate of 5 mm/min. The size of the films was 70 mm length, 10 mm width, with 50 mm distance between two clamps. Five parallel measurements were carried out for every sample.

## RESULTS AND DISCUSSION

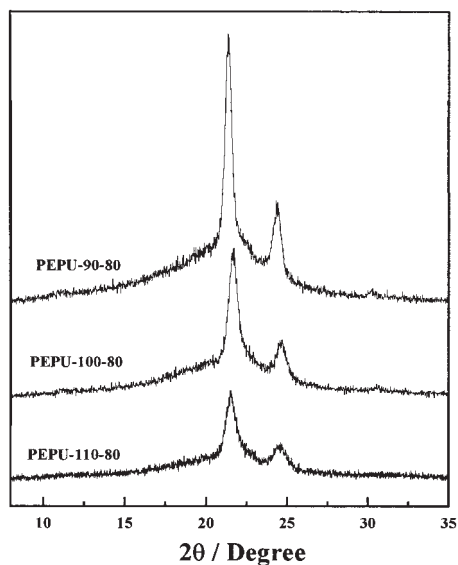
### Effects of reaction temperature on the morphology and properties of PU

To concentrate on the effects of reaction temperature on the PU films, the PU prepolymers were synthesized at different temperatures ranging from 90 to 110°C and then cured at 80°C. PUs are capable of forming several kinds of hydrogen bonds. In all cases, the NH group in the urethane linkage is the donator proton, while the acceptor groups may include urethane containing C=O as well as C=O of the ester linkage in polyester. Almost all of the infrared researches on PU have been focused on two principal vibration regions, namely the NH stretching vibration and the C=O stretching vibration.<sup>18–23</sup> Figure 1 shows the infrared spectra (4000–500  $\text{cm}^{-1}$ ) of PEPU-90-80, PEPU-100-80, and PEPU-110-80 films. For the PU films, the band at 1725  $\text{cm}^{-1}$  is attributed to the free urethane carbonyl stretching vibrations, and the peak centered at 3358  $\text{cm}^{-1}$  corresponds to NH bonded to carbonyl groups. The peak heights of the 1725  $\text{cm}^{-1}$  stretching band decreases in the order of PEPU-110-80 < PEPU-100-80 < PEPU-90-80, indicating that the strength of

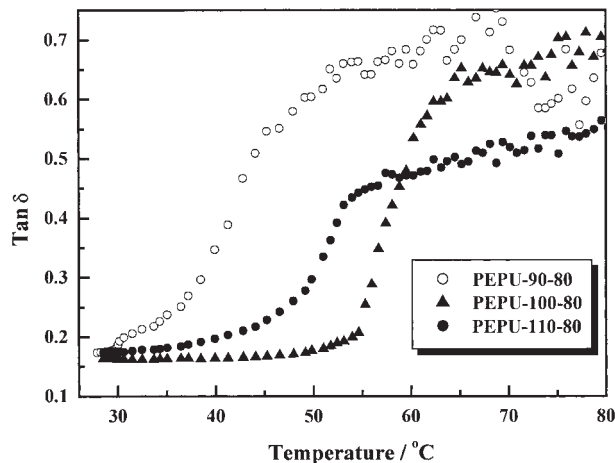


**Figure 1** ATR-FTIR spectra of the PEPU-90-80, PEPU-100-80, and PEPU-110-80 films.

hard segments hydrogen-bonding decreases sequentially from PEPU-90-80 to PEPU-110-80. A reverse behavior has been observed in the stretching band of NH at  $3358\text{ cm}^{-1}$ , which increases in the order of PEPU-110-80 > PEPU-100-80 > PEPU-90-80. The results suggest that the phase mixing between the



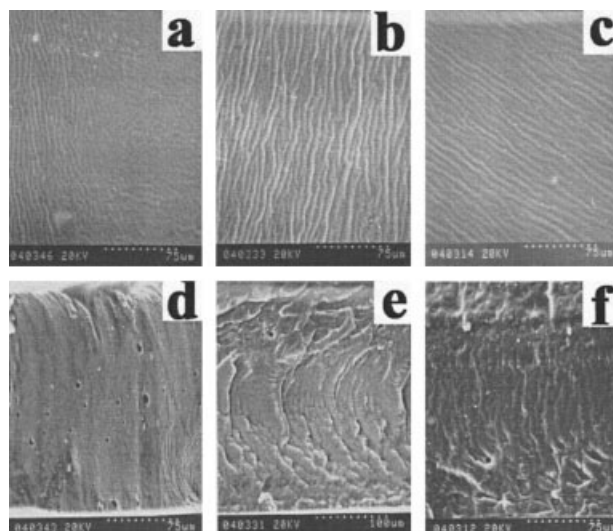
**Figure 2** WAXD spectra of the PEPU-90-80, PEPU-100-80, and PEPU-110-80 films.



**Figure 3**  $\text{Tan } \delta$  as a function of temperature for the PEPU-90-80, PEPU-100-80, and PEPU-110-80 films.

hard and the soft segments of PU enhances with an increase of the reaction temperature.

To evaluate the crystalline state of the films, the data from WAXD measurements are shown in Figure 2. In PUs containing crystalline soft segments and amorphous hard segments, the X-ray scattering is contributed mainly from the crystalline soft segments.<sup>21</sup> In Figure 2, all the WAXD patterns of the PU films show the presence of two major peaks at  $2\theta = 22.02^\circ$  and  $24.58^\circ$ . The two peaks are sharp, corresponding to the order arrangement of PU polyester soft segment. The intensities of the peaks apparently decrease with an increase of the reaction temperature. This explains that the hard segments act as physical crosslinks, and the crosslinking reaction has occurred during the chain-



**Figure 4** SEM photographs for the PEPU-90-80 (surface (a) and cross section (d)), PEPU-100-80 (surface (b) and cross section (e)), and PEPU-110-80 (surface (c) and cross section (f)) films.

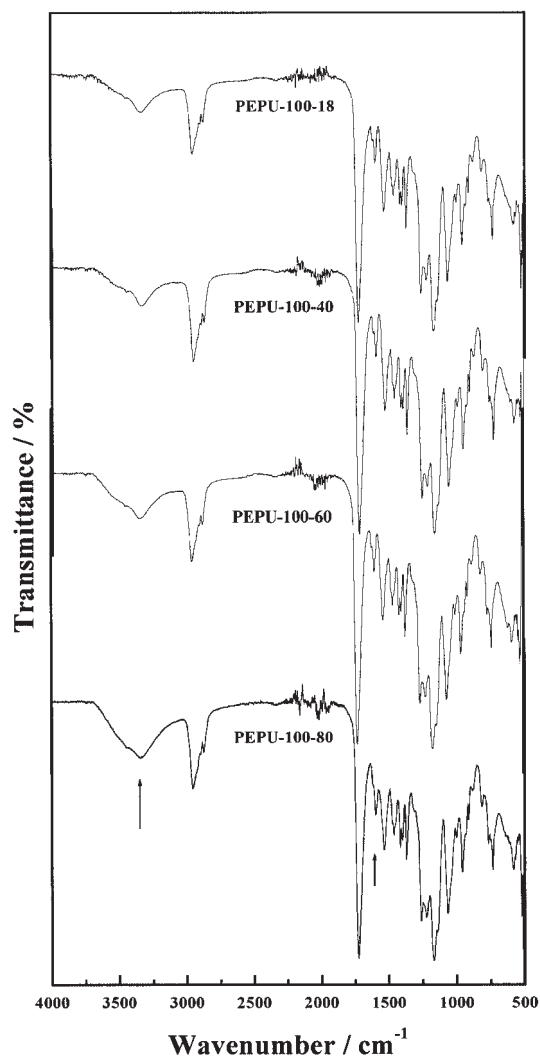


Figure 5 ATR-FTIR spectra for the PEPU-100 films.

extending, resulting in a slower mobility of the soft segments. Generally, when the crystalline component and the amorphous component in a composite material are miscible, its crystallinity index is lower than that of the individual crystalline component.<sup>24,25</sup> Therefore, the decrease of the crystallinity in the PU films suggests a stronger interaction between hard and soft segments to destroy the ordered soft segment, leading to the decrease of the intermolecular packing in the small crystalline domains.

Usually, the  $\alpha$ -relaxation, mechanical loss factor ( $\tan \delta$ ) peak in the DMA thermogram, reflects the glass transition, and may be analyzed to provide information about the motion of molecules. The height and width of the  $\alpha$ -relaxation peak may also be analyzed for the copolymer to observe trends in the crosslink density and network homogeneity.<sup>17,26</sup> The temperature dependence of  $\tan \delta$  from DMA is given in Figure 3, and this illustrates about the peaks associated with glass transition ( $T_g$ ) and

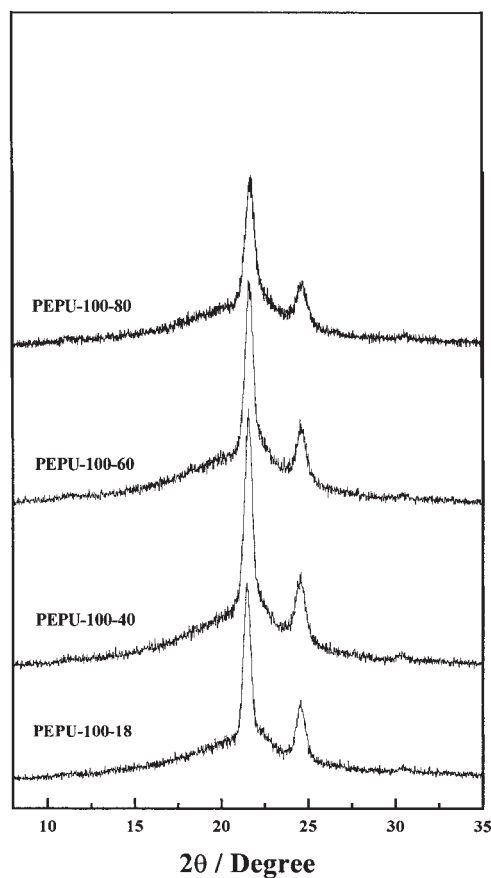


Figure 6 WAXD spectra for the PEPU-100 films.

damping capacity of soft segments.<sup>26</sup> The  $T_g$  values for all films range from 50 to 70°C for the PU films. The shift of transition regions to higher temperature with an increase of reaction temperature from 90 to 100°C can be attributed to the greater amount of hard segments dissolved in the soft segments as a

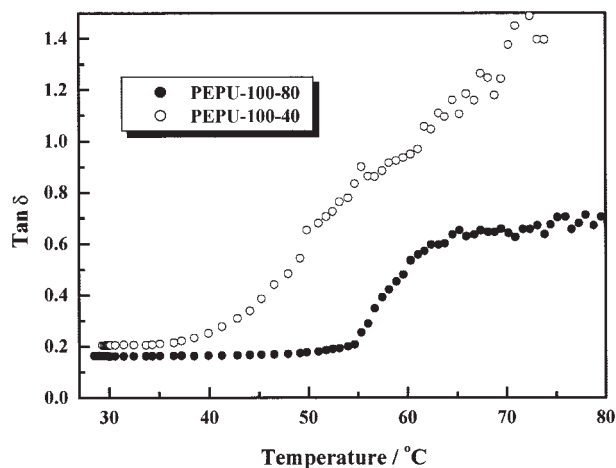
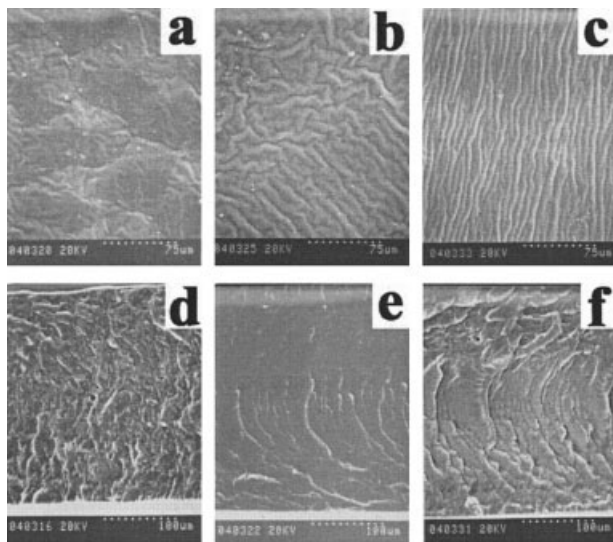


Figure 7  $\tan \delta$  as a function of temperature for the PEPU-100 films.



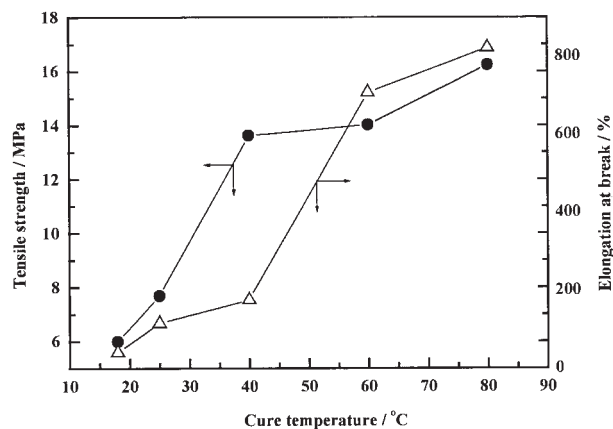
**Figure 8** SEM photographs for the PEPU-100-18 (surface (a) and cross section (d)), PEPU-100-60 (surface (b) and cross section (e)), and PEPU-100-80 (surface (c) and cross section (f)) films.

result of phase mixing between the hard and soft segments. Moreover, as the temperature further increases to 110°C, the intensity of  $\tan \delta$  peak of the PEPU-110-80 film decreases, and the transition region shifts to lower temperature compared with that of PEPU-100-80 film. This suggests that the phase separation between the hard segments and soft segments has enhanced.<sup>17</sup>

Image from scanning electron microscopy is the proof that the system is miscible. Figure 4 shows the SEM photographs of the surfaces and cross sections of PU films. The morphology of PEPU-90-80 is smooth and indicative of a more homogeneous structure. However, the PEPU-100-80 and PEPU-110-80 films display a rather rough surface and cross section. It has been reported that the heterogeneous nature of the materials gives rise to a bimodal distribution of the hard segment.<sup>27</sup> Zawadski and Akcelrud have suggested that rich regions of the hard segment could coexist and be partially dispersed in the soft segmental matrix.<sup>28</sup> Therefore, at elevated temperature, the PEPU-100-80 and PEPU-110-80 films exhibit two phase morphologies containing a continuous, namely, soft rubbery matrix in which hard segments are distributed.

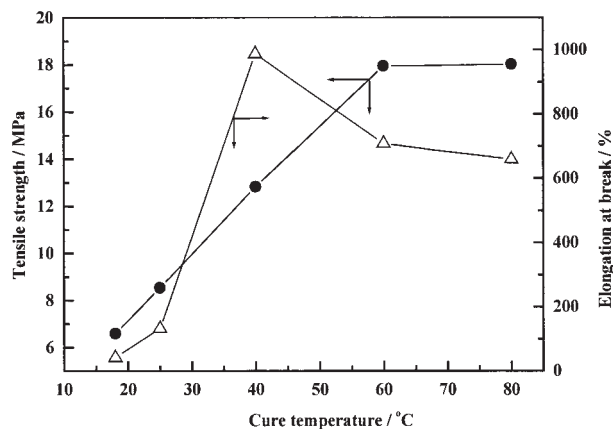
#### Effects of cure temperature on the morphology and properties of PU

To focus on the effects of cure temperature on the morphology and properties of PU films, we have taken PEPU-100 prepolymer prepared at 100°C and cured at the temperature range from 18 to 80°C for 24 h. Hydrogen bonding in PUs has been the subject of

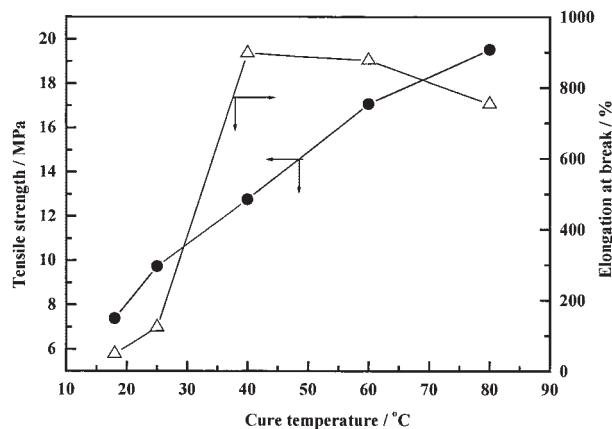


**Figure 9** Effects of cure temperature on the tensile strength (●) and elongation at break (Δ) for the PEPU-90 films.

numerous investigations using infrared spectroscopy, indicating that both the frequency shifts and intensity changes are characteristics of the specificity magnitude of the hydrogen bonds formed.<sup>21-23</sup> Figure 5 shows the infrared spectra of the PEPU-100-18, PEPU-100-40, PEPU-100-60, and PEPU-100-80 films. The intensities of hydrogen-bonded -NH centered at 3358  $\text{cm}^{-1}$  for the films increase as cure temperature increases, suggesting that the phase mixing between the hard and soft segments enhances. For the PU films, the band at 1640  $\text{cm}^{-1}$  is attributed to the hydrogen-bonded C=O formed from the polyester soft segment. The intensities of the peaks are almost the same as or slightly lower than that for the PU films when the cure temperature increases from 18 to 60°C, suggesting that the ordered soft segment structure hardly changes. As the cure temperature further increases to 80°C (above the  $T_g$  of soft segment), the intensity of the peak decreases apparently as a result of the crosslinking caused by the



**Figure 10** Effects of cure temperature on the tensile strength (●) and elongation at break (Δ) for the PEPU-100 films.



**Figure 11** Effects of cure temperature on the tensile strength (●) and elongation at break (△) for the PEPU-110 films.

cure reaction and intermolecular interaction between hard and soft segments. Therefore, the cure temperature at 80°C dominantly influences the crystalline morphology of the PEPU-100 films.

In Figure 6, the WAXD patterns of the PEPU-100-18, PEPU-100-40, PEPU-100-60, and PEPU-100-80 films show two major intense peaks at  $2\theta = 22.02^\circ$  and  $24.58^\circ$ . Both peaks are sharp, corresponding to the order arrangement of PU polyester soft segment.<sup>21</sup> As the temperature increases from 18 to 60°C, the intensities of the peaks are almost the same as or slightly lower than that for the PU films, suggesting no change in crystallinity of soft segment. The intensity of the peak decreases apparently with an increase of the cure temperature further to 80°C (above the  $T_g$  of soft segment). Therefore, when the cure temperature is above 60°C, the strong intermolecular interactions between hard and soft segments for the PU films are supposed to retard the arrangement of the molecular chains in a regular manner for polyester soft domain. This supports the results from the infrared analysis.

Figure 7 shows  $\tan \delta$  as a function of temperature for the PEPU-100 films. When the cure temperature increases from 40 to 80°C for the PEPU-100 films, the height of the  $\tan \delta$  peaks decreases. Because  $\tan \delta$  is the ratio of viscous to elastic moduli, it can be surmised

that the decreasing height is related to a lower segmental mobility of soft segments. Thus it is indicative of a higher degree of crosslinking of hard segments at elevated cure temperature in presence of the cure agent TMP. Moreover, high concentration of crosslinks for the hard segments could inhibit the intermolecular packing of the soft segments, resulting in the shift of transition regions to higher temperature with an increase of cure temperature.

The SEM images of the PEPU-100-18, PEPU-100-60, and PEPU-100-80 films are shown in Figure 8. All of the films display rather rough surfaces and cross sections. However, the morphology of cross section for the PEPU-100-60 film is relatively homogenous compared with other films, indicating a relatively dense architecture in the inner structure. This implies that strong intermolecular interaction has occurred between the hard and soft segments for the PEPU-100-60 film, leading to a good miscibility.

### Mechanical properties of PU

It is important that good mechanical properties of PU are required in many applications. The mechanical properties of PU are influenced by a number of inter-related system parameters, including  $T_g$ , molecular weight between crosslinking point, chemical structure, phase separation, and many other contributing factors.<sup>29</sup> Seymour and Cooper assumed that the phase separation is responsible for the mechanical properties.<sup>30</sup> The mechanical properties of the PEPU-90, PEPU-100, and PEPU-110 films are shown in Figures 9, 10, and 11, respectively, and the experiment data are summarized in Table I. The tensile strength ( $\sigma_b$ ) values for the PEPU-90 films increase from 5.99 to 16.2 MPa, and elongation at break ( $\epsilon_b$ ) increases from 40.6 to 822% with an increase of cure temperature from 18 to 80°C, this suggested that the degree of crosslinking further increased at elevated cure temperature. The  $\sigma_b$  values of both PEPU-100 and PEPU-110 films increase with an increase of cure temperature. Therefore, the addition of TMP molecules allows the network to be formed and tightened, leading to an improvement of the tensile strength of the PU films. Interestingly,  $\epsilon_b$  values of the films PEPU-100 and PEPU-110 increase

**TABLE I**  
Effects of Cure Temperature on the Mechanical Properties of the Films

Temperature (°C)	Tensile strength (MPa)			Elongation at break (%)		
	PEPU-90	PEPU-100	PEPU-110	PEPU-90	PEPU-100	PEPU-110
18	5.99	6.60	7.39	40.6	42.9	49.0
25	7.69	8.54	9.74	116	133	124
40	13.6	12.7	12.8	176	988	898
60	14.1	17.9	17.1	708	709	878
80	16.2	18.0	19.5	822	660	755

with an increase of the cure temperature to 40°C up to maximum values 988 and 898% for the PEPU-100 and PEPU-110 films, respectively. It is noted that the PEPU films cured at relatively lower temperature (40–80°C) have similar mechanical properties as those cured above 100°C in reference.<sup>31</sup> However, the PEPU-90–60, PEPU-100–60, and PEPU-110–60 films cured at 60°C all possess higher tensile strength and elongation at break, compared with the films cured at other temperatures on the whole. The results from Table I also indicate that the relatively higher reaction temperature is favorable to the improvement of the mechanical properties on the whole, resulting from the promotion of the crosslinking reaction. Apparently, for high tensile strength, a certain degree of phase separation is necessary. Thus, by varying the reaction temperature and cure temperature, the PEPU films can be tailored to the mechanical properties of specific applications.

### CONCLUSIONS

Three kinds of PU prepolymers were prepared at 90, 100, and 110°C, respectively, and then the PU prepolymers were crosslinked by TMP successfully and cured at 18, 25, 40, 60, and 80°C to obtain three series of poly(ester-urethane). When the reaction temperature increased from 90 to 100°C, the crystallinity degree of the soft segmental decreased, but interaction between soft and hard segments enhanced, leading to an enhancement of the glass transition temperature of soft domain and tensile strength as a result of the promotion of crosslinking reaction. When the cure temperature was above 60°C, miscibility between soft and hard segments of the films was improved, resulting in lower crystallinity and higher soft segment  $T_g$ 's and tensile strength. On the whole, the PEPU-90–60, PEPU-100–60, and PEPU-110–60 films cured at 60°C all possessed higher tensile strength and elongation at break compared with the films cured at other temperatures. Therefore, reaction temperature and cure temperature play an important role in the improvement of the crosslinking structure and mechanical properties of the semicrystalline PU.

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