CHAPTER XI

EFFECT OF BONDING AGENTS ON THE PROPERTIES OF STYRENE BUTADIENE RUBBER-ALUMINIUM POWDER COMPOSITES

Results of this chapter have been communicated to Journal of Applied Polymer Science
The physicomechanical properties of the metal powder filled polymer composites are inferior due to the lack of proper adhesion and poor dispersion of the filler in the polymer phase [1]. In order to get beneficial properties of rubber vulcanizates, the filler must be uniformly dispersed therein. In addition, poor dispersion may results in certain detrimental effects [2]. These can be summarised as follows (i) reduced product life, (ii) poor performance in service, (iii) poor product appearance, (iv) poor processing characteristics, (v) poor product uniformity, (vi) raw material waste and high finished-product rejection rates and (vii) 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 agents may be mixed with fillers prior to their addition to polymers or they may be added directly to the polymers. Several reports on coupling agents, their uses, mechanism by which they act, substrates, adhesive systems, and theories of adhesion are available [3-7] and most of them are discussed in Chapter III. Wolff [8] made a detailed study on the optimisation of silane-silica compounds, variations of mixing temperature and time during the modification of silica with a silane-coupling agent. The effects of some carbon black/rubber-coupling agents without nitrosogroups have been investigated, and the correlation between the efficiency and chemical structure of coupling agents was discussed by Klasek et al. [9]. 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, modifications of the polymer is reported [10]. Partial epoxidation of natural
rubber has been carried out in order to assess its effect on rubber to brass adhesion [11].

### Table XI.1. Base Formulations of mixes

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Mixes</th>
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<tr>
<td></td>
<td>G</td>
</tr>
<tr>
<td>SBR</td>
<td>100</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>2.0</td>
</tr>
<tr>
<td>Zinc oxide</td>
<td>5.0</td>
</tr>
<tr>
<td>TDQ</td>
<td>1.0</td>
</tr>
<tr>
<td>Aluminium powder</td>
<td>--</td>
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<tr>
<td>Hexamethylene tetramine</td>
<td>--</td>
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<tr>
<td>Resorcinol</td>
<td>--</td>
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<tr>
<td>Si-69</td>
<td>--</td>
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<tr>
<td>Cobalt naphthenate</td>
<td>--</td>
</tr>
<tr>
<td>CBS</td>
<td>1.0</td>
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<tr>
<td>Sulphur</td>
<td>2.2</td>
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SBR - Styrene butadiene rubber
TDQ - 2,2,4-Trimethyl-1,2-dihydro quinoline
Si-69 - bis[3-(trichoxysilyl) propyl] tetrasulphide
CBS - N-cyclohexyl benzthiazyl sulphenamide

In this chapter, the effect of various bonding/coupling agents in aluminium powder filled styrene butadiene rubber composites is presented. The selected systems include, hexamethylene tetramine-resorcinol system (HR), bis[3-(trichoxysilyl) propyl] tetrasulphide (Si-69) and cobalt naphthenate (CoN). The base formulations used are given in Table XI.1. The ratio of hexamethylene tetramine and resorcinol used in this study is in the ratio 1:2. While plotting figures, in the case of HR system, we have taken the amount of resorcinol in the abscissa, whereas the amount of hexa varies according to the ratio. The effect of bonding agents was studied at a
constant aluminium powder loading of 10 phr. The effect of loading of aluminium powder was studied by varying the aluminium powder content from 0 to 40 phr. 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. Mechanical properties like Shore A hardness, rebound resilience, heat build-up, tensile strength etc. have been evaluated, according to the standard procedures as given in Chapter II. Enhancement in adhesion between rubber and aluminium powder is studied by equilibrium swelling in toluene.

**XI.1. Effect of Bonding Agents on Cure Characteristics**

The maximum rheometric torque obtained at 150°C for aluminium powder filled SBR composites are given in Figure XI.1. For 10 phr aluminium powder loaded composites with hexa-resorcinol and Si-69 as bonding agent, the maximum torque, increased continuously whereas in the case of cobalt naphthenate the trend is reversed. From Figure XI.1b it is clear that without the use of any bonding agent the maximum torque increases with aluminium powder loading. At higher loading, both HR-system and Si-69 increased the maximum torque of aluminium powder filled SBR composites. With HR and Si-69, the adhesion between aluminium powder and SBR improved considerably, which increased the maximum torque. The decrease in torque with cobalt naphthenate may be due to its catalytic activity in the oxidation of rubber. The cure rate index (CRI) values, which is a measure of the level of cure of rubber vulcanizate, are shown in Figure XI.2.
Figure XI.1. Variation of maximum rheometric torque in SBR composites as a function of (a) the amount of bonding agent at 10 phr of aluminium powder (b) the amount of aluminium powder
Figure XI.2. Variation of cure rate index in SBR composites as a function of
(a) the amount of bonding agent at 10 phr of aluminium powder (b) the amount of aluminium powder
It is found that all the bonding agents increased the CRI. At 10 phr of aluminium 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.

XI.2. **Effect of Bonding Agents on Tensile Properties**

Figure XI.3 shows the modulus at 200% elongation of aluminium 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 XI.4a and XI.4b. 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 aluminium powder increased the tensile strength of SBR-vulcanizates. This is further increased by the addition of bonding agents. The increase in modulus and tensile strength for these composites in presence of bonding agents are due to better interactions between the filler and the matrix. The elongation at break of the aluminium powder filled SBR compound with and without bonding agents is presented in Figure XI.5. At 10 phr loading of aluminium powder, the elongation at break decreased gradually as the bonding agent increased and the decrease is sharper at higher loading of bonding agent. From Figure XI.5b, we can see that, the aluminium powder loading decreased the elongation continuously due to the decrease in polymer fraction in the composite. The bonding agents again decreased the elongation at break, since the presence of bonding agents caused additional interaction between the aluminium powder and rubber which restrict the elongation of the polymer net works.
Figure XI.3. Variation of 200% modulus in SBR composites as a function of (a) the amount of bonding agent at 10 phr of aluminium powder (b) the amount of aluminium powder
Figure XI.4. Variation of tensile strength in SBR composites as a function of (a) the amount of bonding agent at 10 phr of aluminium powder (b) the amount of aluminium powder.
Figure XI.5. Variation of elongation at break in SBR composites as a function of (a) the amount of bonding agent at 10 phr of aluminium powder (b) the amount of aluminium powder.
XI.3. Effect of Bonding Agents on Swelling Behaviour

Equilibrium swelling ($Q_x$) of aluminium powder filled SBR-vulcanizes with and without bonding agents is presented in Figures XI.6a and XI.6b. Aluminium powder filled SBR having no bonding agent decreased the $Q_x$ values. This is due to the combined effects of reinforcement, additional crosslinking in presence of filler and the decrease in polymer fraction in the composite. The presence of bonding agent again decreased the $Q_x$ 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 Hargopad and Aminabhavi [12]. The degree of cure in a particular filler reinforced vulcanizates can also be calculated by swelling methods. Here also the decrease in equilibrium swelling of aluminium powder filled SBR-compounds in presence of various bonding agents can be explained on 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

\[
Q = \frac{\text{Swollen weight} - \text{Dried weight}}{\text{Original weight} \times 100 / \text{Formula weight}} \quad \text{..... (XI.1)}
\]
Figure XI.6. Variation of equilibrium swelling in SBR composites as a function of (a) the amount of bonding agent at 10 phr of aluminium powder (b) the amount of aluminium powder (solvent, toluene at 27°C)
Figure XI.7. Variation of $1/Q$ values in SBR composites as a function of (a) the amount of bonding agent at 10 phr of aluminium powder (b) the amount of aluminium powder
Figure XI.8. Variation of \( Q_f/Q_0 \) values in SBR composites as a function of (a) the amount of bonding agent at 10 phr of aluminium powder (b) the amount of aluminium powder
Figures XI.7a and XI.7b show 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. This showed that adhesion is maximum with HR system followed by Si-69. According to Lorentz and Parks [13],

\[ \frac{Q_f}{Q_g} = a e^{z} + b \]  

..... (XI.2)

where Q has the same meaning as above, 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. Higher the \( \frac{Q_f}{Q_g} \) values, the lower will be the extent of interaction between the filler and the matrix. Figure XI.8 gives the \( \frac{Q_f}{Q_g} \) values of the SBR-compounds. At 10 phr of aluminium powder loading (Figure XI.8a) the addition of bonding agents decreased the \( \frac{Q_f}{Q_g} \) values, suggesting greater rubber-filler interaction in the composites. At higher aluminium powder loadings (Figure XI.8b), the presence of bonding agent decreased the \( \frac{Q_f}{Q_g} \) values, and the maximum effect is with the HR system. Among the cases studied the ability of the bonding agents to decrease the \( \frac{Q_f}{Q_g} \) values is in the order, HR > Si-69 > CoN. Stronger the polymer-filler interaction lesser will be the voids at the interface, which in turn form less solvent pockets. This confirms that maximum aluminium powder-rubber interaction has occurred when bonding agents are present in the composites. These bonding agents are supposed to act differently to affect the bonding between the filler and rubber. The bonding mechanisms are illustrated in Chapter III.

XI.4. Effect of Bonding Agents on Mechanical Properties

Figure XI.9 shows the Shore A hardness of the composites. As the bonding agent concentration increased, the hardness also increased. From
Figure XI.9b, it is clear that even without any bonding system aluminium 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 aluminium powder with SBR.

Tear strength for SBR-composites containing aluminium powder is shown in Figure XI.10. At 10 phr level of aluminium powder, Si-69 and HR increased the tear strength and is higher in the former case. Aluminium powder increased the tear strength of the SBR composites which is in proportion with its loading. 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 of the polymeric chains. This dual functionality of cobalt naphthenate is reflected in the properties of its compounds.

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

Rebound resilience of the composites is given in Figure XI.12. The maximum decrease in resilience is observed with vulcanizates containing Si-69 followed by HR system, at 10 phr loading of aluminium powder. At higher loadings also the rebound resilience is decreased with aluminium powder for composites with and without bonding agents. As the loading of filler increased, the polymer fraction in the compound decreased, resulting a decreased resilience.
Figure XI.9. Variation of hardness in SBR composites as a function of (a) the amount of bonding agent at 10 phr of aluminium powder (b) the amount of aluminium powder.
Figure XI.10. Variation of tear strength in SBR composites as a function of (a) the amount of bonding agent at 10 phr of aluminium powder (b) the amount of aluminium powder
Figure XI.11. Variation of heat build-up in SBR composites as a function of (a) the amount of bonding agent at 10 phr of aluminium powder (b) the amount of aluminium powder
Figure XI.12. Variation of rebound resilience in SBR composites as a function of (a) the amount of bonding agent at 10 phr of aluminium powder (b) the amount of aluminium powder
XI.5. Analysis of SEM 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 XI.13(a-d).

*Figure XI.13. SEM photographs of tensile fractural surface of 10 phr aluminium powder filled SBR vulcanizates with and without the presence of bonding agents.*

(a) having no bonding agent  
(b) with HR-system  
(c) with Si-69  
(d) with CoN

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These SEM photographs support the improved properties of aluminium powder filled styrene butadiene rubber composites in presence of bonding agents. In the unbonded composite the aluminium powder exists as loose aggregates where as in the bonded composites, aluminium particles are more aligned as compared to unbonded composites. Aluminium powder is more firmly bonded to the rubber matrix with hexamethylene tetramine-resorcinol system (HR) and with silane (Si-69) coupling agent.

**XI.6. Conclusions**

The cure characteristics of aluminium powder filled SBR-composites showed an increase in maximum rheometric torque and cure rate index with aluminium powder loading. Hexa-resorcinol and Si-69 increased the maximum torque while CoN decreased it. Shore A hardness of SBR-aluminium powder composites is increased with loading and is more pronounced in presence of bonding agents. Equilibrium swelling studies showed an improved adhesion between aluminium powder and SBR in presence of bonding agents. The modulus, tensile strength and tear strength increased with aluminium 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-aluminium powder composites showed a marked increase in heat build-up value especially with silane coupling agent. Aluminium powder caused a decrease in rebound resilience of SBR compounds and the decrease is maximum with Si-69 followed by HR system.
References