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Surface Free Energy of Polyethylene After Corona Treatment and its Stability at Different Storage Temperatures

ABSTRACT

Polymeric materials, especially polyethylene, are among the most widely used materials due to their mechanical properties, low price, and chemical resistance. However, its low surface free energy and poor wettability represent a major problem in cases where good adhesion of inks, adhesives, or coatings is necessary. The surface free energy of polymeric materials can be increased, for example, by corona, plasma, or flame treatment. This work focuses on monitoring the changes in the surface free energy of polyethylene film after corona treatment. The stability of this treatment was evaluated over time at different storage temperatures of the treated polyethylene film (10 °C, room temperature, and 40 °C). The surface free energy was evaluated by the sessile drop method based on the evaluation of the contact angles of four liquids (water, ethylene glycol, formamide and diiodomethane) on the OCA 50 device. The results show a significant decrease in the free surface energy during first day after corona treatment.

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KEY WORDS
Surface free energy, polyethylene, contact angle, corona, temperature influence

1. Introduction

Polymeric materials are currently among the most widely used materials worldwide, used in various sectors (packaging industry, construction and building industry, textile industry, agriculture, automotive industry, etc.). The most widely used polymer materials include polyethylene (PE), polypropylene (PP), polyethylene terephthalate (PET), polystyrene (PS), and polyvinyl chloride (PVC). The advantages of polymer materials are their good mechanical properties, chemical resistance, and low price. A significant part of the produced polymer materials must be further processed by printing (packaging of various products, textile materials, floor coverings, electronics, etc.). A general problem with printing on most polymer materials is their low free surface energy and wettability, which represents a fundamental problem in cases where it is necessary to ensure good adhesion and spreading of inks, adhesives, or coatings. The surface free energy of some polymers is summarised in Table 1. In order for a liquid, such as printing ink, to wet the printed surface, its surface tension must be lower than the free surface energy of the printed material. The surface tension of inks depends on the type and composition of inks (for example, inkjet inks 22–45 mN/m, offset inks ~37 mN/m, water based flexographic inks 34–38 mN/m) (Izdebska, 2016). Polar liquids such as water have a higher surface tension and nonpolar one has a lower surface tension.

Table 1
Surface free energy of chosen polymeric films (Izdebska, 2016)

Polymeric film	PP	PE	PVC	PS	PET
Surface free energy (mJ/m²)	29–30	31–36	36–39	43–44	43–47

The surface free energy of polymeric materials and its wettability can be increased by various methods (corona discharge in air, application of low-temperature plasma, flame activation, chemical effect of acid solution,

application of reactive gases – chlorination, fluorination, etc.). In printing, corona discharge treatment is often used to treat the surfaces of polymer printed materials. However, the increasing of the surface free energy and hydrophilic character of treated surfaces is not permanent and there is a noticeable decrease of these parameters in time, and it is called hydrophobic recovery (Guimond & Wertheimer, 2004; Pascual et al., 2008).

Evaluation of the surface free energy of polymers can be done by various methods developed by Berthelot, Anthonow, Girifalco and Good, Fowkes, Owens and Wendt, Wu, Zisman, etc. (Izdebska, 2016). In this paper, the Owens-Wendt method (Owens & Wendt, 1969) was used. This method uses two liquids (one polar and one non-polar) with known surface tensions. According to this method, the polar and dispersive components of the surface free energy (γ) can be estimated (Equation 1),

$$\frac{\gamma_l \cdot (1+\cos(\theta))}{2 \cdot (\gamma_l^d)^{0.5}} = (\gamma_s^p)^{0.5} \cdot \left[\frac{(\gamma_l^p)^{0.5}}{(\gamma_l^d)^{0.5}}\right] + (\gamma_s^d)^{0.5} \quad (1)$$

where ϑ is the contact angle, γ_l is the surface tension of the liquid and γ_s is the surface tension of the solid or the surface free energy. The terms with subscripts *p* and *d* refer to the polar or dispersive component, respectively. Equation 1 is linear equation ($y = ax + b$), where $(\gamma_s^p)^{0.5}$ is the slope of the line and $(\gamma_s^d)^{0.5}$ is the intercept of this line on the *y* axis. The total surface free energy of solid (γ_s) is the sum of polar (γ_s^p) and dispersive (γ_s^d) components $(\gamma_s = \gamma_s^p + \gamma_s^d)$.

This article evaluates changes in the surface free energy of polyethylene film after corona treatment at different storage temperatures (10 °C, room temperature and 40 °C) using the Owens-Wendt method.

2. Experimentals

2.1. Materials

The polyethylene film tested in this paper was from the Czech company GRANITOL and is supplied under the trade name GRANIL O. It is a single-layer non-shrinkable LDPE (low-density polyethylene) film with 60 µm thickness, thermal resistance −50 °C to +85 °C and can be printed with inks.

Four liquids were used for measurements of contact angles on LDPE film. These liquids were distilled water, ethylene glycol (purity > 99.8 %), formamide (> 99.5 %) and diiodomethane (> 99 %). All liquids, except distilled water, were supplied by MERCK.

2.2. Equipment

The Lab Treator ASL 400 TUM from Ahlbrandt (Germany) was used for corona treatment of LDPE film. The device is equipped with a corona unit with two ceramic electrodes, and its speed of movement over the treated material can be changed. The samples were attached to an aluminium table base that serves as a counter electrode. In this work, the speed of movement of the corona unit was 10 m/min at a power 800 W. Corona treatment of the samples under these conditions was always performed twice (immediately after each other). Measurements were carried out at a room temperature.

Goniometer OCA 50EC from DataPhysics (Germany) was used for measuring of contact angles (sessile drop method) of four liquids. For each measurement (before corona treatment, after corona treatment and subsequent measurements over time), 4 samples were prepared and the contact angles of 3 drops of each liquid were measured on each sample. The contact angles of the drops were measured using SCA20 software. Each drop was scanned for 10 seconds (frequency 1 frame per second). The average contact angle values were used to calculate the free surface energy of LDPE using the Owens-Wendt method. The standard deviation was determined for all sample measurements. After corona treatment, contact angles were measured and subsequently the samples were stored under different temperature conditions (10 °C – refrigerator, room temperature – laboratory and 40 °C – oven). Contact angle measurements were performed 2 and 4 hours after corona treatment and next after 1 day, 7 days, 14 days etc. in a period more than two months (see Tables 3, 4, a 5).

3. Results and discussion

First, the surface free energy of the untreated LDPE was measured. Untreated LDPE was measured three times over a five-month period to evaluate stability and repeatability of measurements. The results are presented in Table 2. The results indicate that the surface free energy of untreated LDPE is stable and that the measurement repeatability is very good. The differences between measurements are within the standard deviation. The surface free energy of untreated LDPE was around 26 mJ/cm² and its polar component around 2 mJ/m².

Table 2

Surface free energy (γ_s) of untreated LDPE with polar (γ_s^p) and dispersive (γ_s^d) components. The values in brackets are standard deviations

Measurements	γ_s^p (mJ/m²)	γ_s^d (mJ/m²)	γ_s (mJ/m²)
1	2.0 (0.7)	23.5 (1.5)	25.5 (0.9)
2	2.2 (0.7)	24.0 (0.9)	26.2 (0.7)
3	1.7 (0.4)	24.4 (0.5)	26.1 (0.6)

Tables 3, 4 and 5 summarise the changes in the surface free energy of corona discharge treated LDPE and its decrease over a period of more than two months at room temperature, lower temperature 10 °C (refrigerator) and elevated temperature 40 °C (oven). After corona discharge treatment of LDPE, a significant increase in surface free energy (39–42 mJ/m²) is observed in all measurements, driven by an increase in its polar component (from ~2 mJ/m² to ~12 mJ/m²). The most pronounced decrease in surface free energy is observed for all tested samples during the first day after corona treatment (31.7 mJ/cm² for room temperature, 32.7 mJ/cm² for 10 °C, 31.9 mJ/cm² for 40 °C) and significant changes can be observed as early as 4 hours after treatment. This also corresponds to a significant drop in the polar component, whereas changes in the dispersive component are minor. After more than two months of samples aging, the greatest decrease in surface free energy was observed for samples stored at 40 °C. At the end of this period, the average free surface energy of these samples was 27.8 mJ/cm² (untreated samples ~26 mJ/cm²). The samples stored at room temperature had an average surface free energy 31.6 mJ/cm² and at lower temperature 29.7 mJ/cm². Furthermore, for samples aged at elevated temperatures, a more rapid decrease in free surface energy to values below 30 mJ/cm² can be observed. These values were reached only one week after corona treatment.

The standard deviation of the total free surface energy (γ_s) was low for all measurements (mainly in the range 0.2–0.8 mJ/cm²), indicating good repeatability of the measurements. For each temperature, the standard deviation was calculated based on four evaluated samples.

Table 3

Surface free energy (γ_s) of corona discharge treated LDPE film with polar (γ_s^p) and dispersive (γ_s^d) components in terms of the storage time aged in air at room temperature. The values in brackets are standard deviations

Aging time	γ_s^p (mJ/m²)	γ_s^d (mJ/m²)	γ_s (mJ/m²)
0 hours	12.5 (0.8)	28.5 (0.9)	42.0 (0.4)
2 hours	12.4 (0.4)	29.8 (0.9)	42.2 (0.6)
4 hours	6.8 (2.9)	30.4 (2.7)	37.2 (0.6)
1 day	2.9 (0.2)	28.8 (0.2)	31.7 (0.3)
7 days	2.8 (0.2)	29.5 (0.2)	32.3 (0.2)
21 days	1.9 (0.2)	28.2 (1.1)	30.1 (0.9)
31 days	3.2 (0.5)	28.7 (0.3)	31.9 (0.2)
71 days	3.2 (0.5)	28.4 (0.9)	31.6 (0.4)

Table 4

Surface free energy (γ_s) of corona discharge treated LDPE film with polar (γ_s^p) and dispersive (γ_s^d) components in terms of the storage time aged in air at lower temperature (10 °C). The values in brackets are standard deviations

Aging time	γ_s^p (mJ/m²)	γ_s^d (mJ/m²)	γ_s (mJ/m²)
0 hours	10.9 (2.2)	30.0 (1.9)	40.9 (0.6)
2 hours	5.4 (1.0)	32.6 (1.7)	38.0 (1.0)
4 hours	2.0 (0.3)	31.3 (0.9)	33.3 (0.6)
1 day	2.2 (0.4)	30.5 (1.1)	32.7 (0.7)
7 days	2.3 (0.4)	30.2 (0.8)	32.5 (0.7)
14 days	3.1 (1.5)	28.9 (1.5)	32.0 (0.3)
47 days	3.3 (1.1)	26.2 (1.0)	29.5 (0.4)
69 days	3.5 (1.1)	26.21.0)	29.7 (0.8)

Table 5

Surface free energy (γ_s) of corona discharge treated LDPE film with polar (γ_s^p) and dispersive (γ_s^d) components in terms of the storage time aged in air at elevated temperature (40 °C). The values in brackets are standard deviations

Aging time	γ_s^p (mJ/m²)	γ_s^d (mJ/m²)	γ_s (mJ/m²)
0 hours	12.2 (1.0)	26.8 (0.3)	39.0 (0.8)
2 hours	9.8 (0.5)	28.0 (0.4)	37.8 (0.8)
4 hours	8.0 (0.6)	27.8 (0.3)	35.8 (0.5)
1 day	2.6 (0.5)	29.3 (0.8)	31.9 (0.4)
7 days	2.6 (0.5)	27.3 (0.9)	29.9 (0.6)
14 days	2.2 (0.1)	26.2 (0.3)	28.4 (0.2)
28 days	2.4 (0.3)	26.3 (0.3)	28.7 (0.3)
76 days	2.2 (0.4)	25.5 (0.7)	27.8 (0.6)

4. Conclusions

Increasing the surface free energy and wettability of polymer materials by corona discharge treatment is a commonly used method, for instance, in the printing industry. However, this increase in surface free energy of polymer films is unstable; in the case of non-polar polymers such as polyethylene and polypropylene, the surface free energy decreases relatively quickly, and the hydrophobic surface is restored. This study investigated the effect of temperature and aging time on changes in the surface free energy of LDPE film after corona treatment. Measurements demonstrated a significant decrease in surface free energy within a few hours after corona treatment. In general, the most pronounced changes occurred during the first day after treatment, while the subsequent decrease in the following weeks was slow and gradual. The storage temperature (10°C, room temperature and 40°C) had little impact on the reduction of surface free energy during the first day after corona treatment. However, elevated storage temperatures resulted in a more rapid decrease in surface free energy over the

long term; values below 30 mJ/cm² were reached just one week after corona treatment. These rapid changes in the surface free energy of polymer materials must be taken into account during the processing of polymer films (e.g. printing, lamination, gluing), because the aging time after corona treatment significantly changes the surface properties of the treated materials.

5. References

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