

Properties of Green Fiber Reinforced Polypropylene Nanocomposites Pre-Treated With Acrylonitrile

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Abstract: Green fiber polymer nanocomposites were prepared using green fiber (kenaf fiber), polypropylene (PP) and Halloysite Nanoclay (HN) by single extruder and injection molding technique. Before being used, green fiber was chemically treated with acrylonitrile (AC) for increasing its hydrophobicity and compatibility with composite matrix. The effects of green fiber loading and HN clay incorporation on the properties of developed nanocomposites were investigated. AC pre-treatment reduced hydrophilicity of green fiber which was confirmed through Fourier transform infrared (FTIR) spectroscopy. Scanning electron microscopic (SEM) analyses indicated that the structure and surface morphology of composites were significantly changed when HN clay assimilation into green fiber/PP composites. XRD result revealed that the crystallinity of nanocomposites increased upon HN clay used. Tensile properties of composites were found to be improved for HA clay injection. Water absorption also decreased for HA clay and increased with the increase of GF loading. Agglomerates and micro-voids was largely decreased for the satisfactory interaction of pre-treated GF to PP composites, which enhance dispersion of the fiber in the matrix. Hydrophilic nature of GF was significantly reduced upon AC pre-treatment.

Keywords: *Nanocomposites; Halloysite nanoclay; Tensile property; EDX; SEM*

Introduction: The recent concern toward the deterioration of the environment has generated immense interest on the use of the abundant agricultural residues. An alternative solution to solve this problem is to use these residues as filler/fiber in composites materials. Due to environmental and renewable issues, development of high quality engineering products prepared from natural resources is ever increasing [1,2]. Among all natural fibers, kenaf plants (*Hibiscus cannabinus*) have extensively been planted and used over the past few years. Kenaf fiber has already been identified as a potential raw material due to its some good properties i.e. low density, good stiffness and high tensile properties [3-6]. Research is going on for using lignocellulosic fibers in place of synthetic fibers as reinforcing fillers [1,7,8]. The usage of these natural substances as reinforcing fillers is cheap. It also minimizes the environmental pollution caused by their bio-degradable characteristics [9]. Agriculture by-products such as corn stalk,

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kenaf, rice straw, wheat straw and grass have become potential sources for natural fibers as they are easily available, inexpensive, renewable, environmentally acceptable, non-abrasive and light. The cost of producing lignocellulosic natural reinforced polymer composites is quite low. As a result, these materials have attracted much attention of the researchers and relevant industry [10].

Kenaf fiber was chosen as the green filler material as it is easily obtainable as waste product and has a minimal effect on the environment due to its biodegradable properties [1, 11]. One of the major drawbacks of using kenaf fiber as filling material is its hydrophilic nature that will cause moisture absorption and consequent deformation of the product. For overcoming this problem kenaf fiber was chemically treated with acrylonitrile (AC), which in turn improved the mechanical properties of the composites. Nanotechnology is a promising approach towards developing advanced materials for the current and future engineering products. Polymer nanocomposites possess better thermal, mechanical and chemical properties. Many studies have been carried out on polymer composites using natural and synthetic fiber. However, very little research work has been reported on the preparation of nanocomposites using green fiber, polypropylene (PP) and Halloysite Nanoclay (HN). Therefore, the aim of this work is to develop green nanocomposites using kenaf fiber, PP and HA caly. Finally, the important properties like physical and mechanical properties of developed composites were investigated.

Materials & Method:

Materials: Acrylonitrile (AN) and Halloysite nanoclay (HN) was analytical grade reagent. The thermoplastic polyethylene (PP) matrix was supplied by the Polyolefin Company, Private Limited Singapore in the form of homopolymer pellets. The kenaf, used as reinforcing filler and green fiber (GF), was collected from local market in Malaysia. Halloysite nanoclay (HN) was obtained from Sigma Aldrich Company, products of Inc. (USA), and was used as received.

Kenaf Fiber Pre-Treatment: Kenaf fiber was dried at 105°C for 24 hours for reducing its moisture content. It was then kept in a sealed container. 500g kenaf was submerged into the acrylonitrile solution for 10 minutes. Kenaf was then taken out, washed with soap solution followed by water and finally dried in open air.

Nanocomposites Preparation: Pre-treated kenaf fiber and 3% Halloysite nanoclay (HA) was mixed thoroughly with PP granules in order to make nanocomposites. The PP matrix and pre-treated kenaf fiber were taken in different weight fractions (25%, 30%, 35% and 40%). Composites were prepared by passing the mixtures through a single screw extruder at a constant temperature of 135°C ± 5°C. The extruded composites were cut into 15-20 cm long small pieces and crashed into smaller granules using a grinding machine (Model FFC-23, Machinery Company Limited India). The dried granulates were molded according to DIN EN ISO 572-2 Type 1A and DIN EN ISO 179, Type 1 using the injection molding machine at a molding temperature of 165°C for preparing tensile test specimens.

Test analysis: For EDX and X-ray diffraction (XRD) analysis, a PANalytical XRD diffractometer was used to investigate the crystallinity of composites, where Cu K α ($\lambda = 1.54 \text{ \AA}$) radiation was employed with 2θ varying between 4° to 80° at $5^\circ/\text{min}$. Fourier Transform Infrared Spectroscopy (FTIR) of the untreated and treated kenaf were recorded on a Shimadzu FTIR-81001 Spectrophotometer. The obtained spectra are discussed in the results and discussion section. The interfacial adhesion between the kenaf and PP in manufactured composites were examined using a Scanning Electron Microscope (JSM-6701F) supplied by JEOL Company Limited, Japan. The micrographs were taken at a magnification of 300. Tensile tests were conducted according to ASTM D 638-01 using a Universal Testing Machine (Model: MSC-5/500, Agawn Seiki Company Limited, Japan). The tests were performed at a crosshead speed of 10 mm/min. Water Absorption and biodegradability test was carried out according to ASTM D 570-99 and ASTM G160-12 respectively.

Results and Discussion:

Energy-dispersive X-ray spectroscopy (EDX): Energy-dispersive X-ray spectroscopy (EDX) is an analytical technique used for the elemental analysis or chemical characterization of a sample. With the purpose of confirm the incorporation of Halloysite nanoclay inside the composites the EDX test was conducted. The EDX spectrum of nanocomposites shows two elemental peaks of silicon (Si) (17%) and aluminum (Al) (10%). This observation is expected if one considers the presence of Si and Al nanoparticles in the nanocomposites samples. The Halloysite nanoclay (HN) was mixed into the GF/PP composites. This combination may be responsible for the observed peaks as reflected in the EDX spectrum shown in Figure 1. The overall EDX results confirmed that HA clay was present into the nanocomposites.

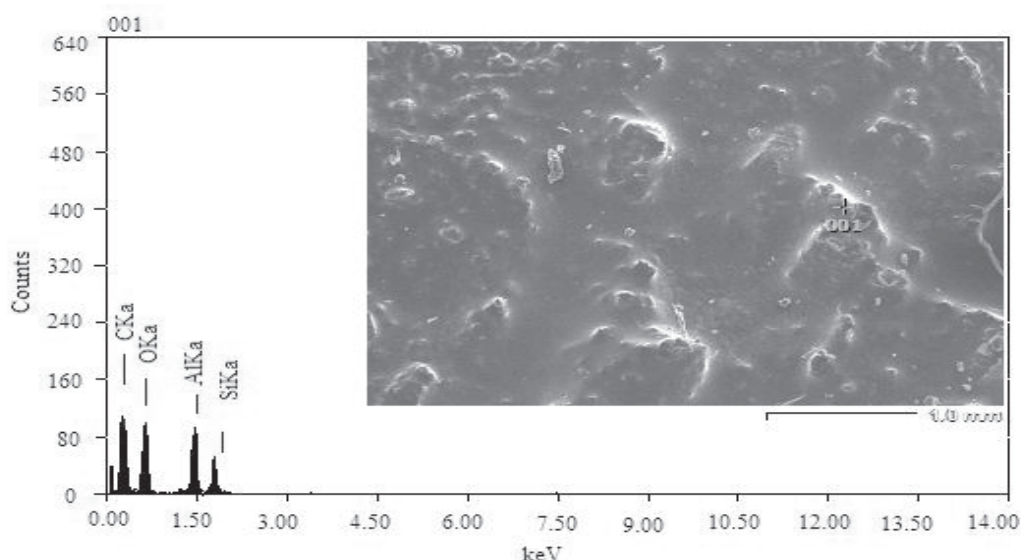


Fig. 1: EDX spectrums of HN clay filled nanocomposites

X-ray diffraction (XRD) analysis: The XRD patterns of composites and HN clay added nanocomposites are shown in figure 2. From figure, it can be seen that the crystallinity values of BF/PP/HN nanocomposites is higher than the BF/PP composites. The crystallinity values of BF/PP composites and BF/PP/HN nanocomposites were 83.30%, and 87.70%. As compared to BF/PP composites, the crystallinity of nanocomposites increased slightly. Moreover, a new peak (2 θ) at 45.2° was observed for BF/PP/HN nanocomposites. This result indicates that the crystallinity of nanocomposites was comprehensively increased when HN caly was added [9].

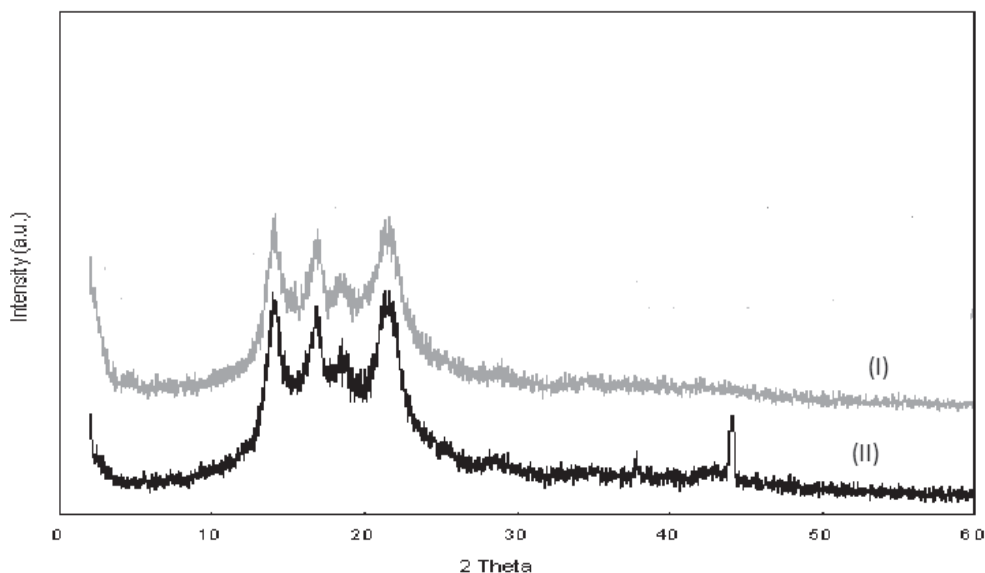


Fig. 2: XRD patterns of (I) BF/PP composites and (II) BF/PP/HN Nanocomposites

Fourier Transform Infrared (FTIR) Spectroscopy: To confirm the chemical reaction between green fiber and AC, FTIR test was carried out and are shown in Figure 3. Green fiber exhibited typical absorption band at the region of 3420 cm^{-1} , 1722 cm^{-1} and 2920 cm^{-1} due to hydroxyl (-OH) stretching, carbonyl (-C=O) stretching and acetylene (=C-H) stretching vibration respectively (spectrum-I). The absorption bands as mentioned above are due to the -OH group in cellulose, carbonyl group of acetyl ester in hemicellulose and carbonyl aldehyde in lignin [12, 13]. Conversely, it was seen that the -C=O stretching vibration peak was moved towards upper wave number with sharp peak intensity upon pre-treated with AC (spectrum-II). AC pre-treated green fiber clearly shows the existence of the characteristic band of cyanoethylation (-CN) group at 2895 cm^{-1} . Furthermore, the absorption band length of -O-H group was reduced and erased to higher wave number with narrowed band intensity. This further confirmed the reaction of -OH groups and of AC. All as discussed above confirmed that the following reaction of green fiber and AC.



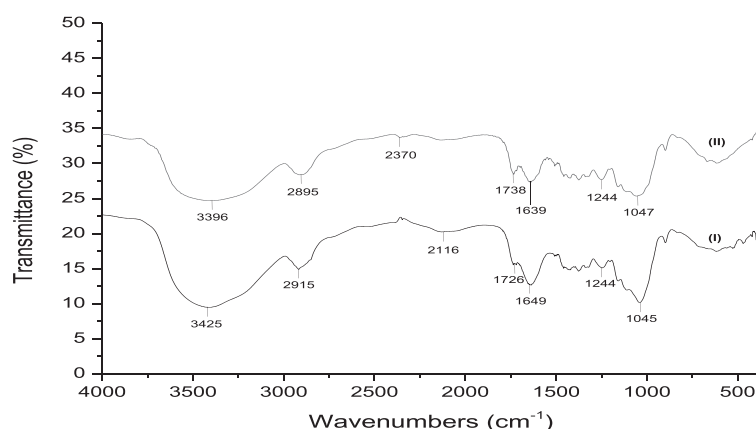


Fig. 3: FTIR spectra of (I) untreated and (II) Pre-treated GF

Scanning electron microscopic (SEM) analysis: In order to investigate the surface morphology of developed composites, SEM test were carried out. SEM micrographs of the BF/PP composites and BF/PP/HN nanocomposites are shown in Figure 4. The green fibers are clearly seen in the composite micrograph because of the weak interaction of green fiber and PP composites as seen in figure 3 (a). It can also be seen that BF filler supplement and deboning of fibers from PP because of the poor interfacial adhesion between polymer and BF fibers [14, 15]. In contrast, the surface morphology was found to be very smooth for the BF/PP/HN nanocomposites. After addition of HN nanoclay, the adhesion and interaction between the fibers and polymer was increase. Smooth fractured surface after the incorporation of HN nanaocalys indicates good adhesion between fiber and polymer matrix [16]. The existence of HN into matrix forced to have good wettability properties, which reduced the formation of voids at the composites interfaces and produced composites with enhance properties [16].

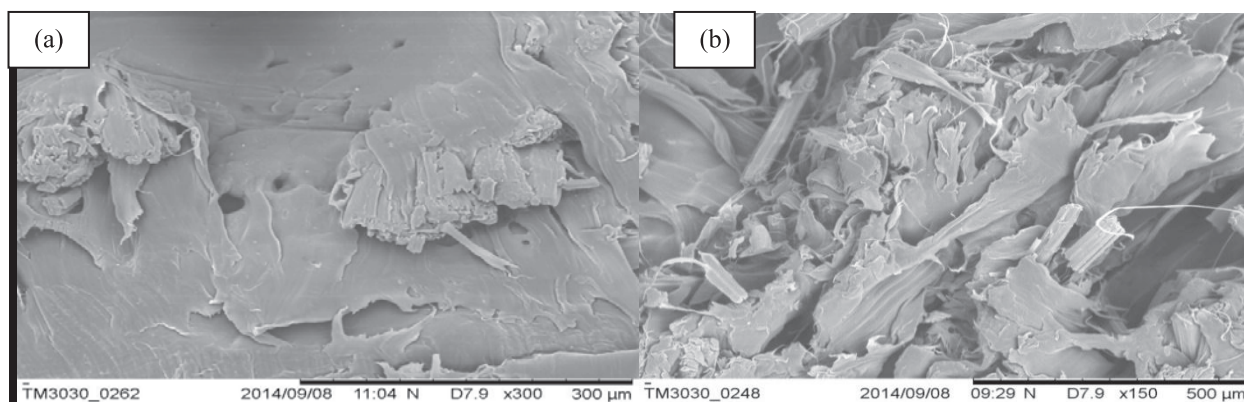


Fig. 4: Typical SEM micrographs of (a) BF/PP composites and (b) BF/PP/HN nanocomposites (at 35% BF content).

Tensile Properties: Tensile strength of both BF/PP composites and BF/PP/HN nanocomposites at different fiber loading are shown in Figure 5. For GF/PP composites, the tensile strength was decreased as increased the BF loading. The similar result was also observed by other researchers [17]. The poor interfacial zone between GF fiber and PP matrix was increased when the fiber load was increased, thus the tensile strength of composites was gradually decreased. This result was also observed in the SEM micrograph which shown in Figure 3. Tensile properties of nanocomposites were significantly increased upon HN clay loaded to composites. The AC pre-treatment also reduced hydroxyl groups form GF, which enhanced interfacial bonding between GF and PP. This in turn increased the tensile strength of the 25% fiber loaded composites. The accumulation of HN clay into GF/PP composites improved the adhesion and interfacial interaction of fiber to polymer matrix. Thus the mechanical properties of the GF/PP/HN nanocomposites were improved [18].

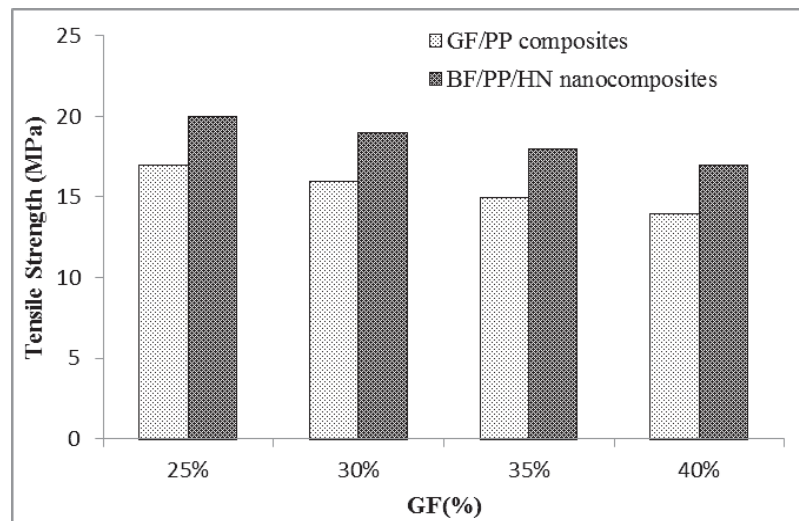


Fig. 5: Variation of tensile strength of GF/PP and GF/PP/HN composites at different green fiber (GF) content

Water Absorption: Figure 6 shows the water-absorption characteristics of developed GF/PP composites and GF/PP/HN nanocomposites at various fibers loading level. The percentage (%) of water absorption increased with increases the GF loading as seen in figure 5 [6, 7]. As stated early, -OH group present in green fiber is the responsible factor for increasing water absorption properties. With the increase of fiber loading to the composites, the number of -OH group was increased, which in turn increased the water absorption. Chemically pre-treated GF reinforced composites had lower water content compared to the untreated composites [7]. Moreover, the addition of HN clay decreased water absorption due to some hydrophilic group was blocked by HN clay particles.

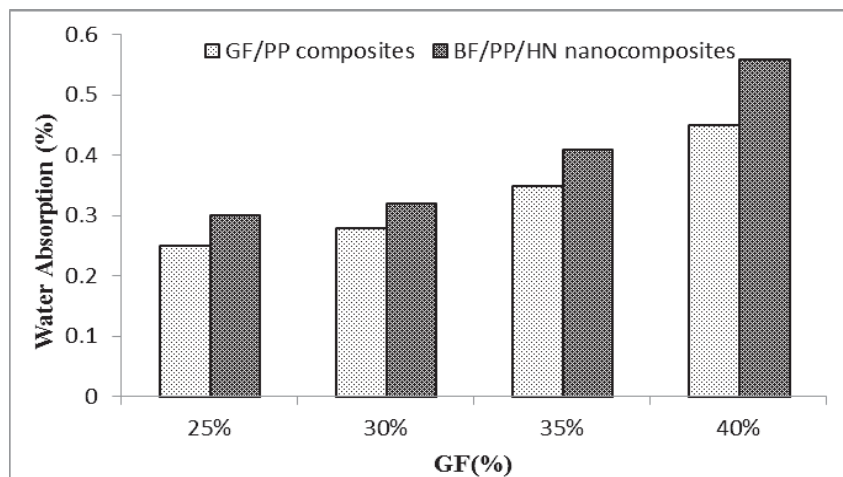


Fig. 6: Variation of water absorption of GF/PP and GF/PP/HN composites at different fiber content.

Conclusions: It can be concluded from present study that the morphological and tensile properties of developed nanocomposites were improved by the addition of HN clay due to the better adhesion and interfacial interaction between fiber-polymer matrixes. The tensile strength of the composites decreased with increase the fiber loading. Among all loading level of fiber, 25% loading had the highest increment of tensile strength. EDX, FTIR and SEM results indicated the changes of morphology after HN clay added. The crystallinity of nanocomposites was increased when HN clay added into GF/PP composites. Furthermore, the water absorption was reduced for the HN clay incorporated product of composite. The developed nanocomposites could be utilized as a potential replacement of plywood or particle board in furniture applications.

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