

ABSTRACT

Ogebule, Oluwaseyi. Ph.D., Purdue University, December 2013. The Effect of Composition on the Linear and Nonlinear Mechanical Properties of Particulate Filled Elastomers. Major Professor: James M. Caruthers.

Engineering elastomers are materials capable of undergoing large deformation upon load application and recovering upon load removal. From car tires to building vibration isolator systems, elastomers are the most versatile of engineering materials. The inclusion of particulate fillers into elastomers enhances their mechanical properties (modulus, tensile strength, toughness, tear resistance, etc) thereby extending their applicability to more demanding functions. The automotive, healthcare, construction, adhesives and consumer products are some of the many industries that produce finished goods containing elastomeric parts.

Despite the various concepts on reinforcement in filled elastomers, a complete understanding of their linear viscoelastic properties and their nonlinear mechanical properties, including stress softening (Mullins), strain dependent dynamic modulus (Payne) and others remains elusive. Furthermore, studies on filled elastomers have failed to produce a unifying perspective on the relationship between the microstructural composition and the observed macroscopic response to deformation. To further the current understanding on the underlying physics of elastomer reinforcement, a comprehensive study on the effect of composition was undertaken.

A major challenge in the application of the Time-Temperature Superposition (TTS) principle for filled elastomers rests on the difficulty of conducting experiments in their linear regime, which could be at strains even lower than 10^{-3} . In this work, the linear viscoelastic behavior of filled elastomers was studied via the successful application of TTS at extremely small strains using the double sandwich shear geometry. Well-defined master curves were constructed for a series of carbon black filled SBR and Polybutadiene elastomers. In addition, an investigation of the effects of filler volume fraction and structure on the full linear viscoelastic response was carried out. A critical analysis of the superposed data showed correlation of linear viscoelastic properties to measurable filler parameters specifically the effective volume fraction, ϕ_{eff} , in which allowed for the first time collapsing

on a single master curve the viscoelastic storage and loss moduli for all filled elastomers studied.

Nonlinear mechanical behavior was investigated on fumed silica filled Poly(dimethylsiloxane) rubber. For the first time, necking was observed for a lightly cross-linked poly(dimethylsiloxane) elastomer filled with 30 phr (parts per hundred rubber) or more of high surface area ($\geq 300 \text{ m}^2/\text{g}$) fumed silica. A series of linear and nonlinear mechanical properties of the necked material were studied including (i) linear and nonlinear dynamic shear analysis including the Payne effect, (ii) uniaxial tension experiments including the Mullins effect, (iii) tensile strength, and (iv) tear resistance via the 'trouser' test. The ultimate properties of the necked material were superior to its un-necked counterpart and both the Mullins and Payne effects were present in the necked material. The dynamic modulus exhibited anisotropy with respect to the direction of the necking deformation, where the anisotropy was not found in fumed silica filled PDMS elastomers that did not neck although the materials were pre-stretched to similar strains. Based upon these experimental observations, it was been postulated that necking occurs due to the breakage of delicate highly branched aggregates at the points of local stress concentrations. The preferential breakage of the most mechanically distressed aggregates will result in a more regular filler-matrix network, giving rise to higher ultimate properties of the necked material. This finding challenges the aggregate breakage postulate as a primary mechanism for the Mullins effect.