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Synthesis and performance of thermoplastic polyurethane based on poly(ethylene carbonate) diol and polycaprolactone diol

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Synthesis and performance of thermoplastic polyurethane based on poly(ethylene carbonate) diol and polycaprolactone diol

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Abstract: The thermoplastic polyurethane (TPU) was prepared through solution polymerization using polycaprolactone diol(PCL) and poly(ethylene carbonate) diol (PECD) as soft segment. PECD was synthesized from carbon dioxide and ethylene oxide. The effect of the relative content of PECD and PCL on the mechanical properties, resilience, solvent resistance and resistance to wet-heat aging properties of TPU was systematically investigated. The results showed that as the content of PCL increased, both the tensile strength and the elongation at break increased, reaching 66MPa and 780% when the content of PCL was 60 wt%. The fixed elongation tensile test showed that the TPU with 30 wt% PCL exhibited the optimal resilience. This result was highly consistent with the results of dynamic thermomechanical analysis(DMA), and the corresponding solvent resistance was markedly enhanced. When the PCL loading reached 50 wt%, the TPU exhibited the optimal cycling stability. PECD/PCL-TPU possessed outstanding resistance to organic solvents. Notably, the sample with 50 wt% PCL maintained a low and balanced swelling rate in toluene, ethyl acetate, butanone, water, and methanol. Thermogravimetric analysis (TGA) showed that the initial decomposition temperature ($T_{5\%}$) of all PECD/PCL-TPUs exceeded 280 ℃, indicative good thermal stability. During the wet-heat aging, these PECD/PCL-TPUs maintained a relatively high strength retention after short aging times. The results after 500 hour of aging indicated that the strength retention rate was positively correlated with the content of PECD.

Keywords: poly(ethylene carbonate) diol; thermoplastic polyurethane; resilience; solvent resistance

Statements and Declarations

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1. Introduction

Carbon dioxide (CO_2) is widely present in the atmosphere and is one of the abundant carbon resources in nature. As an ideal chemical raw material, it has significant application value [1]. With the continuous deepening of global research on the chemical conversion and resource utilization of CO_2, the synthesizing various chemical materials from CO_2 has become a carbon sequestration approach with significant economic benefits, environmental protection significance, and scientific

value [2]. PECD is synthesized through the copolymerization of CO_2 and ethylene oxide (EO)[3]. It is a newly developed low-molecular-weight diol, and its structure contains carbonate bonds and ether bonds. Compared with industrialized poly(propylene carbonate) diol (PPCD)[4, 5], PECD has a more regular chemical structure and is more cost-effective. It has a promising application prospects in the polyurethane industry[6, 7].

TPU is a linear polymer formed by the copolymerization reaction of hard segments and soft segments. Among them, the carbamate bonds in the hard segments can form intramolecular and intermolecular hydrogen bonds, causing the hard segments to aggregate and form physical crosslinking points, which provides TPU with excellent tensile strength, wear resistance[8], heat resistance and other physical properties. Its soft segments are composed of polyether diol, polyester diol or their mixtures, providing TPU with rubber-like elasticity. The hydrogen bonds between TPU molecules can be dissociated when the temperature rises. When the temperature drops, the hydrogen bonds will re-form and undergo physical cross-linking. This enables TPU to be processed through various thermoplastic material processing techniques such as injection molding, extrusion, blow molding, calendering, and thermoplastic molding to produce products of various shapes, making TPU applicable in multiple fields [9].

At present, the traditional polyols used in TPU[10–13] are mainly obtained from petroleum. However, the petroleum refining possess is costly, energy-intensive, and has led to an increasing environmental problems, which has prompted researchers to seek more environmentally friendly alternatives. As a result, the development of sustainable materials has become a research hot topic, which has aroused great interest among enterprises and the academic communities in the utilization of renewable resources.

Currently, using PECD as a polyol for TPU synthesis is an effective application approach. Previously, Xu et al.[14] used PECD to prepare TPU, but the mechanical properties of the product were low and had no practical value. In 2024, He[15] synthesized PECD-TPU using PECD with a CO_2 content of 23% and MDI as raw materials. The overall performance was similar to that of polyether-based TPU. Liu et al.[16] prepared TPU with a molecular weight of approximately 1.4×10^5 by solution polymerization using PECD with a molecular weight of 2100 and a CO_2 content of 30% and MDI. They found that the PECD-based TPU exhibited excellent comprehensive performance. At 33 wt% of hard segment content, the tensile strength reached 66 MPa, and the

elongation at break was 880%, which was higher than that of the traditional high-performance TPU based on PCL and PCDL. Its solvent resistance was also comparable to that of the later. However, this study did not reveal the specific conditions such as the thermal stability and elasticity of TPU.

Researches have showed that PCL-based TPU has excellent elastic and mechanical properties. Regarding the performance improvement of PECD-based TPU and filling the gap in existing research, in this paper, from the perspective of soft segment structure design, using different proportions of PECD and PCL as the soft segments, diphenylmethane diisocyanate (MDI) as the isocyanate, and 1 4-butanediol (BDO) as the chain extender, a PECD/PCL composite TPU was prepared. The effects of different proportions of PCL on the comprehensive performance of TPU was explored, aiming to develop and utilize sustainable polyol to prepare TPU with excellent comprehensive performance and commercial value. The research provides important experimental basis and ratio reference for the preparation of composite thermoplastic polyurethane and its practical application scenarios.

2. Experimental section

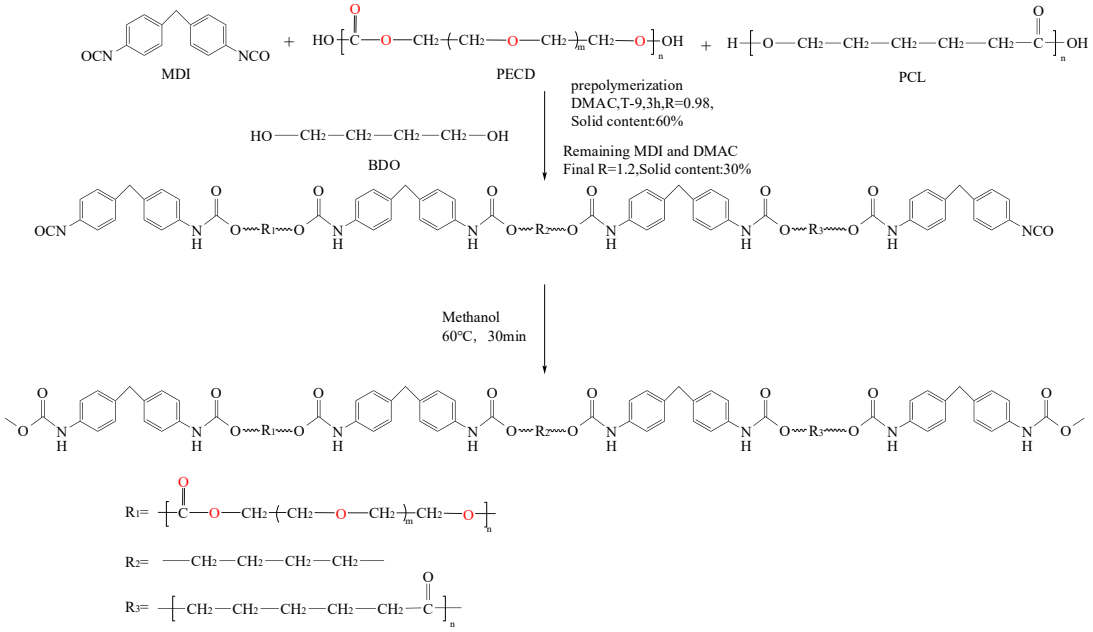
2.1. Material

Poly (ethylene carbonate) diol (PECD, Mn = 3000 g/ mol) was synthesized in our laboratory. polycaprolactone diol (PCL, Mn=2000 g/ mol) was purchased from Ingevity Functional Materials (Zhuhai) Co., Ltd.(Zhuhai, China). Methylenediphenyl Diisocyanate (MDI) was purchased from Wanhua Chemical Group Co., Ltd. (Yantai, China). 1, 4-butanediol(BDO) was obtained from Shanghai Macklin Biochemical Co., Ltd(Shanghai, China). Methanol, N, N-Dimethylacetamide (DMAC) and ethyl acetate were purchased from Tianjin Damao Chemical Reagent Factory (Tianjin, China). Tin (II) 2-ethylhexanoate (T-9), Deuterated chloroform (CDCl3) and tetrahydrofuran were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd (Shanghai, China). Toluene and butanone were purchased from Guangzhou Chemical Reagent Factory (Guangzhou, China). Deionized water was prepared in the laboratory and used as the solvent of solvent resistance test.

2.2. Synthesis of PECD/PCL-TPU

TPU was synthesized by solution polymerization with DMAC as the solvent (As shown in **Scheme 1**) . Firstly, PECD, PCL and BDO were added to a dry three-necked flask equipped with an electric stirrer and stirred in a constant temperature of 30℃ in an oil bath for 30 min to ensure thorough mixing. Subsequently, MDI and T-9 catalyst were slowly added to the flask, and the

reaction temperature was gradually raised to 60℃. The reaction was then continued at a stirring speed of 300 rpm for 3 h. During the pre-polymerization stage, the R value (molar ratio of -NCO/-OH) was set at 0.98, and the solid content of the reaction system was 60wt%. After the reaction reached a stable state, the remaining MDI and DMAC were slowly added to the flask in batches, eventually obtaining a high-viscosity TPU solution with a solid content of 30±1wt%. When the solution reached the preset solid content and viscosity, an excess amount of methanol was introduced to quench the residual free -NCO group. The system was kept at 60°C for 30 min to complete the end-capping reaction. Finally, a polyurethane solution with appropriate viscosity and good fluidity is obtained. The specific feeding formula is shown in Table 1.



Scheme 1 Synthesis route of PECD/PCL-TPUs by solution polymerization method

Table 1 Formulation of TPUs with different ratios of PECD/PCL

Sample \ Material(g)	PECD	PCL	MDI/g	BDO	PECD content in polyols（wt%）
TPU-1	0	40	17.09	3.29	0
TPU-2	8	32	16.96	3.38	20
TPU-3	12	28	16.77	3.42	30
TPU-4	16	24	16.4	3.35	40
TPU-5	20	20	16.72	3.51	50
TPU-6	24	16	16.67	3.55	60
TPU-7	28	12	16.64	3.6	70
TPU-8	40	0	16.49	3.71	100

The solid content of all solutions was30 wt %, the R value was 1.2, and the addition amount of catalyst was 0.5 wt ‰ of the polyols.

2.3. Preparation of TPU films

The polyurethane solution was transferred to a glass beaker, and DMAC was added to adjust its viscosity. After thorough stirring, the mixture was degassed under vacuum for 15 min. Subsequently, the solution was uniformly casting onto a transparent glass plate at a constant speed using a 0.2 mm film applicator. The wet film was cured at 80 ℃ for 8 h and then dried at 120 ° C for 2 h to remove residual DMAC. Finally, a TPU film was obtained.

2.4. Testing and Characterization

^{1}H-NMR spectra were characterized using an AVANCE III 400 MHz superconducting Fourier transform nuclear magnetic resonance spectrometer (Bruker, Germany) with $CDCl_3$ as the solvent. Each spectrum was scanned 16 times. The content of CO_2 in PECD was calculated using the equation (1)[17].

$$F_{CO_2} = \frac{A_{4.3}}{2A_{4.3}+A_{3.7}} \times 100\% \quad (1)$$

The chemical composition of the TPU films were characterized using a N6700 Fourier transform infrared spectrometer (Saiensi Instrument Co., Ltd.). With the wavelength range of 500 to 4500cm^{-1}.

The molecular weight of TPUs were determined by a Waters510 Gel permeation chromatography (GPC, Waters Corporation, USA), using tetrahydrofuran as the mobile phase. The polyurethane solution was diluted by high-purity tetrahydrofuran with a purity higher than 99.9%, and the concentration was adjusted to 3%-5%. Then, it was filtered through a filter membrane with 0.22μm pore size to obtain the sample for detection.

The mechanical properties of the TPU film were tested using a universal testing machine(CMT4204, MTS Systemco., Ltd.). The test was carried out in accordance with the ASTMD412-1998-2002 standard, with the test speed of 200mm/min. The sample is in the shape of a dumbbell, with a length of 25mm and a width of 4mm. It is cut from a film. During the test, five measurements were conducted and the average value was taken as the final result.

The constant elongation tensile-cycle stability performance test was conducted using a universal testing machine (CMT4204, MTS System Co., Ltd.). The test rate was 200mm/min and the deformation rate was set to 100%. During the experiment, the stress-strain curve was recorded, and the elastic recovery rate (ER) was calculated according to the equation (2) (the cut gauge length

L_0 was 16mm, L_1 was the the gauge length when a 100% strain was recorded, and L_2 was the gauge length when zero force was unloaded at the same speed). The sample was in the shape of a dumbbell, with dimensions of 25mm in length and 4mm in width. It was cut from a film. During the test, five measurements was conducted and the average of them was taken as the final result.

$$ER\ (\%) = \frac{L_1 - L_2}{L_1 - L_0} \times 100\% \quad (2)$$

The Dynamic mechanical analysis (DMA) was performed on the DMA+50 dynamic thermomechanical analyzer (Matt Weber, French). The test conditions were -80 to 120℃, with a static load of 3N and an oscillation frequency of 2Hz. The TPU sample strip (approximately 0.3mm×10mm×4mm) was tested in the tensile mode with a heating rate of 10℃/min.

The sample for determining the solvent absorption rate was in the shape of a dumbbell, with dimensions of 25mm in length and 4mm in width. It was cut from a film. The initial mass of each group of sample was recorded as M_1. At 23℃, the samples were soaked in five different solvents for 24 h respectively. After the samples were take out, the solvents on the surfaces were absorbed by filter paper and reweighed immediately, recorded as M_2. The solvent absorption rate was calculated using the following equation (3)[18]：

$$Ds = \frac{M_2 - M_1}{M_1} \times 100\% \quad (3)$$

The contact angle measurements of TPU films were performed using an OCA100 optical contact angle goniometer (DataPhysics Instruments GmbH, Germany). A 5μL of deionized water was dropped on the surface of uniformly thick TPU film sample, and the contact angle of water droplet was recorded. Each sample group was measured three times, and the average value was calculated.

Thermogravimetric analysis (TGA) was conducted in a nitrogen environment (flow rate: 50ml/min) using the TGA 2 analyzer (Mettler Toledo, Switzerland). The temperature range of the test was set from 30 to 600℃, and the heating rate was 10℃/min.

The TPU films were subjected to a double 85 aging resistance test in a constant temperature and humidity chamber (LHS-50CH, Shanghai Yiheng Scientific Instruments Co., Ltd., China). The temperature was set at 85±2℃, the relative humidity was 85±5%RH, and the test duration was 500 hours.

3. Results and discussion

3.1. 1H-NMR analysis

The molecular structure of PECD was characterized by ^{1}H-NMR (As shown in **Fig. 1**). The signal at 4.52 ppm was attributed to the -CH_2- unit of ethylene carbonate. The chemical shifts at 4.20-4.38 ppm (A4.3) belonged to the -CH_2- unit in the carbonate segments, and the chemical shifts at 3.57-3.80 ppm (A3.7) were assigned to the -CH_2- unit in the ether segments. Based on the integrated results of these peak signals, the F_{CO2} of the carbonate group (-COO-) in the PECD polymer chain was calculated according to the equation 1. The results showed that F_{CO2} was 28±1%, which is crucial for the subsequent performance of TPU, as the carbonate groups help to form polarity and intermolecular interactions[19, 20].

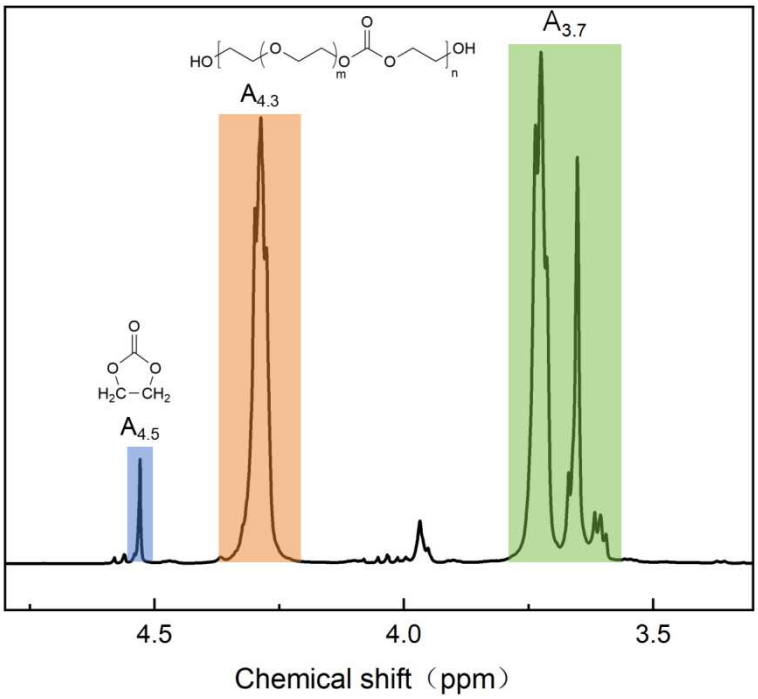


Fig. 1 1H-NMR spectrum of PECD

3.2. FT-IR analysis

The structures of PECD/PCL-TPUs were analyzed by FT-IR spectroscopy, and the results are shown in **Fig. 2**. The FTIR spectra revealed that all TPU samples exhibited nearly identical infrared absorption peak positions after introduction of PCL with different proportions. The asymmetric and symmetrical stretching vibration absorption peaks of methylene (-CH_2-) were at 2865cm^{-1} and 2923cm^{-1}, and the stretching vibration peak of ether group (-C-O-C-) appeared at 1257cm^{-1}. Two characteristic peaks were observed at 1670cm^{-1} and 3330cm^{-1} , which respectively belonged to the

ester group (-C=O-) and carbamate bond (-NH-COO-) of polyurethane. It can be observed that as the proportion of PCL increased, the peak at 1670cm^{-1} became sharper and the intensity rised. The characteristic -NCO peak at 2270cm^{-1} has completely disappeared, indicating that the reaction has been fully completed and there were almost no free -NCO groups remaining. These results conformed that PECD/PCL-TPUs were successfully synthesized.

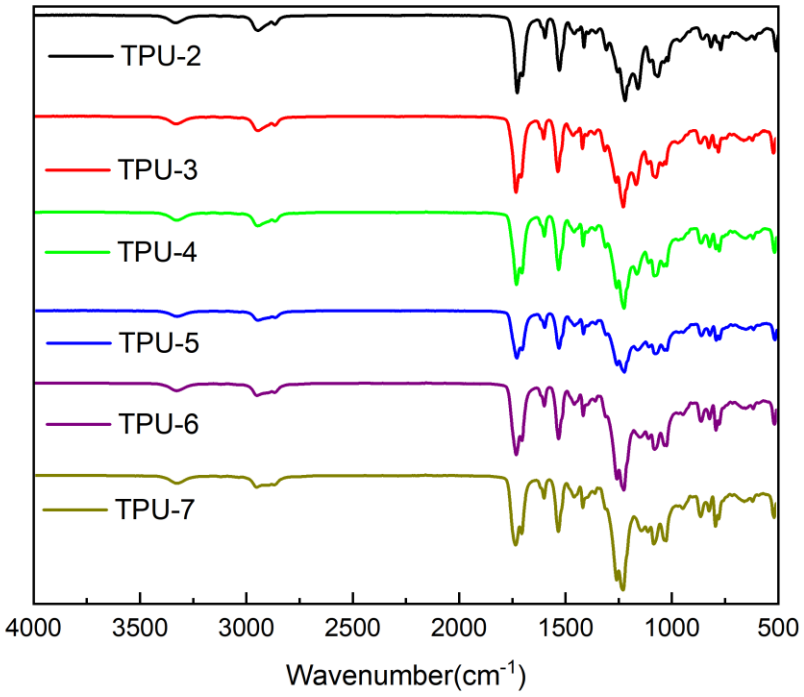


Fig. 2 FT-IR spectra of PECD/PCL-TPUs

3.3. GPC analysis

The relative molecular weights and molecular weight distribution of PECD/PCL-TPU were characterized by GPC, as shown in **Table 2**. The results show that the number-average molecular weights of TPUs were all approximately 100kg/mol, with slight differences in the distribution index.

Table 2 Molecular Weight and Distribution of PECD/PCL-TPUs

Sample	M_n kg/mol	M_w kg/mol	PDI
TPU-1	108	171	1.58
TPU-2	102	171	1.68
TPU-3	108	186	1.72
TPU-4	101	150	1.48

TPU-5	103	166	1.62
TPU-6	100	162	1.61
TPU-7	114	160	1.40
TPU-8	105	150	1.44

3.4. Mechanical properties of PECD/PCL-TPUs

The content of PCL had a great influence on the performances of PECD/PCL-TPU. The mechanical properties of PECD/PCL-TPUs are summarized in **Table 3**.

Table 3 Summary of Mechanical Properties of PECD/PCL-TPUs

Sample	tensile strength (MPa)	elongation at break(%)	100% Tensile strength (MPa)	300% Tensile strength (MPa)
TPU-1	61±2	680±20	3	14
TPU-2	58±2	710±30	3	12
TPU-3	59±2	820±50	4	18
TPU-4	66±3	780±30	4	16
TPU-5	60±3	690±30	4	11
TPU-6	56±2	680±50	4	10
TPU-7	49±2	660±50	4	12
TPU-8	42±2	580±40	5	14

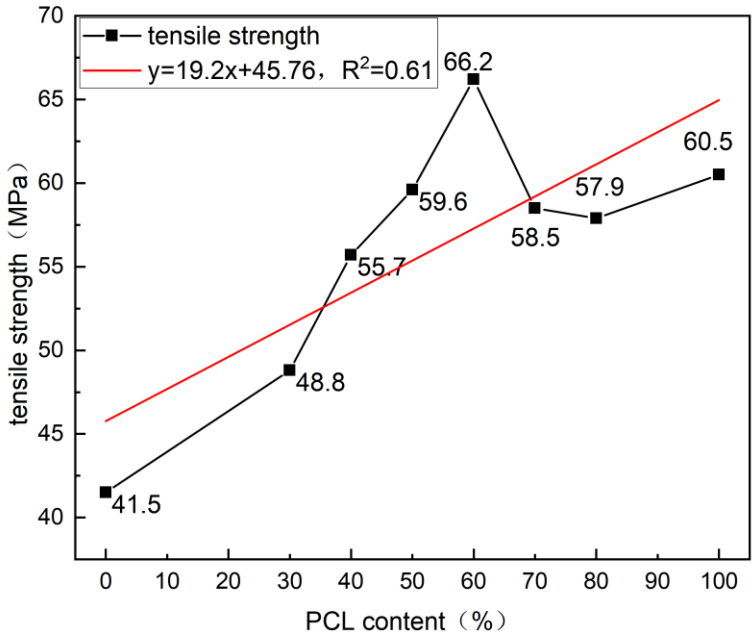


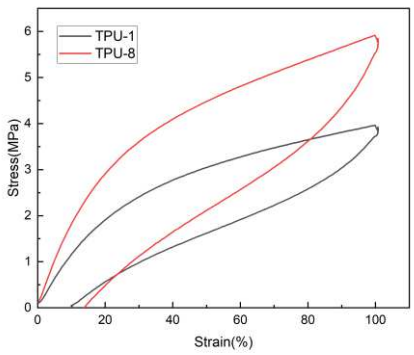
Fig. 3 Trends of tensile strength of PECD/PCL-TPUs

From **Fig. 3** and **Table 3**, it can be observed that as the PCL content increased, the tensile strength of PECD/PCL-TPU first rised and then falled. Among them, the maximum value of TPU-

4 reached 66 MPa. Incorporating an appropriate fraction of PCL as the soft segment can optimize the hard-segment stacking, increase the physical crosslinking density, and significantly enhance the tensile strength. Meanwhile, PECD possesses electron-donating ether bonds, which form strong intermolecular interactions with the ester bonds in the PCL structure[21]. Increasing the content of PCL further reduced the number of electron-donating ether bonds, thereby weakening the intermolecular interactions and resulting in a decline in mechanical properties. TPU-4 achieved the optimal balance of intermolecular forces, thus exhibiting the optimal mechanical strength[22].

3.5. Constant elongation tensile - cycle stability performance test

Constant elongation tensile-cycle stability tests were conducted on the TPU samples, the results are shown in **Table 4** and **Fig. 4 (a~b). It can be seen that** TPU-8 without PCL exhibited the poorest resilience, while the TPUs containing PCL showed improvement to different degrees. **Table 4** revealed that the elastic recovery rate of PECD/PCL-TPUs first decreased and then increased with the rising of PCL content. Among them, the elastic recovery rate of TPU-4 was the lowest, at 89.56%, corresponding to the worst resilience, while the elastic recovery rate of TPU-7 was the highest, reaching 91.28%, corresponding to the best resilience. For PECD/PCL-TPUs, PCL at low content existed in the form of dispersed microdomains. These microdomains can form independent regions enriched with soft segments and hard segments, and construct physical crosslinking points, thereby significantly improving the resilience of TPU. As the content of PCL increased, the compatibility between PCL and PECD improved, accompanied by a reduction in the number of physical crosslinking points, resulting in a decline in resilience. When the PCL content was further increased, PECD gradually existed in the form of dispersed microdomains, its adverse effect on elasticity weakened, and the resilience of TPU gradually recovered.



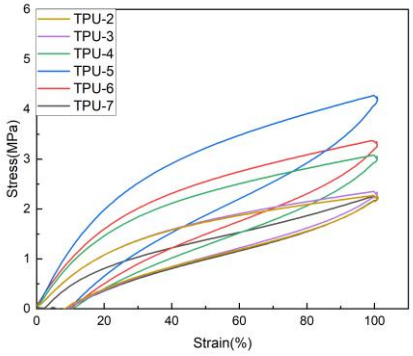


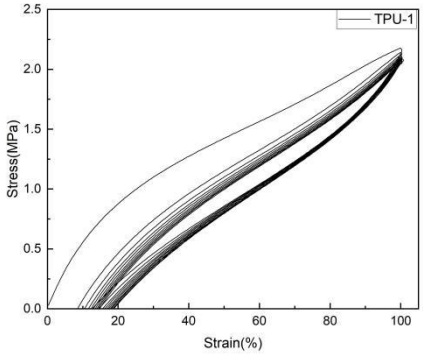
Fig. 4 Hysteresis loops of PECD/PCL-TPUs

Table 4 Cycle elastic recovery rate of PECD/PCL-TPUs

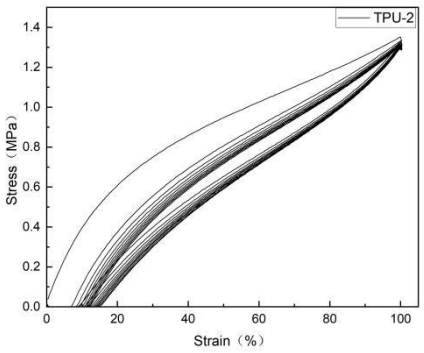
Sample	First cycle elastic recovery rate(%)	Elastic recovery rate after 10 cycles(%)
TPU-1	90.0	81.1
TPU-2	91.1	85.0
TPU-3	90.5	78.7
TPU-4	89.6	86.1
TPU-5	90.5	88.5
TPU-6	90.7	82.6
TPU-7	91.3	76.3
TPU-8	86.0	76.9

As shown in **Fig. 5** (a ~ h) , each TPU sample exhibited the maximum hysteresis loop in the first cycle, and the area of hysteresis loop gradually decreased and stabilized in subsequent cycles, demonstrating typical features of the Mullins effect[23]. After10 cycles, TPU-5 achieved the elastic recovery rate of 88.53%, exhibiting the best cycle stability among all TPUs. This can be attributed to the reversible dissociation of hydrogen bond, which accounted for the initially high energy loss. During the pre-cycling process, a stable hard domain network remained. In this TPU, the ratio of PECD to PCL was 1:1, which afforded superior compatibility between the soft segments, thereby preventing PCL from forming dispersed microdomains and effectively suppressing the PCL stretching-induced crystallization effect (SIC)[24]. In this case, the crystallization of the PCL segment was in the "below critical strain" window. After unloading, the crystallization faded away without accumulating permanent deformation, thus demonstrating the optimal cycling stability.

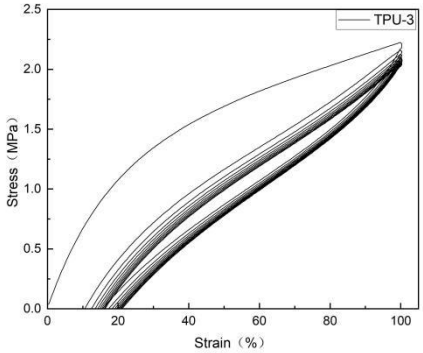
(a)


TPU-1
Stress(MPa)
Strain(%)

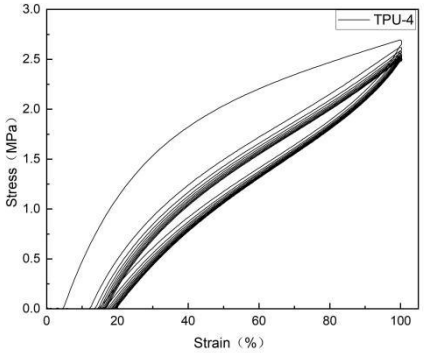
(b)


TPU-2
Stress（MPa）
Strain（%）

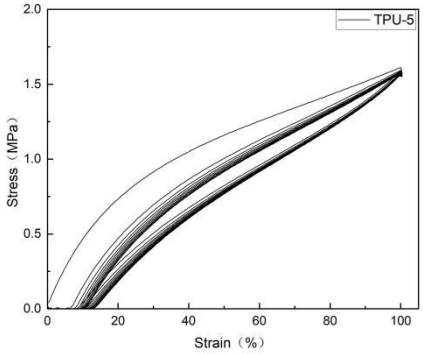
(c)


TPU-3
Stress（MPa）
Strain（%）

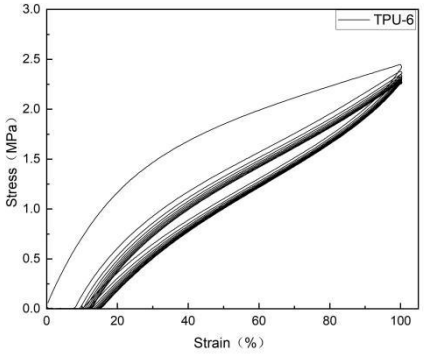
(d)


TPU-4
Stress（MPa）
Strain（%）

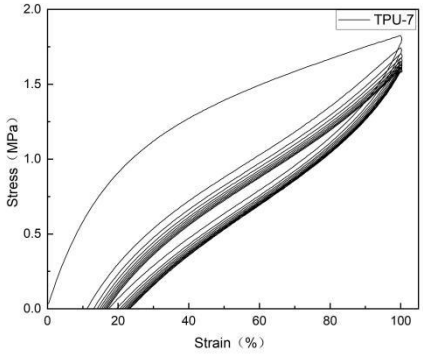
(e)


TPU-5
Stress（MPa）
Strain（%）

(f)


TPU-6
Stress（MPa）
Strain（%）

(g)


TPU-7
Stress（MPa）
Strain（%）

(h)

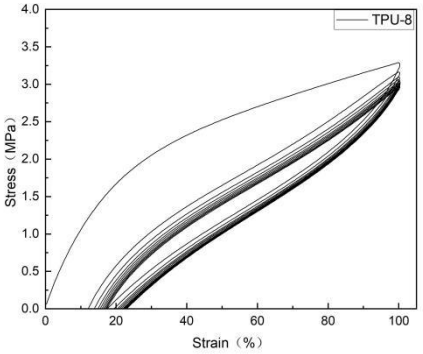

TPU-8
Stress（MPa）
Strain（%）

Fig. 5 (a ~ h) Cycle curves of PECD/PCL-TPUs

3.6. DMA analysis

DMA tests were conducted on the TPUs, and the results are shown in the figure 6. The results in **Fig. 6** (a ~ b) revealed that the storage modulus (E') and glass transition temperature (Tg) of PCL-TPU were both lower than those of PECD-TPUs, demonstrating superior low-temperature flexibility. As the PECD content increased, the E' and Tg of PECD/PCL-TPUs decreased accordingly, reflecting an enhanced degree of phase separation[25]. Therefore, the Tg of the soft segment phase shifted towards a lower temperature. The high modulus and Tg exhibited by TPU-3 may arise from the combined effect of the mixed reinforcement of soft segments and the hydrogen bonds formed by the mutual dissolution and stacking between soft and hard segments[26]. The TPU-7 and TPU-8 possessed similar Tg due to their relatively similar chemical compositions. Notably, TPU-7 showed markedly lower tanδ value, demonstrating that its resilience performance was better. It indicated that the incorporation of PCL had a positive effect on the resilience performance, which was consistent with the results of the fixed-elongation tensile resilience test.

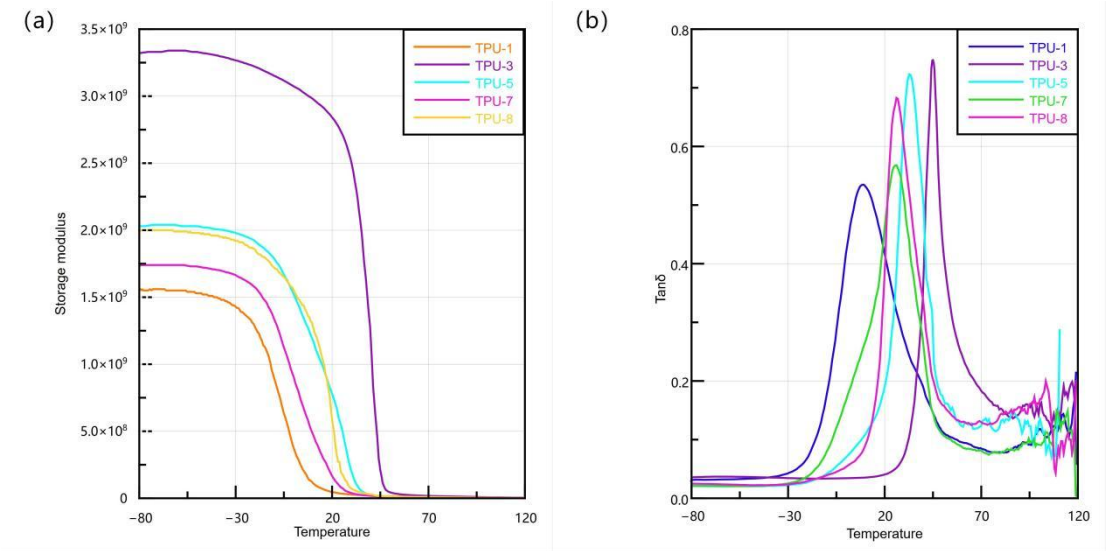


Fig. 6 DMA results of PECD/PCL-TPUs. (a)storage modulus (E') curves of PECD/PCL-TPUs; (b) tanδ curves of PECD/PCL-TPUs

3.7. Solvent absorption rate of PECD/PCL-TPUs

The solvent absorption rates of PECD/PCL-TPUs were tested, and the results are shown in the **Table 5**.

PECD/PCL-TPUs with varied PCL/PECD ratios showed different absorption behaviors toward solvents with distinct polarities, which was mainly related to the proportion of the soft segments.

As the content of PECD increased, the solvent resistance of TPU to non-polar and moderately polar solvents (such as toluene, ethyl acetate, and butanone) significantly improved, while the water absorption rate slightly increased, and the methanol absorption ratio remained basically unchanged. The absorption rates of TPU-7 to ethyl acetate and butanone decreased to 6.1% and 2.2% respectively, demonstrating the optimal resistance to moderately polar solvents. However, due to the dominant role of the hydrophilic chains in PECD, this sample also exhibited the highest water absorption rate of 1.7%.

Table 5 Solvent absorption rates of PECD/PCL-TPUs

Sample	Water(%)	Methanol(%)	Toluene(%)	Ethyl acetate(%)	Butanone(%)
TPU-1	1.0	9.0	20.3	13.8	17.7
TPU-2	0.3	8.8	21.0	14.1	8.4
TPU-3	0.4	7.4	15.8	15.4	4.9
TPU-4	0.6	8.3	15.3	13.3	7.6
TPU-5	0.7	7.2	14.1	14.1	5.4
TPU-6	1.6	7.1	15.1	14.0	4.8
TPU-7	1.7	7.2	13.9	6.1	2.2
TPU-8	1.6	7.7	11.8	17.5	16.5

This ratio not only retained the excellent tolerance of PECD to non-polar/moderately polar solvents, but also effectively inhibited excessive water absorption by introducing PCL, maintaining a low and balanced absorption rate in toluene, ethyl acetate, butanone, water and methanol.

3.8. Analysis of water contact angle test

The water contact angle tests were conducted on PECD/PCL-TPUs, and the results are shown in **Table 6**. The average water contact angles of all samples were within the range of 84.2-87.5°, showing overall hydrophilicity. Compared with the samples with a low PCL content (30%-40%), TPUs with a higher PCL content had a higher water contact angle, that is, enhanced hydrophobicity. This indicated that the introduction of PCL can effectively reduce the surface free energy of TPU and optimize the interaction behavior between the surface and water.

Table 6 Water contact angles of PECD/PCL-TPUs

Sample	Left contact angle (°)	Right contact angle (°)	Average contact angle (°)
TPU-1	75.4±0.2	80.6±0.5	78.1±0.4
TPU-2	85.1±0.2	85.5±0.1	85.3±0.2
TPU-3	86.0±0.7	84.2±0.7	85.1±0.7
TPU-4	86.9±0.9	85.6±1.8	86.3±1.4
TPU-5	88.6±0.3	86.4±1.2	87.5±0.8
TPU-6	84.7±0.5	83.8±0.5	84.2±0.5
TPU-7	84.6±0.9	85.7±1.1	84.2±1.0

TPU-8	84.0±1.1	84.6±1.2	84.3±1.2

3.9. TGA analysis

In order to explore the thermal properties of PECD/PCL-TPUs, TGA tests were conducted on PECD/PCL-TPUs, and the results are shown in the **Fig. 7** and **Table 7.**

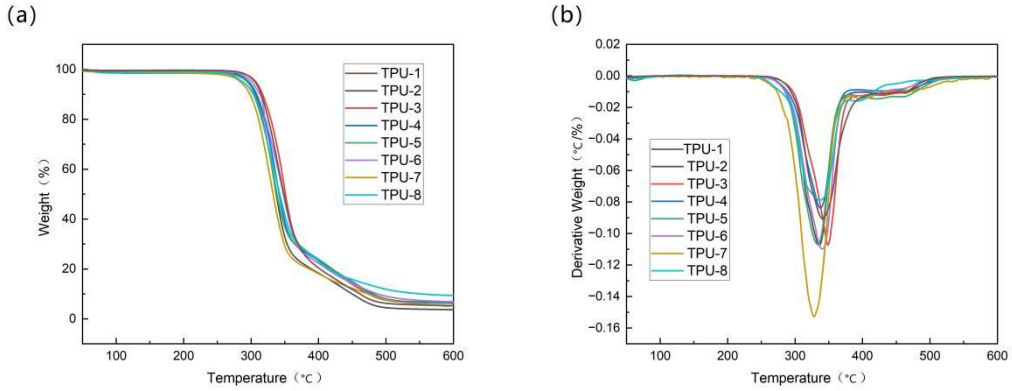


Fig. 7 Thermal degradation behavior of PECD/PCL-TPUs: (a)TG curves;(b)DTG curves.

The initial decomposition temperatures ($T_{5\%}$) of TPUs slightly increased with the increase in PCL content, but the change was not significant. This is mainly because the initial decomposition temperature of the carbonate bond is similar to the thermal decomposition temperature of the carbamate bond, while the thermal decomposition temperature of PCL is relatively high. Therefore, as the PCL content increased, the thermal decomposition temperature slightly rised[27–29].

Table 7 TGA data of PECD/PCL-TPUs

Sample	$T_{5\%}$(℃)	$T_{50\%}$(℃)	$T_{90\%}$(℃)
TPU-1	305.6	348.5	461.5
TPU-2	294.5	337.3	449.8
TPU-3	307.0	350.8	473.6
TPU-4	296.6	341.6	480.6
TPU-5	294.1	338.3	476.3
TPU-6	300.9	347.9	487.8
TPU-7	284.0	332.3	473.7
TPU-8	287.6	342.3	552.3

3.10. Analysis of wet-heat aging resistance test

The wet-heat aging test was performed at 85℃ and 85% relative humidity (RH) to rapidly assess the long-term reliability of the materials in a hygrothermal environment. A 500-hour wet-heat aging test was carried out on five different PECD/PCL-TPUs, and the results are shown in the **Fig. 8**.

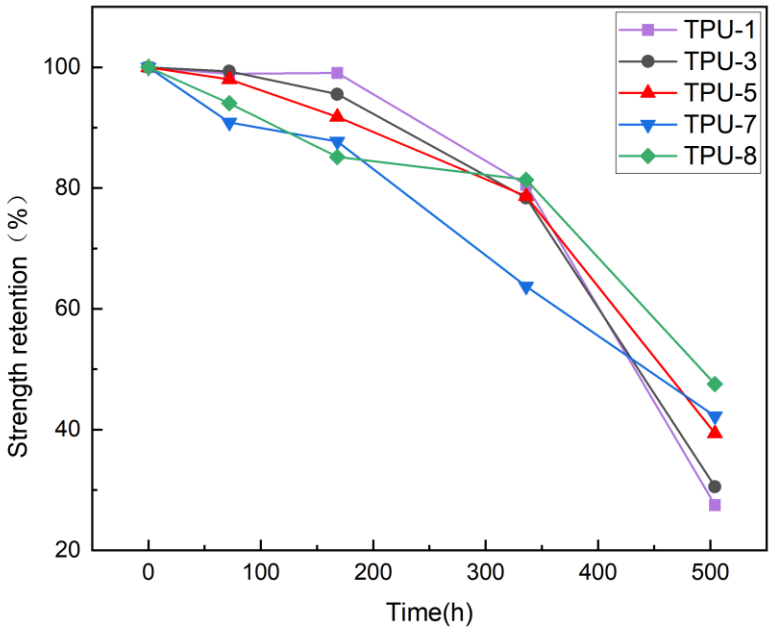


Fig. 8 Wet-heat aging resistance of TPUs

During the pre-aging period (0-168 hours), all the TPU samples exhibited excellent stability, with the tensile strength retention rates exceeding 85%. Among them, TPU-1 showed the best short-term resistance to wet-heat aging . After 168 hours of aging, its strength retention rate was as high as 99%, indicating the thermal oxidative hydrolysis degradation was significantly inhibited within a short period of time. As the aging time extended to 336 h and 500 h, the humid and hot atmosphere accelerated the hydrolysis and breakage of molecular chains, the phase separation of the soft segments, and the increase of interface defects. The mechanical strength of all films continued to decline. At the end of 500h aging, the wet-heat aging resistance of TPU-1 sharply declined, and the strength retention rate droped to 27.5%. In contrast, TPU-8 demonstrated the best resistance to wet-heat aging, maintaining a strength retention rate of 47.5% after 500h.

These results showed that TPU-8 had the best end-point resistance to wet-heat aging. The carbonate bond[30] in its structure has good hydrolysis resistance. However, PECD is inherently strong hydrophilic and has a high water absorption rate, which facilitates water penetration toward carbonate bond, thereby resulting in relatively poor initial resistance to wet-heat aging. PCL has a relative hydrophobicity, increasing the content of PCL can reduce its water absorption. In the early stage of aging (0-168 hours), as the content of PCL increased, the resistance to wet-heat aging

improved. However, as the aging time prolonged, PCL began to undergo hydrolysis, generating carboxylic acids, forming a self-catalytic cycle, which further catalyzed hydrolysis. At this point, as the dosage of PCL increased, the resistance of TPU to wet-heat aging declined. TPU-1 performed the worst in the 500-hour wet-heat aging test.

4. Conclusion

The influence of PECD/PCL ratio on the properties of TPUs was systematically explored. In terms of mechanical properties, the tensile strength of TPUs first increased and then decreased as the content of PCL increased, reaching the peak value of 66MPa when the PCL content was 60 wt%. Combining the fixed elongation tensile test with DMA characterization, the results showed that the best resilience was optimal at 30 wt% of PCL content, and the cycle stability was optimal at 50 wt% of PCL content. The solvent resistance of TPUs has also been improved. The PECD/PCL-TPUs exhibited significantly improved resistance to non-polar and medium-polar solvents. As the content of PECD increased, the absorption rate in solvents such as toluene and ethyl acetate decreased, and the water absorption increased. Among them, the TPU with 50 wt% of PCL exhibited the best comprehensive solvent resistance. The introduction of PCL also increased the water contact angle of TPU to 84.2-87.5°. The initial decomposition temperature of TPU was all above 280℃, and the thermal decomposition mainly occured between 250 and 385℃. In the wet-heat aging test, the strength retention rate of PECD/PCL-TPUs significantly increased during the short-term heat aging period, while the strength retention rate of TPUs after 500-hour of long-term heat aging was positively correlated with the proportion of PECD.

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