

A Comparative Study of Short Nylon Fiber—Natural Rubber Composites Prepared from Dry Rubber and Latex Masterbatch

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ABSTRACT: A novel method for the preparation of short nylon fiber–natural rubber composites was developed in which short fibers chopped to approximately 6 mm were incorporated in the latex stage and processed into sheet form. By this method, mixing cycle time was reduced without compromising the fiber dispersion. Fiber breakage during mixing was reduced. The new composites when compounded with a dry bonding system based on hexamethylenetetramine, resorcinol and hydrated silica

(HRH) showed improved modulus, tensile strength and abrasion resistance compared to conventional composites. Tear strength, resilience, and compression set were similar to the conventional composites. SEM analysis indicated better interaction between matrix and fibers in the case of latex master batch. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 1484–1491, 2008

Key words: natural rubber; latex; nylon; fibers; composites

INTRODUCTION

Short fibers are used as reinforcing fillers in rubber compounds to get products with improved properties. They became very popular because of the possibility of obtaining anisotropic properties, ease of processing, and economy.^{1–3} In rubber, compounding fillers are incorporated on two roll mixing mills or in internal mixers. Typical mixing process involves incorporation, distribution, and dispersion. These are achieved by continuously subjecting the material to shear on a two roll mill or internal mixer. The use of short fibers of glass, rayon, aramid, asbestos, and cellulose as reinforcing fillers in natural, as well as synthetic rubber have been investigated by many researchers.^{1–10} The effect of fiber–matrix adhesion, aspect ratio of fiber, fiber dispersion and orientation, nature of the matrix, and type of fiber on the extent of reinforcement is also studied.^{11–16} All of these studies utilized the traditional mode of fiber incorporation at the time of mixing. Preparation of homogeneous compounds with well-dispersed fibers is time consuming and highly energy intensive. Fillers being the major volume component, it takes about 60–70% of the total energy input of a mixing operation. This calls for development of a less time consuming process for incorporation and distribu-

tion of fibers in the rubber matrix. One method is to incorporate the fibers in the rubber latex itself and then process the latex into conventional sheet form. In this article, we report the features of such an alternate method. Short nylon fiber–natural rubber composites were prepared in the new method. The factors considered in the selection of the composite were the optimum combination of mechanical properties of natural rubber and good strength of nylon fibers and their bondability to the rubber matrix in presence of good adhesion promoters. The cure characteristics and the mechanical properties of these composites are compared with that of the composites prepared by conventional method. The effect of a conventional dry bonding system based on hexamethylenetetramine, resorcinol, and hydrated silica (HRH) has also been investigated.

EXPERIMENTAL

Materials used

Single clone (RRII-105) natural rubber field latex was procured locally. Crumb rubber (ISNR-5) was obtained from the Rubber Research Institute of India, Kottayam, India. Nylon fibers manufactured by SRF, Chennai, India, were chopped to ~ 6 mm length. Zinc oxide, stearic acid, HS (1,2-dihydro-2,2,4-trimethylquinoline), MBTS (Mercptobenzthiazyl disulfide), TMTD (tetramethylthiuram disulfide), sulfur, hexa (hexamethylenetetramine), resorcinol, and hydrated silica used were of commercial grade.

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TABLE I
Formulation

Ingredients	Mix No.							
	A ₁	A ₂	B ₁	B ₂	C ₁	C ₂	D ₁	D ₂
NR ^a	100	100	100	100	100	100	100	100
ZnO	4	4	4	4	4	4	4	4
Stearic acid	2	2	2	2	2	2	2	2
HS	1	1	1	1	1	1	1	1
Fiber ^a	–	–	10	10	20	20	30	30
Silica	–	1.6	–	1.6	–	1.6	–	1.6
Resorcinol	–	2.5	–	2.5	–	2.5	–	2.5
Hexa	–	1.6	–	1.6	–	1.6	–	1.6
MBTS	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6
TMTD	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Sulphur	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5

^a For dry rubber mixes, the fibers were added during mixing. For latex stage composites, the fibers were added to latex equivalent to 100 rubber.

Processing

The field latex was diluted to 12.5% dry rubber content (DRC). A sandwich of alternating layers of latex and short fibers cut to 6 mm length was made and the latex was coagulated using dilute formic acid. The coagulum obtained was squeezed between rollers to remove water. The sheet obtained was dried in an air oven at 40°C for 3 days. Fiber loadings were adjusted to get 10, 20, and 30 phr fiber in the final composites. The composites were then processed like conventional sheet rubber.

Formulation of the mixes is given in Table I. The mixes were prepared according to ASTM D 3182 on a laboratory size two-roll mixing mill. Fibers were extracted by dissolving out the matrix in a solvent and the length distribution of fibers was determined by using stereo microscope and camera.

The energy for mixing was determined by mixing in a Thermo Haake Rheomix. The mixing cycle was limited to 5.5 min at 80°C with a fill factor of 0.75. The fibers were incorporated at 1.5 min and the torque was continuously measured for the remaining time of 4 min. Rotor speed was kept constant at 30 rpm during initial loading time of 1.5 min and then at 60 rpm for the remaining running time of 4 min. The integrated energy input for the free mixing cycle was noted.

Cure characteristics were determined by using Rubber Process Analyser model RPA 2000 at 150°C. Fibers were oriented in the mill direction by passing through the tight nip in the mill at the end of the mixing process. The thin sheets obtained were cut in the required dimensions and stacked one above the other to the desired volume. The sheets were vulcanized at 150°C under a pressure of 180 kg/cm² in an electrically heated hydraulic press to their respective cure times. The samples obtained were tested for mechanical properties according to relevant ASTM

standards. The test samples were prepared such that the fibers are oriented along and across the direction of application of load during testing. Schematic representation of fiber orientation in tensile and tear test samples is given in Figure 1.

RESULTS AND DISCUSSION

Evaluation of processing energy

Figure 2 shows the integrated energy input during the mixing process in the Rheocord mixer. The energy input shows almost a linear increase with time. For the latex stage composite energy input at any time is greater than the dry rubber composite. The higher energy for mixing is because of more restrained matrix resulting from better dispersion of fibers. That higher energy can be input in shorter

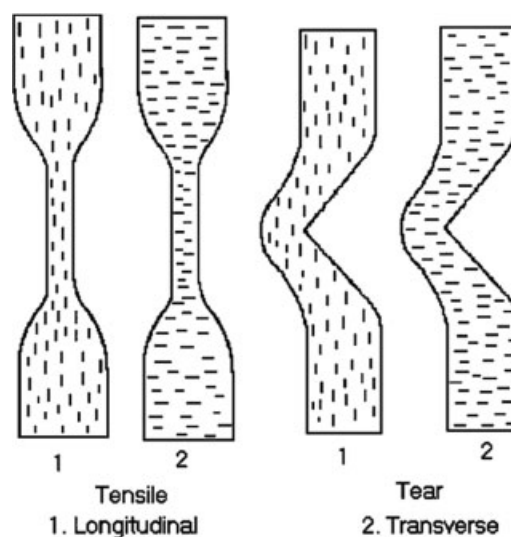


Figure 1 Schematic representation of fiber orientation.

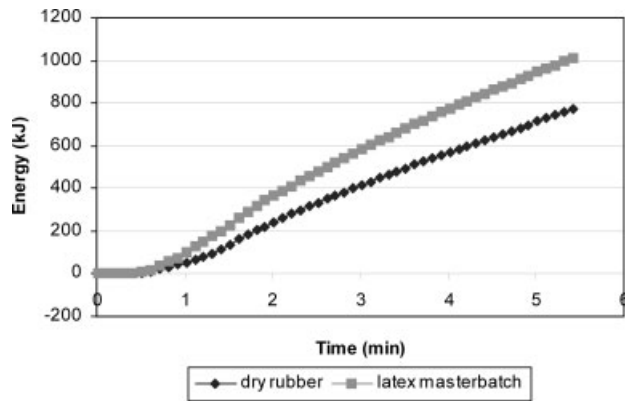


Figure 2 Energy input with time of mixing.

time shows that the total mixing time can be reduced without compromising the filler dispersion.

Fiber breakage analysis

The initial average length of the fibers was 6 mm. Figure 3 compares the distribution of fiber length after milling. The figure shows that average fiber length is 1.5–2.5 mm in the case of dry rubber compound whereas it is 2.5–3.5 mm in the case of latex master batch. This may be attributed to shorter shear history of the latex master batch.

Cure characteristics

Minimum torque

Figure 4 shows the variation of minimum viscosity measured as torque in RPA at 150°C with fiber loading. The minimum torque increases with fiber loading. The relatively higher viscosity of the latex stage composite may be attributed to higher average fiber length and low level of molecular breakdown due to shorter shear history.

Differential torque

Figure 5 compares the differential torque, i.e., maximum torque minus the minimum torque values of

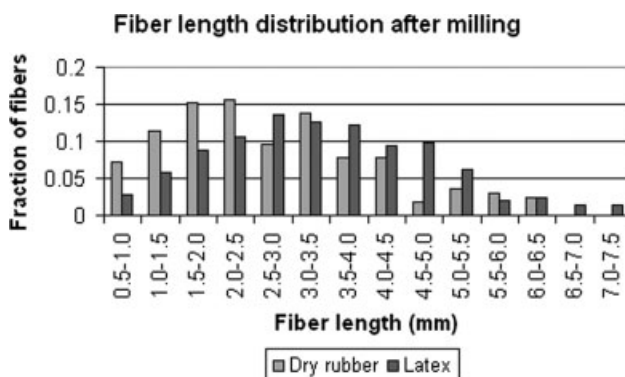


Figure 3 Fiber length distribution after milling.

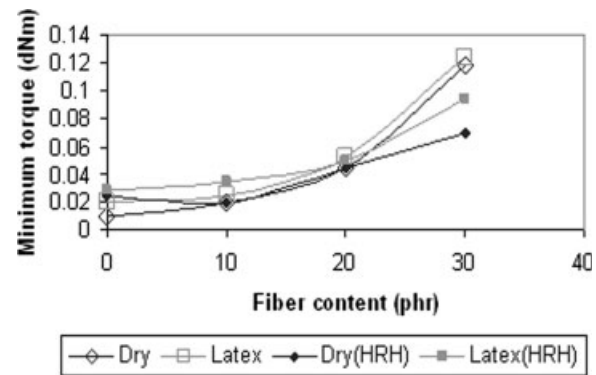


Figure 4 Variation of minimum torque with fiber content.

compounds with and without bonding agent. In both cases, the differential torque increases with the fiber loading. This shows an increasingly restrained matrix with fiber loading. In the compounds without bonding agent, latex master batch show marginally higher differential torque compared to dry rubber compounds. This is because of the lower fiber breakage. For compounds with bonding agent, the differential torque is comparable.

Cure time and scorch time

Figure 6 shows the variation of cure time with fiber loading and Figure 7 that of scorch time. In all the compounds cure time, as a general trend, increases with fiber loading. Compounds with bonding system show higher cure time compared with compounds without bonding system. This is because of the retarding effect of hydrated silica present in the tri-component bonding system, which facilitates enough time for the development of proper bonding between fiber and matrix. In both types of compounds (with and without bonding system), dry rubber composites show marginally higher cure time at all fiber loadings. For all types of composites, scorch time initially decreases and then remains almost constant with fiber loading. The cure and scorch behav-

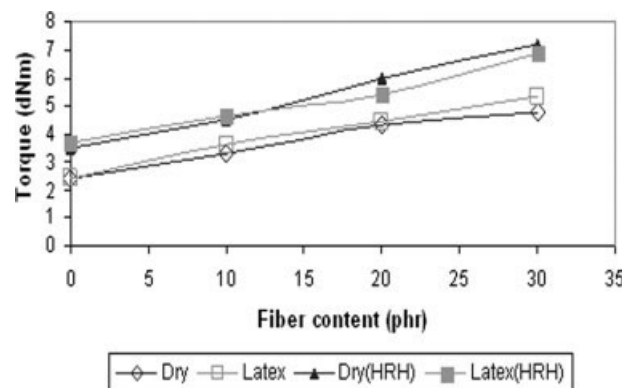


Figure 5 Variation of differential torque with fiber content.

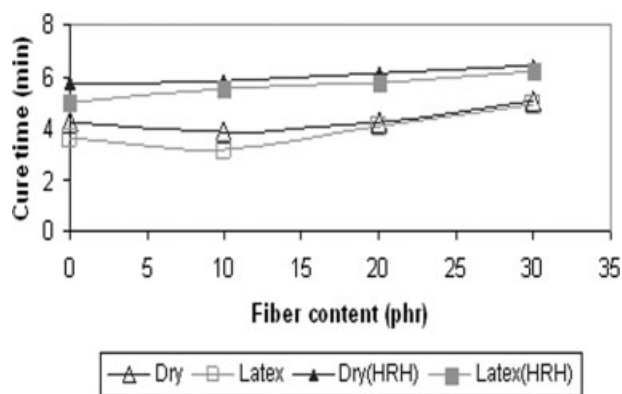


Figure 6 Variation of cure time with fiber content.

iors show that at higher loadings of fiber there is retardation of cure rate. This may be because of the adsorption of curatives by the fibers making them unavailable for crosslinking.

Mechanical properties

Tensile strength

The variation of tensile strength of the composites in longitudinal direction is shown in Figure 8(a). In composites without bonding system tensile strength continuously decreases with the fiber loading. Since the natural rubber matrix is nonpolar the polar nylon fiber will not develop adequate interfacial adhesion to resist the tensile forces at high elongations. So the fibers get easily pulled out from the matrix. The voids thus developed will act as points of weakness effecting earlier failure and reducing the tensile strength. With increase in fiber content the tensile strength is further reduced.

For obtaining more interaction between the fiber and the matrix HRH dry bonding system (Hydrated Silica-Resorcinol-Hexa) was introduced into the rubber matrix. In composites with bonding system, tensile strength in longitudinal direction initially decreases and then increases with the fiber content. Sreeja and Kutty¹⁷ reported similar results with

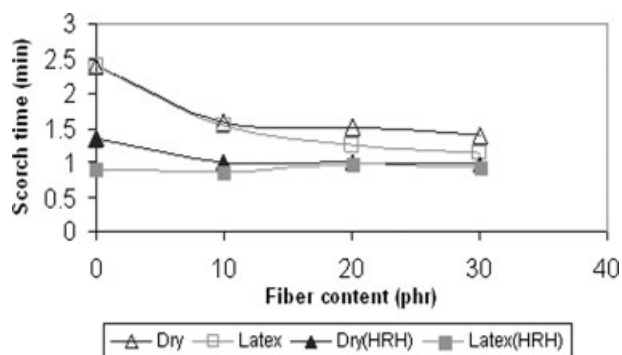
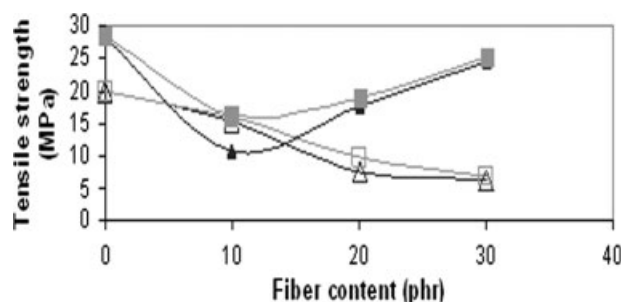
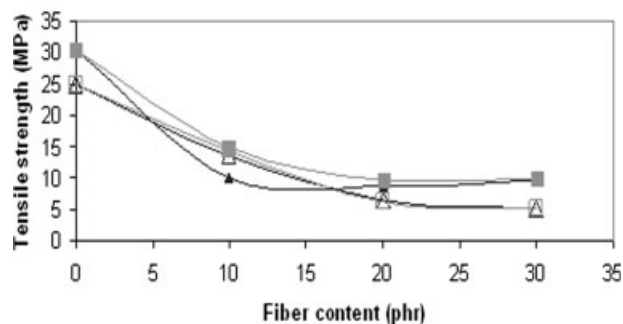


Figure 7 Variation of scorch time with fiber content.



a



b

Figure 8 (a) Variation of tensile strength (longitudinal) with fiber content. (b) Variation of tensile strength (transverse) with fiber content.

treated fibers in dry natural rubber compounds. Initial reduction in tensile strength is because of the interruption of stress crystallization of natural rubber by the short fibers. At higher fiber loadings, the increased reinforcement will offset the reduction in stress crystallization. The latex stage compound shows higher values than dry rubber compound. This is because of lower breakdown of fiber and matrix as a result of lower mixing cycle.

Figure 8(b) shows the variation of tensile strength in transverse direction with the fiber loading. When the fibers are arranged transversely the tensile strength will be provided solely by the matrix. Increase in fiber content will result in the dilution of the matrix which will reduce the tensile strength of the composite. So in the transverse direction, for all composites, the tensile strength shows a decrease with fiber content. In this case, also the latex stage composites exhibit better values due to the lower molecular breakdown of the matrix.

Modulus

Figure 9(a) shows the variation of modulus at 50% elongation of composites without and with bonding system in longitudinal direction. All the composites show an increase in modulus with fiber content. But without bonding system modulus values are substantially low. Without bonding system, dry rubber

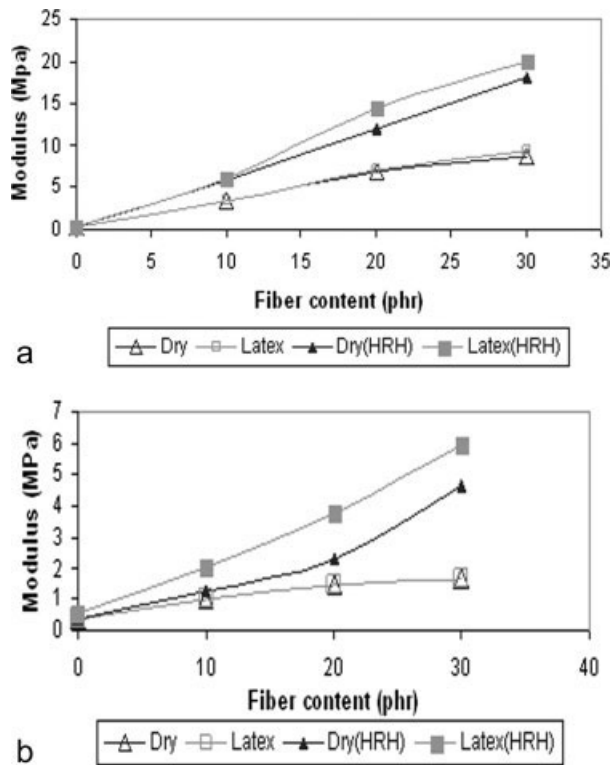


Figure 9 (a) Variation of 50% modulus (longitudinal) with fiber content. (b) Variation of 50% modulus (transverse) with fiber content.

and latex master batch composites show similar values. With bonding system, latex master batch composites show better values than the dry rubber composites especially for 20 and 30 phr loadings. This is attributed to the reduced fiber breakage and lower molecular breakdown of matrix.

Figure 9(b) compares the modulus at 50% elongation in transverse direction of the composites. Transverse modulus is much lower compared with the longitudinal modulus since fibers oriented in transverse direction cannot contribute to the load bearing property of the composites. Among composites with bonding system, latex stage composites have better values than dry rubber composites whereas composites without bonding system show similar values.

Tear strength

Figure 10(a) shows the variation of tear strength with fiber content for systems without and with bonding agent. In the longitudinal direction, the fibers are oriented perpendicular to the crack propagation. When the fiber content increases there will be more and more hindrance to the crack propagation as is evident from the increase in tear strength of the composites. The composites with bonding agent show higher values, as expected. In both the systems, the values are comparable between latex and dry stage composites.

Figure 10(b) shows the variation of transverse tear strength with fiber content. In the transverse direction, fibers are arranged parallel to the crack front and offer less resistance to crack propagation resulting in lower tear strength values than composites with fibers in longitudinal direction.

Elongation at break

Variation of elongation at break in the longitudinal direction with fiber content is shown in Figure 11(a). Elongation at break values exhibit a linear decrease with fiber content for all the types of composites. In composites without bonding agent the voids formed in the matrix, by the easier pullout of the fibers, will act as defects causing earlier breaking of specimens and thus reducing the elongation at break. The latex master batch composites show better values than dry rubber composites since the determining factor is the matrix which encountered lesser shear than the latter. In composites with bonding agent the reinforcing fibers progressively restrict the matrix resulting in a decrease in elongation at break. A sharp reduction in elongation even at 10 phr fiber loading shows improved adhesion between fiber and matrix provided by the bonding agent.

Variation of elongation at break in the transverse direction, with fiber content is shown in Figure 11(b). Here also the elongation at break decreases

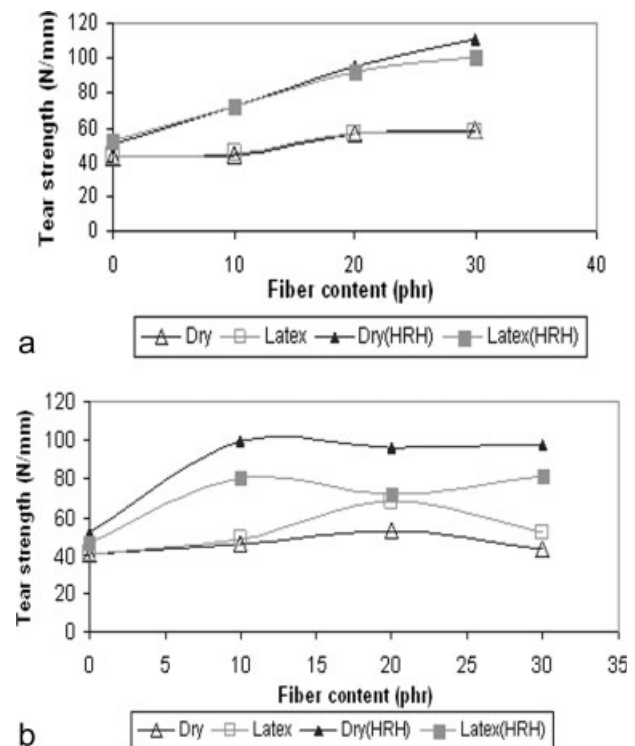


Figure 10 (a) Variation of tear strength (longitudinal) with fiber content. (b) Variation of tear strength (transverse) with fiber content.

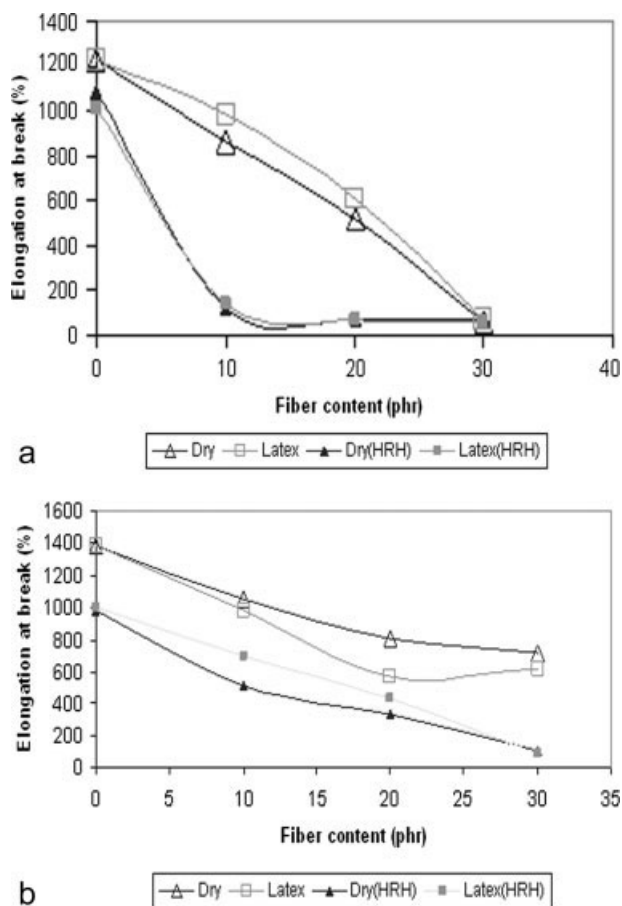


Figure 11 (a) Variation of elongation at break (longitudinal) with fiber content. (b) Variation of elongation at break (transverse) with fiber content.

with fiber content. But the decrease is smaller compared with that of longitudinal composites since transversely arranged fibers are not as effective in restraining the composite.

Rebound resilience

Figure 12 shows the variation of rebound resilience with fiber content. For compounds with bonding

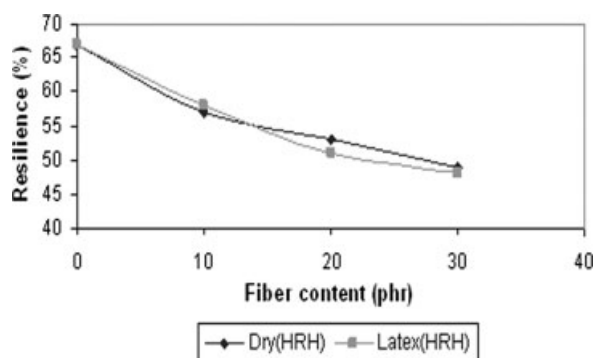


Figure 12 Variation of rebound resilience with fiber content.

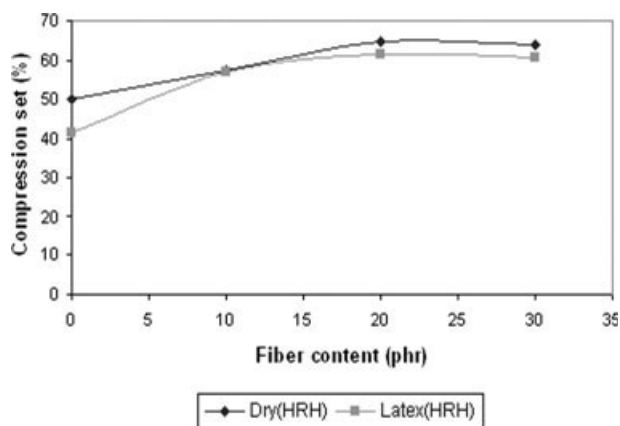


Figure 13 Variation of compression set with fiber content.

agent, rebound resilience decreases with the increase in fiber content. The values are similar for both latex stage and dry stage composites.

Compression set

Figure 13 compares the compression set values of latex master batch and dry rubber composites, both with bonding agent. Compression set increases marginally with fiber content and then remains almost constant. In all compositions except 10 phr

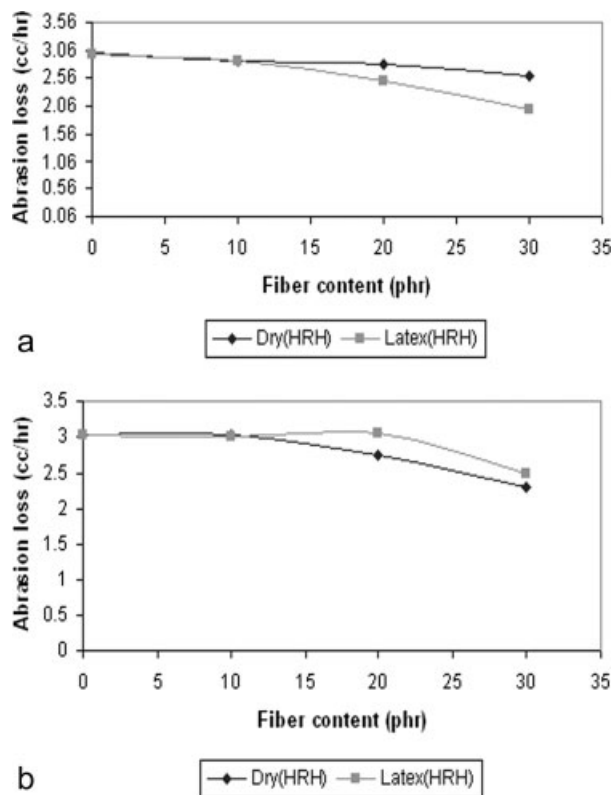


Figure 14 (a) Variation of abrasion loss (longitudinal) with fiber content. (b) Variation of abrasion loss (transverse) with fiber content.

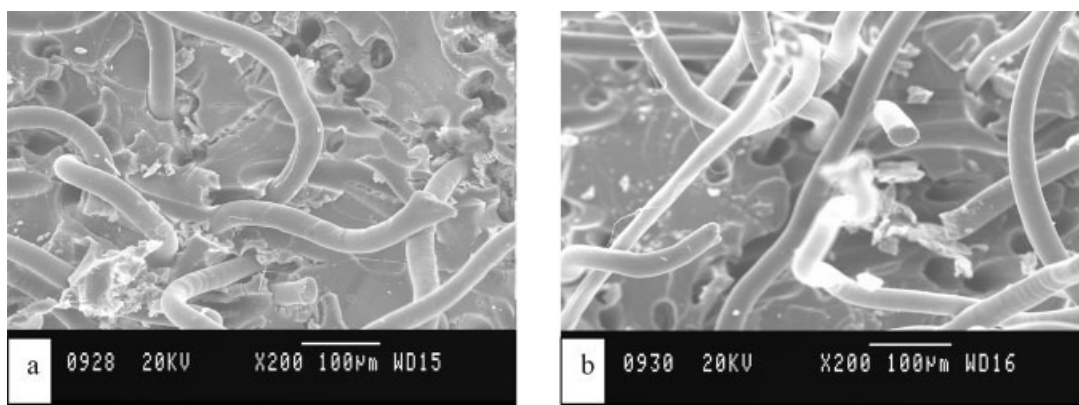


Figure 15 SEM photograph of fracture surface of (a) dry rubber and (b) latex masterbatch specimens.

fiber loading, the latex master batch shows lower set values.

Abrasion resistance

Figure 14(a) compares the abrasion resistance in the longitudinal direction of latex and dry stage composites with fiber content. Abrasion resistance is improved with the introduction of fibers in the case of composites with bonding system. There is remarkable increase for latex master batch compounds compared to dry rubber, especially for 20 and 30 phr. Figure 14(b) shows the abrasion resistance in the transverse direction. In this case, better values are for the dry rubber stage composites than for the latex stage composites. In the transverse orientation during abrasion process whole fibers are removed from the sample along with abraded rubber. Consequently, abrasion loss will be higher than the samples with longitudinally oriented fibers. In the latex stage composites, the interaction between the fiber and the rubber is more. Because of this interaction,

more rubber will be bound together with the fiber and will be removed along with fiber. So latex stage composites will register higher abrasion loss.

SEM analysis

Figure 15 shows the SEM photographs of the fracture surface from tensile specimens of (a) dry rubber and (b) latex masterbatch. From the SEM analysis, it is observed that in latex masterbatch samples the dispersion is more uniform and there are less fiber pullouts from the matrix than dry rubber. This proves that the reduction in mixing time is not affecting the dispersion of fibers but positively contribute to the composite performance. This is more pronounced in the samples with bonding agent. Figure 16 shows the fracture surface of (a) dry rubber and (b) latex masterbatch composites with bonding agent. In composites with bonding system, the adhesion is better compared with those without bonding system, which is apparent from the texture of the fractured surface.

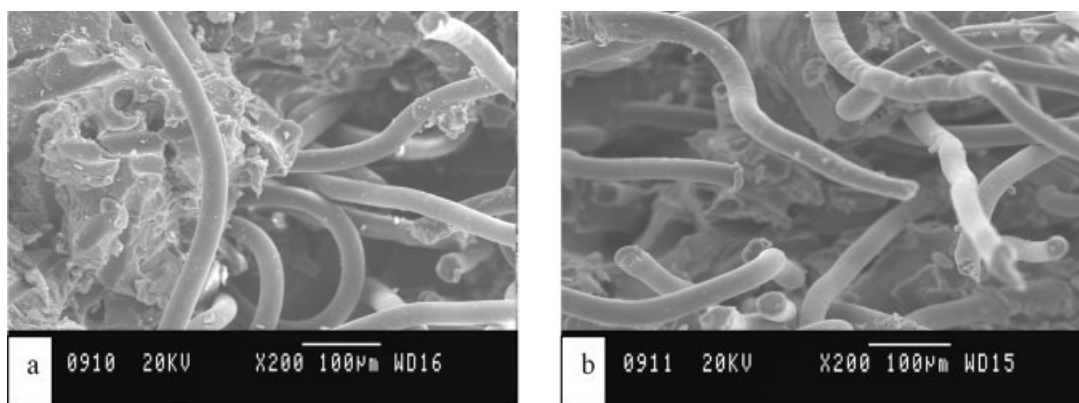


Figure 16 SEM photograph of fracture surface of (a) dry rubber and (b) latex masterbatch specimens (with bonding system).

CONCLUSIONS

From the study following conclusions are drawn. The natural rubber-short fiber composites prepared by latex stage master batching requires less mixing time for proper dispersion of fibers compared to the conventional composites. The fiber breakage during milling is reduced in the case of new method. The composites prepared by the new technique show similar cure characteristics as of the conventional composites. Of the mechanical properties tested, for the composites with dry bonding agent based on HRH, modulus, tensile strength and abrasion resistance show better values indicating better reinforcement. Elongation at break is reduced. Tear strength, resilience, and compression set show more or less similar values. Better interaction between matrix and fibers in the new composites is also indicated by the SEM analysis. The new method proposed is an efficient one to reduce the mixing time and hence to increase the production volume without compromising, and in most cases enhancing, the vulcanizate properties.

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