Effect of Adhesion on the Equilibrium Swelling of Natural Rubber-Aluminium Powder Composites

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ABSTRACT: Equilibrium swelling of natural rubber composites containing aluminium powder has been investigated in a series of aromatic hydrocarbon solvents, such as benzene, toluene, xylene, and mesitylene. These composites were vulcanized by four vulcanizing systems, *viz.* conventional, efficient, dicumyl peroxide, and a mixture, consisting of sulfur and dicumyl peroxide. In each system, the effect of aluminium powder with and without bonding agent was studied. The results showed that addition of bonding agent reduced the swelling considerably, and its effect is more pronounced in the conventional system due to increased adhesion. The dependence of the diffusion coefficient on the crosslinking system and the solvent–polymer interaction parameter were calculated from diffusion data. These results are also indicative of the improved adhesion with hexa-resorcinol–silica bonding system in these composites. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 2427–2438, 1998

Key words: adhesion; swelling; aluminum powder; natural rubber; composites

INTRODUCTION

Metal powders form a class of potential fillers for polymer composites and offer advantages of conducting heat and electricity that suit various specific applications. They provide inherent electromagnetic interference and radiofrequency interference shielding to protect business machines, aerospace components, and computers. Metal powders incorporated polymer composites also have applications like discharging static electricity, heat conduction, electrical heating, converting mechanical to electrical signals, and frictionantifriction materials. These composites have the advantage of high corrosion resistance, lower specific weight, great accessibility, and the ease of making complicated articles.

Numerous articles related to the properties of the conductive filler-polymer composites have ap-

peared recently in the literature.¹⁻⁹ Interest in this field is driven by an increasing industrial demand for materials with tailored physical properties. In these particulate-filled systems, a significant problem is caused by the nonuniform dispersion of the discrete phase in the matrix, giving rise to fluctuations in the composite properties.⁹⁻¹¹ Partial surface modification of the filler by a suitable coupling agent reduces this problem by enhancing surface interaction between the two phases. There exist many coupling agents for this application and, among these, silane,¹² titanate coupling agents,¹³ and chromium(III) fumarato compounds¹⁴ have been found to form strong assemblies. Better adhesion strength in these cases have been explained by a coupling mechanism through interfacial diffusion and interpenetrating crosslinking networks. The use of primarily dispersed resorcinol-formaldehyde resin in rubber compound, along with formalin donor for improving the bonding of rubber to the reinforcing materials, is also reported by Rajan and colleagues.¹⁵ O'Connor¹⁶ and Varghese and col-

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leagues¹⁷ concluded that a bonding system consisting of hexamethylene tetramine (Hexa) and resorcinol is sufficient for getting good fiber-rubber adhesion with cellulosic fibers.

To measure the adhesion between fiber and rubber, many techniques such as H-block and strip adhesion have been used. Although these measurements gave a good relative indication of adhesion, the real effect was overshadowed by the time-dependent nature of the viscoelastic materials. Equilibrium swelling in solvents is another technique that has been used to assess rubberfiller 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 Whitby and colleagues.¹⁸ The sorption and transport of organic solvents by polymer membranes have been studied extensively by Aminabhavi and coworkers.^{19–21} Unnikrishnan and Thomas²² studied the transport of aromatic hydrocarbons through natural rubber (NR) vulcanizates with different vulcanizing systems. Swelling of vulcanized rubber in various liquids has been investigated by Gee²³ and found that the entropy of swelling is independent of the nature of the swelling liquid. Kraus²⁴ determined the degree of cure in particulate filler reinforced vulcanizates by the swelling method. Lorentz and Parks²⁵ also investigated the restriction from swelling exerted by a filler, using carbon blacks in NR vulcanizates. Based on swelling measurements, Parks²⁶ reported that NR vulcanizate loaded with brass powder showed an increase in crosslink density, indicating an interaction or bonding between rubber and brass.

In this article, the equilibrium swelling was evaluated as a means to measure the degree of adhesion between NR and aluminium powder, with and without the presence of Hexa-resorcinolsilica bonding system. Efforts were also made to investigate the effect of different types of crosslinking systems on the phenomenon of diffusion and adhesion. Diffusion and sorption behavior of aromatic hydrocarbons through these composites and the rubber–solvent interaction in terms of interaction parameter have also been presented.

EXPERIMENTAL

NR used for this study was Indian Standard Natural Rubber, light color grade (ISNR-5). Hexa and resorcinol were of laboratory reagent grade. All other ingredients were of commercial grade. Aluminium powder is obtained from Kosla Metal Powder Co. Pvt. Ltd., India, and has a density of 2.7 g cm^{-3} and a particle size of 125 to 200 nm.

NR was vulcanized by four vulcanizing systems, viz. dicumyl peroxide (DCP), conventional (CV), efficient (EV), and a mixture of sulfur and dicumyl peroxide (Mixed) systems. The formulations used are given in Table I. The quantity of resorcinol, silica, and Hexa was varied based on the filler content. The composites were prepared in a two roll mixing mill (150 mm \times 300 mm). To study the effect of different vulcanizing systems on diffusion, the samples were cured to the extent that all of them developed the same rheometric torque²² (40 dNm). Because torque is proportional to crosslink density, it is assumed that all the samples have nearly the same crosslink density. However, this assumption is not always true in the absolute sense, when we compare samples with different crosslinking systems. Thus, we have also used samples cured up to their optimum cure time (t_{90}) for these studies.

For swelling studies, vulcanized composites were cut using a sharp-edged circular die of 1.98 cm diameter. The thickness of the sample was measured using a micrometer screw gauge. The initial weight was taken and immersed in solvents contained in test bottles, kept at constant temperature in an air oven. Samples were removed from bottles at periodic intervals and weighed immediately in an airtight weighing bottle after the wet surface of the sample was dried using a piece of blotting paper. The uptake of the solvent by the composite during swelling was expressed as moles of solvent sorbed by 100 g of composite. This method was found to be more convenient for the comparison of sorption data and was adopted by many researchers. We have conducted the swelling studies in a series of aromatic hydrocarbons (i.e., benzene, toluene, p-xylene, and mesitylene).

RESULTS AND DISCUSSION

The cure characteristics of the composites are given in Table II. Rheometric data of aluminium powder-loaded NR stocks using conventional vulcanizing systems are shown in Figure 1. Loading of aluminium powder increases the maximum torque, while it decreases the scorch time and optimum cure time. In Westlinning and Wolff's

		DCP			CV			ΕV			Mixed			C	7	
Ingredients	A	E	Ι	В	Ŀ	ſ	C	IJ	K	D	Η	Г	\mathbb{F}_2	\mathbf{J}_2	F_3	J_3
NR	100	100	100	100	100	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	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	5.0	5.0
TDQ	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
MOR				0.6	0.6	0.6	1.5	1.5	1.5	0.6	0.6	0.6	0.6	0.6	0.6	0.6
Sulfassan-R							1.0	1.0	1.0							
DCP	4.0	4.0	4.0							1.5	1.5	1.5				
Sulfur				2.5	2.5	2.5	0.6	0.6	0.6	2.5	2.5	2.5	2.5	2.5	2.5	2.5
Aluminum powder		10	10		10	10		10	10		10	10	25	25	50	50
Resorcinol			2.0			2.0			2.0			2.0		5 L		10
Silica			2.0			2.0			2.0			2.0		5 L		10
Hexa			0.75			0.75			0.75			0.75		1.88		3.75
TDQ = 2,2,4-Trime	thyl 1,2-6	dihyrdoqu	uinoline; M	$OR = m_c$	rpholine	benzathia	zyl sulfer	namide; S	Sulfassan-]	R = 4,4'-0	lithiodim	orpholine				

Table I Formulation of Mixes

treatment of rheometric data, the rubber–filler interaction is described in terms of α_F values,

$$\alpha_F = \left[(\Delta L_f / \Delta L_g) - 1 \right] / w \tag{1}$$

 L_f and L_g stand for torque measured with filled stock and gum stock, respectively, and w represents the weight of filler. Westlinning plot is given in Figure 2. The data indicate that the aluminium powder promotes or accelerates the crosslinking of the rubber, with the effect being quite pronounced in the presence of bonding agent.

The sorption curves were obtained by plotting Q_t , mol % solvent uptake per 100 g of polymer against square root of time. The experiments were conducted in benzene, toluene, xylene, and mesitylene, respectively, at 27°C. Because all of the solvents followed the same diffusion pattern, as evident from the shape of sorption curves, the discussion is limited to the diffusion of toluene only. Figure 3(a-d) shows the sorption curves in toluene for the gum vulcanizates and aluminium powder-filled composites with and without bonding agent. It is seen from these figures that, in each system-viz. DCP (mixes A, E, and I), CV (mixes B, F, and J,) EV (mixes C, G, and K), and Mixed (mixes D, H, and L)-the gum compounds absorbed the maximum amount of solvent at equilibrium swelling. This was expected because there is less restriction for the penetrant to enter into the vulcanizate. From Table III, it is clear that the maximum uptake of solvent, Q_t follows the order DCP < EV < Mixed < CV for gum samples. This phenomenon was studied in detail by Unnikrishnan and Thomas,²² and they concluded that the difference in the maximum Q_t values of NR with different crosslinking systems may be due to the different types of crosslinks (i.e., polysulfidic linkage in CV, polysulfidic along with C-C linkage in Mixed, predominantly mono- or disulfidic in EV, and only C-C bonds in DCP). But, for the unbonded systems, Q_t follows the order as $EV \leq DCP < Mixed < CV$; for the bonded system, Q_t follows the order as $EV \leq CV < DCP < Mixed$. This was due to the different effect of aluminium powder with and without bonding agent in different vulcanizing systems. The same trend was obtained when the sorption experiments were conducted using samples cured at their respective optimum cure times.

Mixes	Maximum Torque (dNm)	Minimum Torque (dNm)	Optimum Cure Time at 150°C (min)	Cure Time for 40 dNm at 150°C (min)
А	42	14	26.5	40.0
\mathbf{E}	42	13	27.5	33.0
Ι	47	12	30.0	27.0
В	43	8	16.0	17.0
F	45	7	16.0	15.5
J	52.5	8	13.5	8.5
С	44	5	3.5	3.5
G	46	4	3.5	3.5
Κ	49	3	2.5	2.5
D	47	10	14.0	12.0
Η	47	9	13.5	12.0
L	56	6	13.5	8.0
F_2	47.8	6	15.0	12.0
J_2	55.5	6.5	13.0	8.5
F_3	52	4	14.5	10.5
J_3	59.8	4	13.5	8.0

Table II Cure Characteristics

In each vulcanizing system, at the same loading of aluminium powder, the amount of solvent sorbed by the composite at equilibrium swelling was less for the composites containing bonding agents, compared with that without bonding agent [Fig. 3(a-d)]. On the perusal of sorption curves, an interesting observation can be made on the differences in initial rates of diffusion for different composites. The initial rates of diffusion is faster for composites without bonding agent than with bonding agent. This is due to the fact that, in unbonded rubber-aluminium powder composites, the number of voids at the interface is higher than that in composites with bonding agent. The weak interface allows easy entrance of the penetrant, which acts as solvent pockets at equilibrium.



Figure 1 Rheographs of NR compounds containing aluminium (Al) powder with and without bonding agent.



Figure 2 Westlinning plots of rheometer data. Effect of aluminium powder with and without bonding agent.



Figure 3 Sorption curves in toluene at 27°C: (a) DCP, (b) CV, (c) EV, and (d) Mixed.

Figure 4 shows the effect of aluminium powder with and without bonding agent on the equilibrium swelling in toluene. The effect of bonding agent at 10 phr filler loading was maximum in conventional vulcanization. This was due to the presence of sulfur that may assist the bonding phenomena.

There is a systematic trend in the sorption behavior of liquids of different molecular size, even if the diffusion curves obtained for benzene, toluene, xylene, and mesitylene are the same. In all of the systems, as the penetrant size increased, the uptake (Q_t) decreased (Fig. 5). Benzene showed the maximum, and mesitylene shows the minimum value of Q_t among the solvents used. This type of absorption was also reported earlier by Salmon and van Amerongen.²⁷ We have seen that the effect of bonding agent is more pronounced in the CV sys-

Solvents	Systems	Gum	Unbonded	Bonded
Benzene	DCP	4.40	4.28	3.96
	\mathbf{CV}	5.21	4.78	3.86
	$_{\rm EV}$	4.50	4.06	3.82
	Mixed	4.71	4.52	4.36
Toluene	DCP	4.07	3.73	3.55
	\mathbf{CV}	4.64	4.25	3.42
	\mathbf{EV}	4.09	3.51	3.36
	Mixed	4.24	4.01	3.77
Xylene	DCP	3.77	3.55	3.44
	\mathbf{CV}	4.20	3.87	3.43
	\mathbf{EV}	3.81	3.34	3.24
	Mixed	3.99	3.61	3.49
Mesitylene	DCP	2.79	2.65	2.53
·	\mathbf{CV}	3.26	2.95	2.47
	\mathbf{EV}	2.81	2.57	2.47
	Mixed	3.08	2.86	2.75

Table III Amount of Solvent Absorbed by Composites at Equilibrium Swelling (27°C) in mol %

tem, and the conventional vulcanization is widely used for various applications. Thus, in this study, the effect of aluminium powder at higher loadings is done only with the CV system. As the loading of metal powder increased, the equilib-



Figure 4 Effect of aluminium powder (10 phr) on equilibrium swelling of NR vulcanizates with and without bonding agent. Swelling solvent-toluene at 27°C.



Figure 5 Dependence of maximum mol % uptake on the molecular weight of solvent on the CV system.

rium sorption of the specimens decreased, as shown in Figure 6 and was due to the increased hindrance exerted by the filler at high loading and also due to the high crosslinking due to the



Figure 6 Effect of metal powder on equilibrium sorption with and without bonding agent.

		n at	27°C		$K \times 10^2 ({ m gg}^{-1} { m min}^{-1})$ at 27°C			
	Benzene	Toluene	Xylene	Mesitylene	Benzene	Toluene	Xylene	Mesitylene
А	0.56	0.63	0.65	0.65	6.10	4.04	3.06	2.77
\mathbf{E}	0.56	0.55	0.62	0.62	5.10	5.49	3.51	2.93
Ι	0.55	0.56	0.63	0.66	6.42	4.84	3.29	2.97
В	0.58	0.61	0.66	0.65	4.59	4.03	2.78	2.74
\mathbf{F}	0.59	0.60	0.63	0.62	3.91	4.16	2.73	2.75
J	0.57	0.60	0.63	0.62	4.96	4.21	2.84	3.03
С	0.56	0.57	0.65	0.62	4.72	4.85	2.84	3.19
G	0.57	0.59	0.62	0.62	4.76	4.74	3.02	2.75
Κ	0.59	0.58	0.63	0.62	4.38	5.04	2.96	3.29
D	0.60	0.59	0.66	0.64	4.16	5.00	2.73	3.13
Η	0.59	0.60	0.62	0.62	3.84	3.78	2.86	2.50
L	0.59	0.61	0.63	0.62	4.45	4.07	2.85	2.96

Table IVAnalysis of Sorption Data

better heat conduction. In the bonded and unbonded composites, the liquid uptake decreased gradually, but the reduction was sharp in the case of bonded composites.

To investigate the mechanism of solvent transport in the polymer composites, the sorption results before completion of 50% of the equilibrium have been analyzed using the equation,²⁸

$$Q_t/Q_{\infty} = Kt^n \tag{2}$$

where K is a constant depends on the solvent and the cure system that indicates the structural characteristics of the polymer. Value of the exponent n indicates the type of transport mechanism. A value of 0.5 for n implies the Fickian transport, whereas for a case II transport the value of n is 1.0 and for a value of 0.5 < n < 1.0; the anomalous transport is observed. The least-squares estimation of K and n of eq. (2), given in Table IV, indicate an almost Fickian diffusion mechanism in the systems included in this study.

The diffusion coefficient, D, can be calculated from the Fick's first law for the flux of the penetrant at constant temperature, using the formula.

	$D imes 10^7$			
	$(cm^2 s^{-1})$	ΔH	ΔS	
Samples	(Toluene)	(kJ mol ⁻¹)	$(\mathrm{Jmol}^{-1} \mathrm{K}^{-1})$	χ
А	8.59	0.9685	-23.41	0.3662
\mathbf{E}	5.48	0.9985	-24.39	0.3789
Ι	5.28	0.9192	-23.45	0.4556
В	7.35	0.9947	-24.28	0.3595
\mathbf{F}	5.93	0.9346	-23.13	0.3792
J	5.09	0.9008	-25.06	0.4143
С	7.99	0.8997	-23.56	0.3855
G	6.97	0.8877	-24.89	0.4129
Κ	6.33	0.8988	-25.08	0.4240
D	7.84	0.8930	-23.30	0.3767
Н	5.94	0.8886	-23.98	0.3881
\mathbf{L}	5.56	0.8723	-24.33	0.4425

Table V Values of Diffusion Coefficient (D), Thermodynamic Functions, and Interaction Parameter (χ)



Figure 7 Dependence of temperature on the maximum uptake of toluene.

$$D = \pi \left(\frac{h\theta}{4Q_{\infty}}\right)^2 \tag{3}$$

where Q_{∞} has the same meaning as before, θ is the slope of the linear portion of the sorption curves before attainment of 50% equilibrium, and *h* is the initial sample thickness. The calculated values for *D*, given in Table V, indicate that DCP system has the highest value of *D* and CV has the lowest. Comparing the bonded and unbonded composites, the latter has the lowest *D* value.

The temperature dependence of diffusion in the systems is investigated for the range from 27°C to 70°C, which clearly support the fact that temperature activates the diffusion process (Fig. 7). The rubber–solvent interaction parameter χ has been calculated using the equation²⁹

$$\chi = \frac{(d\phi/dT)\{[\phi/(1-\phi) + N\ln(1-\phi)] + N\phi\}}{2\phi(d\phi/dT) - \phi^2 N(d\phi/dT) - \phi^2/T}$$
(4)

where ϕ is the volume fraction of rubber in the solvent swollen sample at equilibrium swelling, and N is calculated from ϕ using,

$$N = \frac{\phi^{2/3} - 2/3}{\phi^{1/3} - 2\phi/3} \tag{5}$$

These values are listed in Table V. In each system, the χ values are highest for the bonded composites, suggesting the lowest rubber-solvent interaction in the bonded composites.

The enthalpy ΔH and entropy ΔS of sorption were calculated using van Hoffs' relation.

$$\log K_s = \frac{\Delta S}{2.303R} - \frac{\Delta Hs}{2.303RT} \tag{6}$$

where K_s is the maximum mol % uptake of the solvent. The values of ΔH and ΔS are also given in Table V. The negative sign in the entropy of the sorption data suggests the retainment of liquid state structure of solvent molecules even in the sorbed state.²⁹

According to the Lorentz and Parks²⁵ equation,

$$Q_f/Q_g = ae^{-z} + b \tag{7}$$

where Q is defined as grams of solvent per gram of hydrocarbon and is calculated by

$$Q = rac{ ext{Swollen weight} - ext{Dried weight}}{ ext{Original weight} imes 100/ ext{Formula weight}}$$

The subscripts f and g of the above 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. Parks²⁶ also suggested that the value of 1/Q, the

Table VI Values of 1/Q, Q_f/Q_g , and V_{r0}/V_{rf} for Composites with and without Bonding Agent

System	1/Q	$Q_{_f}/Q_{_g}$	V_{r0}/V_{rf}
DCP			
Unbonded, E	0.2522	0.9965	0.9523
Bonded, I	0.2645	0.9504	0.9145
CV			
Unbonded, F	0.2106	0.9980	0.9524
Bonded, J	0.2517	0.8352	0.7979
EV			
Unbonded, G	0.2538	0.9448	0.9309
Bonded, K	0.2557	0.9378	0.8936
Mixed			
Unbonded, H	0.2250	0.9976	0.9800
Bonded, L	0.2264	0.9957	0.9325



Figure 8 Kraus plots of swelling data. Effect of bonding agent in NR-aluminium powder composites.

degree of crosslinking, can also be used to study the adhesion effects. Table VI shows the Q_f/Q_g , and 1/Q values for the composites for different systems. The lowest value of Q_f/Q_g in each crosslinking system is for the composites with bonding agent (i.e., mix I, J, K, and L) that confirms that maximum aluminium powder–rubber interaction has occurred when the bonding agent is present in the composite. The results from the 1/Q values also support this observation. Among the different crosslinking systems, the CV system has the highest Q_f/Q_g value and lowest 1/Q value, suggesting that the Hexa-res-

orcinol-silica bonding system suits well with aluminium powder in NR.

The interaction between rubber and a filler such as carbon black has been investigated by a number of workers using a swelling technique. Assuming the swelling to be completely restricted at the rubber–filler interface due to adhesion, Kraus³⁰ has shown that the degree of restriction on the volume concentration of a reinforcing filler follows an equation of the form,

$$\frac{V_{r0}}{V_{rf}} = 1 - \left[3c(1 - V_{r0}^{1/3}) + V_{r0} - 1\right] \frac{\theta}{1 - \theta} \quad (8)$$

where θ is the volume fraction of filler, and *c* is a constant characteristic of the filler and indicative of the degree of adhesion.

$$\theta = \frac{\text{Volume of filler}}{\text{Total volume of the vulcanizate}}$$
(9)

 V_r is the volume fraction of rubber that was calculated from the equilibrium swelling data using the equation,

$$V_r = \frac{(d - fw)\rho_r^{-1}}{(d - fw)\rho_r^{-1} + A_0\rho_s^{-1}}$$
(10)

where d is the weight after drying out the sample, and w is the weight of the swollen sample. A_0 is the weight of the absorbed solvent, f is the fraction of the insoluble components, and ρ_r and ρ_s are the densities of the rubber and solvent, respectively. When eq. (10) is applied to rubber containing rein-

Mixes	Modulus at 200% Elongation (N mm ⁻²)	Modulus at 300% Elongation (N mm ⁻²)	Tensile Strength $(N mm^{-2})$	Elongation at Break (%)
В	1.05	1.33	23.50	850
F	1.49	1.73	21.29	800
F_2	2.12	2.65	19.85	720
$\bar{F_3}$	3.71	4.01	18.31	600
J	1.97	2.65	24.27	750
J_2	2.65	3.61	19.85	600
$\overline{J_3}$	3.79	5.35	11.71	350

Table VII Tensile Properties of Composites with CV System



(a)

(c)



Figure 9 Scanning electron micrographs of tensile fractural surface of aluminium powder-filled NR vulcanizates with and without the presence of bonding agent: (a) 10 phr aluminium powder having no bonding agent, (b) 10 phr aluminium powder having bonding agent, (c) 25 phr aluminium powder having no bonding agent, (d) 25 phr aluminium powder having bonding agent, (e) 50 phr aluminium powder having no bonding agent.

forcing filler, it is found that V_{rf} of the rubber phase in the swollen gel is always much higher than for the pure gum V_{r0} . So, the ratio V_{r0}/V_{rf} decreases with filler loading. The ratio represents the degree of restriction of the swelling of rubber matrix due to the presence of filler.

From Table VI, it is seen that, in each crosslinking system, the lowest V_{r0}/V_{rf} values are for composites with bonding agent, which is associated with enhanced rubber-filler adhesion due to the presence of bonding agent.

Equation (8) predicts that V_{r0}/V_{rf} should vary linearly with $\theta/1 - \theta$. At high filler loading, the line

deviates from linearity. The theory assumes that the filler particles are far enough, so as not to interact with each other. This is obviously not true at higher loading. According to Kraus' theory, the slope of the straight line will be a direct measure of reinforcing ability of the filler used. The more the adhesion ability, the more the swelling resistance will be. Negative higher slope values indicate a better adhesion effect. From Figure 8, the composites with bonding agent have a higher slope than composites without bonding agent, which shows the increased adhesion. According to this, aluminium powder showed an improved adhesion to the rubber



(e)



Figure 9 (Continued from the previous page)

when we use Hexa-resorcinol-silica as a bonding agent. The resorcinol combines with the methylene donor in the presence of silica and gives a resin with the structure,



when the resin is intimately mixed with rubber adhesion is greatly improved. This is due to the increased polarity of the rubber, which arises from the powerful hydrogen bonding characteristics of the resorcinol resin. This principle makes great improvements in bonds between rubber and various substrate materials, such as metal powders.

It is found from this study that the Hexa-resorcinol-silica bonding system improves the adhesion and the extent of adhesion is different for different crosslinking system. It is found that the effect is more pronounced in the conventional vulcanizing system with 2.5 phr sulfur.

Tensile properties of composites in the CV system are given in Table VII. At low phr of the metal powder, the addition of bonding agent increases the tensile strength. But, as the metal powder loading increases, the tensile strength and elongation at break decreases.

The scanning electron micrographs taken from the fractured surface of tensile pieces are presented in Figure 9(a–f). It can be seen from the scanning electron micrographs that the addition of bonding agent in the aluminium powder is more firmly bonded to the rubber matrix, which gave a smooth surface on failure. In the unbonded composites, the metal powder is seen to exist as a loose aggregate that results in a nonuniform rough surface. However, this effect narrows down when the metal powder loading was increased.

CONCLUSIONS

The effects of aluminium powder on the swelling behavior of NR composites with and without bonding agent in different crosslinking systems are evident from this study. The crosslinking system has an important role in the maximum uptake value, which is in the order CV system > mixed system > EV system \ge DCP system for gum composites. But, the order of maximum uptake value is perturbed in composites filled with aluminium powder with and without bonding agent due to the difference in the effect in different vulcanizing systems. In all of the samples, temperature activates the diffusion process and the maximum uptake value decreases with increase in molecular weight of the solvent. In all of the crosslinking system, the maximum uptake for composites containing bonding agent is substantially lower than the corresponding value for the composites without bonding agent and is more

pronounced in the CV system. The increased aluminium powder content brings about a greater restriction to swelling and the use of a bonding agent further reduced the swelling considerably. The χ values for the composites indicate that the rubber–solvent interaction increases when Hexaresorcinol-silica is used as the bonding agent in each crosslinking system for the aluminium powder-filled NR vulcanizates.

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