Research Article

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Poly(propylene carbonate) networks with excellent properties: Terpolymerization of carbon dioxide, propylene oxide, and 4,4'-(hexafluoroisopropylidene) diphthalic anhydride

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Abstract: Poly(propylene carbonate) (PPC) is an emerging low-cost biodegradable plastic with potential application in many fields. However, compared with polyolefin plastics, the major limitations of PPC are its poor mechanical and thermal properties. Herein, a thermoplastic PPC containing cross-linked networks, one-pot synthesized by the copolymerization of carbon dioxide, propylene oxide, and 4,4'-(hexafluoroisopropylidene) diphthalic anhydride, had excellent thermal and mechanical properties and dimensional stability. The weight-average molecular weight and the polymer yield of the PPC5 were up to 212 kg mol^{-1} and $104 \text{ g}_{\text{polym}} \text{ g}_{\text{cat}}^{-1}$, respectively. The 5% thermal weight loss temperature reached 320°C , and it could withstand a tensile force of 52 MPa. This cross-linked PPC has excellent properties and is expected to be used under extreme conditions, as the material can withstand strong tension and will not deform.

Keywords: poly(propylene carbonate), carbon dioxide, networks, terpolymerization

1 Introduction

Currently, excessive emission of carbon dioxide (CO_2) is contributing to the destruction of ecological balance and threatening the survival of various organisms (1,2). However, CO_2 is a naturally abundant, cheap, recyclable, and non-toxic carbon source involved in various organic reactions (3–6). CO_2 is converted into energy products and chemicals, which are not only conducive to environmental protection but also help in solving the problem of carbon resource shortage (7–12). Its development and utilization have attracted widespread attention worldwide. Inoue et al. (13) first reported the copolymerization of CO_2 and epoxide to produce poly(propylene carbonate) (PPC) in 1969. PPC produced by copolymerization has the unique advantages of being biodegradable and therefore does not pollute the environment, which has attracted worldwide attention. PPC is an emerging low-cost biodegradable plastic with many potential applications, including adhesives, mulch films, packaging, polymer electrolytes, toughening agents, and biomedical materials (14–17).

However, compared with polyolefin plastics, the major limitations of PPC are its poor mechanical and thermal properties. The structural asymmetry of propylene oxide (PO) gives the polymer irregular and poor thermal performance, and PPC's low glass transition temperature (T_g) and amorphism lead to its weak mechanical strength and poor dimensional stability (18). Therefore, a comprehensive modification to enhance the performance of PPC is required to realize its wide application. Much effort has been made to improve the mechanical properties and thermal stability of PPC by chemical modification and physical blending (19–22), which involved mixing PPC with other materials. Physical blending can only adjust the performance of the material within a limited range and it can encounter many problems, such as the poor compatibility of the blended materials, the uneven dispersion of

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nanoparticles, insignificant improvement in performance, and complicated preparation processes. These problems restrict further applications of physical blending of PPC. Chemical modification is the addition of a third unit to the polymerization reaction, which, by adjusting the molecular chain structure of the polymer, can produce a more precise solid and control the structure of the polymer product. Chemical modification methods include ternary copolymerization, cross-linking reactions, chain transfer reactions, block copolymerization, and graft copolymerization. Currently, ternary copolymerization is an important method for modifying aliphatic polycarbonate (23–27).

The 4,4'-(hexafluoroisopropylidene) diphthalic anhydride (6FDA) monomer contains rigid benzene ring groups, and so, the resulting polymer has excellent mechanical properties. The addition of a rigid third monomer gives the resulting PPC better stability, and because it can withstand higher tensile force, there is no significant deformation after the tensile force is released. At the same time, the strong negative electricity of the introduced fluorine atoms and the chemical and thermal stability of the polypropylene carbonate are significantly improved. Experimentally, the dimensional stability and thermal properties of the polymerized product have been significantly improved, and so, the ternary copolymerized polymer can be used in high external tension and high-temperature environments.

2 Materials and methods

2.1 Materials

PO was refluxed over calcium hydride for 8 h, distilled under dried nitrogen gas, and stored over 0.4 nm molecular sieves prior to use. CO₂ (99.99%) was commercially obtained from Shenzhen Shente Industrial Gas Co., Shenzhen, China. Glutaric acid, zinc oxide, and 6FDA were purchased from Aladdin Industrial Corporation, and zinc glutarate (ZnGA) was synthesized according to the literature (28).

2.2 General copolymerization procedure

ZnGA (0.1 g) and a certain proportion of 6FDA were placed in a 250 mL autoclave reactor equipped with a magnetic stirrer and dried for 8 h at 70°C under a vacuum. The autoclave was subsequently carefully purged with nitrogen. Then, 11.6 g of PO was injected into the autoclave, which

was then filled to 3 MPa with CO₂. The copolymerization reaction was stirred at 70°C for 24 h. The reactants were then cooled to room temperature, and the pressure was released. The hard block product, dissolved in trichloromethane containing a 5% hydrochloric acid solution to decompose ZnGA, was precipitated three times in ethanol to remove a small amount of propylene carbonate. This was then dried to a constant weight at 80°C in a vacuum and the yield was calculated.

2.3 Characterization and measurements

Fourier transform infrared (FT-IR) spectrometry (Nicolet 6700; Thermo Scientific) was carried out with attenuated total reflection accessories. Using deuterochloroform as a solvent, proton nuclear magnetic resonance (¹H NMR) spectra were obtained (400M; Bruker). The average molecular weights of the polymers were determined by gel permeation chromatography (Waters 515 HPLC pump and Waters 2414 detector) with tetrahydrofuran as the eluent. The gel contents were determined by the ASTM D2765 method.

Thermogravimetric analysis (TGA) was measured using a simultaneous thermal analyzer (STA 6000; PerkinElmer). Samples were tested under a 20 mL min⁻¹ nitrogen flow from 25°C to 450°C at a heating rate of 10°C min⁻¹. A hot-set test was carried out in an oven. A dumbbell-shaped specimen was loaded with 0.14 MPa and the reference length was marked as L_0 ($L_0 = 20$ mm). The load specimen was then placed in an oven at 60°C. After 15 min, the length between the markers was measured and recorded as L_1 , and the load was released. After 5 min of relaxation at 60°C, when the specimen was no longer shortened at room temperature, the length between the markers was measured and recorded as L_2 . Mechanical properties were tested at 23°C using an electronic tensile tester (CMT 6104) according to ASTM D368. The crosshead speed was 50 mm min⁻¹. The crystallinity and the crystal structure were measured by an X-ray polycrystalline diffractometer with copper (Cu) k-alpha radiation with a wavelength of 1.5418 Å. Scanning electron microscopy (SEM) was used to observe the surface morphologies of the catalysts. The samples were coated with gold and imaged with a Zeiss Ultra Plus field emission scanning electron microscope. Differential scanning calorimetry (DSC) measurements were conducted in the temperature range of 20–100°C at a heating rate of 10°C min⁻¹ on a Q100 TA instrument under 20 mL min⁻¹ nitrogen flow. The gel contents were determined by the ASTM D2765 method. The sample was refluxed in boiled chloroform for 24 h. The

Scheme 1: Synthesis of ZnGA from zinc oxide and glutaric acid.

insoluble proportion was dried to a constant weight at 80°C in a vacuum. The gel content is defined as the weight percentage of the insoluble proportion in the sample.

3 Results and discussion

3.1 Catalysts

Zinc glutarate (ZnGA) was synthesized according to the literature (28). Equal molar ratios of ZnO (8.14 g, 100 mmol) and GA (13.21 g, 100 mmol) were added into 300 mL toluene at 55°C, and the mixture was stirred for 12 h. The filter cake was washed with acetone several times, and then the filter cake was dried in a vacuum oven at 80°C for 8 h. After drying, it was carefully ground with a mortar, sealed, and stored (see Scheme 1).

Figure 1 shows that the FT-IR curve of the ZnGA catalyst: peaks a (1,585 cm⁻¹), b (1,536 cm⁻¹), and c (1,405 cm⁻¹) represent the zinc–carboxylate bond (COO⁻), respectively and peak d represents the carbonyl (C=O) stretching of 1,697 cm⁻¹. The crystal structure of ZnGA was determined by XRD and the diffraction pattern is shown in Figure 2. The XRD analysis was performed to determine the degree of crystallinity of the catalyst and the presence of unreacted

ZnO. In Figure 2, the characteristic peaks of ZnGA are marked with an asterisk, and that of ZnO are marked with a hash. FT-IR and XRD patterns are similar to those of ZnGA reported by Dehghani and Moonhor in a previous paper (29,30), indicating that the ZnGA catalyst was successfully synthesized. The results of the field emission SEM shown in Figure 3 demonstrate that ZnGA catalysts were generated from aggregated small-rectangular plate crystals. These small rectangular plate crystals are uniform in appearance and arranged neatly. This rectangular morphology is similar to the single-crystal ZnGA synthesized via the hydrothermal reactions of zinc perchlorate hexahydrate and glutaronitrile reported by Ree and co-workers (31).

3.2 Synthesis

6FDA was introduced into the polymerization reaction of CO₂ and PO for ternary copolymerization to yield polycarbonates (PPCs) with a cross-linked network structure, where the proportion of 6FDA input and the 6FDA feed proportion did not exceed 5 wt% of PO (see Scheme 2). According to the previous research (8,32,33), one acid anhydride can be copolymerized to connect a carbonate chain in the ternary copolymerization. Therefore, 6FDA can be connected to four polycarbonate chains, and

Figure 1: FT-IR pattern of ZnGA.

Figure 2: XRD pattern of ZnGA.

Figure 3: SEM image of ZnGA.

Scheme 2: Formation of network-shaped poly(propylene carbonate) (PPC) with carbon dioxide (CO_2)/propylene oxide (PO) copolymerization in the presence of 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA).

cross-linking occurs to form a cross-linked polycarbonate. Through experimental characterization, it was found that the cross-linked polycarbonate has excellent thermal properties, mechanical properties, and dimensional stability. FT-IR spectra (see Figure A1 in the Appendix) showed that the characteristic $\text{C}=\text{O}$ peak stretching vibration peaks at $1,775$ and $1,850\text{ cm}^{-1}$ of 6FDA disappear in PPCs, and the characteristic $\text{C}=\text{O}$ peak stretching vibration of the ester bond appear compared to the spectrum of 6FDA. In addition, the success of ternary polymerization was preliminarily

assessed by the state of the polymerized product after the reaction: the PPC was light yellow and viscous. After cross-linking, the PPCs showed a solid state. The ^1H NMR (see Figure A2) spectrum, only representing the soluble components, did not show the signal peak of the 6FDA unit. Because 6FDA formed a gel after the ternary copolymerization, it was insoluble in deuterated chloroform and so the ^1H NMR spectra of PPCs only showed the signals of CO_2/PO copolymers.

The results showed that with a gradual increase in the amount of 6FDA in the polymerization reaction, the yield of the polymer was greatly improved from 25 to $104\text{ g}_{\text{polym}}\text{ g}_{\text{cat}}^{-1}$. A possible reason for this is that with the addition of 6FDA, cross-linkages formed a network-shaped polycarbonate, and as the monomer ratio increased, the degree of cross-linking gradually increased. The gel content in the polymer increased from 0% to 45%, which was the main indicator used to measure the degree of polymer cross-linking (see Table 1). Further, the molecular weights of the copolymers substantially increased, and the molecular weight distribution (M_w/M_n) was lower than PPC. It is worth mentioning that 212 kg/mol is the largest relative molecular weight among the cross-linked PPCs reported to date, indicating that the molecular weight distribution of the produced polycarbonate was relatively uniform.

3.3 Thermal properties

Figure 4 and Figure A4 present the TGA and the DTG curves of the products. For PPC, the 5% weight-loss degradation temperature ($T_{d,5\%}$) was 150°C , and there was one maximum weight-loss degradation temperature

Table 1: Results of copolymerization^a

Sample	6FDA feed ^b	Polymer yield ^c	M_n ^d	PDI ^e	Gel (%)
PPC	0	25	70	2.4	0
PPC1	1	58	184	1.0	23 ± 1.5
PPC2	2	68	189	1.0	36 ± 1.8
PPC3	3	86	205	1.0	37 ± 2.2
PPC4	4	99	205	1.0	38 ± 1.9
PPC5	5	104	212	1.0	45 ± 2.0

^a Polymerization conditions: ZnGA, 0.10 g; PO, 45 mL; CO_2 pressure, 3.0 MPa; 70°C , 24 h. ^b 6FDA feed of PO in the copolymerization (wt%).

^c g polymer/g ZnGA. ^d M_n = number-average molecular weight (kg mol^{-1}), determined by GPC. ^e Polydispersity index = M_w/M_n ; M_w – weight-average molecular weight (kg mol^{-1}), determined by GPC.

Figure 4: TGA curves of PPC and PPCs.

($T_{d,max}$) of 270°C (see Table 2). According to the decomposition mechanism of PPC (34), with an increase of temperature, the pyrolysis and detachment of the polycarbonate chains lead to the weight loss of the PPC materials; however, the $T_{d,5\%}$ and $T_{d,max}$ of each copolymer was over 320°C and almost reached 383°C, respectively. These were significantly higher than the degradation temperatures of the PPC (see Table 2). This significant improvement in the thermal stability was attributed to the formation of cross-links in the PPC matrix by the introduction of 6FDA into the PPC chains since the cross-linking significantly limited the unzipping reaction. The cross-linked polycarbonate carbonate chains restricted the unzipping and detachment of the carbonate chains, while the 6FDA contained a more stable benzene ring and fluorine atoms. Due to the strong electronegativity of the fluorine atoms and the stability of the benzene ring, the produced polycarbonate had better thermal stability; hence, the thermal stability of PPCs was significantly improved. Polycarbonate with good performance can be applied at high temperatures, which broadens the application range of the PPC.

Table 2: Thermal properties of PPC and PPCs

Sample	$T_{d,5\%}$ (°C)	$T_{d,max}$ (°C)	T_g (°C)
PPC	150	270	31
PPC1	300	350	51
PPC2	305	350	52
PPC3	306	350	52
PPC4	310	330	54
PPC5	320	350	52

3.4 Mechanical properties and dimensional stability

The strain–stress curves are presented in Figure 5, Table A1 lists the data. The test results showed that with increasing 6FDA, the mechanical strength of the PPCs was significantly improved from 18.2 up to 51.7 MPa. However, after the tension was released, the elongation at break was significantly reduced, from 312% to 11%, which is a leap-forward improvement in the mechanical properties of PPC materials (see Figure 5). A possible reason for this is that the ternary copolymerization introduced a benzene ring containing a rigid group into the PPC unit, which gave the polymerized material better stability. The PPC chains mainly contained carbonate linkages with small quantities of ether linkages (35,36). The PPC had fewer polar groups, and the interaction between the PPC chains was smaller, so the mechanical strength was weaker. When the PPC underwent the cross-linking reaction to form the cross-linked polycarbonate, the movement between the PPC chains was restricted, thereby greatly improving the mechanical strength.

The low T_g and amorphous nature of PPC not only make it weak mechanically but also easy to deform (37). Hence, for many applications, maintaining the dimensional stability of PPC above 60–70°C is critical. Compared to the PPC, the hot-set elongation of the PPCs dropped sharply from more than 300% to 7%. The permanent deformation was significantly reduced, and there was almost no deformation, which indicated that the cross-linked network significantly improved the thermal stability and dimensional stability of the polymer. Adding

Figure 5: Strain–stress curves of PPC and PPCs.

rigid groups to a copolymerization reaction to synthesize cross-linked polycarbonate can completely and significantly improve the dimensional stability of PPC, which lays a solid foundation for the large-scale application of PPC and subsequent application research.

4 Conclusions

CO₂, PO, and 6FDA were synthesized by ternary copolymerization under the catalysis of ZnGA, and cross-linked polycarbonate PPCs were successfully synthesized by a one-pot method. The obtained cross-linked polycarbonate had excellent thermal and mechanical properties and dimensional stability. The molecular weight reached an unprecedented 212 kg/mol. The thermal decomposition temperature reached 320°C, and it could withstand a tensile force of 51 MPa without degeneration with good dimensional stability. The synthetic cross-linked polycarbonate exhibits excellent properties and can be expected to be used under many extreme conditions as the material can withstand strong tension and will not deform.

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Appendix

Figure A1: FT-IR spectra of 6FDA and PPCs. PPC1–5 presents the copolymer with a 1–5 wt% 6FDA feed of PO in the copolymerization, respectively.

Figure A2: ¹H NMR spectra of poly(propylene carbonate) (PPC) and PPCs.

Figure A3: Photographs of PPC and PPCs.

Figure A4: DTG curves of PPC and PPCs.

Figure A5: DSC curves for PPC and PPCs.

Table A1: Mechanical properties of PPC and PPCs

Sample	Tensile strength (MPa)	Elongation at break (%)	Hot-set elongation (%)	Permanent deformation (%)
PPC	18.2 ± 1.3	312 ± 9	300 ± 7	150 ± 9
PPC1	33 ± 1.5	30 ± 2.1	63 ± 5	7 ± 1.2
PPC2	38.2 ± 1.6	18 ± 1.7	44 ± 3	5 ± 0.3
PPC3	43.8 ± 1.3	17 ± 1.3	20 ± 2	1 ± 0.1
PPC4	48.1 ± 1.7	15 ± 0.7	16 ± 2	0
PPC5	51.7 ± 1.4	11 ± 0.5	7 ± 0.5	0

Figure A6: GPC curves of PPC and PPCs.