Research Article

Effect of Nano-CaCO$_3$ and Talc on Property and Weathering Performance of PP Composites

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Wood plastic composites (WPCs) are increasingly being utilized these days due to their excellent mechanical properties and low maintenance cost. Despite these advantages, poor UV resistance and low impact strength are drawbacks. To overcome these shortcomings, coextrusion technology has recently been applied in the production of WPCs and it has been showing good results. However, further research on the combination of different functional enhancements is still needed. This study, therefore, manufactured polypropylene (PP) composites filled with UV stabilizer and inorganic fillers (i.e., nano-CaCO$_3$ and talc) and then investigated the influence of weathering on the mechanical and morphological properties of the filled composites as a function of filler type and content. UV stabilizer effectively protected the filled composites from UV-induced photodegradation. At 2.5 wt% nano-CaCO$_3$ (NCC), the NCC particles were well dispersed in the PP matrix, thereby improving the mechanical properties of the filled composites. The best results were observed in 2.5 wt% NCC and 10 wt% talc hybrid filled composites. The composites prepared by adding UV stabilizer to the PP matrix together with NCC and talc exhibited high mechanical properties and improved weathering resistance, and, thus, the combination of NCC, talc, and UV stabilizer in the PP matrix is applicable for shell layer to be used in coextruded WPCs.

1. Introduction

Wood plastic composites (WPCs) have received a lot of attention as they combine the properties of wood and plastic. WPCs can be readily manufactured using wood flour (WF) and thermoplastic resins such as polypropylene (PP) and polyethylene (PE) through extrusion, injection, and compression molding [1]. These composites are widely used as nonstructural building materials such as decking, fences, and window frames. Furthermore, the use of WPCs in furniture and automotive industries has been steadily increasing worldwide. Higher contents of WF in WPCs led to improved mechanical properties with lower thermal expansion compared with conventional plastics, but these WF filled composites had disadvantages such as increased moisture absorption percentage and low weathering resistance [2, 3].

To overcome these disadvantages, WPCs with a new shape and structure need to be developed. Coextrusion is a technique to produce optimized products having multilayered structures by connecting two or more extruders to one coextrusion die. The coextrusion die combines molten plastic layers with different properties into one form, thereby producing new products. Recently, in the field of WPCs, studies have been initiated on methods to improve their performance by applying coextrusion technology for manufacturing WPCs with improved characteristics. The coextruded WPCs are composed of a core layer and shell layers, and these WPCs have been found to show better properties than conventional WPCs as the surface has the shell layers fabricated using thermoplastic resins and functional fillers [4].
The shell layer of coextruded WPCs is made of thermoplastic resins such as PP and HDPE and this layer plays an important role in influencing the properties of the entire coextruded WPCs [5]. Coextruded WPCs with shell layers made of pure thermoplastics exhibit higher hydrophobicity than conventional WPCs, but they have low modulus and high thermal expansion capacity [6]. Therefore, many studies have investigated ways to enhance the functionality of the shell layer by adding fillers into it. One such example is the use of CaCO₂ particles to toughen the shell layer, and it was found that the CaCO₂ reinforced thermoplastics had higher mechanical strengths than pure thermoplastic [7]. This toughening was also observed when nanosize CaCO₂ particles were added, leading to enhancements in the mechanical properties of WPCs, such as improved modulus of elasticity (MOE), modulus of rupture (MOR), and impact strength [8–10]. In addition, talc, inorganic plate-shaped filler, has been used as an additive in WPCs to improve their thermal and mechanical properties [11, 12]. Incorporating both talc and CaCO₂ into thermoplastic improved its physical and thermal properties with better weathering resistance compared with the weathering performances obtained by adding only one of these fillers [13].

Thermoplastics such as PP are vulnerable to UV rays. Natural weathering of thermoplastics is caused by the generation of oxygen and light radiation, which is called photooxidation. This photooxidation can produce carbonyl, carboxyl, hydroxyl, and peroxide groups in the polymer. The carbonyl groups in the deteriorated polymers promote degradation. Commercial light stabilizers used for the prevention of photooxidation of PP are classified into three types. These are nickel compounds, 2-hydroxybenzophenone- or hydroxyphenylbenztriazole-based UV absorbers (UVA), and hindered amine light stabilizers (HALS). Among these additives, the use of low molecular weight HALS is most appropriate as light stabilizers in thermoplastics [14] as HALS has excellent photostability due to its ability to reproduce nitroxyl radicals [15].

The aim of this study is to investigate the effect of nano-CaCO₂ and talc on the weathering, mechanical and morphological properties of PP composites with and without HALS for shell layers used in coextruded WPCs.

2. Experimental

2.1. Materials. Polypropylene (PP), trade name HJ700, was supplied by Hanwha Total Petrochemical Co. (S. Korea). It has a melt index of 22 g/10 min (230°C/2.16 kg) and a density of 0.91 g/cm³. Coupling agent, UV stabilizer, nano-CaCO₂, and talc were used as received. Maleic anhydride-grafted polypropylene (MAPP), CM-1120H, was provided by Lotte Chemical Co. (S. Korea) and used as a coupling agent. The molecular weight, melt index, and maleic anhydride ratio were 124,200 g/mol, 80 g/10 min, and 0.5–1.0 wt%, respectively. The UV stabilizer used was Tinuvin 770, which was supplied by BASF (Germany). Tinuvin 770 is a typical HALS UV stabilizer with a molecular weight of 481 g/mol. Nano-CaCO₂ (NCC) of approximately 40 nm was purchased from Dongho Calcium Co. (S. Korea). Talc, KC-5000C, was purchased from Koch Co. (S. Korea), with a specific gravity of 2.58–3.83. Its degree of whiteness and particle size were 97.5% and 3.5 μm, respectively.

2.2. Preparation of Composites. Raw materials were placed into an 11 mm twin-screw extruder (Bautek Co., S. Korea) with L/D ratio of 40 and six temperature zones. The temperature zones of the extruder were 165, 165, 170, 170, 160, and 120°C, respectively. The compounded and extruded raw materials were pelletized using a pelletizer (Bautek Co., S. Korea). The prepared pellets were then fed into a BOY 12M injection molding machine (Dr. Boy GmbH & Co. KG, Germany) to produce specimens. The barrel temperatures of the injection molding machine were 175, 170, 165, and 120°C. II types of composite specimens were prepared by varying the amount of NCC contents, talc, and UV stabilizer. Formulation ratios of the PP-based composites are shown in Table 1.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>PP (wt%)</th>
<th>Tinuvin 770 (wt%)</th>
<th>MAPP (wt%)</th>
<th>Nano-CaCO₂ (wt%)</th>
<th>Talc (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>97.5</td>
<td>0.5</td>
<td>2</td>
<td>5</td>
<td>-</td>
</tr>
<tr>
<td>T10-N2.5</td>
<td>85</td>
<td>0.5</td>
<td>2</td>
<td>5</td>
<td>10</td>
</tr>
<tr>
<td>T10-N5</td>
<td>82.5</td>
<td>0.5</td>
<td>5</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>T10-N10</td>
<td>77.5</td>
<td>0.5</td>
<td>10</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>T10-N15</td>
<td>72.5</td>
<td>0.5</td>
<td>15</td>
<td>15</td>
<td>10</td>
</tr>
</tbody>
</table>

2.3. Mechanical Property. Three mechanical properties were investigated. The Izod impact strength test, the fractured and UV-exposed surfaces of the specimens were observed using a JSM-7401F (Jeol Ltd., Japan) field emission scanning electron microscope (FE-SEM) at acceleration voltages of 5 kV or 10 kV.

2.4. Morphological Property. After the Izod impact strength test, the fractured and UV-exposed surfaces of the specimens were observed using a JSM-7401F (Jeol Ltd., Japan) field emission scanning electron microscope (FE-SEM) at acceleration voltages of 5 kV or 10 kV.

2.5. Color Change Property. Accelerated weathering tests were conducted to test the UV stability of materials using
an ATLAS Ci 3000+ xenon arc UV exposure system (AME-TEK Co., USA) according to ASTM D2565. The equipment has a nozzle for spraying water and UV light sources, and the composite specimens were rotated at 1 rpm within it. Irradiance, humidity, and temperature of the test chamber were maintained at 0.35 W/m², 50%, and 42°C, respectively. UV exposure times were 250, 500, and 1,000 h. After each exposure time, color changes and mechanical properties of the composites were analyzed. The lightness, $L^*$, and chromaticity coordinates ($a^*$ and $b^*$) were measured using CM-700d of Konica-Minolta Co., and the total color difference ($\Delta E^*ab$) was obtained using the following equation:

$$\Delta E^*ab = \sqrt{\left(L_f - L_i\right)^2 + (a_f - a_i)^2 + (b_f - b_i)^2},$$

where $L_f$, $a_f$, and $b_f$ are the lightness and chromaticity coordinates after the UV exposure, respectively, and $L_i$, $a_i$, and $b_i$ are the lightness and chromaticity coordinates before the UV exposure, respectively.

3. Results and Discussion

3.1. Mechanical Property. The impact strengths of the composites before and after accelerated weathering tests are observed in Figure 1. The impact strengths of the composites containing 2.5 wt% NCC were highest regardless of weathering. The impact strength values decreased slightly as the NCC contents increased. Since the NCC particles are very small sizes (average 40 nm), toughening could be obtained when these nanoparticles were evenly dispersed in composite materials, thereby improving impact strengths [7, 9, 10]. However, the addition of large amounts of NCC in the composite makes its dispersion difficult [8]. In the case of NCC-talc hybrid filled composites, the highest impact strength was obtained at 10 wt% talc filled composites. Namely, the addition of NCC decreased impact strength values. Thus, we believe that the incorporation of NCC together with talc into PP matrix makes NCC dispersion more difficult compared with NCC only [10, 16]. After 250, 500, and 1,000 h of accelerated weathering tests, impact strength values of the whole composites seemed to decrease; this decrease was especially pronounced for pure PP. This is because PP, vulnerable to UV light, is affected by moisture and photooxidation during accelerated weathering, which results in the cleaving of its polymer chains. In contrast, the composite with UV stabilizer had a lower rate of degradation than pure PP because the UV stabilizer inhibits the formation of hydroperoxide group and ketone group, which are photoinitiators of PP, through the reprocessing of nitroxyl radicals [14, 15]. Talc and NCC-talc hybrid filled composites showed smaller reduction rates compared with NCC-only filled composites in impact strengths, as accelerated weathering times were longer as shown in Figure 1(b). From the above results, it can be seen that the plate-shaped talc had a significant effect in maintaining the impact strength of the composites even after a long period of accelerated weathering and it acted as an effective functional filler like NCC by preventing decrease in strength [17].

The tensile strength of each composite with different formulation ratios was evaluated as a function of the accelerated weathering test time. Similar to the results of the impact strength, the highest tensile strength was observed in the 2.5 wt% NCC filled composite. However, as the NCC contents increased, the tensile strength decreased; this is probably because when stress was applied during the tensile test, voids were formed around the NCC particles in the composite, which had an unfavorable effect on the strength of the composite, thereby resulting in a decrease in the tensile strength. The incorporation of talc into composites resulted in a higher tensile strength than the composites containing NCC only. This is because the plate-like talc particles acted
as the main reinforcing filler, which makes it more difficult to debond the PP matrix during the tensile test [16, 18]. The tensile strength of NCC-talc hybrid filled composites also tended to decrease as the NCC contents increased. This is because of the result aforementioned about voids around NCC. After 1,000 h of accelerated weathering, tensile strength showed reduced features compared with the tensile strength values before weathering as shown in Figure 2. The highest decrease of tensile strength was observed in pure PP because it was photooxidized by UV light. Among NCC-only filled composites, decreasing rates of impact strength in specimens were higher in 10 or 15 wt% NCC filled composites compared with 2.5 or 5 wt% NCC filled composites. However, the composites containing talc showed a low decreasing rate even after 1,000 h of accelerated weathering. It is believed that inside plate-shaped talc particles effectively protected the talc filled composites from UV light [19].

Figures 3 and 4 show the flexural strength and flexural modulus of various composites, respectively. Unlike the impact strength and tensile strength, significant increases in flexural strength were not observed in NCC-only filled composites regardless of NCC content. However, we found remarkable increases in flexural strength of the talc filled composites compared with NCC-only filled composites. This is probably because the orientation of talc in longitudinal direction during the molding process led to large
improvement in the bending strength. Besides, as the accelerated weathering proceeded to 1,000 h, flexural strength of pure PP significantly decreased, but there were relatively small differences in the flexural strength of the composites containing UV stabilizer. Numbers of cracks were noticeably observed on the surface of pure PP as shown in the SEM images of Figure 6(a), which is differentiated form Figure 5 and this degradation phenomenon was caused by UV-induced photodissociation. On the other hand, the UV stabilizer have little effect on the surface morphology of 15 wt% NCC-only or 15 wt% NCC and 10 wt% talc hybrid filled composites showing a certain degree of cracks observed in Figures 6(d) or 6(f). After 1,000 h of accelerated weathering, the composites with 5 wt% or more NCC contents showed a drastic decrease in their flexural strength. This is believed to be caused by the aggregations of the NCC particles [19]. Also, as shown in Figure 4(b), flexural modulus of talc filled or NCC-talc hybrid filled composites were noticeably increased than pure PP and control without fillers. This is because the fillers were stiffer than PP, thereby improving the stiffness of the composites [17].

3.2. Morphological Property. Figure 7 shows SEM images of fracture surface of various NCC and NCC-talc hybrid filled composites. From the SEM images, it could be seen that the higher the NCC contents in the composites, the less the NCC particles dispersed. Therefore, we believe that adding small amount of NCC into PP composites, such as 2.5 wt%, is more effective in improving the performance of the composites compared with adding large amount of NCC into the PP composites. As the NCC content of the composites became higher than 2.5 wt%, NCC nanoparticles began aggregating more. Also, it can be seen that the orientation of talc particles in impact specimen was more pronounced for the longitudinal direction and the talc orientation seemed to play a major role in improving the impact strength.

The surfaces of tensile specimen were photographed so as to observe the surface changes of the composite both before and after accelerated weathering test. In Figure 6, the pure PP specimen clearly showed numbers of large cracks caused by moisture and UV light. However, the UV stabilizer was effective in protecting the composites against moisture and UV; therefore, the surface changes of these composites were greatly reduced compared with that of pure PP. But after 1,000 h of UV exposure, the specimens containing 15 wt% NCC showed cracks on the surface regardless of the presence of talc. The cracks could be associated with the decrease in the flexural strength of the composites containing more than 2.5 wt% NCC.

3.3. Color Change Property. To determine the color changes of composites before and after accelerated weathering, the color values of two specimens were measured using a colorimeter. $L^*$, $a^*$, and $b^*$ values were obtained from the $L^*a^*b^*$, which is a color value calculation method recommended by the International Commission on Illumination (CIE). The $L^*$ value is expressed as a value from 0 to 100, and the brightness is represented by $a^*$ and $b^*$, which indicates saturation and is represented by a value from −128 to 127. The $a^*$ value indicates red in the positive direction and green in the negative direction, and the $b^*$ value indicates yellow in the positive direction and blue in the negative direction. The color change values after 1,000 h of accelerated weathering are shown in Table 2. The higher filler contents of the composites resulted in a greater overall brightness of the composites. The composites were more blue and green when the higher amounts of NCC particles were incorporated into

![Figure 4: Flexural modulus of pure PP, control, and PP-based composites depending on accelerated weathering time: (a) NCC-only; (b) NCC-Talc.](image-url)
the composites. Also, when the talc was further added to the composites, the color changes were smaller than NCC-only filled composites.

The value of $\Delta E^{*ab}$, which is an index of the change in color, can be obtained using (1) aforementioned in the experimental test method. The degree in the color difference was classified by referring to the US National Bureau Standard Unit 6.0 [20] (Table 3). The color differences in the pure PP after 250, 500, and 1,000 h of weathering show high values of 3 or greater unlike the composites containing UV stabilizer, as can be seen in Figure 8. The UV stabilizer prevented the photooxidation of PP in the composite. The color difference value of the control specimen was less than 1.5 after 1,000 h of accelerated weathering. As the NCC contents increased, the color difference value increased over time. However, the composites containing both talc and NCC exhibited a smaller color change than the composites containing NCC only after 1,000 h of accelerated weathering. This is because the plate-shaped talc mitigated photodegradations of PP matrix and NCC-talc hybrid filled composites were more resistant to
4. Conclusions

The properties of PP-based composites were evaluated by adding NCC and talc as fillers. 2.5wt% NCC filled PP composite showed the highest impact strength and also, the incorporation of plate-shaped talc particles significantly improved flexural properties. The composites with UV stabilizer showed higher weathering resistance after accelerated weathering and we confirmed that the UV stabilizer effectively prevented the deterioration of the mechanical properties of the composite materials. NCC-talc hybrid
Table 2: Color changes after 1,000 h of weathering in PP, control, NCC-only, NCC-talc hybrid filled PP-based composites.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>ΔL*</th>
<th>Δa*</th>
<th>Δb*</th>
<th>AE*ab</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>2.13</td>
<td>-0.51</td>
<td>-1.80</td>
<td>4.02</td>
</tr>
<tr>
<td>Control</td>
<td>0.24</td>
<td>0.25</td>
<td>-1.08</td>
<td>1.10</td>
</tr>
<tr>
<td>N2.5</td>
<td>0.33</td>
<td>0.19</td>
<td>-1.99</td>
<td>1.32</td>
</tr>
<tr>
<td>N5</td>
<td>0.62</td>
<td>0.14</td>
<td>-1.60</td>
<td>2.25</td>
</tr>
<tr>
<td>N10</td>
<td>1.35</td>
<td>-0.03</td>
<td>-2.07</td>
<td>2.41</td>
</tr>
<tr>
<td>N15</td>
<td>1.43</td>
<td>-0.25</td>
<td>-2.20</td>
<td>2.50</td>
</tr>
<tr>
<td>T10</td>
<td>0.09</td>
<td>0.16</td>
<td>-0.68</td>
<td>1.13</td>
</tr>
<tr>
<td>T10-N2.5</td>
<td>0.13</td>
<td>0.14</td>
<td>-1.28</td>
<td>1.24</td>
</tr>
<tr>
<td>T10-N5</td>
<td>0.34</td>
<td>0.02</td>
<td>-1.42</td>
<td>1.61</td>
</tr>
<tr>
<td>T10-N10</td>
<td>0.71</td>
<td>-0.02</td>
<td>-1.77</td>
<td>1.90</td>
</tr>
<tr>
<td>T10-N15</td>
<td>0.90</td>
<td>-0.16</td>
<td>-2.04</td>
<td>2.23</td>
</tr>
</tbody>
</table>

Table 3: Sensitive expressions of color difference by N.B.S Unit 6.0.

<table>
<thead>
<tr>
<th>ΔE*ab</th>
<th>Sensitive expressions of color difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0–0.5</td>
<td>Trace</td>
</tr>
<tr>
<td>0.5–1.5</td>
<td>Slight</td>
</tr>
<tr>
<td>1.5–3.0</td>
<td>Noticeable</td>
</tr>
<tr>
<td>3.0–6.0</td>
<td>Appreciable</td>
</tr>
<tr>
<td>6.0–12.0</td>
<td>Much</td>
</tr>
<tr>
<td>12.0–d</td>
<td>Very much</td>
</tr>
</tbody>
</table>

Our results suggest that NCC-talc hybrid filled composites are highly applicable for shell layers used in coextruded WPCs.

Conflicts of Interest

The authors declare that they have no conflicts of interest.
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References


