CHAPTER VII

DYNAMIC MECHANICAL PROPERTIES OF NATURAL RUBBER-ALUMINIUM POWDER COMPOSITES

Results of this chapter have been communicated to Journal of Polymer Science
Rubber products generally undergo dynamic stress during service and hence their behaviour under dynamic loading is highly important. The informations obtained from dynamic mechanical measurements are of importance to manufactures and users of polymers in structural applications. Of these greater importance is the information provided by the damping, since end-use properties such as vibration dissipation, heat build up, impact resistance and noise abatement are all related to mechanical damping. The dynamic mechanical properties of elastomers are greatly dependent on temperature, frequency, type and concentration of filler and the extent of deformation. Several investigators have studied the dependence of dynamic mechanical properties of rubber vulcanizates on the type and concentration of fillers [1-4] under different test conditions [5]. Studebaker and Beatty [6] studied the effect of compounding on dynamic mechanical properties of rubber. The major compounding variables in this study are the nature of the rubber, nature and amount of ingredients in the curing system, nature and amount of fillers and presence of plasticizers. Viscoelastic studies of short sisal fibre reinforced natural rubber composites have been studied by Varghese et al. [7]. Dynamic mechanical properties of a variety of carbon black-loaded compound over a wide range of frequency and temperature have been reported [8-12]. Manna et al. [13] 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 [14] gives a good report on dynamic mechanical analysis for the characterization of physical properties.
Table VII.1. Formulations of mixes for dynamic mechanical analysis

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<th>Ingredients</th>
<th>GUM</th>
<th>HAF</th>
<th>GPF</th>
<th>ACB</th>
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<th>10Al</th>
<th>20Al</th>
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<th>HR</th>
<th>Si-69</th>
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TDQ - 2,2,4-trimethyl-1,2-dihydroquinoline
Si-69 - bis[3-(triethoxysilyl) propyl] tetrasulphide
Hexa – hexamethylene tetramine
CBS - N-cyclohexyl benzothiazyl sulphenamide
TDI – toluene diisocyanate
Effect of silica filler on the dynamic mechanical properties of ionic elastomer based on carboxylated nitrile rubber was reported [15] and found that the rubber-filler interaction in the cluster region causes striking changes in the variation of $E'$ and $\tan\delta$ with double strain amplitude.

In this chapter, the dynamic mechanical properties of aluminium powder filled natural rubber composites over a wide range of temperatures (30 to 150°C), and also at different frequencies are reported. The effects of loading of aluminium powder and various bonding agents such as hexamethylene tetramine-resorcinol system (HR), bis[3-(triethoxysilyl) propyl] tetrasulphide (Si-69), cobalt naphthenate (CoN) and toluene diisocynate (TDI) on viscoelastic properties have been investigated. For comparison, results of vulcanizates containing conventional fillers are also included. Formulations of the mixes are given in Table VII.1. The experimental viscoelastic data have been compared with theoretical predictions.

**VII.1. Effect of Fillers on Dynamic Mechanical Properties**

The dynamic storage modulus ($E'$), loss modulus ($E''$) and loss factor ($\tan\delta$) 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 frequencies. Figure VII.1 shows the effect of temperature on the storage modulus ($E'$) of the composites containing different fillers. The measurements were carried out at a frequency of 1.0 Hz over a wide temperature range from 30 to 150°C. Increase in storage modulus by the addition of carbon black is also reported by Gandhi et al. [8]. The storage modulus of natural rubber composites with various fillers increased in the order, china clay < aluminium powder < acetylene black < GPF < precipitated silica < HAF.
Figure VII.1. Variation $E'$ with temperature of natural rubber composites with various fillers at a frequency of 1.0 Hz

Figure VII.2. Dependence of $E''$ with temperature of various fillers incorporated natural rubber composites at a frequency of 1.0 Hz
**Figure VII.3. Variation of tanδ with temperature of natural rubber with various fillers at a frequency of 10 Hz**

Similar trends are reflected in the loss modulus ($E''$) and tanδ values of the natural rubber composites containing various fillers and these are shown in Figures VII.2 and Figure VII.3 respectively. 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 (tanδ) is a dimensionless parameter, which is a measure of the ratio of energy lost ($E''$) to energy stored ($E'$) in a cyclic deformation. The storage modulus, loss modulus and tan δ are increased in the same order as that the reinforcing capacity of these fillers in natural rubber vulcanizates. Rubber-filler interaction is a major factor, which influences the dynamic mechanical properties of a compound to greater extend. The rubber-filler interaction increases as the reinforcing capacity increases. Silica filled vulcanizates show modulus and tanδ values close to HAF filled ones. The storage
modulus, loss modulus and tanδ values of aluminium powder filled composites are in between those of acetylene black and clay.

**VII.2. Effect of Aluminium Powder Loading**

Figure VII.4 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 the storage modulus increased. There is a continuous increase in the storage modulus of the composite as temperature is increased above 100°C.

![Figure VII.4. Variation $E'$ with temperature of natural rubber composites with aluminium powder at a frequency of 0.1 Hz](image)

*Figure VII.4. Variation $E'$ with temperature of natural rubber composites with aluminium powder at a frequency of 0.1 Hz*
Figure VII.5. Dependence of $E''$ with temperature of aluminium powder filled natural rubber composites at a frequency of 10 Hz

Figure VII.6. Variation of $\tan \delta$ with temperature of natural rubber composites with aluminium powder at a frequency of 10 Hz
The variation of loss modulus ($E''$) of the same composites at 10 Hz is presented in Figure VII.5. The minimum loss modulus is observed with gum vulcanizate. Presence of aluminium powder in natural rubber composites resulted a higher loss modulus and as the loading of aluminium powder increased the loss modulus also increased. In all cases, as temperature increased, the loss modulus decreased gradually. The damping properties of the vulcanizates can be understood from the plot of tan$\delta$ versus temperature (Figure VII.6). It is interesting to note that the tan$\delta$ values are minimum with gum natural rubber vulcanizates and increased with aluminium powder loading. The variation of storage modulus and loss modulus as a function of aluminium powder loading in natural rubber is shown in Figure VII.7. As the loading of aluminium powder increased, both $E'$ and $E''$ are increased. A similar increase is also observed in the tan$\delta$ values with increased loading of aluminium powder (Figure VII.8). Depending on the strength of natural...
rubber-aluminium powder interaction, physical adsorption and/or chemisorption of rubber molecules on the surface of aluminium powder may take place. This interaction leads to an immobilization of the rubber segments. Kaufman et al. [16] demonstrated the presence of three distinct regions within the polymer characterised 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 definite thickness around the filler. This would result in a rubber shell on the filler surface in which the polymer viscosity is increased and the modulus would be increased. 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 (Figure VII.9).

Figure VII.8. Variation of tanδ with loading of aluminium powder in natural rubber at different temperatures at a frequency of 10 Hz.
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. This results in a higher storage modulus and tanδ in vulcanizates containing higher loading of aluminium powder.

**VIII.3. Effect of Bonding Agents**

Figures VIII.10 and VIII.11 show the effect of various bonding agents on storage modulus and loss modulus of natural rubber containing 10phr aluminium powder respectively. By the addition of bonding agents, the storage modulus and loss modulus are increased, in the order cobalt naphthenate (CoN) < toluene diisocyanate (TDI) < bis[3-(triethoxy silyl)propyl]tetrasulphide (Si-69) < resorcinol-hexa system (HR).
Figure VII.10. Variation of $E''$ with temperature of natural rubber-aluminium powder filled composites with various bonding agents at a frequency of 0.1 Hz.

Figure VII.11. Dependence of $E''$ with temperature of NR-aluminium powder filled composites with various bonding agents at a frequency of 1.0 Hz.
Figure VII.12. *Variation of tanδ with temperature of NR-aluminium powder composites with various bonding agents at a frequency of 10 Hz.*

The increase in storage modulus by the addition of bonding agent is due to the improved adhesion between aluminium powder and the matrix. The damping behaviour of natural rubber vulcanizates containing aluminium powder with various bonding agents is shown in Figure VII.12. The addition of bonding agent increased the tanδ 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 presence of bonding agent restricts the easy slippage of the polymer molecules along the filler surface. The mechanism of the adhesion between natural rubber and these bonding agents are described in section III.
VII.4. Temperature and Frequency on Dynamic Mechanical Properties

In all cases as the temperature increases, the tan$\delta$ values of composites decreased (Figure VII.8). This is due to the increased storage modulus 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 the segmental motion. The viscosity of the polymer decreases and the molecular adjustments take place easily, so that the modulus is decreased and the energy dissipation among polymer molecules will increase with temperature. Also at high temperature the brownian motion increases and the viscosity is low in the polymeric solid permitting an easy segmental movement.

Effects of frequency on dynamic mechanical properties are shown in Figure VII.13. A decrease in storage modulus ($E'$), loss modulus ($E''$) and tan$\delta$ are observed as the frequency is decreased. This phenomenon may be explained by the pseudo-rigidity effect of the frequency. In this effect, the relaxation time (which may be considered as the inverse of frequency) responsible for chain mobility reduces drastically with increasing frequency, which results in temporary "freezing" of the amorphous region.
Figure VII.13. Frequency dependence of $E'$, $E''$ and $\tan \delta$ for natural rubber composites containing 30 phr aluminium powder
Relative moduli; defined as $E'_r/E'_m$, where $E'_r$ is the elastic modulus of the filled vulcanizate and $E'_m$ is that of the gum vulcanizate, can be plotted as a function of volume fraction of the filler. The experimental value can be compared with the modified Kerner equation [17]. 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 are 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 the Poisson's ratio for the rubber as 0.5, at a given volume fraction of filler, $\phi$, the modified Kerner equation can be written as:

\[
\frac{E'_r}{E'_m} = \frac{1 + 1.5A\phi}{1 - A\phi} \quad \ldots \ldots \ (VII.1)
\]

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 VII.14. shows the plot of $E''_m/E''_r$ versus the volume fraction of the filler at 35°C. A linear decrease in $E''_m/E''_r$ with volume fraction was observed according to the following equation.

\[
E''_m/E''_r = 1 - A\phi \quad \ldots \ldots \ (VII.2)
\]

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 we can calculate $E'_r/E'_m$ theoretically.
**Figure VII.14.** \( E'' / E' \) as a function of aluminium powder concentration at 35°C, 10 Hz

**Figure VII.15.** Relative modulus \( E'' / E' \) as a function of aluminium powder concentration at 35°C, 10 Hz
The hydrodynamic interaction model for rubber reinforcement was developed by Guth and Gold [18,19]. The model is described by the equation

\[ E' r = E'_m(1 + \alpha \phi + \beta \phi^2) \] ...... (VII.3)

\( E'_r, E'_m \) and \( \phi \) has the same meaning as the above equation. For Vander Walls types of interaction between rubber and the dispersed filler particles, \( \alpha = 2.5 \) and \( \beta = 14.1 \).

Figure VII.15 shows the experimental and theoretical curves of the storage modulus 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 Guth and Gold model. It is well known that the term '\( \alpha \)' depends on dispersion of the filler particles in the matrix and '\( \beta \)' depends on molecular interaction [19]. Hence, the value of '\( \beta \)' can be used to study the interaction of filler with matrix. In the present case, \( \alpha \), the degree of dispersion is taken as constant (2.5) for a particular loading of aluminium powder since we are given the same procedure and time for mixing. The variation in \( \beta \) with various bonding agents in 10 phr loading of aluminium powder is shown in Table VII.2. It is seen that the \( \beta \) values are remarkably increased by the use of bonding agents due to the increased interaction of aluminium powder with natural rubber in presence of bonding systems.

Zhou et al. [20] introduced a new concept as that of equivalent interfacial thickness, R, as derived from the Halpin-Tsai equation [21]. This concept substantiates the idea that the interface can be understood as a uniform layer, assuming that 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 \( \Delta R \) will stand for stronger interfacial action. \( \Delta R \) is expressed as
\[ \Delta R = R_0 \sqrt{B-1} \]  \hspace{1cm} \text{(VII.4)}

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

\[ \frac{(E'_f/E'_m) - 1}{(E'_f/E'_m) + 2} = B\phi \]  \hspace{1cm} \text{(VII.5)}

where the parameters has the same meanings as above equations. It is clear that \( \Delta R \) is proportion 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 (10phr) composites with various bonding agents are given in Table VII.2. 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.

**Table VII.2. Values of \( \beta \) and \( B \) of NR-aluminium powder composites with bonding agents**

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<tr>
<th>Sample</th>
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<th>( B )</th>
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<tr>
<td>HR</td>
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**VII.6. Conclusions**

Dynamic mechanical properties of natural rubber vulcanizates containing aluminium powder have been investigated and are compared with those of vulcanizates containing conventional fillers. Presence of
aluminium powder increased the storage modulus, loss modulus and tanδ value of natural rubber composites. These properties are also increased with the loading of aluminium powder. Additions of other fillers like HAF, GPF, acetylene black, china clay and precipitated silica to natural rubber increased the storage modulus, loss modulus and tanδ values of 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 (HR), bis [3-(triethoxysilyl) propyl] tetrasulphide (Si-69), cobalt naphthenate (CoN), toluene diisocyanate (TDI) have been investigated. Presence of bonding/coupling agents increases the tanδ values, due to the improved adhesion between rubber and aluminium powder. With increase in temperature, tanδ decreased gradually. Dynamic mechanical properties are also influenced by the frequency of measurements.
References