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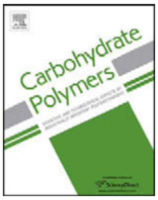

Organically modified nanosized starch derivatives as excellent reinforcing agents for bionanocomposites

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ABSTRACT

Organic modification of starch nanoparticles was carried out at room temperature to obtain nanosized hydrophobic derivatives. The particle size of the modified starch nanoparticles obtained by transmission electron microscopy (TEM) and X-ray diffraction (XRD) was found out to be around 50 nm. The hydrophobic starch derivatives were used to prepare bionanocomposites of natural rubber by mastication process. The properties were compared with composites obtained from untreated starch nanoparticles and carbon black. Up to 30 phr of the fillers were successfully incorporated leading to an enhancement in mechanical as well as thermal properties. Scanning electron microscopy (SEM) revealed single phase morphology of nanobiocomposites indicating compatibility of the filler and matrix. Dynamic mechanical properties were seen as a broad tan delta peak over a large range of temperature. It was observed that modified starch nanoparticles could be a potential substitute for carbon black as reinforcing agents and as promising materials for vibration damping applications.

1. Introduction

Polymer nanocomposites successfully integrate the two concepts of composites and nanometer sized materials. It is accepted that the term 'nanocomposites' describes a class of two-phase materials where one of the phases has at least one dimension lower than 100 nm (Bendahou, Kaddami, & Dufresne, 2010). Due to nanometric size effect these composites display some unique outstanding properties with respect to their conventional microcomposite counterparts. Polysaccharides such as cellulose, starch and chitin are a potential renewable source of nanosized reinforcement. They are naturally found in a semicrystalline state. Aqueous acids can be employed to hydrolyze the amorphous sections of the polymer. As a result the crystalline sections of these polysaccharides are released, resulting in individual monocrystalline nanoparticles (My Ahmed Said Azizi, Alloin, & Dufresne, 2005). The concept of reinforced polymer materials with polysaccharide nanofillers has known rapid advances and considerable interest in the last decade owing to their renewable character, high mechanical properties, low density and diversity of the sources (Bendahou et al., 2010). The use of starch nanoparticles is receiving a significant amount of attention because of the abundant availability of starch, low cost, renewability, biocompatibility, biodegradability and non-toxicity (Chakraborty, Sahoo, Teraoka, Miller, & Gross, 2005). Starch nanocrystals obtained by acid hydrolysis of waxy maize starch have been used as filler in a synthetic polymeric matrix and appeared to be an interesting reinforcing agent (Angellier, Molina-Boisseau, Putaux, Dupeyre & Dufresne, 2005; Dufresne & Cavaille, 1998; Dufresne, Cavaille, & Helbert, 1996). In this context, waxy maize starch nanocrystals have been considered as potential filler for natural rubber (NR), which is one of the most important elastomers widely used in industrial and technological areas (Thakore, Desai, Sarawade, & Devi, 2001). However most of the composites have been prepared by solution blending.

We have mainly concentrated on studying the reinforcement ability of starch by employing commercial mixing methods. Both native starch as well as starch nanoparticles are found to induce excellent reinforcement in natural rubber (Thakore et al., 2001; Valodkar & Thakore, 2010, in press). The main hurdle for the use of starch as a reinforcing phase is its hydrophilicity. Hence, there is a growing interest in organically modified derivatives of polysaccharides for different applications (Thielemans, Belgacem, & Dufresne, 2006; Tsuji & Kawaguchi, 2005; Xu et al., 2010). The amphiphillic nature imparted upon polysaccharides after hydrophobic modification gives them a wide and interesting applications spectrum, for instance as rheology modifier, emulsion stabilizer, surface modifier and as drug delivery vehicles. Chemical modification of starch nanocrystals is reported with various reagents such as anhydrides and fatty acids in organic and aqueous solvents (Namazi & Dadkhah, 2010; Namazi, Mosadegh, & Dadkhah, 2009; Wang et al., 2009). Modification also has been done

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via graft polymerization of caprolactone, poly ethylene oxide, etc. (Fang, Fowler, Tomkinson, & Hill, 2002; Namazi & Dadkhah, 2010; Namazi et al., 2009; Thielemans et al., 2006; Tsuji & Kawaguchi, 2005; Wang et al., 2009; Xu et al., 2010). However most of these modifications require drastic or prolonged reaction conditions which may also lead to agglomeration of the starch nanocrystals.

Hence we preferred to carry out room temperature organic modification of starch nanoparticles obtained by acid hydrolysis. The resulting hydrophobic derivatives were used for the development of bionanocomposite of natural rubber by commercial mastication process. Mastication process is superior because (i) it is environmentally safe due to the absence of organic solvents and (ii) it is compatible with the current industrial process such as extrusion and injection molding. A comparison was made with mechanical and thermal properties of conventional composite counterparts.

2. Experimental

2.1. Materials

Waxy maize starch (containing mostly amylopectin and small traces of amylose), sulfuric acid, 1,4-hexamethylene diisocynate, dibutyl tin dilaureate (DBTDL), acetic anhydride, tetrahydrofuran (THF), toluenesulphonic acid (PTSA) and acetic acid were purchased from Sigma–Aldrich, Bombay. NR and carbon black (CB) were kindly supplied by Mouldtech Rubber Industries, Vadodara.

2.2. Preparation of starch nanoparticles (SNPs)

A given weight of waxy maize starch (SW) was mixed with 3.16 M H_2SO_4. The suspension was continuously stirred for 5 days. It was then washed by successive centrifugation in distilled water until neutrality. SNPs were stored at 4 °C with several drops of chloroform.

2.3. Isocynate modification of SNP (SNI)

The isocyanate modification was carried out as reported elsewhere (Valodkar & Thakore, 2010a). Previously dried SNP (1 mole) and HMDI (1.1 mole) were allowed to react in dry tetrahydrofuran (THF) at room temperature in the presence of catalytic amount of DBTDL under nitrogen atmosphere to form a urethane linkage. The mixture was immediately subjected to ultrasonication to obtain a homogeneous dispersion of isocyanate modified starch nanoparticles in THF. Subsequent lyophilization of the dispersion resulted in dried nanoparticles.

2.4. Acetylated SNP (SNAC)

SNPs and acetic acid were mixed at room temperature. Acetic anhydride was added dropwise to the above mixture. After stirring for few minutes PTSA was added and the reaction mass was stirred for 6 h at 60 °C. The product was filtered and dried at 50 °C under vacuum. Degree of substitution was determined to be 2.7.

2.5. Preparation of bionanocomposites

The bionanocomposites of NR were prepared on two roll mixing mill. The mastication was continued until homogenous composites were obtained. This was followed by vulcanization at 150 °C and ~300 kPa pressure for 7–8 min to obtain rubber composite sheets with 1 mm thickness.

Four sets of bionanocomposites were synthesized using each of waxy corn starch (SW), starch nanocrystals (SNP), HMDI modified starch nanoparticles (SNI) and acetylated starch nanoparticles (SNAC) as reinforcing fillers in NR. Up to 30 phr of fillers were added along with the accelerators such as sulphur (1.8 phr), tetramethylene thiuram disulphide (0.5 phr), mercaptobenzo thiazyl disulphide (1 phr), zinc oxide (5 phr), and stearic acid (1 phr). Composites with carbon black (CB/NR) were also prepared for comparison.

2.6. Characterization of nanoparticles

Size and shape of the nanoparticles were determined by using TEM on a Philips, Holland Technai 20 model operating at 200 kV. The sample for TEM was prepared by putting one drop of the colloidal copper solution onto standard carbon-coated copper grids and then drying under an electric bulb for 30 min. X-ray diffraction (XRD) was determined by using PANalytical 'X'PERT-PRO XRPD. FT-IR spectra of starch and the vacuum dried nanoparticles were recorded as the KBr pellet on the Perkin Elmer RX1 model.

2.7. Characterization of nanocomposites

Stress/strain properties of all the NR composites were measured on a Universal Testing Machine (UTM, Lloyd Instrument) using test specimen in the form of dumbbells according to ASTM standard and procedure (D638). The gauge length was 50.0 mm. The crosshead speed was 10 mm/min at 25 °C and 50% humidity. The data given are the average of five measurements. The surface morphology of the tensile fractured surfaces was examined by means of Jeol Scanning Electron Microscope (JEOL JSM–5610LV). An accelerating potential of 15 kV was used for the analysis of the sample. TGA was recorded on TG–DTA 6300 INCARP EXSTAR 6000 in nitrogen atmosphere in temperature range of 30–450 °C at heating rate of 10 °C/min. DSC was performed on DSC 60 Shimadzu in nitrogen atmosphere in temperature range of −80 to 0 °C at heating rate of 10 °C/min. Dynamic mechanical tests were carried out using NETZSCH DMA 242. The specimen was a thin rectangular strip (15 × 5.1 × 0.959). The range of temperature in which the analysis was carried out between −80 and 0 °C at the frequencies of 1, 5 and 10 Hz in nitrogen atmosphere. The setup measured the complex tensile modulus E^*, i.e., the storage component E' and the loss component E''. The ratio between the two components, $\tan\delta$ was also determined.

3. Results and discussion

Fig. 1A shows TEM images of nanocrystals before (Fig. 1A(a)) and after modification (Fig. 1A(b) and A(c)). After acid treatment process, the native waxy corn starch granules have been destructured and degraded to nanocrystals with a size range of 70–100 nm (Fig. 1A(a)). We did not recognize anymore the platelet shape of unmodified starch particles along with its crystallinity as revealed by XRD. The particles are more individualized and monodispersed than their unmodified counterparts with a size of 50 nm in case of SNI and 40 nm in case of SNAC. The starch nanoplatelets are believed to aggregate as a result of hydrogen bond interactions due to the surface hydroxyl groups (Valodkar & Thakore, 2010b). Blocking these interactions by relatively large molecular weight molecules obviously improves the individualization of the nanoparticles. The decrease in the polar contribution reduces the strength of the interparticle interactions and results in the individualization of the nanoplatelets (Valodkar & Thakore, 2010a).

Fig. 1B shows the XRD pattern of starch and starch modified nanoparticles. The diffraction pattern displays typical peaks of A-type amylose allomorph (Valodkar & Thakore, 2010b). It was characterized by peaks at 2 theta value at 11.23° (0.76 nm) and