Surface Graft Copolymerization of 2-Hydroxyethyl Methacrylate onto Low-Density Polyethylene Film Through Corona Discharge in Air

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ABSTRACT: The corona discharge technique was explored as a means of forming chemically active sites on a low-density polyethylene (LDPE) film surface. The active species thus prepared at atmospheric pressure in air was exploited to subsequently induce copolymerization of 2-hydroxyethyl methacrylate (HEMA) onto LDPE film in aqueous solution. The results showed that with the corona discharge voltage, reaction temperature, and inhibitor concentration in the reaction solution the grafting degree increased to a maximum and then decreased. As the corona discharge time, reaction time, and HEMA concentration in the reaction solution increased, the grafting degree increased. With reaction conditions of a 5 vol % HEMA concentration, 50°C copolymerization temperature, and a 2.0-h reaction time, the degree of grafting of the LDPE film reached a high value of 158.0 $\mu g/cm^2$ after treatment for 72 s with a 15-kV voltage at 50 Hz. Some characteristic peaks of the grafted LDPE came into view at 1719 cm^{-1} on attenuated total reflectance IR spectra ($>$C═O in ester groups) and at 531 eV on electron spectroscopy for chemical analysis (ESCA) spectra (O_{1s}). The C_{1s} core level ESCA spectrum of HEMA-grafted LDPE showed two strong peaks at ~286.6 eV (—C—O— from hydroxyl groups and ester groups) and ~289.1 eV (O═C—O— from ester groups), and the C atom ratio in the —C—O— groups and O═C—O groups was 2:1. The hydrophilicity of the grafted LDPE film was remarkably improved compared to that of the ungrafted LDPE film. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 81: 2881–2887, 2001

Key words: low-density polyethylene film; corona discharge; surface grafting; 2-hydroxyethyl methacrylate

INTRODUCTION

Polyethylene (PE) is a common polymer material. However, its chemically inert surface prevents its applications in some fields, for example, printing or painting, adhesion and biomedical materials, and so forth. Several methods have been developed to overcome this problem, such as flame, corona, or plasma treatment; exposure to ozone or an etching agent; and others. However, among these only surface grafting of the selected monomers provides good control of the prepared surface nature and this is especially important for biomedical applications.[1] The usual methods for surface grafting are chemical graft polymerization and graft polymerization induced by glow discharge,[2,3] UV irradiation,[4,5] and high-energy radiation such as γ rays.[6–8] Chemical graft co-

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polymerization requires a long time, a high temperature, and an organic solvent. Glow discharge treatment requires low pressure in the apparatus. The γ-ray type of radiation needs an expensive apparatus, it activates the substrate as a whole, and this might ultimately affect the final properties. UV irradiation also decreases the mechanical strength of polymer materials.

Corona discharge can be carried out in air by an apparatus ordinarily used in the industry.[9] It can effectively oxidize the polymer surface to produce oxygen-containing groups of ester, ether, ketone, hydroperoxy, epoxy, carboxylic acid, and so forth.[10] Corona discharge seem to be as effective as glow discharge, UV irradiation, and high-energy irradiation in introducing peroxides to a polymer for the subsequent use of graft polymerization. The peroxides formed during corona discharge affect only the surface. Thus, the location of grafting is definitely limited to the surface region of the polymer material without any change of the bulk properties.[11] Very few works have reported on the graft polymerization on polyethylene through corona discharge.[12,13]

Since successful clinical applications of poly(2-hydroxyethyl methacrylate) (PHEMA) were demonstrated in 1960, HEMA has been widely used as an important monomer for polymer surface graft modification to prepare biomedical materials with good mechanical properties and biocompatibility. Therefore, this study investigated corona discharge induced graft copolymerization of HEMA onto low-density PE (LDPE) film and its hydrophilicity.

EXPERIMENTAL

Materials

The LDPE had a melting index of 7.2 g/10 min. The HEMA and benzophenone were chemically pure, and Mohr's salt [$(FeSO_4(NH_4)_2SO_4(6H_2O)$] was analytically pure.

Graft Polymerization

The LDPE powder mixed with 1.5 wt % benzophenone was blown into films on the blow molding unit of a Haake torque rheometer. The prepared LDPE films were activated by a SDCD16-2-10 type corona discharge apparatus (Dalian Radio Factory of China) in air at room temperature (50-Hz frequency, 7-mm gap between electrodes), then they were immersed in HEMA aqueous solution deaerated by nitrogen. The grafting was carried out in a nitrogen atmosphere at a preselected constant temperature. After polymerization for a given time, the films were thoroughly washed with hot distilled water to exclude the residual monomer and the homopolymer on the film surface and then dried in a vacuum oven. The grafting degree was calculated as follows:

$$G = (W - W_0)/S$$

where G, S, W, and W_0 represent the grafting degree ($\mu g/cm^2$), the area (cm^2), the weight before grafting (μg), and the weight after grafting (μg), respectively.

Characterization

Attenuated total reflectance IR (ATR-IR) spectroscopy was carried out with a Nicolet model 560 IR spectrometer. Electron spectroscopy for chemical analysis (ESCA) spectra were obtained on a Kratos XSAM 800 spectrometer, using a monochromatic Al Kα photon source. The static contact angle of the water on the LDPE film was measured at ambient temperature by a contact angle apparatus (model 20913, Erma Optical Works). Distilled water was used for this measurement, and five readings were averaged.

RESULTS AND DISCUSSION

Effect of Corona Discharge Treatment Time and Voltage on Grafting Degree

From Figure 1 it can be seen that the grafting degree increased with increasing corona discharge time within the test time. The active sizes on the film surface increased with the corona discharge time, which initiated graft copolymerization of HEMA on the LDPE surface in the reaction solution.

Figure 2 shows that the degree of grafting increased with increasing corona discharge voltage up to 17 kV in a constant treatment time of 72 s. A further increase of the discharge voltage caused the grafting degree to decrease. The active sites on the film surface increased with the corona discharge voltage, which initiated graft copolymerization of HEMA on the LDPE surface in the reaction solution. However, a corona discharge voltage that was too high caused surface degra-

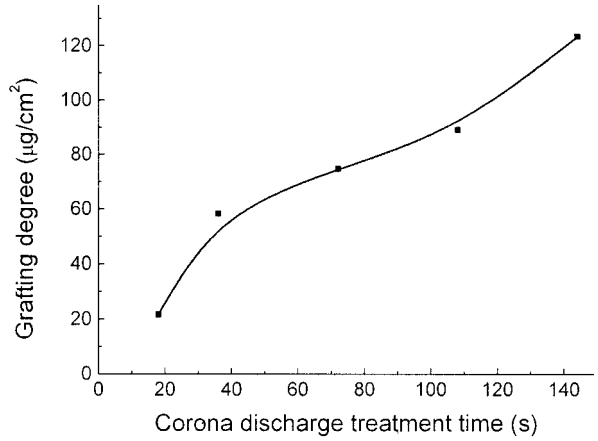

Figure 1 The effect of the corona discharge treatment time on the grafting degree of HEMA onto LDPE films (15-kV corona discharge voltage, 2.0-h copolymerization time, 50°C copolymerization temperature, and 5% HEMA concentration).

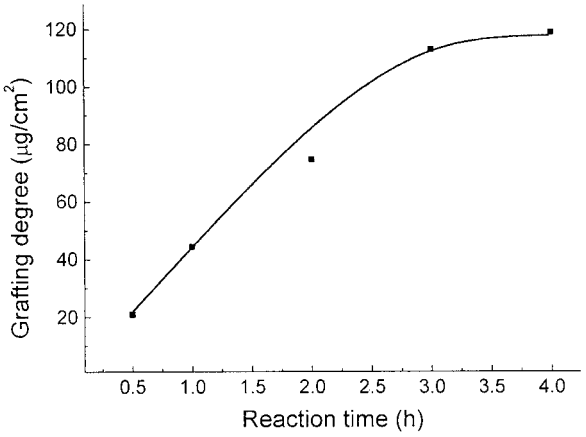

Figure 3 The effect of the reaction time on the grafting degree of HEMA onto LDPE films (72-s corona discharge treatment time, 15-kV corona discharge voltage, 50°C copolymerization temperature, and 5% HEMA concentration).

dation to form low molecular weight oxide, which tended to initiate homopolymerizaion of HEMA in the reaction solution; thus, the grafting degree decreased.

Effect of Reaction Time on Grafting Degree

Figure 3 shows the effect of the reaction time on the grafting of HEMA onto pretreated LDPE films. It is obvious that the grafting degree initially increased with the grafting time, and then tended to level off after about 3 h.

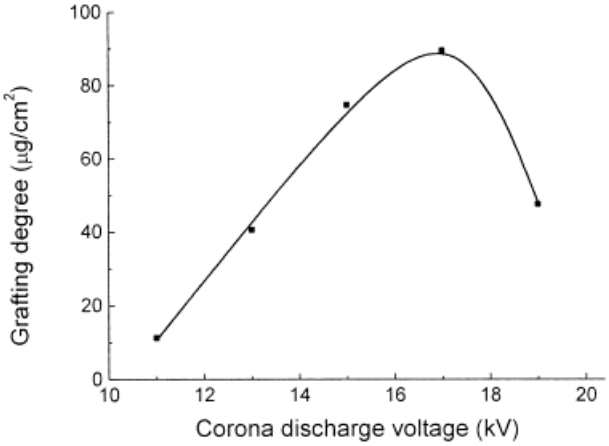

Figure 2 The effect of the corona discharge voltage on the grafting degree of HEMA onto LDPE films (72-s corona discharge treatment time, 2.0-h copolymerization time, 50°C copolymerization temperature, and 5% HEMA concentration).

Effect of Reaction Temperature on Grafting Degree

Figure 4 shows that as the reaction temperature increased the grafting degree increased to a maximum at 60°C and then decreased. The results assumed that an elevated temperature can accelerate the monomer diffusion and the peroxides produced by corona discharge decompose into radicals. As a consequence, a higher grafting degree was achieved. However, a temperature that is too high can cause the homopolymerization of HEMA in the reaction solution, which decreases the grafting degree.

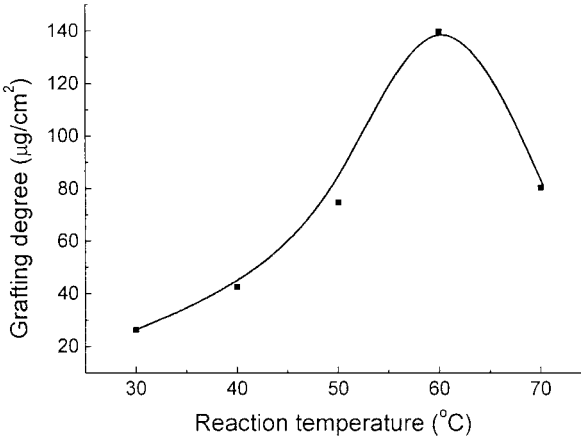

Figure 4 The effect of the reaction temperature on the grafting degree of HEMA onto LDPE films (72-s corona discharge treatment time, 15-kV corona discharge voltage, 2.0-h copolymerization time, and 5% HEMA concentration).

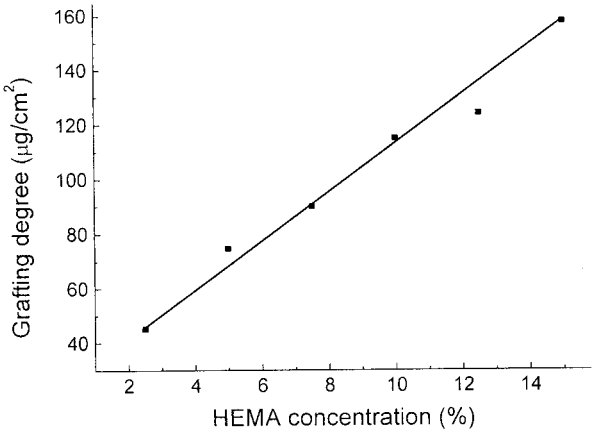

Figure 5 The effect of the HEMA concentration on the grafting degree of HEMA onto LDPE films (72-s corona discharge treatment time, 15-kV corona discharge voltage, 2.0-h copolymerization time, and 50°C copolymerization temperature).

Effect of Monomer Concentration on Grafting Degree

Figure 5 shows that the grafting degree monotonously increased with the monomer concentration. However, the observed result showed that the monomer tended to form HEMA homopolymer during the copolymerization reaction when the concentration was over 20%.

Effect of Inhibitor Concentration on Grafting Degree

It is known that inhibitors are usually added during grafting to minimize homopolymer formation.

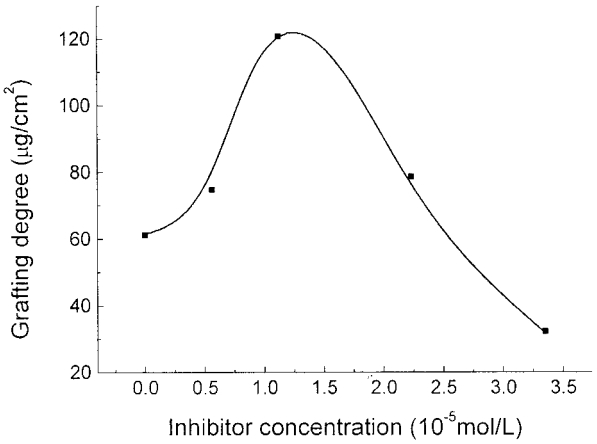

Figure 6 The effect of the inhibitor concentration on the grafting degree of HEMA onto LDPE films (72-s corona discharge treatment time, 15-kV corona discharge voltage, 50°C copolymerization temperature, and 5% HEMA concentration).

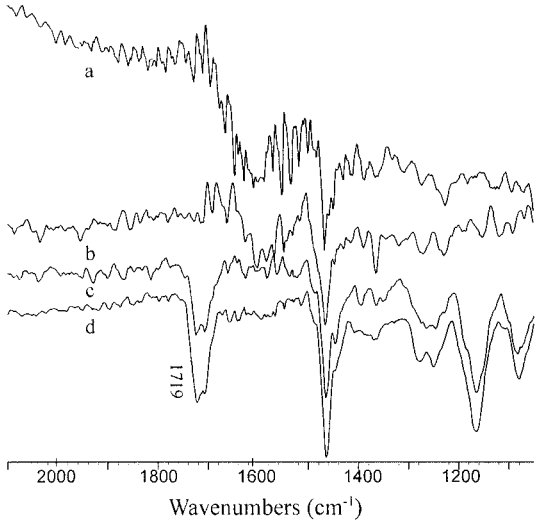

Figure 7 ATR-IR spectra of LDPE films with copolymerization times of (a) 0, (b) 1.0, (c) 2.0, and (d) 3.0 h (72-s corona discharge treatment time, 15-kV corona discharge voltage, 50°C copolymerization temperature, and 5% HEMA concentration).

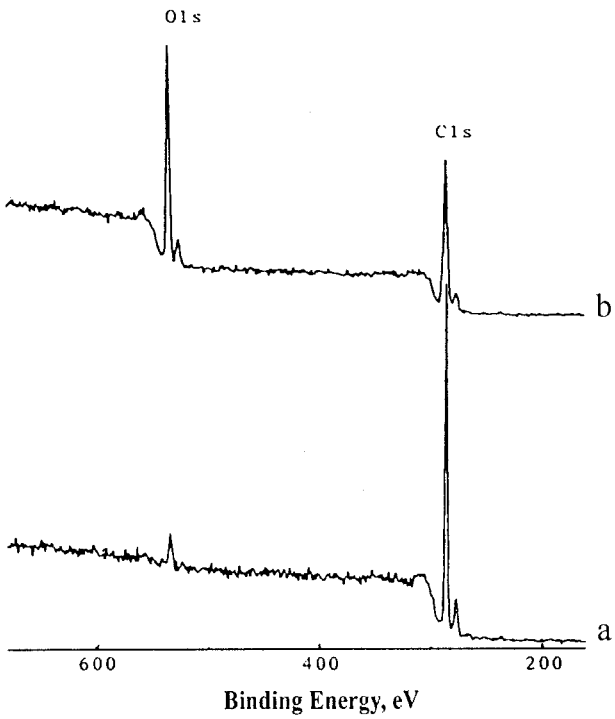

Figure 8 ESCA spectra of LDPE films with copolymerization times of (a) 0 and (b) 2.0 h (72-s corona discharge treatment time, 15-kV corona discharge voltage, 50°C copolymerization temperature, and 5% HEMA concentration).

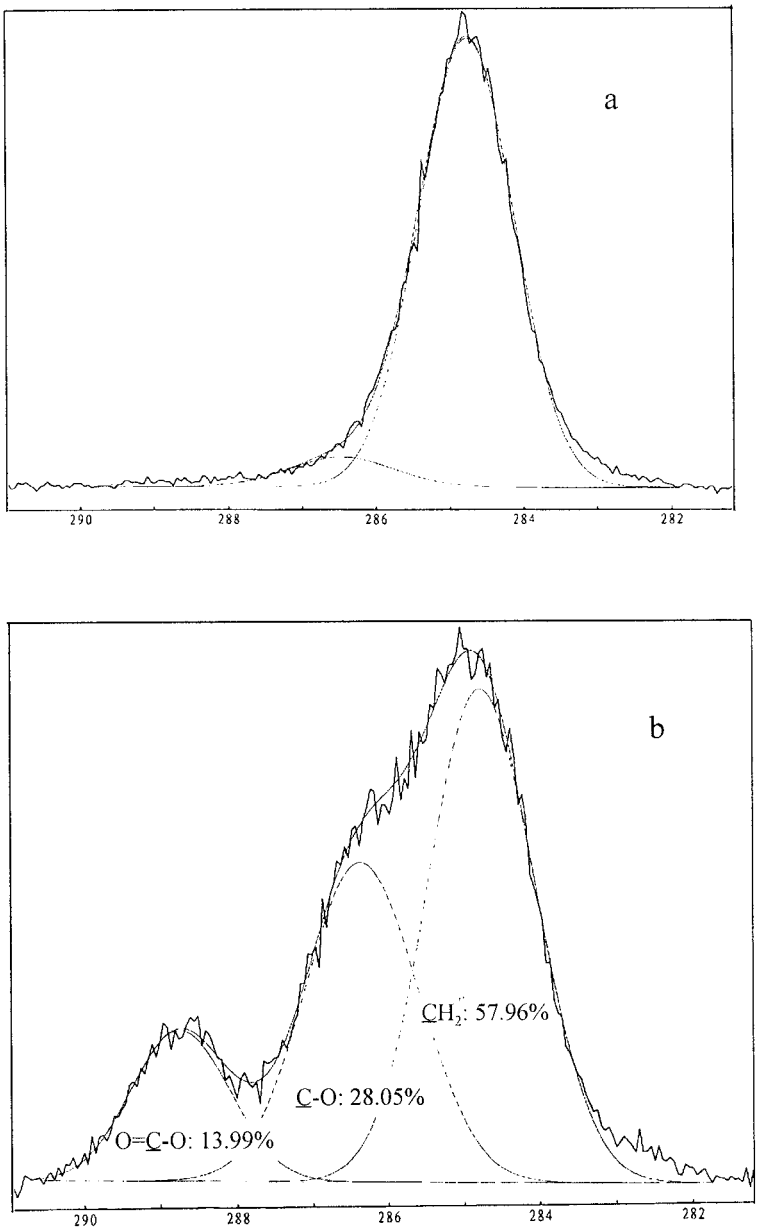

Figure 9 ESCA C_{1s} core-level spectra of ungrafted and HEMA-grafted LDPE films with copolymerization times of (a) 0 and (b) 2.0 h (72-s corona discharge treatment time, 15-kV corona discharge voltage, 50°C copolymerization temperature, and 5% HEMA concentration).

As shown in Figure 6, the degree of grafting increased to a maximum with the increasing concentration of the Mohr's salt and then decreased. We observed that the homopolymer formation monotonously decreased with the increasing concentration of the Mohr's salt. However, at a high Mohr's salt concentration the copolymerization was also inhibited, leading to a lower grafting degree.

ATR-IR Analysis

Figure 7 shows the ATR-IR spectra of the starting LDPE film (Fig. 7, spectrum a) and the HEMA-grafted films (Fig. 7, spectra b–d). The grafted LDPE films showed strong bands at 1791 cm^{-1} that were due to the stretching vibration of $>$C═O in the ester groups. The band strength increased with the reaction time. This was evi-

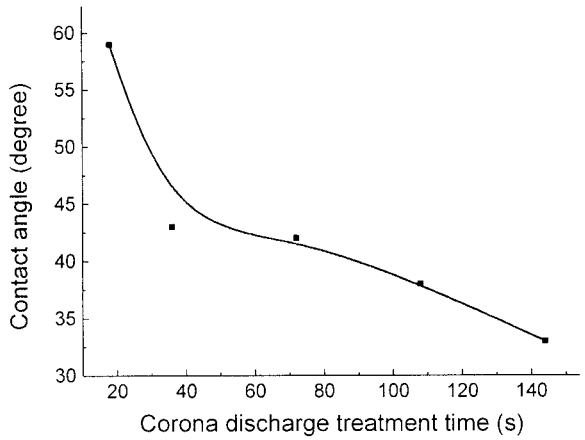

Figure 10 The effect of the corona discharge treatment time on the contact angle of HEMA-grafted LDPE films with water (15-kV corona discharge voltage, 2.0-h copolymerization time, 50°C copolymerization temperature, and 5% HEMA concentration).

dence that the film surface was covered with grafted HEMA.

ESCA Spectra

The ESCA spectra of the starting LDPE film and the HEMA-grafted LDPE films are shown in Figure 8. There was one small O_{1s} peak at about 531 eV in the spectrum of the starting film (Fig. 8, spectrum a), which came from the oxidation during storage and the additives. There was clearly a strong peak at 531 eV assigned to O_{1s} in the spectrum of the grafted film (Fig. 8, spectrum b). Figure 9 compares C_{1s} core level scan spectra of the starting and HEMA-grafted films. The starting film surface had a strong alkyl carbon (—C—C—) peak at ~285.0 eV and a small —C—O— peak at ~286.6 eV. The HEMA-grafted surface showed two strong peaks at higher binding energies. The peaks of the high binding energy region for the grafted surface corresponded to carbon atoms with a single bond to oxygen at ~286.6 eV (—C—O— from hydroxyl groups and ester groups) and carbon atoms with three bonds to oxygen at ~289.1 eV (O═C—O— from ester groups). The contents of C atoms in —C—O— groups and O═C—O groups are 28.05% and 13.99%, respectively, corresponding to the chemical composition of HEMA [(H_2C═C(CH_3)—C(═O)—O—CH_2—CH_2OH)] and PHEMA. The ESCA spectra also demonstrated that the film surface was covered with grafted HEMA.

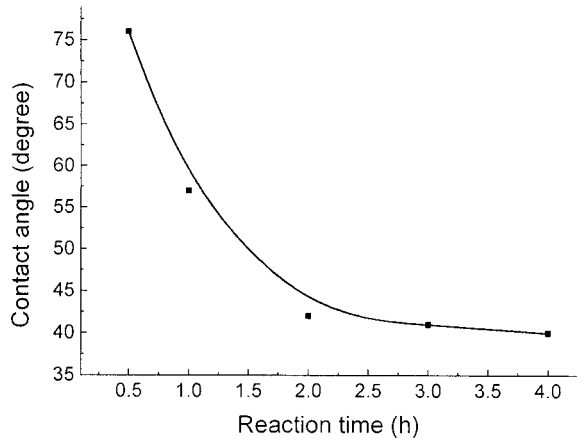

Figure 11 The effect of the reaction time on the contact angle of HEMA-grafted LDPE films with water (72-s corona discharge treatment time, 15-kV corona discharge voltage, 50°C copolymerization temperature, and 5% HEMA concentration).

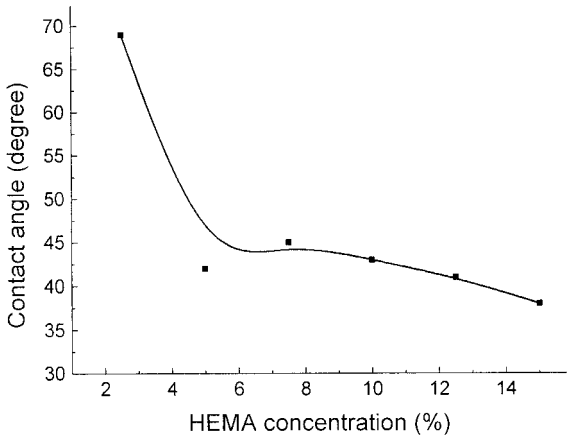

Figure 12 The effect of the HEMA concentration on the contact angle of HEMA-grafted LDPE films with water (72-s corona discharge treatment time, 15-kV corona discharge voltage, 2.0-h copolymerization time, and 50°C copolymerization temperature).

Contact Angle

Figures 10–12 show that, when the corona discharge time, the reaction time, and the monomer concentration increased (i.e., with the increase of the degree of grafting), the contact angles of the grafted LDPE films with water decreased. The hydrophilicity of the LDPE film can be remarkably improved by grafting with HEMA through corona discharge.

CONCLUSIONS

The chemically inert surface of LDPE film can be graft copolymerized with HEMA through corona

discharge. In this way, the grafting degree is increased to a maximum and then decreased by varying the corona discharge voltage, reaction temperature, and inhibitor concentration in the reaction solution. As the corona discharge time, reaction time, and HEMA concentration in the reaction solution are increased, the grafting degree increases. Under the conditions of a 5 vol % HEMA concentration, 50°C copolymerization temperature, and 2.0-h reaction time, the grafting degree of the LDPE film after being treated for 72 s by a 15-kV voltage reaches a high value of 158.0 $\mu g/cm^2$. Some characteristic peaks of the grafted LDPE become visible at 1719 cm^{-1} on the ATR-IR spectra ($>$ C═O in ester groups) and at 531 eV in the ESCA spectra (O_{1s}). The hydrophilicity of the grafted LDPE film is remarkably improved compared to that of the ungrafted LDPE film.

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