Strength of Bonded Joints at Elevated Temperatures after Radiation Cross-linking

M. Bednarik, D. Manas, M. Manas, M. Stanek, A. Mizera, M. Ovsik, and P. Kratky

Abstract—In this study there was found that ionizing beta radiation increased the strength of bonded joints and improved the adhesion properties of low-density polypropylene (LDPE) and high-density polyethylene (HDPE). Bonded joints at elevated temperature (60 °C) were tested. Generally, for the formation of quality bonded joint it is important to wet the adhesive bonding surface well. Wettability is characterized by the contact angle of wetting. The liquid has to have a lower surface tension than the solid in order to be able to wet the solid substance. The measurement results indicated that ionizing beta radiation was a very effective tool for improvement of adhesive properties and increased the strength of bonded joints of studied polymers at elevated temperature (60 °C). Bonded surfaces with ionizing beta radiation doses of 0, 66, 132, 165 and 198 kGy were irradiated. The best results were achieved by irradiation at doses of 165 kGy by which the highest surface energy and the highest strength of bonded joints of HDPE and LDPE were achieved.

Keywords—Surface energy, ionizing beta radiation, strength, bonding, adhesion, polymers, elevated temperature

I. INTRODUCTION

Bonding has experienced tremendous expansion in the field of joining materials in the last years. Because of that expansion bonding is classed as new techniques even when it is in fact very old. [2, 4]

In comparison with conventional joining methods (riveting, welding and screwing) bonding provides a new combination of options and it allows obtaining special shapes and properties which cannot be created by conventional methods of coupling.

Joining materials using adhesive joints offers several benefits, but also limiting factors if compared with using mechanical joints. To decide about the type of coupling it is necessary to consider the advantages and disadvantages of bonding in comparison with traditional joining technique. Among the advantages of bonding especially belong:

1. We can connect the same and dissimilar materials and do not take into account the thickness.
2. Application of adhesives does not undermine the coherence of the connect parts.
3. Watertight and gastight joints may be prepared.
4. It does not disturb profile or aesthetic appearance of bonded file and does not increase its weight.
5. Joints can be transparent or colored and it is possible to achieve their high strength.
6. The load at the joint interface is distributed over an area rather than concentrated at a point.
7. Joints are more resistant to flexural, fatigue, and vibrational stresses.
8. Bonding is often less expensive and faster than mechanical joining.
9. Can be more easily adapted to join irregular surfaces than mechanical joints.

Adhesive bonding has also several technological disadvantages, in comparison with mechanical joints. The disadvantages of bonded joints are the requirements for planeness and cleanliness of surface to be bonded and sensitivity to peel stress. Special surface treatments are required for bonded materials with poor adhesion properties and maximum bond strength is reached after the certain time. [2, 4, 5, 6, 9, 12, 14]

II. EXPERIMENTAL

The aim of the experiment was to examine the effect of beta irradiation on the strength of bonded joints for selected types of materials at elevated temperature (60 °C).

A. Materials

For this experiment low-density polyethylene LDPE DOW – LDPE 780 E and high-density polyethylene HDPE DOW – HDPE 25055E were used.

Low-density polyethylene and high density polyethylene belong to the group of polyolefins. Polyolefins are the largest group of thermoplastics which are often referred to as commodity thermoplastics. Polyolefins consist only of carbon and hydrogen atoms and they are non-aromatic. The two most
important and common polyolefins are polyethylene and polypropylene which are much exploited for its price accessibility of raw materials, good process ability, and advantageous user properties. Polyolefins are for its non-polar character and low surface energy can not be bonded without previous surface treatment. [15, 16, 19]

Polyolefins are usually processed by extrusion, injection molding, blow molding, and rotational molding methods. Polyethylene is used for the production of packaging materials (shrinkable films, pouches), gear wheels, bearings, textile fibers, and toys. Polyethylene is currently the most widely used polymer in the world. [9, 10, 12, 13]

The samples were made by using the injection molding technology on the injection molding machine Arburg Allrounder 420C (Fig. 1). Injection conditions are shown in Table 1.

![Fig. 1 Arburg Allrounder 420C](image)

Table 1 Injection conditions

<table>
<thead>
<tr>
<th></th>
<th>HDPE</th>
<th>LDPE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Injection rate</td>
<td>60 mm/s</td>
<td>50 mm/s</td>
</tr>
<tr>
<td>Injection pressure</td>
<td>800 bar</td>
<td>600 bar</td>
</tr>
<tr>
<td>Injection time</td>
<td>0.4 s</td>
<td>0.4 s</td>
</tr>
<tr>
<td>Cooling time</td>
<td>20 s</td>
<td>30 s</td>
</tr>
<tr>
<td>Mold temperature</td>
<td>40 °C</td>
<td>40 °C</td>
</tr>
<tr>
<td>Holding pressure</td>
<td>600 bar</td>
<td>500 bar</td>
</tr>
<tr>
<td>Cycle time</td>
<td>56.8 s</td>
<td>56.6 s</td>
</tr>
<tr>
<td>Temperature of zone 2</td>
<td>200 °C</td>
<td>190 °C</td>
</tr>
<tr>
<td>Temperature of zone 3</td>
<td>205 °C</td>
<td>200 °C</td>
</tr>
<tr>
<td>Temperature of zone 4</td>
<td>210 °C</td>
<td>210 °C</td>
</tr>
<tr>
<td>Temperature of zone 5</td>
<td>225 °C</td>
<td>215 °C</td>
</tr>
<tr>
<td>Temperature of zone 6</td>
<td>230 °C</td>
<td>220 °C</td>
</tr>
</tbody>
</table>

The samples had the shape and dimensions according to the CSN EN ISO 527 – 2. Before bonding, surfaces of samples were irradiated by ionization beta radiation of doses of 0, 66, 132, 165, and 198kGy at Beta – Gamma Service GmbH & Co. KG, Germany. [3, 6, 7, 10, 11, 14, 17]

![Fig. 2 Testing Specimen](image)

Tab. 2 Specimen dimensions [8]

<table>
<thead>
<tr>
<th>Test specimen parameters</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>b₁ - Width of Gage Length</td>
<td>10 ± 0.2 [mm]</td>
</tr>
<tr>
<td>b₂ - Width of Gripping End</td>
<td>20 ± 0.2 [mm]</td>
</tr>
<tr>
<td>l₁ - Length of gage Length</td>
<td>80 ± 2 [mm]</td>
</tr>
<tr>
<td>l₂ - Distance Between Gripping Ends</td>
<td>104-113 [mm]</td>
</tr>
<tr>
<td>l₃ - Specimen Length</td>
<td>≥ 150 [mm]</td>
</tr>
<tr>
<td>L₀ - Distance of Extensometers</td>
<td>30 ± 0.5 [mm]</td>
</tr>
<tr>
<td>L - Distance of Grips</td>
<td>115 ± 1 [mm]</td>
</tr>
<tr>
<td>h - Specimen Thickness</td>
<td>4 ± 0.2 [mm]</td>
</tr>
<tr>
<td>R - Radius</td>
<td>20 - 25 [mm]</td>
</tr>
</tbody>
</table>
B. Surface treatment by beta radiation

Ionizing beta radiation gives inexpensive commodity plastics and technical plastics the mechanical, thermal, and chemical properties of high-performance plastics. This upgrading of the plastics enables them to be used in conditions which they would not be able to withstand otherwise. The energy-rich beta rays trigger chemical reactions in the plastics which results in networking of molecules (comparable to the vulcanization of rubbers which has been in industrial use for so long). [1, 3, 7, 8]

The energy from the rays is absorbed by the material and cleavage of chemical bonds takes place. This releases free radicals which in next phase from desired molecular bonds. [3, 8, 14, 18, 21]

The irradiation cross-linking of thermoplastic materials via electron beam or cobalt 60 (gamma rays) is performed separately, after processing. Generally, ionizing radiation includes accelerated electrons, gamma rays and X-rays. Radiation processing with an electron beam offers several distinct advantages when compared with other radiation sources, particularly γ-rays and x-rays.

The process is very fast, clean and can be controlled with much precision. There is no permanent radioactivity since the machine can be switched off. In contrast to γ-rays and x-rays, the electron beam can be steered relatively easily, thus allowing irradiation of a variety of physical shapes.

The electron beam radiation process is practically free of waste products and therefore is no serious environmental hazard. These are not only capable of converting monomeric and oligomeric liquids, but also can produce, due to cross-linking, major changes in the properties of solid polymers. The cross-linking level can be adjusted by the irradiation dosage. The absorbed dosage means the value of energy of ionizing radiation absorbed by a unit of mass of the processed material. The unit of absorbed dose is 1 Gray (1 Gy = 1 J/kg).

The main difference between beta and gamma rays is in their different abilities to penetrate the irradiated material. Gamma rays have a high penetration capacity. The penetration capacity of electron rays depends on the energy of the accelerated electrons. Due to electron accelerator, the required dosage can be applied within seconds, whereas several hours are required in the gamma radiation plant (Fig. 3). [3, 34, 35, 36, 37-42]

Beta and gamma rays can be used for the irradiation of polyolefines, polyesters, halogen polymers and polyamides from the thermoplastics group, elastomers and thermoplastic elastomers. Some of them need the addition of a cross-linking agent. Polymers can be classified into two groups according to their response to ionizing radiation. One group exhibits predominant cross-linking, the other predominant chain scission. [1, 3, 34, 35, 36]
C. Wetting contact angle measurements

The angle of contact was measured by using the sessile drop (Fig. 4) and surface energy was determined by OWRK method (Owens – Wendt – Rabel – Kaeble method).

The liquids water, glycerol and ethylene glycol with known $\gamma^p$ (polar component) and $\gamma^d$ (dispersive component) were used for calculating the surface energy of HDPE and LDPE. [2, 4, 11]

<table>
<thead>
<tr>
<th>Liquid</th>
<th>$\gamma^1_l$ (mJ/m$^2$)</th>
<th>$\gamma^d_l$ (mJ/m$^2$)</th>
<th>$\gamma^p_l$ (mJ/m$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Distilled water</td>
<td>72.8</td>
<td>21.8</td>
<td>51.0</td>
</tr>
<tr>
<td>Glycerol</td>
<td>64.0</td>
<td>34.0</td>
<td>30.0</td>
</tr>
<tr>
<td>Ethylene glycol</td>
<td>48.0</td>
<td>29.0</td>
<td>19.0</td>
</tr>
</tbody>
</table>

The height ($h$) and radius ($r$) of the liquids were measured by using microscope and the contact angle was calculated using the following equation:

$$\text{contact angle } (\theta) = \sin^{-1}\left(\frac{2rh}{r^2 + h^2}\right).$$

(1)

The polar and dispersive components of the surface energy of the polymer surface were calculated using methods OWRK:

$$\frac{(1 + \cos\theta)\gamma^1_l}{2\sqrt{\gamma^d_l}} = \sqrt{\gamma^p_l}\frac{\gamma^p_l}{\gamma^d_l} + \sqrt{\gamma^d_l},$$

(2)

where $\theta$ is the contact angle of testing liquids, $\gamma^1_l$ is the liquid surface energy, and $\gamma^p_l$ and $\gamma^d_l$ are the polar and dispersive components of the test liquids. The values of polar and dispersive components of testing liquids are given in Table 1. [2, 11]

Similarly, the solid – surface energy ($\gamma_s$) is expressed in terms of its polar and dispersive components:

$$\gamma_s = \gamma_s^p + \gamma_s^d.$$

(3)

D. Testing the strength of bonded joints

After sample preparation (production and irradiation) contact angles were measured and surface energy was calculated. Then the samples were bonded and their strength was measured. For testing the strength of bonded joints there was used a tensile test on the test machine Zwick 1456. Test conditions were according to the CSN EN ISO 527-1 and CSN EN ISO 527-2. Speed was 10 mm/min and evaluation software was Test Expert Standard. [18, 20, 34, 35, 36]

III. RESULTS AND DISCUSSION

A. Contact angle and surface energy

The variation in contact angle of HDPE for different doses of radiation and for different test liquids is shown in Fig. 1. It shows that the contact angle on the untreated surface is 89.2°, 79.1°, and 66.3° for distilled water, glycerol, and ethylene glycol, respectively. The contact angle values were considerably reduced after irradiation by a dose of 165 kGy to lower values of 57.9°, 54.6°, and 31.1° for distilled water, glycerol, and ethylene glycol, respectively (referring to: Fig. 5).

![Fig. 5 Variation of contact angle with respect to radiation dose for material HDPE](image)
The variation in contact angle of LDPE for different doses of radiation and for different test liquids is shown in Fig. 2. It shows that the contact angle on the untreated surface is 89.2°, 79.2°, and 67.9° for distilled water, glycerol, and ethylene glycol, respectively (referring to Fig. 6).

The contact angle values were considerably reduced after irradiation by a dose of 165 kGy to lower values of 54.7°, 49.3°, and 36.6° for distilled water, glycerol, and ethylene glycol, respectively (referring to Fig. 6).

Fig. 6 Variation of contact angle with respect to radiation dose for material LDPE

It shows that surface energy of untreated surface is 24.2 mJ/m² and 24.5 mJ/m² for water + glycerol and water + ethylene glycol, respectively. Ionization beta radiation increases the surface energy. The surface energy values considerably increased after irradiation by a dose of 165 kGy to higher values of 42.6 mJ/m² for water + glycerol and 43.1 mJ/m² for water + ethylene glycol.

Fig. 7 Variation of surface energy with respect to radiation dose for material HDPE

Fig. 7 shows a plot of surface energy $\gamma_S$ from the measured contact angles on the surface of the HDPE.

It shows that surface energy of untreated surface is 24.2 mJ/m² and 24.5 mJ/m² for water + glycerol and water + ethylene glycol, respectively. Ionization beta radiation increases the surface energy. The surface energy values considerably increased after irradiation by a dose of 165 kGy to higher values of 42.6 mJ/m² for water + glycerol and 43.1 mJ/m² for water + ethylene glycol.

Fig. 8 Variation of surface energy with respect to radiation dose for material LDPE

Fig. 8 shows a plot of surface energy $\gamma_S$ from the measured contact angles on the surface of the LDPE.

It shows that surface energy of untreated surface is 24.1 mJ/m² and 23.2 mJ/m² for water + glycerol and water + ethylene glycol, respectively. Ionization beta radiation increases the surface energy. The surface energy values considerably increased after irradiation by a dose of 165 kGy to higher values of 45.4 mJ/m² for water + glycerol and 45.6 mJ/m² for water + ethylene glycol.

Similar trend was observed for the polar component $\gamma_{pS}$ (refer with: Fig. 9 and Fig.10). The properties such as wettability, adhesion strongly depends upon the surface energy.
Fig. 9 Variation of polar component of surface energy with respect to radiation dose for material HDPE

Fig. 10 Variation of polar component of surface energy with respect to radiation dose for material LDPE

B. Strength of bonded joints of HDPE

Strength of bonded joints is characterized by the maximum burdensome force which endured bonded sample. For bonding of HDPE two-component methacrylate adhesive Cyberbond A806, two-component epoxy adhesive Cyberbond E705, and cyanoacrylate adhesive Cybebrond 2008 were used.

The highest strength of bonded joints samples of HDPE (adhesive Cyberbond A806) have those which were irradiated by a dose of 165 kGy. After the irradiation by a dose of 165 kGy strength is increased by 180 % (referring to: Fig. 12).

The highest strength of bonded joints samples of HDPE (adhesive Cyberbond A806) have those which were irradiated by a dose of 165 kGy. After the irradiation by a dose of 165 kGy strength is increased by 250 % (referring to: Fig. 13).

Fig. 11 Variation of strength of bonded joints with respect to radiation dose (material HDPE at 60 °C, adhesive Cyberbond E705)

The highest strength of bonded joints samples of HDPE (adhesive Cyberbond A806) have those which were irradiated by a dose of 165 kGy. After the irradiation by a dose of 165 kGy strength is increased by 100 % (referring to: Fig. 11).
C. Strength of bonded joints of LDPE

For bonding of LDPE one type of two-component epoxy adhesive of company Cyberbond (E705) and two types of cyanoacrylate adhesives of companies Cyberbond (2008 and 5008) were used.

The highest strength of bonded joints samples of LDPE (adhesive Cyberbond E705) have those which were irradiated by a dose of 165 kGy. After the irradiation by a dose of 165 kGy strength is increased by 200 % (referring to: Fig. 14).

The highest strength of bonded joints samples of LDPE (adhesive Cyberbond 2008) have those which were irradiated by a dose of 165 kGy. After the irradiation by a dose of 165 kGy strength is increased by 150 % (referring to: Fig. 15).

The highest strength of bonded joints samples of LDPE (adhesive Cyberbond 5008) have those which were irradiated by a dose of 165 kGy. After the irradiation by a dose of 165 kGy strength is increased by 350 % (referring to: Fig. 16).

IV. Conclusion

This article describes the effect of beta radiation on the contact angle of wetting, on the surface energy and on the final strength of bonded joints of HDPE and LDPE (at 60 °C). Beta radiation increases the strength of bonded joints of HDPE and LDPE and improves their adhesion properties. The best results were achieved by irradiation at doses of 165 kGy by which the
highest surface energy and the highest strength of bonded joints of HDPE and LDPE were achieved.

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