PERIODIC NANOSTRUCTURES ON POLYETHERIMIDE INDUCED BY AFM NANOLITHOGRAPHY

JUŘÍK Petr*, SLEPIČKA Petr, PŘIBYL Matěj, ŠVORČÍK Václav

*University of Chemistry and Technology, Department of Solid State Engineering, Prague, Czech Republic, EU, *petr.jurik@gmail.com*

Abstract

In this paper we describe a nanopatterning technique of polyetherimide by scanning with the silicon tip in contact mode of atomic force microscopy. Different applied forces were used for the consecutive scanning of the same sample area. The higher applied load the less consecutive scans are necessary for the pattern formation. The most regular pattern on this aromatic polymer substrate was achieved for the applied load 150 nN. The variation of number of scans leads to increase of surface roughness due to mass transport on the polymer surface. The structure formation mapping contributes strongly to development of new applications using nanostructured polymers, e.g. in tissue engineering or in combination with metallization in selected electronics and metamaterials construction.

Keywords: Polyetherimide, atomic force microscopy pattern, nanostructuring

1. INTRODUCTION

The phenomenon of construction of nanopattern by means of scanning with atomic force microscopy is relatively new technique with a pioneer work published in 1992 [1]. Two major approaches can be used for nanopatterning of polymers if we do not consider beam treatment. First approach is that polymer foil can be stretched up like it was recently done with polypropylene [2,3] or we can use simple scanning which for some polymers can lead to ripple pattern creation [4-6]. The construction of surface nanostructures by scanning of a flat surface with a AFM tip was observed confirmed several times for different polymers [6-8]. Increase of volume of layer and frictional response can be quantified with the conclusion that observed plastic deformation induced by the tip-surface interaction has a connection with a second-order phase transition in case thin glassy films [8]. The periodic pattern can be modified by change of the scanning velocity, applied force or angle. Therefore the possibility of periodic pattern of desired dimensions or orientation was proposed [9].

Different models were proposed for the explanation of the nanopatterns formation. The following mechanisms responsible for nanopattern formation induced by interaction of tip with polymer films were proposed: (i) Schallamach waves, (ii) stick-slip behavior, and (iii) fracture-based descriptions [10]. Also different type of AFM tips were used, including special, but also expensive diamond tips, used for nanodots formation on polycarbonate films, where a two-step nanoindentation method to construct controllable and oriented system of 3D nanodot arrays was executed [11]. The interaction of AFM tip with surface of solid material can be also used for modification of biomaterial. DNA molecules have been engineered to mimic the initial stages of mismatch repair [12]. AFM was also used for generating and characterizing of the mechanical properties of cell-derived matrices [13]. The regular ripple pattern can be also realized by means of excimer laser treatment which we realized on several aromatic polymers recently, such as in case ripple pattern on PEN [14] or dot pattern on PES [15], and by heat treatment, realized on PLLA [16]

However, the effect of regular pattern formation has not been observed for polyetherimide (PEI) so far. In this work we used standard Si probe tip of a AFM Veeco CP II equipment to modify PEI surface by scanning with aim to construct regular pattern on the polymer surface. The surface nanostructuring was studied with respect to the applied load with use of standard silicon tip in contact mode. We have determined the optimal scanning parameters for the ripple construction with the dimensions and regularity depending on the applied load and number of consecutive scans of the same area on PEI surface.

2. EXPERIMENTAL: MATERIALS AND MODIFICATION

As a substrate we used polymer polyetherimide (PEI, density 1.27 g cm-3, 50 µm thick foils) supplied by Goodfellow Ltd., Cambridge, Great Britain). For modification and surface morphology determination we used an atomic force microscopy (AFM) technique using a VEECO CP II device. A Si probe CONT-20A tip with the spring constant 0.9 N m-1 was used for the nanolithography experiment. The mean surface roughness (Ra) represents the average of the deviations from the centre plane of the sample.

3. RESULTS AND DISCUSSION

We have studied interaction of silicon tip in contact mode of AFM with PEI substrate. We study the tip-polymer interaction especially from the morphologic point in dependence on the load of the tip on the polymer and the number of consecutive scans applied on the sample. The results reported previously shown the dependence of the applied surface load on the sample on the regular pattern [3]. So far no results on PEI polymer were published.

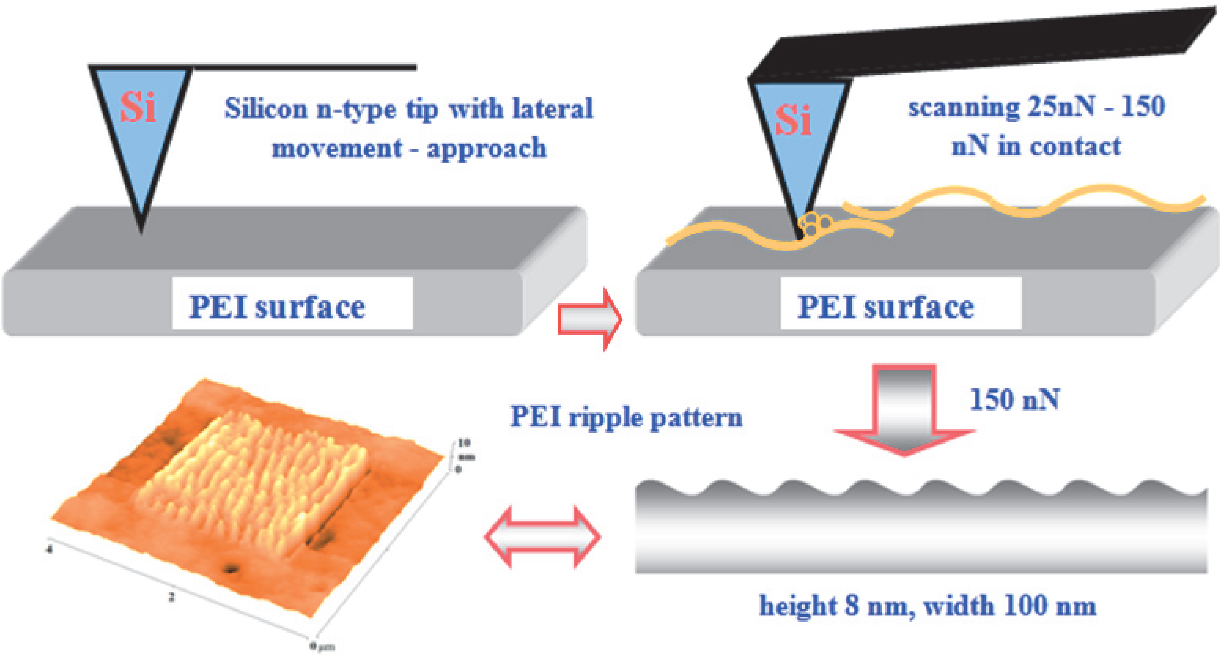

Figure 1 Title The principle of PEI nanopatterning with silicon tip in contact mode

The **Figure 1** describes the treatment of polyetherimide with Si n-type AFM tip and ripple pattern formation. The different types of surface modification connected with mass transfer can be applied. As we have mentioned above, Schallamach waves or stick-slip behavior, and last but not least fracture-based descriptions can be responsible for ripple pattern or regular pattern on polymer surface due to applied force onto the surface due to AFM tip interaction.

On the basis from the **Figure 2**, we can conclude that the optimal number of consecutive AFM scans differ for PEI in the dependence of applied force on the sample. It was observed, that for PEI samples the ripple pattern appeared earlier for the higher applied load, even after the first scan for 150 nN, and with the reduction of applied force the number of consecutive scans increases (**Figure 2**).

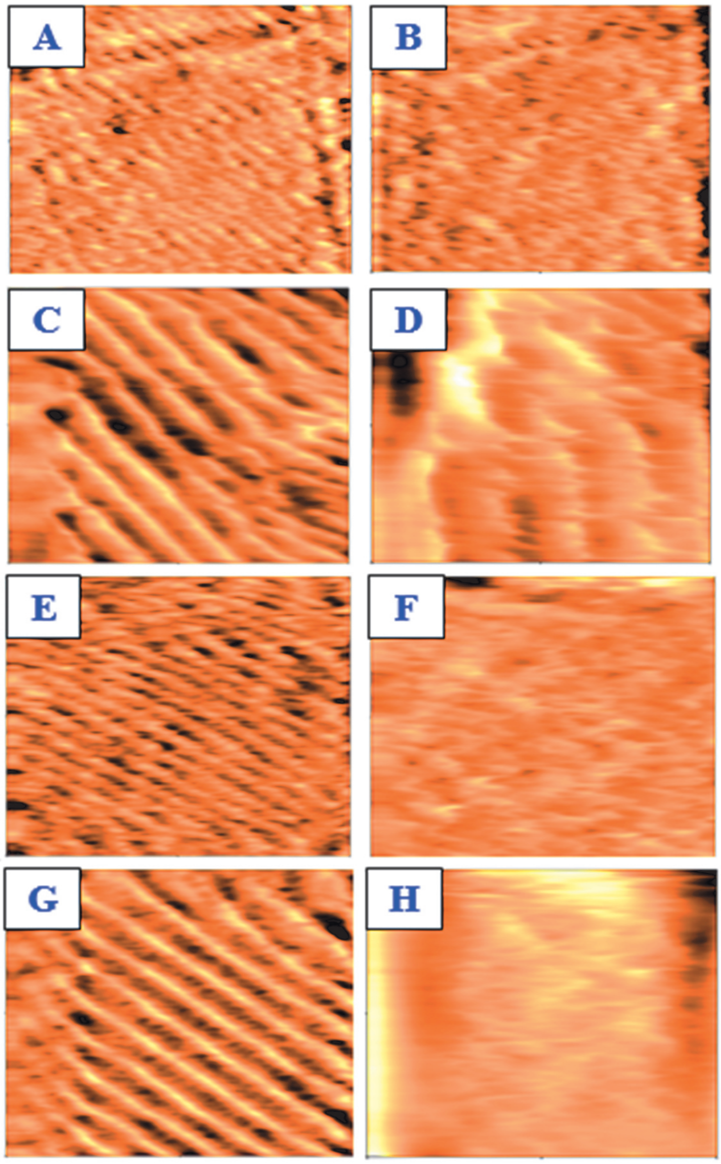

Figure 2 2D AFM images of PEI treated with 25 nN (4th scan - A; 10th scan - B), 50 nN (2nd scan - C; 10th scan - D), 75 nN (2nd scan - E; 10th scan - F) and 150 nN (1st scan - G; 10th scan - H). The 1x1 μm² image was acquired

The construction of ripples on a PEI polymer can be explained by a as stick-slip mechanism [9]. The polymeric material is moved by the probe which forms a precursor wave (see **Figure 1**). The polymer "hill" is constructed in front of the tip. This phenomenon is manifested by the change of mechanical equilibrium and the tip can skip over the ripple which was constructed. In the next stage, which is the next scan line, the forward scan (different y-axis value depends on the number of scan lines on the surface area) the upper part of the polymer is pushed again. These phenomena lead to the formation of a periodic pattern which also depends on the direction of the polymer flow. The precise relation between the mass flow and pattern formation depends on the polymer's mechanical properties. This relation also depends on the shape and dimension of the tip. Also the technique of polymer manufacturing (uniaxially or biaxially oriented foil) can play a significant role.

The shape of the tip can be also modified during the tip movement along the polymer surface if the contact mode is used for the treatment, therefore also some additional effects may also apply.

These effects may appear as irregularities on the modified ripple pattern, and can decrease the quality of ripple pattern on polymer. Due to the tip pressure in combination with material transport in the contact mode, the ripple pattern regularity and quality can also deteriorate for the higher number on scans over the surface. This premise was supported by the experimental observation on the basis that repetitive scanning of the same square (same scanning parameters) increases the roughness of the scanning area (**Figures 2a-h**). Thus, the ripple structure could be formed only in the first stages of scanning, while the more pronounced tip-surface interaction leads to the significant increase of surface roughness, which is more pronounced for higher applied forces. It was determined that the surface roughness increases either with number of consecutive scans and applied force on the polymer surface. The input parameters for optimal nanostructure was estimated for the highest applied load 150 nN, where regular pattern with periodicity of approx. 100 nm and height of approx. 8 nm was achieved (**Figure 4**). The dependence of surface roughness on the applied force of the AFM tip decreases with the force reaching its maximum for applied force 150 nN and 10 consecutive scans of the same area.

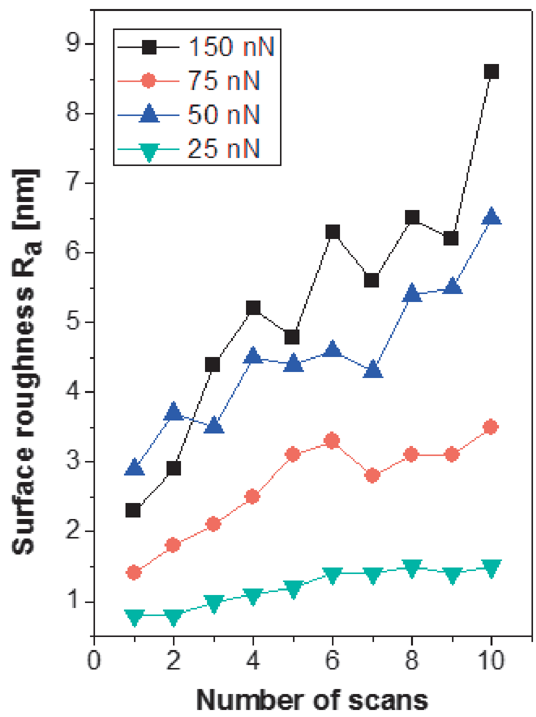

Figure 3 The dependence of the roughness on the number of consecutively applied scans of PEI surfaces for applied loads 25, 50, 75 and 150 nN

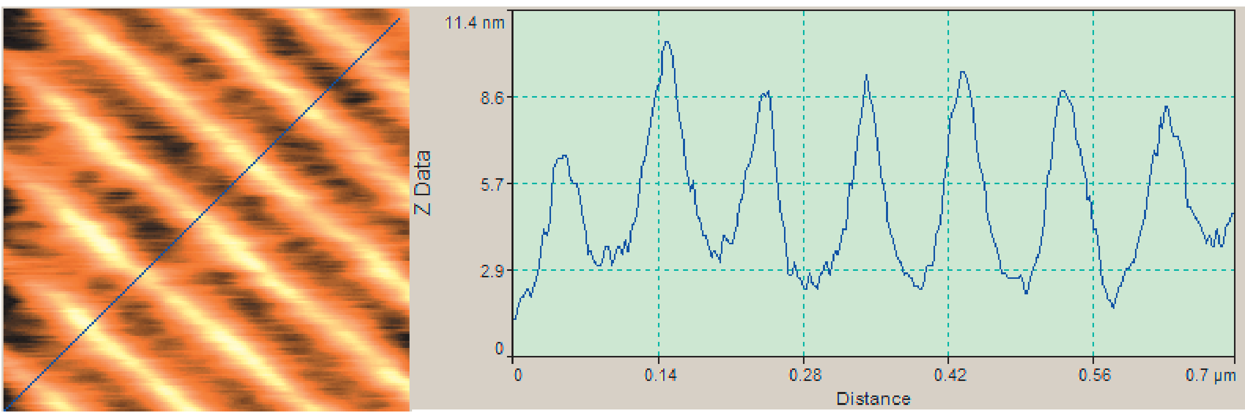

Figure 4 The representative AFM image (A) with line analysis (B) acquired for the PEI sample treated with 150 nN (1st scan, 0.5x0.5 µm2)

4. CONCLUSION

We have confirmed that AFM modification with an appropriate input of scanning parameters can lead to the construction of an ordered ripple pattern on the surface of polyetherimide films. The applied load on the surface of polymer can induce the ripple pattern even after the first scan for higher applied forces, while with decrease of applied force the number of consecutively applied scans increases. The orientation of the ripple pattern is determined by the material re-distribution on the surface that is strictly determined by the shape of the tip and most of all, the applied force on the surface. The relatively uniform pattern on the surface of PEI can be constructed for higher applied forces (up to 150 nN) with the pattern width of approx. 100 nm and pattern height approx. 8 nm. In comparison with the treatment of polymer surface with excimer laser light the scanning with silicon tip was successfully applied for the PEI nanostructuring with low height and relatively uniform shape.

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REFERENCES

[1] LEUNG O.M., GOH M.C. Orientational Ordering of Polymers by Atomic Force Microscope Tip-Surface Interaction, *Science*, 1992, vol. 255, pp. 64-66.

[2] UCHIDA K., MITA K., MATSUOKA O., ISAKI T., KIMURA K., ONISHI H. The structure of uniaxially stretched isotactic polypropylene sheets: imaging with frequency-modulation atomic force microscopy, *Polymer*, 2016, vol. 82, pp 349-355.

[3] AURIEMMA F., DE ROSA C. Stretching isotactic polypropylene: From "cross-ss" to crosshatches, from gamma form to alpha form, Macromolecules, 2016, vol. 39, pp. 7635-7647.

[4] YAN Y. D., GENG Y. Q., HU, Z. J. Recent advances in AFM tip-based nanomechanical machining. International Journal of Machine Tools and Manufacture, 2015, vol. 99, pp. 1-18.

[5] D'ACUNTO M., DINELLI F., PINGUE P. Nanoscale rippling on polymer surfaces induced by AFM manipulation, Beilstein Journal of Nanotechnology, 2015, vol. 6, pp. 2278-2289.

[6] NAPOLITANO S., D'ACUNTO M., BASCHIERI P., GNECCO E., PINGUE P. Ordered rippling of polymer surfaces by nanolithography: influence of scan pattern and boundary effects, *Nanotechnology*, 2012; vol. 23, art. numb. 475301.

[7] WATSON J.A., BROWN C.L., MYHRA S., WATSON G.S. Two-dimensional stick-slip on a soft elastic polymer: pattern generation using atomic force microscopy, *Nanotechnology*, 2006, vol. 17, pp. 2581-2589.

[8] SCHMIDT R.H., HAUGSTAD G., GLADFELTER W.L. Ordered rippling of polymer surfaces by nanolithography: influence of scan pattern and boundary effects, *Langmuir*, 2003, vol. 19, pp. 898-909.

[9] D'ACUNTO M., NAPOLITANO S., PINGUE P., GIUSTI P., ROLLA P. Fast formation of ripples induced by AFM. A new method for patterning polymers on *nanoscale, Materials Letters,* 2007, vol. 61, pp. 3305-3309.

[10] D'ACUNTO M., DINELLI F.,PINGUE P. Nanoscale rippling on polymer surfaces induced by AFM manipulation, *Beilstein Journal of Nanotechnol*ogy, 2015, vol. 6, pp. 2278-2289.

[11] YAN Y., SUN Y., LI J., HU Z., ZHAO X. Controlled nanodot fabrication by rippling polycarbonate surface using an AFM diamond tip, *Nanoscale Research Letters*, 2014, vol. 9, pp. 372-379.

[12] JOSEPHS E.A., ZHENG T., MARSZALEK P.E. Atomic force microscopy captures the initiation of methyl-directed DNA mismatch repair, *DNA Repair*, 2015, vol. 35, pp. 71-84.

[13] TELLO M., SPENLÉ C., HEMMERLÉ J., MERCIER L., FABRE R., ALLIO G., SIMON-ASSMANN P., GOETZ J.P. Generating and characterizing the mechanical properties of cell-derived matrices using atomic force microscopy, *Methods*, 2016, vol. 94, pp. 85-100.

[14] SLEPIČKA P., NEDĚLA O., SAJDL P., KOLSKÁ Z., ŠVORČÍK V. Polyethylene naphthalate as an excellent candidate for ripple nanopatterning, *Applied Surface Science*, 2013, vol. 285B, pp. 885-892.

[15] MICHALJANIČOVÁ I., SLEPIČKA P., VESELÝ M., KOLSKÁ Z., ŠVORČÍK V. Nanowires and nanodots prepared with polarized KrF laser on polyethersulphone, *Material Letters*, 2015, vol. 144, pp. 15-18.

[16] JURIK P., SLEPICKA P., MISTRIK J., JANICEK P., RIMPELOVA S., KOLSKA Z., SVORCIK V. Oriented gold ripple-like structures on poly-L-lactic acid. Applied Surface Science, 2014, vol. 321, pp. 503-510.