A review of use of barrier discharge for modification of surface of polymers

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Abstract. In the framework of this work, a review of the use of a barrier discharge for modifying the surfaces of various polymer products is given. There are various examples of reducing, increasing the wettability angle of modified samples, deforming, smoothing their surface and changing their surface energies.

1. Introduction
Changing the properties of polymer surfaces is an acute issue in many sectors, such as medicine, space technology, oil and gas production. The main objective is whether to increase or decrease the wettability angle.

There are several types of polymer processing: glow discharge, barrier discharge, UV radiation, ozone. A glow discharge requires the absence of foreign particles, i.e. vacuum, which greatly increases the cost of this technology in industry. UV radiation affects the inner layers of the processed material; the processing speed is also several times lower, as when using ozone. Therefore, the barrier discharge is one of the promising industries in practical use.

2. Main part
Different effects and causes of the consequences of processing by a discharge of this type are revealed in different sources:

2.1. Polyimide and fluoroplastic
Modification of a polymer film consisting of a polyimide and fluoroplastic layer [1], followed by sintering under a press, showed that the welded joint significantly increased, but the improved adhesion strength was unstable and fluctuated randomly. The surface of the process polyimide film became more even, large protrusions, scratches, and lesions smoothed out. Such a uniform microrelief is possible when the corresponding defects are melted.

After modification, the Livshitz – Van der Waals surface energy in both polymers sharply decreases, while in PI the acid and base increase, in the fluoroplastic, the acid increases, and the main decreases almost to zero. The unstable adhesion between these polymers can be explained by the increase in acidic surface energy and the repulsion of like charges particles.

The solution to this problem is the mechanical cleaning of the surface of the polyimide. After cleaning the surface of the modified polyimide film (the adhesion to the fluoroplastic does not change much in the cleaned unmodified polyimide film), the adhesion to the fluoroplast becomes high and stable, which is possibly due to the removal of the defective surface layer.
2.2. Polylactide and fluoroplastic
When modifying polylactide (PL-38) [2], (which is used in medicine as temporary implants) by a barrier discharge, first the free surface energy (FSE) decreases, increasing the wetting angle, then it starts to increase, due to which the wetting angle decreases, but remains larger than in the unmodified sample. The time of reaching the peak (the most hydrophobic state) and its value depends on the energy of the discharges and their frequency. With an increase in the intensity of exposure, the peak occurs faster and the wettability angle increases. This is due to the destruction of polar groups on the surface of the material, which create most of the surface energy, followed by recombination under the influence of ozone and plasma.

The situation with fluoroplastic is different. When a polymer is modified, its surface energy, on the contrary, first increases and then decreases, while the contact angle increases to a certain value and does not change anymore. The FSE decreases due to a decrease in polarization energy, but at the same time, the dispersion component slightly increases due to the roughness of the surface. The increase in hydrophobicity, in this case, can be explained by a reorientation from the surface of the polar groups into the interior of the sample, followed by the creation of hydrogen bonds between the oxygen-containing groups.

2.3. Polypropylene
Barrier discharge processing of polypropylene [3] makes its surface coarser. As the modification proceeds, the amount of oxygen in the polymer greatly increases, which then slightly decreases and remains at a stable level. The spectrum of the polymer changes, indicating that part of the carbon has turned into CO or CO2, new elements have been created, such as ketones \([-C = O-]\), acytals \([- (O - C - O) -]\) and carboxyls \([- (C + O) - O-]\).

After a 2-minute processing, the wetting angle significantly decreases from 93.7° to 53.8°. This is due to an increase in oxidized polar groups created by chemical effects in the air from a barrier discharge. In course of time, polypropylene returns part of its hydrophobicity. It’s caused by the relaxation of the orientation of the polar groups of the processing surface. As a result, the wettability angle is 64°, which is 30° less than that of the unprocessed material.

2.4. Polyethylene
A barrier discharge modification of polyethylene [4] reduces its wettability angle: from the first second of processing from 87° to 37°. With further processing, the wettability angle begins to increase. After long-term storage, hydrophobicity approaches its initial values, so processing must be done before the necessary procedures (painting, printing, etc.).

2.5. Polyethylene terephthalate
The influence of plasma to polyethylene terephthalate [5], which is a promising material in medicine, gives a tangible result: surface energy increases more than 4 times. The main part of this energy is polar, because the dispersion component does not exceed 7%. At the same time, hydrophilicity increases significantly: the wettability angle decreases from 72° to 29°. In time, this angle increases to 37 °, which is approximately 2 times smaller than that of the original polymer.

The result can be explained by the destruction of polymer chains on the surface, which are oxidized in the amorphous phase. The \(-C - O-\) and \(-C - C -\) bonds are broken, and the appeared radicals form carboxyl groups at the break points, which determine the level of hydrophilicity.

3. Conclusion
From the above, we can conclude that:
- the modification of polymers by a barrier discharge leads to different results (like increase or decrease the wettability angle)
- the main factors are the type of polymer, the operation mode of the installation (voltage, current, current direction), processing environment
- the surface can become both rougher and smoother
- in time, after processing, different polymers return their hydrophobic properties to different degrees.

References
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