



*Understanding the Viscoelastic Behavior of silica Filled Rubber*  
J.G.de Castro

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# Summary

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Over 10 million metric tons of carbon black and silica nanoparticles are produced each year, mainly to modify polymer mechanical performance for numerous industrial and household applications. We are part of a large consortium that, in collaboration with the tire and automotive industry, tries to develop a completely new understanding of composite rubber materials. Therefore, this thesis presents the PhD research on understanding the viscoelastic behavior of silica filled Nitrile Butadiene Rubber NBR using three different sizes/surface areas in three different regions of deformations: small, medium and very large deformations, i.e. until the break point.

In the first chapter of this thesis we show how big the rubber market is and why it is important to understand the mechanical behavior of filled rubbers. With a big effort of the society to contribute for the reduction of CO<sub>2</sub> and methane, there are many research centers all around the world motivated to find technologies and approaches to bring down the emissions of these gases by at least 60 percent by mid-century. Not only the reduction of those gases is needed but also the developing of low carbon products is essential to tackle climate change.

Chapter 2 describes the characteristics of the compounds we used in this project assessed by means of calorimetry and Small Angle X-ray Scattering SAXS performed in Grenoble, France. The conclusions of this chapter were fundamental for other conclusions and discussions in the subsequent chapters.

At very small deformations, in the linear regime, we can measure the reinforcement of filled rubbers. In Chapter 3 we study how the rescaling of the reinforcement changes with particle size. Mostly nanoscale silica or carbon black particles are used in composite however, the rationale for such small fillers remains unclear because classical elasticity is inherently scale-free. We showed that for a given volume fraction, smaller fillers (or agglomerates) with larger surface area consistently result in the larger reinforcement. Because of the universality of this effect, we proposed a rescaling of the reinforcement that accounts for the microstructure of different composite materials.

Chapter 4 investigates the strain softening observed in our NBR compounds at intermediate deformations during a strain sweep in oscillatory rheology: the modulus decreases with increasing deformation. On the other hand, if the non-linear elastic response is analyzed within a single oscillation cycle (described by Lissajous curves), rubber compounds are reported to exhibit strain hardening. We conclude that the apparent strain hardening is due to the use of a tangent modulus in the LAOS analysis, and the overall rheology remains strain softening. To show that this conclusion is robust, we demonstrate a rescaling of the modulus that collapses the data from all the oscillatory measurements onto a single master curve that clearly exhibits the correct strain softening behavior.

In Chapter 5 we find that small amounts of silica increase the fracture stress and strain, but too much filler makes the material brittle, and consequently fracture at small deformations. Furthermore, we observe that both the fracture energy and the elastic modulus increase monotonically with the filler volume fraction and the tradeoff between the two turns out to be primordial to create the non-monotonic fracture behavior. To rationalize these findings, we first examine the standard Griffith theory for fracture, which uses an energy balance between the elastic energy gained upon propagation of a fracture and the surface energy lost by creating additional interfacial area. From this, we conclude that the energy barrier for the spontaneous nucleation of an initial fracture is so large that thermally-driven fluctuations are much too weak to cause spontaneous breaking at a given stress. We then extend the Griffith theory using an Eyring-type model that incorporates a stress-induced crossing of the energy barrier for crack formation. This allows us to relate the stress at break of a filled rubber to the volume fraction of filler material based only on the fracture energy and modulus of the material, both of which can be separately measured.

In Chapter 6 conclusions and directions for future research are given. We explore specifically what could be done in order to better understand the interaction between filler and polymer matrix. For that we propose the use of additional chemical components (coupling agents) that may form a covalent bond between filler and matrix. Thus, we expect different mechanical behavior in all deformations and we could investigate the polymer filler interaction in more detail by microscopy and spectroscopy under stress.