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Atomic Force Microscopy Investigation of Polystyrene and Polystyrene/PMMA Composites Surfaces

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The surface morphology of polystyrene (PS) before and after u.v.-irradiation was studied by means of Atomic Force Microscopy (AFM). The u.v.-irradiation of PS sample doped with poly(methyl methacrylate) caused distinct changes in surface morphology. The nanometer-scale structures of the rod-like shape bumps of diameter of 300 nm and the height of 75 nm were created. We also showed that the very small forces of 0.2 nN are enough high to modify the surface of PS samples.

Keywords: AFM; Polystyrene/PMMA; UV irradiation

INTRODUCTION

Physical and mechanical properties of plastics depend not only on the chemical structure of polymers but also on their morphology [1,2]. AFM technique is one of more suitable for characterisation of organic material surface [3,4]. The polymer surfaces undergo very often changes due to influence of various environmental factors. Ultraviolet (u.v.) irradiation is one of the most destructive factors and it involves formation of radicals in macrochains followed by a breakdown of chemical bonds [5,6]. The main reactions occurring in polymer upon its exposure to u.v. radiation are main chain scission, oxidation, side groups abstraction or destruction, etc. [5-8]. Because photodegradation of

solid polymers starts in very thin surface layer, it is very important to use the technique enabling to monitor these surface changes.

In this letter, we present the results of our study of morphology changes caused by u.v. irradiation of polystyrene (PS), polystyrene/poly(methyl methacrylate) blend (PS/PMMA). These materials are of interest because of its wide applications and looking for optimal preparation conditions [9]. We were also interested in looking for the possibility of the nanometer-scale structures' formation.

EXPERIMENT

The polystyrene was produced by Oświęcim, Poland. Poly(methyl methacrylate) were obtained by emulsion polymerisation using ammonium persulfate as initiator. Thin polymer films were obtained by casting of 2% benzene (PS, PS/PMMA) solution onto glass plates. After the solvent evaporation samples were dried in vacuum to a constant weight. Then, the samples were u.v.-irradiated by a low-pressure mercury lamp TUV30W (Philips, Holland) during 8 hours. The intensity of incident light (at sample surface) was 4.4 mW/cm^2. The lamp emitted u.v.-radiation of the wavelength 254 nm. All irradiations were performed at the room temperature in air atmosphere. The AFM experiment was performed on both non-irradiated and irradiated samples under ambient air condition using a combined AFM/STM system (OMICRON) working in the constant force topographic mode. We used contact mode silicon cantilevers (NT-MDT).

RESULTS AND DISCUSSION

Figure 1 shows images of PS surface before and after irradiation. Measurement conditions in this case were much more difficult due to a high adhesion force between the AFM tip and the sample surface. Non modified PS surface revealed an array of the randomly distributed holes of the typical diameter of (100±25) nm, and the depth of (1±0.2) nm. They were probably formed during fast solvent evaporation during film preparation. The individual bigger bumps of the diameter from few tens to few hundred nm appeared after irradiation, as shown in Fig. 1b.

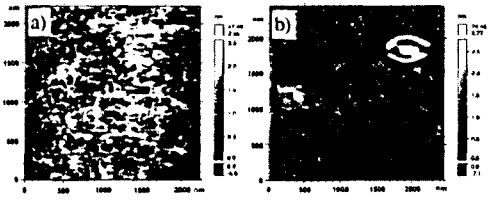

FIGURE 1. AFM top view images of 2.45 μm × 2.45 μm area of PS surface before (a) and after (b) u.v.-irradiation for 8 h.

Their appearance can be explained by a diffusion of low-molecular gaseous blisters towards the polymer surface. When the tip was scanned a few times at the same area ($1\mu m^2$) the parts of the top layer were removed and a small depression (1 nm deep) appeared as shown in Fig. 2. The removed material is localised mainly along the sides of the scanning area, perpendicularly to the direction of scanning, however there are some hillocks inside an abrasion mark. The mechanism of the material removal is most probably the result of abrasion via direct mechanical tip-sample contact. The study of nanometer scale modifications proved that using a force of 0.2 nN in AFM is enough high to modify the PS surface!

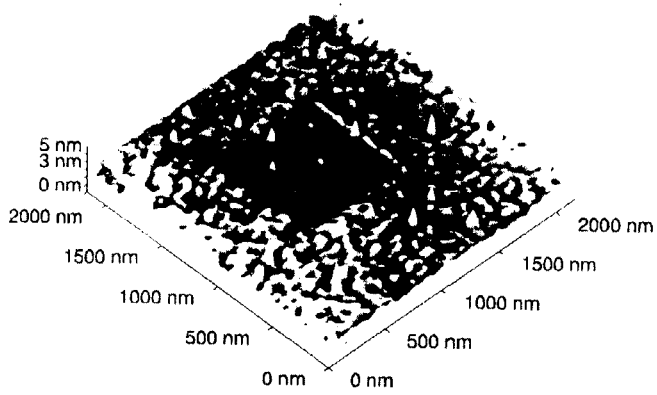

FIGURE 2. AFM quasi-3D image of 2 μm × 2 μm area of PS after few scans of the same area of 1 μm^2 using a loading force of 0.2 nN

The most spectacular changes after u.v.-irradiation were observed in the case of PS/PMMA sample (Fig. 3). The domains in the form of big rounded bumps of 1.2 μm diameter and up to 80 nm in height were observed before irradiation. There were 8 bumps on average on 16 μm^2 covering 64% of the sample area. After irradiation the bumps become distinctly isolated and their shape was changed. The edges of these bumps become steep (nearly orthogonal towards the sample surface) and their height become nearly the same for all of them and was about (74±15) nm. The average diameter of theses rod-like bumps was (300±30) nm. There were 24 bumps on average on 16 μm^2 covering 14% of the sample area. Our interpretation of the observed process is as follows: it is expected, that PMMA component is preferentially adsorbed on SiO_x type substrates (a polar surface) forming homogenous layers with some protruding bumps [9]. These PMMA bumps are surrounded and covered by PS phase. The volatile products which appear due to u.v.-irradiation of the PS component make that the PMMA component is unveiled. The formation

process looks like this one occurring during formation of self-organised semiconductor quantum dots. It could be interesting to investigate these structures via optical spectroscopy methods.

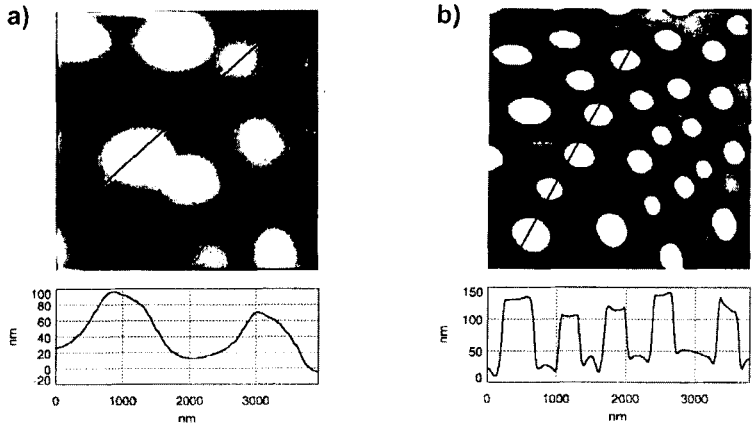

FIGURE 3. AFM top view images of 4 μm × 4 μm area of PS/PMMA sample before (a) and after (b) u.v.-irradiation for 8 h. The cross-line profiles at the bottom of the each image show the shape and dimensions of the observed structures.

CONCLUSION

We conclude that AFM can be effectively used for characterisation of surface nanostructures on irradiated polymers, as well as for their surface modifications in the nanometer scale. Moreover, phase shape and size as well as size distribution in case of immiscible polymer blends can be revealed directly by AFM. Thus, investigation of polymer morphology and its changes caused by u.v.irradiation may have a practical meaning during expectations of life time of polymer articles under use conditions.

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