Abstract

Environment-friendly “green” nano-composites were fabricated from a starch-based, dispersion-type biodegradable resin and cellulose nanofibers. The mixture of the dispersion-type biodegradable resin and cellulose nanofibers were blended well by using a mixer and/or a stirrer. Composites were prepared by conventional hot pressing at a constant temperature of 140°C and at pressures from 10 to 50 MPa. Their flexural strength as well as flexural modulus increased with increasing the molding pressure, and were also affected by fabrication processes. It can be seen that their mechanical properties such as strength and modulus had a good correlation with their sample density. It should be noted that there exists significant effectiveness in the stirrer mixing process, which results in the uniform dispersion of cellulose nanofibers.

1 Introduction

In recent years, there is increasing interest in the development of biodegradable and/or plant-derived composite materials, which we sometimes refer to as “green” composites [1-5], because of strong global demand for creating a resource-circulating society. In the case of the “green” composites, various kinds of natural fibers are being added to biodegradable resins such as poly-lactic acid (PLA) and modified starch to reinforce plant-derived, polymeric matrix materials and improve their mechanical properties.

It is well known that cellulose microfibril is a basic structural unit of all plants and one of the smallest natural fibers. The Young’s modulus of the cellulose microfibril has been measured to be around 140 GPa [6], and also its tensile strength to be 1.7 GPa [7]. From academic and industrial point of view, it is of great interest to examine the possibilities and limitations of nanoscale reinforcement derived from cellulose nanofibers [8-11].

The aim of this study is to develop advanced “green” composites reinforced by cellulose nanoscale fibers, and to examine the effect of processing conditions on their mechanical properties.

2 Experimental methods

2.1 Materials

A starch-based, dispersion-type, biodegradable resin (CP-300, Miyoshi Oil & Fat Co., Ltd.) was used as a matrix material. This thermo-plastic resin is made from an esterified starch prepared from corn grains. Fine resin particles approximately 6 μm in diameter are suspended in a water-based solution, and the average resin content is 40% (w/w), therefore this resin is a viscous liquid.

Table 1. Physical and mechanical properties of biodegradable resin used as matrix.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
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<tbody>
<tr>
<td>Density (g/cm³)</td>
<td>1.18</td>
</tr>
<tr>
<td>Melting point (°C)</td>
<td>58</td>
</tr>
<tr>
<td>Softening point (°C)</td>
<td>57</td>
</tr>
<tr>
<td>Water absorption (%)</td>
<td>2.0</td>
</tr>
<tr>
<td>Tensile strength (MPa)</td>
<td>10</td>
</tr>
<tr>
<td>Tensile elongation (%)</td>
<td>550</td>
</tr>
<tr>
<td>Young’s modulus (GPa)</td>
<td>0.4</td>
</tr>
<tr>
<td>Flexural strength (MPa)</td>
<td>22</td>
</tr>
<tr>
<td>Flexural modulus (GPa)</td>
<td>1.0</td>
</tr>
</tbody>
</table>
Basic properties of this resin are listed in Table 1. Nano-scale cellulosic fibers (Celish KY100-S, Daicel Chemical Industries, Ltd.) were used as reinforcement. This reinforcing fiber was prepared from wood pulp by a number of homogenization processes. The fiber was used as received conditions without any surface treatment. Figure 1 shows macroscopic view of the dried cellulose nano-fibers, on the other hand Fig. 2 shows microscopic view of the same fiber.

Fig. 1. Macroscopic photograph of cellulose nano fiber.

Fig. 2. Microscopic photograph of cellulose nano fiber.

2.2 Fabrication of composites

Figure 3 is a flowchart that we used for fabricating “green” composites. The both biodegradable resin and cellulosic nanofibers were mixed well for 20 minutes by using a home-use mixer. Several specimens were mixed with a low speed stirrer at 300 rpm for 24 hours (stirrer treated composite). Then excess water was roughly removed by a filtering process, followed by drying at 105°C in air (control composite). All samples with fiber loading of 70% (w/w) were prepared by a hot pressing method at the conditions of constant temperature of 140°C and various pressures from 10 to 50 MPa.

Fig. 3. Flowchart for fabrication process.

2.3 Characterization of composites

Quasi-static flexural tests were carried out using an Instron universal test machine (Model 5567) to evaluate the mechanical properties of composites. The flexural strength was measured using a 3-point bending test with a span length of 50 mm and a constant crosshead speed of 1.0 mm/min. Shapes of specimens for flexural tests were 100.0 mm × 15.0 mm × 1.5 mm. Their internal microstructures were examined using a scanning electron microscope (SEM).

3 Results and discussions

3.1 Flexural properties

Figure 4 demonstrates the relationship between flexural strength of composites reinforced by cellulosic nanofibers and molding pressure. The
flexural strength of control composite gradually increases with increasing molding pressure, and almost saturates at the molding pressure of 50 MPa. The pressure dependence of flexural strength for stirrer treated composite is also similar to that of control composite. However the flexural strength of the composite molded at low pressures below 20 MPa has higher than that of control composite. In addition, it should be noted that the stirrer treated composite has higher flexural strength at any molding pressures.

The flexural modulus of control composite material has almost the same pressure dependence as shown in Fig. 5. It can be seen that the flexural modulus for the stirrer treated composite is higher than that for control composite. The difference, however, gradually decreases with increasing the molding pressure showing almost the same manner as the case of flexural strength.

### 3.2 Density

Figure 6 shows the variation of density with respect to molding pressure. In the case of control composite, its density increases with increasing molding pressure with almost the same dependence of the flexural strength as shown in Fig. 4. It is worth noticing that the density difference between control composite and stirrer treated composite is smaller than expected from the results on their mechanical properties (Figs. 4 and 6). It is therefore suggested that there exists another strengthening effect in the stirrer treated composite.

### 3.3 Microstructure

SEM observation shows that control composite has extensive resin rich and poor regions, namely uniform distribution is not achieved. However, no resin rich or poor regions are readily visible in stirrer treated composite. It can be seen that there is considerable difference in internal microstructure and fiber dispersion behavior for the stirrer treated composite, whereas there is almost no significant difference in their density at the molding pressures over 30 MPa (Fig. 6). It can be seen from these results that there is significant effectiveness in a stirrer mixing process, which results in a uniform dispersion of nanofibers.
4 Conclusions

Advanced “green” composites were successfully fabricated from a starch-based, dispersion-type biodegradable resin and cellulosic nanofibers. Flexural strength increases with increasing molding pressure. The increases in flexural properties are attributed partially to increases in sample density. The sample preparation method, especially low speed stirrer treatment, plays an important role in the strengthening of the composites. This stirrer mixing treatment contributes to an improvement in a uniform dispersion of nano-scale fibers in resin matrix.

References


