



Green nanocomposites of natural rubber/nanocellulose: Membrane transport, rheological and thermal degradation characterisations



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ABSTRACT

The membrane transport, rheological and thermal degradation properties of nanocomposites based on natural rubber (NR) latex reinforced with nanocellulose is clearly discussed with theoretical explanations. The concentration of the nanocelluloses in the composites was 2.5, 5, 7.5 and 10 wt%. The cross-linking agents like ZnO, sulphur etc. were used during the composite preparation stage. The existence of the three dimensional network of Zn/cellulose complex in the nanocomposite and its influence on the diffusion, rheological and thermal properties were also discussed. The V_{rf} value of the composite shows an increase from 0.74 (NR) to 0.80 (10% composite) which gives the evidence of the reinforcement of the filler in the matrix. The polarity and the tortuosity of the nanocellulose make the composites resistant to non-polar organic solvents and this behavior is increased with increasing the nanofibre content. The remarkable decrease in the diffusion coefficient and the equilibrium solvent absorption with the addition of nanocellulose is also discussed. Kraus empirical equation was used to ascertain the extent of reinforcement and found the percolation threshold value of the filler is in the range of 4.5–5.9 wt% of nanocellulose.

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1. Introduction

Nanocomposites based on polymeric matrices successfully integrate the concepts of composites and nanometer sized materials. It is well known that the term 'nanocomposite' describes a class of two-phase materials where one of the phases has at least one dimension lower than 100 nm. Scientific reports shown that the commercial interest in fillers for nanocomposites has mainly focused on clay, silica (Pavlidou and Papaspyrides, 2012) and other inorganic based materials. Tremendous works were reported in the last decade about carbon nanotubes (CNTs) reinforced nanocomposites (Lau et al., 2006) and most recently the research works are concentrated in graphene reinforced composites (Nabarun et al., 2012). But in the recent decades, the polymers reinforced with cellulose nanofibres or with its derivatives have attracted many scientists owing to the green environmental issues (Abraham et al., 2012) and the enhanced mechanical, electrical and biodegradation properties because of the nanometric size of the cellulose. The biodegradability, high mechanical properties, low density, and availability from renewable resources and diversity of the sources

(Abraham et al., 2011) of the nanocelluloses have posted them as a competing candidate for polymeric green filler.

Nano reinforced polymer composites are widely used in many engineering applications and hence the study of transport of solvent molecules through these membranes and their flow properties along with the thermal degradation analysis are very important. Diffusion in the composite membrane is a kinetic process depending on the free volume within the material, segmental mobility of polymer chains, tortuosity on the moving path because of the presence of the filler, polarity of the reinforced phase and the size of the penetrant molecule (Smith and Peppas, 1985). The transport properties of various rubber/rubber, thermoplastic elastomers, interpenetrating networks and natural fiber and particulate filled composites have been studied by various researchers (Mathew et al., 2002; Prasanthakumar and Thomas, 2001; Visakh et al., 2012). Transport properties of rubber composites are strongly dependent on the cross-linking, the nature of filler and additives, penetrant size, etc. The hydrophilic –OH groups in the surface of the nanocellulose has the ability to improve the barrier properties of rubber composite materials toward organic solvents according to a tortuous path model in which a small amount of nanocellulose significantly reduces permeant diffusion. In the dispersed system, the individual nanofibre will have very high surface area and as a result the barrier and flow properties get changed. Angellier et al. (2005) have investigated the swelling behavior of natural rubber

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Table 1
Formulation of the cross-linked NR/nanocellulose composite.

	Weight % in the nanocomposite				
	Neat NR	2.5%	5%	7.5%	10%
Centrifuged natural rubber latex	96.5	94	91.5	89	86.5
Potassium hydroxide solution	0.35	0.35	0.35	0.35	0.35
Sulphur dispersion	1.5	1.5	1.5	1.5	1.5
ZDC dispersion	0.75	0.75	0.75	0.75	0.75
ZMBT dispersion	0.6	0.6	0.6	0.6	0.6
Zinc oxide dispersion	0.3	0.3	0.3	0.3	0.3
Nanocellulose dispersion	0	2.5	5	7.5	10

filled with waxy maize starch nanocrystals where they found as the starch content increases, the absorption rate decreases and the starch nanocrystals form a three-dimensional network, resulting in the reduction of swelling capability of the matrix. The reduction of swelling upon the addition of starch nanocrystals has also been suggested as due to the interaction between starch and natural rubber.

The aim of the present study was to analyze the transport properties, viz. toluene and *p*-xylene permeability of nanocomposite films composed of NR and nanocellulose. We have used nanocellulose (Abraham et al., 2011) extracted from banana fiber by steam explosion process as the filler and vulcanizing agents for the cross-linking of the NR matrix at the composite preparation stage. We have adopted reduced sorption curves, diffusion coefficient and Kraus equation for analyzing the result with a theoretical background. The rheological behavior of the nanocomposites which is interconnected to the diffusion characteristics was also discussed. The reinforcement of NR with this bio nano filler will enhance the viscosity of the composite into a considerable extent.

Along with the diffusion analysis and the flow properties, the thermal degradation characteristics of the nanocomposites were also included. For selecting materials with specific applications, the exact knowledge of its thermal characteristics is also important. The demand for products, which could be used in high temperature applications, stimulated the investigations to unravel the relationship between thermal properties and chemical interactions between natural rubber and nanocellulose (Xuefeng et al., 2012). Because of the presence of hydroxyl groups on cellulose it is expected for a higher filler–filler interaction than filler–matrix interaction (Moon et al., 2011). The stability of rubber vulcanizates depend on the environment because degradation is primarily dependent on thermal or thermo-oxidative degradation (Subramaniam et al., 2012; Nashar and Sadek, 2012; Jose et al., 2010). Hence the presence of oxygen in the cellulose molecule will also affect the thermal properties of the nanocomposite.

Green nanocomposites are composed of green renewable materials and are fully biodegradable after its end use. The studied nanocomposite is prepared by nanocellulose (banana fiber) and natural rubber latex. The prepared nanocomposite is completely biodegradable by vermicompost method which is discussed in our earlier manuscript (Abraham et al., 2012). The existence of the Zn/cellulose complex network in the studied NR nanocomposites and its influence on their diffusion, rheological and thermal degradation properties are clearly discussed below with theoretical explanations.

2. Experimental

2.1. Materials

2.1.1. Natural rubber latex, the matrix

Centrifuged latex of natural rubber was kindly supplied by Rubber Board, Kottayam, Kerala, India. It contained spherical particles

with an average diameter around 1 μm , with a dry rubber content of 60 DRC and it contains more than 98% of *cis*-1,4-polyisoprene.

2.1.2. Nanocellulose, the reinforcement

A homogenous (with a diameter of 10–60 nm) dispersion of nanocellulose which is obtained by the steam explosion of the banana fiber is used as the reinforcing material for the nanocomposite (Abraham et al., 2011).

2.2. Composite membrane processing

NR latex/nanocellulose composite membrane were prepared from pre-vulcanized latex (Abraham et al., 2013) by casting on a glass plate followed by drying at ambient temperature. The composite composition is described in Table 1 formulation. The aqueous suspension of the various proportions of nanocellulose, latex and the cross-linking agents were mixed by ball milling followed by ultra sonication. The pre-vulcanization 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 filler (nanocellulose) used. The ball milling process was conducted for 2 h in water medium with ceramic balls (1.5 cm diameter) in stainless steel container (1 L). The speed of the mill was 300 rotations per minute. It is then subjected to ultra-sonication for 10 min in 50% amplitude at room temperature. The mixed aqueous suspension of the nanocomposites poured in to glass plates and dried for 24 h at oven with a temperature of 50–60 °C in order to obtain dry film membranes between 1 mm and 2 mm thick depending on the test and with weight fractions of nanocellulose within the NR matrix ranging from 0 to 10 wt%. Resulting film membranes were conditioned at room temperature in desiccators containing P_2O_5 until tested.

2.3. Scanning electron microscopy (SEM)

SEM analysis of the samples was done by an Analytical Scanning Electron Microscope (A-SEM), ZEISS EVO 60. The Microscope works with tungsten filament and maximum acceleration voltage of 30 kV. The samples were mounted on aluminum stubs and gold-coated with a sputter coater.

2.4. Transmission electron microscopy (TEM)

The size of the elementary particles and its distribution in NR matrix were characterized by transmission electron microscopy (TEM) with a C M 12 PHILIPS HRTEM. For the evaluation of the dispersion of nanocellulose on the dried NR matrix, cryo cutting method was adopted. The cryo cutting of the nanocomposites were done by a thin section of about 100 nm was cut with a diamond knife at $-100\text{ }^\circ\text{C}$ (T_g of NR is ~ 60) to observe the dispersion of nanocellulose inside the rubber matrix.

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