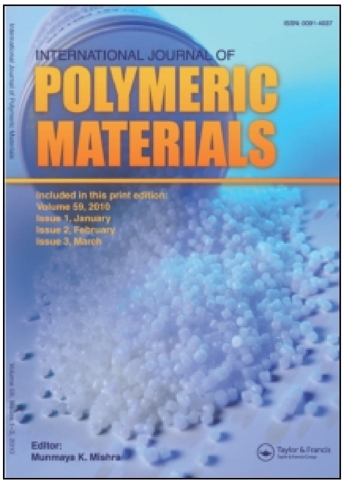

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A. A. Wazzan[a]
[a] Department of Chemical & Materials Engineering, Jeddah, Saudi Arabia

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EFFECT OF VISCOSE SHORT FIBERS REINFORCEMENT ON THE PHYSICO-MECHANICAL PROPERTIES OF NATURAL RUBBER VULCANIZATES

A. A. Wazzan
King Abdulaziz University,
Department of Chemical & Materials Engineering,
Jeddah, Saudi Arabia

The properties of natural rubber (NR) vulcanizates loaded with viscose short fibers were studied using different adhesion systems. It was found that the two systems, HRH (hydrated silica, resorcinol and hexamethylene tetramine) and one of (hydrated silica, m-phenylenediamine and hexamethylene tetramine) were the most effective. The synergistic effect of resorcinol and m-phenylenediamine was also studied. The effect of fiber loading on the mechanical properties of the vulcanizates was also investigated.

Keywords: Natural rubber, viscose, short fiber composites

INTRODUCTION

Although the use of short fibers in compounding started long ago to assist processing and for economic considerations [1], it is only recently that short fibers have attracted the attention of several researchers because of their advantages in mechanical properties, good dispersion and good adhesion to rubber matrix [2–5].

The adhesion between many types of short fibers and most elastomers has been strengthened by the discovery of the tricomponent system (HRH) (hydrated silica, resorcinol and hexamethylene-tetramine) [6–9]. The theory of the adhesion can be explained by in situ formation of resorcinol formaldehyde resin in the rubber vulcanizates [10–12].

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Address correspondence to A. A. Wazzan, King Abdulaziz University, Dept. of Chemical and Materials Engineering, P.O. Box 80204, Jeddah 21589, Saudi Arabia, E-mail: aawazzan@hotmail.com.

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 [13–20].

In the present work the results of our investigation on processing and mechanical properties of natural rubber reinforced with viscose short fibers using HRH and other adhesion systems are reported.

EXPERIMENTAL

Viscose short fibers, produced by Misr Company for artificial silk, Kafer El Dwar, Egypt, chopped to average length of 38, 62 and 100 mm as well as fiber waste, were used. All rubber mixes were prepared on a two roll mill of diameter 470 mm and width 300 mm,

TABLE 1 Effect of Different Adhesion Systems on Viscose Short Fiber

Ingredient Sample No.		M1	M2	M3	M4	M5	M6	M7
Resorcinol		—	—	5	—	—	—	—
Urea		—	—	—	2.7	—	—	—
Thiourea		—	—	—	—	3.5	—	—
Phenol		—	—	—	—	—	4.3	—
m-phenylenediamine		—	—	—	—	—	—	5
Hydrated silica		—	—	5	5	5	5	5
Hexamethylene tetramine		—	—	3.2	3.2	3.2	3.2	3.2
Fiber*		—	25	25	25	25	25	25
Rheometric characteristics								
ML (dNm)		2.3	0.4	1.1	0.9	1.3	0.7	1.2
MH (dNm)		49.5	58.1	70.4	61.0	69.3	57.5	61.2
t_{C90} (min)		14.0	13.6	17.0	8.5	8.5	6.5	11.0
t_{S2} (min)		5.6	5.5	3.0	3.5	1.5	2.3	3.3
CRI (min^{-1})		11.9	12.4	7.1	20.0	14.3	23.2	12.9
Mechanical Properties and Equilibrium Swelling								
Tensile strength, MPa	L	19.7	11.2	8.1	11.4	13.1	12.4	11.2
	T	19.7	10.5	7.6	11.2	10.8	11.4	10.0
Elongation at break, %	L	655	500	150	395	428	467	279
	T	665	515	261	464	443	501	290
Young's modulus, MPa	L	3.2	3.8	18.3	5.4	7.0	3.8	7.7
	T	3.1	2.5	6.7	3.4	3.6	2.9	2.9
Equilibrium swelling, %		328	254	123	212	211	220	146

Base recipe (phr): NR 100, Stearic acid 1.5, Zinc oxide 5, SRF 40, Oil 3, N-isopropyl-N'-phenyl-p-phenylenediamine (IPPD) 1, Cyclo-hexyl-benzo-thiazol-2-sulphenamide (CBS) 0.8, Sulphur 2, *Viscose short fiber denier 1.5, 36 mm. L = Longitudinal Direction T = Transverse Direction.

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 determined using a Monsanto oscillating disc rheometer R-100 [21]. The mechanical properties were determined according to standard methods [22] using the Instron universal testing machine (Model 5586). Swelling was carried out using toluene [23]. Aging of the samples was carried out at 90°C for different time periods in a good aerated oven [24].

RESULTS AND DISCUSSION

I. Effect of different adhesion system on NR-viscose short fibers composites

The difficulties in achieving acceptable adhesion between many types of short fiber and most elastomers have been overcome by the discovery of the tricomponent HRH system. Nonetheless, it is of

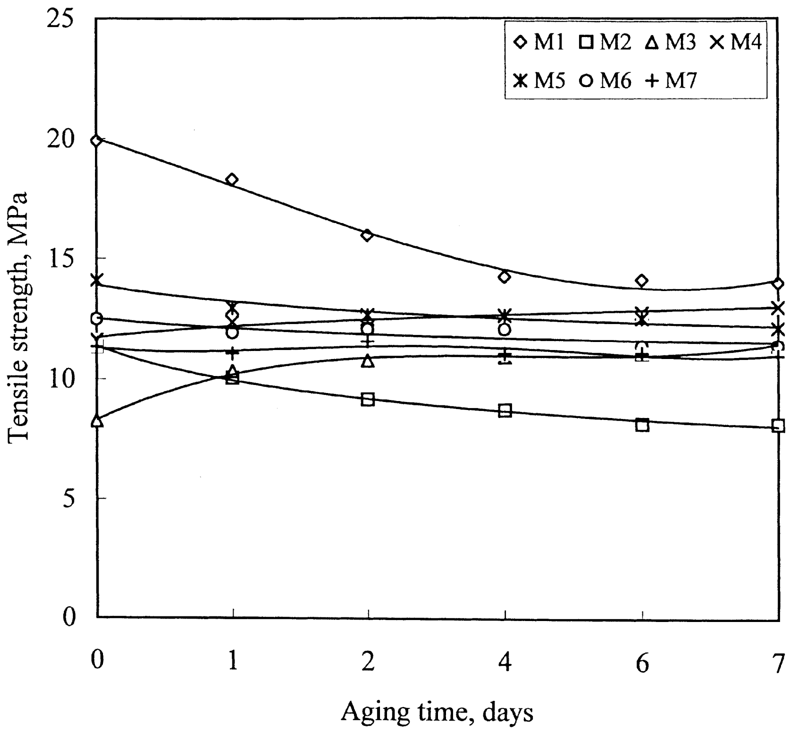

FIGURE 1 The relation between tensile strength vs. aging time.

great interest to replace resorcinol by urea, thiourea, phenol or m-phenylenediamine in equimolar quantities to study the effect of these compounds on the adhesion between NR and viscose short fibers.

The rubber formulations, their rheometric characteristics and physico-mechanical properties of the vulcanizates are shown in Table 1.

From these data, it is clear that urea, thiourea and phenol decrease the optimum cure time and increase the cure rate index, while they slightly decrease elongation at break of vulcanizates. This change can be attributed to the formation of urea formaldehyde, thiourea formaldehyde or phenol formaldehyde resins, which act as a vulcanizing agents. However, the change did not affect the adhesion between fiber and rubber. On the other hand, in terms of enhancement of Young's modulus m-phenylenediamine is shown to be the nearest compound to resorcinol.

The vulcanizates containing the above–mentioned adhesion systems were subjected to thermal oxidative aging at 90°C for different time periods.

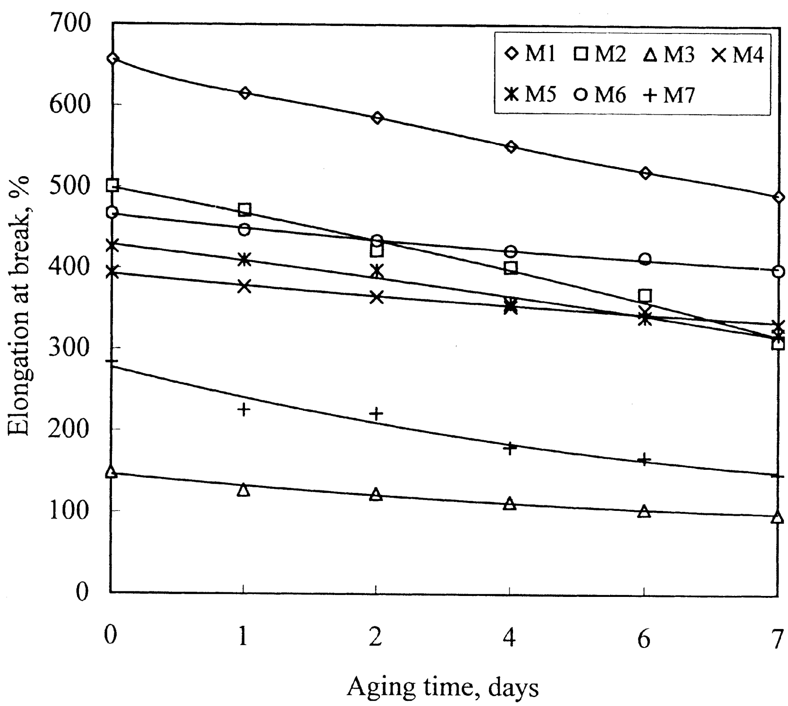

FIGURE 2 The relation between elongation at break vs. aging time.

The physico-mechanical properties and equilibrium swelling were determined and represented in Figures 1–3.

Figures 1 and 2 show the dependence of both elongations at break and the tensile strength in the longitudinal direction on the aging time. It is clear from these curves that both properties for vulcanizates M1 and M2 (i.e. without adhesion system) decrease with aging time, whereas for vulcanizates containing urea, thiourea or phenol the elongation at break decreases with aging time and the tensile strength increased or did not change much with aging time. This may be attributed to further formation of crosslinked resin during aging. On the other hand, the sample containing m-phenylenediamine showed an increase in the tensile strength and a decrease in the elongation. This can be explained by the formation of more resin, which enhances the adhesion between rubber and fiber during aging.

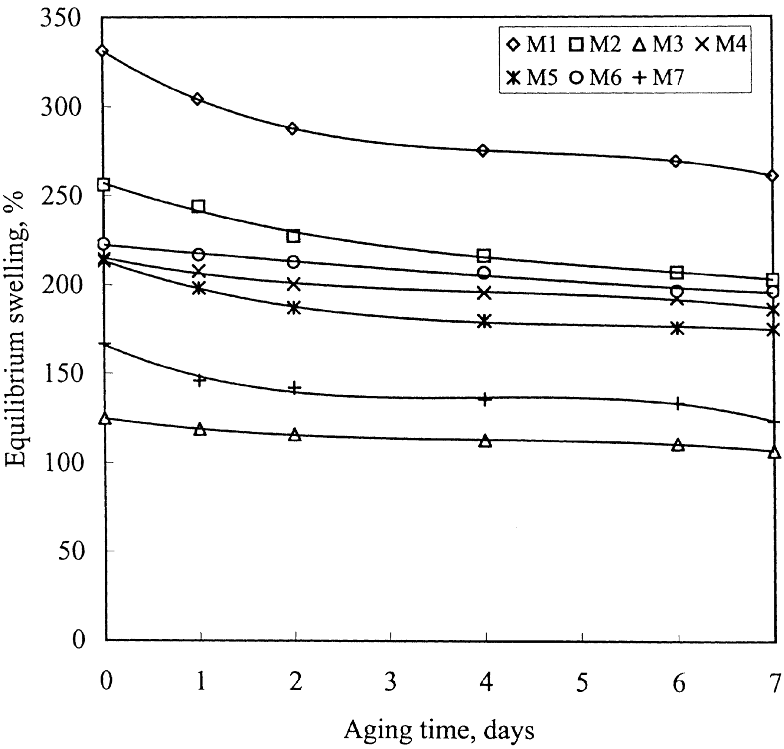

FIGURE 3 The relation between equilibrium swelling in toluene vs. aging time.

TABLE 2 Effect of Combination of Resorcinol and m-phenylenediamine

Ingredient Sample No.	M3	M8	M9	M10	M7
Resorcinol	5.0	3.75	2.5	1.25	—
m-phenylenediamine	—	1.25	2.5	3.75	5.0
Rheometric characteristics					
ML (dNm)	1.1	2.0	2.5	1.0	1.2
MH (dNm)	70.4	66.0	71.0	67.0	61.2
t_{C90} (min)	17.0	17.0	16.0	12.5	11.0
t_{S2} (min)	3.0	2.0	3.0	2.0	3.3
CRI (min^{-1})	7.1	6.7	7.7	9.5	12.9

Basic recipe (phr): NR 100, Stearic acid 1.5, Zinc oxide 5, SRF 40, Oil 3, IPPD 1, CBS 0.8, Fiber 25, Silica 5, Hexamethylene tetramine 3.2, Sulphur 2.

The sample containing resorcinol showed a good stability in both properties during aging.

Figure 3 shows the relation between the equilibrium swelling and aging time. The obtained results are in good agreement with those obtained from the mechanical properties. From the above results it is clear that m-phenylenediamine is the nearest compound to resorcinol in the adhesion power. Therefore, it is of great interest to study the effect of the combination between these two additives on the adhesion

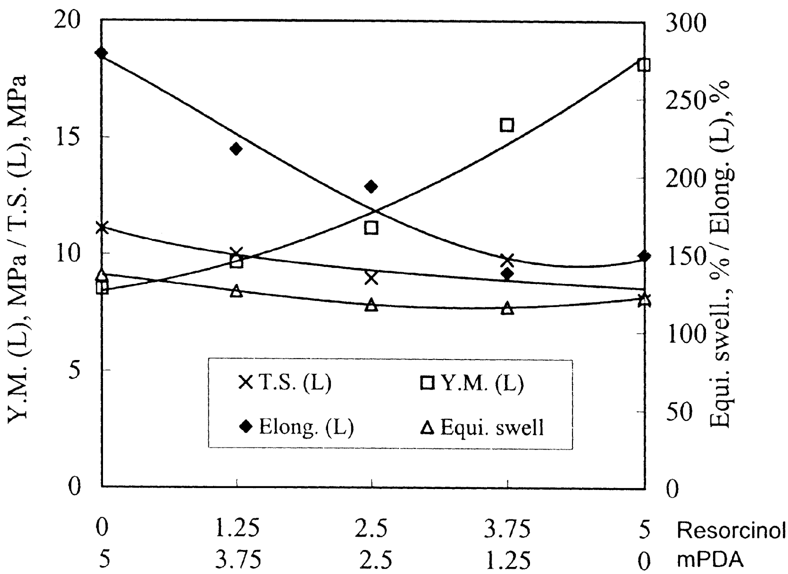

FIGURE 4 Dependence of the physico-mechanical properties on resorcinol/mPDA concentration.

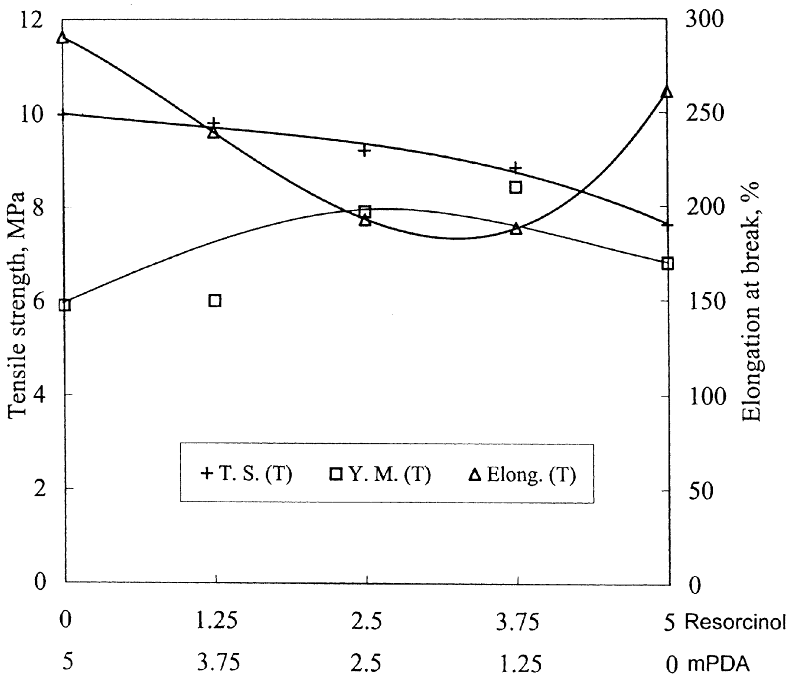

FIGURE 5 Dependence of the physico-mechanical properties on resorcinol/ mPDA concentration.

force. For this purpose, five formulations were prepared containing different ratios of the additives as shown in Table 2. The rheometric characteristics were determined and listed in the same table. From these data it is shown that the increase of m-phenylenediamine (mPDA) concentration above 2.5 phr reduces the optimum cure time. Accordingly, the cure rate index (CRI) also decreases with increased mPDA in the mixture.

The physico-mechanical properties of the vulcanizates are shown in Figures 4 and 5. It is clear from these curves that there is a synergistic effect between the two additives. It is also shown that the ratio 3.75:1.25 of resorcinol: mPDA is the best combination, which leads to highest adhesion between NR and viscose short fibers.

II. Effect of Different Lengths of Viscose Fibers

Viscose short fibers with different lengths and waste viscose fibers were incorporated in NR mixes. The rubber formulations, their

TABLE 3 Effect of Different Lengths of Viscose Fibers

Ingredient Sample No.		M8	M11	M12	M13
Fiber Length (mm)		38	62	100	waste
Rheometric characteristics					
ML (dNm)		2.0	6.0	5.2	6.0
MH (dNm)		66.0	66.0	54.0	63.0
t_{C90} (min)		17.0	17.0	18.0	17.0
t_{S2} (min)		2.0	2.0	2.5	2.0
CRI (min^{-1})		6.7	6.7	6.5	6.7
Tensile strength, MPa	L	10.8	9.5	8.6	11.0
	T	9.7	9.6	8.5	10.1
Elongation at break, %	L	139	167	190	127
	T	191	200	210	170
Young's modulus, MPa	L	18.0	9.6	7.2	19.1
	T	8.7	6.6	5.9	11.2
Equilibrium swelling %		117	118	141	115

Basic recipe (phr): NR 100, Stearic acid 1.5, Zinc oxide 5, SRF 40, Oil 3, IPPD 1, CBS 0.8, Fiber 25, Resorcinol 3.75, mPDA 1.25, Silica 5, Hexamethylene tetramine 3.2, Sulfur 2.

rheometric characteristics and the physico-mechanical properties of the vulcanizates are shown in Table 3.

From these data it is clear that the fiber length has practically no effect on the rheometric characteristics. However, with respect to the mechanical properties it is clear that the shorter the length of fiber, the greater the reinforcement becomes; this is reflected in a higher tensile strength, increased Young's modulus and lower equilibrium swelling. On the otherhand, it is clear that the waste viscose fibers

TABLE 4 Effect of Waste Viscose Fiber Concentrations

Ingredient/Sample No.	M1	M14	M15	M16	M17	M13	M18
Fiber Concentration	—	5.0	10.0	15.0	20.0	25.0	30.0
Rheometric characteristics							
ML (dNm)	2.3	1.2	1.2	1.9	1.2	2.5	2.5
MH (dNm)	49.5	56.0	56.0	58.0	61.0	63.0	70.2
t_{C90} (min)	14.0	19.0	18.0	16.5	16.5	17.0	18.0
t_{S2} (min)	5.6	2.8	2.8	3.0	3.0	2.0	2.5
CRI (min^{-1})	11.9	6.2	7.4	6.7	6.7	6.8	6.5

Basic recipe (phr): NR 100, Stearic acid 1.5, Zinc oxide 5, SRF 40, Oil 3, IPPD 1, CBS 0.8, Resorcinol 3.75, Silica 5, Hexamethylene tetramine 3.2, Sulfur 2, mPDA 1.25.

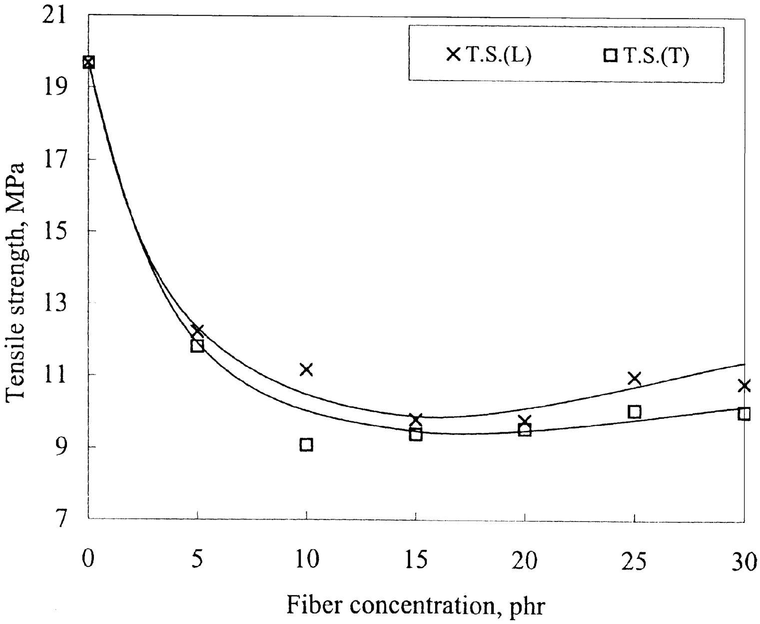

FIGURE 6 Dependence of tensile strength on fiber concentration.

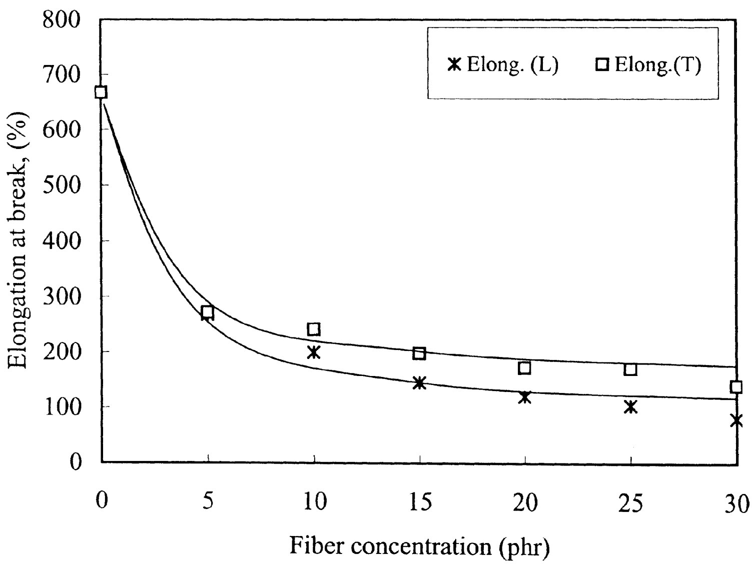

FIGURE 7 The dependence of both longitudinal (L) and transversal (T) elongation at break on the fiber concentration.

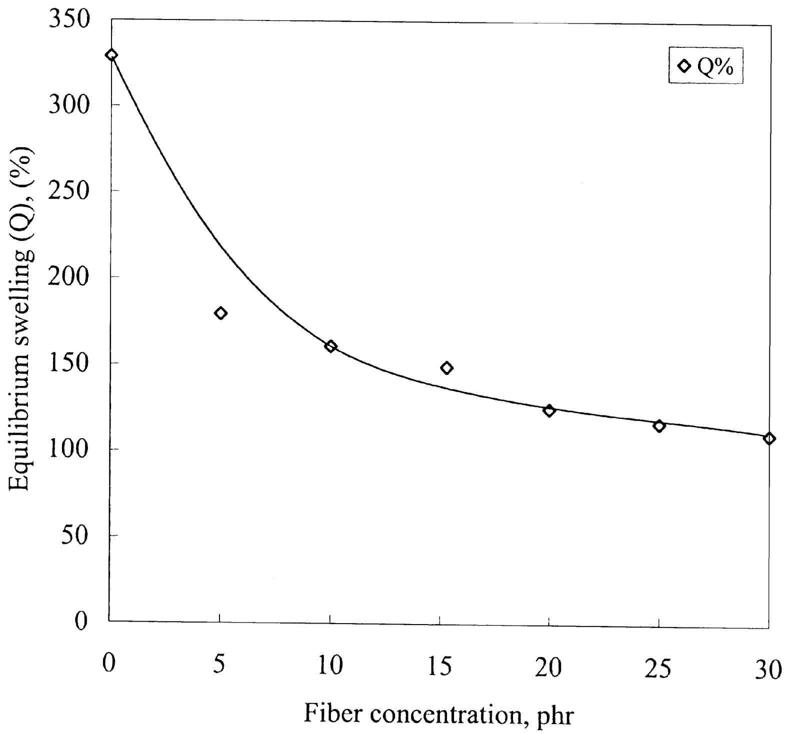

FIGURE 8 The relation between equilibrium swelling in toluene and fiber concentrations.

provide the best overall effect, which can be attributed to the fact that the wastes include different lengths.

III. Effect of Waste Fiber Concentrations

Waste viscose short fibers were incorporated in different concentrations up to 30 phr in the test matrix. The rubber formulations as well as their rheometric characteristics are listed in Table 4. From this table one notices that 5 phr of waste fiber halved the scorch time and extended the optimum cure time but the higher levels had no additional effect on cure kinetics.

The mechanical properties and swelling were determined and represented in Figures 6–8. Figure 6 shows both the longitudinal and transversal tensile strength vs., fiber concentration. One sees that the tensile strength in both directions sharply decreases with loading before reaching at minimum at 15 phr, then there is a slight increase.

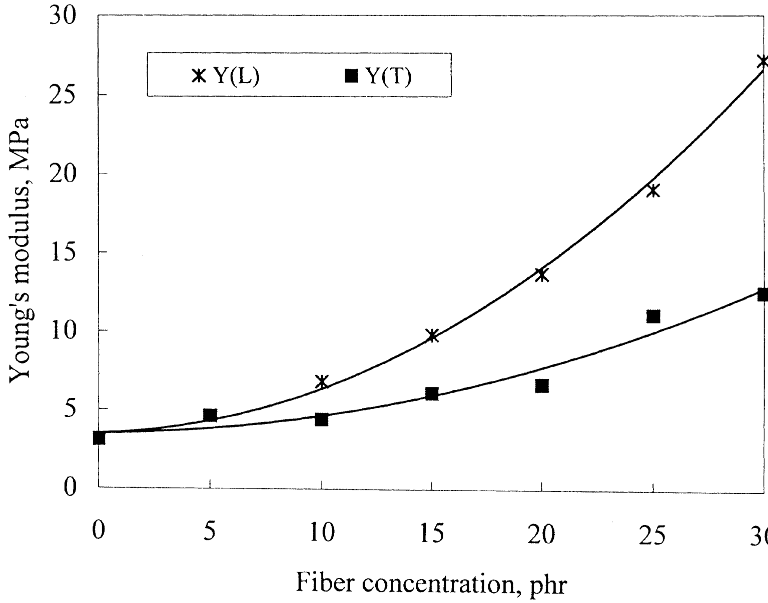

FIGURE 9 Dependence of Young's modulus on fiber concentration.

Figures 7 and 8 show the dependence of both elongations at break and equilibrium swelling in toluene respectively on the fiber concentration. It is clear that both properties sharply decrease with 5 phr fiber and then more slowly.

The curves obtained for Young's modulus are shown in Figure 9, which indicate that Young's modulus increases in both directions with the increase in fiber concentration. Therefore it can be concluded that the increase in fiber concentration leads to NR composites with high stress at low strain.

CONCLUSIONS

The following conclusions can be drawn from the experiments described herein:

1. The ratio 3.75:1.25 of resorcinol: mPDA is the best combination that leads to highest adhesion between NR and viscose short fibers.
2. Decrease of fiber length increases its efficiency in the reinforcement of natural rubber.
3. Waste viscose short fibers are most efficient, which can be attributed to the random distribution of the fiber lengths.

4. Increased fiber concentration reduces both the elongation at break and the tensile strength up to 15 phr, by weight.

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