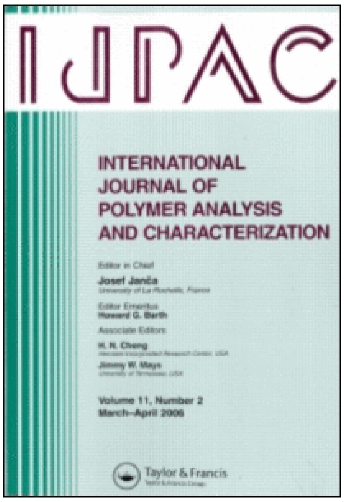

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THERMAL AND MECHANICAL PROPERTIES OF NATURAL RUBBER AND STARCH NANOBIOCOMPOSITES

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Large-scale starch nanoparticles of about 10–50 nm were obtained by acidic hydrolysis of amylopectin-rich cornstarch (waxy starch). They were used to prepare nanobiocomposites with natural rubber by mastication technique. Up to 30 phr (parts per hundred of rubber) of the filler was successfully incorporated leading, to an enhancement in thermo-mechanical properties. Tensile and elongation were even higher than those of conventional composites of untreated waxy starch and amylose-rich starch as well as carbon black at all loadings. SEM revealed single-phase morphology of nanocomposites, indicating extremely uniform mixing. It was observed that starch could be a potential substitute for carbon black as filler.

Keywords: Nanobiocomposite; Nanoparticles; Natural rubber; Starch

INTRODUCTION

There is currently considerable interest in processing polymeric composite materials filled with nanosized rigid particles called “nanocomposites.”[1] Because of the nanometric size effect, these composites have some unique and outstanding properties compared to to their conventional microcomposite counterparts. Natural rubber (NR) is one of the most important elastomers widely used in industrial and technological areas. Carbon black (CB) is the most commonly used reinforcing agent in NR. A variety of clays such as montmorillonite and organoclays[2,3] have been used for preparing nanocomposites of NR. The reinforcement increases with the amount of filler added and also with the reduction in particle size.[4]

Bionanocomposites are novel materials born out of the growing interest in nanomaterials and in the development of materials derived from renewable sources.[5] Polysaccharides such as starch, cellulose, and chitin are potential renewable sources of nanosized reinforcements. The use of starch is receiving significant attention because of its abundant availability, low cost, renewability, biocompatibility, biodegradation, and nontoxicity.[6] Native starch granules contain more or less

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concentric "growth rings" that are readily visible by optical or electronic microscopy.[1] Acid treatment is needed to reveal the concentric lamellar structure of starch granules. The purpose of this treatment is to dissolve away regions of low lateral order so that the water-insoluble, highly crystalline residue may be converted into a stable suspension by subsequent vigorous mechanical shearing action.[7] Dufresne et al.[8,9] obtained starch nanocrystals (SN) from potato starch granules. The insoluble hydrolyzed residue obtained from waxy corn was reported to be composed of crystalline nanoplatelets around 5–7 nm thick with a length of 20–40 nm and a width of 15–30 nm.[10] Starch nanocrystals were used as a reinforcing phase in natural rubber and displayed substantially improved mechanical properties.[11] Composites of NR have also been reported with chitosan.[12,13] However these composites were prepared in aqueous medium using rubber latex.

In the present work, starch nanocrystals were used for preparation of bionanocomposites with NR by mastication technique on a two-roll mixing mill. The thermal and mechanical properties were compared with those of composites prepared using untreated waxy starch (SW), amylose-rich starch (soluble starch) (S), and carbon black (CB). In rubbers, fillers not only reduce the cost of the material but also improve the mechanical and thermal properties of the compounds. It is important to study these properties to develop the right compound and to improve the processability of the resulting compounds for a broad range of applications.

EXPERIMENTAL SECTION

NR and carbon black were kindly supplied by Mouldtech Rubber Industries (Vadodara, India). Waxy cornstarch (9005-25-8-S9679) and soluble starch (9005-25-8-S2004) were supplied by Sigma-Aldrich Bombay (India).

Preparation of Starch Nanoparticles

Waxy cornstarch nanoparticles were prepared by acidic hydrolysis with 3.16 M H_2SO_4 solution.[1] The particles were collected by centrifuging at 10,000 rpm for 5 min at 25°C and washed with distilled water until neutral. They were vacuum dried at 50°C for 24 h.

Preparation of Nanocomposites

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

Three sets of biocomposites were synthesized: starch/NR (S/NR), waxy cornstarch/NR (SW/NR), and starch nanocrystals/NR (SN/NR). Up to 30 phr of fillers was added along with the accelerators such as sulfur (1.8 phr), tetramethylene thiuram disulfide (0.5 phr), mercaptobenzo thiazyl disulfide (1 phr), zinc oxide (5 phr), and stearic acid (1 phr). Composites with carbon black (CB/NR) were also prepared for comparison. The sheets were conditioned at 0% relative humidity (RH) by storing in a dessicator containing anhydrous $CaCl_2$ until being used.

Characterization of Starch Nanocrystals

Size and shape of the nanoparticles were determined by using transmission electron microscopy (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.

Characterization of Composites

The ultimate mechanical properties of all the NR composites were measured on a Universal Testing Machine (UTM, Lloyd Instrument) using test specimens 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 stress at break and the elongation at break were reported for each sample. The data given are the average of 3–5 measurements. The surface morphology of the tensile fractured surfaces was examined by means of a JEOL scanning electron microscope (JEOL JSM-5610LV). An accelerating potential of 15 kV was used for the analysis of the sample. Thermogravimetric analysis (TGA) was recorded on a TG-DTA 6300 INCARP EXSTAR 6000 in nitrogen atmosphere at a heating rate of 10°C/min. Differential scanning calorimetry (DSC) was performed on a Shimadzu DSC 60 at a heating rate of 10°C/min. Water sorption was determined by a method reported elsewhere.[19,20] The results are the average of three measurements.

RESULTS AND DISCUSSION

Characterization of Starch Nanocrystals

Figure 1(a) shows the TEM of insoluble residue obtained after 5 days of H_2SO_4 hydrolysis, which has the shape of parallelepiped nanoplatelets in aggregates of 50 nm. The diffraction pattern in Figure 1(b) displays typical peaks of A-type amylose allomorph.[14] It was characterized by peaks at 2θ value at 11.23° (0.76 nm) and a strong peak at 15.03° (0.57 nm), a double strong peak at 17.2° (0.52 nm) and 17.97° (0.49 nm), and a strong peak at 22.99° (0.39 nm).[15] The average size of the starch nanoparticles determined from the width of the reflection according to the Debye-Scherrer equation was about 10 nm.

Mechanical Properties

It can be seen from Figure 2(a) that as the amount of filler increases the tensile strength (T.S.) increases as expected. For biocomposites it follows the order SN/NR > SW/NR > S/NR. In the case of carbon black composites the initial lower T.S. value rapidly increases from 10 to 30 phr loading but remains lower than that of SN nanocomposites at all levels. This indicates the improved dispersion of the starch nanocrystals in the NR matrix due to small particle size. The slow increase of T.S. in the case of starch-filled composites may be because of

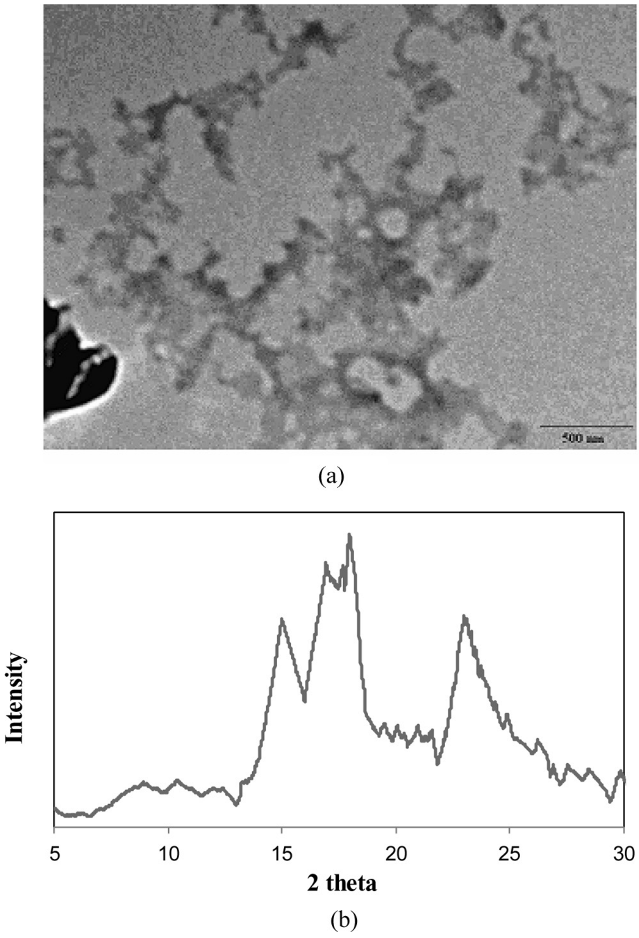
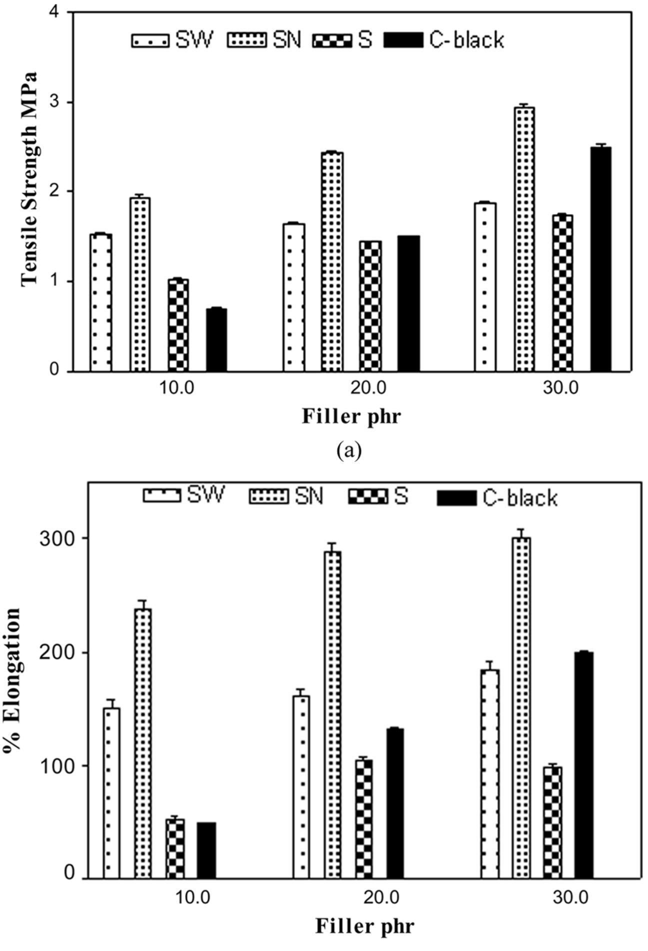


Figure 1. (a) TEM and (b) XRD spectra of starch nanoparticles.

increasing incompatibility of hydrophobic NR with hydrophilic starch at higher loadings. Due to the small particle size of SN, it is well dispersed into the pores of the matrix of NR, due to which the adhesion between the two increases, which in turn increases the stiffness and hence the strength of NR, although SN is hydrophilic in nature. The larger size of native starch does not allow it to be well dispersed into the pores of the NR matrix, so the adhesion between them is not as good as that between SN and NR.

Figure 2(b) shows that as the amount of SW and SN increases the elongation increases along with T.S., which is also seen in carbon black. This is an interesting observation as generally elongation and T.S. show the opposite trend. High starch nanocrystal content seems to preserve the elastic behavior of NR-based composites. Hence, the increase in percent elongation is more progressive than in carbon black. In the case of SW/NR, the increase is because it has high amylopectin content and hence higher molecular weight. Native starch, on



(a)

(b)

Figure 2. Effect of various fillers on (a) tensile strength and (b) % elongation at break of NR.

the other hand, induces a high brittleness of the material and hence the elongation diminishes after 20 phr. This is due to poor compatibility of hydrophobic NR and hydrophilic starch.

It can be said that SN/NR nanocomposites exhibited the highest mechanical strength and elasticity even at higher loading. The decreased size of nanoparticles compensates for the incompatibility arising due to the respective hydrophilic and hydrophobic nature of starch and NR. Due to small particle size, more particles per volume are available. A large amount of surface area will be exposed to the rubber molecules, leading to a huge interfacial volume around the nanofiller, which results in increase in stiffness. This increases the mechanical strength via synergistic effect, and the elasticity is improved because fracture does not occur until much higher elongation has taken place.

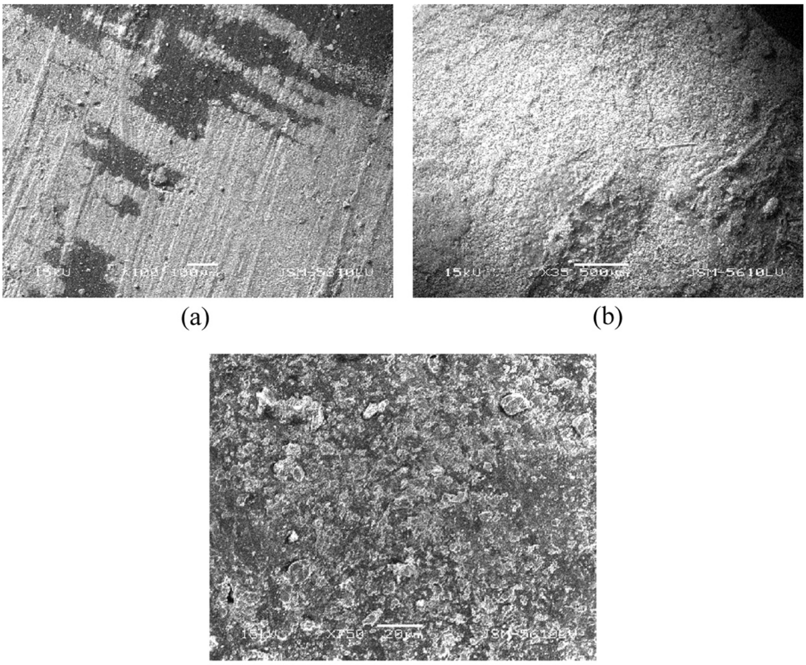
Scanning Electron Microscopy (SEM)

The results of the mechanical properties can be explained on the basis of morphology. The SE micrographs of fractured samples of biocomposites at 30 phr loading are shown in Figure 3. It can be seen that all the biofillers are well dispersed into the polymer matrix. They are very uniform and no cracks or holes were observed on the surface as a result of fracture. Among all, SN/NR composites (Figure 3(a)) exhibited a uniform single-phase morphology with a smooth surface. SW/NR (Figure 3(b)) showed a somewhat rough surface. In the case of native starch composites (Figure 3(c)), relatively coarse, two-phase morphology is seen.

Thermal Properties

Figure 4(a) shows typical TG curves of NR composites at 30 phr loading. All the biocomposites showed an initial mass loss from 150°C to 250°C attributed to elimination of volatile components such as water.[16] As such, the composites were stable up to 250°C. Beyond this temperature, the mass loss can be assigned to the thermal decomposition of natural rubber.[17]

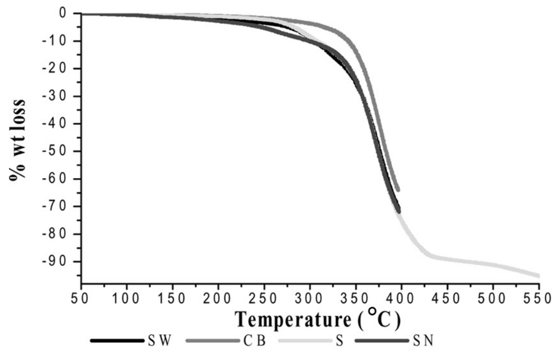
Figure 4(b) shows DSC curve of NR composites at 30 phr filler loading. The T_g of unfilled NR is around −66°C.[18] The T_g increases with incorporation



(a) (b)

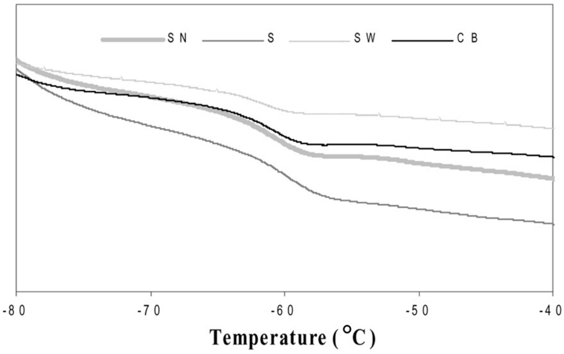
(c)

Figure 3. SE micrographs of NR biocomposites at 30 phr loading of (a) SN, (b) SW, and (c) S.



Composites	% wt.loss			
	1%	2%	5%	50%
S/NR	125°C	176°C	246°C	274°C
SW/NR	138°C	200°C	276°C	375°C
SN/NR	193°C	207°C	272°C	369°C
C-black/NR	208°C	260°C	315°C	382°C

(a)



Composites	Tg(°C)
SW/NR	-58.7
SN/NR	-57.2
S/NR	-57.7
C-black/NR	-58.8

(b)

Figure 4. (a) TGA and (b) DSC curves of all composites at 30 phr loading.

of filler and also with filler loading. This is because of stiffness imparted by the filler, which increases with increasing filler loading. The T_g of SN/NR is highest, followed by S/NR, SW/NR, and carbon black/NR composites. Due to small particle size, there are more SN particles so that a larger surface area is exposed to the NR matrix. This results in increase in stiffness and hence in increase in the T_g of SN/NR composites. All the biocomposites have T_g values comparable to those of carbon black/NR composites even at highest loading.

Table I. Water sorption data of biocomposites

	% Water uptake		
Composites	10 phr	20 phr	30 phr
SW/NR	1.30	0.82	0.60
SN/NR	1.22	0.65	0.34
S/NR	1.88	1.10	0.98

Water Sorption Studies

Water absorption largely depends on the water-soluble or hygroscopic components embedded in the matrix, which acts as a semipermeable membrane. The fiber/matrix adhesion is an important factor in determining the sorption behavior of a composite. Moreover, fiber architecture has also been found to affect moisture absorption. As the bionanofillers used here are highly hydrophilic in nature, water sorption was expected to be high and proportional to filler loading. However, the results of the experiment (Table I) showed an interesting trend. The maximum water uptake is only 1.88%, which is much lower than expected. Further, the water sorption decreases with filler loading. This indicates increasing adhesion between the polymer matrix and filler, which supports the improved mechanical strength with increasing filler content. Also, the high vulcanization temperatures may have introduced certain degree of cross-linking, which decreases the affinity of hydrophilic fillers towards water.

CONCLUSIONS

Starch-based fillers could be successfully incorporated into NR matrix up to 30 phr, by mastication technique. All the biofillers are potential substitutes for CB at 10 phr loading. The addition of only 10 phr of SN in NR induces a reinforcing effect corresponding to more than 20 phr of CB. The decreased size of nanoparticles compensates for the incompatibility arising due to the respective hydrophilic and hydrophobic nature of starch and NR. Hence, nanocomposites of SN showed the best mechanical properties, followed by SW and S. The nanocomposites exhibited a uniform single-phase morphology with a smooth surface. All the biocomposites showed thermal stability up to 250°C and the T_g values were comparable to that of CB/NR composites. Thus, starch nanocrystals are clearly a good substitute for carbon black.

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