

## ABSTRACT

Hysteresis loss and hysteresis loss ratio of natural rubber (*NR*) and styrene-butadiene rubber (*SBR*) vulcanizates having variations of loading of carbon black, precipitated silica, clay, resin and curatives under uniaxial, pure shear and constrained extension modes ( $\lambda_x$ : 1.5 to 2.2 and  $\lambda_y$ : 1.2 to 4.0), and compression have been investigated over a wide range of strain rates ( $3.78 \times 10^{-5}$  to  $210 \times 10^{-3} \text{ sec}^{-1}$ ), strain levels (10 to 300 %), temperatures (298 to 423 K), holding times (0 to 1200 seconds) at constant stress and strain, and cure times ( $t_{90}$  to  $t_{90} + 20$  minutes for tensile specimens and  $t_{90} + 10$  to  $t_{90} + 60$  minutes for heat buildup specimens), as well as under swollen conditions in a few cases. Hysteresis loss under uniaxial deformation increases with an increase in strain rate, filler loading, resin loading (at high rates), crosslink density, and strain level. Hysteresis loss decreases with an increase in temperature and resin loading at high testing temperature. All the data of hysteresis loss of filled *NR* and *SBR* have been found to be superimposable on single master curves with the help of *WLF* shift factor. The master curves can be divided into three regions. The slope of the intermediate region,  $\Delta \log (\text{Hysteresis loss}) / \Delta \log (\text{Reduced rate})$  has been found to be 0.1 for almost all the vulcanizates. Similar master plots have been obtained when the hysteresis loss has been measured at higher cycles and higher extensions and also using the data of hysteresis loss ratio. Carbon black contributes significantly to the hysteresis loss even when the energy dissipation is minimized by swelling. A model for hysteresis loss of rubber vulcanizates under uniaxial loading at medium strain (less than 100%) under dynamic condition has been proposed by using *Boltzmann superposition principle*, *statistical theory of rubber elasticity* and *phenomenological theory*. The theory incorporates both experimental and analytical parameters to quantify hysteresis loss. The model with no adjustable parameter has been successfully tested at various strain rates, strain levels and temperatures using the experimental results for *NR* and *SBR* vulcanizates filled with carbon black, silica, clay, resin and curatives. The material constant,  $M_j^{**}$ , is a function of strain rates, temperatures, number of cycles and is defined as the products of *Young's* modulus and square root of strain rate. The other material constant,  $K^*$ , is independent of temperature, strain rates, strain levels, number of cycles and material composition. The theory of medium strain hysteresis loss based on power law derived from *Boltzmann superposition principle*, *statistical theory of rubber elasticity* and *phenomenological theory*, is then extended to high strain. The numerical predictions from the model equation are then compared with the experimental results and the results from *Ferry's* equation. The unique attributes of this model equation is that the material constants are exactly the same as the materials constants obtained from the model equation at medium strain. Hysteresis loss was also measured at constant strain and constant stress under tensile deformation through variable holding time applied at the tension side of the experiment. Higher hysteresis

loss and hysteresis loss ratio are observed at constant stress than at constant strain. The experimental results for a given vulcanizate, at a given strain rate, number of cycle and strain level are summarized by five parameters: the slopes of the two straight lines, their intercepts upon the hysteresis axis at  $\log_{10} t = 0$  and the time corresponding to the intersection point of the two straight lines,  $t_{crit}$ . Evidence has been produced for the existence of a distinct relaxation process, which occurs within first 120 seconds holding time at room temperature. This process becomes less important, as the strain or the temperature is increased. However, at high temperature another distinct relaxation process has been observed. The values of hysteresis loss under pure shear and constrained extension modes are higher than that under uniaxial loading. Hysteresis loss, hysteresis loss ratio and input energy under pure shear and constrained extension modes increase with an increase in filler loading and extension ratio, and are higher when reinforcing filler is used. A universal expression relating input energy,  $W$ , to the hysteresis loss ( $H_y$ ) as well as hysteresis loss ratio ( $H_y$ ), under uniaxial, pure shear and constrained extensions over the range of extension ratios (below failure point) and number of cycles have been developed. A relationship between heat generation per unit time per unit volume ( $q$ ) of filled rubber vulcanizates and hysteresis loss ( $H_y$ ), specific heat ( $C_p$ ), temperature difference between operating temperature ( $T'$ ) and glass transition temperature ( $T_g$ ), frequency ( $\nu$ ), stroke amplitude ( $SA$ ), thermal conductivity of rubber ( $\lambda$ ), structure of carbon black ( $S_i$ ), surface area of carbon black ( $S_a$ ), *Young's* modulus ( $M_o$ ), weight of carbon black in rubber ( $F'$ ), temperature difference between wall and environment ( $\Delta T$ ) and stress i.e., load per unit area ( $S$ ) has been developed by using *dimensional analysis of Buckingham  $\pi$  theorem* as well as *Rayleigh's method*. The model equation explains the contradictory results of a decrease of heat generation with an increase of hysteresis loss by an increase of modulus, and the increase of heat generation at constant modulus and loading of filler by an increase of surface area of the filler. The data of heat generation calculated theoretically by model equation for unknown *NR* and *SBR* vulcanizates are also in good quantitative agreement (within  $\pm 15\%$ ) with the experimental data. The model equation is also verified by varying the stress and stroke amplitude in the heat generation experiment and shows good accord with the predictions made in model equation.

### Key Words

*Hysteresis loss; Hysteresis loss ratio; Natural rubber; Styrene-butadiene rubber; Carbon black; Input energy; Heat generation; Uniaxial extension; Pure shear deformation; Constrained extension; Compression; Boltzmann superposition principle; Statistical theory of rubber elasticity; Phenomenological theory; Dimensional analysis; Buckingham  $\pi$  theorem; Rayleigh's method*