P115

Atomic force microscopy in the model's development of polymeric functional materials formation on inert supports

T.S. Sazanova[1,2], K.V. Otvagina[1], A.E. Rassadin[2], L.A. Fomin[2,3], I.V. Vorotyntsev[1]

[1]*Nizhny Novgorod State Technical University n.a. R.E. Alekseev, 603950, Nizhny Novgorod, Russia yarymova.tatyana@yandex.ru*

[2]*Nizhny Novgorod Mathematical Society, Nizhny Novgorod, 603950, Russia*

[3]*Institute of Microelectronics Technology and High Purity Materials RAS, 142432, Chernogolovka, Moscow region, Russia*

The development of polymer-based functional materials with tailor-made structure and properties is closely associated with different physical, chemical and material science problems. Fundamental research of polymers structure and their functional properties is needed for the solution of those problems. Since it is known that physical and physical-chemical properties of polymer-based materials not only depend on their chemical nature but also strongly correlate with their surface structure, the study of this effect is an important task.

For example, in the case of gas separation processes, a non-porous polymeric membrane surface has significant contribution to gas transmission properties. It is due to the fact that first stages in gas separation are deposition of permeating gases on a membrane surface and their absorption. The rougher a membrane surface, the larger will be its actual area, and with the growth of this area, the separation speed also increases, that is, permeable properties are improved.

Thus, functional properties of polymeric materials can be controlled by varying their surface roughness (with due regard to their chemical nature). In this context, the most energy efficient and resource-saving way is mathematical modeling. A mathematical model of the "growth" of polymer films (in particular membranes) on a support could allow to identify the necessary structure and roughness of this support to obtain polymeric materials with tailor-made properties without conducting experiments.

To develop and verify such mathematical "growth" model, a polymeric surface can be assessed by atomic force microscopy (AFM). This method is suitable for such study not only because of high lateral and vertical resolutions, but also its ability of gaining quantitative three-dimensional information about topography without destruction of a soft polymer surface. Also, the results of AFM scanning are presented in digital format, which allows them to be processed using statistics methods [1] and to be used for mathematical modeling [2].

In this work, AFM results were used in the development and verification of a model for polymeric membranes formation on inert supports on the example of a range of membranes based on polysulfone (PSU), cellulose triacetate (CTA) and polyvinyl alcohol (PVA) with different roughness and viscosity.

PSU, CTA and PVA flat shits were obtained by corresponding polymer solution casting using automatic coating machine MemcastPlus (Porometr, Belgium) onto inert supports followed by solvent evaporation under equilibrium conditions. Solutions of polymers were prepared in the following proportions: 3, 5, and 7.5% PSU in tetrahydrofuran (THF), 0.75, 1.5, and 3% CTA in glacial acetic acid, 0.75, 1.5, and 3% PVA in water. After the polymer films formation, they were easily peeled off the support and desiccated under vacuum for 24 hours. Each of the polymers was cast on three glass substrates.

Borosilicate glass was chosen as an inert support, due to its chemical, thermal and mechanical stability. Before use the glass was chemically treated in order to obtain certain surface roughness. Glass support 1 was exposed in the 5% hydrofluoric acid solution for 10 min, glass support 2 was exposed in the 15% hydrofluoric acid solution containing 50% ammonium fluoride for 5 min and glass support 3 was exposed under etching paste containing 30% HF, 30% NH_4F, and 15% $BaSO_4$ for 5 min. After etching glass supports were rinsed thoroughly with distilled water in ultrasound bath for 10 min.

The glass supports surface and their roughness were studied by a scanning probe microscope SPM-9700 (Shimadzu, Japan). AFM scanning was performed using a contact mode by silicon

nitride cantilevers OMCL-TR800PSA (Olympus, Japan) with a stiffness coefficient of 0.57 N/m and a typical tip radius of no more than 15 nm (guaranteed - no more than 20 nm), a tip height was 29 microns. The experiments were carried out under ambient conditions. Automatic correction of linear noise was applied during scanning. For checking purposes reproducibility, AFM scanning was carried out on different sites of the studied surfaces. Processing of the obtained AFM images and their analysis were performed by a software SPM Manager ver. 4.02 (Shimadzu, Japan).

The same way, the polymers surface was studied. But since polymeric materials have a loosely-coupled surface structure, AFM scanning was performed using a tapping mode by silicon vibrating cantilevers PointProbe FMR-20 (Nano World Innovative Technologies, USA) with a stiffness coefficient of 1.3 N/m and a typical tip radius of no more than 8 nm (guaranteed - no more than 12 nm), a tip height was 15 microns.

According to the AFM scanning data (height arrays with a dimension of 512 × 512 pixels) of the supports and the polymer films from the most viscous of the presented solutions (7.5% PSU, 3% CTA, and 3% PVA), a “growth” model as a Kardar-Parisi-Zhang (KPZ) one was developed.

The obtained model takes into account chemical and physico-chemical features of an original polymer solution, including its viscosity, a Kuhn segment of a polymer chain (a flexibility measure of macromolecules) and solvent evaporation rate, as well as support roughness used for film formation.

The viscosity of the polymer solutions was determined using SVM 3001 Stabinger Viscometer (Anton Paar, Austria) at 25 degrees Celsius. The evaporation rate of the solvent from the polymer solutions was defined by measuring changes in the solution mass over time. The Kuhn segments were found by reference data.

The model was successfully verified using the AFM images of the polymer films surface obtained on the same supports from the same polymers (but with a lower initial viscosity), good agreement with experimental data was observed.

This work was supported by the RFBR (project No. 18-08-01356 A).

1. T.S. Sazanova, K.V. Otvagina, I.V. Vorotyntsev, *Polymer Testing* **68** (2018).
2. A.E. Rassadin, T.S. Sazanova, A.V. Stepanov, L.A. Fomin, *IOP Conf. Series: Mat. Sci. Eng.* **443** (2018).