

Structures and properties of polycarbonate modified polyether-polyurethanes prepared by transurethane polycondensation

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ABSTRACT: Thermoplastic polycarbonate modified polyether-polyurethane (PEPU) elastomers were prepared by transurethane polycondensation method using poly(oxytetramethylene) glycol of $M_n = 2000$ and dimethyl-hexane-1,6-dicarbamate as the main raw materials, 1,4-butanediol as a chain extender and polycarbonate diol (PCDL) as an additive in the presence of dibutyltin oxide as a catalyst. The effect of the PCDL on the PEPU's structure, intrinsic viscosity, molecular weight, mechanical, optical, and thermal properties, and water resistance were studied. The polycarbonate modified PEPU's showed better mechanical and thermal properties, but lower molecular weight and optical properties than the PEPU's. The PEPU's modified by PCDL1000 exhibited better performance, including mechanical, optical, and thermal properties, than those by PCDL2000. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 42804.

KEYWORDS: elastomers; mechanical properties; optical properties; polyurethanes; thermogravimetric analysis (TGA)

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INTRODUCTION

Thermoplastic polyurethanes (PUs) are synthetic polymer materials which consist of alternating soft polyether or polyester segments and hard segments.^{1–7} Several controllable variables associated with materials, such as chemical structure and molecular weight of polyol,^{4,8–14} can have a profound effect both on the structure and the properties. Therefore, thermoplastic PU is widely used as coatings, adhesives, fibers, and high-performance elastomeric products because of excellent properties with respect to flexibility, heat resistance, and strength with a changing structure of materials, preparation conditions, soft segment molecular weights, and so on.^{15–22} Among electronics fields, there are strong requirements to design flexible PUs which can be used in a wide range of temperature, and this can be successfully carried out by using polyether polyols.^{23–25} When polyether polyol is used as soft segments, the PU will have excellent flexibility and low temperature properties. However, the PU still has defects in mechanical properties.

A substantial effort has gone into improving the mechanical properties and water resistance of polyether-PUs (PEPU's) without significantly sacrificing the molecular weights and optical properties by utilizing a diol mixture of a polyether polyol and a polycarbonate polyol as soft segments.^{26–31} Comparison of the properties of two series of thermoplastic PU elastomers, poly(propylene glycol) (PP)-based PU (PPPU) samples and poly

(oxytetramethylene) glycol (PTMG)-based PU (PTPU) samples, were conducted by Kim *et al.*³² They found that PTMG-based PTPU samples had higher elastomeric behavior than PP-based PPPU samples at the same hard segment content. Erdodi *et al.*³¹ concluded that the addition of PTMG to PIB-based PUs significantly increased both tensile strengths and elongations, while at the same time maintained their good hysteresis behavior.

The main purpose of this work was to study the effect of (polyether and polycarbonate) polyol on the structure and thermal, mechanical, and optical properties of thermoplastic PU elastomers, prepared from dimethyl-hexane-1,6-dicarbamate (HDC) and 1,4-butanediol (BDO) as hard segments, and PCDL and PTMG as soft segments. In this study, we discussed the influence of PCDL content on the properties of PEPU's. The effects of different molecular weight PCDL on the structure and the properties of the PCDL modified PEPU's were also studied.

EXPERIMENTAL

Materials

Polycarbonate diol (PCDL T-6001 (PCDL1000): $M_n = 1000$, Ube Industries, Japan), PCDL (T-6002 (PCDL2000): $M_n = 2000$, Asahi Kasei, Japan), and PTMG ($M_n = 2000$, Hangzhou Sanlong New Material Ltd, China) were used as a polymer glycol. 1,6-Hexamethylene diamine (HDA: > 99.0%, Shanghai Lingfeng Chemical Reagent), zinc acetate dihydrate ($Zn(OAc)_2 \cdot 2H_2O$: > 99.0%, Shanghai Lingfeng Chemical Reagent), and dimethyl carbonate



Scheme 1. The process for the synthesis of HDC.

(DMC: >99.9%, Anhui Tongling Chemical Industry) were employed as materials of HDC. Dibutyltin oxide (DBTO: >99.0%) and BDO (>99.0%) were from Aladdin Reagent.

Synthesis of HDC

Non-phosgene synthesis of HDC from HDA and DMC was realized with $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ as a catalyst. By a reaction distillation process at 366 K for 5 h, 98.21% conversion to HDA and 63.02% yield to HDC could be achieved. This process is described in Scheme 1. The optimized conditions were as follows: the reaction temperature and time was 366 K and 5 h, respectively, the molar ratio of DMC to HDA was 6 : 1, and the amount of $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ catalyst was 0.05 wt % (based on the weight of HDA). The bottom product was further cooled at room temperature until a white mixture was obtained. Then, DMC and catalyst residue were dissolved in the water at 313 K. The desired HDC product could be collected after filtering and vacuum drying. By recrystallization using methanol and vacuum drying of 24 h, the purity of HDC could be above 99%. The structure of HDC was confirmed as $\text{CH}_3\text{O}-\text{CONH}-\text{(CH}_2)_6-\text{NHCO}-\text{OCH}_3$ by the following NMR and Fourier transform infrared (FTIR) data.

^1H NMR (400 MHz, CDCl_3 , d, ppm): 4.71 (b, 2H, $-\text{NHCO}-$), 3.66 (s, 6H, $-\text{OCH}_3$), 3.15–3.47 (q, 4H, $-\text{CH}_2\text{NH}-$), 1.64–1.29(4H,m, $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2-$), 1.29–1.18(4H,m, $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2-$).

^{13}C NMR (500 MHz, CDCl_3 , d, ppm): 157.13 (C=O), 52.50 ($-\text{OCH}_3$), 41.26($-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2-$), 30.36 ($-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2-$), 26.63 ($-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2-$).

FTIR (cm^{-1}): 3341 ($-\text{NH}-$ stretching), 2940, 2860 ($-\text{CH}_2$, $-\text{CH}_3$), 1690 ($-\text{C}=\text{O}-$ stretching), 1530 ($-\text{NH}-$ bending), 1260 (O=C–O stretching).

Synthesis of PUs

The PUs, including PCPU (polycarbonate-PU) and PEPUs, were prepared by a transurethane polycondensation process from HDC, BDO, PCDL, and PTMG where the molar ratio of $-\text{NH}-\text{COO}-$ to $-\text{OH}$ was 1 : 1. The PCPU was synthesized from HDC, BDO, and PCDL while HDC, BDO, PCDL and PTMG with various PCDL content in soft segments (0–50 mol %) were used for the preparation of PEPUs. The PCPU and PEPUs were synthesized as shown in Scheme 2. The prepolymerization reaction was carried out at 383 K for 45 min under a reduced pressure of 0.07 MPa in the presence of a catalytic amount of DBTO, added after careful melting and mixing of reagents. The reaction was followed by a polycondensation reaction at 463 K for 110 min under vacuum. Then the viscous product was poured into a mold composed of a spacer of 2 mm thickness and two solid teflon plates and left to cure at room temperature for 4 h.

Characterization

^1H NMR and ^{13}C NMR Spectra: ^1H NMR and ^{13}C NMR spectra of HDC were recorded using a 400 MHz and 500 MHz Bruker NMR spectrometer with tetramethylsilane as the internal standard in CDCl_3 , respectively.

FTIR Spectroscopy: FTIR spectra, ranging from 4000 cm^{-1} to 400 cm^{-1} , were analyzed with a Nicolet 6700 spectrometer using thin films.

Differential Scanning Calorimetry (DSC): DSC thermograms were obtained with a TA Q200 calorimeter under a nitrogen atmosphere. Samples were dried (0.01 Torr at 313 K overnight) prior to testing, and samples with weights of about 5 mg were used. Samples were cooled from room temperature to 173 K with liquid nitrogen and then heated to 523 K at a heating rate of 10 K/min. Glass-transition temperature (T_{gs}) for the polymer samples were taken as an inflection point on curves of the heat-capacity changes.

Thermogravimetric Analysis (TGA): TGA was performed on an SDT Q600 thermogravimeter in the temperature range from room temperature to 873 K at a heating rate of 10 K/min under a nitrogen atmosphere. Samples with masses of about 18 mg were used.

Gel Permeation Chromatography (GPC): The number (M_n) and weight (M_w) average molecular weights, and the index of molecular weight distribution (M_w/M_n) of the polymers were measured by GPC on a Polymer Laboratories PL-GPC50. Tetrahydrofuran (THF) was used as an eluent (flow rate = 1 mL/min). A GPC universal calibration curve was established using a viscosity detector and polystyrene standards.

Intrinsic Viscosity Analysis ($[\eta]$): The intrinsic viscosity of 0.3 g/25 mL polymer solution in dichloromethane (CH_2Cl_2) was measured in an Ubbelohde viscometer at 298 K. Intrinsic Viscosity ($[\eta]$) was estimated from eq. (1):

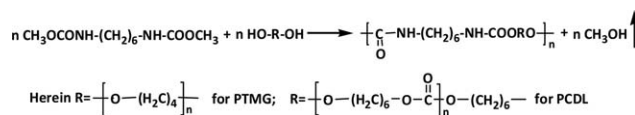
$$[\eta] = \frac{\sqrt{2(\eta_{\text{sp}} - \ln \eta_r)}}{C} \quad (1)$$

where η_r is the relative viscosity ($\eta_r = t/t_0$, where t is the effluxion time of the solution, t_0 is the effluxion time of solvent), η_{sp} is the specific viscosity ($\eta_{\text{sp}} = \eta_r - 1$), and C is the concentration of the polymer solution (g/mL).

Tensile Strength Test: Tensile strength test was investigated on a MTS Systems tensile-testing machine according to Chinese standard GB/T 528-2009 at the speed of 500 mm/min at 298 K. The strength at break (σ_b , MPa) and elongation at break (ε_b , %) of the sheets were recorded.

Hardness Measurement: The hardness of the PUs was measured by the Shore A method at 296 K; values were taken after 15 s.

Transmittance and Haze Measurement: Optical properties of the PUs were acquired with an optical hazemeter WGT-S system (Shanghai Precision and Scientific Instrument, China). The values obtained are the average of at least six determinations.



Scheme 2. The transurethane polycondensation process for the synthesis of PUs.

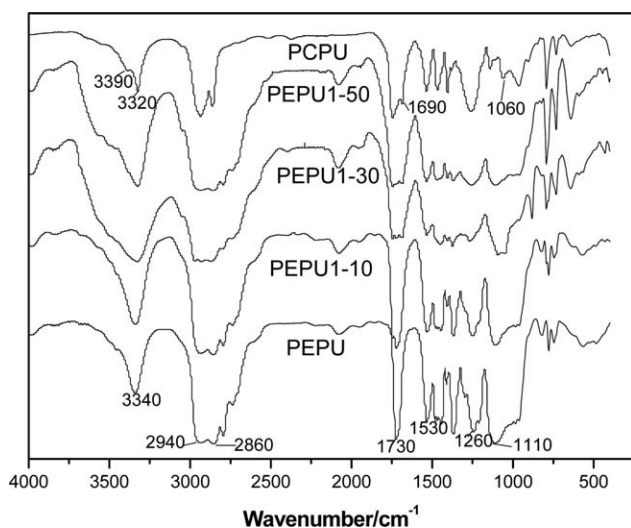


Figure 1. FTIR spectra of PUs.

Water Absorption Behaviors: A water absorption test was carried out under the specification of GB/T 1034-2008. Specimens were dried at 298 K in a vacuum oven for 48 h and then were left to cool at room temperature in sealed plastic bags before weighing their dry weight. Then they were immersed in distilled water at 298 K and 353 K for 15 days, respectively. Weighing on a balance with a precision of 1 mg, weight gains of the specimens periodically removed from the water bath were recorded. Once the measurement finished, the samples were immediately put back to the water path for further measurements. As a result of water absorption, water absorption percentage (WAP) gain at any time t was determined by eq. (2):

$$\text{WAP} = \frac{M_t - M_D}{M_D} \quad (2)$$

where M_D and M_t denote the weight of dry material (the initial weight of materials prior to exposure to water) and the weight of the materials after exposure to water, respectively.

RESULTS AND DISCUSSION

Nomenclature Employed

The nomenclature used for this series is of the form PEPU x - y , where x equals to the molecular weight of PCDL employed (1 = PCDL1000 and 2 = PCDL2000) and y represents the mol % of PCDL (10–50) in soft segments (or PCPU in the case of 100%). For example, PEPU1-10 is a 10% PCDL1000 modified PEPU. When PEPU1s or PEPU2s is used, it stands for the series of PCDL1000 modified PEPUs or the series of PCDL2000 modified PEPUs, respectively.

FTIR Analysis

The FTIR spectra of PEPU, PEPU1s, and PCPU are shown in Figure 1. The infrared research has been focused on the urethane C=O stretching vibration in the amide-I and amide-II region. The absorption bands around 1730 cm^{-1} are related to the C=O stretching vibration in the amide-I region, and those at 3341 cm^{-1} (N–H stretching) and 1530 cm^{-1} (N–H bending) can be ascribed to the N–H vibration in the amide-II region.³³

In the spectra of PEPU and PCPU, the band at 1260 cm^{-1} is assigned to the stretching of O–C–O group, while the band at 1110 cm^{-1} originates from the stretching of ether C–O–C group. As shown in Figure 1, the spectra of PEPUs show no peak at 1060 cm^{-1} (absorption of the C–O–C groups in –NHCOO–). The result indicates that the band at 1060 cm^{-1} of the C–O–C group in –NHCOO– is covered by the band at 1110 cm^{-1} of the ether C–O–C group and that urethane linkages are formed between PU N–H and C=O, suggesting a successful modification. In order of increasing wavenumbers in the amide-I region, two C=O amide-I stretching bands are observed, these are H-bonded carbonyl groups in ordered “crystalline” hard domains (1690 cm^{-1}) and non H-bonded “free” carbonyl groups (1730 cm^{-1}). Figure 1 displays no H-bonded carbonyl stretching in hard domains at 1690 cm^{-1} but a strong free carbonyl stretching at 1730 cm^{-1} in the PEPU spectra, while it displays both C=O amide-I stretching bands in the PCPU spectra. As seen in the spectra of PEPUs, the band at 1690 cm^{-1} sharpens as PCDL1000 content increases, indicating that the vibration associated with H-bonded carbonyl groups in ordered crystalline hard domains increases with the addition of PCDL. Thus, the extent of interurethane interactions is suggested to increase with the increment of PCDL content, so does the phase mixing. Moreover, the PCPU spectra exhibits two weakly separated bands of the N–H stretching at 3390 cm^{-1} corresponding to H-bonded N–H stretching in disordered “amorphous” conformations, and the band at 3320 cm^{-1} corresponding to H-bonded N–H stretching in ordered crystalline domains. However, for PEPU and PEPU1s, only one band at 3341 cm^{-1} connected with N–H vibrations are observed. This result implies that a complex morphology which involves both the PCDL or PTMG soft segment and hard segment is developing with PCDL content increases. It may be due to the contradiction between the smaller degree of PCDL soft segments’ compatibility with hard segments and the stronger interaction of hard segment urethane groups with carbonate groups of oligocarbonate chains than with oligoether chains of ether groups.³⁴

Thermal Properties Analysis

DSC Analysis. The DSC curves of the PUs from the first heating scans (Figure 2) showed distinct glass transition of the soft segment: 199 K for PEPU and 234 K for PCPU, respectively. Indistinct transitions in the DSC curves of PEPU1s, observed in the range of (289–292) K, may be connected both with the melting of soft segments and glass transition of amorphous portion of hard segments.³⁵

For PCPU and the PCDL modified PEPUs, an increase in PCDL content (0 to 50%) resulted in an increase in T_{gs} (199–209 K), suggesting a decrease of the degree of microphase separation.^{1,36} A greater degree of phase mixing may be due to smaller difference in stiffness between soft and hard segment chains owing to higher stiffness of PCDL than PTMG chains. Besides, this may result from the mobility restriction of the soft segment at the hard/soft segment junction because higher crystallization capacity of PCDL segments compared to that of PTMG segments.⁹ It could also be the result of a stronger

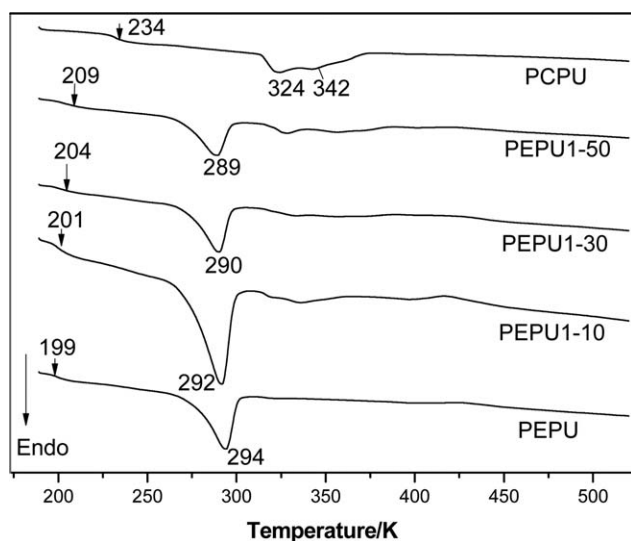


Figure 2. DSC curves of PUs prepared under different PCDL1000 content.

interaction of hard segment with carbonate groups in PCDL than with ether groups in PTMG. And the interaction between hard and soft segments causes an increment of T_{gs} by improving miscibility of the domains.

TGA. The numerical TG data are summarized in Table I, while the TG and the differential TG (DTG) curves are given in Figure 3. For the purpose of comparison, Table I and Figures 2 and 3 also contain data received from PCPU and PEPU. The TG curves of these PUs [Figure 3(a)] show two distinct weight loss, implying at least two stages of degradation occurred in these samples during the heating process.³⁷ The degradation of the first stage (stage 1) and the second stage (stage 2) were around 533 K–(593–638) K and (593–638) K–733 K, respectively, reflected in two peaks in the DTG curves in Figure 3(b) at around (602–628) K and (681–695) K. In the case of the PUs, the first stage can be ascribed to the decomposition of the urethane bonds in hard segments and the second stage is associated with the carbonate or the ether content in the soft segments.³⁸

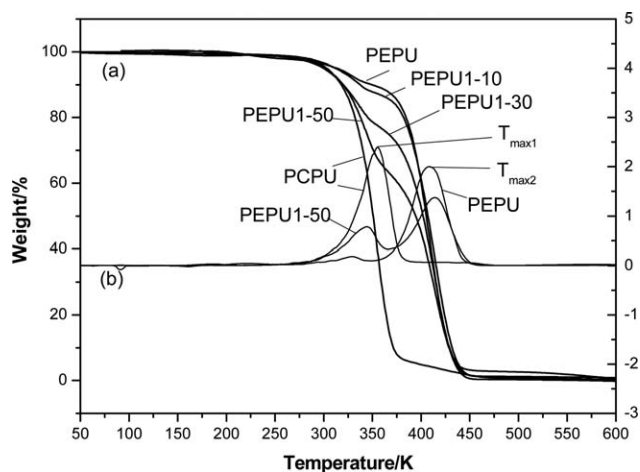


Figure 3. TGA (a) and DTG (b) curves of PUs prepared under different PCDL1000 content.

As can be seen from the TG data in Table I, the PCDL modified PEPUs were characterized by better thermal stability as compared to PCPU or PEPU. Comparing the temperature of 5% weight loss ($T_{5\%}$) of the PEPUs, it can be seen the $T_{5\%}$ of the PCDL modified PEPUs (576–586) K exceeded that of PEPU at 561 K. The peak of the DTG curves [Figure 3(b)] in each stage of degradation (T_{max1} and T_{max2}) is the temperature at which the degradation rate is maximal. Table I shows that T_{max1} and T_{max2} values of the PCDL modified PEPUs clearly exceeded those of PEPU. The increase of PCDL content in the soft segments caused some increment of T_{max1} (602–628 K) and T_{max2} (681–687 K), and stage change of T_{max1} (stage 1–stage 2). Besides, the peak values of the DTG curves in stage 1 and stage 2 (the maximum percentage of weight loss per degree Celsius, T_{mw1} and T_{mw2} , respectively) also represent thermal stability at different stages of the degradation of the samples.^{39–41} The PCDL modified PEPUs had lower T_{mw2} values so the thermal stability of these samples exceeded that of PEPU. However, the PCDL modified PEPUs in stage 1 were less thermally stable than PEPU since they had higher T_{mw1} values. According to the preceding analyses of TG and DTG, two points should be noted.

Table I. Decomposition Temperature of PUs Prepared Under Different PCDL1000 Content

Samples	Temperature of 5% weight loss (K)	Interval of weight loss (K)	T_{max1} (K)	T_{mw1} (%/K)	T_{max2} (K)	T_{mw2} (%/K)
PEPU	561	Stage 1: 533~637 Stage 2: 637~823	602	0.18	681	2.00
PEPU1-10	586	Stage 1: 533~620 Stage 2: 620~733	609	0.24	687	1.82
PEPU1-30	586	Stage 1: 533~597 Stage 2: 597~733	610	0.43	687	1.66
PEPU1-50	576	Stage 1: 533~597 Stage 2: 597~733	617	0.78	687	1.37
PCPU	577	Stage 1: 533~594 Stage 2: 594~733	628	2.39	695	1.21

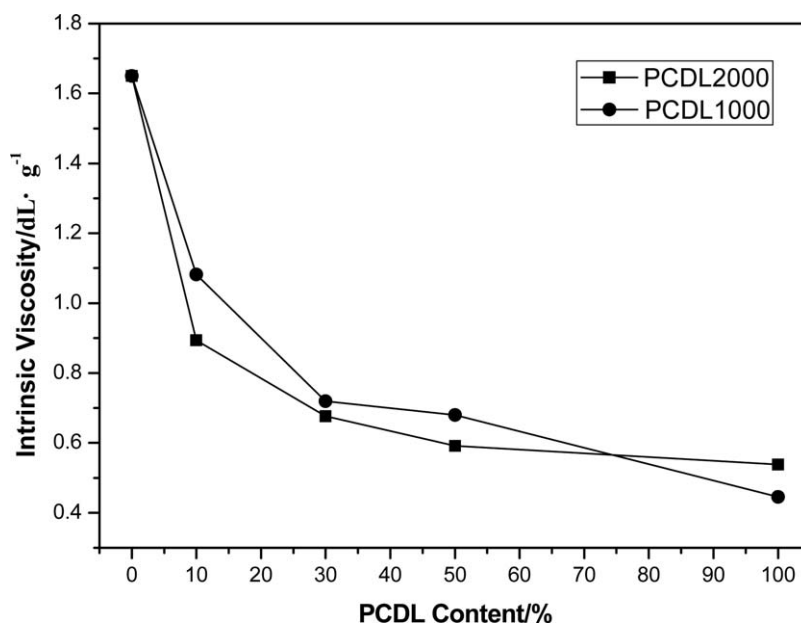


Figure 4. Intrinsic viscosity of PUs prepared under different PCDL content.

First, the PCDL modified PEPUs exhibited higher temperature of 5% weight loss, so these samples are characterized by better thermal stability compared with PEPUs. Second, although the PCDL modified PEPUs had higher T_{mw1} values than the PEPUs, the samples exhibit higher thermal stability because of higher T_{max1} and T_{max2} .

Intrinsic Viscosity and Molecular Weight Analysis

As seen from Figure 4, the intrinsic viscosities of PEPUs are higher than that of PCPU. Moreover, intrinsic viscosity decreased with an increase in PCDL content. High intrinsic viscosity values point to high molecular weights of these polymers, which are confirmed by GPC data received for the PUs soluble in THF (Table II).⁴² Besides, PEPUs displayed higher molecular weights than those of PEPUs. This implies that the shorter segments of PCDL1000 are more compatible than those of PCDL2000, resulting in a greater number of successful reactions and higher molecular weights.⁴³

Mechanical Properties Analysis

Shore A hardness and tensile properties were measured for all the PUs and the data are shown in Tables III and IV. As can be seen from the data, the PCDL modified PEPUs and PCPU showed significantly higher hardness, tensile strength, and elongation at break than those of PEPUs.³² PEPUs revealed tensile

strengths in the range of (7.0–83.8) MPa and elongations at break in the range of (173–2054)%, while PEPUs were characterized by higher tensile strengths in the range of (22.7–149.9) MPa and higher elongations at break in the range of (305–2145)%. Generally, all the PEPUs exhibited much better mechanical properties, including hardness, strength and elongation at break, compared to PEPUs or PCPU. Mechanical properties of these PCDL modified PEPUs were also influenced by the change of the PCDL content. As PCDL content increased in both series of PCDL modified PEPUs, their hardness increased accordingly. A tensile strength value of 149.9 MPa and an elongation at break of 2144% were obtained for PEPUs-10.

These differing mechanical properties result from two different phenomena: first, the materials are greatly influenced by the properties of the employed soft segments, and, second, the resultant morphology of each material affects its tensile properties. To explain further, better tensile properties may be attributed to the increasing degree of phase mixing according to the FTIR analysis (Figure 1). On one hand, some phase separation is required to provide enough physical crosslink sites to impart elastomeric behavior.^{10,44} On the other hand, if the hard and

Table II. Molecular Weights of PUs Prepared Under Different PCDL1000 Content

Samples	$\overline{M}_w \times 10^{-5}$	$\overline{M}_n \times 10^{-4}$	D
PEPU	2.84	15.6	1.82
PEPU1-10	1.46	6.48	2.24
PEPU1-30	1.13	5.78	1.95
PEPU1-50	0.66	2.47	2.67
PCPU	0.39	2.04	1.92

Table III. Mechanical Properties of PUs Prepared Under Different PCDL1000 Content

Samples	Shore A hardness	Tensile strength (MPa)	Elongation at break (%)
PEPU	57.2	2.3	168
PEPU1-10	69.2	149.9	2144
PEPU1-30	79.4	54.9	1467
PEPU1-50	86.5	29.1	305
PCPU	>100	35.2	118

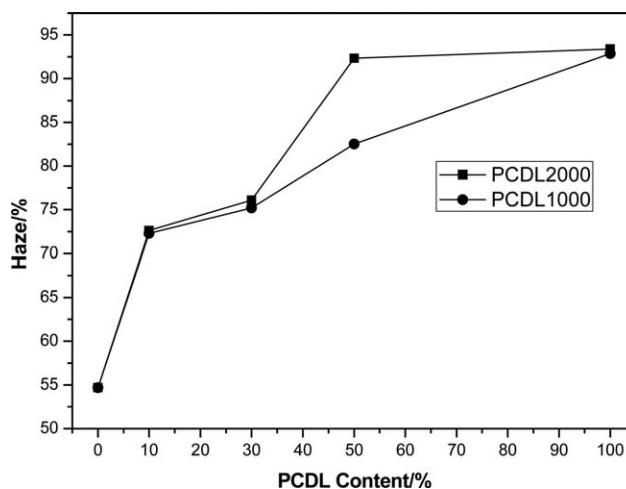
Table IV. Mechanical Properties of PUs Prepared Under Different PCDL2000 Content

Samples	Shore A hardness	Tensile strength (MPa)	Elongation at break (%)
PEPU	57.2	2.3	168
PEPU2-10	74.7	83.9	2054
PEPU2-30	77.9	23.2	306
PEPU2-50	82.9	7.0	173
PCPU	>100	6.2	771

soft domains are extremely immiscible, sharp phase boundaries result and a localization of shear stresses occurs at the narrow interface, giving rise to poor tensile properties. Additionally, another possible explanation of their better mechanical properties could be higher intrinsic viscosities of PEPUs (Figure 4) or crystallization capacity of the soft segment under strain.⁸

Optical Property Analysis

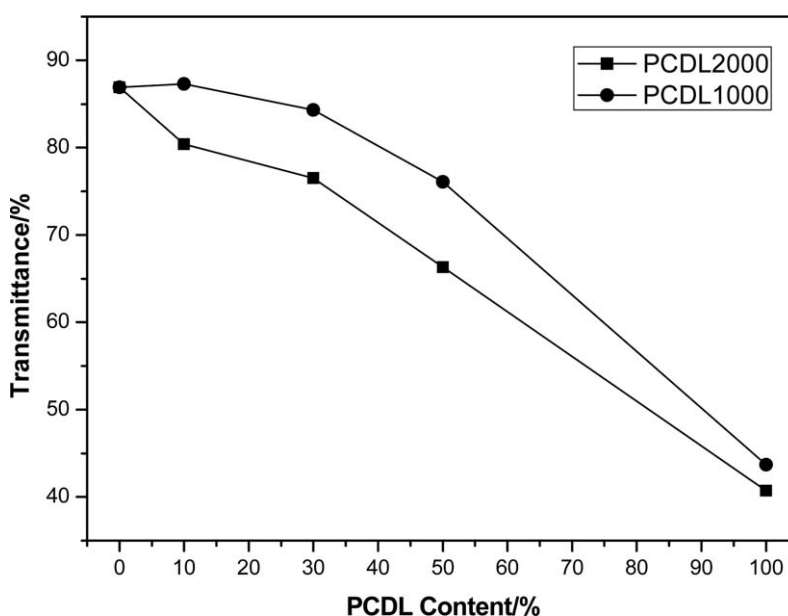
PEPU appeared transparent, however, 10%, 30%, and 50% PCDL modified PEPUs were, respectively, more translucent to nearly opaque in appearance. The visible light transmittance and haze value of PCPU and PEPUs are given in Figures 5 and 6. PEPU2s revealed transmittance in the range of 86.90–66.30% and haze in the range of 54.70–92.35%, while PEPU1s were characterized by higher transmittance (86.90–76.10%) and lower haze (54.70–82.52%). PCPU was opaque, yet very stiff and strong, more like a tough thermoplastic than an elastomer,⁴⁵ which can be explained by the phase separation between PCDL and hard segments and the immiscibility between these two segments. With increasing content of PCDL, the transmittance slightly decreased and the haze value of all the samples increased. The PCDL modified PEPUs displayed lower transmittance

**Figure 6.** Haze of PUs prepared under different PCDL content.

tance and higher haze than those of PEPU, owing to the competition of the two components (PTMG and PCDL) in the interfacial interaction.⁴⁶ Optimum optical properties were achieved when PCDL1000 was employed rather than PCDL2000. This improvement may be due to amorphous soft domains provided by shorter soft segments which corresponded with greater degree of phase mixing.⁴⁷

Water Resistance

Figures 7 and 8 show the water uptake of PUs measured at immersion temperature of 298 K and 353 K, respectively. The curves show that WAP increased rapidly within the first few days of immersion. After 4 days of exposure, the water uptake approached an asymptotic value, at which the maximum WAP (W_m) was reached. As shown in Figure 7, the W_m value of the PEPU was higher than those of the PCDL modified PEPUs. This indicates that PEPU is prone to water absorption, which

**Figure 5.** Transmittance of PUs prepared under different PCDL content.

can be associated with the hydroscopicity of PTMG, which contains —OH and —O—C—O—.⁴⁸ In general, the water uptake of polymers is governed by two theories, that is, (i) the free volume theory (which controlled by the moisture diffusion) and (ii) the interaction theory (which controlled by the chemical bonding, e.g., H-bond).⁴⁹ Upon re-drying, the appearances of all samples were fully recovered and WAPs of PEPU and PCPU fell to 0.38% and 0.24%, respectively. This phenomenon indicates that the incorporation of PCDL into PEPUs decreases the water uptake by the moisture diffusion at 298 K. In other words, the presence of PCDL tends to improve water resistance of the PEPUs at immersion temperature of 298 K.

As can be seen from Figure 8, higher temperature caused higher water absorption in shorter exposure time. It can be observed that numbers of voids and cracking appeared on the fracture surfaces of PCPU, which could not be recovered while cooling to room temperature. This phenomenon can be related to the hydrolytic degradation of PCDL. PCPU could absorb water, resulting in hydrolysis of ester groups, breaking down long macromolecular chains at immersion temperature of 353 K.⁵⁰ Nevertheless, water absorption caused a dramatic increment in WAPs for PEPU and PEPU1-10, but not much change in the morphology. One of the factors could be attributed to the swell ability and absorption ability of PTMG. In other words, higher temperature increases swelling of PEPU structure and subsequently induces higher water absorption. For PEPU1-30 and PEPU1-50, not much change in the morphology appeared which exposed to water absorption at 298 or 353 K, though we can observe slight weight gains (W_m of 2.21% and 2.95% for PEPU1-30 and PEPU1-50 at 353 K, respectively). The improvement of water resistance can be explained by several reasons. One of the reasons is that the presence of PCDL prevents the easy diffusion and penetration of water molecules and results in reduction of water absorption.^{51,52} Another reason is that the formation of H-bonding sites between hard and soft blocks prevents the swelling of the PU samples and subsequently reduces the water penetration.⁵³ In summary, 30–50% PCDL loading reduced water absorption and enhanced the water resistance property of PEPUs.

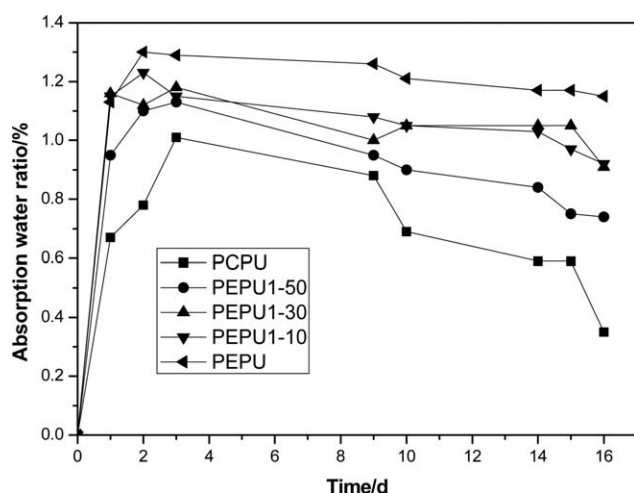


Figure 7. WAP of PUs prepared under different PCDL1000 content at 298 K.

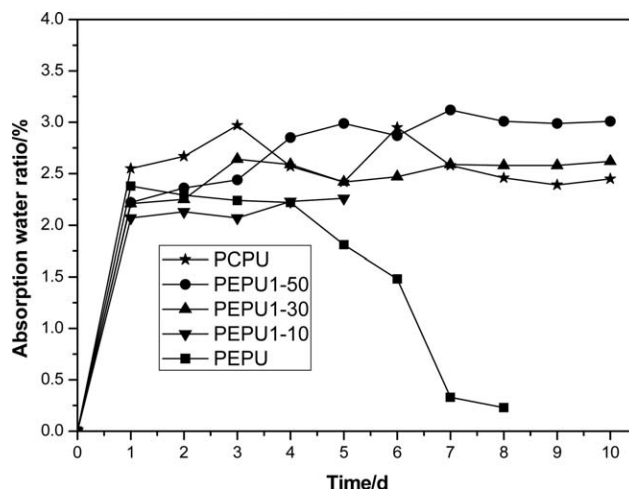


Figure 8. WAP of PUs prepared under different PCDL1000 content at 353 K.

CONCLUSIONS

High molecular weight PCDL modified PEPUs have been successfully synthesized by transurethane polycondensation process from HDC as a hard segment, BDO as a chain extender, and PCDL and PTMG as soft segments. The effect of the PCDL content on the structure and some thermal, mechanical, and optical properties of the PCDL modified PEPUs were studied.

The resulting PUs were colorless, high-molecular-weight (on the basis of intrinsic viscosity values and GPC data) solids. The use of PCDL produced polymers with slightly lower molecular weight but significantly higher tensile strengths and much higher elongations at break. The TG results show that the PCDL modified PEPUs were characterized by higher thermal stability which exhibited higher temperature of 5% weight loss (576–586 K vs. 561 K) and higher T_{max1} and T_{max2} . The PCDL modified PEPUs displayed lower transmittance but better water resistance, owing to its higher concentration of H-bonding sites between both hard and soft blocks. In the case of polymers synthesized from PCDL and PTMG as soft segments, better tensile strengths were achieved when PCDL1000 was employed. The PCDL1000 modified PEPUs showed better mechanical and thermal properties than the PCDL 2000 modified PEPUs.

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