

Creation of nano-dimension structures on the surface of polymer films used in packaging and research of their properties

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Experimental results on researching structure and chemical constitution of surface of polymer films modified by processing with gaseous fluorine are represented in this work. The influence of different modes of fluorination of PE, PVC, PI, PET films on change of their surface properties has been researched by using methods of scanning electron microscopy, MBFIR IR- spectroscopy, evaluation of friction factors.

Introduction

Nowadays in printing industry we observe considerable growth of volumes of printed products with use of polymer films as substrates. Polymer films, being as a rule hydrophobic, are badly wet by inks especially by water-based inks. That's why printing on polymer films requires either preliminary creating extra layers so called primers, or surface modification by processing it with corona discharge. And in the first place, it is connected with the necessity of increasing adhesion strength on the border "polymer film – printing ink". In other words, modification of polymer film surface is not a new direction for printing industry. However, during the process of creating new packaging materials, especially for a number of foodstuffs, requirements to barrier properties of polymer films are constantly being toughened relative to moisture, oxygen, odors.

At present time, increasing barrier characteristics of polymer films used in packaging is achieved by two ways: increasing thickness of packing material or creating extra layers that also increases general film thickness. Analysis of scientific literature displayed the possibility of applying various kinds of modification films surface on nano-dimension level which leads to decreasing permeability of moisture fume, grease, oxygen [1-4]. There are experimental data which are evidence of decreasing permeability of various elastometers whose surface was subjected to such modification. It was of great interest to get experimental data concerning the influence of such modification on the structure and properties of a surface of polymer films (such as PE, PET) used as packing materials.

Methods

Surface modification of polymer films from polyethylene (PE), polyvinylchloride (PVC), polyimide (PI) and polyethylene terephthalate (PET) was carried out by processing it with gaseous fluorine at a special plant on various modes and with different activity degree of processing[5]. Modification of film samples was carried out both from one side of surface and from two sides.

Researches of surface of fluorinated and control film samples which were carried out on scanning electron microscope Stereoscan-360 (10 000 magnification).

Structurally-chemical changes taking place in surface layer of polymer films subjected to modification, were estimated by IR spectroscopy of multirepeatedly broken full internal reflection (MBFIR). Recording IR-spectra of researched films was carried out on IR-spectrophotometer with Fourier-transformer. For recording IR-spectra of surface we used MBCIR add-on device produced on the base of ZnSe crystal. At that, the form of crystal faceting and also ratio of geometric dimensions allowed to get 36 reflections from the surface of researched films.

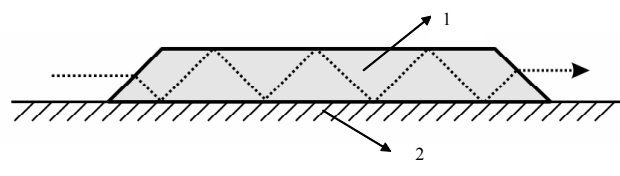


Figure 2: Principle of IR-spectra MBFIR record: 1- ZnSe prism, 2 – polymer film

¹Дехант И., Данц Р., Киммер В., Шмольке Р. ИК-спектроскопия полимеров. М.: Химия, 1976.

It was used data from the monograph «IR-spectroscopy of polymers»¹ during the process of de-cryption. Quantitative analysis of IR-spectra was done with use of program "FSpec", designed for control IR Fourier spectrophotometer and processing spectra.

The evaluation of static and dynamic friction factors was conducted on a special plant [6]. Schematic diagram are represented at fig.3

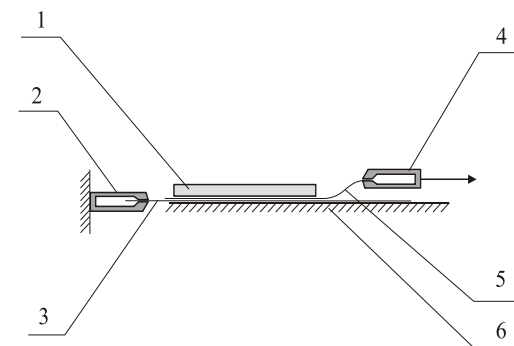


Figure 3: Evaluation of permeability was done by gas chromatography method at temperature 25°C.

Experimental results

The fig. 1 presents the kinetic dependence of modification extent of fluorinated systems. C_A^F – mass of fluorine in polymer per 1 m².

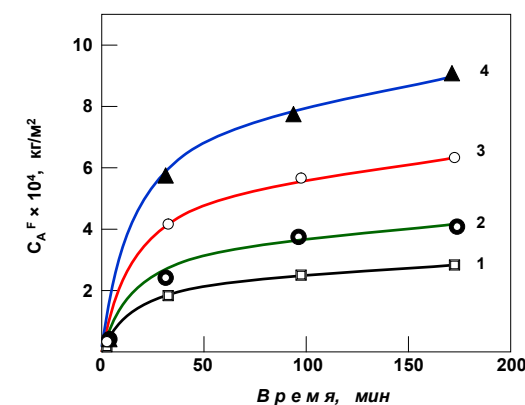


Figure 1: Kinetic dependences of modification extent of fluorination films: PVC (1), PE (2), PI (3) and PET (4) by blend of 15 vol.% fluorine with helium at 20° C

Analysis this dependence it can be marked that polymers take up positions in the following consecution according to extent growth of the fluorination: PVC < PE < PI < PET. Obviously this consecution is determined by polymer macromolecule chemical structure.

Researches of surface of fluorinated and control film samples which were carried out on scanning electron microscope Stereoscan-360, registered that microrelief of surface undergoes essential changes on nano-dimension level during the process of treating by fluorine.

At that, it was discovered that with 10 000 magnifications one can see on photos that surface of fluorinated samples from PE and PVC has open undulation in comparison with relatively smooth surface of not modified samples from PE, PVC, PI and PET.

To the most, it is observed for PE while in case of PVC these changes have more minor and not uniform nature.

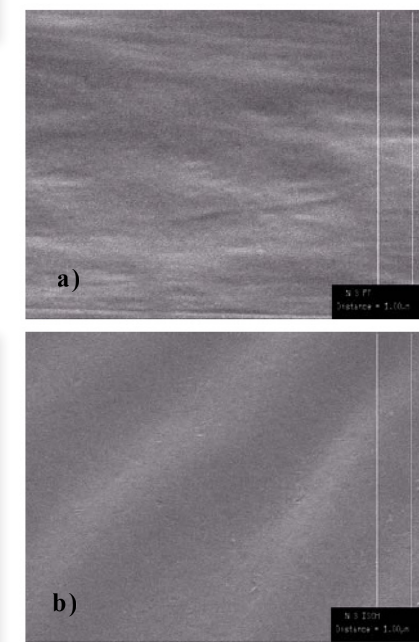


Figure 4: Photos of films from PE: a - initial sample, b - fluorinated samples

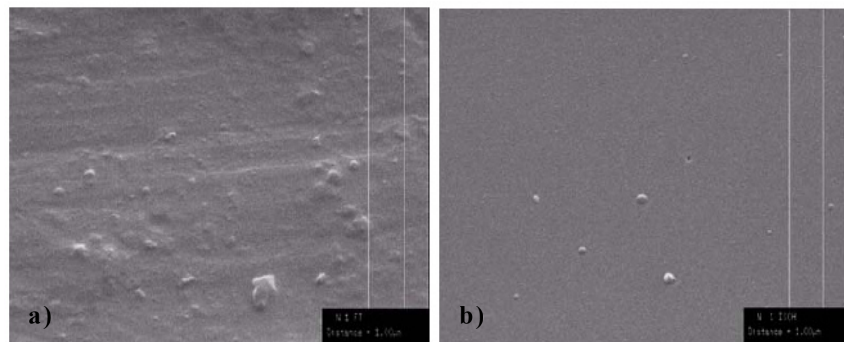


Figure 5: Photos of films from PVC: a - fluorinated samples, b - initial sample

Dimensions of typical surface geometry fragments observable on microscopical shots make up for PE for valleys 500÷700 nm and 500÷1500 nm for high grounds. These dimensions are close to dimensions of crystalline formations which are typical for polyethylene. Whereas such morphological changes of surface are not observed at fluorination of PI and PET. Presumably, manifestation of transformation of surface layer from initial into polyfluorinated in changes of surface structure depends on physico-mechanical properties of a polymer.

Analysis of IR-spectra MBFIR confirmed our assumption about substitution of hydrocarbon onto fluorohydrocarbon composition of macromolecules in surface layer. At this picture you can see IR-spectra of surface of initial and fluorinated PE film samples. On samples subjected to fluorination it is observed appearance of broad intensive band at frequencies in the range of 1100-1300 cm^{-1} . It is evidence of presence of $-\text{CF}-$, $-\text{CF}_2-$ and $-\text{CF}_3$ groups in surface layer.

With increasing duration of fluorination the intensity of a band at frequency range of 1100-

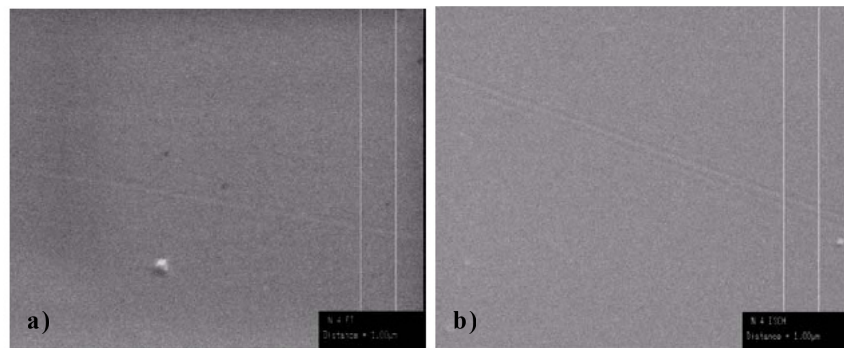


Figure 6: Photos of films from PET: a - fluorinated samples, b - initial sample

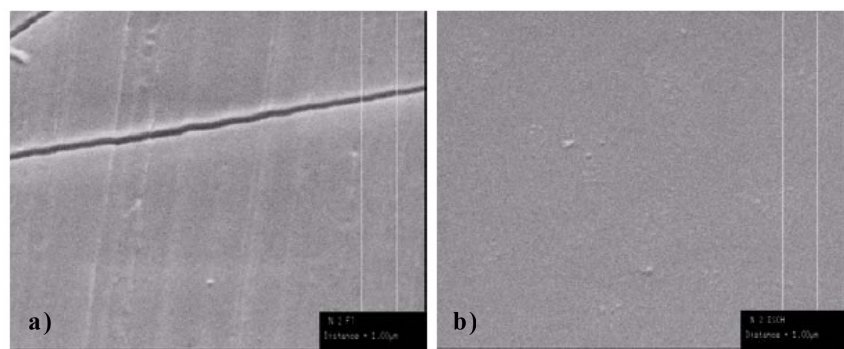


Figure 7: Photos of films from PI: a - fluorinated samples, b - initial sample

1300 cm^{-1} is increased (as it is seen at fig.8), and consequently concentration of $-\text{CF}-$, $-\text{CF}_2-$ and $-\text{CF}_3$ groups is increased. On IR-spectra PET, PI and PVC films it is observed broadening of a stripe in frequency band 1050-1150 cm^{-1} . As in this frequency band besides fluorine-contain-

ing groups there is dichroic stripe (1100-1125 cm^{-1}) owing to fluctuation (C-O) groups, that's why it is not noticeable to observe appearance of new stripes against a background of the dichroic stripe.

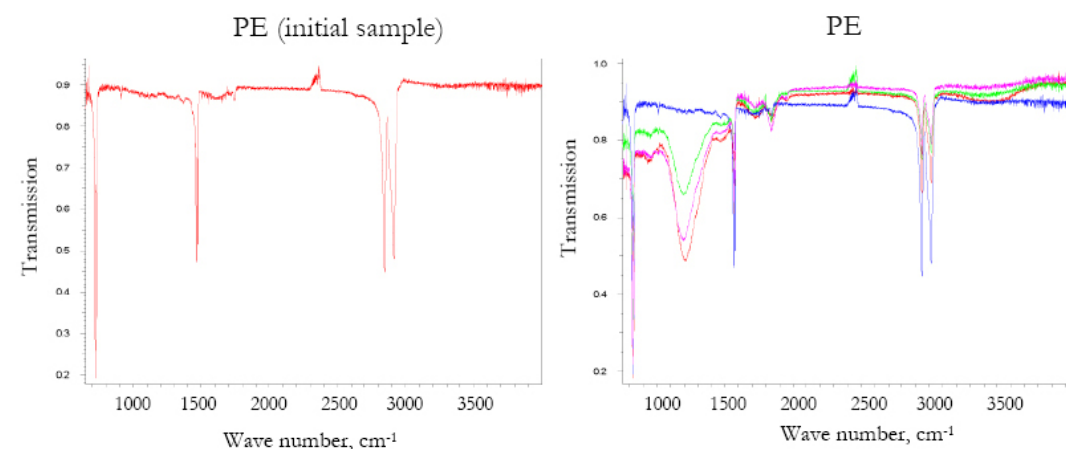


Figure 8: MBFIR IR-spectra of PE

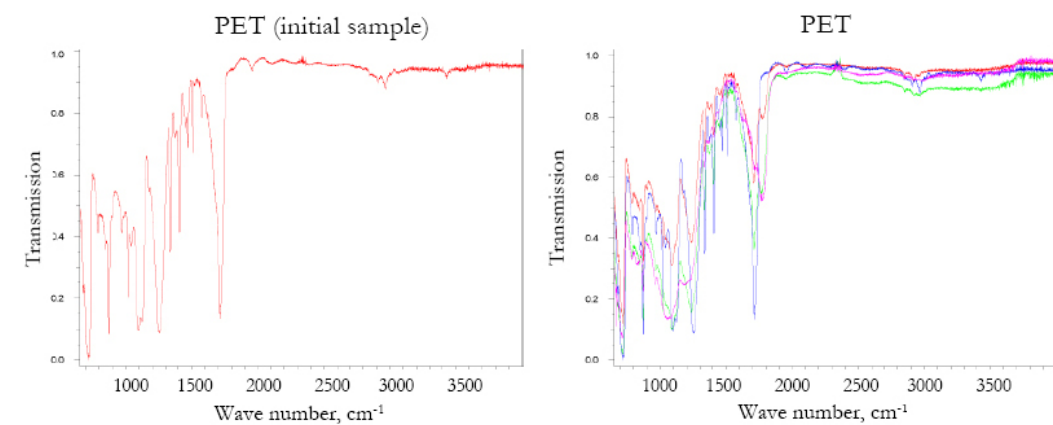


Figure 9: MBFIR IR-spectra of PET

Figure 10: MBFIR IR-spectra of PI

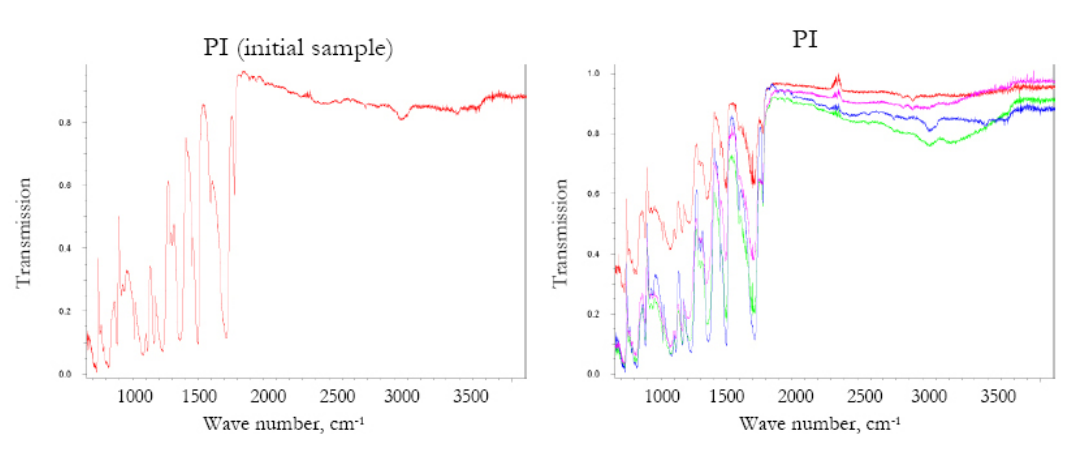
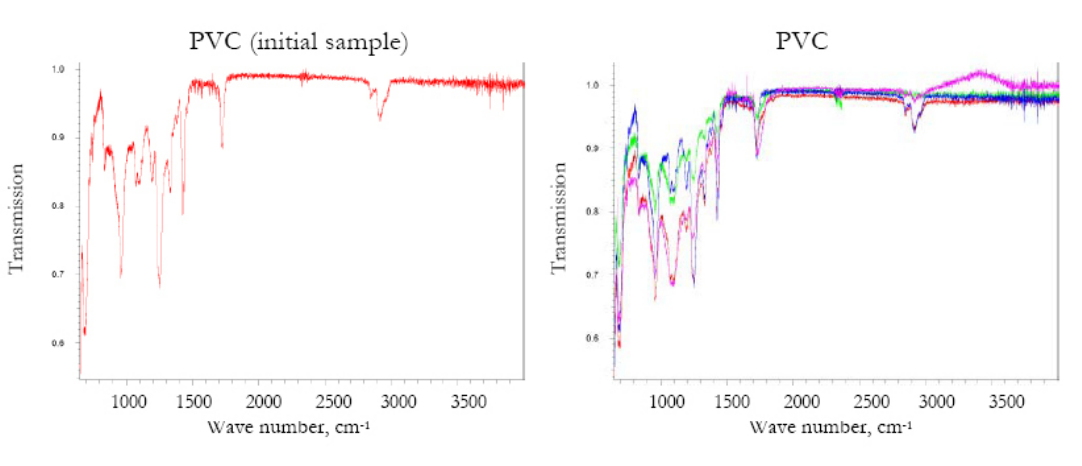


Figure 11: MBFIR IR-spectra of PVC

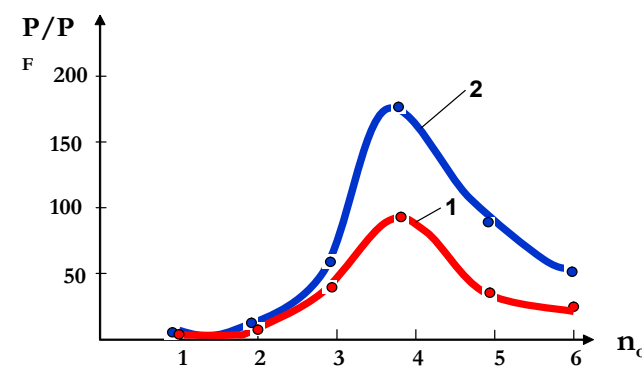


Experimental results of measuring friction factors for some researched samples of polymer films are represented at table 1.

No	Polymer film	μ_s (static)	μ_d (dynamic)
1	2	3	4
1.	PE (initial) PE (fluorinated)	0,60 0,42	0,56 0,40
2.	PET (initial) PET (fluorinated)	0,72 0,38	0,68 0,36
3.	PVC (initial) PVC (fluorinated)	0,63 0,44	0,60 0,40
4.	PI (initial) PI (fluorinated)	0,86 0,65	0,78 0,60

Table 1: Evaluative results of friction factors of polymer films, which are subjected to fluorination

Figure 12: Graph of correlation permeability P/P_F



As it is seen from results represented at table 1, in all cases decreasing values of friction factors is observed.

Analysis barrier properties of initial and fluorinated PE films, it can be marked decreasing of permeability of fluorinated PE for alcohol.

Researching initial and modified samples of PE permeability relative to different alcohols (from methanol till hexanol) it was analyzed the influence of duration of fluorination into correlation permeability P/P_F (fig.12). P - initial polymer permeability coefficient, P_F - fluorinated PE permeability coefficient, n_o - number of carbon atoms in alcohol's molecule, 1 - PE film fluorinated for 40 minutes, 2 - PE film fluorinated for 90 minutes. As it is seen from fig. 12 the highest barrier properties was registered for isobutyl alcohol (4 carbon atoms).

Then estimating barrier properties of initial and fluorinated PE films, it was marked decreasing permeability at fluorination of PE films for oxygen and alcohol (oxygen molecule is larger than alcohol that's why we can expect increasing barrier properties).

Summary

- The research showed the possibility of barrier properties level increasing of some polymer films by modification with gaseous fluorine treating of their surfaces on nano-dimension level.
- Fluorination of polymer film surfaces leads to creation of fluorine-containing groups on the polymer blanket (-CF-, -CF₂- and -CF₃). Their concentration grows with increase of fluorination duration.

- The research directions should be expanded and barrier properties will be analyzed thoroughly in following research.
- Some results can be used in development of multi-layer packing materials with high barrier properties and at general decreasing of thickness of combined film packaging.

List of literature

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