Effect of plasma activation on the surface structure and strength characteristics of polypropylene film

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Central to the chemistry of high molecular weight compounds is the surface modification of polymers, which makes it possible to give the materials new properties without changing their volume chemical and physicomechanical characteristics. One of the most promising methods for surface treatment of polymers is the plasma chemical method [1]. The appearance of new functional groups and active centres as a result of plasma chemical treatment opens up means for the subsequent grafting of molecules of other substances to the polymer that either themselves possess the necessary properties or have functional groups capable of reacting with the modifying compounds [2].

Interaction in the “low-pressure gas-discharge plasma–polymer” system is a complex multistage process. It is known that the depth of penetration of active particles of plasma into the polymer is no greater than a few micrometres [3]. Agents modifying the material under the action of low-pressure plasma are excited particles (molecules, atoms, electrons, ions) and electromagnetic radiation, the energy of which changes in a very wide range, from fractions to hundreds of electron volts.

A new plasma chemical method for treating materials in a plasma–solution system appeared comparatively recently. The method essentially consists in the material that is undergoing modification being placed in an electrolyte solution in which, or over which, a glow discharge is produced by a particular method [3]. In the plasma–solution system, under the action of the discharge, active particles are formed that bombard the surface of the electrolyte. The most active of them dissipate their energy on molecules of the solvent and dissolved substance. As a result, the surface of the polymer is reached by secondary particles, which are characterised by a comparatively narrow energy spectrum.

It is of interest to compare the nature of change in the physicomechanical properties, the surface structure, and the nature of the functional groups formed as a function of the method of plasma chemical treatment of the material. In the present work, investigations were conducted on films of isotactic polypropylene (PP) of grade FND-PP produced in Italy, with a molecular weight of 400 000–700 000 atomic units and a thickness of 15 µm. The procedure for modifying the PP in plasma is described in reference [4].

EFFECT OF PLASMA ACTIVATION ON THE STRENGTH CHARACTERISTICS OF POLYPROPYLENE FILM

The change in surface properties of PP film modified in plasma was monitored from the change in its physicomechanical properties. Mechanical tests were conducted on an RM-30-1 tensile testing machine according to the GOST 14236–86 standard. The results of physicomechanical tests are given in Table 1.

From the data in Table 1 it can be seen that, in PP specimens activated in low-temperature plasma, both in oxygen and in argon, there is a reduction in the value of the breaking elongation. This can be attributed to the fact that, under the action of the discharge, transition from amorphous phase into a “smectic” phase and from a “smectic” phase into an α-crystalline phase occurs. The results obtained give grounds for assuming that short-wave vacuum UV radiation is responsible for the change in volume structure of PP [5]. The action of
the plasma–solution system does not adversely affect
the physicomехanical properties of the polymer. This
indicates that treatment in a plasma–solution system
is milder than treatment in a low-temperature gas
plasma.

Changes in the surface relief of the PP film at all
stages of activation in plasma were monitored by atomic
force microscopy (AFM). To obtain AFM images, use
was made of a Smena scanning probe microscope
and a Multi Mode™ Nanoscope IIIa™ scanning probe
microscope. AFM studies were conducted in tapping
mode in “height” (topography) and “phase contact”
regimes (the AFM tests were conducted in the N. N.
Semenov Institute of Chemical Physics of the Russian
Academy of Sciences under the supervision of Professor
A. B. Solov’eva).

From Figure 1 it can be seen that the film in the initial
state comprises a combination of spherulite-like formations
with an average particle size of 300 nm and with a
more or less homogeneous structure. After modification
of the PP specimen in low-temperature plasma, the
surface of the film becomes more homogeneous, and
its roughness decreases. This occurs on account of the
fact that the relatively coarse spherulite-like structures
that were present in the initial specimen are broken up
into fine structures.

**ACTIVATION OF POLYPROPYLENE SPECIMENS
IN PLASMA**

The plasma–solution system for surface activation of
different materials began to be used comparatively
recently. A feature of this method of plasma treatment
is that surface activation occurs under the action not of
the initial aggressive primary particles but of secondary
particles formed in the electrolyte solution. This makes
it possible to activate the surface of the material under
milder conditions, thereby retaining its initial properties,
and more selectively, with increase in the surface
concentration of some functional groups and decrease
in that of others [6–10].

![AFM images of PP film](image)

**Figure 1.** AFM images of PP film: 1 – surface of initial film; 2 – film activated in oxygen plasma in zone of positive column \(P = 30 \text{ Pa}, I_d = 20 \text{ mA}, t_{\text{specimen}} = 90 \text{ s} \); 3 – film activated in argon plasma in zone of positive column \(P = 300 \text{ Pa}, I_d = 20 \text{ mA}, t_{\text{specimen}} = 5 \text{ min} \); 4 – film activated in plasma–solution system \(I_d = 30 \text{ mA}, t_{\text{specimen}} = 10 \text{ min} \)

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**Table 1. Results of physicomехanical tests of PP specimens after different types of treatment (averaged data from results of 15 measurements)**

<table>
<thead>
<tr>
<th>Measured parameter</th>
<th>Unactivated specimen</th>
<th>(O_2) discharge, (P = 30) Pa, (I_d = 20) mA, (t = 90) s</th>
<th>(\text{Ar}) discharge, (P = 300) Pa, (I_d = 20) mA, (t = 15) s</th>
<th>PSS,† 0.5 M KCl solution, (I_d = 30) mA, (t = 10) min</th>
</tr>
</thead>
<tbody>
<tr>
<td>Working tensile load, N</td>
<td>(6.5 \pm 0.3)</td>
<td>(7.1 \pm 0.3)</td>
<td>(6.9 \pm 0.2)</td>
<td>(6.9 \pm 0.1)</td>
</tr>
<tr>
<td>Breaking elongation, mm</td>
<td>(21.8 \pm 1.1)</td>
<td>(18.0 \pm 0.9)</td>
<td>(19.3 \pm 1.0)</td>
<td>(22.1 \pm 0.2)</td>
</tr>
</tbody>
</table>

* Working rate at break 100 mm/s (constant for all specimens).
† PSS – plasma–solution system.
The error of measurement of the working load and the breaking elongation was \(\leq 5\%\).

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Frustrated total internal reflection (FTIR) infrared spectra of the initial PP films indicate that the polymer contains in its surface layer a small number of hydroxyl and carbonyl groups. Their presence may be due both to natural ageing processes and to the presence in the PP specimens of uncontrolled additives associated with the film production technology.

Judging from the FTIR infrared spectra, activation of the specimens in the plasma–solution system leads to the formation of primary alcohol groups. This is indicated by absorption bands in the 1240 and 1020 cm\(^{-1}\) region. The accumulation of hydroxyl groups in the surface layer of the material is confirmed by changes in the region of the spectrum that corresponds to stretching vibrations of the hydrogen-bound OH groups (3300–3600 cm\(^{-1}\)). Furthermore, surface activation of PP in the plasma–solution system leads to an increase in the intensity of the absorption bands in the 1740 cm\(^{-1}\) region, corresponding to stretching vibrations of the carbonyl groups in the surface layer of the modified polymer. After the treatment of polypropylene in the plasma–solution system, an absorption band in the 1560–1580 cm\(^{-1}\) region appears in the spectrum, which is due to the formation of carboxylate ions.

The activation of PP in low-pressure oxygen plasma, both in the active zone of the plasma and in the zone of flow afterglow, leads to similar results.

The activation of polypropylene films in low-pressure oxygen plasma results in the formation on the surface of the polymer of oxygen-containing groups: C–OH, C=O, –COOH, and so on [11].

FTIR infrared spectra indicate that the treatment of the polymer in oxygen plasma at reduced pressure leads to an increase in absorption in the 2900–3700 cm\(^{-1}\) region, which corresponds to stretching vibrations of the O=H bond, and in the 1600–1800 cm\(^{-1}\) region, which reflects an increase in the concentration of C=O groups in different chemical surroundings. There is an increase in the intensity of absorption in the 900–1400 cm\(^{-1}\) region, corresponding to deformation vibrations of the O=H bond and stretching vibrations of the C=O bond. In the case of activation in low-pressure plasma, double bonds of the vinyl and vinylidene type are formed, the maximum absorption of which falls at 890 and 810 cm\(^{-1}\) respectively.

CONCLUSIONS

Thus, the activation of inert polypropylene films using low-pressure oxygen or argon plasma or a plasma–solution system makes it possible to change the morphological surface structure of the polypropylene film, i.e. to reduce its roughness. Under the action of plasma on the surface of the film, oxygen-containing groups of different nature are formed, by which further modification of the films is possible. Activation in the plasma–solution system does not affect the strength characteristics of the polypropylene film. Changes in the values of the strength characteristics of the initial and plasma-activated specimens lie within the range of experimental error.

REFERENCES