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Development and Characterization of Fly Ash/Crumb Rubber Reinforced Natural Rubber Composite

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The aim of this study is to evaluate the feasibility of utilizing fly ash and crumb rubber derived from tyre waste with natural rubber to develop a composite material with improved properties. The composites were evaluated for morphological, thermal and mechanical properties. It was found that with increase in crumb rubber loading, tensile strength, tear strength, abrasion resistance and skid resistance of the composites increased whereas water absorption, compression set, hardness and density decreased up to 120 phr of crumb rubber concentration. SEM micrographs show that fly ash/crumb rubber reinforced natural rubber composites have enhanced rubber-filler interaction to produce more continuous and interlocked structure than fly ash reinforced natural rubber composite.

Keywords: Fly ash, Crumb rubber, Natural rubber, Composites, Properties.

INTRODUCTION

Fly ash generated by the combustion of pulverized coal in thermal power plants and scrap tyres derived from the used tyres are considered as major environmental pollutants. With increasing demand of electricity and automobiles, the annual production of fly ash and scrap tyres are also increasing in large amount all over the world out of which very less quantity is being utilized for different applications. Therefore, it has become highly essential to develop technologies for bulk utilization of these solid wastes.

Fly ash has many properties like high silica content, particle size distribution, morphology and surface characteristics that make it a suitable material to be used as reinforcing filler in polymer composites [1-4]. Scrap tyres are reprocessed to prepare crumb rubber by different methods like cracker mill process, granular process and micro-mill process [5]. Some studies have shown that crumb rubber can be used in various construction applications [6-10]. It is most commonly used in the asphalt pavement industry. Introduction of crumb rubber into asphalt produce crumb rubber modified asphalt. This rubberized asphalt can then be used as part of the hot mix asphalt to construct roads and highways [11-21]. However, the extent of production of fly ash and scrap tyres is much more than extent of their utilization. Therefore, considerable efforts are required to find solution of the problem by utilizing these wastes in new areas where they can be consumed in large amount.

Sombatsompop and Kumnuantip [22] studied the effect of addition of tyre-tread reclaimed rubber on the properties of two natural rubber compounds with respect to the reclaimed rubber concentration and mastication time. For vulcanized rubbers, it was also observed that 100 % modulus of the rubber increased with reclaimed rubber content. The hardness and heat buildup properties of the vulcanizates increased with reclaimed rubber content whereas the tear strength became independent of the reclaimed rubber. In an another research work of Phadke *et al.* [23] studied the effect of addition of cryoground rubber to natural rubber that causes changes in curing characteristics (decrease in Mooney scorch time, optimum cure time and reversion time) and shows a detrimental effect on most of the vulcanizate properties (tensile, resilience, flex, hysteresis, set and abrasion). Tear strength, however, is not adversely affected by cryoground rubber.

Yilmaz and Degirmenci [24] investigated the feasibility of utilizing fly ash and rubber waste with Portland cement as a composite material for masonry applications and found that the composite containing 10 % Portland cement, 70 and 60 % fly ash and 20 and 30 % tyre rubber particles have sufficient strength for masonry applications. Prasad and Raju [25] have evaluated the performance of flexible pavement on expansive soil subgrade using gravel/flyash as subbase course with waste tyre rubber as a reinforcing material.

Bala *et al.* [26] studied the influence of flyash and waste tyre rubber particles on the behaviour of concrete composite.

The rubber content has been taken in the range of 0 to 40 % as replacement of fine and coarse aggregates while the flyash has been varied from 0 to 30 % for cement. Experimental results showed that the density, compressive strength and bond strength of the concrete decreased while workability increases with increasing rubber content. Addition of fly ash also decreases the density and compressive strength.

The above studies have shown that though extensive research work on use of crumb rubber for construction applications has been carried out, very few research investigations has been carried out where crumb rubber has been used with natural rubber and fly ash to develop composites. In an earlier study Maan *et al*. [27,28] have prepared rubber composites with varying percentage of fly ash (0-600 phr), characterized them for various mechanical properties and optimized the formulation with 400 phr fly ash. In the present study, crumb rubber derived from scrap tyres have been used alone with fly ash for making fly ash/crumb rubber reinforced natural rubber composites. Composites were made using 400 phr concentration of fly ash with varying concentration of crumb rubber in natural rubber matrix and have been studied for morphological, thermal and mechanical properties *viz*., tensile strength, tear strength, skid resistance, abrasion resistance, compression set, hardness, density and water absorption for use in sidewalk pavement tiles, car mats, door mats, *etc*.

EXPERIMENTAL

Crumb rubber having particle size 30 mesh and carbon black content 28 % was procured from Arihant Oil and Chemicals, India. Fly ash was collected from Badarpur Thermal Power Plant, Delhi. The chemical composition of fly ash is given in Table-1. Natural rubber in the form of pale crepe was locally procured. Zinc oxide was procured from SD Fine Chemical Ltd. and stearic acid from Sigma-Aldrich, USA for use as an activator in the compositions. 1,3-Diphenyl guanidine and 2-mercaptobenzothiazole accelerators were procured from Merck Millipore, Germany. Sulfur for use as vulcanizing agent was procured from Merck Millipore, Germany. All the additives were used as such without any further purification.

Preparation fly ash/crumb rubber reinforced natural rubber composite: The composites were prepared by incorporating crumb rubber, fly ash and other additives in natural rubber matrix. The compound recipe is given Table-2. Natural rubber was first masticated on a laboratory two-roll mill for 3-5 min. Subsequently, natural rubber was compounded with crumb rubber and fly ash in the two roll mill for another 10 min. Activators, accelerators and sulfur were then added in the composition and milling was continued for next 15 min. The compounded material was then molded at 160 °C and 30 tons pressure in a compression molding machine in the form of a sheet having dimensions 150 mm × 150 mm × 6 mm. Post curing of prepared fly ash rubber sheet was done at 100 °C for 1 h in an air oven.

Characterization of fly ash-rubber composite: Determination of tensile and tear strength of the composites were carried out using a Universal Testing Machine (H50KT, Tinius Olsen, UK) at a speed of 500 mm/min [29,30].

Scanning electron microscopy (SEM) studies were performed by using EVO 18 Special Edition (Zeiss, Germany) for imaging. The samples were mounted on aluminum stub with the help of double-sided adhesive carbon tapes (Agar Scientific, UK). The mounted samples were exposed to about 20 nm gold coating at 20 mA for 165 s by sputter coater SC7620 (Quorum technologies Ltd., UK) to make them electrically conductive.

The abrasion resistance test was carried out according to ASTM D 4060-10 [31]. Abrasion resistance was calculated as loss in weight after 1000 abrasion cycles. Skid resistance test was performed using Wessex skid resistance tester and reported as the British Pendulum Number (BPN) [32].

Compression set test was carried out at 27 °C for 24 h with the applied compression of approximately 25 % of the original thickness of the specimen [33]. Compression set was calculated from the following formula:

$$\text{Compression set (\%)} = \frac{t_o - t_1}{t_o - t_s} \times 100$$

where, t_o is initial thickness of the test piece (mm), t_1 is thickness of the test piece after recovery (mm) and t_s = height of the spacer (mm).

Hardness of fly ash rubber composite was determined by using a Shore A type Durometer [34]. Water absorption of the samples was determined according to IS 5382 [35].

Thermogravimetric analysis (TGA) was done for the rubber composite using an SDT-TGA analyzer (TA Instrument, USA) at the heating rate of 5 °C/min under the nitrogen atmosphere in the temperature range of 25 to 1000 °C to observe the weight loss at different temperatures.

RESULTS AND DISCUSSION

The various properties of the fly ash/crumb rubber reinforced natural rubber composites are given in Fig. 2 and are also summarized in Table-3.

TABLE-1
COMPOSITION OF FLY ASH

Chemical composition of fly ash											
Components	SiO_2	Al_2O_3	Fe_2O_3	CaO	Na_2O	TiO_2	SO_3	MgO	MnO	K_2O	LOI
Composition (%)	57.4	31.8	4.6	0.6	0.2	1.7	0.1	0.2	0.2	0.6	2.7

TABLE-2
FORMULATIONS OF FLY ASH/CRUMB RUBBER REINFORCED NATURAL RUBBER COMPOSITE

Ingredients	Natural rubber	Fly ash	Crumb rubber	ZnO	Stearic acid	MBT	DPG	Sulfur
Amount (phr)	100	400	0-240	5.0	2.0	0.5	0.2	2.5

TABLE-3
PHYSICO-MECHANICAL PROPERTIES OF FLY ASH/CRUMB RUBBER REINFORCED NATURAL RUBBER COMPOSITES AT DIFFERENT CONCENTRATIONS OF CRUMB RUBBER

Crumb rubber concentration (phr)	Hardness (Shore A)	Density (g/cm^3)	Tensile strength (kg/cm^2)	Weight loss (g)	Skid resistance (BPN)	Compression set (%)	Water absorption (%)	Tear strength (N/mm)
0	88	1.85	28	0.34	50	18	0.80	14.0
40	86	1.74	32	0.18	52	14	0.55	16.4
80	84	1.69	36	0.15	56	9.5	0.33	18.5
120	82	1.65	38	0.14	59	8.0	0.21	20.4
160	81	1.61	35	0.12	61	8.6	0.09	18.8
200	80	1.57	33	0.10	63	9.1	0.06	17.9
240	78	1.55	31	0.10	64	9.5	0.04	17.6

The effect of variation of crumb rubber on tensile strength of natural rubber composites is shown in Fig. 2a. With increase in crumb rubber concentration tensile strength increased up to 120 phr because of the improved reinforcement *i.e.* provided by the carbon black present in the crumb rubber and also the material became more elastic due to the presence of crumb rubber. Thereafter tensile strength decreased marginally with higher loadings of crumb rubber; this may be due to the insufficient voids present in the rubber matrix to hold more crumb rubber particles and consequent less probability of

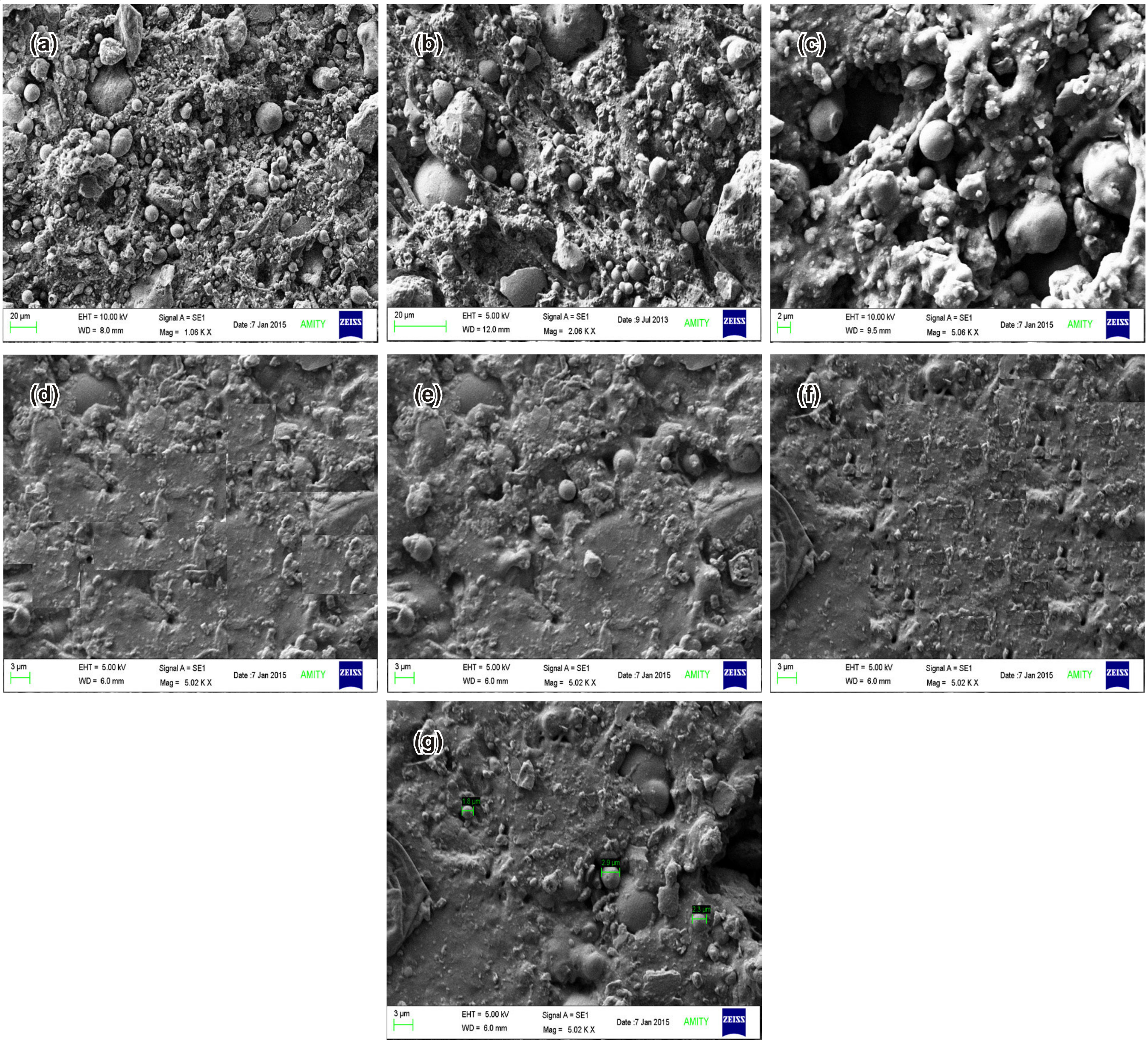

Fig. 1. SEM photographs of fly ash-natural rubber composite with (a) 0 phr crumb rubber; (b) 40 phr crumb rubber; (c) 80 phr crumb rubber; (d) 120 phr crumb rubber; (e) 160 phr crumb rubber; (f) 200 phr crumb rubber; (g) 240 phr crumb rubber at 400 phr fly ash concentration

rubber-filler interaction. Similar trend was observed for the effect of crumb rubber concentration on tear strength of composites as in case of tensile strength and can be explained in similar line (Fig. 2b).

It can be seen from the SEM micrographs given in Fig. 1a-1g that fly ash and crumb rubber are homogeneously distributed in the natural rubber matrix in all the compositions used in the experiments. It is evident that crumb rubber incorporated in the composites improved the dispersion of the ingredients in the matrix resulting in more reinforcement and consequently better physico-mechanical properties as compared to composite having no crumb rubber in its composition (Fig. 1a). It may be due to fact that fly ash/crumb rubber reinforced natural rubber composites have enhanced rubber-filler interaction to produce more continuous and interlocked structure than fly ash reinforced natural rubber composite without crumb rubber.

With increase in crumb rubber concentration, skid resistance of the fly ash/crumb rubber reinforced natural rubber composites increased as shown in Fig. 2c. This may be due to the fact that with the incorporation of crumb rubber in the polymer matrix, the surface of the composite became rough because of the presence of coarser crumb rubber particles on the surface of the composites causing improvement in skid resistance.

Fig. 2d showed that the abrasion resistance increased with increase in concentration of crumb rubber as evidenced by gradual decrease in weight loss. This may be due to the larger surface area of the carbon black present in the crumb rubber for better filler-rubber interfacial adhesion in the composites as evident in the SEM micrographs.

Compression set of the developed composites decreased with increasing concentration of crumb rubber up to 120 phr, this is due to the improvement in reinforcement caused by the crumb rubber particles and thereafter slightly increased as shown in Fig. 2e. This may be due to the insufficient sites in polymer matrix to bind more crumb rubber particles.

From the Fig. 2f, it is observed that with increase in crumb rubber loading, hardness decreased. It is due to the fact that

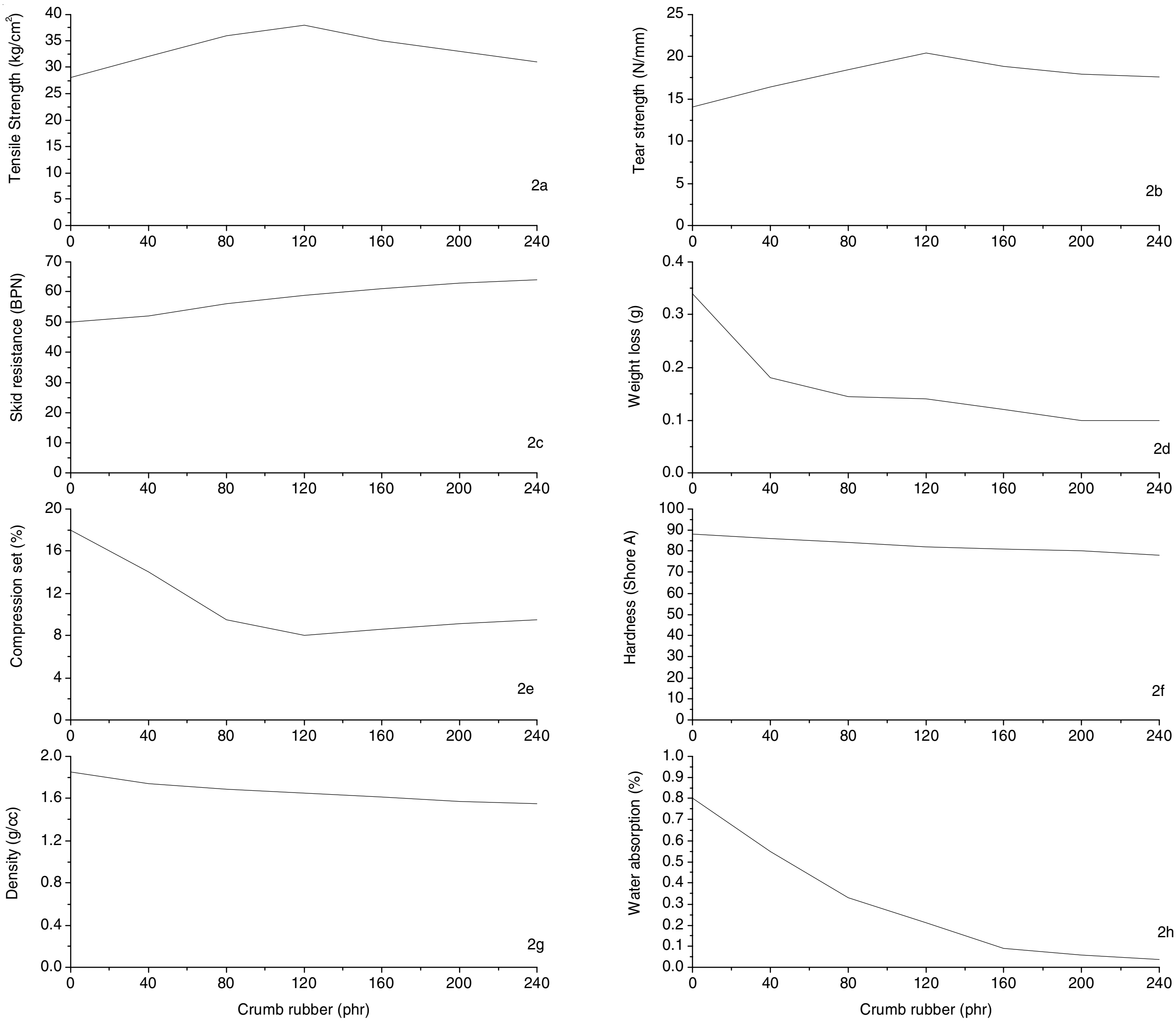

Fig. 2. Properties of fly ash-rubber composite using different crumb rubber concentrations at 400 phr fly ash content (2a. Tensile strength; 2b. Tear strength; 2c. Skid resistance; 2d. Weight loss; 2e. Compression set; 2f. Hardness (Shore A); 2g. Density; 2h. Water absorption)

the presence of crumb rubber increased the overall rubber content in the composite material resulting in more flexible vulcanizates, thereby decreasing the hardness.

The effect of variation of crumb rubber on density of natural rubber composites is shown in Fig. 2g. With increase in loading of crumb rubber density decreased. It is because of the reason of low specific gravity of crumb rubber particles. Water absorption decreased significantly with increase in crumb rubber concentration (Fig. 2h). It may be due to the fact that availability of hydrophilic fly ash surface decreases with increase in hydrophobic crumb rubber loading resulting in overall decrease in water absorption of the composites.

Thermogravimetric analysis was performed to observe the comparative weight loss at different temperatures. Thermogravimetric analysis has also been used to measure the thermal stability and decomposition behaviour of fly ash-rubber composite on heating. The weight loss at the temperature less than 200 °C was due to the release of trapped volatile materials. Then the thermal decomposition of the polymer matrix occurred between 250 and 450 °C. From Fig. 3 it was observed that composites having crumb rubber has less residual mass when compared with composite without crumb rubber at the same temperature range.

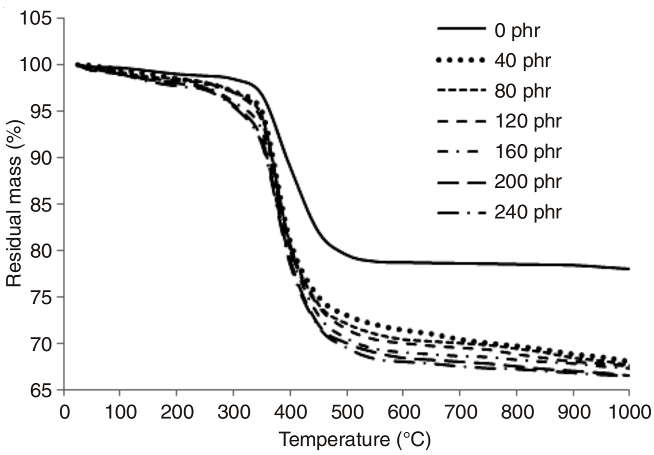

Fig. 3. TGA curve of fly ash-rubber composite at different crumb rubber concentration at 400 phr fly ash content

Conclusion

In this study fly ash/crumb rubber reinforced natural rubber composites were prepared by varying crumb rubber concentration at a particular fly ash loading and characterized for different properties. The experimental observations reveal that with the addition of crumb rubber in the polymer matrix, tensile strength, tear strength, skid resistance and abrasion resistance of the composites increased whereas hardness, compression set and water absorption decreased at upto 120 phr crumb rubber concentration and beyond that decreased or levelled off. Density steadily decreased with increase in crumb rubber content. Incorporation of fly ash and crumb rubber in natural rubber composites results in an economical and light weight material which can be used in applications like jogging tracks, garden hoses, floor mats, tiles, horse trails, *etc*. as these composites are more durable and flexible as compared to traditional materials. The present research work has great potential in lowering the environmental pollution by utilizing the solid wastes like fly ash and tyre waste derived crumb rubber for making value-added products.

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