A swelling study of process-induced and deformation-induced anisotropy of filled rubbers

V. A. Fernandes & D. S.A. De Focatiis
University of Nottingham, Nottingham, United Kingdom.

ABSTRACT: Processed but undeformed rubber specimens were swollen in appropriate organic solvents, and their linear dimensions and mass were recorded before swelling, in the swollen state, and after drying. Rubber specimens were subjected to four load-unload cycles of uniaxial and equibiaxial mechanical deformations, resulting in varying degrees of permanent set depending on the rubber and on the deformation. In the rolled rubbers, anisotropy of swelling was observed in the rolling direction. Likewise, a clear increase in the swelling ratio in the direction of deformation is observed in all the materials during uniaxial deformations, with more minor changes in the other two dimensions. It is possible that equibiaxial deformation allows a higher anisotropy in the two directions of deformation, reducing the thickness swelling observed due to the processing method.

1 INTRODUCTION

It is well known that cross-linked elastomers swell in the presence of organic liquids, and useful relationships between the swelling-induced increase in configurational entropy and the modulus of the rubber were obtained many decades ago by Flory (1942) and Flory & Rehner (1943) using the free energy of chain stretching and mixing in the solvent. Further was presented by Treloar (1950) years later analysing the strain involved. Many uncertainties can be found in this theory to obtain the average molecular weight between cross-links, M_c (Valentín et al., 2008). Nevertheless, it is still one of the fastest and simplest ways to analyse changes in the rubber network under the interaction with a solvent. Other properties such as the entanglements of the chains can be examined using in the Flory-Rehner approach, like the investigation of Schlögl et al. (2014).

Most studies to date have focused on ideal unfilled rubbers, cross-linked to produce an isotropic network of chains (Ogden & Roxburgh, 1999, Qi, 2004). This assumption does not include the induced anisotropy due to deformation. Recent work by Itskov et al. (2006) and Machado et al. (2012) indicates that the network changes to an anisotropic conformation due to stretching of the rubber. Machado et al. (2010) even proved experimentally that up to a 45° turn in the subsequent deformations with respect of the pre-strain, a softening will be exhibited in the mechanical response. Diani et al. (2006) recently adapted their constitutive model to add a strain energy density in order to include the effect of permanent set and anisotropy.

Chai et al. (2013) included the solvent interaction during deformation of a rubber. An obvious decrease in the Mullins effect compared with the mechanical response of dry specimens is observed. These investigations indicate that the deformation history of the material creates changes in the network and can also modify the solvent-polymer interaction.

From the point of view of the manufacturing process, an induced deformation is applied during the vulcanization. This can also lead to an initial anisotropy than can influence in the swelling process and even in the mechanical response.

In this study, the directionality of the swelling phenomenon in a series of commercial filled elastomers is explored. Particular attention was taking to two manufacturing process widely used in the rubber industry: sheet rolling and compression moulding. The deformation-induced anisotropy under uniaxial and equibiaxial stretches deformation are also presented.

2 EXPERIMENTAL SETUP

2.1 *Materials*

Five cross-linked carbon black filled elastomers were studied. Two of these were manufactured by compression-moulding: a sulphur cross-linked oil extended ethylene-propylene-diene rubber com-

pound, EPDM1, and a commercial filled natural rubber compound, NR. Sheets of ~0.5mm in thickness were cross-linked by compression moulding into 150mm × 150mm flash moulds using a Daniels heated press at 160°C for 13 7.50 minutes for EPDM1 and 10 minutes for NR (De Focatiis, 2012). The vulcanization conditions used were recommended by the manufacturers.

Three further elastomers were obtained in sheet form following rolling processes: a nitrile butadiene rubber compound, NBR, a chloroprene rubber compound, CR, and a further ethylene-propylene-diene rubber compound, EPDM2. The materials were provided pre-vulcanized in large 0.5mm thick sheets by J-Flex Rubber Products.

2.2 *Test protocol*

Previous to the swelling experiments, a set of specimens were prepared for uniaxial and equibiaxial tensile testing deformations.

2.2.1 *Tensile testing tests*

A first series of rubber specimens were set for uniaxial tensile deformations using an Instron 5969 tensile testing machine equipped with a 100 N load cell and an Instron counterbalanced travelling extensometer. Uniaxial test specimens were cut from sheets using a hand-operated Wallace specimen cutting press fitted with a dumbbell shape cutter type 1BA according to BS ISO 527-2. Cross-sections were measured using a Hildebrand rubber thickness gauge according to ISO 23529 in the thickness direction, and a calibrated scanner system in the width direction. For the rolled processed materials, the uniaxial deformation was applied parallel to the rolling direction (MD).

A second series of specimens were tested under equibiaxial tensile deformation using the Oxford flexible biaxial stretcher (Buckley & Turner, 1999). Rectangular shape specimens of 85 mm by 85 mm were cut from sheet. Cross-sections were measured using also a Hildebrand rubber thickness gauge.

The test protocol used for both modes of deformation consisted of four loading-unloading cycles up to a maximum strain, ε_u, for uniaxial deformation and, ε_m, for equibiaxial deformation. Five variations of ε_u were studied for uniaxial testing and four for ε_m. Each cycle was unloaded to a force of 0.1 N to avoid buckling. All tests were performed at a nominal strain rate of 0.03 s^{-1} and room temperature (20±0.1°C).

2.2.2 *Swelling experiments*

After the deformation stage, rectangular samples of 20 mm by ~5 mm were cut from the centre of the dogbone shape specimen used for uniaxial deformation, and square samples of 20 mm by 20 mm where cut from the centre of biaxial testing specimens. Four experiments for each condition were tested for uniaxial strains. In the case of the biaxial specimens, four samples for swelling can be taken for each specimen.

Table 1. Solvent properties used for swelling experiments. Density of the solvent ρ_s. Molar volume of the solvent V_s. Solubility parameters for solvent δ_s and polymer δ_p

	EPDM1	EPDM2	NR	NBR	CR
Solvent		Toluene		Dichloro-methane	THF
ρ_s (g/cm^3)		0.867		1.325	9.10
V_s (ml/mol)		106.27		84.93	81.11
δ_s(cal/cm^3)$^{1/2}$		8.91		9.68	9.10
δ_p (cal/cm^3)$^{1/2}$	8.10	8.10	8.30	10.60	9.30

To analyse the influence of manufacturing process, un-deformed rubber specimens were also used for the swelling experiments. The samples were immersed in a specific solvent for each material (see Table 1 for more properties of each solvent) for 48 hours at room temperature (20±1°C). The solvents selected should have a solubility parameter similar to the specific elastomer, allowing a good interaction between solvent and elastomer during the swelling process and equilibrium (Brandrup et al., 1990). The time in between the tensile deformation test and the immersion in the solvent was no more than four hours for all specimens.

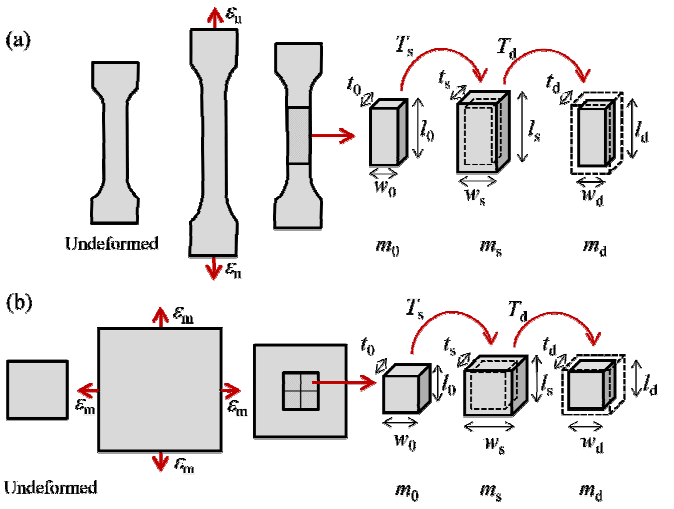

Figure 1. Uniaxial (a) and equibiaxial (b) description of the deformation test and swelling experiment stages for a sample.

The illustration showed in Figure 1 explains the different stages of the experiments and the volumetric dimensions measured. The change in mass due to swelling was recorded using a Mettler Toledo XS105 analytical balance. The volumetric dimensions of each specimen were measured using a calibrated scanner system for the length and width, and a Hildebrand rubber thickness gauge for the thickness.

All parameters were measured in three different stages: the initial stage before the immersion of the elastomers in the solvent; after T_d=48 hours of immersion, and after T_d=48 hours of removing the specimens from the solvent. The swelling ratio, ϕ_s was calculated as the variation of mass after and during swelling stage $\phi_s = m_s / m_d$. Both ϕ_s and the di-

mensional ratios λ were calculated using the values after T_d as reference value for unswollen rubbers. It is assumed that after the swelling process, all oils and soluble additives of the compound were dissolved. The values of the dry stage contain then the pure rubber-filler network. Four swelling experiments for each condition were prepared to calculate the average.

3 EXPERIMENTAL RESULTS

3.1 *Process-induced anisotropy.*

It seems reasonable to think that the manufacturing process can impart a certain degree of anisotropy if a considerable pressure and/or stretching is applied during vulcanization. A compression-moulded vulcanization method implies a high load in the thickness direction, giving a certain liberty of the chain to move in the perpendicular direction. In the case of a sheet rolling technique, a considerable stretching is induced parallel to the rolls, together with the compression in the thickness direction. An easier way to observe the loads for both methods is represented in Figure 2.

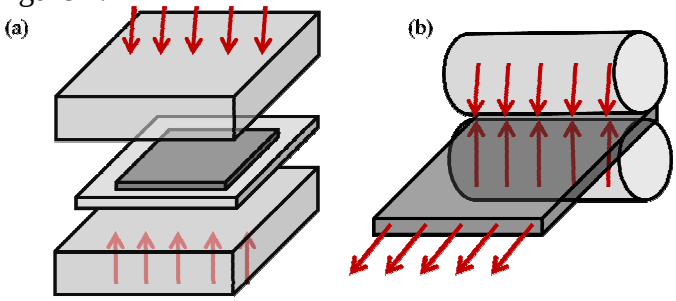

Figure 2. Representation of manufacturing process of (a) compression-moulding and (b) sheet rolling.

In an initial stage, the influence of the manufacturing process can be studied by the analysis of the changes in the dimensions of the samples during the swelling stage. In Figure 3 the ratio of each dimension is reported for all five materials. As is clearly observed, all rubbers swelled more in the thickness direction than in the other directions, related with the fact that in both processing methods, the thickness experiences large change due to compression during moulding and rolling.

For the compression-moulded rubbers, EPDM1 and NR, the swelling is symmetric in the perpendicular directions of the compression. The isotropy in these two directions is expected as the chains have the same degree of freedom to move and accommodate during the vulcanization. It is interesting to notice the highest swelling ratio in the thickness for NR. Even though EPDM1 and NR have the same processing method, they structure and vulcanization conditions differ between then. This observation may indicate that the possibility of anisotropy will be also conditioned by the rubber structure.

In the case of the rolled rubbers, anisotropy of swelling was also observed between the rolling direction and the transverse direction, having the lowest swelling ratio in the direction parallel to the rolling. It is important to remember that the rolling and vulcanization processes are occurring simultaneously. A network with chains slightly oriented in the direction of rolling can be created. As a result, when the swelling equilibrium is reached, the chains can relax moving in a direction opposed to the initial orientation. Consequently, a higher swelling in the perpendicular direction is observed.

Even though the materials have not passed through any induced deformation, they have an initial preconditioning of the network, regardless of being very often described as non-deformed specimens.

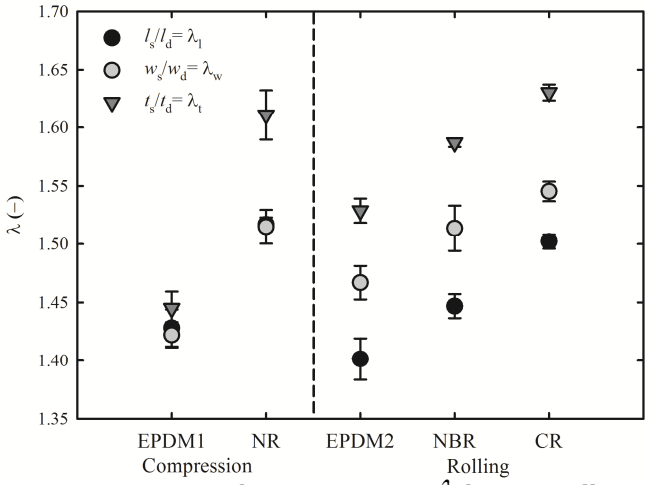

Figure 3. Dimensional ratio variation λ during swelling for rubbers manufactured by compression-moulding and rolling.

3.2 *Deformation-induced anisotropy.*

When a deformation is applied to filled-rubbers, the well-known Mullins effect can be observed in the constitutive response This phenomenon is related with a change in the structure, and that can be attributed to either rearrangement or breaking of the chains (Diani et al., 2009). Any of these theories are still difficult to prove. Swelling experiments after uniaxial and equibiaxial tensile deformation can give an indication of what is occurring in the network if a change in the solvent absorption and volume distribution is observed.

3.2.1 *Swelling ratio variation*

When the swelling ratio, ϕ_s, is calculated from the change in weight during swelling, an evident growth in ϕ_s is observed with increasing of deformation, as it is reported in Figure 4 for the five elastomers. For both modes of deformation, a higher absorption of solvent is presented when the specimen is subjected to higher deformations, giving an insight of a modification in the structure that allows more solvent to be contained within the network expanding the chains. It is possible a change in the free volume of

the network, allowing an increase in the diffusion of the solvent. However, this can be associated with disentanglements of the chains, rupture of filler-rubber, filler-filler and/or rubber-rubber points. Any of the cases, it seem that a permanent change occurs in the system.

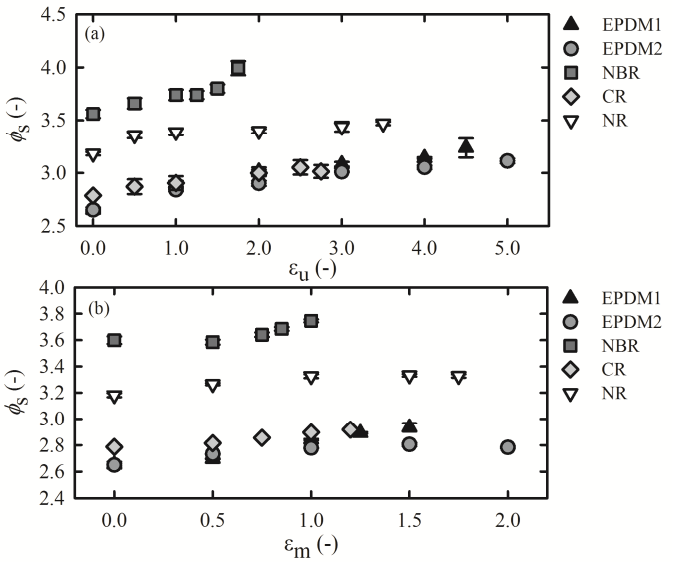

Figure 4. Swelling ratio ϕ_s for rubbers under (a) uniaxial ε_u and (b) equibiaxial ε_m deformations.

3.2.2 *Three-dimensional volume variation*

The anisotropy induced during deformation can be studied using again the variation during swelling in the three dimensions of the sample. By using two modes of deformation, it was possible to notice how the ratio varies depending of the conditioning. The variation of λ are presented for each material in the Figures 5-9 for ε_u and ε_m.

During uniaxial deformation, a clear increase on the swelling ratio in the direction of deformation, λ_l, is observed for all cases. Minor changes in the other two dimensions is reported. Independently of the manufacturing process, there is a clear anisotropy in the direction of the stretch. It is interesting to notice that the values of λ_w and λ_t, independently of the material, tend to merge to a more similar value with the increase of strain. EPDM2 might represent the most obvious anisotropy, with an increase of λ_l around 20%. On the other side, NBR has an increase of no more than 8%. It is also important to notice that NBR is the material with lower ε_u, as the strain to failure is around ε_f=1.95. This restriction does not allow to reach considerable high deformations.

In the case of the equibiaxial deformation, there is a progressive increase in the ratios λ_l and λ_w, and a slight reduction of λ_t. Likewise, λ_l and λ_w will keep more or less the same swelling ratio difference at any strain magnitude for all the compressed and rolled rubbers. As the deformation is equal in both axes, the mechanism occurring is equivalent.

It is necessary to notice that the equibiaxial magnitude ε_m of strain is considerable less than the uniaxial values ε_u. During a simultaneous equibiaxial deformation, the constrains in the two axes increase considerable the energy of the system.

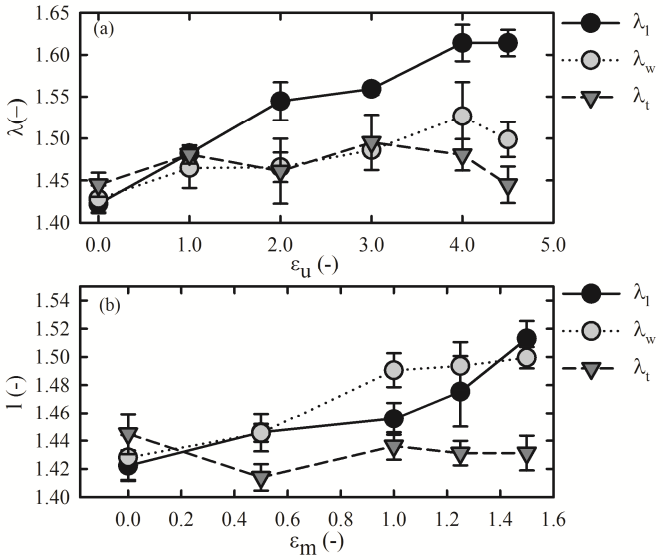

Figure 5. Dimensional ratio λ variation for EPDM1 under (a) uniaxial ε_u and (b) equibiaxial ε_m deformations.

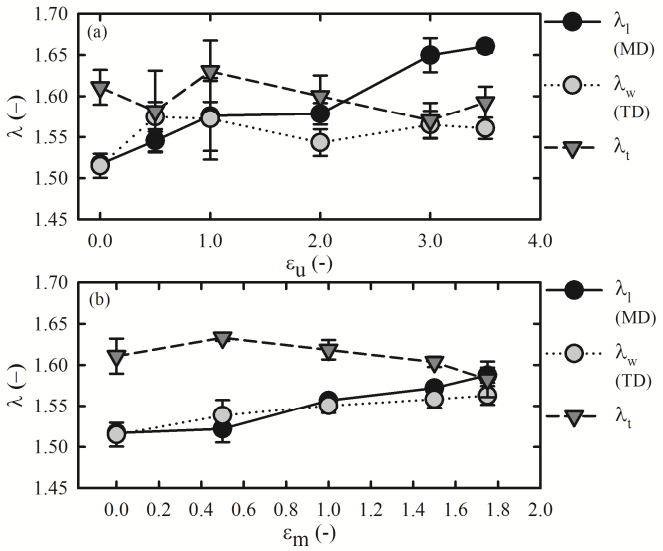

Figure 6. Dimensional ratio λ variation for NR under (a) uniaxial ε_u and (b) equibiaxial ε_m deformations.

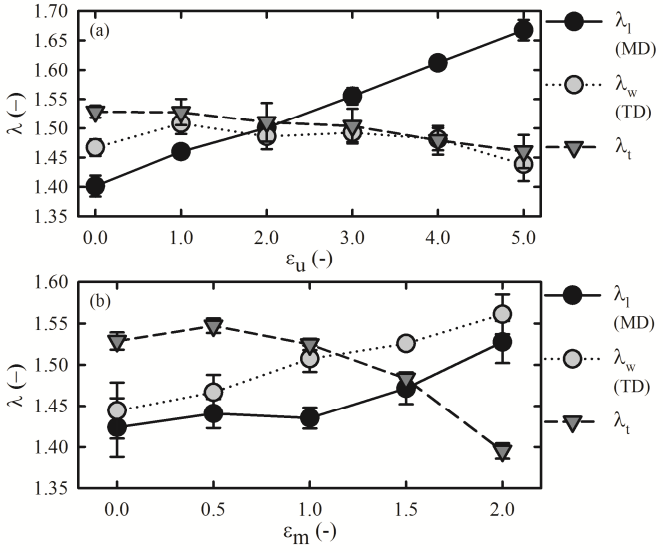

Figure 7. Dimensional ratio λ variation for EPDM2 under (a) uniaxial ε_u and (b) equibiaxial ε_m deformations.

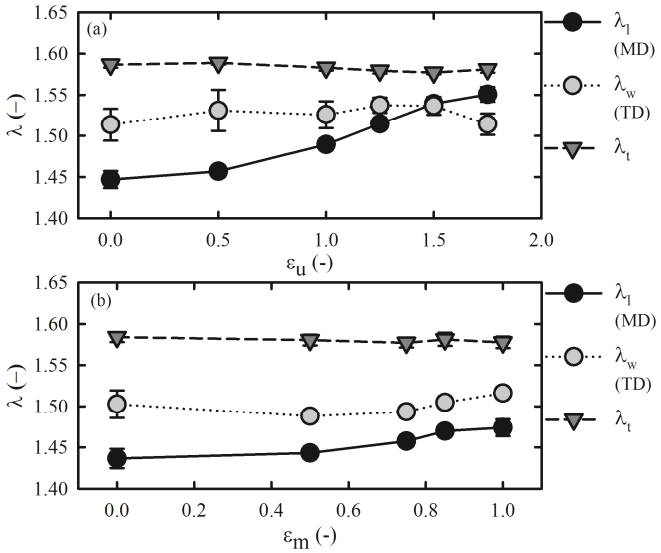

Figure 8. Dimensional ratio λ variation for NBR under (a) uniaxial ε_u and (b) equibiaxial ε_m deformations.

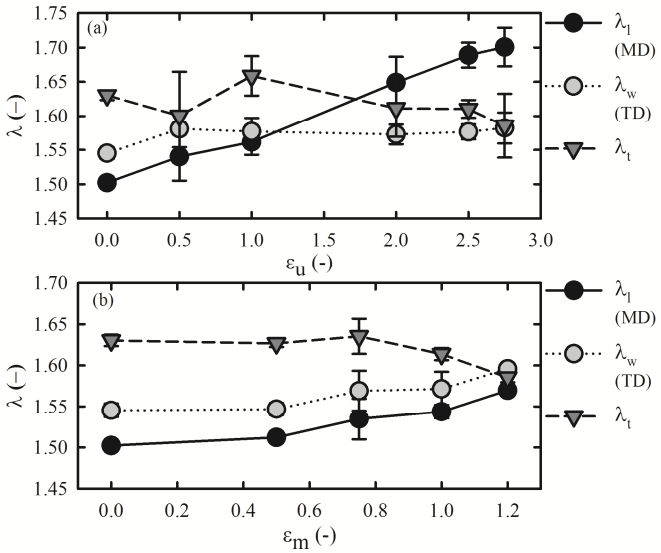

Figure 9. Dimensional ratio λ variation for CR under (a) uniaxial ε_u and (b) equibiaxial ε_m deformations.

4 DISCUSSION

It is clear that stretching a filled rubber will provide a change in the network, creating a visible anisotropy. This can be interpreted as an indicator of damage to either the network of chains or to the filler network in the direction of deformation. To try to understand the mechanism, the system can be described as a rubber matrix with a rubber network and a rubber-filler network. Numerous experimental data and models proposed gives enough evidence that the major contributor to the softening is the filler reinforcement (Diani et al., 2009).

The free energy of the filler-rubber and even the filler-filler (aggregates) interaction is lower that the chains bonds and crosslink joints. In this case, during deformation, the weakest points of the rubber-filler network will be the first ones to detach. Subsequent loads below the previous deformation will then require less energy, showing the softening effect. This do not implies that a rubber-rubber network is not happening simultaneously. The separation of the rubber-filler points can bring a rearrangement of the rubber-rubber network such a chains disentanglements that should be accounted in the mechanism occurring during stretching. In the swelling scenario, the detached of the rubber-filler network points will allow more free volume for the diffusion of the solvent in the stretched direction. The permanent set presented in all materials during the tensile tests is an evidence of a permanent change network.

The experimental data presented here seems to match with the network evolution and anisotropy theory presented by Dargazany & Itskov (2009). The micro-mechanism presented explains a simultaneous deformation and damage mechanics in the rubber-rubber and filler-rubber networks.

The phenomenon observed with the rolled materials as a consequence of manufacturing seems to have a different approach. It is possible that during the manufacturing, there is no change in the rubber-filler network. The vulcanization is still in process, allowing the movement of the chains in the rolling direction instead of the alteration of the rubber-filler network.

5 CONCLUSIONS

It was shown that the swelling experiment can be used to observe the variation in de volume dimensions ratio in order to analyse orientation of the chains. A clear anisotropy is induced during two of the most common manufacturing processes used in the rubber industry. The experimental data showed seems to indicate a more permanent damage occurring during deformation, involving more the rubber-filler unions than damage in the rubber-rubber network.

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