

## CHAPTER II

### LITERATURE SURVEY

Natural rubber in their original state are not suitable for engineering applications since they are hard and brittle at low temperature, and soft at high temperature. When the raw rubber is mixed with filler, sulfur, and other ingredients and vulcanized, it becomes strong and hard. Therefore it can be used for many industrial application in wider temperature ranges. Besides tire production, NR in vulcanized form is used as rubber goods such as mechanical goods, hoses, sole, linings to avoid corrosion in chemical processes, gaskets, etc.

Takino *et al.* (1997) studied on the viscoelastic properties of elastomers and tire wet skid resistance. They recommended that the British Portable Skid Tester (BPST) wet skid resistance of eighteen sulfur curable polymers which might be used for automobile tires. These results have been analyzed in relation to the viscoelastic properties of polymer systems. Analysis of wet skid resistance in term of peak value of  $\tan \delta$  over a prescribed temperature range and abrasion loss was derived from the theory of the rubber friction-was concluded to give a better relationship for a wide range of polymers.

Demichan *et al.* (1994) studied on the selection of inorganic fillers for non-tire rubber compounding. Mathematical models were developed for various inorganic fillers used instead of or together with carbon black in the rubber compounding. The suitable filler for a rubber product can be predicted based on its desired property by using the mathematical and cost models. The selection of fillers for compounds by mathematical and cost models was very important. The use of models saved time and money in the production. Other parameter of the vulcanization process such as cure time,

temperature, compounding ingredients ratio, etc. can also be predicted by such a mathematical approach so that this approach can be applied to various rubber compounding recipes in the non-tire rubber industry.

## **2.1 Carbon Black Filled Vulcanised Rubber**

Pal *et al.* (1982) studied on the effects of carbon black (HAF black, N330)-vulcanization system (conventional and efficient vulcanization (EV)) interactions on NR network structure and properties. They found that at all loadings, modulus, flex cracking resistance, dynamic set and compression set of the conventional system were higher than those of the EV one. But irrespective of filler concentration, heat build up of the EV system was higher than that of the conventional system. At lower loading of filler, a marked difference in values of resilience, hardness, elongation at break, tear and tensile strength was observed between the two vulcanisate systems whereas this difference was minimized at higher loading. At lower loading of filler, abrasion loss of EV system was more than that of the conventional one. Addition of HAF black at 5 phr loading increased total crosslink density and the proportion of polysulfidic crosslinks in the conventional system and higher loadings of filler did not have any further effect of network structure. But at higher loadings, some properties tended to become independent of the vulcanization system. This implied that higher loadings of filler, filler-rubber interaction over shadows the network structure and the properties became independent of vulcanization system and were governed by the filler concentration.

Dannenberg (1986) studied on carbon black tread wear ratings from laboratory test. It was found that a few of the treadwear predictor correlation had the require accuracy to provide a satisfactory alternative to read testing of tires for the wear performance of carbon black, depending on

requirements and circumstances. Correlation based on laboratory rubber testing of rubber mixed and tread compounds are preferred over those based solely on carbon black colloidal and morphological measurements. In Cotton and Dannenberg's correlation of treadwear index with Angle Abrasion measurements of 30 phr compound and heated rebound rubber, and Westinning and Wolff's correlation with rebound resilience, and the Monsanto Rheometer determination of a polymer/filler interaction factor ( $\alpha_f$ ) are satisfactory in any instances for the prediction of the treadwear index behavior of carbon black.

Gonzalez et al. (1996) studied on a new carbon black-rubber coupling agent to improve wet grip and rolling resistance of tires. They reported that the compound *p*-aminobenzenesulfonyl azide (Amine-BSA) was developed as a new type of carbon black to rubber coupling agent. Its incorporation into a rubber compound increased resilience and moduli at low strain, and reduced abrasion loss, while hardness, tensile strength and elongation at break remain essentially unaltered. The behavior of this coupling is confirmed by the dynamic mechanical response of the vulcanisates. The glass transition temperature ( $T_g$ ) of rubber is shifted to higher temperatures. The Amine-BSA compounds may be used in the treads to reduce rolling resistance and improve wet skid resistance. These attributes were estimated from dynamic property measurements.

Ghosh *et al.* (1997) studied on the effect of the modified carbon black on the properties of NR vulcanisate. They found that the rubber-grade carbon black filler HAF (N330) was modified with a plant product (PP; long aliphatic chain substituted phenols) in the presence or absence of hexamine (Hexa) or dicumyl peroxied (DCP) to put a flexible moiety in between the carbon black and the elastomer chain in order to improved some of its processing and reinforcement characteristics. This flexibility offered by the PP decreased slightly the filler-polymer interaction, which decreased the

stiffness of the filler-rubber composite, resulting to improved flex cracking resistance. The modification process was simple and involved cheap materials. It was investigated to show better processing behavior, without any processing aid such as easy incorporation and uniform dispersion in the rubber phase without abnormal heat generation, and also improved vulcanisate properties such as tensile strength, flex checking resistance, and lower abrasion loss, without affecting other properties to significant extent.

Sau et al. (1999) studied the electrical and mechanical properties of conducting carbon black filled composites based on rubber and rubber blends. The electrical and mechanical properties of new conductive rubber composites based on ethylene - propylene - diene rubber, acrylonitrile butadiene rubber (NBR), and their 50/50 (weight ratio) blend filled with conductive black were investigated. The threshold concentrations for achieving high conductivity are explained on basis of the viscosity of the rubber. The electrical conductivity increases with the increase in temperature whereas the activation energy of conduction decreases with an increase in filler loading and NBR concentration in the composites. The electrical hysteresis and electrical set are observed during the heating-cooling cycle, which is mainly due to some of irreversible change occurring in the conductive networks during heating. The mechanism of conduction in these system are discussed in the light of different theories.

## **2.2 Silica Filled Vulcanised Rubber**

Koshy *et al.* (1994) studied the viscoelastic properties such as storage modulus ( $E'$ ), loss modulus ( $E''$ ) and damping ( $\tan\delta$ ) of unfilled and silica-filled blends of NR and ethylene-vinyl acetate copolymer (EVA) which were crosslinked by sulfur and peroxide. They found that the  $\tan \delta$  values of unfilled blends showed two transitions corresponding to EVA and NR

phases. This indicated that the blends are immiscible. It was seen that the addition of silica decreased the  $\tan\delta$  values of samples substantially except that of NR, where a slight increase in  $\tan\delta$  values can be observed at high temperatures. The sharp decrease of  $\tan\delta$  in filled EVA and EVA-rich blends was associated with the decrease in crystallinity of the EVA phase due to the presence of fillers. Increase of the storage and loss moduli of all samples is due to the addition of silica filler.

Bice *et al.* (1997) studied on the effect of precipitated silicas in truck tire treads. They found that the effect of precipitated silicas on reducing rolling resistance is transferable from passenger tire to truck tire tread application. The relative influence of various silicas and their levels upon the balance of compound cure, physical and dynamic properties in a NR-based truck tire formulation was presented. The degree to which the perturbation of the cure system by silica surface area and loading effect was illustrated. The relative influence of silane coupling agent and accelerator level was determined. It was found that increasing the accelerator level, as silica loading is increased and as silica surface area is increased, diminishes the effect of the silane coupling agent upon compound physical properties over the range of study.

Ono *et al.* (1999) had studied on the structure development in silica-filled polyisoprene composites. The rubber phase in the composites was composed of so-called bound and free rubber. Moreover, the bound rubber was composed of multiple phases having different mobilities and the amount of bound rubber and its mobility depended on the sort of silica used. The main mechanism of formation of bound rubber in this composites is considered to be a physical adsorption of rubber molecules on the silica surface. The amount of bound rubber is affected by the state of aggregation of silica particles which is function of particle size and amount of silanol groups on the particles. When the composites were annealed, the amount of

bound rubber increased with increasing annealing temperature due to the development of chemical crosslinks in bound and free rubber phase.

Thammathadanukul et al. (1996) studied on the comparison of silicas modified by the *in situ* polymerization of organic comonomers with those modified by a bifunctional organosilane coupling agent ( $\gamma$ -mercaptopropyl-triethoxy-silane). They found that both techniques increased the compound cure rate, thereby significantly reducing  $T_{90}$  cure time, while also improving tensile properties, tear strength, abrasion resistance, and compression set of the cured compound. The silane-modified silica gave a higher flex-cracking resistance than that of the silicas modified by the *in situ* polymerization of organic monomers whereas the latter silica significantly increased rebound resilience and offered greater overall improvements in rubber compound performance. The rubber compound physical properties obtained using the modified higher surface area.

Tanahashi et al. (1998) studied reinforcement of acrylonitrile-butadiene rubber by silica generated *in situ*. The amount of *in situ* silica introduced in the NBR vulcanizates was limited due to the high polarity of NBR. The presence of  $\gamma$ -mercaptopropyltrimethoxysilane ( $\gamma$ -MPS) in the NBR vulcanizate increased the conversion of tetraethoxysilane (TEOS) in the sol-gel reaction and resulted in the higher amount of *in situ* silica, compared to the system without  $\gamma$ -MPS. The obtained silica was very fine and dispersed very homogeneously. *In situ* sol-gel reaction of TEOS in the NBR vulcanizates mixed with the conventional silica (VN-3) was also carried out. The reinforcement efficiency in this system increased with the increase of the amount of mechanically mixed conventional silica. Interestingly the hysteresis loss decreased by the *in situ* filling of silica.

### 2.3 Mixed Fillers in Vulcanised Rubber

Furtado *et al.* (1995) studied on the effect of filler characteristics in the curing characteristics and physico-mechanical properties of vulcanized composition of styrene-butadiene rubber (SBR) by replacement of silica with mica and a total filler content was kept constant. They have reported that the crosslink density and mechanical properties for the composition in which the proportion of silica was higher than that of mica because of a higher surface areas of silica compared to mica, leading to a better interaction between silica and polymer. The tensile properties were supported by scanning electron microscopy (SEM) observations from the tensile fracture surfaces.

Sombatsompop (1998) studied on the dynamic mechanical properties such as storage modulus ( $E'$ ), loss tangent ( $\tan \delta$ ), etc. of ground flexible polyester polyurethane (PU) foam particles and carbon black-filled rubber vulcanisates. It was found that NR compounds can be reinforced by 60 phr carbon black and 20 phr PU particles of average size 200  $\mu\text{m}$  in order to give similar reinforcing level in the dynamic mechanical properties. The dynamic modulus of the vulcanisates increased and became more pronounced in the transition and the rubbery regions. In the rubbery region, few dynamic losses were seen as a result of the polymer molecular mobility. The dynamical properties were not significantly affected by the type of filler used in this work but were strongly influenced by the use of difference curing systems.

Okel and Waddell (1994) studied on the effectiveness of predicting rubber performance based on measured silica physical properties in silica and carbon black-filled compounds and they provided a detailed understanding of how precipitated silica can be used to enhance the performance of carbon-filled rubber compounds. This study confirmed that

the single best predictor was the primary silica physical property, nitrogen single point Brunauer, Emmelt, Teller (BET) surface area which predicted rubber compound performance. Silica structure, as measured by dibutyl phthalate (DBP) absorption, and nitrogen or mercury total pore volume, can play a secondary role. Increasing silica surface area beneficially increased compound scorch protection, tensile and tear strength, flex fatigue life and aged elongation. Increasing silica surface area adversely increased compound viscosity, heat build up and cure time, and decreased Pico abrasion index. The confidence limits of the predictions was dependent upon the concentration of precipitated silica used in the carbon black-filled rubber compound.