Structural-mechanical AFM mapping of overstressed zones in stretched filled natural rubber

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Abstract

Surfaces of cracks in the stretched natural rubber filled with silica nanoparticles were studied. On the non-deformed material the notches were made and then the sample was stretched and fixed. As the result, the defects propagated deeper into the material and somehow stopped. The polymer matrix in the region of crack is in critical stress-strain state. The surface of such cracks was studied by atomic force microscope in nanomechanical mapping regime. It was found that the stiffness of the polymer in the crack is much higher than the stiffness of the material in the unloaded state. This is due to strain-induced crystallization and orientation of natural rubber. The formation of elastomer strands oriented orthogonal to the axis of the crack was observed. It was shown that the stiffness and structure of the polymer and oriented strands depend both on the filler fraction and the distance from the crack tip.

1 Introduction

Natural rubber (NR) and its vulcanizates are extensively used in rubber industry. Therefore, it is important to understand the mechanisms responsible for material failure and especially to prevent in-service failure of materials. The strain of a polymer in a static crack of the stretched material reaches its limiting value, and any increase of loading may lead to a further growth of the defect. Investigations the structural-mechanical properties of such regions on micro- and nano- levels provide insight into the processes involved into the resistance of NR vulcanizates to failure. Until recently, in situ studies of the microstructure of cracks and ruptures in rubber were performed by SEM under low vacuum conditions [1]. However, this procedure was not effective in achieving high resolution ($< 10\mu m$) necessary to observe changes taking place in the NR samples at the submicron scale. The unique advantage of NR is strain induced crystallization. Application of wide-angle X-ray diffraction (WAXD) has made it possible to evaluate the degree of crystallization of NR around a crack tip with spatial resolution of $100\mu m$ and more [2].
In the present study, we have used complementary high-resolution atomic force microscopy (AFM) allowing not only observation of the structure of cracks till the

scale of separate filler inclusions and oriented polymer fibrils, but also measurement of the stiffness of overstressed zones in the material being in a crystalline phase.

2 Materials and methods

In this work the natural rubber vulcanizates filled with silica oxide (mass fraction 0, 5, 30, and 50 wt. parts) Aerosil (nanoparticles $20nm$ in size) were used. For testing, thin-strip specimens were clamped in a miniature tensile device. Small-size notches were cut at the edges of the specimens, and after that they were stretched and fixed. To observe changes in the material in the crack, an AFM probe was placed in the "bottom" of the crack (Fig. 1).

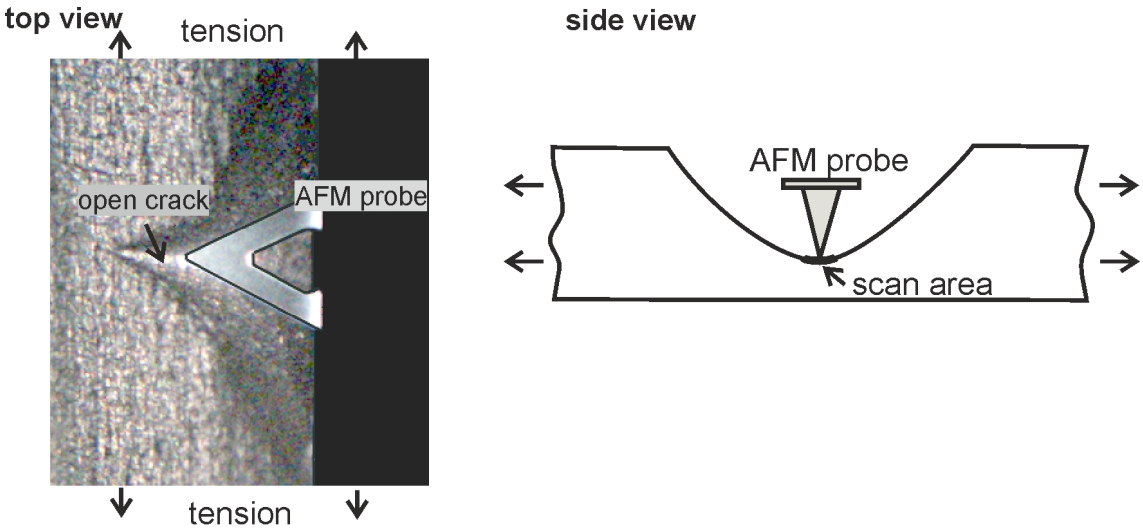

Figure 1: Illustration of AFM crack scanning

The structural-mechanical properties of surfaces were studied with an AFM Dimension Icon in PeakForce regime. Every point on the surface was subjected to nanoindentation, and, apart from a relief height, a force curve $F(z)$ - a relationship between the indentation force F applied by a cantilever to the specimen surface and its vertical displacement z was obtained. The high indentation rate allowed to get rid of undesirable inelastic interactions and to determine the high resolution mechanical characteristics of the material surface. The original algorithms based on the Maugis-Dugdale [3, 4] model of elastic interactions were used to fit the force curves. The result of this processing is the material stiffness at a given point.

According to the assumed properties of the material, AFM cantilevers of different stiffness calibrated by the method of free thermal oscillations were used. Figure 2 presents the examples of force curves obtained in PeakForce mode by scanning the NR surface areas with different stiffness (crystallization degree). The result of the Maugis-Dugdale approximation is shown in Fig.2b: markers - experimental data; lines - model fitting. The negative values of the indentation depth from Fig.2b correspond to the case when the material is entrained by the probe during its retrace.

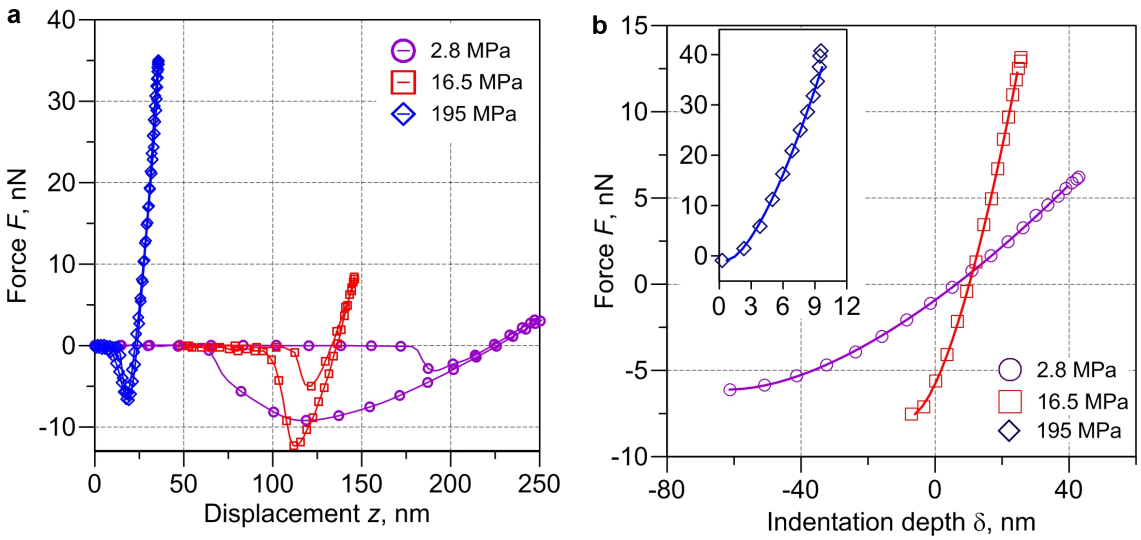

Figure 2: Force curves obtained for NR in different phases (a) and the corresponding identification depth (b)

3 Results

The surface relief and elastic modulus of NR in the area without defects are illustrated in Fig. 3.

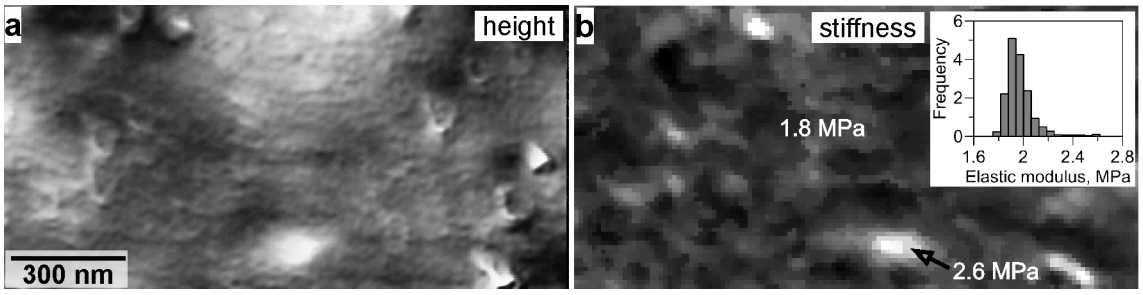

Figure 3: AFM-images of the NR surface height (a) and the map of the elastic modulus (b). Hereinafter the dark areas correspond to low values, while the light areas - to higher values

An inset in Fig.3b shows the distribution of the elastic modulus; its mean value is $2MPa$, which is close to macroscopic measurements. Note that in the elastic modulus map there are relatively soft ($1.8MPa$) and more rigid regions ($2.6MPa$). Probably, this is associated with the local inhomogeneities of crosslinks.
The structural-mechanical properties of the material surface in a cross crack are dependent on a distance away from a sharp crack tip. Figure 4 presents the AFM-images obtained around the crack tip and in the vicinity of the crack opening in the stretched unfilled NR (schematic representation of scan positions are shown in the insets). Near the crack tip there are extended polymeric strands moving from the edges of the crack to its axis and exhibiting a bend towards the crack tip (indicated by вГЧАвГЄ in Fig. 4a). Away from the tip or if the crack has a form of trench crossing the whole sample, the parallel polymer strands and local

longitudinal ruptures occur on the specimen surface.
Measurements have shown that the NR stiffness around the crack tip is 300 MPa, and in the crack opening - 600 MPa. The indentation depth is 9 nm and 5 nm, respectively. Such a high stiffness points to the fact that the material is in an oriented crystalline phase.
The stiffness of the material in a crack reaches its maximum values at a distance of $\pm 3 - 4 \mu m$ away from the rupture axis, and then it reduces sharply. Elastic modulus profiles along one of the crack cross-sections (dashed line) are given in Fig.4.

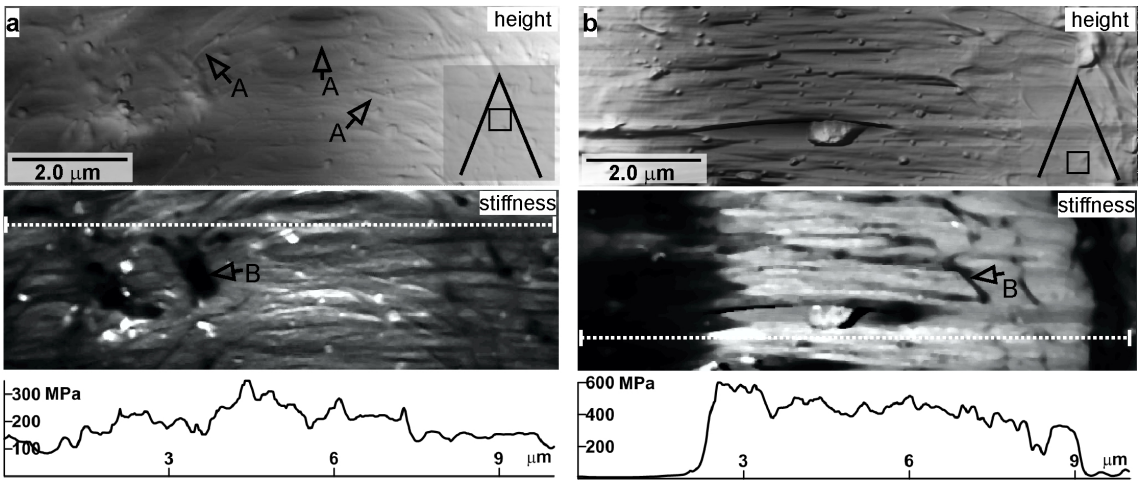

Figure 4: AFM-images of the relief and stiffness in cracks of the unfilled NR around the crack tip (a) and in opening (b). Explanations are provided in the text

The close-up views of strands at the rupture tip are given in Fig. 5b. Their cross-section size is 8...30 nm. The height of the visible part of the strand is 6...8 nm. Figure 5a shows a region at the crack tip that is free of strands (as in the center of Fig. 5b). The image is obtained using a sharp probe. It is seen that the structure of smooth regions in higher resolution is composed of a network of nanofibrils. The maximum visible transverse dimension of a fibril is 4 nm (validity is limited by the size of the probe tip). The height of the visible fibril part is 0.5...0.7 nm. If it is supposed that the fibril has a circular cross-section and rises half its size above the surface, then the true transverse dimension of these fibrils is 1.0...1.4 nm. Contrast in the probe-surface adhesion map is indicative of a difference between the mechanical properties of the polymer in fibrils and the surrounding material. Low adhesion (dark areas) corresponds to a more rigid material.
On the rupture surface there are also parts exhibiting stiffness (B in Fig. 4) less than that of the surrounding material. The stiffness of these structures (Fig.5c) is an order of magnitude lower than the stiffness of the surrounding material. They seem to be partially crystallized fragments of the polymer broken due to crack propagation.
An incorporation of filler into the polymer increases the number of strands in the crack. The rupture surface of NR with 5 wt. parts of filler is characterized by a larger number of strands (Fig.6). The cross-section dimensions of strands are 20...30 nm (Fig. 6a). The stiffness of the strand reaches 800 PËPa, and the stiffness of the surrounding material is 200 PËPa (Fig. 6b).

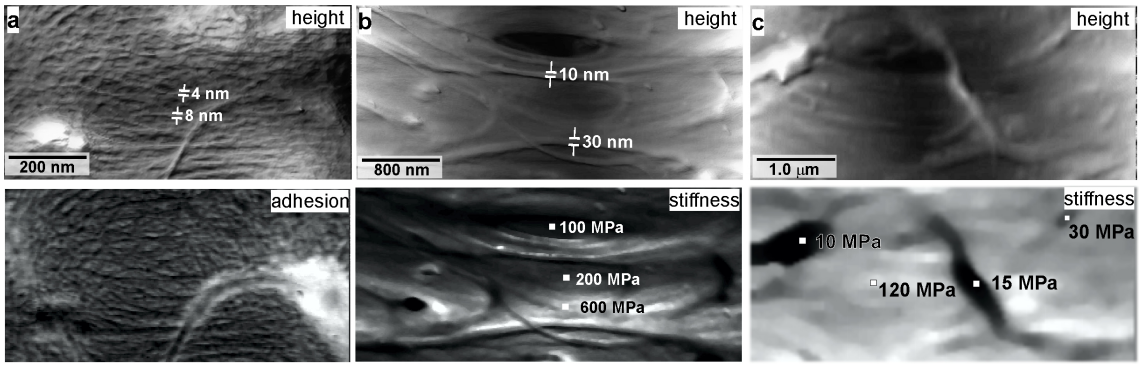

Figure 5: AFM-images of nanofibrills (a), stiff strands (b) and soft regions (c) on the unfilled NR crack surface

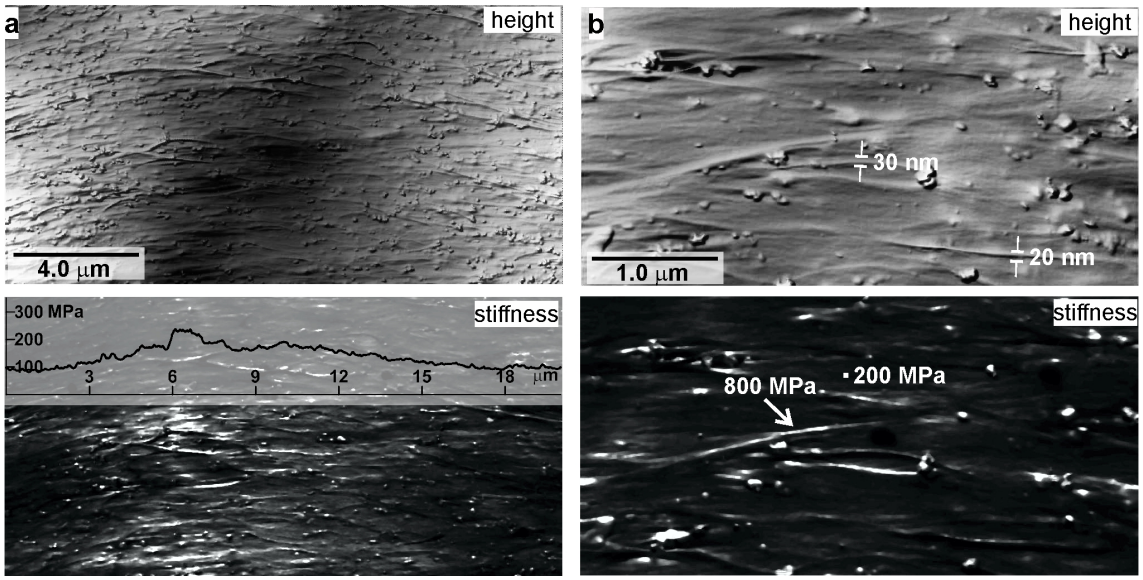

Figure 6: AFM-images of the height (a) and the stiffness (b) of the crack surface of NR with 5 wt. parts of filler

As the filler content increases, the number of strands increases as well and their length decreases. Figure 7a, b presents the images of cracks in NR with 30 and 50 wt. parts of filler. Filler distribution in the material is inhomogeneous, which causes the occurrence of regions with high and low concentration of inclusions. The highest stiffness (600...800 PËPa) appears in the regions free of filler, where the polymer deformation is maximal. The strand sizes are comparable with the sizes of inclusions.

4 Conclusion

The surfaces of cross notches in the stretched natural rubber filled with silica oxide nanoparticles were investigated. Use of atomic force microscopy made it possible to study the structural-mechanical properties of the surface of these cracks. It has been found that the stiffness of the polymer in the crack (200вГ з600 PËPa) is many times

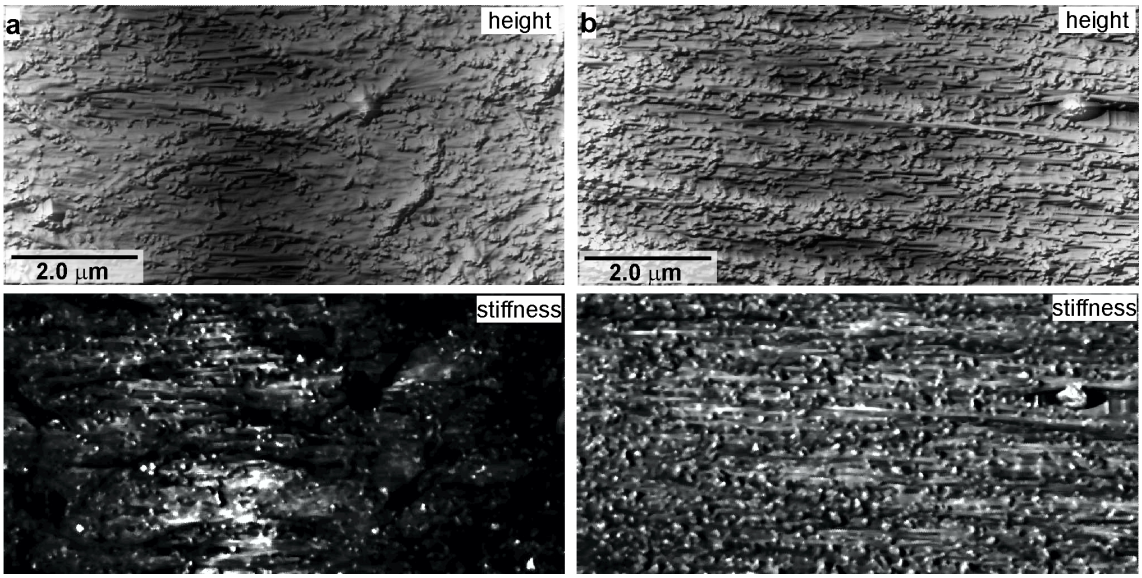

Figure 7: AFM-images of the height and stiffness of cracks in NR with 30 (a) and 50 (b) wt. parts of filler

as large as the stiffness of the material in an unloaded state ($2P$). The generation of the oriented elastomeric strands orthogonal to the rupture axis was observed. It is shown that the polymer stiffness, the structure and stiffness of strands are dependent on the filler concentration, as well as on the distance away from the crack tip.

Acknowledgements

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References

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