

# Effect of ionic liquid 1-butyl-3-methylimidazolium halide on the structure and tensile property of PBS/corn starch blends

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## ARTICLE INFO

### Article history:

Received 27 October 2020

Received in revised form 10 January 2021

Accepted 11 January 2021

Available online 12 January 2021

### Keywords:

Polybutylene succinate

Starch

1-Butyl-3-methylimidazolium halide

## ABSTRACT

As a promising biodegradable resin, poly (butylene succinate) (PBS) is often blended with starch to reduce the cost. In this paper, 1-butyl-3-methylimidazolium halide pre-plasticized corn starch (CS) was blended with PBS to prepare PBS/corn starch blend material modified by ionic liquid (PBS/CS-IL). Ionic liquid (IL) acted as plasticizer and compatibilizer, and the effects of 1-butyl-3-methylimidazolium halide with different halogen anion on PBS/Starch blends were explored. The effects of IL on the structure and tensile property of PBS/Starch blends were evaluated by FTIR, SEM, DSC, TGA and XRD, respectively. Test results showed that the addition of IL significantly reduced the crystallinity of PBS/Starch blends, and the size of starch particles in the PBS matrix was also effectively reduced. IL also acted as a compatibilizer of starch and PBS, and induced the morphology of the blends to change from “sea-island” structure to homogeneous phase. The results of the tensile test showed that compared with the PBS/Starch blend without IL, the elongation at break of PBS/CS-IL increased from 22% to 93%. This study provided a simple and feasible method for the preparation of low-cost PBS bio-composite materials, and provided theoretical support for future industrial production.

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## 1. Introduction

Due to the extensive use of polymer products derived from petrochemistry, especially the packaging products which are difficult to recover, serious plastic waste pollution has been caused, which is also a waste of resources. In recent years, the development of biodegradable polymer materials that can replace traditional petroleum-based plastics has become a research hotspot [1–7]. As a natural polymer, starch is biodegradable, cheap, and is considered to be one of the most potential natural materials to replace traditional petroleum-based plastics [8–12]. Ridhwan Jumaidin [13] added co-grass fiber to Thermoplastic tapioca starch (TPCS) to improve the tensile and flexural properties of TPCS composites, while reducing impact strength and elongation. Small-molecule plasticizers (such as glycerin, water, urea) were added to starch to increase the elongation at break of modified starch materials and facilitate thermoplastic processing, but these starch materials have low tensile strength and are easy to absorb water, making it difficult to industrialize applications [1,2,4,7,14]. Therefore, starch is used to blend with other polymer materials such as polylactic acid (PLA) [1,15],

poly (butylene succinate) (PBS) [16,17], polycaprolactone (PCL) [18], poly (butylene adipate-co-terephthalate) (PBAT) [19].

PBS is a kind of biodegradable polyester and has good mechanical properties and biocompatibility [1,20,21]. It is widely used in disposable medical supplies, lunch boxes, agricultural films, and other fields [3]. However, compared with traditional petroleum-based plastics (For example, polypropylene, polyethylene, polystyrene, polyvinyl chloride), PBS has the defects of high cost [22], low tensile strength, and low stiffness [3]. PBS/Starch blends can reduce the cost and improve the degradation rate of PBS. Unfortunately, PBS with poor hydrophilicity is difficult to be compatible with starch containing hydrogen bonds and more hydrophilic groups. Simply blending starch with PBS will not give the product excellent properties because they are thermodynamically immiscible [23]. In order to solve this problem, compatibilizer or plasticizer should be employed [24]. Yin [23] synthesized MAH grafted PBS (MAH-g-PBS) as an interfacial compatibilizer and prepared the biodegradable TPS/PBS blends, which improved the strength and elongation at break of the blends. Su [16] synthesized starch-g-PBS by conjugating reaction between hydroxyl group, and PBS carboxylic acid terminal group in chloroform at room temperature by using N,N'-dicyclohexylcarbodiimide conjugating agent. Starch-g-PBS led to the sharp change of PBS crystallization, promoted the strong interfacial adhesion and improved the modulus and other properties of blends. Although the graft reaction of PBS or starch can improve the compatibility with starch, the reaction product was often accompanied with the defect of low grafting rate, which led

Abbreviations: PBS, poly (butylene succinate); CS, corn starch; IL, ionic liquid; [BMIM][Cl], 1-butyl-3-methylimidazolium chloride; [BMIM][Br], 1-butyl-3-methylimidazolium bromide; [BMIM][I], 1-butyl-3-methylimidazolium iodide.

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to the increase of raw material cost. In fact, further plasticization was needed in processing and blending [1]. It was also a method to prepare thermoplastic starch by adding various plasticizers (such as water, urea, formamide, polyol) to starch [14,25]. However, these kinds of small molecular plasticizers were easy to migrate out of starch materials, resulting in starch retrogradation after a longer storage time, which reduced the properties of the materials [26–29]. In recent years, some researchers have found that ionic liquid (IL) has a more significant ability to plasticize starch compared with traditional plasticizers.

Ionic liquid (IL) is a kind of low melting point salt, which has the advantages of good stability, non-flammable, non-explosive, easy to recycle and no detectable vapor pressure. According to the study of Sankri et al. [26], the plasticizing mechanism of 1-butyl-3-methylimidazolium chloride on starch was assumed to be that each ion pair  $\text{Cl}^-/[\text{BMIM}]^+$  formed complex interactions with a C–O–H group of starch: the  $\text{Cl}^-$  anion strongly interacted with the hydrogen atom, while the  $[\text{BMIM}]^+$  cation interacted with the oxygen atom. As a result, the intra- and inter-molecular hydrogen bonds of starch chains were disrupted and led to the sufficient plasticization for starch.

Although there are some articles about IL modified starch [16,23,24,30–33], most of them first added IL to starch to obtain thermoplastic starch (TPS), and then blended TPS with bio-based materials under the effect of compatibilizer to obtain composite materials. This method is too cumbersome, and the data on the effects of different structure IL on the structure and properties of pure PBS and PBS/Starch blends are scarce. The focus of this paper is to investigate the effects of different IL on the structure and properties of PBS/Starch blends, and reveal the law of actions of IL 1-butyl-3-methylimidazolium halide with different halogen anion. The destruction of intra- and inter-molecular hydrogen bonds of starch chains by IL with different halogen anions was explained from the electron and volume interaction, which further explained why IL could be used as the compatibilizer or modifier of PBS/Starch blends and provided data and theoretical support for future industrial production.

## 2. Materials and methods

### 2.1. Materials

Corn starch (CS) (moisture content 10.5%; amylose content 27% (w/w, dry basis); purity >99%) was supplied by Aladdin Biochemical Technology Co., Ltd. (Shanghai, China). PBS was obtained from Anqing He Xing Chemical Corp. Ltd. (Anhui, China).  $\bar{M}_n$  (number average molecular weight),  $\bar{M}_w$  (weight average molecular weight), and PDI ( $\bar{M}_w/\bar{M}_n$ ) are 36,657 g/mol, 100,807 g/mol, and 2.75, respectively. 1-Butyl-3-methylimidazolium chloride ( $[\text{BMIM}][\text{Cl}]$ ), 1-butyl-3-methylimidazolium bromide ( $[\text{BMIM}][\text{Br}]$ ), 1-butyl-3-methylimidazolium iodide ( $[\text{BMIM}][\text{I}]$ ) were purchased from Lanzhou Institute of Chemical Physics (Lanzhou, China). All the IL reported purity >99% (mass-fraction).

### 2.2. Sample preparation

The PBS and CS were dried in an oven at 80 °C for 8 h, to prevent excessive hydrolysis which can damage physical properties of the PBS [17]. CS and IL (25 parts of IL per 100 parts of dry starch) were manually mixed, and sealed and stored for 24 h at room temperature. The obtained CS modified by  $[\text{BMIM}][\text{Cl}]$ ,  $[\text{BMIM}][\text{Br}]$  and  $[\text{BMIM}][\text{I}]$  were named as CS-Cl, CS-Br and CS-I, respectively.

Different from the previous two-step method of preparing PBS/Starch blends by researchers [22,24,34], we blended 60 wt% PBS and 40 wt% pure CS or CS modified by ionic liquid (CS-IL) in Rheomix OS Torque Rheometer (Rheocord System 40, HAAKE, Germany) at 135 °C with a rotor speed of 60 rpm for 15 min. The obtained samples were named as PBS/CS, PBS/CS-Cl, PBS/CS-Br and PBS/CS-I, respectively. The formulations of samples are listed in Table 1.

**Table 1**

Proportions of materials used for the preparation of PBS/Starch samples.

Samples	Starch/(wt%)	Ionic liquid	PBS/(wt%)	IL/starch ratio/(wt/wt)
PBS/CS	40	None	60	0.25
PBS/CS-Cl	40	$[\text{BMIM}][\text{Cl}]$	60	0.25
PBS/CS-Br	40	$[\text{BMIM}][\text{Br}]$	60	0.25
PBS/CS-I	40	$[\text{BMIM}][\text{I}]$	60	0.25

Finally, according to previous research, the obtained blend particles were dried at 80 °C for 4 h, and then transformed into dumbbell ( $2 \times 4 \times 75$  mm) and rectangular ( $2 \times 10 \times 75$  mm) shapes by using a micro-injection molding machine (Minijet-Pro, ThermoFisher, Germany) for tensile testing and other measurement experiments. The barrel and mold temperatures during micro-injection molding are 140 and 25 °C, respectively, and the injection and filling pressures are both 450 bar.

### 2.3. FTIR-ATR analysis

FTIR spectrometer (Nicolet is50, Thermo Fisher, USA) equipped with a slide-on ATR accessory was used for the FTIR analysis. The resolution power is  $2 \text{ cm}^{-1}$ , and the scan range is 4000 to  $400 \text{ cm}^{-1}$ .

### 2.4. Differential scanning calorimetry (DSC)

DSC analysis was carried out using DSC8500 (Q200, TA, USA). Samples (3 mg) were placed in sealed aluminum crucibles under nitrogen atmosphere. Each sample was first heated from 30 to 140 °C at 50 °C/min, kept for 5 min to erase the thermal history (first heating process) and then cooled to  $-70$  °C at 10 °C/min, kept at  $-70$  °C for 5 min (first cooling process) and reheated to 140 °C at a rate of 10 °C/min (second heating process). The degree of crystallinity of all samples was calculated using the following equation:

$$X_c = \frac{\Delta H_m}{\omega \times \Delta H^{\circ}_m} \times 100\% \quad (1)$$

where  $\Delta H_m$  is the heat of fusion of different samples,  $\Delta H^{\circ}_m$  is the heat of fusion of 100% crystalline PBS, which is 110.3 J/g (theoretical melting enthalpy) and  $\omega$  is the weight fraction of PBS in the blends [22].

### 2.5. Thermogravimetric analysis (TGA)

Thermal stability was investigated using TGA thermal analysis instrument (TA2950, Du Pont, UK). Test was performed on platinum pans under 25 ml/min nitrogen flow, in the temperature range of 30–600 °C at a heating rate 10 °C/min.

### 2.6. X-ray diffraction (XRD)

The crystallinity of PBS composites was recorded an X-ray diffractometer (Ultima IV, Rigaku, Japan). The measurement was carried out in  $2\theta$  ranges between 5 and 50° with step size of 0.026°. The data of crystallinity ( $X_c$ ) was analyzed by Jade 6.0 software.

### 2.7. Scanning electron microscopy (SEM)

The morphological observation was carried out by scanning electron microscope (JSM-5900LV, JEOL, Japan). Composites were fractured in liquid nitrogen and treated with dimethyl sulfoxide (DMSO) to remove the dispersed starch particles. After the procedure, all samples were washed with distilled water and then dried. Finally, samples were vacuum coated with a thin layer of gold.

## 2.8. Tensile test

Tensile strength and elongation at break were determined according to GB/T1040.1–2018 with a universal testing machine (Instron 5567, MA, USA) at a crosshead speed of 50 mm/min. At least five replicated samples for each PBS/Starch blends were tested and the mechanical parameters were calculated with Bluehill 3 software.

## 2.9. Behavior in water

All samples (10 × 10 × 3 mm) dried at 60 °C for 24 h were immersed in distilled water for 24 h, and the water absorption and solubility were measured [35]. Wet samples were placed on a paper towel for a few minutes to remove excess water. The mass of the original dry sample was recorded as  $W_0$ , and the mass of the sample after water absorption was recorded as  $W_1$ . The wet samples were placed in an oven at 100 °C for 24 h to dry and weigh. The weight of the wet sample after drying was recorded as  $W_2$ . Each group of samples was measured 5 times and the average value was taken. The moisture absorption of the sample was calculated using the following formula (2):

$$\text{Moisture absorption (\%)} = \frac{W_1 - W_0}{W_0} \times 100\% \quad (2)$$

Solubility degree was calculated according to the following formula (3):

$$\text{Solubility degree (\%)} = \frac{W_0 - W_2}{W_0} \times 100\% \quad (3)$$

## 2.10. Statistical analysis

Statistical analysis data were subjected to one-way analysis of variance (ANOVA) using a SPSS computer program (SPSS Statistic 20.0). Post hoc multiple comparisons were determined by the Tukey's test with the level of significance set at  $p < 0.05$ .

# 3. Results and discussion

## 3.1. FTIR spectroscopy

The position change of vibration absorption peaks of different groups in the infrared spectrum can reflect the interaction between IL, starch and PBS. Fig. 1 shows the infrared spectra of pure CS, PBS/CS, and PBS/CS-IL. In the curve of pure CS, the absorption peaks of 3288  $\text{cm}^{-1}$  and 2928  $\text{cm}^{-1}$  were stretching vibration of -OH and asymmetric stretching vibration of -CH in glucose unit, respectively [22]. Footprints of alkenes, esters, aromatic compounds, ketones, and alcohols were found in all PBS/Starch blends, which had different oxygen-containing functional groups, such as OH (3400–3200  $\text{cm}^{-1}$ ), C=O (1765–1710  $\text{cm}^{-1}$ ) and C-O-H (1050  $\text{cm}^{-1}$ ) [36]. When hydrogen bonds are formed between intramolecular or intermolecular, the density of electron cloud is averaged due to the effect of hydrogen bonds, thus the bond frequency decreases, and the vibration peak moves to the low wavenumber direction on the infrared spectrum. On the contrary, when the hydrogen bonds in molecules or molecules are weakened, the absorption peaks of -OH move in the direction of high wavenumber direction on the infrared spectrum [37]. Compared with the spectrum of CS, the absorption peak of hydroxyl group of PBS/CS did not change, and the absorption peak of 1713  $\text{cm}^{-1}$  was attributed to the absorption vibration peak of C=O on the PBS molecular chain, indicating that there was no obvious interaction between PBS and CS. However, the vibrational absorption peak of -OH in PBS/CS-IL shifted to a higher wavenumber direction, from 3289 to 3300, 3312 and 3319, respectively. According to previous study by Liu et al. [24], the reason for this phenomenon may be due to the interaction between

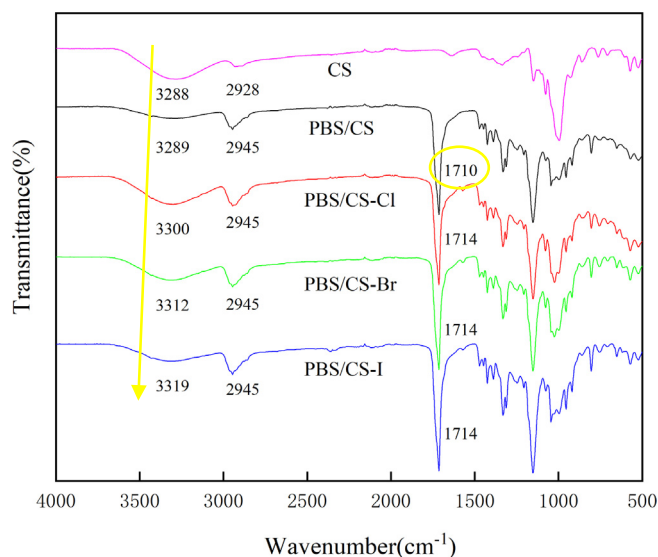


Fig. 1. FTIR spectra for corn starch and PBS/Starch blends.

the cation part [BMIM]<sup>+</sup> in IL and O in starch -OH, and the anion part (Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>) had a certain attraction to H in -OH, which destroyed the original intramolecular and intermolecular hydrogen bonds of starch. At the same time, IL, as small molecules, permeated into the starch molecules and provided free volume of polymer chain segment movement, and the effect of original hydrogen bond was further weakened [38,39]. Comparing the effects of different IL on PBS/CS-IL, [BMIM][I] had the strongest plasticizing effect on starch, which indicated that [BMIM][I] with large volume of iodine atoms had certain advantages under the same electronic effect.

Compared with the C=O (1710  $\text{cm}^{-1}$ ) absorption peak of PBS/CS, the infrared absorption peak of C=O (1714  $\text{cm}^{-1}$ ) of PBS/CS-IL moved in the direction of high wavenumber direction on the infrared spectrum, from 1710 to 1714, which may be due to cations([BMIM]<sup>+</sup>) in IL were attracted by oxygen atoms in C=O, which reduced the electron cloud density of carbon oxygen double bond on carbonyl group. This result is consistent with that of Zhao et al. [30,31]. The FTIR spectra shows that there were no new characteristic peaks except the positions of some original characteristic peaks, which indicated that the IL did not react with the blends to form new groups, but weakened the hydrogen bond of the blends.

## 3.2. Morphological investigation

The morphology of the material will affect its physical properties, especially its mechanical properties are closely related to the micro morphology [21]. In order to further investigate the morphology of PBS/CS and PBS/CS-IL, the microstructure and interfacial adhesion of the blends were analyzed by SEM. The fracture surface micrograph of PBS/CS and PBS/CS-IL after etching is shown in Fig. 2. By comparing the PBS/CS SEM diagram after etching, it is shown that the infiltration of IL can significantly reduce the size of starch granules in PBS matrix. Fig. 2 (a) shows that the untreated CS was dispersed in the PBS matrix with a diameter range of 3–20  $\mu\text{m}$ . However, Fig. 2(b–d) show that the size of CS-IL decreased significantly, and the diameter of 90% starch particles in PBS/CS-I is less than 5  $\mu\text{m}$ . The decrease of CS-IL particle size was attributed to the destruction of starch structure by IL, which weakened the intermolecular interaction force of starch and made starch granules unable to reunite into larger size. Another factor is that the coupling effect of IL can promote the uniform dispersion of starch granules in PBS matrix and limit the collision of small starch granules, similar phenomenon has been confirmed in the experimental results of Zhang et al. [22].



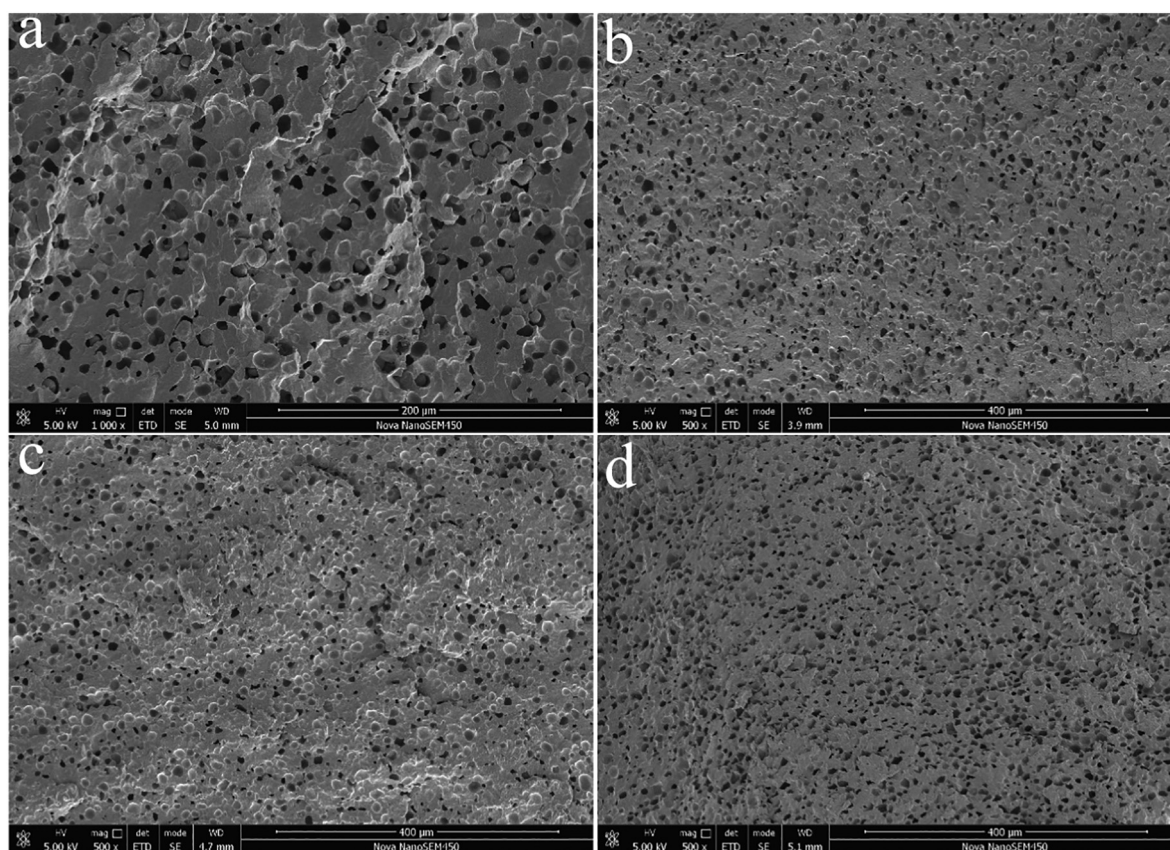


Fig. 2. SEM photograph for: (a) PBS/CS, (b) PBS/CS-Cl, (c) PBS/CS-Br, (d) PBS/CS-I.

### 3.3. Differential scanning calorimetry (DSC)

DSC analysis was used to evaluate the thermal properties and crystallization behavior of PBS/Starch blends. At the same time, in order to explore whether IL has a certain effect on the thermal performance of PBS, we added different IL into PBS (1:50 w/w) and mixed it in HAAKE Rheomix OS Torque Rheometer under the same conditions to obtain PBS modified by IL (PBS-IL: PBS-[BMIM][Cl], PBS-[BMIM][Br], PBS-[BMIM][I]). Fig. 3 shows the first cooling curve and the second heating curve of the pure PBS, PBS-IL, and PBS/Starch blends. The DSC data (Enthalpy of fusion,  $\Delta H_m$ ; crystallinity, Xc; Crystallization temperature, Tc;

Melting temperature, T<sub>m</sub>; Glass transition temperature, T<sub>g</sub>) of samples are shown in Table 2. It can be seen that for PBS the melting enthalpy is 51.3 J/g, and the crystallinity is 46.5%. The crystallinity of PBS/CS, PBS/CS-Cl, PBS/CS-Br and PBS/CS-I is 45.8%, 39.2%, 38.0% and 36.6% respectively. The addition of CS reduced the crystallinity of PBS, which may be due to the fact that CS was purely in the PBS matrix in the form of particles, which hindered the release of PBS molecular chains into the lattice during crystallization [24,36].

Compared with the crystallinity of PBS/CS, the melting enthalpy and crystallinity of the sample modified by adding IL were both reduced, and this result was contrary to that of Liu et al. [24]. Small molecular IL acted

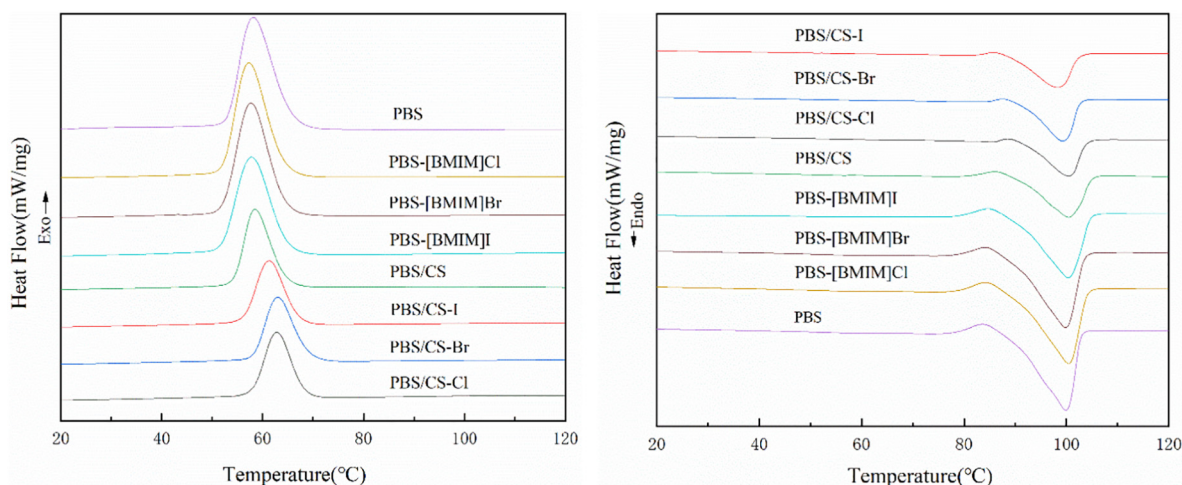


Fig. 3. DSC curves for PBS, PBS-IL and PBS/Starch blends: the first cooling (a) and the second heating scan (b).

**Table 2**

The DSC data of PBS, PBS-IL and PBS/Starch blends.

Samples	$\Delta H_m$ (J/g)	$T_c$ (°C)	$T_m$ (°C)	$T_g$ (°C)	Xc-DSC (%)	Xc-XRD (%)
PBS	51.3 ± 0.5	58.4 ± 0.9	100.3 ± 0.7	−39.9 ± 0.5	46.5 ± 8.5	55.4 ± 7.3
PBS-[BMIM][Cl]	54.6 ± 0.7	57.7 ± 0.1	100.2 ± 0.2	−40.5 ± 0.3	49.5 ± 4.8	58.7 ± 5.2
PBS-[BMIM][Br]	54.6 ± 0.1	57.5 ± 0.8	100.2 ± 0.1	−40.1 ± 0.4	49.5 ± 5.3	58.4 ± 4.3
PBS-[BMIM][I]	54.8 ± 0.1	57.3 ± 0.1	100.2 ± 0.2	−40.7 ± 0.1	49.7 ± 7.5	59.6 ± 6.5
PBS/CS	30.3 ± 0.6	58.7 ± 0.2	100.2 ± 0.3	−41.6 ± 0.5	45.8 ± 7.8	52.7 ± 5.8
PBS/CS-Cl	25.9 ± 0.7	62.8 ± 0.8	102.0 ± 0.8	−40.0 ± 0.4	39.2 ± 7.5	43.1 ± 7.6
PBS/CS-Br	25.1 ± 0.6	61.3 ± 0.3	101.8 ± 0.5	−40.4 ± 0.6	38.0 ± 6.7	41.7 ± 7.5
PBS/CS-I	24.2 ± 0.3	60.9 ± 0.7	100.3 ± 0.7	−40.0 ± 0.2	36.6 ± 4.8	38.6 ± 5.3

as plasticizer of starch, which weakened intra- and inter-molecular hydrogen bonds of starch chains. On this basis, CS-IL was fully dispersed in PBS matrix, the compatibility of CS-IL and PBS was strengthened. It can be seen that the crystallinity of PBS/CS-Cl, PBS/CS-Br and PBS/CS-I is gradually increasing, which may be due to the best compatibility between CS-I and PBS. When PBS crystallized, CS-I had less hindrance to molecular chain. The compatibility of CS-Cl and CS-Br with PBS was not as good as that of TPS-I with PBS. During the crystallization process, they hinder the movement of PBS molecular chain greatly and the chain segments were not easy to be discharged into the lattice, so the crystallinity was reduced. It was necessary to provide the energy needed for the movement of the segments at higher temperatures, so  $T_c$  of the blends was also increased.

In order to further study the effect of IL on the crystallization behavior of PBS, PBS-IL (50:1 w/w) mixture was prepared under the same processing conditions as PBS/Starch blends. After adding IL, the crystallinity of PBS-IL increased, indicating that IL promoted PBS crystallization to a certain extent. The reason can be attributed to the interaction between polar IL and the polar bonds on the PBS chain, which further weakened the intermolecular force of PBS and caused less entanglement of PBS chains and increased mobility of molecules, so that the molecular chain can be effectively discharged into the lattice thus strengthened the crystallinity [24].

In Fig. 3(b), there are two peaks in the melting part of PBS, PBS-IL, and PBS/Starch blends. In this process, there is an exothermic cold crystallization peak, and the corresponding temperature is the cold crystallization temperature. This phenomenon of double melting peaks can be explained by the melting-recrystallization mechanism: at lower temperatures, crystals with relatively poor thermal stability melt first at low temperatures, then crystallize to form crystals with relatively good stability, and finally achieve full melting at relatively high temperatures [40].

### 3.4. Thermogravimetric analysis

The influence of different IL on PBS/Starch blends thermal stability was presented as TGA analysis results in Table 3 and in Fig. 4. The thermal decomposition of PBS/Starch blends shows two stages in the TG diagram. The first thermal decomposition temperature ( $T_{d1}$ ) was between 240 and 300 °C, which was the decomposition stage of starch, the second decomposition temperature ( $T_{d2}$ ) was between 370 and 390 °C, and PBS decomposed at this stage. Pure CS and pure PBS

**Table 3**

Thermal properties obtained by TG analyses of PBS and PBS/Starch blends.

Samples	$T_{d1}$ (°C)	$T_{d2}$ (°C)	Residue at 600 °C (%)
CS	300 ± 3	–	8.83 ± 1.23
PBS	380 ± 2	–	0.18 ± 0.55
PBS/CS	290 ± 2	380 ± 2	4.25 ± 0.58
PBS/CS-Cl	248 ± 3	379 ± 2	10.17 ± 0.42
PBS/CS-Br	255 ± 1	377 ± 2	8.80 ± 0.26
PBS/CS-I	277 ± 1	371 ± 1	7.33 ± 0.24

decomposed at 300 °C and 380 °C respectively. The  $T_{d1}$  of PBS/CS was 290 °C and  $T_{d2}$  was 380 °C. It can be seen that the addition of natural CS does not change the decomposition temperature of PBS, indicating that there was no obvious reaction between them, only a simple physical blending [12,13,24]. Compared with PBS/CS, the  $T_{d1}$  and  $T_{d2}$  of the PBS/CS-IL decreased, and the thermal stability of the blends decreased. The reason for this phenomenon is that after CS was plasticized by IL, the number of intramolecular and intermolecular hydrogen bonds was reduced, the interaction force between the CS molecular chains was weakened, and the thermal stability was reduced [30,31]. The  $T_{d1}$  of PBS/CS-Cl, PBS/CS-Br, and PBS/CS-I were 248 °C, 255 °C, and 277 °C respectively, and the  $T_{d1}$  gradually decreased. It has been seen from the previous analysis that compared with [BMIM][Br] and [BMIM][I], the plasticizing ability of [BMIM][Cl] was the weakest, but the  $T_{d1}$  of PBS/CS-Cl was the lowest. For  $T_{d1}$  PBS/CS-Cl < PBS/CS-Br < PBS/CS-I, the plasticizing effect of IL on starch cannot explain this phenomenon. The reason for this phenomenon may be that the compatibility between CS-Cl and PBS was poor, and the attraction of PBS matrix was less. After temperature rise, it was easier to decompose. However, the compatibility of TPS-Br, TPS-I with PBS is better and they were wrapped by PBS matrix and were not easy to decompose when heated, so  $T_{d1}$  is higher [35,41,42].

The  $T_{d2}$  of PBS/CS-Cl, PBS/CS-Br, PBS/CS-I were 379 °C, 377 °C, 371 °C, respectively. Compared with PBS/CS, the decrease of  $T_{d2}$  in PBS/CS-IL was attributed to the decomposition of CS-IL may produce small polar molecules, which may induce the degradation of PBS. At the same time, PBS/CS-Br, PBS/CS-I, the two stages of thermal decomposition became not obvious. The above phenomenon was attributed to the destruction of IL on starch, meanwhile the cation part of IL had a certain effect on O in C=O of PBS [30], which increased the compatibility between CS-IL and PBS [16,41]. Such that the decomposition of the second stage became less obvious.

### 3.5. XRD analysis

In order to further investigate the effect of IL on the crystal structure of PBS/Starch blends, XRD was employed. The XRD profiles are shown in Fig. 5 and the Xc-XRD values are summarized in Table 2. As for the XRD pattern of neat PBS (Fig. 5), there were three main characteristic diffraction peaks around  $2\theta$  of 19.5°, 21.5°, and 22.5° for  $\alpha$  crystal, corresponding to (020), (021) and (110) planes, respectively [14,34]. Same as previous studies [14,43,44], compared with the XRD pattern of neat PBS, the peak position of PBS/CS was almost the same as that of neat PBS. However, it is noted that the intensity decreased especially at 19.5°, indicating the deterioration on crystallization property of PBS matrix. This might be due to the fact that starch particles hindered the movement of PBS segments during the crystallization process of PBS, which made it difficult for the PBS segments to be discharged into the lattice and caused the decrease of crystallinity. Similar result was reported by Liu et al. [24].

Similarly, the position and number of characteristic peaks of PBS/CS-IL did not change after adding IL, which indicated that the addition of IL did not change the crystal type of PBS/Starch blends and no new crystals

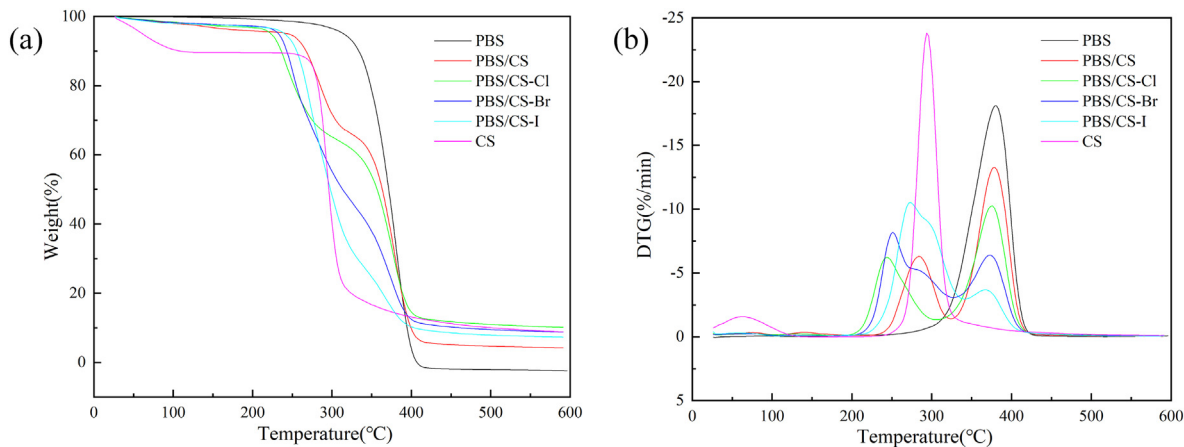


Fig. 4. TGA results of CS, PBS and PBS/Starch blends (a) TG curve (b) DTG curve.

were formed. However, the intensity of the original characteristic peak decreased obviously. Because the peak strength was positively correlated with the crystallinity [45], it indicated that the addition of IL reduced the crystallinity of PBS/Starch system. When CS was plasticized by IL, IL might act as a “compatibilizer” and CS-IL was blended with PBS at high temperature and shear stress, which made CS-IL combine with PBS better. The crystallinity of PBS/CS-I was the lowest among the three kinds of PBS/CS -IL, which may be due to [BMIM][I] had the best plasticizing effect on starch, causing the best compatibility between CS-I and PBS. In the crystallization process of PBS, CS-I had the greatest blocking effect on the movement of PBS segments, and the crystallization ability of PBS decreased, which was consistent with DSC results.

3.6. Tensile test

Fig. 6. shows the tensile strength and elongation at break of PBS/CS and PBS/CS-IL. The tensile strength and elongation at break of PBS/CS were 17.8 MPa and 22.4%, respectively, showing higher hardness and greater brittleness. This was because the compatibility between natural CS and PBS was poor, and the bonding strength between two phases was weak, which showed the mechanical properties of blends both hard and brittle. The poor compatibility and interface interaction

between PBS and CS were the reasons for the decline of the mechanical properties of PBS/CS [22,46]. Therefore, the incompatibility and poor interfacial adhesion of PBS/CS must be eliminated. With the addition of IL, the tensile strength of the PBS/CS-IL decreased slightly and the elongation at break significantly increased. In the three PBS/CS-IL, the tensile strength (MPa) and elongation at break (%) of PBS/CS-Cl, PBS/CS-Br, and PBS/CS-I were 17.0, 16.7, 15.4 and 24, 28, 93, respectively. After adding 20% [BMIM][I], the tensile strength of the PBS/CS-I was 15.4 MPa and the elongation at break increased to 93%, because [BMIM][I] weakened the intermolecular force of starch, and made starch and PBS molecular chain integrate better and the material showed good toughness. This result can also be proved in the analysis of SEM and XRD.

Similarly, Table 4 shows the changes in Young’s modulus of the PBS/Starch blends. This result shows that with the addition of IL, Young’s

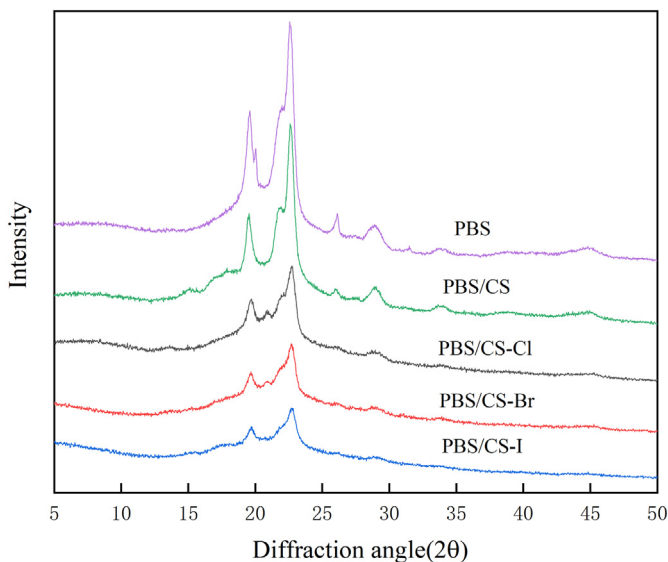


Fig. 5. XRD patterns for PBS and PBS/Starch blends.

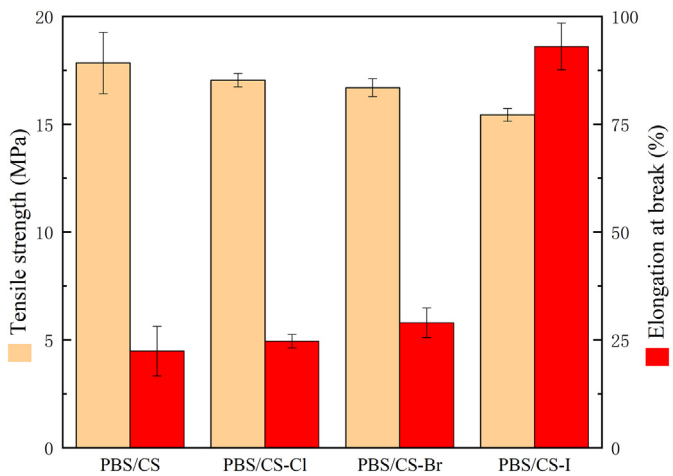


Fig. 6. Mechanical tests result for PBS/Starch blends.

Table 4  
Tensile tests of PBS/Starch blends.

Samples	Tensile strength (MPa)	Elongation at break (%)	Young’s modulus (MPa)
PBS/CS	17.8 ± 0.5	22 ± 3	620 ± 12
PBS/CS-Cl	17.0 ± 0.2	24 ± 1	545 ± 23
PBS/CS-Br	16.7 ± 0.3	28 ± 2	542 ± 21
PBS/CS-I	15.4 ± 0.2	93 ± 3	521 ± 15



**Table 5**  
Sorption and solubility degrees in distilled water.

Samples	Water sorption degree (%)	Solubility degree (%)
PBS	0.33 ± 0.14	0.73 ± 0.52
PBS/CS	13.31 ± 2.36	7.39 ± 1.24
PBS/CS-Cl	10.27 ± 1.25	5.35 ± 1.15
PBS/CS-Br	7.85 ± 0.87	5.53 ± 0.23
PBS/CS-I	3.63 ± 0.36	5.23 ± 0.38

modulus of the blends decreased. This may be because for PBS/CS, starch cannot be uniformly dispersed in the PBS matrix in the form of granules, forming stress concentration points, which was reflected in the high Young's modulus of PBS/CS [47]. However, with the addition of IL, the Young's modulus of PBS/CS-IL decreased significantly. Compared with PBS/CS 620 Young's modulus (MPa), PBS/CS-Cl, PBS/CS-Br, and PBS/CS-I are 545, 542 and 521, respectively. The decrease was mainly attributed to the improved compatibility of PBS and CS-IL. As can be seen from previous SEM, this result was consistent with the results of Shamsuri et al. [32].

### 3.7. Behavior of PBS and PBS/Starch films in water

Water absorption is one of the disadvantages in the application of starch-containing materials. As previously reported [17], inserting the starch component into the PBS polymer had a higher water absorption rate because the starch component may account for 300% of the water absorption rate. As shown in Table 5, the water sorption degree of pure PBS was only 0.33%, and the solubility degree was 0.73%, which showed that PBS, as a hydrophobic resin, had strong water resistance. However, after adding CS, the water sorption degree of PBS/CS was 13.31%. It is obvious that the addition of CS reduced the water-resistance of the material. This was due to the presence of hydroxyl groups in natural CS resulting in higher moisture absorption. Previous studies on the moisture absorption properties of starch biopolymer substrates supported this result [48,49].

The Solubility degree of PBS/CS-IL was almost the same, around 5%, but the Water sorption degree was quite different. This result was consistent with the research results of Zdanowicz et al. [35]. The Water sorption degrees of PBS/CS-Cl, PBS/CS-Br, and PBS/CS-I were 10.27%, 7.85%, and 3.63%, respectively. Compared with PBS/CS, the water-resistance of PBS/CS-IL increased. This may be because IL interacted with the hydroxyl groups of starch itself, reducing the number of hydrogen bonds in the system, and CS no longer formed hydrogen bonds with water molecules. At the same time, as [BMIM][Cl], [BMIM][Br], [BMIM][I] gradually increased the plasticizing effect of CS, the water-resistance of the corresponding composite materials gradually increased.

## 4. Conclusions

In this work, PBS/CS and PBS/CS-IL were prepared and characterized. PBS/CS-IL obtained by adding different IL have obvious differences in the structure and performance of the materials. DSC results revealed that CS interfered with the crystallization of PBS. After IL was added, the crystallinity of PBS/CS-IL was further reduced. XRD results also confirmed this trend. In the FTIR spectra, we found that IL could make the hydroxyl absorption peak of the composite material move to the high wavenumber direction, and the sequence of movement follows PBS/CS < PBS/CS-Cl < PBS/CS-Br < PBS/CS-I. This showed that the plasticizing effect of IL on the PBS/Starch blends material was [BMIM][Cl] < [BMIM][Br] < [BMIM][I]. The tensile test also confirmed this trend. Among them, PBS/CS-I has the best tensile effect. Compared with PBS/CS, PBS/CS-I elongation at break was increased by more than 3 times. The water absorption test also showed that the water-resistance of PBS/CS-IL was improved.

## CRedit authorship contribution statement

**Jin Xu:** Writing-Original draft preparation; Writing-Review & Editing; Investigation.

**Yanfei Chen:** Investigation.

**Yuanfang Tian:** Investigation.

**Zhaojie Yang:** Investigation.

**Zhixin Zhao:** Investigation.

**Wenhao Du:** Investigation.

**Xi Zhang:** Conceptualization; Methodology; Supervision; Writing-Review & Editing.

## Acknowledgements

This research was funded by Applied Basic Research Project of Sichuan Province, [grant number: 2017JY0247].

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