

Preparation of Chlorinated Poly(propylene carbonate) and Its Distinguished Properties*

Xi-hua Cui^{a, b}, Jing Jin^a, Jie Cui^a, Gui-yan Zhao^{a**} and Wei Jiang^{a**}

^a State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China

^b University of Science and Technology of China, Hefei 230026, China

Abstract Poly(propylene carbonate) (PPC), the copolymerization product of carbon dioxide and propylene oxide, was chlorinated for the first time in our laboratory. Nuclear magnetic resonance (NMR) spectroscopy and ion chromatography test showed that chlorine atoms were successfully introduced onto the polymer chains of PPC. We named this newborn polymer material as chlorinated poly(propylene carbonate) (CPPC). It is worth noting that the reaction conditions of the chlorination of PPC were quite mild, which could be easily and simply realized at industrial level. What is more important is that CPPC possessed many more distinguished properties in solubility, wettability, adhesiveness, and gas barrier compared with PPC. For example, the bonding strength of CPPC as thermal adhesive is nearly four times higher than that of PPC for wood, stainless steel and glass. The oxygen permeability coefficient of CPPC exhibits a decrease of 33% compared with that of PPC. Moreover, CPPC is quite stable in air, whereas it could be well biodegraded in soil compared with PPC. These results indicated that CPPC could be widely used in the fields of coating, adhesive, barrier materials and so on, which could greatly promote the development of PPC industry.

Keywords Poly(propylene carbonate); Chlorination; Biodegradability; Adhesive; Gas barrier

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INTRODUCTION

Carbon dioxide is a kind of inexhaustible inexpensive chemical raw material, and it has been recently noted that carbon dioxide is fixed into a chemical material on a large scale. Since Inoue *et al.*^[1] synthesized aliphatic polycarbonates with high molecular weight by using the copolymerization of carbon dioxide and an epoxy compound in 1969, the study on such system has been continuously deepened and developed^[2, 3]. Nowadays, it becomes a research focus in the field of polymer science to synthesize polymer materials by using carbon dioxide as the raw material. For example, poly(propylene carbonate) (PPC), a typical biodegradable material, is an alternating copolymer of carbon dioxide and propylene oxide^[4, 5], and has been put into the stage of industrial production. However, since common PPC has a glass transition temperature (T_g) of 30–40 °C and is amorphous, there are some defects such as poor dimensional stability at high temperature, large brittleness at low temperature, and the like^[6]. PPC is difficult to be used as plastic individually, and is generally used as a modifier for rubber or plastic^[7, 8], which limits its wide development and application. Also due to the above

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** Corresponding authors: Gui-yan Zhao (赵桂艳), E-mail: gyzh@ciac.ac.cn

Wei Jiang (姜伟), E-mail: wjiang@ciac.ac.cn

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disadvantages, PPC is usually blended with other polymers, especially biodegradable polymers, to improve its mechanical properties and thermal stability, and to maintain its biodegradability at the same time. At present, a variety of polymer materials, such as polylactic acid^[9–13], poly(butylene succinate)^[14], poly(3-hydroxybutyrate)^[15], poly(hydroxybutyrate-co-hydroxyvalerate)^[16], starch^[17–19], chitosan^[20] and natural fibers^[21, 22] have been extensively studied to be blended with PPC. The mechanical properties and thermal stability of materials blending PPC with polymers mentioned above can indeed be improved to a certain extent.

Completely different from the modification methods mentioned above, PPC has been successfully chlorinated in our laboratory, which has recently been authorized by the United States (US)^[23], European Union (EU)^[24], Japan^[25] and China patents^[26]. In this paper, we, for the first time, report the preparation of chlorinated poly(propylene carbonate) (CPPC) and its structure and properties. It can be found that the introduction of chlorine atoms greatly changed the properties of PPC such as solubility, wettability, adhesiveness, and gas barrier, *etc.*

EXPERIMENTAL

Materials

Poly(propylene carbonate) (PPC) was obtained from Taizhou Bangfeng Plastic Co., Ltd. (Wenling, Zhejiang, China). Chlorine (Cl₂) was supplied by Hai Jing Chemical Factory (Qingdao, Shandong, China). SiO₂ was purchased from Qingdao Dongyue Rhodia Chemical Co., China. Dichloromethane (CH₂Cl₂; AR) and sodium hydroxide (NaOH; AR) were purchased from Beijing Chemical Co., China. All chemicals were used as received without further purification.

Preparation of CPPC

CPPC was prepared by a gas-solid phase reaction^[27, 28] without any catalyzer in a 200 L enamel reactor. PPC powder (15 kg) and SiO₂ (0.45 kg) were premixed and then chlorine was introduced into the reactor. The chlorination temperature was 60 °C and the chlorination time was 1 h. The excess chlorine gas and resulting hydrogen chloride (HCl) flowed into a container containing 50 L of sodium hydroxide (NaOH) solution.

Characterization

PPC and CPPC samples were characterized by quantitative ¹³C-NMR, ¹H-NMR, distortionless enhancement by polarization transfer (DEPT-135) NMR and ¹³C-¹H heteronuclear single-quantum coherence (HSQC) NMR. All NMR experiments were carried out on a Bruker 400 MHz spectrometer at room temperature with CDCl₃ as the solvent and tetramethylsilane (TMS) as the internal reference. The molecular weight (MW) and molecular weight distribution (MWD) of PPC and CPPC were measured by TOSOH HLC-8220 GPC at 40 °C using THF as eluent (the flow rate was 0.35 mL·min⁻¹) against polystyrene standards. The samples prepared for NMR and GPC characterizations were purified by dichloromethane (CH₂Cl₂) before measurements. The chlorine content of the CPPC before purification by dichloromethane was measured by a Dionex ICS-1000 ion chromatography system (ICS) (Dionex, USA). The glass transition temperature (*T*_g) of PPC and CPPC was measured by differential scanning calorimetry (DSC) (TA Instruments Q2000, USA) under nitrogen atmosphere. First heating was performed from room temperature to 120 °C at a heating rate of 10 K·min⁻¹. Then, the sample was cooled down till -20 °C at a cooling rate of 10 K·min⁻¹. Second heating was performed from -20 °C to 120 °C at a heating rate of 10 K·min⁻¹. The *T*_g of the sample was determined by the midpoint method during the second heating process. Thermogravimetric analysis (TGA) was performed using a thermal analysis instrument (TA Instruments Q50, USA). All samples were heated from room temperature to 600 °C at a rate of 10 K·min⁻¹ under nitrogen atmosphere. Microstructure was observed by field-emission-gun environmental scanning electron microscope (FEG ESEM) (XL30, FEI COMPANY) with an accelerating voltage of 5 kV. The sample surfaces were coated with a thin layer of gold before SEM observation.

Biodegradation Test

Biodegradation experiments were carried out by soil burial test. Specimens for biodegradation test were prepared by hot compression molding and then cut into dumbbell-shape. The thickness of the specimens was 1 mm. The

initial weights of the specimens were measured prior to tests. PPC and CPPC specimens were buried in a rectangular wooden box containing garden soil. The specimens were placed 4 cm under the top soil and 5 cm above the bottom soil. The container was put indoor at room temperature. The soil was watered periodically during the experiment to retain constant humidity. The room temperature and soil temperature (which was measured at a depth of 4 cm) during the period were recorded (see Fig. S1 in supporting information, SI). The total experimental period was 120 days, and the specimens were periodically removed from the box and weighted. In this process, the specimens were thoroughly rinsed in a stream of distilled water and dried at 23 °C in a vacuum oven to constant weight. For contrast, another three dumbbell-shape specimens of PPC and CPPC were exposed to air to be tracked for weight changes.

Wettability Test

Wettability of PPC and CPPC melt on wood, stainless steel and glass was measured by a sessile-drop method with a contact-angle goniometer drop-shape analysis (KRUS GmbH) at 180 °C. Prior to the test, samples were molten and then a drop of polymer melt was put onto the dry substrate surface and kept in an oven at 180 °C for 1 min to get stability.

Lap Shear Adhesion Test

Lap joints were made by placing molten adhesive materials (PPC or CPPC) between two overlapping 9 mm × 85 mm substrates (wood, stainless steel and glass). The size of the overlapping lap joints was 9 mm × 12 mm. The stuck samples were initially kept in an oven at 180 °C for 5 min to get promoted adhesion, and then taken out of the oven to get cooled to room temperature. Contact pressure was maintained during the adhesion process using two 32 mm binder clips which produced a contact stress of 1.2 MPa. Lap shear adhesion test was conducted at 23 °C on Instron 1121 material tester at a cross-head speed of 1 mm·min⁻¹. The shear stress at the break of the lap joint was defined as the fracture strength. Five specimens were tested in each case to obtain a reliable mean value and standard deviation.

Oxygen Barrier Property Test

All prepared films were approximately 800 μm in thickness and cut into a circular shape of 50 cm². The oxygen permeability coefficient (OP) was measured according to GB/T1038-2000 using a DM2/330 Differential and Equal Pressure Method Gas Permeability Tester (Labthink Instruments Co., Ltd., Jinan, China). OP measurements were performed at the constant temperature of 23 °C under dry conditions with Differential Pressure Method to obtain oxygen transmission rate (OTR). OP was calculated as follow:

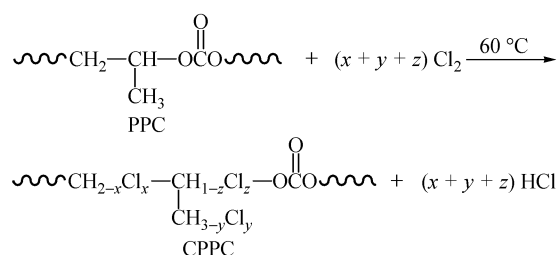
$$OP = \frac{OTR \times e}{\Delta p} \quad (1)$$

where e is the film thickness (μm), and Δp is the oxygen partial pressure difference. The measurements were performed at least four times and the results were averaged.

RESULTS AND DISCUSSION

Chlorination of PPC and Its Molecular Structure

Chlorine (Cl₂) can react with PPC by abstracting the hydrogen atoms from the carbon. As given in Scheme 1, three kinds of hydrogen atoms, *i.e.* the primary, the secondary and the tertiary hydrogen, can react with chlorine. However, the possibility of chlorination reaction is different for different kinds of hydrogen^[29]. It is known that the secondary and the tertiary hydrogen of PPC are more difficult to be abstracted from carbon to form the corresponding stable radicals due to the strong electron-withdrawing ability of —OCOO—. Moreover, PPC possesses abundant primary hydrogen atoms (the ratio for the primary, the secondary and the tertiary hydrogen atoms is 3:2:1). Therefore, it is relatively easier for the primary hydrogen of PPC to be abstracted by chlorine than that for the secondary and the tertiary hydrogen. As a result, the primary hydrogen of PPC is more likely to be replaced by chlorine atoms.



Scheme 1 Chlorination of PPC and its possible molecular structure
 x is an integer of 0–2; y is an integer of 0–3; z is an integer of 0–1.

^{13}C -NMR spectrum of CPPC is presented in Fig. 1(b). For the purpose of comparison, the spectrum of PPC used in this study is also shown in Fig. 1(a). It is seen that two new signals appear at $\delta = 70.6$ (labeled C5) and $\delta = 73.5$ (labeled C6). To assign these new signals, DEPT-135 NMR measurement was conducted on CPPC, as shown in Fig. 1(c). Negative peak is observed for C5 and positive peak is observed for C6, indicating that C5 is assigned to the secondary carbon and C6 is assigned to the tertiary carbon. It is unquestionable that the secondary carbon is assigned to $-\text{CH}_2\text{Cl}$ coming from $-\text{CH}_3$. To further investigate whether the tertiary carbon is ascribed to $-\text{CHCl}-$ or $-\text{CHCl}_2$, we calculated the integral peak area of ^{13}C -NMR spectra of PPC and CPPC (Figs. S2 and S3 in SI). The peak area of C2 that is assigned to the carbon of $-\text{CH}_2-$ for CPPC is almost the same as that of C2 for PPC, which confirms that the tertiary carbon is not ascribed to $-\text{CHCl}-$ from $-\text{CH}_2-$. However, the peak area of C3 assigned to the carbon of $-\text{CH}_3$ is 1.43 for PPC and 1.21 for CPPC based on the peak area of C4, which demonstrates that the tertiary carbon is ascribed to $-\text{CHCl}_2$ from $-\text{CH}_3$. Therefore, we can conclude that the chlorination reaction mainly takes place between chlorine and $-\text{CH}_3$ of PPC, forming $-\text{CH}_2\text{Cl}$ and $-\text{CHCl}_2$. In other words, the molecular structure of the CPPC obtained in our lab is as:

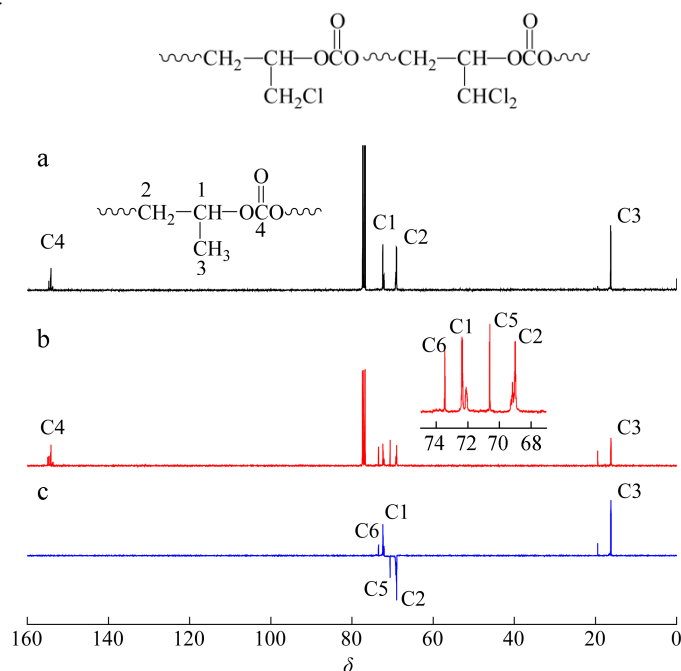


Fig. 1 ^{13}C -NMR spectra of (a) PPC and (b) CPPC, and (c) DEPT-135 NMR spectrum of CPPC

^1H -NMR spectra of PPC and CPPC are shown in Fig. 2. It can be seen that three new signals appear at $\delta = 4.03$ (peak 5), 4.56 (peak 6) and 4.86 (peak 7). ^{13}C - ^1H HSQC NMR measurement of CPPC is used to assign

these new signals (Fig. 3). Strong correlation signals at δ_C/δ_H 70.8/4.03, 70.8/4.57, and 73.1/4.87 correspond to C5/H5, C5/H6, and C6/H7 correlations for CPPC, respectively. Thus, both peak 5 and peak 6 are assigned to the protons of group $-\text{CH}_2\text{Cl}$ which is from the lateral methyl and the terminal methyl, and peak 7 is assigned to the proton of group $-\text{CHCl}_2$. ^1H -NMR results further confirm the existence of $-\text{CH}_2\text{Cl}$ and $-\text{CHCl}_2$ on the CPPC chains. In addition, the signal appearing at $\delta = 1.51$ (peak 4) is assigned to the proton of the terminal methyl group. And the signal appearing at $\delta = 5.31$ (peak 8) is assigned to the proton of dichloromethane, which is used to purify CPPC and not completely removed by vacuum drying. The chlorine content of the CPPC before purification by dichloromethane measured by ion chromatography is 1.7 wt%.

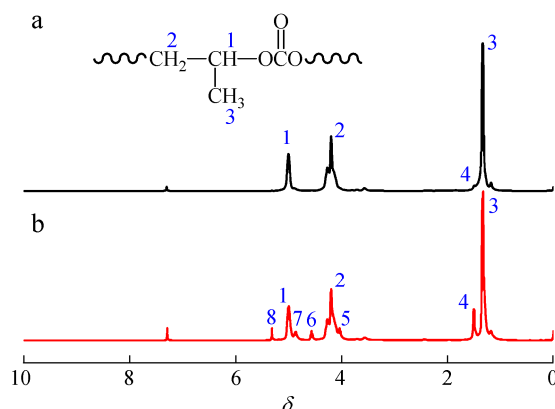


Fig. 2 ^1H -NMR spectra of (a) PPC and (b) CPPC

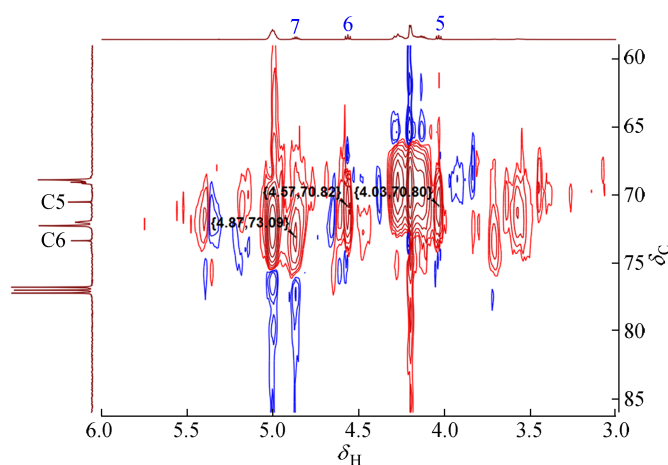


Fig. 3 ^{13}C - ^1H HSQC spectrum of CPPC between δ_C/δ_H 60.0–85.0/3.0–6.0

On the other hand, the chemical shift at $\delta = 19.4$ in ^{13}C -NMR spectrum of CPPC in Fig. 1(b) is ascribed to the terminal methyl group. The peak area of terminal methyl signal peak of CPPC gets increased compared with that of PPC (Figs. S2 and S3 in SI), suggesting the occurrence of degradation with the chlorination of PPC. Figure 4 presents the GPC chromatograms of PPC and CPPC. It can be seen that CPPC presents obviously broader molecular weight distribution (MWD) compared with PPC. The molecular weight (MW) and MWD are listed in Table 1. It is evident that CPPC has both lower number average MW and lower weight average MW, but broader MWD than PPC, further confirming that the degradation reaction occurs during chlorination.

Furthermore, the thermogravimetric (TG) and derivative thermogravimetric (DTG) curves of PPC and CPPC are shown in Fig. 5. The maximum weight loss temperature ($T_{\max}$) of CPPC decreases considerably from

229.5 °C to 213.0 °C. DSC results (Fig. S4 in SI) show that the glass transition temperature (T_g) for PPC is 37.2 °C, whereas it is 28.6 °C for CPPC. The decrease of both thermal stability and T_g results from the degradation of PPC during the chlorination.

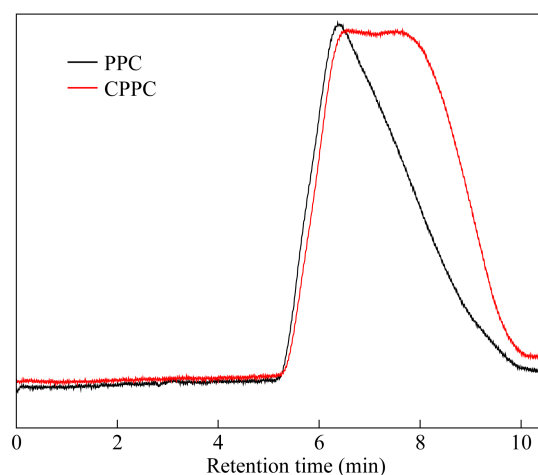


Fig. 4 GPC chromatograms of PPC and CPPC

Table 1 Molecule weight parameters for PPC and CPPC

Sample	$M_n^a \times 10^{-4}$	$M_w^b \times 10^{-4}$	M_w/M_n^c
PPC	9.8	39.9	4.0
CPPC	5.8	26.2	4.5

^a Number average molecular weight, determined by GPC; ^b Weight average molecular weight, determined by GPC; ^c Molecular weight distribution, determined by GPC

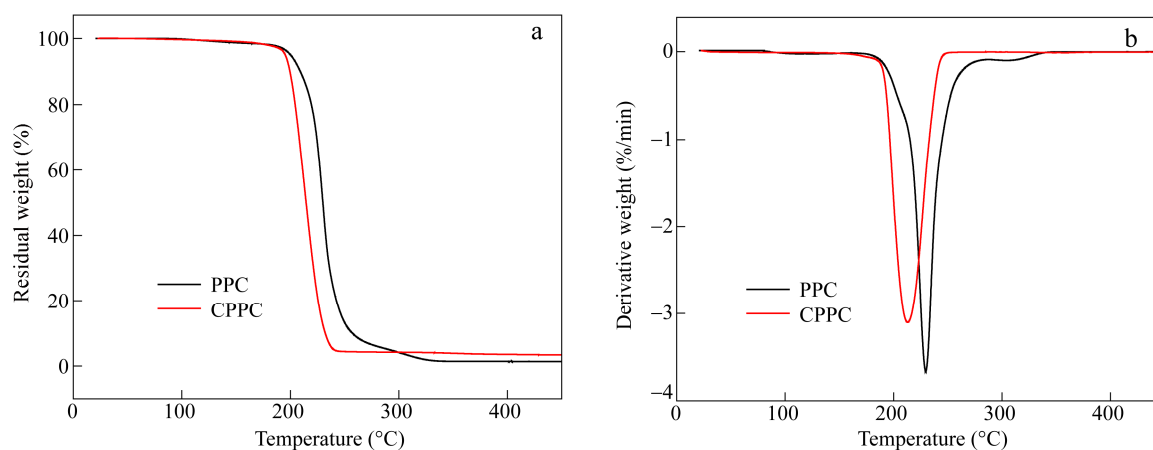


Fig. 5 (a) TG and (b) DTG curves of PPC and CPPC

The above results confirm that chain scission of PPC occurs during the chlorination. However, chlorine atoms were really introduced onto the polymer chains of PPC and CPPC was successfully prepared by this simple gas-solid phase reaction. The chlorine content of the CPPC before purification measured by ion chromatography is 1.7 wt%. It is worth noting that the reaction conditions of the chlorination of PPC are quite mild, such as low reaction temperature (60 °C), atmospheric pressure, no solvent, no catalyzer *etc.*, which can be easily and simply realized at industrial level. What is more important is that many properties of PPC are greatly changed after chlorination as given below, which can widely extend the application fields of PPC.

Biodegradability

Soil burial test was used in this study^[30, 31], and the biodegradability was evaluated through the weight loss of the samples^[32]. For the purpose of comparison, the samples exposed to air were also studied. Figure 6 shows that the weight percent for both the PPC and CPPC specimens exposed to air remains almost unchanged over a period of 120 days, indicating that both PPC and CPPC are stable in air. Moreover, it can be seen that the weight for the PPC samples buried in soil also remains roughly unchanged within 120 days. This is consistent with the results by Lu *et al.*^[31] and Du *et al.*^[33]. They found that PPC degraded obviously under composting conditions or in buffer solution, but was stable in soil at room temperature. However, the weight decreases markedly with test time for the CPPC samples buried in soil. It loses 2.5% weight within 30 days and 12.3% within 120 days. These results can be further confirmed by SEM observation. The surfaces of both the PPC (Fig. 7a) and CPPC (Fig. 7d) samples exposed to air for 120 days are quite flat and smooth. Moreover, no obvious difference can be observed between the exposed and buried PPC samples (Figs. 7a–7c). However, the surface for the CPPC samples buried for 60 days becomes wrinkled and small holes can be observed. When the burying time increases to 120 days, the surface becomes significantly changed.

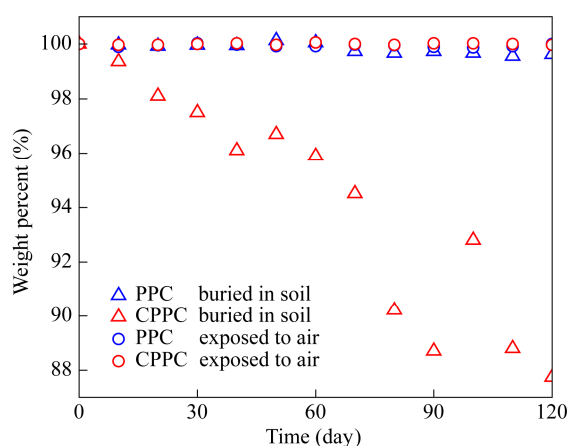


Fig. 6 Weight percent versus test time for PPC and CPPC buried in soil and exposed to air

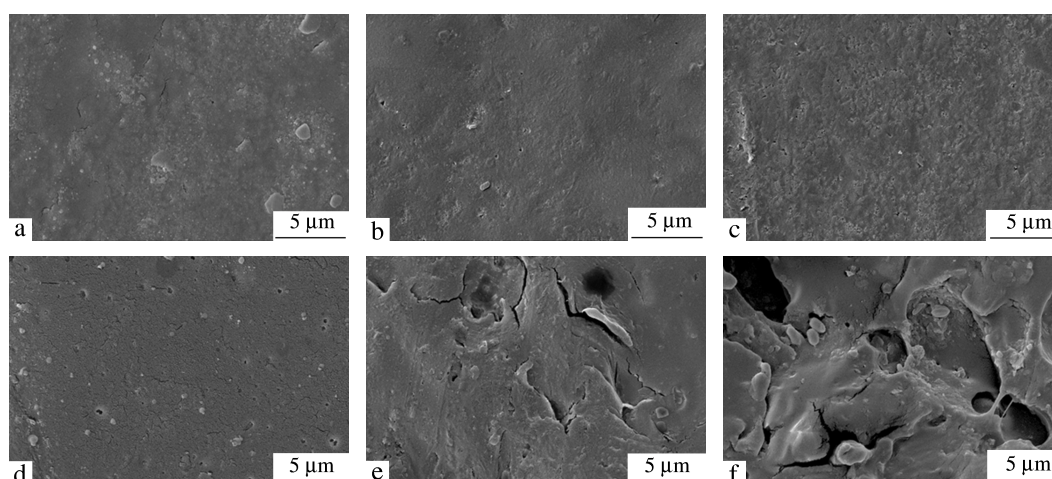


Fig. 7 SEM images of (a) the PPC sample exposed to air for 120 days, (b) the PPC sample buried for 60 days, (c) the PPC sample buried for 120 days, (d) the CPPC sample exposed to air for 120 days, (e) the CPPC sample buried for 60 days, and (f) the CPPC sample buried for 120 days

The above results show that CPPC possesses excellent biodegradability in soil environment. One reason is that the hydrophilicity of PPC can be improved by the introduction of chlorine atoms onto the PPC polymer chains. As a result, more microorganisms can be attached on the surface of CPPC. The other reason is that the molecular weight of CPPC is lower than that of PPC, which is also conducive to biodegradation^[34].

Solubility

To investigate the solubility of PPC and CPPC, four kinds of organic solvents (acetone, tetrahydrofuran, ethyl acetate, and dichloromethane) were chosen to dissolve PPC and CPPC at room temperature. The concentration for all solutions is $5 \text{ mg}\cdot\text{mL}^{-1}$. From Fig. 8, it can be seen that all the PPC solutions are white and with low transparency, indicating poor solubility. However, CPPC can be completely dissolved in these four kinds of solvents and all solutions are clear and transparent. Here, we would like to note that acetone and ethyl acetate are quite common solvents. Good solubility in such solvent can extend the application fields of CPPC as coating and printing materials.

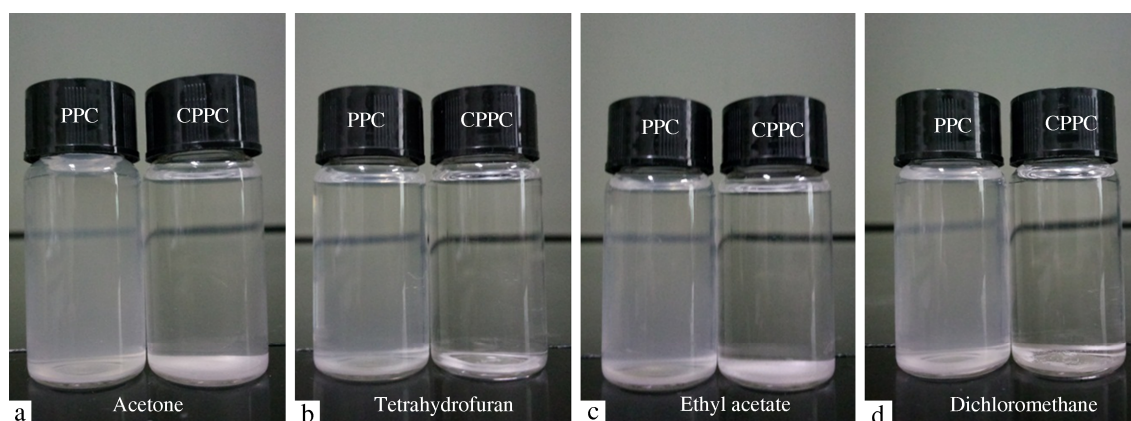


Fig. 8 Solutions of PPC and CPPC in different solvents ($5 \text{ mg}\cdot\text{mL}^{-1}$): (a) acetone, (b) tetrahydrofuran, (c) ethyl acetate, and (d) dichloromethane (The online version is colorful.)

Wettability and Adhesive Property

Wettability is one of the most important properties that determine whether a polymer can be used as thermal adhesive^[35–37]. The wettability of PPC and CPPC melt on wood, stainless steel, and glass surface was measured at 180°C . As shown in Fig. 9, the contact angles for PPC (θ_p) and CPPC (θ_c) measured at 180°C are 65.0° , 14.7° on the wood surface, 40.7° , 12.7° on the stainless steel surface, and 27.4° , 14.5° on the glass surface, respectively. It is revealed that the wettability of PPC melt on these material surfaces can be obviously improved by chlorination.

Figure 10 shows the results of lap shear adhesion test for various materials. It is clear that the adhesive property of PPC can be considerably improved by chlorination. The fracture strength for wood, stainless steel and glass bonded with CPPC is near to 7.4, 3.3 and 2.0 MPa, which is four times higher than that for corresponding substrates bonded with PPC. Furthermore, Fig. 11 presents the images of the fracture surfaces for the wood samples bonded with PPC and CPPC, respectively. From Fig. 11(a), it is seen that the fracture occurs at the interface between PPC and substrate, and the surface of substrate is very smooth. This kind of fracture could be characterized as the interface fracture. However, the fracture occurs within the wood chips (Fig. 11b), indicating that the adhesion between CPPC and the wood substrate is strong enough. These results suggest that CPPC is an ideal thermal adhesive material. Moreover, comparing with the traditional thermal adhesive materials such as ethylene-vinyl acetate copolymer (EVA), polyurethane (PU) *etc.*, CPPC is a kind of green material with low cost.

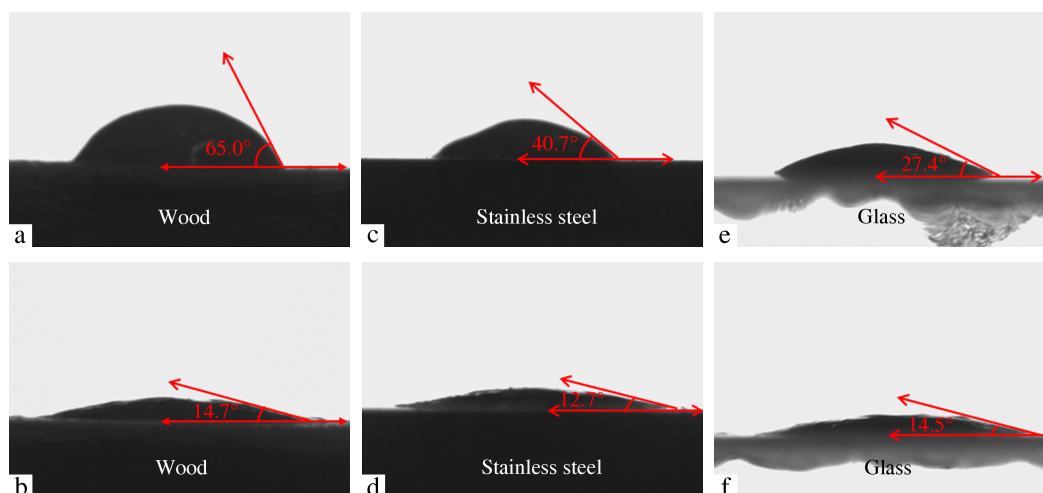


Fig. 9 Images of (a) PPC on wood surface, (b) CPPC on wood surface, (c) PPC on stainless steel surface, (d) CPPC on stainless steel surface, (e) PPC on glass surface and (f) CPPC on glass surface at 180 °C

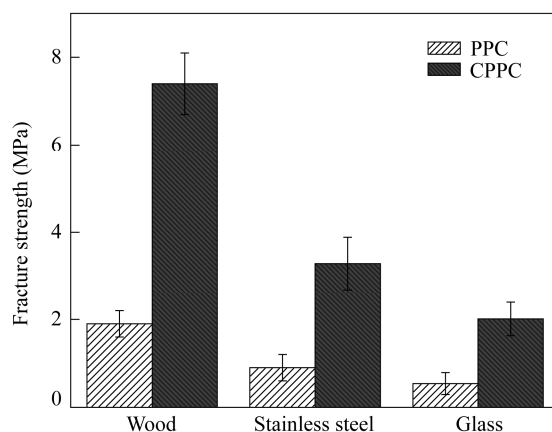


Fig. 10 Fracture strength for different materials bonded with PPC and CPPC

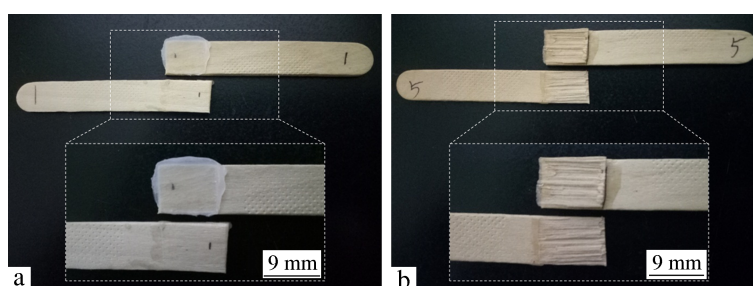


Fig. 11 Fracture surfaces for the wood samples adhered with (a) PPC and (b) CPPC (The online version is colorful.)

Gas Barrier Property

PPC itself possesses good gas barrier property^[38]. For 800 μm thick film, Fig. 12(a) shows that the oxygen permeability of PPC is $1.08 \text{ cm}^3 \cdot \text{cm} \cdot \text{m}^{-2} \cdot \text{day}^{-1} \cdot \text{atm}^{-1}$. According to the calculation based on the data from literature^[39], for 800 μm thick film, the oxygen permeability of high-density polyethylene (HDPE), polyethylene terephthalate (PET), polyamide 6 (PA6), polyvinylidene chloride (PVDC) and polyvinyl alcohol (PVA) is 200, 3.2, 2.4, 0.16 and $0.016 \text{ cm}^3 \cdot \text{cm} \cdot \text{m}^{-2} \cdot \text{day}^{-1} \cdot \text{atm}^{-1}$, respectively. In this study, oxygen permeability coefficient of

CPPC film was also measured at 23 °C and the result is presented in Fig. 12(a). It is seen that the oxygen permeability coefficient changed from $1.08 \text{ cm}^3 \cdot \text{cm} \cdot \text{m}^{-2} \cdot \text{day}^{-1} \cdot \text{atm}^{-1}$ to $0.72 \text{ cm}^3 \cdot \text{cm} \cdot \text{m}^{-2} \cdot \text{day}^{-1} \cdot \text{atm}^{-1}$. That is, the gas barrier property of CPPC can be further improved by chlorination. This can be attributed to the introduction of the chlorine atoms onto the polymer chains of PPC. Gas molecules permeate film through the following three procedures: dissolution, diffusion and desorption as shown in Fig. 12(b). Gas barrier property is mainly determined by the dissolution and diffusion process^[40]. The introduction of chlorine atoms increases the polarity of PPC, which can reduce the dissolution rate of non-polar gas molecules, such as oxygen molecules into CPPC film. Moreover, the size of the chlorine atom is larger than that of the hydrogen atom. Due to the space steric effect, the introduction of chlorine atoms reduces the diffusion rate of gas molecules in CPPC film. Consequently, the gas barrier property of CPPC can be further improved by chlorination.

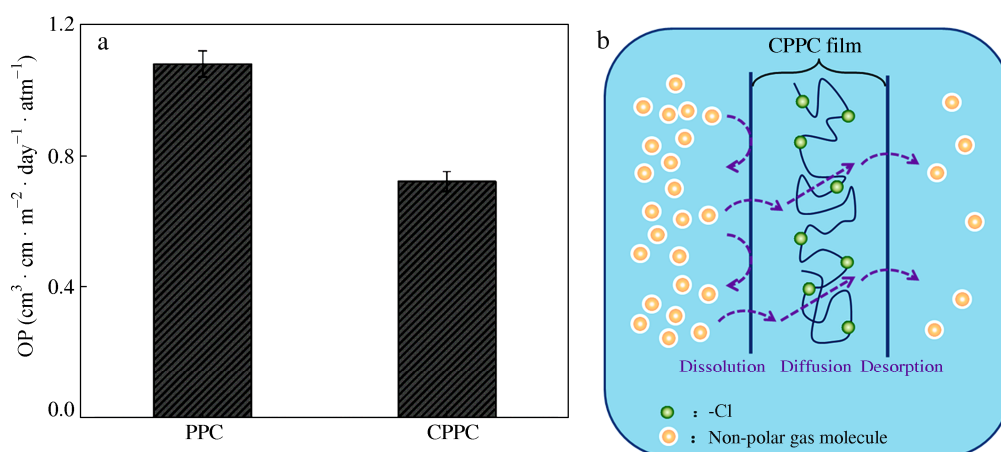


Fig. 12 (a) Oxygen permeability coefficient of PPC and CPPC film; (b) The permeation process of non-polar gas molecules through CPPC film (The online version is colorful.)

CONCLUSIONS

Chlorinated poly(propylene carbonate) (CPPC) was successfully prepared by a gas-solid phase reaction with moderate reaction conditions. The chlorine content of CPPC measured by ion chromatography is 1.7 wt%. The introduction of polar chlorine atoms onto the PPC polymer chains greatly changed the properties of PPC. The biodegradation test shows that the biodegradability of CPPC is superior to that of PPC. CPPC exhibits better solubility in some common organic solvents and better wettability of melt on wood, stainless steel and glass compared with PPC. The shear fracture strength for wood, stainless steel and glass bonded with CPPC is four times higher than that for corresponding substrates bonded with PPC. The oxygen permeability coefficient of CPPC exhibits a decrease of 33% compared with that of PPC. All these distinguished properties can greatly broaden the applications of CPPC in the fields of coating, adhesive, barrier materials, and so on. In sum, the simple preparation process and distinguished properties will make CPPC have bright application prospects.

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