Biopolymers as Effective Fillers in Natural Rubber: Composites versus Biocomposites

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ABSTRACT: Biocomposites of natural rubber (NR) blends were prepared with a variety of fillers obtained from renewable resources by a mastication technique. They were characterized for their mechanical properties and morphologies and compared with composites of the conventional filler carbon black (c-black). The biopolymers exhibited an interesting trend and imparted strength to NR that was quite comparable to c-black. Up to 30 phr of the fillers could be successfully incorporated; this led to enhancements in the mechanical strength. The properties were found to vary with the type and ratio of filler, namely, starch, cellulose, and chitin. The optimum me-chanical strength of the biocomposites was observed at 10 phr. The results were interpreted on the basis of the morphology by scanning electron microscopy, which revealed strong filler–polymer interactions. The moisture-uptake characteristics of the composites were studied. It was found that addition of biofillers did not lead to a significant increase in the moisture absorption. Furthermore, as the adhesion between the polymer matrix and fillers increased, the water uptake decreased. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 3815–3820, 2012

Key words: biopolymers; composites; rubber

INTRODUCTION

Fillers exist in a variety of systems, including organic, biological, biomimetic, and polymeric materials.[1,2] In polymer systems, fillers not only reduce the cost of the material but also improve the mechanical and dynamic properties of the compounds.

Natural rubber (NR) is widely used in industry and is freely and naturally available at low expense. The unique mechanical properties of NR result from both its highly stereoregular microstructure and the rotational freedom of α-methylene C—C bonds and from the entanglements that result from the high molecular weight, which contribute to its high elasticity. The properties of NR can be tailored by the addition of fillers of various surface chemistry and modification of the aggregate size/aspect ratio to suit the application concerned.

Carbon black (c-black) and silica are the main fillers used in the compounding of NR.[3,4] C-black, manufactured by the burning of oil or natural gas in controlled conditions, is the most important reinforcing agent. However, because of its origin from petroleum, it causes pollution and gives a black color to the rubber. Hence, research has been focused on the development of other reinforcing agents to replace c-black in rubber compounds. Silica and other types of fillers have a weaker polymer–filler interaction and are extensively used where a high degree of reinforcement is not essential.[6,7] The use of clay minerals, such as montmorillonite[8,9] and organoclays,[10–12] has also been extended to NR, and they seem to be a potential substitute for c-black.

Biopolymers have received increased interest lately because of more environmentally aware consumers, the increased price of crude oil, and global warming. They are used in variety of applications, such as therapeutic aids, medicines, coatings, food products, and packing materials. A variety of fibers, such as sisal,[13] bamboo,[14] and short coir fibers,[15] have been used to prepare biocomposites of NR. However, the use of polysaccharides as fillers or reinforcing agents in NR has not been extensively reported in the literature.[16,17] Blends of starch with thermoplastic polymers have been prepared in the past by our laboratory.[18,19] Hence, we prepared biocomposites of NR using various polysaccharides, such as starch, chitin, and cellulose, as reinforcing agents. Their properties were compared with conventional composites containing c-black.

Chitin constitutes the structure of the external skeleton in shellfish and insects and is one of the major components of the fibrous material of cellular walls in mushrooms and algae.[20,21] It is estimated that about 10^{10}–10^{11} tons of this polymer are

synthesized each year. Cellulose and its derivatives are an important class of natural macromolecules.[22] Cellulose is the most common component found in the cell walls of higher plants. Starch is a naturally occurring biomaterial that is abundantly available and has a low cost for commercial applications.

EXPERIMENTAL

Materials

NR and c-black were kindly supplied to us by Moldtech Rubber Industries (Vadodara, India). Starch (soluble), microcrystalline cellulose, and chitin from crab shells were supplied by Qualigens Chemicals (Bombay, India).

Preparation of the composites

The composites of NR were prepared on two roll-mixing mills, and the mastication had to be continued for a long time to obtain homogeneous composites. During this process, the temperature was controlled at about 40°C. Three sets of biocomposites were synthesized, namely, starch/NR, cellulose/NR, and chitin/NR biocomposites. These results were then compared with those of a conventional composite, that is, a c-black/NR composite. Up to 30 phr filler was added, along with 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).

This was followed by vulcanization, which was carried out at 150°C for 7–8 min with a hot press. The pressure of the hot press was adjusted ($\sim$ 300 kPa) to obtain rubber composite sheets with a 2 mm thickness.

Characterization

The synthesized composites were tested for various properties.

Hardness

Shore hardness was measured on a Frank hardness tester with a Shore A (Accumet Products, Mumbai, India) durometer at several points on the surface of the specimen. An average of six measurements was taken as the result.

Mechanical properties

The stress/strain properties of all of the NR composites were measured on a universal testing machine (Lloyd Instruments) using test specimen in the form of dumbbells according to ASTM D 638. The gauge length was 50.0 mm. The crosshead speed was
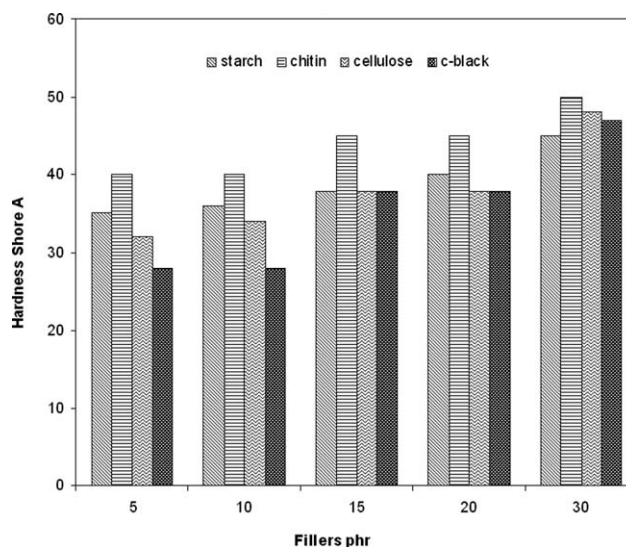
Figure 1 Effect of various fillers on the hardness of NR.

10 mm/min at 25°C and 50% humidity. The data given are the average of five measurements.

Scanning electron microscopy (SEM)

The surface morphology of the tensile fractured surfaces was examined by means of a JEOL scanning electron microscope (JEOL JSM-5610LV, U.K.). An accelerating potential of 15 kV was used for the analysis of the sample.

Density

The density of the biocomposites was determined by the method used for resins.[23]

Water sorption studies

Water sorption was determined by a method reported elsewhere.[24,25]

RESULTS AND DISCUSSION

Hardness

The results of hardness of the various composites are expressed in Figure 1. It was observed that in all of the composites, the hardness increased with increasing concentration of fillers, as expected. Thus, the biofillers did not have any negative effect on the hardness at increased concentration, although the increase was more rapid in case of c-black.

The results of hardness testing led to the following conclusions:

- Up to 30 phr, all of the four biofillers showed superior hardness to c-black.
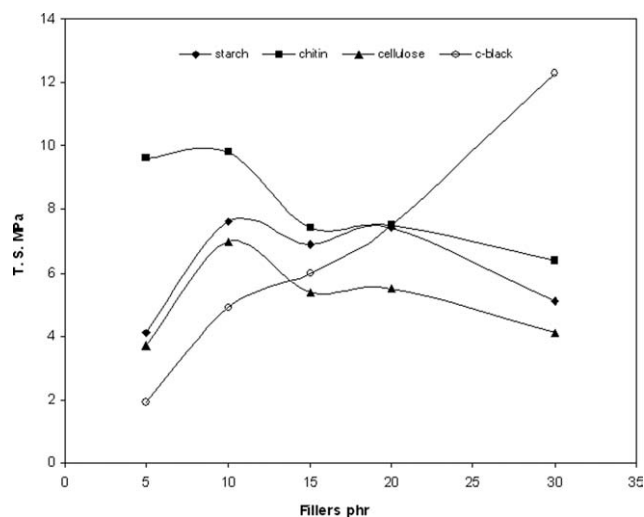- Among the biofillers, chitin showed the best hardness properties followed by starch and cellulose.

Figure 2 Variation of TS of NR with filler loading.

- An increase in parts per hundred resin of c-black led to a steep increase in hardness of NR, whereas the increase was not so pronounced in the case of the biofillers.

Mechanical properties

Tensile strength (TS)

The value for TS for the unfilled rubber was 1.6 MPa. It can be seen from Figure 2 that the composites exhibited a considerably higher TS, even at 5-phr loading, which increased further up to 10 phr. At this filler content, all of the composites had a greater strength than the c-black composite. Among biofillers, the TS imparted by chitin was highest, followed by starch, cellulose, and c-black. The addition of 5 phr of chitin showed a TS greater than 20 phr of c-black. However, unlike hardness, a further increase in the amount of filler decreased the TS except in c-black. This may have been because of the poor compatibility of hydrophilic biopolymers with hydrophobic NR at a higher loading.

Percentage elongation at break

The percentage elongation for unfilled rubber was 93%; this was much lower than that of the composites with 5 phr of any of the fillers (Fig. 3). A trend very similar to TS was observed. The optimum percentage elongation was observed at 10 phr, after which the elongation decreased, along with TS as the concentration of biofiller increased. This was an interesting observation because, generally, elongation and TS show the opposite trend. This once again supported the hypothesis that at higher loadings, the hydrophilic biofillers had poor interaction with NR.
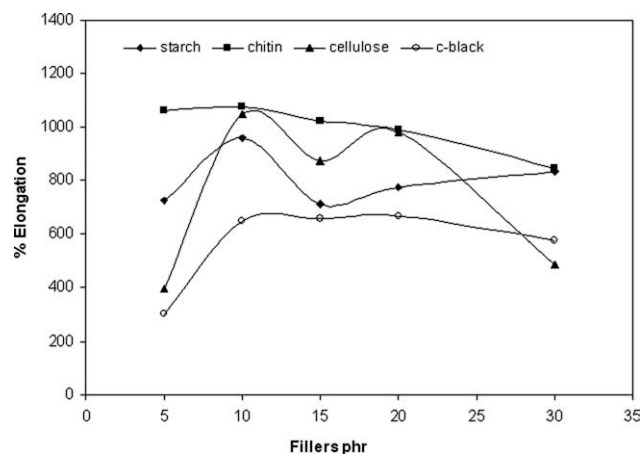

Figure 3 Variation of percentage elongation of NR with filler loading.

Thus, the results of TS and elongation show that the optimum loading of biofillers was 10 phr, and chitin exhibited exceptional mechanical strength, even at minimum loading.

Young's modulus

Young's modulus showed a trend similar to hardness; that is, the modulus increased with increasing filler content, with the highest being at 30-phr loading (Fig. 4). Chitin composites had exceptionally high values of modulus.

SEM

The results of the mechanical properties could be interpreted on the basis of morphology. The SEM micrographs of the composites at 10-phr loading are shown in Figure 5. The micrographs of the biocomposites showed a very uniform morphology like a single phase with no distinction between the matrix and the dispersion phase. However, the composites
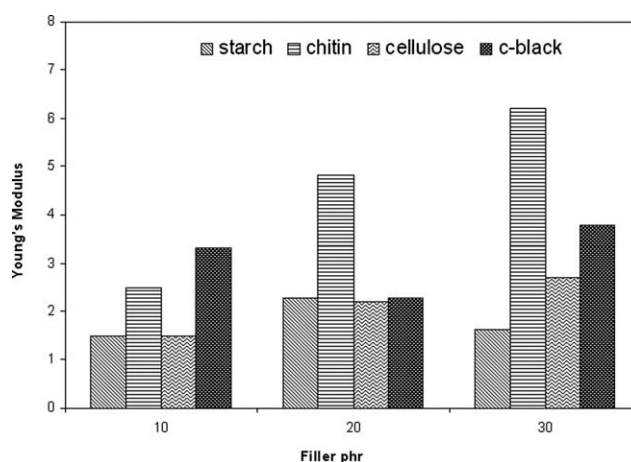

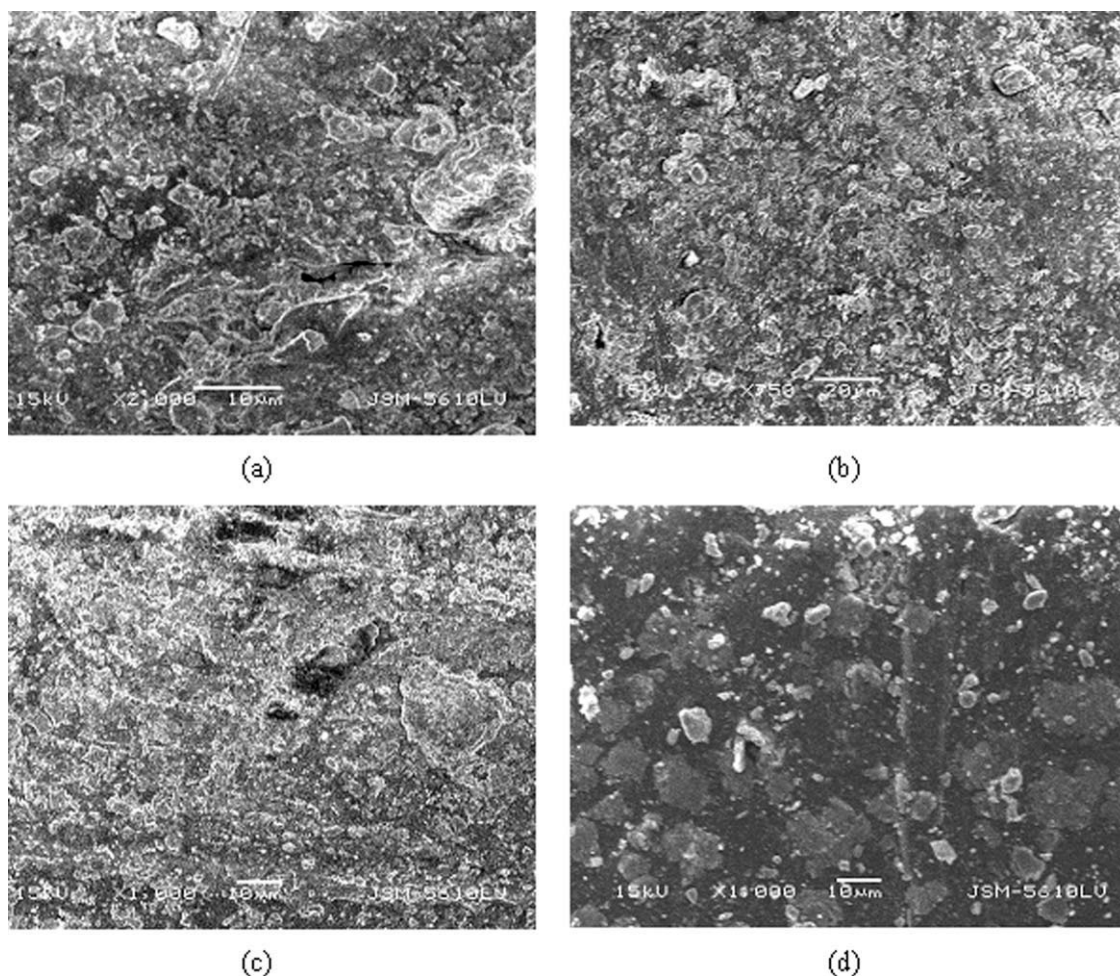**Figure 4** Young's modulus of the NR composites.

Figure 5 SEM micrographs of NRs containing different biofillers at 10 phr: (a) chitin, (b) starch, (c) c-black, and (d) cellulose.

containing chitin and starch [Fig. 5(a,b)] showed better mixing of the two phases among all of the composites. The composite of c-black showed the presence of holes formed during fracture, as evident from Figure 5(c), whereas SEM of the cellulose composite [Fig. 5(d)] showed the presence of particles on the surface; these may have leeched out during fracture. Overall, the biocomposites exhibited strong filler–polymer interaction.

Density

The density data expressed in Figure 6 show that as the percentage of filler increased, the density went on increasing, as expected. Among the biofillers, starch showed the highest density, followed by c-black, chitin, and cellulose. This was again because of the nature and texture of the biofillers.

Water sorption studies

A major drawback of these biopolymers is that they are hydrophilic in nature and, therefore, have an affinity to-

ward moisture; this leads to low degrees of adhesion between the fiber and matrix.[26] A reduction in water uptake was observed, and it was attributed to better compatibilization between the fiber and the matrix.

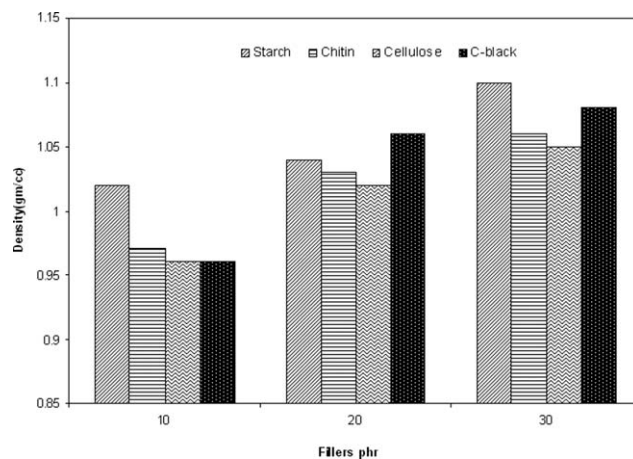Moisture absorption takes place by three types of mechanisms, namely, diffusion, capillarity, and

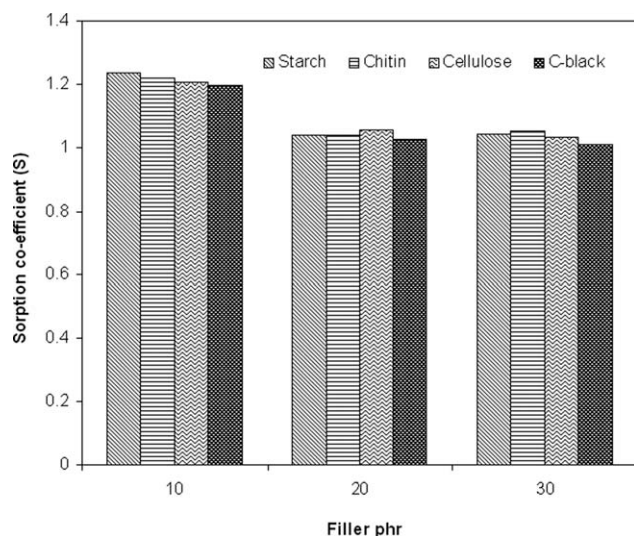**Figure 6** Density of the NR composites.

Figure 7 Effect of biofiller loading on the sorption coefficient of water in the composites.

transport via microcracks.[27] Among the three, diffusion is considered to be the major mechanism. Water absorption largely depends on the water-soluble or hygroscopic components embedded in the matrix; these act as a semipermeable membrane. The fiber/matrix adhesion is an important factor in determining the sorption behavior of composites. Moreover, the fiber architecture was also found to affect the moisture absorption.

As polysaccharides are highly hydrophilic in nature, the water sorption of the composites was expected to be high. Also, it was expected to increase with increasing filler loading. However, the results of the experiment show an interesting trend. As shown in Figure 7, the amount of filler increased as the sorption coefficient decreased. Thus, we could say that as the amount of filler increased, the adhesion between the polymer matrix and filler increased; this led to an increase in hardness and a decrease in the water absorption. Also, the water sorption of the biocomposites was quite comparable to that of the c-black composites. This showed that the biopolymers did not possess the drawback of increased moisture absorption. This further supported the fact that the biofillers could be a potential substitute for c-black.

At 10 phr, the composites of starch showed the highest water sorption, followed by those with chi-

TABLE I
Uptake of Water at Equilibrium (mol %)

Filler	10 phr	20 phr	30 phr
Starch	6.78	5.76	5.79
Chitin	6.73	5.76	5.85
Cellulose	6.63	5.86	5.73
C-black	6.59	5.71	5.61

TABLE II
Volume Fraction of the Polymer in the Solvent-Swollen Sample

Filler	10 phr	20 phr	30 phr
Starch	0.4462	0.4814	0.4642
Chitin	0.4609	0.4843	0.4734
Cellulose	0.4654	0.4818	0.4806
C-black	0.4683	0.4777	0.4773

tin, cellulose, and c-black, as seen from the values of the molar percentage uptake of water expressed in Table I, although the opposite trend was observed in the case of volume fraction of the polymer in the swollen sample (Table II). At 20 phr, the cellulose composites showed higher water sorption than those of starch, chitin, and c-black. At 30 phr, the order was chitin, starch, cellulose, and c-black.

CONCLUSIONS

The results of the mechanical properties show that up to 15 phr, all of the polysaccharides showed superior strength and elongation behavior to that of c-black. Composites with chitin showed the best mechanical properties followed by those with starch and cellulose. The addition of 5 phr of chitin resulted in better mechanical properties than when 20 phr of c-black was used. After 10 phr, the mechanical properties of the biocomposites were deteriorated with further addition of filler. This may have been because of the poor compatibility of hydrophilic biopolymers with hydrophobic NR. On the other hand, increasing quantity of c-black in the composites led to a constant increase in the mechanical properties. SEM study revealed improved morphology, phase mixing, and strong filler–polymer interaction in the case of the biocomposites. As the filler loading increased, the water absorption decreased; this also indicated an increase in adhesion between the polymer matrix and the fillers. The study indicated that the biofillers under investigation were a potential substitute for c-black. The drawback of a hydrophilic nature, which prevents their use at higher loadings, could be overcome by chemical modification.

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