

## Aramid 섬유보강천연고무 및 합성고무복합재료의 기계적 성질

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## Mechanical Properties of Short Aramid Fiber Reinforced Natural and Synthetic Rubber Composites

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**요 약 :** Aramid(4mm) 강화고무(SMR, SBR, NBR, BR, BR/SMR) 복합재료를 open mill에서 혼합 제조하였으며, 제조된 aramid단섬유보강가황고무의 기계적 특성을 섬유함량, 고무종류 및 섬유 표면 처리 효과의 관점에서 검토하였다. BR/SMR계에서는 섬유함량이 10~20 wt %에서 강화효과가 나타났으며, 섬유함량이 20 wt %인 경우 강화효과는 SBR계가 최대였다. 또한, cresol-acetone-phenol계 수용액으로 aramid를 표면처리하여 NBR을 보강시킨 경우엔 미처리 섬유보강에 비해 강도가 2배 이상 증가함을 알 수 있었다.

**Abstract :** Short(4mm) aramid fiber reinforced rubber(SMR, SBR, NBR, BR, BR/SMR) composites have been prepared on a conventional open mill. The effects of fiber concentration, rubber type and fiber surface treatment on the mechanical properties of the vulcanizates were examined. Optimum fiber concentration for reinforcement was approximately 10 wt % for BR/SMR. The most pronounced reinforcing effect at 20 wt % fiber loading was observed for SBR. Surface treated aramid fiber reinforced NBR showed more than twice of the strength of the surface untreated aramid fiber reinforced NBR.

### INTRODUCTION

Short fiber reinforced rubber composites impart useful mechanical properties such as stiffness, strength, modulus, and damping in addition to processing advantage.<sup>1~5</sup> Therefore, the major application of the short fiber reinforcement is directed toward the production of hoses, V-belts

and complex shaped mechanical parts.<sup>6,7</sup>

The reinforcing effect of short fiber is governed by a number of factors ;<sup>7,8</sup> fiber type and length, concentration, adhesion/bonding between fiber and matrix, fiber aspect ratio, orientation and breakage during mixing etc..

Various fibers including glass, rayon, nylon, cellulose, silk and jute have been well incorporated

with natural and synthetic rubbers.<sup>1~9</sup> The proper choice of bonding agents has also been the subject of many investigators.<sup>7,10</sup> However, studies on aramid reinforced rubber are rare.

This paper considers the aramid(sp. gr. 1.45) reinforced SMR(Standard Malaysian Rubber, sp. gr. 0.913), synthetic rubbers such as SBR(Styrene-Butadiene Rubber, sp. gr. 0.933), NBR(Acrylonitrile-Butadiene Rubber, sp. gr. 0.98.) and BR (Butadiene Rubber, sp. gr. 0.890), and rubber blends(BR/SMR). The effects of fiber concentration, type of rubber and surface treatment have been examined in terms of tensile and tear strength, elongation, hardness, wear, heat buildup, and compression set.

## EXPERIMENTAL

Formulations of rubber mixes(Tables 1~5) for SBR, NBR and BR were prepared according to KSM 6517, 6642 and 6515, respectively. Rubber mixes for SMR and BR/SMR were prepared following the conventional methods employed in rubber industry. Mixing operation was carried out on a conventional open mill (150mm×330mm) at 50±5°C, and roll speed ratio of 1:1.25. Plasticity of rubber was lowered by masticating the sample on a cold tight mill for the first five minutes. Aramid fibers, chopped with the length

of 4mm leading to the initial aspect ratio of 250, were then fed. Care was taken to ensure the fiber orientation was approximately equal in all mixes as indicated by the grain direction. Other ingredients were subsequently added following the standard procedures employed in rubber industry.

The mixes were vulcanized at 150°C, 150kg/cm<sup>2</sup> at their respective optimum cure times(5-15min). The optimum cure times were determined from a rheometer(Monsanto R-100). Typical rheographs

**Table 2.** Formulations of SMR Mixes

Sample Code	Content of Mix (parts by wt)	
	C	D
SBR <sup>(1)</sup>	100	100
HAF	50	50
Stearic Acid	1	1
ZnO	3	3
Sulfur	1.75	1.75
BBS <sup>(2)</sup>	1	1
Aramid Fiber	0	20

<sup>(1)</sup> SBR 1502

<sup>(2)</sup> N-t-butyl-2-benzothiazyl sulphene amide

**Table 3.** Formulations of NBR Mixes

Sample Code	Content of Mix (parts by wt)		
	E	F	G
NBR <sup>(1)</sup>	100	100	100
SRF <sup>(2)</sup>	40	40	40
Stearic Acid	1	1	1
ZnO	5	5	5
Sulfur	1.5	1.5	1.5
DM	1	1	1
Aramid Fiber	0	20	0
Coupling Agent <sup>(3)</sup>	0	0	22 <sup>(4)</sup>
Treated Aramid Fiber			

<sup>(1)</sup> N-230 SL

<sup>(2)</sup> Semi-Reinforcing Furnace (carbon black)

<sup>(3)</sup> PR 307 (Dae Bo Chem. Co., Korea)

<sup>(4)</sup> Dry add-on of coupling agent was approximately 10 wt%

**Table 1.** Formulations of SMR Mixes

Sample Code	Content of Mix (parts by wt)	
	A	B
SMR <sup>(1)</sup>	100	100
HAF <sup>(2)</sup>	50	50
Stearic Acid	3	3
ZnO	5	5
Pine tar	4	4
Sulfur	3	3
DM <sup>(3)</sup>	1	1
Aramid Fiber	0	20

<sup>(1)</sup> RSS #3 (Ribbed Smoke Sheets)

<sup>(2)</sup> High Abrasion Furnace (carbon black)

<sup>(3)</sup> Dibenzothiazyl disulfide

**Table 4.** Formulations of BR Mixes

Sample Code	Content of Mix (parts by wt)	
	H	I
BR <sup>(1)</sup>	100	100
HAF	60	60
Stearic Acid	2	2
ZnO	3	3
N-oil <sup>(2)</sup>	15	15
Sulfur	1.5	1.5
BBS	0.9	0.9
Aramid Fiber	0	20

<sup>(1)</sup> KBR 01 (Kumho Petrochem. Co., Korea)

<sup>(2)</sup> Aromatic oil

**Table 5.** Formulations of BR/SMR Mixes

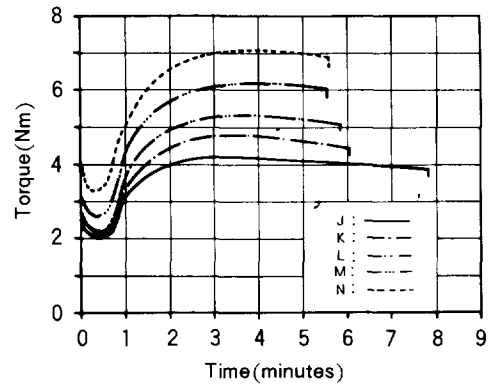
Sample Code	Content of Mix (parts by wt)				
	J	K	L	M	N
BR	60	60	60	60	60
SMR	40	40	40	40	40
Stearic Acid	1	1	1	1	1
Zeosil <sup>(1)</sup>	45	45	45	45	45
ZnO	5	5	5	5	5
DM	2	2	2	2	2
M <sup>(2)</sup>	1	1	1	1	1
Sulfur	2	2	2	2	2
PEG <sup>(3)</sup>	3	3	3	3	3
Process Oil	5	5	5	5	5
Aramid Fiber	0	5	10	20	30

<sup>(1)</sup> White Carbon

<sup>(2)</sup> 2-mercapto benzothiazole

<sup>(3)</sup> Polyethylene glycol

for BR/SMR mixes are shown in Fig. 1. Physical properties of the vulcanizates were measured from standard procedures. Tensile and tear strengths were measured on a Stograph(Shimadzu) following ASTM D412-51T and D624-54. Abrasion tests were done according to NBS method(KSM 6518), and Shore A hardness was measured following ASTM D676-52T procedure. The above tests were carried out at room temperature, and at least five runs were made for each sample. Heat buildup measurements were done in a Goodrich Flexome-


**Fig. 1.** Typical rheographs for BR/SMR mixes.

ter as per ASTM D623-67, method A, i.e, for 25min at 100°C. The compression set was measured at constant strain(25%), 70°C, 22 hours (ASTM D35 95-61). All of the above samples were prepared along the longitudinal direction.

## RESULTS AND DISCUSSION

Typical rheographs of the mixes are given for BR/SMR(60/40 by weight) (Fig. 1). The rheographs show gradual increases of maximum torque with the increase of fiber content. However, as expected, the optimum cure times do not depend on fiber loading, but on sulfur content of the mix, which was kept constant. Essentially the same tendency was observed for other mixes in our experiments, and has been reported by others<sup>9,11</sup> also.

Mechanical properties of the vulcanizates, as a function of fiber concentration, have been examined for BR/SMR(60/40) mix. BR rubber is almost always used in blends with other rubbers. The rubber blends of BR with SMR have been widely employed in tire production. Fig. 2 shows tensile and tear strengths for the BR/SMR vulcanizates. In literature, the fiber loadings at which the composite strength is minimum and equal to matrix value are respectively referred to as minimum and critical loadings. The minimum and critical fiber loadings are function of fiber type, aspect ratio, orientation, and adhesion between fiber and mat-

않고 블랜드물에서 두개의  $T_m$ 만이 관찰됨을 볼 수 있으며, 동일한 경향을 BC-90과 PU-80의 블랜드물에서도 관찰할 수 있었으며 이를 Fig. 12에 함께 도시하였다. 이러한 결과도 BC와 PU에 포함되 동일 구조인 PU블록이 함께 결정화를 형성하

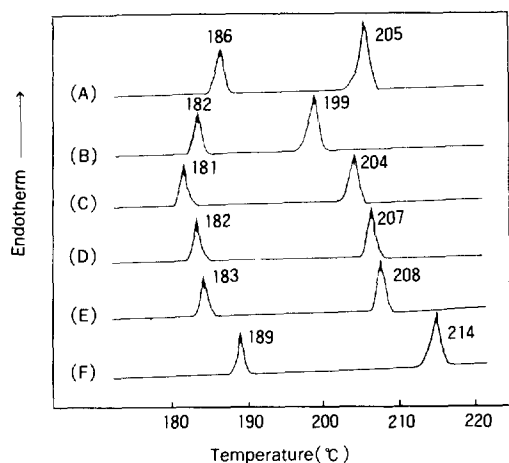


Fig. 11. Melting endothermic peaks of PU-80 / BC-50 blends containing (A) 0; (B) 20; (C) 40; (D) 60; (E) 80; and (F) 100 wt % PU-80.

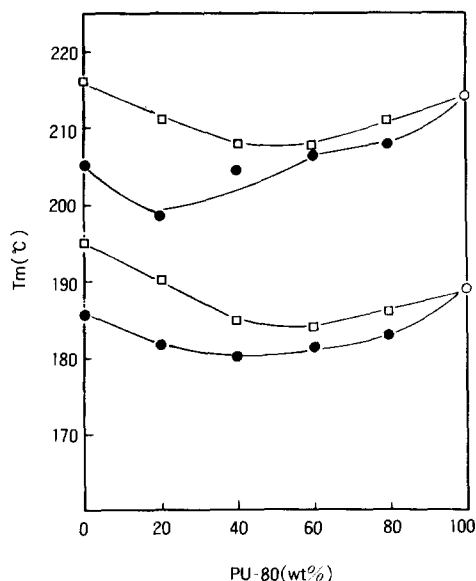


Fig. 12.  $T_m$  of BC / PU-80 blends: (○) BC-50; (●) BC-90.

거나, 한 성분(함량이 적거나 결정화 속도가 느린)의 결정화가 다른 성분에 의해 크게 방해 받아 결정화 하지 못해 한 성분의  $T_m$ 만이 관찰되는 가능성을 제시하나, 앞 PU-60의 블랜드물의  $T_m$ 거동에서 설명한 바와 같이 두 성분의 PU블록이 함께 결정화 할 가능성이 큰 것으로 생각된다.

#### 강온결정화온도( $T_{mc}$ )

230°C에서 1분간 용융시킨 BC-50 혹은 BC-90과 PU-20 블랜드물을 20°C / min로 강온시킬 경우 결정화 피크( $T_{mc}$ )의 조성에 따른 변화를 Fig. 13에 도시하였다. 이 경우 한개의  $T_{mc}$ 가 관찰되었으며,  $T_{mc}$ 가 PU-20의 양이 증가함에 따라 감소함을 볼 수 있다. 녹는점 부근에서의 고분자의 결정화 속도는 녹는점으로 부터의 과냉각 정도에 크게 의존하므로,<sup>13</sup> Fig. 13의  $T_{mc}$ 의 감소는 Fig. 8에서 나타난  $T_m$ 의 감소가 주요 원인임을 알수 있고,  $T_m$ 의 감소가 큰 BC-50의 블랜드물에서  $T_{mc}$ 가 BC-90의 블랜드물에서 보다 더 크게 나타남을 볼 수 있다. Fig. 14에는 BC-50 혹은 BC-90의 PU-40과의 Fig. 15에는 PU-80과의 블랜드물의  $T_{mc}$ 의 변화를 도시하였는데 이 경우도 한개의  $T_{mc}$ 가 관찰되며, 대체로  $T_m$ 이 감소하는 경우  $T_{mc}$ 가 감

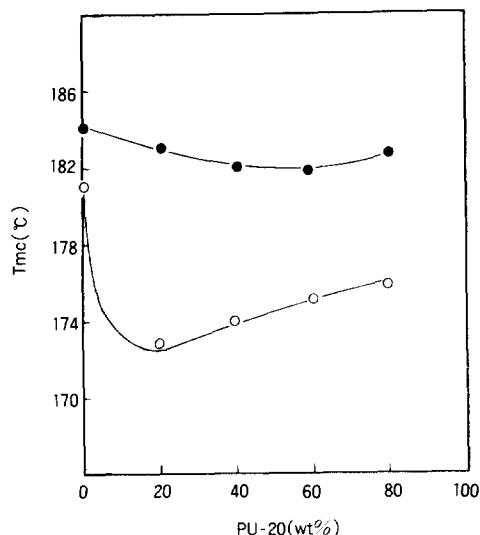


Fig. 13. Variation of  $T_{mc}$  of PU-20 / BC blends: (○) BC-50; (●) BC-90.

rix etc., as mentioned earlier. For the particular system of BR/SMR blend reinforced with short aramid fibers, the minimum and critical concentrations are respectively found to be 5, and 10~20 wt%. A value for critical fiber loading of 10 wt% was also reported by others.<sup>12</sup> Similar observations have been reported for aramid reinforced neoprene<sup>13</sup> and other systems.<sup>8</sup>

At fiber concentration lower than the critical volume, there are not enough fibers to control matrix elongation, and fibers would be subjected to high strain with only small loads and break, and the strength of the elastomeric composite is controlled by the matrix strength. The volume fraction of fiber necessary to recover the matrix strength is 0.1~0.15 depending on the nature of fiber, elastomer, bonding level and state of dispersion. It seems that the present results belong to the general observation.<sup>8</sup>

The tear test can be viewed as a means for estimating the ultimate properties of the composite.<sup>13</sup> The tear strength of the present composites monotonically increases with rubber loading, rapidly at low concentraion and slowly at high concentration. Generally, low fiber loadings can elevate the tear strength effectively, however, at high loadings, strain amplification between closely packed fibers promotes tearing and reduces the strengthening effect.<sup>7</sup> This can actually reduce the tear strength of composite below that of matrix for transversely

oriented sample.

Elongations at break for BR/SMR mixes are shown in Fig. 3. When the fiber loading was increased from 5 to 10 wt%, the elongation at break showed a drastic drop, i.e., from about 500 to 20%, and the value remains almost constant beyond this concentration. It may be noted that the critical fiber loading for strength reinforcement is found slightly above 10 wt% loading, whereas sharp drop in elongation at break was observed at 10 wt%, presumably less than that value, actually. This, in part, may be due to the experimental error, however, the results are not unusual.<sup>14</sup> In fiber reinforced composites, fibers act as load carrier via shear, and hence, depending on the bonding level between fiber and matrix, the strengthening effect would appear at higher concentration than with perfect bonding. On the contrary, the elongational property, more or less, is governed by the strain amplification<sup>1</sup> leading to break at lower concentration than the critical loading for strength reinforcement. Similar results were reported for jute fiber reinforced natural rubber, where strengthening effect was observed at 25wt% loading and sharp drop in elongation at break was noted at 15%.<sup>14</sup> A continuous increase in hardness and decrease in wear is observed with the increase of fiber concentration (Fig. 4) like other short fiber reinforced rubbers.<sup>7</sup>

Heat buildup, caused by cyclic compression, is given in Table 6 together with compression set

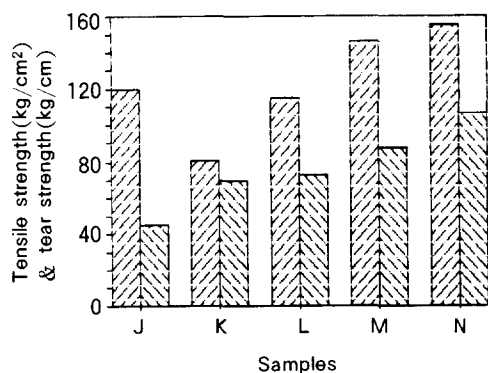


Fig. 2. Tensile(▨) and tear(▩) strengths for BR/SMR mixes.

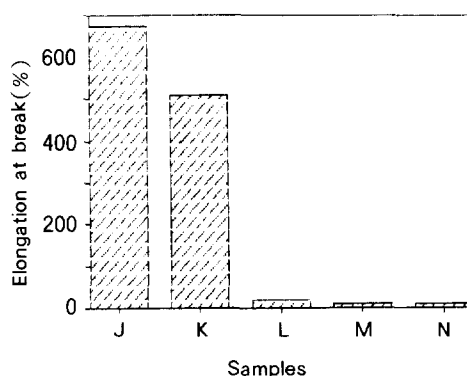


Fig. 3. Elongation at break for BR/SMR mixes.

data. Heat buildup for unreinforced BR/SMR mix is 38.9°C. However, the heat buildup for > 10 wt% reinforced composite was more than 48.9°C (the limit of our facility), and was not measured in our experiment. Heat buildup over 50°C was also reported with aramid fiber reinforced SBR by others.<sup>15</sup> It is likely that the fiber, oriented perpendicular to the stroke, tend to coil<sup>7</sup> together with buckling<sup>16</sup> leading to debonding from the matrix. In the process of coiling of the fiber, part of the applied stress will be absorbed as elastic energy, and the residual will dissipate as heat causing a temperature rise during the compression cycle.

Compression set, measured at constant strain (25%), increases as the fiber concentration increases, due probably to the increased stiffness of the composite. Increasing stiffness requires increasing applied load for the same strain, and this should lead to partial debonding and fiber breakage. The result gives an increase in compression set.<sup>17</sup>

The effect of aramid reinforcement (20 wt%) on

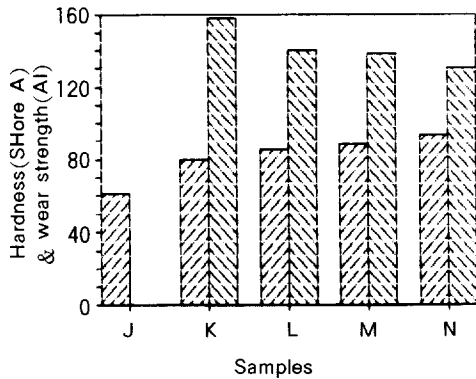


Fig. 4. Hardness (hatched) and wear (solid) strengths for BR/SMR mixes.

Table 6. Heat Build up and Compression Set Data for BR/SMR Mixes

Sample Code	Content of Mix (parts by wt)				
	J	K	L	M	N
Heat Buildup(°C)	38.9	48.9	48.9	48.9	48.9
Compression Set(%)	57.9	62.4	67.4	71.1	90.5

various rubbers is shown in Figs. 5 and 6. Regardless of the type of rubber considered here, tensile and tear strengths of the composites are significantly higher than those of unloaded mixes. Tensile strength is increased by 26(NBR)~62(SBR)%, and tear strength by 55(NBR)~95(SBR)%. In four of the mixes, elongation at break reduced down to order of 10% from 239(SBR)~750(NBR)%. The wear strength (Fig. 6) of the vulcanizates was reduced by approximately 10(SMR)~30%(BR) upon fiber loading at 20 wt%. With regard to strengths, the reinforcing effect of aramid was most pronounced with SBR.

The effect of fiber surface treatment on mechanical properties has been studied for NBR(Figs. 7

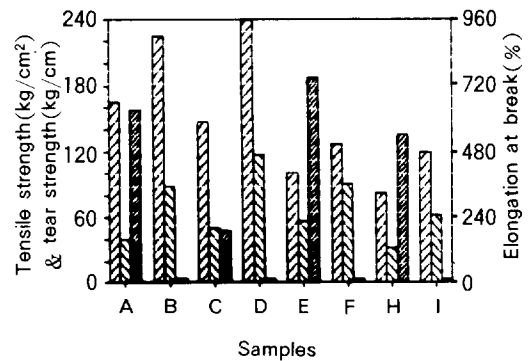


Fig. 5. Tensile (hatched) and tear (solid) strengths, and elongation at break (solid) for SMR, SBR, NBR, and BR mixes.

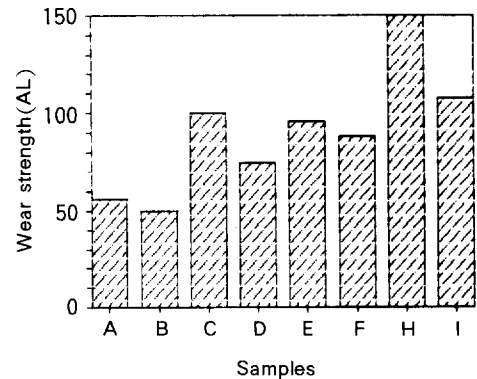


Fig. 6. Wear strength for SMR, SBR, NBR, and BR mixes.

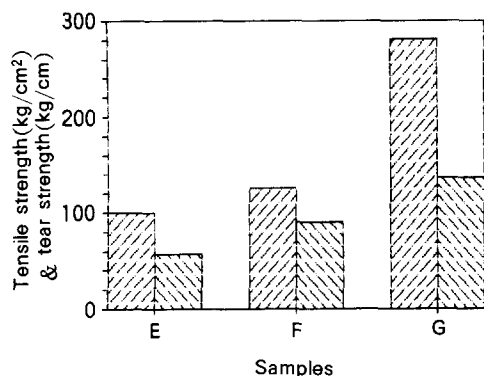


Fig. 7. Tensile(▨) and tear(▩) strengths for NBR mixes.

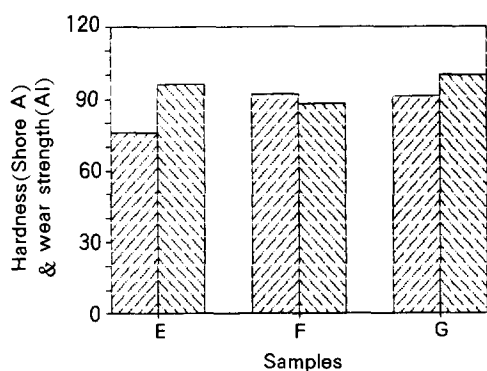


Fig. 8. Hardness(▨) and wear(▩) strengths for NBR mixes.

and 8). The bonding agent employed was a mixture of cresol, acetone and phenol, which has been typically used for nylon fiber. Tensile strength of treated composite is over more than two times of the untreated composite, indicating the interfacial adhesion is essential for the effective reinforcement. This, of course, is through the effective shear stress transfer at interface, fiber as a load carrier and matrix as a load transfer medium. Tear strength and wear resistance have also been

improved by surface treatment. However, the hardness, being as a bulk property, has not been changed by surface treatment.

## REFERENCES

1. L. A. Goettler and K. S. Shen, *Rubber Chem. Technol.*, **56**, 620 (1983).
2. A. Y. Coran, *Rubber Chem. Technol.*, **47**, 396 (1974).
3. A. Y. Coran, K. Boustany, and P. Hamed, *J. Appl. Polym. Sci.*, **15**, 2471 (1975).
4. J. E. O'Connor, *Rubber Chem. Technol.*, **50**, 949 (1977).
5. V. M. Murty and S. K. De, *Rubber Chem. Technol.*, **55**, 287 (1982).
6. L. A. Goettler, R. I. Lieb, and A. J. Lambright, *Rubber Chem. Technol.*, **52**, 838 (1979).
7. D. K. Setua and S. K. De, *Rubber Chem. Technol.*, **56**, 808 (1983).
8. A. Y. Coran, P. Hamed, and L. A. Goettler, *Rubber Chem. Technol.*, **49**, 1167 (1976).
9. N. Arumugam, K. T. Selvy, and K. V. Rao, *J. Appl. Polym. Sci.*, **37**, 2645 (1989).
10. M. J. Nichols and R. F. Ohn, *Adhesive Age*, 31 (June, 1976).
11. V. M. Murty and S. K. De, *J. Appl. Polym. Sci.*, **27**, 4611 (1982).
12. E. Wagner and L. M. Lobeson, *Rubber Chem. Technol.*, **43**, 1129 (1970).
13. S. R. Moghe, *Rubber World*, 187(5), 16(Feb., 1983).
14. V. M. Murty and S. K. De, *J. Appl. Polym. Sci.*, **29**, 1355 (1984).
15. A. P. Foldi, *Rubber Chem. Technol.*, **49**, 379 (1984).
16. P. K. Mallick, "Fiber Reinforced Composite", Dekker, New York, 1988.
17. R. M. Jones, "Mechanics of Composite Materials", Mc Graw-Hill, New York, 1975.