

Comparison of the properties of bioderived polycarbonate and traditional bisphenol-A polycarbonate

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Abstract

The bioderived polycarbonate (ISB-PC) was synthesized via transesterification and polycondensation of isosorbide (ISB) and diphenyl carbonate (DPC), using lithium acetoacetone as catalyst. The resulting ISB-PC exhibited high glass transition temperatures similar to bisphenol A polycarbonate (BPA-PC), and were thermally stable up to 350 °C. The incorporation of isosorbitol into the polymer chain imparted an improved mechanical property of ISB-PC, such as a higher bending and tensile modulus and higher elongation at break. The ISB-PC can be readily cast into transparent films with a tensile strength of 73.3 MPa and a tensile modulus of 534 MPa. The ISB-PC displayed a highly UV transmittance and possessed a blue fluorescence under the UV irradiation. At the same time, ISB-PC also has strong anti-yellowing ability.

1. Introduction

Polycarbonate (PC) is a kind of plastic with superior mechanical and thermal properties. It has been extensively employed in a variety of industries, including electronic and electrical appliances, machinery, aviation, transportation, optical machinery, construction, agriculture, textile, medical and other industries. Bisphenol A-type polycarbonate (BPA-PC), one of the most widely used commercial polycarbonate (PC) materials, can be added to improve the impact resistance, thermal stability, and other properties, which is due to its high performance and low price. It has a wide range of applications in various fields of life, especially food and beverage packaging, optical discs, medical equipment, and sports equipment [1-3].

However, bisphenol A is a derivative of petroleum, which is incompatible with green environmental protection and sustainable development. Moreover, the residual bisphenol A in the product cannot be completely removed because the production process of BPA-PC requires the use of bisphenol A, an environmental endocrine disruptor that is detrimental to organisms [4]. The application of BPA-PC in food packaging and medical treatment is currently banned in many countries [5-6], so the search for BPA-PC substitutes has become a research hotspot. Isosorbide (ISB) is a cyclic aliphatic diol derived from sorbitol through a dehydration reaction. Sorbitol is obtained by hydrogenation of glucose, therefore it can be found in a variety of sources, including starch and cellulose [7]. As a rigid molecule with a chiral structure and nontoxic properties, ISB has extremely stable chemical and thermal properties and excellent optical properties. A variety of polymers with high glass transition temperatures and special properties can be created with it. It is a renewable monomer, with a biological based, and its safety has been proven. It is the only commercially produced carbohydrate diol, which makes it promising as a biologically based monomer for the preparation of polycondensation reactions [8-11]. Ochoa-Gomez et al. for instance, studied the synthesis of isosorbide bis (methyl carbonate) by transesterification of isosorbide and dimethyl carbonate, proving the possibility of synthesizing polycarbonate by ISB [12]. ISB has been used to synthesize isosorbitol polycarbonate (ISB-PC), and the synthesis of polycarbonate isosorbide (ISB-PC) by replacing bisphenol A with isosorbide is expected to promote the application of polycarbonate in food packaging and medical equipment [13-15].

Some studies have been performed on isosorbide-type polycarbonate. For example, a series of ISB copolycarbonates were synthesized by adding flexible hydrogenated bisphenol A (HBPA) into the melting polycondensation of isosorbide and diphenyl carbonate (DPC) using sodium methanol (NaOMe) as a catalyst to reduce the brittleness of ISB-PC [16]. As a tillustration, a series of ISB copolycarbonates were synthesized by adding different catalys to evaluate the impact of various catalysts on the structure and optical properties of synthesized ISB-PC [17]. However, they did not systematically compare isosorbide-based polycarbonate with conventional BPA-based polycarbonate in all aspects. This paper introduces and investigates the melting polycondensation of diphenyl carbonate (DPC) and isosorbide (ISB) to create biobased polycarbonate (ISB-PC). The structure of the homemade ISB-PC was characterized systematically, and the differences in mechanics, thermal deformation, transmittance and yellowness between ISB-PC and BPA-PC were compared.

2. Experimental

2.1. Materials

Isosorbide (ISB, 98%, Shanghai Aladdin Company) and diphenyl carbonate (DPC, 99%, Shanghai Aladdin Company) were used for melting polycondensation with lithium acetyl acetone (LiAcac) as a catalyst and bisphenol A-type polycarbonate (BPA-PC, Jiangxi Jiachen Industry Co., Ltd.). All the above materials can be used directly without further purification except for isosorbitol.

2.2 Synthetic procedures

ISB was distilled and purified at 190°C. After purification, it was sealed to prevent oxidation and reserved in a drying oven. DPC (21.64 g, 0.1 mol), purified ISB (14.6 g, 0.1 mol) and LiAcac (0.0053 g, 5/10000 molar mass of isosorbide) were added to 100 mL three-way bottles with a pilot tube, mechanical stirring and condensing unit at 190 °C. In N₂ atmosphere the reaction was stabilized by rapid stirring at 190°C for 30 min to completely melt the material and cancel N₂, and then the reaction was continued by pumping negative pressure (0.05MPa~0.055MPa) for 30 min. Then, the negative pressure (0.05 MPa to 0.055 MPa) was continued to be pumped for 30 min to react, and the negative pressure was increased (to about 0.065 MPa to 0.07 MPa) and continued to react for 30 min, and then the negative pressure was continued to be increased twice, each time to about 0.015 MPa, for 1 h. Then, the temperature rose to 230 °C, the negative pressure was increased (to 0.085 MPa~0.09 MPa), and the reaction time was 1 h. Finally, the negative pressure of the oil changing pump was adjusted to be less than 300 Pa, and the temperature rose to 240 °C. According to the reaction viscosity, the reaction can be stopped after a certain time under stirring conditions with the following reaction equation:

The molten polycondensation of DPC and ISB will produce the byproduct phenol. In the experiment, the negative pressure pumped by the pump was used to remove the phenol produced in the reaction. The cleaner the phenol removed, the higher the molecular weight of the product obtained and the better the performance

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2.3. Preparation of ISB-PC and BPA-PC film

ISB-PC and BPA-PC resins were placed in an oven and dried at 120 °C for 24 h. The baked samples were covered with polyimide film and clamped on the upper and lower plates with molds. The samples were raised to 240 °C and melted for approximately one minute to allow the material to flow and form fully. Then, the pressure was gradually increased from 0 MPa to 10 MPa, and the gas was not stopped to prevent the generation of bubbles.

2.4. Preparation of ISB-PC and BPA-PC standard splines

First, the PC granules were dried in a vacuum drying oven at 120 °C for 24 h to ensure that the moisture content was lower than 0.02%. After crushing, the granules were granulated, and finally, injection molding was performed. During injection molding, the injection temperature of BPA-PC was set to 270~290 °C, the injection temperature of ISB-PC was set to 210~240 °C, and the injection pressure was set to 35~45 MPa. Finally, a 60 mm×10 mm×4 mm composite tensile spline was obtained.

2.5 Characterization

The microstructure of BPA-PC and ISB-PC films was observed by FT-IR (Nicolet iS10), and the test range was 4000 cm^{-1} ~ 400 cm^{-1} . Nuclear magnetic resonance spectroscopy ($^1\text{H-NMR}$) was conducted using a Bruker Avance 300 MHz spectrometer (USA). Gel permeation chromatography (GPC, PL-GPC220) was utilized to determine the molecular weight. The glass transition temperature of the two films was measured by scanning calorimetry (DSC, DSC 200 F3). In a N_2 atmosphere, the temperature ranges from 30 °C to 300 °C, and the temperature rate is 10 °C/min. Thermogravimetric analysis (TGA, STA 409PC) was used to further analyze the thermal stability of the two films. In a N_2 atmosphere, the temperature ranges from 30 °C to 600 °C, and the heating rate is 10 °C/min. The mechanical properties of the splines were obtained by a CMT4104 mechanical tester (CMT4104) at a speed of 100 mm/min. The measurement was repeated three times to obtain an average value. An XBJ-5.5 impact testing machine was used to test the impact strength of notched splines. A pencil hardness tester (phh -750) was used to measure the scratch resistance of pencils with different hardnesses. A microcomputer-controlled thermal deformation Vica softening point testing machine (HVT302) was used to test the thermal deformation temperature at 120 °C/h, with a temperature upper limit of 280 °C and a weight of 0.238 kg. The transmittance of the two kinds of PC was measured by an ultraviolet visible spectrophotometer (UV-

1800PC). A three-purpose ultraviolet analyzer (ZF-1S) was used to irradiate 254 nm ultraviolet light, and a colorimeter (ZB-A) was used to test the yellowness at different irradiation times. Each measurement was repeated three times to take the average value.

3 Results and discussion

3.1 Molecular weight and chemical structure

FT-IR spectra for ISB-PC and BPA-PC are depicted in Figure 2. The ether bond's C-O-C stretching is measured at 1250 cm^{-1} . The vibration absorption peaks of the benzene ring are 1510 cm^{-1} and 1600 cm^{-1} . All samples exhibited absorption bands at 1770 cm^{-1} corresponding to the C=O stretching of carbonyl bonds. The peaks for the asymmetric and symmetric stretching of aliphatic -CH₂ and -CH are two absorptions near 2980 cm^{-1} and 2870 cm^{-1} . The weight average molecular weight (M_w), number average molecular weight (M_n) and the polydispersity index (PDI) of ISB-PC measured from the GPC analysis were 49987 g/mol, 27095 g/mol and 1.84, respectively. This indicates that good mechanical properties plausible possessed by ISB-PC.

The structural properties of ISB-PC and BPA-PC were also studied by liquid phase ¹H NMR spectroscopy with CDCl₃ as the solvent. As examples, the typical ¹H NMR spectra of ISB-PC and BPA-PC are shown in Fig. 3, respectively. A characteristic peak at $\delta = 3.8\text{-}4.1$ ppm represented the protons attached to primary carbons in the furan ring of ISB-PC, (i.e., peak 1 and 6 in Fig. 3), and the proton attached to the secondary carbon in the furan ring of ISB-PC was identified at 4.55 ppm, (i.e., peak 4 in Fig. 3). The chemical shift at $\delta = 4.8$ ppm can also be assigned to the proton attached to the secondary carbon in the furan ring of ISB-PC (i.e., peak 3 in Fig. 3). An intense characteristic peak at $\delta = 5\text{-}5.1$ ppm resulted from the proton attached to two opposite secondary carbons in the furan ring of ISB-PC (i.e., peak 2 and 5 in Fig. 3). Furthermore, the intensity of the proton on the benzene ring in the terminal phenoxy structure in the ISB-PC is 7.2 and 7.42, (i.e., peak c and d in Fig. 3). Therefore, the results show that ISB and DPC were polymerized to generate the target polymer ISB-PC.

3.2 Thermal properties

The thermal properties of BPA-PC and ISB-PC polymers were tested by DSC and TG, and the results are shown in Figure 4 and Figure 5. As shown in Figure 4, the T_g value of the synthesized ISB-PC polymer measured by DSC is 145.8 °C and that of the BPA-PC polymer is 146.1 °C, which shows that the homemade ISB-PC has reached commercial demand and means that ISB-PC has more application scenarios, such as liquid crystal display fields. As shown in Figure 5, the synthesized ISB-PC sample was degraded in a N₂ atmosphere in the next step, and the weight loss rate reached 100%. Before 350 °C, there was no obvious thermal grain loss in ISB-PC samples, which was due to the presence of adjacent furan rings in ISB-PC molecules, which increased the rigidity of the chain structure in the macromolecular structure. BPA-PC began to lose weight at approximately 500 °C. This is because BPA-PC contains

benzene rings, which do not move easily and therefore have better thermal stability than ISB-PC. The temperature of the copolymer with 5% weight loss ($T_{d,5\%}$) was determined by thermogravimetric analysis. The bond energy of C=C is higher than that of the fat bond, so the $T_{d,5\%}$ of BPA is 496°C, higher than that of ISB-PC 350 °C.

3.3 Mechanical properties

The mechanical properties of BPA-PC and ISB-PC were compared by tensile, bending and impact tests. The tensile strength, tensile modulus and elongation at break of BPA-PC are clearly shown in Figure 6, and their values are repeated in the table. The tensile strengths of ISB-PC and BPA-PC were 73.3 MPa and 57.8 MPa, and the bending strength was 103.1 MPa and 86.9 MPa, respectively. In general, the elasticity of polymers is influenced by a combination of rigidity and molecular weight [18]. The ISB-PC has good stability and high tensile strength, which is the result of the high molecular weight, rigidity and low polarity of the homoperic polymer. Moreover, the stereochemically guided connection between the long chain molecules and the internal hydrogen bond network of the sugar group in ISB also makes ISB its own characteristic compound with high elasticity resilience.

Table 1 shows that the impact strength of ISB-PC is 7.4 kJ/m², which is smaller than that of BPA-PC (14 kJ/m²). This is because the methyl groups in the structure of bisphenol A give the PC-BPA macromolecular chains greater flexibility, so the impact strength is high. By testing the pencils hardness of two kinds of PC samples, the ISB-PC hardness is 3 H, and the BPA-PC hardness is 2 H. This indicates that the hardness of ISB-PC is higher. Experiments show that with the increase in the content of the rigid molecule ISB, the hardness level of the pencil is higher, indicating that the rigidity of ISB is the main component of hardness. At the same time, the general hardness is higher, the better the scratch resistance, so it also shows that ISB-PC scratch resistance is better than BPA-PC.

3.4 Transmittance and yellowness

The ultraviolet spectrophotometer showed that both ISB-PC and BPA-PC had better light transmittance because polycarbonate, as an amorphous polymer, had better light transmittance. However, the transmittance of ISB-PC is 91.3%, which is better than BPA-PC's transmittance of 88.6%. Generally, polymers containing benzene rings have a higher refractive index than aliphatic polymers, but the presence of benzene rings makes their dispersion more serious. The Abbe number is inversely proportional to the degree of dispersion, and most resins with high Abbe numbers are aliphatic resins. Therefore, the comprehensive optical characteristics of ISB-PC are better.

The two kinds of PC were irradiated under 254 nm ultraviolet light for the same time, and the yellowness test was carried out by colorimetry. The results showed that with increasing irradiation time, the yellowness of both kinds of PC increased from negative to positive. The growth rate of ISB-PC was slower and finally stabilized at 0.44, while the growth rate of BPA-PC was faster. It stabilized at 4.42 to 4.43.

Additionally, during the test, it was found that under ultraviolet light, ISB-PC appeared blue and BPA-PC appeared yellow. After 192 h of exposure, ISB-PC showed little change, while BPA-PC showed more serious discoloration, from colorless and transparent at the beginning to yellow.

4. Conclusion

In this study, the melt polycondensation method was adopted to allow ISB and DPC to conduct bulk polymerization under the action of the catalyst LiAcac. Following investigation, the ISB and DPC isomolar reaction, when the molar mass of catalyst accounted for 0.05% ISB, was the best reaction ratio. The incorporation of isosorbide into the polymers not only make the product more friendly to the environment, but also markedly raised their mechanical property, including a higher bending and tensile modulus and higher elongation at break. The results of pencil hardness test showed that ISB-PC also had a higher hardness rating. The DSC results showed that the homemade ISB-PC had a T_g comparable to that of BPA-PC. The ISB-PC displayed a highly UV transmittance and possessed a blue uorescence under the UVirradiation. At the same time, ISB-PC also has strong anti-yellowing ability. However, as a result of the structure of ISB itself, the test results also demonstrate that the impact steength of ISB-PC is lower than that of BPA-PC, necessitating the addition of other monomers for copolymerization or modification to improve these properties.

Declarations

Acknowledgment

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Data Availability Statement

Some or all data, models, or code generated or used during the study are available from the corresponding author by request.

All author declare no conflict of interest.

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Table

Table.1. Mechanical properties of ISB-PC and BPA-PC

Samples	ISB-PC	BPA-PC
Tensile modulus (MPa)	534	466.7
Tensile strength (MPa)	73.3	57.8
Elongation at break (%)	68	21.1
Flexural modulus (MPa)	2710	2200
Bending strength MPa	103.1	86.9
Impact strength (kJ/m ²)	7.4	14

Figures

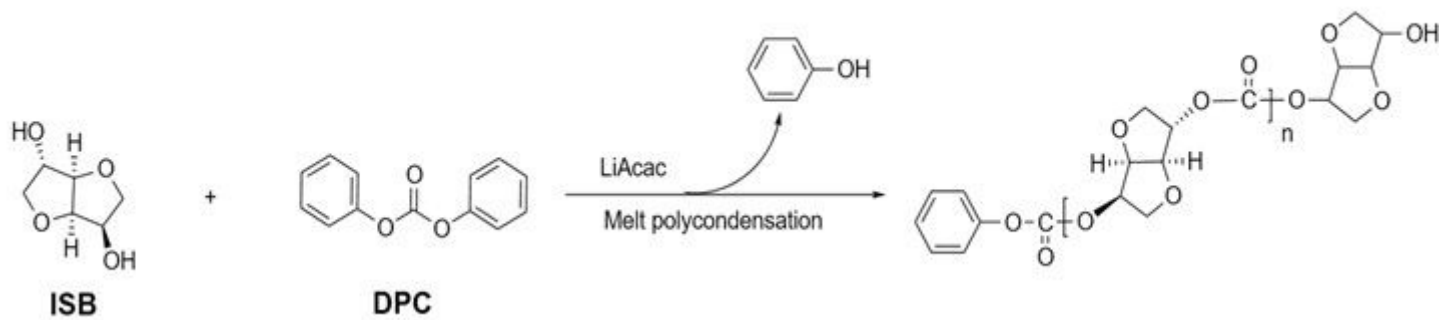


Figure 1

The route for the synthesis of bioderived polycarbonate (ISB-PC).

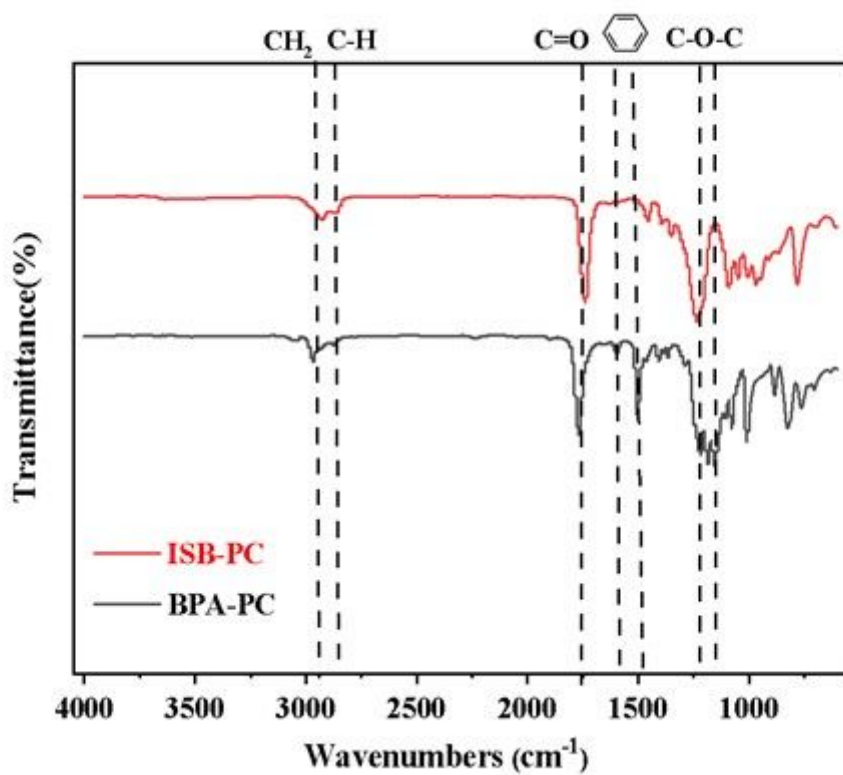


Figure 2

The FTIR spectra of ISB-PC and BPA-PC.

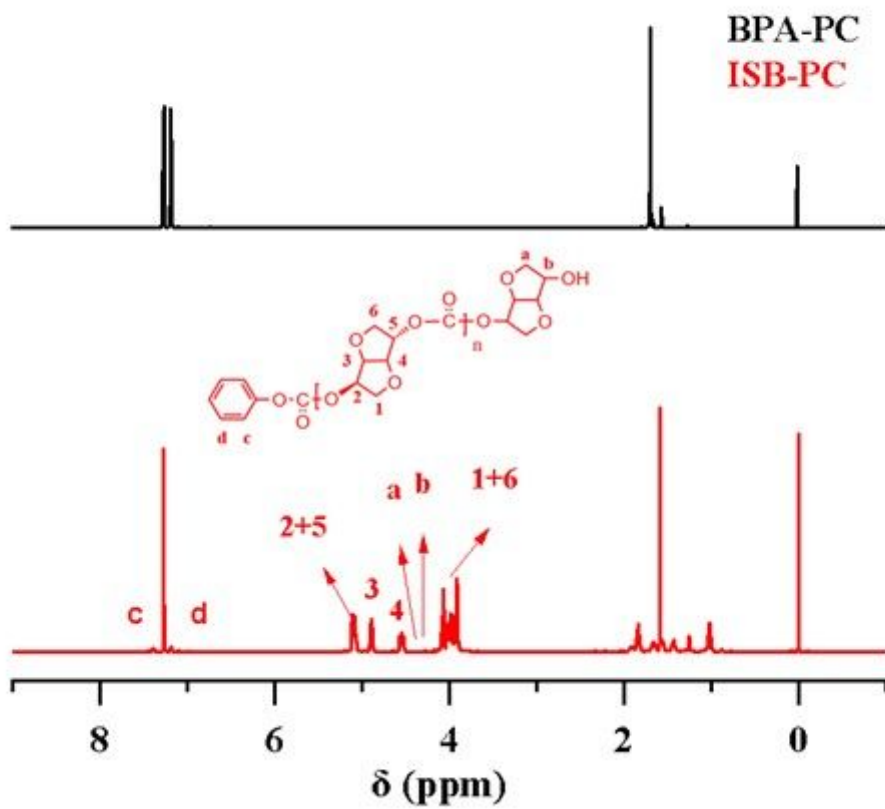


Figure 3

The ¹H-NMR spectra of ISB-PC and BPA-PC.

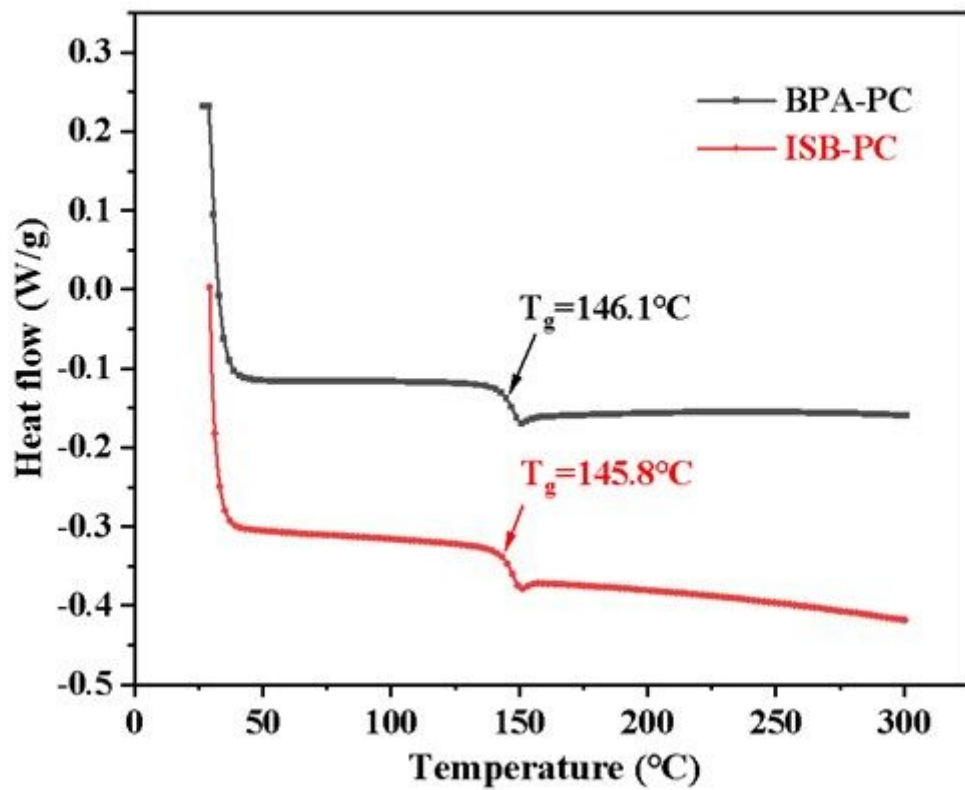


Figure 4

DSC curves of ISB-PC and BPA-PC.

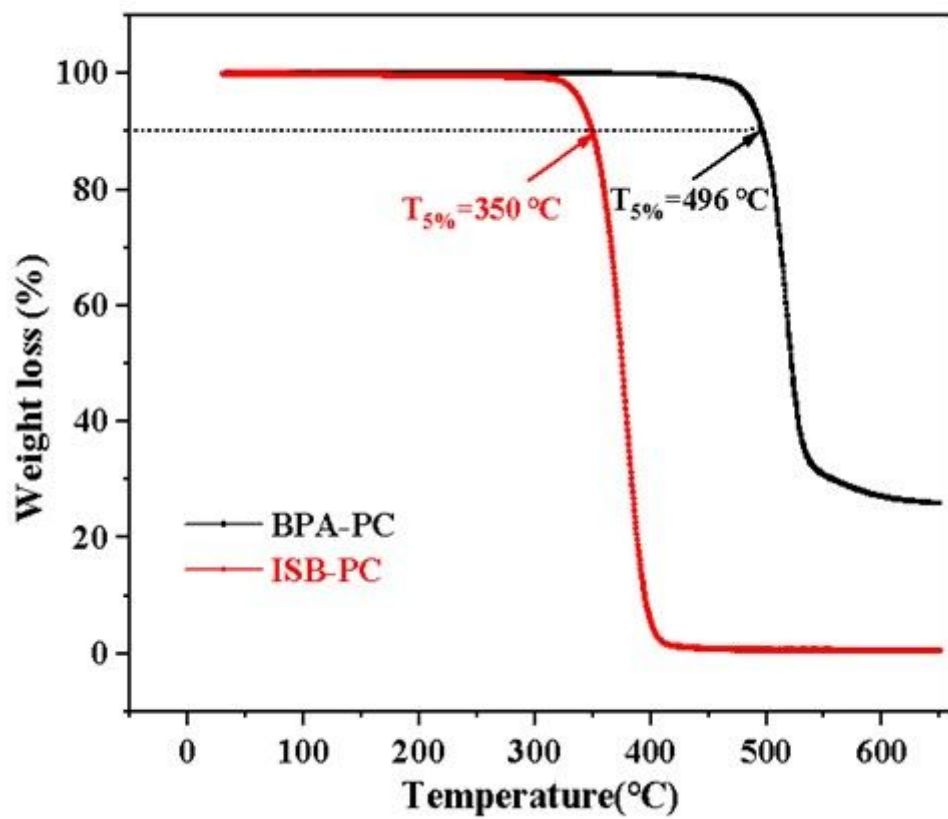


Figure 5

TG curves of ISB-PC and BPA-PC.

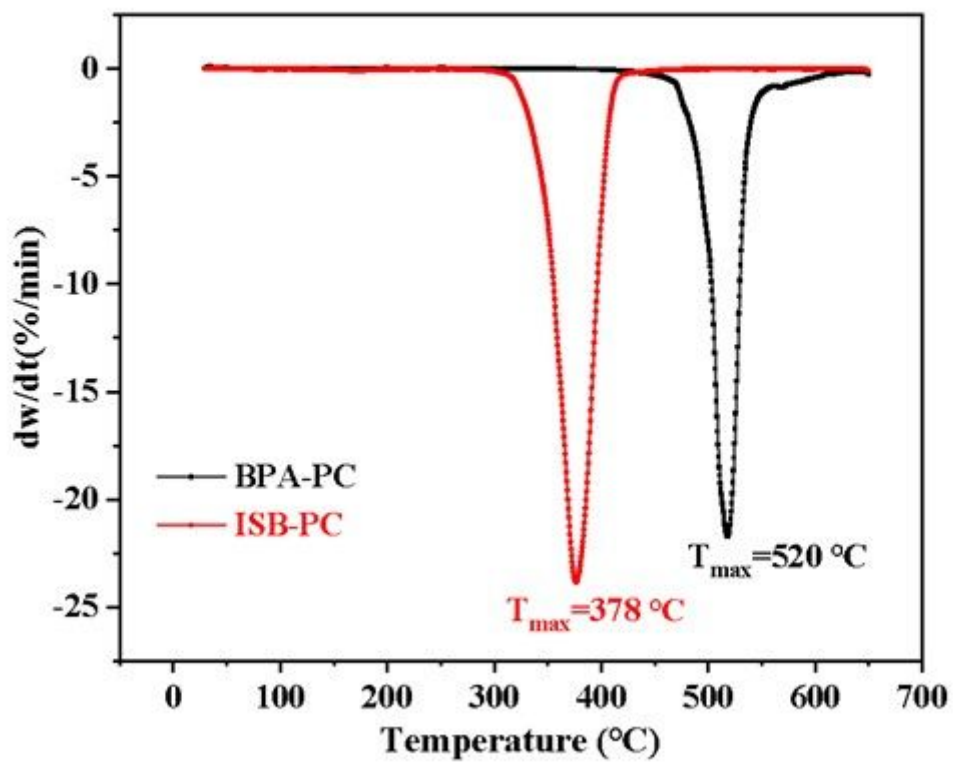


Figure 6

DTG curves of ISB-PC and BPA-PC.

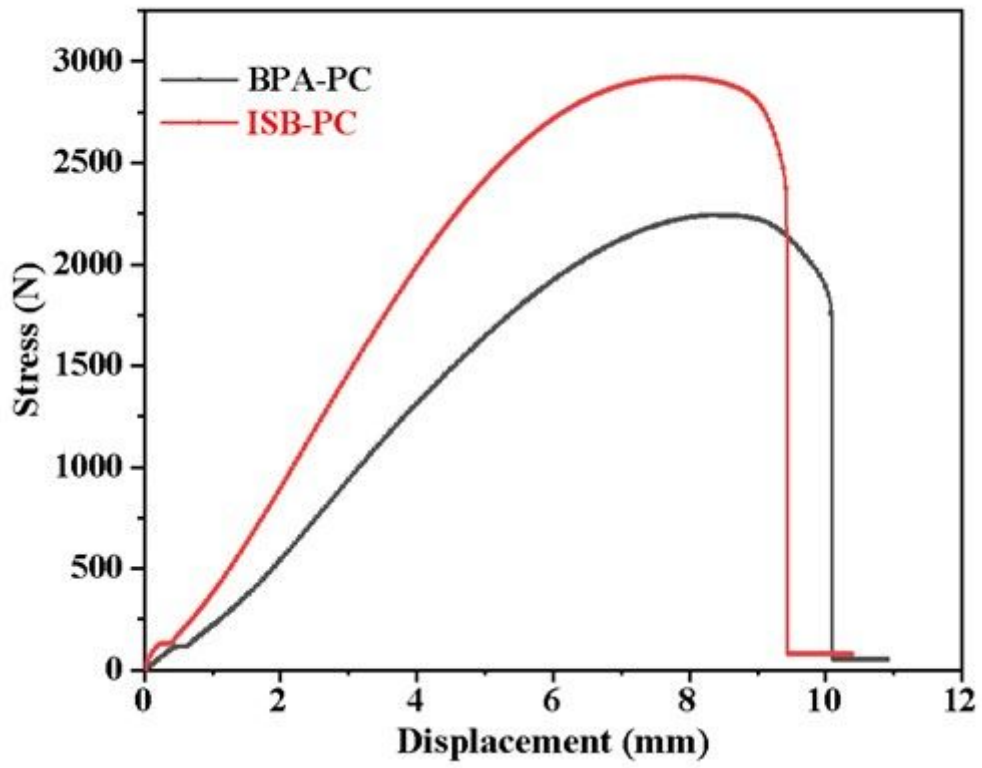


Figure 7

Tensile stress-strain curves of ISB-PC and BPA-PC

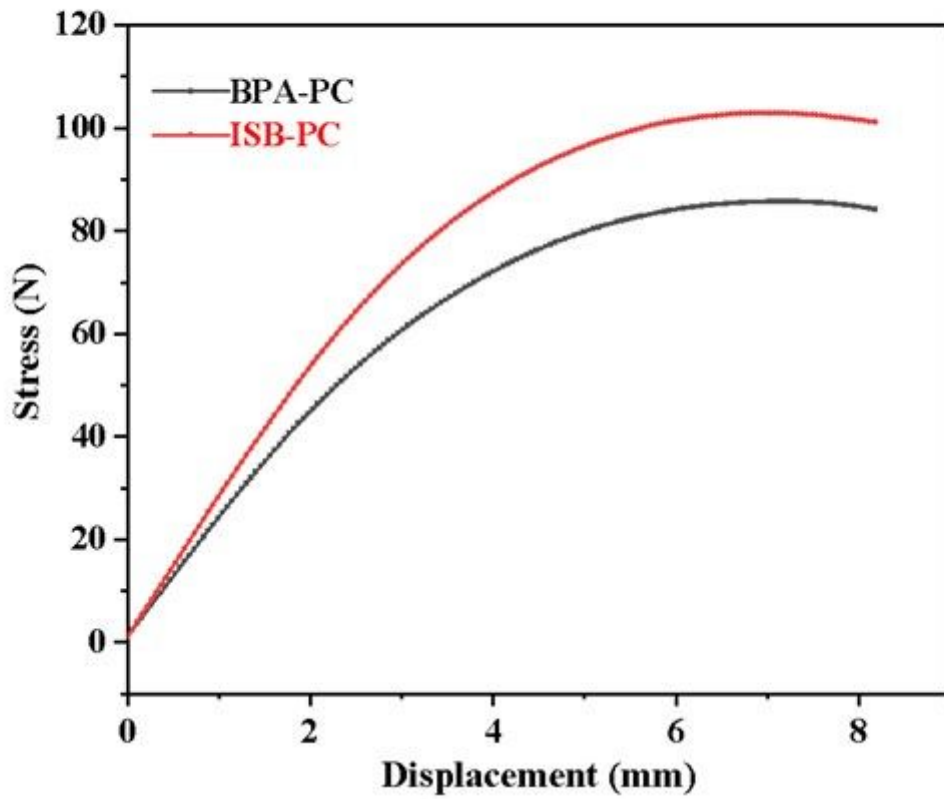


Figure 8

Bending stress-strain curves of ISB-PC and BPA-PC

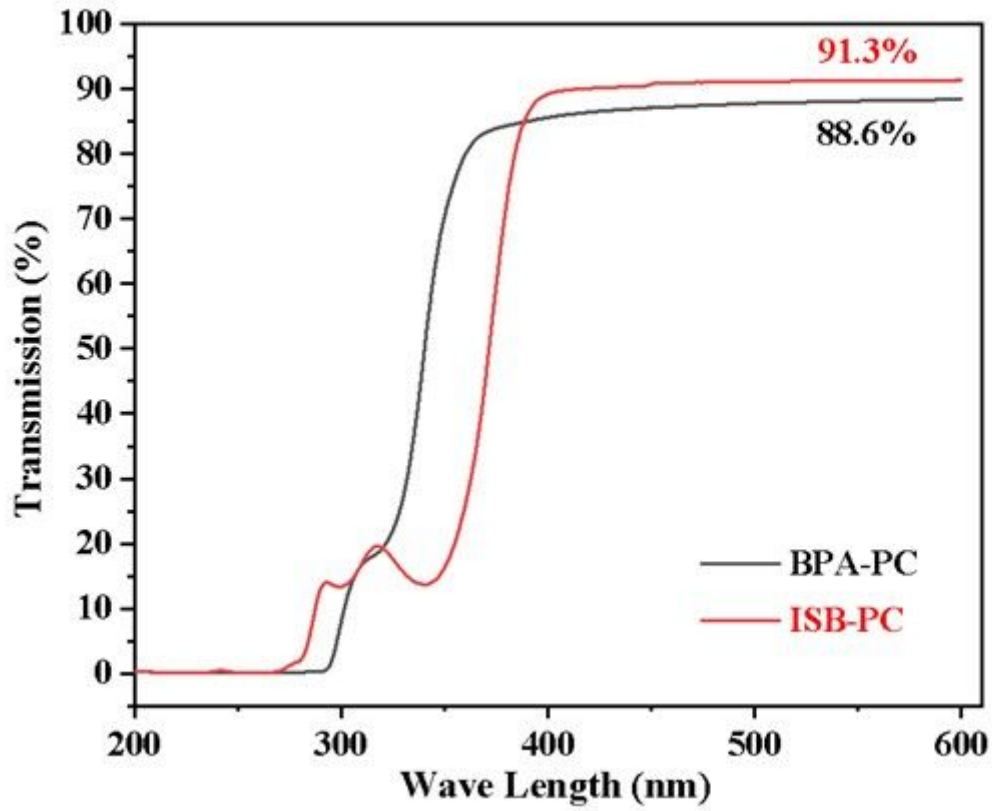


Figure 9

Transmittance of BPA-PC and ISB-PC films varies with wavelength

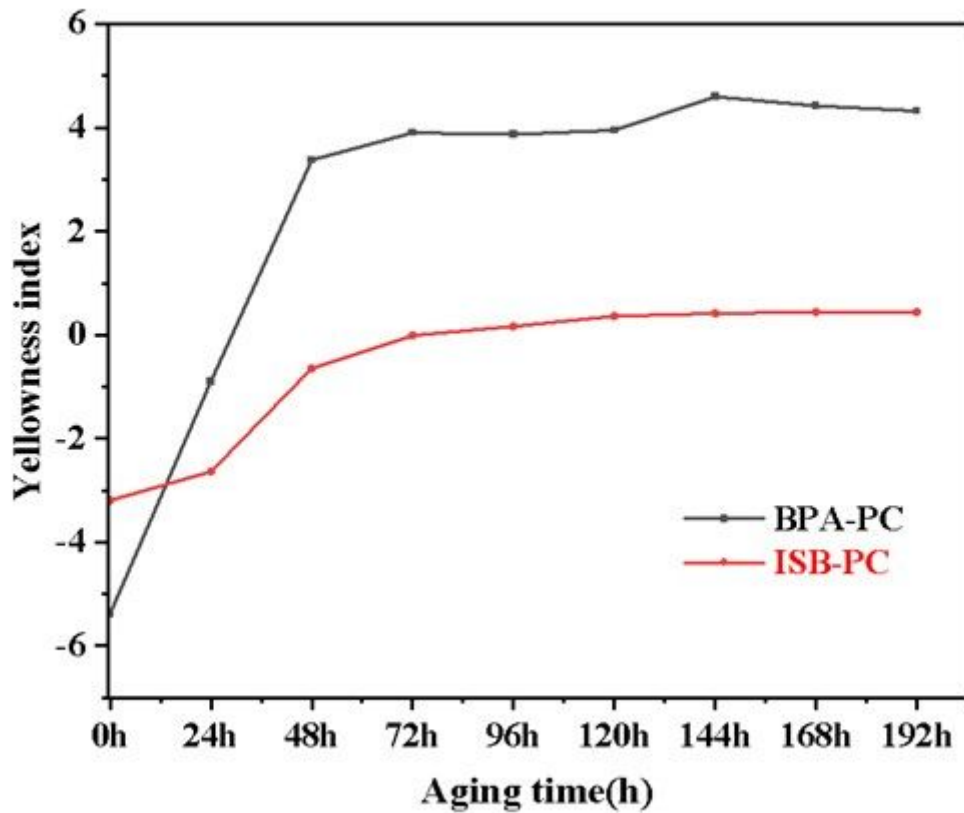


Figure 10

Relationship between the yellowness index of BPA-PC and ISB-PC films with irradiation time

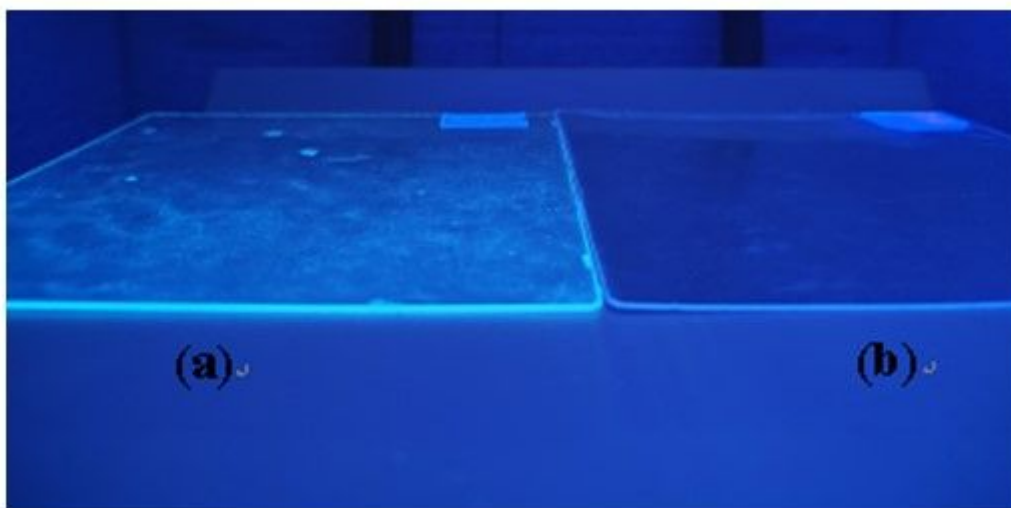


Figure 11

Photographs of polymer film irradiated under 254nm UV-light for 0 hours: (a) BPA-PC and (b) ISB-PC

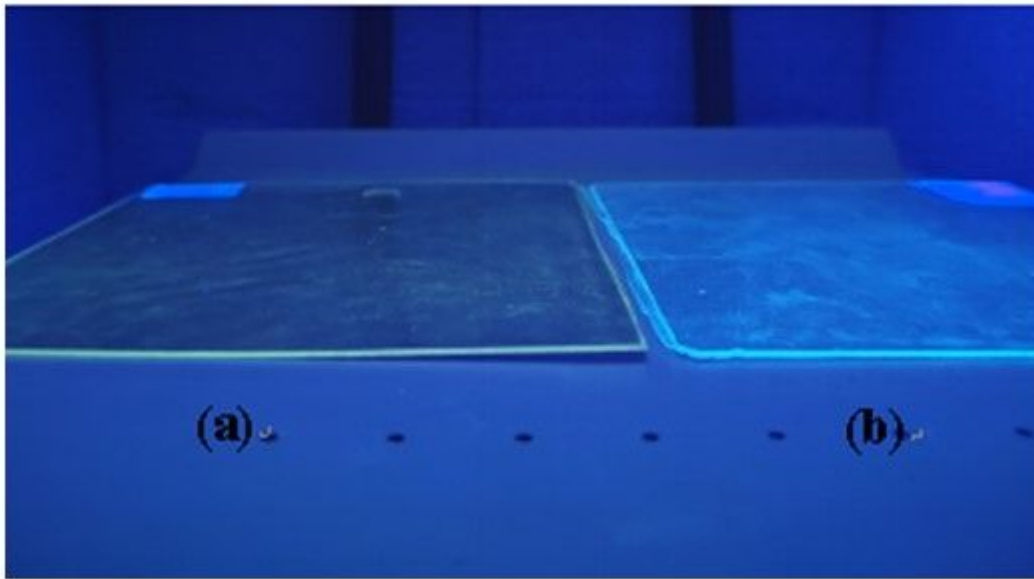


Figure 12

Photographs of polymer film irradiated under 254nm UV-light for 192 hours: (a) BPA-PC and (b) ISB-PC

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