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# SELECTED PROBLEMS OF LOW-TEMPERATURE PLASMA MODIFICATION OF POLYPROPYLENE FILM PROPERTIES

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A b s t r a c t. Biaxially oriented PP film (BOPP) was treated by low-temperature plasma generated by corona discharches in air. The specific treating energy changed from to 0 to 15 kJ/m$^2$. The influence of specific treating energy on free surface energy, oxidation degree of outer layer (OL) of polymer and surface roughness of treated film has been investigated. The free surface energy was determined by Owens – Wendt's and van Oss – Good's methods. The oxidation degree of OL was determined by XPS method and surface roughness by AFM method. The influence of specific treating energy on adhesive strength of joints with treated film was also investigated.

K e y w o r d s: low-temperature plasma, modification of polypropylene film properties.

## INTRODUCTION

The polymers belong to materials of low free surface energy. For majority of them the energy value does not exceed 40 mJm$^{-2}$ and for polyethylene (PE) and polypropylene (PP) this value attains 30 – 33 mJm$^{-2}$. The prevailing part of polyolefins is used for making variety of goods including packaging by using such operations like gluing, laminating, printing. The general principle [1] is already known after which the achievement of good adhesive properties needs the free surface energy of the plastic material higher by 10 mJm$^{-3}$ than free surface energy of paints, glues or lacquers used. This dependence does not occur for majority of paints and lacquers made by using alcoholic solvents, especially for paints with ecologically friendly water solvents. In this situation a surface layer modification of the plastic products is needed to enable sufficient adhesive strength between plastic surface and paint, lacquer or glue. One of the methods of such modifying is subjecting plastic surface to low-temperature plasma generated by corona discharges. This method also known as corona treatment or surface activation is generally used for modifying such products like: films, plates, tubes, profiles, i.e., for products mostly made by extrusion. Very often the corona treatment device [2]

is integral part of the whole technological line. The low-temperature plasma method has several advantages the main of them are [3]:

- high output capacity up to 30 $ms^{-1}$,
- possibility of bilateral film treatment in one process,
- easy change-over of surfaces to be activated,
- adjustable discharge power and therefore the change of property range to be modified,
- no environmental hazard.

The stream of low-temperature plasma onto the plastic surface causes significant changes in chemical as well as physical properties of the outer layer (OL) of plastic products effecting higher strength of adhesive joints. The main changes are [4, 5]:

- cleaning surface and removing weak interface layer,
- generation of functional polar groups,
- increase of surface roughness,
- cross-linking of the polymer chains,
- formation of intermediate surface consisting of low-molecular-weight compounds on the OL.

The quantitative range of changes depends on treatment conditions of the product to be activated, constructional features of the treating device, properties of the plastic material and environmental factors in which the process is carried on.

The main treatment process condition is specific discharge energy. The paper concerns the results of BOPP film treating process, especially of influence of specific corona-discharge energy on free surface energy of OL, oxidation degree of OL, film surface roughness and strength of adhesive joints where one of the elements was treated BOPP film.

## EXPERIMENTAL

### The objective of the research

The objective of the research was the determination of dependence of free surface energy, oxidation degree of OL, surface roughness and adhesive joints strength vs. specific treating energy. The subject of the research was the 40 μm thick BOPP film, type Bifol AG 4001 of Polish production from ORLEN S.A. in Płock [6].

### Methods applied

1. The modification of surface properties of the PP film to be tested has been carried out on the experimental treating stand [7]. There were 12 samples prepared for tests, the first of which (denoted as $x_1$) was reference sample (not treated). The

others were treated with alternative specific energy: 0,3; 0,5; 0,8; 1,2; 1,6; 2; 3; 5,0; 7,5; 10 and 15 kJ/m$^2$, respectively. These samples were denoted as $x_2$, $x_3$.....$x_{15}$, respectively. The specific treating energy ($E_j$) was determined after equation (1) by changing the corona discharge power (P) and film transfer speed (v) of width (l) in the electrode gap [7]:

$$E_j = P/lv \qquad (1)$$

The frequency of voltage supply for discharge electrodes was 35 kHz, the electrode gap was 2,0±0,2 mm, the ambient temperature when treating was kept within 23±2$^0$C at the relative humidity 50±3%.

2. The measurement of wetting angle was carried out using goniometer type G10 of Krüss GmbH directly after treating film in 22±2$^0$C at the relative humidity 50±3%. As measuring liquids water distilled twice, diiodomethane, glycerin and α-bromonaphthalene were used. The capacity of liquid droplet was 3 mm$^3$.

3. Free surface energy was calculated after following methods: Owens – Wendt's and van Oss – Good's [1, 7].

4. The determination of oxidation degree of OL was carried out by photoelectron spectroscopy using spectroscope Escolab 210 of VG Scientific in the Institute for Organic and Physical Chemistry of Polish Academy of Sciences in Warsaw. The tested samples were subjected to X-ray radiation using $AlK_\alpha$ of quantum energy 1486,6 eV. To diminish the PP degradation occurring under radiation the nominal power of X-ray tube has been lowered by 20%. The pressure in the test chamber of the spectrophotometer was reduced to the level $2 \div 3{,}6 \cdot 10^{-6}$ Pa.

5. The investigation of geometrical structure of the surface has been carried out by AFM method using atomic forces microscope type UHV STM/AFM of Omicron GmbH provided with measuring point made of silicon nitride ($Si_3N_4$) with the radius ca.10 nm. The point has been fixed on the flexible lever of stiffness 1N/m. The tests were carried on in the Institute of Physics of Technical University of Poznań. For roughness estimation the average arithmetical roughness profile ($R_a$) has been admitted [8]. Moreover, the mean square deviation of the roughness profile ($R_q$) has also been determined. 5 samples, denoted as $x_1$, $x_4$, $x_7$, $x_{10}$ and $x_{12}$ were subjected to tests. For each sample 3-dimensional pictures were done, of areas 1, 4 and 16 μm$^2$, respectively. The roughness profile was made using samples of area 1 and 4 μm$^2$.

6. The adhesive strength of joints with treated film was tested by tear-off method. The conditions were following: tear-off angle – 180°, the length of the tested joint – 150 mm, the width of the tested joint – 25 mm [9]. The tests were carried on using testing machine Tiratest model 2160. The grip traverse speed was 300 mm min$^{-1}$. During the measurement the average tear-off force was registered.

The film to be tested was torn-off from the double-sided adhesive tape type L 2139 glued to an aluminum plate.

The tear-off specific work (W) was determined using following equation [7]:

$$W = 2 \cdot F \cdot l/s \cdot l = 2 \cdot F/s \quad (2),$$

where: W – specific tear-off work, F – average tear-off strength, s – width of the film to be torn-off, l – active length of the sample to be torn-off.

## RESULTS

### Results of investigating free surface energy

The results of investigating free surface energy vs. specific treating energy was presented in Fig. 1. Raising the specific treating energy causes the increase in free surface energy of the tested film; however, the course of changes in free surface energy may be divided into two separate ranges. In the first range, at the lower specific treating energy ranging from 0 to 2 $kJm^{-2}$ the great increase in free surface energy occurs. The second range at the specific treating energy from 2 to 15 $kJm^{-2}$ reveals smaller changes in free surface energy. Its value strongly depends on calculation method; however, the best conformity after both methods can be observed within the range from 0 to 1 $kJm^{-2}$. The values of free surface energy beyond this range strongly differ from each other. The results are smaller after Owens – Wendt's methods than after van Oss – Good's. At the applied specific treating energy of 15 $kJm^{-2}$ the values are 54 and 73 $kJm^{-2}$, respectively.

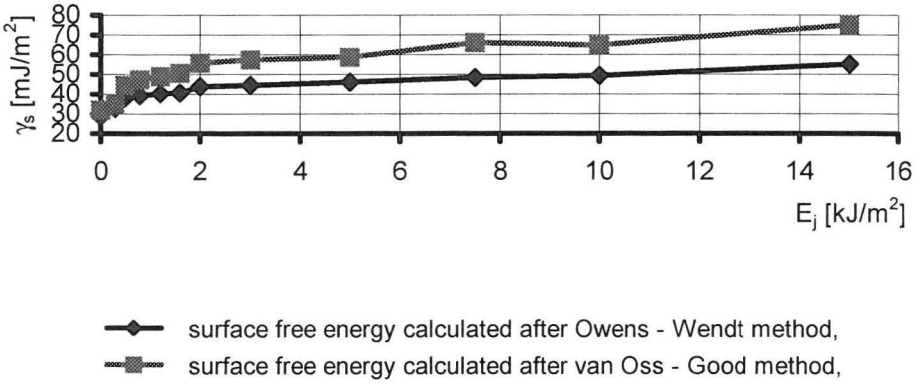


**Fig. 1**. Dependence of free surface energy of Bifol AG 4001 film vs. specific treating energy.

**The results of investigating oxidation degree of the OL.**

The oxidation degree of the OL of tested film was presented as an O/C quotient (in %) (oxygen atoms/carbon atoms). Figure 2 shows that oxidation degree of the OL increases with increasing specific treating energy. This process occurs in the whole range of changes in treating energy, however, it is faster within the range from 0 to 5 $kJm^{-2}$. This increase is a result of increasing number of oxygen atoms in the OL causing formation of functional polar groups, mainly alcoholic, ketones and aldehydes.

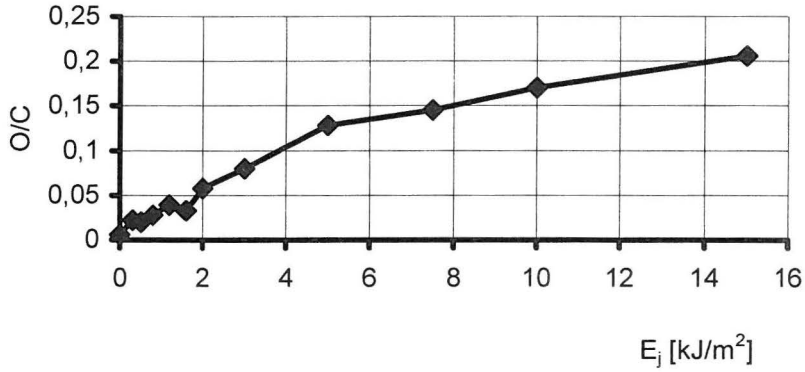


**Fig. 2.** Dependence of O/C quotient vs. specific treating energy for Bifol AG 4001 film.

**Results of geometric structure of the surface of treated film.**

The dependence of surface roughness of investigated film vs. specific treating energy was presented on Fig. 3.

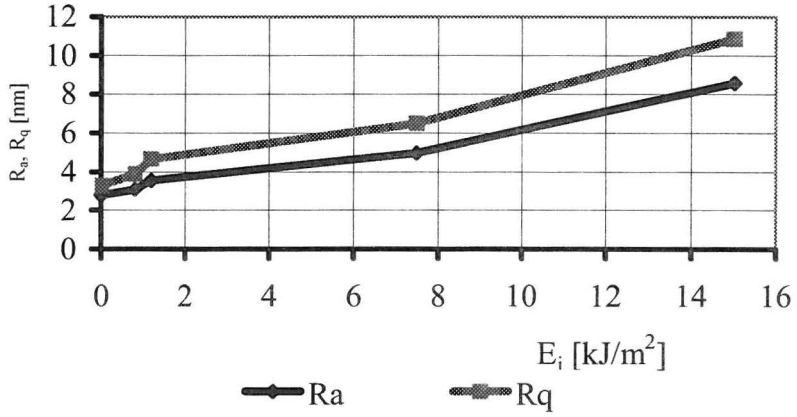


**Fig. 3.** Dependence of surface roughness of Bifol AG 4001 film vs. specific treating energy.

The $R_a$ and $R_q$ parameters increase with increasing specific treating energy. For $E_j$ changes within 0 to 1,2 $kJm^{-2}$ the increase is much faster than for other changes in specific treating energy. The visual analysis of pictures of film surface and its comparison with results from Fig. 3 shows that treating process causes structural changes in film surface geometry, however, the assessment of those changes is not fully liable because of only mechanical performance that is not fully characteristic for the investigated surface.

**Results of adhesive strength of joints with treated film**

After each tear-off test the elements of destroyed joints have thoroughly been analysed. The observations have been carried out using photometric microscope type Amplival of magnification 320 times. For samples denoted $x_1$ to $x_9$ it has been found that the adhesive collapse of the joint occurred on ca. 95% interface area: double-sided adhesive tape – treated film. For samples $x_{10}$, $x_{11}$, $x_{12}$ the joint collapse was of decohesive character because of the delamination of the double-sided adhesive tape. Those results have been rejected. The results of adhesive strength were collected on Fig. 4. It shows that the increase of tear-off strength depends on increase of specific treating energy. This increase is almost of linear character and the values are 350 $Jm^{-2}$ and 1795 $Jm^{-2}$ for samples $x_1$ and $x_9$, respectively.

The tear-off work calculated after equation (2) is the sum of adhesive work, deformation work of the film, work loss for overcoming electrostatic interaction and work loss for heating up the torn-off film.

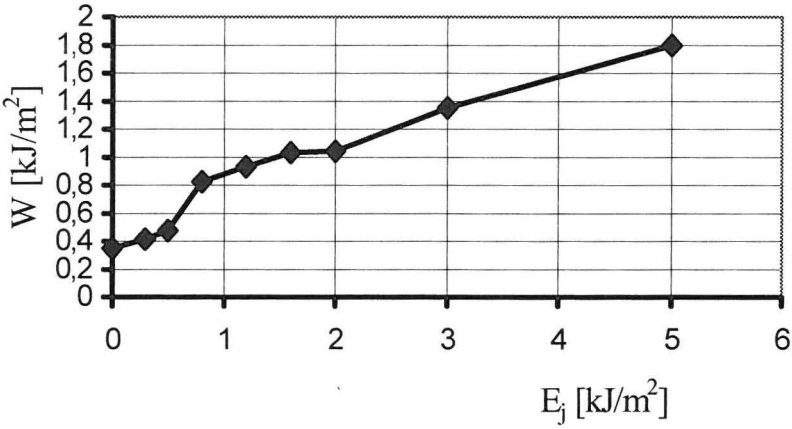


**Fig. 4.** Dependence of specific tear-off work vs. specific treating energy for Bifol AG 4001 film.

## CONCLUSIONS

1. The method of treating biaxially oriented PP film surface with low temperature plasma generated by corona discharges in air causes such changes in properties of the OL like free surface energy, oxidation degree and roughness. The properties have significant influence on the strength of adhesive joints one element of which is above-mentioned film. The range of changes in individual parameters mainly depends on specific treating energy.
2. The increase of specific treating energy causes increase in free surface energy of the tested film. Its values also depend on method of calculation used. In the lowest range of specific treating energies the increase in free surface energy is the fastest.
3. The results of free surface energy calculated after two methods conform each other for specific energies up to 1 $kJm^{-2}$. Free surface energy of the treated film surface calculated after van Oss – Good's method may attain 72 – 73 $mJm^{-2}$ at the highest specific treating energy applied (15$kJm^{-2}$), however, the results calculated after Owens – Wendt's are much lower and attain ca. 53 $mJm^{-2}$.
4. Oxidation degree of investigated OL measured as an (O/C) quotient of atoms number (in %) occurring in the OL increases with increasing specific treating energy. The oxidation degree determined in this way does not exceed 21%.
5. The roughness of the treated film measured using $R_a$ and $R_q$ parameters increases with increasing specific treating energy. The results of those parameters range from 3 nm to 11nm. From the visual analysis of the surface pictures one can see that surface area increases with increasing treating energy.
6. The strength of adhesive joints in which one of the elements is the treated film increases, approximately in linear form, with increasing specific treating energy. The measure of this strength is a tear-off work the maximal value of which attains ca. 1,8 $kJm^{-2}$.

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# WYBRANE ZAGADNIENIA MODYFIKOWANIA WŁAŚCIWOŚCI FOLII POLIPROPYLENOWEJ METODĄ PLAZMY NISKOTEMPERATUROWEJ

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S t r e s z c z e n i e. Folię polipropylenową dwukierunkowo orientowaną (BOPP) aktywowano w wyładowaniu koronowym o jednostkowej energii od 0 do 15kJm$^{-2}$, w atmosferze powietrza. Badano zależność swobodnej energii powierzchniowej, stopień utlenienia warstwy wierzchniej (WW) i chropowatość powierzchni aktywowanej folii, a także wytrzymałość adhezyjną złącz z aktywowaną folią od jednostkowej energii aktywowania. Swobodną energię powierzchniową określano metodami Owensa – Wendta oraz van Ossa – Gooda. Stopień utlenienia WW badano metodą XPS, a chropowatość powierzchni metodą AFM.

S ł o w a k l u c z o w e: plazma niskotemperaturowa, modyfikowanie właściwości warstwy wierzchniej folii.