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Effect of Corona Discharge Treatment on the Dyeability of Low-density Polyethylene Film

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Abstract

The purpose of this work is to investigate the surface modification of LDPE film *via* corona discharge treatment and subsequent graft polymerization, and their effect on the resulting dyeability is studied in terms of the surface functional groups, surface energetics, and acid-base interaction between the modified LDPE and the dyes used.

Introduction

Low-density polyethylene (LDPE) is widely used in various applications due to abundant supply, low cost, good processability, low energy demand for processing, and resistance to chemicals and harsh environments. Recently, the packaging industry demands mostly LDPE because of its high specific modulus and strength where it is used directly or in the form of laminates with aluminium foil, paper, etc. However, its surfaces are inert and hydrophobic, and need to be made more hydrophilic in nature, e.g., to improve printability, paintability, or adhesion to adhesives or inorganic substances (1).

The surface modification of LDPE film could be accomplished in a number of ways, but corona discharge treatment and subsequent graft polymerization onto the surface can be possibly one of the most suitable ways of modifying the polymer surface for obtaining permanent alternated surface, especially for improving water wettability.

Experimental

An additive-free low-density polyethylene (LDPE, 250~300 μm thickness, Hanyang Chemical Co., Korea) film was used as the polymeric substrate for the preparation of the gradient surface.

The acid and base dyeing agents used were, respectively, the Acid Red 42 (C. I. 17070, Bayer) and Basic Green 1 (C. I. 42040, Aldrich Chemical Co.,) without further purification for dyeing of LDPE film.

The corona discharge powers were varied within 0 (LDPE 0), 50 (LDPE 50), 100 (LDPE 100), 150 (LDPE 150), and 200 watt (LDPE 200) at 100 kHz.

The acrylic acid monomer solution (Junsei Chem. Co., Japan) was prepared by dissolving 10 wt.% monomer in purified water.

The surfaces of LDPE film were analyzed using XPS (ESCA LAB MK-Ⅱ, VG Scientific Co.).

Contact angle was measured using the sessile drop method (12) on a Rame-Hart goniometer. For this work, the total surface free energies (or surface tension) and their London dispersive and specific (or polar) components for the wetting liquids are shown in Ref. (2).

To investigate the dye uptake, the corona-treated LDPE film were dyed for 1 h at 80℃. The dye concentrations were varied within 0.5 g/l, 1.0 g/l, 2.0 g/l, and 3.0 g/l. The film rinsed with water to remove the dyes that had not bonded with the sites of dye sorption of the film. The color strengths of dyed LDPE film were measured using a colorimeter (Spectraflash 500, U.S.A.). The reflectance measurements expressed as *K/S* value were determined by applying the Kubelka-Munk equation: (3)

$$K/S = (1-R)^2 / 2R \quad (1)$$

where, K is the absorption coefficient, S the scattering coefficient, and R the decimal fraction of the reflectance of the colored sample.

Results and Discussion

Table 1 represents the XPS results of the chemical compositions of corona-treated LDPE surfaces grafted by acrylic acid. As a result, the content of oxygen and the O_{1S}/C_{1S} composition ratios increase with increasing the corona discharge power, while the content of nitrogen remains nearly constant. This is clearly attributed to the introduction of polar oxygen groups on the corona-treated LDPE film surfaces.

Figure 1 shows the *K/S* values dyed with color pastes of acid dye for different concentrations. The *K/S* values do not significantly increases with increasing the corona power and the concentration of dye. This is due to the acidification of LDPE film grafted by acrylic acid after corona treatment.

Table 1. Chemical Compositions of the Corona-treated LDPE Film Surfaces from XPS

Samples	Element (%)			O_{1S}/C_{1S} (%)
	C_{1S}	O_{1S}	N_{1S}	
LDPE 0	91.2	7.4	1.4	8.1
LDPE 50	77.9	20.7	1.4	26.7
LDPE 100	69.4	29.1	1.5	41.9
LDPE 150	65.5	33.1	1.4	50.5
LDPE 200	64.8	33.5	1.7	51.7

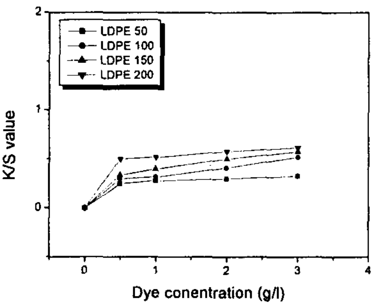

Fig. 1. Relationship between *K/S* value and dye concentration of corona-treated LDPE films dyed with Acid Red 42.

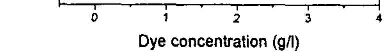

Fig. 2. Relationship between *K/S* value and dye concentration of corona-treated LDPE films dyed with Basic Green 1.

Meanwhile, Figure 2 shows the *K/S* values dyed with color pastes of basic dye for different concentrations. As a result, the corona treatment does lead to a significant increase of *K/S* value, which can be related to the effect of acid-base interaction between acidic corona-treated LDPE film and basic dye (4). Also, the *K/S* increase of corona-treated LDPE film with the corona discharge power can be attributed to the introduction of acidic polar component, resulting in creating the active sites at the surface of LDPE films and the interaction between the modified LDPE film and $-NH_3$ in basic dye.

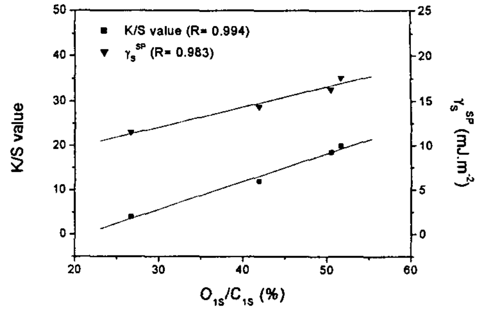

Fig. 3. Dependence of the *K/S* value dyed with basic dye and the specific component of surface free energy on O_{1S}/C_{1S} ratio (R = coefficient of regression).

A good linearity between the O_{1S}/C_{1S} ratio and the resulting *K/S* value or specific component of surface free energy is Figure 3. As mentioned above, it is a consequence of the increasing the specific component on surface free energy or acidic character of LDPE films, resulting in increasing the content of oxygen and dyeability of LDPE film.

Conclusions

The effect of corona discharge treatment on the LDPE surface properties has been studied in the context of XPS, contact angles, and dyeability. As a result, it is found that the introduction of acidic polar groups and the increasing of O_{1S}/C_{1S} on the corona-treated LDPE film is resulted from grafting with acrylic acid. These functional groups lead to an increase in the specific component of surface free energy or acidic character of LDPE surface, resulting in an immense increase in the *K/S* value of dyeability when basic dye agent is used. This is again confirmed by the acid-base intermolecular interaction between acidic functional group of LDPE surface and $-NH_3$ in basic dye after this treatment system.

References

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