Indian Journal of Natural Rubber Research, **15**(2) : 109-118, 2002.

DYNAMIC MECHANICAL PROPERTIES OF ALUMINIUM POWDER FILLED NATURAL RUBBER COMPOSITES

V.S. Vinod, Siby Varghese, Baby Kuriakose, Sabu Thomas and Gabriel Groeninck

Vinod, V.S., Varghese, S., Kuriakose, B., Thomas, S. and Groeninck, G. (2002). Dynamic mechanical properties of aluminium powder filled natural rubber composites. *Indian Journal of Natural Rubber Research*, **15**(2) : 109-118.

The dynamic mechanical properties of natural rubber vulcanizates containing aluminium powder have been compared with those containing conventional fillers. Storage modulus, loss modulus and loss factor increased continuously with increase in aluminium powder loading. The effect of various bonding agents like hexamethylene tetramine-resorcinol system, bis [3-(triethoxy silyl) propyl] tetrasulphide, cobalt naphthenate and toluene diisocyanate have been investigated. Presence of bonding agents increased the dynamic modulus and mechanical loss due to improved adhesion. With increase in temperature mechanical loss decreased. Variation in testing frequency affects dynamic properties, which decreased as the frequency decreased. Various theoretical models have been used to fit the experimental viscoelastic data.

Key words: Aluminium powder, Composites, Natural rubber, Viscoelasticity.

Vinod, V.S, Siby Varghese (for correspondence), Baby Kuriakose, Rubber Research Institute of India, Kottayam– 686 009, India; Sabu Thomas, Mahatma Gandhi University, Kottayam, India and Gabriel Groeninck, Laboratory of Macromolecular and Structural Chemistry, Department of Chemistry, Catholic University of Leuven, Belgium.

INTRODUCTION

Measurement of dynamic mechanical properties helps in understanding the behaviour of elastomers under cyclic loading and temperature. The modulus information obtained from dynamic mechanical testing is of importance to manufacturers and users of polymers in structural applications. Of greater importance is the information on damping, since such end-use properties as vibration dissipation, heat build-up, impact resistance and noise abatement are related to mechanical damping. Rubber products generally undergo dynamic stress during service. Therefore, their behaviour under dynamic loading is highly important. The dynamic mechanical properties of elastomers are strongly dependent on temperature, frequency, type and concentration of filler and the extent of deformation. Several investigators studied the dependence of dynamic mechanical properties of rubber vulcanizates on the type and concentration of fillers (Ulmer *et al.*, 1973; Ferry and Fitzgerald, 1982) under different test conditions (Mukhopadhyay *et al.* 1993). Studebaker and Beatty (1974) studied the effect of basic compounding on dynamic mechanical properties of rubber. The major compounding variables involved in this study were nature of the rubber, nature and amount of ingredients in the curing system and type and quantity of fillers and plasticizers. Viscoelastic studies on sisal fibre reinforced natural rubber composites were reported by Varghese *et al.* (1992). Dynamic mechanical properties of a variety of carbon black–loaded compounds over a wide range of frequency and temperature have been reported (Gandhi and Salovery, 1988; Nagata *et al*, 1987). Manna *et al.* (1998) studied the effect of strain on the dynamic mechanical properties of ENR-carbon black mixture with special reference to the role of oxidation of the filler surface in the formation of rubber-filler bonds. Blaine *et al.* (1998) reported on dynamic mechanical analysis for the characterization of physical properties. Effect of silica filler on the dynamic mechanical properties of ionic elastomer based on carboxylated nitrile rubber was reported by Mandal *et al.* (1995) who found that the rubber filler interaction in the cluster region causes striking changes in the variation of E′ and tan δ with double strain amplitude.

In recent years metal powder filled rubber composites have received considerable attention (Bhattacharya and Chaklader, 1982 & 1983; Parks, 1982; Delmonte, 1961; Nobile *et al.*, 1988). These composites offer the advantage of conducting heat and electricity, which suits various applications involving dissipation of electrostatic charge, development of friction-anti-friction materials and protection from electromagnetic waves. Incorporation of conductive fillers in rubber has advantage in moulding of thick articles like dock fenders, solid tyres, etc. The increased conductivity reduces the cure time required for thick rubber articles and gives uniform cure throughout the material (Vinod *et al.*, 2001). In addition to the incorporation of metal powder, other methods adopted for increasing the conductivity of polymers are: i) incorporation of conductive blacks (Norman, 1970), ii) synthesis of ionic conductive polymers (Simon, 1991), iii) addition of conductive polymeric powders (Meyers, 1986) etc. Poor adhesion and non-uniform dispersion of the discrete phase in the matrix cause fluctuation in the composite properties. This can be overcome by using coupling/bonding agents (Rajan *et al.*, 1988; Alex and Mathew, 1989), which increase the rubber-filler interaction. The use of resorcinol-hexa-silica system to improve adhesion between natural rubber and aluminium powder in various vulcanization systems was reported by Vinod *et al.* (1998). Buchen (1959) gave a detailed list of various agents for bonding rubber to metal.

In the present work the dynamic mechanical properties of aluminium powder filled natural rubber composites over a wide range of temperature (30 to 150°C) and at different frequencies have been studied. The effects of loading of aluminium powder and various bonding agents on viscoelastic properties have been investigated. For comparison, results from vulcanizates containing conventional fillers are also included. Finally the experimental viscoelastic data have been compared with theoretical predictions.

MATERIALS AND METHODS

Natural rubber used for this study was Indian Standard Natural Rubber, grade-5 (ISNR-5). Aluminium powder, (Khosla Metal Powder Co. Pvt. Ltd., India) having a density of 2.7 g cm^{-3} and a particle size ranging from 125 to 200 nm was used for this study. The bonding agents, viz. hexamethylene tetramine, resorcinol, bis [3-(triethoxy silyl) propyl] tetrasulphide (Si-69), cobalt naphthenate (CoN) and toluene diisocyanate (TDI) were of laboratory reagent grade. The other ingredients were of commercial grade. Formulations of the mixes are given in Table 1. The mixes were prepared on a two-roll mixing mill, 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.

Vulcanized rectangular specimens (50 X 8 mm) having a thickness of 4 mm were used for the experiment. The dynamic storage modulus (E′), loss modulus (E″) and loss factor (tan δ) were measured as a function of temperature at various frequencies using a Dynamic Mechanical Analyser (Model DMTA-MKII, Polymer Laboratories, U.K.). The properties were determined over a temperature range of 30 to 150° C, with a dynamic tension strain amplitude of 0.1% and at a heating rate of 2 °C min^{-1}. The tensile properties were tested on a 'Zwick' Universal Testing Machine (Model 1474) at a crosshead speed of 500 mm/min at 27 ± 2°C, according to ASTM D-412-80.

Table 1. **Formulation of mixes**

Ingredient	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	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
Aluminum 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
Si-69 - Bis[3-(triethoxysilyl) propyl] tetrasulphide
CBS - N-cyclohexyl benzothiazyl sulphenamide
GPF - General purpose furnace black
Hexa - Hexamethylene tetramine
HAF - High abrasion furnace black
TDI - Toluene diisocyanate

RESULTS AND DISCUSSION

Dynamic storage modulus, loss modulus and loss factor were measured as a function of temperature at three frequencies viz. 10, 1.0 and 0.1 Hz. All these parameters have the same pattern of change with temperature at all the frequencies studied. Figure 1 shows the effect of temperature on the storage modulus of the composites containing different fillers at a frequency of 1.0 Hz over a temperature range of 30 to 150°C. Increase in storage modulus by the addition of carbon black was also reported by Gandhi and Salovery (1988). It is clear that storage modulus of natural rubber composites with various fillers followed the order, china clay < aluminium powder < acetylene black < GPF < precipitated silica < HAF. Similar trends are reflected in the loss modulus and tan δ values of the natural rubber composites containing various fillers and the tan δ plot is shown in Figure 2. Storage modulus (E′) is a measure of the elastic energy stored or recovered in a cycle of deformation. The loss modulus (E″) measures the energy dissipated or lost as heat. Loss tangent (tan δ) is a dimensionless parameter, which is a measure of the ratio of energy lost to energy stored in a cyclic deformation. Storage modulus, loss modulus and tan δ are increased in the same order as that of the reinforcing capacity of these fillers in natural

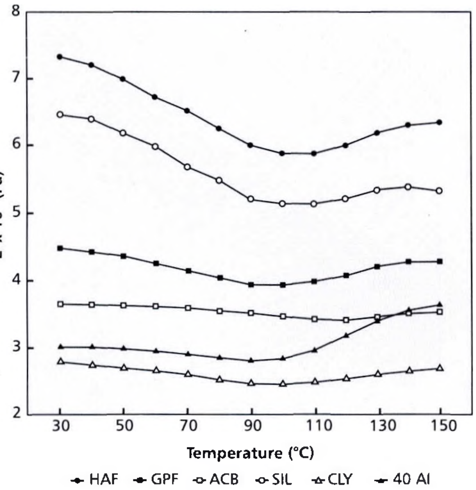

Fig. 1. Variation of E′ with temperature of natural rubber composites with various fillers at a frequency of 1.0 Hz

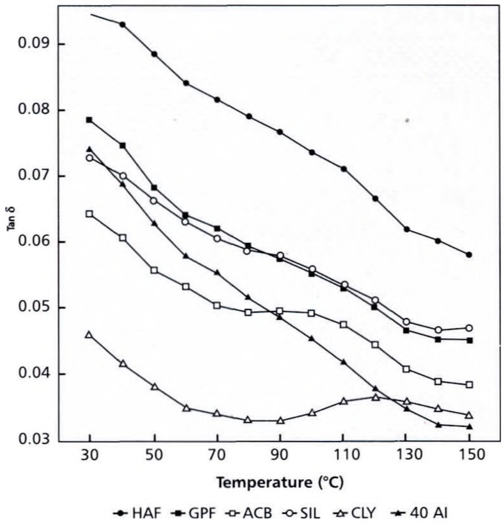

Fig. 2. Variation of tan δ with temperature of natural rubber with various fillers at a frequency of 10 Hz

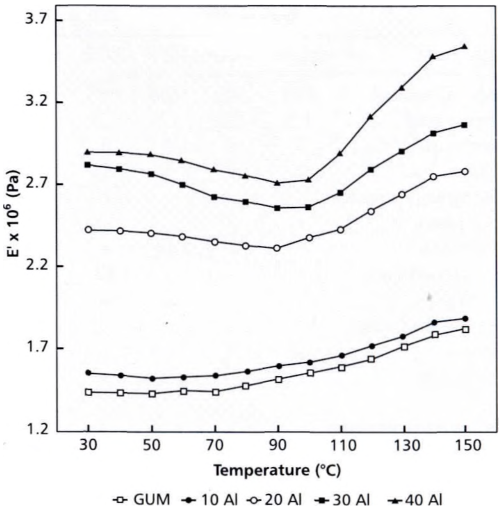

Fig. 3. Variation of E′ with temperature of natural rubber composites with aluminium powder at a frequency of 0.1 Hz

rubber. Rubber-filler interaction is a major factor, which determines the dynamic mechanical properties of a compound. The rubber-filler interaction increases as the reinforcing capacity increases. Silica filled compounds show modulus and tan δ values close to HAF filled ones. Wang (1998) made a comparison of carbon black and silica on dynamic mechanical properties of hydrocarbon rubbers. Acetylene black is usually used as a conductive black, but it is not much reinforcing. Storage modulus, loss modulus and tan δ for the aluminium powder filled composites were found to be in between those of acetylene black and clay filled ones.

It is generally observed that concentration of filler can influence the temperature dependence of the composite. Figure 3 shows the effect of temperature on storage modulus of aluminium powder filled natural rubber vulcanizates at 0.1 Hz. The gum vulcanizate has the lowest storage modulus. As the loading of aluminium powder increased storage modulus increased. Presence of aluminium powder in natural rubber composites resulted a higher loss modulus and as the loading of aluminium powder increased loss modulus also increased. In all cases, as the temperature increased loss modulus decreased gradually. The damping properties of the vulcanizates can be understood from the plot of tan δ versus temperature (Fig. 4). It is interesting to note

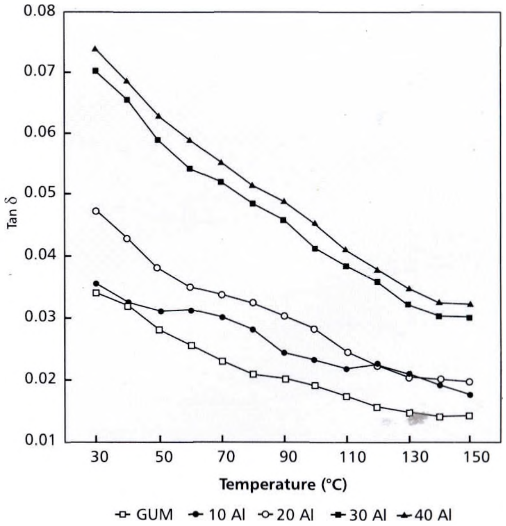

Fig. 4. Variation of Tan δ with temperature of natural rubber composites with aluminium powder at a frequency of 10 Hz

that the tan δ values are minimum with gum natural rubber vulcanizate and increased with aluminium powder loading. An increase in the tan δ values is observed with increased loading of aluminium powder (Fig. 5). Depending on the strength of natural rubber-aluminium powder interaction, physical adsorption and/or chemisorption of rubber molecules may take place on the surface of aluminium powder. This interaction leads to an effective immobilization of the rubber segments. Kaufman *et al.* (1971) demonstrated the presence of three distinct regions within the polymer characterized by different degrees of molecular mobility: a region of mobile rubber, an outer shell surrounding the filler which is less mobile, and a hard inner shell where the motion of rubber segments is extremely restricted. This resembles a rubber shell model of a definite thickness around the filler. This would result in a rubber shell on the filler surface in which the polymer viscosity is increased resulting in increased modulus. Generally, it can be assumed that the modulus of the inner shell is very high and decreases gradually with increasing distance from the filler surface (Fig. 6). In the case of natural rubber-aluminium powder composites, as the aluminium powder loading increases the mobile region decreases and the sites for natural rubber-aluminium powder interaction increase, resulting in a higher storage modulus and tan δ in vulcanizates containing higher loading of aluminium powder.

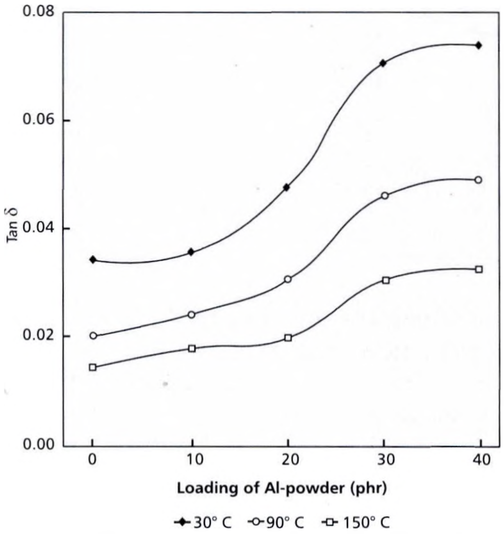

Fig. 5. Variation of tan δ with loading of aluminium powder in natural rubber at different temperature

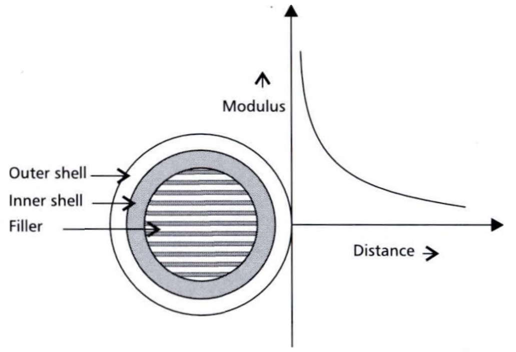

Fig. 6. Schematic representation of rubber shell model

Figure 7 shows the effect of various bonding agents on storage modulus of natural rubber containing 10 phr of aluminium

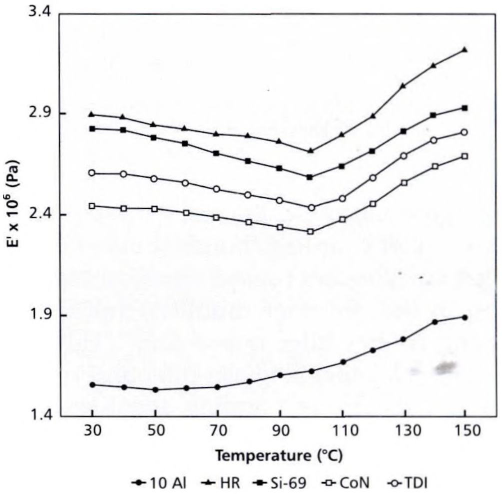

Fig. 7. Variation of E′ with temperature of natural rubber aluminium powder composites with bonding agents at a frequency of 0.1 Hz

powder. By the addition of bonding agents, the storage modulus is increased, in the order resorcinol-hexa system (HR) > bis [3-(triethoxy silyl) propyl] tetrasulphide (Si-69) > toluene diisocyanate (TDI) > cobalt naphthenate (CoN). The increase in storage modulus by the addition of bonding agent is due to the improved adhesion between aluminium powder and the rubber matrix. The damping behaviour of natural rubber vulcanizates containing aluminium powder with various bonding agents is shown in Figure 8. The addition of bonding agent increased the tan δ values. The presence of coupling/bonding agent in the filled vulcanizates caused significant reduction in the polymer mobility due to the strong rubber-filler interaction. This improved adhesion between filler and rubber in the presence of bonding agent restricts the easy slippage of the polymer molecules along the filler surface.

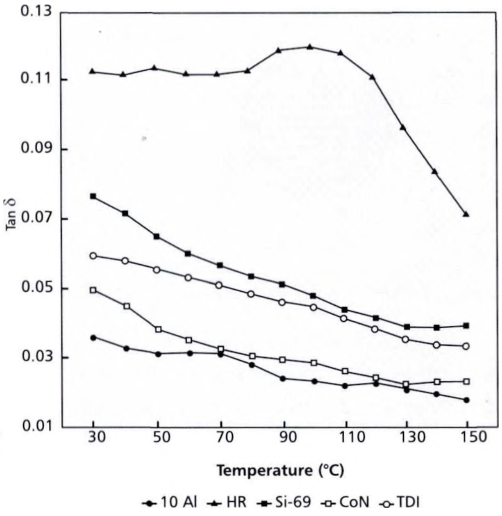

Fig. 8. Variation of tan δ with temperature of NR-aluminium powder composites with bonding agents at a frequency of 10 Hz

Tensile properties of the composites are shown in Table 2. At 40 phr loading, HAF and silica filled compounds have higher tensile strength compared to the aluminium powder filled one, whereas the clay filled composite has the lowest tensile strength. The loading of aluminium powder slightly increased the tensile strength value. The bonding agents increased the tensile strength of natural rubber-aluminium powder composites in the order, Si-69 >HR system >TDI >CoN. Modulus of the composites also followed the same trend. Elongation at break decreased with increased loading of aluminium powder due to the polymer dilution effect, and the bonding agent further decreased the maximum elongation.

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

Sample	Modulus, 300% (MPa)	Tensile strength (MPa)	Elongation at break (%)
GUM	2.8	20.1	800
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
HAF	18.0	27.9	375
GPF	17.0	25.5	356
ACB	15.6	24.0	378
CLY	6.3	20.0	490
SIL	8.3	26.0	409
HR	5.7	25.4	715
Si-69	4.5	26.2	642
CoN	4.3	22.3	750
TDI	4.3	23.1	733

In the case of resorcinol-hexa system, the resorcinol combines with the methylene donor to give a resin *'in situ'* during vulcanization, which binds the rubber and the metal powder. This is due to the increased polarity of the rubber, which arises from the powerful hydrogen bonding characteristics of the resorcinol resin. Silane coupling agents are quite effective in reactive polymer systems since they contain polar silanol groups capable of adhering to the surface of glass, metal, etc. and a hydrocarbon part which can interact with the rubber matrix. The addition of isocyanate to rubbers initiates a chemical reaction, which might account for the bonding in the matrix. It is suggested that the isocyanate radical itself united with the hydrated oxide layers on the surface of the metal. Cobalt naphthenate can also be used to promote metal adhesion, which creates increased polarity in the matrix. The relatively low improvement resulting from the addition of cobalt naphthenate is due to the catalytic oxidative power of this substance, which leads to polymer degradation.

In all the cases as the temperature increases, the tan δ values of composites decreased (Fig. 5). This is due to the increased storage modulus caused by the continued crosslinking of the rubber composites as the temperature increased. The increased interface adhesion in presence of bonding agents again increased the storage modulus. With increase in temperature the free volume increases and the polymer chain mobility is increased. When the temperature reaches a certain level, the free volume of the polymer increases more rapidly than the volume expansion of the molecules, facilitating segmental motion. The viscosity of the polymer decreases and the molecular adjustments take place easily, so that modulus is decreased and the energy dissipation among polymer molecules will increase with temperature. Also at high temperature Brownian motion increases and the viscosity decreases in the polymeric solid permitting easy segmental movement.

Effects of frequency on dynamic mechanical properties are shown in Figure 9. A decrease in storage modulus, loss modulus and tan δ are observed as the frequency is decreased. This phenomenon may be explained by the pseudorigidity effect of the frequency. In this effect, relaxation time (which may be considered the inverse of frequency) responsible for chain mobility reduces drastically with increasing frequency, which results in temporary "freezing" of the amorphous region.

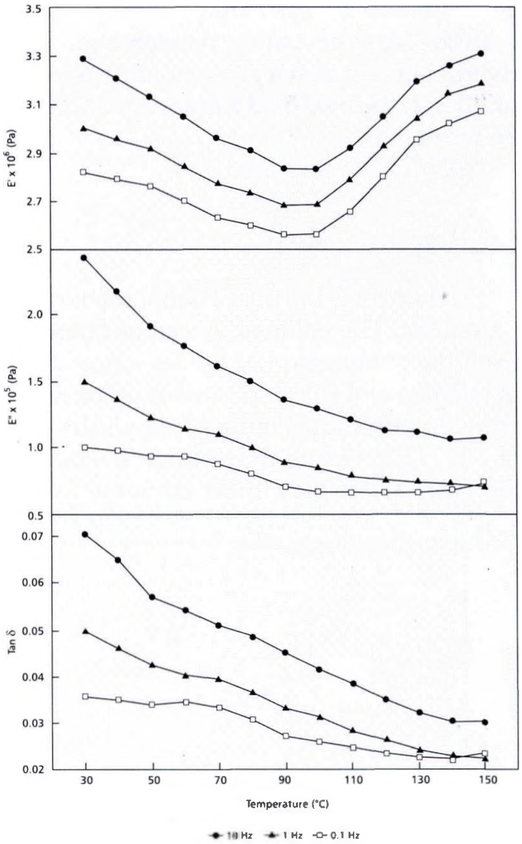

Fig. 9. Frequency dependence of E', E" and tan δ for natural rubber composites containing 30 phr alumiumum powder.

Relative moduli defined as E'_ϕ / E'_μ, where E'_0 is the elastic modulus of the filled vulcanizate and E'_μ is that of the gum vulcanizate, can be plotted as a function of the volume fraction of the filler. The experimental value can be compared with the modified Kerner equation (Ziegel and Romanov, 1973). Kerner considered that a filler particle is surrounded by a shell of matrix material, which merges into a medium that has the elastic properties of the composite. Particles adhere to the matrix but do not interact with one another. The complexity of the Kerner equation has been simplified by restricting its applicability to the rubbery state of the filled compounds and assuming that the dynamic modulus of the filler greatly exceeds that of the polymer matrix. Now, assuming Poisson's ratio for the rubber as 0.5, at a given volume fraction of filler, ϕ, the modified Kerner equation can be written as,

$$\frac{E'_\phi}{E'_\mu} = \frac{1+1.5A\phi}{1-A\phi} \qquad (1)$$

where, A is the filler-rubber interaction parameter. The value of 'A' can be obtained from the comparison of the loss moduli E″ of unfilled and filled specimens at the reference temperature. Figure 10 shows the plot of E''_μ/E''_ϕ versus the volume fraction of the filler at 35⁰C. A linear decrease in the E''_μ/E''_ϕ with volume fraction of filler was observed according to the following equation,

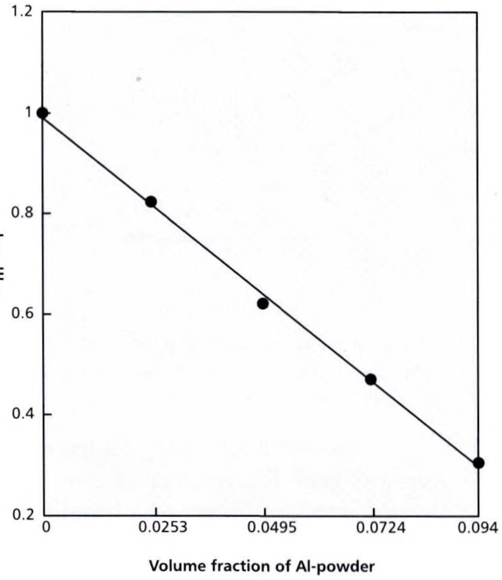

Fig. 10. Em″/Ef″ as a function of aluminium powder concentration at 35⁰C, 10 Hz

$$E''_\mu/E''_\phi = 1 - A\phi \qquad (2)$$

where, A is the same interaction parameter term used in the first equation. The value of A is obtained from the slope of the line and is found to be 7.4. Using this value it is possible to calculate E'_ϕ/E'_μ theoretically. The hydrodynamic interaction model is described by the equation,

$$E'_\phi = E'_\mu\,(1+\alpha\phi+\beta\phi^2) \qquad (3)$$

E'_ϕ, E'_μ and ϕ has the same meaning as in the previous equation. For Vander Walls type of interaction between rubber and the dispersed filler particles, α=2.5 and β=14.1.

Figure 11 shows the experimental and theoretical curves of the E'_ϕ / E'_μ values' of NR-aluminium powder composites as a function of volume fraction of aluminium powder. It is seen that the experimental values are close to the model described by equation (3). It is well known that α depends on dispersion of the filler particles in the matrix and β depends on molecular interaction.

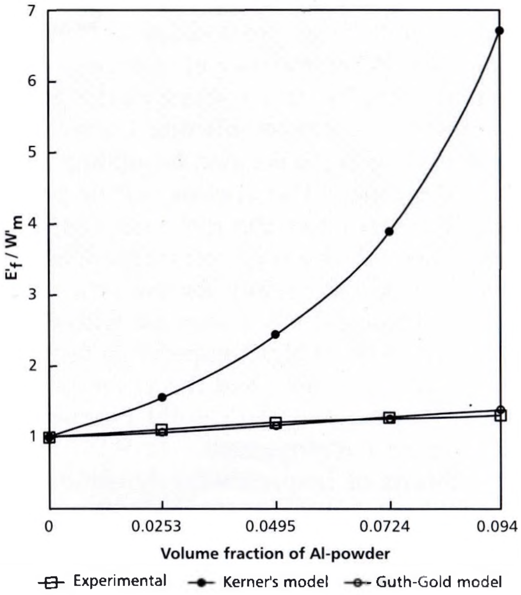

Fig. 11. Relative modulus E′f/E′m as a function of aluminium powder concentration at 35⁰C, 10 Hz

Hence, the value of β can be taken to study the interaction of filler with matrix. In the present case, α, the degree of dispersion is constant (2.5) for a particular loading of aluminium powder since we have given the same time for mixing. The variation in β

with various bonding agents in 10 phr loading of aluminium powder is shown in Table 3. It is seen that β values are remarkably increased by the use of bonding agents due to the increased interaction of aluminium powder with natural rubber in the presence of bonding systems. Property variation in filler-reinforced materials generated at the interface is a consequence of an increment in filler radius in such a way that greater interfacial thickness (ΔR) will stand for stronger interfacial action (Short, 1981).

Table 3. **Values of β and B of NR-aluminium powder composites with bonding agents**

Sample	β	B
10 Al (without bonding agent)	15.5	1.027
HR	1471.0	9.917
Si-69	1401.4	9.584
CoN	980.0	7.396
TDI	1165.0	8.395

ΔR is expressed as

$$\Delta R = R_0 \sqrt{(B-1)} \qquad (4)$$

where, R_0 is the filler radius and B can be determined using the equation,

$$\frac{(E'_\phi/E'_\mu) - 1}{(E'_\phi/E'_\mu) + 2} = B\phi \qquad (5)$$

Other parameters have the same meanings as in Equation 1. It is clear that 'ΔR' is proportional to the value of 'B'. A comparison of 'B' values will give an idea about the rubber-filler interaction. The calculated 'B' values for NR-aluminium powder (10 phr) composites with various bonding agents are given in Table 3. The 'B' values increased with the use of bonding agents which follow the order, HR-system >Si-69 > TDI >CoN. This again supported the increased interaction of aluminium powder with natural rubber by the use of bonding agents.

CONCLUSION

Dynamic mechanical properties of natural rubber vulcanizates containing aluminium powder have been investigated and compared with those of vulcanizates containing conventional fillers. Presence of aluminium powder increased the storage modulus, loss modulus and tan δ of natural rubber composites. These properties are increased with the loading of aluminium powder. Also, additions of other fillers like HAF, GPF, acetylene black, china clay and precipitated silica increased the storage modulus, loss modulus and tan δ values of natural rubber vulcanizates. The increase follows the same order as that of the reinforcing capacity of these fillers. The filler-rubber interface has a vital role in determining the viscoelastic properties of the composites. The effect of various bonding agent viz. hexamethylene tetramine- resorcinol system, bis [3- (triethoxysilyl) propyl] tetrasulphide, cobalt naphthenate and toluene diisocyanate have been investigated. Presence of bonding/coupling agents increases tan δ values, due to improved adhesion between rubber and aluminium powder. With increase in temperature, tan δ decreased gradually. Dynamic mechanical properties are also influenced by the frequency at which measurements are made.

REFERENCES

Alex, R. and Mathew, N.M. (1989). Effect of silane coupling agents on mechanical properties and polymer filler interaction in silica filled ENR. *Kautschuk Gummi Kunststoffe*, **42**: 674-676.

Bhattacharya, S.K. and Chaklader, A.C.D. (1982). Review on metal filled plastics, Part I. Electrical conductivity. *Polymer Plastic Technology Engineering*, **19 (1)**: 21-51.

Bhattacharya, S.K. and Chaklader, A.C.D. (1983). Review on metal filled plastics, Part II. Thermal properties. *Polymer Plastic Technology Engineering*, **20 (1)**: 35-59.

Blaine, R.L., Gill, P.S., Hassel, R.L. and Woo, L. (1998). A new dynamic mechanical analysis system for characterisation of physical properties. *Journal of*

Applied Polymer Science, (Applied Polymer Symposium), **34**: 157-171.

Buchen, S. (1959). *Rubber to Metal Bonding. Lockwood and Son Ltd, London.* pp. 166-249.

Delmonte, J. (1961). *Metal/Polymer Composites.* Van Nostrand Reinhold, New York. pp77-131.

Ferry, J.D. and Fitzgerald, E.R. (1982). Dynamic mechanical properties of carbon black loaded butyl rubber and polyisobutylene. *Rubber Chemistry and Technology*, **55**, 1403-1412.

Gandhi, K. and Salovery, R. (1988). Dynamic mechanical properties of polymers containing carbon black. *Polymer Engineering Science*, **28**: 877-887.

Kaufman, S., Schtiehter, W.P. and Davis, D.P. (1971). Nuclear magnetic resonance study of rubber-carbon black interaction. *Journal of Polymer Science*, Part A2, **9**: 892-839.

Mandal, U.K., Tripathy, D.K. and De, S.K. (1995). Effect of silica filler on dynamic mechanical properties of ionic elastomer based on carboxylated nitrile rubber. *Journal of Applied Polymer Science*, **55**: 1185-1191.

Manna, A.K., De, P.P., Tripathy, D.K. and De, S.K. (1998). Hysteresis and strain dependent dynamic mechanical properties of ENR filled with surface oxidised carbon black. *Journal of Applied Polymer Science*, **70**: 723-730.

Meyers, R.E. *U.S.Patent*, **4 617**: 353 (Oct . 14, 1986)

Mukhopadhyay, K., Tripathy, D.K. and De, S.K. (1993). Dynamic mechanical properties of silica filled ethylene vinyl acetate rubber. *Journal of Applied Polymer Science*, **48**: 1089-1103.

Nagata, N., Kobatake, T., Watanabe, H., Ueda, A. and Yoshioka, A. (1987). Effect of chemical modification of solution polymerised rubber on dynamic mechanical properties in carbon black filled vulcanizates. *Rubber Chemistry and Technology*, **60**: 837-855.

Nobile, M.R., Nicodemo, L. and Nicolais, L. (1988). The effect of the applied field on the electrical properties of metal polymer composites. *Polymer Composites*, **9 (2)**: 139-143.

Norman, R.H. (1970). *Conductive Rubbers and Plastics.* Elsevier Publishing, Amsterdam. pp30-125.

Parks, C.R. (1982). Brass powder in rubber vulcanizates. The effect on adhesion. *Rubber Chemistry and Technology*, **55**: 1170-1179.

Rajan, S., Shridhran, P. and Rao, A.S. (1988). Resorcinol formaldehyde resin for bonding of different reinforcements to rubber compounds. *Rubber Reporter*, **13**: 5-7.

Short, D. (1981). *Fibre Composite Hybrid Materials.* Mc Millan Publishing Co., New York. p 69.

Simon, H.P. *U. S. Patent* **5010**: 139 (April 23 , 1991)

Studebaker, M.L. and Beatty, J.R. (1974). Effects of compounding on dynamic mechanical properties of rubber. *Rubber Chemistry and Technology*, **47**: 803-824.

Ulmer, J.D., Chirico, V.E. and Scott, C.E. (1973). The effect of carbon black type on the dynamic properties of natural rubber. *Rubber Chemistry and Technology*, **46**: 897-926.

Varghese, S., Kuriakose, B., Thoms, S. and Koshy, A.T. (1992). Dynamic mechanical properties of short sisal fibre reinforced natural rubber composites. *Indian Journal of Natural Rubber Research*, **5**: 18-24.

Vinod, V.S., Varghese, S. and Kuriakose, B. (1998). Effect of adhesion on the equilibrium swelling of natural rubber aluminium powder composites. *Journal of Applied Polymer Science*, **70**: 2427-2438.

Vinod, V.S., Varghese, S. and Kuriakose, B. (2001). Effect of aluminium powder on filled natural rubber composites. *Rubber Chemistry and Technology*, **74**: 236-248.

Wang, M.J. (1998). Effect of polymer-filler and filler-filler interaction on dynamic properties of filled vulcanizates. *Rubber Chemistry and Technology*, **71**: 520-589.

Ziegel, K.D. and Romanov, A. (1973). Modulus reinforcement in elastomer composites: Inorganic fillers. *Journal of Applied Polymer Science*, **17**: 1119-1124.