The investigation of the light radiation caused polyethylene based materials deterioration by means of atomic force microscopy

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Abstract. The impact of the environmental conditions on the materials used in various devices and constructions, in particular in electrotechnical applications, has an critical impact in terms of their reliability and utilization range in specific climatic conditions. Due to increasing utilitarian requirements, technological processes complexity and introducing new materials (for instance nanomaterials), advanced diagnostic techniques are desired. One of such techniques is atomic force microscopy (AFM), which allows to study the changes of the roughness and mechanical properties of the surface at the submicrometer scale, enabling the investigation of the degradation processes. In this work the deterioration of selected group of polyethylene based materials have been measured by means of AFM, as the samples were exposed to the simulated solar light and UV-C radiation. Such an analysis of the environmental conditions impact on the deterioration process using AFM methods for various versions of specific material was not presented before.

1. Introduction

The issue of the reliability and utilization economy of various products, is one of the major concerns of each consumer. A number of works aimed at improvement and verification of those factors have been performed [1-3]. The major impact on the product’s performance, including the lifetime is the durability of used materials. The continuous progress in material development requires verification of their various properties, including the resistance to the environmental conditions, as one of the essential factors in terms of outdoor applications. Due to the need of the insight into the decomposition of tested materials and nanomaterials in particular, advanced diagnostic methods can provide useful information. Such an approach, based on utilization of atomic force microscopy, was already presented in various works, aimed at observation of the nanoscale impact of light radiation, increased temperature or high voltage on the surface of tested samples [4-10]. Also, the molecular-scale wear of the material due to repetitive load could be observed [11]. In addition, specific methodology solutions

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were developed in order to improve the analysis quality [12-15]. However, systematic works, providing step-by-step observation of the material’s deterioration are so far rare. In this work, the investigation of three types of polyethylene based materials are presented. The impact of the simulated solar and UV-C radiation was verified in terms of the roughness and stiffness changes. Moreover, the wettability of the surface, as the roughness-related phenomena was measured. Obtained results allowed to notice various resistance of tested materials to the applied conditions, as the added compounds improve their properties. In addition, one can conclude various dynamics of the surface degradation. Moreover, the force spectroscopy measurements provided unique data allowing to identify both: detachment of the microparticles and the appearance of the electrostatic charge embedded in the material, related to the polymer chains breaking. Therefore, the superior role of atomic force microscopy in the investigation of the materials deterioration process was shown.

2. Experimental results

2.1. The preparation of the samples and the exposition the light radiation

Three materials have been prepared in order to perform the experiment: all materials are based on the linear low density polyethylene (LLDPE – DFDA 7540 from Dow Chemical Company). The material marked “PE” is the pristine polymer. The composite “PE+UV” contains the UV-stabilizer (UV 6014 LD from Polyplast Muller) in amount of 5 wt. %. The “PE+UV+MMT” was filled with the UV-stabilizer and the montmorillonite (Cloisite 15A from Southern Clay). The composite PE-UV was prepared in a single-screw extruder. The technology of PE-UV-MMT was a two-stage process. First the montmorillonite was introduced into polyethylene matrix in a twin-screw extruder, than this material was homogenized with the UV stabilizer in the single-screw extruder. The samples of the two composites, as well as the pristine polymer were formed by press moulding by 40 tons at 150 °C for 6 min. The samples were placed in two independent chambers providing simulated solar radiation emitted by the xenon lamp, and UV-C radiation emitted by evanescent lamp. Following basic parameters of the radiation conditions were applied: Xenon lamp (Xe): \( \lambda_{\text{range}} = 300-800 \text{ nm} \) and 38,5 W/m\(^2\), UV lamp (UV): \( \lambda = 235 \text{ nm} \) and 9 W/m\(^2\). In order to observe the deterioration progress, the following time periods were applied: 100, 200 and 500 hours.

2.2. AFM topography analysis

The morphology analysis was performed using DI 3000 AFM, working at ambient conditions, in tapping mode. To perform the measurement, following probes were used: Nanosensors Pointprobes, \( f_{\text{res}} = 306-353 \text{ kHz} \), \( k = 43-68 \text{ N/m} \). Scanning area was 3 \( \mu \text{m} \) x 3 \( \mu \text{m} \) (fig. 1a, b), as it provided desired resolution allowing to observe nanometer-scale features, and avoid the influence of micrometer/millimeter-scale objects related to the form imperfections (fig. 1c).

![Figure 1](image-url)  
Figure 1. The examples of the surface scans 3\( \mu \text{m} \) x 3\( \mu \text{m} \) (a, b) and 50\( \mu \text{m} \) x 50\( \mu \text{m} \) (c).
In order to obtain statistically relevant data, at least 20 scans for each case were acquired. For each image, the roughness parameters were calculated, including $\text{Sq}$ (Root Mean Square) and $\text{Sbi}$ (Surface Bearing Index). The median, second and third quartiles were calculated. The data was processed using SPIP software from Image Metrology company [16]. No data revealing the influence of the fabrication process like presented in figure 1c was taken into account. Obtained results are presented in figure 2.

![Figure 2. Roughness parameters (Sq and Sbi) changes of investigated samples.](image)

Despite relatively large distribution of analyzed factors caused by the surface non-homogeneities, one can observe specific changes of the roughness. The $\text{Sq}$ parameter reveals non-monotonic behavior, where at the first stages the roughness decrease is observed, and when the deterioration process continues, the increase occurs. Such phenomena may seem surprising, however it was observed before, when the polycarbonate sample was tested in terms of the UV light resistance [13]. One can argue, that the first parts of the surface that deteriorates, are elevated, exposed and fragile areas. Once they are gone and $\text{Sq}$ reaches minimum, the holes start to appear due to further degradation, and the roughness increase. One has to be aware, that in case of presence of any fillers, such a process may
show different progress tendency. Obtained results allowed to observe exceptions from general behavior, as samples PE+UV/Xe and PE+UV+MMT/Xe aged using Xenon lamp reveal reversed tendency. Such a phenomenon could be caused by a presence of UV stabilizer, which increased the resistance of the material against the radiation, however the impact of the thermal interaction could lead to some level of surface’s degradation. However, in following steps, the surface become more flat with the majority of holes (see Sbi discussion below). Rapid increase of Sq in case of PE+UV+MMT sample irradiated with UV, may be related to the MMT particles uncovering, which as relatively big objects may have a major contribution in the roughness changes.

The Sbi parameter, which is related to the bearing properties, in general increases, therefore one can conclude, that the upper part of the surface flattens continuously, however the amount and size of holes increase (also indicated by Ssk parameter not shown here). In addition, one can also notice general behavior, where the UV light causes larger relative changes of the surface roughness due to its higher energy, than Xenon lamp light. It should be also stressed, that the presence of the additives did not influence significantly the surface roughness. Po particular improvement of the roughness changes was observed after UV stabilizer added.

2.3. AFM surface stiffness determination

The force spectroscopy measurements allowed to determine the changes of the surface stiffness. CSG30 probes from NT-MDT, \( f_{\text{res}}=48 \text{ kHz} \) \( k_{\text{nom}}=0.6 \text{ N/m} \). In order to calculate the real spring constant, thermal noise method was used. For each case approximately 300 force curves have been acquired (10 in single spot) in order to provide statistically reliable outcome. Figure 3 shows the examples of acquired curves, revealing unique phenomena such as the microscale cracking (a) of the surface due of the applied force, or appearance of the electrostatic force due to the decomposition of the polymer chains (b). It should be stressed, that no other measurement technique allows to obtain such a results. Further investigations performed by means of electrostatic force microscopy (EFM) may provide valuable information concerning the way this phenomena develops. It should be underlined, that the electrostatic forces mapping provided by EFM allows to detect locally accumulated charge in insulating materials [17, 18].

Figure 4 shows the stiffness changes of investigated materials. This parameter was determined basing on the slope of the tip-sample interaction in repulsive forces range. Acquired data was processed in order to obtain statistical information about the average value and the median. Obtained results allow to observe complex, non-monotonic changes of the mechanical properties of the surface. At the first stage the stiffness increases. This particular phenomena can be related to the deterioration of relatively soft, elevated features, weakly attached to the surface. Following, as the abovementioned features are gone and the degradation process continues, the material’s surface stiffness decreases due to the activation of the radicals and the molecular chains decomposition.
The changes of the stiffness of investigated materials. The differences in the process dynamics can be seen between certain samples and exposition conditions. All samples exposed to UV light show reversed “V” shape, revealing both phases of the process. One should be aware, that in case of Xenon lamp exposition, deep deterioration of the material, caused by the raised temperature, can’t be detected straightforward using force spectroscopy tool, however, the presence of the material cracks or discontinuities, may be revealed as the tip-sample interaction events in the repulsive force range. As expected, the dynamics of the stiffness changes is higher for the UV light exposition. It can be also seen, that the addition of MMT provided higher stiffness, allowing to obtain better durability of the material.

2.4. Wettability angle determination
In addition to the roughness data, the wettability angle was determined, as it also plays essential role in the degradation of the material in outdoor applications. The measurements were performed using the home-made setup containing CCD-camera based microscope and digitally controlled deionized water dispenser. For each sample at least 10 angles have been acquired in order to provide statistical analysis. The graphs showing the wettability changes are presented in figure 5.

The wettability angle, as expected, decreases along with the radiation period, proving the roughness increase of the investigated surface. Therefore, in general this result confirms the roughness increase. Such a technique, however, due to the presence of millimeter scale features related to the fabrication process (fig. 1c), can not provide such an insight into the morphology changes as the AFM methods deliver. Again, the UV radiation caused more dynamic changes of measured factor than Xenon lamp light. It should be underlined, that UV stabilizer may present a limited performance in terms of presence of UV-C radiation. There must be stressed, however, that the study of the resistance of
materials to such a wavelength are useful, as certain object can be exposed to such conditions for instance in medical facilities.

3. Summary and outlook
Performed experiments allowed to trace the changes of the morphological and mechanical properties of the PE and PE based samples at the submicrometer scale. Acquired data delivered unique information about the deterioration of the investigated materials due to exposition to both: Xenon and UV-C light sources. The multi-stage process in both: roughness and stiffness changes was observed. Observed degradation phenomena contained UV radiation curing and polymer chains breaking, preliminary surface smoothing and the then the holes appearance. Also, the impact of presence of UV stabilizer and MMT nanoparticles was verified. It should be stressed, that no such complex study was performed so far. Additionally performed wettability tests provided confirmation of the surface’s roughness development.

Further research will be performed in order to obtain more detailed information about various aspects of the materials deterioration. Long term tests may provide the better insight into the process in terms of understanding the role of various nanofillers. In particular, the detailed study of the appearance of the electrostatic forces will be carried out, using the electrostatic force microscopy technique. It should be stressed, that the presence of the electrostatic field may have a considerable consequence in terms of the ageing process as well as the aggravation of the material’s performance as the insulator. Presented investigation are particularly valuable in terms of observation of the behaviour of the nanomaterials, where the submicrometer scale parameters can deliver essential information.

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Acknowledgments
Presented experiments were performed within frames of IEL statutory work.