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AFM Investigation of Epoxy Fracture Surfaces Indicating Nanoplasticity

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Epoxy fracture surfaces are investigated by nanomechanical atomic-force micrsocopy (AFM). Apparent *nodules* on these surfaces are likely AFM tip-convolution artifacts, which might also explain apparent modulus inhomogeneities. No modulus inhomogeneities are found on smooth ultramicrotome cuts. Investigation of a copolymer shows, however, that existing inhomogeneities can be measured indeed. AFM investigation results in plastic deformation of ultramicrotome cuts already at low forces of 50 nN, which results in a blunt topographic image and an apparently increased modulus. This suggests that thin, sharp surface features are present on ultramicrotome cuts which are plastically deformed upon AFM investigation. Super-sharp AFM imaging showed a presumably more representative image of the investigated fracture surfaces, which showed numerous depressions and vertical steps a few nanometers high. This suggests that even brittle epoxy exhibits some plasticity at the nanometer scale upon fracture.

Keywords: Polymer, Epoxy, Fracture mechanics, High resolution, Atomic-force microscopy (AFM).

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1. INTRODUCTION

Fracture surfaces have long since been investigated to obtain information on fracture mechanisms. This was, however, always difficult for unfilled thermosetting polymers like epoxy as their brittleness results in very smooth fracture surfaces. Trials to measure epoxy fracture surfaces by transmission electron microscopy of C–Pt replicates suggested that those exhibited a *nodular* morphology, which was interpreted as a sign of an inhomogeneous modulus distribution [1]. Recent atomic-force microscopy (AFM) studies seemed to support this observation [2]. Fig. 1 shows an AFM image of an epoxy fracture surface apparently showing *nodules*.

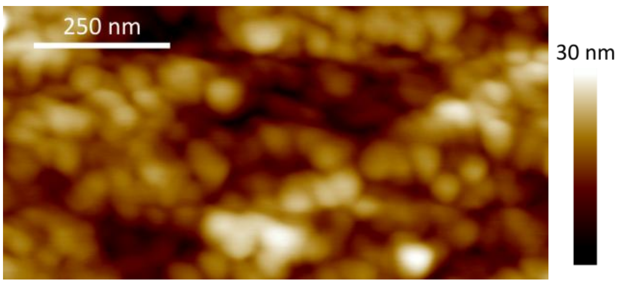

Fig. 1 – Topographic AFM image of an epoxy fracture surface, imaged with hard contact, apparently showing a nodular morphology (reprinted with permission [3])

However, later work suggested that these nodules were more likely just AFM artifacts [3]. The present work aims at adding to this discussion and drawing a clearer image of the real fracture surfaces of epoxies and the underlying fracture mechanisms.

2. EXPERIMENTAL PROCEDURE

The investigated epoxy system was a mixture of 100 parts by mass (pbm) diglycidyl ether of bisphenol A (Epikote 828 LVEL from Momentive), mixed with 89.2 pbm methyl tetrahydrophthalic anhydride curing agent and 2.00 pbm 1-methyl imidazole catalyst, which was cured at 120 °C for 8 h.

Fracture surfaces were created by manual fracturing of pre-cracked samples. Ultramicrotomy was done at room temperature with a *Reichert-Jung Ultracut* ultramicrotome using a *Diatome ultra 35°* diamond blade at 1 mm/s. A sample of acrylonitrile styrene acrylate (ASA, trade name *Luran S*) was cryo-ultramicrotomed at −110 °C.

Nanomechanical AFM investigation was done with a *MultiMode 8 AFM* from *Bruker* with a 10-μm piezo scanner in the *Peak-Force Tapping* mode, which allows scanning at given (low) contact forces and recording force–distance curves at each pixel. AFM was done in three different ways: *Soft contact* imaging was done with silicon nitride AFM probes (*ScanAsyst-Air* from *Bruker*, nominal spring constant 0.4 N/m, nominal tip radius 2 nm) at forces below 1 nN; *hard contact* imaging was done with silicon AFM probes (*RTESPA* from *Bruker*, 40 N/m, 8 nm) at forces of approx. 50 nN, resulting in deformations of 2–3 nm; and *super-sharp* imaging was done with high-resolution AFM probes (*HiRes-C19/Cr-Au* from *MikroMasch*, 0.5 N/m, < 1 nm) at forces of well below 1 nN. When imaging with hard contact, the force–distance curves are fitted to a Derjaguin–Muller–Toporov (DMT) model to determine the material's modulus at each pixel. The stated average roughness R_a was calculated from topographic AFM images of 1000 × 500 nm² for comparison.

3. RESULTS AND DISCUSSION

3.1 Tip convolution

Fig. 2 shows the very same surface as given in Fig. 1, but scanned with soft contact, thus providing higher resolution. A nodular morphology appears to be present again, but the nodules appear much smaller this time.

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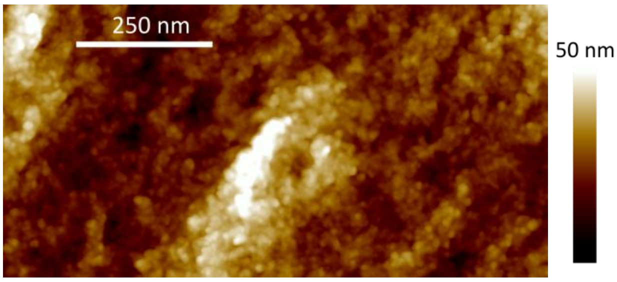

Fig. 2 – Topographic AFM image of the same surface as in Fig. 1, but imaged with soft contact; the nodules remain, but they appear much smaller now (reprinted with permission [3])

This shows that the nodular morphology visible in Fig. 1 is an AFM artifact rather than a real surface feature.

The reason for this difference lies most likely in the *tip convolution* AFM artifact, as shown in Fig. 3: If the surface features have a similar scale as the AFM probe tip, the measured image will always be a convolution of the real surface and the AFM tip. For an approximately paraboloid AFM tip, the measured surface will appear nodular. As the tip radius was much smaller for soft contact imaging, the resulting nodular artifacts appeared much smaller as well.

The very same effect results in artificially inhomogeneous modulus distribution. Fig. 4 shows a modulus image gathered simultaneously with the topographic image in Fig. 1. It appears to show pronounced modulus inhomogeneities, with the apparently hard areas being in topographic valleys. However, the underlying DMT model assumes a planar surface and can thus be used on very smooth surfaces only. The apparently harder regions in Fig. 4 are likely in positions where the AFM tip touches the surface in more than one contact point simultaneously, thus experiencing much higher resistance to deformation, which gives the appearance of a harder region.

It turned out that AFM modulus measurement is indeed very sensitive to surface roughness. Even very smooth polished surfaces ($R_a \cong 1$ nm) showed apparent modulus inhomogeneities that correlated with the surface topography, in particular if the contact forces were low and the material was therefore not deformed strongly enough by the AFM tip. If very smooth ultramicrotome

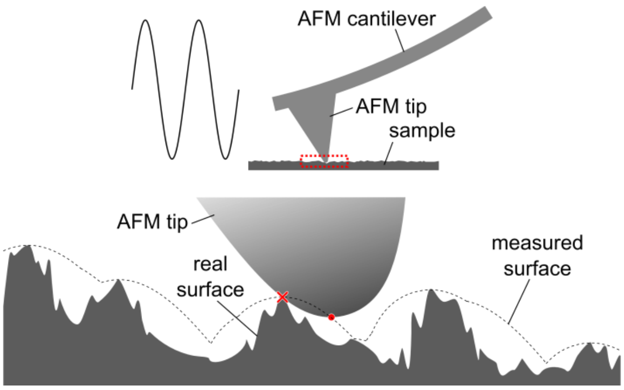

Fig. 3 – Schematic illustration of an AFM tip scanning a rather rough surface, resulting in a tip-convolution artifact; the small circle highlights the supposed contact point, while the cross highlights the actual contact point between the AFM tip and the surface (reprinted with permission [3])

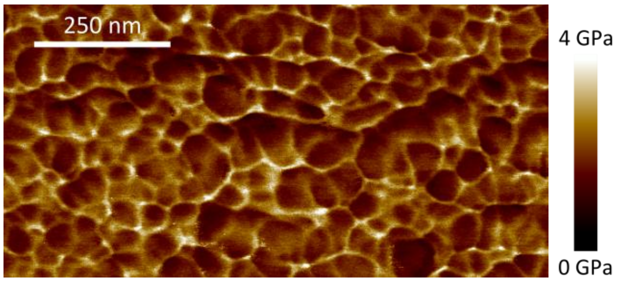

Fig. 4 – AFM modulus image gathered simultaneously with the topographic image in Fig. 1 with hard contact; the measured modulus appears to be very high in the topographic valleys (reprinted with permission [3])

cuts ($R_a < 0.5$ nm) were investigated, a homogeneous modulus distribution was measured for all investigated epoxy systems.

3.2 Real inhomogeneity and fragile features

Considering this effect, one might doubt whether it is actually possible to measure modulus inhomogeneities with nanomechanical AFM at all. Fig. 5 shows the topographic and the modulus image of the cryo-ultramicrotome cut ASA sample. A subsurface elastomeric particle causes a clear soft region which resulted in only little topographic effect upon cryo-ultramicrotomy. This shows that modulus (actually stiffness) inhomogeneities of a few hundred MPa can be measured at resolutions of below 100 nm.

The rectangle visible in the center of Fig. 5 stems from plastic deformation from an earlier AFM scan, which took place even though the contact forces were always kept as low as 50 nN. This plastic deformation causes the topographic image to look blunt and the modulus to appear slightly higher. Both effects can be explained by the presence of very thin, sharp features on

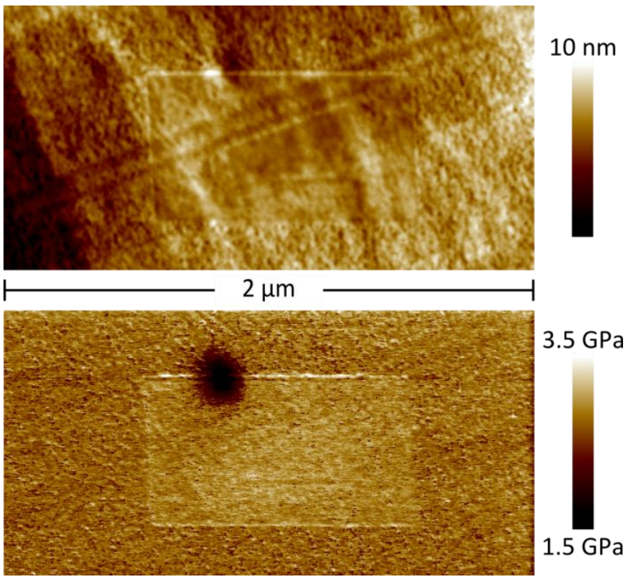

Fig. 5 – AFM height and modulus image of cryo-ultramicrotomed ASA gathered with hard contact; a subsurface elastomeric particle causes a clear soft region with minimum topographic effect; the center rectangle stems from plastic deformation by an earlier AFM scan (image courtesy of the author)

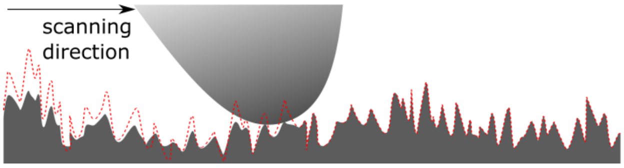

Fig. 6 – Schematic illustration of an AFM tip scanning a surface with sharp features that undergo plastic deformation already at low contact forces

the surface, as outlined in Fig. 6. In the scanned region, these sharp features have been flattened. When the surface is scanned for the second time, the absence of sharp features makes it appear blunter and as the easily deformable features are gone, the modulus will appear to be higher. This effect cannot be fully avoided if a certain deformation is necessary, like for modulus imaging. This suggests that the even smooth ultramicrotome cuts exhibit sharp features at the sub-nanometer scale.

3.3 Super-sharp AFM imaging

While the soft-contact image in Fig. 2 is less affected by tip convolution, apparent nodules are still visible in it. However, while the nodular shape of these features is most likely artificial, the features themselves are real. In order to determine the real shape of these surface features, the fracture surfaces must be imaged with super-sharp AFM tips. Fig. 7 shows an AFM image of the same surface as in Fig. 1 and 2, imaged that way.

This image shows the opposite of what the standard AFM images suggest. Rather than nodules, it shows numerous depressions and nearly vertical steps of a few nanometers height. Notably, AFM artifacts like tip convolution cannot result in depressions like these, thus this image might represent the real fracture surface.

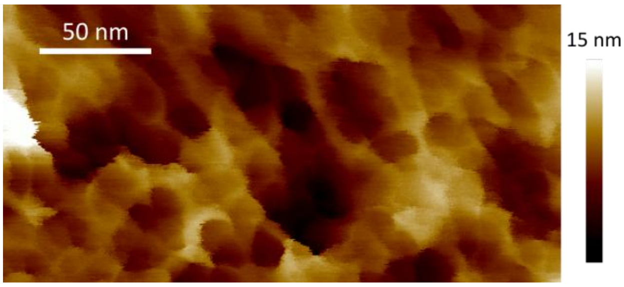

Fig. 7 – Topographic AFM image of the same surface as in Fig. 1 and 2 obtained with supersharp AFM tips

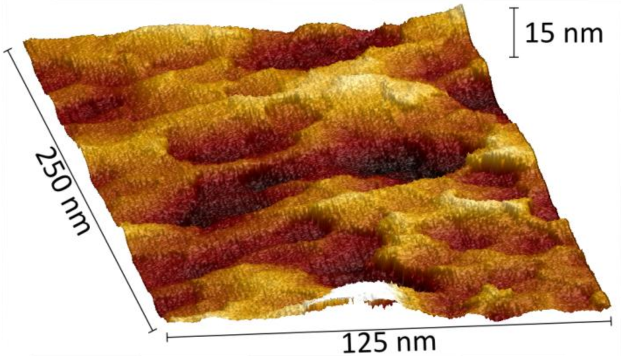

Fig. 8 – 3D view of the image in Fig. 7 (all axes drawn to scale)

The three-dimensional view of these data in Fig. 8 suggests that this material has undergone significant plastic deformation at the nanometer scale. The question to what extent epoxy undergoes plastic deformation has long since been raised [4]. These data suggest that even very brittle epoxy systems exhibit some plasticity, even if it's only at a very small scale (*nanoplasticity*, *nanoductility*). It should be noted, however, that the shape of a fracture surface depends on the crack velocity, which can vary strongly along the crack path. This image might thus represent only a small fraction of the whole fracture surface.

3.4 Simulated tip convolution

Tip convolution of a surface can be simulated by a dilation algorithm, which calculates $A \oplus B$, where A is a given surface and B is an assumed AFM tip geometry [5]. Using the highly resolved image from Fig. 7 as A and an assumed paraboloid AFM tip with a tip radius of 2 nm as B, we obtain the image in Fig. 9, which resembles that obtained with soft contact in Fig. 2 (note the different magnifications). The fact that the apparent nodules appear again in Fig. 9 supports the assumption that the observed nodules are entirely due to tip convolution.

Fig. 9 – Tip convolution simulated by a dilation algorithm on the data in Fig. 7

4. CONCLUSIONS

Scientists have long since been speculating on the shape of the fracture surfaces of brittle thermosetting polymers like epoxy. Observations of a nodular morphology were most likely afflicted by measurement artifacts, like tip convolution.

Likewise, an apparently inhomogeneous modulus distribution within the material can be explained by AFM artifacts. As long as only very smooth surfaces are investigated (R_a < 0.5 nm), like ultramicrotome cuts, no modulus inhomogeneities are measured.

Investigation of ASA showed that existing modulus inhomogeneities can indeed be measured with this method. Plastic deformation during an AFM scan stems most likely from thin, sharp features on the surface, which deform plastically already at low forces of approx. 50 nN. This suggests that even smooth ultramicrotome cuts exhibit very sharp features at the sub-nanometer scale.

Investigation of fracture surfaces with super-sharp AFM probes suggests that even very brittle epoxy undergoes plastic deformation at the nanometer scale upon fracture, which results in numerous depressions and almost vertical steps of a few nanometers height.

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