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Names and affiliations of applicants (* indicates experimentalists):

J.M. Chenal*, L. Chazeau*, C. Gauthier*, G. Vigier*

Groupe d'étude de métallurgie Physique et de Physique des matériaux, Bâtiment Blaise Pascal, INSA de Lyon, 20 avenue Albert Einstein, 69621 Villeurbanne Cedex France

Report:

In many applications fillers strengthen natural rubber. It is well established that the introduction of specific fillers such as carbon blacks in natural rubber can strongly increase its rigidity, its abrasion resistance, tear strength and stress at break. The improvement of the physical and mechanical properties of natural rubber in presence of fillers is known to depend on several parameters such as filler volume fraction, specific surface, and topology of filler's structure. The question, which is assessed, is the relation between the mechanical improvement due to fillers and their effect on strain induced crystallisation. In spite of the importance of this phenomenon, strain induced crystallisation in filled NR has not been much studied.

In order to better understand the role of fillers, in situ measurements, during tensile tests, of filled and unfilled samples by wide angle X-ray scattering were performed to characterize the development of the microstructure according to strain ratio. A homemade stretching machine allowing the symmetric deformation of the sample was used to probe by X-ray the same sample position during stretching at 0.25 min^{-1} strain rate. The development of the crystallinity (using the simplified method of Mitchell), the evolution of the crystallite dimensions (thanks to the Scherrer formula) and orientation of the crystallite were calculated from the two-dimensional (2D) WAXS patterns, which were recorded by a CCD Camera.

In a practical point of view, filler could be considered as multifunctionel crossing point. At first, we studied the effect of crosslink density on the strain induced crystallisation process of unfilled NR. An outstanding progress of the crystallization takes place; when the crosslink density decreases, the rate of crystallization increases, then decreases, figure 1a. Thus, we show up two different crystallization regimes according to crosslink density. Moreover, we have plotted for all unfilled samples, figure 1b, the average molecular weight between the network crosslinks (M_c) obtained by swelling versus the crystallite volume (V_c).

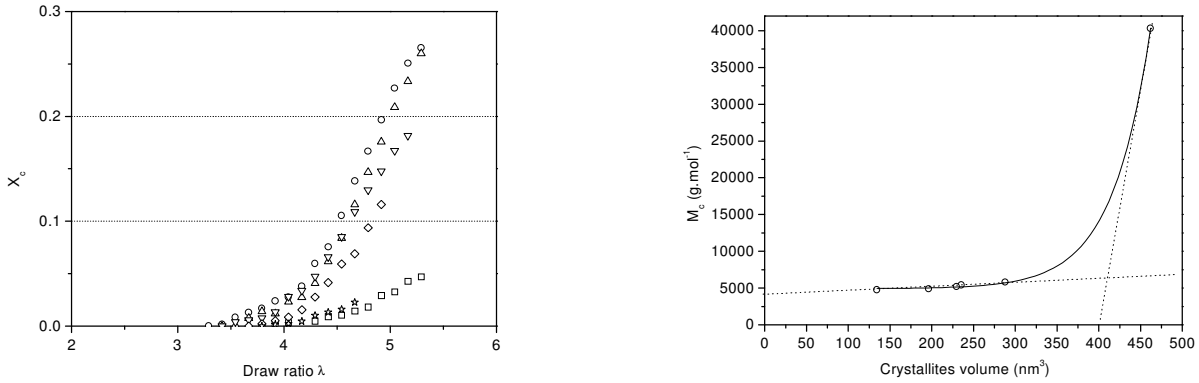

Figure 1 : (a) Effect of network-chain densities (ν x 10^4 mol/cm^3) on crystallization behavior of samples: (≤) 0.23, ( ) 1.61, (ρ) 1.71, (σ) 1.80, (↓) 1.91, (¬) 1.95
(b) Variation of average molecular weight between the network crosslinks versus crystallites volume deduced from our experiments.

The increase V_c in relation to M_c can also be divided in two regimes. At high crosslink density (M_c < 6000 g.mol^{-1}), Mc governs the growth of crystallite volume; on the other hand at weak crosslink density (M_c > 6000 g.mol^{-1}) Vc becomes quasi-independent of M_c. It is interesting to note that the critical value of M_c (~6000 g.mol^{-1}), which separates the two regimes of V_c growth, is closed to the molecular weight between physical entanglements in natural rubber (M_e~7000 g.mol^{-1}). This means that physical entanglements may contribute substantially to the properties of natural rubber after a weak crosslinking, since the crosslinking process traps the entanglements.

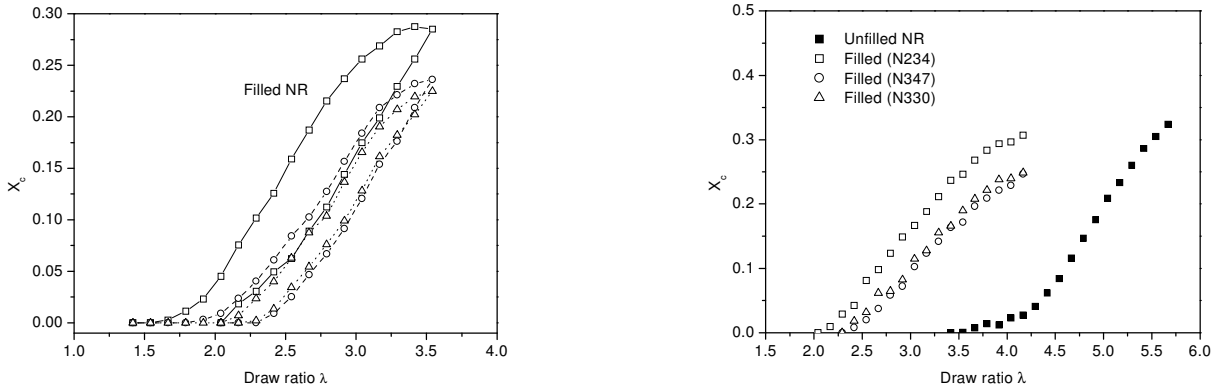

Figure 2 : (a) Crystallinity (X_c) change during successive cycles as a function of the draw ratio.
(b) specific surface and Crystallinity measured as function of draw ratio

The study of the filled NR (carbon black) during dynamics experiments enabled to understand the effect of the stress softening (so-called Mullins effect) on strain induced crystallization. In a mechanical standpoint, after the first mechanical cycle a drop of stress, which is explained by the decohesion between matrix and fillers, is observed. During different cycles, the crystallinity, figure 2a, shows a conspicuous difference between the first

cycle and the other cycles. One concludes that the Mullins effect only plays a major role during stress-induced crystallization and during melting.

The effect of the aggregate structure and the surface area of filler has also been evaluated. One observes, figure 2b, that the onset strain of crystallization is shifted to a smaller value by filling with carbon black. This fact confirms that fillers act as amplificatory of local draw ratio. Moreover, we highlight the importance of the interface between fillers and natural rubber. The higher the carbon black surface area (N234), the smaller the onset of crystallisation and the higher the crystallization of filled sample. Consequently high surface area filler should enhance mechanical properties of the filled sample by increasing crystallinity.

We are in process of preparing three publications on the work performed at ESRF