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STRESS RELAXATION IN ALUMINIUM POWDER FILLED NATURAL RUBBER COMPOSITES

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Stress relaxation measurements in tension were made on aluminium powder filled natural rubber vulcanizates and the results were compared with those containing high abrasion furnace black, general purpose furnace black, acetylene black, china clay and precipitated silica. A two-stage relaxation mechanism was observed in all cases except for the unfilled stock. The rate of relaxation increased with aluminium powder loading. The relaxation process was also found to be influenced by the presence of bonding agents such as hexamethylene tetramine-resorcinol system, bis [3-(triethoxy silyl) propyl] tetrasulphide, cobalt naphthenate and toluene diisocyanate. Composites containing bonding agents showed a slower rate of relaxation and higher cross-over time than those without bonding agents. This is due to the improved adhesion of aluminium powder with natural rubber in presence of bonding agents, which was confirmed by the equilibrium swelling values and scanning electron photomicrographs.

Key words: Aluminium powder, Composites, Natural rubber, Stress-relaxation.

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INTRODUCTION

The behaviour of composites consisting of an insulating polymer and conductive filler is quite interesting as such materials offer advantages of conducting heat and electricity. Higher thermal and electrical conductivity of these polymeric composites make them suitable for many applications such as dissipation of electrostatic charge, protection against electromagnetic radiation and development of friction-antifriction materials. The importance of conductive polymeric systems has been well documented (Norman, 1970; Crossman, 1985; Nobile *et al*, 1988; Lee, 1992 and Lin *et al*, 1993). Incorporation of conductive fillers in rubber offers advantages in the moulding of thick rubber articles like dock fenders and rice polishers. The increased thermal conductivity reduces the cure time of thick rubber articles and gives uniform cure throughout the material (Vinod *et al.*, 2001). The conductivity of polymers can be increased by adding conductive blacks, intrinsically conductive polymer or metallic powders (Meyers, 1986). Polymer based composites are more cost effective, less corrosive than metals and have easy processability. Fluctuation in composite properties is observed with particulate-filled polymer systems due to poor adhesion and non-uniform dispersion of the discrete phase in the matrix. Addition of a suitable coupling/bonding agent reduces this problem by enhancing surface interaction between the two phases. The use of silane coupling agent for improving polymer-filler interaction in silica-filled epoxidised natural rubber was reported (Alex and Mathew, 1989). Buchan (1959) presented a detailed study of various bonding agents for enhancing adhesion between rubber and metal. Resorcinol-silica-hexamethylene tetramine has been used for improving the adhesion between natural rubber and aluminium powder in various vulcanization systems (Vinod *et al.*, 1998; 2000).

Stress relaxation properties assume importance in static and dynamic applications under stress. The stress under a constant deformation decays by an amount substantially proportional to the logarithm of the period under deformed state. Stress relaxation of a material is found to be dependent on various factors such as composition of the mix including the amount and type of fillers (Sircar *et al*, 1971; Gregory, 1977) nature and type of crosslinks, crosslink density, hysteresis behaviour of the compound (Gent, 1963), type of plasticizers and antioxidants used and testing conditions such as temperature, strain level and strain rate (Kutty and Nando, 1991). Kalfayan et *al.* (1974) described stress relaxation as a tool to study ageing characteristics, since it gives an idea about the rates of network scission and formation during ageing. Bhagawan *et al.* (1987) studied the stress relaxation behaviour of short jute fibre-nitrile rubber composites and reported the existence of a two-stage relaxation pattern. Kutty and Nando (1991) reported stress relaxation behaviour of short kevlar fibre reinforced thermoplastic polyurethane and proposed two and three step relaxation mechanisms for the unfilled and filled stock respectively. Varghese *et al.* (1994) studied sisal fibre reinforced natural rubber composites and reported the existence of a single-relaxation pattern for the unfilled stock and a two stage mechanism for the fiber filled composites. It is also reported that bonding agents influence the relaxation process. The cross-over time from one mechanism to the other is less for composites containing bonding agents compared to those without. (Suhara *et al.*, 1998). Cotton and Boomstra (1965) studied stress relaxation in rubber containing reinforcing fillers and summarized that, in raw rubber, reinforcing carbon blacks decrease the rate of relaxation, while in cured rubbers its effect is very small.

In the present work the stress relaxation behaviour of aluminium powder filled natural rubber composites is reported in comparison with compounds containing conventional fillers. Efforts were also made to investigate the effect of various bonding agents such as hexamethylene tetramine-resorcinol system (HR), bis [3-(triethoxysilyl) propyl)] tetra sulphide (Si-69), cobalt naphthenate (CoN) and toluene diisocyanate (TDI) on the stress relaxation behaviour of natural rubber-aluminium powder composites.

MATERIALS AND METHODS

Natural rubber used for this study was Indian Standard Natural Rubber, grade 5 (ISNR-5). Aluminium powder, (M/s Kosla Metal Powder Co. Pvt. Ltd., India) having a density of 2.7 g per cm^3 and a particle size ranging from 125 to 200 nm was used for the study. The bonding agent, such as hexamethylene tetramine, resorcinol, bis [3-(triethoxy silyl) propyl)] tetrasulphide (Si.-69), cobalt naphthenate and toluene diisocyanate were of laboratory reagent grade. All other ingredients were of commercial grade.

The base formulations are given in Table 1. The mixes were prepared in a two-roll laboratory model open mixing mill (150x300mm). The mixing time and the number of passes were maintained the same for all the mixes 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. Dumb-bell shaped test pieces (ASTM D 412) were punched out from the moulded sheet. The stress relaxation measurement was carried out in a 'Zwick' Universal Testing Machine (Model 1474). The samples were pulled to a desired strain level at a strain rate of approximately 0.061s^{-1} and the decay of stress as a function of time was recorded assuming σ_0 and σ_t as the stress at zero time and at that time, t respectively. Tensile properties were tested on the same machine at 25$\pm$2°C and at a cross - head speed of 500mm/min as per ASTM D - 412-80. A JEOL Scanning Electron Microscope (Model JSM 5600 LV) was used to examine the fractured surface of the tensile specimen.

Table 1. **Formulations of mixes**

Ingredient	GUM	HAF	GPF	ACB	CLY	SIL	10 Al	20 Al	30 Al	40 Al	HR	Si-69	CoN	TDI
Natural rubber	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	1.5
Zinc oxide	5	5	5	5	5	5	5	5	5	5	5	5	5	5
TDQ	1	1	1	1	1	1	1	1	1	1	1	1	1	1
Aluminium powder	-	-	-	-	-	-	10	20	30	40	10	10	10	10
HAF black	-	40	-	-	-	-	-	-	-	-	-	-	-	-
GPF black	-	-	40	-	-	-	-	-	-	-	-	-	-	-
Acetylene black	-	-	-	40	-	-	-	-	-	-	-	-	-	-
China clay	-	-	-	-	40	-	-	-	-	-	-	-	-	-
Precipitated silica	-	-	-	-	-	40	-	-	-	-	-	-	-	-
Hexa	-	-	-	-	-	-	-	-	-	-	1	-	-	-
Resorcinol	-	-	-	-	-	-	-	-	-	-	2	-	-	-
Si-69	-	-	-	-	-	-	-	-	-	-	-	1	-	-
Cobalt naphthenate	-	-	-	-	-	-	-	-	-	-	-	-	1	-
TDI	-	-	-	-	-	-	-	-	-	-	-	-	-	1
CBS	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6
Sulphur	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5

TDQ : 2,2,4-Trimethyl 1,2-dihydroquinoline
TDI : Toluene diisocyanate
CBS : N-cyclohexyl benzothiazyl sulphenamide
Hexa: Hexamethylene tetramine

RESULTS AND DISCUSSION

Tensile properties of the composites are shown in Table 2. At equal loading (40 phr) HAF and acetylene black filled composites have higher tensile strength compared to the aluminium powder filled one, whereas the clay filled composite has lower tensile strength value. As the loading of aluminium powder increased, the tensile strength value increased and more so in the presence of bonding agents. The improvement was in the order, Si-69> HR - system> TDI> CoN. The modulus values of the composites also showed the same trend. Elongation at break decreased with aluminium powder loading, and the presence of bonding agent further reduced it. The improved tensile properties in the presence of bonding agents are due to the improved adhesion of aluminium powder with natural rubber. In the case of HR system, resorcinol combines with the methylene donor to form a resin *insitu* during vulcanization, which makes significant improvements in the adhesion between rubber and aluminium powder. With Si-69, the polar silanol groups are capable of interacting with the surface of the metal powder and the hydrocarbon part interacts with the rubber matrix, which imparts better adhesion. The mechanism of improved adhesion in presence of cobalt salts and isocyanates are unknown, but it is assumed to be achieved through increased polarity.

Table 2. **Tensile properties of the composites**

Mix	300% Modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)
GUM	2.8	20.1	800
HAF	18.0	27.9	375
GPF	17.0	25.5	356
ACB	15.6	24.0	378
SIL	8.3	26.0	409
CLY	6.3	20.0	490
10 Al	4.0	20.7	790
20 Al	5.5	21.4	751
30 Al	6.4	22.0	660
40 Al	6.5	22.2	550
10 Al HR	5.7	25.4	715
10 Al Si-69	4.5	26.2	642
10 Al CoN	4.3	22.3	750
10 Al TDI	4.3	23.1	733

Figure 1 gives the stress relaxation plots of the gum vulcanizate at different strain levels. It is seen that the experimental points for the gum compound fall on a straight line, showing that the relaxation process involved only a single mechanism. There are two important mechanisms that can lead to stress relaxation in a cross-linked elastomer (Meier and Kaster,1984); chemical stress relaxation due to chain scission, crosslink scission or crosslink formation and physical stress relaxation due to molecular rearrangement requiring little primary bond formation or breakage. At typical ambient temperatures, the rate of chemical relaxation in a rubber like substance is very small, and the relaxation behaviour is dominated by physical process. The rate of stress relaxation at all the extensions studied was almost constant. The mechanism, therefore, is physical probably involving the protracted rearrangement of molecular chains (Gent, 1963).

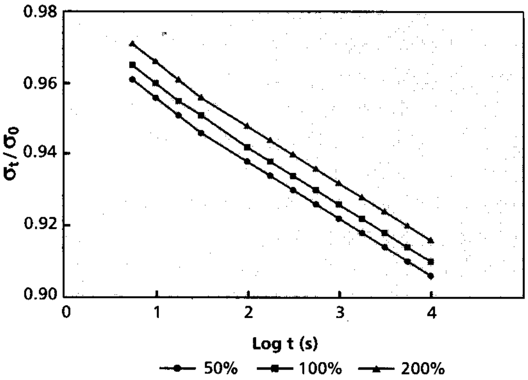

Fig. 1. Stress relaxation curves of natural rubber gum vulcanizate (mix GUM) at various strain levels.

The stress relaxation plots for natural rubber composites containing 40 phr of aluminium powder is shown in Figure 2. Unlike in the gum composite the experimental points of the aluminium powder filled vulcanizates fall on two intersecting straight lines. The stress relaxation curves consisting of two straight lines of unequal slopes indicate the existence of a different relaxation mechanism in the case of the filled composites, one that operates at shorter time and another becoming prominent at the later stages of relaxation. The point of intersection of these two straight lines is the time at which a change over from one mechanism to another takes place.

The stress relaxation plots for various filler incorporated natural rubber vulcanizates are presented in Figure 3. All the filled vulcanizates followed a two-stage relaxation mechanism. It must arise from the progressive failure of rubber-filler attachment either at the surface of the filler or by rupture of the rubber molecules attached to them. The relaxation properties of filled vulcanizates must in some way be related to the relaxation characteristics of filled rubber. This agrees with the concepts of Mullins and Tobin (1965) that the deformation behaviour of filled rubbers can be represented by models in which the rubbery portion of filled vulcanizate is made up of two parts, 'soft' and 'hard' domains. The principal deformation occurring in the soft component displays the same deformation characteristics as is seen in unfilled vulcanizates. At the same time, in the hard domains the effective volume of the filler is the volume of the filler itself as well as the volume of the combined rubber layer, *ie.* the rubber adsorbed on the filler particles. The greater the activity of the filler, the larger the combined layer and the effective size of the particles. These adsorbed

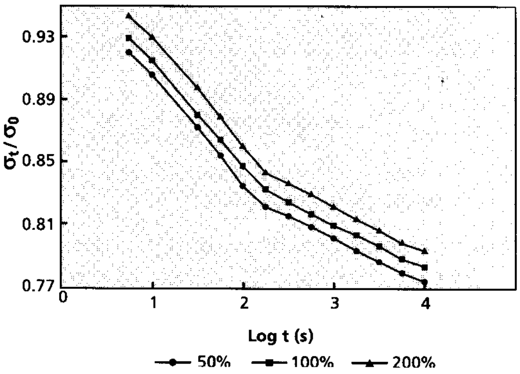

Fig. 2. Stress relaxation curves of 40 phr aluminium powder filled NR composite (mix 40 Al) at various strain levels

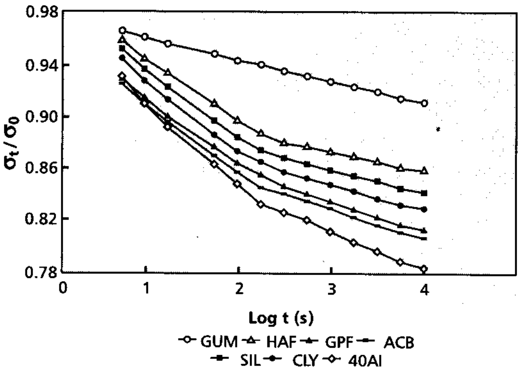

Fig. 3. Stress relaxation curves of natural rubber composites with various fillers at 100% elongation.

(bound) layers of rubber seem to be less elastic and tougher than the unbound rubber in the soft domains. In the filled portion of rubber domain there are relaxation nodes or knots formed through contact between filler and rubber chains. Here the relaxation process takes place through breaking away or through adhesion of segments of the rubber chains to the filler particles. The initial relaxation may be arising out of the combined effect of the orientation at the hard-soft and filler-matrix interfaces, whereas the second one may be due to the flow of soft matrix under tension at longer times.

The slope and intercept of the relaxation curve gave the characteristics of the mixes. The slopes and intercepts were calculated using a linear regression method. The contribution by an earlier process of relaxation is calculated by dividing the difference of the two intercepts by the intercept of the first line at t = 1. The values obtained by this method are given in Table 3. It is seen that in all cases the earlier slope is greater than the later. The rate of relaxation is faster in the case of first stage. This shows that relaxation, as indicated by the slope, is found to be independent of the strain levels up to 200%. The independence of relaxation at lower strain levels has been reported earlier in the case of natural rubber (Gent, 1963). The rate of relaxation is minimum in the gum vulcanizates and maximum in the aluminium powder filled sample. The contribution to initial mechanism and cross over times of natural rubber with various fillers followed the order, HAF>acetylene black>GPF>silica> aluminium powder>clay.

The effect of aluminium powder loading on stress relaxation at 100% strain in natural rubber vulcanizates is shown in Figure 4. The slope and intercept values of these composites are presented in Table 4. All the stocks show a two-step relaxation mechanism as indicated by two intersecting straight lines of different slopes. The rate of relaxation in the second stage is always lower than in the first stage. With increase in aluminium

Table 3. **Stress-relaxation measurements**

Sample	Slope			Intercept			Contribution to initial mechanism (%)	Cross over time (s)
	Early	Later	Difference	Early	Later	Difference		
GUM, 50%	0.0167	-	-	0.9727	-	-	-	-
GUM, 100%	0.0167	-	-	0.9766	-	-	-	-
GUM, 200%	0.0167	-	-	0.9827	-	-	-	-
40 Al, 50%	0.0656	0.0297	0.0359	0.9702	0.8918	0.0784	8.08	210
40 Al, 100%	0.0609	0.0297	0.0312	0.9700	0.9018	0.0682	7.03	199
40 Al, 200%	0.0606	0.0297	0.0309	0.9815	0.9128	0.0687	7.00	191
HAF	0.0442	0.0157	0.0285	0.9882	0.9109	0.0773	7.82	273
GPF	0.0474	0.0227	0.0247	0.962	0.8932	0.0688	7.15	223
ACB	0.0484	0.0231	0.0253	0.9587	0.8884	0.0703	7.33	236
CLY	0.0519	0.0194	0.0315	0.9725	0.9044	0.0681	7.00	188
SIL	0.0483	0.0184	0.0299	0.9847	0.9146	0.0701	7.12	211

powder content, the slope at the first stage is increased. This shows that the rate of relaxation increases with aluminium powder content. At a lower aluminium powder content, even though filler matrix interface is higher compared to the unfilled stocks, the matrix gets diluted, resulting in less reinforcement. Similar observations have been reported earlier (Cotton and Boonstra, 1965) for reinforced rubber vulcanizates. From Table 4 it is clear that cross-over time and the contribution to initial mechanism gradually increased with the increase in aluminium powder loading.

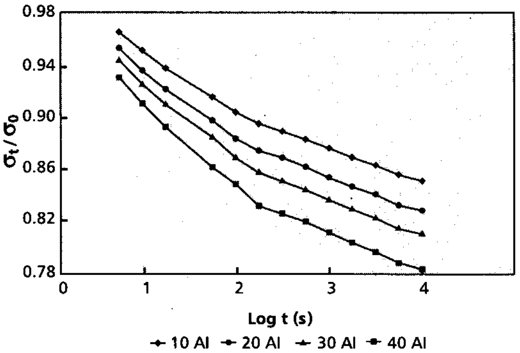

Fig. 4. Stress relaxation curves of natural rubber composites aluminium powder at 100% elongation.

The variation of relaxation behaviour with various bonding agents is shown in Fig. 5 and the corresponding slope and intercept values are given in Table 4. All the composites contain 10 phr of aluminium powder and the experiment was conducted at 100% elongation. The mixes with bonding agents show two stage relaxation pattern which indicates that two types of mechanism are operating in the process. However, the early relaxation rate of the composites is found to be affected by the presence of bonding agents. This is because the filler-matrix bond in the composites, containing bonding agent, is stronger. The composites containing bonding agents show a slower rate of relaxation than those having no bonding agents. This reflects the increased adhesion between natural rubber and aluminium powder in presence of the bonding agents. Improved adhesion by the use of various bonding agents was reported earlier (Vinod *et al.*, 2001; Varghese *et al.*, 1994; Suhara *et al.*, 1998) which support the present obser-

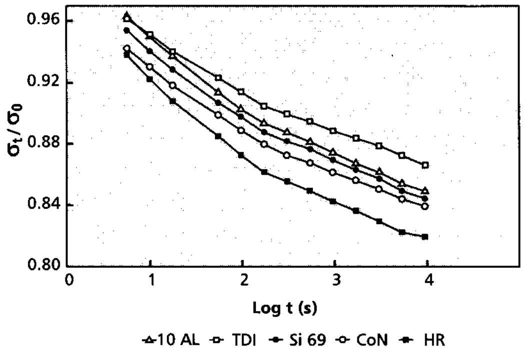

Fig. 5. Effect of bonding agents on the stress relaxation curves of NR-aluminium powder (10 Al) composites at 100% elongation.

Table 4. **Effect of aluminium powder loading on stress-relaxation measurements at 100% elongation**

Sample	Slope			Intercept			Contribution to initial mechanism (%)	Cross over time (s)
	Early	Later	Difference	Early	Later	Difference		
10 Al	0.0442	0.0257	0.0185	0.9945	0.9532	0.0413	4.15	133
20 Al	0.0495	0.0267	0.0228	0.9856	0.9345	0.0511	5.18	158
30 Al	0.0541	0.0277	0.0264	0.9799	0.9206	0.0593	6.05	177
40 Al	0.0609	0.0297	0.0312	0.9700	0.9018	0.0682	7.03	199
HR	0.0438	0.0248	0.0190	0.9696	0.9186	0.0510	5.26	223
Si-69	0.0406	0.0241	0.0165	0.9802	0.9297	0.0505	5.14	201
CoN	0.0387	0.0221	0.0166	0.9683	0.9197	0.0486	5.01	198
TDI	0.0348	0.0203	0.0145	0.9889	0.9401	0.0488	4.93	191

vation. By comparing the cross-over times of various mixes with and without bonding agents, it is possible to have a clear idea about the level of adhesion between the aluminium powder and natural rubber in these compounds. Vulcanizates containing bonding agents always registered a higher cross-over time. Initial relaxation is faster in a weak interface and hence a low cross-over time is realized for unbonded composite. In a strong interface as that exists in mixes containing bonding agents, the initial relaxation process is long and takes more time for the initiation of the second phase of the relaxation process.

The improved adhesion of natural rubber and aluminium powder in these composites can be understood from the swelling measurements. The swelling of the composites containing bonding agents was conducted in toluene at 27ºC, and the equilibrium swelling values obtained are given in Fig. 6. Various factors like, cross link density, nature of polymer, nature of solvent, presence of fillers, system of vulcanization etc. affect the swelling values. For a particular filler in a polymer at a given loading, a comparison of the equilibrium swelling values gives an idea about the adhesion between the polymer and the filler. In natural rubber - aluminium powder composites containing bonding agents, the equilibrium swelling values followed the order HR system<Si-69<CoN<TDI. This suggests a strong rubber- aluminium powder interaction through improved adhesion, which in turn reduces solvent pockets and voids at the interface. The improved adhesion is also clear from the scanning electron photomicrographs of these composites. The fractured surface of the tensile test pieces of the composites were examined by means of a scanning electron microscope (SEM). The SEM photographs are given in Fig. 7 (a-e). It is seen that in the unbonded composite the aluminium powder exists as loose aggregates and causes a non-uniform rough surface. The photographs of the composites with bonding agents showed that the filler particles are more aligned when compared to unbonded composites. In composites with hexamethylene tetramine-resorcinol system and Si-69, the aluminium powder is more firmly bonded to the rubber matrix and gave a smooth failure surface. The SEM photographs support the improved properties of aluminium powder filled natural rubber composites in the presence of bonding agents.

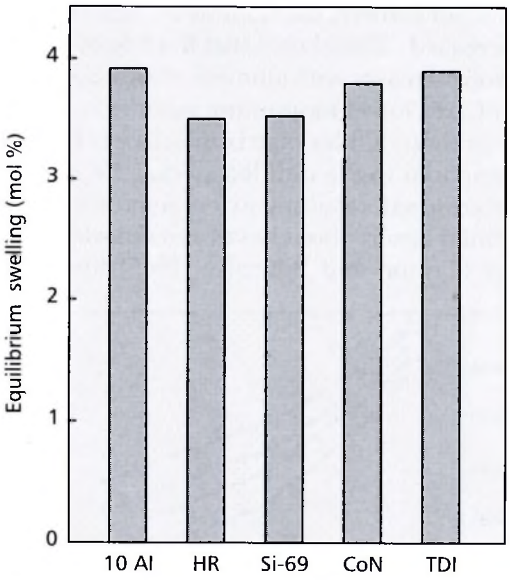

Fig. 6. Equilibrium swelling values of NR-aluminium powder composites with various bonding agents

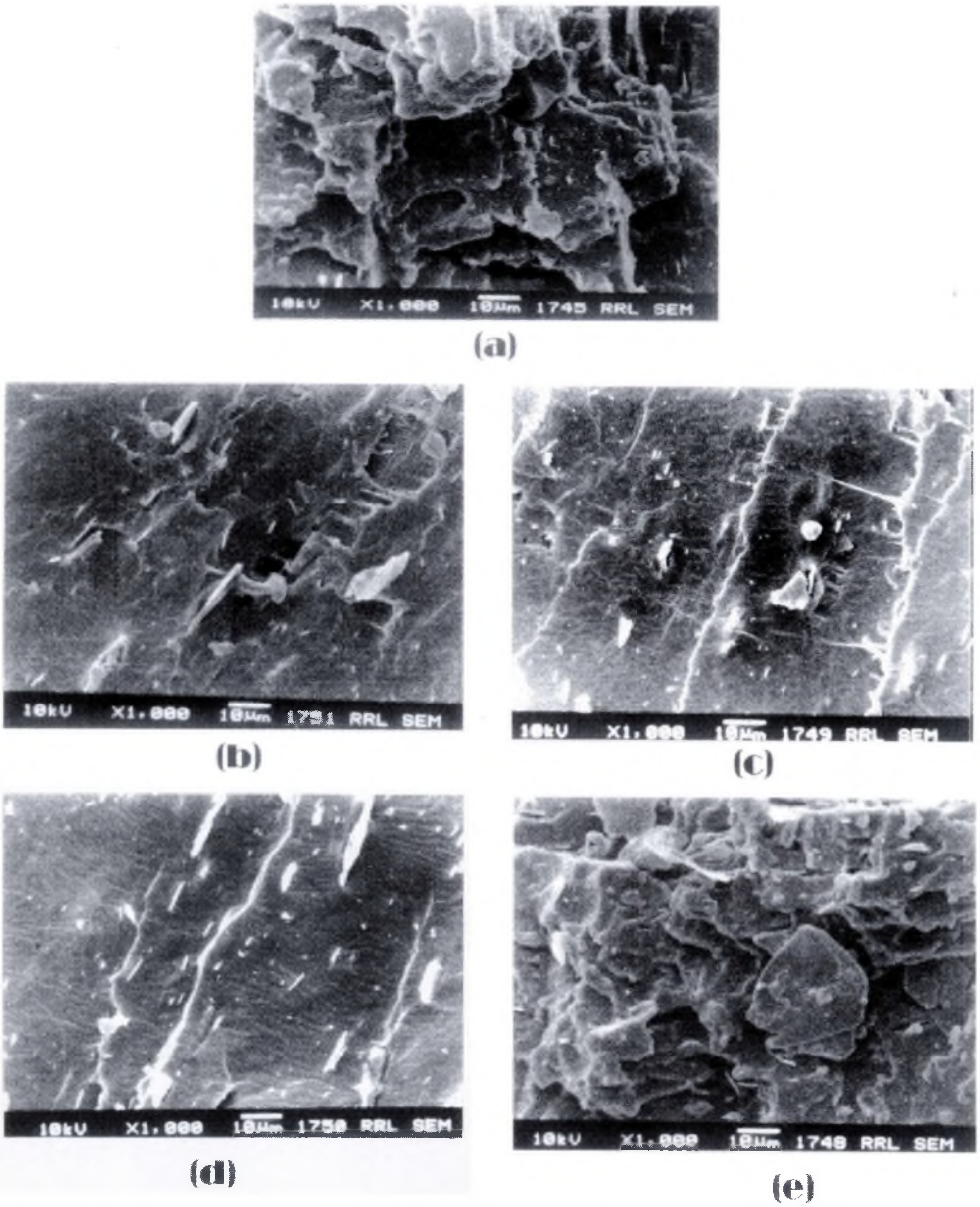

Fig. 7. SEM photographs of tensile fractured surface of 10 phr aluminium powder filled natural rubber composites; a: having no bonding agent, b: with HR system, c: with Si-69, d: with TDI and e: with CoN.

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