The Relationship Between Surface Structure and Characteristics of Plasma-Polymerized Films Investigated by Means of Probe Microscopy

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The relationship between the surface morphology of the polymer films formed on steel substrates in glow-discharge plasma in heptane and their physico-chemical and mechanical characteristics was studied by means of the AFM, XPS, the chemical technique, and contact angle measurements. It was assumed that the variation of the surface morphology and film characteristics with τ_{pl} is connected with the deformation of the films in the process of relaxation of internal stresses growing as the degree of cross-linking increases. Protruding macromolecular fragments were detected on the film surfaces, with their quantity, shape and sizes reflecting the degree of the polymer strain. If some critical polymer strain is exceeded, the coalescence of a macromolecular sample, as well as deterioration of strength and protective characteristics of films takes place.

1. Introduction

In spite of abundance of studies on the structure and characteristics of plasma-polymerized films the investigation of their surface structure is the subject of just a few of them though the knowledge of the surface morphology may shed extra light on the mechanism of thin films formation and the reasons for their destruction. The majority of studies along this line use mostly electron microscopy. However, the currently developing technique of atomic force microscopy (AFM) is more informative, allowing to obtain three-dimensional images of material surfaces at higher resolution as well as investigate different material characteristics [1].

The purpose of the present work is to study the relationship between surface structure and physico-chemical and mechanical characteristics of the films prepared in glow-discharge plasma of heptane under the conditions of varied plasma

treatment duration, by means of atomic force microscopy (AFM) combined with other up-to-date techniques.

2. Experimental

The films were deposited on an insulated substrate (sample) representing a plate of low-carbon steel with the ferrite-perlite structure (carbon content 0.22%, grain size 7–10 μm), having an air-oxidized layer. Prior to plasma treatment the samples were rinsed in heptane. A bell-type reactor with a displacement of 200 cm^3 and the external disposition of electrodes separated by 90 mm was used for plasma treatment performed in a dynamic mode with the samples being equidistant from the electrodes. Prior to the experiment the system had been pumped off to 4.66 Pa and then a monomer (heptane) with the pressure before the discharge onset equal to 13.3 Pa at a steady-state flow (p_0) was introduced. To control the heptane flow before and after glow-discharge plasma (GDP) excitation by rf-field with the frequency of 40.68 MHz a needle dosimeter was used. The discharge power was 70 Wt. The plasma treatment duration (τ_{pl}) was varied in the range of 0.5–10 min. The chromel-copel thermocouple was used to control the sample temperature during plasma treatment.

The P4-Solver NT-MTD apparatus and the techniques described in Ref. [2] were used to study the topography, roughness, thickness, hardness, and surface polarity changes of the films by means of AFM. The silicon probes CS12 of the same company having the cantilever dimensions of $200 \times 40 \times 2$ μm and a force constant 3.0 N/m were used. The tip curvature radius was ≈ 10 nm. The root mean square roughness (S_g) was taken as the characteristic of surface roughness. The film hardness was assessed by measuring the least force pressing the tip to the sample, at which a specific rectangular pit remains after scanning of the selected area 0.5×0.5 μm on the film with the area 6×6 μm. In this case the investigation was started with the loading of 0.9 μN and one scan with the subsequent increase of the number of scans until the film destructed, with a maximum of 5 scans. If the film preserved its integrity a new area was scanned under the increased loading with a top value of 3.2 μN. The surface polarity changes were assessed by the changes in the sample-probe interaction force (F_z) observed in the process of measuring the force-distance curves in a local force spectroscopy mode [2] no less than in 10 surface sites. The film thickness (h) was determined by measuring the depth of a scratch left by a copper needle [2]. The data spread here made up 20%. A microscope with the $28^\times$ magnification was used to evaluate the film-to-sample adhesion, with the film exterior in the locus of scratching by a copper needle taken as a criterion.

The chemical composition of the sample surfaces was studied by means of

the previously described XPS-analysis [3].

The film permeability was determined as follows. 10 μl of aqueous solution containing 5 g/l $CuSO_4 \cdot 5H_2O$ and 1 g/l strong H_2SO_4 was deposited on the film and the time of contact release of copper and H_2-bubbles was fixed. The value reciprocal to the time of release of these reaction products was taken as the film permeability (P). Since in the majority of cases a symbate release of Cu and H_2 took place and some of the films had a red colouring hindering the control of Cu release, the results of P calculations obtained taking into account the time of H_2-bubbles appearance have been presented in the paper. A 16× magnification was applied for microscopic measurements; the results of three measuring cycles were averaged.

A conventional goniometric technique was used to determine the water contact angle (θ). It was found that in the range of the drop volume from 2 to 5 μl the values of θ remain unchanged. The average θ-values measured from three surface parts at a drop volume of distilled water equal to 2 μl are cited in the paper.

3. Results and Discussion

The investigations have shown that as one passes from the steady-state monomer flux to the one observed under the conditions of the discharge the initial reactor pressure $p_0 = 13.3$ Pa drops down to $p_g = 12.5$ Pa within several seconds (remaining stable from this point on), which may evidence a relatively high degree of heptane-to-polymer conversion [4,5]. Judging by the XPS-data indicating the presence of C- and O-atoms in the analyzed layers and the absence of Fe-atoms, the polymer film thickness is no less than 10 nm. The oxygen content in the layers analyzed is $9 \pm 2\%$ at all values of τ_{pl} in correlation with the XPS-data for the film polymerized from the plasma of hexane [6]. The C-OH-groups (binding energy $E_b = 286.7 \pm 0.2$ eV in the C1s-spectrum and 533.5 ± 0.2 eV in the O1s-spectrum [7]) represent the main oxygen-containing fragment of the films. The content of other oxygen-containing fragments, namely, C=O ($E_b = 287.9 \pm 0.3$ eV in the C1s-spectrum and 532.2 ± 0.2 eV in the O1s-spectrum) and C(O)OH ($E_b = 290 \pm 0.2$ eV in the C1s-spectrum [7]), of which many IR- and XPS-investigations of the films polymerized from the plasma of alcanes are indicative [4–6,8], does not exceed 3% in all the cases. Although the content of oxygen do not practically change with τ_{pl} there is a dependence between the values of θ and τ_{pl} (Fig.1, curve 1). A seeming contradiction between the stability of polar groups content and variations in the surface wetting ability is presumably associated with the XPS sensitivity to a surface layer ≈ 10 nm thick while θ is measured by a purely surface technique. A drop in the wetting

ability of a plasmapolimerized film in air is known to be basically associated with a reorientation (by rotation) of polar O-containing groups inside the matrix [4]. A water drop deposited onto the film surface during θ-measurements gives rise to the reorientation of hydrophilic sites (their outcrop to the surface). τ_{pl}-determined changes in θ of the films having approximately equal contents of polar groups (as in our experiments), are therefore indicative of their different reorientation abilities, i.e. structural differences of the films prepared at different τ_{pl}. With this circumstance in mind, the experimental results obtained can be interpreted as follows. The increase of τ_{pl} causes a gradual increase (with the simultaneous increase of θ) of branches and cross-links characteristic of the plasmapolymerized hydrocarbons [4], resulting in a state where no rotation of hydrophilic groups around a polymer chain virtually occurs (θ takes an extreme value of $103 \pm 3°$ characteristic of the hydrophobic extruded polyalkene films [9,10]). At $\tau_{pl} > 3$ min the degree of cross-linking might have taken higher values but this cannot reduce the rotation of practically already static polar groups, i.e. increase the surface hydrophobicity (no increase of θ is observed). The longer is τ_{pl} the larger is the film thickness (Fig.1, curve 2). However, the speed of the film thickness growth decreases in direct proportion to τ_{pl} (Fig.1, curve 3). The dependences found are representative of the process of deposition of thin films onto insulated substrates under the conditions of glow discharge [5] and may be associated with the fact that during growth of the film the substrate is heated (Fig.1, curve 4) resulting in partial etching of the film [5,11] and in reduced adsorption of the particles involved in heterogeneous stages of the film growth [4,5,12,13].

The film structural changes in the growth period are reflected in the surface morphological changes and film characteristics. The surface of the initial sample consists of cavities and hills interconnected by a net of grooves presumably associated with defects of treatment prior to the investigation. $F_z > 0$ for all the surface regions which is natural for hydrophilic iron oxides.

However, during the initial stages of plasma treatment ($\tau_{pl} < 1$ min) a thin polymer layer ($h < 200$ nm) virtually reproduces the substrate topography with a somewhat increased S_g (Fig.1, curve 5). The roughness increase may be proposed to result from the film deformation owing to relaxation of tensile internal stresses arising in the process of the film formation under the plasma conditions [4]. It may be assumed in view of a weak S_g increase that the film macromolecule chain segments possess high mobility, characteristic of the polymers with low degree of cross-linking. During the F_z measurements "sticking" of a probe tip is observed on a part of the film surface. Such a strong adhesive contact may evidence the incomplete monomer polymerization, with the possible formation
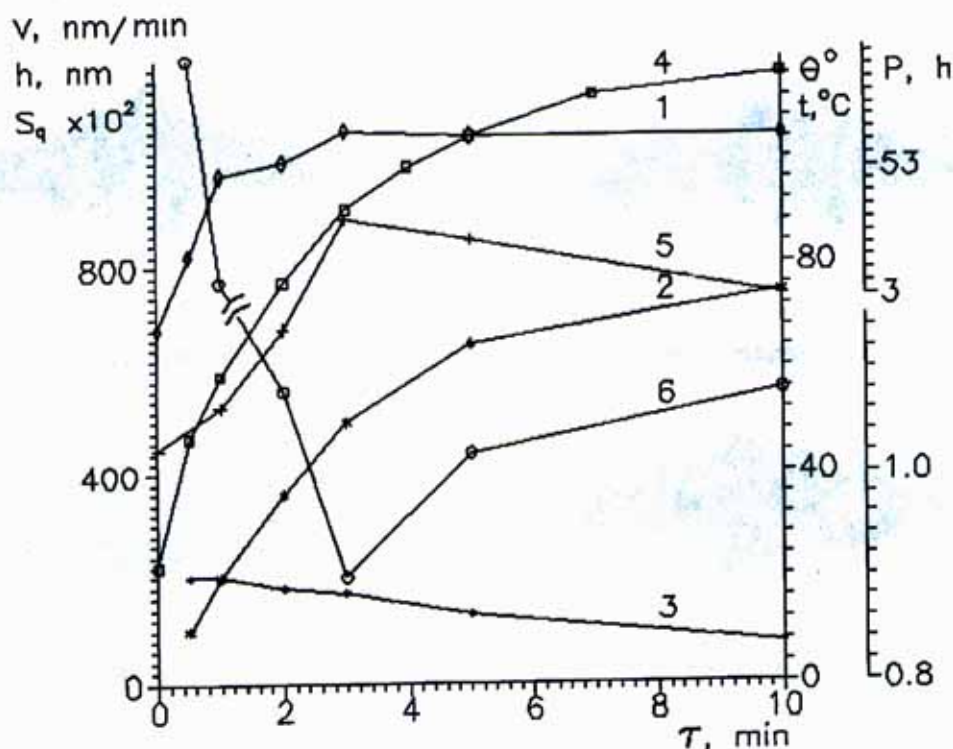
Figure 1. The plasma polimerization duration dependence of water contact angle θ (1), thickness H (2), deposition rate V (3), temperature (4), mean root square roughness S_g (5), and permeability P (6) of a heptane film.

of short oligomer chains. The other film regions are characterized by F_z in the range between 0 and 15 nN, which is typical of a combination of hydrophobic and hydrophylic surfaces, respectively. It is the formation of the film with such a structure that may explain both low hardness (0.9 μH/1) (Table 1) and high permeability (Fig.1, curve 6) almost similar to that of the iron oxide layer on the initial sample. High film-to-substrate adhesion is simultaneously observed.

For a film with $h = 200$ nm ($\tau_{pl} = 1$ min) the most typical topographical specific feature consists in individual cone fragments 20–35 nm in height (Fig.2a). Cone cutting off at 1.8 μN has demonstrated their uniform structure and hardness similar to that on other film regions. At apexes and cuts $F_z = 0$. These results evidence that the cones represent macromolecular fragments without polar groups. Furthermore, small hemispherical structures are discernible on the surface. These very hemispheres are presumably the main cause of increase of S_g measured on a film surface free of the cones. The resulting film is

a

b

c

d
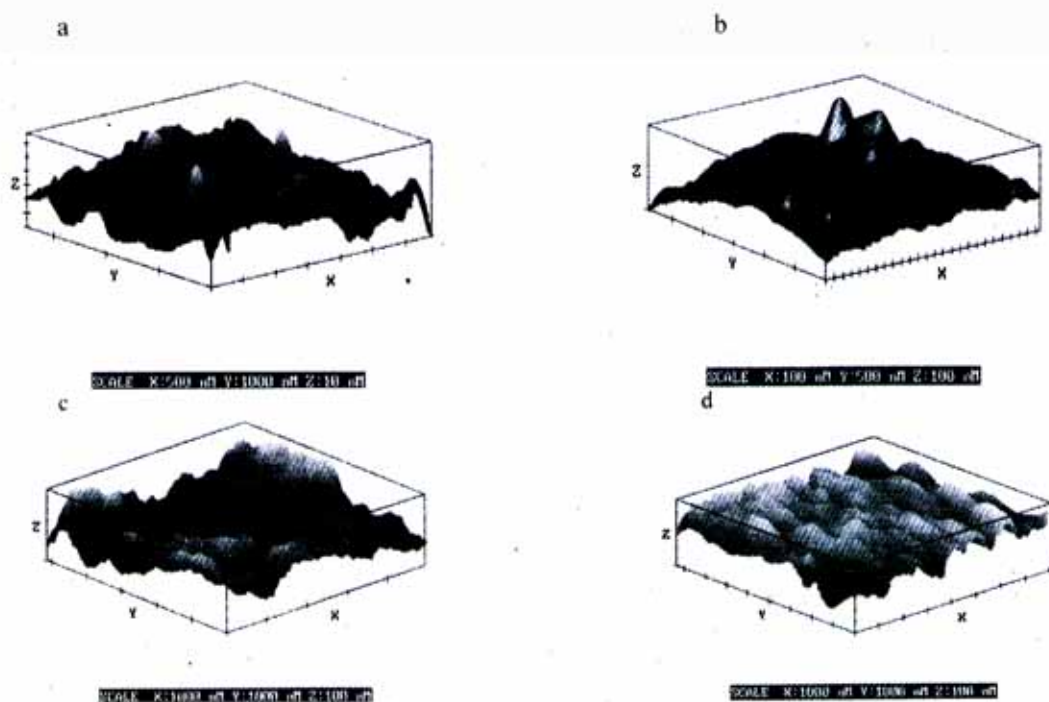
Figure 2. The AFM-image of the surface of the heptane plasma-polymerized film. Plasma polymerization duration, min: a − 1; b − 2; c − 3; d − 5.

characterized by the surface hydrophobicity and hardness increase, and the permeability decrease (Fig.1), which evidence the growth of the branching degree and cross-linking. F_z ranging from 0 to 90 nN was measured for one part of surface regions with no possibility to measure it for the other part in view of the film "stickiness". Furthermore, "thinning out" of an image (traces of a tip at 0.45 μN) has been discovered during the AFM-imaging, that evidences low film surface density. The results obtained indicate that the film is a heterogeneous one and includes at least two layers. The first layer with a certain degree of cross-links that is formed on the substrate surface is the one that determines strength properties and protective characteristics of the general heterogeneous film. The second layer on top of this first one is believed to be an oligomeric layer with a thickness comparable to the depth of a pit taking its origin in the process of a film hardness measurement. For the sample under study this value is ∼ 10 nm, i.e. no more than 4–6% of the heterogeneous film thickness. The results obtained may apparently confirm one of the concepts of the activation-

τ_{pl}, min	Hardness*	Force of film-probe interaction			Adhesion to substrate
		"Sticking" of a probe in the film	F_z		
			0	> 0	
0	0.45	−	−	+	−
0.5	0.9/1	+	+	+	smooth edges of cuts, the film does not crumble devolve or peel
1.0	1.8/1	+	+	+	
2.0	1.8/3	+	+	+	
3.0	1.8/5	−	+	−	the film slightly devolves, no peeling is observed
5.0	0.9/5	−	+	−	nonuniform edges of cuts, the film devolves significantly, no peeling is observed
10.0	0.9/1	−	+	−	

Table 1. Characteristics of polymer films prepared in plasma of heptane at a pressure of 13.3 Pa and power 70 Wt. *Numerator: the force pressing the probe to the sample surface; denominator: number of the probe scans.

recombination model of a stationary growth of a polymer film [14]. According to this model, the processes stimulating the growth of a film mass take place in its surface layer (several monolayers in thickness) with the density low at the gas phase interface and increasing with depth to the values of bulk density. The growth of branching and cross-linking degrees in the first film layer results in the decreased freedom of molecular reorganization and, hence, in the appearance of stress relaxation sites in the film region with increased surface energy. It may be proposed that the relaxation of internal stress is accompanied by the release of energy required for the formation of free chemical bonds — the growth sites (GS) of polymer film formed under the conditions of steady-state discharge (in addition to energy released in the process of recombination of positive ions derived from plasma with electrons [12]). Presumably the cones and hemispheres represent the fragments of a growing polymer film, with their quantity, shape, and dimensions reflecting the degree of polymer strain and the presence of surface regions with different surface energies. The film growth to 360 nm does not change its adhesive characteristics, but results in further film strengthening (while a layer ($\leq$ 10 nm thick) of "sticky" compounds still remains at the surface), improvement of protective characteristics and surface topography changes. Aside from individual cones as high as 50 nm and a lot of small hemispherical structures closely-located cones formed presumably at the expense of coalescence of several cones (Fig.2b), appear on the film surface. Similar morphological changes were observed in the process of the AFM-imaging

of the growth of Ge-nanoislands on Si-substrates [15]. In agreement with Ref. [15], we may suppose that the film thickness growth is accompanied by a further increase of cross-linking degree and internal stresses and, hence, the number of stress relaxation sites. The cone coalescence partially releases the stresses, which in its turn decreases the total energy of these structures.

In view of these premises, further τ_{pl} increase ensuring yet higher cross-linking degree could well be supposed to cause the growth of the number of cones with the formation of extended structures (combs, for example) under their coalescence (Fig.2 c). The topography will reflect high degree of roughness of coalesced groups. The structure of such a film should be characterized by the reduced permeability, considerable strength (due to the increased cohesion) [16] and high surface hydrophobicity. In fact, all these points are characteristic of the film formed at $\tau = 3$ min ($h = 500$ nm) (Fig.1,2c), with zero F_z for all the film regions. A poorer film adhesion (Table 1) is explained by the fact that high internal stresses arising in such a film begin to exceed the adhesion forces connecting a polymer layer and a substrate. For a film with $h \geq 500$ nm this excess is presumably low giving only a slight adhesion deterioration. However, the internal stresses in the films formed at $h \geq 650$ nm ($\tau \geq 5$ min) are so extremely high that a large number of cones forming under coagulation provides a relatively smooth surface (Fig.2d). Apart from a sharp degradation of adhesive characteristics, the film hardness also drops (Table 1). This indicates that the internal stresses begin to exceed the cohesion forces as well, resulting in cracking of the polymer layer, which partially releases the internal stresses. Cracking should have increased the film permeability (which is indeed observed) and surface roughness (Fig.1). In reality, however, a noticeable drop of S_g is observed. Note that under our conditions a decrease in S_g was typically registered near 90°C (Fig.1), close to the temperature at which partial destruction of the films prepared in plasma from benzene (80° C) [5] occurs as well as of the polyethylene film (prepared by a conventional rolling-compression technique) treated by oxygen plasma [11]. Generally the value of surface roughness may be supposed to be the result of at least two processes: it is increased by the deformational processes, and it is reduce by the film etching. The observed S_g decrease at $\geq 90°C$ is presumably associated with the film etching during its formation in plasma [4].

4. Conclusions

1. The relationship between surface morphology of the polymer films formed on steel substrates in glow-discharge plasma in heptane and their physico-chemical and mechanical characteristics has been studied by means of the AFM,

XPS, the chemical technique, and contact angle measurements.

2. It has been assumed that variation of the surface morphology and film characteristics with τ_{pl} is connected with the deformation of the films in the process of relaxation of internal stresses growing as the degree of cross-linking increases. Protruding macromolecular fragments have been detected on the film surfaces, with their quantity, shape and sizes reflecting the degree of the polymer strain.

3. If some critical polymer strain is exceeded, the coalescence of a macromolecular sample, as well as deterioration of strength and protective characteristics of films has been shown to take place.

Acknowledgements

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