JAN GOŁĘBIEWSKI, MARIAN ŻENKIEWICZ
Institute for Plastics Processing "Metalchem"
ul. M. Skłodowskiej-Curie 55
87-100 Toruń

Influence of corona treatment energy and storage time on the changes of the contact angle of activated polystyrene film

RAPID COMMUNICATION

Summary — Corona treatment was applied to modify surface of general purpose polystyrene (GPPS) film to improve its molecular interaction with lacquers, paints and adhesives. Results of corona treatment unit energy (E_j) effect on changes in the contact angle of the film using water, glycerol, diiodomethane and α-bromonaphthalene as well as results of changes in the contact angle occuring during six weeks storage after corona treatment have been presented. The significant influence of *Ej* on the contact angle changes, especially when tested with water and glycerol (polar liquids) has been found. It turns out from presented results that the wettability suitable for technical purposes can be obtained when *Ej* values reach *ca.* 1.2 kJ/m^2. Due to gradual disappearance of the activation process effects, storage time of the tested film can not be longer than 2 weeks.
Key words: polystyrene film, surface layer modification, corona treatment, wettability, contact angle.

Nowadays the consumption of polystyrene (PS) in Europe reaches *ca.* $3.5 \cdot 10^6$ tons/year comprising 10% of the consumption of all polymers [1]. This polymer is amorphic, brittle and transparent. The surface layer (SL) of PS is hydrophobic and therefore this polymer belongs to materials characterized of low surface free energy. Two varieties of PS are generally used in the packaging industry , *i.e.* high impact polystyrene (HIPS) and general purpose polystyrene (GPPS) being the virgin PS modified by means of elastomers. Compared to virgin PS, the GPPS has better mechanical properties and HIPS is impact resistant [2]. Majority of PS is used for film production for food packaging purposes. Domestic HIPS consumption in 2001 did not exceed $7 \cdot 10^4$ tons, including 55% of the total amount transformed into films and subsequently into packagings. Packagings are produced primarily by thermoforming using gluing and printing.

Because of hydrophobic properties of SL, the wettability of PS is not sufficient for paints and lacquers normally used in technology. This is particularly true for paints and lacquers with water based solvents, preferred due to the ecological requirements [3]. This feature makes using PS for printed, glued or laminated packagings difficult without prior SL modification. Therefore, the main aim of SL modification of PS film is to alter the physical and chemical structure of the material towards increasing molecular interactions between film and paint, lacqeur or adhesive, thus improving the wettability of PS film. The most known methods of SL modification of PS packagings are flame and corona treatment [4—6].

The corona treatment method [3, 5] consists in exposing SL of PS to short-lasting (0.01—0.10 s) corona discharges in air under standard atmospheric pressure. The method is mostly used directly prior to printing of PS film. Corona treatment is also used during film extrusion and corona treatment device is an integral part of the technological line for this process [7]. The basic parameters of the treatment are:

— Specific treatment energy, defined as a quotient of discharge energy and surface to be treated. Depending on kind and amount of additives in polymer (especially slip agents) and properties of paints, lacqeurs or adhesives, the polymer materials are treated with specific treatment energy in the 0.5—3.0 kJ/m^2 range.

— Transport speed of the material to be treated through the discharge gap. In the industrial lines such speed does not exceed several dozen m/min.

— Gap width between the electrodes within the 1.5—3.0 mm range.

— Parameters of the corona treatment device, especially power and frequency of the generator, number and shape of the high voltage electrodes, kind of insulating material of the earthing electrode. As a rule the generator power does not exceed several kW and frequency of the corona discharges ranges 15—35 kHz.

The literature does not give any information concerning relationships of contact angle of GPPS *versus* specific energy of corona treatment and contact angle *versus* storage time. To fill up this gap we present herewith the selected results of our works concerning those phenomena.

The aim of the work was to establish the relationship of contact angle of GPPS *versus* specific energy of corona treatment and to investigate the changes of the treating effect in time. Several different tests have been conducted in order to establish the changes in the contact angle.

EXPERIMENTAL

Material

The investigated material was three-layered PS film of 0.2 mm thickness, extruded by the slotted extrusion head in MiA Folia Company (Poland). The external layer was 0.02 mm thick and made of GPPS, whereas the two other layers were made of mixture HIPS/GPPS (75:25). The film was subsequently used in production of thermoformable packagings, mainly for dairy industry. Dimensions of the film samples to be tested were 100 × 20 mm.

Test methods

Modification of the tested film SL was carried out on a special test stand, the description of which is given in reference [5].

The corona treatment was carried out with specific treatment energy of 0.5, 1.2, 3.0 and 5.0 kJ/m^2. Energy (E_j) was set by changing corona discharge power (P) and by changing transport speed (v) of the film of width (l) in the gap between the electrodes. Its value is determined according to the following formula [3]:

$$E_j = \frac{P}{lv} \quad (1)$$

Frequency of the discharging voltage was 35 kHz, electrode gap was 2.0±0.2 mm; ambient temperature was kept at 23±2°C at relative humidity of 50±3%.

Contact angle measurements were carried out directly after corona treatment of GPPS film and after 1, 2, 4 and 6 weeks, respectively, using type G10 goniometer made by Krüss GmbH. Film to be treated was conditioned at 22±2°C and relative humidity of 50±3%.

The following test liquids were used: twice distilled water (W), glycerol (G), diiodomethane (D) and α-bromonaphthalene (B), *i.e.* liquids usually applied in tests of surface properties. The volume of liquid droplet was 3 mm^3.

RESULTS

Influence of the of E_j value on contact angle changes in GPPS film using different test liquids has been presented in Fig. 1. Results show that, irrespectively of test liquids, the greatest changes in contact angle occur when E_j is changed in the 0—1.2 kJ/m^2 range. However, the highest rate of changes in the contact angle was seen for water and glycerol at 35° and 30°, respectively. At E_j values above 1.2 kJ/m^2 the chages were significantly smaller; in case of diiodomethane such angle remained practically constant.

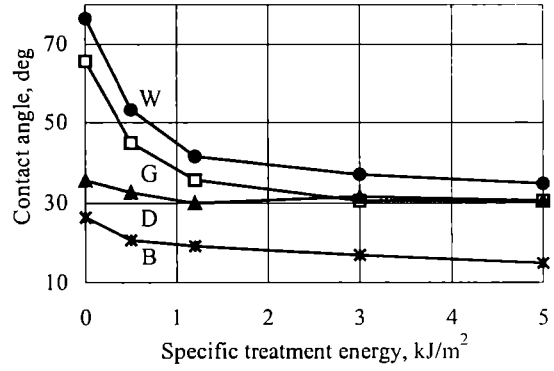

Fig. 1. Influence of specific treatment energy on the contact angle of non-treated GPPS; liquids: W — twice distilled water, G — glycerol, D — diiodomethane, B — α-bromonaphthalene

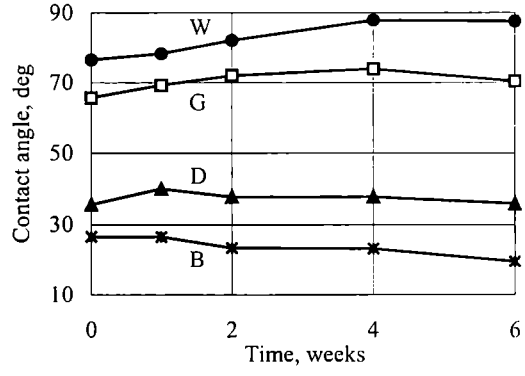

Fig. 2. Influence of storage time on the contact angle of GPPS film (explanations as in Fig. 1)

Figure 2 presents the influence of storage time on the contact agle for untreated GPPS film. Measurements of the contact angle were performed directly after film extrusion and one, two, four and six weeks later.

Results show that contact angles increase during the first four weeks after extruding GPPS with the two polar

test liquids, *i.e.* water and glicerol, by 11° and 8°, respectively. No further changes were reported in the next two weeks. The reported changes might have been caused by migration of slip agents to the film surface.

Significantly smaller contact angle changes occur in case of non-polar liquids, *i.e.* diiodomethane and α-bromonaphthalene [8]. However, unlike diiodomethane, contact angle measured by α-bromonaphthalene slightly decreases in time. This was due probably to the stronger interaction between α-bromonaphthalene molecules and additive molecules (migrating to the surface of polymer material) than interaction between molecules of this liquid and molecules of GPPS.

Changes in contact angle in time post treatment of GPPS film are presented in Figs. 3—6. When the GPPS film was treated with low energy values (E_j = 0.5 and 1.2 kJ/m^2 — Figs. 3 and 4) changes in contact angle were similar to those observed for non-treated samples (Fig. 2). The interpretation of this phenomenon can follow similar lines.

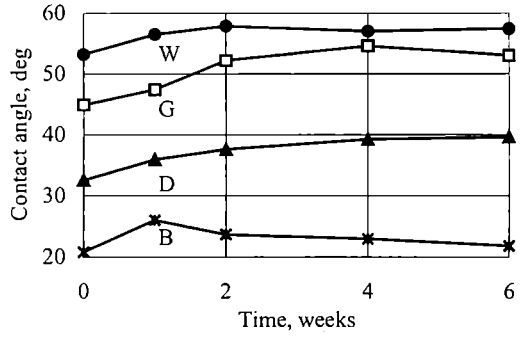

Fig. 3. Influence of storage time on the contact angle of GPPS film treated with E_j = 0.5 kJ/m^2 (explanations as in Fig. 1)

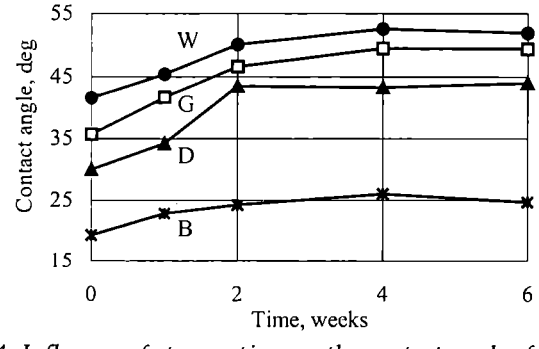

Fig. 4. Influence of storage time on the contact angle of GPPS film treated with E_j = 1.2 kJ/m^2 (explanations as in Fig. 1)

Contact angle for the treated samples with higher specific treatment energy values (E_j = 3.0 and 5.0 kJ/m^2 — Figs. 5 and 6) increases over the whole time period. The highest increase is observed for glycerol (16.7° and 18.3°, respectively), slightly lower in the case of diiodomethane and water (13.5 °, 15.6° and 10.3°, 11.9°, respectively), and the smallest for α-bromonaphthalene (9.7° and 7.8°).

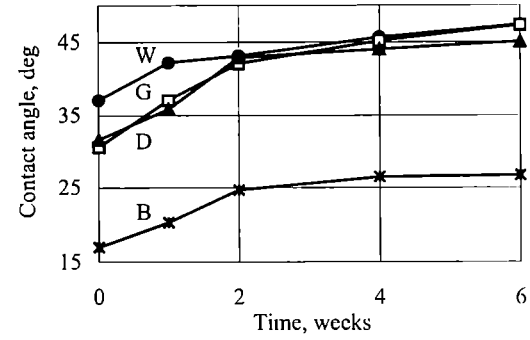

Fig. 5. Influence of storage time on the contact angle of GPPS film treated with E_j = 3.0 kJ/m^2 (explanations as in Fig. 1)

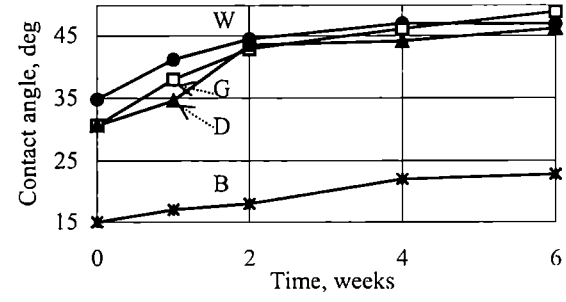

Fig. 6. Influence of storage time on the contact angle of GPPS film treated with E_j = 5.0 kJ/m^2 (explanations as in Fig. 1)

Basing on above mentioned results one can presume that in the case of more modified (oxidized) SL in treated GPPS film, reactions running in this layer, associated with decomposition of polar functional (hydrophilic) groups, continue for a long period of time after the corona treatment. Confirmation of this thesis needs further tests concerning changes in composition of SL in treated GPPS, *e.g.* by photoelectron spectroscopy or by mass spectroscopy of secondary ions, what will be the subject of our further investigation.

CONCLUSIONS

Presented results of investigating changes in the contact angle of GPPS film carried out within 6 weeks from its treatment date allow to formulate the following conclusions:

— GPPS film treating by corona discharge causes increase of wettability of SL what can be confirmed by changes in the contact angle of this layer by different test liquids.

— Changes in wettability of treated GPPS film depend on specific treatment energy. Highest changes of wettability have been observed for energy values in the range up to 1.2 kJ/m^2. Such value should be applied in the industrial processes of treating GPPS films.

— Changes in contact angle measured by polar test liquids (*i.e.* water and glycerol) in the energy range up to 3 kJ/m^2 are significantly greater than changes measured by non-polar test liquids (*i.e.* diiodomethane and α-bromonaphthalene).

— Treating effect of the GPPS film decreases in time, what can be proved by increasing contact angle of this film. The extent of those changes depends on specific treatment energy. Most significant changes were observed within first two weeks from the time of treatment. Typically, when specific treatment energy exceeded 1.2 kJ/m^2 contact angle increased for all test liquids within the test period.

— Storage time for GPPS film from its time of treatment with energy values of 1.2 kJ/m^2 should not exceed 2 weeks.

REFERENCES

1. AMI Press Release 5.12.2001, *Polimery* 2002, **47**, 455.
2. Szlezyngier W.: "Plastics", Oficyna Wyd. Politechniki Rzeszowskiej, Rzeszów 1996, p.150—151 (in Polish).
3. Żenkiewicz M.: "Adhesion and Modification of Surface Layer of Polymers", WNT Warszawa 2000, p. 127, 171—178 (in Polish).
4. Żenkiewicz M.: *Polimery* 2000, **45**, 81.
5. Gołębiewski J.: "Investigation of Influence of Low-temperature Plasma on Selected Properties of Surface Layer of Polypropylene Film", Doctor's Thesis. Politechnika Lubelska 2000, p. 9, 24—35 (in Polish).
6. Chi-Ming Ch.: "Polymer Surface Modification and Characterization", Hanser Publishers, Wien 1994, p. 265.
7. Żenkiewicz M., Lutomirski S.: *Polimery* 2001, **46**, 244.
8. Kuczmaszewski J.: *Polimery* 2001, **46**, 792.

Received 1 IX 2002.