Reinforcement of Natural Rubber with Nylon 6 Short Fibers

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SYNOPSIS

The properties of natural rubber vulcanizates reinforced with nylon 6 short fibers were studied. It was found that the stress of vulcanizates decreased with initial fiber loading, followed by an increase with increasing the amount of fiber. The effect of reinforcing carbon black HAF on the physicomechanical properties was studied in the presence and absence of hydrated silica.

INTRODUCTION

Rubber products generally undergo dynamic stress during service. Their resistance to dynamic load application is important. Most rubber products are composites, reinforced with textiles. Recently, short-fiber reinforcement has been found to be a suitable alternative to continuous cord reinforcement for processing economy and design flexibility.[1]

The adhesion between many types of commercial fibers and most elastomers has been overcome by the discovery of the tricomponent system[2-4] consisting of hexamethylenetetramine, resorcinol, and high-surface-area hydrated silica (HRH system).

The mechanical properties of the composites, such as modulus, tensile strength at break, and ultimate elongation, depend on fiber orientation, fiber aspect ratio, and adhesion between fiber and matrix.[5-9]

In this paper, we report the results of our investigation on mechanical and swelling properties of natural rubber (NR)-reinforced by nylon 6 short fibers. The effects of bonding agent, fiber ratio, and reinforcing carbon black have been studied.

EXPERIMENTAL

Nylon 6 fibers, denier-6, produced by Misr Company for Artificial Silk-Kafer El Dwar, Egypt, chopped to about 113 mm were used. All rubber mixes were prepared on a two-roll mill of diameter 470 mm and width 300 mm, with speed of slow roll at 24 rev/min and gear ratio of 1 : 1.4. The role temperature was kept at about 50°C during mixing. Care was taken to ensure fiber orientation in the mill direction. The rheometric characteristics of NR mixes were studied[10] using a Monsanto oscillating disc rheometer R-100. The mechanical properties were determined according to standard methods[11] using an electronic Zwick tensile testing machine (model 1425). Swelling was conducted using toluene.[12] Aging of the samples was carried out at 100°C for 48 h in a good air-heated oven.[13]

RESULTS AND DISCUSSION

I. Effect of Bonding Agents on NR Vulcanizates

The compounds of the tricomponent system (HRH) were added to NR mixes successively, then nylon 6 fibers were added in a ratio of 20 phr and compared with the rubber mix containing the same ratio of fibers without the adhesion system. The rubber formulations, as well as their rheological characteristics and the physicomechanical properties of the vulcanizates, are shown in Table I. From these data, one can determine the following:

(a) Effect of Silica

The addition of silica leads to a slight increase in the cure time and a high increase in the scorch time, which can be attributed to the acidic nature of silica. On the other hand, both longitudinal (warp) and

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Table I Effect of HRH System on the Properties of NR Vulcanizates

	Formulation No.					
	1	2	3	4	5	6
NR	100	100	100	100	100	100
ZnO	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2
Resorcinol	—	—	5	5	5	—
Silica	—	5	5	5	5	—
Fiber (nylon 6 113 mm)	—	—	—	—	20	20
CBS	0.8	0.8	0.8	0.8	0.8	0.8
Sulfur	2	2	2	2	2	2
Vulcacite H	—	—	—	3.2	3.2	—
Rheometric properties						
ML (dN m)	2.5	4	3	4	2	2
MH (dN m)	57.5	57	35	58	85	77
tc90 (min)	18	20.5	22.5	21	12.5	15.5
ts2 (min)	8	12	4	3.25	3.5	7.5
CRI (min)	10	13.3	5.4	5.6	11.1	12.5
Physicomechanical properties						
Tensile strength (L) (MPa)	17.8	19.8	10.5	15.9	11.0	8.42
Elongation (L) (%)	700	700	800	630	50	100
Tensile strength (T) (MPa)	16.8	21.6	10.2	19.3	5.7	5.1
Elongation (T) (%)	700	700	700	620	300	400
Q (%)	386	350	496	337	168	261

transversal (weft) tensile strength are increased while the equilibrium swelling in toluene is slightly decreased.

(b) Effect of Resorcinol

The addition of resorcinol with silica results in a significant decrease in maximum torque, scorch time, cure rate index, and tensile strength. However, the swelling in toluene is increased.

(c) Effect of Hexamethylenetetramine (HMTA)

The addition of hexamethylenetetramine with the resorcinol and hydrated silica increases the maximum torque compared with the control sample 1; it also decreases both the elongation at break and the equilibrium swelling in toluene. On the other hand, the addition of HMTA does not affect, practically, the scorch time, the optimum cure time, and the cure rate index when compared with sample 3.

Table II Effect of Fiber Concentration on the Rheometric Characteristics of NR Formulations

	Formulation No.						
	4	7	8	9	5	10	11
Nylon 6 fiber	—	5	10	15	20	25	30
ML (dN m)	4	2	3.75	2.5	2	3	2.5
MH (dN m)	58	60	70	80	85	98	90
tc90 (min)	21	16.5	17	16	12.5	15.5	15.5
ts2 (min)	3.25	3.5	3.75	4.5	3.5	4	4.25
CRI (min^{-1})	5.6	7.69	7.54	8.7	11.1	8.7	8.88

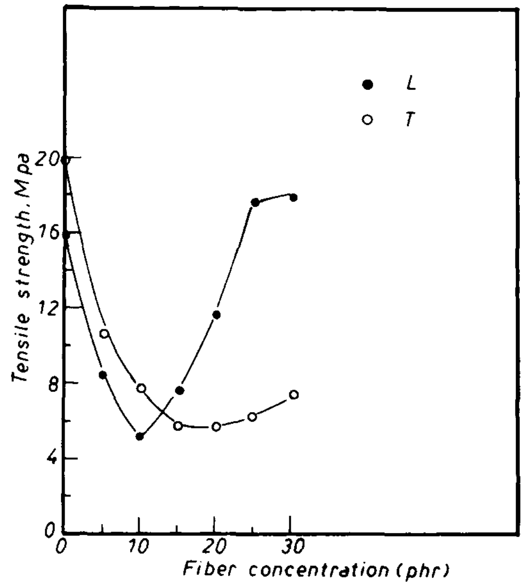

Figure 1 The dependence of both longitudinal (L) and transversal (T) tensile strength on the fiber concentration.

(d) Effect of Nylon 6 Fibers

The loading of fibers in conjunction with the HRH system (sample 5) showed that the maximum torque and cure rate index were increased. Also, the addition of fibers reduced the longitudinal elongation,

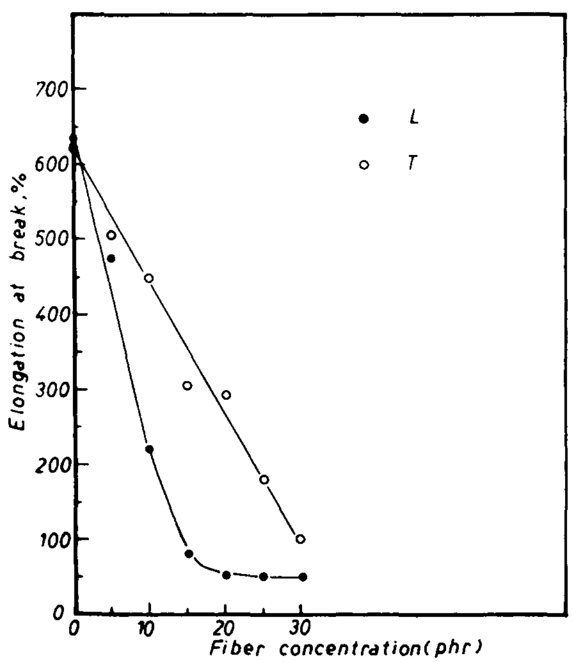

Figure 2 The dependence of both longitudinal (L) and transversal (T) elongation at break on fiber concentration.

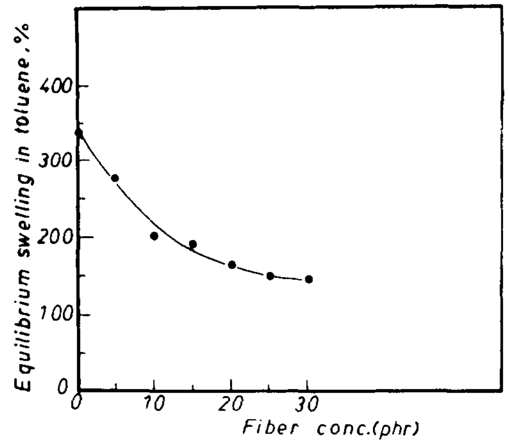

Figure 3 The dependence of equilibrium swelling in toluene on fiber concentration.

the equilibrium swelling in toluene, and the transverse tensile strength.

Comparing these results with that obtained for sample 6, which contains fibers without the adhesion system HRH, indicates that the bonding between fibers and the rubber matrix is necessary to obtain high stress at low extension, which is very important in most rubber articles reinforced by textile.

II. Effect of Nylon Fiber Loading on the Properties of NR Composites

Nylon 6 fibers were incorporated in different ratios up to 30 phr in NR mixes to study the effect of fiber loading on the properties of the vulcanizates. Table II shows the rheometric characteristics of the mixes.

The rubber mixes were vulcanized at $142 \pm 1°C$ for their optimum cure time. The mechanical prop-

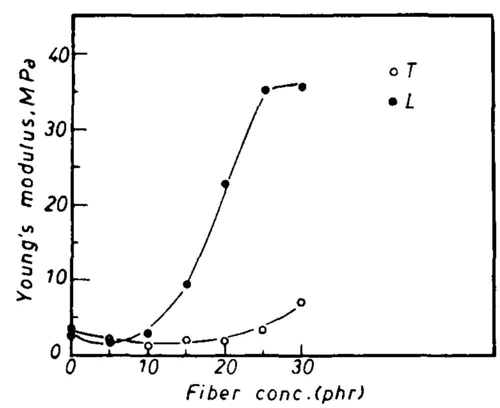

Figure 4 The dependence of Young's modulus on the fiber concentration.

Table III Effect of Carbon Black and Silica on NR Vulcanizates

	Formulation Nos.									
	12	13	14	15	16	17	18	19	20	21
Silica	—	5	5	5	5	5	—	—	—	—
HAF	—	—	10	20	30	40	10	20	30	40
Processing oil	—	—	3	3	3	3	3	3	3	3
Rheometric characteristics										
ML (dN m)	1.5	1.5	2	2	3	3	1.5	1.5	2	3
MH (dN m)	80	89	87	87	96	104	84	94	90	102
tc90 (min)	13	14	14	17.5	17	16.5	15	14.5	15.5	16.5
ts2 (min)	3.5	3.75	3.5	3.75	3.5	3.5	3.25	3.25	3	3.25
CRI (min^{-1})	10.53	9.76	10	7.27	7.41	7.69	8.51	8.89	8	7.55
Percent of the retained properties after aging at 100°C for 48 h										
Tensile strength (L) (%)	129.7	94.0	92.7	95.4	96.3	84.8	92.6	99.7	94.4	101.3
Tensile strength (T) (%)	106.8	93.5	92.0	91.6	109.0	90.6	94.1	111.0	100.6	87.8
Q (%)	105.3	112.3	104.9	109.4	105.5	95.6	113.4	106.1	108.2	107.7

Base recipe: NR, 100; ZnO, 5; stearic acid, 2; resorcinol, 5; Nylon 6 fiber, 25; CBS, 0.8; S, 2; vulcacite H, 3.2; PBN, 1.

erties were determined and represented in Figures 1 and 2. Figure 1 shows both longitudinal and transverse tensile strengths vs. fiber concentration. It is clear that the longitudinal tensile strength sharply decreases as the fiber concentration is increased up to 10 phr, then it is highly increased with further increasing fiber up to 25 phr. On the other hand, the transverse tensile strength is decreased up to 15 phr fiber, then a slight increase is observed with further increase of fiber concentration. Figure 2 shows that the longitudinal elongation at break is sharply decreased with the increase of the fiber concentration up to 20 phr, then it remains constant. On the other hand, the transversal elongation decreases linearly with increasing fiber loading.

The equilibrium swelling in toluene was determined and is presented in Figure 3. The equilibrium swelling decreased with increasing amount of fiber in the matrix. This can be attributed to the fact that the fibers do not swell in toluene.

Figure 4 shows the relation between the Young's modulus of the rubber vulcanizates and the fiber concentration in the rubber matrix. One can see that Young's modulus in the longitudinal direction is slightly decreased in the initial fiber loading, then increases sharply with further increase of the fiber concentration up to 25 phr. In the transverse direction, it is shown that the increase of fiber concentration leads to a slight increase in Young's modulus.

These results are in a good agreement with tensile strength data.

III. Effect of Carbon Black and Silica

To study the effect of carbon black on the properties of vulcanizates as well as the bonding between rub-

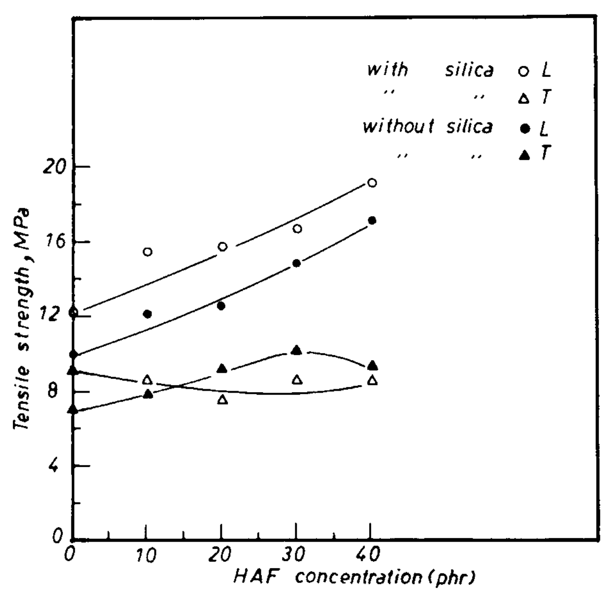

Figure 5 The dependence of tensile strength, both longgitudinal (L) and transversal (T), on HAF concentration.

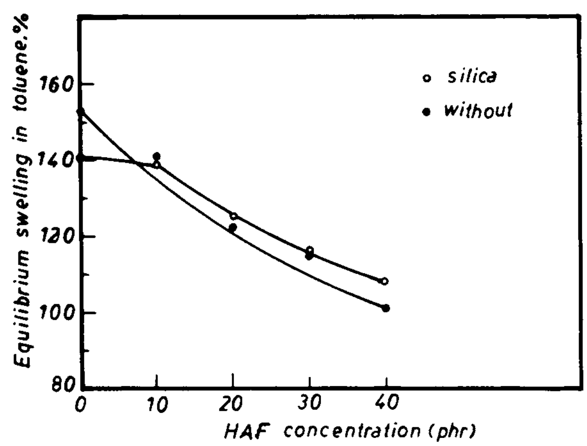

Figure 6 The dependence of equilibrium swelling in toluene on HAF concentration.

ber and fibers, HAF was added in different concentrations up to 40 phr, in the presence and the absence of 5 phr silica. These NR mixes were loaded with 25 phr nylon 6 fibers. The formulations and the rheometric characteristics of NR mixes are given in Table III. It is clear that the addition of HAF increases the maximum torque while it decreases the cure rate index.

Figure 5 depicts the dependence of both longitudinal and transverse tensile strength on the concentration of carbon black. These results indicate that as the carbon black concentration increases the longitudinal tensile strength increases, while it does not affect significantly the transverse tensile strength. On the other hand, it is clear that the addition of silica together with HAF improves the tensile strength. This indicates the necessity for silica to obtain a good adhesion between rubber and fibers.

The equilibrium swelling in toluene decreases with increasing the concentration of HAF in the absence and the presence of hydrated silica as shown in Figure 6.

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