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ORIGINAL PAPER

Novel CO_2-based low-molecular weight poly (propylene carbonate) diol (PPCD) for two-component polyurethane adhesive

Chaozhi Wang[1] · Hualin Li[1] · Zhenhong Huang[1] · Zhu Ding[1] · Zonglin He[1] · Baohua Liu[1] · Jiaoyan Ai[1] · Lina Song[1]

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Abstract

The subject of this study was the application of a novel CO_2-based low-molecular weight poly (propylene carbonate) diol (PPCD) in the field of adhesive. Two-component polyurethane adhesive (PPCD-PU) was prepared with PPCD and polymethylene polyphenyl polyisocyanate (PAPI) as raw materials, propylene carbonate diol (PCD-EDA) as extender. The effects of the molecular weight, carbonate linkage content of PPCD and content of PCD-EDA on the properties of PPCD-PU were also investigated. The results showed that the novel CO_2-based low-molecular weight poly (propylene carbonate) diol had higher carbonate linkage content (35%). The PPCD-PU synthesized by the PPCD had good adhesion performance, and the lap shear strength reached to 15 MPa. The addition of PCD-EDA not only improved the bonding properties of the adhesive, but also made PPCD-PU adhesive achieved higher lap shear strength in a shorter curing time. When the amount of PCD-EDA was 20 wt.%, the lap shear strength increased to 17 MPa, and the lap shear strength increased significantly from 3.7 to 10.6 MPa after curing at 80 °C for 30 min. Water absorption rate of PPCD-PU film was about 1.7%, and the lap shear strength was almost unchanged after 24 h of immersion in water. The temperature of 5%-weight loss of PPCD-PU was 284 °C, and the glass transition temperature was 79.3 °C. All the polyurethane adhesives obtained performed good heat and water resistance.

Keywords Poly (propylene carbonate) diol · CO_2-based polyol · Low-molecular weight · Polyurethane adhesive · Carbonate linkage content

Introduction

As a greenhouse gas, utilization of CO_2 has attracted global attention due to growing environmental concerns. It is urgent to take effective measures to reduce carbon dioxide content. Propylene carbonate (PC) is produced by the reaction of CO_2 and propylene oxide (PO) in the presence of catalysts and is also a by-product in the synthesis of poly (propylene carbonate) diol (PPCD). PPCD, a CO_2-based polyol and a high-profile green polymer, is synthesized by the copolymerization of CO_2 and PO (Lu et al. 2012). As one of the emerging low-cost and eco-friendly polymer materials, the copolymer has attracted extensive attention both in industry and academic research. In general, according to the utilization, the products of the copolymerization of PO and CO_2 fall into two categories: One is poly (propylene carbonate) (PPC) with high molecular weight and high carbonate linkage content (≥ 99 wt.%), which has good biodegradability. The other is PPCD with lower molecular weight as raw material for polyurethane industry, whereas much less attention has been paid on controlled synthesis of

✉ Baohua Liu
baohua@gdut.edu.cn

Chaozhi Wang
474853401@qq.com

Hualin Li
2506411696@qq.com

Zhenhong Huang
1052890325@qq.com

Zhu Ding
1055362823@qq.com

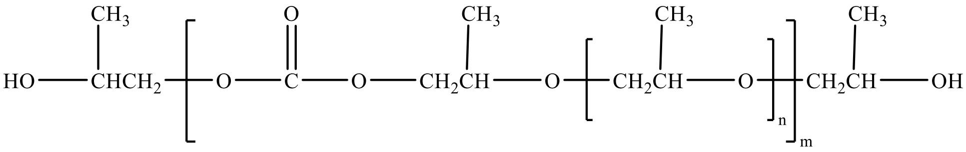
Zonglin He
310251392@qq.com

Jiaoyan Ai
aijy@gdut.edu.cn

Lina Song
Songlina@gdut.edu.cn

[1] School of Materials and Energy, Guangdong University of Technology, Guangzhou 510006, Guangdong, People's Republic of China

Scheme 1 Molecular structure of PPCD



low-molecular weight PPCD (Mn ≤ 2000 g/mol), especially the high carbonate linkage content and low by-product content (Meng et al. 2016; Li et al. 2011; Langanke et al. 2014; Liu et al. 2020; Qin et al. 2015).

Most of the polyols currently used for polyurethane synthesis are polyether polyols and polyester polyols (Datta and Haponiuk 2010; Datta and Leszkowski 2008). Recent report showed that the production of polyurethanes using polycarbonate polyols instead of traditional polyesters and polyether polyols can reduce greenhouse gas emissions by 11–19% and save fossil resources by 13–16% (Assen et al. 2014). Therefore, it is of great significance to prepare polyurethane from CO_2-based polyols (Orgilés-Calpena et al. 2016a).

Polyurethane adhesives can be prepared as single or two-component, and the former is of the moisture-curing or hot-melt types, in which the reaction group is exposed to air moisture after cross-linking structure (Bhagavathi et al. 2021; Ren et al. 2013; Kläusler et al. 2014; Wongsamut et al. 2020; Fuensanta et al. 2019). The latter is of the two-component polyurethane adhesive system consists of both components separately and is blended only shortly prior to application, and one of the components is usually a pre-polymer (Bockel et al. 2020; Bliem et al. 2018; Derikvand et al. 2013; Silva et al. 2010). Due to their excellent adhesion and outdoor durability, polyurethane adhesives have been widely used in textile, food packaging, footwear industry, coating, automotive and other industries in recent years (Tian et al. 2022; Nacas et al. 2019; Orgilés-Calpena et al. 2016a; Chen et al. 2016; Boutar et al. 2017). This adhesive is characterized by the presence of urethane groups in its structure, which has excellent bonding properties (Bockel et al. 2020; Sheikhy et al. 2013).

At present, there were few studies on the application of PPCD in polyurethane adhesives, most of the reports on reactive hot-melt polyurethane adhesive. The molecular weight of PPCD used was only as low as 2000 g/mol and bonding properties of polyurethane adhesive needed to be further improved. (Orgilés-Calpena et al. 2016b; Liu et al. 2017). The lower molecular weight PPCD has not been reported in the field of polyurethane adhesives. The structure of propylene carbonate diol, which is obtained by ring-opening reaction of PC and diamine, contains urethane groups (Wang et al. 2013; Wazarkar et al. 2016; Włoch and Datta 2017). It is expected to be used as extender to obtain PPCD-PU with better bonding properties. He et al. used PC and diamine to prepare several different PCDs as extenders for the modification of PPCD-based waterborne polyurethane (WPU), effectively improving the mechanical properties of WPU (He et al. 2022).

In this article, PU pre-polymer was synthesized through various novel CO_2-based low-molecular weight poly (propylene carbonate) diol (PPCD) (Mn = 500 ~ 2000 g/mol) with different carbonate linkage contents and low by-product (≤ 1%). The propylene carbonate diol (PCD-EDA) was used as extender to modify the PU pre-polymer. Then, two-component polyurethane adhesive was prepared with the PU pre-polymer as the component A. The comprehensive properties of the resulting two-component polyurethane adhesive were characterized. Synthetic of low-molecular weight PPCD with a higher carbonate linkage content and the problem of by-product utilization have been solved. The prepared PPCD-PU adhesive has good bonding and thermal properties.

Experimental

Materials

A several different novel poly(propylene carbonate) diol (PPCD-500, PPCD-1000, PPCD-1000-b, PPCD-1000-c, PPCD-1500 and PPCD-2000, average Mn = 500 ~ 2000 g/mol) was supplied by Guangdong Dazhi Environmental Protection Technology Co., Ltd. (China). All PPCDs have the same structure, but there are differences in their molecular weight, carbon linkages content and by-product content. The structure of poly (propylene carbonate) diol is illustrated in Scheme 1. Ethylenediamine (EDA)(AR) was purchased from Guangzhou Chemical Reagent Factory (China). Polymethylene polyphenyl polyisocyanate (PAPI) was purchased from Wanhua Chemical Group Co., Ltd. (China), PAPI mainly used to prepare aliphatic polyurethane, and NCO content is 30.5 ~ 32 wt.%. Dibutyltin dilaurate (DBTL) was purchased from Aladdin Company. Polyether ternary alcohol (N303, average Mn = 350 g/mol, hydroxyl value = 480 ± 30 mgKOH/g, viscosity = 600 ± 80 mPa·s) was purchased from Jining Hongming Chemical Reagent Co., Ltd. (China). 3A molecular sieve activated powder was purchased from Luoyang Jalon Micro-nano New Materials Co., Ltd. (China).

PPCD was synthesized from CO_2 and PO catalyzed by Zn-Co bimetallic. Novel poly (propylene carbonate) diol was produced in cooperation with Guangdong Dazhi Environmental Protection Technology Co., Ltd. PPCD with different low-molecular weights (500 ~ 2000 g/mol) could be prepared by new process, the mole content of carbonate linkages (−COO) in the copolymer was more than 35%, and the percentage content of by-product was less than 1%.

Carbonate linkages (F_{COO}) and the percentage content of by-products (W_{PC}) of different PPCDs were calculated by Eqs. 1 and 2, as shown in Table 1. In Table 1, the W_{PC} data proved that we successfully prepared PPCDs with by-product content less than 1%. With the increase in F_{COO} in the molecular structure of PPCD, its viscosity keeps rising, because the PPCD molecular structure contains a large number of ether bonds and carbonate linkages. The increase in −COO content means that the content of strong polar carbonate linkages increases, while the content of ether linkages decreases. The interaction between molecules leads to the chain segments movement decreasing. As a result, the viscosity of the resin increases accordingly. F_{COO} is an important index of the bonding property of PPCD-PU adhesive, and the viscosity is a reference for the construction conditions.

Poly (propylene carbonate) diol was vacuum dehydrated for 2 h at 110 °C before use. Polyether ternary alcohol was dehydrated by molecular sieve before use. 3A molecular sieve activated powder was treated at 250 °C for 3 h before use.

Preparation of two-component polyurethane adhesive

Preparation of PCD-EDA extender

Based on the related studies, PCD-EDA was obtained by ring-opening reaction of propylene carbonate (PC) and EDA (Wang et al. 2013; Wazarkar et al. 2016; He et al. 2022). The synthetic schemes of the PCD-EDA are shown in Scheme 2.

Table 1 Properties of different PPCDs

Sample	Average Mn (g/mol)	F_{COO} (%)	W_{PC} (%)	Viscosity (mPa·s)
PPCD-500	500	32.99	0.79	190,000 ± 3000
PPCD-1000	1000	35.03	0.21	230,000 ± 5000
PPCD-1500	1500	35.35	0.11	250,000 ± 5000
PPCD-2000	2000	35.30	0.22	290,000 ± 7000
PPCD-1000-b	1000	27.08	0.24	70,000 ± 3000
PPCD-1000-c	1000	23.54	0.74	13,000 ± 2000

PC (204.18 g) and EDA (60.10 g) with molar ratio of 2:1 were charged into a 500-ml three-necked flask equipped with digital stirrer and a nitrogen inlet. The mixture was heated up to 80 °C and reacted for 3 h until the optimal yield was reached. At 80 °C, the reaction of PC and EDA was rapid, and the solid content of the product reached more than 96.5 wt.% in a relatively short time (1 h). About 3 h after the reaction, the yield reached more than 99.2 wt.%, and the reaction was basically complete. The synthesis had a higher yield, and the product did not need an isolation procedure. Moreover, studies have shown that PC will not react with isocyanate group under the condition of catalyst and 80 °C (Wang 2015). The prepared PCD-EDA is solid state at room temperature, and the melting point is about 60 °C. PCD-EDA was used as small molecule extender.

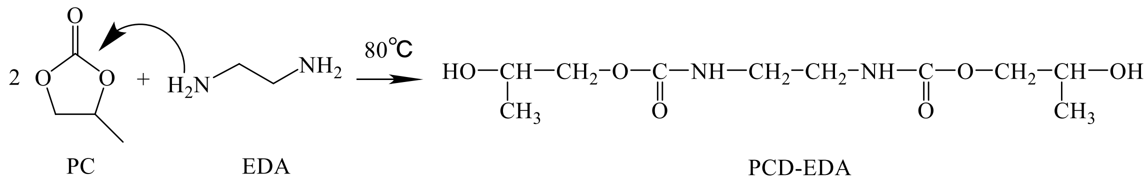
The structure of PCD-EDA was characterized by FTIR and ^{1}H NMR, and the results are shown in Fig. 1.

In Fig. 1a, the overlap peaks at 3330 ~ 3500 cm^{-1} are characteristic peaks of −OH and −NH. The peaks at 1687 cm^{-1}, 1265 cm^{-1} and 1068 cm^{-1} were characteristic absorption of the C=O, C−O, and C−O−C groups, respectively, indicating the formation of urethane groups.

In Fig. 1b ^{1}H NMR (400 MHz, $CDCl_3$, δ): 3.07 (a, 2H, CH_2), 3.99 ~ 4.01 (b, 2H, CH_2), 3.55 ~ 3.64 (c, H, CH), 4.77 ~ 4.84 (d, H, OH), 5.90 ~ 6.10 (e, H, NH), 1.01 ~ 1.05(f, 3H, CH_3). The ^{1}H NMR spectrum of PCD-EDA showed signals at 5.90–6.10 ppm and 4.77–4.84 ppm corresponding to the −NH− groups in the urethane groups and the −OH groups in the carbonate linkages. Accordingly, the structure of PCD-EDA was further confirmed.

Preparation of component A

The polyurethane pre-polymer was prepared by a 'one shot' method polymerization process. PPCD, PCD-EDA and PAPI were charged into a 500-ml three-necked flask equipped with a mechanical stirrer, a nitrogen inlet and a thermometer. The reaction temperature was raised to 50 °C, and the mixtures were stirred at 400 rpm at this temperature for about 10 min to mix well. The reaction mixtures were heated up to 90 °C under a nitrogen atmosphere and reacted for approximately 4 h until the theoretical NCO content of the pre-polymer



Scheme 2 Ring-opening polymerization of PC and EDA to PCD-EDA

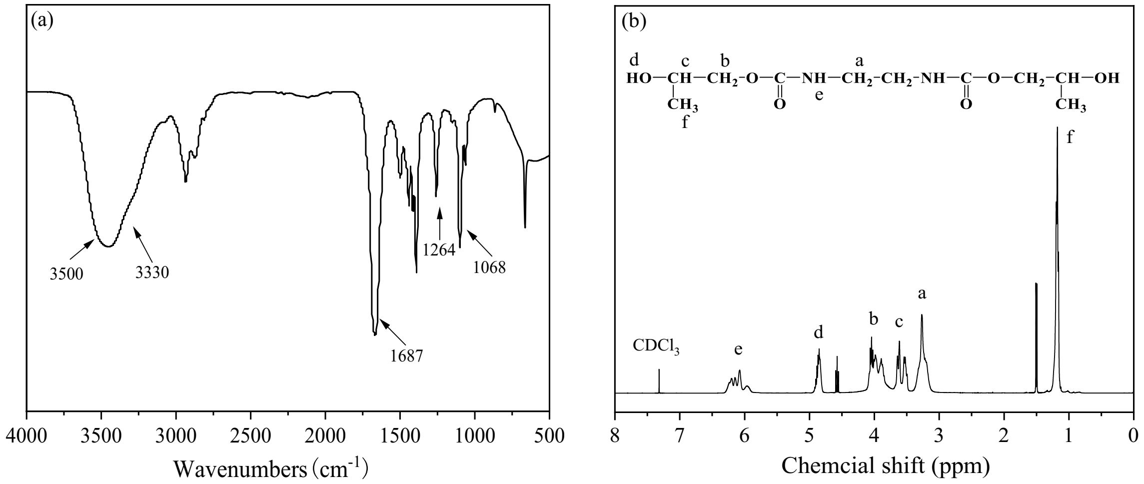


Fig. 1 FTIR and ^{1}H NMR spectrum of PCD-EDA

was reached to achieve pre-polymer, where NCO content was detected by 'di-*n*-Butylamine-Actone' method. After the reaction, the pre-polymer (component A) was sealed with nitrogen and stored for later use.

Preparation of component B

Curing agent (N303), catalyst (DBTL) and filler (3A molecular sieve activated powder) were charged into a 500-ml three-necked flasks equipped with a mechanical stirrer, after the mixtures (component B) stirred at 400 rpm for 30 min under room temperature and vacuum, and then sealed with nitrogen and stored for later use.

Preparation of PPCD-PU

The two-component polyurethane adhesive was prepared by mixing components A and B with the isocyanate index of 1.0–1.01. The masses of raw materials are listed in Table 2. The reaction route for the PPCD-PU adhesive is illustrated in Scheme 3.

The PPCD-PU adhesives were used as adherents to attach two stainless steels with a size of 100 mm × 25 mm × 2 mm. Two stainless steels were put together to form an overlap area of 25 mm × 12.5 mm after brushing the PPCD-PUs on the overlap area of the sheets, and the thickness of adhesive layer was 0.2 mm. The assemblies were curing at 80 °C for a preset time (0.5 h, 3 h, 6 h, 12 h and 24 h).

Characterizations

Transform infrared spectrometers (FTIR)

The composition analyses of PPCD and PU films were performed using a Nicolet 6700 Fourier-transform infrared spectrometers (FTIR, Thermo Fisher Scientific, America) at the scan range of wavenumber from 500 to 4000 cm^{-1}.

Nuclear magnetic resonance (NMR)

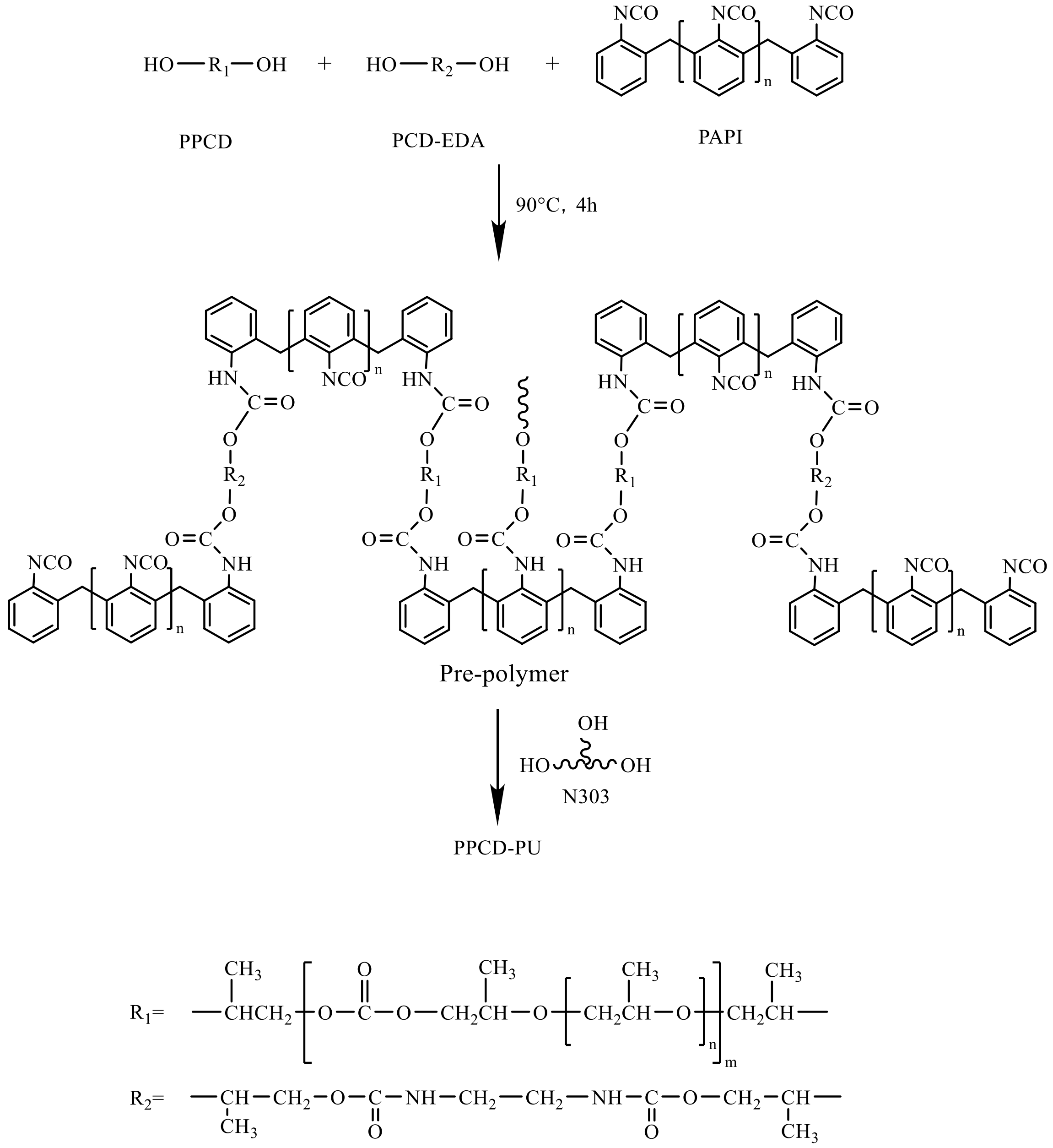
To extend the chemical structure understanding of poly (propylene carbonate) diol, the nuclear magnetic resonance (NMR) spectrum was characterized by a Bruker Avance III HD 400 (400 MHz) instrument using tetramethylsilane as an internal standard at ambient temperatures. The samples of PPCD were dissolved by deuterium chloroform ($CDCl_3$) for a ^{1}H NMR experiment.

Lap shear strength

Lap shear strength of rigid-to-rigid bonded assemblies tests of PPCD-PU adhesives were carried out using the universal mechanical testing machine (CMT4204, MTS SYSTEM Co., Ltd.). The test speed was (5.0 ± 0.5) mm/min. The arithmetic mean of 5 tests was used as the test result.

Shore hardness

Hardness testing method: The hardness of samples was measured by LX-D-type shore hardness tester. Based on the standard requirement, the average value was taken by testing five points. The distance of each two points was no less than 6 mm.



Scheme 3 Reaction route for the PPCD-PU

Viscosity

Viscosity of PPCD and the mixture of components A and B were measured by Brookfield viscometer at 25 °C. The average data of three experimental measurements were taken as the viscosity.

Water resistance

Determination of lap shear strength after water absorption. Rigid-to-rigid bonded assemblies of PPCD-PU adhesives were cured at 80 °C for 24 h and then immersed in water for 24 h at room temperature.

Water absorption ratio was performed at room temperature. The PPCD-PU films were cut into 2 cm × 2 cm and weighted (m_1). After 24 h immersion in

Table 2 Feeding mass and NCO content in the synthesis of PPCD-PU

Sample	Component A (g)			Component B (g)		
	PPCD	PCD-EDA	PAPI	N303	Catalyst	Filler
PPCD-PU-1	40 (PPCD-500)	0	87.6	56.4	0.03 wt.% of N303	30 wt.% of N303
PPCD-PU-2	40 (PPCD-1000)	0	65.2	46.5		
PPCD-PU-3	40 (PPCD-1500)	0	57.6	43.1		
PPCD-PU-4	40 (PPCD-2000)	0	54	41.6		
PPCD-PU-5	40 (PPCD-1000-b)	0	65.2	46.5		
PPCD-PU-6	40 (PPCD-1000-c)	0	65.2	46.5		
PPCD-PU-7	40 (PPCD-1000)	2	71.5	50.2		
PPCD-PU-8	40 (PPCD-1000)	4	78	54		
PPCD-PU-9	40 (PPCD-1000)	6	84.2	57.5		
PPCD-PU-10	40 (PPCD-1000)	8	90.6	61.2		

water, the films were dried with filter paper and weighted (m_2). The water absorption was calculated according to:

$$\text{Water absorption } (\%) = \frac{m_2 - m_1}{m_1} \times 100\%$$

Thermogravimetric analysis (TGA)

The thermal properties of the PPCD-PU films were characterized by thermal gravimetric analysis (TGA) (STA 409PC, Germany) under N_2 atmosphere (flow rate: 50 mL/min). The experiment temperature ranged from room temperature to 600 °C at a heating rate of 10 °C/min.

Dynamic mechanical analysis (DMA)

The thermal properties of the PPCD-PU films were also determined by dynamic mechanical analysis (DMA) (Metravib DMA861, France) in the tension mode (5 N of static force) at 1 Hz. The samples were heated from 0 to 150 °C at a rate of 5 °C/min.

Results and discussion

FTIR spectrum of PPCD and PPCD-PU

The structures of poly (propylene carbonate) diol and the corresponding PPCD-PU films were characterized by FTIR, and the results are shown in Fig. 2.

In Fig. 2, the peaks at 1749 cm^{-1} and 1270 cm^{-1} were attributed to the characteristic absorption of −C=O bond and −C−O− bond in the carbonate linkages, respectively. The peak at 1073 cm^{-1} was assigned to the stretching vibration −C−O−C− in PPCD molecular chain, and the broad peak at approximately 3448 cm^{-1} indicated the existence of −OH. The disappearance of the peaks near 3448 cm^{-1} and 2270 cm^{-1} indicated the complete reaction of the hydroxyl group and isocyanate group. The appearance of the absorption peak at 3308 cm^{-1} indicated the formation of urethane groups (−NHCOO−). The results confirmed the formation of PPCD-PU.

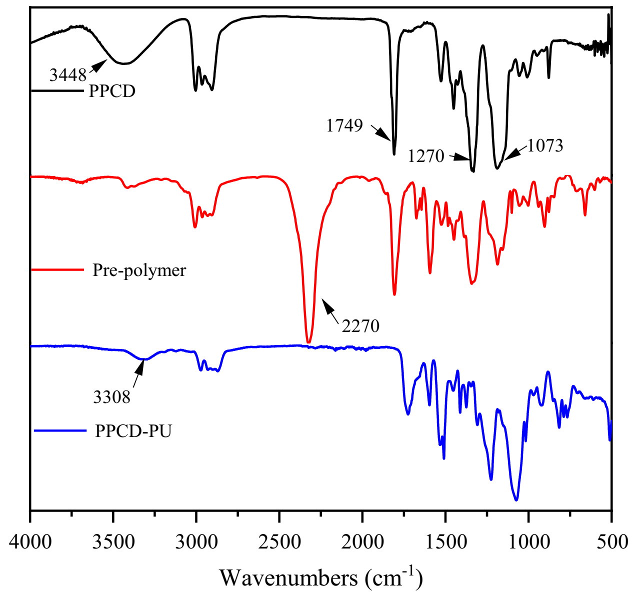


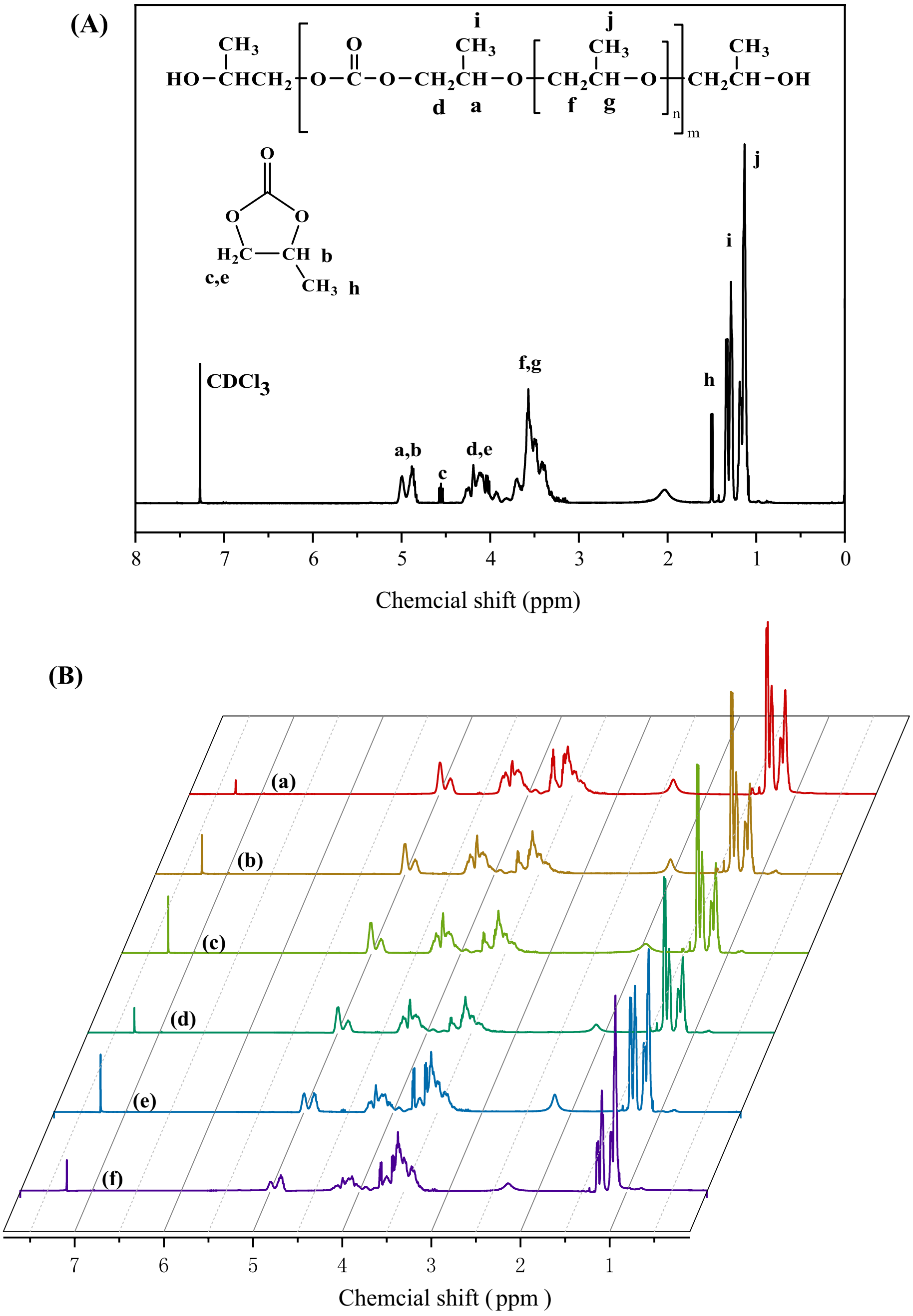
Fig. 2 FTIR spectrum of PPCD and PPCD-PU

^{1}H NMR spectrum of PPCD

The molecular structure of poly (propylene carbonate) diol was characterized by NMR. In Fig. 3, ^{1}H NMR (400 MHz, $CDCl_3$, δ): 4.82 ~ 5.08 (a, H, CH), 4.88 (b, 1H, CH), 4.6 and 3.98 ~ 4.35 (c, e, 2H, CH_2), 3.9 ~ 4.35 (d, 2H, CH_2), 3.27 ~ 3.77 (f, g, 3H, CH_2, CH), 1.5 (h, 3H, CH_3), 1.24 ~ 1.4 (i, 3H, CH_3), 1.0 ~ 1.23 (j, 3H, CH_3).

According to the peak area of ^{1}H NMR spectrum, the content of carbonate linkages (F_{COO}) and the percentage

Fig. 3 **A** ^{1}H NMR spectrum of PPCD. **B** ^{1}H NMR spectrum of different PPCDs. (a) PPCD-500; (b) PPCD-1000; (c) PPCD-1500; (d) PPCD-2000; (e) PPCD-1000-b; and (f) PPCD-1000-c



content of by-products (W_{PC}) in PPCD molecular chain were calculated, based on the integrated area of the peaks of CH ($\delta = 4.82 \sim 5.08$) and CH_2 ($\delta = 3.9 \sim 4.35$) in the polycarbonate unit ($A_{5.0}$ and $A_{4.2}$), the peaks of CH_2 ($\delta = 4.6$) in the propylene carbonate unit ($A_{4.6}$) and the peaks of CH and CH_2 ($\delta = 3.27 \sim 3.77$) in the polyether unit ($A_{3.5}$). The relevant calculation formulas are shown in Eq. 1 and 2.

$$F_{\mathrm{COO}} = \frac{A_{5.0} + A_{4.2} - 2 \times A_{4.6}}{2 \times A_{5.0} + A_{4.2} - 2 \times A_{4.6} + A_{3.5}} \tag{1}$$

$$W_{PC} = \frac{102 \times A_{4.6}}{2 \times A_{5.0} + A_{4.2} - 2 \times A_{4.6} \times 102/3 + A_{3.5} \times 58/3 + 102 \times A_{4.6}} \tag{2}$$

Effect of different PPCDs on the properties of PPCD-PU

PPCD-PU was prepared from PPCD with different molecular weights or F_{COO}. The effects of different molecular weights of PPCDs on the properties of the PU adhesive are analyzed in Table 3. With the increase in PPCD molecular weight, the

Table 3 Effect of molecular weight of PPCD on properties of PPCD-PU

Sample	Molecular weight (g/mol)	NCO content (wt.%)	Viscosity (mPa·s)	Shore D (HD)	Lap shear strength (MPa)
PPCD-PU-1	500	16	14,800	80	14.1
PPCD-PU-2	1000	16	29,600	76	15.0
PPCD-PU-3	1500	16	49,200	74	14.9
PPCD-PU-4	2000	16	61,400	70	15.3

viscosity of the mixture of components A and B increased, whereas the shore hardness of PPCD-PU decreased. Because with the increase in PPCD molecular weight, the increase in relative content of PPCD (the soft segment) leads to the increased of the molecular chain flexibility and intersegment entanglement.

Similarly, the pre-polymer of PPCD-PU-1 to PPCD-PU-4 had the same NCO content, resulting in the same number of polar linkages (−NHCOO−) formed. In this case, PPCD-PU-2 to PPCD-PU-4 were prepared from PPCD with similar F_{COO}, so the lap shear strength was basically the same, up to about 15.3 MPa. However, the F_{COO} of PPCD-500 was lower than that of PPCD-1000 to PPCD-2000, so the lap shear strength was relatively low.

In Tables 1 and 3, the viscosity of PPCD and PPCD-PU increased with the increase in molecular weight. The polyurethane adhesive prepared by PPCD-1000 has performed excellent bonding properties moderate viscosity and convenient construction. Therefore, PPCD-1000 was preferred for subsequent studies.

The content of −COO in PPCD has great influence on the performances of PPCD-PU. When keeping the molecular weight of PPCD as 1000 g/mol and NCO content of pre-polymer as 16 wt.%, the effects of the different F_{COO} on the properties of PPCD-PU adhesives were studied. The results are shown in Table 4.

With the increase in F_{COO}, the bonding properties of the adhesive improved obviously. This was consistent with the reported results of preparing reactive hot-melt polyurethane adhesives with different carbonate linkage contents of PPCD (Liu et al. 2020). The side methyl group coupled with inferior molecular regularity cause PPCD as soft segment forms amorphous state in polyurethane (Ma et al. 2017). However, with the increase in the mole content of carbonate linkages in the molecular chain of PPCD, the intermolecular interaction force increases. It is easier to form hydrogen bonds of intramolecular and intermolecular and had greater molecular cohesion. Although the crystallinity of PPCD-based polyurethane is inferior, the mechanical properties of it are still excellent.

Effect of content of PCD-EDA on the properties of PPCD-PU

PCD-EDA has symmetrical molecular structure, short carbon chain and contains more polar linkages (−NHCOO−). After being added to PPCD-PU, the density of polar linkages in the molecular structure of polyurethane increased. As a result, it was easier to form hydrogen bonds, which improves the bonding properties of polyurethane adhesive and the viscosity and shore hardness increased. The results are shown in Table 5. When the addition amount of PCD-EDA was 20 wt.% of PPCD, the lap shear strength was 17.0 ± 0.5 MPa.

Effect of curing time on the properties of PPCD-PU

The lap shear strength of PPCD-PU at 80 °C for different curing times (0.5 h, 3 h, 6 h, 12 h and 24 h) is shown in Fig. 4. The lap shear strength of all PPCD-PU adhesives increased with the prolongation of curing time. PPCD-PU without PCD-EDA showed lower lap shear strength in short time curing. When the amount of PCD-EDA was 20 wt. %, the lap shear strength of 80 °C curing for 0.5 h increased significantly from 3.7 to 10.6 MPa and curing for 24 h increased from 15 to 17 MPa. The molecular structure of PCD-EDA had high content and dense distribution of urethane groups, which made PPCD-PU had more polar linkages before curing, and forms more hydrogen bonds with

Table 4 Effect of F_{COO} of PPCD on properties of PPCD-PU

Sample	F_{COO} (%)	NCO content (wt.%)	Viscosity (mPa·s)	Shore D (HD)	Lap shear strength (MPa)
PPCD-PU-2	35.03	16	29,600	76	15.0
PPCD-PU-5	27.08	16	20,600	75	10.3
PPCD-PU-6	23.54	16	12,500	76	8.5

Table 5 Effect of PCD-EDA content on basic performance of PPCD-PU

Sample	PCD-EDA content (wt.%)	NCO content (wt.%)	Viscosity (mPa·s)	Shore D (HD)	Lap shear strength (MPa)
PPCD-PU-2	0	16	29,600	76	15.0
PPCD-PU-7	5	16	35,600	80	15.3
PPCD-PU-8	10	16	48,300	82	15.8
PPCD-PU-9	15	16	62,400	84	16.6
PPCD-PU-10	20	16	78,300	86	17.0

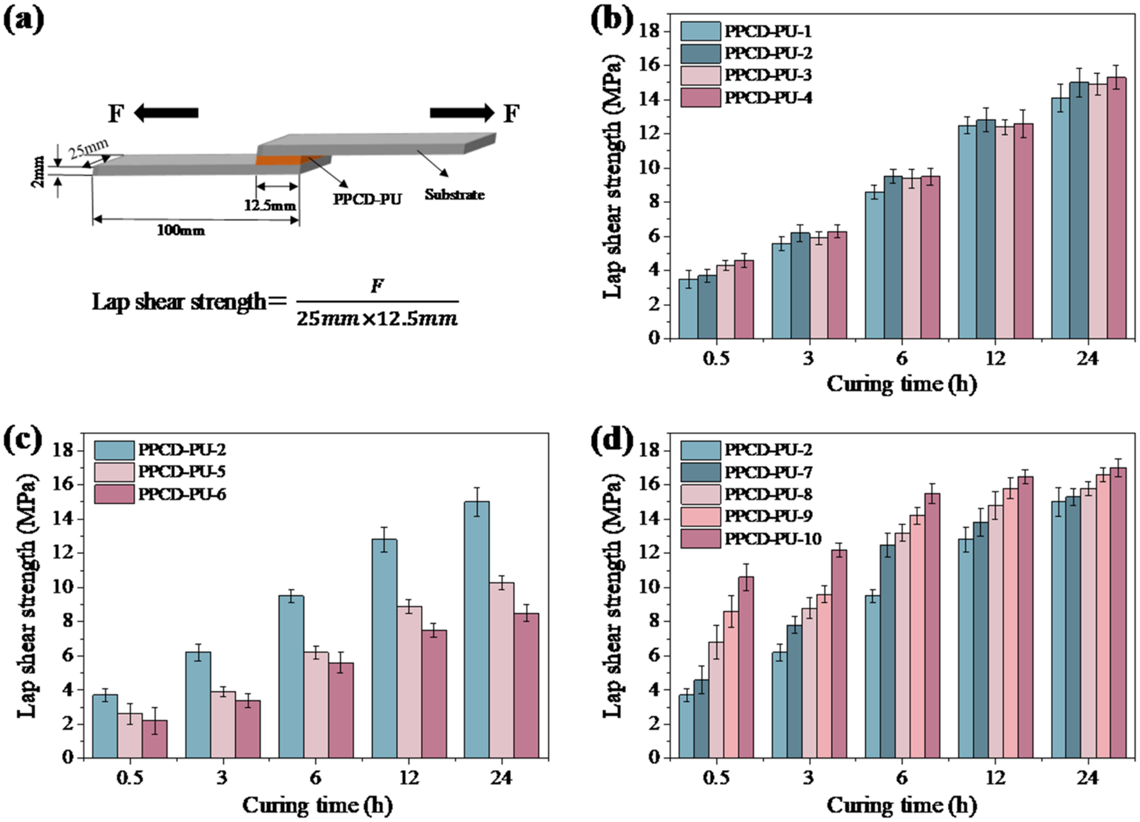


Fig. 4 **a** Lap shear strength tests, **b–d** Lap shear strength of PPCD-PU-1 ~ PPCD-PU-10 at 80 °C for different curing times

the substrate in a shorter curing time to improve the bonding properties. This means it can be used in the case of requiring a short time to achieve high bonding strength.

Water resistance of PPCD-PU

The water resistance test results of PPCD-PU are shown in Table 6. From Table 6, water absorption rate of PPCD-PU-2 film was about 1.7% and the lap shear strength was almost unchanged. The F_{COO} of PPCD and the content of extender PCD-EDA had little effect on water resistance of PPCD-PU. For one thing, the enhancement of the intermolecular force resulted from the increasing polar linkages (−COO and −NHCOO−), which prevented water penetration, thus improved water resistance and maintained the same lap shear strength (He et al. 2022). For another, polyurethane

Table 6 Water resistance of PPCD-PUs

Sample	Lap shear strength (MPa)	Water absorption (%)
PPCD-PU-2	15.0	1.7
PPCD-PU-6	8.5	1.9
PPCD-PU-10	16.9	1.6

with cross-linked molecular chain prevents water from permeating into inner of film, so that PPCD-PU with higher cross-linking degree had better water resistance.

Thermal analysis

TGA analysis can give information not only on thermal stability of polyurethanes, but also on decomposition steps related to the different stability of the soft and hard segments.

TGA was used to analyze the thermal stability of the PPCD-PU films prepared by different PPCDs, and the results are shown in Fig. 5 and Table 7. From PPCD-PU-2, 5 and 6, the thermal decomposition temperature decreased slightly with the increase in F_{COO}. When F_{COO} increases from 27 to 35%, the initial decomposition temperature of PPCD-PU decreases by 11.3 °C, revealing that the carbonate linkage content has great influence on the thermal properties. Due to carbonate linkages had lower thermal stability than ether linkages, the increase in carbonate linkage content led to low thermal stability of PPCD-PU-2. However, all PPCD-PUs showed good thermal stability, which was almost identical and comparable to the reported results (Liu et al. 2020).

Table 7 TGA data of PPCD-PUs

Sample	$T_{5\ wt.\%}$ (°C)*	$T_{10\ wt.\%}$ (°C)*	$T_{50\ wt.\%}$ (°C)*
PPCD-PU-2	284.0	297.3	372.5
PPCD-PU-5	295.3	309.1	370.6
PPCD-PU-6	299.8	314.5	367.0
PPCD-PU-8	279.6	294.5	366.3
PPCD-PU-10	274.6	290.6	372.5

*$T_{5\ wt.\%}$ temperature of 5%-weight loss; $T_{10\ wt.\%}$: temperature of 10%-weight loss; and $T_{50\ wt.\%}$: temperature of 50%-weight loss

From PPCD-PU-2, 8 and 10, with the content of extender PCD-EDA, the initial decomposition temperature of PPCD-PU decreased slightly with the increase in the addition amount, which was because PCD-EDA provided more urethane groups for PPCD-PU, while the thermal decomposition temperature of urethane groups is lower.

The loss tangent (tan *δ*) and storage modulus (*E*') of the PPCD-PU films were explored by DMA, and the temperature corresponding to the peak of tan δ is defined as glass transition temperatures (T_g). The results are shown in Fig. 6 and Table 8. With the increase in F_{COO}, the T_g of PPCD-PU increased significantly. However, with the increase in PCD-EDA

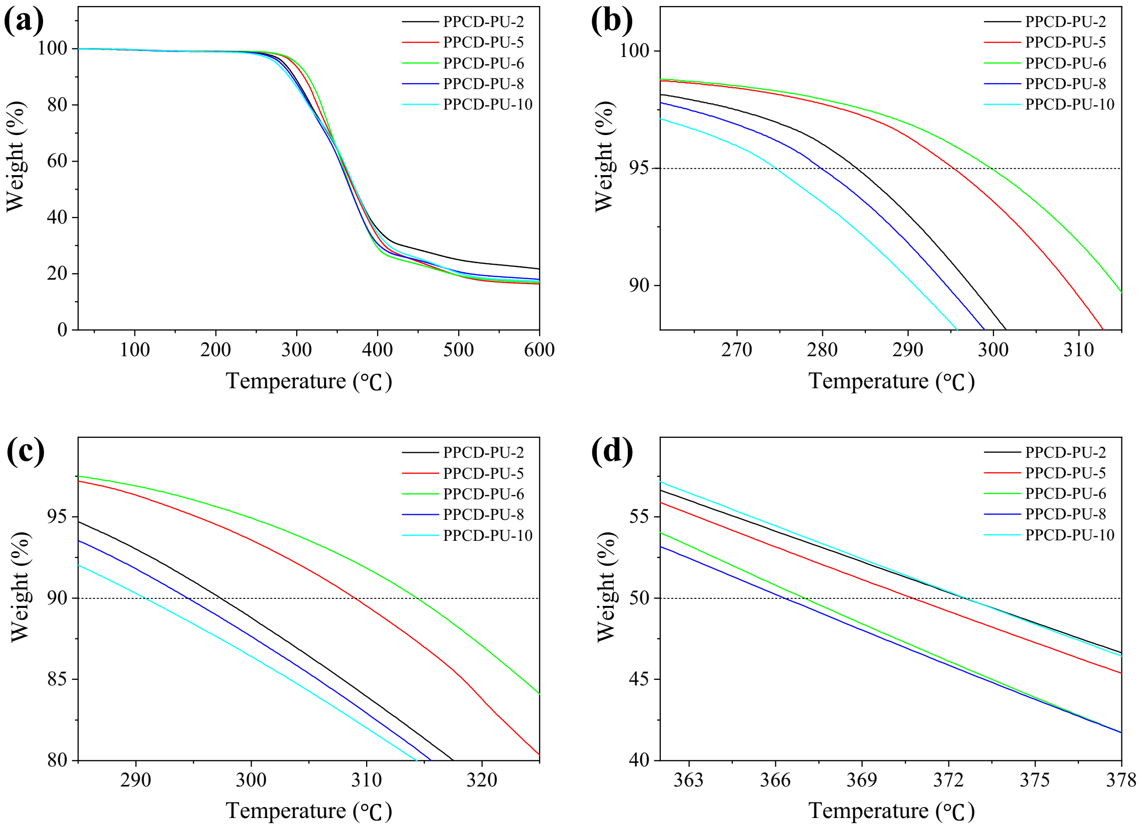


Fig. 5 TGA of PPCD-PUs

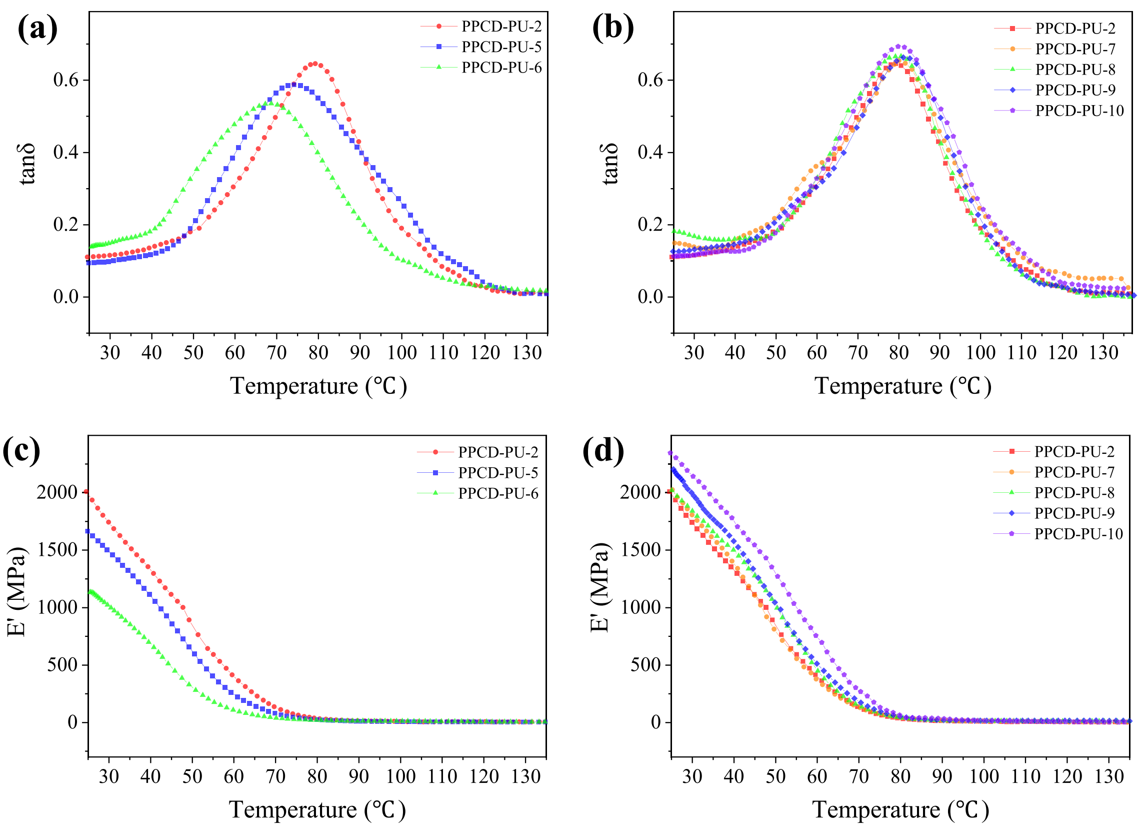


Fig. 6 DMA of PPCD-PUs. **a** and **b** Loss tangent (tan δ), **c** and **d** Storage modulus (E')

Table 8 DMA data of PPCD-PUs

Sample	T_g (°C)	Tan δ peak magnitude	E' (MPa) at 25 °C
PPCD-PU-2	79.3	0.645	1984.5
PPCD-PU-5	74.2	0.587	1660.0
PPCD-PU-6	68.7	0.535	1128.4
PPCD-PU-7	80.0	0.654	2013.4
PPCD-PU-8	80.5	0.666	2023.8
PPCD-PU-9	81.1	0.662	2202.3
PPCD-PU-10	79.9	0.693	2312.2

content in the pre-polymer, T_g of PPCD-PU did not change significantly. The E' of PPCD-PU increases with the increase in F_{COO} and PCD-EDA content, indicating that the increase in polar carbonate linkages and urethane groups contents increased the intermolecular force and hydrogen bond force, resulting in the improvement of PPCD-PU storage modulus.

Conclusions

A series of PPCD-PUs adhesive were successfully prepared by using poly (propylene carbonate) diol (PPCD) as soft segment. The results showed that the lap shear strength of the prepared adhesives was significantly affected by the content of polar carbonate linkages in the raw materials and the content of the extender PCD-EDA, but not sensitive to the molecular weight. However, the viscosity of the products is much more sensitive to the molecular weight. Compare the properties of sample PPCD-PU-6, PPCD-PU-5 and PPCD-PU-2 adhesive prepared. When the carbonate linkage content increased from 23.5% to 35%, the lap shear strength increased from 8.5 to 15 MPa, and the glass transition temperature increased from 68.7 to 79.3 °C, but the temperature of 5%-weight loss decreased from 299.8 to 284 °C. It indicated that PPCD-PU-2 prepared from PPCD with high carbon dioxide content not only has excellent lap shear strength, but also has good thermal properties. After being soaked PPCD-PU in water at room temperature for 24 h, the water absorption rate of PPCD-PU-2 film was 1.7%, and the lap shear strength was basically not affected, which indicated that it had good water resistance. The addition of extender PCD-EDA can make PPCD-PU have higher bonding properties in a short curing time. Compare the sample PPCD-PU-2 and PPCD-PU-10, when the PCD-EDA content increased from 0 to 20 wt.%, the lap shear strength of short curing (0.5 h) and final curing (24 h) increased significantly from 3.7 and 15 to 10.6 and 17 MPa, respectively. But the viscosity of the sample increased significantly. However, the decomposition temperature and the glass transition temperature were roughly constant. The bonding properties of PPCD-PUs were obviously improved by PCD-EDA.

Declarations

Conflict of interest The authors declare no conflict of interest.

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