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Time-resolved mechanical spectroscopy of epoxidized natural rubber/SiO<sub>2</sub> composite / Arrigo, Rossella; Malucelli, Giulio. - ELETTRONICO. - (2022). (Intervento presentato al convegno XXIV Convegno Nazionale dell'Associazione Italiana di Scienza e Tecnologia delle Macromolecole tenutosi a Trento (Italia) nel 4-7 settembre 2022).

*Availability:*

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# TIME-RESOLVED MECHANICAL SPECTROSCOPY OF EPOXIDIZED NATURAL RUBBER/SiO<sub>2</sub> COMPOSITE

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## Introduction

The macromolecular architecture of polymers and polymer-based multiphase systems can be characterized through the study of their rheological behavior, due to the singularity of the relationship between macromolecular motions and the relaxation dynamics of polymer chains [1]. This is particularly evident in the rheological response at low frequency, which reveals distinct information about the macromolecule dynamics due to the possibility of probing the slow relaxations of the predominant portion of the material [2]. However, since measurements by conventional rheological tests require very long experimentation time, the analysis is only suitable for polymers exhibiting a high structural stability within the duration of the tests. It has also been demonstrated that conventional frequency sweep tests are not accurate when an event involving a mutation takes place during the measurement within a time interval that exceeds the natural relaxation time of the polymer [3]. Several studies over the last two decades have shown that the “true” rheological behavior of the so-called transient polymers can be obtained using time-resolved mechanical spectroscopy (TRMS), in which the frequency-dependent rheological functions are obtained by subjecting the material to successive frequency sweeps over a realistic time schedule for this type of evaluation. The data collected for each frequency are then plotted as a function of the acquisition time and extrapolated to “zero” time to obtain a fundamental rheological parameter for the material, alongside the time dependency function for structure evolution [4].

In this work, we exploited TRMS to obtain an accurate characterization of the rheological behavior of an ENR composite containing 25 mol% of epoxy groups and reinforced by 10 wt.% of silica particles. To this end, the relaxation spectrum of the material was acquired to evaluate the effect of the embedded particles on the dynamics of ENR macromolecules. Besides, TRMS was used to assess the possibility of utilizing the changes in rheological parameters occurring by the thermal treatment received by the melt during the test as a method to probe the effect of silica particles on cross-linking and chain scission reactions taking place in the matrix.

## Results and discussion

To gain an insight into the evolution of the microstructure of ENR/SiO<sub>2</sub> composite in the melt state and to evaluate the possible influence of the interaction phenomena between silica and ENR on the relaxation kinetics of the latter, the material was

subjected to different successive frequency sweep measurements in order to obtain the weighted relaxation spectra. Looking at the resulting spectra, shown in Figure 1, it is noted that the tail appearing at long relaxation time gradually increases alongside a broadening of the incomplete peak related to the relaxation of ENR macromolecules. These features indicate a progressive elastic dominant behavior evidenced by the appearance of slower relaxation modes of the ENR matrix.

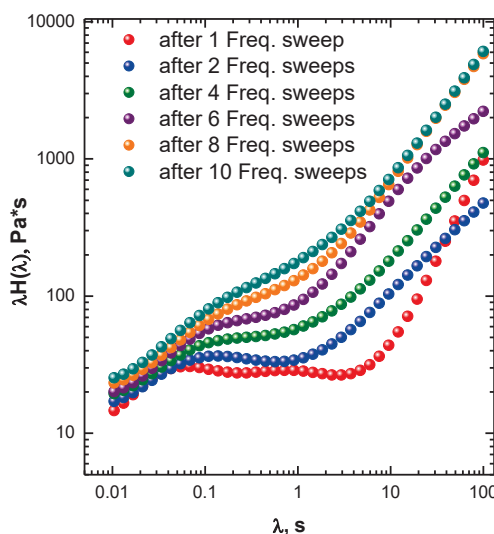


Figure 1: Weighted relaxation spectra for ENR+SiO<sub>2</sub> system subjected to subsequent frequency sweep measurements.

To further inspect the phenomena relative to the observed progressive restriction of the ENR relaxation dynamics, the data of the consecutive frequency sweep measurements were re-arranged by applying TRMS procedure, from which plots of the variation of  $G'$  and  $G''$  with time were obtained. Then, the respective isochronal modulus values were calculated as the intercept between a vertical line at a specific time  $t$  and the curves interpolating the experimental data. Furthermore, the modulus values at time zero were also estimated. Figure 2 shows the curves of the isochronal storage modulus calculated at different times during TRMS measurements, alongside the calculated  $G'$  value at time zero. The TRMS data clearly highlight not only the enhanced the elastic behavior acquired by the melt with increasing the exposure time to high temperature, but also the vanishing effect of the thermal treatment at much higher frequencies, where the fast relaxations take place. These two effects are not revealed by conventional single-frequency runs.

The collected data are indicative of the possible occurrence of two concurrent phenomena, involving the combined effect of the embedded silica particles and the ENR network evolution, which give rise to a progressive magnification of the elastic rheological behavior.

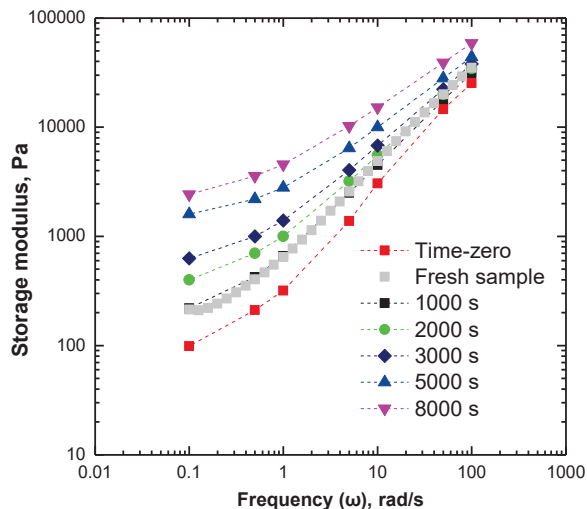


Figure 2: Isochronal storage modulus for ENR+SiO<sub>2</sub>, collected at different times during TRMS tests.

In particular, the flattening of the  $G'$  curves in the low frequency region can be taken as indicative of a gradual slowing down of the relaxation kinetics of the ENR macromolecules, since the decrease in the slope of the storage modulus curve is often associated with the restriction of the polymer chain motion, resulting from the presence of strong interfacial bonding and highly dispersed particles. To support the occurrence of strong interactions between ENR macromolecules and the embedded particles, and the possible formation of hydrogen bonds involving OH groups onto silica surface and oxirane rings of the matrix, ATR-FTIR spectra were collected for both unfilled ENR and ENR + SiO<sub>2</sub> composite, before and after the thermal treatment. The obtained results suggested the occurrence of ring opening reactions of the epoxy groups during the thermal treatment and strong interactions between silica particles and ENR. Furthermore, the decrease of the slope of  $G'$  curves in the terminal region can be associated with thermal-induced gelation reactions (i.e., cross-linking) for ENR in the pristine state (unfilled) during TRMS measurements, leading to a progressive increase of the cross-linking degree of the matrix [5]. Aiming at evaluating the critical time for gelation in the ENR+SiO<sub>2</sub> composite, the Winter–Chambon criterion was applied, and the obtained data were compared to those of unfilled ENR. The multi-frequency plots of  $\tan\delta$  against time for the ENR + SiO<sub>2</sub> system are presented in Figure 3, from which the intersection point (i.e., the gel time) is identified at around 6500 s. Measurements performed under the same testing conditions for unfilled ENR indicated that the gel point appears at around 1500 s [5]. The estimated increase for the

time required to reach the gelation for the composite system can be expected from a possible acceleration of chain scission reactions in the ENR matrix, due to the acidic nature of the SiOH groups on the surface of the silica particles. These exert a catalytic effect on the opening of the oxirane groups, which brings about the cleavage of the -C-C- bond at the contiguous -CHOH-CHOH- groups.

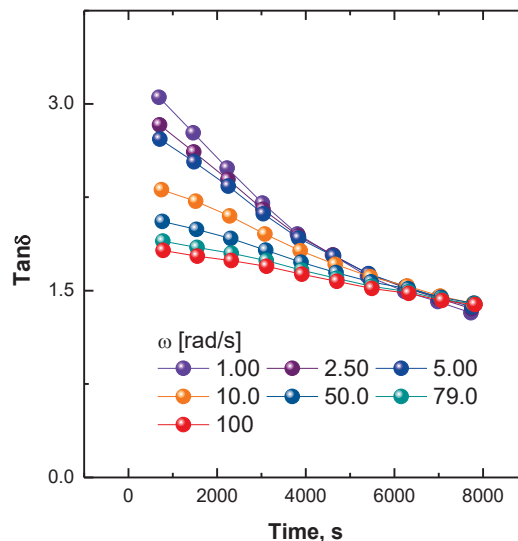


Figure 3: Multi-frequency plot for the variation of  $\tan\delta$  as a function of time for ENR+SiO<sub>2</sub> system.

## Conclusions

In this work, TRMS was employed to study the rheological response on an ENR-based composite containing 10 wt% of silica particles, within both linear and non-linear rheological regimes. The data revealed a remarkable effect of the silica particles on the macromolecular dynamics of the ENR matrix, which has been attributed to the formation of a matrix/polymer interphase exhibiting highly impeded relaxations. At the same time, the analysis of the storage and loss modulus curves obtained through TRMS sweeps for both the ENR+SiO<sub>2</sub> composite and the pristine ENR has shown that the silica particles exhibit a catalytic effect on the degradation of the ENR matrix. This effect was evidenced from an increase in gelation time. The obtained data provide useful insights for the applications of silica reinforced ENR and particularly on the role of silane coupling agents, which may extend beyond the enhancement of interfacial adhesion to include stabilizing effects.

## References

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