

Fracture toughness and strain induced structure modification in silica filled rubbers

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The fracture behaviour of a unfilled and silica filled IR was studied performing uniaxial tensile test on notched pure shear specimen up to rupture. Tests were performed on both pristine material and on material that has been previously cyclically deformed, to evaluate the effect of strain-induced structure modification on the compound's fracture toughness.

Introduction

Filled rubbers show the *Mullins effect*, that is the stress-softening phenomenon that can be observed when reloaded after a preliminary loading-unloading cycle [1]. Several physical interpretations have been proposed to explain the softening including bond ruptures, chains slipping over the filler, filler-cluster rupture, network rearrangement, chain disentanglement and retraction.

These mechanisms also cause energy-dissipation and they contribute to increase the material's fracture toughness. It would be thus expected that if preliminary cyclic deformation is applied to a filled rubber, this could affect its fracture behaviour.

Aim of this work was to verify this effect for a silica-filled polyisoprene rubber in relation to the filler content.

Materials and methods

Silica filled compounds based on a polyisoprene (IR) were kindly supplied by Pirelli S.p.A. Different contents of ZeoSilica1165 were considered, as detailed in table 1, where the amount of the coupling agent Si69® (triethoxysilpropyltetrasulfide-silane, TESPT) used for each compound is also indicated. The compounds were vulcanized for 10 minutes at 170°C.

Table 1: Compounds composition

Compound	Silica content (phr)	Silica volume fraction, ϕ	TESPT content (phr)
IR0	0	0	0
IR22	22	0.091	1.76
IR37	37	0.145	2.96
IR45	45	0.172	3.60

Uniaxial tensile tests were performed on a Housfield dynamometer at the displacement rate of 50 mm/min, using dumbbell specimens having 1 mm thickness and a gauge length of 14 mm. As shown in figure 2a, where the nominal stress-strain curves of the different compounds are reported, IR0 shows a quite fairly detectable crystallization-induced stress relaxation [2]: it was thus possible to determine, for the unfilled compound, the strain at the onset of the strain induced crystallization which turned out to occur at $\varepsilon_{SIC\ onset} = 5$ in agreement with literature data [3].

For the filled compounds, which do not show any crystallization-induced stress relaxation, the strain at SIC onset was determined, in a first approximation, using the following equation [4]

$$\varepsilon_{filled\ compound} = \varepsilon_{rubber\ matrix} \left(1 - \phi^{1/3}\right) = \varepsilon_{SIC\ onset_IR0} (1 - \phi^{1/3})$$

considering that, at SIC onset, the strain of the rubbery matrix in the filled compound is equal to the strain of the rubber in the unfilled one at SIC onset.

By plotting the reduced stress $\sigma^* = \frac{\sigma_n}{\left(\lambda - \frac{1}{\lambda^2}\right)}$ versus $\frac{1}{\lambda}$ (figure 2b), where $\lambda = 1 + \varepsilon$ is the applied draw ratio, the strain at the maximum chain extension, ε_{M_ex} , was determined for each compound as the strain at σ^* upturn according to [2].

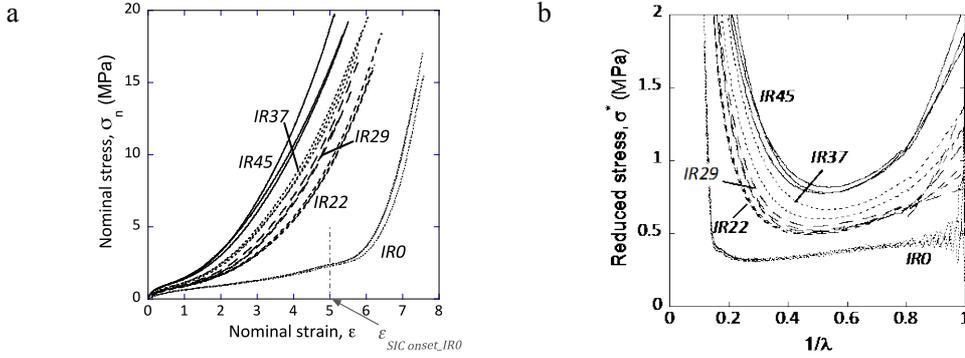


Figure 2: Stress strain curves (a) and Mooney-Rivlin (b) plot for the pristine compounds.

Loading-unloading tests were performed on pure shear (PS) specimens (100x20x1mm). Different values of the maximum applied strain were considered in the range (15 – 200)%. A displacement rate of 50 mm/min was adopted in both the loading and the unloading step. For each compound the dissipated energy fraction was measured as a function of the applied strain. A series of ten loading-unloading cycles was carried out, at 50 mm/min, to cause pre-strain softening of the compounds: the values of the maximum strain applied in each series, that will be referred to as $\varepsilon_{pre-strain}$ in the following, were fixed within the range (15 – 200)%.

Fracture tests were performed following a fracture mechanics approach. Pure shear (PS) specimens (100x20x1mm) having a 22mm notch were adopted to determine J-integral values at fracture onset. The notch was introduced with a razor blade just before the test. Tests were performed at a displacement rate of 50 mm/min. Crack onset was detected from video-recording of the tests. Digital image correlation analysis was performed to measure the value of the strain at crack onset, $\varepsilon_{crack\ onset}$, at the nearest distance possible from the crack tip with this technique (0.23 mm in this case).

As previously done [5], the fracture toughness, J-integral, at crack onset was evaluated from the load displacement curves using the expression:

$$J_c = \frac{U}{B(W - a_0)}$$

in which U is the strain energy, B is the notch plane thickness, a_0 the notch length and W the specimen width.

Fracture tests were performed both on pristine materials and on materials that have been previously pre-strain softened.

All the mechanical tests on PS specimens were performed on an Instron 1185 dynamometer.

Results and discussion

Figure 3a reports the strain values at maximum chain extension, ε_{M_ex} , the strain values at strain induced crystallization onset, $\varepsilon_{SIC\ onset}$, and the strain values at crack onset, $\varepsilon_{crack\ onset}$, for the different pristine compounds (as for the latter strain, it was measured close to the tip of the crack).

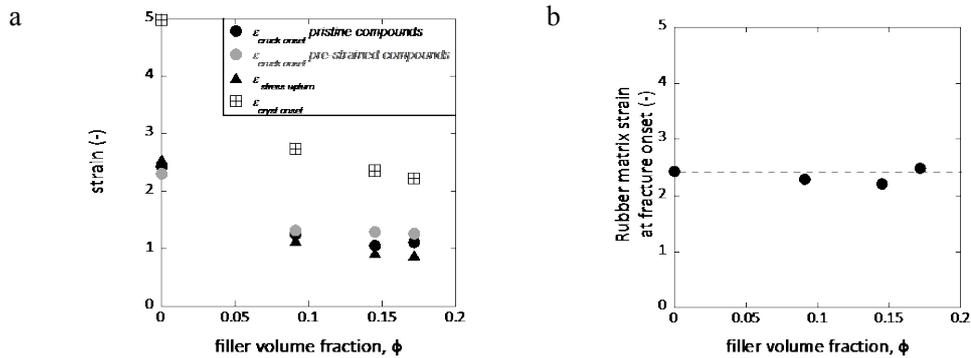


Figure 3 (a) Comparison between the strain at maximum chain extension and at crystallization onset for the pristine compounds and the strain at crack onset for both the pristine and the pre-strain softened compounds.

(b) Rubber matrix strain at crack onset in the pristine and the pre-strain softened compounds ($\epsilon_{rubber\ matrix} = \epsilon_{compound}/(1 - \phi^{1/3})$).

It can be observed that the strain at fracture initiation of the filled compounds is (i) lower than that of the unfilled rubber, (ii) close to the strain at which the maximum chain extension occurs but (iii) smaller than the strain at crystallization onset.

Taking into account the strain amplification due to the presence of the rigid particles of the filler, the strain of the rubber matrix in the filled compounds is close to that of rubber in the unfilled one (figure 3b).

In figure 4a the fracture toughness of pre-strain softened compounds are plotted versus the value of the applied $\epsilon_{pre-strain}$ and compared to those of the pristine compounds ($\epsilon_{pre-strain} = 0$).

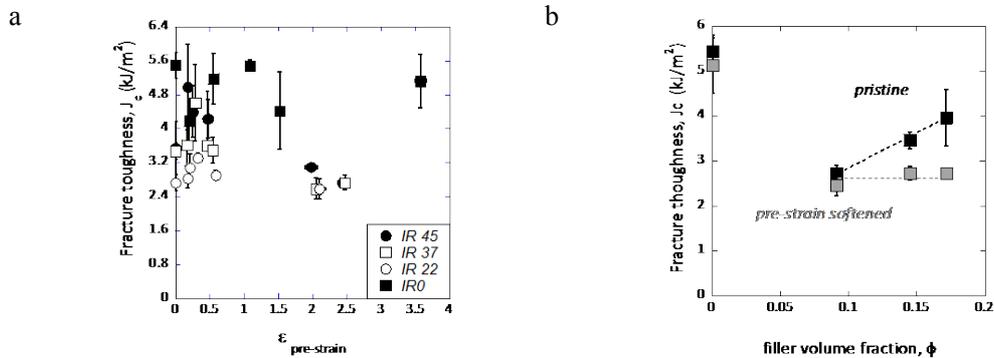


Figure 4 Fracture toughness as a function of pre-strain deformation (a) and filler content (b).

It can be observed that pre-strain softening affects the filled compounds fracture toughness only if it has been performed at a strain higher than the strain at crack onset of the relevant pristine materials (all occurring around 1%), that is if $\epsilon_{pre-strain} > \epsilon_{crack\ onset\ pristine}$. For these conditions: (i) J_c does not seem to be significantly dependent on either the filler content or the value of $\epsilon_{pre-strain}$, (ii) the strain at crack onset for the pre-strained compounds is similar to that of the pristine ones (figure 3a). In figure 4b J_c is plotted as a function of the filler content for both pristine and the pre-strain softened compounds for which $\epsilon_{pre-strain} > \epsilon_{crack\ onset\ pristine}$. It can be observed that the fracture toughness of the filled compounds is always lower than that of the unfilled one. Further, for the pristine compounds, J_c increases with the filler content, while for the pre-strained compounds it seems to be fairly constant and close to the fracture toughness of IR22.

The increase in the pristine compounds J_c observed as filler content increases could be correlated with the dissipative deformation of the structure, which characterizes these silica

filled compounds. In figure 5 the dissipated energy fraction, measured for each compound at its $\epsilon_{crack\ onset}$, is plotted versus the filler content for both pristine and pre-strain softened compounds: for the latter the dissipated energy is fairly constant, not affected by the filler content and close to that of the unfilled compound, while for the pristine compounds, the dissipated energy increases with the filler content.

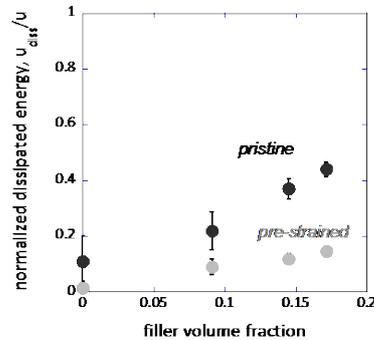


Figure 5 Dissipated energy fraction at crack initiation vs. filler content.

Referring to literature [6], small strain modulus dependence on filler content (data not reported in this contribution) suggests that for filler content higher than 0.09 the material has a “supernetwork” structure, characterized by bound rubber connection zones bridging particles clusters. The higher the filler content, the more extended the “supernetwork” and the higher the energy dissipation related to the network rupture. In the pre-strain softened compounds, the “supernetwork” structure has been destroyed and the rubber matrix dissipates similarly, irrespective of the filler content.

Conclusions

The obtained results suggest that:

- the energy dissipation, related to the super network rupture, is responsible for the higher fracture toughness found in pristine materials in comparison to that of the pre-strained compounds;
- the strain at the crack tip at fracture onset is nearly the same for pre-softened and pristine compounds and further seems to occur when the matrix rubber reaches a critical value.

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