AFM relaxation studies of rubber vulcanisates

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Overview

Stress relaxation in silica-filled epoxidized natural rubber (ENR 25), natural rubber (SMR L) and synthetic rubber, polybutadiene (cis-BR) was examined using the depth-sensing indentation method with a pyramidal diamond tip. In this study, the force-displacement curve was obtained as each material was indented by 2µm and this indentation held for a period of time before being released. Stress relaxation was observed as a decrease in force during a hold period at maximum strain. From the known geometry of the indentor tip, the stress was calculated and Hardness and Elastic Modulus were estimated.

Surface topography (AC mode)

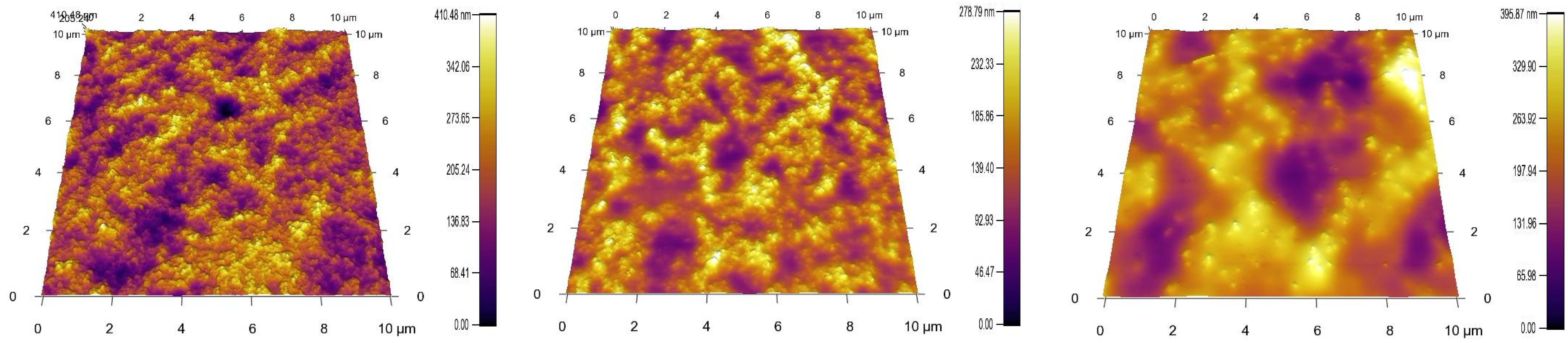


Figure 1. AFM topography images of silica-filled rubbers; ENR 25, SMR L and cis-BR; 10µmx10µm scan area; cantilever AC240TS Olympus (k=2N/m, f_o=70kHz)

Direct measurement of area function

- Ideal tip geometry yields the following area-to-depth ratio: $A_c = 24.5h_c^2$
- Real tips are not perfect! Therefore indenting tip is placed as sample and imaged with high aspect ratio AFM tip.

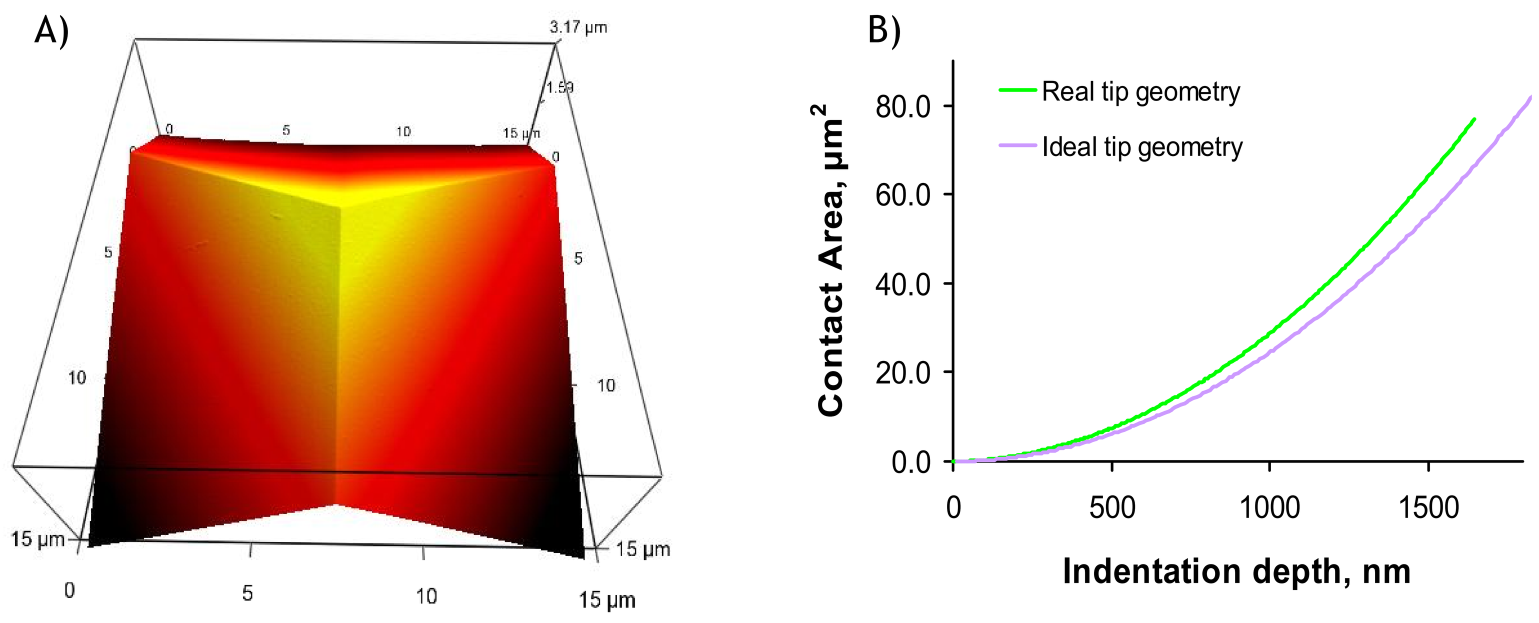
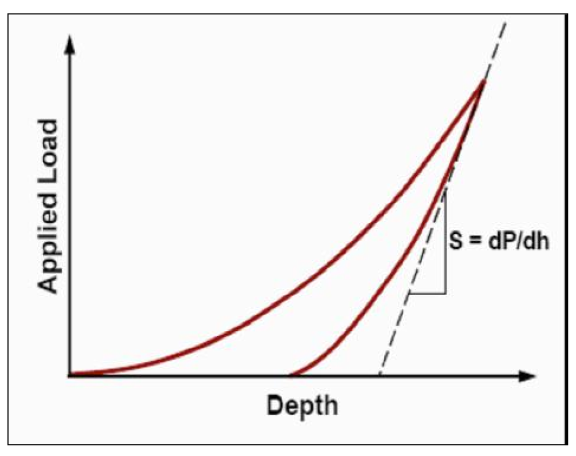


Figure 2. A) AFM image of Berkovich tip; B) Area function for Berkovich tip

Olivier and Pharr model

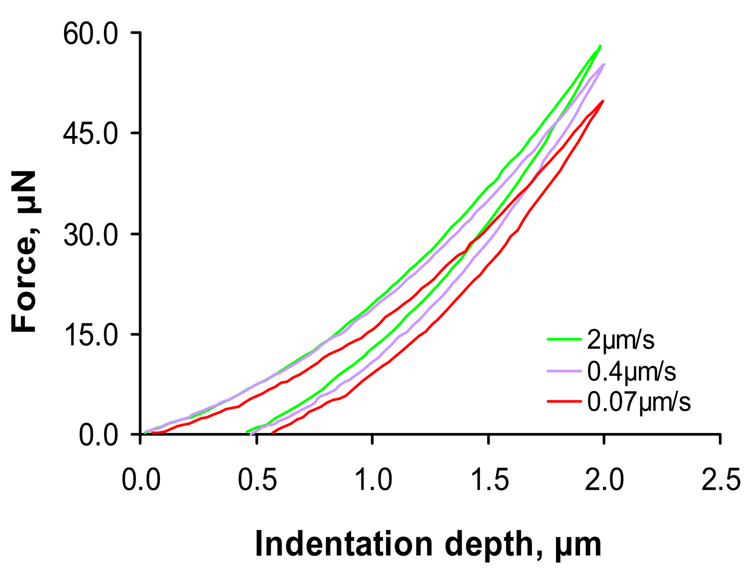


- Fitting the unloading portion of the load displacement data with a power-law relation
- Obtaining the reduced Modulus, E_r from the stiffness, S, and the projected Contact Area, A_c (where E is the Young modulus and ν is the Poisson ratio, i and s refer to the indenter and sample respectively)

$$S = \frac{dP}{dh} \qquad E_r = \frac{\sqrt{\pi}}{2\beta}\frac{S}{\sqrt{A_c}} \qquad \frac{1}{E_r} = \frac{(1-\nu^2)}{E_i} + \frac{(1-\nu_i^2)}{E_s}$$

Figure 3. Olivier & Pharr model for data analysis

Effect of loading rate on Modulus and Hardness of filled ENR 25



Loading rate µm/s	P_{max} µN	Hardness MPa	Young's Modulus MPa
2	58.56	1.43	6.59
0.4	55.47	1.24	6.37
0.07	50.26	1.08	5.84

Figure 4. Force vs. indentation depth

- The slower the loading rate the more the material can relax over that time
- For viscoelastic material a pause time has to be applied at maximum indentation before unloading

Indentation stress relaxation in silica-filled vulcanisates and Conventional stress relaxation at 10% strain (Instron)

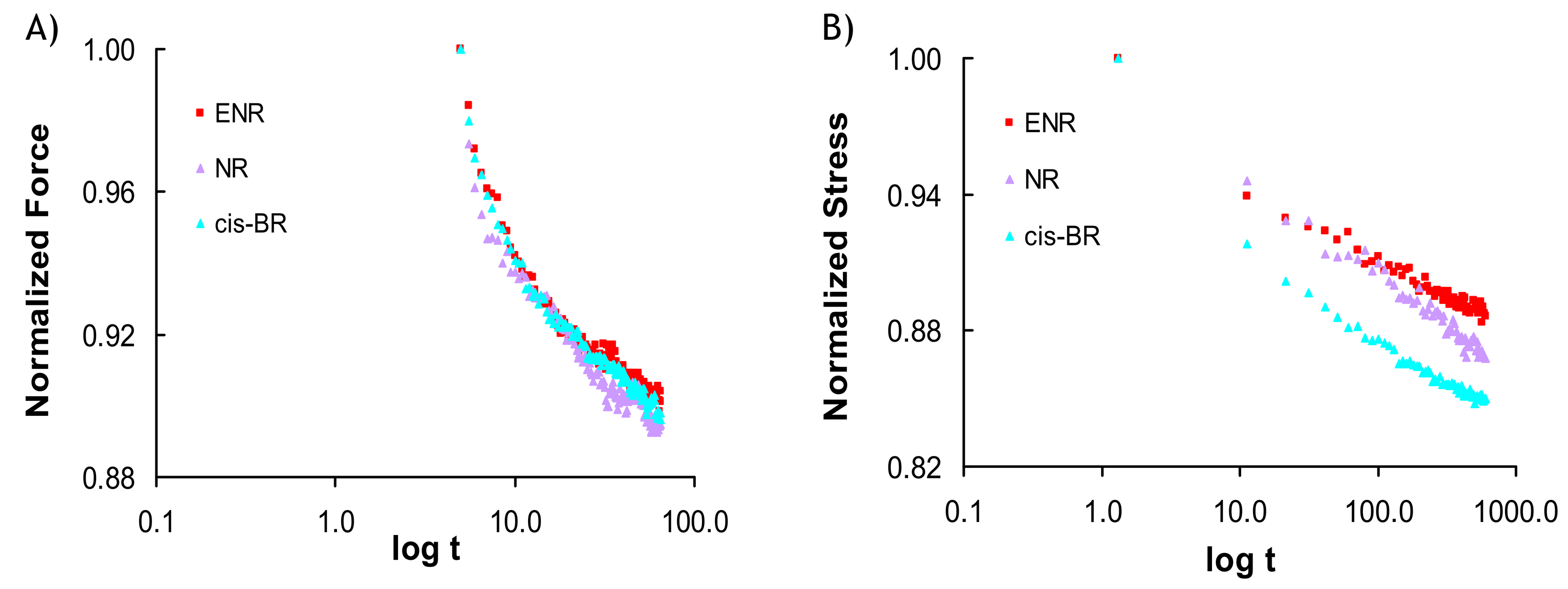


Figure 5. A) Indentation and B) Conventional (10% strain) stress relaxation

- Conventional stress relaxation measurement shows that the weaker polymer-filler interaction the greater relaxation is observed
- No significant difference between rubbers was observed in indentation stress relaxation

Influence of pause time on Hardness

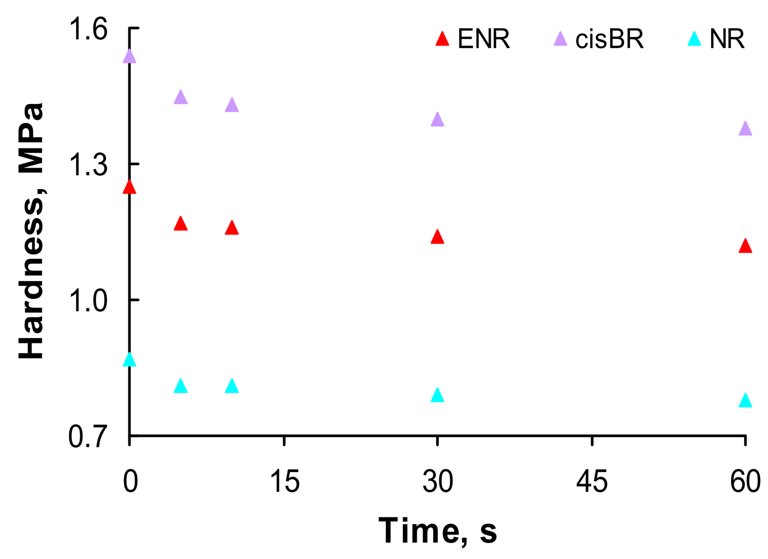


Figure 6. Hardness vs. pause time

- For all compounds a decrease in hardness with pause time is observed
- In each case 60s of pause time is sufficient to reduce relaxation
- Cis-BR compound appears to be harder than ENR 25 and NR

Comparison of Hardness tests

Sample	Hardness IRHD	Hardness MPa
ENR 25	52	1.12
NR	52	0.775
cis BR	57	1.38

Wallace Microhardness tester
Spherical tip (diameter 0.4mm)
Load 153.3 mN

Asylum Research Nanoindenter
3-sided pyramid, Berkovich tip
Radius of curvature <50nm
Max. Indent. 2µm

- In both tests cis-BR compound appears to be harder compared to ENR 25 and NR
- Non-uniform filler distribution affects the measure of Hardness on a micro scale

*IRHD- International Rubber Hardness Degrees

Conclusions

- Effect of loading rate on Modulus and Hardness has been showed for ENR 25 compound.
- Due to the relaxation process a decrease in Hardness value with pause time was observed for these three rubbers.
- Nanoindentation is a small-scale, localised measurement, thus the data might be expected to differ from that given by the standard rubber tests. Non-uniform filler distribution or humidity level may affect micro/nanoindentation measurements (hardness, relaxation) hence further investigations at controlled humidity conditions are required.