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Degradation behaviour of natural rubber–aluminium powder composites: effect of heat, ozone and high energy radiation

V.S. Vinod, Siby Varghese*, Baby Kuriakose

Rubber Research Institute of India, Kottayam, Kerala 686 009, India

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Abstract

Properties such as resistance towards heat, ozone and gamma radiation and flame resistance of aluminium powder filled natural rubber composites were studied. Aluminium powder filled natural rubber composites showed better retention of mechanical properties after thermal ageing compared to other fillers like HAF, GPF, silica and acetylene black. Tensile strength of natural rubber (NR)–aluminium powder vulcanizates increased slightly after ageing for 7 days at 70 °C due to the slow and continued crosslinking, but on prolonged ageing, chain scission predominated, which decreased the tensile strength. These composites also have better resistance towards ozone exposure. The cracks generated due to ozone exposure are small and discontinuous in aluminium powder filled vulcanizates, whereas the cracks are deeper, wider and continuous for other filler incorporated samples. Effects of various bonding agents namely hexamethylene tetramine-resorcinol system (HR), bis [3-(triethoxysilyl) propyl] tetrasulfide (Si-69), cobalt naphthenate (CoN) and toluene diisocyanate (TDI), on the ageing characteristics of natural rubber-aluminium powder composites were studied and it was found that these composites have better resistance towards heat, ozone, and gamma irradiation.

Keywords: Natural rubber; Aluminium powder; Degradation

1. Introduction

Natural rubber (NR), unlike many other polymers, is highly susceptible to degradation, due to the presence of double bonds in the main chain. Degradation of NR is accelerated mainly by heat, humidity, light, ozone, radiation etc. In routine technological evaluation, rubber vulcanizates are subjected to accelerated ageing tests to get information about the service life. This problem was well recognized by Baker [1] who examined the effect of temperature on the ageing behaviour of natural rubber compounds. Effects of high-energy radiation, thermal and ozone exposure in natural rubber composites containing sisal fibre were reported [2]. Many of the chemically unsaturated rubbers are prone to attack by even the minute quantities of ozone present in the atmosphere. Such attack not only detracts from the surface appearance of rubber products but also causes loss of physical properties, especially in thin-walled articles.

NR, when properly compounded either with suitable waxes or antioxidants, will have ozone resistance as good as or even better than many synthetic rubbers [3]. Degradation of NR by radiation is also a serious problem, mainly from gamma ray irradiation, which is usually used in sterilization. With gamma ray irradiation high molecular weight materials may decompose. The mechanism of characteristic changes in gamma ray irradiated polymer, including degradation and crosslinking has been studied by Shintani and Jakamura [4]. The effects of temperature and environmental factors on the performance of polymers and various degradation reactions including their mechanisms are available in the literature [5–10].

Introduction of fillers into polymers leads to a wide range of interactions arising at the polymer-filler interface. These dispersed fillers considerably influence the properties of the polymer composites, including their degradation and stability. The major factors that control these properties are the surface chemistry of the filler, nature, shape and size of particles, size distribution and specific surface area etc [11]. For many material applications information is needed on the thermal properties such as thermal conductivity, heat capacity, electrical conductivity etc. In such cases conductive polymers acquire wide acceptability. These composites have applications like dissipation of electrostatic charge, devel-

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* Corresponding author. Fax: +91-481-353-327.
E-mail address: rrii@vsnl.com (S. Varghese).

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opment of friction-anti-friction materials, protection from electromagnetic waves [12], and also give uniform curing and reduce the cure time of thick rubber articles [13]. Various methods are available to increase the conductivity of rubbers [14–16]. One of the best and easy methods is incorporation of metal powders. Poor adhesion and non-uniform dispersion of the discrete phase in the matrix cause fluctuation in the composite properties [17]. This can be overcome by using coupling/bonding agents [18–22], which increases the rubber-filler interaction.

In the present work we report the ageing properties of aluminium powder-filled natural rubber composites. Resistance towards heat, ozone, gamma-irradiation and flame resistance were studied. Effects of loading of aluminium powder and various bonding agents have been investigated. For comparison of results, vulcanizates containing conventional fillers are also included in the study.

2. Experimental

NR used for this study was Indian Standard Natural Rubber, Grade 5 (ISNR-5) the specification of which is given in Table 1. The bonding agents, hexamethylene tetramine, resorcinol, bis [3-(triethoxy silyl) propyl] tetrasulfide (Si-69), cobalt naphthenate and toluene diisocyanate were of laboratory reagent grade. All other ingredients were of commercial grade. Aluminium powder was obtained from M/s Kosla Metal Powder Co. Pvt. Ltd, Pune, India, and had a specific gravity of 2.7 and a particle size of 127 to 300 nm.

The base formulation used is given in Table 2. The mixes were prepared in a two- roll mixing mill, and the bonding agents were added at the time of mixing. The samples were cured to their optimum cure time at 150 °C as obtained from Monsanto Rheometer R-100. Tensile properties of the vulcanizates were measured on a 'Zwick' Universal Testing Machine (Model 1474) at a crosshead speed of 500 mm/min as per ASTM D 412-80. For thermal ageing, tensile specimens of the vulcanizates were kept in an air oven, maintained at 70 °C. The tensile strength of the aged samples was determined, after conditioning the samples for 24 h. Resistance to ozonolysis was studied using an ozone test chamber manufactured by MAST Development Company, USA. The ozone concentration used was 50 pphm. The ozonised oxygen generated in the ozoniser by a UV quartz lamp is collected in a separate chamber where the sample is exposed. For gamma irradiation, the samples were kept in a gamma chamber, for the required time. The flammability test was carried out using an SR-FTA flammability tester by ASTM D 2863-77 method.

3. Results and discussion

Fig. 1 illustrates the decrease in tensile strength and modulus (300%) due to thermal ageing for natural rubber

Table 1
Characteristics of natural rubber

Parameters	Value
Dirt content, % by mass	0.04
Volatile matter, % by mass	0.50
Nitrogen, % by mass	0.30
Ash, % by mass	0.40
Initial plasticity, P_0	38
Plasticity retention index, PRI	78

Table 2
Formulation of mixes[a]

Ingredients	GUM	HAF	GPF	ACB	CLY	SIL	10Al	20Al	30Al	40Al	HR	Si69	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	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	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
Aluminum powder	–	–	–	–	–	–	10	20	30	40	10	10	10	10
HAF	–	40	–	–	–	–	–	–	–	–	–	–	–	–
GPF	–	–	40	–	–	–	–	–	–	–	–	–	–	–
Acetylene black	–	–	–	40	–	–	–	–	–	–	–	–	–	–
China clay	–	–	–	–	40	–	–	–	–	–	–	–	–	–
Precipitated silica	–	–	–	–	–	40	–	–	–	–	–	–	–	–
Hexa	–	–	–	–	–	–	–	–	–	–	1.0	–	–	–
Resorcinol	–	–	–	–	–	–	–	–	–	–	2.0	–	–	–
Si-69	–	–	–	–	–	–	–	–	–	–	–	1.0	–	–
Cobalt naphthenate	–	–	–	–	–	–	–	–	–	–	–	–	1.0	–
TDI	–	–	–	–	–	–	–	–	–	–	–	–	–	1.0
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
Sulfur	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

[a] TDQ, 2,2,4-trimethyl-1,2-dihydroquinoline; HAF, high abrasion furnace black; GPF, general purpose furnace black; Hexa, hexamethylene tetramine; Si-69, bis[3-(triethoxysilyl) propyl] tetrasulphide; TDI, toluene diisocyanate; CBS, N-cyclohexyl benozthiazyl sulphenamide.

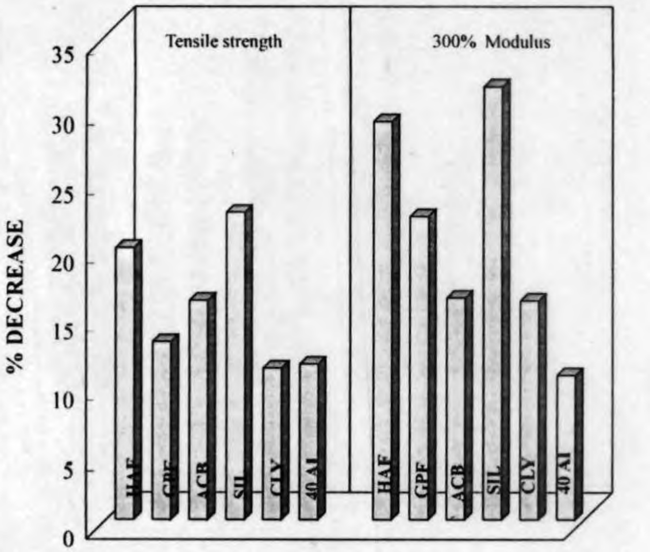

Fig. 1. Percentage decrease in tensile strength and modulus (300%) of NR vulcanizates containing various fillers, after ageing at 70 °C for 14 days.

composites containing 40 phr loading of various fillers. After keeping at 70 °C for 14 days, the percentage decrease in tensile strength of the natural rubber composites containing various fillers followed the order clay < aluminium powder < GPF < acetylene black < HAF < silica. The results showed that clay and aluminium powder-incorporated vulcanizates have better retention of mechanical properties after ageing compared to other fillers. The action of oxygen on natural rubber is activated by heat. For assessing the long-term serviceability of the vulcanizates, variation in modulus along with the variation in tensile strength is helpful. From the figure it is clear that the percentage decrease in 300% modulus due to ageing follows the order, aluminium powder < clay < acetylene black < GPF < HAF < silica. This showed that aluminium powder-filled natural rubber composites have minimum loss in its properties compared to other fillers. The influence of temperature is not direct, as in normal chemical reactions in promoting the reaction but it is mainly an indirect effect, which finally leads to polymer degradation.

Variation in tensile strength after thermal ageing of natural rubber vulcanizates containing different loadings of aluminium powder is shown in Fig. 2. An increase in tensile strength is observed with aluminium powder filled samples at all loadings. The higher retention in tensile strength (> 100%) of the vulcanizates, after ageing at 70 °C for 7 days could be due to the continuing cross-linking of the elastomer. Ageing for 14 days at 70 °C results in a decrease of tensile strength at all loadings. However, the filled samples showed better retention than the gum sample. Fig. 3 shows the variation in modulus (300%) of the aluminium powder-filled vulcanizates. From the figure it is clear that as the loading of aluminium powder increased, the modulus also increased. The increase in modulus is due to the higher extent of cross-links formed in the composites, due to the increased thermal conductivity in the presence of aluminium powder. During thermal ageing the gum composite gradually loses their modulus due to degradation. In aluminium powder filled vulcanizates an increase in modulus is observed after 7 days ageing and a decrease after 14 days ageing at 70 °C, the same trend as in the case of the tensile values after ageing. In rubber compounds, temperature causes two competing reactions namely cross-link formation and scission of

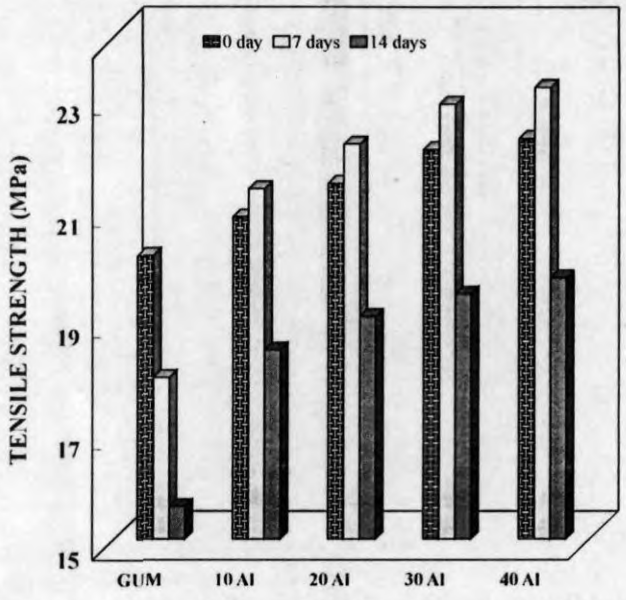

Fig. 2. Variation in tensile strength of aluminium powder filled NR composites after ageing at 70 °C.

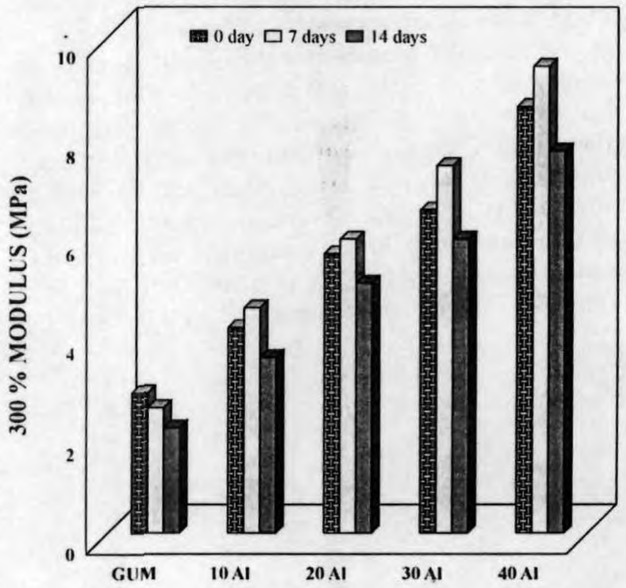

Fig. 3. Variation of modulus (300%) of aluminium powder filled NR composites after ageing at 70 °C.

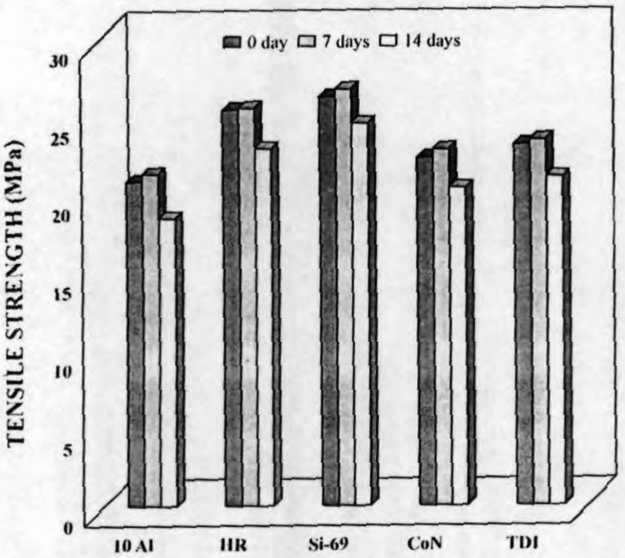

Fig. 4. Dependence of tensile strength with ageing at 70 °C for NR–aluminium powder (10 phr) composites containing bonding agents.

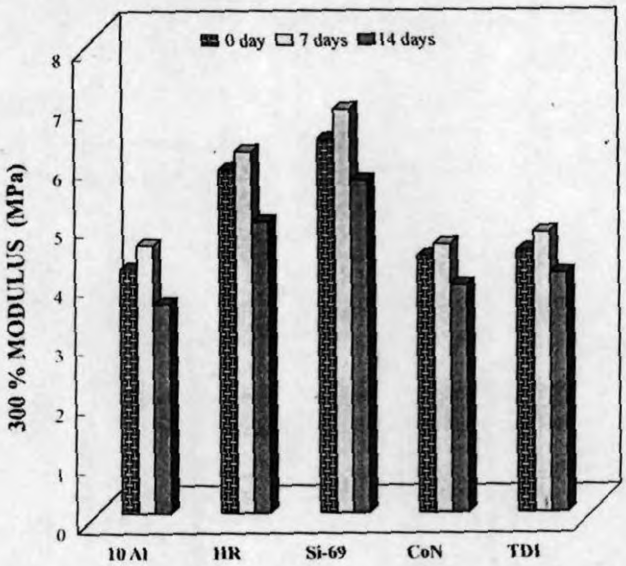

Fig. 5. Dependence of 300% modulus with ageing at 70 °C for NR–aluminium powder composites containing bonding agents.

chains. The slight increase and then decrease in tensile strength and modulus values of these composites can be explained on the basis of these processes. At lower periods of ageing the extent of main chain scission is less and effect of cross-linking predominates but at longer periods the reverse situation occurs resulting in lower retention of tensile strength and modulus.

Fig. 4 shows the tensile strength of NR–aluminium powder composites containing different bonding agents, after ageing. The bonding/coupling agents used were hexamethylene tetramine-resorcinol system (HR), bis [3-(triethoxy silyl) propyl] tetra-sulfide (Si-69), cobalt naphthenate (CoN) and toluene diisocyanate (TDI). The 300% modulus of these composites and its variations due to thermal ageing are presented in Fig. 5. It is seen that both the tensile strength and modulus slightly increased in all cases after ageing at 70 °C for 7 days. Further ageing at the same temperature caused more polymer degradation than crosslink formation resulting in a decrease in tensile strength and modulus. Variations in composite properties with type of bonding agents are observed with particulate-filled systems, which is due to the poor adhesion and non-uniform dispersion of the discrete phase in the matrix. Interface modification of the composites partly by a suitable coupling/bonding agent reduces this problem by enhancing surface interaction between the two phases. This is clear from Table 3, in which the equilibrium swelling in toluene of the vulcanizates at 27 °C are presented. This can be taken as a measure of adhesion between the polymer and particulate fillers. The improved adhesion between the discrete phases of a composite containing bonding

Table 3
Properties of the composites[a]

Sample	T_{90} (min)	Tensile strength (MPa)	Hardness (shore A)	Heat build -up (°C)	Q∞ in toluene (mol%)	LOI (n%)
GUM	18.0	20.1	42	07	4.060	16.4
HAF	15.0	27.9	50	38	2.807	18.4
GPF	16.5	25.5	48	24	2.928	18.2
ACB	14.5	24.0	50	38	2.888	18.0
SIL	17.5	26.0	46	26	3.098	18.1
CLY	20.0	20.0	38	20	3.321	18.2
10 Al	17.5	20.8	43	09	3.732	17.3
20 Al	16.0	21.4	49	13	3.311	17.4
30 Al	15.0	22.0	51	17	2.960	17.8
40 Al	14.0	22.2	53	19	2.792	18.2
HR	09.0	25.4	46	15	3.320	17.3
Si-69	12.0	26.2	46	18	3.340	17.5
CoN	10.0	22.3	44	17	3.600	17.4
TDI	16.0	23.1	45	15	3.710	17.4

[a] See Table 2 footnote for abbreviations.

agents is evident in the low values for swelling these composites than the corresponding composite without bonding agent (compound 10 Al). The improved adhesion causes fewer solvent pockets resulting a low value of equilibrium swelling.

Some of the main properties of the composites are given in Table 3. The addition of aluminium powder gradually decreased the optimum cure time, which was further reduced by the addition of bonding agents. Among the various fillers used (40 phr) aluminium powder filled vulcanizates had the maximum hardness value. It is also interesting to note that the 40 phr aluminium powder loaded natural rubber compound has only half the value of heat build up than the corresponding 40 phr HAF black loaded compound. Silane coupling agents are quite effective in reactive polymer systems; they contain polar silanol groups capable of adhering to the surface of glass, metal etc. and hydrocarbon groups which interact with the rubber matrix. The addition of isocyanate to rubbers initiates a chemical reaction, which might feasibly account for the bonding of particulate fillers to the matrix. It is suggested that the isocyanate group itself combines with the hydrated oxide layers on the surfaces of the metal. Cobalt naphthenate can also be used to promote metal

Table 4
Variation in the elongation at break values (%) of the composites after ageing at 70 °C[a]

Sample	0 Day	7 Days	14 Days
GUM	800	790	760
HAF	370	370	360
GPF	360	340	330
ACB	380	370	350
SIL	450	440	430
CLY	490	480	470
10 Al	790	790	780
20 Al	750	750	730
30 Al	660	640	620
40 Al	550	540	540
HR	720	700	700
Si-69	640	630	620
CoN	750	730	710
TDI	730	720	700

[a] See Table 2 footnote for abbreviations.

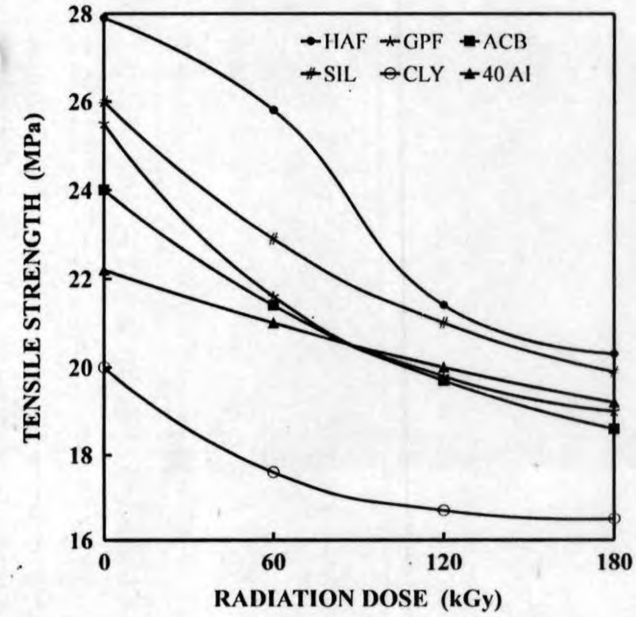

Fig. 6. Variation in tensile strength with gamma irradiation for NR–vulcanizates containing different fillers.

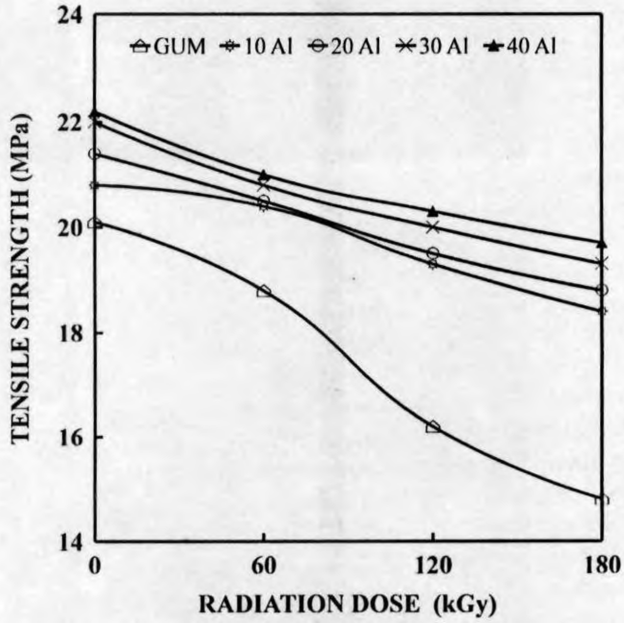

Fig. 7. Effect of gamma radiation on natural rubber–aluminium powder composites.

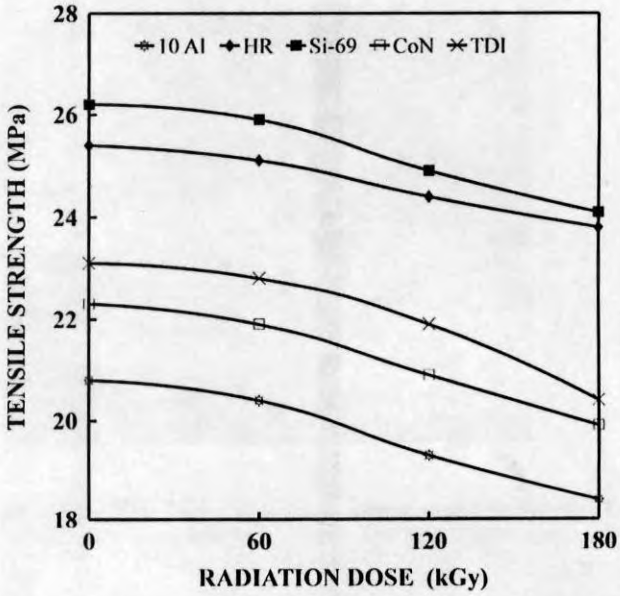

Fig. 8. Variation in tensile strength with gamma radiation for NR–aluminium powder composites containing bonding agents.

adhesion, which creates an increased polarity in the matrix. It is also reported that CoN is an effective oxidation catalyst for natural rubber [23]. The comparatively lower tensile properties of the vulcanizates-containing CoN may be due to this effect.

The elongations at break (%) values of the composites are presented in Table 4. It is seen that the elongation at break (EB) is maximum for gum vulcanizate and the loading of aluminium powder decreased the elongation at break. The presence of bonding agent further decreased the EB. The improved adhesion in the presence of bonding agent restricts the mobility of polymer segments, which finally results in a reduction in elongation. The thermal ageing caused a slight reduction in the

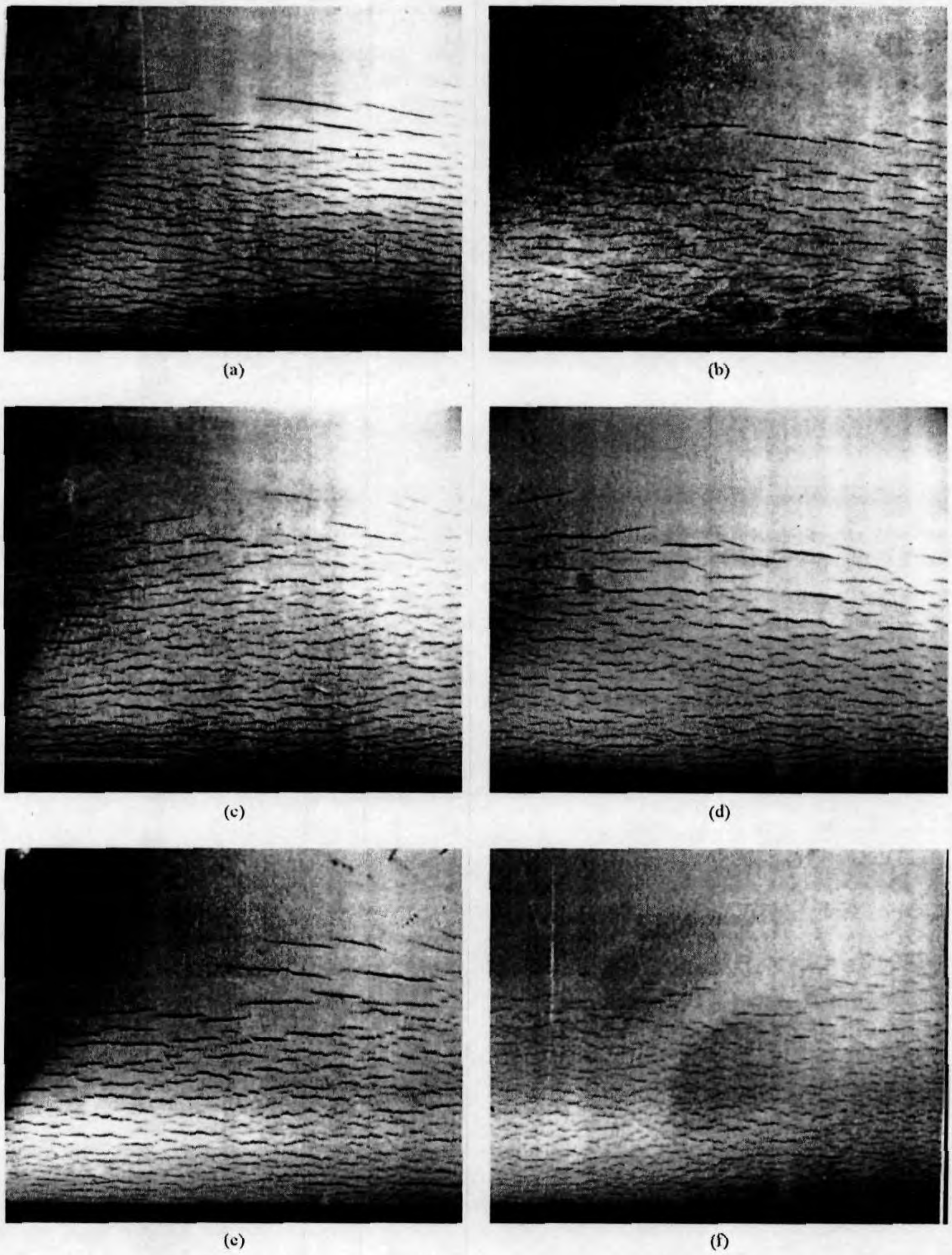

Fig. 9. Optical photomicrographs of ozone exposed (10 h) NR–vulcanizates containing 40 phr fillers: (a) high abrasion furnace black; (b) general purpose furnace black; (c) acetylene black, (d) precipitated silica, (e) china clay and (f) aluminium powder.

elongation at break in all cases. Both cross-link formation and main chain scission at high temperature causes reduction in polymer elongation. We have seen that the tensile strength and modulus are slightly increased by ageing due to additional (7 days at 70 °C) crosslinks formed during the ageing period. This additional cross-links reduced the elongation of these composites. Ageing at 70 °C for 14 days further decreased the maximum elongation, but here the main mechanism involves the chain scission due to polymer degradation as evident from the loss in tensile strength values.

The limiting oxygen index (LOI) values of natural rubber composites containing aluminium powder are given in Table 3. The LOI is defined as the volume fraction of oxygen in an oxygen-nitrogen atmosphere that will just support steady candle-like burning of a material. It has been widely applied as a measure of polymer flammability [24]. All fillers including aluminium powder increased the LOI value of the gum compound and LOI value increased with aluminium powder loading. But the addition of bonding agent was found to have less effect on the LOI values.

The effect of γ-radiation on the tensile properties of various fillers incorporated vulcanizates is given in Fig. 6. Gamma irradiation caused a decrease in tensile strength for all compounds, but the extend of decrease is different. From the figure it is clear that the percentage decrease is minimum for aluminium powder filled compounds, whereas in other cases a sharp fall in tensile strength was observed. Though gamma irradiation can cause crosslinking and polymer degradation, the reduction in tensile value shows that chain scission leading to polymer degradation is the main reaction here. Fig. 7 shows the effect of gamma radiation on tensile strength of natural rubber-aluminium powder composites at different loadings. The tensile strength of the gum was reduced sharply from the original value after a radiation doze of 180 kGy. At all loadings, aluminium powder imparted better resistance towards γ-radiation than the gum samples. The effect of various bonding agents on NR–aluminium powder composites towards gamma radiation is shown in Fig. 8. Here also the radiation caused a reduction in the tensile strength, the same trend as observed in composites having no bonding agent.

To assess the ozone resistance of the aluminium-filled vulcanizates, test samples having 20% strain were exposed to ozonized air of 50 pphm ozone concentration. Characteristic cracking in rubber is not observed unless a tensile strain is imposed during exposure, and once the strain is exceeded, a crack will grow at a constant rate independent of additional strain, and for many rubbers in direct proportion to ozone concentration [3]. In the case of NR aluminium powder composites it is seen that cracks developed on the surface of all the samples as early as two hours of exposure to ozone. However, the nature and intensity of cracks due to ozone attack are different for various vulcanizates. Optical photographs of the surfaces of vulcanizates after 10 h of ozone exposed samples are presented in Figs. 9(a)–(f). In the case of aluminium powder incorporated samples the cracks are small and discontinuous whereas continuous and deep cracks are observed in the vulcanizates having no aluminium powder. This may due to the higher extent of cross-links formed in these composites, due to the higher thermal conductivity of aluminium powder. The presence of aluminium powder as an inert particle in the elastomer prevents the growth of cracks along the polymer. A growing crack in the reactive phase must, sooner or later encounter an inert particle and come to a halt, further propagation being possible only by the crack circumventing the particle or jumping over it. Except for very small particles circumvention is unlikely, since it would involve the crack propagating parallel to the applied stress, i.e. in a direction involving a minimum release of elastic stored energy [25]. The length of cracks in the reactive phase will, however, be governed by the density and nature of the unreactive particles present in the polymer. From the photograph it is clear that incorporation of aluminium powder will impart better ozone resistance compared to other filler incorporated vulcanizates. The same trend is observed with vulcanizate containing bonding agents.

4. Conclusions

Compared to other fillers, aluminium powder filled natural rubber composites retained their mechanical properties after thermal ageing. Ageing of NR–aluminium powder composites at 70 °C for 7 days slightly increased the tensile strength due to the continued crosslinking in the composite, but degradation predominates on prolonged ageing, resulting a decreased tensile strength. The maximum elongation is found to decrease due to prolonged ageing. The LOI values are increased by the incorporation of various fillers including aluminium powder. Gamma radiation caused a decrease in tensile strength for all compounds, but is minimum for aluminium powder incorporated samples. The trend remains same irrespective of aluminium powder loading and presence of various bonding agent. Optical photographs of ozone exposed samples showed that in aluminium powder filled vulcanizates, the cracks developed are small and discontinuous, where as in other samples the cracks are deep, wide and continuous.

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