

## THE STUDY OF THE SURFACE TRANSFORMATION OF SOME POLYMERS BY HIGH FREQUENCY DISCHARGE PLASMA<sup>1)</sup>

J. VLECHA<sup>2)</sup>, M. MASTHUBA<sup>2)</sup>, E. LAPČEK<sup>2)</sup>, A. LODES<sup>2)</sup>,  
P. KRUPA<sup>2)</sup>, Bratislava

The surface of polypropylene and some other materials was modified using  $O_2(N_2)$  dc plasma and studied by measuring the contact angle, absorption spectra, and by means of microscopy, iodometric titration and thermic analysis. The great changes of the surface properties are assumed to be caused by the formed hydroperoxide, by carbonyl and carboxyl groups, also by surface crosslinking and physical destruction.

### ИЗУЧЕНИЕ ПРЕОБРАЗОВАНИЯ ПОВЕРХНОСТИ НЕКОТОРЫХ ПОЛИМЕРОВ ПОД ВЛИЯНИЕМ ПЛАЗМЫ ВЫСОКОЧАСТОТНОГО РАЗРЯДА

В работе изучается изменение поверхности полипропилена и некоторых других материалов под влиянием высокочастотной плазмы  $O_2(N_2)$ , а также приводятся результаты измерений угла смачивания, спектров поглощения и при помощи микроскопии фодометрического титрования и термического анализа. Предполагается, что большие изменения поверхностных свойств обусловлены образованием перекиси водорода, групп карбонильных и карбоксильных, а также образованием сетчатой структуры поверхности и физическим разрушением.

### I. INTRODUCTION

The study of kinetics and mechanisms of photochemical reactions in polymer materials has lately made much progress [1]. The exposition by UV light (~ 10 hours) leads to the changes of the physical and chemical surface and of the bulk properties like wettability, stress-strain, surface density of polar groups, etc. [2—6].

<sup>1)</sup> Contribution presented at the 3rd Symposium on Elementary Processes and Chemical Reactions in Low Temperature Plasma in Krákovo. September. September 22—26, 1980.

<sup>2)</sup> Department of Chemical Engineering ČHTE SVST, Jánska 1, 880 37 BRATISLAVA, Czechoslovakia.

These phenomena result probably from the surface concentration of carbonyl ( $C=O$ ) and hydroperoxide ( $-OOH$ ) chromophores and other groups. Carlsson et al. [3] proposed and proved the mechanism of polypropylene monofilaments photooxidation. From this mechanism there is evident the possibility of crosslinking of the surface layers. The electron microscopy of monofilaments [4] has shown changes of morphology and degradation of the surface.

The low temperature plasma treatment of polymer surfaces is studied because of the ability to modify a polymer surface without affecting their bulk properties. It can be presumed that the high speed of plasmochemical surface reactions results from high plasma effectivity — solid surface energy transfer by electrons, excited atoms and ions collisions.

The choice of the polymer material was determined by a definite requirement of surface transformation of isotactic polypropylene. We have in mind the increase of its polarity and improvement of its surface colourability.

## II. METHODS

For the plasma-thin polymer film interaction it is necessary to use a plasma with a low temperature of neutral particles, hence we employed high frequency oxygen and nitrogen plasma generated by a hf inductively coupling plasma generator ( $\sim 10$  MHz). The scheme of the experimental equipment is in Fig. 1. The flow of

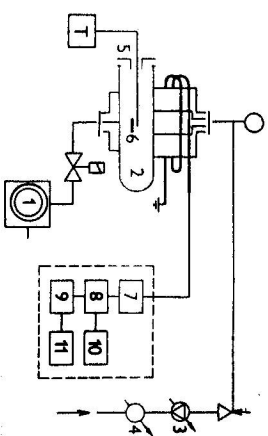


Fig. 1. Scheme of the experimental equipment for the plasma modification of polymer films. 1 - oil pump, 2 - quartz vacuum chamber, 3 - flowmeter, 4 - manostat, 5 - thermocouple Ni-Cr-Ni, 6 - sample, 7 - reflected power measuring, 8 - oscillator, 9 - voltage source, 10 - tuning capacitor, 11 - power regulator.

the working gases ( $O_2$ ,  $N_2$ ) was regulated between  $(0.7-3.2) \times 10^{-5} m^3/s$  and the pressure in the vacuum chamber was changed from 460 to 1200 Pa. The active hf discharge burned inside four arms of the quartz chamber and so the plasma in the polymer sample position was homogeneous. The power of the generator was regulated from 39 to 240 W. The plasma temperature was measured by a Ni-Cr-Ni thermocouple 5 mm above the sample and its value was in the range 297—423 K. The polymer samples (polyethylene, polypropylene, PVC, polyvinyl alcohol, carboxymethyl cellulose) was exposed to the plasma from a few seconds to 15 minutes. We studied commercial polypropylene with a biaxial orientation (Hercules) and other commercial polymers.

By measuring the contact angle  $\Theta$  and other surface properties we determine the degree of surface transformation after the plasma application. The contact angle of the  $H_2O$  drop was measured by a KERNCO instrument (U.S.A.). The angle was measured five times in five places. The value  $\Theta$  was determined statistically.

By means of polarization microscopy and scanning electron microscopy we obtain the picture of the topographical, morphological changes of the surface and of the degree of the polymer surface degradation. Microscopical observations were carried out by a CARL ZEISS Jena polarization microscope and by SEM JEOL J. S. 35. The greatest magnification of SEM was 4000.

Some samples were submitted to thermal analysis on a METTLER thermoanalyzer. DTA (differential thermal analysis) and DTG (derivation thermogravimetry) were performed with 5 mg of a polymer film with an air flow of 7 l/h and a heating velocity of  $10^\circ/min$ . The standard for DTA was  $Al_2O_3$ .

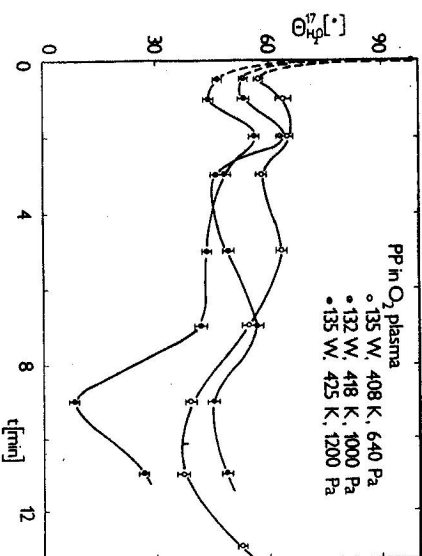


Fig. 2. Contact angle ( $\Theta_{H_2O}$ ) versus time of  $O_2$  plasma application for the polypropylene.

## III. RESULTS

We have ascertained that a change of hydrophilicity is the most effective change of the polymer surface properties after plasma application. A marked diminishing of the contact angle was observed for every mentioned polymer. Isotactic polypropylene was the most completely studied. Contact angle dependences on the time of exposition in  $O_2$  plasma are in Fig. 2. We suppose that the polymer transformation has a high velocity. This assumption is verified by the measured results in Fig. 3, where short exposition times (seconds) are sufficient. This fact results also from Fig. 4 for PVC exposed to  $O_2$  plasma. The saturated states of contact angle

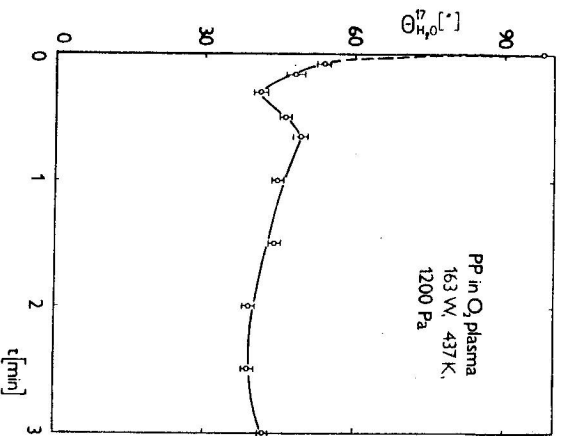


Fig. 3. Contact angle ( $\Theta_{H_2O}^{17}$ ) versus time of O<sub>2</sub> plasma application for the polypropylene.

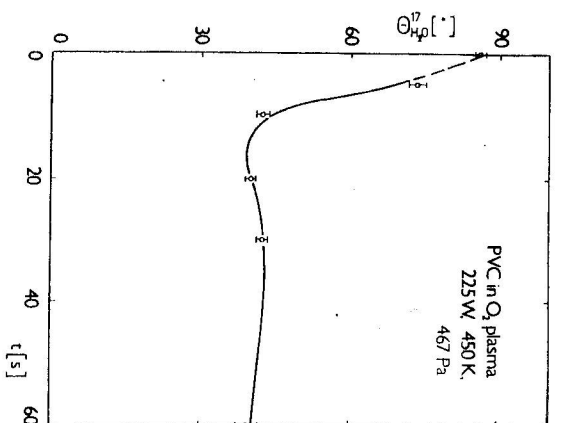


Fig. 4. Contact angle ( $\Theta_{H_2O}^{17}$ ) versus time of O<sub>2</sub> plasma application for the PVC.

time dependences are also evident. It is also evident that the contact angle decreases when the power of the plasma generator increases.

To determine the causes of these phenomena we followed the morphology of polymer surfaces. In Fig. 5 and Fig. 6 there are photographs of polymer surfaces obtained by a polarization microscope and SEM at different stages of transformation.

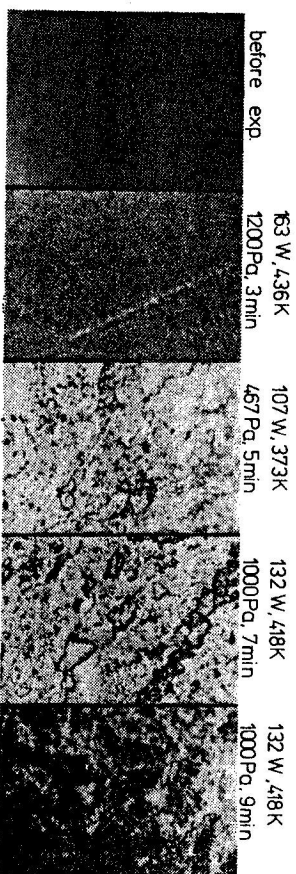


Fig. 5. Photograph of polypropylene surface obtained by polarization microscope. Magnification —350.

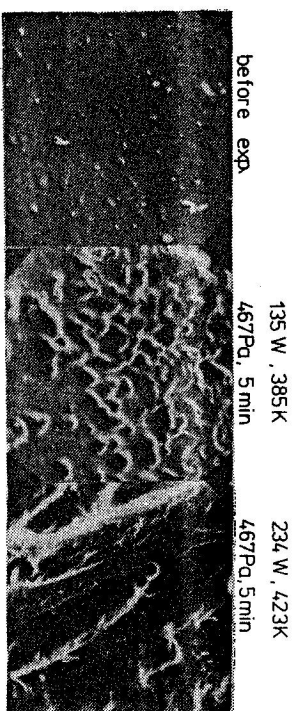


Fig. 6. Photograph of polypropylene surface obtained by SEM. Magnification —4000.

#### IV. DISCUSSION

The effect of low temperature plasma treatment on a polymer surface is a common result of the photo-chemical effect of UV light generated by plasma and the physical contact of electrons, excited atoms and ions with the polymer surface. In the case of oxygen plasma the singlet and triplet O<sub>2</sub> (<sup>1</sup>O<sub>g</sub><sup>+</sup>, <sup>1</sup>Δ<sub>g</sub><sup>+</sup>, <sup>3</sup>O<sub>g</sub><sup>+</sup>) and the atoms O are important in any energetic state. Most important is the effect of singlet oxygen, which performs the intensive oxidation of the exposed material. The hf discharge leads to the perturbation of the classical energy distribution in the plasma system and to the dissipation of energy among its subsystems. The importance of electrons, excited atoms and molecules increases. The energetical particles knock the surface of the exposed material and their physical effect leads to the desorption of molecules of the physically coupling gases. (The excitation of these molecules cannot be eliminated). Defect metastables (free radicals, discharge centres, etc.) can be created by this mechanism.

The high intensity of thermal motion creates the conditions for a statically random and uniform treatment of the polymer surface as it is evident from Fig. 5. The mechanical discontinuity increases with exposition time prolongation. The big block loss results from a nonuniform orientation of the internal tension.

From the UV, IR absorption spectroscopy, thermal analysis and iodometrical titration it is evident that polymer surface properties are changed not only by physical processes, but also by chemical reactions. The spectroscopical measurements show the inevitability of the multireflection method. Periodical changes of absorption with exposition time synchronized with changes of the contact angles indicate the process of the periodical oxidation of the surface layer and its destruction. Precise measurements are impaired by surface splitting and by dispersion and interference effects. The method of single transition does not make the quantitative analysis of the observed chemical changes possible. The same reason (the chemical changes were recorded only in layers ~10—100 nm [7]) has

limited the applicability of iodometric titration. This chemical method has shown only a slight increase of hydroperoxide concentration on the transformed layer. The decrease of velocity of thermo-oxidation degradation (see the DTG curves in the Fig. 7) signalizes the increase of crosslinking intensity of the polypropylene surface. The broadening of the DTG curves is also caused by crosslinking effects. The results of DTA confirmed the assumption about the change of surface morphology.

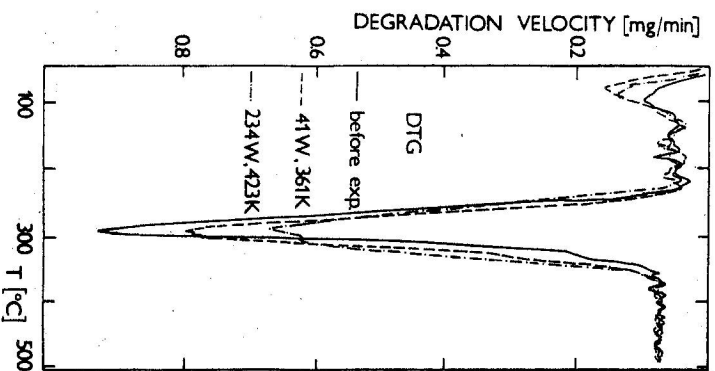


Fig. 7. DTG curves for polypropylene (466 Pa, exp. time - 5 min.)

The use of nitrogen *ht* plasma did not prevent oxidation of the polymer surface. Contact angle dependences on the time of exposition in both oxygen and nitrogen plasmas were equivalent. The high contents of  $O_2$  in technical nitrogen and oxygen desorbed from the walls of the reaction chamber [8] prevented an inert atmosphere.

The importance of photochemical reactions for wavelengths  $>200$  nm was excluded by means of quartz glass. The effect of UV light with  $<200$  nm is doubtful.

From the above discussion it may be concluded that: a) the changes of the macroscopical properties of polymer surfaces after plasma application are the result not only of chemical but also of morphological changes in the thin surface layer; b) plasmochemical treatment of polymer surfaces is more marked and faster than the photo-chemical one.

#### ACKNOWLEDGEMENTS

The authors are indebted to Doc. Ing. M. Košík, CSc. for DTG and DTA measurements.

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Received October 20th, 1980