# Effect of the Molecular Structure of Polyurethane Elastomers on the Thermomechanical Properties of PUE/PC Blends

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**ABSTRACT:** Polyurethane elastomers (PUEs) based on 4,4′-diphenylmethane diisocyanate (MDI), 1,4-butanediol (BDO) and two kinds of aliphatic polycaprolactone (PCL) diols with molecular weight of 1000 Da and 2000 Da have been synthesized and melt-blended with polycarbonate (PC). The compatibility of PC and PUEs was investigated by differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA) and scanning electron microscopy (SEM). The results indicated that the glass transition temperature ($T_g$) of PC decreased by 0–40°C when 0–10 wt % of PUEs incorporated into the PC matrix. Phase separation in the blends was not detected by means of DSC characterization, but measurements of DMA and SEM indicated that phase separation existed in the blends of PC and PUEs synthesized with 1000 Da PCL-diol. As for PUEs/ PC blend in which 2000 Da PCL-diol as PUEs' soft segments, it turned from completely compatible to partially when the NCO/OH ratio for the PUEs prepolymer was increased from 2 : 1 to 4 : 1. The compatibilities of PC and PUEs were greatly influenced by the molecular weight of polyols and the ratio of NCO/OH in the PUE prepolymer, higher molecular weight of polyols and lower NCO/OH ratio resulted in better compatibility. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 412–420, 2012

**Key words:** polycarbonates; polyurethane elastomers; blends; compatibility; glass transition

## INTRODUCTION

Polymer blends and composites have been extensively studied in recent dozens of years in both the academic and industrial communities due to the fact that new materials with good properties can be developed in relatively shorter time and with a minimum investment. It is well known that bisphenol-A PC is an important engineering thermoplastic with excellent clarity, high heat-deflection temperature, and toughness in thin sections. However, its ultraviolet (UV) and chemical resistance are limited and it is notch sensitive and susceptible to strain crazing. Furthermore, PC is difficult to process due to its high melt viscosity originating from its rigid molecular chains and its high $T_g$. Blending with another polymer to regulate the properties of PC should be an advisable way to overcome its drawbacks.

Many researches have been carried out about utilizing elastomers[1,2] or thermoplastic[3–5] to modify PC. Chang[1] has pointed out that the ductile-brittle transition temperature (DBTT) of the notched impact strength decreased with an increase of PC molecular weights and elastomer content when PC was modified with MBS elastomer; meanwhile, the modified PC had higher impact strength than the unmodified counterpart if the failure was in the brittle mode but had lower impact strength if the failure was in the ductile mode. Cho[6] has used core-shell rubber particles to modify PC and concluded that an optimum particle size and 4 wt % rubber phase content of the modifier could impart maximum toughness for the notched PC. Furthermore, Zhou[7] has found that reactive modification of PC with a hydroxyl functionalized siloxane (PDMS) in the melt state would obtain a novel blend with superior flow and excellent low temperature impact strength.

PUEs are promising modifiers for PC because they can meet a wide range of physical and chemical property depending on their components. In the case of such two-component system, miscibility or compatibility is first under consideration. Shyu and coworkers[8] have reported that PC and PU semi-interpenetrating polymer networks (semi-IPNs)

showed improved compatibility compared with their linear blends, a higher ratio of NCO/OH and lower molecular weight of polyols in PU prepolymer resulted in better compatibility and finer phase domains in their linear blends and semi-IPNs. However, the choice of modifiers is limited in case to maintain the transparency of PC. Fambri has first modified PC with PUEs based on aliphatic PC-diols and polypropylene glycols as soft segments. The results indicated that PUEs were miscible with PC up to 20 wt % and decreased the $T_g$ by about 30°C (at 10 wt % PUEs in blends), which was considered suitable for the practical modification of processing and mechanical properties of transparent PC.[9] Later, Fambri has synthesized PUEs consisting of aliphatic PC-diols and tetramethylene glycols as soft segments to form miscible blends with PC. Single phase existed in the blends with the content of PUEs up to 10 wt % and the $T_g$ of PC also decreased by about 30°C. Furthermore, the strong interaction among constituents has caused an increase in modulus of the blends at temperature below $T_g$ in both dynamic and static mechanical tests, which phenomena is usually regarded as "antiplasticization" effect.[10]

With regard to above researches about PC modified with PUE, the miscibility between them is intensively depended on the molecular chain structure of PUE. Moreover, Ahn[11] has already pointed out that the hard-segment portion of PUE was immiscible with PC in the absence of interchange reaction. Thus, PUE possesses both PC miscible and immiscible segments within their chain structures on condition that miscible polyester glycols are chosen as the soft segments of PUE. As we all known, poly(ε-caprolactone) (PCL) and PC blends are miscible in their amorphous phase, which is confirmed by the fact that only one $T_g$ can be detected in their blends.[12] So it is expected that the compatibility between PUE and PC could be adjusted by utilizing PCL-diols as soft segments of PUE.

In this study, a series of PUEs were synthesized via utilizing aliphatic PCL-diol and MDI extended by BDO, and then they were melt-blended with PC. The aim of this work is to regulate the miscibility of PUEs with PC by varying the molecular structure of PUEs. The influence of NCO/OH ratio for the PUE prepolymer and molecular weight of PCL-diols on the compatibility of the blends was investigated. The phase morphologies, thermal and mechanical properties of blends were studied via scanning electron microscopy (SEM), differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), and mechanical tests. In addition, the influence of the PUEs incorporation on the PC optical transparency was also investigated.

## EXPERIMENTAL

### Materials

MDI and dibutyltin dilaurate (DBTDL) catalyst were purchased from Aldrich and used as received. PCL-diols (CAPA 2100 and 2200) were obtained from Solvay (England) with an average molecular weight of 1000 and 2000 Da, respectively, and they were dehydrated under vacuum at 110°C for 2 h before use. BDO, toluene and $n$-hexane were purchased from Shanghai Chemical Reagent (Shanghai, China). BDO was distilled under reduced pressure. Toluene was dried over 4 Å molecular sieves and distilled from sodium benzophenone ketyl for further purification.

Bisphenol-A PC manufactured by Bayer, Makrolon 3103, with a molecular weight $\overline{M}_n = 32,000$ g mol$^{-1}$ and $\overline{M}_w/\overline{M}_n = 1.59$, was employed in this work. Its $T_g$ is 148.2°C, measured by DSC.

### Synthesis of PUEs

PUE was synthesized by the prepolymer method in toluene. To prepare the prepolymer, MDI and PCL-diol were first dissolved into toluene under mechanical stirring at room temperature, and then the reaction temperature was raised to 60°C and the mixture was allowed to react for 1 h with the existence of DBTDL. The prepolymer was subsequently chain extended with BDO at 60°C for 3 h. After the extended chain reaction was completed, some additional toluene was added followed by precipitation of the final product into a 10-fold excess of $n$-hexane and then the product was dried under vacuum at 60°C for 1 week.

### Preparation of PUEs and PC blends

Before blending, PC and PUEs were dried in a vacuum oven at 100 and 60°C for 24 h, respectively. The blends of PC and PUEs were prepared by melt mixing with a Haake Rheomix 600 (Karlsruhe, Germany) with a batch volume of 50 mL. The components were mixed at a twin screw speed of 60 rpm for 5 min at 220°C. The mixing fractions of PUEs in blends were set at 2.5, 5.0, and 10.0 wt %. After blending, all samples were cut into small pieces and cooled to room temperature under an air atmosphere. Also, the original PC was subjected to the same mixing treatment to obtain a reference sample.

All blending samples were compression-molded into sheets with thicknesses of 1.0 ± 0.1 mm for various tests under a hot press at 220°C, a hold pressure of 8 MPa and a hold time of 3 min, followed by quenching to room temperature between two thick metal blocks. The dried synthesized PUE films with thicknesses of 1.0 ± 0.1 mm were also obtained

**TABLE I**
**Chemical Compositions and Molecular Weights of PUEs**

| Polyurethane elastomers | Molar mass of PCL (Da) | Molar ratio of MDI/PCL/BDO | HS (wt %) | $\overline{M}_n \times 10^{-3}$ (g mol$^{-1}$) | $\overline{M}_w/\overline{M}_n$ |
|---|---|---|---|---|---|
| PUE12 | 1000 | 2 : 1 : 1 | 37.2 | 85 | 2.49 |
| PUE13 | 1000 | 3 : 1 : 2 | 48.0 | 49 | 2.47 |
| PUE14 | 1000 | 4 : 1 : 3 | 56.0 | 33 | 2.24 |
| PUE22 | 2000 | 2 : 1 : 1 | 22.8 | 77 | 2.26 |
| PUE23 | 2000 | 3 : 1 : 2 | 31.7 | 49 | 2.83 |
| PUE24 | 2000 | 4 : 1 : 3 | 38.9 | 45 | 2.69 |

through compression mold at 180°C for thermal and mechanical measurements.

## Characterization

Gel permeation chromatography (GPC) was performed on a Waters 1525 fitted with two columns (Styragel HT3 and HT4 N,N'-dimethylformamide (DMF) 7.8 × 300 mm² column) connected in a series and 2414 refractive index detector with TEDIA DMF containing 0.05M LiBr as mobile phase. The inherent viscosities were measured with an automatic Ubbelohde viscometer thermostated at 25°C.

DSC measurements were performed on a TA Instrument Differential Scanning Calorimetry Q200 (USA) with a Universal Analysis 2000 under a continuous dry nitrogen purge (50 mL min$^{-1}$). Indium was used for temperature and enthalpy calibration. All samples were sealed in aluminum pans with mass in the range of 5–10 mg. All measurements were conducted at a scan rate of 10°C min$^{-1}$ following heat-cool-heat procedure from −80–250°C. $T_g$s were determined by the midpoint of enthalpy change during the second heating.

DMA was carried out on DMA/SDTA861$^e$ (Mettler Toledo, Switzerland) in the tensile mode. The samples were scanned from −100 to 180°C at a frequency of 1 Hz and a heating rate of 3°C min$^{-1}$. The shape of the film samples was rectangular (∼ 4.0 × 9.0 × 1.0 mm³). The storage modulus ($E'$) and loss factor (tan δ) were recorded as a function of temperature.

The morphologies of the fracture surfaces of the neat PC and blends were characterized by SEM using a Model XL30 ESEM (Philips) at an accelerating voltage of 15 kV. The samples were frozen well in liquid nitrogen and quickly broken off to obtain a random brittle-fractured surface. A layer of gold was sputter-coated uniformly over all fractured surfaces before observations.

Uniaxial tensile tests were performed on an 8.9-kN screw-driven universal testing machine (1211, Instron, Canton, MA) equipped with a 10-kN electronic load cell and mechanical grips. The tests were conducted at room temperature with a crosshead rate of 5 mm min$^{-1}$. At least five specimens (∼ 20.0 × 4.0 × 1.0 mm³) for each sample were tested and the results were averaged.

The light transmittance and haze value of the sheets of the original PC and PUEs/PC blends were measured with a haze-gard plus (BYK-Gardner) at room temperature.

## RESULTS AND DISCUSSION

### Characterization of PUEs

The PCL-based PUEs were prepared via a two-step synthesis process. All samples can dissolve completely into polar solvents such as DMF and tetrahydrofuran, which proved that there was no covalent crosslinking in their molecular structure. Table I gives the basic properties of these synthesized PUEs. According to the two PCL-diols with different molecular weight and three different isocyanate index R values (that is, the NCO/OH molar ratios for the PUE prepolymer), six kinds of PUEs were synthesized for blending. The R values were set at 2 : 1, 3 : 1, and 4 : 1, and the corresponding PUEs were called PUE12 (PUE22), PUE13 (PUE23), and PUE14 (PUE24), respectively. The first number denotes the thousand digital of a molecular weight of the PCL-diols and the second one represents the R value. So the MDI/PCL/BDO molar ratios in these PUEs were 2/1/1, 3/1/2, and 4/1/3, respectively. The number average molecular weights $\overline{M}_n$ of all PUEs were higher than 30 × 10³ g mol$^{-1}$ and there was a decreasing trend in $\overline{M}_n$ with increasing the isocyanate index R value. Definitely, the index R represented the molar ratio of MDI and PCL-diol. Once R was increased, the molar ratio of PCL-diol and BDO was lowered, that is to say, the proportion of the chain-extender BDO was raised which had low molecular weight compared with PCL-diol in the PUE macromolecular chain, thus the $\overline{M}_n$ of PUE was dropped. The hard segment content of each PUE is also shown in Table I. For PUEs with 1000 Da PCL-diol, PUE12 with the lowest isocyanate index R contained about 37.2 wt % hard segments (HS), and with increasing the R value, the HS component increased to 48.0 wt % for PUE13 and 56.0 wt % for PUE14.
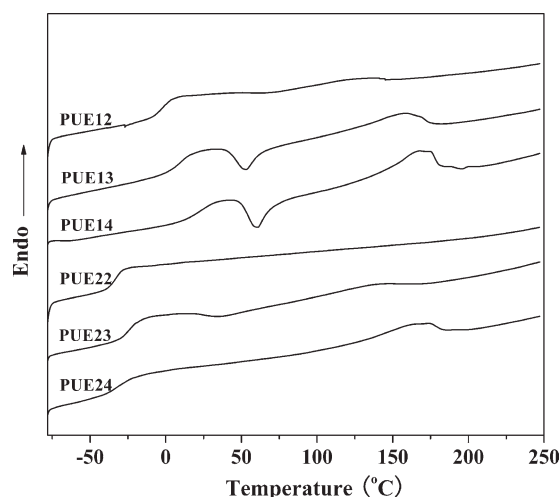
**Figure 1** Second-heating DSC thermograms of PUEs at a $10°C\ min^{-1}$ heating rate.

The thermal behavior of all PUEs was examined by means of DSC. Figure 1 shows the second heating scan thermograms of PCL-based PUEs, and the defined $T_g$, $T_{cc}$, and $T_m$ values are given in Table II. In general, for PUEs with 2000 Da PCL-diol, the $T_g$s were significantly lower than those of PUEs with 1000 Da PCL-diol. In these two PUE series, an increase in $T_g$ was observed with increasing the $R$ value, namely with decreasing the soft segment PCL content. Particularly, the $T_g$ of PUE23 was higher than that of PUE22 and PUE24. Usually, the lower the content of soft segments in PUE, the higher the $T_g$ belonging to soft segments, resulting from the lowered degree of microphase separation. While, another crucial factor should be considered into account: crystallization of chain segments in PUEs. The depression of PCL-diols crystallization in segmented polyurethanes had already been studied in Li's reports, and the limit of PCL molecular weight was in the range of 2000–3000 below which the PCL segments were not able to crystallize at the usual processing conditions, and this limit exhibited a slight increase with increasing hard-segment content of polyurethanes.[13] Now there was also no melting behavior for soft segments in the second heating

scan thermograms. Whereas, melting behavior for the hard segments existed in PUEs except in PUE22. In addition, there was cold crystallization in PUE23 but no in PUE24, suggesting that the PUE24 had faster crystallization rate than PUE23 did, so the degree of microphase separation was higher in PUE24, which is the reason of the $T_g$ of PUE23 higher than that of PUE24. In these six kinds of PUEs, only PUE22 had no endothermic peak in the thermogram, so it is considered to be mainly amorphous. This maybe relate to the low content of the hard segments in PUEs. Through Table I, it can be noted that the PUE22 contained about 23 wt % of hard segment, while in the other five kinds of PUEs, the hard segment contents were all higher than 30 wt %, and the endothermic peak became stronger with the hard segment contents increasing. There was similar result in previous report that thermoplastic PUEs based on PCL-diol as soft segment were semicrystalline and amorphous with more than 40 wt % and lower than 20 wt % of hard segment, respectively.[14] As regards to the mechanical properties of PUEs, they are exhibited through stress–strain measurements, also listed in Table II. Obviously, low modulus and high strain at break are characteristic of rubbery materials. Along with the isocyanate index $R$ value increasing and the PCL-diol chain length decreasing, the tensile modulus and strength increased and the elongation at break decreased.

## Blends of PC with PUEs

The extent of miscibility of components in PUE/PC blends prepared via melt blending was investigated through thermal and dynamic mechanical analyses. Figures 2 and 3 show the DSC thermograms of PUE12/PC and PUE22/PC blends with different compositions. The DSC thermograms revealed only one glass transition in any of the prepared blends. This result does not unambiguously prove a single-phase character of the blends because a small amount of an immiscible component (say, less than 10 wt %) can be hardly detected as the second glass transition. The original PC is an amorphous polymer

**TABLE II**
**Thermal and Mechanical Properties of PUEs**

| Polyurethane elastomers | $T_g$ (°C) | $T_{cc}$ (°C) | $T_m$ (°C) | Tensile modulus (MPa) | Tensile strength (MPa) | Elongation at break (%) |
|---|---|---|---|---|---|---|
| PUE12 | −2.0 | 44.8 | 121.0 | 46.6 ± 6.8 | 15.1 ± 2.0 | 1040 ± 50 |
| PUE13 | 10.9 | 53.2 | 157.7 | 50.1 ± 5.2 | 49.7 ± 6.5 | 810 ± 50 |
| PUE14 | 22.2 | 60.7 | 167.0 | 43.3 ± 3.2 | 101.1 ± 7.6 | 540 ± 40 |
| PUE22 | −32.7 | – | – | 13.8 ± 4.5 | 7.1 ± 5.1 | 1100 ± 40 |
| PUE23 | −24.2 | 38.0 | 137.5 | 36.1 ± 4.8 | 18.0 ± 3.0 | 980 ± 20 |
| PUE24 | −30.8 | – | 162.6 | 41.4 ± 2.9 | 42.7 ± 6.7 | 910 ± 30 |
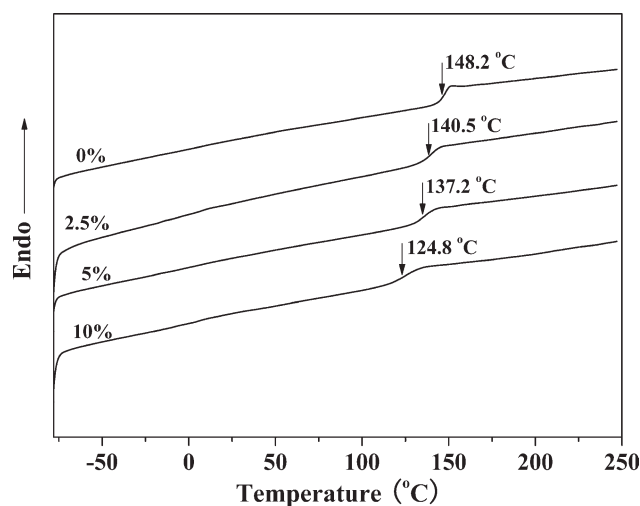
**Figure 2** Second-heating DSC thermograms of PUE12/PC blends at a 10°C min$^{-1}$ heating rate.

and shows the $T_g$ at 148.2°C. The $T_g$s of PUE12 and PUE22, obtained from the above results, were −2.0°C and −32.7°C, respectively. After the addition of PUE into PC, the $T_g$s of the blends decreased continuously along with the PUE content increasing and the $T_g$s of the PUE22/PC blends were lower than those of the PUE12/PC blends at the same PUE content. Taking PC with 10 wt % PUE22 and PUE12 as an example, it decreased by 40°C in the former blend and 23°C in the latter one compared with the original PC. This result may root from the miscibility between PC and PCL which have been extensively studied, and been regarded by many authors as fully miscible on account of the single $T_g$ in the entire composition range in the liquid and amorphous states.[12,15] The soft segment PCL chain length is longer in PUE22 than in PUE12, and both of the two PCLs with different molecular weight existed in
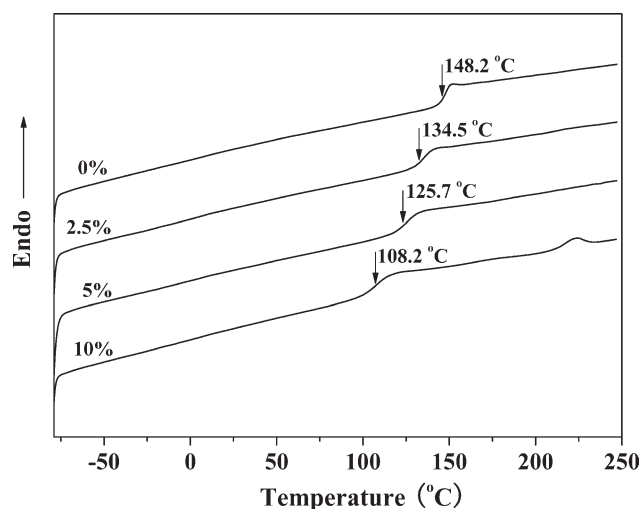


**Figure 3** Second-heating DSC thermograms of PUE22/PC blends at a 10°C min$^{-1}$ heating rate.

an amorphous state in the PUEs, therefore, the $T_g$s of PC declined more when blended with PUE22. For the blend of PC with 10 wt % PUE22, an endothermic peak at about 223°C appeared, which was attributed to the melting behavior of PC. The crystallization of PC has been investigated by many authors.[16,17] It is indicated that PUE22 induced the crystallization of PC in this blend. Usually it is ascribed to the increasing rate of polymeric segmental motion resulted from the plasticization effect like PEO[18] or PCL[19] on PC.

Utilizing DMA to evaluate the miscibility between PC and PUE is another more favorable way, because the sensitivity of DMA is much higher than that of DSC.[20]

Figures 4 and 5 show the temperature dependence of $E'$ and tan δ for the PUE12/PC and PUE22/PC blends at a frequency of 1 Hz. It is obvious that the dynamic $E'$ of PUE was lower than that of PC besides the $E'$ of PUE12 at the glassy state which was close to that of PC. In addition, the $E'$ of PUE12 steeply decreased at around −3°C which was assignable to the α-relaxation (that is, the glass transition) of the soft segments of PUE12, and it was at around −30°C for PUE22. There were tan δ peaks in the tan δ versus temperature curves corresponding to this α-relaxation of the soft segments for PUEs.

After addition of 2.5 to 10 wt % PUEs into PC, the $E'$ of the blends in the glassy state were all close to that of the origin PC and nearly independent of the PUE fraction; the $T_g$ for PC was gradually shifting to
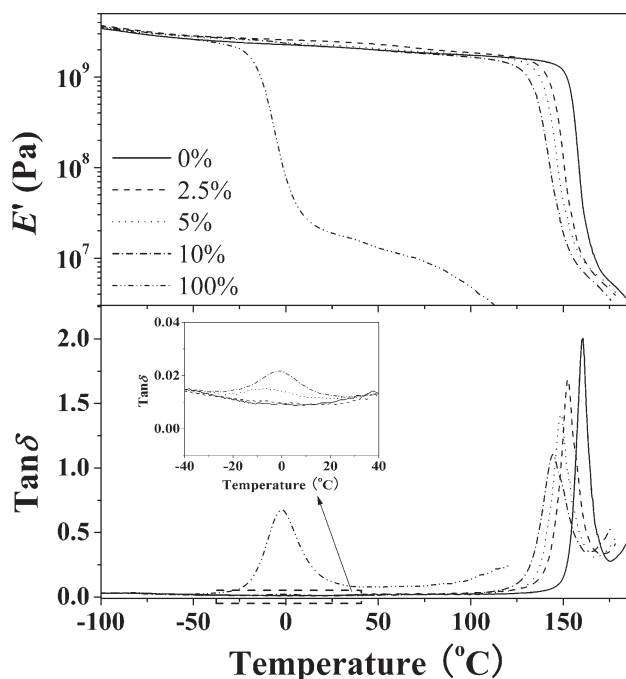


**Figure 4** Effect of the PUE12 mass fraction on the temperature dependence of storage modulus ($E'$) and loss tangent (tan δ) for the PUE12/PC blends.
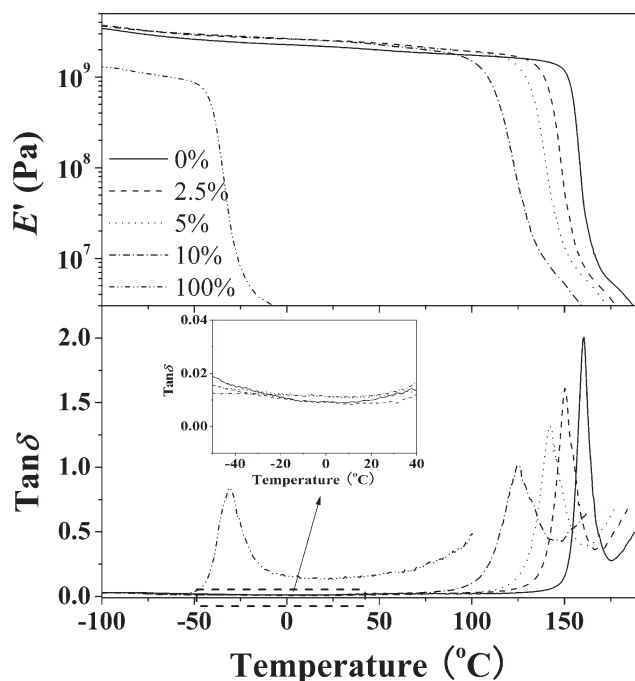
**Figure 5** Effect of the PUE22 mass fraction on the temperature dependence of storage modulus ($E'$) and loss tangent (tan δ) for the PUE22/PC blends.

lower temperature from at about 160°C for the original PC with the height and width of the tan δ peaks gradually declined and broadened, respectively. Furthermore, the $T_g$s of PC were lower when blended with PUE22 than with PUE12 at the same PUE content. It decreased by 35°C for PC containing 10 wt % PUE22 and only by 15°C when incorporating the same portion of PUE12. This may be related with the flexibility of the PUE chain segments. The density of urethane groups which have high polarity and rigidity is doubtless higher in PUE12 than in PUE22 due to the difference in the soft segment chain length. Therefore, the molecular chains were more flexible in PUE22 than in PUE12, which resulted in the PC chain segments possessing greater mobility in PUE22/PC blends.

Whereas, there were other significant differences in the dynamic mechanical behavior of PUE12/PC and PUE22/PC blends. From the enlarged plot inserted in Figure 4, it can be seen that the glass transition for PUE12 still existed when its content was higher than 2.5 wt % and only shifted slightly to higher temperature. This suggested that PC was merely partially compatible with PUE12 while the case in PUE22/PC blends was dissimilar since the glass transition of PUE22 entirely disappeared which was distinguished from the inserted plot in Figure 5. It means that PC and PUE22 were completely compatible.

The influence of the prepolymer isocyanate index $R$ on the miscibility of PUE and PC was studied by DMA on PC blends containing 10 wt % PUEs which are based upon 2000 Da PCL-diol (in Fig. 6). As the NCO/OH ratio was increasing from 2 : 1 to 4 : 1, the α-relaxation peaks of PUE initially vanished and then appeared, simultaneously the extent of the PC peaks shifting toward lower temperature reduced. Thus, the NCO/OH ratio also governs the miscibility between PUE and PC; the lower NCO/OH ratio leads to better compatibility. It favors Ahn's conclusion that the MDI-BDO hard segment portion was immiscible with PC in the absence of interchange reaction,[11] whereas, it is opposite to the Shyu's viewpoint that higher NCO/OH ratio resulted in better compatibility in PC and PU linear blends and semi-IPNs.[8]

It is well know that the properties of the blends are highly dependent on the phase structure and interface adhesion between two polymers. Figure 7 shows the SEM images of the brittle fractured surfaces for the original PC and PC blends containing 10 wt % PUE12 and PUE22. The original PC exhibited a smooth and featureless fractured surface without much deformation [Fig. 7(a)], and PC blended with 10 wt % PUE12 displayed a distinct two-phase morphology [Fig. 7(b)]. It is a pity that the PUE12 particles were detached from the PC matrix leaving the empty holes during the cryo-fracture process. The spherical-shaped holes were very finely dispersed in PC matrix, with diameters ranging from 0.3 to 0.6 μm. This indicated that the interfacial adhesion was weak in PUE12/PC blends. Whereas, the fracture
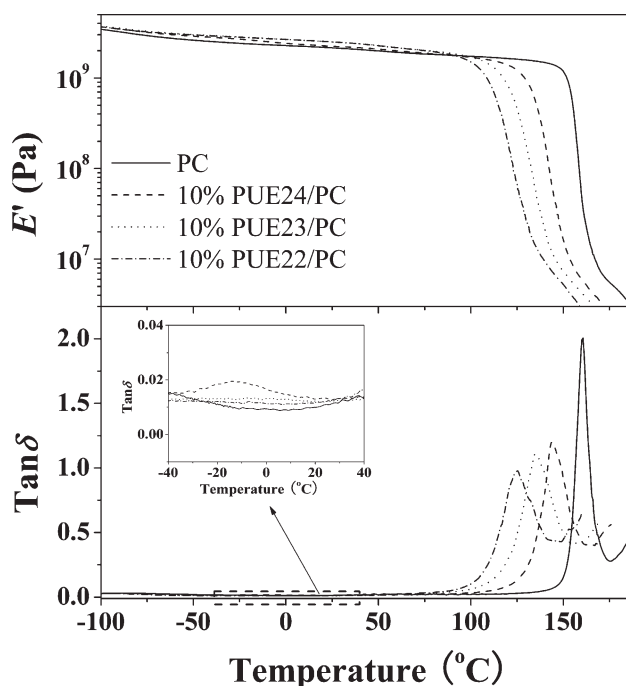


**Figure 6** Temperature dependence of storage modulus ($E'$) and loss tangent (tan δ) for the PC blended with 10 wt % PUEs.
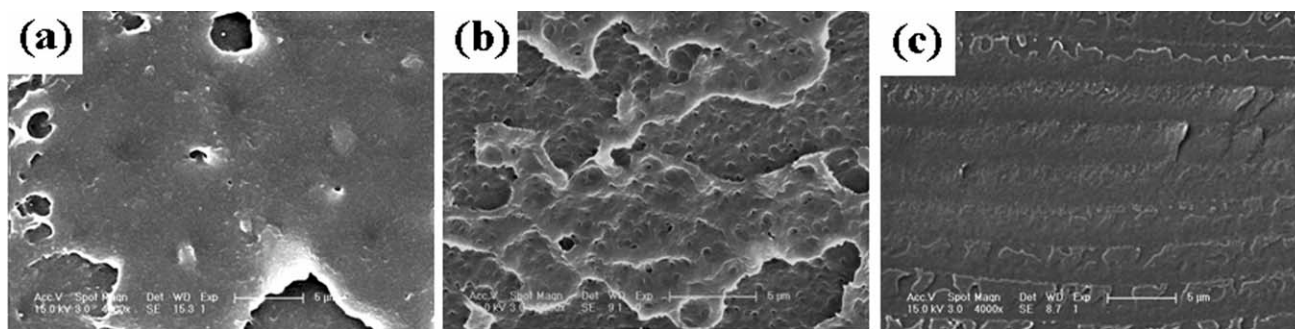
**Figure 7** SEM micrographs of (a) the original PC and PC blended with 10 wt % (b) PUE12, and (c) PUE22.

surface of PC with 10 wt % PUE22 exhibited homogeneous just like the original PC [Fig. 7(c)], and it was impossible to discern the component PUE22 from the PC matrix. The results of SEM were consistent with the dynamic mechanical analysis.

Figure 8 shows the two-phase morphology of PUE14/PC blends with different component ratio using SEM for observation. The PUE14 phase domain with 0.3 to 0.5 μm diameters was seen to be dispersed uniformly in the continuous matrix of PC. The number of PUE14 particles increased when increasing PUE14 content from 2.5 to 10 wt %, while the particle size distribution was always narrow in the whole composition range. What differed from the PUE12/PC blend was that there were legible interface existing between the two phases, and the PUE14 spherical particles were embedded into the PC matrix. This suggested that the cryogenic fracture was unable to pull out the rubber particles from the matrix. Thus, it can be concluded that the interfacial adhesion between the two phases increased along with the increase of NCO/OH ratio for the PUE prepolymer. So it is reasonable to speculate that there was some interaction existing within the two constituents, and the formation of hydrogen bonds between urethane and carbonate groups is most likely.[10,21] This hydrogen bonding interaction got stronger when increasing the NCO/OH ratio.

Mechanical property is related to the morphology, domain size, and size homogeneity of the polyblends.[22] The tensile properties of the PUEs/PC blends in which 1000 Da PCL-diol was utilized for the soft segments of the PUEs are given in Table III and the representative stress–strain curves of the PUE14/PC blends which had the best overall mechanical properties are illustrated in Figure 9. It can be seen that the original PC exhibited a yield maximum, accompanied by the formation of necking which was continuously followed by cold drawing and strain hardening. The addition of PUEs was not significantly changed the tensile behavior of PC. The yield maximum that is, yield stress took on a little decrease when compared with the original PC. Tensile strength of the PUEs/PC blends presented a decreasing trend with increasing the PUEs content. Tensile moduli of the blends were all close to that of the original PC, which was corresponding to the case of dynamic storage moduli at room temperature. The elongation at break for these blends correlated with the NCO/OH ratio and weight fraction of PUEs. An initial increase followed by a decrease was observed with an increase in PUE content, and for PUE13/PC and PUE14/PC blends, addition of 2.5 wt % PUE exhibited the maximum elongation at break, while for PUE12/PC blends, the optimal addition was 5 wt %. In most of previous reports about PC modified with rubber or elastomer, the addition of less than 10 wt % modifier usually led to the optimal results.[1,6,23]

PC is one of a few transparent engineering thermoplastics in commercial products, but most PC-based polyblends are translucent or opaque owing
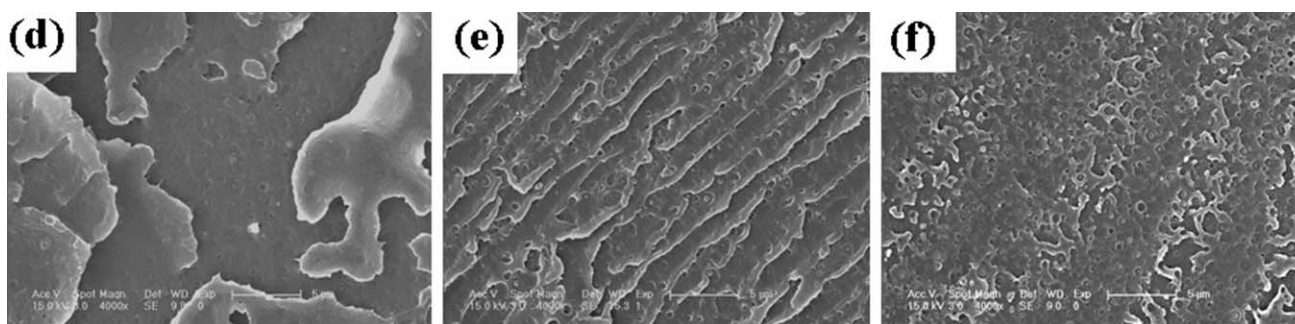


**Figure 8** SEM micrographs of PUE14/PC blends, (d) 2.5/97.5, (e) 5/95, and (f) 10/90.

**TABLE III**
**Tensile Properties of the PUEs/PC Blends**

| Samples | | Tensile strength (MPa) | Tensile modulus (MPa) | Elongation at break (%) |
|---|---|---|---|---|
| PC | | 62.4 ± 0.3 | 1270 ± 55 | 84 ± 6 |
| PUE12/PC | 2.5/97.5 | 62.1 ± 1.5 | 1420 ± 40 | 82 ± 8 |
| | 5/95 | 60.8 ± 1.6 | 1180 ± 55 | 96 ± 3 |
| | 10/90 | 58.3 ± 0.7 | 1160 ± 65 | 58 ± 4 |
| PUE13/PC | 2.5/97.5 | 61.5 ± 1.7 | 1180 ± 45 | 96 ± 8 |
| | 5/95 | 59.1 ± 2.0 | 1150 ± 55 | 95 ± 8 |
| | 10/90 | 54.3 ± 0.1 | 1240 ± 60 | 75 ± 9 |
| PUE14/PC | 2.5/97.5 | 62.0 ± 2.0 | 1260 ± 65 | 105 ± 5 |
| | 5/95 | 60.7 ± 1.2 | 1250 ± 70 | 96 ± 3 |
| | 10/90 | 60.9 ± 1.4 | 1310 ± 70 | 93 ± 3 |

to the characteristics of multi-phase structure inside the PC matrix. So the miscibility of PC with PUEs in the blends prepared by melt mixing is also indirectly estimated by the optical properties of the blend sheets. The visible light transmittance and haze value of the original PC and PC blended with PUE12 and PUE22 are plotted in Figure 10. The transmittance of the original PC was about 90%, and it was only slightly decreased after addition of PUE. Moreover, the largest decrease in transmittance was just 5% when 10 wt % PUE12 added to PC. Comparatively speaking, the optical difference among the original PC and PC blends was further manifested by the haze value. When the content of PUE12 or PUE22 was less than 5 wt %, only some sort of increase was happened in the haze value of blends compared with 4% for the original PC. Apparently at 10 wt % loading, it was sharply increased to 23% for PUE12 and it was only to 7% for PUE22. This result accorded with the heterogeneous phase structure in PUE12/PC blends and homogeneous in PUE22/PC blends. In view of this, the heterogeneous structure had insignificant influence on the

transmittance but dramatic effect on the haze value of polyblends.

## CONCLUSION

Blends of PC and PUEs (0–10 wt %) were prepared by melt blending in which PUEs were synthesized from MDI, BDO, and PCL-diols with molecular weight of 1000 and 2000 Da. The crystallization of PCL-diol has been suppressed and the melting behavior belonging to the hard segments has emerged in PUEs. This study showed that the miscibility between PC and PUEs was correlated with the molecular weight of PCL and the prepolymer isocyanate index $R$. The compatibilities can be improved by using higher molecular weight of polyols and lower NCO/OH ratio in PUE prepolymer. Increasing the molecular weight of PCL from 1000 to 2000 Da, the phase structure of PUEs/PC blends turned from a two phase into a single phase when $R$ fixed at 2, which was observed from the DMA and SEM results. SEM studies also showed that it became more and more difficult for PUE spherical particles
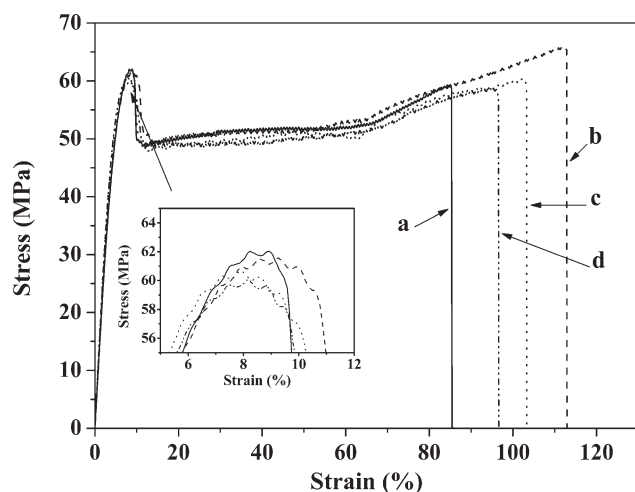


**Figure 9** Stress–strain curves for the PUE14/PC blends, (a) 0/100, (b) 2.5/97.5, (c) 5/95, and (d) 10/90.
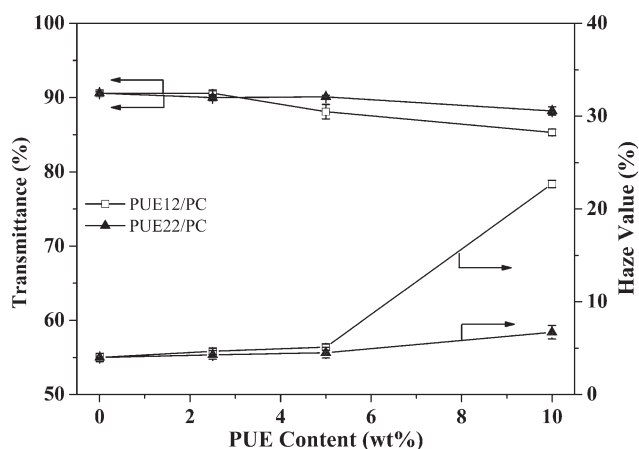


**Figure 10** Effect of the PUEs concentration on the transparency and haze for the PUEs/PC blends.

detached from the PC matrix when increasing the NCO/OH ratio in PUEs/PC blends in which PUEs were synthesized from 1000 Da PCL-diol. The tensile strength and modulus were not significantly decreased when increasing PUEs content to 10 wt % in PC blends and the elongation at break exhibited an initial increase and then a decrease. The optical transparency tests showed that the transmittance of blends had only a slight decrease upon the addition of PUEs into PC and the haze vale was remarkably affected by the phase structure of blends.

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