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Assessment of adhesion in natural rubber-aluminium powder composites by equilibrium swelling in aliphatic solvents

V. S. VINOD, S. VARGHESE*, B. KURIAKOSE
Rubber Research Institute of India, Kottayam, Kerala, India-686 009

Equilibrium swelling was tried as a means to measure the adhesion between natural rubber (NR) and aluminium powder in their composites. NR-aluminium powder composites which contained four vulcanising systems, viz., conventional (CV), efficient (EV), dicumyl peroxide (DCP) and a mixture consisting of sulphur and dicumyl peroxide (mixed) and hexa-resorcinol-silica as dry bonding system were evaluated for this. A series of aliphatic solvents like pentane, hexane and heptane were used to study the equilibrium swelling of the composites. The results showed that addition of bonding agent reduced the swelling and are more pronounced in conventional system, due to the increased adhesion. The scanning electron microphotographs revealed more uniformity of the metal powder in the matrix in presence of hexa-resorcinol silica bonding system. © *2000 Kluwer Academic Publishers*

1. Introduction

For many material applications, information is needed on their properties such as thermal conductivity, heat capacity, electrical conductivity etc. Conducting polymer composites made by the incorporation of metal powders into polymers are an emerging group of engineering materials suitable for applications such as electromagnetic interference (EMI) and radio frequency interference (RFI) shielding to protect business machines. They are also used for conduction, electrical heating, discharging static electricity, friction anti-friction materials, and for converting mechanical to electrical signals. These composites have high corrosion resistance coupled with ease of making and they need only single step moulding.

Conductive filler-polymer composite has become an interesting field of research and numerous papers have been appeared in the literature [1–9]. In metal powder filled systems, the major problems are non-uniform dispersion of the powder and poor adhesion [9, 10]. between the polymer and the filler surfaces. There are many methods to achieve better rubber to metal adhesion. These include chemically or physically modifying the existing metal surface, use of a suitable coupling agent [11, 12] which enhances the surface interaction between the two phases and also by incorporating special additives into the rubber which promote the chemical bonding. Rajan *et al.* [13] reported the use of primarily dispersed resorcinol-formaldehyde in rubber compound along with formalin donor for improving the bonding of rubber to the reinforcing materials.

Equilibrium swelling of composites in solvents is a technique which has been used to assess the rubber filler adhesion, since the filler, if bonded is supposed to restrict the swelling of elastomers. Aminabhavi and co-workers [14–16] have made a detailed analysis of the diffusion process in various rubbery polymers. The rate of solvent diffusion within a polymer matrix is controlled by factors such as structure of polymer, type of crosslinking, crosslinking density, penetrant size, presence of fillers, temperature [14–16] etc. A large number of studies have been reported in the literature about the effect of fillers on the sorption behaviour of elastomers [17, 18] Generally, it is observed that the presence of an active filler reduces the extend of equilibrium swelling. The influence of size and shape of the penetrant molecules was described by Saleem *et al.* [19] and it is found that the equilibrium sorption of sorbents decreases linearly with increase in penetrant molecular size. It is also found that temperature activates the phenomenon of diffusion according to the Arrhenius equation [14]. The effect of the type of crosslinking system on the phenomenon of diffusion is studied in detail by Unnikrishnan *et al.* [22], Mathai *et al.* [20] and George *et al.* [21] Based on swelling measurements, Parks [23] reported that natural rubber vulcanisate loaded with brass powder showed an increase in crosslink density indicating an interaction or bonding between rubber and brass. The adhesion between rubber and short glass and asbestos fibres has been studied by Das [24] using restricted swelling measurements. Equilibrium swelling studies by Varghese *et al.* [25] showed that a bonding

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[*] Author to whom all correspondence should be addressed.

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system consisting of hexamethylene tetramine and resorcinol is very effective for getting good fibre-rubber adhesion.

The main objective of the present study is to investigate the effect of hexamethylene tetramine-resorcinol-silica bonding system in natural rubber aluminium powder composites and to examine equilibrium swelling technique as a means to measure the degree of adhesion between natural rubber and aluminium powder. Efforts were also made to assess the effect of different vulcanising systems on bonding. Diffusion and sorption behaviour of a series of aliphatic hydrocarbon, viz., *n*-pentane, *n*-hexane and *n*-heptane through these composites are also presented.

2. Experimental

2.1. Materials

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

2.2. Sample preparation

NR was vulcanised by four vulcanising systems viz. dicumyl peroxide (DCP), conventional (CV), efficient (EV) and a mixture of sulphur and dicumyl peroxide (Mixed). The formulations used are given in Table I. The quantity of resorcinol silica and hexa varies on the filler content. The composites were prepared in a two roll mixing mill (150 × 300 mm). To study the effect of different vulcanising systems on diffusion, the samples were cured to the extend that all of them developed the same rheometric torque [20] (40 dNm). Since torque is proportional to the 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. Hence we have also used samples cured up to their optimum cure time (t_{90}) for these studies.

2.3. Sorption experiments

Vulcanised composites were cut using a sharp edged circular die of 1.98 cm diameter. The thickness of the samples was measured using a micrometer screw gauge. The initial weight was taken and immersed in solvents contained in test bottles, kept at constant temperature. The samples were periodically removed from the test bottles, adhering solvent was blotted off the surface, and the samples were weighed in air tight bottles on a highly sensitive electronic balance and immediately replaced into the test bottles. The time for each weighing was kept to a minimum of 30–40 seconds in order to eliminate the error due to the escape of solvent from the samples. This procedure was continued until no more liquid uptake by the polymer was noted. The quantity of solvent absorbed was expressed in moles of solvent sorbed by 100 g of the polymer material.

3. Results and discussion

Rheometric data of aluminium powder loaded natural rubber stocks in conventional vulcanising systems are shown in Fig. 1. Aluminium powder incorporation causes a decreases in scorch time and optimum cure time and an increase in maximum torque. The cure characteristics are presented in Table II. Westlinning and Wolff treated the rheometric data in terms of α_F values to describe the rubber-filler interaction. The α_F is given as

$$\alpha_F = \frac{[\Delta L_F/\Delta L_g) - 1]}{W}$$

L_F and L_g stand for torque measured with filled stock and gum stock respectively and W represents the weight of filler. Fig. 2 shows the Westlinning plot which indicates that the aluminium powder promotes or

TABLE I Formulation of mixes

Ingredients	DCP			CV			EV			MIXED			CV			
	A	E	I	B	F	J	C	G	K	D	H	L	F_2	J_2	F_3	J_3
Natural rubber	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
Aluminium powder	-	10	10	-	10	10	-	10	10	-	10	10	25	25	50	50
Resorcinol	-	-	2.0	-	-	2.0	-	-	2.0	-	-	2.0	-	5	-	10
Silica	-	-	2.0	-	-	2.0	-	-	2.0	-	-	2.0	-	5	-	10
Hexa	-	-	0.75	-	-	0.75	-	-	0.75	-	-	0.75	-	1.88	-	3.75

TDQ – 2,2,4-trimethyl 1,2-dihyrdoquinoline; MOR – Morpholine benzathiazyl sulfenamide; Sulfassan-R – 4,4′-dithiodimorpholine; DCP – Dicumyl peroxide; Hexa – Hexamethylene tetramine.

TABLE II Cure characteristics

Mixes	Max. Torque (dNm)	Min. torque (dNm)	Optimum cure time at 150°C (min)	Cure time for 40 dNm at 150°C (min)
A	42	14	26.5	40.0
E	42	13	27.5	33.0
I	47	12	30.0	27.0
B	43	8	16.0	17.0
F	45	7	16.0	15.5
J	52.5	8	13.5	8.5
C	44	5	3.5	3.5
G	46	4	3.5	3.5
K	49	3	2.5	2.5
D	47	10	14.0	12.0
H	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

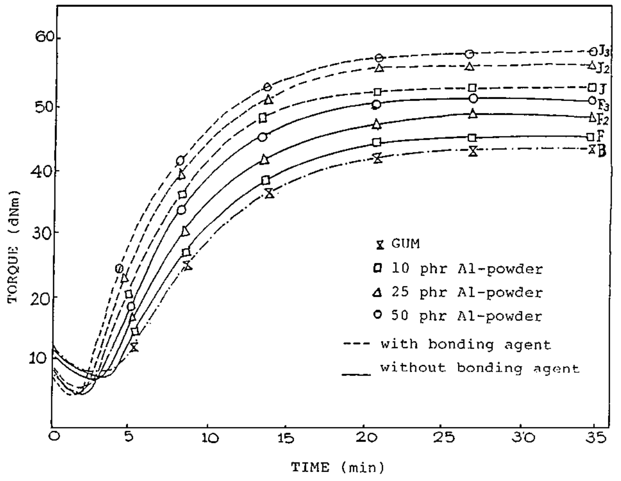


Figure 1 Rheographs of natural rubber compounds containing aluminium powder with and without bonding agent.

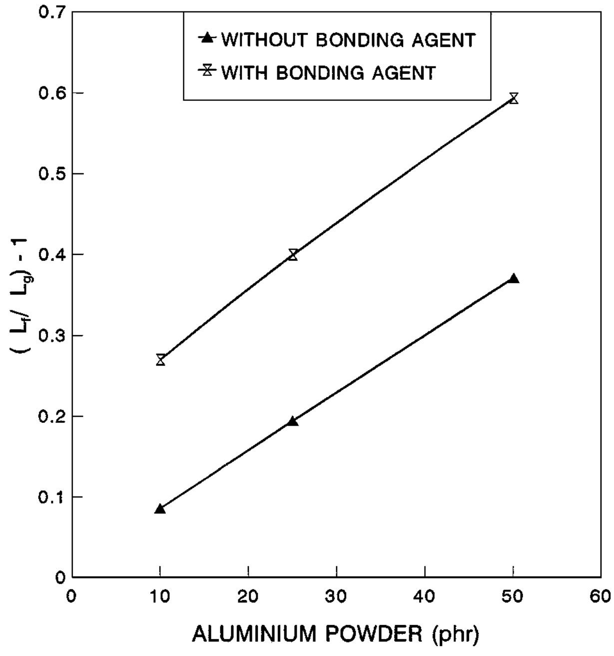


Figure 2 Westlinning plots of rheometer data. Effect of aluminium powder with and without bonding agent.

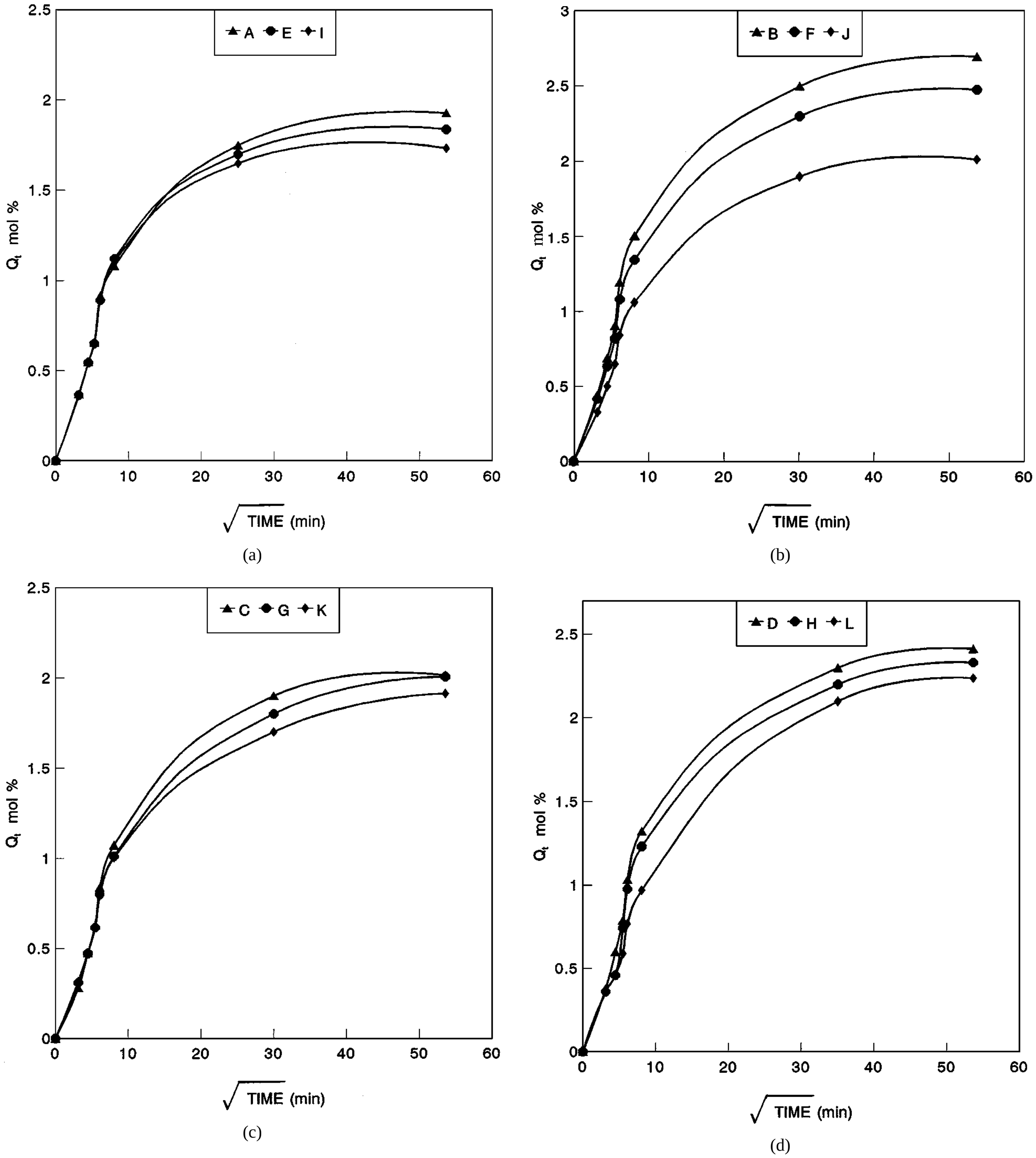
TABLE III Amount of solvent sorbed by comparison at equilibrium swelling (27°C) in mol%

Solvents	Cure system	Gum	Unbonded	Bonded
Pentane	DCP	1.42	1.30	1.29
	CV	1.88	1.68	1.38
	EV	1.50	1.46	1.37
	Mixed	1.68	1.58	1.48
Hexane	DCP	1.58	1.47	1.38
	CV	2.19	1.94	1.57
	EV	1.69	1.66	1.52
	Mixed	2.02	1.85	1.77
Heptane	DCP	1.93	1.84	1.73
	CV	2.69	2.48	2.01
	EV	2.01	2.00	1.92
	Mixed	2.41	2.33	2.23

accelerates the crosslinking process and the effect being quite pronounced in presence of hexa-resorcinol-silica as the bonding system.

Fig. 3 shows the sorption curves, which were obtained by plotting Q_t (solvent uptake per 100 g of polymers) versus square root of time, in heptane at 27°C. Though the experiments were done in pentane and hexane, the discussion is limited only to heptane since the other solvents also followed the same diffusion pattern. It is seen from the sorption curves that in each system, viz. DCP (mixes A, E and I) CV (mixes B, F and J) EV (mixes C, G and K) mixed, (mixes D, H and L) the gum compounds absorbed the maximum amount of solvent at equilibrium swelling. This was expected since there is less restriction for the penetrant to enter into the polymer. The $Q_{\propto}$ values as from Table III follow the order DCP < EV < mixed < CV for gum and unbonded samples, which may be due to the different types of crosslinks. i.e. polysulphidic linkage in CV, polysulphidic along with C-C linkage in mixed, predominantly mono or disulphidic in EV and the C-C bonds in DCP. For bonded systems the Q_t follows the order DCP < EV < CV < mixed, which may be due to the different effect of bonding agents in different vulcanising systems.

The decreased swelling in filled polymeric systems may results from one or more of four causes [26]. (i) The filler may cause an increase in crosslinking efficiency of the vulcanising agent, thus leading to additional polymer to polymer crosslinks; (ii) the presence of filler may enhance the degree to which existing polymer to polymer crosslinks or physical chain entanglements (or both) restrict swelling of the rubber; (iii) the filler may alter the affinity of the swelling agents for the rubber; (iv) the filler may restrict the swelling of the rubber because of adhesion of rubber to the filler surface either by physical interaction or through the formation of rubber to filler bonds. The presence of bonding agents again complicates the system and may affect all these factors. In the present case the loading of aluminium powder is kept constant and the compound is cured to the same level in such a way that all of them develop the same rheometric torque. Thus the qualitative measurement of the enhanced adhesion in presence of a bonding agent in a filler-rubber composite is reasonable.



(a)

(b)

(c)

(d)

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

The effect of hexa-resorcinol-silica bonding system on the solvent absorption with 10 phr of aluminium powder in each vulcanising system is shown in Fig. 4. In each vulcanising system, with same loading of aluminium powder the equilibrium sorption is less for composites containing hexa-resorcinol-silica as bonding system than composites without bonding agents. This is because in unbonded rubber-aluminium powder composites the voids at the interface is higher than that containing bonding agent. The weak interface allows easy entrance of the penetrant which act as solvent pockets at equilibrium. The effect in reducing the solvent uptake is maximum in conventional vulcanisation and this may be due to the presence of excess sulfur present in the conventional system which may assist the bonding phenomenon. The effect of bonding agent with aluminium powder on equilibrium swelling is given in Fig. 5. At high loadings, only CV-system is selected since the effect of bonding agent is more effective in CV-system and conventional vulcanisation is widely used for various applications. As the loading of metal powder increased, the equilibrium sorption of the specimens decreased. This was due to the increased hindrance exerted by the high filler content and the better heat conduction of the aluminium powder which causes high crosslinking. The reduction in equilibrium sorption is sharp in the case of bonded composites than unbonded, which shows

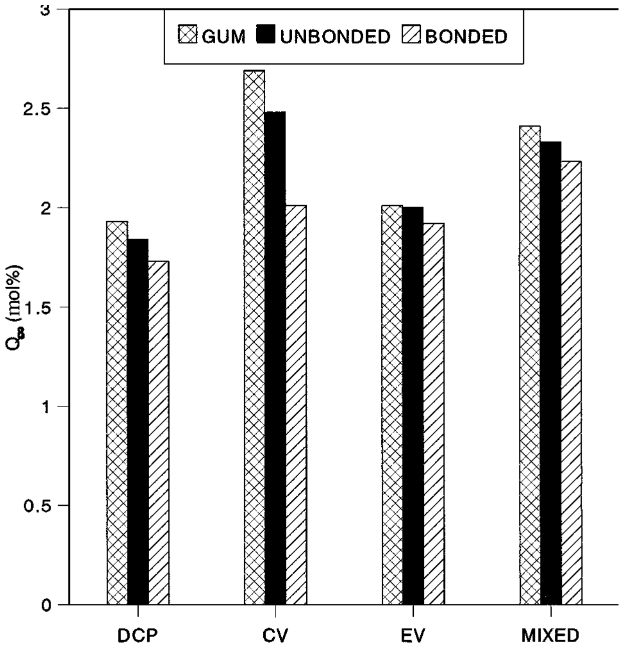


Figure 4 Effect of aluminium powder (10 phr) at equilibrium swelling of NR vulcanisates with and without bonding agent. Swelling solvent-heptane at 27°C.

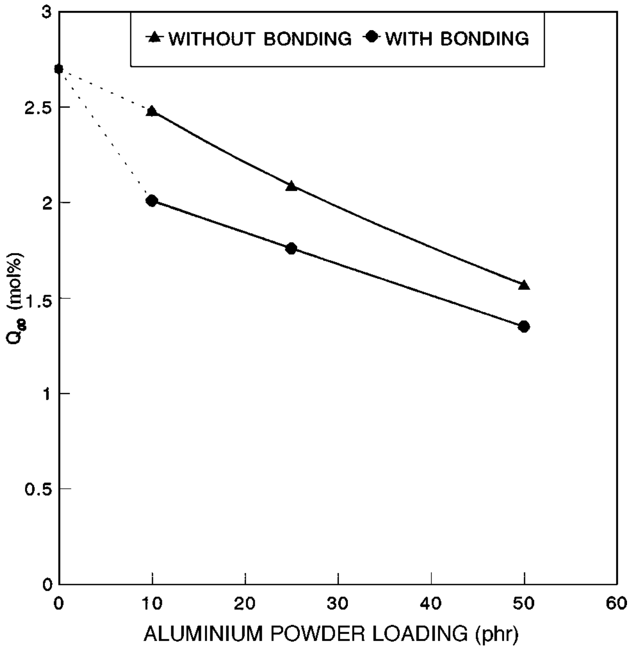


Figure 5 Effect of aluminium powder on equilibrium sorption with and without bonding agent.

the improved adhesion on adding hexa-resorcinol-silica.

From the initial linear portion of the sorption curves, the effective diffusivity D of the polymer-solvent system was calculated using the equation [27]

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

where θ is the slope of the linear portion of the sorption curve and h is the initial thickness of the polymer sample. The variation of diffusion depends on the nature of the penetrant molecule, in addition to the different crosslinks present in the polymer. The calculated values of D, given in Table IV, indicate that DCP system has the highest value of D and CV has the lowest. Comparing the bonded and unbonded composites, lowest value of D is with bonded compounds. The permeability coefficient P can be computed from the following equation [28]

TABLE IV Values of diffusion constant, permeation coefficient and rate constant at 28°C in heptane

	System	$D \times 10^7$ (cm^2/sec)	$P \times 10^7$ (cm^2/sec)
DCP	Gum	9.39	18.15
	Unbonded	8.56	15.76
	Bonded	8.31	14.42
CV	Gum	6.20	16.74
	Unbonded	4.84	11.99
	Bonded	4.59	9.25
EV	Gum	7.65	15.41
	Unbonded	5.67	11.37
	Bonded	5.55	10.65
Mixed	Gum	6.33	15.28
	Unbonded	4.69	10.94
	Bonded	4.58	10.25

$$P = DS$$

Where S is the solubility or sorptivity, which is maximum saturation sorption values and has been calculated as

$$S = \frac{M_\mathrm{s}}{M_\mathrm{p}}$$

where M_s is the mass of the penetrant at equilibrium swelling and M_p is the mass of the polymer sample. The permeability coefficient shows the net effect of sorption and diffusion process. The values of P are included in Table IV, which show that the bonded composites have lower values than the unbonded composites.

According to Lorentz and Parks [29]

$$\frac{Q_\mathrm{f}}{Q_\mathrm{g}} = ae^{-z} + b$$

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

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

The subscripts f and g of the above equation refer to filled and gum vulcanisates respectively. z is the ratio by weight of filler to rubber hydrocarbon in the vulcanisate while a and b are constants. The higher the $Q_\mathrm{f}/Q_\mathrm{g}$ values, the lower will be the extent of interaction between the filler and the matrix. Table V shows the values for composites in heptane at 27°C. The lowest value of $Q_\mathrm{f}/Q_\mathrm{g}$ in each crosslinking system is for the composites with bonding agent which confirms

TABLE V Values of $1/Q$ and Q_f/Q_g

System	Sample	$1/Q$	Q_f/Q_g
DCP	Unbonded	0.4663	1.044
	Bonded	0.4748	1.025
CV	Unbonded	0.3319	1.041
	Bonded	0.3921	0.846
EV	Unbonded	0.4075	1.085
	Bonded	0.4088	1.081
Mixed	Unbonded	0.3476	1.052
	Bonded	0.3494	1.046

that maximum aluminium powder-rubber interaction has occurred when the bonding agent is present in the composite. The highest difference between the bonded and unbounded composites is obtained in CV-system, which shows that the effect of bonding is maximum in CV system. Parks [23] also suggested that the value of $1/Q$, the degree of crosslinking, can be used to study the adhesion effects, and is given in Table V. The results from $1/Q$ values also support the above observations. All these results shows that aluminium powder showed an improved adhesion to the rubber when we use hexa-resorcinol-silica as a bonding agent, and the bonding system is more effective in conventional system of vulcanisation. The resorcinol combines with methylene donor in presence of silica which binds the rubber and the filler.

During vulcanisation the resin diffuses uniformly within the rubber phase. This increases the polarity of the rubber due to the powerful hydrogen bonding with resorcinol resin. This makes great improvements in bonds between rubber and various substrate material such as metal powders.

TABLE VI Values of Van't Hoff parameters

System	Sample	ΔH (kJ/mol)	ΔS (J/mol)
DCP	Gum	3.29	−21.86
	Unbonded	3.29	−22.21
	Bonded	3.29	−22.70
CV	Gum	3.85	−17.23
	Unbonded	4.78	−14.72
	Bonded	4.19	−18.30
EV	Gum	3.33	−21.33
	Unbonded	2.60	−23.78
	Bonded	1.09	−29.12
Mixed	Gum	2.55	−22.49
	Unbonded	2.74	−22.17
	Bonded	2.43	−23.49

TABLE VII Tensile properties of composites with CV system

Sample	Modulus at 200% elongation (N/mm^2)	Modulus at 300% elongation (N/mm^2)	Tensile strength (N/mm^2)	Elongation at break (%)
B	1.05	1.33	23.50	850
F	1.49	1.73	21.29	800
F_2	2.12	2.65	19.85	720
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
J_3	3.79	5.35	11.71	350

The effect of molecular size of the penetrant on the sorption behavior is given in Fig. 6. As the number of carbon atoms of the *n*-alkanes increases from 5 to 7, the equilibrium sorption values increases. This type of studies are reported by Salmon and Van Amerongen [30].

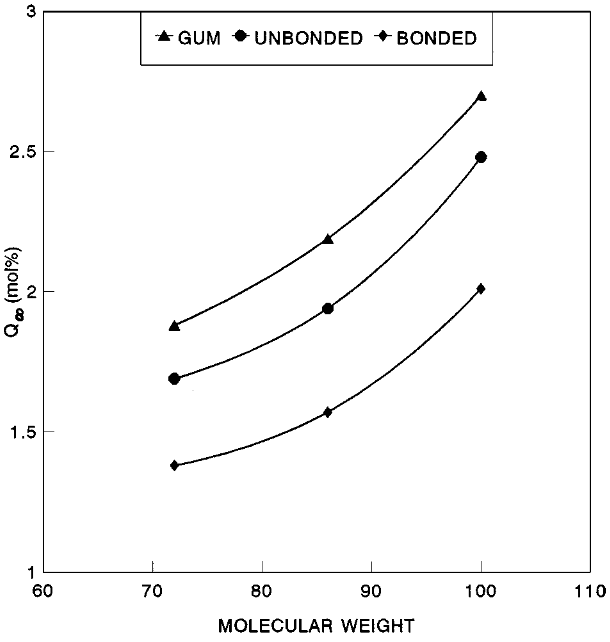


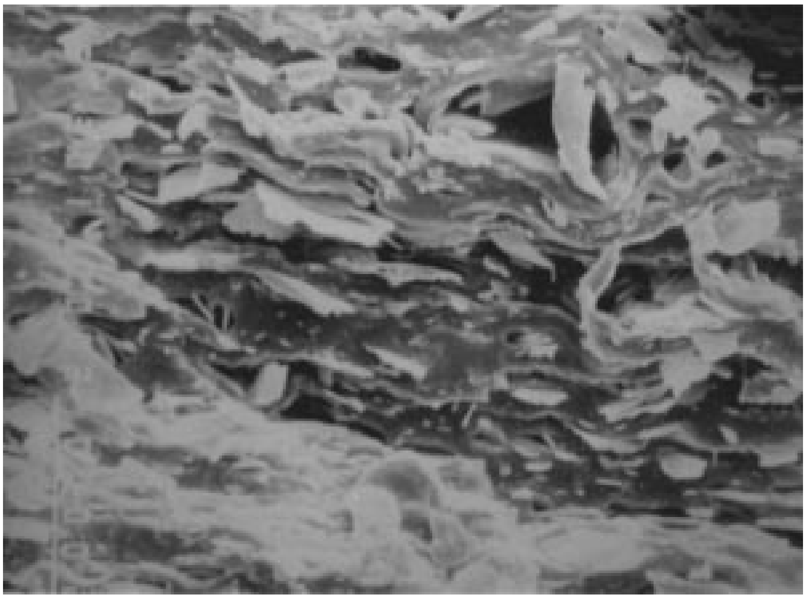
Figure 6 Dependence of maximum mol per cent uptake on molecular weight of solvent, in CV system.

The enthalpy and entropy of these composites were calculated using Van Hoffs equation,

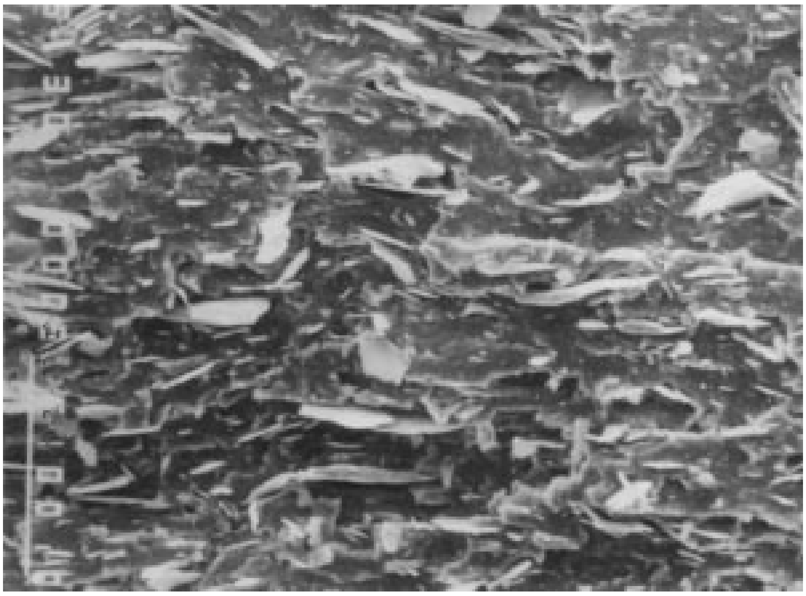
$$\log K_s = \frac{\Delta S}{2.303\text{R}} - \frac{\Delta H_s}{2.303\text{RT}}$$

where K_s is the maximum mole per cent uptake of the solvent. The values of ΔH and ΔS are given in Table VI. The negative sign of entropy of the sorption data suggests the retainment of liquid structure of solvent molecules even in the sorbed state.

Table VII gives the tensile properties of composites in CV-system. The modulus at 200% and 300% elongation are increased on adding hexa-resorcinol-silica as the bonding agent. At low loading of the metal powder the addition of the bonding agent increases the tensile strength, but as the metal powder loading increases, the tensile strength decreases. The fractured surfaces of tensile pieces of the composites with and without bonding agent were examined by a scanning electron microscope. The SEM photographs are given in Fig. 7a–b. It can be seen from the SEM photographs that the filler particles are more aligned on adding bonding agents compared to unbounded composites. The effect narrows down as the metal powder loading was increased. In composites with hexa-resorcinol-silica, the aluminium powder is more firmly bonded to the rubber matrix which gave a smooth surface on failure, whereas in the unbonded composites the metal powder is seen to



(a)



(b)

Figure 7 SEM of tensile fracture surfaces of aluminium powder filled natural rubber vulcanizates with and without the presence of bonding agent: (a) 25 phr aluminium powder having no bonding agent, and (b) 25 phr aluminium powder having bonding agent.

exist as loose aggregates which results a non-uniform, rough surface.

4. Conclusion

Differences in swelling behaviour of natural rubber aluminium powder composites with and without bonding agent in different vulcanisation systems are evident from this study. The crosslinking system has an important role in the maximum uptake value of gum vulcanisates which is in the order CV-system > mixed system > EV system > DCP system. The maximum uptake value increases with increasing molecular weight of the aliphatic solvent in the series pentane, hexane and heptane. In all systems the equilibrium swelling value decreases by the addition of aluminium powder, which again decreased in presence of hexa-resorcinol-silica as bonding system. The decrease in equilibrium swelling is greater in CV system which shows that the hexa-resorcinol-silica bonding system is more effective in conventional vulcanisation. The scanning electron microphotographs showed that the metal powders are of aligned uniformly throughout the matrix by the addition of hexa-resorcinol-silica as the bonding system.

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