

Preparation and Characteristics of Paper-based Biodegradable Plastics

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The aim of this work was to make biodegradable plastics from renewable resources. Paper-based biodegradable plastics were produced *via* a sol-gel process by using zinc chloride solution. The optimum conditions were a zinc chloride concentration of 65%, reaction temperature of 70 °C, reaction time of 5 s, aging time of 3 h, and glycerol concentration of 10%. Fourier transform infrared spectroscopy (FT-IR) and wide-angle X-ray diffraction (XRD) revealed that no chemical reaction occurred and the crystal form of the cellulose remained cellulose I, but the degree of crystallinity decreased. Compared to other biodegradable plastics, these paper-based biodegradable plastics had better mechanical properties and greater biodegradability.

Keywords: Cellulose; Gel fibers; Biodegradable plastics; Zinc chloride

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INTRODUCTION

Plastics have been widely used because of their mechanical properties and features such as low cost, durability, and processability (Gómez and Michel Jr. 2013). Most plastics are made from synthetic or semi-synthetic long chain polymeric molecules and are resistant to biological degradation (Shah *et al.* 2008). The widespread utilization of plastics has posed a serious environmental pollution problem (Ishigaki *et al.* 2004; Leejarkpai *et al.* 2011). Therefore, more and more researchers are focusing on developing eco-friendly materials to produce biodegradable plastics. The biodegradable materials can be classified as renewable sources (polysaccharides and proteins), chemically synthesized (polyacids and polyesters), microbial synthesized (bacterial cellulose), and biopolymer blends (Salmoral *et al.* 2000; Satyanarayana *et al.* 2009; Li *et al.* 2014; Urtuvia *et al.* 2014). Several biodegradable plastics have been introduced to the market, such as starch-based and polycaprolactone plastics. However, biodegradable plastics directly produced from cellulose are rarely reported.

Cellulose is the most abundant natural resource and has been widely used in many fields because of its low cost, biodegradability, biocompatibility features, *etc.* Some applications are based on dissolution of cellulose, and many solvent systems have been developed (Zhang *et al.* 2005; Jin *et al.* 2007; Lindman *et al.* 2010; Casarano *et al.* 2011; Lu and Shen 2011; Medronho and Lindman 2014a). These utilizations are mostly based on the complete dissolving and regenerating process. Nevertheless, partial dissolution of cellulose provides another method for potential application (Mathew *et al.* 2012; Zhu *et*

al. 2013). By partially dissolving the cellulose, followed by a regeneration process, the cellulose fibers will keep their fibrous shape and be covered by regenerated fibrillar fibers. Massive hydrogen bonds will form between fibers. That is, there is a potential opportunity to make materials from cellulose that have excellent mechanical properties and biodegradability.

In this study, zinc chloride solution was used as the solvent for cellulose. Paper-based biodegradable plastics (PBP) were produced by partially dissolving the cellulose and regenerating it *via* a sol-gel process. During this process, the structure of the fibers remained intact and the regenerated fibrillar gel fibers provided excellent mechanical properties. Furthermore, the optimum preparation conditions were investigated, and the properties of PBP were tested.

EXPERIMENTAL

Materials

Raw paper was composed of cotton fibers with a beating degree of 35 SR. The properties of the raw paper were as follows: basis weight, 115 g/cm²; thickness, 0.15 mm; and apparent density, 0.77 g/cm³. The zinc chloride solution was prepared by dissolving solid zinc chloride in distilled (DI) water. The zinc chloride was AR grade and produced by Shanghai Xinbao Chemical Reagent Co., Ltd. The plasticizer was glycerol, which was AR grade and produced by Shanghai Jiuyi Chemical Reagent Co., Ltd.

Methods

Preparation of paper-based biodegradable plastics

The raw paper was dried in an oven at 105 °C for 6 h to remove the moisture content. The solid zinc chloride was added to DI water and stirred for 30 min. Several solution concentrations were investigated, at 50 wt%, 60 wt%, 65 wt%, 70 wt%, and 75 wt%. Zinc chloride solutions in the glass culture dish were heated in a digital thermostat water bath to the desired temperatures (55, 65, 70, 75, or 80 °C). The raw paper was immersed into the zinc chloride solution for various lengths of time (1 s, 5 s, 10 s, 20 s, 30 s). Then, the resulting paper was taken out, excessive liquid on the surface was wiped away, and the paper was then exposed to the air for aging (0, 1, 2, 3, 4, 6, 8 h). Afterwards, the paper was immersed into DI water at room temperature to change from sol to gel and ions removal. After 60 min of gelation and washing, the paper was transferred into a plasticizer solution for another 60 min to convert the paper into paper-based biodegradable plastic. The overall preparation process is illustrated in Fig. 1.

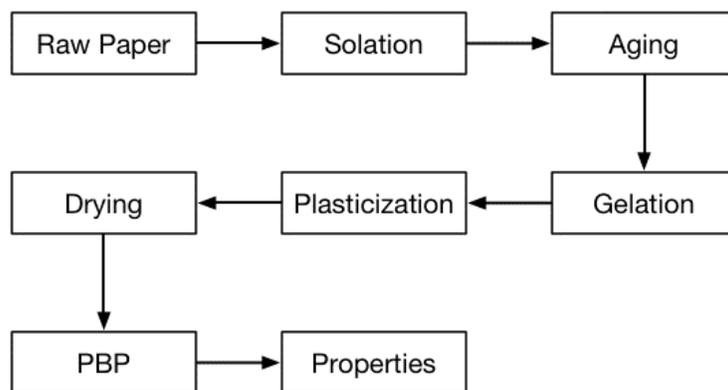


Fig. 1. Scheme for preparation of PBP

Cellulose dissolution rate

The cellulose dissolution rate was used to evaluate the cellulose dissolving solvent and optimize the dissolving conditions. The raw paper was pre-dried, and the initial weight was recorded as W_1 . The raw paper was immersed into the zinc chloride solution at specific conditions and was then taken out and washed with DI water to remove zinc chloride. The resulting sample was dried in an oven at 105 °C for 6 h, and the weight was recorded as W_2 . The cellulose dissolution rate was calculated using the following equation.

$$\text{Cellulose Dissolution Rate (\%)} = (W_1 - W_2)/W_1 \times 100 \quad (1)$$

Scanning electron microscopy (SEM) analysis

The PBP was frozen in liquid nitrogen, fractured, and vacuum dried. The sample was sputtered with gold and then examined with a FEI Quanta 200 device (USA), operated at 20 kV.

Fourier transform infrared (FT-TR) analysis

The dried PBP powders were embedded in KBr pellets and were analyzed using a Nicolet IR-360 FTIR spectrometer from Thermo Nicolet (wavenumber range from 4000 to 500 cm^{-1}).

XRD analysis

X-ray diffraction (XRD) measurements were conducted at a scanning speed of $2\theta = 0.2^\circ/\text{min}$ using a Rigaku Geigerflex RADIIB diffractometer with Ni-filtered Cu K α radiation ($\lambda = 0.15418 \text{ nm}$).

Mechanical properties analysis

The mechanical properties of PBP were determined following the standard test methods in the Chinese plastic industry (tensile strength: GB/T 1040.1-2006 (2006); elongation: HG2-163-65 (1965); water absorption: GB/T 1034-2008 (2008); folding numbers: GB3904-83 (1983)). All mechanical properties tests were performed in duplicate.

Biodegradability analysis

The biodegradability was characterized by outdoor burial test, and the biodegradable properties of PBP were measured with respect to the tensile strength and mass loss. Two PBP samples were cut with sample sizes of 10 mm × 10 mm and 180 mm × 200 mm. The 10 mm × 10 mm sample was used for the mass loss measurement, and the 180 mm × 200 mm sample was used for the tensile strength testing. The samples were dried in an oven, and the initial dry mass was recorded. The soil burial testing was conducted inside a cabinet at room temperature, and the soil used in the experiments was taken from local flowerbeds (Nanjing Forestry University, Nanjing, Jiangsu). The samples were buried at a depth of 100 mm. A set volume of non-chlorinated tap water was added to the cabinet every three days to maintain the moisture content of the soil.

The samples were removed from the soil weekly and carefully washed and dried in air. The 10 mm × 10 mm sample was weighed to calculate the mass loss, and a 15 mm × 20 mm sample was cut from the 180 mm × 200 mm sample to measure the tensile strength loss according to GB 1040-79,

$$\text{Mass loss (\%)} = [(W_0 - W_s)/W_0] \times 100, \quad (2)$$

where W_0 is the sample initial weight, and W_s is the sample weight after biodegradation.

RESULTS AND DISCUSSION

Parameters of PBP Manufacture

Effect of zinc chloride concentration

It has been reported that the water content has a significant impact on the dissolution of molten salt hydrates and concentrated aqueous salt solutions (Leipner *et al.* 2000; Lu and Shen 2011). To find the best condition for PBP preparation, different concentrations of zinc chloride solutions were investigated at 70 °C for 5 s. As shown in Fig. 2, with increasing zinc chloride concentration, the cellulose dissolution rate increased dramatically, indicating the great impact of zinc chloride concentration on cellulose dissolution. When the concentration was lower than 60%, the cellulose was barely dissolved, whereas when the concentration increased to the range of 60% to 70%, the cellulose dissolution rate increased from 5.2% to 79.5%, which means that most of the cellulose had been dissolved in the solution. In this study, the objective was to keep the cellulose fibers skeleton structure intact, such that the regenerated fibrillar gel fibers can act as an adhesive to provide good mechanical properties. Thus, completion of the dissolving process was not expected. When the concentration was 65%, the cellulose dissolution rate was 25.3%. The cellulose was partially dissolved, and the other part was swollen at this concentration (Fischer *et al.* 2003). Thus, the optimum zinc chloride concentration was determined to be 65%.

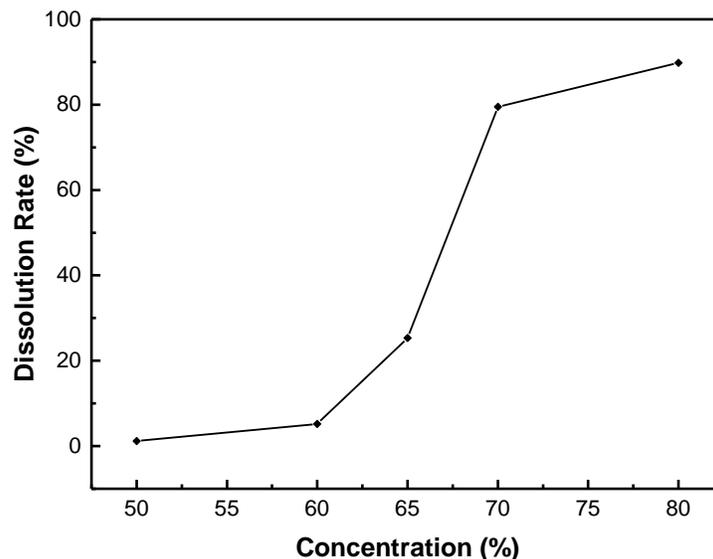


Fig. 2. Effect of zinc chloride concentration on cellulose dissolution

Effect of reaction time

A suitable reaction time is necessary for cellulose swelling and dissolution. If the reaction time is too short, the cellulose will not be swollen completely, whereas a long reaction time may cause cellulose decomposition. Neither outcome is desirable. Figure 3 displays the cellulose dissolution rate at different reaction times (1 s, 5 s, 10 s, 20 s, 30 s) at 70 °C in 65% zinc chloride solution. The dissolution rate increased sharply from 1 s to 10 s. After 10 s, the dissolution rate decreased. Zinc chloride molecules in the solution will penetrate into the amorphous and crystalline regions, which break the intra- and inter-molecular hydrogen bonds and cause the swelling and dissolution of the cellulose (Zhu *et al.* 2013). The breakage of hydrogen bonds mostly occurred in the amorphous region in the first 10 s. Therefore, the dissolution rate increased sharply after 10 s. From 10 s to 30 s, the zinc chloride molecules continuously saturate the crystalline region. Compared to the amorphous region, the hydrogen bonds in the crystalline region are relatively stable and hard to break, but the cellulose eventually can be completely swollen and dissolved. At 5 s, the dissolution rate was 20.2%, as discussed above. Five seconds was therefore chosen as the best reaction time.

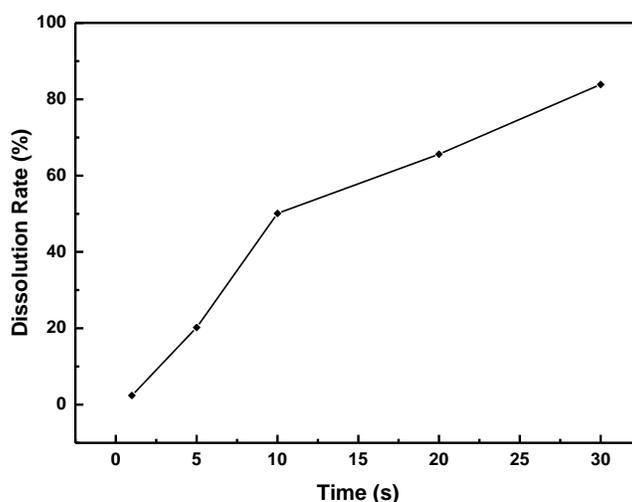


Fig. 3. Effect of reaction time on cellulose dissolution

Effect of reaction temperature

In addition to the zinc chloride concentration and reaction time, temperature can affect cellulose swelling and dissolving as well (Medronho and Lindman 2014b). The cellulose dissolution behavior at different temperatures (55 °C, 65 °C, 70 °C, 75 °C, 85 °C) was investigated, and results are displayed in Fig. 4. The cellulose dissolution rate was negligible when the reaction temperature was below 65 °C but it increased sharply from 65 to 75 °C. When the reaction temperature was above 75 °C, the rate of cellulose dissolution tended to level off. It is not hard to draw the conclusion that reaction temperature has a significant influence on the dissolving process. The driving force of cellulose dissolving was strengthened with increasing temperature in zinc chloride solution (Medronho and Lindman). Most of the cellulose was dissolved (70%) when the temperature was 75 °C; therefore, the growth rate slowed when the temperature was over 75 °C. In this study, the cellulose dissolution rate was 21.7% at 70 °C; thus, 70 °C was chosen as the optimum reaction temperature with zinc chloride concentration 65% and reaction time 5 s.

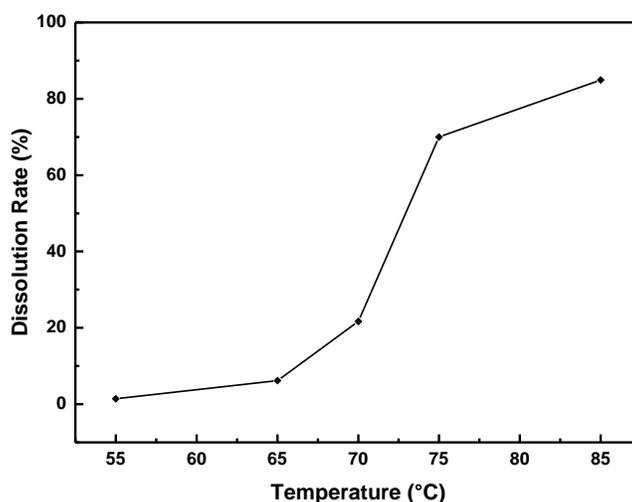


Fig. 4. Effect of reaction temperature on cellulose dissolution

SEM analysis after gelation

SEM was used to characterize the surface morphology of the PBP prepared at the optimum conditions discussed above. Micrographs taken with magnifications of 500 and 1500 are shown in Fig. 5. The skeleton structure of the cellulose fibers remained intact, and the fibrillar gel fibers were regenerated among the skeleton fibers after gelation. The remaining cellulose fibers constituted a three-dimensional network structure, and the fibrillar gel fibers were distributed as adhesive. Massive hydrogen bonds were formed to provide excellent mechanical properties (Zhu *et al.* 2013). In addition, in the presence of a considerable amount of micropores, soil water and microbes can easily penetrate into the PBP and cause degradation.

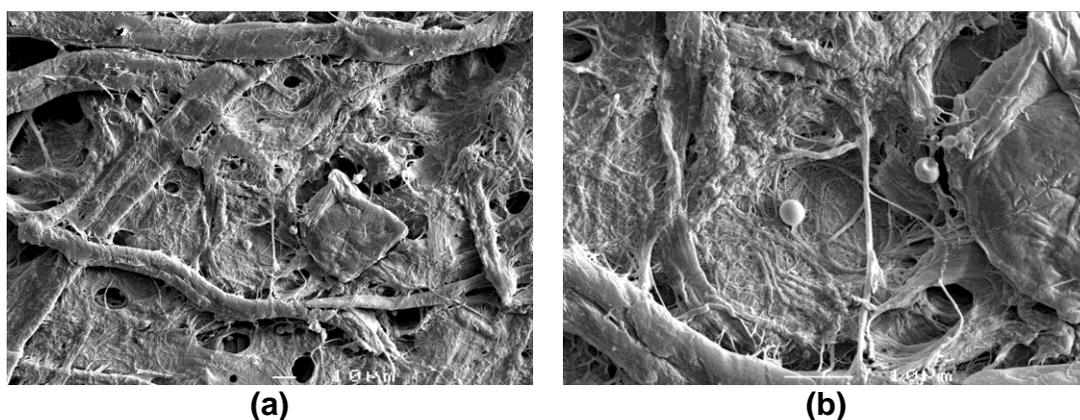


Fig. 5. SEM photomicrographs of PBP after gelation

Effects of aging time

The aging process is indispensable for further mild swelling and dissolving of cellulose. The paper was taken from the zinc chloride solution and exposed in air for different aging times (0, 1, 2, 3, 4, 6, 8 h). The effect of aging time on the tensile strength, burst strength, and elongation of PBP was investigated, and results are shown in Figs. 6. PBP exhibited the best tensile strength, burst strength, and elongation after aging for 3 h. During aging from 3 h to 8 h, the tensile strength decreased from 9.45 to 7.77 MPa; the burst strength decreased from 410 to 325 kPa; and the elongation decreased from 170.1% to 125.6%. It is possible that the zinc chloride molecules continuously and mildly saturated the cellulose when the paper was exposed to air.

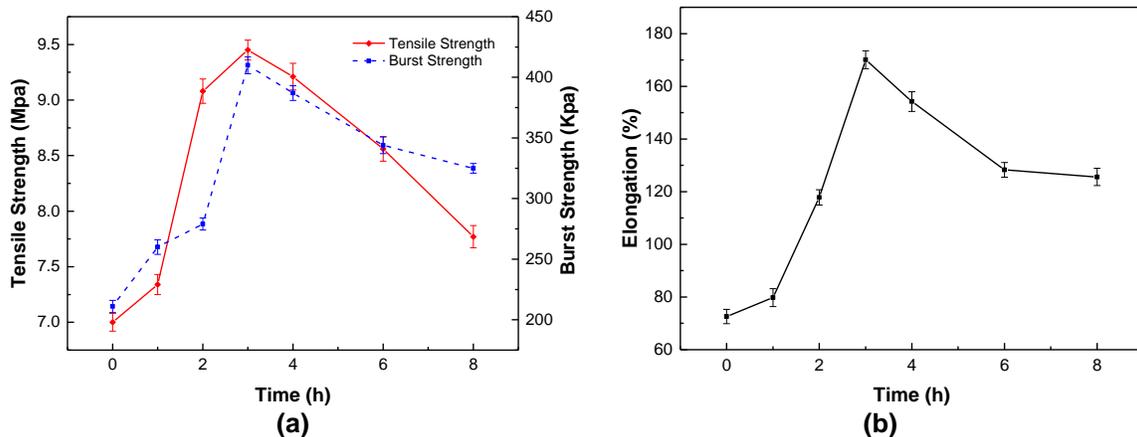


Fig. 6. Effect of aging time on tensile strength, burst strength, and elongation of PBP

When the aging time was increased, more and more cellulose fibers were swollen and dissolved, and the skeleton structure of cellulose fibers was destroyed, leading to decreases in the mechanical properties of PBP. Thus, the optimum aging time was determined to be 3 h.

Effects of plasticizer

Without the plasticization process, the PBP was too brittle to be used as a plastic because a large amount of hydrogen bonds were formed, preventing its use as a substitute for commercial plastics. Therefore, glycerol was used as a plasticizer, and glycerol/ethanol solution was prepared to reduce the viscosity for better penetration. The effects of various contents of glycerol were investigated, with results shown in Figs. 7. The PBP shrank during the drying process, which caused the tensile strength to increase even without glycerol; however, the PBP was brittle, which leads to low burst strength and elongation capability. As shown in Fig. 7, the tensile strength continually decreased with increasing glycerol concentration, whereas the burst strength and elongation reached the maximum value when the glycerol concentration was 10% (tensile strength was 13.7 MPa, burst strength was 438 kPa, and elongation was 181.8%). Thus, the optimum glycerol concentration was determined to be 10%.

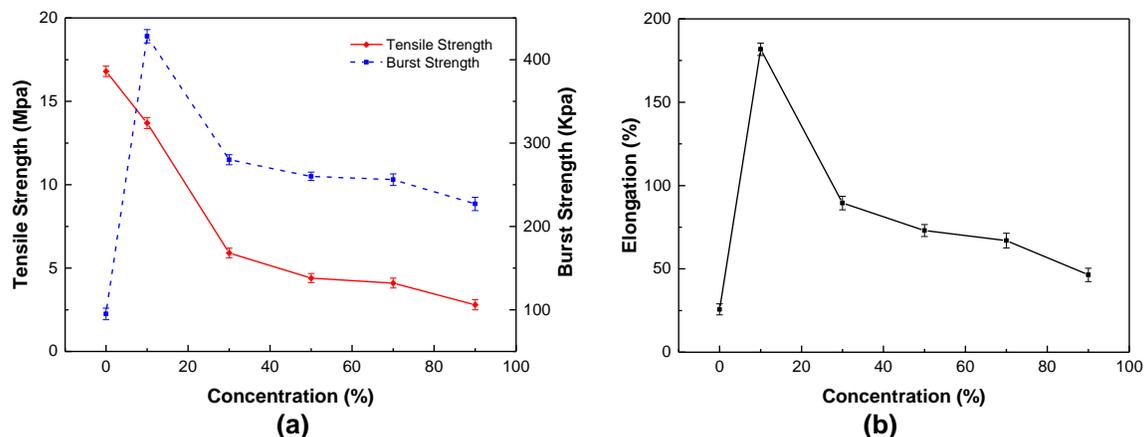


Fig. 7. Effect of glycerol concentration on tensile strength, burst strength, and elongation of PBP

Characterization of Paper-based Biodegradable Plastics

Fourier transform infrared spectroscopy (FT-IR)

FT-IR was used to determine the chemical changes in cellulose. The spectra of raw paper and PBP are displayed in Fig. 8. The FT-IR spectra of PBP were similar to that of the raw paper, which indicated that the cellulose structures had no remarkable differences between them. The stretching vibration of strong hydrogen-bonded hydroxyl groups was observed at approximately 3600 to 3000 cm^{-1} for both spectra. The maximum absorption peak of strong $-\text{OH}$ stretching was at 3423 cm^{-1} . The band at 2920 cm^{-1} , assigned as $-\text{CH}$ stretching, and the peak at 1635 cm^{-1} were observed because of water in the amorphous region. The bands at 1417, 1160, and 1113 cm^{-1} indicated that the cellulose crystal structure of both raw paper and PBP was cellulose I (Carrillo *et al.* 2004). Therefore, it was concluded that no significant extent of chemical reaction occurred and no cellulose derivative was produced during the gelation process.

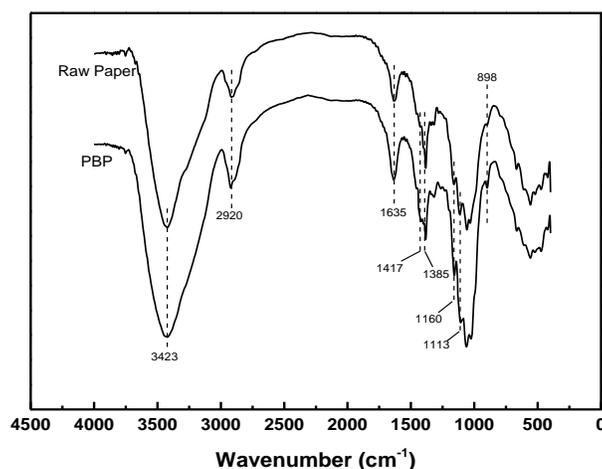


Fig. 8. FT-IR spectra of PBP and raw paper

X-ray diffraction (XRD)

The XRD patterns of raw paper and the PBP are shown in Fig. 9. The raw paper showed three strong peaks, at 15.1°, 16.5°, and 22.8°, corresponding to the {101}, {10 $\bar{1}$ }, and {002} orientations of the typical cellulose I structure. The PBP also showed three strong peaks, at 14.8°, 16.4°, and 22.5°, indicating that the cellulose crystal also belongs to cellulose I. As expected, the crystal structure of cellulose did not change during the sol-gel process, which is in agreement with the FTIR results. Furthermore, according to the XRD data, the cellulose crystallinity of PBP decreased to 74.8% compared to 81.6% of the raw paper, indicating a decrease in cellulose crystallinity when using the zinc chloride solution (Zhang *et al.* 2005).

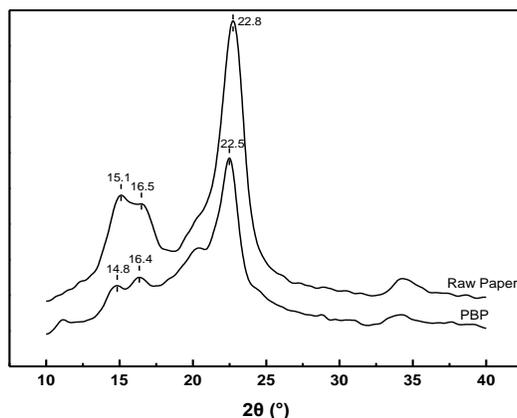


Fig. 9. XRD patterns of raw paper and PBP

Comparison of mechanical properties of PBP and other biodegradable plastics

The mechanical properties of PBP were tested using the standard test methods in the plastic industry to compare with corn-based biodegradable plastics (CBP) and starch-based biodegradable plastics (SBP). As shown in Table 1, the PBP had better tensile strength, elongation, and folding strength compared to CBP and SBP. As discussed above, the formation of large amounts of hydrogen bonds during the gelation process and the three-dimensional network structure led to excellent mechanical properties for the PBP. Although the low water absorption value of PBP may cause a low degradation rate, the degradability is still dominated by cellulose itself.

Table 1. Mechanical Properties of PBP, CBP, and SBP

	Tensile Strength (MPa)	Elongation (%)	Water Absorption (%)	Folding Strength (Times)
PBP	13.7±0.4	181.8±3.7	5±1	800±8
CBP	7.5±0.3	12.1±1.9	10±2	30±2
SBP	10.1±0.3	27.0±2.3	14±2	30±3

Values are mean ± standard deviation.

Biodegradability analysis

The biodegradability was investigated with respect to the mass loss and tensile strength decrease of the PBP, and the results are displayed in Fig. 10. The PBP exhibited excellent biodegradability; the mass loss reached 57.3% after PBP was buried in soil for nine weeks. The microorganism destroyed the structure and reduced the strength of hydrogen bonds, so that the cellulose decomposed gradually. The tensile strength was also measured after nine weeks, showing a decrease to 0.46 MPa. The mass loss curve

implies that the PBP keeps degrading with the extension of time. Accordingly, we can speculate that the PBP is completely biodegradable.

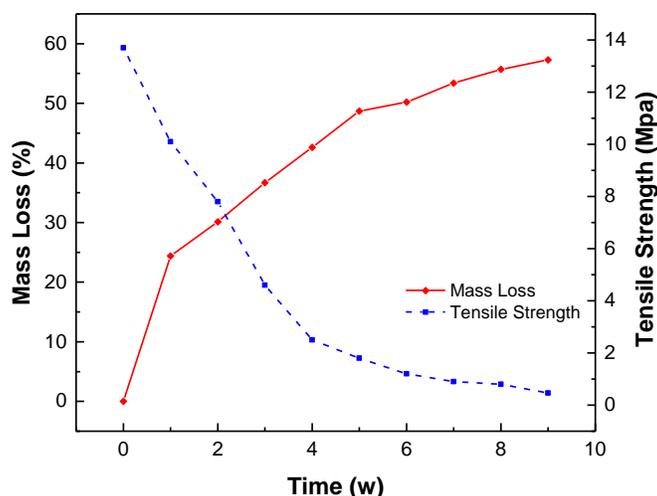


Fig. 10. Mass loss and tensile strength decrease with degradation time

CONCLUSIONS

1. Paper-based biodegradable plastics were prepared *via* a sol-gel process using a zinc chloride solution. The optimum conditions were determined to be a zinc chloride concentration of 65%, reaction temperature of 70 °C, reaction time of 5 s, aging time of 3 h, and glycerol concentration of 10%.
2. The PBP showed excellent mechanical properties compared to other biodegradable plastics and great biodegradability.
3. FT-IR and XRD results revealed that the cellulose crystalline remained cellulose I, whereas the crystallinity decreased.
4. This method provides a new option for producing environmentally friendly biodegradable plastics.

ACKNOWLEDGMENTS

The authors are grateful for the financial support of the National Natural Science Foundation of China, Grant No.031105010 and the Priority Academic Program Development of Jiangsu Higher Education Institution (PAPD)

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Article submitted: September 29, 2014; Peer review completed: January 8, 2015;

Revisions accepted: March 16, 2015; Published: March 31, 2015.

DOI: 10.15376/biores.10.2.2982-2994