Modifying the Properties of Polypropylene-Wood Composite by Natural Polymers and Eggshell Nano-particles

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SUMMARY

In this research, physical, thermal and mechanical properties of polypropylene composites modified with natural polymers such as starch and corn are studied. Also, the effect of adding eggshell nano-particles as fillers is investigated. 4 weight percentage of maleic anhydride as a compatibilizer of polypropylene was used in order to improve mechanical properties. Polypropylene-wood composites have been introduced as new sources of raw materials in various industries and have found their way through many applications such as automotive, building and furniture’s industries. This polymer by itself or in combination with various resistant has good heat resistance, great flexibility at low temperatures and resistance against oxidation and ultraviolet radiation. In the current research, bending and tensile tests were utilized for physical and mechanical examinations and also in order to evaluate surface morphology, SEM test was used. Results show that adding maleic anhydride and eggshell nanoparticles instigates improvement in mechanical properties as well as better adhesion between polymer, starch and corn particles.

Keywords: Composite, Polypropylene, Morphology, Eggshells Nano-Particles.

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INTRODUCTION

Polypropylene-wood composites have been introduced as new sources of raw materials in various industries and have found their way through many applications such as automotive, building and furniture industries. This polymer by itself, or in combination with various flame resistant, has a good heat resistance, great flexibility at low temperatures and resistance against oxidation and ultraviolet radiation. Wood-plastic composites (WPCs) are composite materials made of wood fiber/wood flour and thermoplastics such as polyethylene (PE), polypropylene (PP), polyvinyl chloride (PVC) etc. [1]. Recently, adding fibers and natural fillers to plastics to reduce manufacturing cost has been taken into consideration [2]. Various investigations have been conducted into improvement of wood-plastic composites, most of which has been concentrated on production of polyethylene, polypropylene [3, 4]. Mixing polymers and preparation of polymer blends in order to utilize advantages of various polymers and improve their properties have been widely a matter of debate [5, 6]. Studying the effect of maleic anhydride on the mechanical properties of polyethylene and cellulose fibers composites shows that maleic anhydride as compatibilizer improves the mechanical properties of the composites considerably [7]. A huge amount of wood waste is produced each year and their use in plastic industries not only reduces cost of production, but also improves various properties of WPCs [8]. Melt viscosity of polypropylene mixed with inorganic fillers and wood has been investigated by many researchers trying to predict a model for that. Viscosity changes and also filled polymer melt flow index changes are functions of the particles size and Geometric shape of the filler particles. Polypropylene is a thermoplastic material with applications in food packaging, healthcare and pharmaceutical industries owing to economic reasons and ease of shaping process. Therefore, palm fiber wastes are used to reduce the costs and enhance the mechanical properties of polypropylene. Starch being one of the most important natural polymers is considered because of being biodegradable and cheap [9, 10]. To prevent destruction during process starch was mixed up with glycerol. Also maleic anhydride graft polypropylene copolymer (PP-g-MA) was used as a compatibilizer for better connection (starch and corn fiber) between hydrophilic and hydrophobic polypropylene.

Materials

Propylene which was linked to maleic anhydride made by Solvay Belgian company having melt flow index equal to 64 (gr/min), and density equal to 0.91 (gr/cm3) were prepared. Maleic anhydride manufactured by Karagin (Iran) and Karabond EHM was also used.
Mechanical Tests

Test results based on standards are listed in Table 1.

Mechanical tests were performed with universal testing machine (tensile, compression and bending machine), Model GT-7001-LC, in andisheye Bartar Company. Izod impact test was performed using machine made by GTECH of Taiwan in the Institute of Andisheye Bartar. In order to perform stretch and impact tests, injection molding apparatus (KRAUS MAFFEI KM model) having L/D equal to 1, was used.

Table 1. Mechanical tests requirements and relevant standards

<table>
<thead>
<tr>
<th>Standard</th>
<th>Velocity (mm/min)</th>
<th>Width (mm)</th>
<th>Thickness (mm)</th>
<th>Length (mm)</th>
<th>Test</th>
</tr>
</thead>
<tbody>
<tr>
<td>ISO 527</td>
<td>50</td>
<td>10</td>
<td>4.03</td>
<td>115</td>
<td>strain</td>
</tr>
<tr>
<td>ISO 527</td>
<td>2</td>
<td>9.98</td>
<td>4.04</td>
<td>64</td>
<td>bending</td>
</tr>
<tr>
<td>ISO 180 – Izod</td>
<td>-</td>
<td>-</td>
<td>3</td>
<td>4</td>
<td>impact</td>
</tr>
</tbody>
</table>

Methodology

Firstly, compound was prepared using a blender for mixing polymer with antioxidant physically. In special cases, compound’s soot should be entered into the blender. After hybridization, the samples were removed from the apparatus followed by formation of samples using hot press machine or injection device. Maleic anhydride was used as polypropylene compatibilizer (Table 4). The percentages of materials are depicted in Table 1. The Polypropylene sample was mixed with 1, 3 and 5 weight percentages of starch in any stage, as well as corn, malic anhydride and egg shell nano-particles as are shown in Table 2. Samples were placed in a vacuum oven for 4 hours in order to achieve dehumidification process. In current research, two screw extruder manufactured by Werner Company were used, Table 5 shows its physical structures. Polypropylene along with lubricant and compatibilizer from the main feeding were inserted into extruder and also corn and starch were added to molten polymer from feeding side. Formulation ratio was adjusted by assistance of weigh feeding apparatus that controlled both main and side feedings. Extruded material was cooled using water bath followed by crushing seeds. Obtained seeds were injected into samples to conduct tests after being dried for 24 hours at 80°C, (Figure 1). Composite samples were cracked in liquefied nitrogen and microscopic examination was performed to analyze the fractures on their surfaces. PP-g-MA produced by Grankyn company was used as a compatibilizer with ratio of 7/1 maleic anhydride. Characteristics are shown in Table 3.
Table 2. The compound percent of samples

<table>
<thead>
<tr>
<th>Samples No.</th>
<th>Propylene %</th>
<th>Corn %</th>
<th>Starch %</th>
<th>Eggshell nanoparticles %</th>
<th>Compatibilizer %</th>
<th>Foaming agent</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>50</td>
<td>46</td>
<td>0</td>
<td>0</td>
<td>4</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>50</td>
<td>44</td>
<td>0</td>
<td>0</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>4</td>
<td>50</td>
<td>33</td>
<td>10</td>
<td>1</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>5</td>
<td>50</td>
<td>21</td>
<td>20</td>
<td>3</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>6</td>
<td>50</td>
<td>9</td>
<td>30</td>
<td>5</td>
<td>4</td>
<td>2</td>
</tr>
</tbody>
</table>

Table 3. Characteristics of starch

<table>
<thead>
<tr>
<th>Unit</th>
<th>Maximum standard</th>
<th>Characteristic</th>
</tr>
</thead>
<tbody>
<tr>
<td>wt%</td>
<td>14</td>
<td>Moisture</td>
</tr>
<tr>
<td>wt%</td>
<td>0.3</td>
<td>Ash</td>
</tr>
<tr>
<td>wt%</td>
<td>2</td>
<td>Acidity</td>
</tr>
<tr>
<td>wt%</td>
<td>0.7</td>
<td>Proteins</td>
</tr>
<tr>
<td>-</td>
<td>Minor</td>
<td>Fat</td>
</tr>
<tr>
<td>-</td>
<td>4.5-7</td>
<td>pH</td>
</tr>
</tbody>
</table>

Table 4. Characteristics of corn

<table>
<thead>
<tr>
<th>Ash</th>
<th>Extracted material</th>
<th>Lignin</th>
<th>Cellulose</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.5 wt%</td>
<td>24.7 wt%</td>
<td>18 wt%</td>
<td>41 wt%</td>
</tr>
<tr>
<td>Wall thickness (μm)</td>
<td>Cellular hole diameter (μm)</td>
<td>Diameter of fibers (μm)</td>
<td>Length of fibers (mm)</td>
</tr>
<tr>
<td>3.48</td>
<td>11.59</td>
<td>18.346</td>
<td>0.936</td>
</tr>
</tbody>
</table>

Figure 1. Schematic of samples
### Table 4. Characteristics of maleic anhydride graft polypropylene copolymer

<table>
<thead>
<tr>
<th>Mol. Wt (Mn)</th>
<th>Density (g/mL)</th>
<th>Melt point (°C)</th>
<th>Maleic anhydride (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>~3,900 by GPC</td>
<td>0/934</td>
<td>156</td>
<td>1/7</td>
</tr>
</tbody>
</table>

### Table 5. Characteristics two-screw extruder

<table>
<thead>
<tr>
<th>Length</th>
<th>L/D</th>
<th>Screw speed</th>
<th>Maximum output rate</th>
<th>Heating elements</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 M</td>
<td>40</td>
<td>120 RPM</td>
<td>70 kg</td>
<td>6 #</td>
</tr>
</tbody>
</table>

### RESULTS AND DISCUSSION

#### Physical, Mechanical and Bending Properties Tests

One of the most common methods to assess bending modulus is bending test. In this method, the sample is placed between two fulcrums and force is imposed from the top and middle of two fulcrum and force entered from the top and middle of two fulcrum. In this state, lower level of sample was under tension and upper-level was under pressure. If compressive and tensile modulus of the sample are equal, then the tension in the center of sample axis will be zero. Physical and mechanical properties of polypropylene in Table 6 have been presented. In Figures 2 to 7 it can be observed that adding corn, starch and eggshell nano-particles instigates a decrease in bending.

### Table 6. Physical and mechanical properties of polypropylene composite

<table>
<thead>
<tr>
<th>Samples</th>
<th>Bending module (MPa)</th>
<th>Bending strength (MPa)</th>
<th>Tensile modulus</th>
<th>Tensile strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>522.57</td>
<td>7.249</td>
<td>6.08</td>
<td>17.42</td>
</tr>
<tr>
<td>2</td>
<td>1185.63</td>
<td>15.711</td>
<td>7.09</td>
<td>20.45</td>
</tr>
<tr>
<td>3</td>
<td>1224.27</td>
<td>15.908</td>
<td>6.68</td>
<td>19.8</td>
</tr>
<tr>
<td>4</td>
<td>1190.47</td>
<td>15.293</td>
<td>7.1</td>
<td>19.1</td>
</tr>
<tr>
<td>5</td>
<td>1025.55</td>
<td>13.713</td>
<td>1.66</td>
<td>18.49</td>
</tr>
<tr>
<td>6</td>
<td>925.1</td>
<td>12.478</td>
<td>12.41</td>
<td>19.59</td>
</tr>
</tbody>
</table>

#### Impact Test

According to ASTM 256 standard as Table 7 shows, Izod impact test was performed at room temperature. Obtained results related to impact test of polypropylene composites in Figure 8 are presented.
Figure 2. Bending test of polypropylene composite (sample 1)

Figure 3. Bending test of polypropylene composite (sample 2) containing malic anhydride and corn
Figure 4. Bending test of polypropylene composite (sample 3)

Figure 5. Bending test of polypropylene composite (sample 4) containing malic anhydride, corn and eggshells nanoparticles
Figure 6. Bending test of polypropylene composite of (sample 5) containing malic anhydride, corn and eggshells nanoparticles

Figure 7. Bending test of polypropylene composite of (sample 6) containing malic anhydride, corn and eggshells nanoparticles
Table 7. Impact test of polypropylene composites based on ASTM 256 standard

<table>
<thead>
<tr>
<th>Samples</th>
<th>Impact test (J/m)</th>
<th>Test condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>17.55</td>
<td>Iso180</td>
</tr>
<tr>
<td>2</td>
<td>30.86</td>
<td>Humidity percent: 45.1</td>
</tr>
<tr>
<td>3</td>
<td>14.88</td>
<td>Temp: 22.2oC</td>
</tr>
<tr>
<td>4</td>
<td>51.43</td>
<td>Touch back width: 8 mm</td>
</tr>
<tr>
<td>5</td>
<td>222.9</td>
<td>Weights: 1</td>
</tr>
<tr>
<td>6</td>
<td>55.28</td>
<td>Touch Radius: 0.25 mm</td>
</tr>
</tbody>
</table>

Figure 8. Impact Test of polypropylene composites containing glycerol and starch

Tensile Test

Tensile test was performed according to ASTM D638 standard using a puller ZWICK 1458 at ambient conditions and room temperature at a speed of 10 (mm/min) as shown in Figure 9 and Figure 10. As can be observed, by increasing the percentage of corn to polypropylene in samples 2 and 3, tensile properties improved. Tensile properties increased when starch and also 1,3 and 5 weight percent of eggshells nano-particles are added into the samples (4), (5) and (6). Sample (5) showed a decrease in these properties owing to agglomeration of particles.
Thermal Gravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) of the samples was done in a Shimadzu TGA-50 thermal analyzer using a scanning rate of 10°C/min heating rate under nitrogen with 20 mL/min flow rate, from room temperature to 800°C. ASTM E1131 Standard PL-1500 apparatus was used in order to investigate thermal properties of polypropylene-wood nano-composites and the effects of natural polymers and eggshells nano-particles on thermal stability of composites. In Figures 11, 12 and 13 the results of thermal stability of samples...
Figure 11. Thermal test results of sample (4)

Figure 12. Thermal test results of sample (5)
containing various percentage of eggshells nano-particles, starch and corn are represented. Thermal resistance of sample (4) and (5), with 1 and 3 weight percentage of eggshells nano-particles respectively, increased dramatically owing to network formation of eggshells nano-particles in polypropylene matrix. Conversely, increasing the amount of eggshells nanoparticles in sample 6 from 3 wt% to 5 wt% instigates a decrease in thermal stability because of micro-structure disturbance of nano-composites due to increase in viscosity and also agglomeration of nanoparticles.

Results of the Scanning Electron Microscopy (SEM)

Distribution of polypropylene composites is analyzed by studying SEM images. Morphology test results are shown in the following figures. Figures 14 to 23 show the SEM images of composite samples. The following figure shows the SEM images of composite samples. In samples containing eggshells nano-particles, corn, starch and polypropylene-wood, a differences (the highs and lows) can be observed at the broking level showing wood particles breaking instead of splitting them and it means that a good connection between wood of eggshells nano-particles and corn, starch and the matrix have existed and

![Graph showing thermal test results of sample (6)](image)

**Figure 13.** Thermal test results of sample (6)
Figure 14. Sample 1 SEM test with magnification of 20 µm

Figure 15. Sample 1 SEM test with magnification of 50 µm

Figure 16. Sample 2 SEM test with magnification of 20 µm
Figure 17. Sample 2 SEM test with magnification of 50 µm

Figure 18. Sample 3 SEM test with magnification of 50 µm

Figure 19. Sample 3 SEM test with magnification of 200 µm
Figure 20. Sample 4 SEM test with magnification of 20 µm

Figure 21. Sample 4 SEM test with magnification of 50 µm

Figure 22. Sample 6 SEM test with magnification of 20 µm
in samples 4, 5 and 6, these differences have been reduced and the surface be further smoother.

CONCLUSIONS

In general, by creating cross-link, tensile properties of polypropylene will be improved, especially at high temperatures. The results obtained show that the tensile strength and fracture strain of samples containing cross-linked are higher than samples without it at high temperatures. Indeed, an optimum amount of peroxide is needed to achieve the desired tensile properties. By increasing natural polymers such as starch, corn and eggshells nano particles as fillers, physical and mechanical properties will be improved.

REFERENCES


