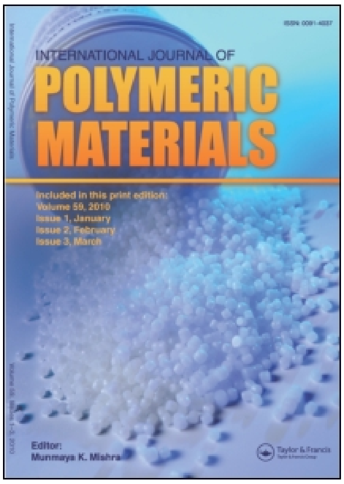

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Flyash as a Co-Filler for Elastomer Composites

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Flyash as waste mineral product was studied to use as a filler. The possibility of partial replacement of active filler (carbon black) by cheaper product (flyash) was investigated. The physico-mechanical properties of SBR composites with constant content of carbon black and varying content of flyash have been studied. It was found that small addition of carbon black exhibited an effective increase in activity of flyash as filler. The results showed that flyash could be utilized for partial replacement of conventional fillers.

Keywords: carbon black, flyash, SBR composite, co-filler

INTRODUCTION

Expanding industrial activities create a continual demand for improved materials that satisfy increasing strength requirements. The polymer composite materials gained importance in industrial applications by fulfilling the properties requirements.

Filled elastomers are a very important class of composite materials for engineering applications, because of their unique mechanical properties, such as elastic behavior at very large deformation, energy absorbing capability, and so on. In the recent past, price escalations combined with the sporadic and possible future shortage of resins and petroleum feedstock have hinted at an urgent need for more economical utilization of fillers. Composite systems offer a means of

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extending the available volume of resins while improving many of their properties in association with economic advantages.

Many types of fillers are in use for enhancement of properties. Carbon black is the most widely used filler in rubber industries. Carbon black is popular due to its higher surface area and particulate nature, which imparts high reinforcing ability. But nowadays, more attention is being paid to non-black mineral fillers like silica [1], clay [2], and mica [3] due to high prices and monotonous color of carbon black. In the search of reducing cost of composites, new materials are being considered to replace totally or partially the conventional ones as a simple economical measure or to impart some desirable properties [4–5].

Flyash is a well-known mineral noted for its very fine particle size with outstanding electrical, heat, and chemical resistance. Most varieties of flyash contain silica and alumina as a major constituent with oxides of potassium, sodium, and phosphorous in various proportions depending on the source and variety of coal [6].

Traditionally, flyash has been used as filler in the construction [7] and agriculture [8] sectors. More recently its use as filler in epoxy [9–12] and thermoplastics [13–14] has been studied, but studies on its use in rubber are still rare [15–17]. This article presents results from the partial replacement of carbon black in SBR. The results of mechanical properties are discussed in the light of polymer filler interaction and morphology study of fracture surfaces of the composites.

EXPERIMENTAL

Materials

Elastomer

Styrene butadiene rubber [SBR Hyundai Techlen 1502] manufactured by Goodyear Tyre and Rubber Company, USA, was used.

Fillers

Carbon black (Grade N-330) from Degussa Corporation (Akron OH, USA), was used in this work. Flyash was procured from Thermal Power Station (Deepnagar, Bhusawal [MS], India). Physico-chemical properties of flyash and carbon black are shown in Tables 1 and 2, respectively.

Other Chemicals

Other chemicals such as stearic acid, zinc oxide, sulphur, dimercaptobenzothiazil disulphide (MBTS), zinc-N-dimethyl dithio

TABLE 1 Physico-Chemical Properties of Flyash

Properties	Observations
Color	Gray
Particle shape	Spherical
Average particle size (μM)	4–5
Bulk density (g/cc)	0.8
Specific gravity	2.1–2.6
Moisture content (%)	4.0–5.0
pH	7.0–7.5

TABLE 2 Physico-Chemical Properties of Carbon Black

Properties	Observations
Grade	N-33
Color	Black
Average particle size (nM)	28
BET surface area (m^2/g)	75
DBP absorption (ml/100 g)	103
pH	7.0–7.5
Type	HAF (Furnace)

carbamate (ZDEC), and phenyl-β-naphthyl amine (PBN) used in the work were manufactured by Bayer India Limited.

Preparation of Mixes and Test Sample

Flyash was dried at 120°C and carbon black at 125°C for 2 h immediately before use. Mixes formulations are given in Table 3. Mixing was carried out on a two-roll mill at a friction ratio 1.2:1. Mixes were cured for 35 min in an electrically heated hydraulic press at 140°C under pressure of 10 MPa.

Characterization of the Composites

The cured sheets were conditioned at 27°C and at relative humidity of 65% for 24 h before being subjected to testing of the mechanical properties. Tensile properties were determined according to ASTM D-412 on UTM-2302 supplied by R&D Equipment Ltd., Mumbai. The crosshead speed was 50 mm/min. Hardness was determined

TABLE 3 Formulation

Materials	Phr
SBR	100
i Lubricant	2.0
ii Activator	3.0
iii Accelerator	0.6
iv Accelerator	0.5
v Oxidant	1.0
vi Curing agent	1.8
filler	Variable

Stearic acid (i), Zinc oxide (ii), MBTS (iii), ZDEC (iv), PBN (v).

using Shore-A scale of Durometer hardness tester according to ASTM D-2240.

Morphological Study

Studies on the morphology of the tensile fracture surfaces of the composites were carried out using a Cemeca SU 30 Scanning Electron microscope. The objective was to obtain some information regarding filler dispersion and bonding quality between filler and matrix and to detect the presence of microdefects, if any. The fractured ends of the specimen were sputter coated with a thin layer of gold to avoid electrostatic charging during examination.

Polymer–Filler Interaction

Polymer–filler interaction was studied to understand the reinforcement phenomenon in the elastomer composites.

Samples weighing 0.2–0.3 grams were allowed to swell in excess toluene at room temperature until equilibrium swelling was achieved. Then the swollen samples were weighed and solvent was removed by drying for six days at room temperature and were weighed again. The volume fraction of rubber in the swollen vulcanizate (V_r) was then calculated by the following relation:

$$V_r = \frac{(D - FT)/\rho_r}{(D - FT)/\rho_r + A_0/\rho_s}$$

where T is the sample weight, D is deswollen weight, F is weight fraction of the insoluble component, and A_0 is the weight of the absorbed solvent corrected for swelling increment. The densities of rubber and solvent are represented by ρ_r and ρ_s, respectively.

RESULTS AND DISCUSSION

Physico-mechanical properties for the SBR compositions with varied content of flyash (0–50 phr) (with fixed quantity of carbon black [10 phr]) are graphically represented in Figures 1 through 4, and are summarized in Table 4.

Elongation and tensile strength data from carbon black–flyash–SBR formulations showed better results when 20 phr flyash and 10 phr of carbon black were used. It is noteworthy that these results are better than those shown by composites containing carbon black (10 phr) and flyash (10–120 phr) separately [18]. However, as the flyash content was increased beyond 20 phr, a decrease of tensile properties was observed. These properties are substantially affected by changes in crosslink density [19]. Tensile strength increases with crosslink density up to some intermediate crosslink density and then decreases with further crosslink formation. On the other hand, modulus increases continuously as the crosslink reaction progresses. This behavior is in good agreement with the data obtained by polymer–filler

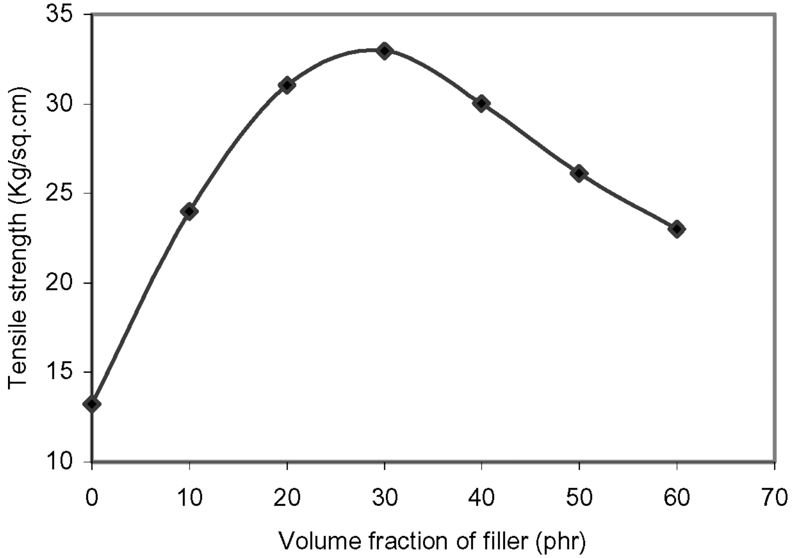


FIGURE 1 Tensile strength as a function of volume fraction of filler.

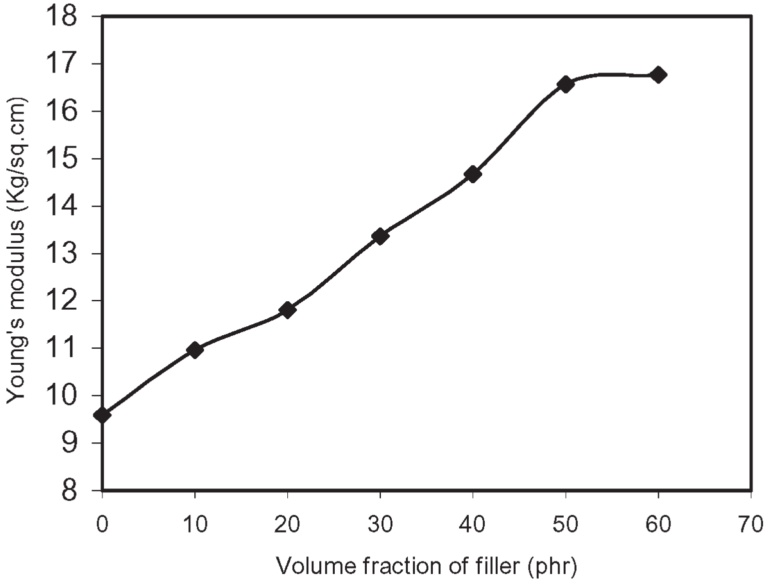


FIGURE 2 Young's modulus as a function of volume fraction of filler.

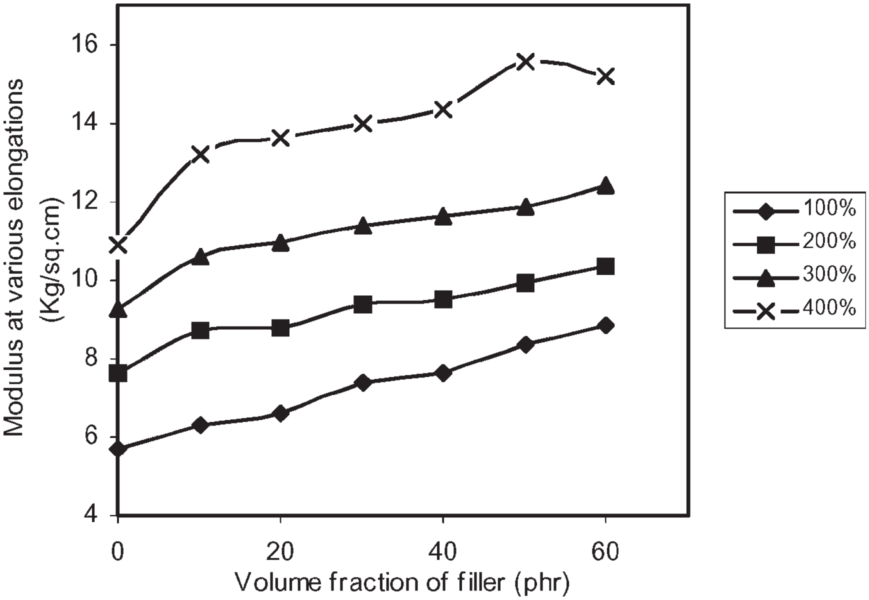


FIGURE 3 Modulus at various elongations as a function of volume fraction of filler.

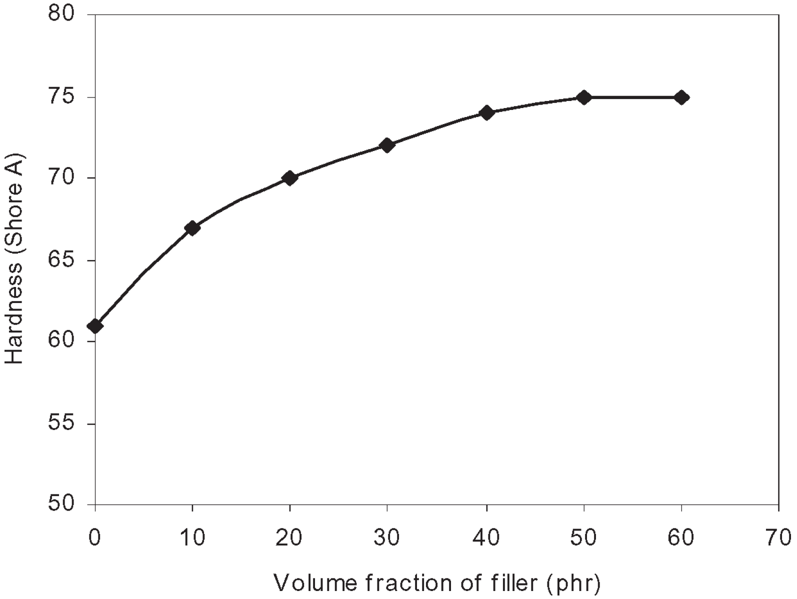


FIGURE 4 Hardness as a function of volume fraction of filler.

interaction studies, where the composition 20–10–100:flyash–carbon black–SBR seems to have the highest crosslink density.

Elongation at break shows a maximum value with formulation 20:10 flyash:carbon black as fillers and decreases in the presence of higher content of flyash. However, with only flyash as a filler, this

TABLE 4 Technical Properties of Filled Composites

Phr of carbon black:flyash	Tensile strength kg/cm^2	Young's Modulus kg/cm^2	Modulus at 100% kg/cm^2	Modulus at 200% kg/cm^2	Modulus at 300% kg/cm^2	Modulus at 400% kg/cm^2	Hardness Shore-A	Volume fraction of swollen rubber (V_r)
0:0	13.22	9.59	5.71	7.63	9.26	10.92	61	0.1832
10:0	24.00	10.96	6.28	8.72	10.62	13.19	67	0.1850
10:10	31.05	11.80	6.60	8.77	10.97	13.63	70	0.1725
10:20	32.96	13.36	7.37	9.37	11.36	13.99	72	0.1669
10:30	30.02	14.67	7.60	9.50	11.63	14.34	74	0.1531
10:40	26.13	16.56	8.35	9.95	11.87	15.52	75	0.1528
10:50	23.03	16.77	8.86	10.37	12.40	15.16	75	0.1469

property presents a high value, probably due to a decrease in the crosslink density [18].

The similarity of the hardness value for all compositions was already expected as compositions, either containing pure carbon black or with flyash, show very high magnitudes, ranging from 72 to 80, compared to gum vulcanizate at 57 only.

These behaviors can be explained considering that the physico-mechanical properties of the vulcanizates depend on the filler characteristics as well as on polymer properties, chemical compositions, operational conditions, and adhesion degree [19].

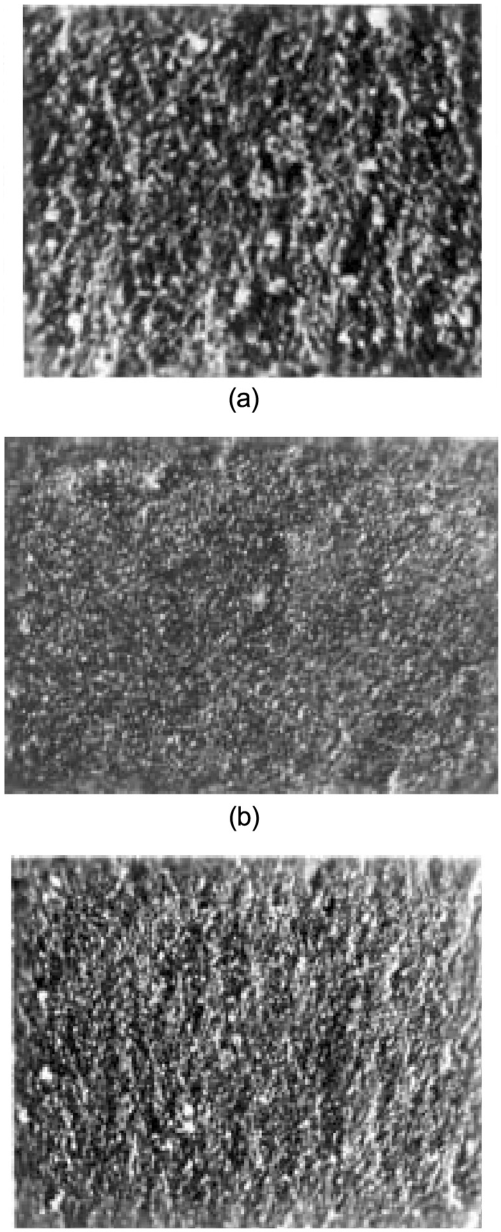
The most important filler characteristics are size, shape, specific surface area, and a combination of the size distribution and shape; that is, the particles packing ratio. The fillers used in this work were of very different primary characteristics, as can be seen in Tables 1 and 2. As is well-established, carbon black has much greater surface area compared to that of flyash. This is primarily due to two factors, namely porosity of structure of carbon black and its very small particle diameter (of the order of 20–30 nm) compared with the rigid structure of flyash and relatively large particle size (2–4 μm).

The combination of these two fillers is presumed to form a dense structure with the voids between flyash particles being occupied by carbon black and polymer. Thus the structure of filler and co-filler provided a favorable packing for reinforcement. This favorable orderliness was naturally dependent on the quantity of flyash and carbon black, which was at its best at the 10:20 carbon black–flyash composition.

Further work relating to interaction of co-fillers with other rubbers is being conducted.

The polymer–filler interaction, that is, the adhesion degree at the surface of the two components also exerts a considerable influence on the mechanical properties of vulcanizates [20]. Information about the nature of this adhesion and the relationship between structure and mechanical properties can be obtained by scanning electron microscopy of fracture surface of the composites [21–23].

Figure 5 shows tensile fractographs of flyash–carbon black–filled compositions. The failure pattern changes in presence of filler (Figure 5a–c). The presence of debonded flyash particles indicates poor polymer–filler interaction (Figure 5c) whereas in SBR–carbon black–flyash composition (Figure 5b) straight fracture path and rough failure surface show higher polymer–filler interaction, which results in good mechanical performance. The fracture surface of the formulations with 20 phr of flyash and 10 phr of carbon black (Figure 5b) is very similar to that of the composition, which contains only carbon black (Figure 5a).



(a)

(b)

(c)

FIGURE 5 Scanning electron micrographs of composites.

As flyash loading increases (at the expense of carbon black), the straight fracture path decreases and a greater number of debonded flyash particles appear in the SEM fractograph of the tensile fracture surface, which support the tensile properties.

Figure 5c shows some pits, which appear on the surface of flyash–carbon black compositions. This photograph shows the poor polymer–filler interaction in the high flyash–SBR compositions and the enhancement of the pits size as more flyash is incorporated, which corroborates the mechanical behavior.

CONCLUSION

This investigation proved that flyash can be a cheap low active filler and be recommended as a partial replacement of carbon black in SBR formulations.

It was established that the otherwise less useful filler flyash could act as a benevolent co-filler in combination with carbon black. The properties of the vulcanizates are retained (in fact improved) up to 40-phr addition of flyash. This means that the percentage of carbon black can be reduced to save cost. Optimum (highest) improvement was observed for composition of 10:20 carbon black–flyash ratio. The improvement was observed up to 8% whereas higher quantities of flyash also showed reinforcement at 10:40 carbon black–flyash ratio.

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