PREPARATION AND CHARACTERIZATION OF GREEN NANOCOMPOSITES BASED ON CELLULOSE NANOFIBRE AND NATURAL RUBBER LATEX

E. Abraham[1,2], L.A.Pothan[2], S. Thomas[3]

[1] *Trent Biomaterials Research Program, Trent University, Peterborough, Ontario, Canada*
[2] *Department of Chemistry, Bishop Moore College, Mavelikkara, Kerala, India 690 101*
[3]*School of Chemical Sciences, Mahatma Gandhi university, Kottayam, Kerala, India 686 560*

Keywords: Natural rubber, Nanocellulose, Biocomposites

Abstract:
Cellulose nanofibres (CNF) with a diameter 10-60 nm were used as reinforcing elements in natural rubber (NR) latex along with cross linking agents to prepare bionanocomposite films. The effect of CNF loading on the mechanical and dynamic mechanical (DMA) properties of NR/CNF nanocomposite was studied. The morphological, crystallographic and spectroscopic changes were also analyzed. A mechanism is suggested for the formation of the Zn-cellulose complex as a result of the deprotonation of the cellulose which is originated during the composite formation.

1. Introduction

There is currently a considerable interest in processing polymeric composite materials filled with rigid particles having at least one dimension in the nanometer range. Because of the nanometric size effect, these composites display some unique properties with respect to their conventional microcomposite counterparts [1]. In the context of both biomass valorization and nanocomposite materials development, cellulose nanofibres used as a filler in a polymeric matrix appear to be an interesting reinforcing agent [2,3]. We have prepared CNFs by a patented steam explosion technique in order to extend their use in nanocomposite applications [4]. They consist of crystalline nanofibres about 10-60 nm diameter with a length of few micrometers. When compared with glass fibers, silica and carbon black, CNF as reinforcing filler in composites has many advantages: low cost, low density, easy processability, and little abrasion to equipment, renewability, and biodegradability.

2. Materials and testing methods

Centrifuged latex of natural rubber was kindly supplied by Rubber Board, Kottayam, Kerala, India. A homogenous CNF (with a diameter of 10-60 nm) dispersion which is obtained by the steam explosion of the banana fibre is used as the reinforcing material.

2.1.   Film Processing.

NR Latex/CNF composite films were prepared from prevulcanised latex (in accordance with the reported formulation [5] of crosslinking agents) by casting on a glass plate followed by drying at ambient temperature. The prevulcanization of the compounded latex was conducted at 70°C for 2 h using water bath with constant gentle stirring. The sample numbers 0, 2.5, 5, 7.5 and 10 indicate the weight percentage of fillers (CNF) used.

2.2.   Testing Methods:

Various analysis like Scanning electron microscopic (SEM),Atomic force microscopy (AFM),Fourier transform infrared spectroscopy (FTIR), X-ray diffraction analysis,Mechanical testing, Dynamic mechanical analysis were conducted to characterize the properties of the filler and the prepared composite.

3.   Results and Discussion

3.1.   Morphology of nanocomposite films

The morphology of NR/CNF composite materials and the distribution level of the filler within the matrix were evaluated by SEM and AFM. Fractured surface of nanometric reinforced rubbers were observed by SEM in order to know how particles were oriented inside the composites together with the possible examination of rubber-nanofibre bonding after the mechanical evaluation. SEM of the tensile fracture surface of 2.5% CNF nanocomposite is shown in Fig. 1. CNF coated with NR latex are clearly seen from the picture. CNF appear like white tubes, whose concentration is a direct function of the cellulose content in the composite. We can observe that the distribution of the filler in the matrix is almost homogeneous. It is the key property for expecting good mechanical properties.
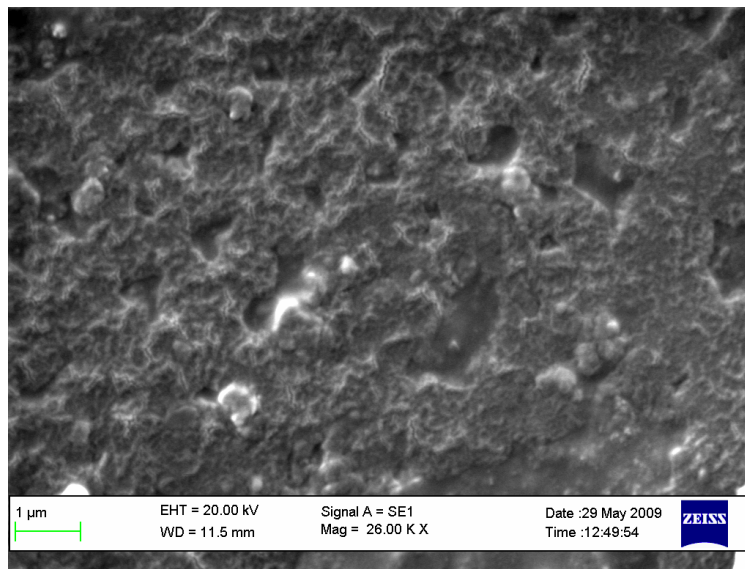

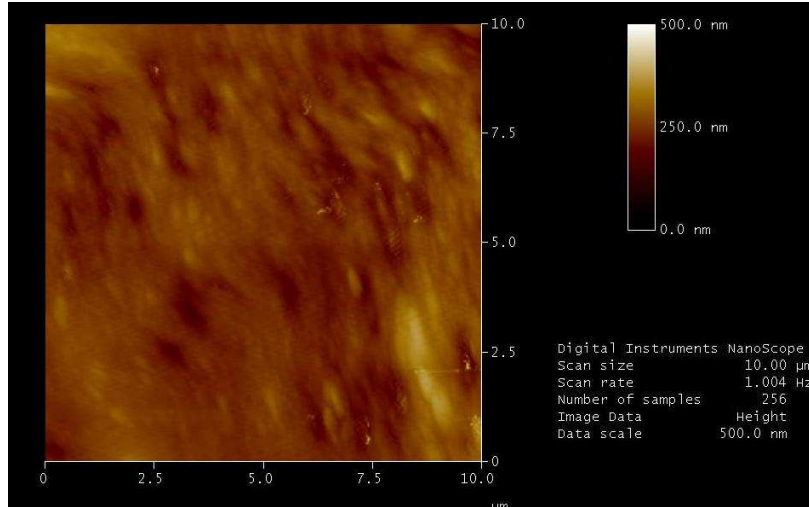Figure 1: SEM of the tensile fracture surface of 2.5% CNF Nanocomposite

Figure 2: AFM (Height image) of 10% CNF Nanocomposite

AFM analysis of the bulk film prepared at normal temperature enabled detailed information of the CNF in the matrix. Figure 2 is the AFM images of 10% CNF nanocomposites. It shows the presence of a homogeneous dispersion of CNF along with some agglomeration of nanofibres in the composite.

3.2. *Deprotonation of cellulose and formation Zn-cellulose complex*

It is reported that the cellulose can be dissolved in aqueous solvent systems containing metals such as copper and zinc in Cuam and Cuen solutions [6]. The dissolution mechanism involves deprotonation of C_2-OH and C_3-OH during the metal complex formation. The deprotonation of cellulose is taking place at alkaline medium with the presence of copper and zinc [7]. The accelerators and crosslinking agents like Zinc dithiocarbamate (ZDC), zinc mercaptobenzothiozole (ZMBT) and zinc oxide (ZnO) were used in the nanocomposite preparation stage to generate active sites in the NR backbone for the crosslinking of the matrix. These accelerators not only make active sites in the NR backbone by breaking the C=C double bond but also have a major role in the deprotonation of the CNF and make them participate in the crosslinking network. Besides, ball-milling followed by ultra-sonication caused an increase of amorphous phase of cellulose, making breakage of inter and intramolecular hydrogen bonds which could produce a large number of free OH groups at the surface of CNF. The resultant OH groups at the cellulose surface were activated, and could form complexes with Zinc (II) during pan-milling. The incorporation of fillers causes interruption in the alignment process of rubber chains. When filler loading is increased, weak interfacial regions between filler surface and rubber matrix through this complex are formed. The resultant Zn-cellulose complex diminishes the crystalline nature of the composite and dispersed with metal ion.

3.3. *XRD analysis of the NR/CNF composites*

X-ray patterns were collected for different compositions of NR/CNF and are displayed in Figure 3. The diffractograms of unfilled natural rubber and pure CNF were added as references. The diffraction pattern recorded for a film of pure CNF obtained by pressing freeze-dried nanofibres

displays typical peaks of A-type amylose allomorph [8]. It is characterized by a strong peak at 2θ = 17.9°, a very strong peak at 25.07°. The natural rubber film displays a typical behavior of a fully amorphous polymer. It is characterized by a broad hump located around 2θ = 18°. By adding CNF, the peaks corresponding to A-type amylose allomorph completely disappear and this is unexpected. The clear dispersion of the CNF in the matrix of natural rubber latex leads to the sinθ value becoming zero. This shows that during the composite formation with CNF, the natural rubber and cross linking agents makes some additional chemical interactions with the CNF which leads to the loss of crystalline nature of the cellulose as well as the entire composite.
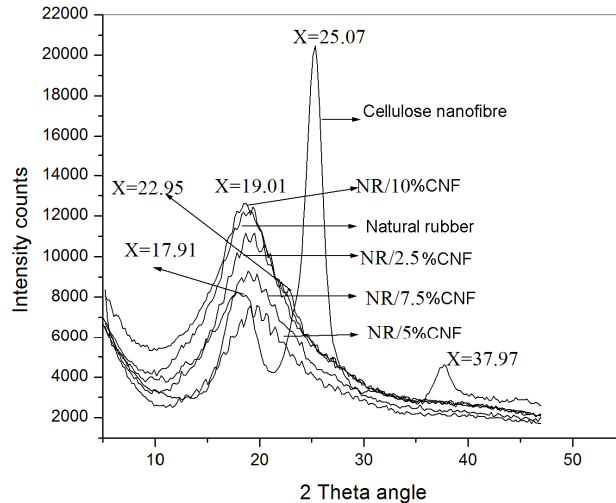

Figure 3: XRD analysis of the nanocomposites

3.4 . Fourier Transform infrared (FTIR) Analysis
The FTIR transmittance spectra of NR and its composites with CNF reveals the formation of some weak chemical reactions between zinc metal and CNF. The corresponding spectrum of CNF is blue-shifted to 3400 cm^{-1} in the spectrum of the composite and the hydroxyl groups of CNF might have some important role in this shift. These phenomena confirm that CNF is successfully activated by crosslinking agents to react with accelerator, zinc metal to form zinc-cellulose complex. The intermolecular hydrogen bonds are broken during composite formation making more hydroxyl groups accessible. The vibrations of C=O stretching peak at 1671 cm^{-1} is almost absent in natural rubber but its intensity shows a gradual increase with increase in the percentage of CNF which reveals the formation of the complex.

3.5. Mechanical properties of the composite
The tensile strength values of natural rubber nanocomposites at different filler loading are shown in Fig. 4. Stress vs. strain curves show that the nanocomposites present initial modulus and tensile strengths greater than NR. The presence of hydroxyl groups in the CNF is responsible for its inherent hydrophilic nature. Since the matrix, NR latex is in its liquid form with its highest tendency of hydrophilicity, the compatibility between the hydrophobic natural rubber and hydrophilic CNF is compromised to some extent. As a result, it becomes very easy to compound hydrophilic CNF dispersion with natural rubber latex along with other cross linking agents which

are aqueous medium. This results in an efficient nanocomposite with good interfacial bonding. As the NR is reinforced with CNF, some interactions are formed between the filler and the crosslinking agents and thereby matrix, which consequently increase the tensile strength [9]. The mechanism suggests a three dimensional network of NR/Zn/CNF which increases the mechanical properties of the composite.Furthermore, incorporation of fiber into the polymer matrix reduces the matrix mobility, resulting in stiffness of the composite. As a result, Young's modulus increase with increasing the filler content of the composites and the percentage of the elongation is regularly decreased with increasing the cellulose content. The gum rubber shows a 900% elongation but the 10% nanocomposite shows ~ 270% of elongation.

The increment of stress level was due to the interaction between the CNF and the rubber through Zn-cellulose complex. A good interface between the CNF and the rubber is very important for a material to stand the stress. As described above, CNF are highly strong materials compared to other types of fillers thus making them good candidate as nano fillers. Under load, the matrix distributes the force to the CNF which carry most of the applied load. The synergic effect of rubber-rubber, rubber-cellulose and cellulose-cellulose interactions give excellent mechanical properties to nanocomposites.
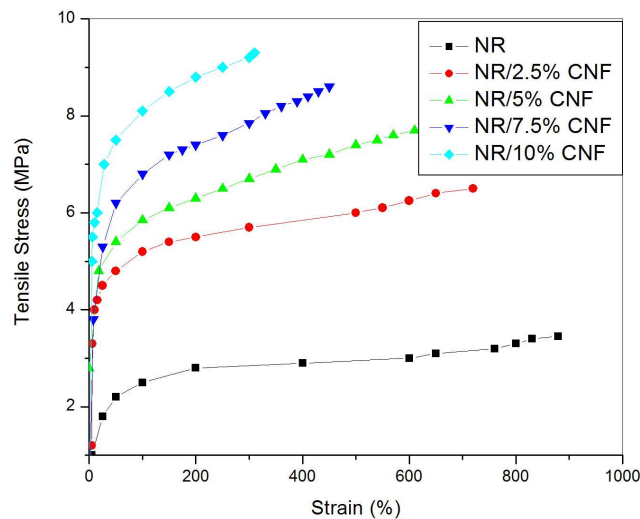

Figure 4: Mechanical properties of the nanocomposites

3.6. Dynamic mechanical analysis of NR/CNF composites
Dynamic mechanical analysis (DMA) is carried out to study the composite structure and performance under various temperatures. The increase in values of E′ with fiber loading indicates that mobility of the polymer chain is decreased in the presence of fibers and thereby the T_g is shifted to higher temperatures. It has been observed that the incorporation of solid crystalline filler into a polymer matrix may increase or decrease the mechanical damping of the polymer [10]. In the present study also, Fig. 5, it was seen that, E□ of all the nanocomposites are greater than that of gum rubber. Fiber incorporation increases the storage and loss modulus, which indicates the higher heat dissipation in the CNF reinforced NR nanocomposites compared to that

5

of gum rubber. The storage and loss modulus of nanocomposites exhibits a significant drop in the transition zone in addition to the shift in the peak towards higher temperature. The height (peak intensity) and position of E□ peaks of these nanocomposites vary with fiber loading.
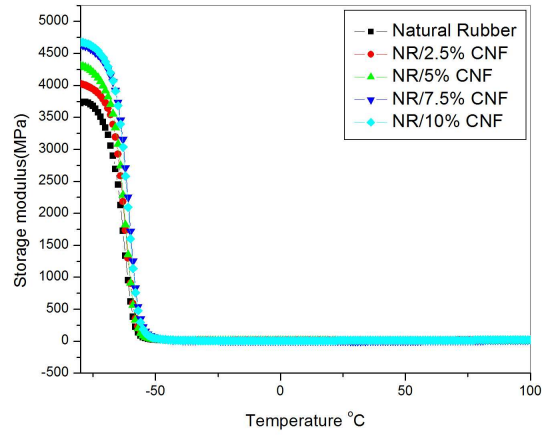

Figure 5: Effect of fibre loading on storage modulus of the nanocomposites.

Thus it is clear that heat dissipation increases with fiber loading in CNF reinforced NR nanocomposites. The increase in damping at the interface with nano fibre loading can be explained by the fact that the larger the interfacial area, the more energy loss there is. The values of storage modulus increase with fiber incorporation in the low temperature region for the composites compared to that of gum. The nanocomposite exhibits an enhancement of the modulus over the temperature range investigated, indicating the elastic responses of pure NR towards deformation and are strongly influenced by the presence of cellulose dispersion. This behavior also reflects the strong confinement of CNF dispersion on the rubber molecules and the existence of a Zn-cellulose complex.

4. Conclusion

Nanocomposite materials were obtained by casting and evaporating a mixture of NR latex and aqueous suspension of cellulose nanofibrils. The filler was evenly distributed in the composite structure which is evident from SEM and AFM analysis. The increase of CNF content in the NR matrix causes a drastic influence in the mechanical properties of the composite, increasing the Young's modulus and tensile strength of materials, but decreases the characteristic rubber elongation. XRD analysis reveals that the nanocomposites of NR with CNF as filler along with the cross linking agents will lead to the loss of crystallinity of the whole composite because of the uniform dispersion of the latter. The formation of a Zn-cellulose complex is anticipated as a result of the deprotonation of the cellulose, during the composite formation which makes the nanocomposites with good mechanical and dynamic mechanical properties. The enhancement in modulus of the composites even below the glass transition temperature of NR proves the strong reinforcing tendency of CNF in the NR latex matrix. The strong stress level involved in DMA experiments is sufficient to explain the extent of rubber-cellulose interactions.

References:

[1] Dufresne A., Cavaille J.Y., Helbert W. New Nanocomposite Materials: Microcrystalline Starch Reinforced Thermoplastic. *Macromolecules,* **29**, 7624-7626 (1996).

[2] Philippe T., Christian E., Zimmermann T. Functional Polymer Nanocomposite Materials from Microfibrillated Cellulose. Advances in Nanocomposite Technology, ISBN, **978-953-307-347-7**. 319-334 (2010).

[3] Angellier H., Molina-Boisseau S., Putaux J.L., Dupeyre D., Dufresne A. Starch Nanocrystal Fillers in an Acrylic Polymer Matrix. *Macromolecular Symposium,* **221**, 95-104 (2005).

[4] Abraham E., Deepa B., Pothan L.A., Jacob M., Thomas S., Cvelbar U., Anandjiwala R. Extraction of nanocellulose fibrils from lignocellulosic fibres: A novel approach. *Carbohydrate Polymers,***86**,1468-1475 (2011).

[5] Stephen R., Varghese S., Joseph K., Oommen Z., Thomas S. Diffusion and transport through nanocomposites of natural rubber (NR), carboxylated styrene butadiene rubber (XSBR) and their blends. *Journal of Membrane Science,* **282**, 162–170 (2006).

[6] Klemm D., Philipp B., Heinze T., Heinze U., Wagenknecht W. Comprehensive Cellulose Chemistry, **Volume 1**, *Fundamentals and Analytical Methods*, Wiley-VCH, Weinheim (1998).

[7] Ning-Jun C., Xu Q., Chee-Shan C., Gong C.S., Chen L.F. Cellulose hydrolysis using zinc chloride as a solvent and catalyst. *Applied Biochemistry. and Biotechnology*, **45-46**, 521-530 (1994).

[8] Xu Q., Chen L.F. Ultraviolet spectra and structure of zinc–cellulose complexes in zinc chloride solution. *Journal of Applied Polymer Science,* **71**, 1441–1446 (1999).

[9] Jamil M.S., Ahmed I., Abdullah I. Effects of rice husk filler on the mechanical and thermal properties of liquid natural rubber compatibilized high-densitypolyethylene/natural rubber blends. *Journal of Polymer Research*, **13**, 315–21 (2006).

[10] Otaigbe J.U. Dynamic mechanical response of a thermoplatic sheet molding compound-glass fiber composite. *Polymer Engineering Sciences*, **31**, 104–109 (1991).