Effect of Bonding Agents on Styrene Butadiene Rubber–Aluminum Powder Composites

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ABSTRACT: Effects of various bonding agents—such as the hexamethylene tetramine–resorcinol system (HR), bis[3-(triethoxysilyl) propyl] tetra sulfide (Si-69), and cobalt naphthenate (CoN)—on the mechanical properties of aluminum powder filled styrene butadiene rubber composites were studied, giving emphasis on concentration of bonding agent and loading of aluminum powder. Shore A hardness, modulus, tensile strength, tear strength, heat buildup, etc., were increased by the loading of aluminum powder, and the presence of bonding agents again increased these properties. Rebound resilience and elongation at break were decreased by the addition of aluminum powder. Equilibrium swelling studies showed an improved adhesion between aluminum powder and styrene butadiene rubber (SBR) in presence of bonding agents. Among the various bonding agents used in this study, silane coupling agent (Si-69) and hexamethylene tetramine–resorcinol (HR) system were found to be better for aluminum powder filled SBR vulcanizates. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 85: 519–529, 2002

Key words: styrene butadiene rubber; aluminum powder; bonding agents; adhesion

INTRODUCTION

It is well known that addition of conductive filler enhances properties such as thermal conductivity,[1] electrical conductivity,[2] heat capacity and radiation shielding of a polymer composite. Conductive fillers normally used in polymers include carbon blacks,[3] intrinsically conductive polymeric powders,[4] and metal powders.[5] The increased thermal conductivity has special application in rubber to impart uniform curing in thick rubber articles within shorter periods of vulcanization time. Powdery metals are the best among other fillers in improving the thermal conductivity.[6] Metal powder filled polymer composite has high corrosion resistance, lower specific weight, and ease of processability. A detailed account of various applications of metal–polymer composites was given by Delmonte.[7]

The physicomechanical properties of the metallic powder filled polymer composites are inferior due to the lack of proper adhesion and poor dispersion of the filler in the polymer phase.[8] In order to get beneficial properties of rubber vulcanizates, the filler must be uniformly dispersed therein. In addition, poor dispersion may result in certain detrimental effects. These can be summarized as follows: (1) reduced product life, (2) poor performance in service, (3) poor product appearance, (4) poor processing characteristics, (5) poor product uniformity, (6) raw material waste and high finished-product rejection rates, and (7) excessive energy usage. The application of coupling agents, for the surface modification of fillers and reinforcement in polymers, has generally been suggested for improving the mechanical strength and chemical resistance of composites. Coupling

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Table I Formulation of Mixes[a]

Ingredients	Mixes			
	WOB	HR	Si-69	CoN
Styrene butadiene rubber	100	100	100	100
Stearic acid	2.0	2.0	2.0	2.0
Zinc oxide	5.0	5.0	5.0	5.0
TDQ	1.0	1.0	1.0	1.0
Aluminum powder	10	10	10	10
Hexamethylene tetramine	—	1.0	—	—
Resorcinol	—	2.0	—	—
Si-69	—	—	2.0	—
Cobalt naphthenate	—	—	—	2.0
CBS	1.0	1.0	1.0	1.0
Sulphur	2.2	2.2	2.2	2.2

[a]TDQ: 2,2,4-trimethyl-1,2-dihydro quinoline; Si-69: bis[3-(triethoxysilyl) propyl] tetrasulphide; CBS; N-cyclohexyl benzothiazyl sulfenamide.

agents may be mixed with fillers prior to their addition to polymers or they may be added directly to polymers. Several reports on coupling agents, their uses, mechanism by which they act, substrates, adhesive systems, and theories of adhesion are available.[9–13] Alkoxy silane coupling agents[14–16] have been used to modify the interface between wood fibers and polymers. Wolf[17] made a detailed study on the optimization of silane coupling agents in silica filled compounds with mixing temperature and time. The effects of some carbon black/rubber coupling agents have been investigated, and the correlation between the efficiency and chemical structure of coupling agents is discussed by Klasek et al.[18] To get an acceptable level of adhesion strength, in cases where the adhesion between the materials is usually low due to the low polarity of the polymer, modification of the polymer is reported.[19] Partial epoxidation of natural rubber has been carried out in order to assess its effect on rubber to brass adhesion.[20]

In this article, we report the effect of various bonding/coupling agents in aluminum powder filled styrene butadiene rubber composites. The selected systems include the hexamethylene tetramine–resorcinol system (HR), bis[3-(triethoxysilyl) propyl] tetrasulfide (Si-69), and cobalt naphthenate (CoN). Enhancement in adhesion between rubber and aluminum powder is studied by equilibrium swelling in toluene. Mechanical properties like shore A hardness, heat buildup, and tensile strength have been evaluated.

EXPERIMENTAL

Styrene butadiene rubber used for this study was SBR-1502 grade. Aluminum powder was obtained from M/s Kosla Metal Powder Co. Pvt. Ltd., India, which has a specific gravity of 2.7 and particle size of 127–300 nm. The bonding agents, such as hexamethylene tetramine, resorcinol, Si-69, and cobalt naphthenate, were of laboratory reagent grade. All other ingredients were of commercial grade.

The base formulations used are given in Table I. The quantity of hexamethylene tetramine and resorcinol used in this study is in the ratio 1:2 throughout this study. While plotting figures, in the case of HR system, we have taken the amount of resorcinol in the abscissa, whereas the amount of hexa varied according to the ratio. At higher loadings of aluminum powder, the concentration of bonding agent varied as the multiples of the ratio of filler to bonding agent used in the base formulation. The composites were prepared in a two-roll mixing mill (150 × 300 mm) and the bonding agents were added at the time of mixing. The samples were cured up to their optimum cure time at 150°C as obtained from a Monsanto Rheometer R-100. The mechanical properties such as hardness and heat buildup were tested according to ASTM D-2240-80 and ASTM D-623-93, respectively. Tensile and tear properties were tested using a "Zwick" Universal Testing Machine (Model UTM 1474) at 25 ± 2°C at a cross-head speed of 500 mm/min, as per ASTM D-412-80 and ASTM D-624-81 test methods, respectively. For

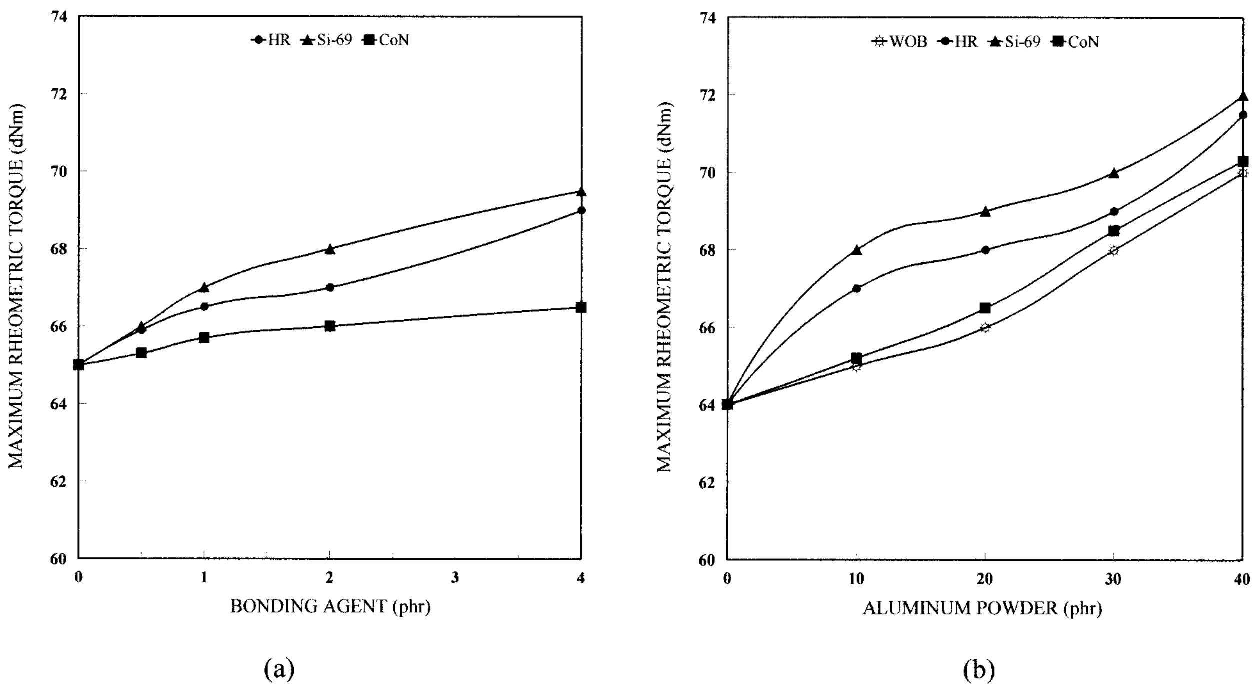


Figure 1 Variation of maximum rheometric torque in SBR composites as a function of (a) bonding agent at 10 phr of aluminum powder and (b) the amount of aluminum powder.

swelling studies, vulcanised pieces were cut circularly by means of a sharp-edged die. The initial weight was noted and immersed in toluene at 27°C. After attaining the equilibrium swelling, the sample was taken out and the swollen weight is noted after the wet surface is dried using a blotting paper.

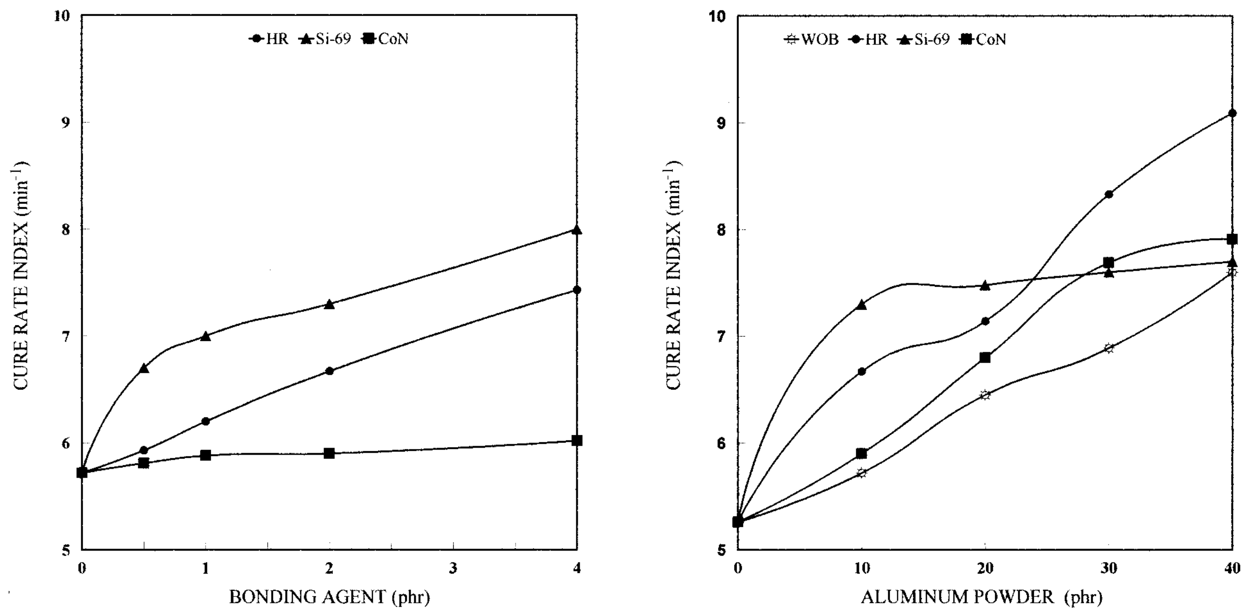
RESULTS AND DISCUSSION

Effect of Bonding Agents on Cure Characteristics

The maximum rheometric torque values obtained at 150°C for aluminum powder filled SBR composites are given in Figure 1. For 10 phr loaded composites of aluminum powder containing bonding agents, the maximum torque increased continuously. From Figure 1(b) it is clear that without the use of any bonding agent the maximum torque increases with aluminum powder loading. At higher loading, both the HR system and Si-69 increased the maximum torque of aluminum powder filled SBR composites. The increase is minimal with cobalt naphthenate, which may be due to its catalytic activity in the oxidation of rubber. The cure rate index (CRI) value, which is a direct measure of the nature of cure of the rubber vulcanizate, is shown in Figure 2. It is found that all the bonding agents increased the CRI. At 10 phr of aluminum powder loading the CRI is in the order Si-69 > HR > CoN. But at higher loadings, HR is found to be better in increasing the CRI, which may be due to the action of hexa as a secondary accelerator.

Effect of Bonding Agents on Tensile Properties

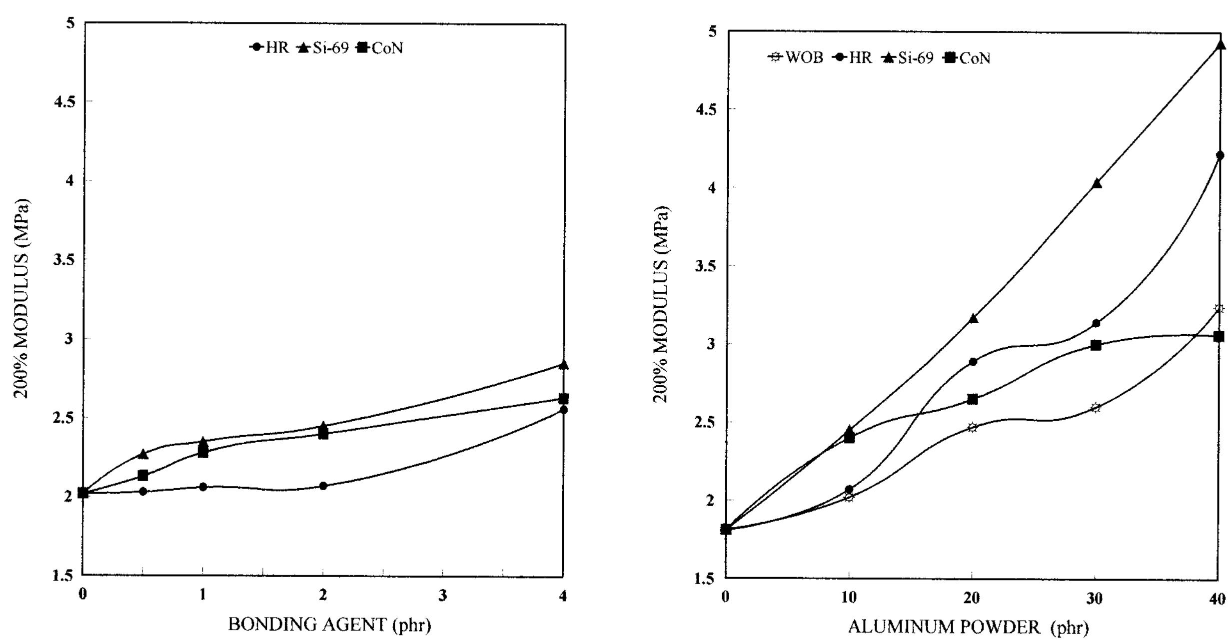
Figure 3 shows the modulus at 200% elongation of aluminum powder filled SBR composites in presence of various bonding agents. The modulus values are found to be increased by the addition of bonding agents. The tensile strength of the composites is given in Figures 4(a) and 4(b). As in the case of modulus, here also the presence of bonding agents increased the tensile strength and maximum effect is observed with silane coupling agent. It is also noted that even without any bonding agent, the addition of aluminum powder increased the tensile strength of SBR vulcanizates. The increase in modulus and tensile strength for these composites in the presence of bonding agents are due to the extra interactions between the filler and the matrix. The elongation at break of the aluminum powder filled SBR compound with and without bonding agents is presented in



(a) (b)

Figure 2 Variation of cure rate index in SBR composites as a function of (a) bonding agent at 10 phr of aluminum powder and (b) the amount of aluminum powder.

Figure 5. At 10 phr loading of aluminum powder, the elongation at break decreased gradually as the bonding agent increased and the decrease is sharper at higher loading of bonding agent. Aluminum powder loading decreased the elongation due to the decrease in polymer frac-



(a) (b)

Figure 3 Variation of 200% modulus in SBR composites as a function of (a) bonding agent at 10 phr of aluminum powder and (b) the amount of aluminum powder.

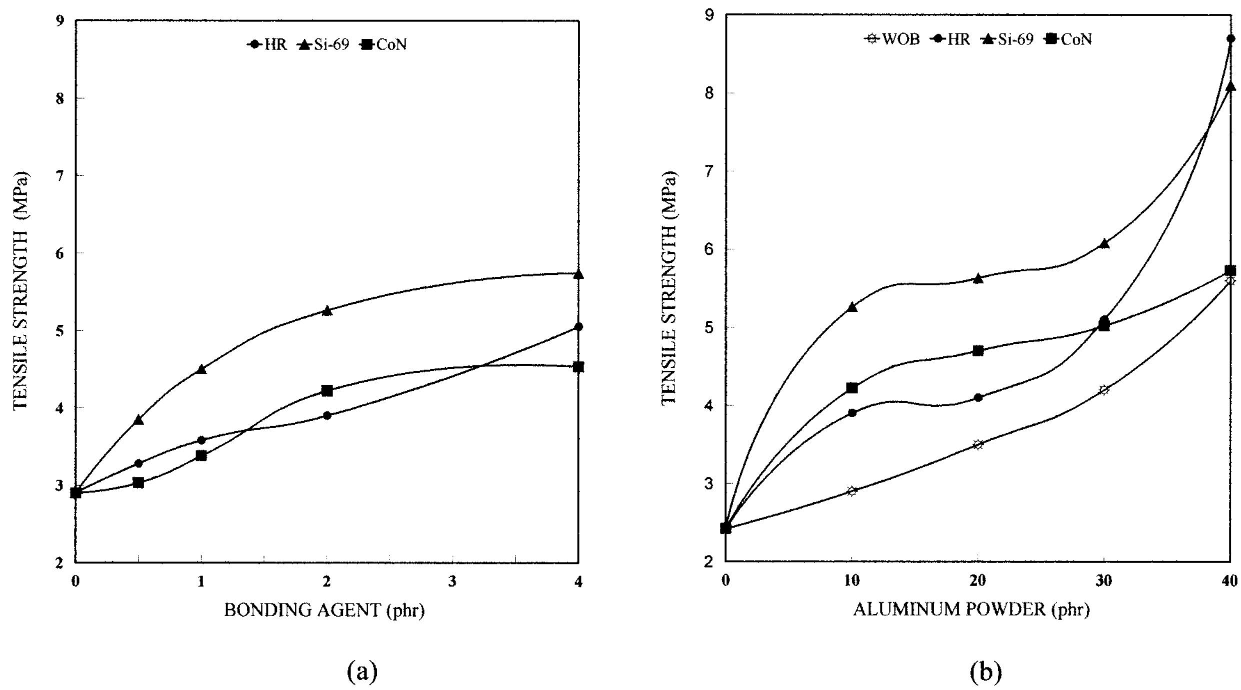


Figure 4 Variation of tensile strength in SBR composites as a function of (a) bonding agent at 10 phr of aluminum powder and (b) the amount of aluminum powder.

tion in the composite. The bonding agents again decreased the elongation at break, since the presence of bonding agents caused additional interaction between the aluminum powder and rubber that restricts the elongation of the polymer networks.

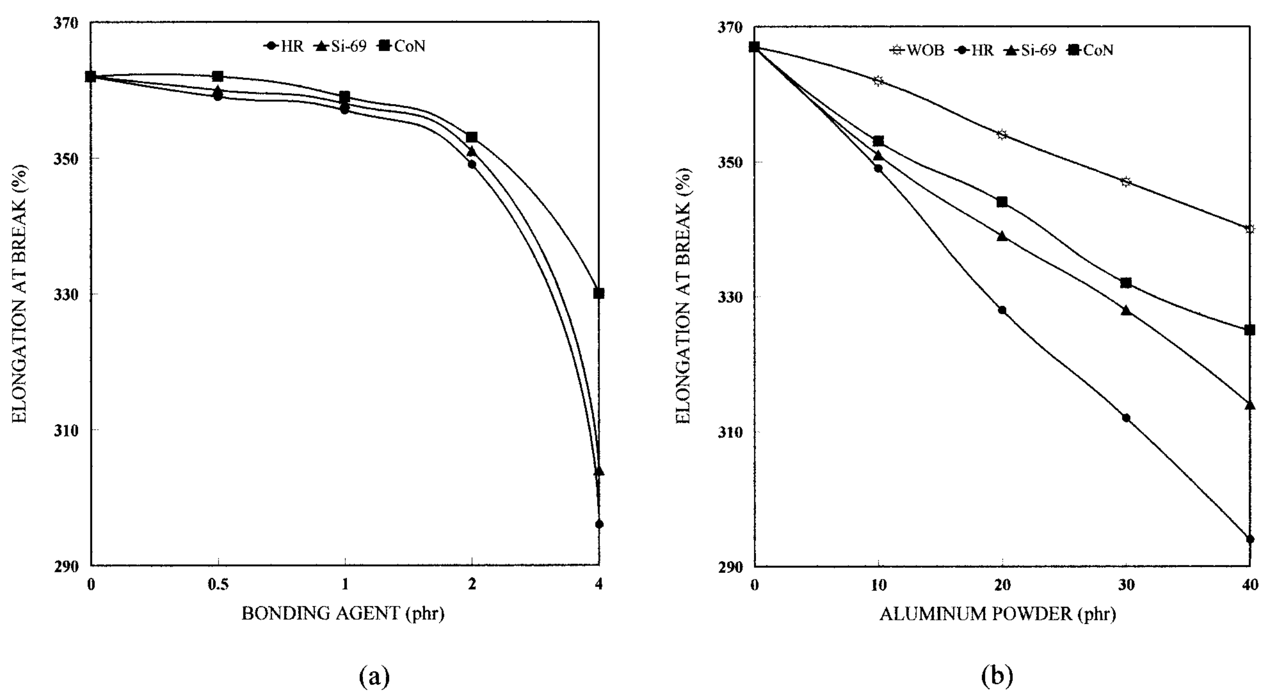


Figure 5 Variation of elongation at break in SBR composites as a function of (a) bonding agent at 10 phr of aluminum powder and (b) the amount of aluminum powder.

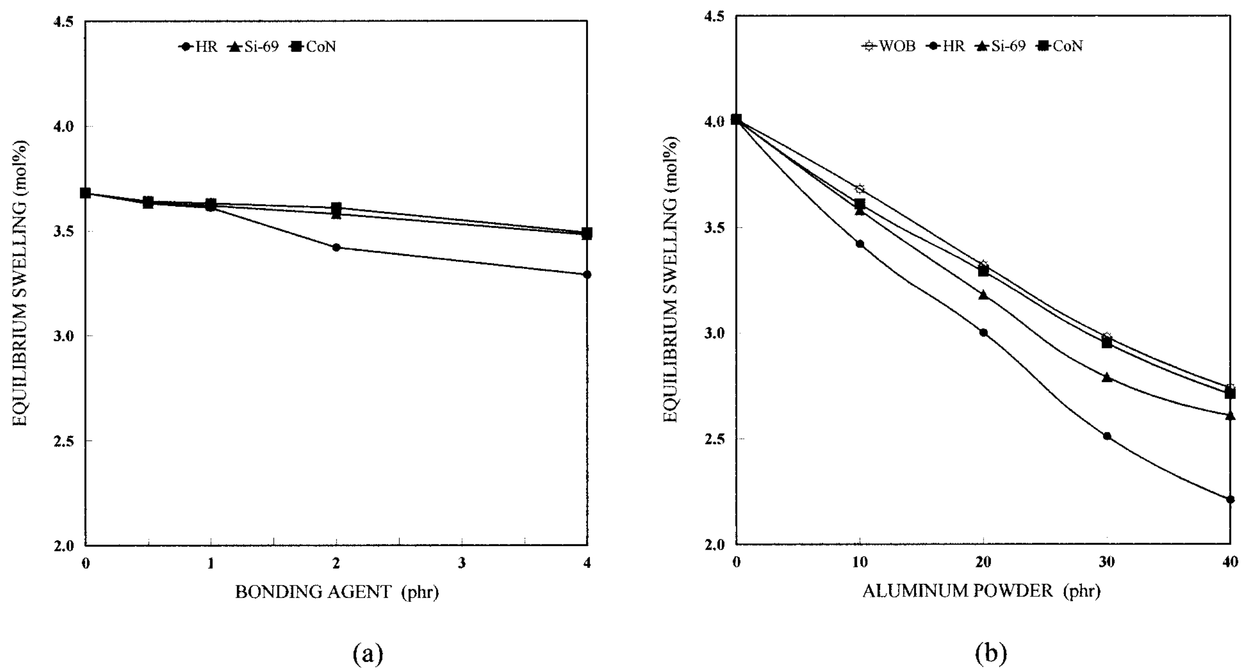


Figure 6 Variation of equilibrium swelling in SBR composites as a function of (a) bonding agent at 10 phr of aluminum powder and (b) the amount of aluminum powder (swelling solvent, toluene at 27°C).

Effect of Bonding Agents on Swelling Behavior

Equilibrium swelling (Q_∞) of aluminum powder filled SBR vulcanizates are presented in Figures 6(a) and 6(b). Aluminum powder filled SBR having no bonding agent decreased the Q_∞ values. This is due to the combined effect of reinforcement, additional crosslinking in the presence of filler, and the decrease in polymer fraction in the composite. The presence of bonding agent again decreased the Q_∞ values, the maximum decrease is found with HR system followed by Si-69. Equilibrium swelling in solvents can be taken as a means to assess rubber–filler adhesion, because filler—if bonded—is supposed to restrict the swelling of the elastomers. Swelling of rubber vulcanizates in a wide range of solvents has been studied by Hargoppad and Aminabhavi.[21] The degree of cure in a particular filler reinforced vulcanizate can also be calculated by swelling methods. Here also the decrease in equilibrium swelling of aluminum powder filled SBR compounds in the presence of various bonding agents can be explained by the improved adhesion. The value of $1/Q$, the degree of crosslinking, can also be used to study the enhancement in adhesion, where Q is defined as grams of solvent per gram of hydrocarbon at equilibrium swelling and is calculated by

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

Figure 7 shows the $1/Q$ values of the composites with different bonding systems. In all cases the $1/Q$ values follow the order, HR > Si-69 > CoN. According to Lorentz and Parks,[22]

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

where Q has the same meaning as above, and the subscripts f and g of the equation 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. Figure 8 gives the Q_f/Q_g values, of the SBR compounds. At 10 phr of aluminum powder loading (Figure 8a) the addition of bonding agents decreased the Q_f/Q_g values, suggesting greater rubber–filler interaction in the composites. At higher aluminum powder loadings [Fig. 8(b)], the presence of bonding agent decreased the Q_f/Q_g values, and the maximum effect is with the HR system. In all cases the ability of the bonding agents to decrease the Q_f/Q_g values is in the order HR > Si-69 > CoN. A strong polymer–filler interaction reduces the voids at the interface. This confirms that maximum aluminum powder–rubber interaction has occurred when bonding agents are present in the composites.

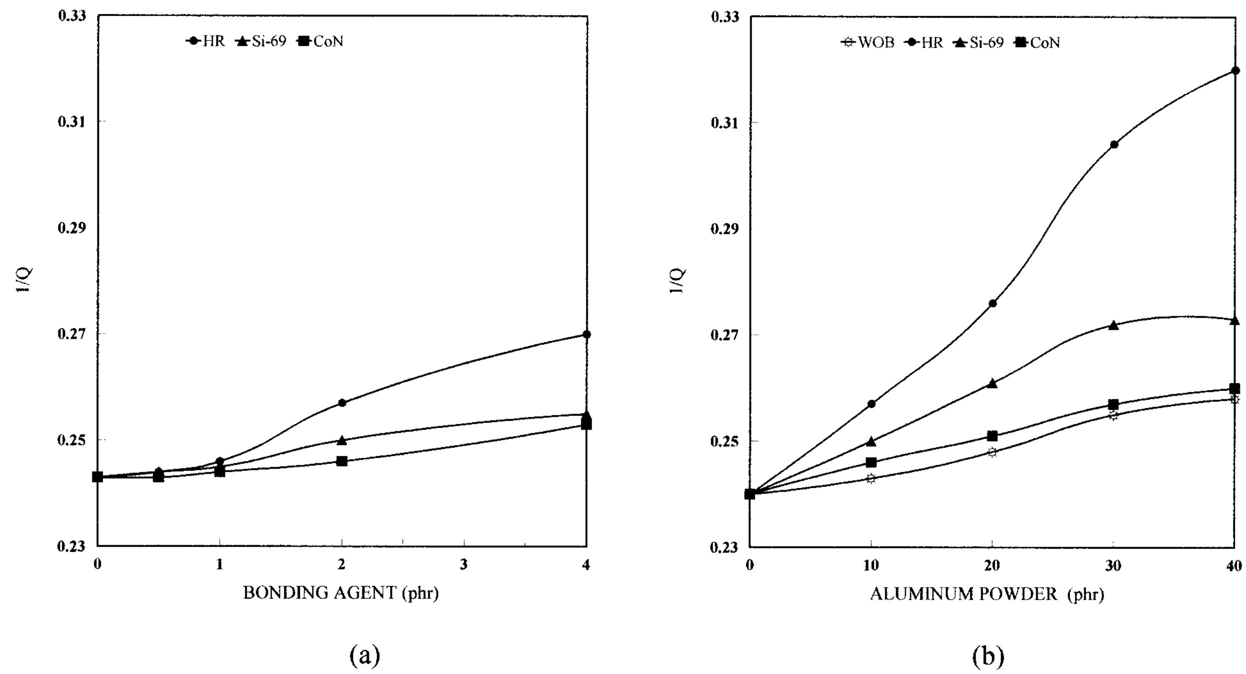


Figure 7 Variation of 1/Q values in SBR composites as a function of (a) bonding agent at 10 phr of aluminum powder and (b) the amount of aluminum powder.

The presence of bonding agents increased the filler–rubber interaction. These bonding agents are supposed to act differently to affect the bonding between the filler and rubber. In the case of HR system, the condensation reaction of hexamethylene tetramine and resorcinol produces a resin *in situ* during vulcanization by the joining of resorcinol nuclei and methylene from hexa, which

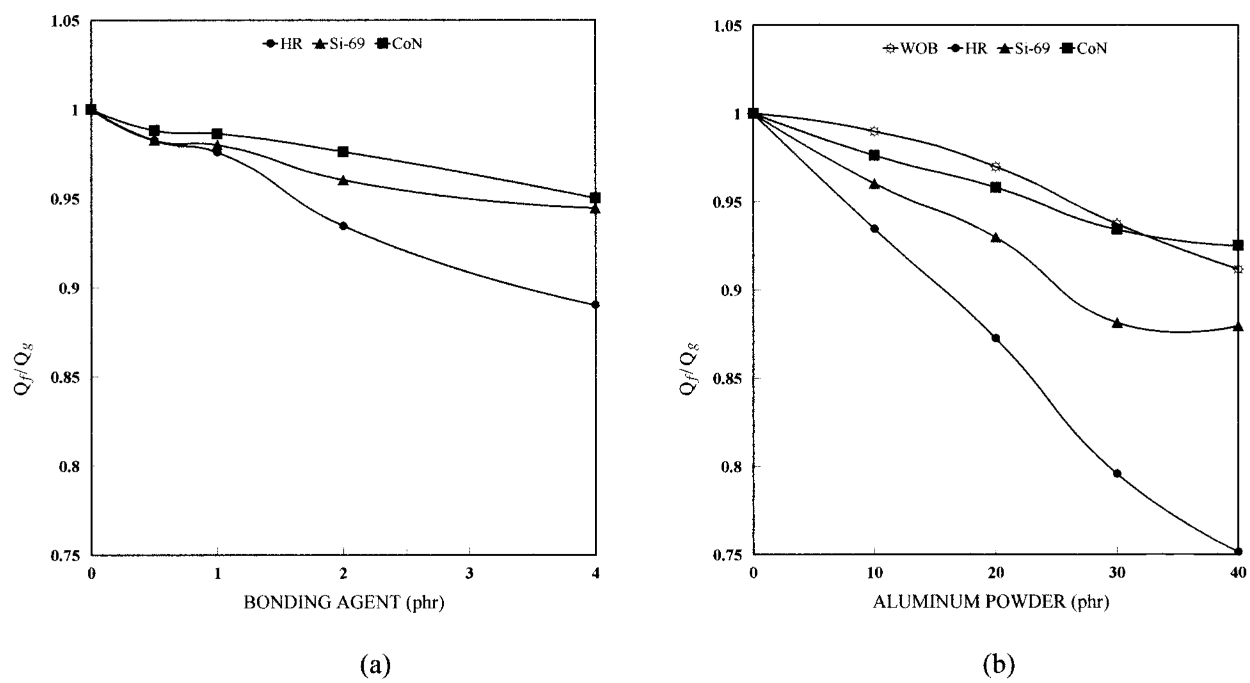


Figure 8 Variation of Q_f/Q_g values in SBR composites as a function of (a) bonding agent at 10 phr of aluminum powder and (b) the amount of aluminum powder.

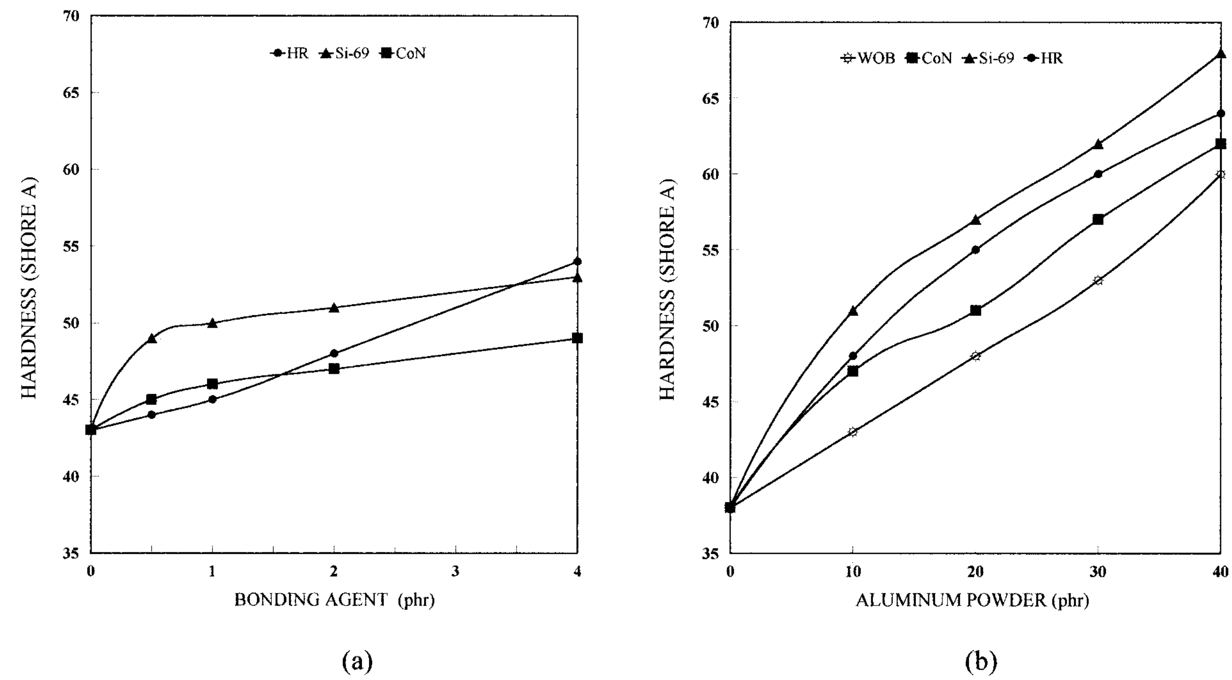


Figure 9 Variation of hardness in SBR composites as a function of (a) bonding agent at 10 phr of aluminum powder and (b) the amount of aluminum powder.

improves the adhesion between rubber and the filler. This is due to the increased polarity of the rubber, which arises from the powerful hydrogen-bonding characteristics of the resorcinol resin. This makes great improvements in bonds between rubber and various substrate materials

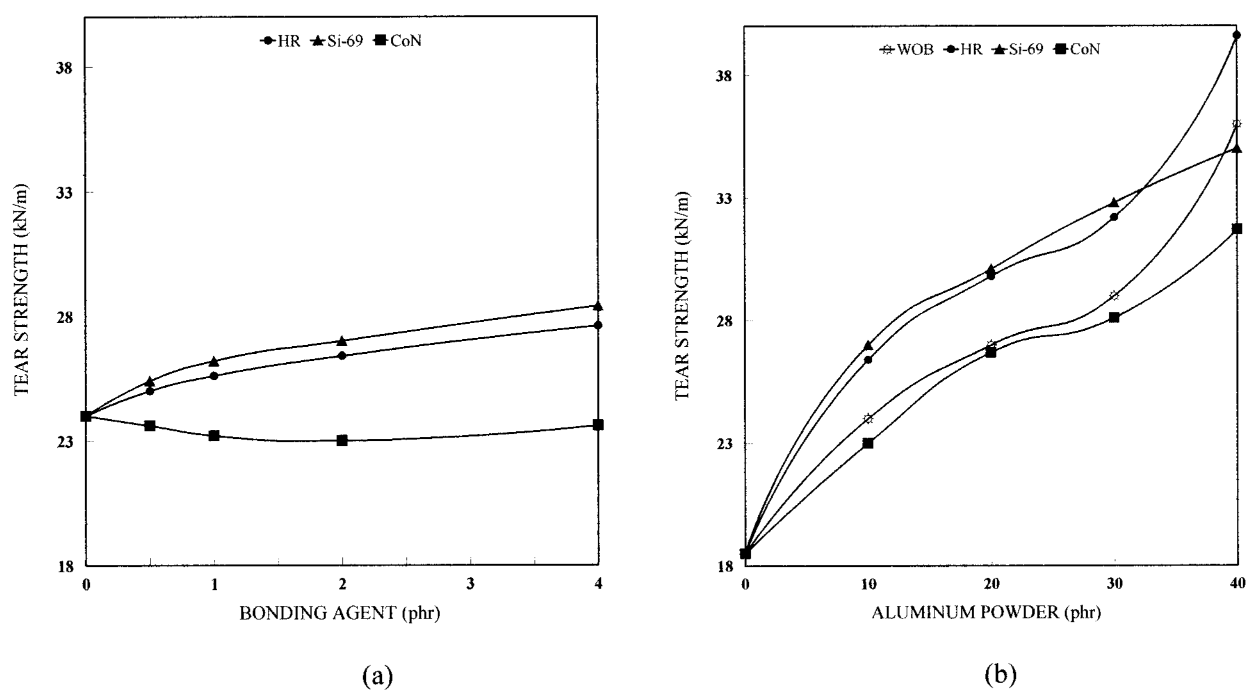


Figure 10 Variation of tear strength in SBR composites as a function of (a) bonding agent at 10 phr of aluminum powder and (b) the amount of aluminum powder.

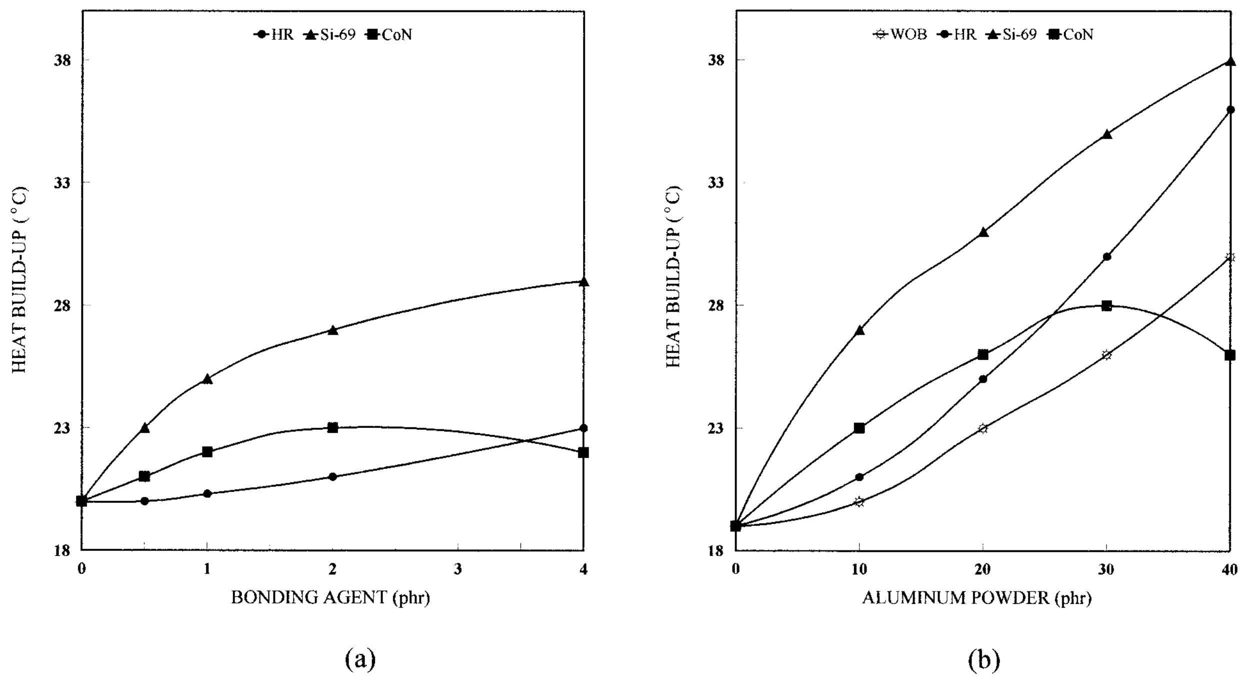


Figure 11 Variation of heat buildup in SBR composites as a function of (a) bonding agent at 10 phr of aluminum powder and (b) the amount of aluminum powder.

such as metal powders. The coupling mechanism with silanes involves a twofold reaction of silanes with both the organic polymer and the metal substrate. The organo functional silane must be compatible with the organic phase so that the silane becomes part of the polymer. The silane, by coreacting with the polymers, modifies the polymer morphology at the interface, which facilitates the stress transfer at the interface. The equilibrium theory of bonding suggests a reversible hydrolytic mobility of silanols at a mineral surface and the silane modified tacky interface provides a strong bond to the mineral surface.[23] Cobalt salts are used commercially in elastomeric stocks to promote metal adhesion. It is believed that such salts will create an increased polarity, which would improve the adhesion properties.

Effect of Bonding Agents on Mechanical Properties

Figure 9 shows the shore A hardness of the composites. As the bonding agent concentration increased, the hardness also increased. From Figure 9(b), it is clear that aluminum powder increased the hardness. This is due to the higher extent of crosslinking in the polymeric phase. The presence of bonding agents further increased the hardness due to the increased adhesion of the aluminum powder with SBR.

Tear strength for SBR composites containing aluminum powder is shown in Figure 10. At 10 phr level of aluminum powder, Si-69 and HR increased the tear strength and is higher in the former case. Aluminum powder increased the tear strength of the SBR composites which is in proportion with its loading. The hexa-resorcinol system and Si-69 increased the tear strength, but in the case of cobalt naphthenate, a lower value of tear strength is recorded compared to the control compound. The enhancement of tear strength with HR and Si-69 are due to the improved adhesion. But with CoN, the adhesion effect might have been over shadowed by the catalytic oxidation reaction taking place on the main chain.[24] This dual functionality of cobalt naphthenate is reflected in the properties of its compounds.

The heat build-up values, in Figure 11, showed a marked increase with Si-69 at 10 phr loading of aluminum powder. Heat buildup increased with loading of aluminum powder. Composites bonded with HR and Si-69 have high value of heat buildup especially, at high loading of aluminum powder. Cobalt naphthenate increased the heat buildup up to 30 phr of aluminum and then a slight decrease is observed.

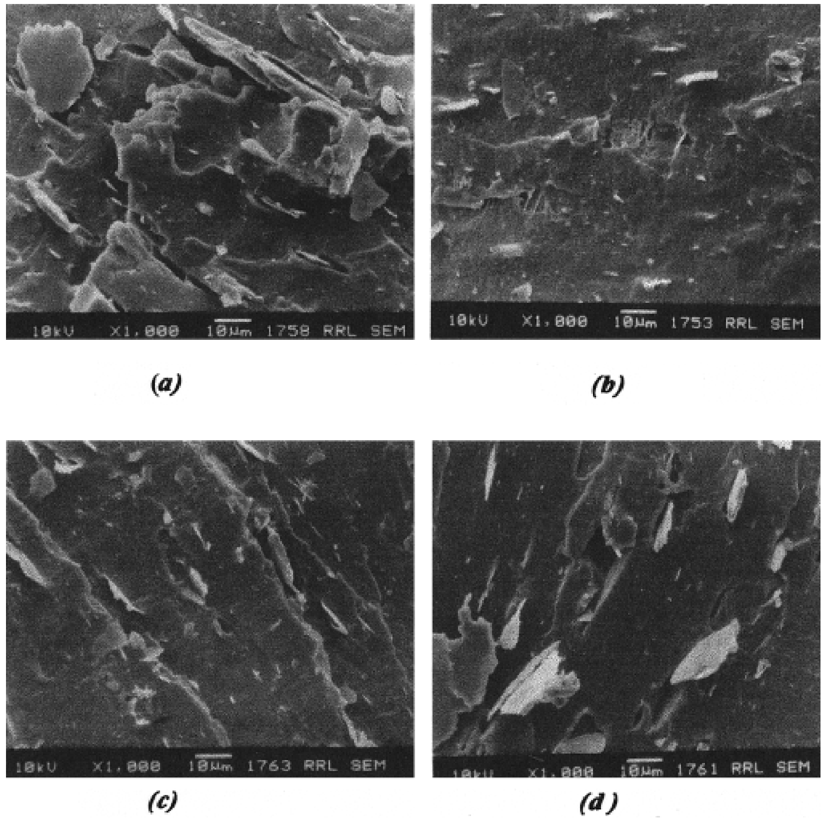


Figure 12 SEM photographs of tensile fractured surfaces of 10 phr aluminum powder filled SBR vulcanizates (a) having no bonding agent, (b) with the HR system, (c) with Si-69, and (d) with CoN (magnification ×1000).

Analysis of Scanning Electron Microscope Photographs

The fractured surface of the tensile pieces of the composites was examined by scanning electron microscope (SEM). The SEM photographs are given in Figures 12(a–d). These SEM photographs support the improved properties of aluminum powder filled styrene butadiene rubber composites in the presence of bonding agents. In the unbonded composite, the aluminum powder exists as loose aggregates whereas in the bonded composites, aluminum particles are more aligned as compared to unbonded composites. Aluminum powder is more firmly bonded to the rubber matrix with the HR and with the Si-69 coupling agent.

CONCLUSIONS

The cure characteristics of aluminum powder filled SBR composites showed an increase in maximum rheometric torque and cure rate index with aluminum powder loading. Shore A hardness of SBR-aluminum powder composites is increased with loading and is more pronounced in presence of bonding agents. Equilibrium swelling studies showed an improved adhesion between aluminum powder and SBR in the presence of bonding agents. The modulus, tensile strength, and tear strength increased with aluminum powder loading, and these properties were further improved with HR and Si-69 bonding systems. The improved adhesion restricts the chain movements, which caused a decrease in elongation at break in presence of bonding agents. SBR-aluminum powder composites showed a marked increase in heat build-up value especially with the silane coupling agent.

REFERENCES

1. Sundrom, D. W.; Lee, Y. D. J Appl Polym Sci 1972, 16, 3159.
2. Yang, L.; Schruben, D. L. Polym Eng Sci 1994, 34, 1109.

3. Lee, J. C.; Nakajima, K.; Ikehara, T.; Nishi, T. J Appl Polym Sci 1997, 65, 409.
4. Meyers, R. E. U.S. Patent, 4, 617, 353, Oct. 14, 1986.
5. Mukhopadyay, R.; De, S. K.; Basu, S. J Appl Polym Sci 1976, 20, 2575.
6. Norman, R. H. Conductive Rubbers and Plastics; Elsevier Publishing: Amsterdam, 1970.
7. Delmonte, J. Metal/Polymer Composites; Van Nostrand Reinhold: New York, 1961.
8. Han, C. D.; Van Pen Seghe, T.; Shete, P.; Raw, J. R. Polym Eng Sci 1981, 21, 196.
9. Meberkia, S.; Vipulanandan, C. Polym Eng Sci 1994, 34, 1287.
10. Pal, P. K.; Chakravarty, S. N.; De, S. K. J Appl Polym Sci 1983, 28, 659.
11. Ranney, M. W.; Pagano, C. A. Rubber Chem Technol 1971, 44, 1080.
12. Raj, R. G.; Kokta, B. V.; Groulean, G.; Daneault, C. Polym Plast Technol Eng 1990, 29, 339.
13. Varghese, S.; Kuriakose, B.; Thomas, S.; Joseph, K. Rubber Chem Thenol 1995, 68, 37.
14. A. D.; Beshay, B. V.; Kokta, C. Daneault, Polym Comp 1985, 6, 261.
15. Morel, S. H. Plast Rubber Proc Appl 1981, 1, 179.
16. Schneider, M. H.; Brebner, K. I. Wood Sci Technol 1985, 19, 67.
17. Wolf, S. Rubber Chem Technol 1982, 55, 967.
18. Klasek, A.; Spacek, J.; Curile, R.; Kafka, S. J Appl Polym Sci 1996, 61, 1137.
19. Breuis, D. U.; Briggs, D. Polymer 1981, 22, 7.
20. Boscott, D. A.; Lebrte, R. S. Eur Polym J 1990, 26, 201.
21. Hargoppad, S. B.; Aminabhavi, T. M. J Appl Polym Sci 1991, 42, 2329.
22. Lorentz, O.; Parks, C. R. J Polym Sci 1961, 50, 299.
23. Pluddemann, E. P. Appl Polym Symp 1972, 19, 75.
24. Naunton, W. J. S. The Applied Science of Rubber; Edward Arnold Publishers: London, 1961.