Aluminium powder · Bonding agents · Nitrile rubber · Thermal conductivity

Effects of bonding agents like hexamethylenetetramine-resorcinol system, bis[3-(triethoxysilyl)propyl] tetrasulfide and toluene disocyanate on the properties of aluminium powder filled nitrile rubber composites were investigated. Shore A hardness, tear strength and tensile properties were increased by the use of bonding agents. Incorporation of aluminium powder increased the thermal conductivity and the resistance towards thermal ageing. Presence of bonding agent decreased the equilibrium swelling due to the improved adhesion between aluminium powder and nitrile rubber.

**Aluminium Powder Filled Nitrile Rubber Composites: Effect of Bonding Agents**

The horizon of application of polymers has been widened with the recent discovery of metal-filled polymers in which the inherent thermal and electrical characteristics of polymers have been substantially modified. Metal powder incorporated polymer composites have applications like heat conduction, electrical heating, and discharging static electricity. These composites have the advantage of high corrosion resistance, lower specific weight, great accessibility and ease of processing. The higher thermal conductivity imposed by metal powders in rubber composites is useful in the vulcanization of thick articles [1]. This helps to reduce the additional vulcanization time needed for the curing of thick rubber products and imparts uniform curing throughout the material, which offers longer service life to the product. Special conductive blacks can be used in significant amount to produce conductive rubbers [2–5]. Conductivity of such composites is found to be less than that of metal powder incorporated composites. Numerous articles related to the properties of metal powder-polymer composites have appeared in the literature [6–10].

Good rubber-filler interaction is necessary for obtaining good physical and mechanical properties. In particulate filled systems an improved interaction of the filler with the matrix can be achieved through the use of bonding/coupling agents [11, 12]. The use of resorcinol-silica-hexamethylene tetramine as a bonding agent to improve the adhesion between natural rubber and aluminium powder along with various vulcanization systems was reported by the authors [13]. It is found that this bonding system is most effective in conventional vulcanization system due to the high level of sulphur to accelerator ratio. Maity and Ghosh [6] used titanate coupling agent for the surface treatment of silver powder in polypropylene. Modifications of the polymer also enhance the rubber-filler interaction. Introducing a functional group can improve the adhesion between rubber and filler by enhancing the surface interaction between the phases. Bosscott and Lebrie [14] carried out partial epoxidation of natural rubber in order to assess its effect on rubber-to-brass adhesion with out sacrificing the desirable physical properties of the rubber.

Effects of various bonding/coupling agents like hexamethylenetetramine- resorcinol (HR), bis[3-(triethoxysilyl)propyl] tetrasulfide (Si-69) and toluene disocyanate (TDI) on NBR-aluminium powder composites are reported in this article.

**Experimental**

Nitrile rubber used was Europrene N 3945. Hexamethylenetetramine (hexa), resorcinol, bis[3-(triethoxysilyl)propyl] tetrasulfide and toluene disocyanate were of laboratory reagent grade. Aluminium powder was obtained from M/s Kosla Metal Powder Co. Pvt. Ltd, India. It has a specific gravity of 2.69 and particle size 127 to 200 nm. Other ingredients and fillers were of commercial grade.

The base formulations used are given in Tab. 1. The dosages of hexa and resorcinol were in the ratio 1:2 throughout this study. At higher loadings of aluminium powder, the concentration of bonding agent varied as the multiples of the ratio of filler to bonding agent used in the base formulation. While plotting the figures, in the case of HR-system we have taken the amount of resorcinol on the abscissa, where as the hexa varies according to the ratio. The composites were prepared in a two-roll mill (150 × 300 mm). The compounds were cured upto their optimum cure time at 150°C. The mechanical properties were tested according to the respective ASTM procedures. Thermal conductivity...
was measured using quick thermal conductivity meter, “Kemtherm” QTM D-3 (Kyoto Electronics, Japan). Flammability was tested by SR-FTA Flammability Tester. “Zwick” Universal Testing Machine (model 1474) was used at 500 mm/min to determine the tensile properties (ASTM D-412-80). For swelling studies, the samples were cut circularly by means of a sharp edged circular die. The initial weight of the sample was taken and immersed in toluene at 27°C. After attaining the equilibrium swelling (at equilibrium swelling, weight of the sample does not change with time) the sample was taken out and the swollen weight was noted after the wet surface was dried using a blotting paper. It is then expressed as number of moles of solvent absorbed by 100 g of the polymer. The ageing resistance was determined by keeping the tensile test pieces at 70°C for 7 days. The percentage retention in tensile strength is calculated to assess the ageing resistance.

### Results and discussions

Thermal conductivity of aluminium powder incorporated nitrile rubber compounds are given in Tab. 2. As the loading of aluminium powder increased, the thermal conductivity also increased. Bonding agents, like hexamethylene tetramine-resorcinol system (HR-system), bis[3-(triethoxysilyl) propyl] tetrasulphide (Si-69) and toluene diisocyanate (TDI) have only a slight effect on thermal conductivity. Resistance to flammability, measured as limiting oxygen index (LOI), are shown in Tab. 2. Limiting oxygen index (n) is defined as the volume fraction of oxygen in an oxygen-nitrogen atmosphere that will just support steady candle like burning of a material. From the Table, it is clear that, as the loading of aluminium powder increased the LOI of NBR-composites. The bonding/coupling agents slightly decreased the LOI and the maximum decrease was found with Si-69.

Shore A hardness values of the composites are shown in Figs. 1a and 1b. At a given loading (Fig. 1a) as the concentration of bonding agent increased the hardness increased. The maximum increase was observed with HR-system followed by Si-69 (Fig. 1b). On increasing the loading of aluminium powder, sharp increase in Shore A hardness was observed. The bonding/coupling agents such as, hexa-resorcinol system, Si-69 and TDI further increased the hardness values.

Tear strength for aluminium powder filled NBR-composites are shown in Figs. 2a and 2b. The bonding/coupling agents increased...
The improved adhesion with HR system is due to the formation of a resin by the condensation reaction of hexamethylene tetramine and resorcinol. It has the following structure. (Scheme 1)

When the constituents are intimately mixed with rubber, a resin is formed during vulcanisation, which increases the bonding between the constituents [17]. This makes great improvements in bonds between nitrile rubber and aluminium powder. The coupling mechanism with silanes involves two-fold reaction with both the organic polymer and the mineral substrate. The organo functional silane must be compatible with the organic phase so that the silane becomes part of the polymer. The silane by co-reacting with the polymers modifies the polymer morphology at the interface to improve stress transfer. The silane coupling agent, bis-[3-(triethoxy silyl) propyl] tetrasulphide has the following structure. (Scheme 2)

The silane triol formed by hydrolysis of trialkoxy silane coupling agent has unique bonding capability with mineral surfaces [11]. This makes great improvements in adhesion between nitrile rubber and aluminium powder. Isocyanate are used in elastomeric compounds to improve the bonding [18]. Adhesion of isocyanate to rubbers initiates a chemical reaction, which might...
Fig. 5. Modulus (300 %) of NBR-composites as a function of (a) the amount of bonding agent, at 10 phr Al powder (b) the amount of aluminium powder with and without bonding agents

Fig. 6. Elongation at break of NBR-composites as a function of (a) the amount of bonding agent, at 10 phr Al powder (b) the amount of aluminium powder with and without bonding agents

Conclusions

A marked increase in thermal conductivity was obtained with incorporation of aluminium powder in NBR-compounds. These composites had higher limiting oxygen index values than the gum vulcanizate. The bonding agents like hexamethylene tetramine-resorcinol system, bis[3-(triethoxysilyl)]propyl) tetrasulphide, and toluene diisocyanate increased the ShoreA hardness, 300 % modulus, tensile strength, tear strength etc. and the increase was found in the order; HR-system > Si-69 > TDI. At a given loading of aluminium powder these properties increased gradually as the concentration of bonding agent increased. The equilibrium swelling in toluene decreased as the bonding agent concentration increased at a given loading, and the same pattern was observed at higher loadings of aluminium powder. These results suggested an improved aluminium powder-nitrile rubber interaction/adhesion in presence of bonding agents. The aluminium powder filled NBR-composites showed better resistance towards oxidative ageing.

References