ELASTOMERIC NANOCOMPOSITES: POTENTIAL OF CHITIN AND CELLULOSE NANOSTRUCTURES AS REINFORCING PHASE

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Abstract

Cellulose and chitin are abundant, natural, renewable and biodegradable polymers which could be broken down into nano sized crystalline entities, using a top-down approach. In most cases, an aqueous suspension of these nano crystallites are prepared by acid hydrolysis process and has high specific mechanical properties making them potential reinforcements in various polymer matrices. In this work, we present the processing and characterization of nanoreinforcements from waste materials such as cellulose and chitin and their polymer nanocomposites using natural rubber matrix (NR) or synthetic rubber matrix, carboxylated styrene butadiene rubber (XSBR). The isolated chitin whiskers had a length ranging from 100 to 500 nm and diameter ranging from 10 to 80 nm and cellulose nanowhiskers had diameters between 4-14 nm. The addition of 4.32 wt of % chitin nanowhiskers resulted in an improvement of 1400 % for tensile strength. The cellulose nanowhiskers gave good mechanical and tensile improvements on NR matrixes and Atomic force microscopy (AFM) was carried out to examine the size and structure of chitin and cellulose nanowhiskers and scanning electron microscopy (SEM) used for the morphological study of both type of nanocomposites. It may be concluded that the biobased nanostructures have great potential in reinforcing natural and synthetic elastomers and the reinforcing potential depends on the dispersion and distribution of the nanocrystals in the matrix as well as the interaction between the phases.

1. Introduction

In the recent years increased attention has been paid to the development of bionanocomposite materials for several industrial applications, such as automotive, construction, or packaging using biomaterials. Biobased nano materails are very promising materials for making nanocomposites. In literature, several works have been reported with these biomaterials reinforcements in various polymer materials. [1] These biomaterials have shown potential to improve the physicochemical as well as the technological properties of plastics and rubber matrices. In our work mainly focusing on the elastomer based nanocomposites. In rubber based composites we always using carbon black and other inorganic and organic nanoparticles, but these materials are causes pollution and other environmental problems. In this context the biomaterials such as cellulose and chitins are very good alternatives. The uses of biomaterials extracted from different natural sources as cassava bagasse [2], sugar cane bagasse [3], rachis of palm tree [4]. Crab shell chitin [5] and Syngonanthus nitens (Capim Dourado) [6] as reinforcement agent in natural rubber-based nanocomposites have reported. employing nanoparticles as a reinforcing agent in natural rubber-based nanocomposites,.

It can be seen that most of these studies use latex blending technique without vulcanization, for the bionanocomposite preparation. There are no reports available on vulcanised rubber based cellulose nanocomposites prepared by master batch processing and two-roll mill mixing, which has potential to be adapted for commercial scale processes. In the current study NR based bamboo nano-cellulose reinforced materials were prepared using a master-batch in latex followed by compounding using two roll mixing mill. Further more, the crosslinking of NR matrix by vulcanization might lead to natural rubber based green nanocomposites with mechanical properties and thermal stability required for practical applications.

Carboxylated styrene-butadiene rubber latex (XSBR latex) is one of the most important elastomers widely used in industrial and technological areas. SBR latex is a copolymer of styrene and butadiene. SBR lattices are prepared by the emulsion polymerization of the desired ratios of butadiene styrene monomers together with the required modifiers and catalysts. Carboxylic-modified styrene-butadiene lattices (XSBR) find uses where adhesion to textile fibers is important. The reinforcement of the XSBR latex with chitin whiskers (CW) combines the elastic behavior of the XSBR rubber with the high strength and stiffness of the chitin whiskers.

In the current report, we present the processing of cellulose nanofiber (CNF), cellulose nanowhisker (CNW), chitin nanowhiskers-based rubbers nanocomposites and their tensile and thermal properties.

2. Experimental section
Materials
Two biomaterials were used as the reinforcement for the preparation of nanocomposites, cellulose and chitin. Waste bamboo cellulose pulp was supplied by Piravam Paper Mill, Kerala, India and had diameters in the range of 10-20 μm. α-Chitin powder was supplied by Marine Chemicals, Cochin, Kerala, India. Natural Rubber (NR) was supplied in latex and solid from by RRI, Kottayam, Kerala, India, and used as matrix material. Carboxylated styrene butadiene rubber latex (XSBR) was supplied by Apar Industries Ltd., Bombay, Maharashtra, India.

Methods

Case-I (Nanocellulose preparation)
Cellulose nanowhiskers were prepared by acid hydrolysis of the bamboo pulp using the method developed by Bondeson et al [7]. The bamboo pulp was washed, drained and treated with 64 % H_2SO_4 and the hydrolysis was carried out by heating the suspension at 45 °C for 130 min. The removal of excess acid was achieved by repeated centrifugation with distilled and dialysis against distilled water.. We have already reported this in our recent works [8,9].

Cellulose nanofibres (CNF) were obtained through mechanical fibrillation of bamboo pulp. The pulp was dispersed homogeneously in distilled water using a laboratory shear mixer (Silverson L4RT, Silverson Machine Ltd., England), and then a slurry with a cellulose concentration about 1% w/w was ground using a super masscolloider (MKCA6-3, Masuko Sanyo Co, Ltd., Japan). In the present study the fibrillation was done using contact mode grinding, where the final gap distance between the stones (from 0-point) was further decreased by 10 μm during the grinding. The grinding speed was approximately 3600 rpm and the total processing time was around 20 minutes. We have reported this preparation method in our recent paper [8,10]

Case-II (Nanochitin preparation)
Nanochtin were prepared following the procedure reported by Nair and Dufresne. [7] The chitin powder was first stirred and boiled with 5-wt % aqueous KOH solution for 6 h. Then, the specimens were rinsed with distilled water and filtered. Following this treatment, chitin samples were bleached with 17 g of $NaClO_2$ in 1 L of distilled water mixed with 27 g of NaOH in 75 ml of acetic acid completed with 925 ml of distilled water. The suspension was heated at 80 °C for 2 h under stirring; this procedure was repeated three times. The chitin whisker suspensions were prepared by hydrolyzing the purified chitin sample with 3 N HCl at the boil under stirring for 1.5 h. After acid hydrolysis the suspensions were dialyzed for 2 h in distilled water and then overnight in running water. An additional dialysis by dialysis bag for 12 h by changing the distilled water every 2 h was performed until a pH = 6 was reached. The dispersion of whiskers was completed by three successive

Preparation of Nanocomposites

Case-I (Cellulose based nanocomposites)
The processing of NR- cellulose nanocomposites were reported in our earlier studies. [9]. Nanocomposites of cellulose fibres (CNF) and nanowhiskers (CNW) with solid natural rubber as a matrix were prepared via a two-step process involving (a) master-batch preparation in NR latex and (b) compounding of the master batch with solid NR and vulcanizing agents using a two-roll mill followed by subsequent curing.

(a) Master batch preparation: In the master batch processing step NR latex and CNF/CNW in aqueous medium are mixed together well to obtain a uniform dispersion of CNF/CNWs in NR latex. The concentration of the latex and CNWs was adjusted to have

a final CNF/CNW concentration of 10 wt%. This dispersion is then coagulated using 1% formic acid. The coagulated mass is separated out by dried in an oven. This master batch is then powdered and used for the next processing step. NR latex without CNF/CNWs was also prepared by the same method and was used as the control master-batch for comparison. The detailed formulations of the master batch are given below.

(b) Compounding: In this step the compounding of the master batch with solid natural rubber and vulcanizing agents was carried out using a two-roll mixing-mill. The used formulations are given in table-1. The nanocomposite compositions were adjusted during this process by diluting the master-batch with appropriate amount of solid NR. The cure time for the vulcanization was determined using a Monsanto rheometer and optimum curing times (t_{90}) was calculated and pressed into vulcanised sheets using a compression moulding in hydraulic press. The nanocomposite preparation steps are schematically represented in figure-1.

Sample code	Solid NR (phr)	MB		ZMBT (phr)	ZnO (phr)	Sulphur (phr)	ZDC (phr)	Stearic Acid (phr)
		NR (phr)	CNF/CNW (phr)					
NR	80	20	0	0.5	0.2	1.5	0.75	2.5
NR-CNW/CNF$_{2.5}$	87.5	10	2.5	0.5	0.2	1.5	0.75	2.5
NR-CNW/CNF$_5$	75	20	5	0.5	0.2	1.5	0.75	2.5
NR-CNW/CNF$_{10}$	50	40	10	0.5	0.2	1.5	0.75	2.5

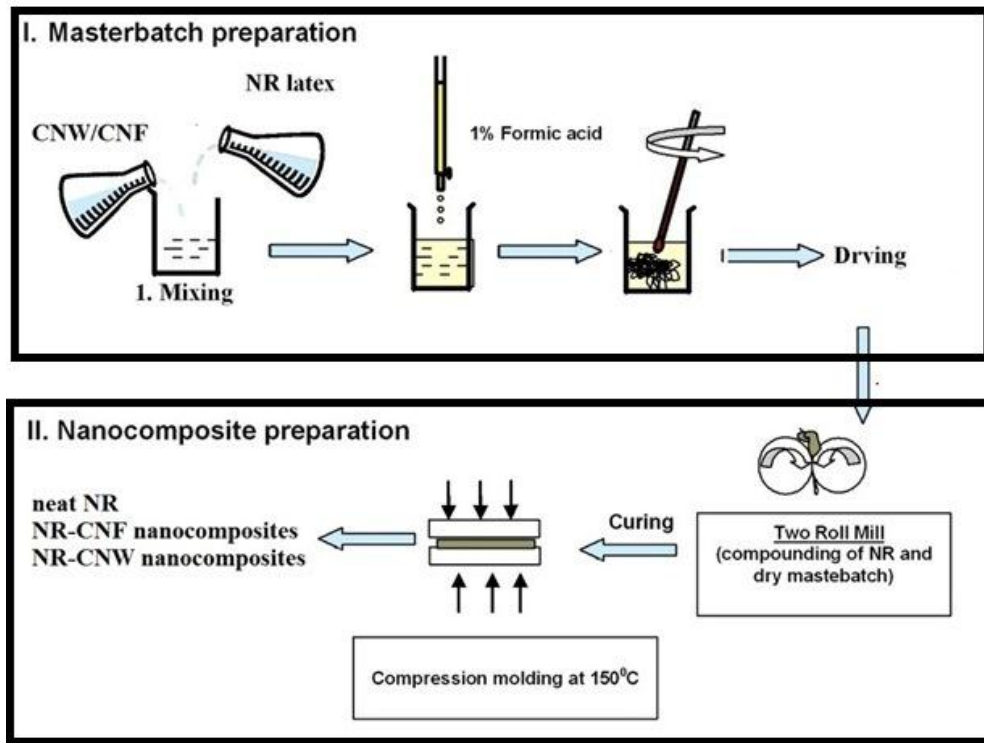**Table-1:** Formulations for the prepared materials

**Figure-1.** Schematic representation of nanocomposites preparation

Case-II (Chitin based nanocomposites)

The XSBR latex was used as matrix and the chitin suspension was introduced in to the latex and stirred for 2 hours, casted in Petri dishes. The solid nanocomposite films were obtained by evaporating the water by drying in an oven at 40 ^{0}C. In all these concentration, volume fraction of the XSBR latex was kept constant. Composites were prepared by changing the volume fraction of chitin whiskers suspension from 2.16 wt% to 4.32 wt%. The pure XSBR matrix is also prepared and used as the control.

3. Result and discussion.
Morphology
Atomic force microscopy (AFM) image of the prepared nanocellulose, nanocellulose fiber and chitin whiskers are shown in figure-2 [9,10]. In nanocellulose are nano-sized whiskers that are well separated and having diameters between 4 and 14 nm and the size for the nanocellulose fibers, having diameters between 23 and 42 nm. For chitin nanowhiskers a broad distribution in length (L) ranging from 100 to 500 nm and diameter (D) ranging from 10 to 80 nm.

(a) (b) (c)
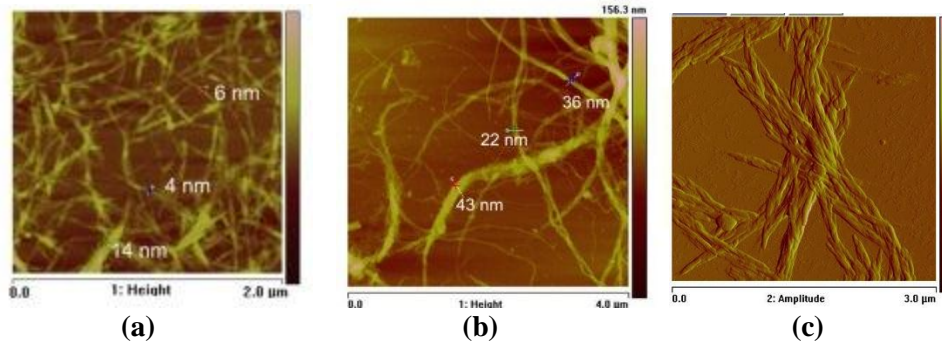
Figures-2. AFM images of (a) cellulose nanowhiskers (b) cellulose nanofibrils (c) nanochitin whiskers

Tensile tests
Typical stress vs strain curves for all type of nanocomposites are shown in figure-3 (9). The stress continuously increases with the strain; the tensile strength of resulting nanocomposites was increases with increase in filler content (see figure 2a). The figure indicates that addition of fillers to matrix, results in increased strength with increasing nanowhisker content. The tensile strength was increased from 9.21 MPa to 17.32 MPa with increase in cellulose nanowhisker content 0–10 wt%. The modulus of elasticity of the nanocomposite was increased steadily with the addition of CNWs and improved from 1.7 MPa to 3.8 MPa with increase in cellulose nanowhisker content from 0 to 10 wt.%.

In the case of chitin nanocomposites was increased from 0.5 MPa to 7.5 MPa with increase in chitin nanowhisker content 0–4.32 wt%. (Figure 2b) The modulus of elasticity increased with the addition of chitin whiskers and improved from 1.5 MPa to 38.5 MPa with increase in chitin nanowhisker content from 0 to 4.32 wt.%, from this result we can say that very small weight percentage of biomaterials in rubber matrixes shows good strength than neat rubber matrixes. For the chitin based nanocomposites, the mechanical performance is attributed to the formation of a rigid chitin network resulting from three-dimensional hydrogen bonding between chitin whiskers and XSBR latex.
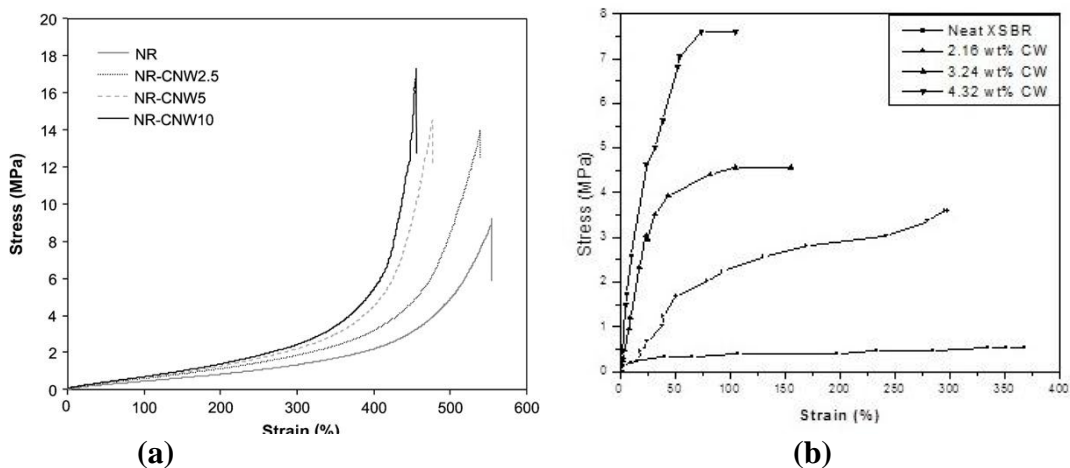
(a)   (b)

Figure-3. Stress vs strain cures of the matrix and the nanocomposites (a) NR-Cellulose whiskers   (b) XSBR-chitin whiskers

Thermal properties

It was observed that the thermal stability increased with increasing nanowhisker content; and the decomposition temperature of nanocomposites at different stages increased upon the addition of cellulose whisker (figure-4) [9]. This positive impact of cellulose nanowhiskers on thermal stability of NR may be explained by decreased mobility of NR phase in the vicinity of the cellulose nanowhiskers. The lowering of NR chain mobility might in turn lead to slower diffusion of degradation products from the system. The same trend shows that the chitin nanowhiskers/XSBR nanocomposites.
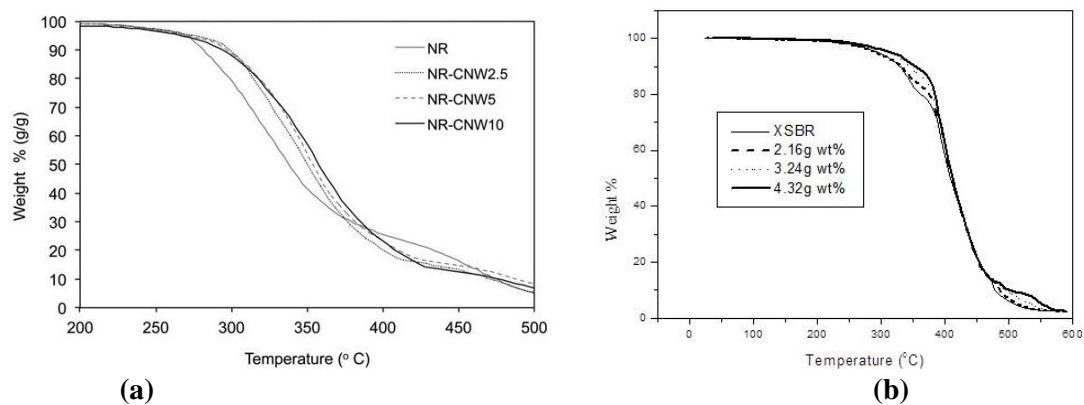

(a)   (b)

Figure-4.TGA cures of (a) NR-Cellulose nanowhiskers, (b) XSBR-Chitin nanowhiskers

Conclusions

Nanosized cellulose whiskers and fibers and chitin nanowhiskers were successfully prepared from bamboo pulp and crab macro fibers respectively by acid hydrolysis and those whiskers were used as the reinforcing phase in rubber matrix. The morphology and size of nano cellulose and nanochitin were studied using AFM. The tensile strength and modulus values increased addition of both whiskers, accompanied by a moderate decrease in elongation at break. TGA data shows that the thermal stability of the both

type of nanocomposites, thermal stability increased with increasing cellulose and chitin nanowhiskers.

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