

Effect of Blending Thermoplastic Elastomer with Natural Rubber Compound and Studies of Short Fiber Reinforced Rubber Composite

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SYNOPSIS

Rubber engineers face difficulties in scorching and vulcanizing during rubber processing, particularly of natural rubber (NR). Therefore, this work tried to solve these problems by blending thermoplastic rubber with NR compound. The results indicated that the scorch resistance of the NR was improved by blending the thermoplastic elastomer styrene-ethylene/butylene-styrene (SEBS). However, its mechanical properties were not found to be improved. Therefore, this study was extended to understand the reinforcement effects of short fiber carbon and glass fibers, on the mechanical properties of the thermoplastic elastomer with NR compounds. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Modification of elastomers by blending has drawn attention because of the possibility to improve the end-use properties of existing elastomers. Elastomer with plastic blends, however, have some difficulties in the vulcanizing reaction, elasticity, etc. Although blending plastics to make a toughened polymer has been very popular,¹⁻³ these blends have many difficulties with processability, compatibility, etc.^{4,5}

Since World War II, the development of fiber reinforced composites has made available polymers lighter than aluminum and stiffer than steel. Generally, the short fiber reinforced rubber composites have become popular in industrial fields because of their processing advantages, and technical properties have been greatly improved in strength, stiffness, modulus, and damping.⁶⁻⁸

Various fibers have been incorporated with natural (NR) and synthetic rubbers.⁹⁻¹² However, few studies on fiber reinforced thermoplastic rubber are found in the open literature. Therefore, this study tried to ascertain the advantages of reinforced rubber composites in NR and thermoplastic elastomer blends. When rigid high modulus materials are in-

corporated into a lower modulus matrix, their mechanical properties are improved. Thus, this study investigated the short carbon fiber, glass fiber, and composites of carbon black reinforced NR and styrene-ethylene/butylene-styrene (SEBS).

The experimental results showed the improvement of the scorch resistance with NR/SEBS blended compared with NR compound, but the mechanical properties were not improved. Carbon and glass fiber reinforced composites showed much better mechanical properties than unreinforced materials.

EXPERIMENTAL

Materials

NR, SMR-L (Standard Malaysian Rubber-L), and a synthetic block copolymer, SEBS, were used in this study. We used the SEBS (KRATON FG 1901X) thermoplastic elastomer of Shell Chemical Company, which is a triblock copolymer consisting of polystyrene end blocks and a poly(ethylene/butylene) midblock. The typical properties of SEBS are summarized in Table I.¹³ We used a carbon black (HAF-330), a carbon fiber, and a glass fiber as a reinforcing material. The surface of the fibers was

Table III Properties for NR/SEBS/Carbon Black and NR/Carbon Black

Properties	Sample	
	F (NR/SEBS/Carbon Black)	G (NR/Carbon Black)
Mooney viscosity ML 1 + 4 at 125°C	22.6	19.5
Scorch time at 125°C (min)		
t_5	24.6	14.2
t_{35}	27.5	16.5
Δt	2.9	2.3
Optimum cure time at 160°C (min)		
T_{90}	6.0	6.4
T_{10}	3.6	3.0
Maximum torque (kg _f ·cm)	57	50
Hardness (shore A)	56	53
Specific gravity (-)	1.07	1.07
Tensile modulus (kg _f /cm ²)	89	90
Elongation at break (%)	630	620

The viscosity of the NR/SEBS/carbon black blend was slightly higher than that of the NR/carbon black compound. This indicates that the viscosity increases by adding SEBS to NR/carbon black. The hardness also slightly increased by adding the SEBS. However, we could not find a way to improve the other mechanical properties such as tensile modulus and elongation at break. A big difference was found in scorch resistance and cure time. Generally, the elastomers have problems with scorch during processing. Scorch is defined as a premature vulcanization that may occur during the processing of the rubber compound due to accumulated effect of heat and time. The characteristics of scorch are taken from Mooney cure curves as follows: t_5 is the time to scorch at MV + 5 units, t_{35} is the time to scorch at MV + 35 units, and Δt is the cure index $t_{35} - t_5$. We compared the scorch time at 125°C for the NR compound with NR/SEBS one. By blending SEBS with the NR compound, the scorch time increased by almost two times. This means the scorch resistance was greatly increased by blending. The optimum cure time was shortened by adding the thermoplastic rubber, meaning that the operation time can be decreased by blending.

Effect of Short Fiber Reinforcement in Rubber Compounds

The rheographs of the rubber mixtures are shown in Figure 1. The rheographs show a gradual increase up to the maximum torque and then a plateau. While

the maximum torque increases by adding the carbon black, it is minimally affected by adding glass fiber and carbon fiber. The reason can be explained by the amount of loading materials, 30 parts of carbon black but only five parts of fibers.

From Figure 1, we determined the optimum cure time from T_{90} , which represents the time to reach 90% of the maximum torque value. The optimum cure time is summarized in Table IV. The optimum cure time is obtained by adding 2 min to T_{90} . The results indicated that the optimum cure time for all samples will be approximately 8 min at 160°C for carbon black filled rubber. The unfilled polymer takes 2 min longer. However, the effect of the loading with carbon and glass fiber did not appear. The reason can be explained by the special function of carbon black and the loading amount.

The Mooney viscosity of the compounds is shown in Figure 2. The carbon black filled rubber shows higher viscosity than the unfilled polymer. Also the reinforced fibers increased the viscosity.

The scorch characteristics of samples are summarized in Table IV. The scorch time of the carbon black filled rubbers at 125°C was 28 min, but the scorch time for all unfilled rubber was approximately 50 min. The order of cure value index is glass fiber reinforced > carbon fiber reinforced > no fiber composites for both the carbon black filled and unfilled materials. The results indicate that the dominating factor is carbon black because of the higher concentration of carbon black than fibers in the rubber compounds. Figure 3 shows the dynamic mechanical

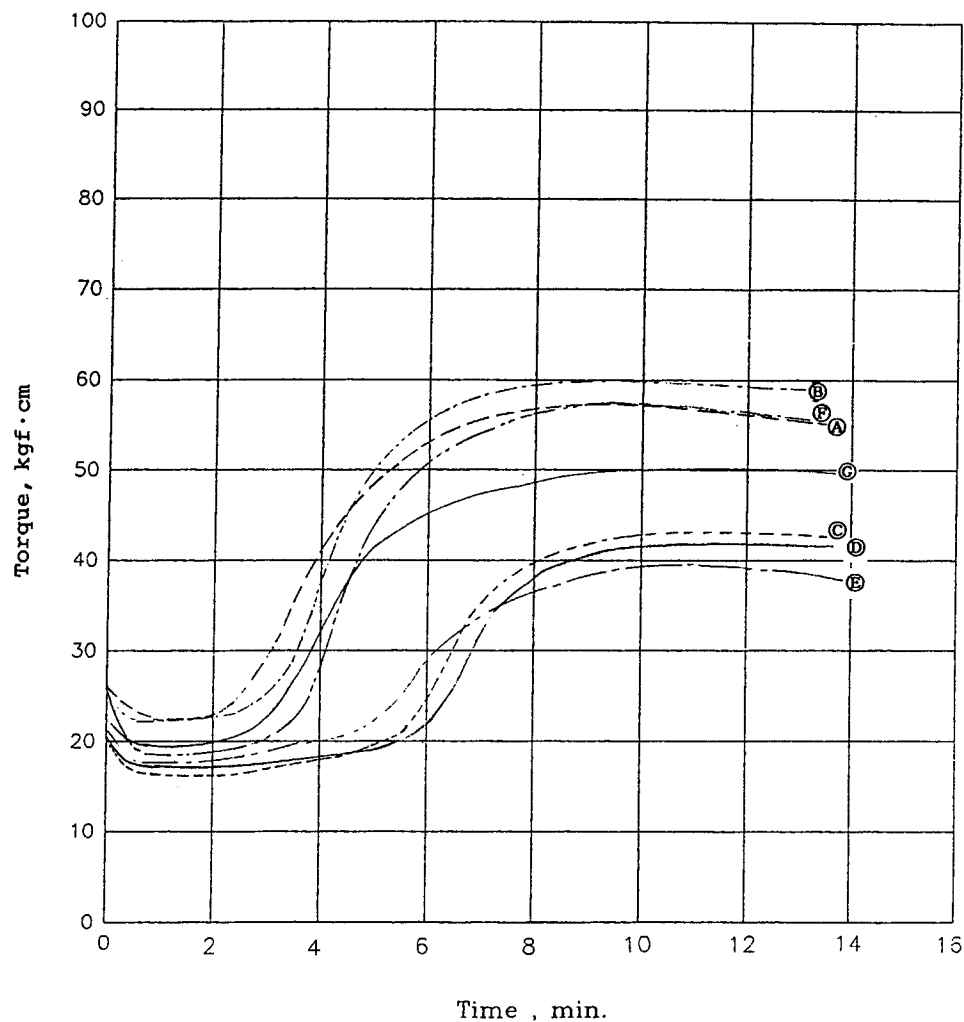


Figure 1 Rheographs of the rubber mixtures in this study.

Table IV Thermal Properties for Samples

Properties	Sample					
	A	B	C	D	E	F
Scorch time at 125°C (min)						
t_5	25	24	44	38	45	25
t_{35}	28	28	52	50	51	28
Δt	3	4	8	12	6	3
Optimum cure time at 160°C (min)						
T_{90}	6.4	6.1	8.3	8.5	7.8	6.0
T_{10}	3.4	3.1	5.2	5.4	5.4	3.6

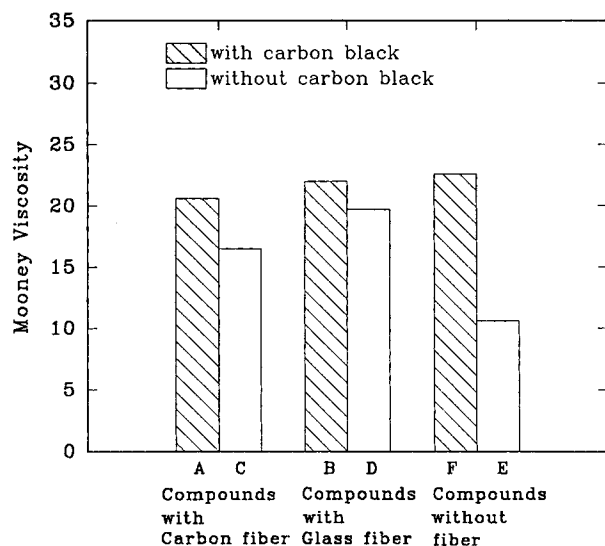


Figure 2 Mooney viscosity of rubber samples.

properties at 1-Hz frequency. The results indicate that elasticity increased with reinforcing materials added. E' (storage modulus) represents the elastic energy stored and E'' (loss modulus) the energy dissipated in a cyclic deformation. Figure 4 show the storage modulus against temperature at 1-Hz frequency. At low temperature (below T_g) all samples except the glass fiber loaded material show almost the same value. However, the order of increase in the storage modulus was $D < C < B < A$ at above T_g . This result indicates that the carbon black filled

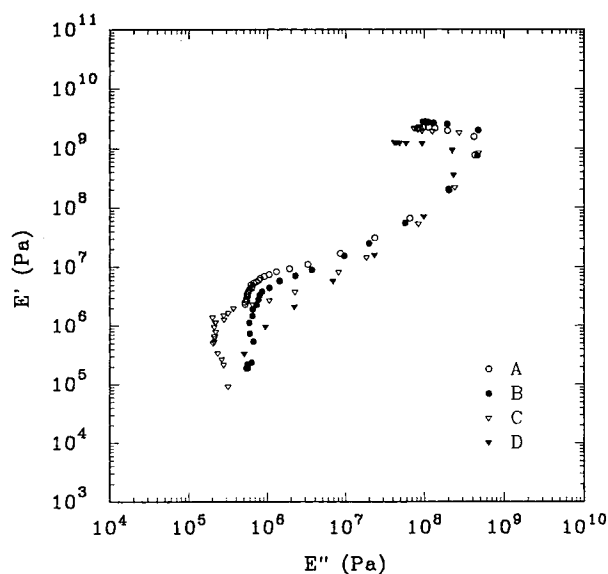


Figure 3 Storage modulus (E') against loss modulus (E'') for fiber loaded composites.

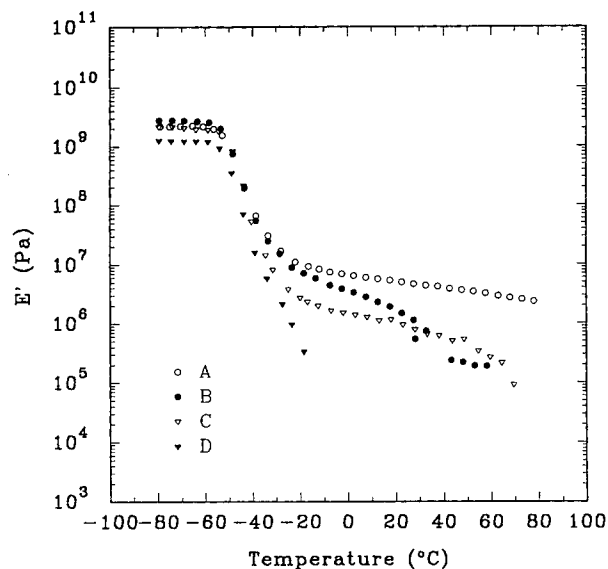


Figure 4 Storage modulus (E') against temperature for fiber loaded composites.

elastomers show higher modulus than unfilled elastomers. The transition behavior of the rubber mixtures is shown in Figure 5. This result indicates the damping peak for NR chain relaxation at -45°C . The behavior of the glass fiber loaded materials (B and D) is more unstable than for the carbon fiber loaded materials (A and C) as the temperature increases.

Figure 6 shows the optical micrographs of the fiber reinforced composites. All micrographs show a discontinuous phase natural rubber matrix and

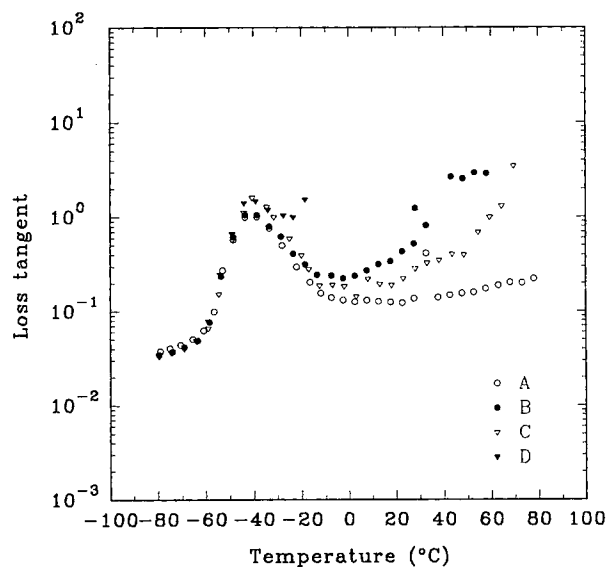


Figure 5 Loss tangent ($\tan \delta$) against temperature for fiber loaded composites.

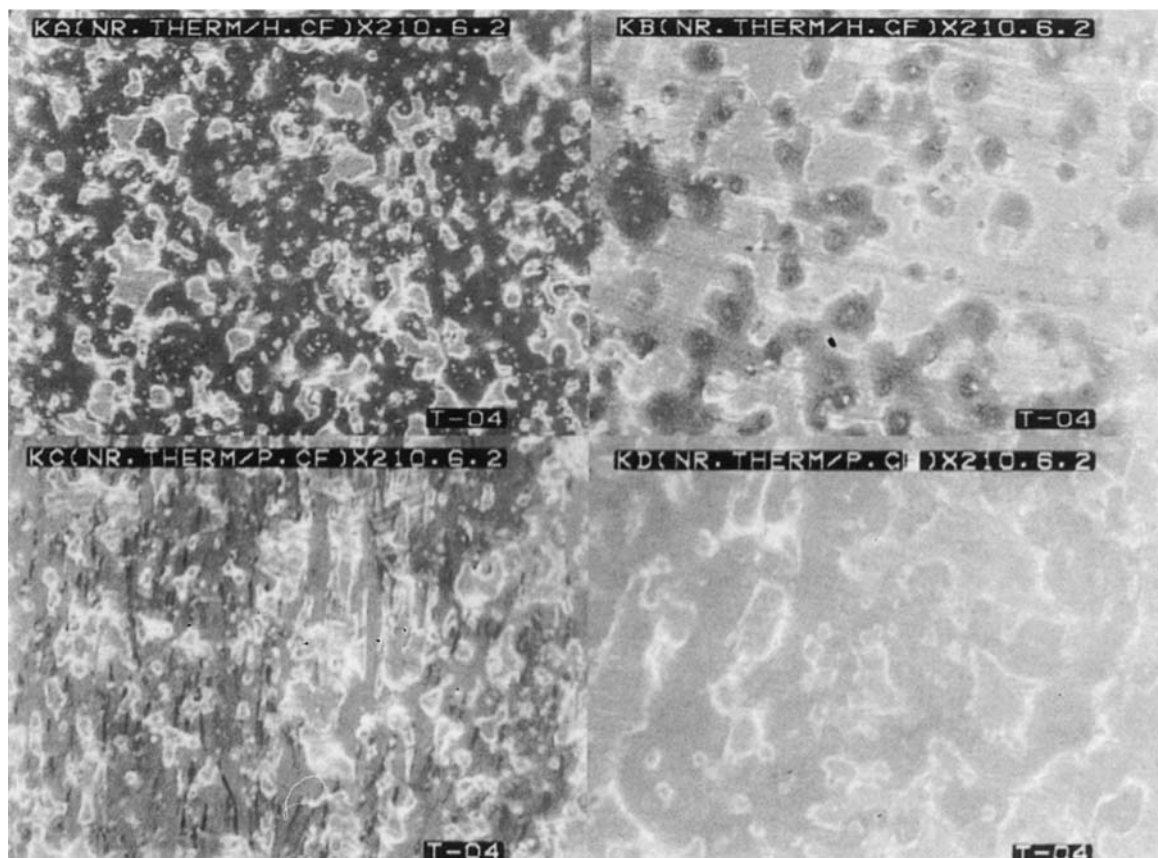


Figure 6 Optical micrographs for fiber loaded composites. (A–D): Sample numbers in Table II.

SEBS domain. Therefore, the NR/SEBS blend is an immiscible system. This is also apparent from the dynamic viscoelastic behavior in Figures 3 and 4.

Micrographs in Figure 6 for the carbon black filled polymer (A and B) show that the carbon black is well dispersed in the mixtures. Micrograph (C) shows that the carbon fiber orientation is in the machine direction. However, we could not observe the carbon fiber state of micrograph A because of the large amount of carbon black dispersed compared to the carbon fiber, and the colors of carbon black and carbon fiber are the same. The glass fibers were not observed because of their transparency. However, we may expect that the fibers are in the machine direction like the carbon fiber in graph (C).

Generally, the specific gravity (sp gr) of a multicomponent blend is an average of each component. The specific gravity of the compounds increases with carbon black loading because specific gravity of the carbon black used is 1.86. In the case

of the glass fiber (sp gr 2.1) or carbon fiber (sp gr 1.8) reinforcement, the specific gravity of the composites slightly increases, which is shown in Figure 7. One of the main advantages of the reinforced composite is the high modulus. Figure 8 shows that loading carbon black, carbon fiber, and glass fiber elevated the tensile modulus effectively. In the composites without carbon black, the obtained modulus is in the order of $C > D > E$. The modulus of carbon black filled composite shows that loading the carbon fiber was effective in the improvement of modulus.

Elongation at break for samples is shown in Figure 9. Both carbon blend and fiber loading reinforcement reduced the elongation. The order of the elongation is in the order of $E > D > F > C > B > A$. The results indicate that the glass fiber loaded composites showed higher values of elongation than carbon fiber loaded composites.

In fiber reinforced composites, fibers act as load carriers via shear, to transfer the applied stress, leading to high modulus. On the contrary, the elon-

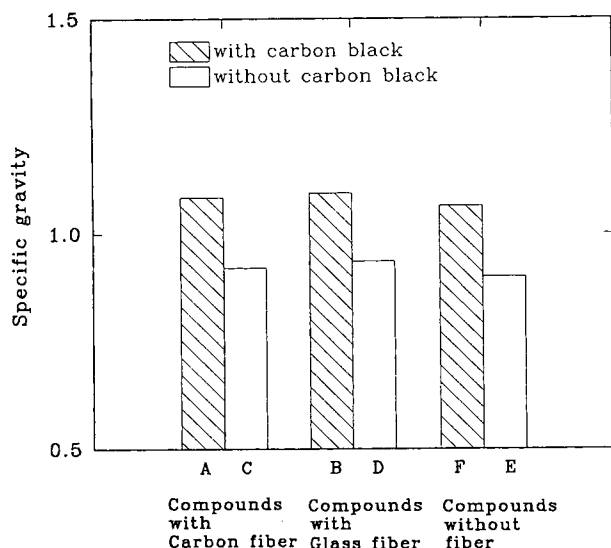


Figure 7 Specific gravity for rubber samples.

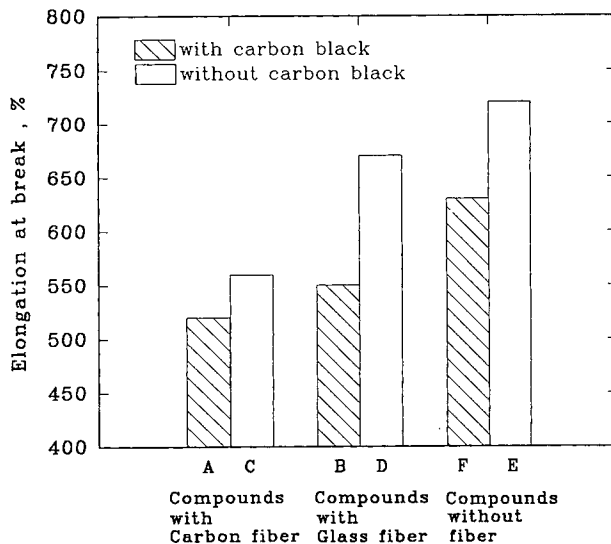


Figure 9 Elongation at break for the rubber samples.

gation is subject to strain amplification, leading to lower break elongations.

The hardness increases in the order of $E < D < F \approx C < B < A$ (Fig. 10). Notably, the hardness of the 5% of carbon fiber loaded composite (C) is almost equal to that of the 30% carbon black filled one (F). However, the glass fiber loaded composites are softer than the carbon black loaded composites. Therefore, we found that the carbon fiber loading was more effective for the improvement of hardness of the composites.

CONCLUSIONS

In comparison with NR/carbon black and NR/SEBS/carbon black compounds, the scorch time at 125°C of the NR/SEBS/carbon black was twice that of the NR/carbon black compound. The optimum cure time decreased by adding the SEBS to the NR/carbon black compound. However, the mechanical properties, modulus, and elongation were not improved by blending SEBS with NR/carbon black compound. Therefore, we investigated the effect of the short fiber reinforcing in the compounds. The experimental data indicated that the mechan-

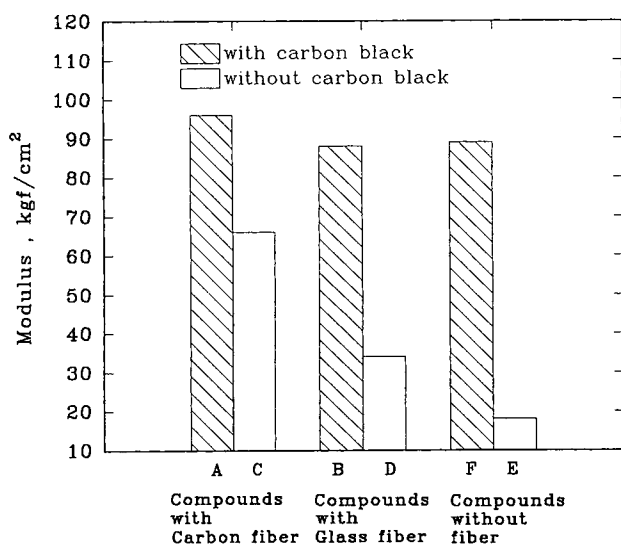


Figure 8 Modulus of the rubber samples.

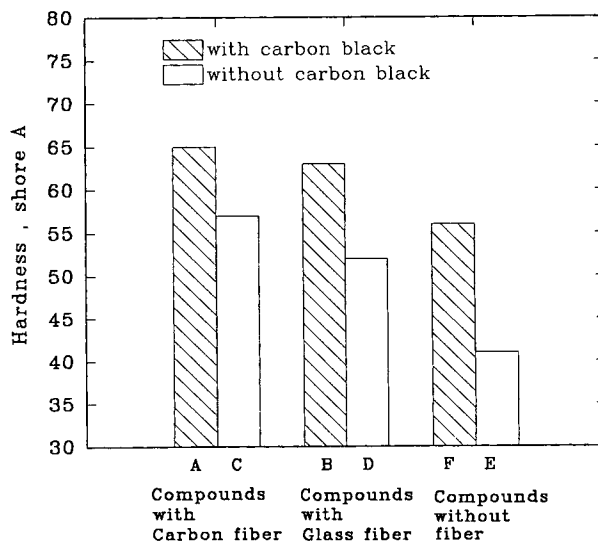


Figure 10 Hardness for the rubber samples.

ical properties, such as modulus, hardness, and damping, were much increased by reinforcing fibers. Carbon fiber especially was more effective than the glass fiber.

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