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Wettability and surface free energy of a radiation-modified polyethylene film

Summary — Effects of the electron radiation generated by a high-voltage linear accelerator on wettability and surface free energy (*SFE*) of low-density polyethylene (PE-LD) film were studied. Radiation doses of 25, 50, 100, 250, and 500 kGy were used. Water, glycerol, formamide, diiodomethane, and α-bromonaphthalene were applied as measuring liquids for contact angle measurements. The calculations of *SFE* were made by Owens-Wendt and van Oss-Chaudhury-Good methods, using the results of measurements of contact angle with various systems of the measuring liquids. Wettability tests were also performed. It was found that the contact angle decreased with the rising radiation dose for all the measuring liquids and the shapes of these dependences were similar. However, significant quantitative differences were observed. The largest changes in the contact angle were detected for the dose range of up to 50 kGy. *SFE* values when measured by different methods and various measuring liquids differed generally in the whole range of the doses applied. Therefore, the surface free energy cannot be accepted as an absolute measure of the thermodynamic state of the surface layer of radiation-modified PE-LD film. Its values can be compared with one another only when they were determined using the same method and the same measuring or standard liquids.

Key words: polyethylene film, radiation-induced modification, wettability, surface free energy.

The value of the surface free energy (*SFE*) is commonly accepted as a measure of the thermodynamic state of the surface layer (SL) of a polymeric material and criterion for evaluation of changes occurring in this layer upon its modification [1]. In industry, polymers are being modified mainly by corona discharge in air or treatment with flame or low-temperature plasma, under the conditions of low pressure and atmosphere of suitable gas or gases mixture [1—3]. The modification processes are aimed mostly at changing the hydrophobic properties into hydrophilic ones, increasing *SFE* values and, thus, improving adhesion properties of the materials. The latter enables successful printing, gluing, and laminating of polymers, including polymer films widely used in packaging [4, 5].

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 [6]. A substantial progress made in the construction of low-energy electron accelerators enabled this method to be applied also in modification of polymer films [7, 8]. Due to the film irradiation, properties of the film 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 [9—11].

The SL oxidation leads to *e.g.* increase in both wettability and *SFE* of a polymer film. Changes in these parameters can be evaluated using various techniques, including direct measurements of the contact angle with use of different measuring liquids and subsequent calculation of *SFE* mostly by Owens-Wendt (OW) method [12] or by van Oss-Chaudhury-Good (vOCG) one [13]. In industry, the reference liquid (RL) method, known as a wettability test, is commonly applied [14, 15]. In our previous papers [16, 17] the effects of electron-beam irradiation on *SFE* of polypropylene and poly(ethylene terephthalate) films were presented. In this report it has been well established that similar effects arised when polyethylene film was irradiated by means of electron-beam.

The objective of this work was to study the effect of the electron radiation, generated in a high-voltage linear accelerator, on wettability of PE-LD film with water, glycerol, formamide, diiodomethane, and α-bromonaphthalene. The next steps were to calculate the surface free energy of this film with OW and vOCG methods, and to compare the results obtained by these methods using different systems of measuring liquids to those ones calculated by RL method.

EXPERIMENTAL

Materials

A low-density polyethylene (PE-LD) 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/cm^3 (23 °C), melt flow rate 0.2—0.4 g/10 min (21.19 N, 190 ± 0.5 °C), molecular weight $6 \cdot 10^5$ Da, and crystallinity 40—50 %. The film was formed by means of the blowing extrusion with a blowing factor of 2.7.

Contact angles were determined using the following liquids:

— doubly distilled water ("Aqua purificata", Maggie Co., Poland),

— glycerol ($C_3H_8O_3$, 99 %, Fluka Chemie GmbH, Switzerland),

— formamide ($HCONH_2$, 98 %, Sigma-Aldrich GmbH, Germany),

— diiodomethane (CH_2I_2, 99 %, Sigma-Aldrich GmbH, Germany),

— α-bromonaphthalene ($C_{10}H_7Br$, 97 %, Sigma-Aldrich GmbH, Germany).

Measuring liquids and the corresponding contact angles were specified as W (water), G (glycerol), F (formamide), D (diiodomethane), B (α-bromonaphthalene) and Θ_W, Θ_G, Θ_F, Θ_D, and Θ_B, respectively. The systems of the measuring liquids were denoted using the letters relating to the liquids involved in the systems.

The following mixtures of reference liquids were applied:

— methanol (CH_3OH, 99 %, Sigma-Aldrich GmbH, Germany) and water, for *SFE* range of up to 29 mJ · m^{-2};

— ethylene glycol ethyl ether ($C_2H_5OC_2H_4OH$, 99 %, Sigma-Aldrich GmbH, Germany) and formamide, for *SFE* range of 30—56 mJ · m^{-2};

— formamide and water, for *SFE* range of 57—73 mJ · m^{-2}.

Equipment

Contact angles were measured using G-11 goniometer (Krüss GmbH, Germany). LAE 13/9 linear accelerator (former USSR) was used to irradiate the examined films. The maximum electron energy was 13 MeV, controllable energy covered the range of 5—13 MeV and average power of the electron beam was 9 kW.

Methods

The film samples were irradiated in the atmospheric air and at ambient temperature (23 °C), *i.e.* under conditions characteristic for industrial technology. To avoid the film overheating 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 surrounding 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 non-irradiated (P_0) and irradiated with various doses (P_1—P_5) are specified in Table 1.

Table 1. Radiation doses absorbed by samples of the films examined

Sample symbols	P_0	P_1	P_2	P_3	P_4	P_5
Dose, kGy	0	25	50	100	250	500

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 mm^3. 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.

Wettability was measured according to standard procedures [14, 15]. A reference liquid in the form of a strip 10 mm wide and 200 mm long was placed with a brush on an examined surface. The time that elapsed from the moment of placing the strip to the moment the strip became divided into drops was measured with a stopwatch. The reference liquid was selected from those which the measured time was within *ca.* 2 s. Surface free energy of the selected liquid was considered as a measure of wettability and assumed to be equal to *SFE* of the film. The measurements were performed 24 h after the irradiation procedure was completed. The ambient temperature was 23 ± 2 °C and the relative humidity of an air 50 ± 3 %. *SFE* values of the studied polymer films were calculated by OW and vOCG methods. The values of *SFE* (γ_L) and its components, relevant to the measuring liquids and used in the calculations, are shown in Table 2 and 3 [18].

Table 2. Surface free energy (γ_L) and its dispersion (γ_L^d) and polar (γ_L^p) components (in mJ · m^{-2}) for applied measuring liquids used for the calculations by OW method

Liquid	γ_L	γ_L^d	γ_L^p
W	72.8	21.8	51.0
G	64.0	37.0	27.0
F	58.0	39.0	19.0
D	50.8	48.5	2.3
B	44.4	44.4	0.0

Table 3. Surface free energy (γ_L) and its components relating to the interactions of Lifshitz-van der Waals (γ_L^{LW}), acid-base (γ_L^{AB}), Lewis acid (γ_L^+), and Lewis base (γ_L^-) (in mJ · m^{-2}) for applied measuring liquids used for the calculations by vOCG method

Liquid	γ_L	γ_L^{LW}	γ_L^{AB}	γ_L^+	γ_L^-
W	72.8	21.8	51.0	25.5	25.5
G	64.0	34.0	30.0	3.92	57.4
F	58.0	39.0	19.0	2.28	39.6
D	50.8	50.8	0.0	0.0	0.0
B	44.4	44.4	0.0	0.0	0.0

RESULTS AND DISCUSSION

Contact angle

The values of contact angle, when plotted versus the dose used to irradiate PE-LD film, decreased monotonically over the entire dose range (*i.e.* up to 500 kGy) for all the applied measuring liquids (Fig. 1). The scale of the contact angle variations depended on the kind of the measuring liquid and is specified in Table 4. For the dose of 250 kGy, the following inequality was obeyed: $\Theta_W > \Theta_G > \Theta_F > \Theta_D > \Theta_B$. 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^{-1} 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 and equalled 0.04 (for W and F), 0.03 (for G), and 0.02 (for D and B) deg · kGy^{-1}.

Table 4. Variation ranges of contact angle for applied different measuring liquids (OW method), caused by radiation

Liquid	Range of contact angle, deg
W	105—54
G	89—60
F	82—42
D	60—44
B	35—13

For non-irradiated PE-LD film, the differences between the contact angle 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, Θ_W values were the highest as compared to the contact angles of remaining liquids and in the range of above 200 kGy Θ_W was only slightly lower (by less than 6°) as compared to Θ_G. The values of Θ_W and Θ_G were close to each other, independently on the dose used for the film irradiation. Contact angles of α-bromonaphthalene were clearly lower with respect to those of the other liquids. The difference between Θ_W and Θ_B decreased from 70 to 41° with the dose rising from 0 to 500 kGy.

Surface free energy

The results of *SFE* calculations are presented in Fig. 2—4. The results show that independently on a calcula-

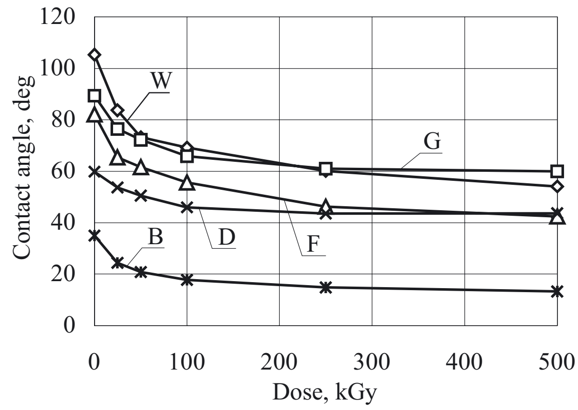

Fig. 1. The effect of electron radiation dose and kind of measuring liquid on contact angle of PE-LD film

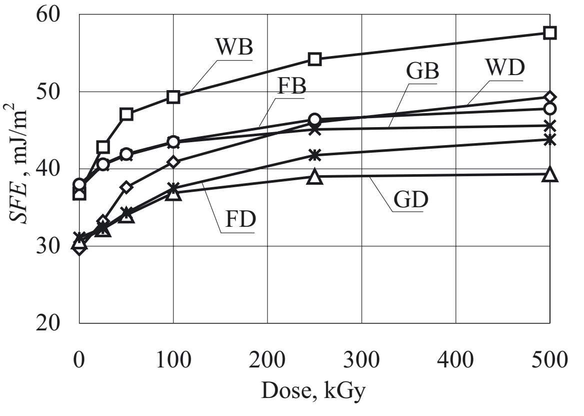

Fig. 2. Surface free energy (SFE) of PE-LD film for various systems of measuring liquids, calculated by OW method, versus electron radiation dose

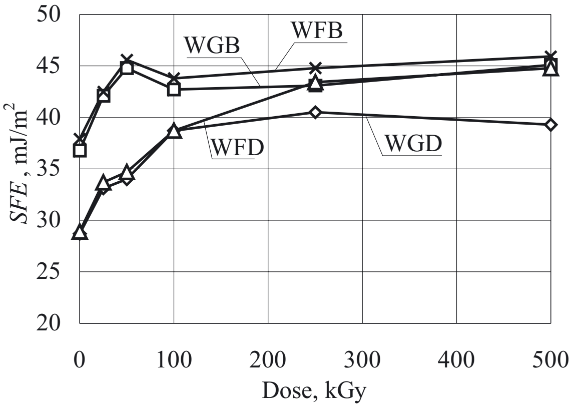

Fig. 3. Surface free energy (SFE) of PE-LD film for various systems of measuring liquids, calculated by vOCG method, versus electron radiation dose

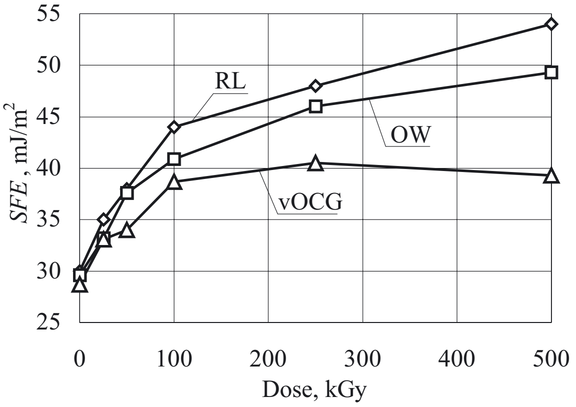

Fig. 4. Surface free energy (SFE) of PE-LD film, calculated either by RL, OW (for WD system) or vOCG (for WGD system) method, versus electron radiation dose

tion method and measuring liquid, surface free energy of PE-LD film increased with the radiation dose generally in the entire dose range. The highest rate of this increase was observed in the range of up to 50 kGy. The scale of changes of *SFE* values differed in relation to both the calculation method and the set of measuring liquids.

Table 5. Variation ranges of surface free energy (*SFE*) for applied systems of measuring liquids (OW method), caused by radiation

System of liquids	Range of *SFE*, mJ $\cdot$ m^{-2}
WD	29.6—49.3
WB	36.8—57.6
GD	30.6—39.3
GB	37.5—45.6
FD	31.1—43.8
FB	38.0—47.8

SFE values obtained using OW method for different systems of measuring liquids are shown in Fig. 2 and their variation ranges in Table 5. Table 6 presents the relative changes of *SFE*, calculated with respect to *SFE* values derived from the contact angles for the WD system. In the case of the system containing B and a polar component (W, G, or F), the values of *SFE* were higher by 8—29 % compared to those found when D was used instead of B. If different polar liquids were combined with the same dispersion liquid (D or B), differences in *SFE* were clearly smaller (Table 6). Differences between *SFE* values for the consecutive samples (P_0—P_5) generally decreased with the rising radiation dose (Fig. 2). The maximum differences in *SFE* obtained with different systems of measuring liquids for the investigated samples were 28—37 % with respect to *SFE* values calculated from the contact angle for WD system.

Table 6. Effect of radiation dose on relative changes of *SFE* values (in comparison with WD system) for applied systems of measuring liquids (OW method)

System of liquids	Dose, kGy					
	0	25	50	100	250	500
WD	1.00	1.00	1.00	1.00	1.00	1.00
WB	1.24	1.29	1.25	1.21	1.18	1.17
GD	1.03	0.97	0.90	0.90	0.85	0.80
GB	1.27	1.22	1.11	1.06	0.98	0.92
FD	1.05	0.97	0.91	0.92	0.91	0.89
FB	1.28	1.22	1.11	1.06	1.01	0.97

In 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 surface free energy depend on the kind of the measuring liquids used (Fig. 5 and 6). When a system containing D (WD, GD or FD) was used in the contact angle measurements, then the resulting *SFED* component did not increase noticeably with the radiation dose. When B was included in the system, then the other constituent did not influence *SFED* values. This was due to the assumption that

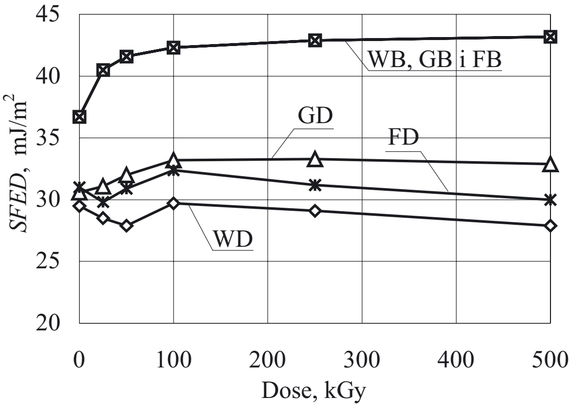

Fig. 5. Dispersion component (SFED) of surface free energy of PE-LD film for various systems of measuring liquids film, calculated by OW method, versus electron radiation dose

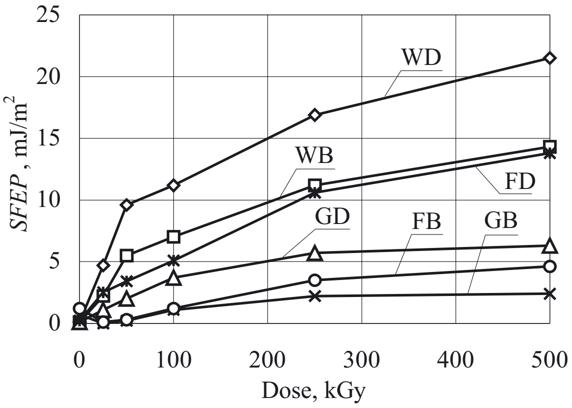

Fig. 6. Polar component (SFEP) of surface free energy of PE-LD film for various systems of measuring liquids, calculated by OW method, versus electron radiation dose

γ_L^p = 0 for B (Table 2). In this case, *SFED* increased by 6.5 mJ · m^{-2} when the radiation dose raised from 0 to 500 kGy.

Unlike *SFED*, *SFEP* component increased with the radiation dose for each system of the measuring liquids. In the dose region of up to 50 kGy, the increase in *SFEP* was the highest when WD system was used and gradually became smaller in the case of WB, FD, and GD. For GB and FB, *SFEP* values were approximately constant. Over the entire dose region (0—500 kGy), *SFEP* increased by 21.4 (maximum) and 1.7 (minimum) mJ · m^{-2} for WD and GB, respectively.

Table 7. Variation ranges of surface free energy (*SFE*) for applied systems of measuring liquids (vOCG method), caused by radiation

System of liquids	Range of *SFE*, mJ · m^{-2}
WGD	28.7—39.3
WGB	36.8—45.1
WFD	28.9—44.8
WFB	37.9—45.9

When vOCG method was applied, the results for the measuring liquid systems containing G and F together were disregarded since the calculated relevant *SFE* values were several times as high as those for the remaining systems and differed significantly from the literature data. This confirms a controversy over the results obtained by this method and explanation of it requires a separate investigation. *SFE* results obtained for the particular systems of measuring liquids are shown in Fig. 3 whereas their variation ranges in Table 7. The relative changes in *SFE*, calculated with respect to *SFE* values derived from the contact angles measured for WGD system, are listed in Table 8. It was found that the values of *SFE* for WGB and WFB were close to each other over the entire dose range. The same was observed in the case of WGD and WFD systems within the dose region of up to 100 kGy. The values of *SFE* were clearly higher when the systems of liquids 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 systems 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.

Table 8. Effect of radiation dose on relative changes of *SFE* values (in comparison with WGD system) for applied systems of measuring liquids (vOCG method)

System of liquids	Dose, kGy					
	0	25	50	100	250	500
WGD	1.00	1.00	1.00	1.00	1.00	1.00
WGB	1.28	1.27	1.32	1.10	1.06	1.15
WFD	1.01	1.02	1.02	1.00	1.07	1.14
WFB	1.32	1.28	1.34	1.13	1.11	1.17

In Fig. 4, *SFE* data determined by RL method are shown together with those calculated by OW (for WD system of liquids) and vOCG (for the WGD system) methods. *SFE* derived by three methods increased with the radiation dose over the entire dose range except the region above 250 kGy in the case of vOCG method. *SFE* values obtained using RL method were the highest while those obtained using vOCG method, the lowest. *SFE* values of the film samples irradiated with dose of 25 kGy and calculated by OW and vOCG methods were approximately equal to each other whereas the value of *SFE* in the case of RL method was by 5.5 % higher. Over the dose range of 25—100 kGy, *SFE* increased at the rates of 0.07—0.12 mJ · m^{-2} kGy, reaching the values of 38.7, 40.9 and 44.0 mJ · m^{-2} in the case of the methods vOCG, OW, and RL, respectively. In the dose range of above 100 kGy, *SFE* values obtained by OW and RL methods were similar, differing by less than 10 % with respect to the data determined by former method. Differences between *SFE* values calculated using the three methods increased with the radiation dose. Considering vOCG and RL methods, the differences were 1.3 and 14.7 mJ · m^{-2} for the non-irradiated film sample and that irradiated with the 500 kGy dose, respectively, or 4.3 and 27.2 % relative to *SFE* values determined by RL method. In general, the values of *SFE* determined by RL method were higher by 1—10 % and 4—37 % than those calculated by OW and vOCG methods, respectively.

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

Apparently, the observed differences in *SFE* values determined by 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/PE-LD film and varying upon the modification of the film surface layer, 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 film surface layer due to electron radiation [9, 10].

CONCLUSIONS

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

— The values of the contact angle for PE-LD film 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 surface free energy of PE-LD film, increasing monotonically with the radiation dose, depend on both the method applied (OW, vOCG, or RL) and the system of measuring liquids. The differences between the results obtained by particular methods and systems of liquids generally increase with the radiation dose.

— The increase in the surface free energy values obtained using OW method is caused mostly by the rise in their polar component (*SFEP*), especially in the case of the measuring systems of liquids containing water (WD and WB). A noticeable rise in the dispersion component (*SFED*) occurs in the case of the systems including α-bromonaphthalene (WB, GB, and FB) and only for the radiation doses of up to 50 kGy.

— When 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 systems containing diiodomethane (WGD and WFD) or α-bromonaphthalene (WGB and WFB) are used. Application of GFD and GFB systems yields the results that require further investigation, including theoretical studies and experimental verification.

— RL method gives the highest values of surface free energy, OW — medium ones (with use of WD system), and vOCG — the lowest ones (with use of WGD system). In the dose range of up to 50 kGy, the differences between *SFE* values obtained by RL and OW methods are slight.

— The surface free energy obtained using the mentioned methods cannot be accepted as an independent physical quantity determining a thermodynamic state of the surface layer of PE-LD film modified with the electron radiation. The surface free energy 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 by the same method and using the same measuring or reference liquids.

— The results and conclusions presented in this work are similar to those obtained by us in the investigation of polypropylene and poly(ethylene terephthalate) films [16, 17].

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