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EXECUTIVE SUMMARY OF THE THESIS

Influence of silanization and sulfur content on curing kinetics and Payne effect in silica-filled styrene-butadiene rubbers

TESI MAGISTRALE IN MATERIALS ENGINEERING AND NANOTECHNOLOGY – INGEGNERIA DEI MATERIALI E DELLE NANOTECNOLOGIE

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1. Introduction

Elastomeric materials filled with reinforcing particles are widely employed in industrial applications such as tires and damping devices, where rubber compounds are subjected to cyclic deformations over a broad range of amplitudes and frequencies. Under these conditions, these materials exhibit complex behaviour due to their nonlinear response arising from the interplay between the polymer matrix, the filler and their interactions. This phenomenon is known as the "Payne effect". Among reinforcing fillers, silica has gained increasing importance, particularly in "green tires". However the polar nature of silica leads to strong filler-filler interactions and poor compatibility with non-polar elastomers such as styrene-butadiene rubber (SBR). To overcome these limitations, various strategies have been developed, among which the most relevant approach is the use of bifunctional organosilane coupling agents such as TESPT. This thesis explores the nonlinear relationship between the components of the shear dynamic modulus and the strain amplitude in torsional oscillatory experiments on SBR with varying TESPT contents (3.75, 6 and 8.25 phr) in both uncured and cured states. The study first investigates the dependence of the curing kinetics on the TESPT and sulfur content and then analyses the evolution of the storage and loss moduli with strain amplitude aiming to separate the contributions of the filler-filler network, the filler-rubber interface and the chemical crosslink network. The experimental results are further interpreted through harmonic analysis methods and parametric fitting based on the Leblanc-Nijman model, providing a quantitative description of the strain-dependent nonlinearity.

A key aspect of this master's thesis is the systematic investigation of how silanization level and sulfur content influence both curing kinetics and the nonlinear viscoelastic response of silica-filled SBR. Particular attention is devoted to identifying these

compositional variables roles in the filler-filler network, in the filler-rubber interface and in the chemical crosslink network and more in general on the Payne effect in both uncured and cured states. Through harmonic-based analysis and parametric modeling, the study aims to provide a quantitative framework capable of clarifying the strain-dependent evolution of these mechanisms.

2. Theoretical background

The Payne effect [1], named after the scientist who brought to the attention the reduction of the storage modulus in filled elastomers under oscillatory shear at high strain amplitudes. After an initial linear viscoelastic plateau (G'_0), the storage modulus decreases progressively with increasing strain, while the loss modulus, after the linear region at low amplitudes (G''_0) typically exhibits a local maximum before decreasing at lower values than G''_0. This behaviour is commonly interpreted as the macroscopic manifestation of the progressive breakdown of the filler-filler network formed by weak physical interactions between aggregates.

Since G' and G" are defined within the hypothesis of linearity, where the response to a sinusoidal input must be sinusoidal, in filled rubbers under large amplitude oscillatory shear (LAOS) the storage and loss moduli should no longer be interpreted as material functions, but just as effective descriptors of the elastic and dissipative contributions of the response. However, in nonlinear conditions the stress signal can be expressed as a linear combination of sinusoidal functions (Fourier series), where higher odd harmonics appear in addition to the fundamental one. The relative intensity of these harmonics, particularly that of the third harmonic, which is often the dominant one associated to the nonlinear behaviour is measured through the ratio I_3/I_1. This information is significant towards the identification and quantification of the non linearity, but not towards the understanding of the behaviour of the filled rubber during the cycle. To obtain a more physically meaningful interpretation of intra-cycle nonlinearities, the stress response can be decomposed using Chebyshev polynomials as proposed by Ewoldt et al. [2]. This approach separates the elastic and viscous contributions and introduces dimensionless indices that quantify intra-cycle strain stiffening/softening and shear thickening/thinning effects, allowing the evolution of nonlinear mechanisms within each oscillation cycle to be characterized. Finally, if the interest is towards the investigation of the interactions involving filler and matrix, the most physically grounded approach is provided by the LeBlanc-Nijman model [3], which models the Total Torque Harmonic Content (TTHC), defined as the sum of higher odd harmonics normalized to the fundamental component, as a function of the shear strain amplitude. The model describes the harmonic growth as the result of a filler contribution and a polymer contribution, and its parameters offer insight into the transition from filler-dominated to matrix-dominated behaviour. Since the third harmonic generally dominates the nonlinear response, the strain dependence of TTHC closely reflects that of I_3/I_1.

3. Materials and methods

The study was carried out on styrene-butadiene rubber (SBR) reinforced with 75 parts of filler per hundred parts of rubber in weight, differing in silane coupling agent (TESPT) content. Five formulations were analyzed: three base compounds with different TESPT levels (3.75, 6 and 8.25 phr) respectively called "L", "M" and "H" and two sulfur-adjusted variants, in which the elemental sulfur content was increased in compound L (L_c) and reduced in compound H (H_c) to balance the total sulfur contribution provided by TESPT. This approach allowed the independent evaluation of the effects of silanization and total sulfur content on curing kinetics and nonlinear viscoelastic response. Both uncured and cured states were investigated in order to distinguish the contributions of the physical filler network from those of the chemical crosslink network. The experiments were performed using a Rubber

Process Analyzer (Premier RPA) from Alpha Technologies operating in strain-controlled torsional mode. The applied shear strain followed a sinusoidal trend ($\gamma(t) = \gamma_0 \sin(\omega t)$) characterized by a strain amplitude (γ_0) and a frequency (ω). The shear stress response is measured and elaborated by the system software that converts it into fundamental viscoelastic parameters such as the storage modulus (G'), the loss modulus (G'') and the loss tangent (tan δ). A minimum specimen mass of 5.75 g was selected to ensure stable torque measurements and to avoid signal collapse observed at large strain amplitudes for lower masses. Two types of tests were performed: first, curing kinetics was investigated under isothermal conditions (170°C for about 30 min) to determine characteristic vulcanization parameters such as characteristic times to reach 10% and 90% of the total torque increase (t_{10}, t_{90}) and the effective cure interval ($\Delta t = t_{90} - t_{10}$). The evolution of the torque during vulcanization at constant strain amplitude (0.1%, so in the linear regime) was monitored to evaluate the influence of TESPT and sulfur content. This vulcanization process was followed by a controlled slow cooling (from 170°C to 50°C in 25 min) to avoid any thermal shock or excessive internal stresses. Second, large amplitude oscillatory shear (LAOS) tests with increasing strain amplitude (from 0.1% to 1000% for uncured samples and from 0.1% to 200% for cured samples) were performed at 50°C and at constant frequency (0.5Hz) to study the effect of TESPT and sulfur content on the Payne effect and more in general to characterize the nonlinear viscoelastic behaviour through the application of harmonic analysis techniques.

4. Experimental Results

4.1. Curing kinetics

The curing behaviour of the investigated compounds is analyzed in terms of the characteristic curing time t_{10}, t_{90} and $\Delta(t_{90} - t_{10})$ reported in Table 1. The results clearly indicate that the curing rate primarily depends on TESPT content, with higher silanization levels leading to faster vulcanization, rather than the sulfur content, that has no influence in compounds with low-content of TESPT and only a marginal effect in high-content TESPT compounds. This result is consistent with the dual role of TESPT as both sulfur donor and coupling agent. However, the limited influence observed increasing the sulfur content alone suggests that in these compounds the coupling function is the dominant contribution. By promoting rubber-silica coupling and enhancing filler dispersion it increases the availability of reactive sites near the filler surface and reduces the adsorption of curatives on the silica surface, improving the efficiency of the curing system. Interestingly compound M appears closer to L than to H in terms of curing kinetics, suggesting a non-linear dependence on the TESPT content.

Table 1. Characteristic curing time to reach 10% and 90% of the total torque increase together with the effective cure interval ($t_{90} - t_{10}$)

	t10% [sec]	t90% [sec]	Δt [sec]
L	62.04	1060.60	998.56
M	68.17	1024.07	955.90
H	54.27	761.23	706.96
Lc	50.67	1053.27	1002.60
Hc	44.97	788.60	743.63

4.2. Payne effect in uncured compounds

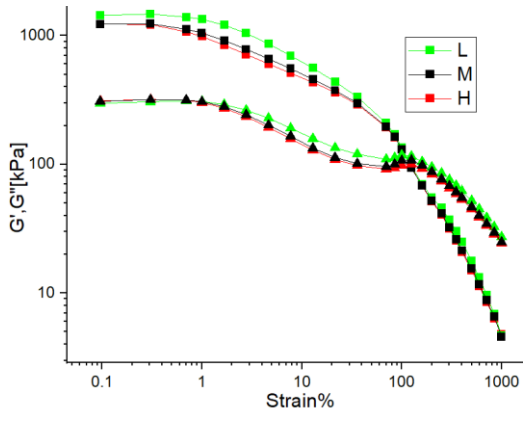

Figure 1. Storage (squares) and Loss (triangles) moduli pre-cure for compounds L, M and H

In the uncured state, amplitude sweep tests show that at small strain amplitudes both G′ and G″ present a plateau, limited to the first two points (0.1% and 0.3%), that defines the linear viscoelastic region. Beyond this region, the material enters the nonlinear regime where the Payne effect occurs. As the strain amplitude increases, G′ decreases monotonically over the entire explored range, consistently with the progressive breakdown of the filler-filler physical network. G″ presents a first, barely visible, local maximum close to the onset of nonlinearity, followed by a gradual decrease up to approximately 70% of strain. Near the crossover condition (tan $\delta \approx 1$, G′ ≈ G"), G″ increases again exhibiting a second, more pronounced relative maximum, attributed to matrix-related nonlinear dissipation, since the filler network is considered largely disrupted. Comparing different formulations, within the linear regime, compound L exhibits the highest storage modulus (G'_0) compared to M and H, indicating a stronger filler-filler network when TESPT content is low. Accordingly, the first, barely visible, local maximum of G″ at the onset of nonlinearity is shifted to slightly higher strain for L, as a more robust filler network requires a larger deformation to initiate significant bond breakage. By further analyzing the LAOS response through Lissajous plots, the onset of nonlinearity can be qualitatively confirmed, becoming detectable for strain amplitudes greater than 0.7%, where the loops start to deviate from a regular elliptical shape. Notably, the loop at 70% strain appears relatively "clean" and elliptical, suggesting the presence of a transition zone in which the filler-filler network is largely disrupted, while matrix-related nonlinearities have not yet emerged and become observable only at higher strain amplitudes. The existence of this transition neutral zone is further supported by the Chebyshev-based LAOS indices S and T, that quantify intra-cycle strain stiffening/softening and intra-cycle shear thickening/thinning, and by the harmonic ratio analysis I_3/I_1, showing values really close to zero at around 70% strain. In order to obtain a quantitative description with physically interpretable parameters, the uncured data were analyzed using the LeBlanc-Nijman model.

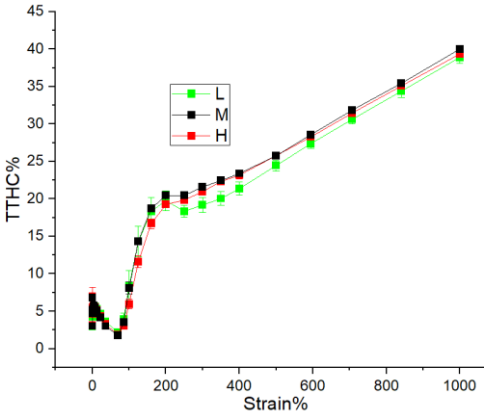

Figure 2. TTHC pre-cure versus on the strain amplitude for compounds L, M and H

The fit was restricted to strain amplitudes $\gamma_0 \geq 125\%$, where the experimental trend is consistent with the theoretical shape assumed by the model. The fitted parameter α, describing the final slope of the TTHC-strain amplitude curve, where matrix is expected to dominate follows the order $L > M > H$. This indicates that higher TESPT content is associated with a less steep increase of nonlinearity at the highest strains: while the matrix contribution continues to raise the TTHC, the filler-rubber contribution remains active up to larger deformations in strongly coupled systems decreasing the final slope. The same trend is observed for parameter B, which governs the magnitude of the local maximum around 200% of strain and, in particular, makes the transition less smooth. The ordering $B_L > B_M > B_H$ therefore indicates a more abrupt transition for the low-TESPT compound. This further supports that, in strongly coupled compounds, filler-rubber interactions decay at higher strains, in agreement with the reported sensitivity of B to the quality of filler dispersion [3]. Finally, the parameter TH_m, representing the asymptotic harmonic content at large strains, increases with TESPT content ($TH_{m\_L} < TH_{m\_M} < TH_{m\_H}$). This is consistent with higher interfacial coupling efficiency and a larger bound-rubber fraction in high-TESPT compounds,

which enhance polymer-filler friction that lead to greater harmonic distortion in the matrix-dominated regime. As a final remark, compounds differing only in elemental sulfur content do not exhibit appreciable differences in the uncured response, confirming that sulfur variations alone do not affect the pre-cure mechanical behaviour and nonlinear signatures. In addition, an interesting trend emerges for the intermediate formulation M. Contrary to what is observed in the curing kinetics, for most of the parameters considered, M lies much closer to H than to L, and in several cases it overlaps with H. This suggests a non-linear, dependence of the analyzed response on TESPT content.

4.3. Payne effect in cured compounds

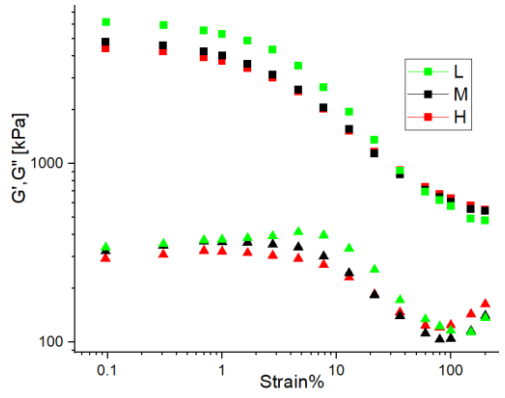

Figure 3. Storage (squares) and Loss (triangles) moduli post-cure for compounds L, M and H

The cured compounds exhibit a similar evolution of G′ and G″ than that observed in the uncured state at low strains, while it differs at high strains. At large strain amplitudes G′ no longer decreases monotonically, instead, it approaches a second plateau at high strain amplitudes that is attributed to the permanent chemical crosslink network. In the same region where G′ reaches a plateau, G″ starts to increase, indicating enhanced dissipation once the response becomes increasingly governed by the stretched crosslinked matrix. As in the uncured case, in the linear region, low-TESPT compounds show higher G'_0 values, and the first local maximum of G″ associated with the onset of nonlinearity is shifted to higher strain, consistent with a stronger filler-filler network at lower TESPT content. At large amplitudes, however, the ordering reverses: compound H exhibits the highest G′ value in the final plateau and the highest G″ value, indicating a stronger chemical network. Analyzing sulfur-balanced formulations (Lc, M and Hc) it's possible to decouple the role of TESPT from the effect of crosslink density. In this case, in the high-amplitude region corresponding to the second G′ plateau, the curves of all three compounds seems to converge and also the differences in G″ in this region are markedly reduced, suggesting that the sulfur adjustment effectively compensates for the TESPT-driven differences in network density. The Chebyshev analysis provides complementary insight: higher TESPT content leads to higher intra-cycle strain stiffening (larger S), consistent with stronger interfacial coupling. While considering sulfur-balanced compounds, it can be observed that the general dependence of the S parameter is instead mainly controlled by the crosslinking density. Finally, the LeBlanc-Nijman analysis of the total harmonic content (TTHC) provides a quantitative confirmation of the trends discussed above.

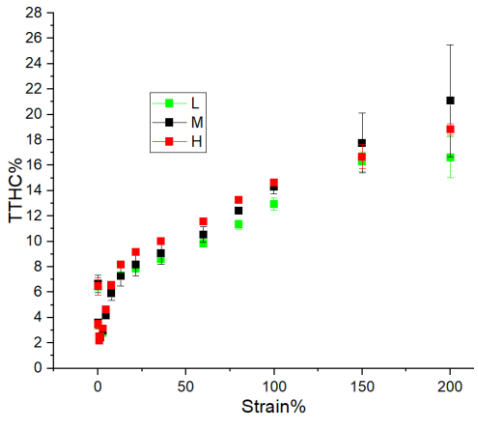

Figure 4. TTHC post-cure versus on the strain amplitude for compounds L, M and H

The parameter B follows the ordering $B_L > B_M > B_H$, the same trend observed for the uncured compounds, suggesting that even after cure the lower-TESPT materials retain a higher degree of interfacial heterogeneity. The parameter C is also higher for the low-TESPT compounds, indicating that the transition towards a matrix-controlled response occurs at lower strain in poorly coupled systems, whereas higher silanization stabilizes the filler-rubber interphase and shifts this transition to larger deformations. In contrast, the asymptotic parameter TH_m primarily follows the crosslink

density ranking ($H > M > L$), confirming that the high-strain nonlinear response in the cured state is governed mainly by the permanent chemical network. A minor residual influence of the coupling agent can still be detected when comparing sulfur-balanced formulations (Hc > Lc for TH_m), which can be attributed to the remaining contribution of filler-rubber coupling to the nonlinear dissipation at large deformations. The intermediate formulation M again shows an asymmetric positioning between L and H, depending on the specific metric considered. In terms of the storage modulus G'_0, M consistently lies much closer to H than to L, indicating that the stiffness at low strain amplitudes (still dominated by the filler network) responds in a strongly non-linear manner to TESPT content. Conversely, when examining nonlinear descriptors such as I_3/I_1 and the Chebyshev parameters, M approaches L for selected strain amplitudes. Overall, the behaviour of compound M supports the conclusion that the dependence on TESPT is not strictly linear across the investigated range, and that different response metrics may saturate at some TESPT levels.

5. Conclusions

This work investigated how TESPT content and elemental sulfur level affect curing kinetics and nonlinear viscoelasticity in silica-filled SBR, combining conventional dynamic analysis with harmonic-based parameters (I_3/I_1, Chebyshev indices) and LeBlanc-Nijman modelling of TTHC. Curing results show that TESPT is the principal factor for the formation of an effective network, consistent with its coupling function, that promotes rubber-silica coupling and enhance filler dispersion increasing the availability of reactive sites near the filler surface and reducing the adsorption of curatives on the silica surface. In the uncured state, the response is dominated by the progressive breakdown of the filler-filler network: the low-TESPT compound exhibits the strongest Payne effect (consequence of a higher G'_0), while differences progressively diminish as the strain amplitude increases. These final differences can be detected and analyzed thanks to Leblanc-Nijman modelling, which highlights properly the effect of TESPT on increasing filler-rubber coupling, whose interactions reduce at higher strains. After cure, the behaviour reflects the combined contributions of residual filler structure, interfacial coupling and the chemical crosslink network. The emergence of a second high-strain G′ plateau highlights the dominance of the chemical network after filler-filler network is reduced, and the convergence of sulfur-balanced formulations at high strain indicates that TESPT mainly affects low-strain reinforcement and interfacial efficiency rather than providing a distinct advantage at large deformations. Finally, the intermediate formulation M response does not scale linearly between L and H across all the analyzed parameters, suggesting a non-linear, potentially with a saturating value, dependence of reinforcement efficiency on TESPT within the investigated range.

References

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