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Surface Channel Microstructures in Polymer Films for Fluid Transport

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Abstract -The methods of heterogeneous microstructure formation on the surfaces of polymer films via their modification with gaseous fluorine have been considered. The successive fluorination and sulfonation of polyolefin films allows the synthesis of heterounit bi- and polyfunctional molecular fragments, thereby providing controlled chemical structuring at the nanolevel within a macromolecular segment. The combined use of the above methods of polymer-surface modification and intermediate film deformation under uniaxial tension results in the formation of surface microzones with fluorinated and sulfonated structures. Fluorinated and sulfonated microzones are formed via mechanical fracture of the fluorinated layer before sulfonation or via shielding of the polymer surface before sulfonation according to a given pattern through photolithographic methods. The practical applications of polymer films with heterogeneous surface structures are discussed.

***Keywords*:** surface, channel, microstructure, polymer films, fluid transport, fluorination, sulfonation

1. Introduction

Recently, in polymer technology, there has been an evident change in the production of flexible functional film materials and devices on flexible polymer substrates. The aforementioned products are used in power engineering (light-emitting materials, solar cells), medicine (materials with incorporated drugs and other special ingredients, functionalized membranes, medical transdermal films), electronics (chips, materials for matrix radiation receivers), analytical equipment (active elements of devices for mon itoring of optical, electrical, and mechanical characteristics; chemical sensors), consumer products (chips for everyday electronic devices, materials for intelligent packaging, “labels” for information coding, etc.).

The great interest in the surface structurization of polymers has arisen owing to the versatility of synthetic and biological polymers and to the possibility to design new high-resolution polymer structures. The polymer structures can be obtained via structurization of reactive molecular precursors and their polymeriza- tion immediately on the surface or through the self-assembly of block copolymers. At present, this field is being developed intensively. The current progress in polymer structurization via photolithography and other printing methods, self-assembly of block copolymers, and the action of thermal or electromagnetic fields on thin polymer films has been thoroughly discussed in a number of papers and reviews (Nie Z., Kumacheva E,. 2008; Shimoda T., et al. 2003; Menard E., et al. 2007; Bloomstein T. M., et al. 2006).

2. Experimental Results and Discussion

In the experiments, LDPE, HDPE, PP, and PET film samples were used Fluorination was performed with elementary fluorine via the developed method (Nazarov V. G., et al. 1996), and sulfonation was performed as described in (Nazarov V. G. 1997). The modification intensity was characterized by the degree of surface fluorination, C_A^F, and the degree of surface sulfonation, $C_A^{SO_3H}$, which are equal to the ratio of the gain in the sample mass to the sample sur- face area. During sulfonation of heterogeneous (non-fluorinated) zones of prefluorinated samples, the sulfonation degrees were estimated from control samples of the same polymers.

The quantitative analysis of the content of individual elements in the surface layers of modified polymers was conducted via X-ray photoelectron spectroscopy (XPS) on a Jeol JPS-9200 spectrometer (Japan) equipped with a semispherical analyzer and a double-anode X-ray gun. The spectrometer resolution was 0.9 eV at the Ag3d level for MgK_{α} X-ray radiation; the analysis depth was 2 nm. The morphological changes in the surface structures were analyzed via AFM microscopy in the semicontact mode (C3M Solver BIO, ZAO NT-MDT, Zelenograd) with the use of NSG 01 silicon probes with a gold coating (a needle-curve radius of 10 nm).

The polymer surface was visualized with a Stereoscan-360 scanning electron microscope (Cambridge Instrument) after the preliminary coating of polymer films with a thin (5 to 10 nm) gold layer. Photographs were taken in the visual spectral region with a POLAM R-312 optical polarization microscope at 20× magnification and an Olympus CX41 optical microscope (Japan) with a video camera.

Metallic layers with patterns were formed on polymer films via standard photolithographic methods (Gotra Z. Yu. 2001) that use spraying with NiCr alloy (Nichrome). The deposition of the metallic layer was performed on a magnetron spraying unit in argon under a vacuum of 2×10^{-2} mm Hg at 300 V for 60 min. For photolithography, a Sp-15 positive photoresist was used.

The method of formation of heterogeneous surface microstructures with different degrees of localization suggests an intermediate thermal or deformational effect on the prefluorinated polymer film. It was shown that, as a result of thermal and deformational effects on a polymer with a fluorinated or sulfonated surface, the continuity of the surface layer deteriorates (Nazarov V. G. 1998). The thermal and deformational effects on the prefluorinated polymer with a controlled size and number of “uncovered” zones of the initial nonfluorinated polymer (hereinafter called “defects” of the modified surface layer) followed by sulfonation of these defects result in heterogeneous macrostructures with high degrees of fragment localization and in intermediate surface areas with transient polarities. The deformational stretching of fluorinated films, which allows the targeted control of the ratio of fluorinated and sulfonated zones on the polymer surface, is given as an example of the used methods.

The thorough study of the stretching of surface fluorinated polyolefin films showed that these films can be assigned to “solid coating on pliable substrate” systems that feature deformation accompanied by surface structuring of a specific type (Volynskii and A.L., Bakeev N.F. 2005). The surface images recorded during stretching of fluorinated films of LDPE, HDPE, PET, and PP exhibit pronounced surface structuring with the characteristic regular relief (Fig. 1) (Nazarov V. G., et al. 2012). The images were obtained on a scanning electron microscope.

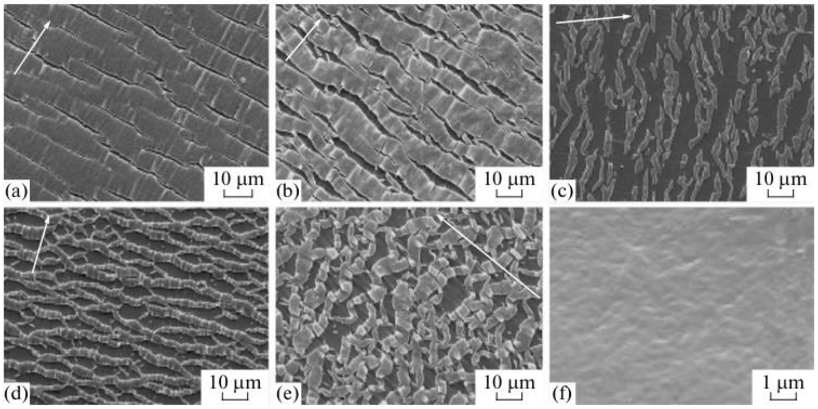

Fig. 1. Surface images of various films: (a) LDPE, (b) HDPE, (c) PET, and (d) PP fluorinated for 0.5 h and then stretched by 100%; (e) fluorinated HDPE after stretching by 200%; (f) fluorinated LDPE before stretching. Arrows indicate the stretching directions.

It is seen that, under uniaxial tension, the fluorinated surface layer is separated into fragments similar in size and 8–15 μm in width. The mentioned character of the fluorinated layer fracture is observed at

100% stretching with neck formation, and at further sample stretching up to 200%, additional fragmentation of the layer is absent, as was shown with the HDPE film fluorinated for 6 h (Figs. 1b, 1e).

From analysis of Fig. 1, it may be concluded that the surface area of the opening zone of the pristine polymer is mainly determined by the degree of stretching of the fluorinated HDPE film. For fluorinated zones, the surface tension is as high as 18 mN/m; for sulfonated zones, it is as high as 65 mN/m.

Further large and reliable structures are formed as a result of the targeted fracture of the fluorinated surface layer during a mechanical action, for example, via the use of metallic needles with different diameters and shapes followed by sulfonation. Through variation in the sulfonation time and intensity, the conditions for the reaction occurring mainly in the uncovered zones of the pristine polymer may be found. With this procedure, on the surface of an LDPE film fluorinated for 3 h, zones with destroyed fluorinated layers in the form of bands and nets were obtained. The general view of the surface pattern formed after sulfonation and the character of the sulfonation zones are shown for the example of the LDPE film with bands (Fig. 2).

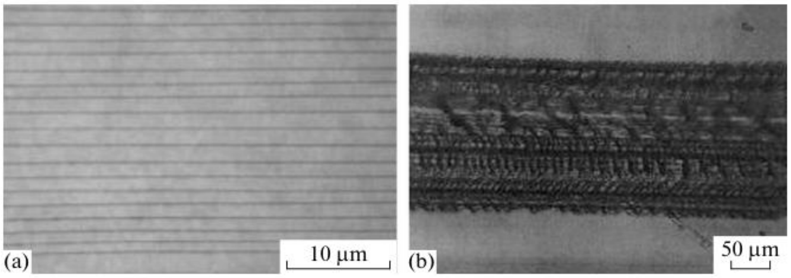

Fig. 2. Images of fluorinated LDPE films obtained on a POLAM R-312 optical polarization microscope: (a) with bands made by steel needles with subsequent sulfonation, no magnification; (b) with a sulfonated band, 50× magnification. The sulfonated bands of the pristine polymer are dark.

As Fig. 2b shows, at the chosen diameter (200 μm) of the needle used for destruction of the fluorinated PE layer, the formed bands are 200–250 μm in width. The zone of sulfonated bands varies in color, a result that is related to the nonuniform sulfonation due to polymer-surface defects that appear during the mechanical action of the steel needle.

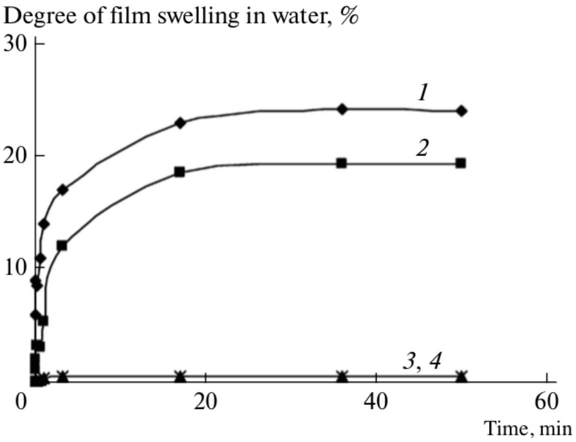

Fig. 3. Kinetics of swelling of (*1–2*) LDPE films with sulfonation degrees of $CA^{SO_3H} = 5.8 \times 10^{-3}$ and (*2*) 2.1×10^{-3} kg/m^2, (*3*) the pristine LDPE film, and (*4*) the successively fluorinated ($C_A{}^F = 4.7\times10^{-4}$ kg/m^2) and sulfonated ($CA^{SO_3H} = 1.1\times10^{-4}$ kg/m^2) LDPE film in water.

For polymer films with mosaic surface modification, the differences in the physicochemical properties of fluorinated and sulfonated zones can be used. Unlike fluorinated zones, the sulfonated zones can sorb water to a significant extent, with the amount of adsorbed water being proportional to the degree of sample sulfonation, and made microfluid transport. Figure 3 shows the kinetics of swelling of LDPE sulfonated films with different sulfonation degrees in water. It is evident that the sorption by sulfonated films occurs rapidly and that equilibrium swelling is attained within 30 min. Thus, at a specific configuration of the sulfonated zones, it is possible to create a system for the targeted transport of water and aqueous solutions through sulfonated channels on the surface of a chemically stable fluorinated LDPE film.

3. Conclusions

The analysis of the results shows that the optimum combination of methods of polymer surface fluorination and sulfonation, the order of their application, and the use of other intermediate operations may be considered a promising line that allows the formation of heterogeneous (mosaic) surface structures with the maximum hydrophobic and hydrophilic properties at the microlevels. Some preliminary results suggest that such approaches are promising for the synthesis of matrices for the control of nanoparticle self-assembly from their colloid solutions in microfluid devices, in surface controlled metal cat- ion sorption, and in medicine. Further investigation, evidently, may open additional lines of application of similar surface structures.

The problem of both spontaneous and forced defect formation in the modified surface layer is an individual poorly known line of investigation. The optimum technological implementation of the forced development of defects may make it possible to form mosaic (heterogeneous) structures on the molecular level, nanolevel, and macrolevel in the surface layers owing to successive targeted modification with different reagents and some additional operations and process stages. Evidently, the resultant structures will be substantially different from both block copolymer and polymer blend structures. The study of the formation of step uniform and gradient surface structures is of interest as well. Generally, it may be concluded that the controlled surface modification of polymers is a promising line in the synthesis of new functional polymers and hybrid components of structurally unified multilayer systems with an intrinsic combination of positive properties of the pristine polymer matrix and the endowed high characteristics of surface layers.

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