

NOTE

Studies on Replacement of Silica by Carbon Black in the Tricomponent Dry Bonding System of Short Fiber–Rubber Composites

INTRODUCTION

Compounding of rubbers with short fibers offers strength and stiffness to the soft and tough rubber vulcanizate.^{1–4} The properties and performance of short fiber-reinforced rubber composites depend mainly on: (a) concentration and type of fiber^{3,5,6}; (b) aspect ratio of the fiber after mixing⁷; (c) orientation of the fiber in the composites⁸; (d) state of dispersion^{2,9}; and (e) degree of adhesion of the fiber to the rubber matrix.¹⁰ Campbell¹¹ has reviewed short fiber reinforcement of rubber. The reinforcement of natural rubber (NR), carboxylated nitrile rubber (XNBR), and styrene–butadiene rubber (SBR) by short jute fiber has been studied by De and co-workers.^{5,6,12–14} It has been observed that proper bonding of the fiber with rubber is essential for optimum composite properties. Adhesion of fiber with rubber matrix is dependent on the bonding system used, the nature of the fiber, and type of rubber. Resorcinol–hexamethylenetetramine–silica tricomponent dry bonding system is generally used in short fiber–rubber systems.¹⁵ In this case silica is believed to act as a controller for resin formation (that is, reaction of resorcinol and hexamethylenetetramine) and helps in developing adhesion between rubber and fiber.¹⁶ Murty and De¹² reported that silica is not an essential component to develop adhesion between fiber and rubber in the presence of carbon black in natural rubber–jute fiber system. In the present work, the role of carbon black in promoting adhesion between rayon fiber and natural rubber has been studied. The main problem in studying adhesion in the case of short fiber reinforcement is that it cannot be measured quantitatively. However, one can assess the adhesion level only qualitatively. The rheometric curves and the shape of stress–strain curves offer a good indication of adhesion.¹⁴ More recently the adhesion level has been assessed by the study of fracture surfaces using scanning electron microscopic (SEM) technique.¹³

In this paper we have studied the effect of carbon black as a substitute for silica in the tricomponent dry bonding system for rayon fiber–natural rubber composites. Technical properties, stress–strain curves, and SEM observations of tensile fracture surfaces were used to assess the orientation of fibers and degree of fiber–rubber bonding.

EXPERIMENTAL

Rayon yarn (Denier 1650) as supplied by Century-Rayon, Bombay, chopped to 6 mm length was used as the reinforcing fiber. Mixing was done in an 150 mm × 330 mm open mixing mill. Nip gap, mill roll speed ratio, and the number of passes were kept the same in all the mixes. While preparing the mixes, care was taken to ensure fiber orientation in the grain direction in all the mixes. Breakage of fiber takes place during mixing and the aspect ratio of the fiber decreases from 240 to 55. Details of mixing, vulcanization, and testing procedures have been summarized elsewhere.^{12,17}

The scanning electron microscopy (SEM) studies were carried out with a Philips 500 Model Scanning Electron Microscope.¹³ Figure 1 shows the type of test specimens, orientation of fibers and the fracture surface exposed to SEM.

RESULTS AND DISCUSSION

Formulations of the mixes are given in Table I. Curing characteristics from rheographs (Fig. 2) are summarized in Table II.

Rheometric Characteristics. Rheograph of mix A (only fiber) shows sufficient scorch safety but low maximum rheometric torque. This indicates that fiber alone cannot give good adhesion with the rubber matrix. But the addition of the bonding agent, resorcinol, and hexamethylenetetramine (mix B), decreases the scorch safety and increases the maximum rheometric torque. Further addition of silica (mix C) causes marginal increase in the scorch safety and modulus. It is believed that the silica filler functions as controller of resin formation (that is, reaction of resorcinol and hexamethylenetetramine), which helps in bonding the fiber with the rubber matrix. By decreasing the quantity of resorcinol and hexamethylenetetramine (mix D), scorch safety can be increased to

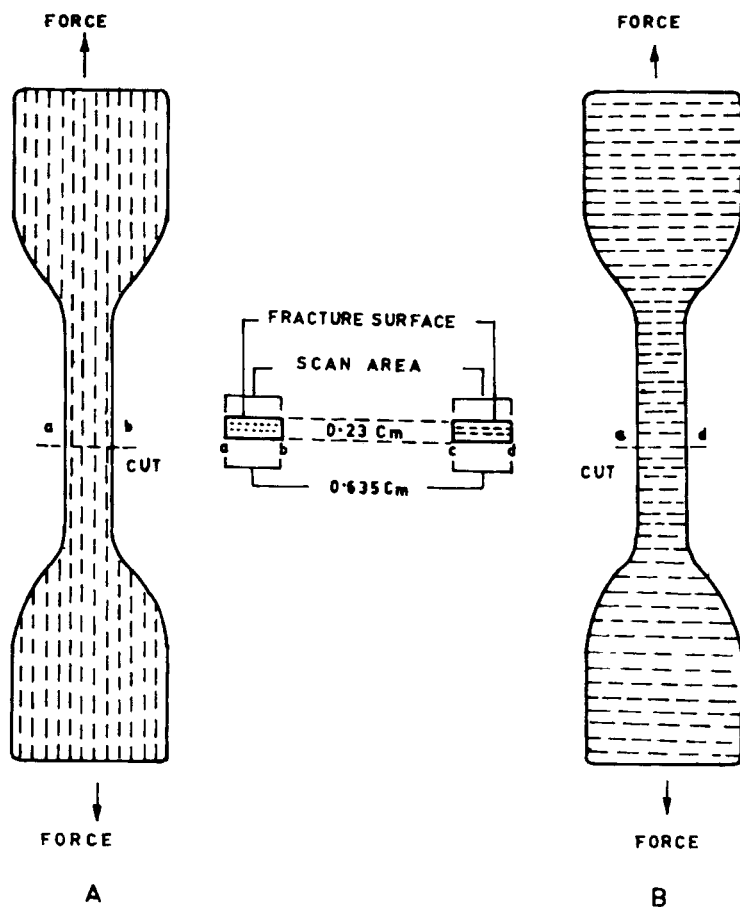


Fig. 1. Tensile specimens showing fiber orientation, fracture surface, and scan area: (A) longitudinal direction; (B) transverse direction.

TABLE I
Formulations of Mixes

Mix no.	A	B	C	D	E
Natural rubber ^a	100	100	100	100	100
Zinc oxide	5	5	5	5	5
Stearic acid	2	2	2	2	2
Rayon fiber	40	40	40	40	40
Silica ^b	—	—	5	5	—
Carbon black ^c	—	—	—	—	5
Resorcinol	—	5	5	2.5	5
Hexamethylenetetramine	—	3.2	3.2	1.6	3.2
CBS ^d	0.8	0.8	0.8	0.8	0.8
Sulfur	2.0	2.0	2.0	2.0	2.0

^a Crumb rubber, ISNR Grade 5, supplied by the Rubber Research Institute of India, Kottayam.

^b Vulcasil-S, supplied by Bayer (India), Ltd., Bombay.

^c N 330, HAF black, supplied by Phillips Carbon Black, Ltd., Durgapur.

^d Accicure HBS, *N*-cyclohexylbenzothiazolesulfenamide, supplied by the Alkali and Chemical Corporation of India, Ltd., Rishra.

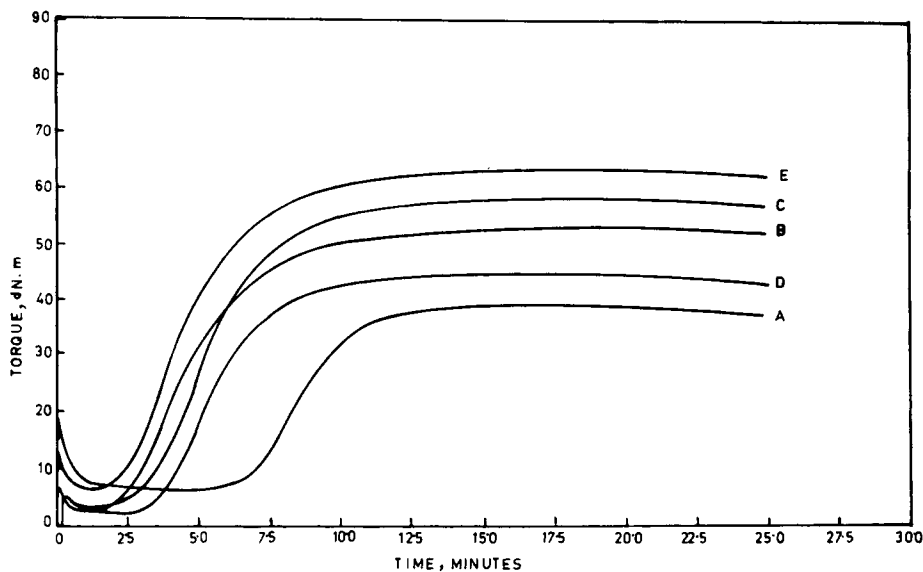


Fig. 2. Rheographs of mixes A, B, C, D, and E at 150°C showing the effect of the bonding agent.

some extent, but, at the same time, the rheometric torque decreases which may lead to deterioration of physical properties. It has been reported earlier that optimum loading of bonding agent is essential for proper bonding of fiber with rubber.⁶ When silica is replaced by black (mix E), scorch safety decreases but the maximum rheometric torque increases. This increase in torque cannot be the filler effect, because carbon black loading was only 5 phr. It has been observed earlier¹² that carbon black, like silica, improves adhesion by minimizing the resin formation and controlling it to low molecular weight species.

Stress-Strain Study. The stress-strain curves of different vulcanizates are shown in Figure 3. These curves clearly show that fiber-rubber adhesion does not take place in the absence of bonding agent (mix A). But resorcinol and hexamethylenetetramine together (without silica) can bond the fiber with the rubber matrix (mix B) to a considerable extent. At the same time, in the presence of silica, the amount of bonding agent has also some effect on the extent of bonding (mix C versus mix D). But the use of carbon black filler in place of silica (mix E) shows the highest degree of bonding. The orientation of fiber in the matrix in the presence of carbon black is higher than that in presence of silica. This is indicated by the difference in elongation at break in the transverse (across the grain direction) and longitudinal (along the grain direction) directions. The orientation of the fibers has been assessed visually by SEM observation of the fracture surface of the tensile specimen (mix E), fractured along the grain direction (Fig. 4) corresponding to portion c-d of Figure 1.

Physical Properties. The physical properties of the composites are reported in Table III. In presence of fiber alone (mix A), the tensile strength of the matrix is poor and the anisotropy of the properties³ is not observable. But with the addition of resorcinol and hexamethylenetetramine

TABLE II
Curing Characteristics of the Mixes at 150°C

Mix no.	A	B	C	D	E
Rheometric scorch time (min)	6.3	2.0	2.5	3.0	1.8
Maximum rheometric torque (N·m)	8.60	11.75	11.86	9.94	14.12
Optimum cure time (min)	11.0	8.0	9.0	8.3	8.0

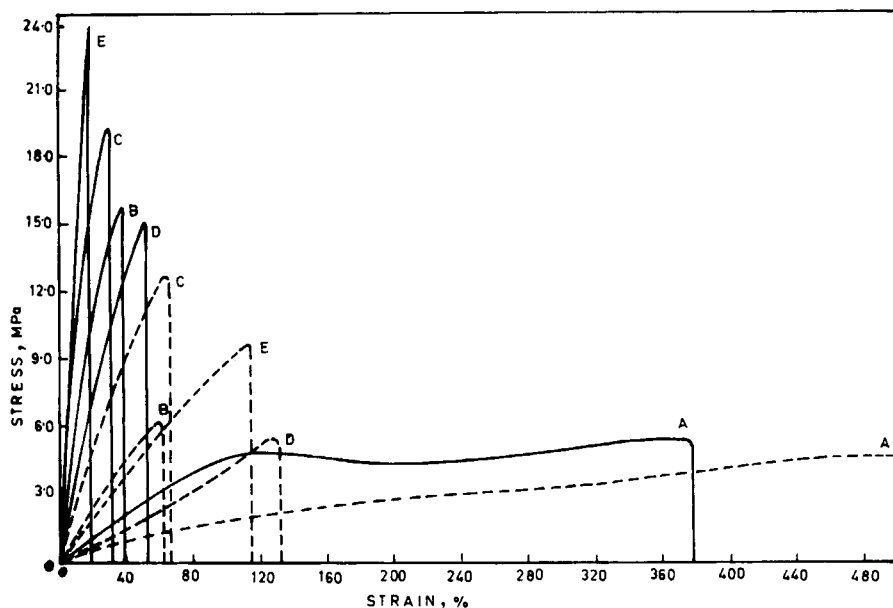


Fig. 3. Stress-strain curves of mixes A, B, C, D, and E showing the effect of the bonding agent: (—) L; (---) T.

(mix B), tensile and tear properties and hardness increase, while elongation at break and heat buildup decrease. Presence of silica (mix C) further improves the physical properties. With a decrease in the amount of bonding agent (mix D), the properties decrease. The presence of carbon black (mix E) provides the best combination of properties of the composite. Tensile strength, tear strength, and hardness increase, while heat buildup decreases in the presence of carbon black.

In general, tensile strength and tear strength increase and heat buildup decreases as the degree bonding of fiber with the rubber matrix is progressively improved.

SEM Studies. Figure 5 is the SEM photomicrograph of the tensile fracture surface of mix A (without bonding agent). It shows a long stem of fiber left after pulling out of the fiber from the rubber matrix. The presence of the free fibers on the surface indicates poor adhesion between the fiber and rubber in the absence of bonding agent. When the fibers are not well bonded with the matrix, the distribution of stress will not be uniform, and the effective function of fibers as reinforcing agents cannot be observed. The matrix failed at very low stress, and fibers get separated from the matrix under stress. Addition of bonding agents (mix C) changes the failure mechanism of the composites which is reflected in the fracture mode. Photomicrograph (Fig. 6) shows (mix C) fiber



Fig. 4. SEM photomicrograph of the tensile fracture surface; fiber orientation in the transverse direction (mix E).

TABLE III
Physical Properties of the Rayon-Natural Rubber Composites with Varying Amount of Bonding Agent and Filler

Mix no.	Fiber orientation	A	B	C	D	E
Tensile strength (MPa)	L ^a	5.72	16.50	19.40	15.60	24.20
	T	4.65	6.30	12.30	5.30	9.50
Elongation at break (%)	L	380	35	25	50	18
	T	500	55	60	130	120
Tear strength (kN/m)	L	35.2	55.3	57.6	57.8	63.5
	T	24.5	37.6	44.0	42.3	38.6
Heat buildup ΔT ($^{\circ}\text{C}$)	L	50	41	35	44	30
	T	54	36	39	49	37
Hardness (shore A)	N ^b	78	85	85	82	90

^a L means longitudinal and T means transverse direction.

^b Normal to the fiber orientation in the matrix.

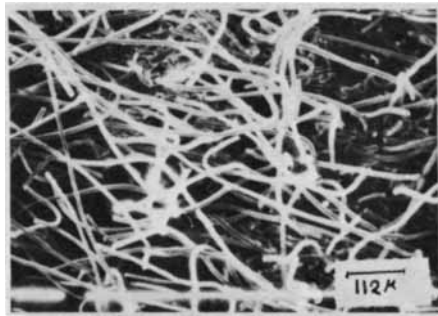


Fig. 5. SEM photomicrograph of the tensile fracture surface, the long stem of fiber showing poor bonding (mix A).



Fig. 6. SEM photomicrograph of the tensile fracture surface, the presence of cavities and fiber breakage showing good adhesion (mix B).

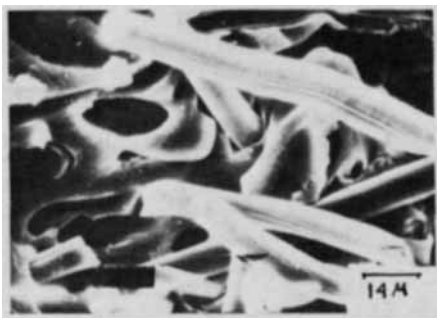


Fig. 7. SEM photomicrograph of the tensile fracture surface, showing fiber pullout due to debonding (mix C).

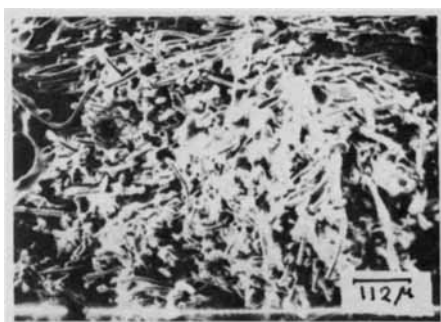


Fig. 8. SEM photomicrograph of the tensile fracture surface, showing improved adhesion of the fiber to the rubber matrix (mix E).

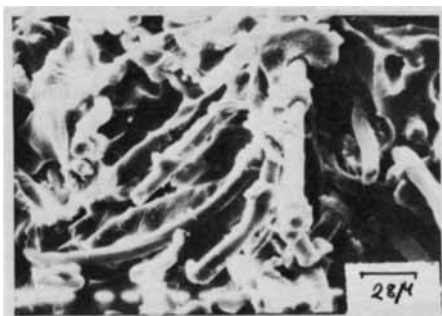


Fig. 9. SEM photomicrograph of the tensile fracture surface, showing strongly bonded fibers with the rubber matrix (mix E).

breakage and cavities on the surface. The bonded fibers in the composites break under stress rather than coming out as long stems. The stress is transferred from matrix to the fiber through interface bonding during tension. This results in breakage of fiber. However, the interface bonding between the fiber and matrix may also fail, and the fibers may also come out leaving the cavities on the surface. This is made more clear at higher magnification (Fig. 7). When silica filler is replaced by carbon black (mix E), the general characteristics of the fracture surface do not change. However, the flow of the matrix decreases, and the fibers show better adhesion with rubber (Fig. 8). Photomicrograph (Fig. 9) clearly shows improved adhesion between the fiber and the rubber matrix.

References

1. A. Y. Coran, K. Boustany, and P. Hamed, *Rubber Chem. Technol.*, **47**, 396 (1974).
2. G. C. Derringer, *Rubber World*, **165**, 45 (1975).
3. J. E. O'Connor, *Rubber Chem. Technol.*, **50**, 945 (1977).
4. J. W. Sheeler, *J. Elast. Plast.*, **9**(3), 267 (1977).
5. D. K. Setua and S. K. De, *Rubber Chem. Technol.*, **56**, 804 (1983).
6. V. M. Murty and S. K. De, *Rubber Chem. Technol.*, **55**, 287 (1982).
7. K. Boustany and A. Y. Coran, U. S. Pat. 3,709,845 (1973).
8. S. R. Moghe, *Rubber Chem. Technol.*, **49**, 1160 (1976).
9. T. J. Leo and A. M. Johansson, U. S. Pat. 4,263,184 (to Wyrough and Loser Inc.) (1981).
10. D. D. Dunnom, Hi-Sil Bulletin, PPG Ind. Inc., No. 35, 1967.
11. J. M. Campbell, *Prog. Rubber Technol.*, **41**, 43 (1978).
12. V. M. Murty and S. K. De, *J. Appl. Polym. Sci.*, **27**, 4611 (1982).
13. S. K. Chakraborty, D. K. Setua, and S. K. De, *Rubber Chem. Technol.*, **55**, 1286 (1982).
14. V. M. Murty and S. K. De, *J. Appl. Polym. Sci.*, **29**, 1355 (1984).
15. N. L. Hewitt, *Rubber Age (Jan)*, 59 (1972).
16. J. R. Creasy, D. B. Russell, and M. P. Wagner, *Rubber Chem. Technol.*, **41**, 1300 (1968).
17. R. Mukhopadhyay, S. K. De, and S. N. Chakraborty, *Polymer*, **18**, 1243 (1977).

A. PATTABHI RAMAYYA
SUNITY K. CHAKRABORTY
SADHAN K. DE

Rubber Technology Centre
Indian Institute of Technology
Kharagpur-721302
India

Received August 10, 1983

Accepted October 14, 1983