SBR · Aluminium powder · Physical properties · Thermal conductivity

Effect of aluminum powder on the properties of SBR composites was studied and compared with other fillers like high abrasion furnace black (N 330) and acetylene black. Increase in hardness, tear strength and tensile strength of SBR vulcanizates followed the order N 330 black > acetylene black > aluminum powder. A marked increase in thermal conductivity was obtained with aluminum powder filled vulcanizates, which reduced the vulcanization time required for thick rubber articles and imparted uniform curing throughout the material. Use of hexamethylene tetramine- resorcinol as bonding agent, imparted better properties for the composites. Aluminum powder incorporated vulcanizates also showed good resistance towards thermal ageing.

Eigenschaften von mit Aluminiumpulver gefüllten SBR-Compositen

SBR · Aluminiumpulver · physikalische Eigenschaften · thermische Leitfähigkeit

Der Einfluss von Aluminiumpulver auf die Eigenschaften von SBR-Compositen wurde im Vergleich zu anderen Füllstoffen wie HAF- und Acetylen-Ruß untersucht. In Gegenwart von Aluminiumpulver wurde ein Anstieg des Drehmoments und eine Verminderung der optimalen Vernetzungszeit beobachtet. Die Zugabe von Hexamethylentetramin-resorcinol als Kopplungsagens erhöht diesen Effekt. Ein Anstieg der Härte, der Zugfestigkeit und der Weiterreissfestigkeit von SBR-Vulkanisation wurde in der Reihenfolge HAF > Acetylenruß > Aluminiumpulver beobachtet. Die Gegenwart von Aluminiumpulver führt zu einem beachtlichen Anstieg der thermischen Leitfähigkeit, die eine kürzere Vulkanisationszeit und eine einheitlichere Vernetzung bei dickwandigen Artikeln erlaubt. Durch den Einsatz des Kopplungsagens werden zudem die Eigenschaften verbessert. Wie Quellungsmessungen zeigen geht dieses auf eine bessere Haftung.

Properties of Aluminum Powder Filled Styrene Butadiene Rubber Composites

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Conductive polymer composites are widely appreciated by their ability to conduct both heat and electricity, which ideally suit for conduction, friction-antifriction materials and for converting mechanical to electrical signals. During vulcanization, increased thermal conductivity helps to attain uniform curing and reduction in vulcanization time of thick articles. Investigations have been carried out to increase the thermal and electrical conductivity of the polymers [1–5]. Usual methods employed to increase the conductivity of polymers involve intrinsically conductive macromolecules [6], or addition of large amounts of conductive fillers like carbon black [7, 8], metallic fiber [9] and metallic powders [10]. Lu and Xu [11] reported that thermal conductivity of polyurethane composites filled with alumina or carbon fibers is about 50 times more than that of pure polyurethane. The advantage of metal powders over other fillers is that they provide good electrical and thermal conductivity in the composite [12–15]. Maity and Mahapatro [16] reported on the thermal characteristics and crystallization behaviour of silver and nickel filled isotactic polypropylene.

A large number of variables, such as, size, shape, nature and state of distribution of the filler, adhesion and thermal compatibility of the phases etc. characterize the system and some of them have strong influence on the properties of the composites [17]. It is seen that improvement in adhesion between the filler and matrix imparts better properties to the composite. We have recently reported the use of various bonding systems for improving the adhesion between natural rubber and aluminum powder [18, 19]. Reports about silane coupling agents, their use, mechanism by which they act, adhesive systems and theories of adhesion are also available [20].

Unlike other metal powders, aluminum is neutral towards rubber composites and is available in powder form. Its specific gravity is in the range of other fillers such as clay, whiting, talc etc. In this paper, the effects of aluminum powder on styrene butadiene rubber composites were studied. For comparison, the properties of commonly used high abrasion furnace black (N 330) and conductive acetylene black incorporated SBR vulcanizates were studied. Efforts were also made to investigate the effect of hexa methylene tetramine-resorcinol system (HR) as a bonding agent in SBR-aluminum powder composites.

Experimental

SBR-1502 grade was used as the matrix rubber. Aluminum powder (Kosla Metal Powder Co. Pvt. Ltd, India) with a specific gravity of 2.69 and a particle size ranging from 127 to 200 nm was used. Fillers and other ingredients were of commercial grade. Formulations used are given in *Tables 1a* and *1b*. The composites were prepared in a two-roll mill (150 × 300 mm). The compounds were cured up to their optimum cure time (t_{90}) at 150 °C. Mechanical properties were measured according to ASTM procedures. [Hardness – ASTM D – 2240 – 81, Heat build-up – ASTM D – 623 – 93. Tear strength – ASTM D – 624-81].

Table 1a. Formulation of mixes

Ingredients	GUM	HF1	HF2	HF3	HF4	AC1	AC2	AC3	AC4
Styrene butadiene rubber	100	100	100	100	100	100	100	100	100
Stearic acid	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Zinc oxide	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
2,2,4 Trimethyl-1,2-dihydroqunoline	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
N 330 black	–	10	20	30	40	–	–	–	–
Acetylene black	–	–	–	–	–	10	20	30	40
N-cyclohexyl benzothiazyl sulphenamide	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Sulphur	2.2	2.2	2.2	2.2	2.2	2.2	2.2	2.2	2.2

Table 1b. Formulation of mixes

Ingredients	Al 1	Al 2	Al 3	Al 4	AB1	AB2	AB3	AB4	HAA	HAB	HAC
Styrene butadiene rubber	100	100	100	100	100	100	100	100	100	100	100
Stearic acid	1.5	1.5	1.5	1.5	1.5	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	5.0	5.0	5.0	5.0	5.0
2,2,4 Trimethyl-1,2-dihydroqunoline	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
N 330 black	–	–	–	–	–	–	–	–	30	20	10
Aluminum powder	10	20	30	40	10	20	30	40	10	20	30
Resorcinol	–	–	–	–	1.0	2.0	3.0	4.0	–	–	–
Hexa methylene tetramine	–	–	–	–	0.5	1.0	1.5	2.0	–	–	–
N-cyclohexyl benzothiazyl sulphenamide	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Sulphur	2.2	2.2	2.2	2.2	2.2	2.2	2.2	2.2	2.2	2.2	2.2

Table 2. Analysis of rheometric curves

Sample	Max.Torque, dNm	t_{90}, min	RIT, min	CRI, min^{-1}
GUM	64	30.0	10.0	5.26
HF1	66	27.0	6.5	5.32
HF2	78	25.0	5.0	5.43
HF3	85	24.0	4.5	5.55
HF4	92	21.0	4.0	5.70
AC1	65	30.0	7.5	5.20
AC2	76	30.0	7.0	5.16
AC3	84	29.0	6.0	5.10
AC4	91	28.0	5.5	5.00
Al 1	65	28.0	7.0	5.72
Al 2	66	24.0	6.0	6.45
Al 3	68	21.0	5.0	6.89
Al 4	70	17.0	4.0	7.60
AB1	67	19.0	3.5	6.67
AB2	68	16.0	2.5	7.14
AB3	69	14.0	2.0	8.33
AB4	71.5	12.0	1.5	9.09

Tensile properties of the vulcanizates were measured using Universal Testing Machine ('Zwick' UTM Model 1474) at a crosshead speed of 500 mm/min at 25 °C as per ASTM D 412-80. The thermal conductivity of the samples was determined using a quick thermal conductivity meter, 'Kemtherm' QTM D-3 (Kyoto Electronics, Japan). For ageing studies, tensile specimens of the samples were kept in an air oven at 70 °C for 7 and 14 days. The tensile strength of the aged samples was determined, after conditioning the aged sample for 24 hours. To study the difference in extent of crosslinking between the surface and interior portions during the vulcanization of thick articles, a rubber cube having 25.4 × 25.4 × 25.4 mm size was moulded by giving additional 5 min to the optimum cure time (t_{90+5}). The cube was then sliced to thin sections and the surface and central slices were subjected to swelling in toluene up to equilibrium at 27 °C. The mol% absorptions of the penetrant were calculated and compared.

Results and discussion

The cure characteristics of the composites are given in *Table 2*. The maximum torque values are found to be increased by the fillers used N 330 black, acetylene black and aluminum powder. The optimum cure time decreased as the loading of fillers increased. This effect is more pronounced in presence of aluminum powder. The addition of hexa-resorcinol as a bonding agent further decreased the cure time, due to the accelerating effect of hexamethylene tetramine. The rheometric induction time (RIT) was decreased in the same trend as shown by the optimum cure time. The cure rate index (CRI) was increased with N 330 black and aluminum powder while it decreased with acetylene black.

Shore A hardness of SBR vulcanizates containing N 330 black, acetylene black and aluminum powder as fillers are given in *Table 3*. The increase in hardness is in the order N 330 black > acetylene black > aluminum powder. The presence of hexa-resorcinol increased the hardness of aluminum powder filled compounds. Since the particle size of aluminum powder used is much higher than that of N 330 black and acetylene black, the contribution to hardness increase by reinforcement is found to be lower for alu-

Table 3. Tensile properties of the compounds

Sample	Modulus (200 %) MPa	Tensile strength, MPa	Elongation At break, %	Hardness, Shore A	Resilience, %	Tear Strength, kN/m
GUM	1.81	2.42	367	38	61.4	18.5
HF1	2.83	7.30	340	44	58.1	28.4
HF2	3.20	10.6	310	51	57.4	36.1
HF3	6.20	21.2	300	59	55.7	47.9
HF4	8.60	23.7	253	65	52.2	58.7
AC1	2.02	5.40	360	43	59.0	25.2
AC2	3.10	8.70	350	50	57.9	33.7
AC3	5.90	14.3	326	58	56.7	43.7
AC4	7.01	16.1	310	63	54.8	55.8
Al 1	2.02	2.90	362	43	60.1	24.0
Al 2	2.47	3.50	354	48	58.1	27.0
Al 3	2.60	4.20	347	53	56.8	29.0
Al 4	3.24	5.60	340	60	55.1	36.0
AB1	2.07	3.90	349	43	58.2	26.4
AB2	2.89	4.10	321	49	57.0	29.8
AB3	3.14	5.10	312	57	55.9	32.2
AB4	4.22	8.70	294	62	53.8	39.6

minum powder. The hardness of aluminum powder filled SBR-composites is mainly due to the higher extent of crosslinks achieved through better thermal conductivity. The rebound resilience of the composites was found to be decreased with filler loading (Table 3). The presence of hexa-resorcinol system improved the adhesion between the rubber and the matrix, which increased the hardness but decreased the resilience. Variation in tear strength of SBR vulcanizates with loading of N 330 black, acetylene black and aluminum powder is shown in Table 3. The tear strength of N 330 black and acetylene black filled vulcanizates is higher than that of aluminum powder filled one due to the higher reinforcing capacity of these fillers. However the tear strength of aluminum powder filled composites can be improved by the use of hexa-resorcinol system as bonding agent.

Fig. 1 shows the thermal conductivity values of the SBR compounds. It is clear from the figure that the fillers increased the thermal conductivity with loading. The thermal conductivity increase is in the order, aluminum powder > acetylene black > N 330 black. The aluminum powder filled compounds have the thermal conductivity much higher than the conductive acetylene black filled ones. SBR filled with 40 phr aluminum powder has a thermal conductivity, which is twice than that of N 330 black filled compound. The use of hexa-resorcinol system does not have much influence on the thermal conductivity. The thermal conductivity values correlate with the electrical conductivity [21]. The volume resistivity values of SBR composites with different loadings of N 330 black, acetylene black and aluminum powder are given in *Fig. 2*. The volume resistivity found to be decreased with loading of fillers. The aluminum powder filled compound has the lowest resistivity values compared to N 330 black or acetylene black filled composite. This indicates that the electrical conductivity showed the same trend as that of thermal conductivity with the addition of aluminum powder. The heat build up values of these composites are presented in *Fig. 3*. The maximum heat build up is for N 330 black filled composites followed by acetylene black and then aluminum powder. Lower reinforcement and the higher thermal conductivity of aluminum powder filled compounds account for the low heat build-up value. The presence of bonding agent, hexa-resorcinol, increased the heat build up due to the improved adhesion. In all cases it is noted that the loading of fillers increased the heat build up values.

The mole per cent absorption of toluene at 27 °C is given in *Fig. 4*. The loading of each type of filler decreased the equilibrium swelling. The aluminum powder filled SBR vulcanizates showed a higher equilibrium swelling value than N 330 black and acetylene black filled compounds due to the lower extent of reinforcement. But the use of resorcinol-hexa bonding system considerably decreased the equilibrium swelling (Q_∞). The equilibrium swelling is restricted by

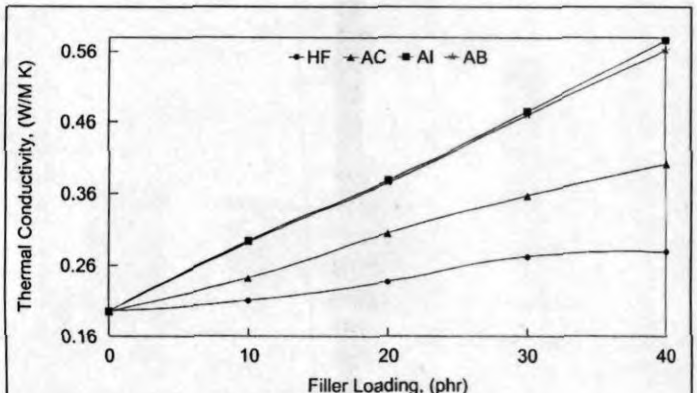

Fig. 1. Thermal conductivity of SBR composites with different loadings of N 330 black, acetylene black and aluminum powder.

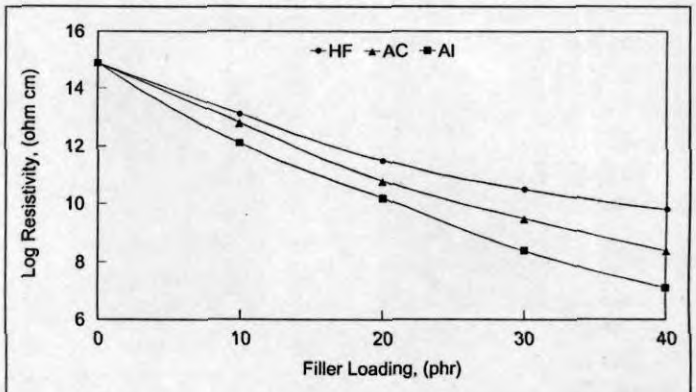

Fig. 2. The volume resistivity of SBR composites with N 330 black, acetylene black and aluminum powder.

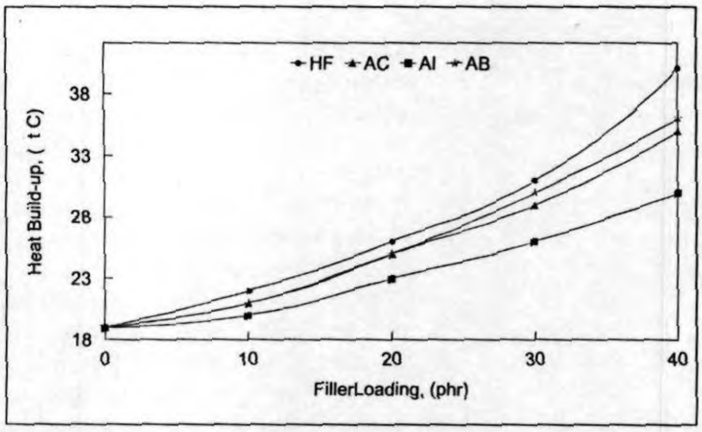

Fig. 3. Heat build-up values of SBR-vulcanizates containing N 330 black, acetylene black and aluminum powder.

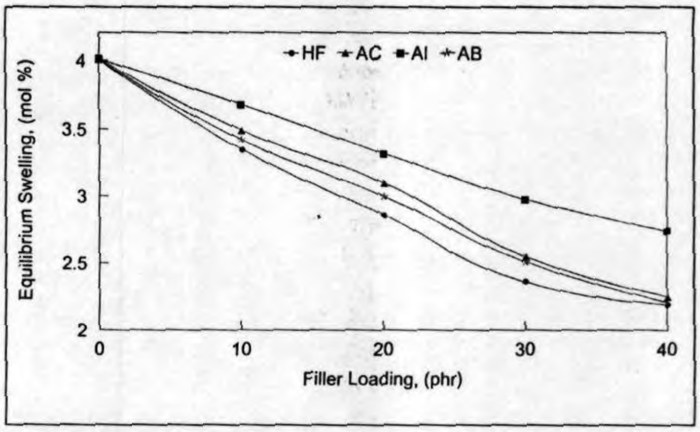

Fig. 4. Equilibrium swelling values of SBR composites with different loadings of N 330 black, acetylene black and aluminum powder. (swelling solvent, toluene at 27 °C)

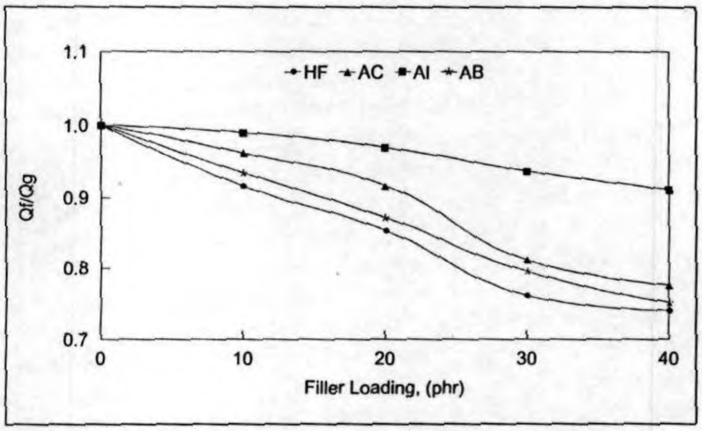

Fig. 5. Q_f/Q_g values of the composites of SBR with loading of N 330 black, acetylene black and aluminum powder.

the adhesion between the filler and the matrix [22]. This is described by

$$Q_f/Q_g = a\,e^{-z} + b$$

where, Q is defined as the weight of solvent uptake per gram of polymer and the subscripts f and g refer to filled and gum vulcanizates respectively; z is the ratio by weight of filler to rubber hydrocarbon in the vulcanizate, whereas a and b are constants.

The higher the Q_f/Q_g values, the lower will be the extent of interaction between the filler and the matrix. *Fig. 5* shows the Q_f/Q_g values of the SBR vulcanizates. The Q_f/Q_g values are lower for N 330 and acetylene black filled vulcanizates compared to aluminum powder filled ones in the absence of bonding agent at a particular loading. It is very interesting to note that the hexa-resorcinol bonding system decreased the Q_f/Q_g value of aluminum powder filled SBR compounds. This is evidently due to the higher extent of adhesion between the rubber and aluminum powder. The improved adhesion is explained through the *insitu* formation of a resin during vulcanization. The hydrogen bonding characteristics of the resin increased the polarity of the rubber, whic makes better adhesion between rubbe. and various substrate materials.

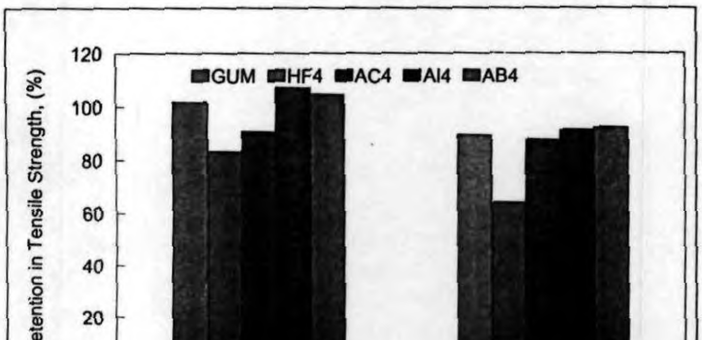

Fig. 6. Percentage retention in tensile strength after ageing at 70 °C of composites of SBR.

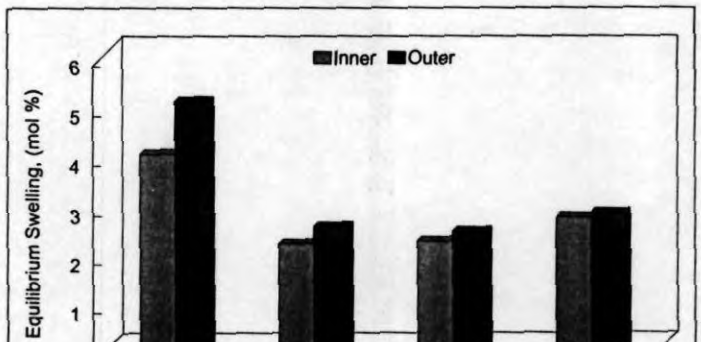

Fig. 7. Equilibrium swelling (Q_∞) values of inner and outer layers of 25.4 mm cube of SBR compounds, vulcanized for additional 5 minutes to optimum cure time.

Table 4. Properties of SBR vulcanizates containing different proportions of N 330 black and aluminum powder

Properties	Al 4	HAA	HAB	HAC	HF4
Aluminum powder, phr	40	30	20	10	0
N 330, phr	0	10	20	30	40
Maximum torque, dNm	70	75	80	84	92
t_{90}, min	17	18	19	20	21
RIT, min	4.0	4.0	4.0	4.0	4.0
CRI, min^{-1}	8.33	7.69	7.14	6.67	5.70
Hardness, Shore A	60	62	63	64	65
Tear strength, k Nm^{-1}	39.1	41.2	48.0	55.5	58.7
Rebound resilience, %	55.1	54.7	54.4	53.2	52.2
Heat build-up, ΔT °C	30	32	34	37	40
Thermal conductivity, W/(mk)	0.576	0.550	0.445	0.314	0.279
Equilibrium swelling, mol %	2.74	2.70	2.62	2.55	2.19
Modulus, (200 %), MPa	3.24	3.6	4.6	5.2	8.6
Tensile strength, MPa	5.6	9.3	19.7	22.8	23.7
Elongation at break, %	344	323	309	293	283

Tensile properties of the composites are given in Table 3. Addition of N 330 black, acetylene black and aluminum powder increased the tensile strength. The maximum increase is observed with N 330 black followed by acetylene black and minimum for aluminum powder. This is due to the difference in reinforcing capacity of these fillers due to the difference in their particle size. It is observed that as the particle size decreased the tensile strength increased. Lower particle size gives higher surface area, which enhances the reinforcement. In the case of aluminum powder, the particle size is higher than that of N 330 black and acetylene black. However the use of hexa-resorcinol improved the tensile strength in aluminum powder filled SBR vulcanizates. The modulus for 200 % elongation shown in the Table 3 follows the same trend as the tensile strength values. The maximum elongation value of the composite is decreased with filler loading. The use of bonding agent decreases the elongation at break values of aluminum powder filled composites considerably. This is because the improved adhesion does not allow the free movement of the polymer chains under a stress.

Ageing effects of these vulcanizates are presented in *Fig. 6*. The action of oxygen on rubber is slow at room temperature, but is activated by heat. To assess the ageing resistance, the samples were aged at 70 °C for 7 and 14 days in an oven, and the retention of tensile strength was evaluated. The gum composite retained the tensile strength after ageing for 7 days at 70 °C. N 330 black and acetylene black filled SBR vulcanizates did not retain their original tensile strength after ageing at 70 °C for 7 days. It is interesting to note that the tensile strength values of aluminum powder filled compounds increased after ageing at 70 °C for 7 days. Ageing for prolonged period, 14 days at 70 °C, caused a decrease in the percentage retention in tensile strength. In the prolonged ageing period also the maximum retention is with the aluminum powder filled vulcanizates compared to N 330 black and acetylene black. The higher tensile strength retention after ageing at 70 °C for 7 days of the aluminum filled vulcanizates could be due to slow, continued crossslinking of the elastomer, but at prolonged ageing the polymer degradation overcomes the crosslinking, resulting in a decrease in tensile strength.

A higher thermal conductivity of rubber compound is very important in the vulcanization of thick articles, since it results a material with more uniform crosslinking. To study this, test pieces were taken from the outer surface and central portion of a rubber cube having 25.4 mm size, which was vulcanized with 5 min additional time to the optimum cure time. The extent of crosslinking in these specimens was assessed by equilibrium swelling (Q_∞). The results are given in *Fig. 7*. In the gum compound, there exists a large difference in the Q_∞ values, between of the central and outer portions of the cube. A higher difference in Q_∞ values indicates uneven curing of the inner and outer portions of the cube. This difference is less in the case of N 330 black and acetylene black filled vulcanizates, but these vulcanizates also did not attain a uniform crosslinking. In the case of aluminum powder filled compound the difference in extent of crosslinking between the interior and surface portions becomes almost zero as evident from the Q_∞ values. In principle the 25.4 mm cube needs more than 5 min additional time for the complete vulcanization. The increased thermal conductivity thus helps to reduce the vulcanization time of thick rubber articles and gave uniform curing throughout the material.

A single material may not meet all the requirements for potential filler in a rubber compound. SBR vulcanizates having higher thermal conductivity and better strength can be obtained by the combination of aluminum powder and N 330 black. Properties of SBR vulcanizates containing different proportions of N 330 black and aluminum powder are given in Table 4. In all cases, the total filler content is fixed to 40 phr. Maximum torque, optimum cure time, hardness, tear strength, heat build up and tensile strength were decreased by the successive replacement of N 330 by aluminum powder. A marked increase in thermal conductivity is observed with the substitution by aluminum powder. Other properties like CRI, rebound resilience, equilibrium swelling and elongation at break were also increased by the substitution of N 330 black by aluminum powder. The above property changes reveal the combined effect of the thermal conductivity and reinforcement ability of these fillers. From knowledge of the combined effect of these fillers we can select a particular combination that suits for a specific application.

Conclusions

Presence of aluminum powder as a filler in SBR composites results an increase in rheometric torque and a decrease in optimum cure time, and these effects were more pronounced in presence of hexa-resorcinol as a bonding agent. Hardness, tear strength, tensile strength etc are higher for N 330 black filled vulcanizates followed by acetylene black and aluminum powder. These properties of aluminum powder filled vulcanizates can be improved by the use of a bonding agent.

A marked increase in thermal conductivity is observed with aluminum powder filled composites. The heat build up is minimum for aluminum powder filled compounds. The equilibrium swelling values and Q_f/Q_g values showed a better adhesion between SBR and aluminum powder in presence of hexa-resorcinol as bonding system. Ageing studies of these composites revealed that aluminum powder filled SBR vulcanizates have better resistance towards heat ageing compared to N330 and acetylene black. The higher thermal conductivity helps to reduce the vulcanization time of thick rubber articles and also imparts uniform curing throughout the material. The coupled effect of strength and other technological properties along with higher thermal conductivity can be obtained by the use of appropriate combinations of both N330 black and aluminum powder in the compound.

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