Characteristics of films obtained in plasma of some saturated hydrocarbons. AFM investigation.

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The polymeric coatings obtained in the low temperature plasma of organic molecules can be used for effective metal protection. However to successfully use these coatings one should be aware of the correlation between the structural features of plasma-forming monomers and the physico-chemical characteristics of the resulting polymeric coatings. In [1] the influence of plasma-treatment regimes on the protective capability and physico-chemical characteristics of the polymeric films deposited in the plasma of heptane was investigated. The objective of this work is to deduce a relationship between the length of a monomer molecular chain (in saturated hydrocarbons) and the physico-chemical characteristics of plasma-polymerized coatings, by means of atomic force microscopy (AFM).

Experimental and specimens

The films were deposited on an insulated substrate (sample) representing a plate of low-carbon steel. A bell-type reactor with a displacement of 200 cm^3, 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, then a monomer with the pressure before the discharge onset 12.8 Pa at a steady-state flow (p_0) was applied. Methane, pentane, heptane, octane, nonane, undecane were studied as the series of saturated hydrocarbons. The discharge power was 40 Wt. The plasma treatment duration (τ_{pl}) was 5 min. The P4-Solver NT-MTD apparatus and the techniques described in [1] were used to study the topography, roughness (S_q), thickness (H), strength (St) and the changes in the film surface polarity as measured by means of AFM by the changes in the force of interaction between a sample and a probe (F_z). 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 deposition 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**).

Experimental results and discussion

The investigations have shown that while passing from a steady-state monomer flow to a monomer flow in discharge conditions the initial reactor pressure p_o decreases to p_g for the whole hydrocarbon family. The p_g / p_o value varies within the range of 0.99-0.91 (Fig.1), which is indicative of a relatively high level of a monomer-to-polymer conversion. However the peak conversion level is observed when the number of carbon atoms in a saturated carbon molecule (C) is equal to 9. Maximum film thickness (H) exactly corresponds to this value (Fig.1).

The film strength increases with C with a sharp increase at C=7. After the film deposition the surface is less rough in contrast with the initial steel substrate ($S_q = 10$) (Fig.1), which evidences a considerable film thickness and a changed surface morphology. In the case of the methane deposition the surface represents a number of cones located mainly along the substrate scratches (Fig.2), $F_z = 0$. This film is characterized by the combination of hydrophobic and hydrophilic surfaces. With all the other films $F_z = 0$. No substrate pattern is observed at C >7. The possible reason may be the coalescence of the cones with the resultant roughness decrease. The least film roughness is observed at C = 11 (Fig. 2 d).

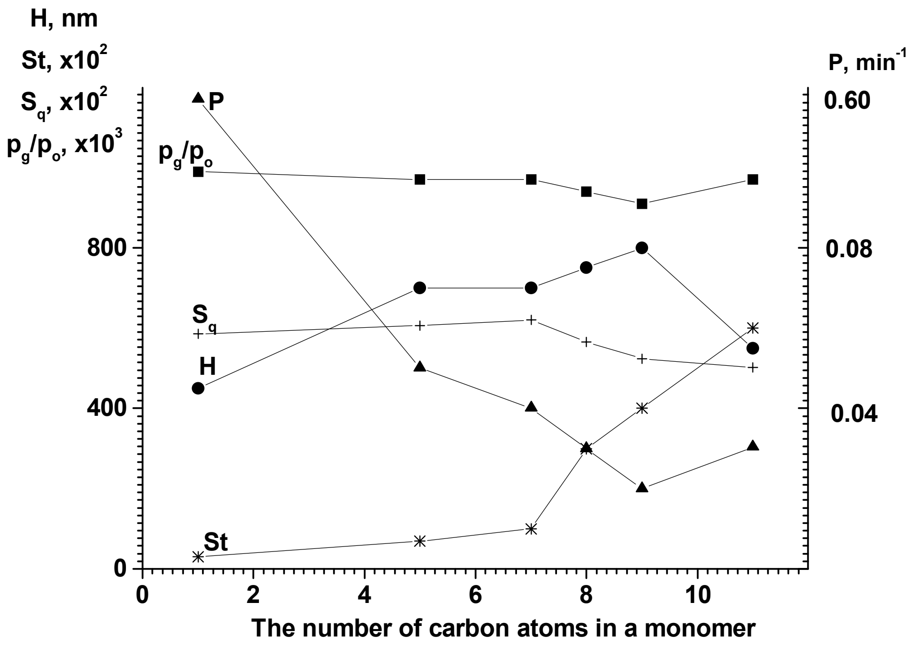

Fig. 1 The number of carbon atoms in a monomer dependence of thickness H, mean root square roughness S_q, permeability P, strength St, relative pressure p_g / p_o.

The results obtained demonstrate that as the hydrocarbon molecule chain length increases the structural changes associated with the quantity of branches and cross links take place in the film. The monomer molecule length growth to C=9 increases the deposition rate, thickness, cross-linking degree, and, as a result, the strength of the plasma-deposited film. The film permeability decreases in a symbate manner (Fig. 1). At further C growth the cross-linking degree and the polymer strength also increase with the unwanted increase however in the film permeability. This can be ascribed to the film thickness decrease, owing to the lower rate of monomer-to-polymer conversion along with the annihilation of the film surface layers during the plasma-deposition. The annihilation depends on the increase of the film internal stresses, which start surpassing cohesive forces. The film in the process destructs, hence, the film thickness and roughness decrease.

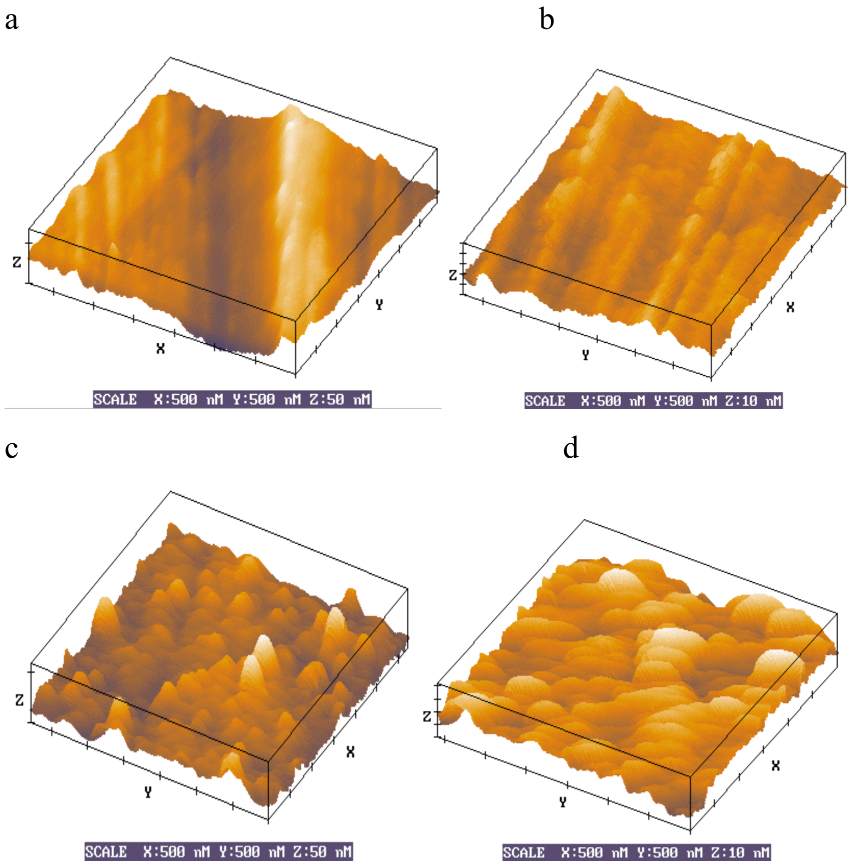

Fig. 2 The AFM-image of the surface of the plasma polymerized film. a - insulated substrate, b – metan, c – pentan, d – undecan.

Conclusions

The investigations cited have shown that the cross-linking degree and the strength of the plasma-deposited film increase with the chain length of the saturated hydrocarbon.

In conditions of fixed plasma-treatment regimes there is an optimum hydrocarbon chain length that provides the highest protective capability of the plasma-deposited films.

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1. A.M. Lyakhovitch, A.V. Dorfman, S.G. Bystrov, V.I. Povstugar //Phys.Low-Dim. Struct., 3/4(2001) p.277-286