

## 나노 케나프 셀룰로오스가 폴리프로필렌 복합소재의 물성 증가에 미치는 영향

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### Nano-Kenaf Cellulose Effects on Improved Mechanical Properties of Polypropylene Composite

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**초록:** 나노입자크기의 케나프섬유를 폴리프로필렌에 첨가하였을 시, 복합소재의 물성변화를 관찰하였다. 천연크기의 케나프섬유를 나노입자크기의 케나프섬유로 대체하였을 시, 그 복합소재의 인장강도, 휨강도, 충격강도, 열변형온도가 증가한 반면에, 용융지수, 연신율(%), 충격강도 등이 감소하였다. 이는 나노입자크기의 케나프섬유가 폴리프로필렌과 접촉하는 표면적의 증가와 섬유표면에 존재하는 휘발성 추출물질 등의 불순물의 감소에 따른 것으로 판단된다.

**Abstract:** The effects of nano size kenaf cellulose fiber on mechanical property of polypropylene (PP) composite were investigated. The addition of nano-kenaf in place of natural kenaf showed higher tensile strength, flexural strength, impact strength, and heat deflection temperature compared to the natural kenaf filled PP composite, while it shows lower melt flow index, elongation%, and flexural modulus. These seemed to be due to the increased surface area of nano-kenaf fiber contacting PP matrix and reduced impurities such as volatile extractives on the fiber surface.

**Keywords:** nano-kenaf fiber, wood plastic composites, polypropylene, mechanical property.

## Introduction

Cellulose nano fibers, which consist mainly of carbohydrate, are as strong as steel and as bendable as plastics and they show high specific strength and stiffness.<sup>1-4</sup> Calculated elongation modulus of nanocellulose is 137 GPa.<sup>5</sup> Nanomaterials create novel and major breakthroughs in material science. Especially, organic nanocelluloses are difficult to produce and handle. However, pure nanocellulose is harmless for human and it is biocompatible. Possible applications of nanocellulose are bio-nanocomposites (e.g. paper nanocoatings and nanobarriers), materials used in the high strength thin film, low coefficient of thermal expansion (CTE) film, and translucent composite, new

materials for electronics, components for food and cosmetic, medical/pharmaceutical, hygiene/absorbent, emulsion/dispersion, and oil recovery, etc.

The typical main applications for wood-plastic compounds (WPCs) are decks, consumer goods, car interior parts, housewares, construction materials, etc. WPCs have many inherent benefits such as consistent material quality and attractive visual appearance. In the case of WPC decks, additional positive attributes include ease of installation, absence of splinters and the fact that periodic pressure washing is not needed. Cellulose reinforced polymer composites are now generally accepted for automotive applications such as door liners/panels, outside doors, parcel shelves, boot liners, glass windows, tires, etc.<sup>6,7</sup>

Authors have reported kenaf concentration effects on PP compound<sup>8</sup>; however, there have been limited research reports

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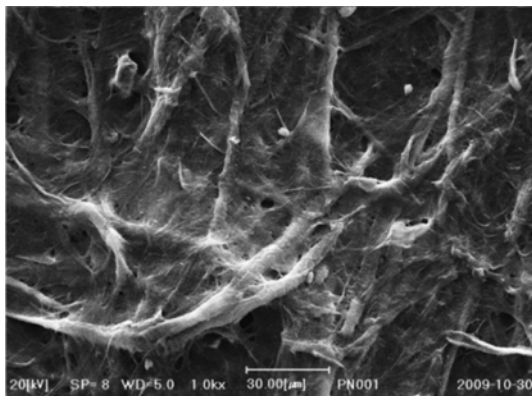
on use of nano-cellulose reinforced PP composite upon mechanical property improvements. This is due to limited availability of nano fibers from natural fiber.

We investigate nano-kenaf fiber reinforced PP composites upon mechanical property compared to natural kenaf fiber filled ones.

## Experimental

The polymer used in this study was polypropylene (PP), supplied by Samsung Total Co., Korea (grade BJ-500). The melt flow index (M.I.) of this polymer after extrusion process was 15 g/10 min in 1 inch PVC die with 5.0 kg at 190 °C (ASTM D 1238). The nano-kenaf containing kenaf (here after we call this as nano-kenaf) used in this study was supplied by Sue Trading Co., South Korea<sup>9</sup> and scanning electron microscope (SEM) photograph of nano-kenaf fibers mixed with large diameter fibers used in this study are shown in Figure 1. The diameter of nano-kenaf measured from electron microscope ranges from 100 nm to 10 μm (nano-kenaf fibers were mixed with big size kenaf fibers) with average aspect ratio of 1000-10000 from the supplier. The average length, density and bulk density of kenaf supplied by the manufacturer were 7 cm, 1.42 g/cm<sup>3</sup> and 0.85-0.90 g/cm<sup>3</sup>, respectively. The kenafs were pre-dried in a vacuum oven for 2 hrs at 100 °C. The moisture content of both kenafs after drying was 5.7%.

Hankuk EM co-rotating twin screw extruder (model STS32HS-40-2V/SF/IF/SNP2/CPC) was used for mixing the nano-kenaf and PP at a mixing temperature of 190 °C. The screw speed and feeding volume were set to 150 rpm and 100 g/min, respectively. The mixing formulations are summarized in Table 1.



**Figure 1.** SEM photograph of nano-kenaf fibers mixed with large diameter fibers (30 μm scale bar).

**Table 1. Mixing Formulations of Nano-kenaf Filled PP Compounds**

Composition (wt%)		
Kenaf 20	Nano-kenaf 20	
Natural kenaf (>100 μm)	Nano-kenaf (100 nm~10 μm)	PP
20	0	80
0	20	80

For the elongation test, dumbbell shape specimens were prepared following ASTM D 638 method using an injection molding machine. The processing temperature, mold temperature, injection pressure, and holding time to injection were set to 180 °C, 56 kg/cm<sup>2</sup>, and 20 sec, respectively. The dimension of the injection molding bar was width (13 mm)/length (57) (total length (190 mm))/thickness (3.18 mm) following ASTM D 638 Type V<sup>1</sup>. Melt flow index (M.I.) was measured by using a melt index tester manufactured by CEAST in Italy following ASTM D 1238 & ISO 1133. An Universal Testing Machine (model SFM-10) manufactured by United Co., USA was used for elongation test at room temperature. The mechanical test curves were obtained from the dumbbell shaped specimens following ASTM D 638. The tensile strength (stress maximum) (kg/cm<sup>2</sup>), elongation% (strain maximum), flexural strength (kg/cm<sup>2</sup>), flexural modulus (kg/cm<sup>2</sup>), of each compound was measured. The impact strength (KJ/m<sup>2</sup>) was measured by using an Izod impact test machine manufactured by CEAST in Italy following ASTM D 256. The heat deflection temperature (HDT) test measures the deflection temperature of a specimen sample as of ASTM D648. HDT was measured by using a Bending Stress Load manufactured by CEAST in Italy following ASTM D 648.

## Results and Discussion

Figure 2 shows the M.I. of each compound. At the same concentration (kenaf 20 wt%), the M.I. of the nano-kenaf filled compound was significantly lower than that of the kenaf, i.e. M.I. [nano-kenaf 20 (3.0) < kenaf 20 (14.6)].

Figure 3 shows the tensile strength (stress maximum) (kg/cm<sup>2</sup>) of each compound. The tensile strength of the nano-kenaf 20 compound was 12.7% higher than that of the kenaf 20, i.e. T.S. [nano-kenaf 20 (384.6) > kenaf 20 (341.4)].

Figure 4 shows the elongation (E.)% (strain maximum) of each compound obtained from an Instron tester. The elongation% of the nano-kenaf filled compound was 8.2% lower

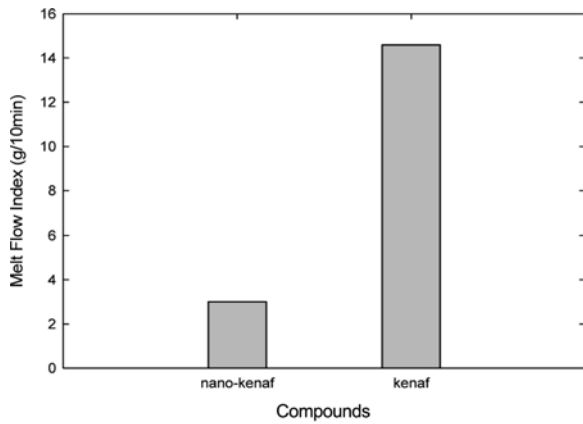


Figure 2. Melt flow index (M.I.) of each compound.

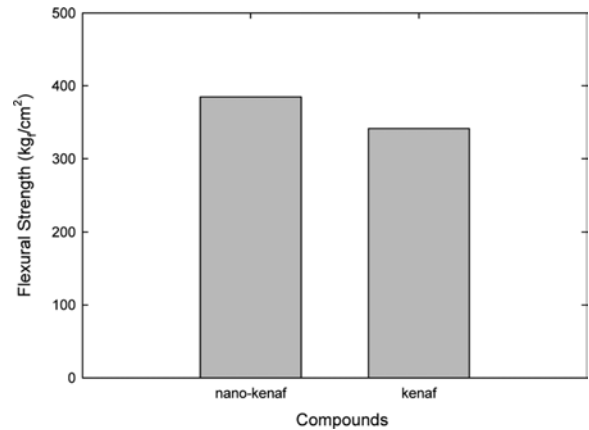


Figure 5. Flexural strength of each compound.

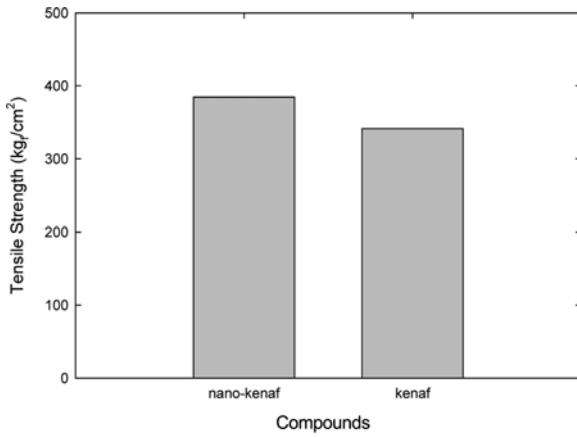


Figure 3. Tensile strength (stress maximum) (kg<sub>f</sub>/cm<sup>2</sup>) of each compound.

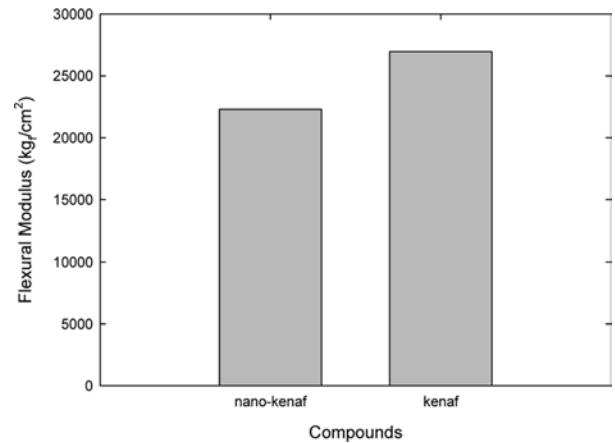


Figure 6. Flexural modulus of each compound.

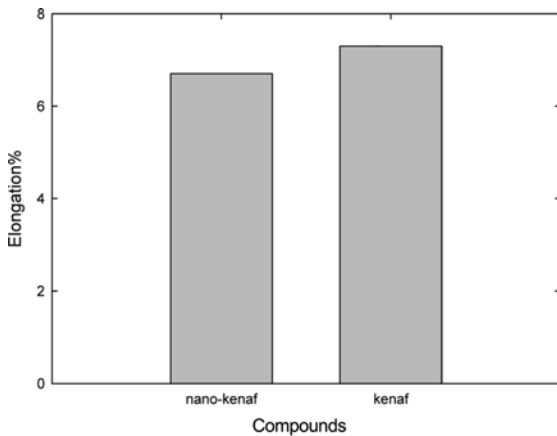


Figure 4. Elongation% (strain maximum) of each compound.

than that of the kenaf, i.e. E.% [nano-kenaf 20 (6.7) < kenaf 20 (7.3)].

Figure 5 shows the flexural strength (F.S.) (kg<sub>f</sub>/cm<sup>2</sup>) of each

compound obtained from an Instron tester. The flexural strength of the nano-kenaf 20 was 7.6% higher than that of the kenaf 20, i.e. F.S. [nano-kenaf 20 (571.9) > kenaf 20 (531.5)].

Figure 6 shows the flexural modulus (F.M.) (kg<sub>f</sub>/cm<sup>2</sup>) of each compound obtained from an Instron tester. The flexural modulus of the nano-kenaf 20 was 17.3% lower than that of the kenaf 20, i.e. F.M. [nano-kenaf 20 (22291) < kenaf 20 (26956)].

Figure 7 shows the impact strength (I.S.) (KJ/m<sup>2</sup>) of each compound obtained from an Izod impact tester. The impact strength of the nano-kenaf filled compound was 23.9% higher than that of the kenaf, i.e. I.S. [nano-kenaf 20 (5.7) > kenaf 20 (4.6)].

Figure 8 shows the HDT of each compound. While the HDT of the kenaf 20 was 142.0 °C, that of the nano-kenaf was 142.6 °C. Thus there was no significant HDT difference between nano-kenaf and kenaf filled PP compounds, i.e. HDT [nano-kenaf 20 (142.6) ≥ kenaf 20 (142.0)]; however the HDT

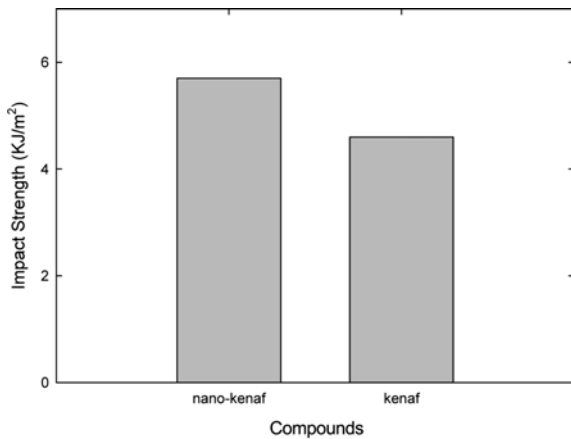


Figure 7. Impact strength of each compound.

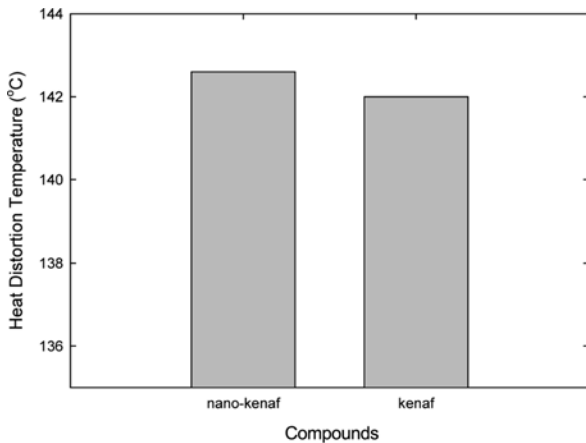


Figure 8. HDT of each compound.

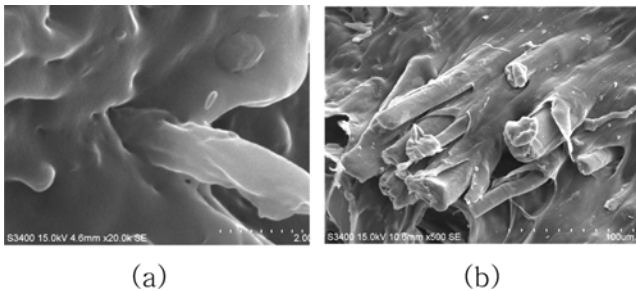


Figure 9. SEM photographs of (a) nano-kenaf (2 μm scale bar); (b) kenaf filled PP composite (100 μm scale bar).

of the nano-kenaf 20 was slightly higher than that of the kenaf 20.

Figure 9 shows SEM photographs of nano-kenaf and kenaf filled PP compounds. The interfacial adhesion between kenaf fiber and PP was not good for both nano-kenaf and kenaf filled systems due to chemical composition differences between two materials. The interfacial adhesion of nano-kenaf with PP

seemed relatively better than that of the kenaf with PP.

High surface area particle filled polymer composites show higher mechanical property compared to low surface area filled one at the same volume.<sup>10-12</sup> This is due to increased surface area contacting between fiber and polymer matrix, which leads to reduction of polymer chain mobility, which provides reduced entropy of mixing  $\Delta S_M$  and as a result increased Gibbs free energy  $\Delta G_M$  between fiber and PP.<sup>10</sup> Nano-kenaf has high surface area than the kenaf at the same volume loading. Kenaf consists of cellulose (45-47%), hemicelluloses (21-23%), lignin (8-13%) and other extractable ingredients such as pectin and wax. These chemical contents vary depending on size, type, harvest season and location, etc. During the nano-kenaf manufacturing process, the water channels in kenaf fiber are destroyed and volatile extractives present in the natural kenaf are eliminated. The elimination of volatile extractives implicates removal of impurities, which hinder spherulite formation on the fiber surface. Yosomiya argued that poor adhesion of a material is due to presence of low surface tension material such as impurities or adsorbed water layers.<sup>13</sup> This leads to interfacial dewetting between fiber surface and polymer matrix. The dewetting surface is responsible for crack propagation, which leads to composite failure.<sup>14,15</sup> As stated above the spherulite formation on the fiber surface implicates more adhesion of PP on the cellulose surface. This gives better mechanical properties of the compound.<sup>16</sup> It is well known that natural fiber consists of cellulose, lignins and various contain extractable chemicals including fatty acids, water, sugars, starches, oils, resins, waxes, pectins, tannins, amino acids, proteins, etc. range from 5 to 20 wt%.<sup>17-19</sup> The adhesion between natural wood particle and matrix polymer is hindered by not only lignins, but also volatile extractives. These lead to poor adhesion between fiber and polymer matrix.<sup>16,20-22</sup> It has been confirmed by researchers that volatile extractives are present in natural fiber<sup>18,23,24</sup> and they are responsible for decrease of mechanical property of the compound.<sup>20-22,25,26</sup> Volatile extractives consist of low molecular weight polymers and act as a plasticizer (e.g. oils) and/or dewetting agent (e.g. waxes) depending on compatibility with polymer matrix. They are present in cellulose channels and gradually migrate out on cellulose surface as a function of time, temperature and concentration following Fick's law and then the mobility of PP chain in the compound increases, which matches with higher elongation% of kenaf fiber compared to nano-kenaf fiber filled PP composite. The SEM photographs show higher interfacial adhesion of nano-kenaf with PP compared to kenaf filled sys-

tem, which matches with better mechanical properties (e.g. higher-tensile strength, -flexural strength, and -impact strength) of nano-kenaf/PP system over kenaf/PP system. Overall, the high surface area per unit volume of the nano-kenaf apparently contributed improvement of interfacial adhesion between kenaf surface and PP and this clearly seemed responsible for high mechanical properties compared to the natural kenaf fiber filled system. And further effective interfacial adhesion between nano-kenaf fiber surface and PP chain seemed occurred due to reduced level of impurities such as low molecular weight volatile extractives on the nano-kenaf surface.

### Conclusions

The nano-kenaf fiber added PP compound showed higher tensile strength, flexural strength, impact strength, and HDT; however, it showed lower M. I., elongation%, and flexural modulus compared to natural kenaf fiber filled PP system. These seemed due to increased surface area of nano-kenaf fiber contacting PP matrix and removed volatile extractives on the fiber surface.

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