

# Use of scanning area related multiple degradation profiles for AFM assessment of polystyrene/PC<sub>61</sub>BM nanocomposite surface deterioration

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In this paper, we present a novel approach developed in order to increase the reliability and accuracy of AFM investigation of morphological changes in a nanocomposite due to exposure to the media causing its degradation. By precise sample positioning and repetitive determination of the roughness changes at specific spots, we were able to create space-related degradation profiles. As the multi-step experiment based on exposure/scanning cycle was performed, we were able to observe a unique response of investigated samples revealing spatial inhomogeneity of the material. In order to present the measurement methodology, we used polystyrene samples containing various quantities of PC<sub>61</sub>BM nanofiller (0 %, 5 %, 10 % and 20 % of mass proportion), which was exposed to 370 nm UV radiation. Obtained data can be recognized as specific fingerprints of investigated materials. The solution based on creation and analysis of degradation profiles can be particularly useful for diagnostics of nanomaterials and nanocomposites to test their resistance to various conditions.

Keywords: *atomic force microscopy; surface roughness; precise positioning; surface degradation; polystyrene nanocomposite*

## 1. Introduction

Atomic force microscopy (AFM) is a very universal diagnostic tool used in surface imaging at micro- and nanoscale. Quantitative 3D topography reconstruction along with the resolution superior to alternative measurement methods, make it very effective in terms of performing a variety of research. One of interesting fields of AFM application is observation of morphological changes due to exposure to certain media. A number of works have been presented in this field [1–12]. The impact of UV and simulated solar radiation [1–6], temperature [7], heavy ions [8], or other environmental conditions [9, 10] was verified. Also the influence of AFM scanning tip on mechanical properties of micrometer-scale polymer features [11] and the progress of electropolishing [12] were successfully investigated that way. The diversity of applied conditions and tested materials proves the versatility of this technique as well as the usability of obtained results.

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One should be however aware, that the information obtained using AFM may be inaccurate, as the morphological properties of surface may differ in various spots of a sample. Therefore conducting research using the outcome of a single measurement may lead to false conclusions. This issue can be overcome by taking a series of measurements and processing it using statistical tools [5, 6, 12]. In such a case, one can also obtain some insight into the distribution of analyzed parameters. There are, however, several issues to be solved if one desires accurate and reliable information about the course of surface changes. One of the major reasons for a specific uncertainty level is material inhomogeneity at this scale. It means, that some measurements taken at randomly chosen locations of a sample may provide the outcome strongly influenced by the local properties of the surface, but not representative for the material. Therefore, using precise positioning of the sample in order to image specific spots at every stage of material degradation is the best way to achieve the knowledge about how the material reacts to specific media with high degree of confidence [13–15].

Such approach is particularly important when nanomaterials and nanocomposites are investigated, and specific sub-micrometer inhomogeneity of the those materials is one of their particular properties.

In this paper, we present the use of degradation profiles obtained using precise sample positioning as a response to the metrological need of accurate information about the deterioration process of polystyrene/BC<sub>61</sub>BM nanocomposite caused by the UV radiation. In order to achieve a reasonable amount of information, the degradation profiles were acquired separately at ten spots, providing unique insight into the morphology changes with particular attention to inhomogeneous material response due to its local properties. We have shown that the analysis of averaged response would provide significantly worse detection sensitivity and would lead to data misinterpretation. The analysis of the degradation profiles performed using this approach, should be one of useful data sources in materials science. The level of coherence of the profiles revealed the way the surface deteriorates with particular emphasis on the process homogeneity, as it indicates material diversity in observed spots. To the best of our knowledge, no such experiment has been reported so far.

## 2. Experimental

According to our previous works, the polymer-nanofiller composite is the best candidate to observe inhomogeneous material degradation phenomena in controlled fashion. In particular, PC<sub>61</sub>BM as the nanofiller revealed very interesting ability to create complex features perfectly fitting for such a kind of experiment [16–18]. In order to perform the experiment, four polystyrene/BC<sub>61</sub>BM samples with various mass proportions have been prepared. For the fabrication process, PC<sub>61</sub>BM 99.5 % (Solenne BV), chloroform HPLC (Sigma Aldrich) and polystyrene (commercially available sheets) were used. Firstly, 400 mg of polystyrene was dissolved in 5 mL of chloroform. Next, the obtained solution was divided into 5 vials 1 mL each. Based on the polymer weight (80 mg),

percent of PC<sub>61</sub>BM addition was calculated to obtain desired PCBM concentration. Solutions containing 0 mg for reference sample, 4 mg for 5 %, 8 mg for 10 %, and 16 mg for 20 % were prepared. Then PC<sub>61</sub>BM was added to the vials and sonicated for 20 min. Dispersion of PCBM in PS was spin-cast on clear glass substrate at 1500 rpm for 25 s. The prepared samples were dried at room temperature for 1 h. The thickness of fabricated nanocomposite films was measured using AFM by measuring the profile of scratched line. The obtained average value was in range of 1.5  $\mu\text{m}$  to 1.7  $\mu\text{m}$ . It should be underlined, that at the micrometer scale one can expect natural materials-related inhomogeneity. In case of polymers, the fabrication parameters affect the polymerization process and may cause the occurrence of areas revealing mechanical, optical and chemical properties different from the majority of the material. Such a problem arises when an inspected area is relatively small, which is the case of AFM surface investigation.

The samples were subjected to a cyclic experimental procedure: first the series of scans at chosen locations were performed, then the samples were exposed to the UV radiation and scanned again at the same locations. The process was repeated until five exposition procedures after the initial scan revealing the  $t = 0$  h state. The idea of the procedure is shown in Fig. 1. It must be emphasized that in order to monitor the reliability of the surface imaging, the reference sample was imaged along with the investigated ones. As no roughness changes were observed in the case of the reference sample, one can assume, that the obtained data of the investigated samples were consistent and reliable.

The measurements were performed using Dimension 3000 AFM system equipped with 100  $\mu\text{m} \times 100 \mu\text{m}$  scanner, in a tapping mode in air, at room temperature of approximately 25  $^{\circ}\text{C}$  and relative humidity 35 %. This approach allowed us to minimize the wear of the scanning tip as well as to perform sample modification. The scanner was calibrated using a standard silicon grid from NT-MDT Company. The NanoSensors Point-probes with the following properties: nominal tip radius  $r_{\text{tip}} = 10$  nm, resonance frequency range

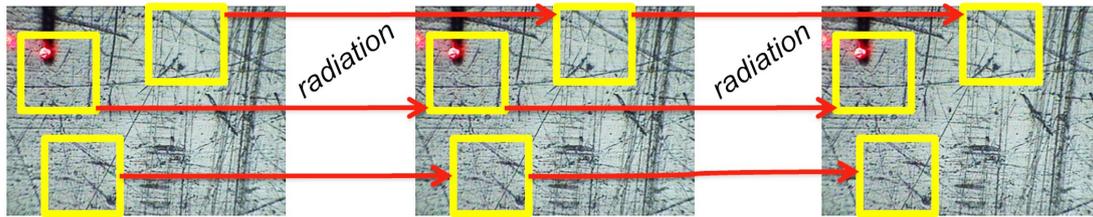


Fig. 1. The idea of cyclic scanning of specific areas and exposure to UV radiation.

of  $f_{\text{res}} = 306 \text{ kHz}$  to  $353 \text{ kHz}$ , and spring constant  $k = 43 \text{ N}\cdot\text{m}^{-1}$  to  $68 \text{ N}\cdot\text{m}^{-1}$  were used. The scanning area  $3 \mu\text{m}$  was applied in order to observe clearly the surface changes with at least  $10 \text{ nm}$  resolution. The data were processed using SPIP software from Image Metrology Company [19]. Root mean square roughness  $S_q$  was determined for each acquired image and used for the determination of profile deterioration. The obtained data were analyzed in terms of presence of artifacts indicating the scanning tip wear or contamination, which could lead to false analysis of the results. No source of potential threads of such a kind was identified.

In order to cause the degradation of the samples, the investigated samples were exposed to UV radiation of  $370 \text{ nm}$  at illuminance of approximately  $160 \text{ lux}$ . The fluorescent lamp was used for that purpose. Due to relatively large energy of the applied radiation, the dynamics of the deterioration process was expected to cause noticeable changes within few hours.

### 3. Results

In order to verify the outcome of the process, FMM (force modulation microscopy) technique [20, 21] was used to see mechanical differences between the polystyrene matrix and  $\text{PC}_{61}\text{BM}$  features. Fig. 2 shows the topography and amplitude response of the force modulation. The observed features are as expected. It has to be stressed that the obtained images were analyzed in terms of the presence of artifacts in FMM image in relation to the possible topography-FMM crosstalk. No evidence of false results was found. The topography image was processed using 2D FFT filter in order

to remove the wavy artifacts related to the interference of laser beam used for detection of scanning probe deflection.

The examples of topography measurement results are shown in Fig. 3. Sample  $0 \%$  is shown before and after  $105 \text{ h}$  of radiation exposure, respectively. A significant change in morphology can be noticed. However, the analysis of deterioration process in relation to specific scanning areas, provides much more complex description of the material response. Therefore, the degradation profiles were prepared based on the acquired data. For each material a set of profiles was prepared, basing on  $S_q$  roughness parameters calculated for each scanned spot, at each stage of the exposure to UV light. As the result, the set of ten curves (degradation profiles) was obtained for each sample, revealing the roughness changes individually at every spot. The coherence of the curves reveals the level of material homogeneity, as any deviation from a typical shape is related to the presence of some addition or other inhomogeneity in the material.

The degradation process profiles are shown in Fig. 4 to Fig. 7. For the reference sample ( $0 \%$  of  $\text{PC}_{61}\text{BM}$ ), one can notice a relatively high coherence of the majority of obtained profiles, however some exceptional behaviors can be also observed at  $40 \text{ h}$  and  $105 \text{ h}$  of exposure. The presence of two roughness increase fractions at  $16^{\text{th}}$  and  $40^{\text{th}}$  hours may be related to the presence of various fractions of polymer with different chain lengths and difference of UV light resistance as well as their morphological response (depolymerization of shorter chains requires less energy and causes smaller surface changes). One can argue,

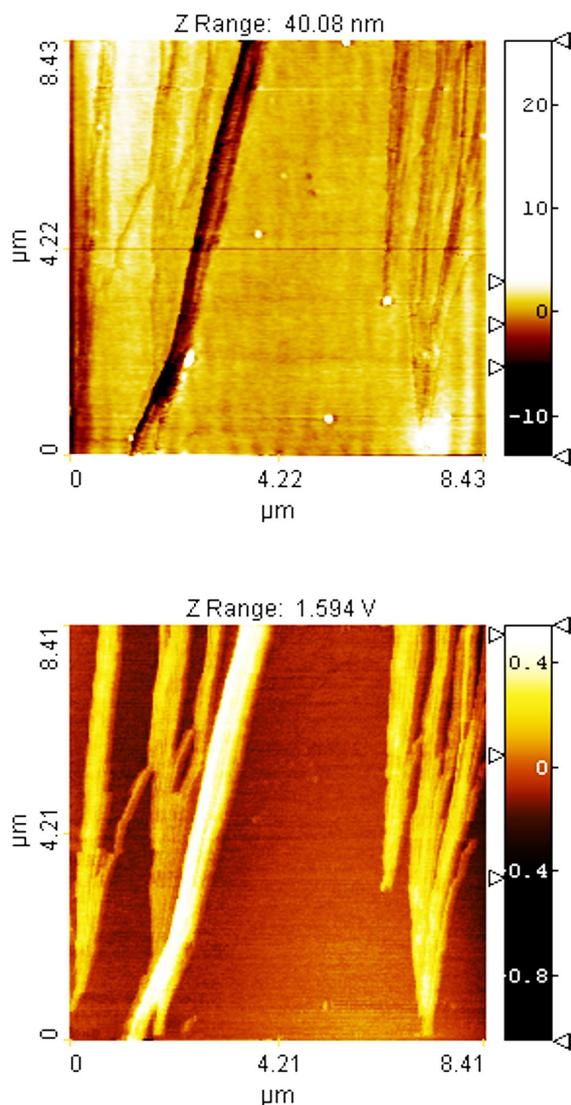


Fig. 2. The topography (top) and FMM amplitude (bottom) images of 20 % PC<sub>61</sub>BM sample.

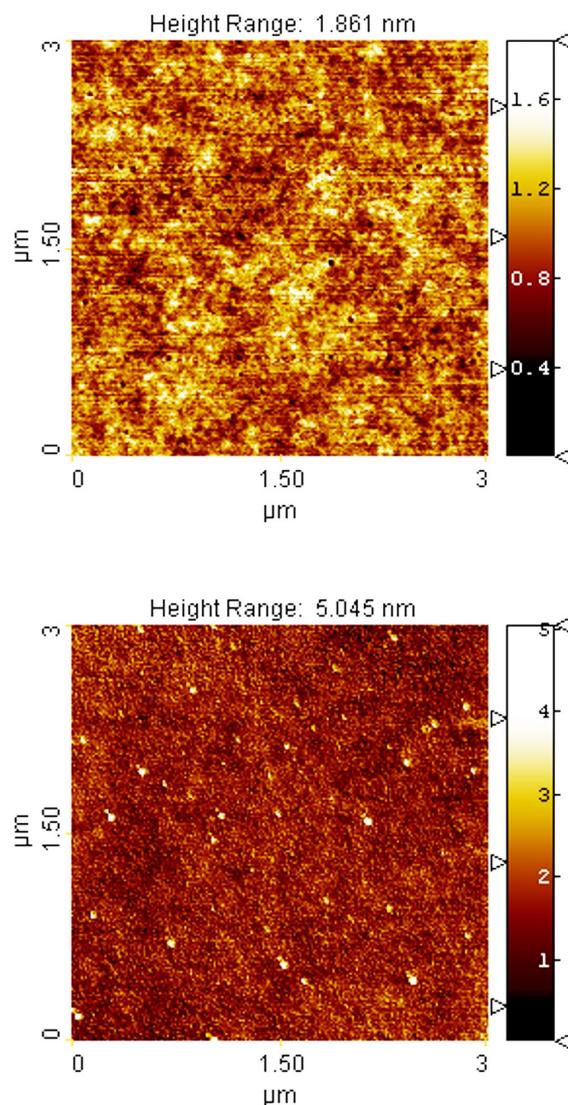


Fig. 3. Examples of topography of the reference sample before (top) and after (bottom) 105 hours of UV exposure.

that in this particular case, two specific fractions of profiles can be distinguished. However, it can be considered, that shortening the exposure time could reveal more peaks of the roughness increase. In general, it can be seen, that for each  $S_q$  increase event, several profiles maintain low values, showing an alternative behavior. It should be underlined, that the local roughness increase at 40<sup>th</sup> hour appears for every sample. Also for the majority of the samples, the roughness increase is visible

at 81<sup>st</sup> hour. However, along with increasing the PC<sub>61</sub>BM quantity, the dispersion of the profiles increases. The higher content of nanofiller can be also noted at the initial stage of the experiment ( $t = 0$ ) as the increased roughness value, up to 10 nm, while the reference and 5 % samples (Fig. 4 and Fig. 5) have not revealed the  $S_q$  bigger than 4 nm. As mentioned before, the presence of two profiles fractions can be clearly seen at the final stage of the experiment for 20 % and

40 % samples (Fig. 6 and Fig. 7). The analysis of presented deterioration profiles enables following the impact of the nanofiller on the surface degradation process, and in particular, its influence on the presence of local inhomogeneity revealing different responses to UV light. One can see, that calculating the average value for the whole group of results would cause the loss of precious information. So far, the average-based approach is common for reported investigations, therefore no comparison with these unique processes was possible.

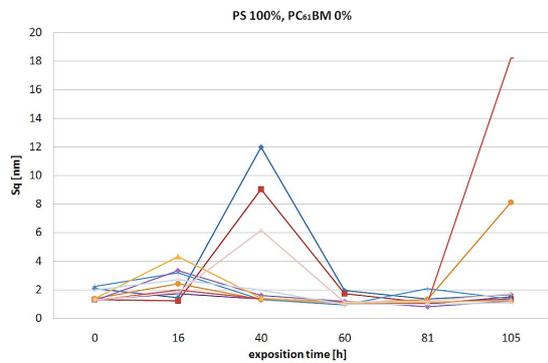


Fig. 4. The degradation profiles of the reference sample.

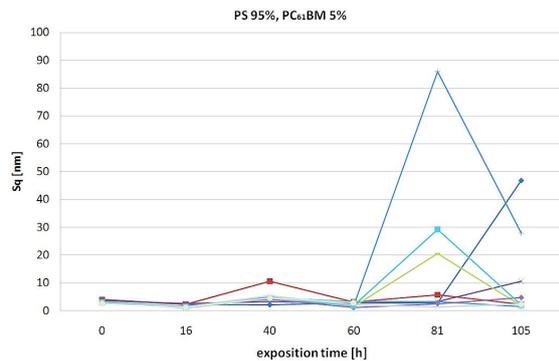


Fig. 5. The degradation profiles of 5 % PC<sub>61</sub>BM sample.

The presented observation allows us to confirm a great improvement in metrological aspect of AFM observation of materials deterioration, as the detection sensitivity and data confidence is significantly better.

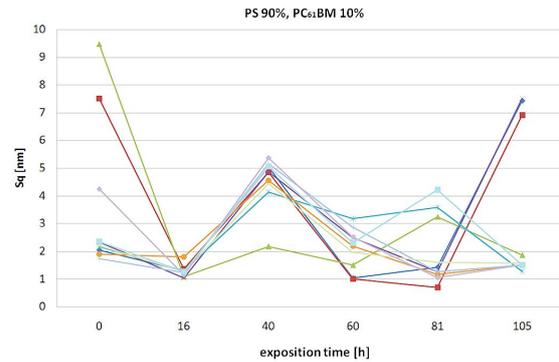


Fig. 6. The degradation profiles of 10 % PC<sub>61</sub>BM sample.

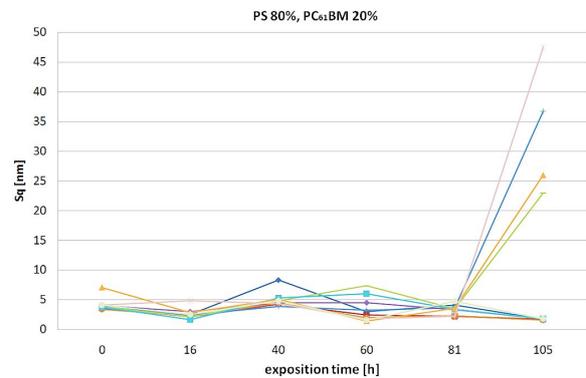


Fig. 7. The degradation profiles of 20 % PC<sub>61</sub>BM sample.

## 4. Conclusions

In this paper, we presented the results of unique AFM diagnostic procedure providing complex information about the degradation of materials at nanoscale. By analyzing a series of profiles of roughness changes at specific areas defined by means of precise sample positioning, one is able to diagnose the samples with high degree of confidence. Unlike in case of experiments basing on the analysis of single measurements or using an outcome of few measurements taken at randomly chosen locations, the obtained results enable comparative analysis of degradation profiles, which allows us to confirm the reliability of obtained information and exclude the influence of any kind of error sources, which could lead to misconclusions. We showed, that in case of non-monotonous

degradation process, such a method is essential, in particular in case of materials containing fillers. By comparing pure polystyrene with the samples containing various quantities of PC<sub>61</sub>BM, we could see that the degradation profiles are modified and one can distinguish some fractions of the profiles most likely related to the quantity of the filler at a certain spot. Such confirmation is very useful, as the surface degradation profiles are complex and reveal many non-monotonous areas of the roughness changes, which has not been reported by other teams at adequate level of certainty. Moreover, when inhomogenous materials are considered, it is possible to distinguish some groups of degradation profiles, related to areas revealing specific amount of nanofiller at imaged area. Therefore we claim, that in terms of research in the field of materials science, presented technique should be very useful in the investigations of the nanomaterials and nanocomposites. According to our knowledge, this method has not been practically used so far. Further investigation of nanocomposites using other diagnostic methods, such as micro/nano-Raman analysis, may provide valuable data for investigation of deterioration process.

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