알카리로 처리된 나노케냐프 섬유가 PP 복합소재 내에서 기계적 물성 변화에 미치는 영향

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(2014년 6월 4일 접수, 2014년 7월 7일 수정, 2014년 7월 19일 채택)

Effects of Alkali Treated Nano-kenaf Fiber in Polypropylene Composite upon Mechanical Property Changes

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(Received June 4, 2014; Revised July 7, 2014; Accepted July 19, 2014)

초록: 나노케냐프 섬유가 포함된 셀룰로스 섬유를 알카리(NaOH)로 처리 후 PP 수지에 첨가하여 물성에 미치는 영향에 대하여 조사하였다. 알카리를 섬유에 처리한 효과로는 M.I., 신장율, 충격강도가 증가하는 반면 인장강도, 휨모듈러스, 열변형온도가 처리하지 않은 섬유에 비해 감소하였다. 알카리를 나노섬유에 처리하였을 때 섬유표면의 불순물과 화학물질을 제거하여 섬유표면의 특성을 변화시켜서 나노섬유와 PP 수지간의 계면간 접착력을 감소시키고 PP의 특성을 변화시키는 것으로 보인다.

Abstract: The surface of nano-kenaf containing cellulose fibers was treated with alkali (NaOH) and their effects on the physical properties of the polypropylene (PP) composite were investigated. The treatment of alkali on the fibers increased the melt flow index (M.I.), elongation%, and impact strength, while it decreased the tensile strength, flexural modulus and heat deflection temperature (HDT) of the compound compared to the untreated one. It seemed the alkali treatment on the nano-kenaf fiber changed the character of the fiber due to removal of impurities and chemicals on the surface and resulted in decreased interfacial adhesion between the nano-fiber surface and the PP matrix and changed the character of the PP.

Keywords: alkali treatment, nano-kenaf, polypropylene, mechanical property, interfacial adhesion.

Introduction

Cellulose fibers are known to low cost, renewability, biodegradability, low specific gravity compared to mineral particles. The typical main applications for cellulose added plastic compounds are car interior parts, consumer goods, housewares, construction, decking, etc. Practical use of celluloses are in the manufacturing of automotive textiles in order to replace the non-degradable, non-recyclable contents of salvaged automobiles to the biodegradable content due to increased social awareness of environmental problems.[1] 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.[1,2] About 30 components of a car are manufactured from cellulose reinforced composites for the recent automotives.[3] Increasing modulus and improving durability of the composite are essential problems that need to be addressed in order for the continued growth of the field such as automotive parts, building, construction applications, etc.

Kenaf fibers have been typically a major source of rope, twine, fishing net, strap, fabric, paper, etc. 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

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season and location, *etc*. Currently they are used for a variety of biocomposites purposes.

The cellulose nano fibers are as strong as steel and as bendable as plastics and they show high specific strength and stiffness.[4-7] Cellulose is a linear, stereo-regular polysaccharide connected with repeated D-glucopyranose units linked by 1,4-β-glucoside bonds. Calculated elongation modulus of nanocellulose is 137 GPa.[8] Nanomaterials create novel and major breakthroughs in material science. Especially, organic nanocelluloses are difficult to produce and handle, however, they are harmless for human due to biocompatibility. Possible applications of nano-cellulose are bio-nanocomposites, high strength thin film materials, low coefficient of thermal expansion (CTE) film, translucent composite, new materials for electronics, paper nanocoatings & nanobarriers, components for food and cosmetics, medical/pharmaceutical, hygiene/absorbent, emulsion/dispersion, oil recovery, *etc*. There have been few research results on obtaining nano-cellulose from wood due to complex constituents in wood cell walls, complicated treatments, and results difficult to interpret. Nano-scale crystallites obtained from cellulose are easily *co*-crystallize laterally and aggregate. They also are to phase transform through alkalization, dissolution, and chemical modification.[9] There have been several known techniques for making nano-cellulose from plants. (1) Mechanical treatment or chemical-mechanical treatment for nanofibrillation.[2,10] (2) Series of chemical treatment, hydrolysis of cellulose, followed by mechanical disintegration or ultrasonification.[11-17] (3) Combination of acid hydrolysis and high-pressure disintegration. (4) Dissolving techniques.[18-20] (5) Cryo-crushing processes of hydrolyzed cellulose.[21,22] (6) Repeated milling of the pulp in water over a long period of time.[23,24] (7) Enzymatic pretreat-ment of cellulose fibers, followed by mechanical splitting in water by means of special high-shear mills or refiners.[23,25,26]

There have been many research reports of the treatment of alkali on cellulose fibers and applications of these in polymer composites.[2,10-17,27-35] For chemical treatment of cellulose, the focus has been mainly on changes of characteristics of cellulose surface by removing impurities on the cellulose fiber, which results in more hydroxyl groups (active sites) exposure on the cellulose fiber.[10-17] There have been no published reports uses of nano-cellulose filled polymer composite for characterization because the nano-cellulose fibers has been typically obtained in lab scale thus the yield was so small not enough to put into polymer matrix.

The addition of nano-kenaf in place of natural kenaf increased mechanical properties such as tensile strength, flexural strength and flexural modulus while it decreased flowability, elongation% and impact strength.[36-38] There have been no published research reports on nano-cellulose treatment with alkali and reinforcement in PP upon mechanical property changes.

In this research, we investigate alkali (NaOH) treated nano-kenaf containing fiber reinforced PP composites upon mechanical property changes compared to untreated one.

Experimental

Materials. 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 size kenaf mixed with micron size kenaf fibers (here after we call this as nano-kenaf)
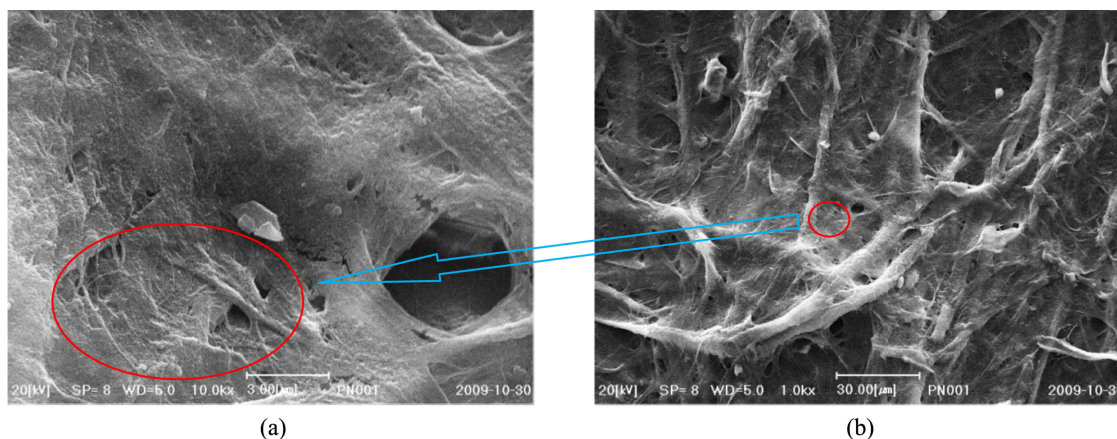

(a)   (b)

Figure 1. Photographs of (a) nano-kenaf fibers (3 μm scale bar); (b) nano-kenaf fibers mixed with kenaf fibers (30 μm scale bar).

used in this study was supplied by Sue Trading Co. (S. Korea)[38] and photographs of these nano-kenaf fibers are shown in Figure 1. The diameter of nano-kenaf measured from electron microscope ranges from 100 nm to 10 μm with average aspect ratio of 1000-10000 from the supplier. The nano-kenaf was treated with NaOH mixed with distilled water (nano-kenaf: NaOH:water = 2.5:0.3:97.2 wt%) for 24 h and then washed with enough distilled water. And the cellulose was dried out in an oven for 24 h.

Mixing. Hankuk EM co-rotating twin screw extruder (model STS32HS-40-2V/SF/IF/SNP2/CPC, screw diameter 32 mm, L/D 40) was used for mixing compounds, the NaOH nano-kenaf/PP (20/80 wt%) and nano-kenaf/PP (20/80 wt%), at a mixing temperature of 190 °C. The screw speed and feeding volume were set to 150 rpm and 100 g/min, respectively.

Injection Specimen Preparation. For the elongation test measurement, 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 kgf/cm^2, and 20 sec, respectively. The dimension of the injection molding bar was 13×57×190×3.18 mm (width(W) ×length(L)×total length(TL)×thickness(T)) following ASTM D 638 Type V[1].

Melt Flow Index. M.I. was measured by using a melt index tester manufactured by CHAST in Italy following ASTM D 1238 & ISO 1133. Each compound was pressed with 5.0 kg load at 190 °C and the weight passed through an orifice for 10 min was measured.

Mechanical Property. For the measurement of elongation properties, an Universal Testing Machine (model SFM-10) manufactured by United Co., USA was used at room temperature. The cross-head speed for mechanical strength test was set to 50 mm/min. The mechanical test curves were obtained from the dumbbell shaped specimens type ASTM D 638. Average value of 10 specimens of each compound was presented. The tensile strength (stress maximum) (kg$_f$/cm^2), elongation% (strain maximum), flexural strength (kg$_f$/cm^2), flexural modulus (kg$_f$/cm^2), and impact strength (kJ/m^2) of each compound was measured. The dimension of the impact strength specimen was 127.0×12.7×6.35 mm ($L×W×T$). The impact strength (kJ/m^2) was measured by using an IZOD impact test machine manufactured by CHAST in Italy following ASTM D 256. A notched sample was placed in a cantilevered beam and an arm held at a specific height (constant potential energy) was released. The arm hit the sample and broke it. From the energy absorbed by the sample, its impact strength was determined. The impact strength was calculated following eq. (1).

$$\text{IZOD Impact strength (kJ/m}^2) = \frac{\text{Energy absorbed by the sample}}{\text{Area of specimen}} \quad (1)$$

The % change of mechanical property was calculated following eq. (2);

$$\% \text{ Change} = \frac{\text{(Treated nano-kenaf)-(Nano-kenaf)}}{\text{Nano-kenaf}} \times 100 \quad (2)$$

Heat Deflection Temperature (HDT). The heat deflection temperature (HDT) test measures the deflection temperature of a specimen ($L×W×T$ (127.0×12.7×6.35 mm)) as of ASTM D648. HDT was measured by using a Bending Stress Load manufactured by CHAST in Italy following ASTM D 648. The test specimen was loaded in three-point bending holder in the edgewise direction. The stress applied on the sample was at 1.82 MPa, and the temperature was increased at 2 °C/min until the specimen deflected by 0.254 mm.

Scanning Electron Microscope (SEM) Characterization. A scanning electron microscope (SEM, Philips Co.) was used to qualitatively characterize the fiber dimension of the nano-kenaf and fracture surface of NaOH treated nano-kenaf and PP. The specimens were coated with gold coating using a Sputter Coater.

Results and Discussion

Flowability (Melt Flow Index). Figure 2 shows the M.I. of
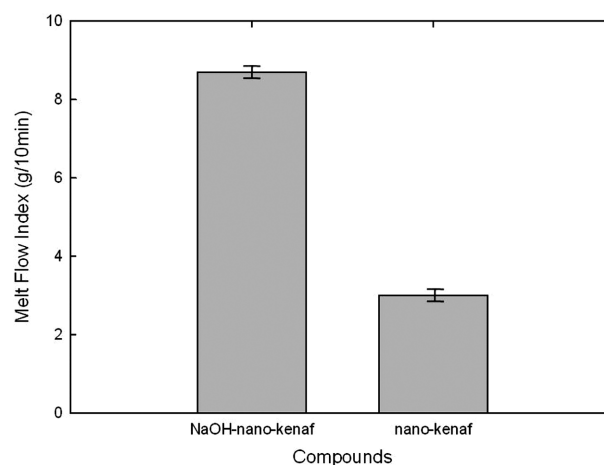

Figure 2. Melt flow index (M.I.) of NaOH treated nano-kenaf/PP and untreated nano-kenaf/PP compound.

each compound. At the same concentration (nano-kenaf 20 wt%), the M.I. of the alkali treated nano-kenaf filled compound was significantly higher than that of the nano-kenaf, *i.e.* M.I. [NaOH nano-kenaf (8.7) < nano-kenaf (3.0)]. We presume this was due to morphology change of the PP chain by the introduction of alkali, which resulted in increased chain mobility of the compound. We will discuss about this in discussion section related with the mechanical property changes of the compound.

Mechanical Property. Figure 3 shows the tensile strength (T.S.) (stress maximum) (kg_f/cm^2) of each compound obtained from an Instron tensile tester. The tensile strength of the NaOH nano-kenaf compound was 11.7% lower than that of the nano-kenaf, *i.e.* T.S. [NaOH nano-kenaf (339.7) > nano-kenaf (384.6)]. This seemed due to decreased chain strength of the
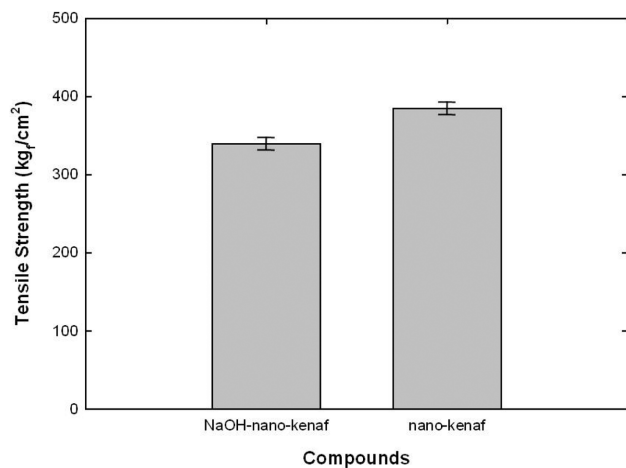
compound presumably by introduction of the NaOH in the compound.

Figure 4 shows the elongation (E.)% (strain maximum) of each compound obtained from an Instron tester. The elongation% of the NaOH nano-kenaf compound was 2153.7% higher than that of the nano-kenaf, *i.e.* E.%. [NaOH nano-kenaf (151.0) > nano-kenaf (6.7)].

Figure 5 shows the flexural strength (F.S.) (kg_f/cm^2) of each compound obtained from an Instron tester. The flexural strength of the NaOH nano-kenaf was 27.3% lower than that of the nano-kenaf, *i.e.* F.S. [NaOH nano-kenaf (415.8) > nano-kenaf (571.9)].

Figure 6 shows the flexural modulus (F.M.) (kg_f/cm^2) of each compound obtained from an Instron tester. The flexural modulus of the NaOH nano-kenaf was 35.6% lower than that

Figure 3. Tensile strength (stress maximum) of NaOH treated nano-kenaf/PP and untreated nano-kenaf/PP compound.

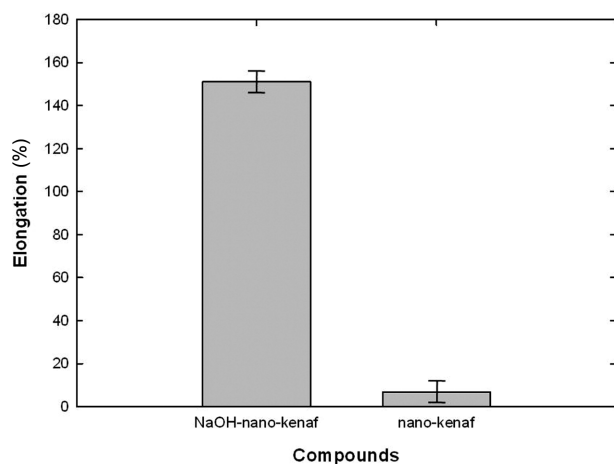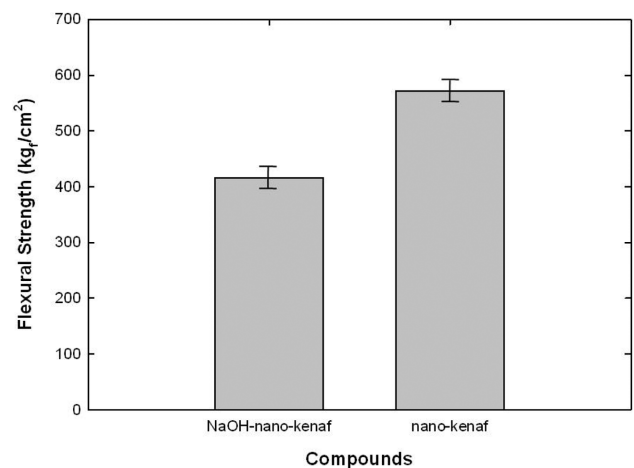**Figure 5.** Flexural strength of NaOH treated nano-kenaf/PP and untreated nano-kenaf/PP compound.

Figure 4. Elongation (strain maximum) of NaOH treated nano-kenaf/PP and untreated nano-kenaf/PP compound.
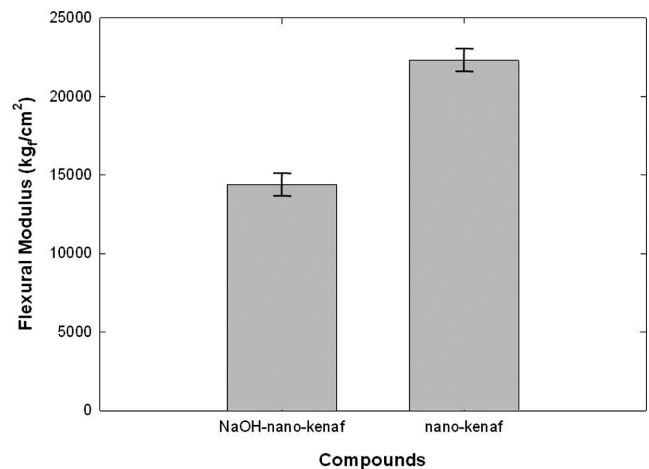

Figure 6. Flexural modulus of NaOH treated nano-kenaf/PP and untreated nano-kenaf/PP compound.
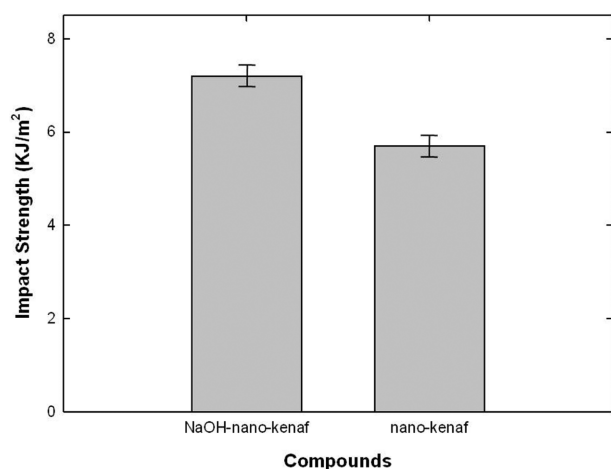
Figure 7. Impact strength of NaOH treated nano-kenaf/PP and untreated nano-kenaf/PP compound.
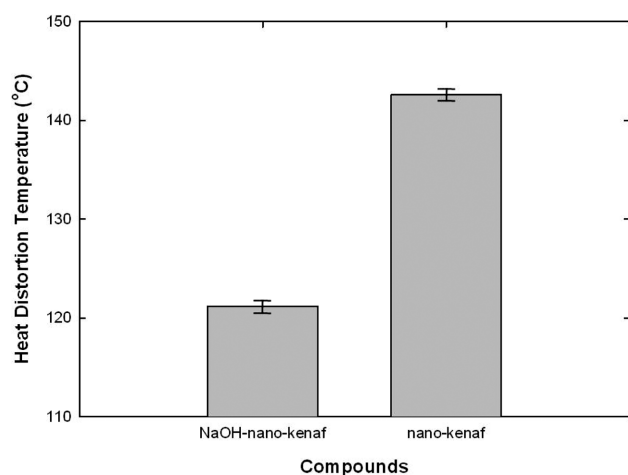

Figure 8. HDT of NaOH treated nano-kenaf/PP and untreated nano-kenaf/PP compound.

of the nano-kenaf, *i.e.* F.M. [nano-kenaf (14360) < kenaf (22291)].

Figure 7 shows the impact strength (I.S.) (kJ/m^2) of each compound obtained from an IZOD impact tester. The impact strength of the NaOH nano-kenaf filled compound was 26.3% higher than that of the nano-kenaf, *i.e.* I.S. [NaOH nano-kenaf (7.2) > nano-kenaf (5.7)].

Mechanical property changes of NaOH treated nano-kenaf/PP compound as shown in Figures 3 through 7 will be discussed in discussion section.

Heat Distortion Temperature (HDT). Figure 8 shows the HDT of each compound. While the HDT of the NaOH nano-kenaf was 121.2 °C, that of the nano-kenaf was 142.6 °C. Thus the treatment of alkali on nano-kenaf surface decreased the

Table 1. Formulation and Comparison of Physical Properties of the Alkali Treated Nano-kenaf and Untreated Nano-kenaf

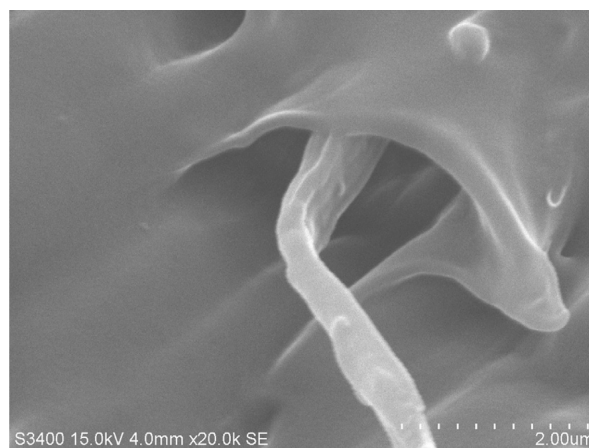|	Alkali treated nano-kenaf (100 nm~10 μm)	Untreated nano-kenaf (100 nm~10 μm)
Composition (weight %) nano-kenaf/PP	20/80	20/80
Melt flow index (M. I.) (g/10 min)	8.7 (+190%)	3.0
Tensile strength (kg$_f$/cm^2)	339.7 (-11.7%)	384.6
Elongation%	151.0 (+2153.7%)	6.7
Flexural strength (kg$_f$/cm^2)	415.8 (-27.3%)	571.9
Flexural modulus (kg$_f$/cm^2)	14,360 (-35.6%)	22,291
IZOD impact strength (kJ/m^2)	7.2 (+26.3%)	5.7
HDT (°C)	121.2 (-14.9%)	142.6
Sp.Gr.	0.99	0.95

Figure 9. SEM photograph of interface between NaOH treated nano-kenaf and PP matrix (2 μm scale bar).

HDT of the compound.

Physical properties of the NaOH treated nano-kenaf and untreated nano-kenaf compounds are summarized in Table 1.
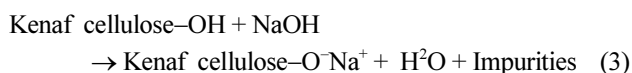
Interfacial Adhesion. Figure 9 shows SEM photograph of fracture surface of NaOH treated nano-kenaf filled PP composite. The photograph showed poor interfacial adhesion between nano-kenaf and PP matrix.

In this research, the NaOH treated nano-kenaf filled PP composite showed lower tensile strength, flexural strength, flexural modulus, and HDT, while it showed higher M.I., elongation%, and impact strength compared to the untreated nano-kenaf

filled PP composite.

Natural fiber consists of cellulose, lignins and various con-tain extractable chemicals including fatty acids, water, sugars, starches, oils, resins, waxes, pectins, tannins, amino acids, pro-teins, *etc*. range from 5 to 20 wt%.[39-44] They hinder the adhe-sion between natural wood particle and matrix polymer. This leads to poor adhesion between fiber and polymer matrix.[45,46] It has been confirmed by studies that volatile extractives are present in natural fiber[40,47,48] and they are responsible for decrease of mechanical property of the compound.[27,42,45,47,49] Yosomiya argued that poor adhesion of a material is due to presence of low surface tension material such as impurities or adsorbed water layers.[50] This leads to interfacial de-wetting between fiber surface and polymer matrix. The de-wetting sur-face is responsible for crack propagation, which leads to com-posite failure.[51,52] The diameters of kenaf fibers we have used in this study are ranges 100 nm to 10 μm, which consists of mixture of nano size kenaf fibers and micron size kenaf fibers. In this experiment, the treatment of alkali on nano-kenaf fiber surface removed the impurities on nano-kenaf surface. During the nano-kenaf manufacturing process, the water channels in the kenaf fiber are destroyed and volatile extractives present in the natural kenaf channels are eliminated. The elimination of volatile extractives implicates removal of impurities on fiber surface; however, the residue impurities in the undestroyed kenaf channel may not clearly removed, thus this migrated on the fiber surface afterward and leads to poor interfacial adhe-sion between the fiber and the PP. Thus it doesn't seem help further reinforcement of the PP composite.

NaOH has been well known chemical for removal of lignins and other volatile extractives on natural fiber surface. When alkali removes impurities on natural fibers, more active sites, hydroxyl groups, which can react with other chemicals such as coupling agents or polar character homogenizers, are exposed to polymer matrix. Further treatment of nano-kenaf with NaOH triggers reaction between accessible -OH groups of the kenaf and -OH groups of the alkali according to following pro-posed chemical reaction[28,33-35] as shown in eq. (3).

$$\text{Kenaf cellulose–OH} + \text{NaOH}$$
$$\rightarrow \text{Kenaf cellulose–O}^-\text{Na}^+ + \text{H}_2\text{O} + \text{Impurities} \quad (3)$$

And the character of kenaf fiber surface changes from hydrophilic to salt, which is less hydrophilic.

The addition of alkali into polymer solution decreases the viscosity and viscoelastic properties of the solution. Alkali

Table 2. NaOH Treatment Effects on Sisal Filled PP Composites[53]

Chemicals/Time	Bending strength (MPa)	Bending modulus (GPa)
Reference sample	30	1.5
NaOH/50 h	24	1.1
NaOH/500 h	18	1.05

neutralizes with negative ion on polymer molecular to a critical concentration and it provides positive ions to polymer molec-ular and the positive ions decrease the viscosity of polymer by charge shield.[29,31] The treatment of NaOH reduces bending strength and bending modulus of cellulose (sisal) filled PP composites as shown in Table 2.[53] Our result, NaOH treated nano-kenaf filled PP composite, showed the same trend of above others.[53] We also observed poor interfacial adhesion between NaOH treated nano-kenaf and PP surface as shown in Figure 9. There was other research result that showed a poor interfacial adhesion between alkali treated fiber (beech) and PP phase.[30] They showed higher tanδ values of alkali treated fiber/ PP composite through temperature range -60~150 °C com-pared to untreated fiber/PP composite, which the alkali treat-ment facilitate the interaction between filler-polymer and lowers the degree of adhesion, *i.e.* poor bonding leads to dis-sipation of energy. The alkali treatment on the cellulose fibers reduced the hydrophilic nature of the fibers as illustrated in eq. (3) and this resulted in better dispersion of the nano-fibers in the polymer matrix. This phenomenon leads to higher impact strength (kJ/m^2) compared to untreated compound. Overall, our results, NaOH treated nano-kenaf/PP composite, showed the same trend compared to micron size fiber filled PP systems as explained above.[29,30,31,53]

In this research, the positive ion (Na^+) seemed form a charge shield on nano-kenaf surface and superfluous positive ions affected the PP property compared to untreated nano-kenaf filled system, which was directly connected to reduced vis-cosity and viscoelastic property of the compound. We pre-sumed the degree of hydrophilic character of the nano-kenaf was depended on the concentration of NaOH. As the NaOH concentration was increased to a certain level, the impurities on the fiber were removed from the surface thus more hydroxyl groups were exposed on the cellulose surface; how-ever, as the NaOH level was higher than this level the exposed hydroxyl group reacted with the positive ions (Na^+) and the surface was covered with the positive ions (Na^+), which was responsible for less hydrophilic surface.

Conclusions

In this research, we investigated alkali treated nano-kenaf fiber effects on physical property of the PP compound.

The NaOH treated nano-kenaf filled PP composite showed lower tensile strength, flexural strength, flexural modulus, and HDT than the nano-kenaf filled PP composite, while it showed higher M.I., elongation%, and impact strength. The treatment of alkali on nano-kenaf surface removed impurities and chemicals on the surface and positive ion (Na^+) changed the character of the fiber and PP.

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