Aluminum Powder Filled Nitrile Rubber Composites

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ABSTRACT: Effect of aluminum powder on the properties of nitrile rubber (NBR) composites and the role of bonding agent viz. hexamethylene tetramine-resorcinol has been investigated. Shore A hardness of the aluminum powder filled composites is lower than that of high abrasion furnace (HAF) and acetylene black (ACB) filled nitrile rubber composites and can be increased by the addition of bonding agent. Equilibrium swelling decreased considerably by the use of hexamethylene tetramine-resorcinol, suggesting an improved nitrile rubber–aluminum powder adhesion. A marked increase in thermal conductivity is obtained with the incorporation of aluminum powder. Increased thermal conductivity reduced the additional time needed for the vulcanization of thick rubber articles and imparted uniform curing throughout the material. In nitrile rubber, the modulus and tensile strength followed the order HAF > ACB > aluminum powder. Combination of HAF and aluminum powder in NBR gave composites with good thermal conductivity and mechanical properties. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 91: 3156–3161, 2004

Key words: composites; diffusion; rubber; swelling; thermal properties

INTRODUCTION

Metallic fillers are a special type of particulate fillers that impart special qualities to polymer composites. These fillers enhance properties such as thermal conductivity, electrical conductivity, response to magnetic fields, heat capacity, etc. A detailed report on production, processing, properties, and application of metal/polymer composites is given by Delmonte.[1] The higher conductivity of these composites has opened up new areas of applications, such as shielding materials to absorb electromagnetic radiation,[2] and making friction–antifriction materials. In many industrial processes, antistatic conveyor belts, made of conductive rubber, are used for eliminating static electricity. Metal-filled composites are used as antistatic materials in airplane tires and blades to dissipate the electrostatic charges accumulated during flight.[3] Boron containing polymers display outstanding heat and oxidation resistance and can be used at elevated temperatures.[4] Reports regarding the properties of metal containing polymers are available.[5–14] In certain cases a significant amount of carbon black[15–18] is used to produce conductive rubbers. Special conductive blacks like acetylene black are used for these purposes. Hassan et al.[19] studied the thermal effects of a blend of natural rubber and styrene butadiene rubber mixed with lamp black and general purpose furnace black. Incorporation of conductive fillers into rubber has other advantages during the molding of thick articles such as dock fenders, solid tires, roll covers, etc. The increased conductivity leads to uniform curing throughout the material, which gives better service life for the products.

Polymer-based composites can, in fact, fulfil the complex requirements of easy processability, good mechanical properties, and appropriate electrical and thermal conductivities. The conductivity can be adjusted, which offers enormous design flexibility for part fabrication. In many particulate-filled systems the mechanical properties are highly affected[20] due to poor dispersion and lack of interaction between the filler and the matrix. This can be successfully overcome by the use of various coupling/bonding agents.[21] Better adhesion strength in these cases has been explained by a coupling mechanism through interfacial diffusion and interpenetrating networks. Among the various systems, early-dispersed resorcinol formaldehyde resin,[22] silane and titanate coupling agents,[23] and chromium fumarato compounds[24] have been found to form strong assemblies.

In this article we report the properties of aluminum powder filled nitrile rubber composites in comparison with high abrasion furnace black N330 grade black and a conductive acetylene black filled composite. Effects of a bonding system consisting of hexamethylenetetramine and resorcinol were also studied.

EXPERIMENTAL

Nitrile rubber used was Europrene N 3945 supplied by Enichem Elastomerics (Southampton, UK). It is made by cold polymerization technique and the acrylonitrle content of the rubber was 39%. The Mooney

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viscosity of the rubber [ML (1 + 4) 100] was 45. Aluminum powder (purity 99.85%) was obtained from M/s Kosla Metal Powder Co. Pvt Ltd. (India). It has a specific gravity 2.69 and a particle size of 127 to 200 nm. Fillers and other ingredients were of commercial grade. The base formulation used is given in Table I. Hexamethylenetetramine (hexa) and resorcinol are in the ratio 1 : 2 for 4 vol loading of aluminum powder. The composites were prepared in a laboratory model two-roll mixing mill (150 × 300 mm) at a frictional ratio of 1 : 1.25. The total mixing time for all mixes was kept at 10 min and the temperature of mixing (26°C) was maintained constant by circulating cold water through the rollers. All the samples were cured at 150°C up to their optimum cure time, (t_{90}) as obtained from a Monsanto Rheometer (RX-100). The maximun and minimum values of the rheometric torque were directly read from Monsanto rheograph. Mechanical properties such as hardness, rebound resilience, and heat build up were tested according to the respective ASTM standards. The tensile properties of the vulcanizates were measured using a Zwick Universal Testing Machine (Model 1474 at a crosshead speed of 500 mm/min at 25°C as per ASTM: D 412–80. The flammability test was carried out using an SR-FTA Flammability Tester. The thermal conductivity of the samples was determined using a Kemtherm QTM D-3 supplied by Kyoto Electronics (Japan). For swelling studies, vulcanized composites were cut using a sharp-edged circular die. The initial weight was taken and immersed in toluene at constant temperature (27°C). After attaining equilibrium, which was ensured by the constant weight of the swollen specimen, the sample was taken out and weighed immediately after the wet surface of the sample was wiped using a piece of blotting paper. The equilibrium swelling was calculated, as moles of solvent sorbed by 100 g of the polymer, to assess the extent of crosslinking. A rubber cube having 25.4-mm size was molded by giving additional time (5 min) over the optimum cure time. The cube was then sliced into thin sections. The outer and central portions were taken and subjected to swelling in toluene up to equilibrium.

TABLE I
Base Formulation

Ingredients	Parts per hundred rubber
Nitrile rubber Europrene N 3945	100
Stearic acid	1.5
Zinc oxide	5.0
TDQ[a]	1.0
Filler[b]	Variable
Resorcinol	Variable
Hexamethylene tetramine	Variable
CBS[c]	1.0
Sulfur	1.5

[a] TDQ, 2,2,4-trimethyl-1,2-dihydroquinoline.

[b] Fillers : N 330 black (HAF), ACB, and aluminum powder.

[c] CBS, *N*-cyclohexyl benzothiazyl sulfenamide.

RESULTS AND DISCUSSION

The maximum values of the rheometric torque obtained with different fillers like N 330 black (HAF), acetylene black (ACB), and aluminum powder in nitrile rubber (NBR) compounds are given in Table II. HAF, ACB, and aluminum powder increased the maximum torque with increased loading, due to the reinforcement effect. Presence of hexa and resorcinol (HR-system) as bonding agent further increased the torque value of the compound containing aluminum powder. This is due to the increased interaction (physical) between aluminum powder and nitrile rubber in presence of the HR system.[9–11] Also, hexa acted as a secondary accelerator for vulcanization of rubbers.[13] The presence of hexa accelerated the vulcanization and formed more crosslinks, which resulted in a high torque. This is made clearer by the higher hardness and rebound resilience of the aluminum powder filled composites containing the bonding agent compared with those of HAF and ACB filled ones.

Figure 1 shows the Shore A hardness versus volume of various fillers in nitrile rubber. In all cases, the hardness increased with loading. The increased hardness with HAF and ACB is mainly due to the reinforcement. Since the particle size of the aluminum powder is much higher than that of HAF and ACB, the contribution to the hardness by reinforcement is considered to be lower for aluminum powder. The maximum decrease in resilience (Fig. 2) occurs with HAF followed by ACB and the minimum decrease occurs with aluminum powder. This is in the same order as that of the reinforcement capacity of these fillers. The lesser increase in hardness and lesser decrease in rebound resilience by aluminum powder is mainly due to the increased thermal conductivity of the vulcanizates, which leads to high crosslink density. Addition of the HR system to aluminum powder filled composite increased the hardness and decreased the rebound resilience, due to the improved interaction between aluminum powder and nitrile rubber.

Figure 3 gives the tear strength values of NBR-composites with HAF, ACB, and aluminum powder. The volume loading of the fillers increased the tear strength values in the order HAF > ACB > aluminum powder. The lower values of tear strength for aluminum powder filled nitrile rubber composites are due to the higher particle size of the filler. Addition of bonding agent improved the interaction between aluminum powder and the rubber, which increased the tear strength.

TABLE II
Properties of the NBR Composites

Sample[a]	300% modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)	Maximum torque (dNm)	LOI (*n*)
GUM	2.10	9.8	628	49	18.0
4 vol. HAF	2.83	14.6	622	51	18.1
8 vol. HAF	4.34	20.0	659	54	18.3
12 vol. HAF	12.2	23.7	486	59	18.8
16 vol. HAF	16.6	22.4	383	61	19.2
4 vol. ACB	5.59	13.3	618	56	18.1
8 vol. ACB	7.74	15.3	554	59	18.4
12 vol. ACB	8.6	16.2	458	61	18.9
16 vol. ACB	10.4	18.1	416	63	19.3
4 vol. AIP	2.16	10.0	627	50	18.3
8 vol. AIP	2.28	10.2	620	51	18.7
12 vol. AIP	2.42	10.6	614	53	19.8
16 vol. AIP	2.70	11.1	605	54	20.6
4 vol. AIP + HR	2.94	10.9	573	54	18.2
8 vol. AIP + HR	3.57	11.4	532	57	18.5
12 vol. AIP + HR	4.33	12.8	498	59	19.1
16 vol. AIP + HR	5.73	14.0	389	60	20.0

[a] ACB, acetylene black; ALP, aluminum powder; HAF, high abrasion furnace black; HR, hexamethylene tetramine-resorcinol system.

Equilibrium swelling values of the composites in toluene at 27°C are given in Figure 4. The maximum uptake of the solvent by the composite at equilibrium swelling was expressed as moles of solvent sorbed by 100 g of the composite. Among the fillers used, the ability to decrease the equilibrium swelling is found in the order aluminum powder with HR system > ACB > HAF > aluminum powder without bonding system. The presence of active filler reduces the extent of equilibrium swelling.[12–14,25] Various factors such as structure of polymer, type of crosslinking, crosslink density, penetrant size, temperature, rubber-filler interaction, etc. are found to influence the equilibrium swelling of rubbers.[26,27] The marked decrease in equilibrium swelling of the aluminum powder filled NBR composites by the addition of hexa-resorcinol is due to the higher extent of crosslinking and the increased interaction between aluminum powder and nitrile rubber by adhesion. The use of resorcinol-formaldehyde resin for bonding of different materials with rubber compounds was reported by Rajan et al.[28] It is reported that resorcinol combines with methylene donor to form a resin during vulcanization. This increases the polarity of the rubber, which makes great improvement in bonds between rubber and various substrate materials such as metals.

Thermal conductivity values of nitrile rubber compounds containing HAF, ACB, and aluminum powder are shown in Figure 5. As the volume loading of the

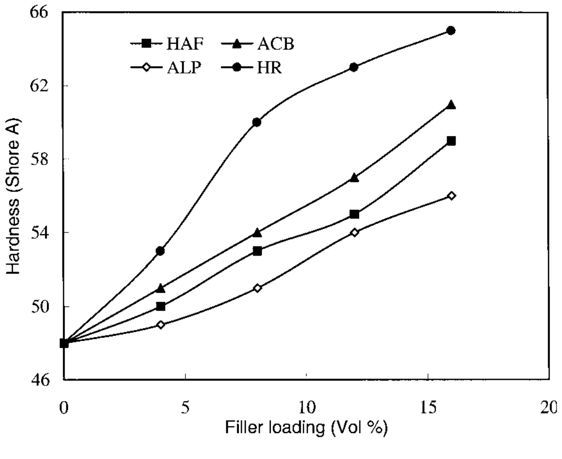

Figure 1 Variations of Shore A hardness values of NBR composites containing various fillers versus filler loading (vol %).

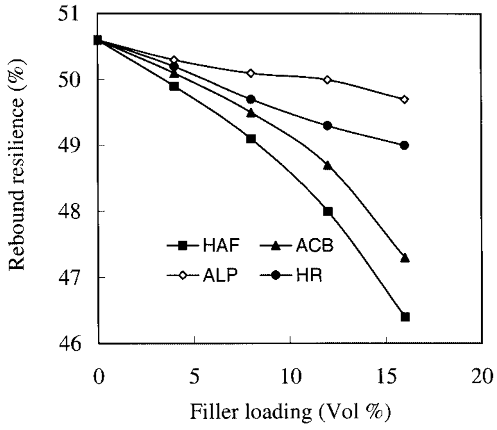

Figure 2 Plots of rebound resilience as a function of filler loading in NBR composites.

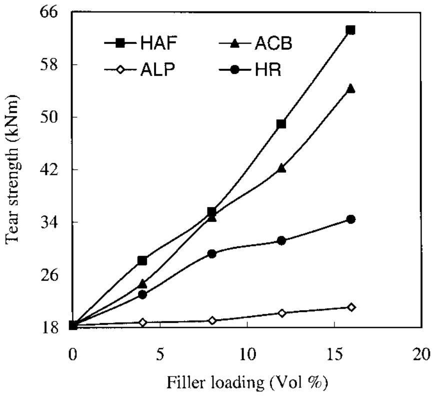

Figure 3 Dependence of tear strength on filler loading in NBR composites.

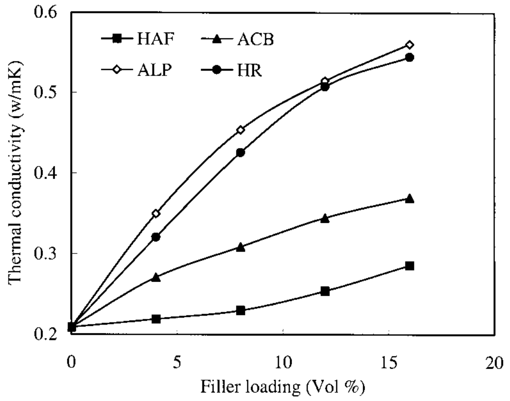

Figure 5 Plots of thermal conductivity of NBR composites containing various fillers against filler volume (%) loading.

fillers increased the conductivity also increased. At the same volume loading, even the conductive ACB imparted lower thermal conductivity than aluminum powder to nitrile rubber compound. Aluminum powder filled nitrile rubber composites have thermal conductivity values almost double that of HAF filled ones, at the same volume loading. Addition of hexa -resorcinol slightly decreased the thermal conductivity of aluminum powder filled NBR composites (Fig. 5).

Thermal conductivity of rubber compound has a major role for the uniform crosslinking of thick articles. Since rubbers are poor conductors of heat, the interior portion of thick rubber articles may not be sufficiently crosslinked and hence additional time is given for their vulcanization. As a result, the surface of the article becomes overcured whereas the interior portion may be in a state of undercure. Moreover it requires additional time for molding and thus expending additional energy and reducing the output. This can be successfully overcome by the addition of conductive fillers such as aluminum powder. This was illustrated in nitrile rubber cube having 25.4 mm size, vulcanized by providing 5 min additional time over the optimum cure time. The central and outer pieces of the cube were taken and subjected to equilibrium swelling. The results are given in Figure 6. The lower difference in equilibrium swelling between inner and outer portion showed less difference in their crosslink density, i.e., almost the same curing state. From the figure it is clear that the maximum difference is with the gum nitrile rubber samples. Even with the conductive ACB, 9% difference in Q_∞ values (which indirectly show the crossliking) between the inner and outer portions of the cube was observed. Aluminum powder filled compound showed almost the same extent of curing in the surface and interior portions of the cube. Actually the 25.4-mm cube needs more than 5 min of additional time over the optimum cure time. The addition of aluminum powder thus minimized the cure time for thick articles and gave uniform curing throughout the material.

Tensile properties of the composites are given in Table II. As the volume loading of the fillers increased,

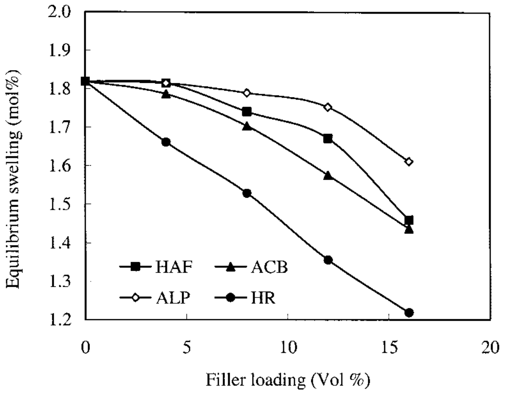

Figure 4 Variation of equilibrium swelling versus filler loading in NBR vulcanizates.

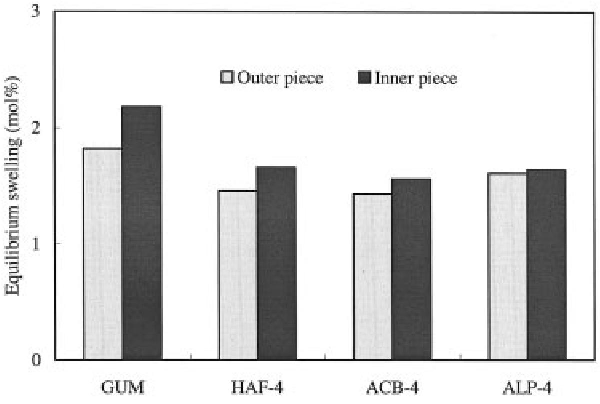

Figure 6 Equilibrium swelling (Q_∞) values of inner and outer pieces of a cube (25.4 mm in size) of NBR composites containing 40 phr of various fillers, vulcanized for an additional 5 min to optimum cure time.

TABLE III
Properties of NBR Vulcanizates Containing Different Proportions of HAF and Aluminum Powder

Properties	HAL-0	HAL-1	HAL-2	HAL-3	HAL-4
Al-powder, (volume loading)	0	4	8	12	16
HAF, (volume loading)	16	12	8	4	0
Maximum torque, (dNm)	61	47	38	31	26
Hardness (Shore A)	59	59	58	57	56
Tear strength (kNm^{-1})	63.3	38.3	37.3	28.3	21.1
Rebound resilience (%)	48.8	50.1	50.6	49.9	49.7
Thermal conductivity (W/mk)	0.286	0.380	0.430	0.511	0.561
Modulus (300%), (MPa)	16.6	6.8	4.9	3.4	2.7
Tensile strength (MPa)	22.4	20.9	17.2	14.5	11.1
Elongation at break (%)	383	419	484	512	605
Equilibrium swelling in toluene at 27°C (mol %)	1.460	1.504	1.532	1.578	1.612

the tensile strength and modulus at 300% elongation increased. This increase followed the order HAF > ACB > aluminum powder. The presence of hexaresorcinol as bonding agent increased both the modulus and the tensile strength. This is due to the improved interaction of aluminum powder with nitrile rubber in the presence of the HR system. The elongation at break values showed a decrease with volume loading of the fillers. In the cases of aluminum powder filled composites, the addition of bonding agent marginally decreased the elongation at break, as a strong interface restricts the mobility of the polymer chains. The results from the flammability test are given in Table II. The limiting oxygen index (LOI) is defined as the volume fraction of oxygen in an oxygen–nitrogen atmosphere that will just support steady candle-like burning of a material. As the volume loading of the fillers increased the LOI also increased, which followed the order, aluminum powder > ACB > HAF. This is because, as the amount of the polymer decreases, more and more oxygen is required for the steady burning of the material. The addition of hexaresorcinol decreased the LOI value of aluminum powder filled nitrile rubber composites.

Table III shows the properties of NBR-vulcanizates containing different proportions of HAF and aluminum powder where the total volume of filler is kept constant (16 volume loading). The maximum torque, Shore A hardness, tear strength, tensile strength, and modulus are found to be decreased by the substitution of HAF by aluminum powder. A marked increase in thermal conductivity is obtained when HAF is replaced by aluminum powder. These results showed that composites of nitrile rubber having good thermal conductivity and mechanical properties could be obtained by the use of appropriate combination of fillers such as HAF and aluminum powder.

CONCLUSION

Marked increase in thermal conductivity is obtained with aluminum powder filled composites, which is almost double the value of corresponding HAF filled composites. This increased thermal conductivity of aluminum powder filled rubber compound reduced the additional time required for the vulcanization of thick rubber articles and imparted uniform curing throughout the material. The order of increasing the tensile strength and modulus of NBR-composites for various fillers followed the series HAF > ACB > aluminum powder, which reflected the reinforcing capacity of these fillers. The addition of bonding agent increased both modulus and tensile strength due to the improved interaction between aluminum powder and nitrile rubber. The rebound resilience of NBR-composites is maximum with aluminum powder compared to ACB or HAF. The addition of hexa and resorcinol improved the adhesion between aluminum powder and nitrile rubber as evident from the lower equilibrium swelling values. The combination of HAF and aluminum powder in nitrile rubber gave composites having both good thermal conductivity and mechanical properties.

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