



Preparation and characterization of potato starch nanocrystal reinforced natural rubber nanocomposites



K.R. Rajisha^a, H.J. Maria^b, L.A. Pothan^c, Zakiah Ahmad^d, S. Thomas^{b,e,*}

^a Department of Chemistry, CMS College, Kottayam, Kerala, India

^b School of Chemical Sciences, Mahatma Gandhi University, Priyadarsini Hills, Kottayam, Kerala, India

^c Department of Chemistry, Bishop Moore College, Mavelikara, Kerala 690101, India

^d UiTM, Mara Malaysia, 40450 Shah Alam, Selangor, Malaysia

^e Centre for Nanoscience and Nanotechnology, Mahatma Gandhi University, Priyadarsini Hills, Kottayam, Kerala, India

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ABSTRACT

Potato starch nanocrystals were found to serve as an effective reinforcing agent for natural rubber (NR). Starch nanocrystals were obtained by the sulfuric acid hydrolysis of potato starch granules. After mixing the latex and the starch nanocrystals, the resulting aqueous suspension was cast into film by solvent evaporation method. The composite samples were successfully prepared by varying filler loadings, using a colloidal suspension of starch nanocrystals and NR latex. The morphology of the nanocomposite prepared was analyzed by field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM). FESEM analysis revealed the size and shape of the crystal and their homogeneous dispersion in the composites. The crystallinity of the nanocomposites was studied using XRD analysis which indicated an overall increase in crystallinity with filler content. The mechanical properties of the nanocomposites such as stress–strain behavior, tensile strength, tensile modulus and elongation at break were measured according to ASTM standards. The tensile strength and modulus of the composites were found to improve tremendously with increasing nanocrystal content. This dramatic increase observed can be attributed to the formation of starch nanocrystal network. This network immobilizes the polymer chains leading to an increase in the modulus and other mechanical properties.

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1. Introduction

Nanocomposite materials find considerable interest recently among researchers and industrialists. Synthetic nanomaterials lack easy processability, biocompatibility, and biodegradability and hence have limitations compared to natural nanomaterials. Biodegradable nanocomposites which have superior thermal, barrier and mechanical properties can be synthesized from biopolymer and nanosized reinforcements. They are formed by the combination of natural polymers and inorganic solids which possess at least one dimension in the nanometer scale. Similar to conventional nanocomposites, which involve synthetic polymers, these biohybrid materials exhibit improved structural and functional properties of great interest for different applications. The

properties inherent to the biopolymers, biocompatibility and biodegradability, open new prospects for these hybrid materials with special incidence in regenerative medicine and environment friendly materials (green nanocomposites). Research on bionanocomposites can be regarded as a new interdisciplinary field closely related to significant topics such as biomineralization processes, bioinspired materials, and biomimetic systems. The upcoming development of novel bionanocomposites introducing multifunctionality represents a promising research topic that takes advantage of the synergistic effect of biopolymers with inorganic nanometer-sized solids. Raw materials often used for these new nanostructured composites are natural polymers; clay and nanowhiskers of chitin and cellulose. A possible source of inspiration for the design of new high performance bionanomaterials is due to the fact that they offer excellent reinforcement [1].

Starch is an abundant biopolymer, which is totally biodegradable. Starch nanocrystals obtained from starch have been used as fillers in polymeric matrices leading to desired reinforcing effect [2–4]. During the last decade, nano-material derived from natural polymers have been used as reinforcement in polymers and have been named as “green” bionanocomposites [5]. Many research

* Corresponding author. Centre for Nanoscience and Nanotechnology, Mahatma Gandhi University, Priyadarsini Hills, Kottayam–686560, Kerala.

Tel.: +9447223452/+481 2730003.

E-mail addresses: sabuchathukulam@yahoo.co.uk, sabupolymer@yahoo.com, sabuchathukulam@yahoo.co.uk (S. Thomas).

works published in the area of starch based bionanocomposites show the relevance on this topic in the current scenario of polymer research [6–9]. Chitin, cellulose and starch are the crystalline residue that can be obtained from different natural polysaccharides with a uniform structure after acidic or alkaline hydrolysis. These nanoparticles from different sources have different geometrical characteristics. For example, the nanocrystals obtained from cellulose [10] and chitin [11] have a rod shaped structure while that of starch have a platelet shaped structure [12].

However, nanocrystals from polysaccharides have the limitation of being hydrophilic and hence are incompatible with hydrophobic polymeric matrices. Therefore, the nanocrystal–matrix interface is usually the weakest point in a biocomposite, which results in the poor performance of the final composite. In order to improve the compatibility between the reinforcing phase and the polymer matrix, the nanoparticles can be physically or chemically modified [12]. An effective method for chemical modification is to graft polymer chains from the matrix directly onto the surface of reinforcing nanoparticles before composite preparation [13]. The formation of a continuous interphase between polysaccharide phase and the polymer matrix phase can improve interfacial adhesion. In addition, entanglements between grafted and ungrafted polymer chains are expected to occur if the molar weight is high enough. By this approach, nanocomposite materials with high content of reinforcing nanoparticles can be prepared. The main polysaccharides of interest as materials for nanocomposite preparation are starch and cellulose, but an increasing attention is also given to the application of the other biopolymers such as chitin and chitosan [14].

Starch is a well-known polymer naturally produced by plants in the form of granules which can be obtained mainly from maize, potatoes, corn, and rice. The properties of these starch granules vary from plant to plant, but are generally composed of, amylose (in most cases about 20% of the granule), and amylopectin. Amylose that builds up to 15–35% of the granules in most plants is a primarily linear polysaccharide with α -(1–4)-linked D-glucose units. Amylopectin is a highly branched molecule, with α (1–4) linked D-glucose backbones and exhibits about 5% of α (1–6)-linked branches, which have a profound effect on the physical and biological properties. Amylose is semi crystalline and soluble in hot water while amylopectin is insoluble in hot water. During its biodegradation, starch undergo enzyme-catalysed acetal hydrolysis where the α -1,4 link in amylopectin is attacked by glucosidases.[15]. The structural differences between these two polymers contribute to significant differences in starch properties and functionality

The focus of this work is to process nanocomposite materials consisting of natural rubber filled with potato starch nanocrystals which are completely biodegradable and thereby replacing the conventionally used carbon black (manufactured by burning oil or natural gas in controlled conditions). In the past decades, research works were focused on the development of other reinforcing agents to replace carbon black in rubber compounds. Recently, Novamont (Novara, Italy), working in partnership with Goodyear Tire and Rubber, has developed tires using nanoparticles derived from corn starch, partially replacing the conventional carbon black and silica used in making tires. This patented innovation, called Biotred, not only presents environmental advantages but also reduces the rolling resistance of tires [16]. Many attempts have been reported to blend polysaccharide nanocrystals with polymeric matrices [17–20]. The resulting nanocomposite materials display outstanding mechanical properties and thermal stability. For example, starch nanocrystals consist of crystalline nanoplatelets about 6–8 nm thick with a length of 20–40 nm and a width of 15–30 nm [20]. They have been used as a new kind of fillers, showing interesting reinforcing and barrier properties in natural rubber [21–23].

In this approach, potato starch nanocrystals constitute another possible filler for natural rubber which can have an admirable contribution in developing new environmental friendly strong composites [5].

Starch nanocrystals, the nanoscale biofiller derived from native starch granules, have been compounded with many different kinds of polymer matrices. The intrinsic rigidity of starch nanocrystals, special platelet-like morphology, strong interfacial interactions, and the percolation network organized by nanocrystals, contribute to the mechanical performance, thermal properties, solvent absorption, and barrier properties of the composites [24].

In the present work, a new nanocomposite based on natural rubber filled with potato starch nanocrystals was prepared. The nanocrystals were characterized by TEM and XRD. By varying the weight percentage of starch nanocrystals in the NR matrix the surface morphology, swelling behavior, and crystallinity of the various composites were investigated. The mechanical properties of the composites were also analyzed.

2. Experimental

2.1. Materials

Natural rubber latex was kindly supplied by Rubber Research Institute of India (RRI, Kottayam, India). It contained spherical particles of natural rubber with an average diameter around 1 μm , and the dry rubber content determined was about 60 wt %. The density of dry NR, was 1.4 g cm^{-3} , and it contained ~98% of *cis*-1,4-polyisoprene. Potato starch powder was purchased from Luba chemicals, Mumbai. Other chemicals like 36 N H_2SO_4 , BaCl_2 , sodium azoture (protectant against microorganisms) etc. needed for the preparation of starch nanocrystals were obtained from local sources.

2.2. Preparation of potato starch nanocrystals

Potato starch nanocrystals were prepared by sulfuric acid hydrolysis of native potato starch powder. About 36 g of potato starch granules were mixed with 250 ml of 36 N H_2SO_4 for 5 days at 40 °C, with a stirring speed of 100 rpm. The aqueous suspension was washed by successive centrifugation with distilled water until neutrality (confirmed by litmus paper testing). At this stage, starch suspension can be believed to be broken into nanocrystals, which changes the refractive index of the solution which is evident from the opaque nature of the suspension. The dispersion was completed by a further 10 min ultrasonic treatment in a B12 Branson sonifier. The resultant aqueous suspension constituted of starch fragments with a homogenous distribution in size. The solid fraction of this aqueous suspension had a weight concentration of about 3.4 wt %.

2.3. Preparation of NR latex/starch nanocrystal nanocomposite films

The aqueous suspension of potato starch nanocrystal and the NR latex were mixed in various proportions at ambient temperature using a mechanical stirrer (IKA-RW 28). The mixing was carried out for 15 min to ensure uniform dispersion. Then the mixture was kept for 1 h in order to ensure homogenization and also for the sedimentation of impurities. The mixture was stored under vacuum and stirred on a rotavapor for 10 min in order to degass the mixture and to avoid the formation of irreversible bubbles during water evaporation. The films with uniform thickness were obtained by casting on a glass mold and was evaporated at 40 °C in a ventilated oven for 4–6 h and then heated at 60 °C under vacuum for 2 h. The resulting films were conditioned at room temperature

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