

A Simple Method for Producing High-Performing End-Capped and Cross-Linkable Poly (Propylene Carbonate)

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ABSTRACT

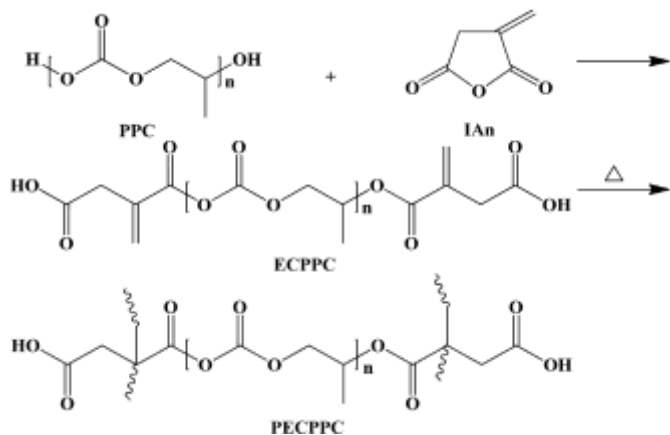
The modification of poly(propylene carbonate) (PPC) using itaconic anhydride (IAN) was initially accomplished by solution blending, followed by direct heating, resulting in high-performance end-capped and cross-linkable PPC (PECPPC). The structure of PECPPC was determined by FTIR and ¹H NMR after a thorough investigation of the interaction of PPC with IAN. To enhance PPC performance, a simple approach that uses end-capping and cross-linking can be created. According to studies made using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA), the glass transition temperature (T_g) and thermal decomposition temperature (T_d) of PECPPCs are both much higher than those of PPC and rose with the amount of IAN present. The end-capping and cross-linking procedures significantly improved the mechanical characteristics of PPC, as demonstrated by tensile tests; the highest tensile strength of PECPPC4 is 37.5 MPa. Additionally, compared to PPC, ECPPC4 demonstrates a higher rate of hydrolysis in phosphate buffer solution (PBS). It is shown that the method of perfectly modifying PPC with IAN by combining end-capping and cross-linking is effective.

Keywords: Poly(propylene carbonate)Itaconic anhydride,End-cappingCross-linking

1. Introduction

The alternative copolymer poly (propylene carbonate, or PPC), which is made of propylene oxide (PO) and carbon dioxide (CO₂), has received a lot of interest due to its high value-added fixation of CO₂ as well as its biodegradability and biocompatibility [1e3]. PPC offers a lot of promise for use in the creation of plastic, elastomers, fibre, adhesives, polymer electrolytes, and other materials [4e6]. The weak thermal stability and mechanical qualities of PPC, however, have restricted its practical use [7]. So many methods—including physical blending [8], terpolymerization [9, 10], end-capping [11], cross-linking [12], etc.—have been devised to enhance PPC performance. Despite numerous successes, it is now exceedingly difficult to change the material profile of PPC fitting for present applications [13e15].

According to reports, the main chain random scission and unzipping degradation of PPC is the mechanism for its heat disintegration [16e19]. The terminal hydroxyl end group's "back-biting" attack on the carbonyl group is the cause of PPC's chain-unzipping breakdown. Consequently, end-capping techniques have been developed to improve PPC's thermal performance. These techniques work by interacting with the PPC's terminal hydroxyl groups in a way that prevents the unzipping reaction. Yao et al. [20] showed that blending the melt with a tiny amount of maleic anhydride improved the thermal stability and mechanical qualities of PPC (MA). The reason is that while pure PPC would drastically degrade in molecular weight during the melt process, PPC can be end-capped with MA simply and while maintaining its molecular weight through simple melt mixing. Jiang et al. [21] investigated the reactive extrusion processes used to create three different end-capped PPC types using MA, phthalic anhydride (PA), and pyromellitic dianhydride (PMDA), respectively. The findings demonstrated that every end-capped PPC performed better mechanically and thermally than PPC. In the meantime, cross-linking techniques can be used to enhance the thermal and



Scheme 1. Preparation of ECPPC and PECPPC.

2. Experimental

Materials

CO₂ with a purity of 99.99% was commercially obtained without further purification. Propylene oxide (PO) of 99.5% purity stored over 0.4 nm molecular sieves prior to use. Itaconic anhydride (IAN) was purchased from Alfa Aesar China (Tianjin) Co., Ltd., which of 97% purity and used without purification. Solvents such as ethanol and chloroform were of analytical reagent grade and used as received.

Sample preparation

PPC was synthesized from the copolymerization of CO₂ and propylene oxide catalyzed by zinc glutarate at 60 °C for 40 h. End-capped PPC (ECPPC) was prepared from PPC with IAN by solution blending at 60 °C for 4 h. The viscous solution was concentrated by using a rotary evaporator to give a proper concentration and precipitated out by pouring the concentrated solution into vigorously stirred methanol. The as-made ECPPC was filtered and dried under vacuum at 80 °C for 10 h. Then, the end-capped and cross-linkable PPC (PECPPC) was prepared from ECPPC with the direct heating treatment under vacuum at 100 °C for 6 h.

Characterization

FTIR spectra of polymers were obtained by the Digilab Merlin FTS 3000 FT-IR infrared spectrometer. ¹H NMR spectra of the

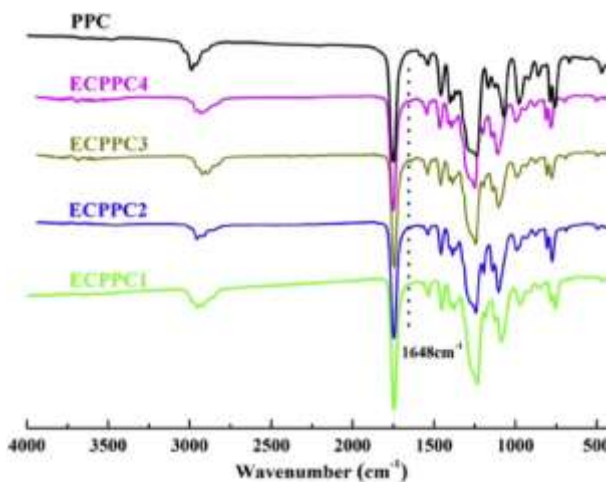


Fig. 2. FTIR spectra of PPC and ECPPCs.

mechanical performance of PPC. For example, Hao et al. [22] reported that the cross-linked poly(propylene carbonate) (PPC) was prepared using polyaryl polymethylene isocyanate as a cross-linking agent. The resulted cross-linked PPC showed higher thermal performance and mechanical properties compared with pure PPC. It is demonstrated that both end-capping and cross-linking techniques with simple processing and low cost are efficient to improve the performance of PPC [23]. To amplify, it is worthwhile to develop a facile strategy with the combination of end-capping and cross-linking techniques to the complete modification of PPC.

Itaconic anhydride (IAN) is one of nontoxic, environmentally friendly and renewable resource [24,25] can be used to prepare polymer materials by ring-opening polymerization [26] or radical polymerization [27]. We recently reported the preparation of cross-linkable aliphatic polycarbonates by one-step strategy from the terpolymerization of CO₂, propylene oxide and IAN, which ascribes to the cross-linking of active exo-type double bond of IAN under copolymerization conditions [28]. It is suggested that IAN can be used for further modification of PPC by the combination of end-capping and cross-linking techniques, which provide a facile route to acquire high performance PPC. Herein, the modification of PPC with IAN by solution blending following with direct heating treatment was firstly investigated. The results showed that IAN can be employed as a reactive agent for significantly improving the performance of PPC by end-capping and cross-linking. The reaction mechanism of PPC and IAN including end-capping and cross-linking was confirmed. It is demonstrated that the strategy with the combination of end-capping and cross-linking techniques is effective to the modification of PPC.

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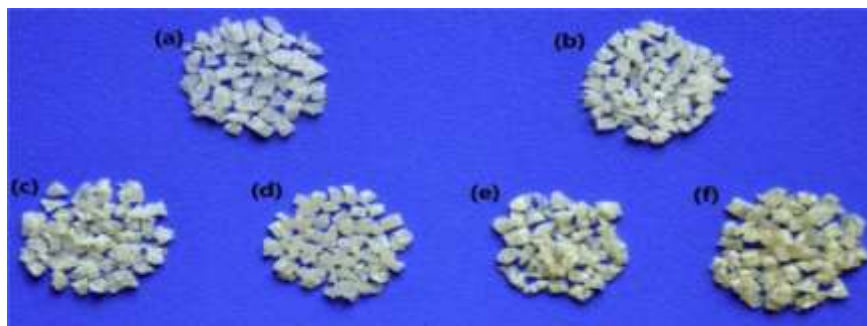


Fig. 1. Macro-morphologies of the samples of (a) PPC³, (b) ECPPC⁴, (c) PECPPC¹, (d) PECPPC², (e) PECPPC³ (f) PECPPC⁴ (³ they correspond to PPC and IAN with the weight ratio of 100/0, 100/10, 100/2, 100/5, 100/8 and 100/10, respectively).

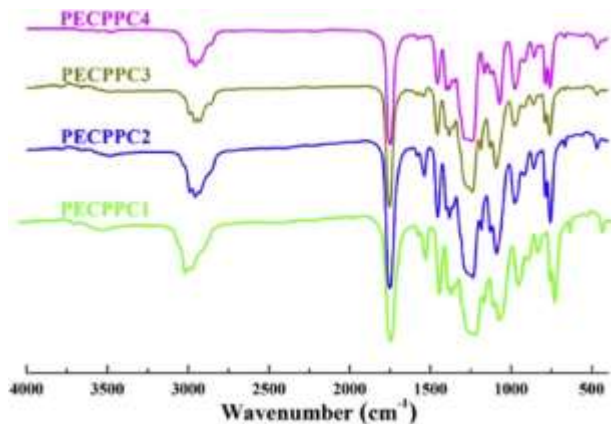


Fig. 3. FTIR spectra of PECPPCs.

products were recorded on a Bruker DRX-400 NMR spectrometer using tetramethylsilane as an internal standard and d-chloroform (CDCl_3) as solvent. Thermogravimetric analysis (TGA) measurements were performed in a PerkinElmer TGS-2 under a protective nitrogen atmosphere. The temperature ranged from 50 °C to 500 °C at a heating rate of 10 °C min^{-1} . Differential scanning calorimetry (DSC) measurements were carried out using a Q100 TA instrument under a high purity nitrogen flow of 40 mL min^{-1} over the temperature range -50 °C to 150 °C at a heating rate of 10 °C min^{-1} . The T_g of the sample was taken as the onset of the change in heat capacity as a function of temperature. The mechanical properties were tested at 23 °C and relative humidity of 50 ± 5% using a CMT 6104 electronic tensile tester with a computer controlling system which was equipped with a 10 kN electronic load cell and mechanical grips according to the ASTM standard. The cross-head speed was 50 mm min^{-1} . The data were recorded as the average value of five parallel determinations. Degradation experiments were carried out by means of the buffer solution processes. The initial weights (W_0) of the specimens were measured prior to tests. Thin-film specimens were prepared by casting 5 wt% PPC and PECPPC4 chloroform solution. Fifteen milligrams of the PECPPC4 film (10 × 5 × 0.5 mm) and 5 mL of phosphate buffer ($\text{NaH}_2\text{PO}_4/\text{Na}_2\text{HPO}_4$, pH 7.4) were placed in a test tube. The container was then placed in a thermostatic bath regulated at 37 °C. The films were removed from the buffer solution for various specified durations. Upon washing with redistilled water, they were dried at room temperature under vacuum to constant weight. The film specimens, from buffer solution experiments, were dried with filter paper after washing with redistilled water and weighed (W_1). The film specimens were dried in a vacuum oven to a constant weight (W_2). The amounts of water absorbed by the specimens were determined from the equation:

$$\text{Weight loss } \delta\% = \frac{W_0 - W_2}{W_0} \times 100\% \quad \text{Water sorption } \delta\% = \frac{W_1 - W_2}{W_2} \times 100\%$$

3. Results and discussion

Reaction of PPC with IAN

The synthetic strategy developed for end-capping PPC (ECPPC)

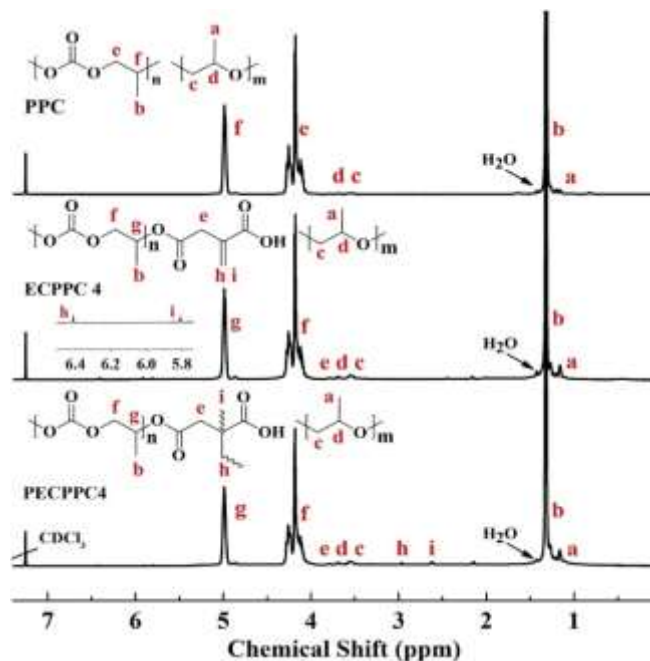


Fig. 4. ^1H NMR spectra of PPC, ECPPC4 and PECPPC4.

proportions by solution blending. PECPPCs were prepared from ECPPCs by the direct heating treatment. PPC, ECPPCs and PECPPCs are whole mass polymers and seem like (a), (b), (c), (d), (e) and (f) in Fig. 1 (a) showed PPC special white, but ECPPC4 (b) and PECPPCs including (c), (d), (e) and (f) appear yellow. Moreover, the colour of PECPPCs becomes darker with the increasing content of IAN, which ascribe to the cross-linking of the active double bond in the end of ECPPC chain by thermal initiation. It is noted that the resulted end-capped and cross-linkable PPC can dissolve in many solvents including chloroform, tetrahydrofuran, acetone and dimethyl sulfoxide, indicating that the micro-crosslinking structure of PECPPCs.

The structure of ECPPC was characterized by FTIR spectroscopy. As shown in Fig. 2, compared with PPC, the new characteristic absorption of ECPPC at 1648 cm^{-1} is assigned to the unsaturated double bonds stretching vibration, demonstrating the end-capping reaction of PPC with IAN. Furthermore, the post-modification of ECPPC was performed by the direct heating treatment at 100 °C for 6 h to provide end-capped and cross-linkable PPC, and denoted as PECPPC1, PECPPC2, PECPPC3 and PECPPC4, respectively. As shown in Fig. 3, the characteristic absorption at 1648 cm^{-1} disappeared in the FTIR spectra of PECPPCs, which ascribed to the cross-linking of the unsaturated double bonds in the end of ECPPC by thermal initiation.

and post-modification PPC (PECPPC) is illustrated in Scheme 1. ECPPCs were prepared from PPC with IAN in different weight

To further investigate the end-capping and cross-linking reaction of PPC with IAn, ^1H NMR spectroscopy of PPC, ECPPC4 and ECPPC4 was tested as shown in Fig. 4. The absorption peaks at 1.34, 4.18, and 5.00 ppm were assigned to CH_3 , CH_2 , and CH in the carbonate unit, respectively; two weak peaks at 5.81 and 6.41 ppm of ECPPC4 was assigned to the two protons of $\text{C}=\text{C}$ double bonds, indicating the end-capping of PPC with IAn. Compared with

Table 1
 Properties of PPC and ECPPCs.

Sample	$T_{d-5\%}$ (°C)	T_{d-max} (°C)	T_g (°C)	Elongation at break (%)	Tensile strength (MPa)
PPC	194.7	241.5	34.3	594.2	6.3
ECPPC1	196.1	242.5	34.4	550.6	9.4
ECPPC2	236.3	243.5	35.0	492.1	11.5
ECPPC3	251.2	266.7	35.3	445.2	13.4
ECPPC4	261.8	271.3	36.8	367.7	16.1

ECPPC4, peaks of PECPPC4 at 2.62 and 2.99 ppm assigned to methylene protons generated by cross-linking of the double bonds in ECPPC, indicating the successful preparation of cross-linkable PPC. It is demonstrated that the strategy for the modification of PPC by solution blending following with the direct heating treatment is available to synthesize end-capped and cross-linkable PPC.

Fig. 6. DSC curves of PPC, ECPPC4 and PECPPCs.

Thermal properties

To confirm the end-capping effect on PPC with IAn, thermal performance of ECPPC was firstly investigated. Thermogravimetric analysis (TGA) was conducted to assess the thermal degradation behavior of ECPPCs. As shown in Table 1, TGA parameters showed the expected increase on the thermal stability of PPC by end-

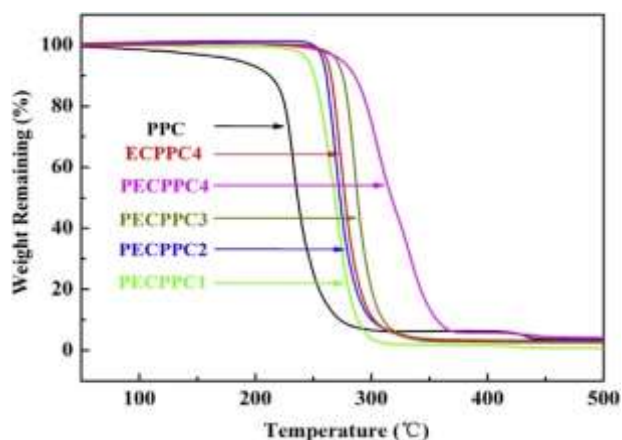
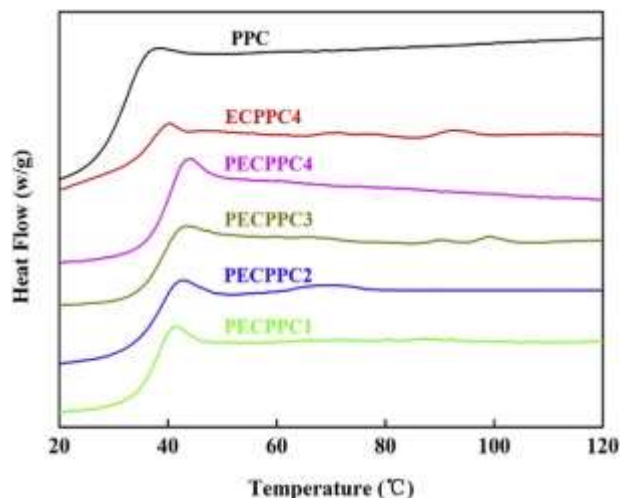


Fig. 5. TGA curves of PPC, ECPPC4 and PECPPCs.

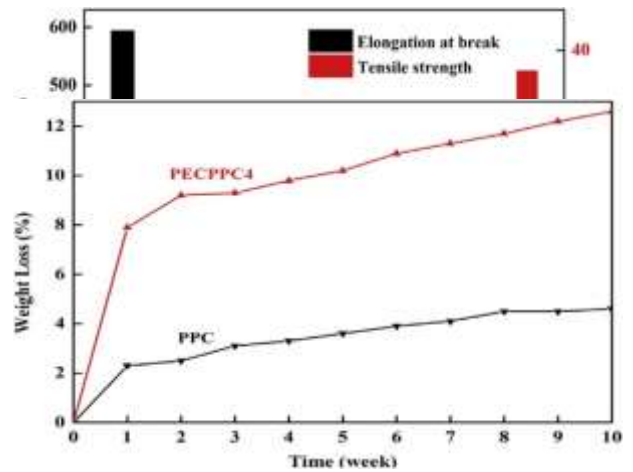


capping. It is clear that the thermal stability of ECPPCs is higher than that of PPC. The thermal decomposition temperature of ECPPCs increased with increasing IAn content. ECPPC4 exhibits the highest thermal decomposition temperature (5% weight loss temperature, $T_{d-5\%}$; and maximum weight loss temperature, T_{d-max}) of $T_{d-5\%}$ of 261 °C and T_{d-max} of 271 °C, respectively. The end-capping restrains the backbiting process and depresses the unzipping reaction of aliphatic polycarbonate, leading to a highly thermal stable PPC. Meanwhile, The glass transition temperature (T_g) of ECPPCs and PPC were measured by differential scanning calorimetry (DSC). Table 1 showed that T_g of ECPPCs increase with increasing amount of IAn content is higher than that of PPC.

In contrast, the post-modification by cross-linking can further enhance the thermal performance of PPC. As shown in Fig. 5, PECPPCs exhibit superior thermal stability. Especially, PECPPC4 with the highest thermal decomposition temperature of $T_{d-5\%}$ of 274 °C and T_{d-max} of 317 °C is much higher than that of ECPPC4, indicating the positive effect for the modification of PPC with IAn by end-capping and cross-linking. Correspondingly, the highest T_g of PECPPC4 is 44 °C (Fig. 6), owing to the cross-linking effect can

Fig. 7. Mechanical properties of PPC, ECPPC4 and PECPPCs.

Fig. 8. Weight loss versus time for ECPPC4 and PPC in buffer solution.



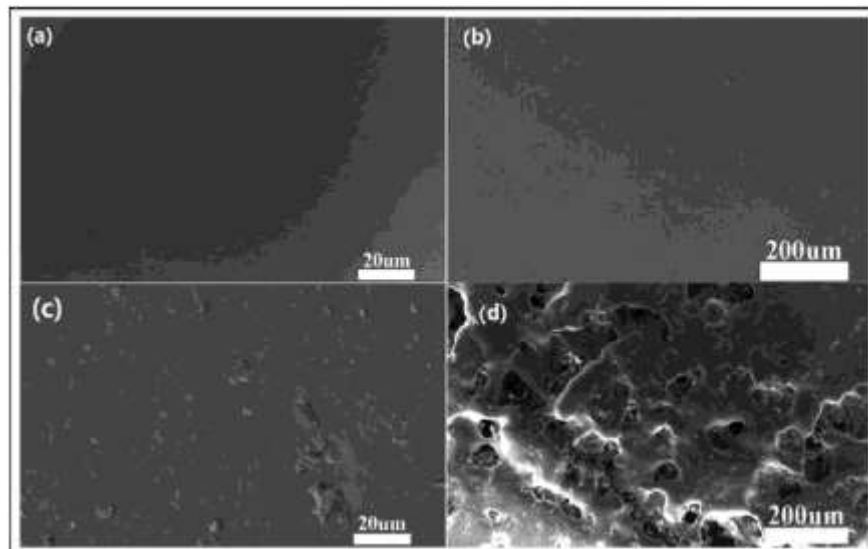


Fig. 9. SEM images of PPC and PECPPC4 films after degradation: (a) PPC 0 weeks; (b) PECPPC4 0 weeks; (c) PPC 10 weeks; (d) PECPPC4 10 weeks.

prevent the flexible carbonate linkage of PPC backbone from rotating. It is demonstrating that the post-modification with cross-linking is very efficient to improve the thermal performance of PPC.

Mechanical performance

To further confirm the end-capping and cross-linking effect for the modification of PPC with IAn, the mechanical performance of PECPPCs, ECPPCs and PPC was also studied. As shown in Fig. 7 and Table 1, the static mechanical properties of the resulted PPC and modified PPC were measured in terms of tensile strength and elongation at break. The end-capping following with cross-linking technique for the modification of PPC with IAn made huge enhancement on the mechanical performance of PPC, leading to the high strength PPC. The highest tensile strength of PECPPC4 reached 37.5 MPa together with an elongation at break of 290%, indicating the reinforcement of PPC with IAn by end-capping and cross-linking.

Degradation behavior

Generally, we consider that cross-linking is available to enhance thermal and mechanical performance of polymer materials but decrease the degradability. Encouraged by our recent reports [28], the degradability of ECPPC4 was determined in the phosphate buffer solution (PBS) of pH 7.4 at 37 °C for 10 weeks. As shown in

Fig. 10. Water sorption versus time for PECPPC4 and PPC in buffer solution.

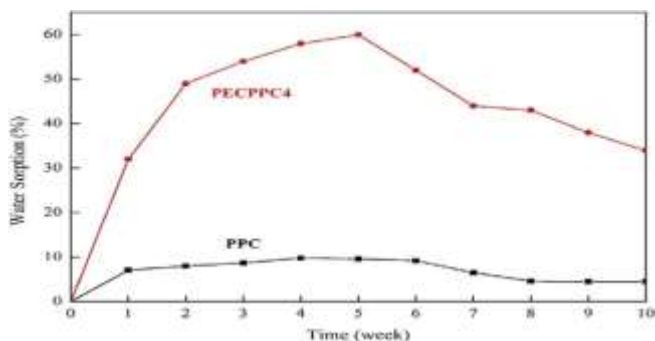


Fig. 8, PECPPC4 exhibit the high hydrolytic degradability compared with PPC. After 10 weeks, the weight loss increased up to 12.68%, which was significantly higher than that of PPC of 4.62%. Fig. 9 shows SEM images of PPC and PECPPC4 before and after into PBS for 10 weeks. The SEM images in good accordance with the results of weight loss of PPC and PECPPC4 taken into PBS. It is obviously that numerous large cavities can be observed in the surface of PPCPEC4 taken into PBS after 10 weeks, showed the higher hydrolysis rate of PPCPEC4 than that of PPC in PBS. It is considered that the high hydrolytic degradability of PECPPC4 presumably arises from the introduction of IAn into the end of PPC. Moreover, the water sorption of polymer materials plays a key role to enhance the degradation rate in burial or immersion, generally used to evaluate the hydrophilicity of examined samples. As shown in Fig. 10, the water sorption of PECPPC4 is far superior to that of PPC, which also indicates that the decrease in water sorption of PECPPC4 at 5 weeks due to the degradation in PBS.

4. Conclusion

In this work, itaconic anhydride (IAn) was firstly used for the preparation of end-capped and cross-linkable PPC by the solution blending following with the direct heating treatment. Structure and properties of the modified PPC was extensively investigated. The results showed that the strategy with the combination of end-capping and cross-linking techniques is efficient to the perfect modification of PPC. TGA and DSC parameters showed the superior thermal performance of PECPPCs compared with PPC. PECPPC4 with T_g of 44 °C exhibits the highest thermal decomposition temperature of $T_{d-5\%}$ of 274 °C and T_{d-max} of 317 °C, respectively. Meanwhile, the end-capped and cross-linkable PPC exhibits excellent mechanical properties, and the highest tensile strength of PECPPC4 is 37.5 MPa. Furthermore, it is noted that PECPPC4 presents the higher hydrolysis rate in PBS than that of PPC. These findings provide an effective and facile strategy to improve the performance of PPC fitting for existing applications.

Conflict of interest

The authors declared that they have no conflicts of interest to this work.

References

- [1] Y.H. Xu, L.M. Lin, M. Xiao, S.J. Wang, A.T. Smith, L.Y. Sun, Y.Z. Meng, Synthesis and properties of CO₂-based plastics: environmentally-friendly, energy-saving and biomedical polymeric materials, *Prog. Polym. Sci.* 80 (2018) 163e182.
- [2] C.M. Kozak, K. Ambrose, T.S. Anderson, Copolymerization of carbon dioxide and epoxides by metal coordination complexes, *Coord. Chem. Rev.* 376 (2018) 565e587.
- [3] Y. Li, Y.Y. Zhang, L.F. Hu, X.H. Zhang, B.Y. Du, J.T. Xu, Carbon dioxide-based copolymers with various architectures, *Prog. Polym. Sci.* 82 (2018) 120e157.
- [4] X.B. Lu, W.M. Ren, G.P. Wu, CO₂ Copolymers from epoxides: catalyst activity, product selectivity, and stereochemistry control, *Acc. Chem. Res.* 45 (2012) 1721e1735.
- [5] X.Y. Huang, J.Y. Huang, J.F. Wu, X.Y. Yu, Q.Z. Gao, Y. Luo, H. Hu, Fabrication and properties of polybutadiene rubber-interpenetrating cross-linking poly(propylene carbonate) network as gel polymer electrolytes for lithium-ion battery, *RSC Adv.* 5 (2015) 52978e52984.
- [6] K.R. Deng, S.J. Wang, S. Ren, D.M. Han, M. Xiao, Y.Z. Meng, A novel single-ion-conducting polymer electrolyte derived from CO₂-based multifunctional polycarbonate, *ACS Appl. Mater. Interfaces* 8 (2016) 33642e33648.
- [7] A.J. Kamphuis, F. Picchioni, P.P. Pescarmona, CO₂-fixation into cyclic and polymeric carbonates: principles and applications, *Green Chem.* 21 (2019) 406e448.
- [8] C. Jiang, Y.S. Zhang, X.F. Xiao, Z. Cai, P. Yu, High-performance hydroxypropyl black liquor lignin/poly (propylene carbonate) bio-composites with enhanced natural degradability, *Polym. Test.* 72 (2018) 348e356.
- [9] Y.L. Liu, M. Xiao, S.J. Wang, L. Xia, D.M. Hang, G.F. Cui, Y.Z. Meng, Mechanism studies of terpolymerization of phthalic anhydride, propylene epoxide, and carbon dioxide catalyzed by ZnGa, *RSC Adv.* 4 (2014) 9503e9508.
- [10] P.F. Song, H.D. Xu, X.D. Mao, X.J. Liu, L. Wang, A one-step strategy for aliphatic poly(carbonate-ester)s with high performance derived from CO₂, propylene oxide and L-lactide, *Polym. Adv. Technol.* 28 (2017) 736e741.
- [11] O. Phillips, J.M. Schwartz, P.A. Kohl, Thermal decomposition of poly(propylene carbonate): end-capping, additives, and solvent effects, *Polym. Degrad. Stab.* 125 (2016) 129e139.
- [12] P.F. Song, S.J. Wang, M. Xiao, F.G. Du, L.Q. Gan, G.Q. Liu, Y.Z. Meng, Cross-linkable and thermally stable aliphatic polycarbonates derived from CO₂, propylene oxide and maleic anhydride, *J. Polym. Res.* 16 (2009) 91e97.
- [13] P. Ohlendorf, A. Ruyack, A. Leonardi, C.J. Shi, C. Cuppoletti, I. Bruce, A. Lal, C.K. Ober, Transient fiber mats of electrospun poly(propylene carbonate) composites with remarkable mechanical strength, *ACS Appl. Mater. Interfaces* 9 (2017) 25495e25505.
- [14] M. Scharfenberg, J. Hilf, H. Frey, Functional polycarbonates from carbon dioxide and tailored epoxide monomers: degradable materials and their application potential, *Adv. Funct. Mater.* 28 (2018) 1704302.
- [15] R. Muthuraj, T. Mekonnen, Carbon dioxide-derived poly(propylene carbonate) as a matrix for composites and nanocomposites: performances and applications, *Macromol. Mater. Eng.* 303 (2018), 1800366.
- [16] W.H. Luo, M. Xiao, S.J. Wang, S. Ren, Y.Z. Meng, Thermal degradation behavior of Copoly(propylene carbonate-ε-caprolactone) investigated using TG/FTIR and Py-GC/MS methodologies, *Polym. Test.* 58 (2017) 13e20.
- [17] G.A. Luinstra, Poly(propylene carbonate), old copolymers of propylene oxide and carbon dioxide with new interests: catalysis and material properties, *Polym. Rev.* 48 (2008) 192e219.
- [18] X.L. Lu, Q. Zhu, Y.Z. Meng, Kinetic analysis of thermal decomposition of poly(propylene carbonate), *Polym. Degrad. Stab.* 89 (2005) 282e288.
- [19] X.H. Li, Y.Z. Meng, Q. Zhu, S.C. Tjong, Thermal decomposition characteristics of poly(propylene carbonate) using TG/IR and Py-GC/MS techniques, *Polym. Degrad. Stab.* 81 (2003) 157e165.
- [20] M.J. Yao, F. Mai, H. Deng, N.Y. Ning, K. Wang, Q. Fu, Improved thermal stability and mechanical properties of poly(propylene carbonate) by reactive blending with maleic anhydride, *J. Appl. Polym. Sci.* 120 (2011) 3565e3573.
- [21] G. Jiang, J. Feng, M.D. Zhang, S.D. Zhang, H.X. Huang, Structure, and thermal and mechanical properties of poly(propylene carbonate) capped with different types of acid anhydride via reactive extrusion, *RSC Adv.* 6 (2016) 107547e107555.
- [22] Y.P. Hao, H.H. Ge, L.J. Han, H.Y. Liang, H.L. Zhang, L.S. Dong, Thermal, mechanical, and rheological properties of poly(propylene carbonate) cross-linked with polyaryl polymethylene isocyanate, *Polym. Bull.* 70 (2013) 1991e2003.
- [23] H.B. Chang, Q.S. Li, C.J. Xu, R.M. Li, H.X. Wang, Z.W. Bu, T. Lin, Wool powder: an efficient additive to improve mechanical and thermal properties of poly(propylene carbonate), *Compos. Sci. Technol.* 153 (2017) 119e127.
- [24] S. Kumar, S. Krishnan, S.K. Samal, S. Mohanty, S.K. Nayak, Itaconic acid used as a versatile building block for the synthesis of renewable resource-based resins and polyesters for future prospective: a review, *Polym. Int.* 66 (2017) 1349e1363.
- [25] S. Kumar, S.K. Samal, S. Mohanty, S.K. Nayak, Synthesis and characterization of itaconic-based epoxy resins, *Polym. Adv. Technol.* 29 (2018) 160e170.
- [26] A.M. Voutchkova, T.G. Osimitz, P.T. Anastas, Toward a comprehensive molecular design framework for reduced hazard, *Chem. Rev.* 110 (2010) 5845e5882.
- [27] F. Kucera, J. Petrus, J. Matlakova, J. Jancar, Itaconic anhydride homopolymerization during radical grafting of poly(lactic acid) in melt, *React. Funct. Polym.* 116 (2017) 49e56.
- [28] P.F. Song, X.D. Mao, X.F. Zhang, X.G. Zhu, R.M. Wang, A one-step strategy for cross-linkable aliphatic polycarbonates with high degradability derived from CO₂, propylene oxide and itaconic anhydride, *RSC Adv.* 4 (2014) 15602e15605.