

MORPHOLOGY AND MOLECULAR STRUCTURE OF POLYURETHANE FILMS TREATED WITH A GLOW DISCHARGE PLASMA

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We have determined the major physicochemical changes occurring in polyurethane surface layers when treated in a glow discharge plasma. We have shown that along with etching and degradation processes in the polymer, there is also redistribution of hydrogen bonds as well as an increase in the concentration of carbonyl groups and the degree of self-association of urethane fragments. We conclude that the established physicochemical changes are due mainly to selective etching of the surface layers on exposure to UV radiation and the flux of charged particles generated in the glow discharge.

Key words: plasma treatment, glow discharge, polyurethane, molecular structure, IR spectroscopy, morphology, etching.

Introduction. Treatment of polymer materials in a glow discharge plasma is an effective technological means for surface activation which is often used to improve the strength of the adhesive bond in vacuum metallization [1], glueing, and formation of multilayer adhesive systems [2], and for surface modification and etching [3]. The major processes occurring on treatment in a discharge that have an effect on the adhesive activity of the surface include charging of the surface layers [2, 4]; degradation of the macromolecules due to exposure of the polymer to ions, electrons, electromagnetic radiation, or external electric fields [5]; chemical reactions involving radicals or ions, occurring in the surface layers [5, 6]; desorption of low-molecular weight compounds [5]. The activation effect, its mechanism and the nature of its appearance depend to a significant extent on the nature of the polymer and the treatment parameters. Thus in [2, 5], it was established that the dominant effect on the degree of activation comes from the charge state of the surface and formation of electret structures.

In addition, the retention of surface activity over long time periods and the marked change in the surface morphology [7] indicate a possible effect on their properties from chemical changes in the composition and structure of the layers treated in a glow discharge.

The aim of this work was to determine the changes in chemical composition, molecular structure, morphology, and properties of polyurethane surface layers that occur when they are treated in a glow discharge plasma.

The Experiment. The polymer films were formed by heating the original polyurethane powder (Desmopan 385) to a temperature of 160°C under vacuum between two pieces of aluminum foil. After cooling down under vacuum, the aluminum foil was removed by dissolving it in the base NaOH, followed by washing in distilled water.

Plasma treatment of the films formed was carried out in a low-frequency ($f = 1$ kHz) glow discharge created in a residual air atmosphere. The distance between electrodes was 7 cm, the discharge current density was 0.5 A/m². The samples were placed on a grounded electrode. The treatment time was set up to 30 min.

The molecular structure of the polyurethane films was studied on a Vertex-70 IR Fourier spectrophotometer (Bruker) and a Hyperion IR microscope (Bruker) using standard procedures. The C–H stretching vibration band at $\nu = 2920$ cm⁻¹ in the CH₂ groups was selected as the internal standard for the IR studies of the polyurethane films. This choice of the band was based on recommendations given in [8, 9] and the plotted experimental dependence of the op-

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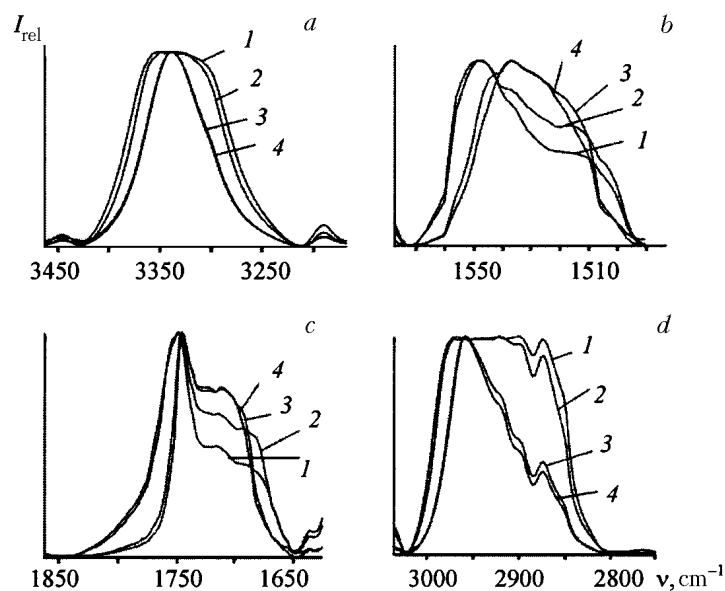


Fig. 1 IR spectra of polyurethane films after plasma treatment for 0 min (1), 10 min (2), 20 min (3), and 30 min (4).

tical density of the 2920 cm^{-1} absorption band on the polymer layer thickness. We established that this dependence is linear with coefficient of determination $R^2 > 0.97$.

The microscopic studies of the films were carried out using a Solver P 47 PRO atomic force microscope (NT-MDT, Zelenograd, Russia). Fractal analysis of the morphological images was done by measuring area and perimeter in the horizontal cross section with maximum number of individual clusters not contacting the boundaries of the image. The monofractal dimension of the cross section D_f was determined by the procedure in [10].

The surface energy of the films formed was measured by the Fowkes method [11].

Discussion of Results. Treatment of polyurethane films in a glow discharge plasma leads to marked changes in the molecular structure. In particular, we established that as the treatment time increases, there is a marked decrease in the width of the absorption band responsible for stretching vibrations of NH groups that are associated as a result of formation of intermolecular H bonds (Fig. 1a). Simultaneously with the decrease in the width of the 3338 cm^{-1} absorption band on exposure to the plasma discharge, its relative optical density decreases (Table 1).

An increase in the plasma treatment time for the polyurethane film is also accompanied by a monotonic decrease in the relative optical density of the 3348 cm^{-1} band responsible for absorption of NH groups that are not bound in a hydrogen bond (Table 1).

A double absorption peak is detected in the region of the bending vibrations of the NH groups ($1600\text{--}1490\text{ cm}^{-1}$) in the IR spectrum of the polyurethane films (Fig. 1b), where the high-frequency component may be due to absorption of bound NH groups while the low-frequency component may be due to absorption of unbound NH groups [12]. As the plasma treatment time increases, the width of the double absorption band decreases with a shift of the band toward lower frequencies. In this case, treatment promotes a significant (by more than 1.4 times) change in the ratio of the optical densities of the absorption bands responsible for the bending vibrations of unassociated and associated NH groups (Table 1), and also a marked decrease in the width of the low-frequency component of the double absorption peak.

In the region of vibrations of the carbonyl groups, we observe splitting of the bands into two components with maxima at 1748 and 1705 cm^{-1} (Fig. 1). The ratio of the areas for the low-frequency and the total absorption bands, provided that the absorption coefficients are equal at these frequencies, is the fraction of carbonyl groups bound to NH groups [13, 14]. The degree of self-association of urethane fragments can also be judged from the parameter R , equal to the ratio of the optical densities of the 1705 cm^{-1} and 1748 cm^{-1} bands. An increase in the plasma treatment time for the polyurethane films is accompanied by a significant decrease in the width of the absorption band in the

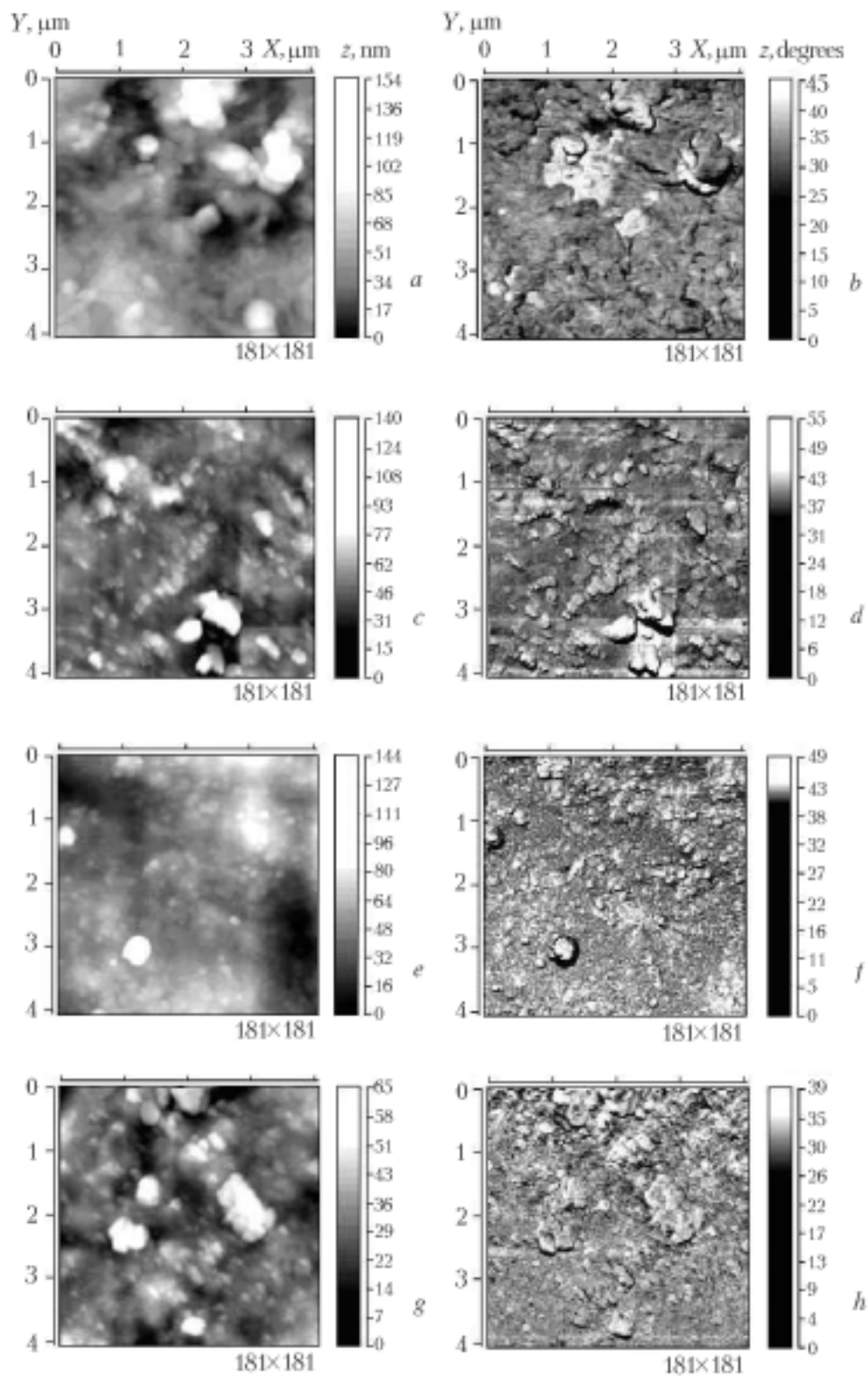


Fig. 2 AFM images of the surface of polyurethane films [(a, c, e, g) topography; (b, d, f, h) phase contrast) after plasma treatment for 0 min (a, b), 10 min (c, d), 20 min (e, f), and 30 min (g, h).

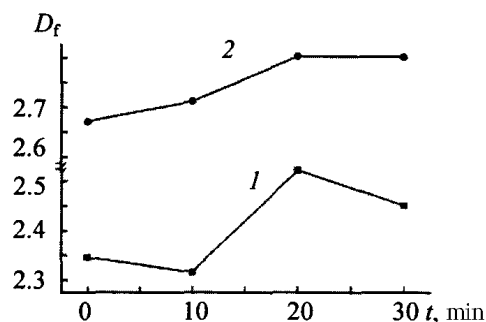


Fig. 3 Dependence of the monofractal dimension of the surface cross section on the plasma treatment time: 1) from topography data; 2) from phase contrast data.

TABLE 1 Relative Optical Densities of Absorption Bands in IR Spectrum of Polyurethane Films for Different Plasma Treatment Times

Treatment time, min	ν , cm^{-1}						$R = D_{1705}/D_{1748}$
	$\nu(\text{CH}_3)$	$\nu(\text{NH})_{\text{assoc}}$	$\nu(\text{NH})_{\text{unassoc}}$	$\delta(\text{NH})_{\text{assoc}}$	$\delta(\text{NH})_{\text{unassoc}}$	$\nu(\text{CO-O-C})$	
	2783	3338	3448	1548	1521	1080	
0	1.78	1.71	0.10	1.29	0.66	0.26	0.50
10	1.32	1.39	0.06	1.03	0.66	0.18	0.65
20	0.76	1.29	0.04	1.61*	1.35*	1.25	0.75
30	0.75	1.34	0.02	2.12*	1.56*	1.64	0.74

*After a 20 min treatment, $\nu = 1541 \text{ cm}^{-1}$ for the $\delta(\text{NH})_{\text{assoc}}$ absorption band and $\nu = 1519 \text{ cm}^{-1}$ for $\delta(\text{NH})_{\text{unassoc}}$; after 30 min, 1538 cm^{-1} and 1519 cm^{-1} respectively.

considered region, and an increase in the degree of self-association of the urethane fragments (the parameter R) (Table 1).

Plasma treatment of the polyurethane film has a significant effect on the structure of the hydrocarbon fragments of the polymer. In the region of absorption for the CH groups ($3020\text{--}2800 \text{ cm}^{-1}$), as the treatment time increases there is a significant decrease in the width and optical density of a number of absorption bands (Fig. 1d). In particular, we see a significant decrease in the optical density of the 2874 cm^{-1} absorption band responsible for the C–H stretching vibrations in the CH_3 group [9]. The IR spectra of polyurethane films that have undergone prolonged plasma treatment (20–30 min) are also characterized by high values of the optical densities for the absorption of stretching vibrations of ester (CO–O–C) groups (Table 1).

Figure 2 shows the AFM images of polyurethane films that have undergone activation treatment in a glow discharge plasma; these images indicate that etching of the surface layer occurs. After treatment, we established that more relief structures with extended surface area are formed on the surface (Fig. 2c–h), compared with the smoother structural formations observed in the original film (Fig. 2a and b).

With the aim of describing the morphological changes occurring, we calculated the fractal dimension of the cross sections in the AFM images of the surface of the treated film (Fig. 3). We see that as the treatment time increases for the polyurethane film, the monofractal dimension (and consequently the "ruggedness" of the structural formations) obtained from the topography and phase contrast data increases.

Due to the finite dimensions of the studied fields, the fractal dimension of the cross sections in the phase contrast images is higher than the fractal dimension obtained from the topography data. This is primarily explained by the larger number of observed structural formations revealed in the phase contrast mode. However, with such an approach,

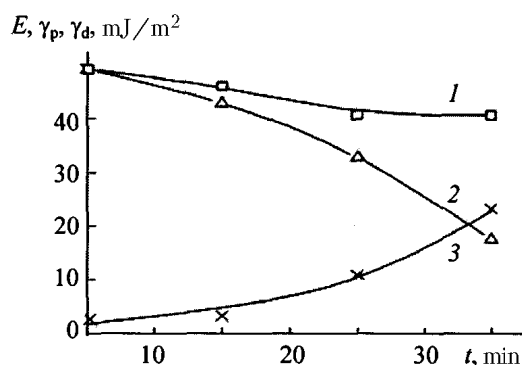


Fig. 4 Dependence of the surface energy E (1), its polar component γ_p (2), and its dispersive component γ_d (3) on the plasma treatment time.

we may trace substantial morphological changes both from the topography data and from the phase contrast data. First of all, the morphology of the film changes significantly after 10 min of treatment. Secondly, during treatment, we observe etching not only of the smooth substrate but also of large cluster formations in the original film (Fig. 2).

An increase in the plasma treatment time leads to a decrease in the surface energies of the polyurethane films (Fig. 4), despite the increase in the ester group content in the molecular structure (Table 1) established by IR spectroscopy; this suggests a change in the structure of the surface layers after etching, a redistribution of polar groups in them.

Conclusion. When polyurethane films are treated in a glow discharge plasma, we observe redistribution of the hydrogen bonds, a decrease in the concentration of hydrocarbon fragments in the surface layers and an increase in the concentration of carbonyl groups and their activity in interaction with NH groups with formation of hydrogen bonds, and a significant increase in the concentration of ester groups (by more than 5 times).

We should consider the decrease in surface energy of the films during treatment as a consequence of processes occurring on exposure to the components of a glow discharge: etching, redistribution of hydrogen bonds, self-organization of urethane fragments. Based on fractal analysis data, the results of an estimate of the surface energy, and the morphology, we can conclude that the established physicochemical changes are due mainly to selective etching of the surface layers on exposure to UV radiation and the flux of charged particles generated in the glow discharge.

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