Research Article

Preparation of Polyvinyl Alcohol/Xylan Blending Films with 1,2,3,4-Butane Tetracarboxylic Acid as a New Plasticizer

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Miscible, biodegradable polyvinyl alcohol (PVA)/xylan blending films were firstly prepared in the range of the PVA/xylan weight ratio from 1:2 to 3:1 by casting method using 1,2,3,4-butane tetracarboxylic acid (BTCA) as a new plasticizer. The properties of blending films as functions of PVA/xylan weight ratio and BTCA amount were discussed. XRD and FT-IR were applied to characterize the blending films. Experimental results indicated that tensile strength (TS) and elongation at break (EAB) of blending films decreased along with the decrease of the PVA/xylan weight ratio. Both of TS and EAB firstly increased and then decreased as the amount of BTCA was increased. More importantly, blending films were biodegraded almost by 41% with an addition of 10% BTCA in blending films within 30 days in soil. For all hydroxyl functionalized polymers (xylan and PVA), their molecular interactions and miscibility with BTCA endowed blending films with the biocompatibility and biodegradability. Therefore, these blending films are environmentally friendly materials which could be applied as biodegradable plastics for food packaging and agricultural applications.

1. Introduction

In recent years, to meet the requirements for environmental protection, multifunctional utilization of natural resources, and increased pressure from related strict laws, efforts have been made to develop biodegradable composite plastic products by incorporating biocompatible polymers as an alternative to conventional synthetic plastic materials derived from petroleum [1, 2]. Moreover, there is an increasingly important trend to explore natural renewable raw materials for the food industries and nonfood industries owing to their sustainable and biodegradable features.

Xylan is derived from hemicellulose which is one of the three primary components of the plant cell wall [3] and many researchers paid extensive attention to the exploration of xylan because of its abundance and biodegradability. Hemicelluloses (mainly xylans and mannans) were used as sustainable packaging materials and more hydrophobic films with the low water vapor and oxygen permeability could be obtained [4, 5]. Xylan films modified by long-chain anhydride were prepared [6]. Modified xylan had better film-forming performance and the tensile strength had increased and moisture-sensitive properties had been lessened due to long carbon chains modification. Xylan has poor film-forming ability and pure xylan films were brittle due to the hydroxyl groups present in each of their repeating units [7]. To solve this problem, different types of plasticizers such as oligosaccharides, polyols, some organic acids, lipids, and ether were added in order to improve mechanical performance of biopolymers films [8–11]. It was found that mechanical properties of xylan-based films were strengthened by blending with nanosized particles [5]. More hydrophobic butylated xylan films were prepared by Peresin et al. [11]. The water sensitivity and wetting behaviour of the xylan derivatives were altered during etherification. Mikkonen et al. [12] studied arabinoxylan films plasticized with glycerol and sorbitol; they found that an increase in the total plasticizer content resulted in more permeable films.

Polyvinyl alcohol (PVA) is excellently fit for blending with natural polymers as it is highly polar and controllable in water solutions [13]. Additionally, it is a biocompatible synthetic crystalline polymer with high tensile strength and flexibility [14]. Several investigations have been carried out on blending PVA with other biopolymers, such as PVA/chitosan [15], PVA/starch [16, 17], and PVA/gelatin [18]. Modification and biocompatibility of PVA/chitosan films were investigated by Zhuang et al. [15]. It was observed that the addition of PVA could improve the film's flexibility and wettability. All prepared PVA/chitosan films were biocompatible. Moreover, the tensile strength (TS) of the PVA/starch films increased about 60% without additives, while EAB decreased about 420.5% [17]. And the films were degraded by about 45–65% after 165 days in soil. Thus, the blending of PVA and natural polymers could improve the properties of natural polymers films for widening the application of films. However, few researchers have made attempts to study biomaterial films by blending PVA with xylan.

1,2,3,4-Butane tetracarboxylic acid (BTCA) is one of polycarboxylic acids (PCAs). BTCA as a crosslinking agent was used to produce a cotton fabric, and the treated fabric showed a reasonable hydrophobicity [19]. Water-resistant hemicelluloses (HC) films were prepared with about 10-11% of BTCA [20]. The water vapor permeability of HC films with a modification of BTCA reduced about twice the untreated films. The effects of BTCA on hydrophobic cellulose fabric by scanning electron microscopy were investigated and the better durable fabric was obtained [21]. So the addition of BTCA could have important effects on the properties of films and fabrics.

In view of the issue mentioned above, the objective of our study was to prepare miscible and biodegradable PVA/xylan blending films by casting method with the addition of BTCA as a plasticizer for improving the properties of blending films. The influences of the PVA/xylan weight ratio and BTCA amounts on the blending films properties were discussed. The mechanical properties, water vapor permeability, the degree of solubility, thermal stability, and degradability were evaluated for PVA/xylan blending films.

2. Experimental

2.1. Materials. Beech wood xylan ($M_w \sim 130,000$ g/mol) and PVA (M_w of 146,000~186,000 g/mol) were purchased from Sigma Aldrich (Germany) and used without further purification. BTCA was supplied by Aladdin Reagent Company Limited (Shanghai, China). Anhydrous calcium chloride ($CaCl_2$) and sodium chloride (NaCl) were of analytical-reagent grade and obtained from Guangzhou Chemical Reagent Factory (Guangzhou, China). Deionized water was used in the preparation of the blending films.

2.2. Blending Films Preparation. The PVA/xylan blending films were prepared by solution casting method. A predetermined amount of PVA was added to ultrapure water. The mixture was stirred for 0.5 h at room temperature and then heated at 95°C for 1.5 h. After PVA was dissolved completely,

Table 1: Detailed composition and abbreviations of PVA/xylan blending films.

Samples	PVA : xylan	BTCA (%)
P3X1	3 : 1	20
P2X1	2 : 1	20
P1X1	1 : 1	20
P1X2	1 : 2	20
PX0	3 : 1	0
PX5	3 : 1	5
PX10	3 : 1	10
PX15	3 : 1	15
PX25	3 : 1	25
PX30	3 : 1	30

xylan was added. After 30 minutes, BTCA as a new plasticizer was added in the mixture solution. The resulting solution reacted at 75°C for 4 h and then poured onto a $110 \times 110 \times 7$ mm teflon mould. Water was dried slowly in a ventilated oven at 40°C overnight. All films were obtained with a uniform thickness and were stored at 23°C with 50% RH at least 48 h prior to all measurements. The blending films with different PVA/xylan weight ratio and BTCA amounts were shown in Table 1.

2.3. Method of Characterization

2.3.1. Tensile Strength (TS) and Elongation at Break (EAB). TS and EAB of films were evaluated using a tensile testing machine (Instron Universal Test Machine Model 5565, USA) fitted with a 100 N load cell. Five samples (110 mm length, 150 mm width) of each film were cut by a paper cutter (FQ-QZD15, Sichuan, China). The crosshead speeds of 30 mm and 20 mm/min were used for testing the mechanical properties. The maximum load and the final extension at break were used for calculation of TS and EAB, respectively.

2.3.2. Water Vapor Permeability (WVP). The WVP assessment was determined according to a gravimetric method and performed as described by Kayserilioğlu et al. [22] with minor modification. Film specimens were clamped on the top of polyethylene bottles containing 3 g anhydrous $CaCl_2$ to maintain 0% RH inside the bottle, followed by sealing the film over the edge of bottle with vaseline. And then the bottles were located in a dryer at 23°C and 75% RH. The RH was maintained by placing 500 mL of saturated NaCl solution in the bottom of the dryer. The bottle was weighed every 24 h, and WVP value was calculated by

$$\text{WVP} = \frac{\Delta w \times L}{(\Delta t \times A)}, \tag{1}$$

where WVP was water vapor permeability ($g \cdot \mu m \cdot cm^{-2} \cdot h^{-1}$). $\Delta w / \Delta t$ was the gain rate of bottle (g/h). A was exposed area of the film (cm^{-2}). L was the mean thickness of the film (μm).

2.3.3. The Water Absorption (WA), Solubility (S), and Water Content (WC). A certain quality (m_0) of oven-dried

PVA/xylan blending films was cut into $2 \times 2 \, \text{cm}^2$ and dipped in 20 mL ultrapure water for 24 h at room temperature. Then we wiped off the excess moisture in the surface of the swollen samples and weighed the weight (m_1). Afterward, the soaked films were dried again at 105°C to the constant weight (m_2). The water absorption (WA) and solubility (S) are calculated with

$$\text{WA} = \frac{(m_1 - m_2)}{m_0},$$
$$S\,(\%) = \frac{(m_0 - m_2)}{m_2} \times 100. \tag{2}$$

Water content was determined at 23°C and 50% RH for two days when the weight of the films was regarded as m. Then the samples were dried at 105°C to reach constant weight (m_3). Water content (WC) was calculated as follows:

$$\text{WC}\,(\%) = \frac{(m - m_3)}{m_3} \times 100\%. \tag{3}$$

2.3.4. Thermogravimetric Analysis (TGA). A simultaneous thermal analyzer (TGA Q500, TA Instruments, New Castle, USA) was used for the thermogravimetric analysis of blending films. Film samples of approximately 9~11 mg were cut into pieces and heated at a rate of 10°C/min from room temperature to 600°C under a nitrogen atmosphere (a flow rate about 20 mL/min). All films were conditioned at 23°C/50% RH for one week before TGA.

2.3.5. FTIR Spectra. Film samples were cut into pieces (10 mm × 10 mm) and dried in the infrared drying oven. FTIR spectra were measured on a Fourier transform spectrophotometer (Nicolet 750, Florida, USA). The absorbance spectrum (4000–400 cm^{-1}) was acquired at 4 cm^{-1} resolution and recorded for a total of 32 scans, using Attenuated Total Reflectance technique (see Figure 5).

2.3.6. X-Ray Diffraction. X-ray patterns of PVA, xylan, and PVA/xylan blending film were analyzed using an X-ray diffractometer (Bruker, model D8 advance) with Cu Kα radiation at a voltage of 40 kV and 40 mA. The measurements were made with scattering angles of 3–40° and a scanning speed of 2°/min. The samples were dried and stored in a desiccator before testing.

2.3.7. The Degradability of Blending Films in Soil. The degradability of blending films was determined by soil burial degradation. 3×3 cm squares were cut from the cast film and buried in the soil at the depth of 10 cm in a gardening pot. The pot was exposed to atmospheric conditions for 30 days. The time required for blending films to disintegrate was recorded. To determine the weight loss in specimens, films were first dry-cleaned with a brush and the weight was recorded. A specimen of each sample was quickly cleaned and then the sample was dried in an oven at 70°C to constant weight and
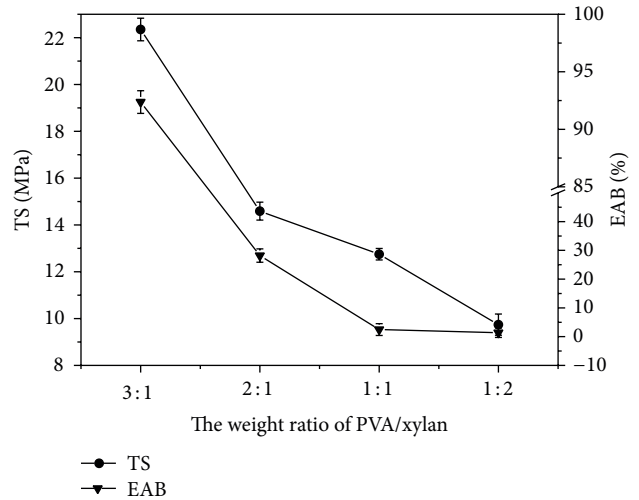

Figure 1: The effect of the weight ratio of PVA/xylan on TS and EAB of blending films with 20% BTCA.

allowed to equilibrate in desiccators prior to weighing. The degradation degree (the weight loss) was determined by

$$\text{Weight loss}\,(\%) = \frac{m_{\text{ini}} - m_{\text{dry}}}{m_{\text{ini}}} \times 100\%, \tag{4}$$

where m_{ini} is the initial weight of the film sample before burial and m_{dry} is the dry weight of the sample after burial for known days.

3. Results and Discussion

3.1. Mechanical Properties. The thickness of blending films which has a significant influence on mechanical properties of the PVA/xylan blending films was measured by Lorentzen & Wettre thickness gauge (Sweden) for precise specimens (55–60 μm). The effect of the weight ratio of PVA/xylan on TS and EAB of the blending films with the addition of 20% BTCA is shown in Figure 1. The results indicated that TS and EAB of the blending composite films decreased obviously along with the decrease of the weight ratio of PVA and xylan from 3:1 to 1:2. The reason explained was that PVA has high tensile strength with hydrogen bonds and xylan is brittle and amorphous with its acetyl and feruloyl groups, as well as α–D–glucopyranosyl uronic acid or 4–O–methyl ether [4, 10, 23]. The values of TS and EAB reached to 22.4 MPa and 92.4%, respectively, as the weight ratio of PVA and xylan was 3:1.

Figure 2 shows the effect of BTCA content on TS and EAB of blending films at the PVA/xylan weight ratio of 3:1. When BTCA content was 0%, the lowest value of EAB was obtained while relatively high TS value was present. With increasing BTCA content to 5%, a decrease in TS and an increase in EBA were observed. With a further increment of BTCA amount from 5% to 30%, both TS values and EAB increased first and then decreased in the range of 16.4–22.4 MPa and 45.5%–92.4%, respectively. It could be explained that polymer-polymer interactions strengthen intermolecular forces at the
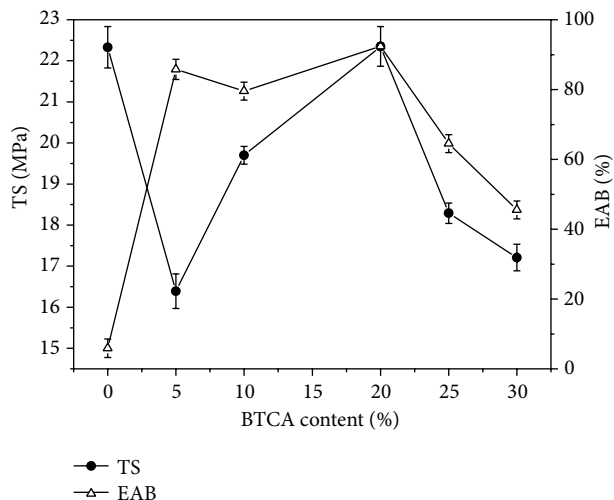
Figure 2: The effect of the BTCA content on TS and EAB of the blending films.

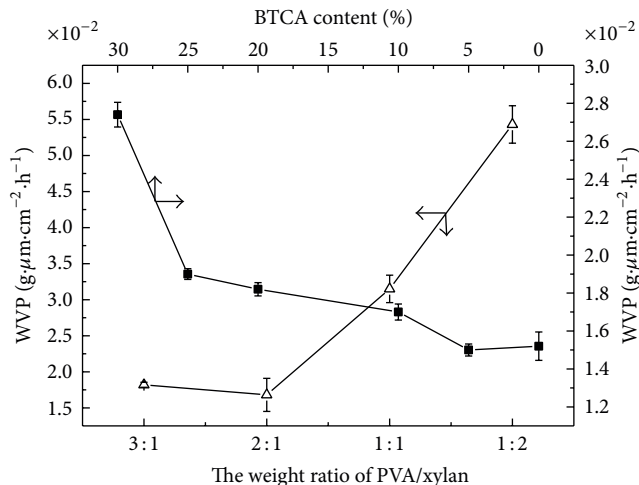Figure 3: The effect of the weight ratio of PVA/xylan and the BTCA content on WVP.

Table 2: The WA, S, and WC of all the PVA/xylan blending films.

Samples	WA	S (%)	WC (%)
P3X1	0.45	19.16	8.53
P2X1	0.62	22.35	10.53
P1X1	0.84	26.38	11.65
P1X2	0.93	30.15	12.31
PX0	1.30	37.29	7.44
PX5	1.18	26.74	11.62
PX10	1.07	26.76	16.59
PX25	0.34	25.51	9.12
PX30	0.31	31.22	9.27

beginning of adding BTCA. Subsequently, the formation of polymer-plasticizer interactions among the macromolecules restrained intermolecular mobility and revealed the decrease of TS and EAB [24]. When BTCA amount reached 20%, TS and EAB obtained their maximum values simultaneously which were higher than the PVA/polysaccharides (angico gum and/or cashew gum) blended films investigated by Silva et al. [25]. Moreover, the addition of BTCA provided the hydroxyl-rich chemicals with carboxyl functional groups. Yoon et al. [26] verified that additives of the films with hydroxyl and carboxyl groups were stronger and more flexible than those with only hydroxyl groups. Thus BTCA had the important impact on mechanical properties of PVA/xylan blending films.

3.2. WVP Measurement. WVP is an important parameter of film for potential applications such as food packaging. Figure 3 illustrates the effect of the weight ratio of PVA/xylan and the BTCA content on WVP. Clearly, WVP was decreased slightly and then increased sharply with the weight ratio of PVA/xylan changing from 3 : 1 to 1 : 2 at the 20% BTCA content. The lowest value was achieved to $0.017\,\text{g·μm·cm}^{-2}\text{·h}^{-1}$ when the PVA/xylan weight ratio was 2 : 1 (P2X1), and the highest value was $0.054\,\text{g·μm·cm}^{-2}\text{·h}^{-1}$ at the PVA/xylan weight ratio of 1 : 2 (P1X2). These results could be attributed to the changes in the functionality properties of the blending films prepared in the different PVA/xylan weight ratio. Clearly, BTCA had a remarkable influence on WVP. When the BTCA content was 5%, WVP of PVA/xylan blending films had the lowest values for $0.015\,\text{g·μm·cm}^{-2}\text{·h}^{-1}$ at the PVA/xylan weight ratio of 3 : 1. This meant that WVP decreased with addition of a little amount of BTCA. This result might be attributed to the water-resistant nature of BTCA. Nevertheless, the WVP increase was directly proportional to the BTCA content in the range of 10%–25% and then incremented sharply up to the highest values of $0.0274\,\text{g·μm·cm}^{-2}\text{·h}^{-1}$ at the content of 30% BTCA. The

higher plasticizer content resulted in more permeable films [27]. Mikkonen et al. [12] gained the same conclusions. This may be due to the formation of intermolecular interactions of BTCA and polyhydroxylic compounds with the increase of BTCA content.

As reported in the literature, García et al. [28] speculated many factors such as polymeric chain mobility and specific interaction between the functional groups of the polymers had effects on WVP. The decrease of WVP may be due to the formation of new interchain interaction. Ghasemlou et al. [29] decreased WVP and improved barrier properties of starch films up to 50% relative to the control sample by adding *Zataria multiflora* Boiss (ZEO) or *Mentha pulegium* (MEO). They thought that the hydrogen and covalent interactions between the starch network and these polyphenolic compounds might limit the availability of hydrogen groups to form hydrophilic bonds with water.

3.3. The WA, S, and WC Determination. The WA, S, and WC of all the PVA/xylan blending films are shown in Table 2. These data were used to further analyze barrier properties of blending films according to the experimental design previously presented (Table 1). When the BTCA content

maintained 20%, the WA increased gradually with the weight ratio of PVA and xylan from 3 : 1 to 1 : 2. Comparatively, the highest WA value reached to 1.30 for the blending films in the PVA/xylan weight ratio of 3 : 1 without the addition of BTCA. When the weight ratio of PVA and xylan was 3 : 1, WA values were decreased along with BTCA amount increasing from 5% to 30%. So the addition of BTCA could efficiently reduce WA of blending films. It was due to increasing moisture barrier properties with addition of BTCA. The solubility of blending films is a crucial influencing factor for potential application such as food packaging. In most cases, water solubility should be lower in order to improve the water resistance and integrity of films, especially for packaging foods [30]. As we can see from Table 2, water solubility increased steadily from 19.16% (P3X1) to 30.15% (P1X2) with 20% BTCA. The increase of the solubility can be explained by the increase of content of hydroxyl groups with the increase of xylan in the blending films. The weight ratio of PVA and xylan was chosen for 3 : 1 which was superior to others as the solubility decreased up to 19.16%, lower than results of 20% solubility studied by Alves et al. [18]. Then S decreased with increasing BTCA content from 0% to 25%. However, when BTCA content reached 30%, the water solubility had a sudden increase which might be due to increment of hydrophilicity of blending films with high concentration of BTCA. Additionally, water content increased gradually with increasing weight ratio of PVA and xylan. For plasticized films, the addition of 20% BTCA to blending films (P3X1) was able to obtain relatively lower water content for 8.53%. This is interpreted as a result of interactions between BTCA and the PVA/xylan composite film matrix, which reduces in the film's affinity for water and limits the accessibility of water molecules in the films [31]. With a further increase of BTCA concentration, the film matrix exposed more hydroxyl groups and increased water uptake. Unplasticized samples had lower water uptake (7.44%).

3.4. Thermogravimetric Analysis (TGA).

Thermogravimetric analysis is a standard technique to determine the composition or thermal stability of materials. The results of TGA and DTG curves of PVA/xylan blending films with different BTCA contents and PVA/xylan weight ratios are illustrated in Figure 4. The pure PVA/xylan films (PX0) exhibited apparently two-step degradation. With the degradation of PVA and xylan chains, the first step region occurred at around 250–330°C, and then carbonization of polymer matrix at the high temperature around 390–470°C formed the second degradation region. In contrast, the BTCA-plasticized films (P3X1, P1X1, and PX10) had three-step degradation process without obvious demarcation line. Four degradations peaks for PX0, P3X1, PX10, and P1X1 were observed at 316, 441, 361, and 433°C, respectively. The sudden drop in weight with increasing temperature occurred between 250 and 400°C. The decrease of hydrogen bonds may lead to the decreasing thermal stability of films, because the rupture of hydrogen bonds requires more energy during thermal degradation [6]. As expected, the total weight loss of the plasticized PVA/xylan films was lower than that of pure composite film (PX0).
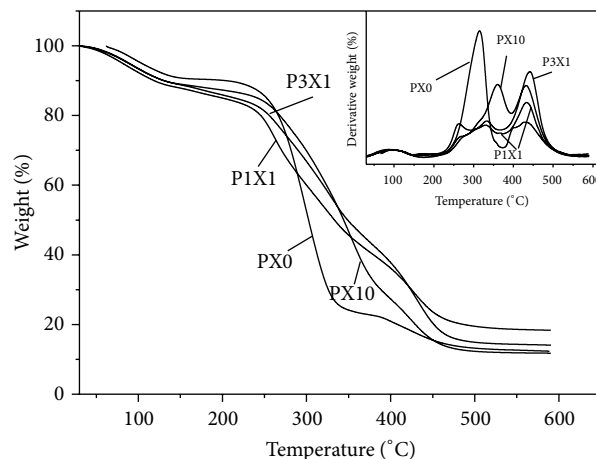

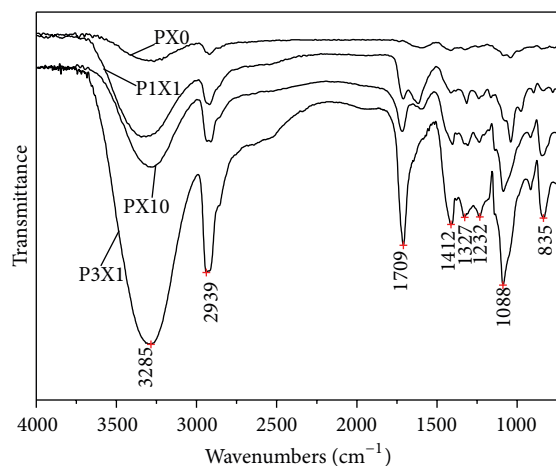FIGURE 4: TGA and DTGA curves of PVA/xylan blending films.

FIGURE 5: FTIR spectra of PVA/xylan blending films.

This might be due to the incorporation of the BTCA which stabilized the composites at high temperature.

3.5. FTIR Spectroscopy.

FTIR spectroscopy was used to examine the interactions between PVA/xylan and BTCA. The broad band at 3285 cm^{-1} originates from the stretching of –OH groups; this peak was larger than the film PX0 due to overlapping stretching of hydrogen bonds, O–H stretching of the composite films [32], which shifts 22 cm^{-1} compared with that of unplasticized PVA/xylan (3263 cm^{-1}). It indicated that BTCA interacted with PVA/xylan films matrix, and the hydroxyl groups between PVA and xylan were partially destructed [33]. And the peak at 2939 cm^{-1} is assigned to CH– stretching. A sharp brand at 1709 cm^{-1} is the C=O bond and suggested the presence of a carbonyl group mainly from BTCA in the film matrix and the C=O bond stretching was stronger with the increase of BTCA which had similar trend with –OH stretching. The absorption bands at 1412 cm^{-1} in P3X1 can be attributed to O–H, C–H bending from PVA structure and the absorption bands at 1327 cm^{-1}, 1232 cm^{-1}
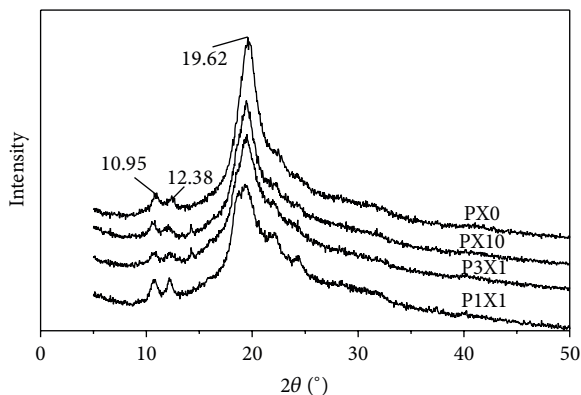
FIGURE 6: X-ray diffraction of PVA/xylan blending films.

to δ (OH) with C–H wagging, respectively. The brands from 835 to 1088 cm^{-1} corresponded to the C–O bond stretching.

3.6. X-Ray Diffraction. X-ray diffractograms of PVA/xylan blending films are shown in Figure 6. As observed, three main diffraction peaks (2θ about 10.95°, 12.38°, and 19.62°) were seen in the X-ray diffraction pattern. The unplasticized films had the highest intensity values corresponding to different regions. When the BTCA content increased from 10% to 20%, the intensity of crystalline peaks decreased a little and the diffraction patterns were quite similar and showed no significant differences with the presence of plasticizer (BTCA). However, the peak became wider and amorphous when the weight ratio of PVA and xylan reduced to 1:1. Furthermore, under this condition, two new peaks appeared at 2θ between 20° and 25°. These changes demonstrated an interaction between the components. The interaction restricted the mobility of the polymer chains and may lead to a considerable slowing of the recrystallization of the matrix during the drying process. This changes the crystalline structure of the composite films. Crystallinity analysis indicated that the xylan in the samples was semicrystalline [34]. Peng et al. [35] also found that the xylan films were semicrystalline.

3.7. Film Deterioration in Soil. The current study focused on increasing biocompatibility and degradability of blending films by adding biodegradable biopolymers. All the films had the same size and shape to prevent the external effects on biodegradation of films [36]. The dependence of degradation of PVA/xylan blending films with different BTCA contents as a function of time is presented in Figure 7. The test was carried out for 30 days of burial in soil under prevailing environmental conditions. For unplasticized films (PX0), the biggest characteristic of their decomposition rate was faster than plasticized films (PX10, PX30) in a beginning dozen days and then the weight loss gradually fell behind those that were plasticized by BTCA. After deterioration in soil about 12 days, blending films with 10% BTCA had higher weight loss ratio and showed a clear advantage. When the films were deteriorated for half a month, weight loss of PX10 reached 31.7%, while PX0 and PX30 were 28.5%, 26.6%,
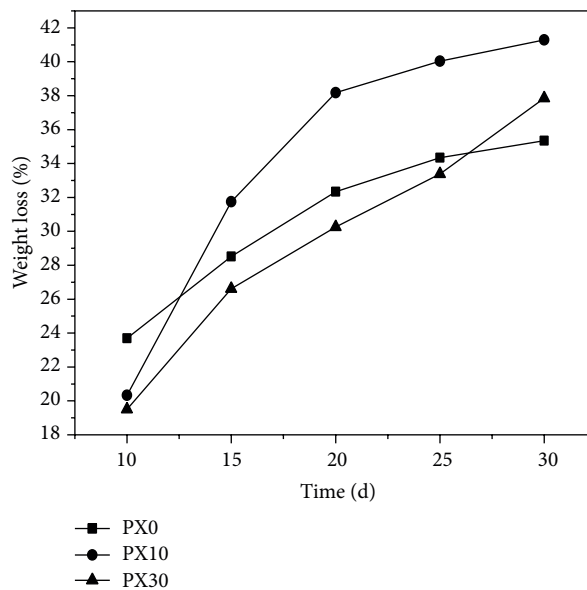

FIGURE 7: The effect of the different BTCA contents on the degradation of PVA/xylan blending films.

respectively. The weight loss of the PX30 films increased by 13.4% during the last 5 days in a month and rapidly surpassed the PX0 films. Eventually, the PX10 films were biodegraded by 41.29% within 30 days and the degree of disintegration was considerable. Chai et al. [16] investigated effects of the content of modified starch on the biodegradation of the PVA/modified starch blending films and the optimal degree of degradation was obviously below 40% within 30 days. The films with 30% BTCA also achieved 37.8%, while the weight loss of untreated films (PX0) was 35.3%, inferior to the plasticized films. Therefore, the addition of BTCA had a positive influence on degradation of PVA/xylan blending films. Imam et al. [37] explained that the addition of a plasticizer in formulations lowered the overall extent of degradation in composites. Also, biopolymers themselves like xylan have stronger biocompatibility and stimulate PVA degradation in soil.

4. Conclusions

PVA/xylan blending films by casting method were successfully synthesized by using BTCA as a new plasticizer. It was found that TS and EAB values reduced with the weight ratio of PVA/xylan from 3:1 to 1:2. Additionally, under the condition of optimal weight ratio of PVA/xylan for 3:1, both TS and EAB increased firstly and then decreased along with the increasing BTCA content. WVP was decreased first and then increased sharply with the decreasing weight ratio of PVA/xylan. The effect of BTCA content on WVP had similar tendency. The WA values were decreased along with increasing BTCA amount due to moisture barrier properties with addition of BTCA. The thermal stability of the plasticized blending films had improved. FTIR and XRD indicated the presence of interactions and structural changes between

BTCA and PVA/xylan matrix. During deterioration in soil for 30 days, PVA/xylan blending films achieved 41.3% weight loss. In summary, the PVA/xylan blending films performed desired mechanical properties and excellent biocompatibility and biodegradation, which indicate that PVA/xylan blending films have promising applications for food packaging and agricultural mulch owing to their sustainable and ecofriendly features.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.
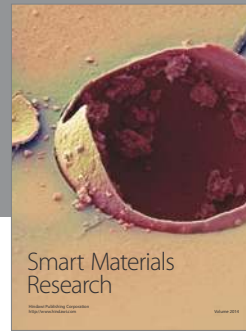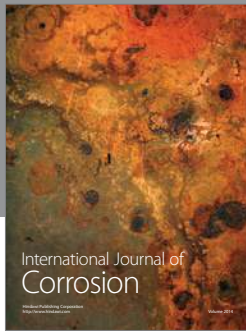
Acknowledgments

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