

# Real-time Crystallization of Organoclay Nanoparticle Filled Natural Rubber under Stretching

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## ABSTRACT

The inclusion of clay nanoparticles (nanoclay) in cross-linked natural rubber (NR) induces an early promotion and enhancement on crystallization under uniaxial deformation. We evaluate and monitor the molecular structure of the polymer network and its changes during elongation by using in-situ synchrotron radiation. Nanoclay introduces an increase of the crystalline content and a dual crystallization mechanism related to the alignment of the nanoparticles during stretching. This study could be the starting point on the designing of a new generation of elastomers materials without the trade-off exhibited in conventional rubber composites.

**Keywords:** natural rubber, nanoclay, crystallization.

## 1 INTRODUCTION.

Layered-silicate nanofillers can improve the physical, mechanical, and thermal properties of polymeric matrices.<sup>[1-3]</sup> This behavior has been explained by the formation of a reinforcing nanofiller network (exfoliated or/and intercalated), within which the polymer chains are confined. However, this explanation is not sufficient to paint a complete picture of the reinforcing mechanism taking place in many systems.

The inclusion of highly anisotropic clay nanoparticles (nanoclay) in NR decreases the network defects and induces an early promotion and enhancement on crystallization under uniaxial deformation. We evaluate the molecular structure of the polymer network and its changes during uniaxial deformation by using dielectric spectroscopy and in situ synchrotron X-ray diffraction, respectively.

## 2 MATERIALS AND METHODS.

The dispersion of the layered silicate on NR was studied by X-ray diffraction (XRD) and Transmission Electron Microscopy (TEM). The viscoelastic properties at low deformation of the materials were studied by Dynamic-Mechanical Analysis (DMA). The distribution of the NR network components was determined by Dielectric Spectroscopy (DS) and the crystallization coupled to mechanical elongation was monitored by in-situ Wide-Angle X-ray (WAXD) synchrotron radiation.

## 3 RESULTS AND DISCUSSION.

By XRD (Figure 1) and TEM studies (Figure 2) we have evidenced that rubber chains easily penetrates into the layered silicate leading intercalate structures and partial exfoliation.

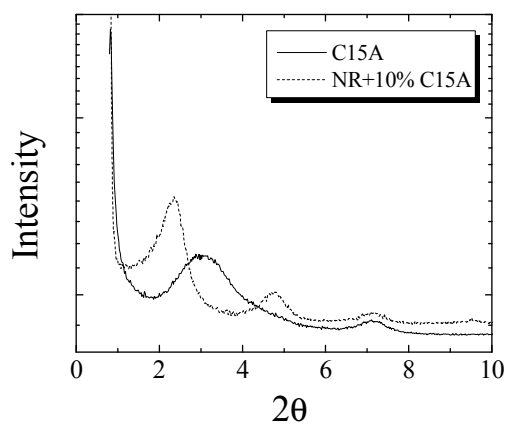


Figure 1. XRD patterns for organoclay (C15A) and for the nanocomposite (NR+10% C15A).

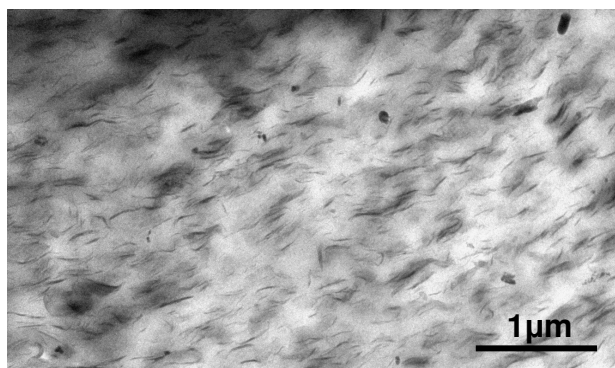


Figure 2. TEM image of NR/C15A nanocomposite.

Dielectric relaxation experiments (Figure 3) of dry and swollen specimens provided a qualitative evaluation of the degree of homogeneity on the network components through the distribution of relaxation times corresponding to the segmental and normal mode.

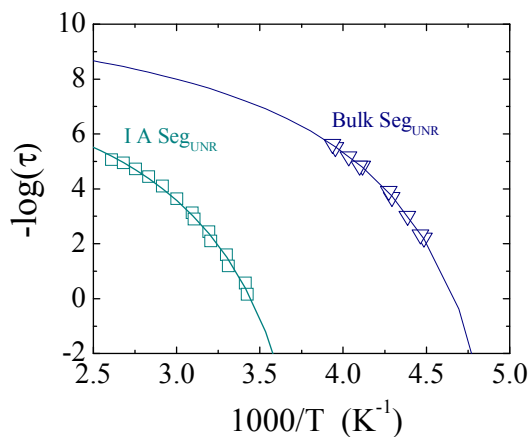


Figure 3. Arrhenius plot of bulk NR's segmental mode and interfacially adsorbed (I. A.) rubber chains.

The results from the study of the induced-crystallinity in the NR materials during uniaxial elongation by synchrotron radiation were rationalized, among others parameters, in terms of the degree of order imposed by the nanoclay on the distribution of the topological constrains of the polymer network as a consequence of a better distribution of the curatives on the NR matrix during the mixing procedure.

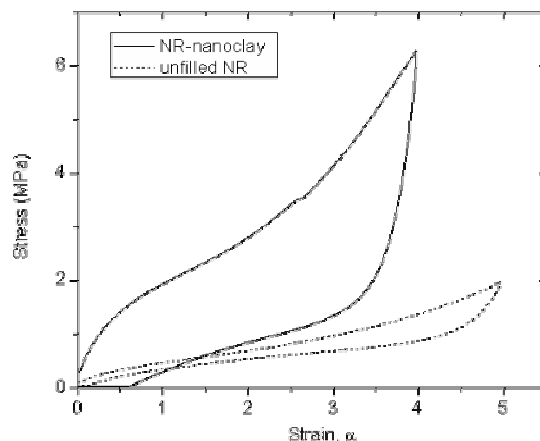


Figure 4. Stress-strain curves for the NR nanocomposites and for the unfilled sample.

In order to understand the improvement of the mechanical properties (Figure 4) we investigated the possibility of any bound rubber formation on the outer surface of fillers like in carbon black or silica bids composites. Evidences have been found in the nanocomposites by dielectric spectroscopy and the existence of a possible relaxation mode suggests a strong adhesion with the fillers (interfacially adsorbed polymer IA) that corresponds to a glass transition substantially higher than the bulk glass transition (Figure 3). Further investigation of the meaning and properties of that mode is underway.

## REFERENCES

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