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# Rheological Behaviour of Short Silk Fiber Filled Rubber Compounds

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Rheological behaviour of rubbers (natural (NR), nitrile (NBR) and polychloroprene (CR)) and short silk fiber filled rubber compounds have been studied. The shear viscosity-shear rate relationship of both non-fiber filled and short fiber filled rubber compounds obey power law model for fluids and is similar to that of short fiber filled polymer melts. The effect of fiber concentration on the shear viscosity is more pronounced at lower shear rates. Both extrudate deformation and die swell become less on the addition of fibers to the mixes and the improvement is more significant at higher fiber concentrations. Extent of fiber breakage by the shear force during mixing is severe and is similar for all the rubbers.

## INTRODUCTION

Short fiber-reinforced rubber composites have gained importance in the last few years because of their processing advantages and good technical properties like strength, stiffness, elastic modulus, creep rate, damping and anisotropy in the physical properties.<sup>1-7</sup> In all these studies emphasis has been put more on the technical properties of the fiber-rubber composites rather than on their flow and rheological characteristics in the unvulcanized state. The need for rheological studies in making a logical choice of polymer for various processing conditions has been indicated by Brydson.<sup>8</sup> Recently,

Setua *et al.* have reported their studies on short silk fiber reinforced natural, nitrile and polychloroprene rubber composites, wherein the processing advantages and enhancement in technical properties achieved due to the addition of short fiber in the rubber mixes have been studied.<sup>9-12</sup> Studies on the correlation between rheology and processing and on the rheological behaviour of polymer melts, fiber filled polymer melts, short glass fiber reinforced polystyrene melts and fiber filled thermosetting compounds have also been made.<sup>13-20</sup> Crowson and Folkes<sup>21</sup> have studied the fiber orientation resulting from convergent, divergent and shear flows. Maschmeyer and Hill<sup>22</sup> reviewed the rheological characteristics of fiber filled high viscous silicone oil. The effects of rubber particles, carbon black and non-black fillers on the flow properties of rubbers and polymer melts have also been studied.<sup>23-29</sup> Various factors affecting the die swell, melt fracture and deformation of the extrudates have been reported by different research groups.<sup>30-35</sup> But limited studies have so far been made on the rheological and extrusion behaviours of short fiber filled rubber compounds.<sup>36-38</sup>

In this paper the results of the studies on shear viscosity, extrudate distortion, die swell values and extent of fiber breakage during mixing of short silk fiber filled natural rubber, nitrile rubber and polychloroprene rubber compounds have been reported.

## EXPERIMENTAL

### Preparation of the mixes

The formulations of the compounds used are given in Table I. Mixes were prepared in a Brabender Plasticorder (model PLE 330), fitted with a cam type (W 50H) mixing head. Details of the mixing sequence are given in Table II. Pieces of the size of  $5.0 \times 5.0 \times 2.0$  mm were cut from the sheets for measuring the flow properties.

### Rheological measurements

The rheological measurements were carried out using a capillary rheometer MCR 3210 attached to an Instron Universal testing machine (model 1195). A capillary having a length to diameter ratio

TABLE I  
Formulations of the mixes

Rubber type	NR <sup>a</sup>				NBR <sup>b</sup>				CR <sup>c</sup>		
Amount of silk fiber, <sup>d</sup> phr	0	5	10	20	0	5	20	0	5	20	

<sup>a</sup> Crumb natural rubber, ISNR-5, obtained from Rubber Research Institute of India, Kottayam.

<sup>b</sup> Nitrile rubber, PERBUNAN N 3307 NS, supplied by Bayer Ltd., West Germany.

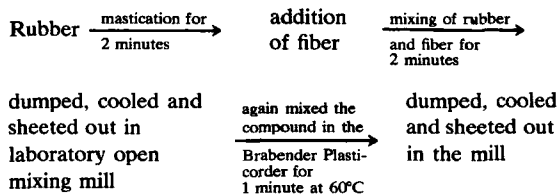
<sup>c</sup> Neoprene rubber, WM-1 grade, supplied by Bengal Waterproof Ltd., Panihati, Calcutta.

<sup>d</sup> Mulberry type of silk fiber, obtained in filatures of Silk Khadi Mondol, Bishnupur, West Bengal.

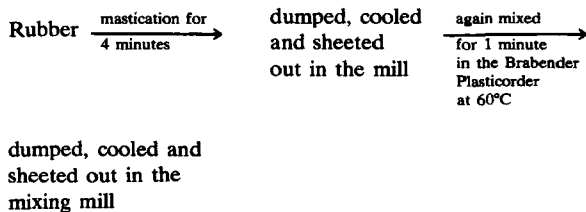
TABLE II  
Mixing sequence

RPM of the rotor	60
Temperature of mixing	60°C
Total time of mixing	5 minutes

1) Mixes with fiber:



2) Mixes without fiber:



( $l_c/d_c$ ) of 40 with an angle of entry of  $90^\circ$  was used for this study so as to minimise capillary end effects. In order to minimise the exposure of the compounds to heat, a gradation in temperature across the length of the barrel was maintained. The temperature difference between the upper and middle zone and that between the middle and lower zone was maintained at  $5^\circ\text{C}$  using a thermocouple attached to a three action current adjusting type control unit. The sample for testing was placed inside the barrel of the extrusion assembly and forced down to the capillary with a plunger attached to the moving crosshead. In the present case, depending on the diameter of the rheometer barrel ( $\frac{3}{8}$  inch), a preheating time of five minutes was found to be adequate for all the samples. After the warming-up period the sample was extruded through the capillary at preselected speeds of the crosshead which varied from 5 to 500 mm per minute. The sample height in the barrel before extrusion was kept the same in all the experiments and the machine was operated to give three different plunger speeds (viz., 5, 50 and 500 mm per minute) from lower to higher speed with a single charge of the material. Forces corresponding to specific plunger speeds were recorded using a strip chart recorder assembly. The forces and the crosshead speeds were converted to shear stresses ( $\lambda_w$ ) and shear rates ( $\dot{\gamma}_w$ ) at wall respectively by using the following equations involving the geometry of the capillary and the plunger and assuming that (i) the fluid, which is incompressible with zero velocity at wall, flows parallel to the axis of the barrel and (ii) all energy is consumed within the capillary and the flow is isothermal. Then,

$$\lambda_w = \frac{F}{4A_p(l_c/d_c)}$$

$$\dot{\gamma}_w = \frac{3n' + 1}{4n'} \times \frac{32Q}{\pi d_c^3}$$

where  $F$  is the force applied at a particular shear rate,  $A_p$  is the cross-sectional area of the plunger,  $l_c$  is the length of the capillary and  $d_c$  is the diameter of the capillary.  $Q$ , the volume flow rate was calculated from the velocity of crosshead and cross-sectional area of the plunger,  $n'$ , the flow behaviour index, is defined by  $n' = d(\log \lambda_w)/d(\log \dot{\gamma}_{w,a})$ , where  $\dot{\gamma}_{w,a}$  is the apparent shear rate at wall and is given by  $32Q/\pi d_c^3$ .  $\dot{\gamma}_{w,a}$  is obtained experimentally and with

the help of regression analysis  $\lambda_w$ , the shear stress at wall, may also be calculated. The shear viscosity of the compounds is then calculated as

$$\eta = \frac{\lambda_w}{\dot{\gamma}_w}$$

Bagley's<sup>39</sup> correction for the entrance pressure losses was not made as the correction factor becomes small for capillaries with higher  $l_c/d_c$  ratio.

### Die swell measurements

The extrudates were collected as they emerged out of the capillary die; care was taken to avoid any further deformation or stretching of the extrudates. The die swell measurements were repeated frequently during the course of equilibrium period and a relaxation period of 24 hours at room temperature (30°C) was found to be sufficient for establishing a steady state, after which no change in the swelling values occurred even after an interval of six days from the time of the experiment. After the relaxation period the diameters of the extrudates were measured at several points using an Olympus stereo binocular microscope (model VB 454). An average of six readings was taken as the diameter ( $d_e$ ) of the extrudate. The percentage die swelling was calculated as the ratio of the diameter of the extrudate to that of the capillary ( $d_e/d_c$ )  $\times 100$ .

## RESULTS AND DISCUSSION

### Shear viscosity

The bargraphs, Figure 1, show the effect of fiber loading on shear viscosity for different rubbers at different shear rates. From Figure 1, it is evident that irrespective of the type of the rubbers all the mixes show pseudoplastic nature as the shear viscosity decreases with increase in shear rate at the same fiber concentration. This dependence is similar for all rubbers viz., NR, NBR and CR. Effect of fiber concentration on shear viscosity is more prominent at lower shear rates (e.g., at 30 sec<sup>-1</sup>) compared to those at higher rates of

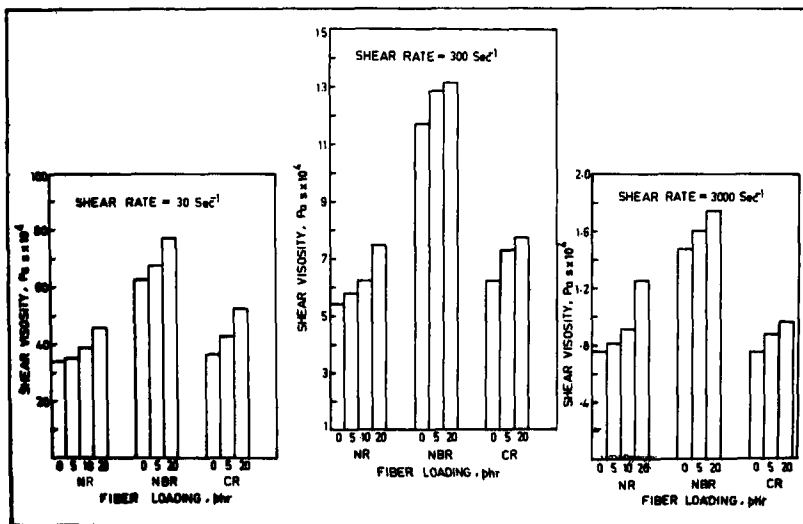


FIGURE 1 Bargraphs showing the effect of fiber loading on shear viscosity for different rubbers at three different shear rates.

shear (e.g.,  $300 \text{ sec}^{-1}$  and  $3000 \text{ sec}^{-1}$ ). At all rates of shear, mixes of NBR show higher shear viscosities than the corresponding mixes of NR and CR while only at  $3000 \text{ sec}^{-1}$  NR compounds show higher shear viscosities than CR compounds. This is possible due to the higher amount of strain crystallization in NR compared to that in CR at very high shear rates. The nature of changes in shear viscosities due to the addition of fibers to different rubber mixes at various shear rates are in line with the earlier observations on glass fiber reinforced polystyrene melts by Chan *et al.*<sup>19</sup> and on short glass fiber filled thermoplastics by Crowson and Folkes.<sup>21</sup>

### Extrudate distortion

The photograph of the extrudates extruded from the capillary for different mixes at three different shear rates is shown in Figure 2. For the gum mixes at all shear rates CR shows maximum extrudate distortion followed by NBR and NR. Extrudate distortion, in the case of NR is significant only at  $3000 \text{ sec}^{-1}$  while that of NBR is negligible at  $30 \text{ sec}^{-1}$  but increases gradually with increasing shear

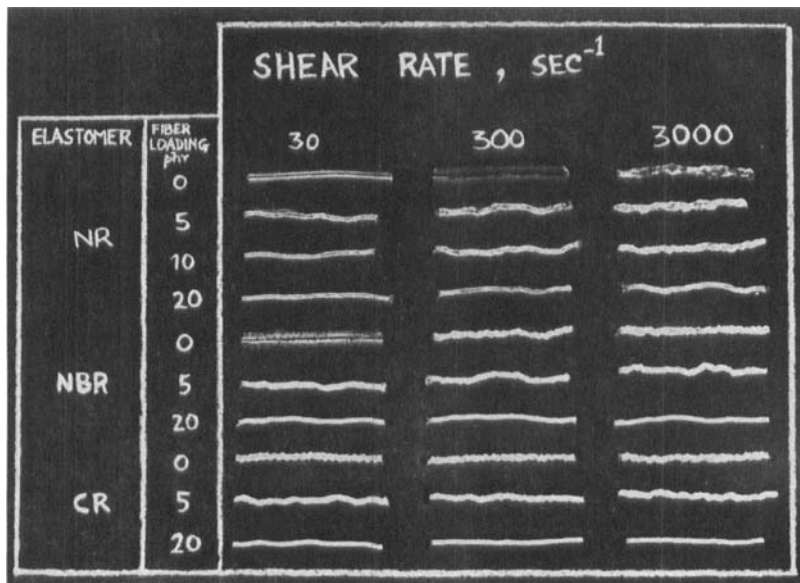


FIGURE 2 Photograph of the extrudates extruded from different mixes at three different shear rates.

rate. For all rubbers, extrudate distortion reduces with the addition of fibers in the mixes. Extrudate distortion at a particular shear rate decreases with increase in fiber concentration and at a particular fiber concentration increases with the increase in shear rates. At  $30 \text{ sec}^{-1}$  NR mixes containing either 5 phr or 20 phr of silk fiber show lowest extrudate distortion followed by NBR and CR. However, at higher shear rates e.g., at  $300 \text{ sec}^{-1}$  and  $3000 \text{ sec}^{-1}$  for both fiber concentrations, the trend in the extent of extrudate distortion is reversed.

$$\text{CR} < \text{NBR} < \text{NR}$$

### Die swell

Percentage die swell values for different mixes are shown in Figure 3. Die swell for the gum rubber mixes increases with increasing shear rates for all rubbers. At all the shear rates NBR shows higher percentage of die swell values than CR. NR shows higher die swelling than NBR and CR at shear rates of  $300 \text{ sec}^{-1}$  and



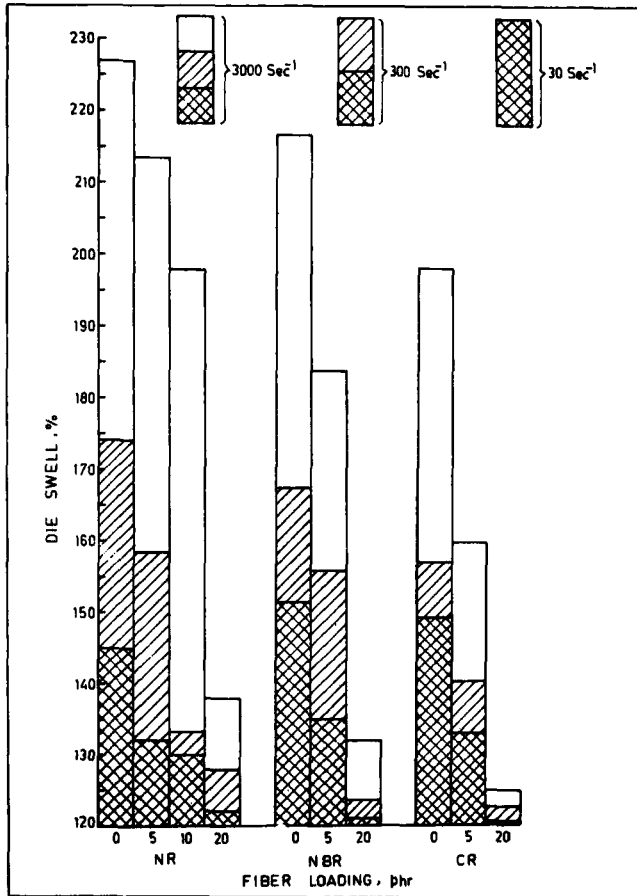


FIGURE 3 Bargraphs showing the percentage die swell values for different mixes at three different shear rates.

3000 sec<sup>-1</sup> unlike that at 30 sec<sup>-1</sup>. For the fiber filled mixes for all rubbers percentage die swell increases with increase in shear rates at a particular fiber loading and decreases with increase in fiber loading at a particular shear rate. At 5 phr fiber loading a similar trend, as observed for the mixes without fiber, in percentage die swell values for NR, NBR and CR is observed although the amount of swelling is greatly reduced by the addition of fibers to the mixes. However, at

20 phr fiber loading percentage die swell is significantly reduced and NR shows consistently higher values than NBR and CR for all shear rates. The results of die swell studies are in agreement with the earlier observations made by Chan *et al.*<sup>40</sup>

### Fiber breakage

Shear force during mixing in the Brabender caused breakage of the fibers. Extent of fiber breakage was determined by dissolution of the fiber-rubber mixes in benzene in the case of NR and in chloroform in the cases of NBR and CR, followed by extraction of the fibers and examination of fiber length distribution by a polarizing microscope under reflected light (model Leitz HM-Pol). It was found that the variation of the mean aspect ratio (length to diameter ratio of the fiber) from its original value of 500 to 65 (for NR), 68 (for NBR) and 70 (for CR) with the volume loading of fiber was negligible and the fall remained unchanged during the process of extrusion through the capillary. However, no change in average fiber diameter (0.012 mm) occurred either during mixing or during extrusion.

### CONCLUSIONS

The following conclusions can be drawn from the preceding discussion.

- 1) The shear viscosity-shear rate relationship of rubbers (NR, NBR and CR) and short fiber-rubber compounds obeys power law model for fluids and is similar to that of short fiber filled polymer melts.
- 2) The effect of fiber loading on the shear viscosity is more pronounced at low shear rates e.g., at  $30 \text{ sec}^{-1}$ .
- 3) Resistance to shape distortion of the extrudates increases on the addition of fibers to the mixes.
- 4) Fiber filled extrudates show lower die swell than the unfilled mixes and negligible die swell is observed at higher fiber concentrations e.g., at 20 phr.

5) Extent of fiber breakage during mixing is severe and the fall in mean aspect ratio is more or less similar for all the rubbers.

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