Preparation and Properties of Biodegradable Planting Containers Made with Straw and Starch Adhesive

Guofeng Wu, Enhui Sun, Hongying Huang, Zhizhou Chang, and Yueding Xu

A biodegradable planting container made with rice straw and starch adhesives modified by polyvinyl alcohol was studied in this paper. The effect of heat treatment and polyamide resin on the properties of planting containers was investigated. The physical property and biodegradability were characterized by means of hygroscopicity, FTIR, degradability, and the thermogravimetric analysis. The results showed that the dry strength of planting containers increased as a result of both treatments. The wet strength of planting containers increased as a result of heat treatment, while the wet strength of planting containers decreased as a result of polyamide resin. The hygroscopicity of planting containers decreased with heat treatment and polyamide resin. The effect of heat treatment was more obvious than the effect of polyamide resin. It was observed that the peak intensity and position were changed for the 3400 cm\(^{-1}\), 2900 cm\(^{-1}\), 1640 cm\(^{-1}\), 1500 cm\(^{-1}\), 1400 cm\(^{-1}\), and 1050 cm\(^{-1}\) under the treatment of polyamide resin. The weight loss of specimens treated with polyamide resin was larger because of the presence of nitrogen in the resin. The appearance of planting containers showed the heat treatment containers were not easily prone to mildew when used for planting. The thermogravimetric analysis (TGA) showed that heat treatment can improve the thermal stability, while the polyamide resin was shown to promote the degradation of planting containers.

Keywords: Planting containers; Biodegradable; Starch adhesive; Heat treatment; Polyamide resin

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INTRODUCTION

In recent years there has been growing interest in the use of biodegradable materials to reduce pollution caused by plastic waste. Countless plastic containers are discarded once the plant dies or is replanted. Therefore, there is a significant need to produce biodegradable planting containers for the nursery industry. A biodegradable planting container can be planted directly into the soil, which reduces labor costs. Biodegradable materials include bio-resin, cellulose, soy protein, and lactic acid (Lubick 2007). Other examples of biodegradable container materials include spruce fibers, sphagnum peat, wood fiber and lime, grain husks, rice hulls, 100\% recycled paper, non-woven degradable paper, dairy cow manure, corn, and hull (Evans and Hensley 2004). Naturally occurring soil microorganisms break down these materials and produce carbon dioxide, water, and biomass (Huang et al. 2013). A disadvantage of degradable containers is that they are more expensive than plastic containers and break or tear easily in a wet environment (Evans and Hensley 2004). The planting containers must be in good condition when they are used for the seeding process. Ultimately, as natural
biodegradable materials, planting containers made from straw and starch resin can be degraded by microorganisms in the soil without causing pollution when the containers are no longer needed.

Starch adhesives are an important component in producing planting containers. The renewable raw materials are bonded together by a degradable adhesive mixture. The degradable adhesive can be developed from renewable agricultural resources (Pan et al. 2005). Starch is a perfect biopolymer that is extensively used as binders (Imam et al. 2001; Markéta et al. 2008; Shen et al. 2012; Moubarik et al. 2010; Wang et al. 2012). Starch adhesive has the advantage of being less costly than synthetic resins and more environmentally friendly due to its biodegradability. When incorporated with 5 to 15% resins such as urea formaldehyde, the starch adhesive can be used for cartons where water resistance is important (Sunday and Adannaya 2010). Therefore, starch must be developed to improve the strength and water resistance of starch-based adhesive (Liu et al. 2012; Liu and Li 2007). Chai et al. (2009) showed that the addition of starch modified by sodium trimetaphosphate could increase its water uptake. The graft copolymerization of synthetic polymers onto a starch back bone is one of the best ways of improving the bonding properties of starch. There are many reports on the synthesis, characterization, and properties of starch graft copolymers (Athawale and Lele 2000; Gong et al. 2006; Kuokkanen et al. 2011). Crosslinking modification is an efficient and commonly used approach to improve the water resistance of starch and polyvinyl alcohol (Samaha et al. 2005). With an addition of 20 wt% modified starch, the blend had a maximum weight loss during enzymatic degradation. It was found that the degradability was enhanced with the addition of the starch (Chai et al. 2009).

Heat treatment can modify the components of the straw. The dimensional stability tends to be improved at the expense of some chemical degradation. Higher levels of stability and water repellence are obtained by heat treatment, which has been widely used to improve the water repellence of wood (Devi et al. 2003). Durability and dimensional stability of wood can be improved after it is heated at a temperature of 180 °C to 230 °C without chemical additives. Disadvantages of this treatment include a decrease in mechanical properties and color changes. Straw has the same components as wood, such as lignin, cellulose, and hemicelluloses. The cellulose, hemicelluloses, and lignin of straw can be destroyed at different temperatures. Destruction of lignin and cellulose is slower and needs a higher temperature than that for hemicelluloses (Mburu et al. 2008).

Polyamide resins are well known for their ability to adhere to many types of fabrics. Major application areas for polyamide resins include shoes, automotive products, packaging, electrical/electronics, and wood working (Lin and Gunasekaran 2010). They have a relatively high and sharp melting point along with high shear resistance. The sharp melting point allows easy application at higher temperatures with faster bonding upon cooling. These resins are excellent for resistance to washing and dry cleaning solvents. The polyamide resins have a higher softening point and higher adhesion strength (France et al. 2010). They can also enhance the properties of planting containers.

In this paper, a new and environmentally friendly starch-based adhesive and straw was used to produce biodegradable planting containers. Heat treatment and polyamide resin were introduced to improve the properties of planting containers. The main objective was to prepare and analyze biodegradable planting containers.
EXPERIMENTAL

Preparation of Starch Adhesive

About 4800 g of dried corn starch and 7200 g of distilled water were mixed in a four-necked, flat-bottomed 20-L stainless steel reaction kettle, and the mixture was stirred at 60 °C for 30 min. The pH of the mixture was adjusted to 6.0 with hydrochloric acid (0.5 M), and then the temperature was increased to 70 °C. The starch was allowed to gelatinize for 30 min at 70 °C, and then 4.8 g of ferrous sulfate was added to the reaction kettle. Then, 288 g of hydrogen peroxide was added to oxidize the gelatinized starch, and the mixture was stirred for 60 min at 80 °C. Finally, the polyvinyl alcohol (PVA-1799, Shanghai Shuo Xiang Plastic Co., Ltd., China) solution (384 g of polyvinyl alcohol dissolved in 2176 mL distilled water) and 2.4 g sodium borate were added to the reaction kettle. When the temperature had cooled to 50 °C, 9.6 g of potassium persulfate was added to the polyvinyl alcohol solution. After the mixture was stirred for 60 min at 80 °C, the system was allowed to cool to room temperature and the pH was adjusted to 6.0.

Preparation of Straw Biodegradable Planting Containers

Two types of planting containers were prepared. In the first formula (named as A), about 5000 g rice straw powder (2 mm) and 4500 g starch adhesive were blended in a mixing tank. Then, 500 g urea-formaldehyde resin and 200 g paraffin wax were added as a wet strength agent and a release agent, respectively. In the second formula (named as B), was used for the planting containers and comprised 5000 g rice straw powder (2 mm), 4500 g starch adhesive, 500 g urea-formaldehyde resin, 200 g paraffin wax, and 600 g commercial polyamide resin. Polyamide resin (650, Southwest Chemical CO. LTD. Jiangxi province, China) was used as a reinforcing agent. The mixed material was blended in the mixing tank at 65 to 70 °C for 30 to 45 min until the moisture content of the blended materials was about 15%. Then the mixed materials were placed in a hot-press machine with four-cavity molds at 120 °C under a pressure of 13 MPa for 2 min. There were three compressions and decompression states in the formation of planting containers.

Heat Treatment of Biodegradable Planting Containers

Heat treatment in a drying oven in the laboratory was set to 130 °C, 150 °C, and 170 °C and was used to improve the water resistance of the straw planting containers. Twenty specimens were prepared for each treatment condition. The labels A0, A1, A2, and A3 stand for the planting containers without polyamide resin, and some properties have been reported by Huang (2013). B0, B1, B2, and B3 are the planting containers with polyamide resin, treated at 130 °C, 150 °C, and 170 °C, respectively.

Properties of Starch Adhesive and Biodegradable Planting Containers

The shear strength in dry and wet state, viscosity, solid content, and pH value of starch adhesives were determined according to GB/T 14074 - 2006 (Testing methods for wood adhesives and their resins, China). The dry and wet tensile strength of planting container was determined according to GB/T 1447-2005 (Fiber – reinforced plastics composites determination of tensile properties, China).

Hygroscopicity of Biodegradable Planting Container

The heat-treated specimens and untreated specimens were conditioned at 25 °C ± 2 °C and 97% relative humidity in desiccators for 15 days. The specimens were immediately weighed at an accuracy of 0.0001 g. The hygroscopicity of the planting containers was calculated using the following equation,

\[
\text{Hygroscopicity(\%)} = \frac{m - m_0}{m_0} \times 100
\]  

(1)

where \( m \) is the specimen weight after absorption and \( m_0 \) is the specimen weight before immersion. Each reported \( m_0 \) was an average value from 10 replications.

FTIR Characterization

FTIR spectra were measured directly from untreated and treated wood using a Tensor 27 (Bruker, Germany) device in the range of 4000 to 400 cm\(^{-1}\). Pellets were prepared from the mixtures of the samples and KBr (1:100 in weight). Then, 32 scans were accumulated at a resolution of 2 cm\(^{-1}\).

Degradability

The degradability of samples was studied by evaluating weight loss over time in the soil at a depth of 10 cm for 90 days. The weight of the samples after degradation in soil was determined. The soil on the samples was carefully removed, and the samples were washed gently with distilled water. The samples were dried in a drying oven until a constant weight was obtained. Weight loss of the samples was used to indicate the degradation rate during the soil burial test. The weight loss was calculated using the following equation,

\[
\text{Weight Loss(\%)} = \frac{m - m_0}{m_0} \times 100
\]  

(2)

where \( m_0 \) is the specimen weight after degradation and \( m \) is the specimen weight before degradation.

Thermogravimetric Analysis

The thermal stability of the planting containers was assessed with a TGA instrument (SII-7200, Japan). The temperature range was from 50 °C to 580 °C at a heating rate of 20 °C/min. These tests were carried out in a nitrogen atmosphere (20 mL/min) to prevent thermoxidative degradation. The sample pan was placed on the Pt basket in the furnace, and approximately 5 mg of material was used for each measurement.
RESULTS AND DISCUSSION

Properties of Starch Adhesive

Compared with amino resins such as urea or melamine, starch adhesive has low strength and viscosity. However, the bonding strength and water resistance of the starch based adhesive can be improved with polyamide resins (mass ratio 500 parts resin to 4500 parts starch), as shown in Table 1. The starch adhesive mixed with polyamide resin (SA-P) had significantly higher shear strength than that without polyamide resin (SA). The shear strength was increased from 0.93 MPa to 1.18 MPa in a dry state and from 0.08 MPa to 0.12 MPa in a wet state. The changes in shear strength suggested that polyamide resin increased the bonding strength of the adhesive. Apparently, the bonding strength was related to the adhesive’s viscosity, solid content, and pH value (Table 1). The properties of starch adhesive mixed with polyamide resin were better than the properties of pure starch adhesive. The improvement was caused by the grafting reaction of the starch-based adhesive. The grafted copolymer of the starch-based adhesive system may play an important role in the improvement of the adhesive properties (Wang et al. 2012).

Table 1. Properties of Starch Adhesives

<table>
<thead>
<tr>
<th>Properties</th>
<th>Shear strength in dry state /MPa</th>
<th>Shear strength in wet state /MPa</th>
<th>Viscosity/mPa·s</th>
<th>Solid content/ %</th>
<th>pH values</th>
</tr>
</thead>
<tbody>
<tr>
<td>SA(SD)</td>
<td>0.93(0.09)</td>
<td>0.08(0.01)</td>
<td>340.5(13.5)</td>
<td>28.3(8.7)</td>
<td>2.7</td>
</tr>
<tr>
<td>SA-P(SD)</td>
<td>1.18(0.12)</td>
<td>0.12(0.03)</td>
<td>370.2(14.7)</td>
<td>34.8(9.8)</td>
<td>2.9</td>
</tr>
</tbody>
</table>

PSA : starch adhesive  PSA-P : starch adhesive mixed with polyamide resin

Mechanical Properties of Biodegradable Planting Containers

The dry and wet tensile strengths are important for planting containers. Table 2 shows the tensile strengths of planting containers. The A groups have been reported by Huang (2013). It has been proved that the dry and wet tensile strengths increased as a result of the heat treatment. The hemicelluloses and cellulose polymers may be broken up during heat treatment (Awoyemi et al. 2009). The temperature increased to an enhanced bonding capacity. The high dependency of bonding capacity on curing temperature was confirmed by prior studies with starch adhesives (D’Amico et al. 2008).

The addition of polyamide resin also plays an important role in dry and wet tensile strengths, and the results are shown in Table 2. The dry and wet strengths of planting containers with polyamide resin were higher than the control specimens. Compared to the heat treatment, the B0 and B1 groups exhibited higher tensile strength, while B2 and B3 had lower tensile strength. That is because the polyamide resins were hot melt adhesive, and the tensile strength of planting containers may be destroyed with higher temperature treatment. Lower temperature promotes full curing of the polyamine resin (Espy 1994; Sroog 1991).
**Table 2. Dry and Wet Tensile Strengths of Planting containers**

<table>
<thead>
<tr>
<th>Specimen</th>
<th>A0</th>
<th>A1</th>
<th>A2</th>
<th>A3</th>
<th>B0</th>
<th>B1</th>
<th>B2</th>
<th>B3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry strength (MPa)</td>
<td>3.80</td>
<td>4.00</td>
<td>5.06</td>
<td>5.93</td>
<td>3.91</td>
<td>4.21</td>
<td>4.27</td>
<td>4.56</td>
</tr>
<tr>
<td>(SD)</td>
<td>(0.77)</td>
<td>(0.62)</td>
<td>(0.72)</td>
<td>(0.79)</td>
<td>(0.87)</td>
<td>(0.65)</td>
<td>(0.75)</td>
<td>(0.78)</td>
</tr>
<tr>
<td>Wet strength (MPa)</td>
<td>0.19</td>
<td>0.40</td>
<td>0.76</td>
<td>1.35</td>
<td>0.76</td>
<td>0.57</td>
<td>0.71</td>
<td>0.72</td>
</tr>
<tr>
<td>(SD)</td>
<td>(0.06)</td>
<td>(0.12)</td>
<td>(0.28)</td>
<td>(0.30)</td>
<td>(0.19)</td>
<td>(0.19)</td>
<td>(0.16)</td>
<td>(0.23)</td>
</tr>
</tbody>
</table>

**Hygroscopicity of Biodegradable Planting Containers**

The major drawback of biodegradable planting containers is their water absorption tendency. The planting containers should be hydrophobic to a certain extent. Heat treatment can decrease the hygroscopicity for straw and wood. The effect of heat treatment has also been reported on planting containers (Huang et al. 2013), which is shown in Fig. 1 (A groups). The hygroscopicity of untreated specimens was 46.6% for A0 at the end of 15 days, while treated specimens had values of 41.9%, 34.4%, and 31.9% for A1, A2, and A3, respectively.

The influence of heat treatment on the planting containers with polyamide resin is also shown in Fig. 1 (B groups), which revealed the percentage of hygroscopicity for 15 days at room temperature at 97% relative humidity. The hygroscopicity of treated samples was lower than that of control samples. The value of the untreated specimen was 43.2% for B0 at the end of 15 days, while treated specimens had values of 42.6%, 40.9%, and 39.6% for B1, B2, and B3, respectively. The results also indicated that the heat-treated specimens absorbed less water than the untreated one. The hydroxyl groups are the main reason for water absorption (Wu et al. 2010). Heat treatment may reduce the hydroxyl groups. However, the hygroscopicity of containers with polyamide resin is higher than that without polyamide resin. That is because the polyamide resin contains amino and acylamino, which are hygroscopic.

**FTIR Analysis**

Figure 2 shows the changes of functional groups of planting containers with heat treatment (A groups); this topic has been discussed by Huang (2013). The band at 3400 cm\(^{-1}\) was significantly smooth and moved toward a lower wavenumber, and the vibration frequency of the aliphatic C-H groups (2900 cm\(^{-1}\)) was slightly increased. The decrease in the intensity at 1640 cm\(^{-1}\) is the reduction of the carbonyl (C=O) stretching vibration absorption peak, indicating hemicelluloses degradation. The peak at 1500 cm\(^{-1}\) can be attributed to the free methoxy groups of modified starch, which remained in the reaction between starch adhesives and straw. It could be concluded that methoxy groups of starch participated in the reaction during the heat treatment. This produced an efficient network of intercross-links between straw and starch adhesives, resulting in high bond strength (Imam 2001).
The changes of functional groups with polyamide resin were also shown in Fig. 2 (B groups). Some changes are similar to the A groups, which has been explained by Huang (2013). The FTIR curves of B0 showed the presence of bands at 3400 cm\(^{-1}\) for –OH stretching and 2900 cm\(^{-1}\) for C-H stretching. In the spectrum of B3, the peak at 3600 cm\(^{-1}\) was sharp and moved toward a lower wavenumber. The peak at 3400 cm\(^{-1}\) was quite smooth. The absorption peak at 1400 cm\(^{-1}\) corresponds to amide (N-C=O), which is from the polyamide resin. This is due to the band between the functional groups of the polyamide resin and the hydroxyl (-OH). It explained the hygroscopicity of planting containers with polyamide resin was higher than that without polyamide resin.

![Fig. 2. Infrared spectra of planting containers](image)

**Degradability**

The weight loss of planting containers without polyamide resin (A groups) were 83.65%, 79.36%, 76.92%, and 74.83%, respectively (Huang 2013), which was shown in Fig. 3. The specimens with heat treatment had a lower degradation rate because the microorganisms had been restrained and destroyed by the high temperature in the planting container.

The addition of polyamide resin showed higher weight loss rate than A groups, which were 92.42%, 87.39%, 85.49%, and 83.47% for B0 to B3. It was due to the existence of nitrogen in the polyamide resin. Nitrogen plays an important role in the reproduction of microorganisms. The appropriate carbon/nitrogen ratio provided suitable growth conditions. The rapid degradation was similar to the composting process. Straw and starch adhesives contain carbon that can satisfy living microorganisms. The samples with polyamide resin decomposed quickly as a result of nitrogen in the polyamide resin. The addition of polyamide resin promoted the degradation of containers after it was discarded.

![Fig. 3. Weight loss of planting containers with different treatments](image)
The fact that the addition of polyamide wet-strength resin generally resulted in higher degradation relative to the control samples provides evidence regarding the relative importance of two likely contributing factors. Cured polyamide resin can be expected to strengthen the containers, possibly increasing the mechanical resistance to infestation and growth of microorganisms. However, if growth is limited by the availability of fixed nitrogen, then the amide resin could be expected to promote biodegradation by supporting growth. The present results suggest that the second mechanism was more dominant under the conditions considered.

Figures 4 and 5 showed the appearance of planting containers over time. Vegetables were planted in the containers, and were placed in the laboratory. Water was added every day to encourage growth. The containers containing polyamide resin seemed to easily accumulate mildew. However, the heat treatment could prevent degradation of the planting containers. The microorganism degradation time was four, six, eight, and ten days for samples A0, A1, A2, and A3, respectively, and the amount of microorganisms in B0, B1, B2, and B3 were larger than those in A0, A1, A2, and A3. This result demonstrated that the polyamide resin can promote the degradation of the planting containers. It can also be found that accumulation and degradation of planting containers enhanced the survival ability of microorganisms when the plants grow. Both of the results showed the polyamide resin played an important role in the degradation of planting containers.

**Figure 4.** The appearance of planting containers during the seeding process (A0, A1, A2, and A3)

**Figure 5.** The appearance of planting containers during the seeding process (B0, B1, B2, and B3)

**Thermogravimetric Analysis**

Figure 6 shows the thermal stability of planting containers. The influence of heat treatment on planting containers has been discussed by Huang (2013). Results indicate that the thermal stability was improved by heat treatment. The residual quality of A0 and A3 were 27.92% and 29.65%, respectively.

The residual quality of planting containers with polyamide resin was 28.45% and 31.79% for B0 and B3, respectively (Fig. 6). The maximum decomposition rates for A0, A3, B0, and B3 were 1493.14 μg/min, 867.33 μg/min, 1167.01 μg/min, and 745.98 μg/min, respectively, while the approximate peak temperatures were 357.47 °C, 363.19 °C, 358.88 °C, and 358.22 °C, respectively. However, the maxima of DTA were 357.47 μV, 363.19 μV, 358.88 μV, and 358.22 μV, respectively. There is a sharp peak at 310 °C for B groups, while the peak for A groups is more gradual. The improved thermal stability was probably because more cross-linking reactions occurred and a high degree of structural order was produced between straw, starch adhesives, and polyamide resin.
CONCLUSIONS

1. Planting containers made from rice straw and starch adhesive were judged to be suitable for widespread use in agriculture and horticulture because of their water resistance and good mechanical performance.

2. Results suggested that polyamide resin in the starch adhesive increased the bonding strength. The polyamide resin also played an important role in increasing both the dry and wet tensile strengths of the planting container at 130 °C. The heat treatment has a better effect on the dry and wet strengths than the polyamide resin at 150 °C and 170 °C.

3. The addition of polyamide resin contributed to higher hygroscopicity as a result of the low water resistance of polyamide resin.

4. The addition of polyamide resin led to a higher weight loss rate because of the existence of nitrogen in the polyamide resin, which provides the appropriate carbon/nitrogen ratio for suitable growth conditions of microorganisms.

5. FTIR analysis showed that the hydrogen and carbonyl contents decreased as result of heat treatment. The amide (N-C=O) was formed between the functional groups of the polyamide resin and the hydroxyl. TGA analysis showed that the thermal stability was improved because of cross-linking reactions during heat treatment.

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