Use of Aluminium Powder in Thick Rubber Articles For Uniform Curing and Reducing Cure Time

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ABSTRACT

Properties of aluminium powder filled natural rubber composites were studied and are compared, with those containing commonly used fillers viz. high abrasion furnace black, general purpose furnace black, acetylene black, china clay and precipitated silica. Maximum thermal conductivity for the compound was obtained by using aluminium powder and the vulcanizates were comparatively better resistant towards oxidative degradation and thermal ageing. The role of aluminium powder in uniform curing and reduction in vulcanization time of thick rubber articles was studied in detail. The rubber articles selected for this study were dock fender and rice polisher brake, which were moulded according to standard specifications. Replacement of a fraction of the filler content of these products by aluminium powder showed a marked increase in thermal conductivity. This increased thermal conductivity reduced the additional time needed for the vulcanization of thick rubber articles and imparted uniform curing throughout the material. Use of aluminium powder did not adversely affect the mechanical properties of the composites. Thus use of aluminium powder in rubber compounds saves energy in the vulcanization of thick rubber articles by reducing the vulcanization time and enhances the service life of such rubber products.

INTRODUCTION

The horizon of application of polymer composites has been widened with the introduction of thermal and electrical conductivity into these composites. The methods currently used to increase the conductivity of polymers is to fill them with specific conductive additives such as metallic powders[1], carbon blacks[2], ionic conductive polymers[3] etc. Among these, metal powders are the best in improving the conductivity. Powdery metal filled polymer composites have the advantage of high corrosion resistance, lower specific weight, great accessibility and ease of moulding. Higher heat and electrical conductivity made it suitable for various specific applications like discharging static electricity, electrical heating, converting mechanical to electrical signals, friction-antifriction materials and shielding from electromagnetic waves[4]. In addition to these, incorporation of conductive fillers into rubber has other advantages in moulding of thick articles like dock fenders, tyre retreads, roll covers, rice polishers, solid tyres etc. 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[5]. As a result, the surface of the article becomes overcured (highly crosslinked) whereas the interior portion may be in a state of undercure (poorly crosslinked). Moreover it requires additional time for moulding and thus expending additional energy and reducing the output. This can be successfully overcome by the addition of conductive fillers like metal powders to rubber compounds which will enhance the heat conduction and lead to uniform curing of thick articles.

Among the metal powders silver, copper and aluminium are the best conductors of heat. But silver is costly and copper is a pro-oxidant in natural rubber. Aluminium is neutral towards natural rubber and is available in powder form. Its specific gravity is in the range of other fillers such as clay, whiting, talc etc. and is easy to mix with rubbers. To investigate the role of aluminium powder in reducing the vulcanization time and

Key words : Natural rubber, Aluminium powder, Vulcanization, Thermal conductivity.

attaining uniformity in curing of thick articles, we have selected two thick natural rubber products-dock fender and brake of rice polisher. Dock fender[6], is used for gentle docking of ships. When a ship docks, the fender system must be able to withstand sudden heavy load in varying directions. The energy absorbing medium is a large cylinder of vulcanized natural rubber. Rice polisher brake is a long rectangular soft rubber block placed in an abrasive cone polisher between the wiremesh segments for restricting motion of brown rice around the rotating abrasive cone. Both these products suffer serious problems due to uneven curing during vulcanization. Here, we tried to improve this, using aluminium powder which is a conductive filler. Mechanical properties of the aluminium powder incorporated natural rubber vulcanizates were also noted and are compared with other commonly used fillers like high abrasion furnace black, general purpose furnace black, acetylene black, china clay and precipitated silica.

MATERIALS AND METHODS

Natural rubber used was Indian Standard Natural Rubber (ISNR-5). The fillers and other ingredients were of commercial grade. Aluminium powder was obtained from M/s. Kosla Metal Powder Co. Pvt. Ltd., India and has a density of 2.69 g cm^{-3} with a particle size of 127 to 200nm. Formulations used are given in Tables I and II.

Table I Formulation of Mixes

Ingredients	HAF	GPF	ACB	CLY	SIL	ALP
Natural rubber	100	100	100	100	100	100
Stearic acid	1.5	1.5	1.5	1.5	1.5	1.5
Zinc oxide	5.0	5.0	5.0	5.0	5.0	5.0
2,2,4-Trimethyl 1,2-dihydro quinoline	1.0	1.0	1.0	1.0	1.0	1.0
High abrasion furnace black	40	-	-	-	-	-
General purpose furnace black	-	40	-	-	-	-
Acetylene black	-	-	40	-	-	-
China clay	-	-	-	40	-	-
Precipitated silica	-	-	-	-	40	-
Aluminium powder	-	-	-	-	-	40
Morpholine benzothiazyl sulphenamide	0.6	0.6	0.6	0.6	0.6	0.6
Sulphur	2.5	2.5	2.5	2.5	2.5	2.5

Table II Formulation of Mixes

Ingredients	DCL	DAL	RCL	RAL
Natural rubber	100	100	100	100
Stearic acid	1.5	1.5	1.5	1.5
Zinc oxide	5.0	5.0	5.0	5.0
2,2,4-Trimethyl 1,2-dihydroquinoline (TDQ)	1.0	1.0	1.0	1.0
N-Isopropyl N1-phynyl para-phenylene diamine	0.5	0.5		
High abrasion furnace black (HAF)	30	30		
Fast extrusion furnace black (FEF)	40	20		
Silica		-	30	20
China clay			20	10
Aluminium powder		20		20
Diethylene glycol (DEG)			1.0	1.0
Naphthenic oil	2.0	2.0	2.0	2.0
Resorcinol		2.0		2.0
Hexamethylene tetramine		0.75	-	0.75
Dicyclohexyl benzthiazyl sulphenamide	0.8	0.8	1.0	1.0
Pre-vulcanization Inhibitor (PVI-50)	0.2	0.2	0.2	0.2
Sulphur	2.5	2.5	2.25	2.25

DCL - Dock fender-control
DAL - Dock fender - with aluminium powder
RCL - Rice polisher brake-control
RAL - Rice polisher brake-with aluminium powder

The composites were prepared in a two-roll mixing mill and were cured upto their optimum cure time at 150°C as obtained from a Monsanto Rheometer R-100. Mechanical properties such as tensile strength, tear strength, hardness, heat build-up, rebound resilience etc. were studied according to their respective ASTM procedures. Tensile and tear properties were tested on a Zwick Universal Testing Machine (Model 1474) at 25 ± 2°C and at a cross head speed of 500 mm/min. The ageing resistance was determined by keeping the tensile test pieces at 70°C for 7 and 14 days, conditioning the aged sample overnight and then testing the tensile properties. Resistance to ozonolysis of the composites was studied using an ozonetest chamber manufactured by MAST Development Company, USA at 50 pphm ozone concentration. The thermal conductivity was determined using Quick Thermal Conductivity Meter (Kemthem QTM D-3) supplied by Kyoto Electronics, Japan. To study the crosslinking pattern in thick rubber articles a pilot study was conducted with rubber cubes of

5cm size which were moulded by giving varying vulcanization times. The cubes were then sliced to thin sheets. The outer and central layers were subjected to swelling in toluene upto equilibrium. Rice polisher brake was moulded in a size of 4 x 4.5 x 46 cm at 150°C in a hydraulic press.

Dock fender samples with 12.5cm ID x 25 cm OD and having a length of 250 cm, were moulded by wrapping the compounded sheet on a steel mandrel and then steam curing at 55psi pressure in an autoclave. These were then sliced to obtain outer and inner layers for studying the cross-link density.

RESULTS AND DISCUSSIONS

Thermal conductivity values of natural rubber composites containing various fillers (40 phr) are given in Figure 1. It is clear that thermal conductivity is much higher for aluminium powder filled composites than other filler incorporated vulcanizates

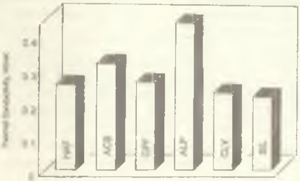


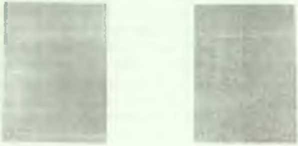
Figure 1. Thermal conductivity of NR-vulcanizates with various fillers (40 phr).

Table III shows the mechanical properties of various filler incorporated natural rubber composites. The maximum rheometric torque and equilibrium swelling in toluene for aluminium powder filled compound was found to be same as that containing HAF at the same loading. Among the fillers used in this study, the maximum shore A hardness is obtained with aluminium powder. Better properties of NR compounds containing aluminium powder is due to the higher extend of crosslinking rather than reinforcement. Since the particle size of the aluminium powder used is much higher than that of HAF and silica, the contribution by reinforcement is considered to be lower for aluminium powder. This is also reflected in the higher rebound resilience of the aluminium powder filled composites. Normally, rubber vulcanizates, with increasing reinforcing filler content, its rebound resilience decreased. The higher extend of crosslinking gave higher rebound resilience for aluminium powder filled NR-vulcanizates. The tensile strength with various fillers in NR follows the order HAF>silica>GPF>acetylene black>aluminium powder>clay. The maximum elongation is also better for aluminium powder filled compounds. It is very interesting to note that aluminium powder filled composites have only half the heat build-up value compared to corresponding HAF or acetylene black filled compounds. Hence, the use of aluminium powder in rubber compounds can reduce the heat build-up in products.

Table III Properties of NR-vulcanizates with various fillers (40 phr)

Property	HAF	GPF	ACB	SIL	CLY	ALP
Maximum torque,dNm	44	42	46	46	36	44
Hardness, IRHD	50	48	52	44	38	53
Rebound resilience, %	53.2	59.0	58 4	57.0	59.7	69 0
Equilibrium swelling, mol%	2.80	2.93	2.89	3.10	3 32	2.80
DIN abrasion loss, mm³	132	147	165	155	309	229
Tensile strength, Mpa	27.9	25 5	24.0	26.0	20.0	22 2
Elongation at break, %	374	356	378	445	490	447
Tear strength, kNm⁻¹	53.1	48.9	50.1	50.0	37.8	38 9
Heat build-up °C	38	23	38	26	20	19
Retention in tensile strength, % (14 days at 70°C)	80.2	87.4	85.8	77 7	89.0	88.7

Optical photographs of 10 hours of ozone exposed natural rubber vulcanizates containing aluminium powder and HAF are shown in Figure 2. Cracks were developed on the surfaces of both the samples even after two hours of exposure to ozone. However, the nature and level of cracks developed due to ozone attack are different for various vulcanizates. In the case of aluminium powder filled vulcanizates, the cracks are small and discontinuous whereas in HAF filled sample the cracks are deep, wide and continuous. This is due to higher level of crosslinking in the aluminium powder filled vulcanizates. The increased crosslinks effectively prevents the generation of cracks and its growth in the surfaces of aluminium powder filled vulcanizates. After keeping at 70°C for 14 days, the percentage retention in tensile strength of the natural rubber composites followed the order clay > aluminium powder > GPF > acetylene black > HAF > silica (Table III). The results showed that clay and aluminium powder retained the mechanical properties of NR even after aging compared to other fillers.



(a) (b)

Figure 2. Optical photographs of ozone exposed NR composites containing
a) 40 phr aluminium powder and
b) 40 phr HAF

The important properties of the composites of dock fender and rice polisher brake are given in Table IV. The optimum cure time did not change in the dock fender and rice polisher brake compounds with the addition of aluminium powder. As per the standard specification, the dock fender material requires a minimum tensile strength of 16 MPa, elongation at break of 350%, a maximum hardness of 72 IRHD, and a compression set of not more than 25 per cent after 22 hours at 70°C. The base formulation was designed to meet all these specifications. Substitution of a part of the filler by aluminium powder marginally improved the properties like compression set and heat build-up. The hardness and rebound resilience are increased whereas the equilibrium swelling decreased for the aluminium powder incorporated sample. These are due to the increased amount of crosslinking with the better conduction of heat, and due to the increased adhesion between natural rubber and aluminium powder in presence of hexamethylene tetramine-resorcinol system. Use of hexamethylene tetramine-resorcinol as bonding system increased the interaction between natural rubber and aluminium powder through improved adhesion between the component materials[7]. Resorinol combines with methylene donor to give a resin, formed *insitu* during vulcanization, which binds the rubber and the metal powder[8].

Table IV Properties of dock fender and rice polisher brake compounds

Property	DCL	DAL	RCL	RAL
Optimum cure time, T^{90}, min	12.5	12.5	18 0	18.0
Max torque, dNm	100	99	63	65
Rheometric induction time, min	3.0	2.5	3 0	2.5
Cure rate index, min^{-1}	12.5	12 5	7 1	7.1
Hardness, IRHD	70	72	49	51
Modulus (300%), M Pa	18 1	17.5	3.7	6.3
Tensile strength, M Pa	23.6	21.6	19.0	19 6
Elongation at break, %	357	367	788	735
Tear strength, kNm^{-1}	56 4	54 6	52.1	50 4
Compression set, %	23.8	21 7	32.0	30 5
Heat-build up, ΔT°C	39	37	21	20
Rebound resilience, %	53.2	54.0	59.7	60.3
DIN abrasion loss, mm^3	83	139	164	169
Equilibrium swelling (toluene at 27°C), mol%	1.705	1.669	3 150	2 901
Retention in tensile strength, %				
a) 7 days at 70°C	100	102	101	102
b) 14 days at 70°C	78	88	85	87

It is seen that, the resistance towards thermal ageing of the composites is improved by the addition of aluminium powder. After keeping at 70°C for 7 and 14 days, the percentage retention of tensile strength is higher in the case of aluminium powder incorporated compound. This is true for both dock fender and rice polisher compounds (Table IV).

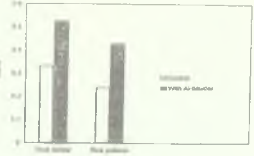


Figure 3. Thermal conductivity increase of the composites by the replacement of 20 phr HAF with A1-powder

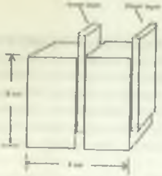
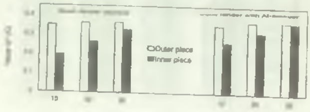


Figure 4. **Samples from inner and outer layers for swelling studies**

Substitution of a part of the filler (20 parts) by aluminium powder markedly increased the thermal conductivity (Figure 3). Between the control compounds, DCL showed better thermal conductivity due to the presence of carbon blacks. Compound 'RCL' contained silica and china clay which are having lower conductivity compared to carbon black. The increase in thermal conductivity due to addition of aluminium powder is almost identical in both the compounds. Thermal conductivity of rubber compound is very important in the vulcanization of thick article as it helps to achieve uniform crosslinking. To study the extent of crosslinking in thick articles, 5 cm cubes were moulded by giving various additional times for vulcanization. Test pieces from the outer surface and central portion were taken [Figure 4] and were assessed for crosslink density by swelling method. Parks[5] suggested that the value of 1/Q gives an idea about the degree of crosslinking, where Q is given by

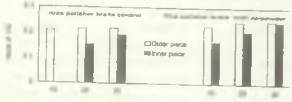
$$Q = \frac{\text{Swollen weight - Dried weight}}{\text{Original weight x 100/Formula weight}}$$

The effect of aluminium powder on the 1/Q values of the centre and outer layers of the 5 cm rubber cube are shown in Figure 5 and 6 respectively. As the additional time given for vulcanization increases, the difference between 1/Q values of the centre and surface layers decreased. Less difference in 1/Q values suggests that the surface and centre portions have almost the same crosslink density. It is very interesting to note that this difference decreased by the substitution of a part of the filler (20 phr) by aluminium powder. Even after giving 30 minutes additional time over the optimum cure time, the control compounds of both the dock fender and rice polisher brake, had appreciable difference in



Additional time for vulcanization (min)

Figure 5. **1/Q values of inner and outer pieces of 5 cm cube of dock fender compound with and without aluminium powder**



Additional time for vulcanization (min)

Figure 6. **1/Q values of inner and outer pieces of 5 cm cube of rice polisher brake compound with and without aluminium powder**

crosslink density between the outer and inner portions. Aluminium powder incorporated compound attains almost the same crosslink density for the inner and outer portions on giving 30 minutes additional vulcanization time. The same result can be observed on comparing the equilibrium swelling Qα data. This result confirms that the use of aluminium powder imparts uniform crosslinking in thick articles through increased thermal conductivity. This technique also helps to reduce the vulcanization time of thick rubber articles.

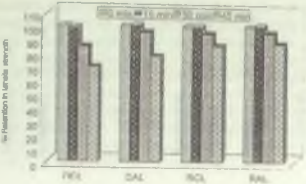


Figure 7. Percentage retention of tensile strength after giving additional time over optimum cure time over optimum cure time for moulding

Usual procedure for the vulcanization of thick articles is to give additional time over the optimum cure time for vulcanizing the interior portions. Conventionally 5 min additional time is given for every additional 6 mm thickness at 150°C. By this practice, the surface which is in contact with the hot mould becomes over cured and gets degraded, as evident from the percentage retention of tensile strength after giving additional time for moulding (Figure 7). In all cases as the additional time given over optimum cure time increased, the percentage retention gradually decreased. This reduction in tensile strength is due to the degradation of the polymer exposed to higher temperatures for longer times. The same trend is reflected in other properties also. This observation emphasises the need for reduced vulcanization time of thick articles.

Figure 8. Photograph of dock fender and rice polisher brake

Figure 8 shows the photograph of dock fenders and rice polisher brakes that were moulded to study the effect of aluminium powder. In these cases also, the outer surface and central portion were sliced to obtain test pieces and were subjected to swelling studies to assess the crosslink density. The results are presented in Table V.

Table V

Sample	Cure time (min)	Qα outer	Qα [illegible]	Diff in Qα	1/Q outer	1/Q inner	Diff. in 1/Q
Dock fender	45	1.604	1.693	0.089	0.362	0.342	0.020
control (DCL)	60	1.590	1.648	0.058	0.363	0.351	0.012
Dock fender with Al-powder (DAL)	45	1.589	1.638	0.049	0.364	0.353	0.011
Rice polisher control	40	3.151	3.927	0.776	0.208	0.167	0.041
(RCL)	[illegible]	3.020	3.272	0.252	0.216	0.200	0.016
Rice polisher with	40	2.700	2.817	0.177	0.244	0.234	0.010
Al-powder (RAL)	50	2.543	2.555	0.012	0.257	0.255	0.001

Substitution of 20 phr of FEF black with aluminium powder in this compound decreased the difference in crosslinking between the outer and interior portions, as evident from the Qα and 1/Q values of DAL. It is evident that the DAL compound attained almost uniform crosslinking at a lower vulcanization time than that without aluminium powder. This is more clear in the case of rice polisher brake material. The difference in 1/Q and Qα values of the outer and interior portions of the rice polisher brake is minimum in the case of aluminium powder incorporated compound. It is seen that vulcanization at 150°C for 40 minutes gives better uniformity in crosslinking in the RAL compound that the control compound vulcanized for 50 minutes. This again confirms that aluminium powder imparts uniform curing and reduce the vulcanization time for thick articles. It is also noted that the effect of aluminium powder is best reflected when it is used in combination with non black fillers, which are less conductive than carbon blacks.

CONCLUSIONS

Use of aluminium powder in natural rubber compounds imparts higher thermal conductivity than HAF, GPF, acetylene black, china clay and silica fillers. Aluminium powder filled NR-vulcanizates have better resistance towards thermal ageing and oxidative degradation. Uniform curing and reduction in vulcanization time of thick rubber articles such as dock fender and rice polisher brake was successfully achieved with the use of aluminium powder as a conductive filler. Marked increase in thermal conductivity is obtained by the replacement of 20 phr of the filler by aluminium powder, which helps to attain uniform curing of thick rubber products, such as dock fender and rice polisher brake, as indicated by swelling experiment conducted using test pieces taken from outer and inner portions of a 5 cm rubber cube. The mechanical properties of vulcanizates were determined and found that substitution of a part of the filler with aluminium powder did not adversely affect the properties to any significant level. All these results strongly support the findings that increased thermal conductivity of aluminium powder incorporated rubber compound imparts uniform curing throughout the material, and which, in turn, reduces the total vulcanization time for thick rubber products. Thus, use of aluminium powder in rubber compounds can considerably save the amount of heat energy required for the vulcanization of thick articles and can enhance the service life of such products.

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