Nonlinear Viscoelastic Behaviour of Rubber Composites

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Polymer Nanocomposites
A polymer nanocomposite consists of a polymer filled with particles that have at least one dimension less than 100 nm.

Spheres (0D) 
TiO$_2$, SiO$_2$

Rods (1D)
CNT, halloysite

Layers (2D)
Clay
Fillers used in rubber reinforcement

Silica, Carbon black

- Large surface area
- Smooth nonporous surface

Layered Silicates (Clays)

- Idealized structure for montmorillonite

Schematic view of aggregate formation between adjacent fumed silica particles through hydrogen bonding

(Jana, S. C.; Jain, S. Polymer 2001, 42, 6897)

Hoffman et al. 1933, 86, 340.

Dynamic Viscoelastic Properties

- The introduction of fillers in rubbers significantly changes the dynamic properties.

  **Significance?? Tires**

- Dynamic properties of filled elastomers are directly related to sliding friction and rolling resistance of tires.
- Fuel efficiency, Safety, Durability
- Sliding Friction, Wet traction (Safety)
- Rolling Resistance (Fuel efficiency)

  - Increasing “tan δ at 0°C”- wet traction
  - Decreasing tan δ at 60° C- rolling resistance
  - Optimization of tan δ at one temp. negatively affects on the other temp.
Payne Effect

The effect of amplitude dependence on the dynamic viscoelastic properties of filled rubbers is referred to as the Payne Effect. (Payne, A. R. J. Polym. Sci. 1962, 6, 57). There is a decrease in dynamic storage modulus of filled elastomers with increasing deformation amplitude.

Kraus (1984) proposed an empirical model based on the agglomeration/deagglomeration kinetics of filler aggregates, assuming a van der waal’s type interaction between the particles.

Influence of the nature of interface

- One of the most effective coupling agents for sulfur cured compounds filled with non black fillers is bis-(3-triethoxysilyl propyl)tetrasulphide (TESPT)-Si-69
- The chemical modification of the silica particles by means of the coupling agent reduces the amplitude of the Payne effect.

L. Bokobza and Rapoport, 2002
Figure 2. Influence of silica modification on the interaction elastomer-filler of SBR-2 and SBR-2(ep7).

Tatiana et al.
Figure 3. Influence of the epoxidized rubber content on a) storage modulus and b) loss modulus, considering a rubber compound filled with 60phr of silica.

Figure 6. Influence of the silica polarity on the rubber-filler interaction of an elastomer with 7mol% of epoxy groups –SBR-2(ep7)-.
Figure 4. Schema of a proposed mechanism for the epoxidized rubber-silica interaction.
Effect of Temperature

Temperature dependence of the storage modulus for natural rubber filled with 50 phr CB


According to Cassagnau, the nonlinear behaviour can be associated with both mechanisms of chain disentanglements and filler-network break down depending on the filler concentration and amplitude deformation.

Payne effect, variation of the storage modulus vs. deformation at different silica concentrations, $\omega = 10$ rad/s (a) EVA/xylene: 100/0, melt EVA, $T = 140^\circ$C; (b) EVA/xylene: 78/22, $T = 21^\circ$C; (c) EVA/xylene: 92.5/7.5, $T = 21^\circ$C

(P. Cassagnau Polymer 45, 2003)

The storage modulus is less strain-dependent in the low strain region for $\gamma < 1\%$ whereas a strain-dependence behaviour occurs over two decades at high strains.
Idealized form of a typical elastic modulus curve

Strain amplitude dependence of $G^*$ of N 115 at different loadings for SBR (a) green compound, (b) vulcanizate.

The storage modulus vs. strain amplitude for MWCNT-filled NR films Measured at room temperature


Schematic representation at low and high filler loading.
NR/Silica nanocomposites

Strain dependence of the storage modulus

\[(E'_0 - E'_\infty)\] increases with increase in silica content


Strain dependence of loss modulus

Schematic representation of (a) the breakdown of aggregates and desorption of rubber chain segments from the filler surface in silica filled NR system (b) multiple points of attachments of rubber chains at the silica surface converting to the single points of attachments on straining.

AFM height image of NR filled with 20 phr nanosilica
Effect of temperature on the Payne effect

![Graph showing the effect of temperature on the Payne effect](image)

The amplitude of the Payne effect decreases dramatically with temperature


Application of the model of variable network density

![Diagram showing the connection of network chains to the filler particle](image)

Fig.1: Connection of network chains to the filler particle raises the network density in the region

Fig.2: The white (black) spots mean free (occupied) interaction positions on the filler surface (left). The chains are attached in the succession of their number. After a certain time many isolated sites available for unstable bonds (grey spots) remain on the surface (right)

(Maier, P.G.; Goritz, D. Kautschuk Gummi Kunststoffe 1996, 49, 18)
Assumptions

- The existence of a distribution of differently strong links between filler particles and segments of elastomer chains
- The increasing desorption of the chains with increasing amplitude leads to a reduced network density
  - The basic idea of Langmuir’s theory was used.
  - The number of isolated interaction sites at the filler surface is constant
  - The sites should be equal regarding the bond energy
  - Every site is able to interact with only one segment of a macromolecule
  - The occupation of the neighboring isolated sites does not influence the adsorption.
  - The desorption should not be influenced by the neighbouring positions

The storage modulus of a filled rubber is given by

\[ E' = N k_B T \]

with \( N \): network density ; \( k_B \): Boltzmann constant  \( T \): temperature in K

According to the model, the network density of a filled vulcanised elastomer

\[ N = N_c + N_{st} + N_l \]  \hspace{1cm} (1)

where \( N_c \) is the chemical network density, \( N_{st} \), the density of network chains caused by stable bonds at the filler surface, \( N_l \) and density of unstable bonds between chains and filler.

\[ E' (\gamma) = \left( N_c + N_{st} + N_l (\gamma) \right) k_B T \]  \hspace{1cm} (2)

The dependence of the modulus on the deformation amplitude could be written as

\[ E (\gamma) = E'_{st} + E'_{l} / (1 + cy) \]  \hspace{1cm} (3)

\[ E'_{st} = \left( N_c + N_{st} \right) k_B T \] \hspace{1cm} \text{and} \hspace{1cm} E_i = N_{10} k_B T
Storage modulus Vs. strain amplitude for NR/Silica

The solid lines represent the curve fits according to the model.


Effect of Temperature

NR/Silica composites

The solid lines represent the curve fits according to the model.
The temperature dependence of the density of unstable bonded chains is written as an Arrhenius law according to

\[ N_{10}(T) = N_{100} e^{-E_j/k_B T} \]

where \( N_{100} \) is a constant characterising the density of unstable bonds and is independent of temperature and the deformation amplitude; \( E_j \) is the activation energy of desorption.

### Table: Fit parameters as a function of temperature

<table>
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<th>Temperature (K)</th>
<th>( N_{s+Nst/10^{20}} (1/cm^3) )</th>
<th>( N_{lo/10^{20}} (1/cm^3) )</th>
<th>( c )</th>
<th>Chi^2/DoF</th>
<th>R^2</th>
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</table>

NR/Silica (\( E = 0.09 \) eV)

**References**

Mullins effect


- The load required to produce a given stretch during the secondary reloading is smaller than that required to produce the same stretch during the primary loading.

[Image: Energy dissipation phenomena (Mullins effect).

Different physical mechanisms for stress softening

- Mullins and Tobin considered the material to be composed of soft and hard regions of rubber, with most of the strain taking place in the soft regions.
- During deformation, the fraction of the hard regions is continuously broken and transformed into the soft phase. Softening as the breaking of bonds between chains and the fillers. He argued that the short chains must break when they are fully extended before the long ones (Mullins, L., Tobin, N.R., 1957. Rubber Chem. Technol. 30, 555)

The stress softening is due to the breaking of bonds between chains and the fillers. The short chains must break when they are fully extended before the long ones. (Bueche, F., 1960, J. Appl. Polym. Sci. 4, 107.)
Mullins effect at small and moderate deformations observed on a 50 phr carbon-black filled SBR submitted to cyclic uniaxial tension.

Diani et al., European Polymer Journal 45 (2009) 601–612

Two loading–unloading cycles performed on 8.3 wt% filled film. The modulus at low-strain strongly decreases after the first loading, suggesting a disruption of the nanotube network. A permanent deformation is observed after first loading.

Physical explanations of the Mullins effect

- Bond rupture
- Molecular slipping
- Filler rupture

Disentanglement

Double layer model
Conclusions

- The amount and morphology of the fillers played a major role on the Payne effect. Silica forms stronger and more developed filler-filler network and the breakdown of these networks results in larger Payne effect.
- Enhanced Payne-like behaviour has been observed for gum vulcanizates at room temperature where there are no filler-filler and no filler-polymer interactions, which are typically associated with filled vulcanizates. This is explained by the effect of chain disentanglements on straining.
- The model of variable network density has been applied and the calculated activation energy is found to be within the range of Van der Waal's interaction energy.
- The number of unstable fixed chains adsorbed on the filler surface is also responsible for the reduction in modulus with increase in temperature.
- In addition to the contribution from filler-filler network, there are a lot of factors which affect the non-linear viscoelastic behaviour including the breakdown of different networks namely filler-filler networks, weak polymer-filler networks, chemical networks and entanglement networks.

Conclusions

- The stress softening, commonly known as the Mullins effect, is observed usually in filled rubberlike materials after the first load.
- Experimental observations have shown that the Mullins effect induces a permanent set and some anisotropy.
- The Mullins effect is a softening that occurs in rubbers during the first deformation. It goes with residual strain and induced anisotropy.
- Contrary to the commonly reported allegation that Mullins softening is observed in filled and unfilled rubbers, only filled rubbers and pure gums that crystallize have shown some Mullins softening until now.
- The phenomenon is reversible, since materials heal when exposed to high temperature in vacuo or to solvent swelling.
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