Synthesis and Characterization of a Novel Polyurethane Elastomer Based on CO_2 Copolymer

Shouping Xu,[1,2] Min Zhang[1]

[1]*Guangzhou Institute of Chemistry, Chinese Academy of Science, Guangzhou 510650, China*
[2]*Graduate School of Chinese Academy of Science, Beijing 100049, China*

ABSTRACT: Novel poly(ethylene ether carbonate) polyurethane elastomers (PEC-PUE) based on methylene diphenyl diisocyanate (MDI) and poly(ethylene ether carbonate) diol (PEC) were prepared and characterized. The diol PEC was a new material obtained by copolymerization of ethylene oxide and CO_2 in the presence of polymer supported bimetallic catalyst (PBM). When the diol PEC reacted with MDI and with 1,4-butanediol as the chain extender, a novel polyurethane elastomer can be formed. The elastomer was characterized by FTIR and ^1H NMR. The mechanical properties were studied by tensile set and the thermal properties were studied by TGA. Results of the tests indicated that mechanical strength of the elastomer can be improved by adjusting the ratio of NCO/OH. The thermal stability as well as tensile strength (TS) decreased sharply after being exposed to moisture and with bonded water in the polymer structure. It was also discovered that as the bonded water evaporated, both the thermal stability and TS would recover. Moreover, shape memory behaviors of the elastomer were also studied, and it was found that all the samples tested returns to its original shape in 100 s. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 3818–3826, 2007

Key words: elastomer; polyurethane; polycarbonates; thermogravimetric analysis

INTRODUCTION

The consumption of all fossil fuels will lead to CO_2 formation, and CO_2 itself has little value by far but contributes much of the greenhouse effect. Any success in feasible CO_2 utilization will attain double benefits, slowing down the increasing rate of greenhouse gases in the atmosphere and utilizing the carbon resource better.

Pioneered by Inoue et al.[1] in 1969, the copolymerization of CO_2 and epoxides to form aliphatic polycarbonates has induced an increasing interest as an efficient way of utilizing CO_2. The catalyst design has been regarded as the driving force during the past decades and many progresses have been made in this area.[2–6] Among all the catalysts reported, polymer supported bimetallic catalyst (PBM)[7,8] are known to catalyze the copolymerization of carbon dioxide and epoxides, and produce aliphatic polycarbonate diols in mild conditions.

Compared with these traditional ways of producing polycarbonate, this method has its advantage. First, without phosgene used or produced it is environmental friendly; second, by using CO_2 as one of the main materials it saves natural resource; third, it cut down the cost of polycarbonate diols. Moreover, the produced aliphatic polycarbonate diols possess designed numbers of hydroxyl end groups, and can be used for the preparation of various polyurethane materials.[9–11]

Aliphatic polycarbonate polyurethane like other kinds of polyurethane, consists of a soft phase and a hard phase. The hard segment is formed as a result of the interaction of the Methylene diphenyl diisocyanate (MDI) with 1,4-butanediol (BDO) or trimethylolpropane (TMP), while the soft segment is made up of ether, ester, and carbonate groups.[12] Furthermore, comparing with the ether and ester groups the use of carbonate group will be to likely improve the resistance to hydrolysis and oxidation of the material.[13,14] And it provided the medical device industry with practical alternatives to subsistent polyurethanes.[15,16]

With these characteristics, the aliphatic polycarbonate polyurethane can be used in a wide variety of industrial products, including industrial parts, building materials, sports goods, medical equipment, and even artificial tissues. However, polycarbonate polyurethane has not been put into large scale utili-

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zation until now. The expensive cost of aliphatic polycarbonate diols might be one of the most important reasons. Because polycarbonate diols were usually obtained either by polycondensation of phosgene with diols or transesterification of five-membered cyclic carbonates with diols,[17–19] which was not only detrimental to the environment but also energy consuming.

Although polycarbonate diols produced by copolymerization of carbon dioxide and epoxides under the catalyzing of PBM can cut down the cost, as a material for preparing polyurethane, it is brand new. A lot of studies have to be carried out in this field. In the article, much attention has been paid on the mechanical, thermal, and hydrolytic properties of the novel polycarbonate polyurethane elastomer based on the CO_2 copolymer diols. Since the novel elastomer may be potential for surgery and tissue repair, shape memory behaviors were also studied.

EXPERIMENTAL

Materials

Ethylene oxide was commercially obtained and was dried over 4 Å molecular sieves, as to keep the water content less than 400 ppm (determined by Kart Fisher titration). CO_2 was also a commercial product and its purity was 99.99 (wt %). Methylene diphenyl diisocyanate (MDI) was purchased from Qingdao Chemical Co. (Shangdong, China), and was used without further purification. 1,4-butanediol (BDO) and trimethylol propane (TMP) were purchased from Shanghai Feiya Co. (China), and were dried separately for 3 h at 100°C, under reduced pressure. Polymer supported bimetallic catalyst (PBM) was prepared according to a reported method.[7]

Preparation of the polycarbonate diols

Poly(ethylene carbonate) polyols PEC was synthesized by copolymerization of ethylene oxide and CO_2 in the presence of PBM catalyst (Scheme 1) in a 5 L autoclave according to reported procedures.[7,8] Unreacted ethylene oxide was removed and recovered by a reported method.[20] The residual catalyst (≤2%) in PEC was deactivated by hot water treat-

ment. Then the polycarbonate diols were dried at 70°C under vacuum for 4 h. All of the works are easy to handle, because the PEC diol is liquid at room temperature.

### Preparation of poly(ethylene ether carbonate) polyurethane elastomers

APC-PUE was prepared using a two step bulk polymerization procedure (Scheme 2). PEC polyols 105 g (0.05 mol) was filled in a 500-mL four-necked flask equipped with a stirrer, a vacuum resource, a thermometer, and N_2 inlet. As the polyols was heated to 60°C, calculated amount of MDI was added into the flask, and was vigorously stirred for 15 min. Then the reaction temperature was elevated to 75°C, after another 15 min the NCO terminated prepolymers can be obtained.

Calculated amounts of BDO or TMP, or their mixture were finally added to the system as chain extender and crosslinker. It was allowed to react further for about 5 min until the reaction mixture became viscous. The synthesis process was better to be carried out under reduced pressure. Finally the product should be conditioned in a steel mold under vacuum at 70°C for 4 h, and then 100°C for 1 h. After cooling, the newly produced polyurethanes were used for testing.

Measurement

The average molecular weight was determined by a Waters GPC instrument, equipped with a TSK gel Super HM-H*4 column and a RI detector, the eluent was DMF, the flow rate was 0.5 mL/min, the operation temperature was set to be 40°C, and the molecular weight was calibrated with polystyrene standards.
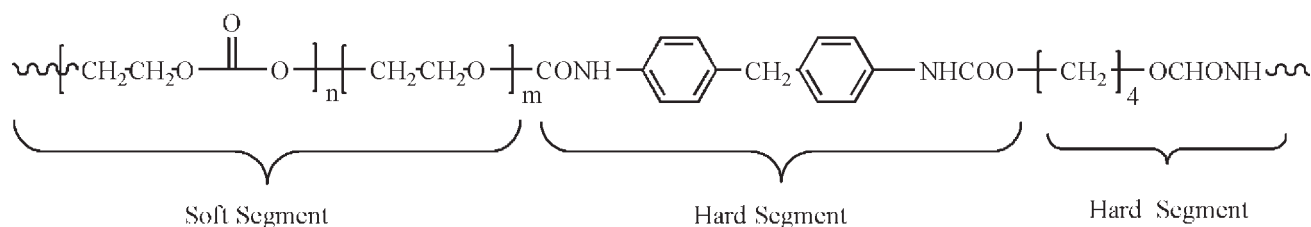
^{1}H NMR spectra were recorded by DIX-400 spectrometer (Bruker, Germany). Tetramethylsilane (TMS) was used as an internal standard material, and measuring temperature and frequency were 25°C and 400 MHz, respectively. The measuring conditions of the materials were the same, except the solvent. In the test of PEC, $CDCl_3$ was used, and in the test of poly(ethylene ether carbonate) polyurethane elastomers (PEC-PUE), DMSO was used as solvent.

R=H or CH₃　　　　　　　　　　　　　　　　　　　　　（APC-Diol）
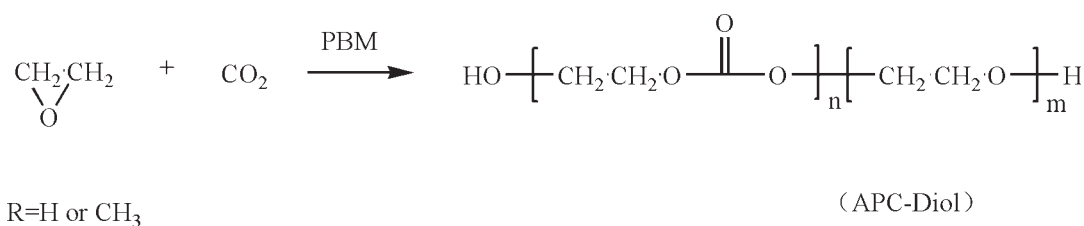
Scheme 1 Synthesis procedure of PEC.
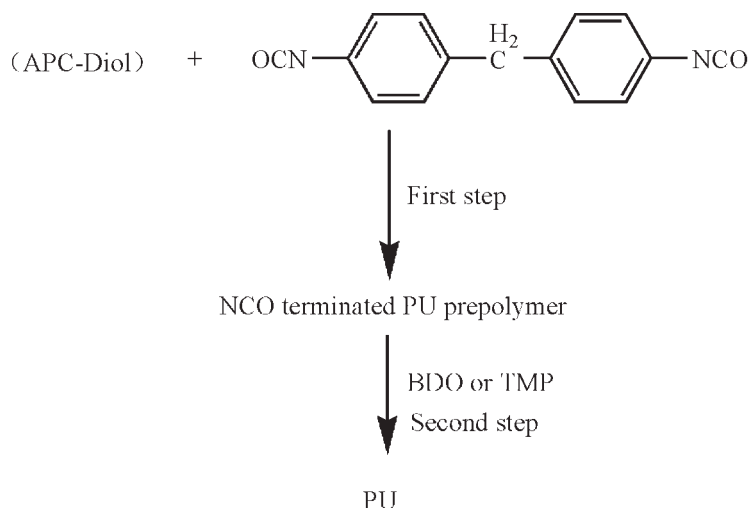
Scheme 2   Synthesis procedure of PEC-PUE.

^{13}C Nuclear magnetic resonance (NMR) spectroscopy was performed on a Bruker AMX-400 (100 MHz) spectrometer and CDCl$_3$ was used as the solvent.

The IR spectra were recorded on a WQF 410 Spectrophotometer made in Beijing China, using the KBr pellet technique.

Stress/strain properties of all the polyurethanes were measured on a standard testing machine provided by Shenzhen Xinsansi Co.

The thermal stability was examined by the gravimetric analysis (TGA) using the Perkin-Elmer Pyres 1.

RESULTS AND DISCUSSION

Characterization

Characterization of PEC

The hydroxyl value (HV, mg KOH/g polymer) was measured by titration. First 0.5 g PEC was added to 20 mL solution of pyridine/acetic anhydride with the ratio 89/11 (v/v) in a 100 mL round-bottomed flask. And equipped the flask, with a vertical reflux condenser and a magnetic stirrer then the flask should be heated in boiling water bath for 2 h. The mixture was cooled to room temperature and then 25 mL of cold distilled water was added into the system. This solution was titrated against 0.5N KOH solution using phenolphthalein as indicator. A blank was also performed using the same steps without the sample.[21] The data from the average of five measurements was 58.5 mg KOH/g, and the M_n value calculated by determination of the end groups was 2085.

According to the GPC results, the M_n of PEC produced from ethylene oxide and CO$_2$ in the presence of PBM is around 2000, and the poly dispersity is 1.17, which coincident with the M_n value calculated by determination of the end groups.

The structure of PEC was verified by ^{1}H NMR. Deuterated chloroform (CDCl$_3$) was used as solvent, tetramethylsilane (TMS) was used as an internal standard material. Measuring temperature and frequency were 25°C and 400 MHz, respectively.

According to ^{1}H NMR spectrum, peaks at 4.33 and 4.24 ppm belong to the protons of —COO—CH$_2$CH$_2$—O— group, the sharp peaks at 3.62 and 3.61 ppm are due to the protons of the —O—CH$_2$CH$_2$—O— group. And calculated from the integral, the novel polyol was confirmed to have a high content of COO segment, molar ratio of —COO—CH$_2$CH$_2$—O— group/—O—CH$_2$CH$_2$—O— group is 1 : 1, as shown in Scheme 1, in the PEC structure the ratio of m/n is 1 : 1.

And it's possible to assign all the ^{13}C NMR lines in the ^{13}C NMR spectroscopy. Carbons of the carbonyl is 155.4 ppm; carbons α to carbonate oxygen, β to ether oxygen, 62.4 ppm; carbons β to carbonate oxygen, α to ether oxygen, 68.6 ppm; and carbons α to ether oxygen, β to ether oxygen, 77.3 ppm; besides, carbons of the end group (CH_2OH), 61.3 ppm.

Characterization of PEC-PUE

Effective labeling was confirmed by ^{1}H NMR (Fig. 1), the measuring conditions were the same as the measurement of PEC except the solvent. DMSO was used instead of $CDCl_3$ in this test.

As shown in Figure 1, chemical shift at 7.28 and 7.05 ppm (aromatic protons belong to the phenylene derivative from MDI) were presented. And at 2.49 ppm (protons of methylene derivative from MDI) also appeared. Peaks at 4.33 and 4.24 ppm belong to the protons of $-COO-CH_2CH_2-O-$ group, and peaks at 3.62 and 3.61 ppm belong to the protons of the $-O-CH_2CH_2-O-$ group, respectively.

^{13}C NMR spectroscopy of the PU is more complicated than that of PEC. ^{13}C NMR (100.613 MHz, $CDCl_3$), 155.4 ppm belongs to carbons of ($O-CO-O$), 154.4 ($O-CO-NH$), 115–140 (aromatic carbons), 61.5–77.3 (CH_2O), 40.2 (CH_2N) ppm.

The polymer structure was also characterized by Fourier transform infrared spectrophotometer (FTIR). The infrared spectra of the synthesized PU thin films on KBr disc in the zone 400–4000 cm^{-1} are presented.

As shown in (Fig. 2), the following bands can be observed: 3347 cm^{-1} (NH stretching band assigned to hydrogen bonded NH groups), 2800–3000 cm^{-1} (asymmetric CH_2 stretching: 2975 cm^{-1}; symmetric CH_2 stretching: 2851 cm^{-1}), 1751 cm^{-1} (C=O of $-O-CO-O-C$ stretching vibrations, which is quite strong and overlaps with the C=O of $-NH-CO-O$ stretching vibrations), 1500–1600 cm^{-1} ($\delta_N-_H + \nu_C-_N + \nu_C-_C$).[22]

Absorption at 1226 cm^{-1} is the typical urethane $C-N$ stretch. The peak at 1263 cm^{-1} is ($C-O-C$ of

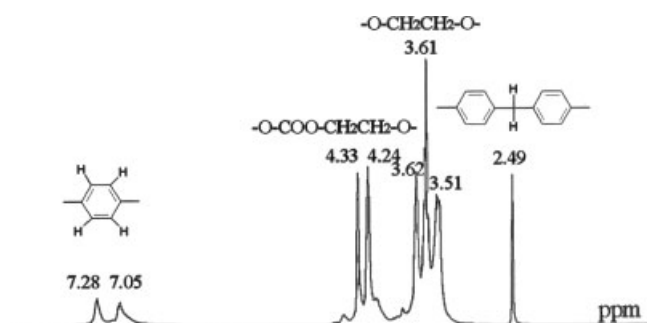**Figure 1** ^{1}H NMR spectrum of PEC-PUE. The PU tested was produced from PEC, MDI, and BDO, and the molar ratio of PEC : MDI : BDO is 1 : 2 : 1.
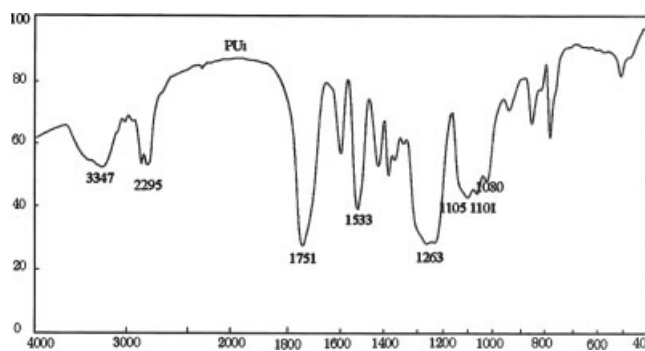

Figure 2 FTIR spectrum of PEC-PUE. The PU tested was produced from PEC, MDI, and BDO, and the molar ratio of PEC : MDI : BDO is 1 : 2 : 1.

$CO-O-C$),[23] and it is also a significant character of PU_1 (PEC-PUE, which was produced from PEC, MDI and BDO, the molar ratio of PEC : MDI : BDO is 1 : 2 : 1), which shows the existence of a lot of carbonate carbonyl. And peaks around 1101 cm^{-1} are ether $C-O-C$ stretch, 1101 cm^{-1} and 1080 cm^{-1} urethane $C-O-C$ stretch.[24]

FTIR and ^{1}H NMR spectra were both consistent with the proposed structures of the diols and elastomer (Scheme 1 and Scheme 2).

Mechanical properties of PEC-PUE

Stress/strain properties of all the polyurethanes were measured on a standard testing machine provided by Shenzhen Xinsansi Co. Dimensions of the sample were 50 × 4 × 2 mm^3 and the crosshead speed was 100 mm/min at 25°C and 50% humidity. The data given are the average of five measurements.

On the basis of the specific materials, MDI, PEC, and BDO, influence on tensile strength (TS) and elongation at break were studied and discussed to obtain higher performance elastomers.

Influence of R

R, the isocyanate index, is the ratio of the equivalents of NCO groups to OH groups,[25–26] and the calculating formula is R = (NCO)/(OH of BDO and TMP and PEC). For the following studies R [isocyanate index, which is the ratio of NCO/(OH of PEC, BDO and TMP)] was varied from 0.96 to 1.14.

It was shown in Figure 3, as R increases, TS increases and the peak can be observed when R reaches 1.10. However, elongation at break decreases straightly. The reason for improvement in the values of TS may due to the occurrence of allophanate formation. When R ≤ 1, NCO groups and OH groups will react to form urethane; if R > 1, the excess NCO groups will react with urethane groups
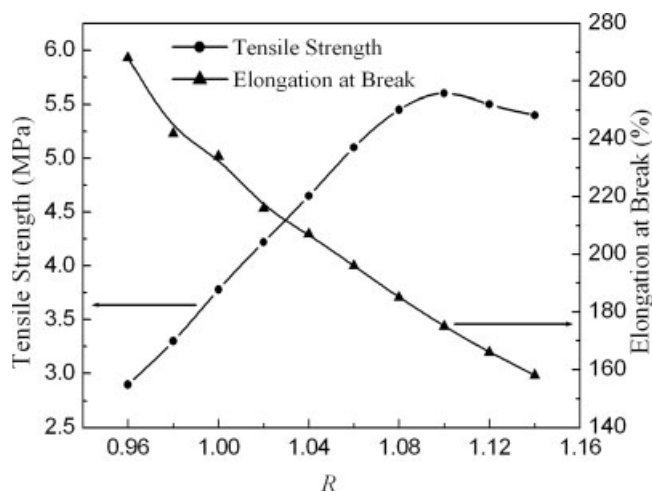
Figure 3 Influence of R on mechanical properties of PEC-PUE. Materials used were PEC, MDI, and BDO, and R varied from 0.96 to 1.14, while molar ratio of PEC : BDO keeps 1 : 1.

and form allophanate linkages, and each allophanate linkage is a potential crosslink point (Scheme 3).[25,26]

However, an excessive amount of allophanate linkages increase viscosity of the system and negative effects show up. First, the pot-life of the polymerization decreases, because the viscosity increases, polymers are likely to become solidified in the reactor; second, when viscosity increases, the movement of functional groups will be affected and the average molecule weight will decrease; third, as crosslinking happens elongation at break decreases straightly. As a result, different R values can be chosen to fulfill different requirement of TS and elongation.

Influence of R_1

R_1 [Isocyanate index during the preparation of isocyanate terminated PU prepolymers, which is the

ratio of NCO/(OH of PEC only)], the preisocyanate index, is the ratio of the equivalents of NCO groups to OH groups during the preparation of isocyanate terminated PU prepolymers and the calculating formula is $R_1 = (NCO)/(OH \text{ of PEC only})$. As shown in Figure 4, while the isocyanate index R equals 1, increasing in R_1 means the increase of MDI and chain extender, and the increase of hard segment.

Results in Figure 4 indicate that as the concentration of hard segments increases, TS and elongation at break of the elastomer both rise. In the polyurethane structure, the hard segment is formed by the MDI and chain extender, and increase in the hard segment will increase the intermolecular attraction, which is mainly the hydrogen bonding between —NH and —C=O. Because of the enhancement of intermolecular attraction, mechanical properties of the elastomer improved.

But the mechanical properties did not increase constantly, especially the elongation. It dropped when R_1 was around 2.1. As concentration of the polyol decreases, crosslink between each separate chain will increase. As a result, the linear decreases in elongation and increases in TS, the polymer becomes increasingly hard as well. At the beginning of the process, some slight increase can be observed about the elongation, it might be because the TS was not strong enough to support the stretch.

Influence of chain extenders

Until now, chain extender used has been BDO, which is a difunctional component and is always used as chain extender in the PU field. It is known that some crosslink will enhance the TS. In the following studies except for difunctional BDO trifunctional TMP was also used as chain extenders.

In this article, BDO content, which is (OH of BDO)/(OH of BDO and TMP), was used to measure
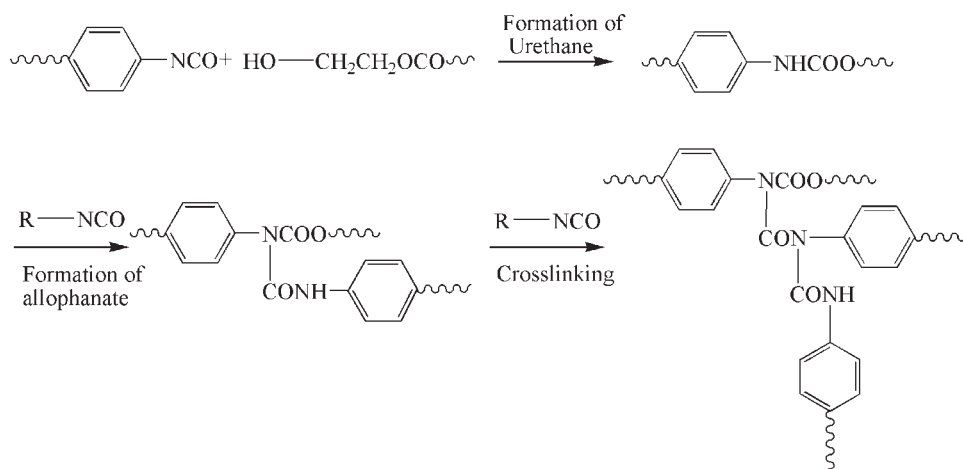
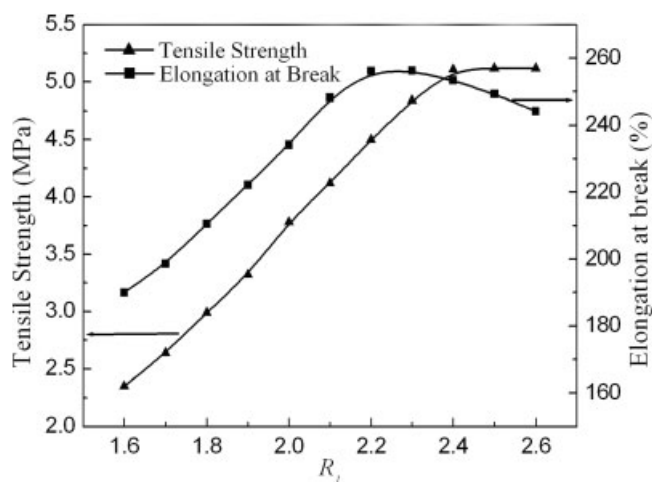**Scheme 3** Crosslinking of the polymer chains when $R > 1$.

Figure 4 Influence of R_1 on mechanical properties of PEC-PUE. Materials used were PEC, MDI, and BDO, and R_1 varied from 1.6 to 2.6, while R remains 1.

different ratios of difunctional and trifunctional components, and its influence on mechanical properties has also been studied. As shown in Figure 5, BDO based elastomers showed higher elongation, but lower TS than TMP based elastomers.

The reason might be that, BDO is a difunctional component, while TMP is a trifunctional component, which will lead to the formation of network in polymers. When the network is formed, flexibility of the polymer will be reduced, and the elongation will decrease accordingly. However, the influence on flexibility of chain extender is much smaller. Prepolymers reacted with BDO will give rise to complete chain extended species, while reacted with TMP, crosslinking will happen.[27] As a result, BDO based elastomers showed higher elongation but lower TS than TMP based elastomers.

However, as Figure 5 shows, the largest TS happens when the BDO content is a bit more than 90%, TMP only takes a little part. It is possibly because that if TMP is used as a chain extender and crosslinker, the intermolecular linkage will be enhanced, but the flexibility of the polymer chain will be decreased. Besides, the chain of TMP molecule is quite short, so in the synthesis process when the linkage is formed, blocks will be formed and will obstruct the reaction of some functional groups. As a result, the largest TS appears when TMP takes only 10% of all the chain extenders and crosslinkers.

Hydrolysis properties

In the following research studying the properties of the PEC-PUE, chips tested are all PU_1 samples, that is BDO was used as chain extender, and the molar ratio of MDI : BDO : PEC was 2 : 1 : 1.

The hydrolytic stability was tested as follows, polymer chips (dimensions were $50 \times 4 \times 2$ mm^3) were immersed respectively, in HCl solvent with pH = 4.0, NaOH solvent with pH = 9.5, and distilled water at 50°C. After a period of 6 days, the films were then taken out and the surplus surface water was removed by a filter paper, the swelling percentage was determined from the weight increase.[28]

$$\text{Swelling (\%)} = (W_1 - W_0)/W_0 \times 100$$

where W_0 is the weight of the original film and W_1 is the weight of the film at equilibrium swelling. And the mechanical decrease can be observed from the change of TS.

$$\text{TS decrease}^1 \text{ (\%)} = (P_0 - P_1)/P_0 \times 100$$

where P_0 is the TS of original film and P_1 is the TS of the film at equilibrium swelling.

Then the above swelled films were rinsed thoroughly with distilled water and dried in vacuum at 80°C for 4 h, the degree of degradation was determined by weight loss.[28]

$$\text{Loss (\%)} = (W_2 - W_0)/W_0 \times 100$$

where W_0 is the weight of original film and W_2 is the weight of dried films after degradation. And the mechanical decrease can be observed from the change of TS as well.

$$\text{TS decrease}^2 \text{ (\%)} = (P_0 - P_2)/P_0 \times 100$$

where P_0 is the TS of original film and P_2 is the TS of dried films after degradation.
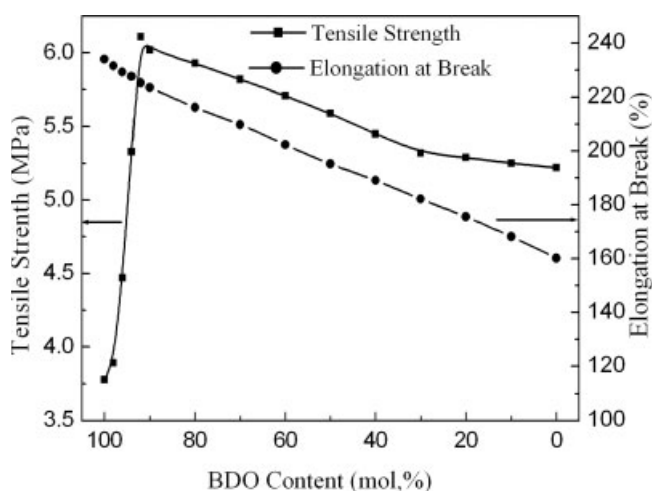

Figure 5 Influence of chain extenders on mechanical properties of PEC-PUE. Materials used were PEC, MDI, BDO, and TMP, the content of BDO and TMP was changed, while R remains 1, R_1 remains 2.

Water contained in the PU after immersion in water for some time can be divided into two kinds free water and bonded water,[29] and the bonded water has been proved to have notable effect on polymer's mechanical properties.[30,31]

As shown in Table I, the TS decreased sharply with moisture, when BDO was used as chain extender the hydrogen bonding between —NH and —C=O may be the main connection between each individual polymer chains, and when this bond was weakened by the interference of H_2O (Scheme 4),[29,30,32] TS decreased. However, if the bonded water was moved out of the system, the mechanical properties recovered.

Compare the samples listed in Table I, the PUEs exposed to acid solvent and distilled water seem to be more stable than the one exposed to basic solvent, which means the PEC-PUE can stand the acid better than the alkalescence. One of the reasons might be that, the hydrolysis of carbonate linkages in PEC-PUE produces carbonic acid,[19,31] and the existence of acid in original solvent will prevent further decompose of the carbonate linkage because of the balance. But in the NaOH solvent, when the pH = 9.5, some acid produced by hydrolyzation will be used for neutralization before getting the balance, that is say more of the PU will be hydrolyzed in based solvent. As a result, polyurethane containing carbonate units has higher hydrolytic stability in acidic solvent.

Thermal properties

The thermal stability was examined by the gravimetric analysis (TGA) using the Perkin-Elmer. Samples

TABLE I
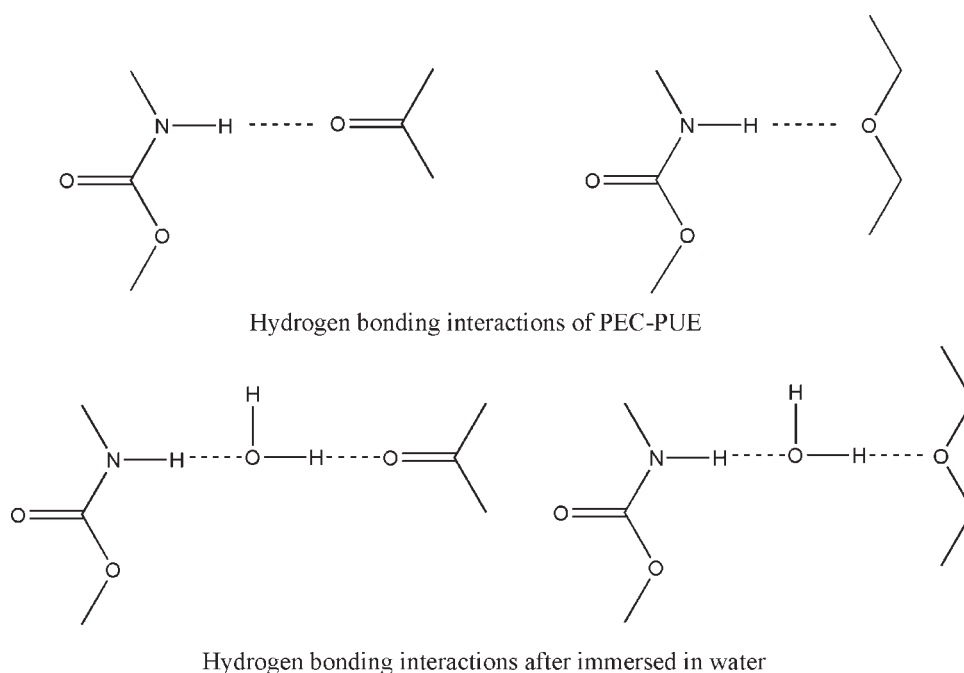**Changes Observed After Immersion in Water for 6 days**

pH	Swelling (%)	Loss (%)	TS decrease[1]	TS decrease[2]
4.0	2.97	2.42	9.9	0
6.8	3.75	3.06	10.2	0
9.5	4.92	5.70	11.3	3.1

PEC-PUE samples tested was produced from PEC, MDI, and BDO, and the molar ratio of PEC : MDI : BDO is 1 : 2 : 1.

weighing 20–25 mg were heated at a constant heating rate of 20°C/min in nitrogen atmosphere. All of the samples were hold at 50°C for 1 min and then heated to 600°C at a rate of 20°C/min.

In Figure 6, PU_1 is PEC-PUE, which was produced from PEC, MDI and BDO, the molar ratio of PEC : MDI : BDO is 1 : 2 : 1, PU_2 is PU_1 immersed in distilled water for 6 days, and PU_3 is PU_2 dried in vacuum for 4 h at 80°C. The PU_2 trace, on which the onset temperatures is the lowest among the three samples, which indicates thermal property as well as the mechanical properties decreases with moisture.

The PU_3 trace is the TGA results of hydrolyzed sample dried in vacuum at 80°C for 4 h, and the PU_1 trace is the TGA results of original sample. These two lines almost superpose against each other, which means first, heated to 80°C and dried in vacuum for 4 h is an effective way to remove bonded water from the polymer; second, the thermal stability of the PEC-PUE will recover to the original state when the bonded water is moved away by heating; third, the elastomer is quite stable when exposed to

Hydrogen bonding interactions of PEC-PUE

Hydrogen bonding interactions after immersed in water

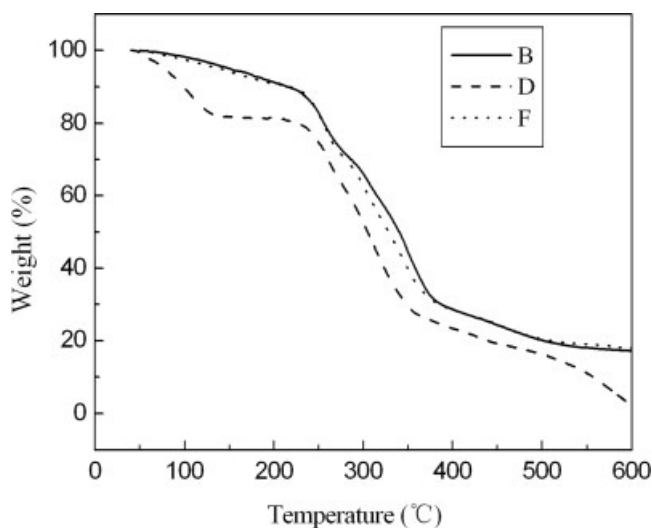**Scheme 4** Hydrogen bonding interactions before and after swelling.

Figure 6 TGA traces of PEC-PUE. PU$_1$ is PEC-PUE, which was produced from PEC, MDI, and BDO, the molar ratio of PEC : MDI : BDO is 1 : 2 : 1, PU$_2$ is PU$_1$ immersed in distilled water for 6 days, and PU$_3$ is PU$_2$ dried in vacuum for 4 h at 80°C.

water, the 6 day's hydrolysis has caused little influence on the polymer's thermal properties.

The observed results show that the existence of H$_2$O in the elastomer will decrease the thermal stability as well, this phenomenon might also due to the insert of H$_2$O between the linkage of polymer chains, which resulted into weakening the crosslinking band of C=O and NH (Scheme 4). Therefore, thermal stability deceased accordingly.

Shape memory properties

PEC-PUE was also made into bars for shape memory test and the dimensions are 20 × 5× 3 mm^3.

As shown in Scheme 2, the PEC-PUE has two separated phases, one of which exhibits a higher thermal transition which is responsible for the permanent shape, and the other shows a lower thermal transition which enables the movement and fixation of the temporary shape.[33,34] The movement and fixation of the soft segment may contribute to the shape memory behavior.

On the basis of the results of differential scanning calorimetry (DSC) tests, which were carried out on a Seiko 220 DSC instrument at a constant heating/cooling rate of 20°C/min. T_g of the soft segment of PEC-PUE appears around −4.5°C. So similar to other TISMPs (thermal induced shape memory polymers) based on T_g, PU$_1$ can be deformed at a temperature above its T_g, and the deformation can be fixed at a temperature below T_g, (its mechanism is describedas follows: the polymer can retain temporary shape by deformation at the temperature above its T_g, and cooled down below T_g; then if heated above T_g, the

material will return to its original shape[35]). When the deformed sample was heated to a temperature above T_g, PU$_1$ could return to its original shape.

In this study, the temperature below the T_g is −8°C, temperature above the T_g is 25°C, and the deformation is folding the sample to 180°.

Under the experimental conditions, almost all the deformed bars returned to their original shape in 100 s, which indicates that the polycarbonate polyurethane has good shape-memory properties. The shape recovery ratio of the polyurethane, which is (splayed angle)/180°, kept over 95% after repeated tests of the same sample for more than 20 times.

CONCLUSION

Under the catalyzing of PBM, the ethylene oxide and CO$_2$ can be copolymerized and a kind of polycarbonate diol (PEC) can be produced.

A series of elastomers (PEC-PUE) based on the polycarbonate diol were synthesized and characterized. The novel material was proven to have a high content of carbonate segment, which contribute to the soft segment of the elastomer. Mechanical, hydrolytic, thermal, and shape memory properties were also studied, and conclusions made from these tests are as follows:

1. Mechanical strength of the elastomer can be improved by increasing the ratio of NCO/OH, however, elongation at break will decrease.
2. TS will be enhanced by increasing the percentage of TMP in chain extender, and the largest TS exists when the ratio of BDO : TMP equals 9 : 1.
3. PEC-PUE was quite stable when exposed to acid solvent and distilled water, when bonded water existed in their structure, mechanical, and thermal properties both decreased slightly, but if the bonded water evaporated, they would recover.
4. The PEC-PUE has good shape memory property.

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