Mechanical Properties of Natural Rubber Filled with Flyash

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ABSTRACT: The mechanical properties of flyash-filled natural rubber were investigated and compared with those filled with calcium carbonate. A number of composites with varying percentage of the fillers were prepared using a two-roll mill and molded on compression molding press. Specimens were subjected to mechanical testing. The properties studied were tensile strength, modulus at various elongations, hardness, density, etc. From the results it was observed that flyash-filled composites were better in mechanical properties compared to those filled with calcium carbonate. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 85: 995–1001, 2002

Key words: elastomers; fillers; mechanical properties

INTRODUCTION

Influence of particulate filler on deformability of a polymer was earlier considered to be purely hydrodynamic. However, later it was proven that specific interaction between the filler and matrix is very important in imparting reinforcement. A relatively easy way to improve mechanical properties of a polymer is generally achived by incarporating fillers. In general, inorganic fillers are applied to improve the stiffness.[1] The most generally used fillers in rubber industries are carbon black, silica, calcium carbonate, zinc oxide, magnesium oxide, talc, mica, resins, etc.[2–8] A study on the chemical nature of a filler on mechanical properties of filled polybutadiene has been reported.[9] Besides the above-referred fillers flyash has also been studied as a filler in PP/PMMA/FA blends[10] and elastomers.[11,12]

In this study, composites of natural rubber filled with flyash with different compositions have been prepared and the effect of incorporation of flyash on mechanical properties has been determined. The results are compared with those of natural rubber–calcium carbonate-filled composites. Because flyash is a waste product generated in very huge quantities (by thermal power stations) it is posing a problem of disposal. The relevance of this study could help in solving the problem of disposal of flyash up to a certain extent, and the polymer industry will get the most economical filler.

EXPERIMENTAL

Materials

The reference filler microcarb-ls-5010 (calcium carbonate, filler grade) was manufactured by 20 Microns Ltd., Vadodara, India. Flyash (the filler under study) was procured from Thermal Power Station, Deepnagar, Bhusawal (MS) India. Other chemicals used were manufactured by Bayer India Ltd. The Following recipe was used to make the composites.

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Recipe

Constituent	phr
Natural rubber	100
Stearic acid	3
Zinc oxide	5
Sulphur	3
Mercaptobenzothiazyldisulphide	1
Phenyl β naphthyl amine	1
Filler	variable
Curing time.	40 min.
Curing temp.	140°C

Preparation of Sheet/Specimens

A two roll mill was used for compounding and mixing. The compounded material was kept in a mold, and was cured under pressure and heat (dimensions of 150 × 150 × 3 mm). The temperature of the compression mold was kept at 140°,[13,14] and the curing was carried out for 40 min. The molded sheets were subjected to conditioning for 24 hs. The dumbbell-shaped specimens in conformation with ASTM D-412 were subjected to Universal Tensile Machine for measurement of tensile strength, modulus at different percentage elongations, etc.

MEASUREMENTS

Tensile properties were measured on a computerized Universal Testing Machine. The tests were carried out according to a ASTM D-412 test procedure. Hardness was measured by Durometer (Shore-A), while density was measured by the conventional emersion method.

Scanning Electron Microscopy (SEM)

To study the extent of dispersion of the filler in the composites, SEM studies were carried out by a vacuum sputtering technique, and the specimens were scanned on a Cemeca (France) model SU-30. Figures 7 and 8 show Scanning Electron Micrographs (SEM) of the composites containing the maximum volume fraction of fillers viz. flyash and calcium carbonate, respectively.

Particle Shape Analysis

Particle shape analysis was carried out for flyash and calcium carbonate. It was analyzed using Olympus Microscope STM-312. From the photograph it was observed that the particle shape of the flyash is spherical while for calcium carbonate it was random, as shown in Figures 9 and 10.

RESULTS AND DISCUSSION

Mechanical properties like tensile strength, modulus at 100, 200, and 300%, elongation at break,

Table I Mechanical Properties of Natural Rubber–Flyash Composites

Volume Fraction	Tensile Strength (MPa)	Modulus at 100% (MPa)	Modulus at 200% (MPa)	Modulus at 300% (MPa)	Modulus At 400% (MPa)	Elongation %	Hardness (Shore-A)	Density (g/cc)
0	3.610	0.518	0.800	1.076	1.345	1597	41	0.9552
0.105	9.152	0.505	0.765	1.014	1.276	1587	45	1.0366
0.142	9.713	0.543	0.822	1.071	1.315	1622	46	1.0583
0.207	12.128	0.598	0.952	1.260	1.716	1630	48	1.0751
0.248	12.080	0.595	0.949	1.324	1.717	1597	49	1.1002
0.312	13.320	0.654	1.030	1.382	1.760	1570	52	1.1453
0.353	12.928	0.703	1.086	1.447	1.867	1502	55	1.1921
0.455	10.220	0.845	1.196	1.533	1.850	1467	60	1.2375
0.459	10.017	0.823	1.230	1.522	1.730	1458	63	1.2563
0.499	8.587	0.867	1.221	1.526	1.847	1255	63	1.2659
0.510	8.003	0.833	1.211	1.485	1.729	1401	65	1.2874
0.557	7.148	0.784	1.206	1.392	1.531	1384	67	1.3133
0.559	7.842	0.772	1.091	1.331	1.659	1448	67	1.3243
0.571	7.466	0.771	1.048	1.230	1.582	1209	69	1.3361
0.574	7.230	0.967	1.075	1.233	1.504	1065	69	1.3460

Table II Mechanical Properties of Natural Rubber–Calcium Carbonate Composites

Volume Fraction	Tensile Strength (MPa)	Modulus at 100% (MPa)	Modulus at 200% (MPa)	Modulus at 300% (MPa)	Modulus at 400% (MPa)	Elongation %	Hardness (Shore-A)	Density (g/cc)
0	3.610	0.518	0.800	1.067	1.345	1597	41	0.9557
0.122	3.940	0.403	0.647	0.857	1.067	1277	43	1.0186
0.139	4.095	0.420	0.607	0.823	1.052	1154	44	1.0411
0.203	4.479	0.422	0.788	1.103	1.417	1231	44	1.0619
0.229	4.952	0.428	0.882	1.328	1.404	1370	46	1.0829
0.259	5.127	0.472	0.770	1.067	1.382	1260	48	1.1038
0.279	5.880	0.471	1.188	1.539	1.904	1144	50	1.1241
0.318	6.545	0.795	1.201	1.597	1.785	1264	51	1.1462
0.349	6.387	0.804	1.262	1.651	1.794	1160	55	1.1878
0.391	5.758	0.850	1.348	1.750	2.214	1231	60	1.2412
0.448	5.372	0.885	1.330	1.697	2.212	1361	65	1.2812
0.529	4.200	0.509	0.805	1.050	1.312	1174	70	1.3229

hardness, and density of flyash and calcium carbonate-filled natural rubber were studied, the results of which are shown in Tables I and II, respectively.

Tensile Strength

It was observed that in both cases (as the volume fraction of filler increased) tensile strength of the composite increased initially and decreased subsequently (after attaining the maximum magnitude) as the volume fraction of filler in the compoisites (Fig. 1). This was not unexpected because, at a low volume fraction of the filler the matrix material was in large quantity, so that all filler particles were capable of being completely wetted by the matrix material while at higher volume fractions of the filler the matrix (i.e., elastomer) was incapable of wetting the filler. This resulted in heterogeneity in the composites leading to deterioration of properties.

The results also indicated that flyash-filled composites showed better tensile properties than the calcium carbonate filled composites. The rate of increment in tensile strength was much higher for flyash-filled composites. The maximum in ten-

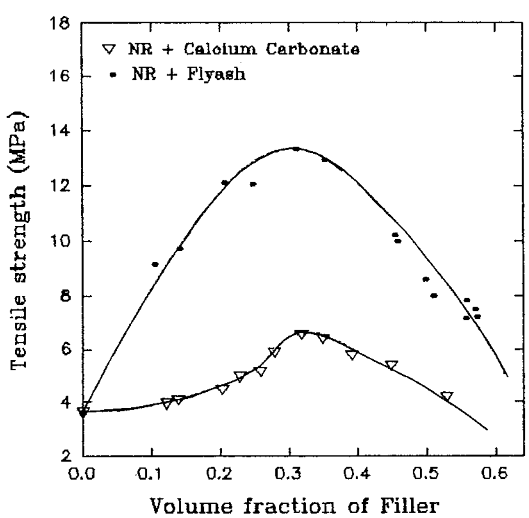

Figure 1 Tensile strength as a function of volume fraction of the filler.

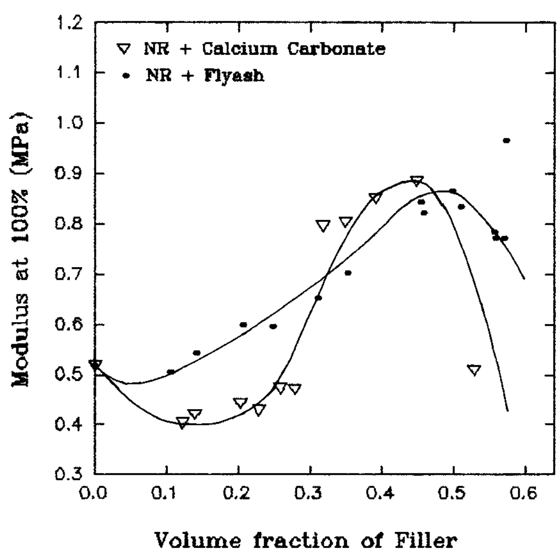

Figure 2 Modulus at 100% as a function of volume fraction of the filler.

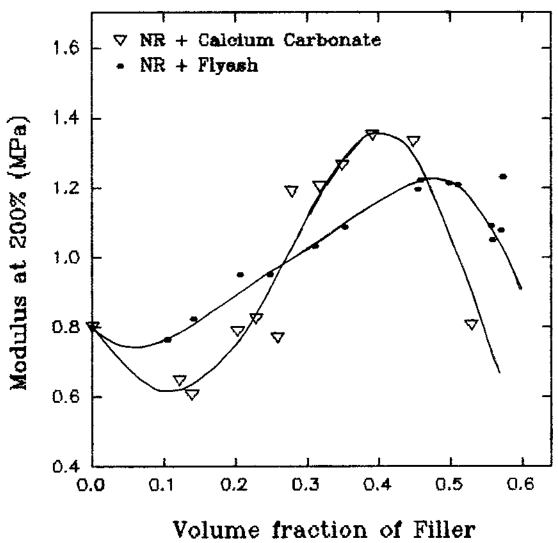

Figure 3 Modulus at 200% as a function of volume fraction of the filler.

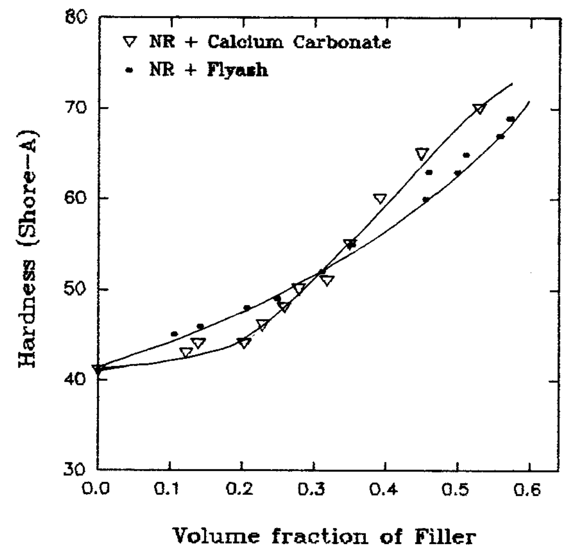

Figure 5 Hardness as a function of volume fraction of the filler.

sile strength occured at the same volume fraction of filler in both cases. The values for the flyash-filled composite is 13.32 MPa, while for calcium carbonate-filled composite it is only 6.54 MPa. The higher values shown by flyash-filled composites can be attributed to spherical shape of the particle, which provided substantial wetting, whereas calcium carbonate particles being random in shape, the composites showed low strength (Figs. 9 and 10).

Modulus at Various Elongations

Figures 2, 3, and 4 showed effect of filler on modulus at 100, 200, and 300% elongation for the natural rubber–flyash-filled composites and natural rubber–calcium carbonate-filled composites, respectively. It was observed that modulus at various elongations of composite initially decreased with filler incorporation. The rate of decrement in the case of calcium carbonate-filled composites

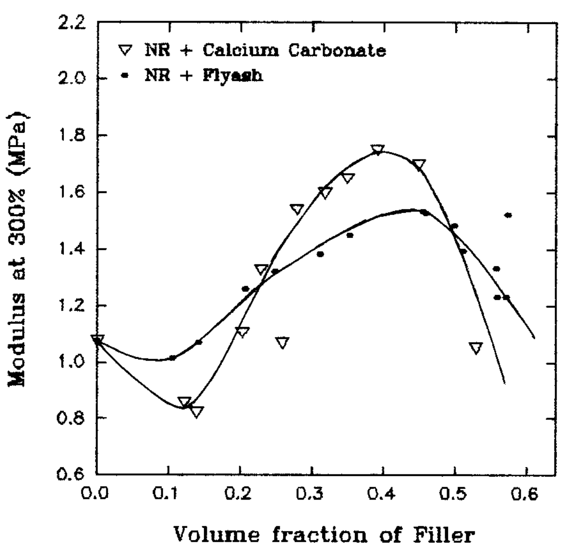

Figure 4 Modulus at 300% as a function of volume fraction of the filler.

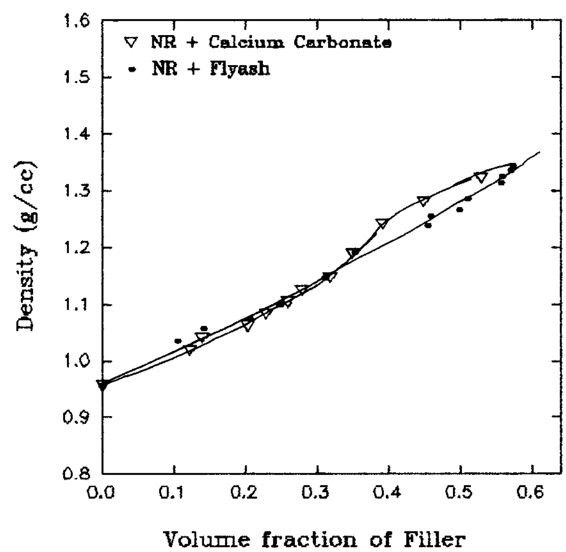

Figure 6 Density as a function of volume fraction of the filler.

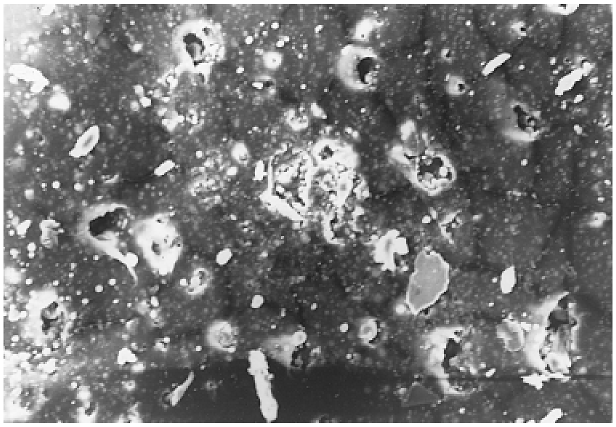

Figure 7 SEM of natural rubber–flyash composite at volume fraction 0.571.

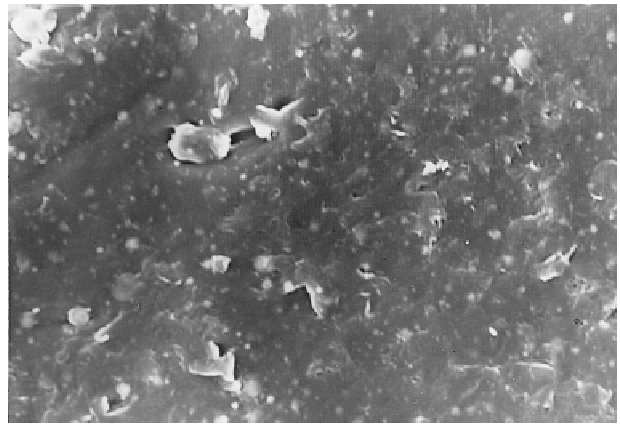

Figure 8 SEM of natural rubber–calcium carbonate composite at volume fraction 0.529.

was higher for all the three elongations (100, 200, and 300%). This was rather surprising, as fillers are customerily added to enhance the modulus. Eirich[15] has summarized a general study of composites, and clarified that the presence of load-bearing or dissipating microelements with their phase boundaries lead to a decrease in microstress concentration. At higher volume fraction of filler stresses tended to initiate local rupture and microdomain boundaries. However, these are too small to cause fracture on a microscopic scale. Thus, cracks are limited by microinhomogeneity and cannot proceed very far without encountering modulus changes diverting their path and reducing their energy. It was also observed that from Figures 2, 3, and 4 during the volume fraction 0.2 to 0.3 that the moduli values of calcium carbonate-filled composites surpasses the moduli values of flyash-filled composites. This could be due to a stiffer nature of calcium carbonate than the flyash, and the phenomenon is seen to shift from volume fraction of 0.3 (in the case of 100% elongation) to 0.2 (in the case 300% elongation) gradually. This shifting can be assigned to the reduction in relative stretchability of composites with elongation.

Hardness

The hardness of flyash-filled natural rubber and calcium carbonate-filled natural rubber are shown in Figure 5. It was observed in both cases that hardness increased as the volume fraction of filler increased. This is because of a rigid nature

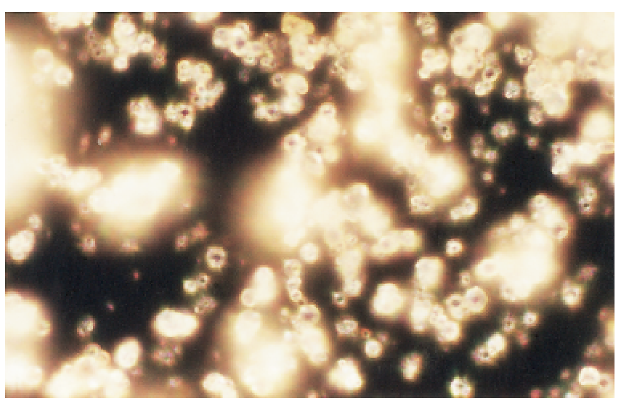

Figure 9 Particle shape analysis of flyash. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

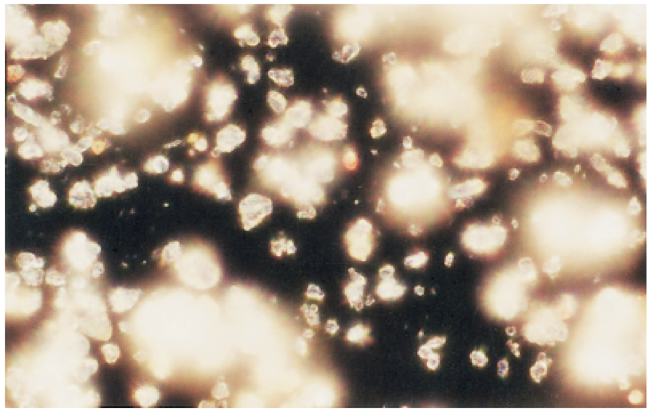

Figure 10 Particle shape analysis of calcium carbonate. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

of the filler, as the fillers are inorganic metal oxide in nature.

Density

The results of density are shown in Figure 6. It was observed that result of flyash-filled natural rubber and calcium carbonate-filled natural rubber shows an increase in density as the volume fraction of the filler increases.

Scanning Electron Microscopy Study

The photographs of SEM are shown in Figures 7 and 8. Figure 7 is related to natural rubber-filled with flyash at a volume fraction of 0.571 with ×-285 (magnification), and Figure 8 shows natural rubber filled with calcium carbonate at a volume fraction of 0.591 with ×-498 (magnification), respectively. A large number of bright/white spots are seen on the surface situated in matrix material, i.e., natural rubber. These bright spots indicate dispersion of flyash in the matrix material. The difficulty in proper dispersion can be attributed to low viscosity of raw rubber.[16] Some formation of agglomerates are also seen due to the filler being very fine in particle size, and excessive addition is probably responsible for the formation of agglomerates. These agglomerates may also be responsible for lower values of modulus. In the case of natural rubber filled with calcium carbonate, less agglomerates are formed (evident from Fig. 8) compared to flyash-filled composites. Thus, higher values of moduli in the case of calcium carbonate-filled composites are justified. The formation of agglomerates is responsible for lowering the tensile properties of the composites.

CONCLUSION

In this work it was observed that addition of filler increased the tensile strength and modulus so as to reach maximum, and then property decreased with increasing the volume fraction of the filler. The composites undergo transition from a continuous phase to a discontinuous phase as the volume fraction of the filler increases. The increase in properties is due to the wetting of the filler with matrix material while dewetting between the filler and matrix materials causes the decrease. Flyash-filled natural rubber showed better results than those of calcium carbonate-filled composite. Hence, flyash could be utilized as a filler, which is, of course, an economical one, and simulteneously, its consumption as filler will definitely help in reducing environmental pollution and financial burdan involved in its disposal.

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