Communications

Cellulose Nano Whiskers from Grass of Korea

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Introduction

Polymer composites form a fascinating interdisciplinary area by bringing together biology and material science for wide verity of applications ranging from construction to biomedical technology.[1,2] A deliberate interest in the development of eco-friendly material motivated the efforts toward research on cellulose composites[3] due to its cheap, sustainable, recyclable, degradable nature and remarkable reinforcing properties at 167.5 GPa of Young's modulus along the chain axis per theoretical estimations.[4] The use of natural fiber for technical applications like automobile industry is restricted due to its incompatibility with generally hydrophobic host matrix and increase in weight of resulting products which provide a poor cost performance ratio. After resolving the incompatibility issues up to a satisfactory extent by adequate modification either in host or filler, it was assumed that dispersion and material properties may be enhanced with reduction in the size and increase in surface area by introducing nano fillers. Nano size (5-20 nm cross sections with length to several μm depending on source) rod like cellulose crystallites particles, known as cellulose nano whiskers (CNW), can be extracted from laterally stabilized fibrils bundle by removing amorphous region through controlled acid hydrolysis.[5] These whiskers have been employed in reinforcing several polymers,[6] which result in comparatively better mechanical properties. Nevertheless, such fibers have conquered many obstacles

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against industrial practices due to time consuming preparation procedure with very low yield, commercial unavailability, and most importantly, comparative higher cost through expensive source such as tunicate,[7] bacterial,[8] algal (valonia),[9] brown algae (Oomycota)[10] and commercially available microcrystalline cellulose.[11] The low yield and availability of raw materials of these sources generally inhibit the penetration of this tremendous reinforcer for the development of daily use biodegradable products. The current attempt was made to obtain the cellulose nano whiskers from the cheapest source, grass of Koera for the first time, which may further broaden the use of these bio fillers ranging from commodity to constructive applications.

Results and Discussion

Cellulose whisker extraction[12] of grass of Korea (genus Zoysia, species japonica and tenuifolia[13] from ground of Seoul National University) was carried out by boiling for 1 h in 2% (w/w) NaOH which was soaked in alkali (5%, w/w) for 2 days, and grass powder (after sieving through 45 μm pore size) was de-waxed by equal proportion of ethanol and water. Cellulose microfibrils are embedded in pectin / hemicellulose matrix and alkali treatment solubilized the pectin by converting carboxylic to corresponding carboxylate and by decreasing the intermolecular hydrogen bonding. The bleached powder (chlorite solution, 1.7% w/w in water, mixed with equal amount of acetate buffer and diluted with 1 liter of distilled water[14] at 70 °C till colored chromospheres was removed) was subjected to acid treatment for 15 min at 55 °C with 65% H_2SO_4 solution in a two-necked round bottom flask, equipped with mechanical stirrer and inter gas outlet and inlet. This material was centrifuged at 3,600 rpm until supernatant became turbid (the supernatant was removed from sediment and replaced by distilled water each time). After hydrolysis, the obtained product was dialyzed for 14 days in running water. Dialyzed product was mixed with distilled water and freeze-dried followed by sonication for 15 min at 9×10% cycle every 7.5 min by keeping inert atmosphere in a cool water bath. SEM in Figure 1(a)-(c) clearly illustrates the shape and size of fibrils under examined area before sonication where fibrils remain attached with each other. These strands appeared to join together by two possible means; some residual cementing materials or electrostatic attraction. The average width of strands ranges from 110-200 nm consists of many closed pack nanofibrils. Moreover, such type of morphology of cellulose fibers has not been detected using SEM in the previous attempts of cellulose whiskers extractions.[7-11,14] These kinds of small fibrils may come out only after hydrolytic removal of amorphous cellulose near the surface.[15] Sonica-
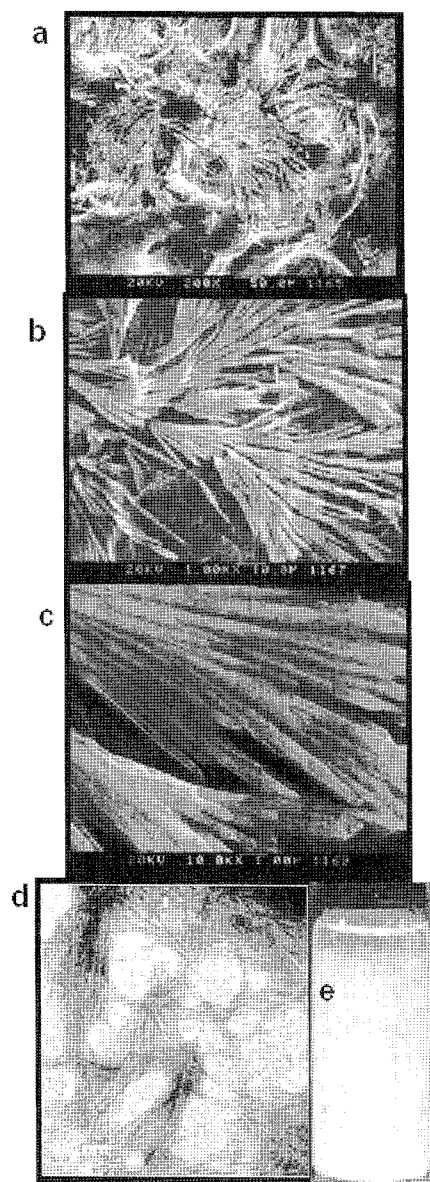
Figure 1. (a),(b),(c), SEM micrographs of cellulose fibers after hydrolysis at different magnifications. (d), (e) TEM micrographs of cellulose whiskers (0.1% (w/w) suspension in water on carbon grid) and suspension of cellulose whiskers after sonication respectively.

tion reduces the aggregation of fibrils significantly exposing several needle shaped nano entities as in TEM from Figure 1(d). Those remain in different lengths (180-300 nm) and width (less than 10 nm). Close aggregation of nanofibrils reveals increased tendency of association in individual whisker. This size of CNW is similar to the reports where nano whiskers were taken out from different sources.[11,16,17] The agglomeration of nano whiskers during TEM analysis may be induced by removal of water which allows them to agglomerate.

Figure 1(e) showed the suspension of CNW in water as a

result of nematic liquid crystalline alignment. The colloidal behavior of cellulose crystal suspension has been examined under crossed polarized light and the repulsion forces in nano crystals having charges on their surface are found responsible for this phenomenon.[18] Crystalline nature of whiskers was monitored by XRD to measure the periodicity of cellulose chains and diffractograms of untreated (vacuum dried after passing through sieves and refluxing in ethanol and water solution for 10 h) and treated grass are presented in the Figure 2(a). In native grass, two well-defined peaks could be observed at $2\theta = 22.3$ and $2\theta = 34.5$ degrees with broader shoulder at $2\theta = 16.4$ degree, which can be correlated with (200) and (023) or (004) crystallographic planes respectively. Moreover, broader shoulder at 16.4 degree may be due to (110) or ($\overline{1}10$).[19] XRD reflection collected for final samples, exhibited two additional peaks at $2\theta = 15.5$ and $2\theta = 16.2$ degree for the (110) and ($\overline{1}10$) plane, and sharp peaks reflect the presence of comparatively higher crystallinity. It has been observed that the broader reflection profile results from smaller crystal size which explains the merging of two peaks as a shoulder.[10] Therefore, the number of cellulose chains present on the surface as amorphous region are less than the chains contributing to the crystalline structural integrity. It has been found that when cellulose has more amorphous portion in the form of lignin, hemicelluloses, etc., the two peaks smeared and resulted one broad shoulder.[19] Thus, treated material has more crystalline part compared to non-treated one, which confirmed the selective removal of amorphous portion during acid hydrolysis. Further the peak pattern of 110, ($\overline{1}10$), 200 reflections are similar with that of wood cellulose[10] where individual crystallites come out with comparatively larger degree than that of original micro fibrils due to higher freedom of motion. The overall FT-IR (Figure 2(b)) gives characteristic of cellulose I and the spectrum at 3600-3200 cm^{-1} region becomes broader due to hydroxyl groups with large area under the peak where a detectable shifting toward higher frequency must be attributed to the increase in exposed hydroxyl groups after removing cementing materials in grass fibers. Untreated fiber showed the peaks around 1738, 1590, 1245 cm^{-1} assigned to carboxylic acid or ester, acetyl and methyl ester groups respectively those were vanished (except at 1600 cm^{-1} which may superimpose with 1590 cm^{-1}) after treatment indicating removal of hemicellulose and pectin. The band at 1042 cm^{-1} may be attributable for -C-O, -C-C-, or -C-OH bending in hemicelluloses. Additionally the vibration peak at 1257 and 1510 cm^{-1} for benzene ring and C-O stretching of lignin were tremendously reduced due to the elimination of lignin from the treated fiber.[20] The reduction of peak around 2915 cm^{-1} for -C-H stretching gives another indication of hemicellulose removal. The disappearance of -CH$_2$ bending vibration at 1440 cm^{-1} was attributed for lignin extraction. Significant reduction of broad absorption in the region of 1600 cm^{-1} after treatments proves the contribution
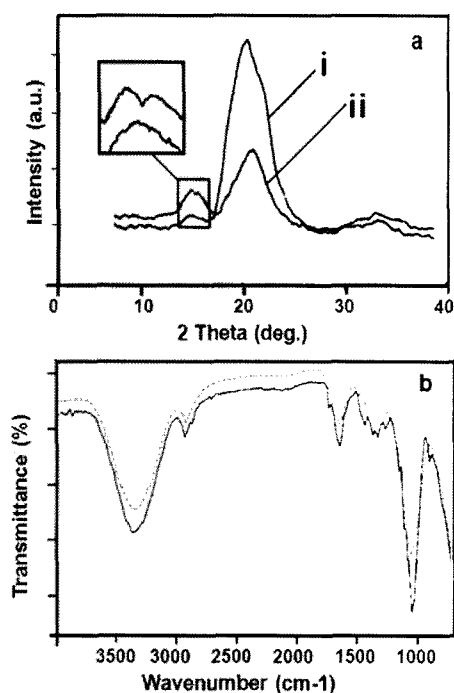
Figure 2. (a) XRD diffractogram of cellulose whiskers (i) and untreated grass fiber (ii), (b) FT-IR spectra of two different region of treated and untreated grass (Carboxyl and Hydroxyl region, --- treated — untreated).

from functional groups of remaining surrounding materials in the existence of this peak whereas complete disappearance of this peak was not observed in our case as has been reported.[20] Cellulose nano whiskers showed two well separated pyrolysis processes and degradation occurred to a wider temperature range starting from 220 to 280 °C, and other between 330-500 °C with initial moisture loss at 120 °C.

The substantial weight loss at 335 °C was due to degradation of cellulose. Untreated fiber exhibited many steps of degradation at 110 °C, intermediate loss at 280 °C and at 352 °C. The degradation of hemicellulose was not observed for nano whiskers due to removal of hemicellulose during alkali treatment. Nano crystals start decomposition at lower temperature than microcrystals due to the increasing numbers of free end chains at the surface, being liable to earlier decomposition whereas the thermal resistance can be increased by neutralizing the sulphate groups.[21] The increase in first degradation temperature, corresponds to moisture in whiskers must be attributable to the strong adhesion of moisture molecules in highly exposed fibers of more surface area.

Research is in progress to study the effect of percentage load, chemical treatments (esterification of nanofibers with various chain lengths) on the properties of different biodegradable and non-biodegradable polymer matrixes after filling with nano fibers. Cellulose whiskers from grass represent the cheapest source to obtain ecofriendly filler for polymers in fabrication of constructive materials. The crystalline cel-

lulose may have its significant applicability for direct compression tableting in pharmaceutical industry and co-processing with other excipients which are expected to improve the performance of material in direct compression, because of its low chemical reactivity.[22] These cellulose nano whiskers not only show a high potential toward the development of materials where cost and low yield are expected to counterbalance by inexpensive source, but also explore the possibility of bio-nanocomposites preparation for disposable commodity applications.

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