



Study on Copolymer from Cyclic Butylene Terephthalate and Polycaprolactone by In-situ Polymerization

Haijun Zhou,* Jinling Wang, Yujie Liu, Zhengyang Chen and Jiaoxia Zhang*

Abstract

In this experiment, polycaprolactone (PCL) toughened poly (cyclic butylene terephthalate) (pCBT) composites were prepared by in-situ polymerization through vacuum molding process. The effect of the catalyst content, polymerization temperature and the content of PCL on the performance of PCL/pCBT composites was discussed. The results show that the crystallinity of composites with 7.5 wt % polycaprolactone is lower, the elongation at break is higher and the toughness has been improved compared with pure pCBT. The mechanical properties obtain the evident improvement at 210 °C. When the catalyst amount is 0.5 wt %, the copolymers have the high molecular weight and their toughness is the best.

Keywords: Polycaprolactone, Cyclic butylene terephthalate, Copolymer, In-situ polymerization

Received: 19 August 2021; 27 September 2021; Accepted: 05 October 2021.

Article type: Research article.

1. Introduction

In the recent years, thermoplastic composites get more attention for their advantages such as shock resistance, toughness, secondary processing, and added recycling options through reprocessing and so on. However, the high viscosity of thermoplastic resin hinders fiber impregnation and their molding process.^[1-4] It is necessary to decrease viscosity during impregnation.^[5] The cyclic butylene terephthalate (CBT) is a low viscosity cyclic oligomer, which can obtain thermoplastic poly (butylene terephthalate) (PBT) quickly after adding a catalyst by in-situ polymerization, so the low viscosity and its thermoplastic properties makes the CBT resin a very promising material to prepare thermoplastic composites.^[6,7] The low viscosity of the CBT in its oligomeric state makes it can polymerize to obtain polymerized CBT (pCBT) by resin transfer molding (RTM) process which are normally suitable for thermosetting resins.^[8]

The isothermal processing below the melting point of pCBT is feasible because the melting temperatures of the CBT oligomer is lower than that of pCBT and the conversion from oligomers to pCBT is adequately fast at relatively low temperatures. Polymerization and crystallization of pCBT simultaneously may occur according to the degree of supercooling and the reaction speed,^[9,10] which ultimately

result in the lower toughness of pCBT than commercial PBT.^[11] The toughened polymers is already obtained by blending toughened resin,^[12,13] rubber,^[14] inorganic filler^[15-17] and copolymerization with other polymer.^[18,19]

Polycaprolactone (PCL) begins to get attention due to its excellent biodegradable property and processability since 1960s. PCL is a hydrophobic, semi-crystalline polymer, whose crystallinity tends to decrease with increasing molecular weight.^[20] The comprehensive advantages of good solubility, low melting point (59–64 °C) and exceptional blend-compatibility has stimulated PCL extensive research in the material and biology field.^[21,22] Wu *et al.*^[21] reported that the nonisothermal crystallization kinetics, crystallization morphology, and melting behavior of pCBT copolymerized with PCL. The PCL is a strong hindrance on the crystallization of pCBT. The vacuum assisted resin transfer molding (VARTM) technique was used by Beast^[23] to prepare pCBT/PCL composites based on CBT and PCL. The result shows that the pCBT/PCL exhibit obvious toughening effect when the content of PCL is 7 wt% to obtain a much tougher material. In our experiment, the novel pCBT/PCL copolymers were prepared based on in-situ polymerization to by vacuum molding process. The effect of PCL content, catalyst content and polymerization temperature on the properties of materials is discussed. At last, we explore the relationship between the molecular weight and crystallinity and the mechanical properties of the copolymer.

2. Experimental

School of Materials Science and Engineering, Jiangsu University of Science and Technology, Zhenjiang 212003, China.

*E-mail: zhjx@163.com (H. Zhou);

myzjx0359@163.com (J. Zhang)

2.1 Materials

The CBT oligomer (CBT100) in this study was supplied by Star-Better (Beijing) Chemical Materials Co. Ltd. The number of repeating units varies from two to seven, resulting in its melting range from 135 °C to 190 °C. Polycaprolactone (Esun220L) was purchased from Guanghua Weiye Industrial Co. Ltd in Shenzhen, having an average molecular weight $M_w = 2000$ g/mol and melting range from 45 °C to 55 °C, and was kept in a desiccator. A butyl tin chloride dihydroxide (XB3) used as catalyst was obtained from ChangZhou Chemistar Chemistry Technology Co. Ltd. All materials were used as received without purification.

2.2 Preparation of PCL/PCBT copolymers

The process used in this experiment was the vacuum molding process. CBT oligomers were put in to a flask and melted at 190 °C, then PCL was added and the mixture rapidly stirred for a few minutes until well mixed. The catalyst was then added and continues to stir for 30s. The mixture was then removed from the flask and filled into the mold of vacuum molding machine which preheated to specified reaction temperature (190-220 °C). The mold was vacuumized and kept the vacuum to start polymerization. The pressure cannot be kept constant during the continuously increasing viscosity, so we should pay attention to adjusting to keep the pressure constant. The temperature and pressure were kept for 30 min, in order to complete the polymerization reaction and to allow for cold crystallization. At last, the mold was allowed to cool to 80 °C by cooling water and obtained the plates. The list of experimental samples with preparation conditions is shown in Table 1.

Table 1. The list of experimental samples.

sample	amount of PCL (wt%)	amount of catalyst (wt%)	Temperature (°C)
1	4.5	0.5	210
2	6	0.5	210
3	7.5	0.5	210
4	9	0.5	210
5	7.5	0.3	210
6	7.5	0.4	210
7	7.5	0.5	210
8	7.5	0.6	210
9	7.5	0.5	190
10	7.5	0.5	200
11	7.5	0.5	210
12	7.5	0.5	220

2.3 Characterization

The samples were investigated by Fourier transform-infrared (FTIR) spectrometer on a FT-5200 provided by DIGILAB Company (America) using KBr tablet method. The scan range was from 500 cm^{-1} to 4000 cm^{-1} .

The intrinsic viscosity of pCBT was measured by JC522-1835 Ubbelohde viscometer. The solvent was mixture of

1,1,2,2-tetrachloroethane and phenol (mass ratio was 2:3). The solvent concentration was 0.1 g/dL. The experiment was under the temperature of 30 ± 0.1 °C. The molecular weight was calculated as following Mark-Houwink empirical formula^[24]:

$$[\eta] = KM^\alpha$$

M — Viscosity-average molecular weight, $[\eta]$ — Intrinsic viscosity, $K = 21.5 \times 10^{-3}$ mL/g, $\alpha = 0.89$.

X-ray diffraction analysis were obtained with a XRD-6000 diffractometer (SHIMADZU, Japan) with $\text{Cu K}\alpha$ radiation at a scanning rate of $5^\circ/\text{min}$, $\lambda = 0.154056$ nm. The X-ray tube voltage was 40 kV, the tube flow was 30 mA, and the scan range was from 5° to 50° with a scanning speed of $2^\circ/\text{min}$. The degree of crystallinity of pCBT/PCL copolymers were calculated by MDI Jade 5.0 software (Material Data, USA).

Tensile tests and flexural tests were performed severally according to GB/T1040.4-2006 and GB/T9341-2008, on a universal electromechanical testing machine with a 30kN load range (CMT 4304, Mets industrial systems (China) Co., Ltd). The tensile sample size was 100 mm \times 25 mm \times 2 mm, and the bracing sheet size was 100 mm \times 25 mm, the test speed was 2 mm/min. The flexural sample size was 100 mm \times 15 mm \times 2 mm, the ratio of span and thickness was 16:1, the loading rate was 2 mm/min.

3. Results and Discussion

In order to investigate the reaction mechanism, the raw materials and products were characterized by FTIR. The Fig. 1 shows FTIR spectra of CBT, CBT/PCL blends and pCBT/PCL copolymer. It can be found that CBT, CBT/PCL blends and pCBT/PCL copolymer all have ester absorption band at 1772 cm^{-1} , but the ester absorption peak of pCBT/PCL copolymer is stronger and sharper than the other two. In addition, in the pCBT/PCL copolymer spectra, the out-plane flexural vibration absorption peak of O-H in carboxylic acid at 918 cm^{-1} and the out-plane flexural vibration absorption peak of O-H in dissociative-hydroxyl at 770 cm^{-1} indicates that the CBT and PCL generate linear polymer and form free end group through the esterification reaction.

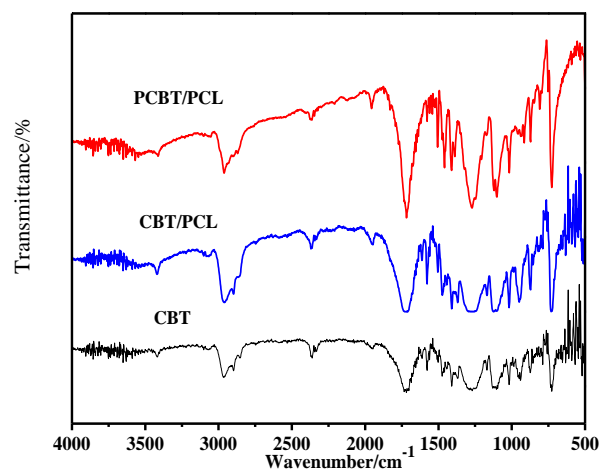


Fig. 1 FTIR spectra of raw material and copolymer of CBT and PCL.

The intrinsic viscosity of pCBT/PCL copolymer was detected with 1,1,2,2-tetrachloroethane and phenol as solvent (Fig. 2). For general polymers, the viscosity and the average molecular weight are positively proportional. We calculated the average molecular weight of the polymer based on Mark-Houwink empirical formula, and the results are shown in Fig. 3. It can be found that, with the increase of PCL content, the intrinsic viscosity and average molecular weight of copolymers decreases gradually. When the content of PCL is more than 7.5%, the intrinsic viscosity almost no longer decreases (Figs. 2a and 3a). This is mainly because the esterification rate of CBT and PCL is far less than CBT ring-opening polymerization rate. PCL impede the ring-opening polymerization rate that lead to reduce the growth of molecular chains. For a further increase of the amount of PCL, ring-opening polymerization esterification rate of CBT and PCL trends to stabilization, so intrinsic viscosity exhibit a substantially unchanged trend. Figs. 2b and 3b shows the effects of the catalyst with different content on the intrinsic viscosity and average molecular weight. It is evident that with the catalyst content increase up to 0.5%, the intrinsic viscosity and average molecular weight of the copolymer increases gradually from 4.43×10^4 to 5.42×10^4 . When further increasing catalyst content, the intrinsic viscosity and average molecular weight hardly change. With the amount of catalyst increase, esterification reaction rate of CBT and PCL increases due to the more active center which accelerate molecular chain growth leading to the increases of the copolymer molecular weight. When the catalyst is 0.5 wt%, active center in the

reaction system is sufficient to enable the polymers to achieve higher molecular weight. So further increase catalytic amount, the intrinsic viscosity of the product remains almost unchanged. Figs. 2c and 3c show the influence of different polymerization temperature on the intrinsic viscosity and average molecular weight of pCBT/PCL copolymer. It can be found that the intrinsic viscosity and average molecular weight of pCBT/PCL copolymer increases gradually with the increasing of reaction temperature. But they keep stable when the temperature higher than 210 °C. Because when the temperature reaches 210 °C, the activity of active centers reaches saturation and there will be no effect on intrinsic viscosity by further raising the temperature.

XRD was utilized to clarify the crystallinity of the pCBT/PCL copolymer. The XRD diffraction patterns of pCBT/PCL are shown in Fig. 4. There are no obvious new diffraction peaks of PCL. The diffraction patterns of pCBT/PCL copolymers strongly exhibit the same tendency that of the pure pCBT (Figs. 4a and 4d), only the intensity of diffraction peaks are different. The results indicate that the good compatibility between pCBT and PCL make the copolymer reveal the lattice of pure pCBT. PCL only increase the amorphous region and reduce the crystal area of pCBT/PCL copolymer. The temperature and catalyst content also had no significant effect on the crystallization peak of the pCBT (Figs. 4b, 4c and 4d). Those results mean that these resins all have the same crystal configuration, varying only in the degree of crystallization.

XRD was utilized to clarify the crystallinity of the

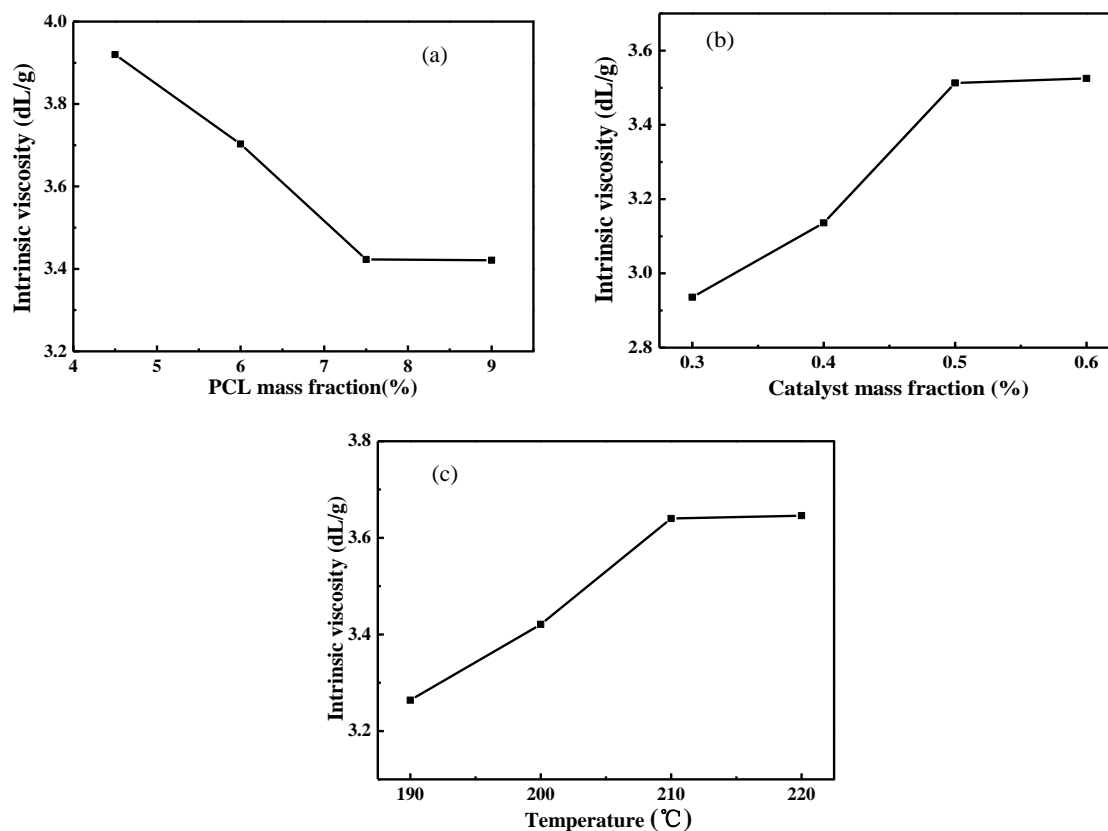


Fig. 2 Intrinsic viscosity-PCL mass fraction, catalyst mass fraction and Temperature of pCBT/PCL copolymer.

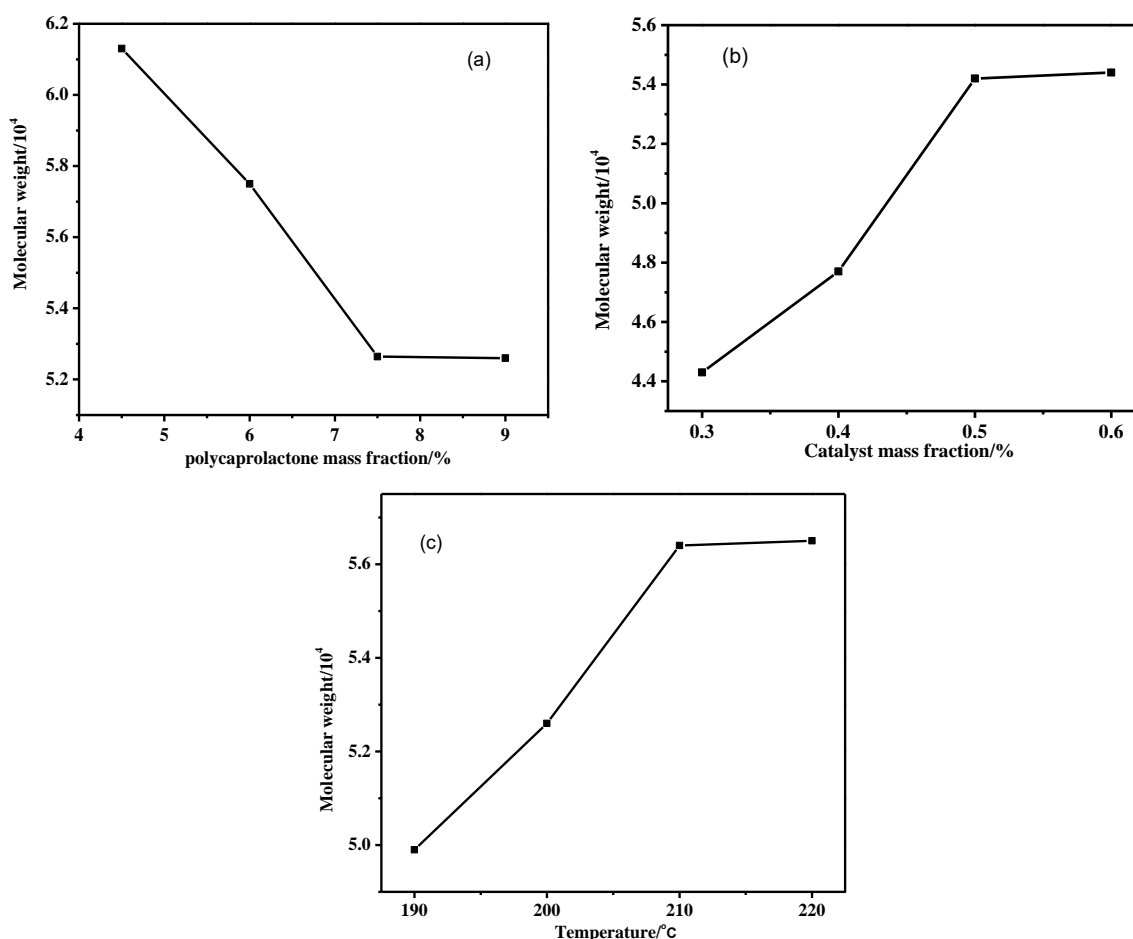


Fig. 3 Average molecular weight of pCBT/PCL copolymer with different experimental condition.

pCBT/PCL copolymer. The XRD diffraction patterns of pCBT/PCL are shown in Fig. 4. There are no obvious new diffraction peaks of PCL. The diffraction patterns of pCBT/PCL copolymers strongly exhibit the same tendency that of the pure pCBT (Figs. 4a and 4d), only the intensity of diffraction peaks are different. The results indicate that the good compatibility between pCBT and PCL make the copolymer reveal the lattice of pure pCBT. PCL only increase the amorphous region and reduce the crystal area of pCBT/PCL copolymer. The temperature and catalyst content also had no significant effect on the crystallization peak of the pCBT (Figs. 4b, 4c and 4d). Those results mean that these resins all have the same crystal configuration, varying only in the degree of crystallization.

Figure 5 describes the crystallinity of pCBT/PCL copolymer calculated from the area of the crystal diffractive peak and the full peak using the XRD diffraction peak. It can be found that the degree of crystallinity consistently decrease whether increasing the PCL content or enhancing catalyst or rising reaction temperature. The polymer molecular weight increase and the branched crosslinking structure of segment increase when increasing the PCL content, enhancing catalyst and rising reaction temperature which leads to the increase of melting point. So it is difficult to crystallization at ungenerous supercooling, which result in the decrease of crystallinity.

Especially when the reaction temperature is increased up to 210°C, the crystallinity decreases significantly.

At last, the mechanical properties of pCBT/PCL copolymer were discussed. The Fig. 6a displays that tensile strength decrease and tensile modulus increase in breaking elongation ratio with the content increase of PCL. Because the adding of PCL reduces the molecular chain growth, and results in the decrease of molecular weight, the amount of molecular chain entanglement point is also reduced. So a lower energy also causes tensile failure. In addition, the decreased crystallinity of copolymer (can be seen from Fig. 4a) with the increasing amount of PCL increase their toughness, so the elongation at break is improved. When the content of PCL is 7.5 wt%, comprehensive mechanical properties are up to the best which corresponded closely to that reported by Baets *et al.*^[23]

As can be seen from Figs. 6b and 6c, the tensile strength and tensile modulus of materials continuously decrease with the increase of the amount of catalyst and rising the temperature. But the elongation at break continuously improves. With the increase of catalyst content, the active center increase of pCBT molecular chains result in the long linear flexible polymer. So the tensile fracture energy correspondingly reduces the tensile strength and tensile modulus become decrease. In addition, the decreased

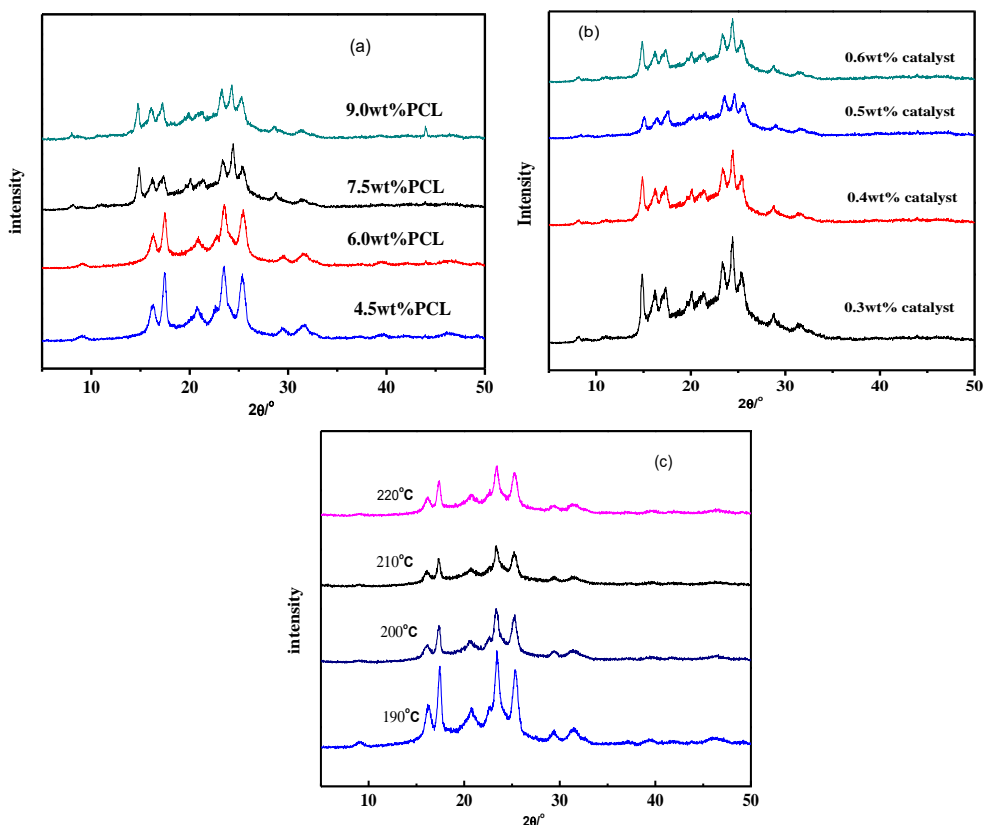


Fig. 4 X ray diffractogram of copolymer prepared by different PCL mass fraction, catalyst and polymerization temperature.

crystallinity of copolymer with the addition of catalyst (can be seen from Figs. 4a and 4c) increase their toughness, so the elongation at break is improved. When the content of catalyst is 0.5 wt%, comprehensive mechanical properties are up to the best. Further increasing the content of catalyst up to 0.6 wt%,

the rate of polymerization rate is to achieve balance, crystallinity tends to be stable, so compared to the 0.5 wt%, the elongation at break have a weak decrease. The copolymers display the highest elongation and best toughness when the reaction temperature is 210 °C.

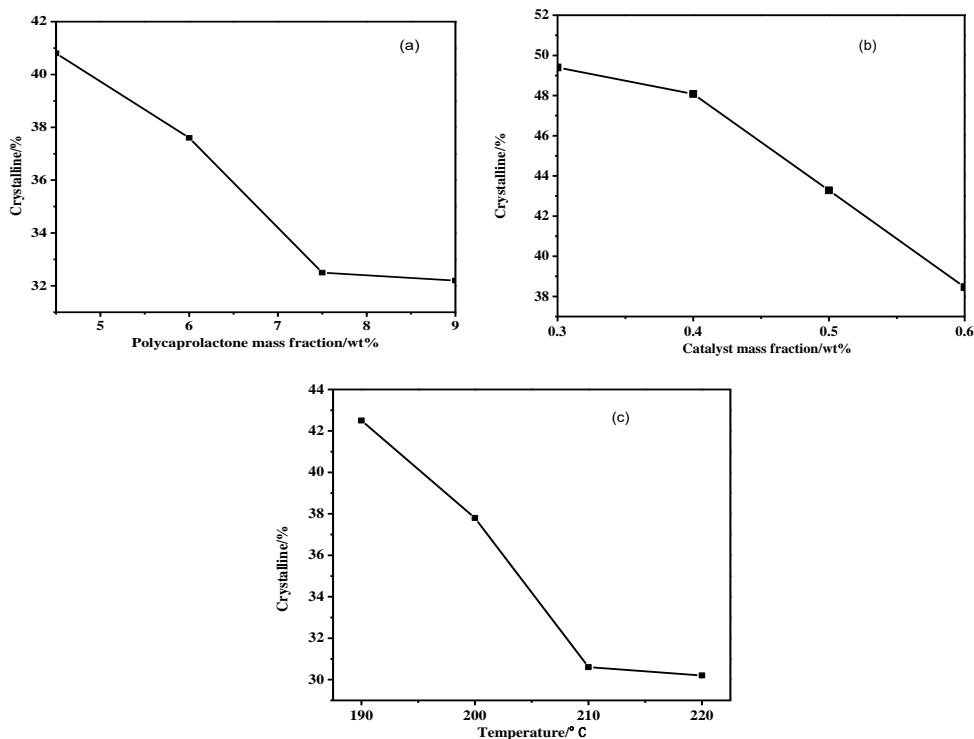


Fig. 5 The crystalline of copolymers prepared by different PCL mass fraction, catalyst and polymerization temperature.

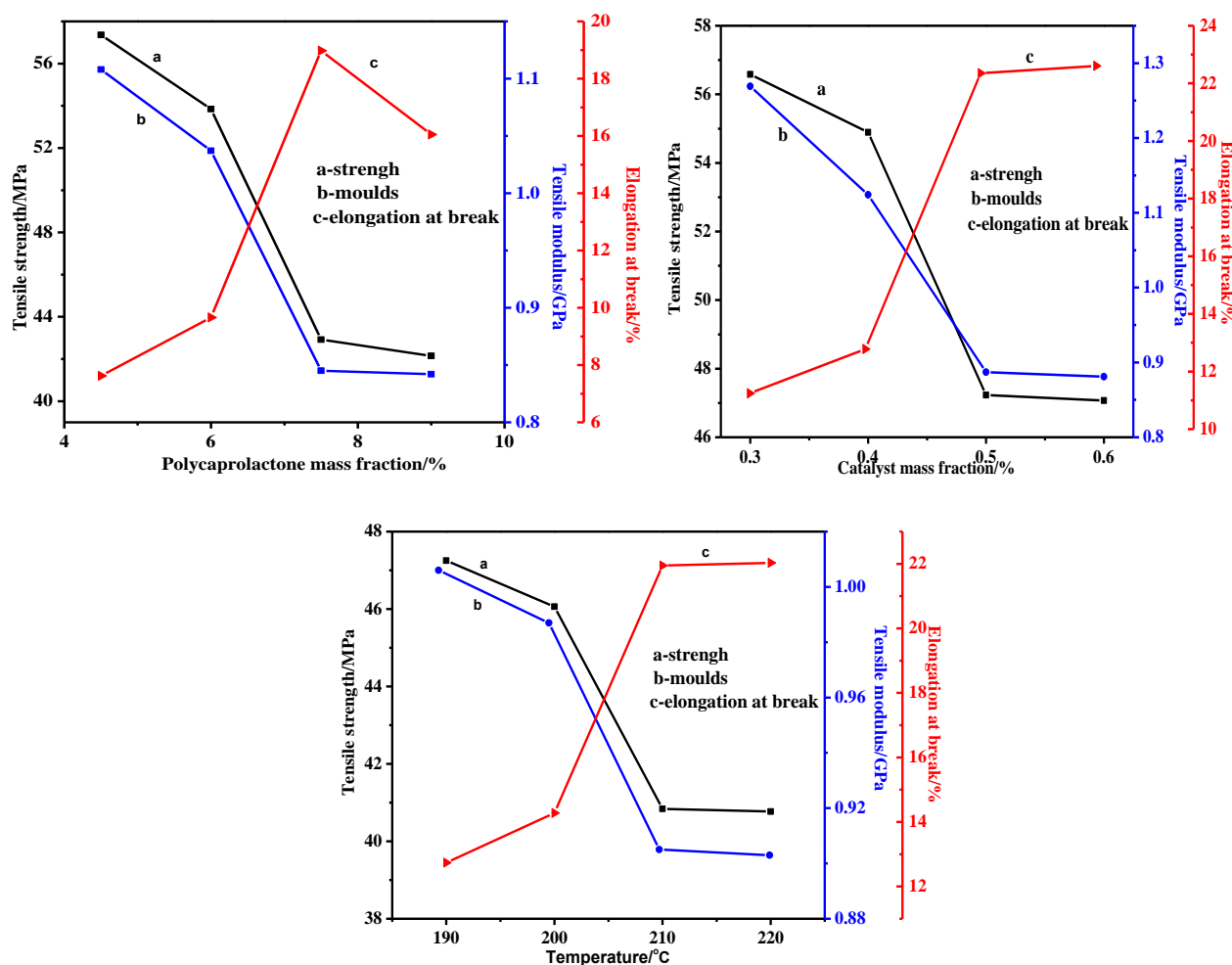


Fig. 6 The mechanical properties of copolymers prepared by different PCL mass fraction, catalyst and polymerization temperature.

The above discusses the effects of experimental conditions on the mechanical properties of copolymers. Below the relationship between structure and mechanical performance is discussed further. Fig. 7 shows the effect of molecular weight and crystallinity on the properties of the copolymers under different experimental conditions. The effect of the crystallinity on the mechanical properties of the pCBT/PCL copolymers is consistent (Figs. 7b, 7d and 7f). The mechanical strengths of all samples increase with the crystallinity. The crystallinity increases the order of copolymers reducing the toughness of the material, and therefore, the elongation at break is reduced. But the effect of molecular weight on the mechanical properties of copolymers shows different trends. When the other conditions remain unchanged and only the PCL content is increased, the tensile strength and modulus rise with increasing molecular weight. Instead, changing the catalyst content and the reaction temperature are reversed (Figs. 7a, 7c and 7e). For general polymers, the mechanical strength increases generally with the molecular weight.^[25,26] However, for copolymers, the proportion of different polymers affects more on the mechanical strength than the molecular weight. Therefore, when the content of PCL is different, the mechanical strength does not rise as the molecular weight increases. For the change of catalyst and reaction temperature,

due to the consistent content of PCL, the chain segment movement is difficult and the mechanical strength increases with the increasing molecular weight. Finally, we plotted the relationship between molecular weight-crystallinity and mechanical properties of pCBT/PCL copolymers without considering the experimental conditions (Fig. 8). As the molecular weight increases, the overall tensile strength and modulus volume exhibit a trend of decreasing first and then increasing (Fig. 8a). The elongation at break shows the opposite trend. When the molecular weight reaches about 50,000, the elongation at break is at a maximum. The pCBT/PCL copolymers show optimal toughness, but have the lowest intensity at this time. The relationship between crystallinity and mechanical properties is not very obvious, and the mechanical performance will also be affected by the PCL content. However, pCBT/PCL copolymers still show the optimal tensile strength and modulus at 40.8% of crystallinity (Fig. 8b). The pCBT/PCL copolymers show a high mechanical strength at the 7.5 wt% of PCL, 0.3 wt % of catalyst and 190 °C of reaction temperature. That means that mild reaction conditions contribute to the polymer crystallize to obtain the appropriate molecular weight, thus exhibit excellent mechanical properties.

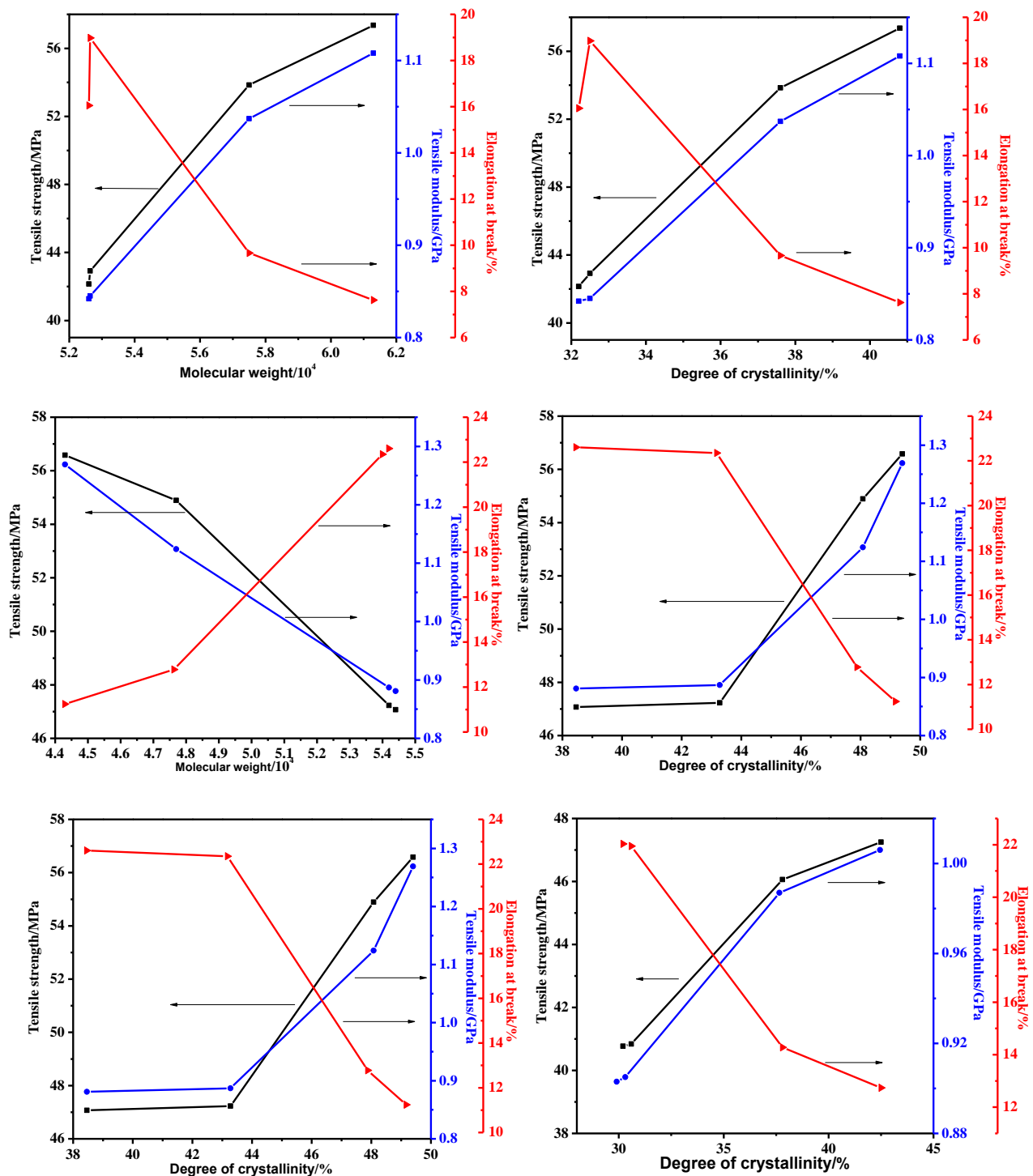


Fig.7 The mechanical properties of copolymers- molecular weight and degree of crystallinity based on different PCL mass fraction (a and b), catalyst mass fraction (c and d) and polymerization temperature (e and f).

4. Conclusions

The pCBT/PCL copolymers were prepared by in-situ polymerization. When the PCL mass fraction is 7.5 wt%, there are a low crystallinity of copolymer and a high breaking elongation, and there would be no effect on mechanical properties of pCBT/PCL copolymers by increasing the mass fraction of PCL. The molecular weight and the breaking elongation ratio constantly increase along with the copolymerization temperature rising, but the crystallinity and

the tensile strength and modulus strength shows a trend of gradually decrease. The copolymer had the highest elongation and best toughness when the reaction temperature reaches up to 210 °C. With enhancing the catalyst, the properties of pCBT/PCL exhibit the similar trend with rising the reaction temperature. When the molecular weight reaches about 50,000, the elongation at break is at a maximum. The pCBT/PCL copolymers still show the optimal tensile strength and modulus at 40.8% of crystallinity.

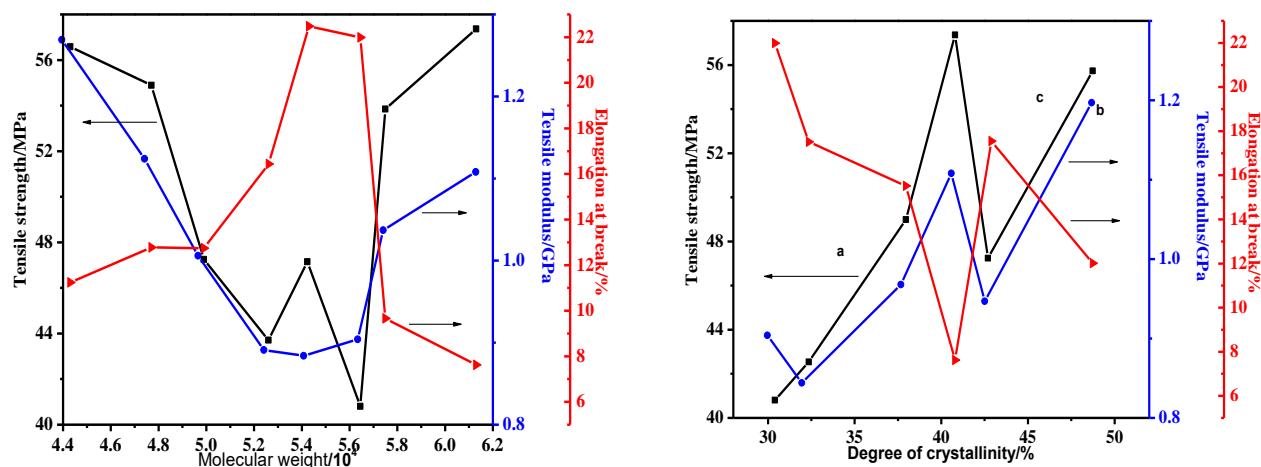


Fig. 8 The mechanical properties of copolymers vs the molecular weight (a) and degree of crystallinity (b).

Conflict of Interest

There is no conflict of interest.

Supporting Information

Not applicable.

References

- [1] A. Miller, G. A. Gibson, *Polymers & Polymer Composites*, 1996, **4**, 459-481.
- [2] A. Toda, *Polymers*, 2021, **13**, 152, doi: 10.3390/polym13010152.
- [3] H. Gu, X. Xu, H. Zhang, C. Liang, H. Lou, C. Ma, Y. Li, Z. Guo and J. Gu, *Engineered Science*, 2018, **1**, 46-54, doi: 10.30919/es.180308.
- [4] J. Zhang, W. Zhang, L. Wei, L. Pu, J. Liu, H. Liu, Y. Li, J. Fan, T. Ding and Z. Guo, *Macromolecular Materials and Engineering*, 2019, **304**, 1900374, doi: 10.1002/mame.201900374.
- [5] Z. Zhang, J. Zhang, S. Li, J. Liu, M. Dong, Y. Li, N. Lu, S. Lei, J. Tang, J. Fan and Z. Guo, *Composites Part B: Engineering*, 2019, **176**, 107338, doi: 10.1016/j.compositesb.2019.107338.
- [6] G. Lanciano, A. Greco, A. Maffezzoli and L. Mascia, *Thermochimica Acta*, 2009, **493**, 61-67, doi: 10.1016/j.tca.2009.04.004.
- [7] H. E. N. Bersee and K.V. Rijswijk, *Composites Part A: Applied Science and Manufacturing*, 2007, **38**, 666-681, doi: 10.1016/j.compositesa.2006.05.007.
- [8] C. Yan, L. Liu, Y. Zhu, H. Xu and D. Liu, *Journal of Thermoplastic Composite Materials*, 2018, **31**, 181-201, doi: 10.1177/0892705717697774.
- [9] J.H. Youk, R.P. Kambour and W.J. MacKnight, *Macromolecules*, 2000, **33**, 3594-3599, doi: 10.1021/ma991838d.
- [10] J. Baets, M. Dutoita, J. Devaux and I. Verpoest, *Composites Part A: Applied Science and Manufacturing*, 2008, **39**, 13-18, doi: 10.1016/j.compositesa.2007.09.013.
- [11] Z. Jiang, S. Siengchin, L.-M. Zhou, M. Steeg, J. Karger-Kocsis and H.C. Man, *Composites Part A: Applied Science and Manufacturing*, 2009, **40**, 273-278, doi: 10.1016/j.compositesa.2008.12.003.
- [12] S. A. Samsudin, S. N. Kukureka and M. J. Jenkins, *Journal of Thermal Analysis and Calorimetry*, 2013, **114**, 1307-1315, doi: 10.1007/s10973-013-3111-6.
- [13] S. Li, L. Zhang, S. Shang, H. Zhou, J. Zhang, P. Wei, H. Xue, X. Hu and J. Wang, *ES Materials & Manufacturing*, 2019, **4**, 20-24, doi: 10.30919/esmm5f218.
- [14] D. Xu and J. Karger-Kocsis, *Tribology International*, 2010, **43**, 289-298, doi: 10.1016/j.triboint.2009.06.008.
- [15] H. Fang and F. Wu, *Journal of Applied Polymer Science*, 2014, **131**, 2929-2938, doi: 10.1002/app.40849.
- [16] A. K. Kalkar, V. D. Deshpande and B. S. Vatsaraj, *Thermochimica Acta*, 2013, **568**, 74-94, doi: 10.1016/j.tca.2013.06.019.
- [17] J.-X. Zhang, Y.-X. Liang, X. Wang, H.-J. Zhou, S.-Y. Li, J. Zhang, Y. Feng, N. Lu, Q. Wang and Z. Guo, *Advanced Composites and Hybrid Materials*, 2018, **1**, 300-309, doi: 10.1007/s42114-017-0007-0.
- [18] W. Huang, Y. Wan, J. Chen, Q. Xu, X. Li, X. Yang, Y. Li and Y. Tu, *Polymer Chemistry*, 2014, **5**, 945-954, doi: 10.1039/c3py00932g.
- [19] T. Abt, M. Sanchez-Soto and A. Martínez de Ilarduya, *European Polymer Journal*, 2012, **48**, 163-171, doi: 10.1016/j.eurpolymj.2011.10.017.
- [20] E. Piskin, *Journal of Biomaterials Science, Polymer Edition*, 1995, **6**, 775-795, doi: 10.1163/156856295X00175.
- [21] C.-M. Wu and C.-W. Huang, *Polymer Engineering & Science*, 2011, **51**, 1004-1013, doi: 10.1002/pen.21910.
- [22] A. Toda, K. Taguchi, K. Nozaki, X. Guan, W. Hu, Y. Furushima and C. Schick, *Polymer*, 2020, **192**, 122303, doi: 10.1016/j.polymer.2020.122303.
- [23] J. Baets, A. Godara, J. Devaux and I. Verpoest, *Polymer Degradation and Stability*, 2010, **95**, 346-352, doi: 10.1016/j.polymdegradstab.2009.11.005.
- [24] F. Samperi, C. Puglisi, R. Alicata and G. Montaudo, *Polymer Degradation and Stability*, 2004, **83**, 11-17, doi: 10.1016/s0141-3910(03)00167-8.
- [25] J. Liu, J. Zhang, J. Tang, L. Pu, M. Lu, L. Xu and Z. Guo, *ES Materials & Manufacturing*, 2020, **10**, 29-38, doi: 10.30919/esmm5f912.

[26] M. Ashizawa, Y. Zheng, H. Tran and Z. Bao, *Progress in Polymer Science*, 2020, **100**, 101181, doi: 10.1016/j.progpolymsci.2019.101181.

Author information



Haijun Zhou received his BS (1998) from North University of China (NUC), he got his MS (2001) in chemical engineering and technology from North University of China (NUC), and then he got his Ph.D. (2005) in Material Science from Tongji University in China. In 2010, he worked as a visiting scholar at the Admiral Makarov

National University of Shipbuilding. Dr. Zhou is an associate professor at the School of Materials Science and Engineering, Jiangsu University of Science and Technology. His research interests focus on the synthesis of resin matrix composites, polymer microsphere, etc.



Jiaoxia Zhang received her B.S. (2003) from North University of China (NUC), he got her M.S. (2008) and Ph.D. (2011) in Materials Science from Northwestern Polytechnical University of (NPU) IN China. In 2017-2018, he worked as a visiting scholar at the University of Tennessee Knoxville. Dr. Zhang is an

associate professor at the School of Materials Science and Engineering, Jiangsu University of Science and Technology. Her research interests focus on the polymers and their composites; Energy storage materials, photocatalytic technology, etc.

Publisher's Note: Engineered Science Publisher remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.