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Influence of electron radiation on surface free energy of low density polyethylene film

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Materials

ABSTRACT

Purpose: of this paper is to study the effect of the electron radiation, generated in a high voltage accelerator, on surface free energy (SFE) of low density polyethylene film.
Design/methodology/approach: An LAE 13/9 linear accelerator (former USSR) was used to irradiate the examined polyethylene film. The maximum electron energy was 13 MeV, controllable energy range, 5-13 MeV, and average power of the electron beam, 9 kW. The contact angles were measured with a G 11 goniometer (Krüss GmbH, Germany) using doubly distilled water, glycerol, formamide, diiodomethane, and α bromonaphthalene. The calculations of SFE were done by means of the Owens Wendt or the van Oss-haudhury-Good methods.
Findings: The value of the SFE for the polyethylene film, increasing monotonically with the radiation dose, depends on both the applied method of calculation and the set of measuring liquids. The differences between the results obtained with these two methods and sets of liquids generally increase with the radiation dose.
Research limitations/implications: The SFE value of polyethylene film depends not only on the intermolecular interactions originating in several outer atomic layers of the film but also on the intermolecular interactions occurring in the measuring liquids and on the way of performing investigations. Thus, it may be compared only when determined with the same method and using the same measuring liquids.
Practical implications: The results of presented research allow determining the recommendations referring to the optimization of irradiation technology of low density polyethylene film.
Originality/value: The differences in the SFE values calculated with the Owens Wendt and the van Oss Chaudhury-Good methods depend not on only on the kind of the calculation method but also on the kind of measuring liquid used in contact angle measurement.
Keywords: Engineering polymers; Surface free energy; Quality of adhesive joints; Electron beam irradiation

1. Introduction

Modification of polymer materials by means of ionizing radiation is already known for many years and it is still a subject of intensive research. Such modification improves the mechanical, thermal and electrical properties [1]. A substantial progress made in the construction of low-energy electron accelerators enabled this method to be applied also in modification of polymer films [2,3]. Due to the film irradiation, properties of the film surface layer (SL) change; oxidation of this layer is one of the most important processes occurring upon this treatment. The extent of oxidation depends significantly on the radiation dose, which was shown previously [4].

The SL oxidation leads to, e.g., increase in both wettability and surface free energy (SFE) of a polymer film. Changes in these parameters can be evaluated with various techniques, including direct measurements of the contact angle with use of different

measuring liquids and subsequent calculation of SFE mostly with the Owens-Wendt (OW) method [5] or with the van Oss-Chaudhury-Good (vOCG) method [6]. In our previous papers [7,8] effects of electron-beam irradiation on the SFE of polypropylene film and some problems of calculations of SFE of polymeric materials were presented.

The aim of this work was (i) to study the effect of the electron radiation on wettability of an low density polyethylene (LDPE) film with water, glycerol, formamide, diiodomethane, and α-bromonaphthalene, (ii) to calculate the SFE of this film with the OW and vOCG methods, and (iii) to compare the results obtained with these methods using different measuring liquids.

2. Materials, apparatus and methods of tests

A LDPE film, 150 μm thick, produced from parent polyethylene, Malen-E (PKN Orlen SA, Płock, Poland) was selected for the measurements. The polymer was obtained by a high-pressure polymerization. Its density was 0.918-0.921 g/cm3 (23 C), melt flow rate, 0.2-0.4 g/10 min (21.19 N, 190 ± 0.5° C), molecular weight, 6×105, and crystallinity, 40-50%. The film was formed by means of the blowing extrusion with a blowing factor of 2.7.

The contact angles were determined using the following liquids: doubly distilled water, glycerol, formamide, diiodomethane, and α-bromonaphthalene. The letters W, G, F, D, and B were used to stand for relevant measuring liquids and the corresponding contact angles were specified as ΘW, ΘG, ΘF, ΘD, and ΘB, respectively. The sets of the measuring liquids were denoted using the letters relating to the liquids involved in the sets.

The contact angles were measured with a G-11 goniometer (Krüss GmbH, Germany).

An LAE 13/9 linear accelerator (former USSR) was used to irradiate the examined films. The maximum electron energy was 13 MeV, controllable energy range, 5-13 MeV, and average power of the electron beam, 9 kW.

The film samples were irradiated in the atmospheric air and at ambient temperature (23° C), i.e., under conditions characteristic of industrial technology. To avoid an excess increase in the film temperature when applying large radiation doses, the irradiation was repeated with relatively small doses (25 kGy) until the expected total doses were achieved. Thus, the applied way of the film modification was not an adiabatic process: during the successive breaks in the irradiation procedure, the released heat dissipated into the surroundings and the sample temperature increased relatively little. For an irradiation procedure, a film specimen (50×42 cm) was placed in an aluminum container that was put on a conveyor able to move with a controlled speed through the radiation zone. The samples P0, P1, P2, P3, P4, and P5 were irradiated with doses 0, 25, 50, 100, 250, and 500 kGy, respectively.

The measurements of the contact angle, considered as the advancing contact angle, were carried out 24 h after the irradiation procedure was completed. The volume of the drop placed with a micropipette on the surface of an examined sample was 3 mm3. The time that elapsed from the moment the drop was placed to the moment of the read-out of the contact angle was within the range of 30-60 s for all the measurements. Twelve measurements were performed for each sample; the lowest and the highest values were disregarded and the remaining ten were used to calculate the arithmetic mean, variance, and standard deviation, the last quantity being 3° or less.

The SFE values of the studied polymer films were calculated with the OW and vOCG methods. The values of SFE and its components, relevant to the measuring liquids and used in the calculations, were accepted from literature [9].

3. Results and discussion

3.1. Contact angle

The values of the contact angle, when plotted against the dose used to irradiate the LDPE film, decreased monotonically over the entire dose range (i.e., up to 500 kGy) for all the applied measuring liquids (Fig. 1).

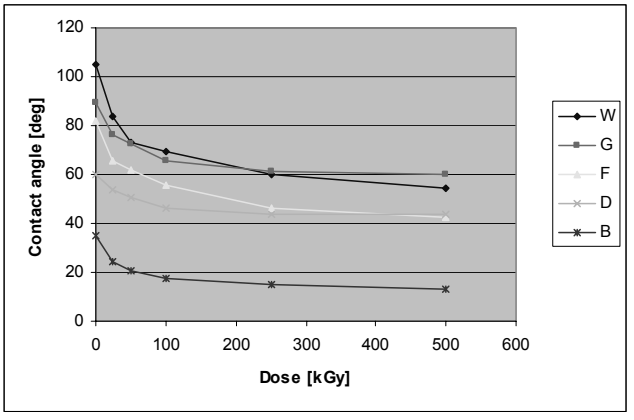

Fig. 1. Contact angle of various measuring liquids versus electron radiation dose for the LDPE film

For the dose of 250 kGy, the following inequality was obeyed: ΘW > ΘG > ΘF > ΘD > ΘB. In the range of up to 50 kGy, the average rate of the contact angle decrease was 0.64, 0.34, 0.41, 0.19, and 0.28 deg/kGy for the liquids W, G, F, D, and B, respectively. In the range of above 50 kGy, the average rate of the decrease was significantly lower.

For the non-irradiated LDPE film, the differences between the contact angles related to the particular measuring liquids were clearly larger than those for irradiated samples. In the range of the radiation doses of up to 200 kGy, the ΘW values were the highest as compared to the contact angles of remaining liquids and in the range of above 200 kGy, ΘW was only slightly lower (by less than 6°) as compared to ΘG. The values of ΘW and ΘG were close to each other, independently of the dose used for the film irradiation. The contact angles ΘB were clearly lower with respect to those of the other liquids. The difference between ΘW and ΘG decreased from 70 to 41° with the dose rising from 0 to 500 kGy.

3.2. Surface free energy

Independently of a calculation method and measuring liquids, SFE of the LDPE film increased with the radiation dose generally in the entire dose range (Figs. 2, and 4). The highest rate of this increase was observed in the range of up to 50 kGy. The scale of changes in the SFE values differed in relation to both the calculation method and the set of measuring liquids.

The SFE values obtained with the OW method for different sets of measuring liquids are shown in Fig. 2.

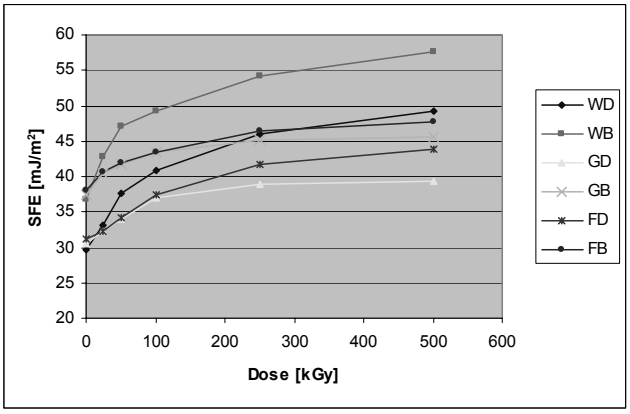

Fig. 2. Surface free energy (SFE) of the LDPE film, calculated with the OW method for various sets of measuring liquids, versus electron radiation dose

Differences between the SFE values for the consecutive samples (P0-P5) generally decreased with the rising radiation dose. The maximum differences in SFE obtained with different sets of measuring liquids for the investigated samples were 28-37% with respect to the SFE values calculated from the contact angle for the WD set.

In the OW method, SFE of a solid is assumed as a sum of the dispersion (SFED) and polar (SFEP) components. Contributions of these components to the overall SFE depend on the kind of the used measuring liquid. When a set containing D (WD, GD or FD) was used in the contact angle measurements, then the resulting SFED component did not increase notably with the radiation dose. When B was included in the set, then the other constituent did not influence the SFED values. In this case, SFED increased by 6.5 mJ/m2 when the radiation dose was raised from 0 to 500 kGy

Unlike SFED, the SFEP component increased with the radiation dose for each set of the measuring liquids (Fig 3). In the dose region of up to 50 kGy, the increase in SFEP was the highest when the WD set was used and gradually became less in the case of WB, FD, and GD. For GB and FB, the SFEP values were approximately constant. Over the entire dose region (0-500 kGy), SFEP increased by 21.4 (maximum) and 1.7 (minimum) mJ/m2 for WD and GB, respectively

When the vOCG method was applied, the results for the measuring liquid sets containing G and F together were disregarded since the calculated relevant SFE values were several times as high as those for the remaining sets and differed

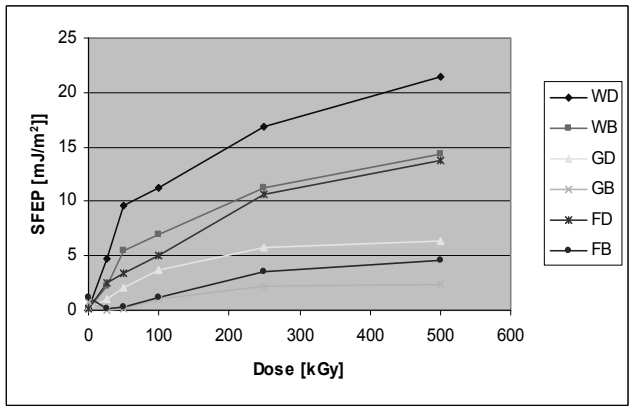

Fig. 3. Polar component (SFEP) of SFE of the LDPE film, calculated with the OW method for various sets of measuring liquids, versus electron radiation dose

significantly from the literature data. This confirms a controversy over the results obtained with this method [10]. The SFE results obtained for the particular sets of measuring liquids are shown in Fig. 4.

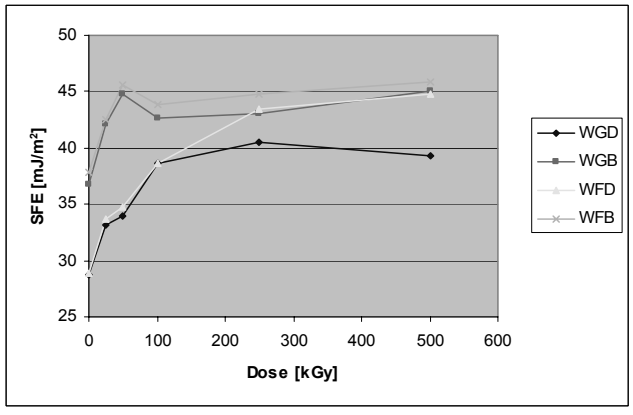

Fig. 4. Surface free energy (SFE) of the LDPE film, calculated with the vOCG method for various sets of measuring liquids, versus electron radiation dose

It was found that the values of SFE for WGB and WFB were close to each over the entire dose range. The same was observed in the case of the WGD and WFD sets within the dose region of up to 100 kGy. The values of SFE were clearly higher when the sets containing B (WGB and WFB) were used instead of those including D (WGD and WFD). Thus, the kind of the dispersion liquid determined the resulting SFE values. Differences in SFE for the sets containing D or B were especially large (27-32%) when the film samples were irradiated with the doses of up to 50 kGy. Replacing G with F affected SFE insignificantly.

In Fig. 5, the SFE data calculated with the methods of OW (for the WD set) and vOCG (for the WGD set) are presented. The SFE derived with these methods increased with the radiation dose over the entire dose range except the region above 250 kGy in the

case of the vOCG method. The SFE values obtained with the OW method were higher than those with the vOCG method. Differences between the SFE values calculated using the two methods increased with the radiation dose.

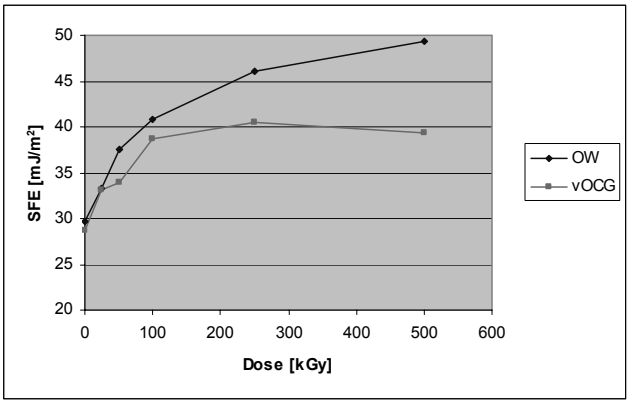

Fig. 5. Surface free energy (SFE) of the LDPE film, obtained with the methods of OW (for the WD set), and vOCG (for the WGD set), versus electron radiation dose.

Usually, the values of SFE obtained with the OW and vOCG methods and using various sets of measuring liquids differed significantly from one another. Their characteristic feature was that the SFE values determined with use of the sets containing B were distinctly higher than those in the case of D. Moreover, the SFE values calculated with the OW method and using the WB set were clearly higher as compared with those obtained with use of the remaining sets.

Apparently, the observed differences in the SFE values determined with different methods were not caused by experimental errors since the same values of contact angles were used for all the calculations. Intermolecular interactions, occurring in the system of a measuring liquid/LDPE film and varying upon modification of the film SL, differed for the particular liquids and were presumably responsible for the mentioned differences. Changes in the intermolecular interactions resulted, in turn, from qualitative and quantitative variations in functional groups, which occurred in the LDPE film SL due to electron irradiation [11].

4. Conclusions

The following general conclusions may be drawn from the presented results:

- The values of the contact angle for the LDPE and all the applied measuring liquids decrease monotonically with the rising radiation dose. The rate of this decrease depends on the kind of the liquid and is the highest in the dose range of up to 50 kGy.
- The values of the SFE for the LDPE, increasing monotonically with the radiation dose, depend on both the applied method (OW or vOCG,) and the set of measuring liquids. The differences between the results obtained with the particular methods and sets of liquids generally increase with the radiation dose.
- The increase in the SFE values obtained with the OW method is caused mostly by the rise in their polar component (SFEP), especially in the case of the measuring sets containing water (WD and WB). A notable rise in the dispersion component (SFED) occurs in the case of the sets including α-bromonaphthalene (WB, GB, and FB) and only for the radiation doses of up to 50 kGy.
- When the vOCG method is applied, the calculation results for the samples irradiated with the doses of up to 100 kGy differ insignificantly from one another provided the sets containing diiodomethane (WGD and WFD) or α-bromonaphthalene (WGB and WFB) are used.
- The SFE value depends not only on the intermolecular interactions originating in several outer atomic layers of the film but also on the intermolecular interactions occurring in the measuring liquids and on the way of performing investigations. Thus, it may be compared only when determined with the same method and using the same measuring or reference liquids.

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