Surface Modification of Polyethylene Terephthalate Film by CO_2 Laser-Induced Graft Copolymerization of Acrylamide

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ABSTRACT: Graft copolymerization of acrylamide onto polyethylene terephthalate (PET) using a CO_2 pulsed laser was performed to improve water wettability. After laser irradiation in air, the films were placed in the aqueous solution of monomer and then heated to decompose peroxides formed onto the irradiated PET film. Peroxide density was determined spectrophotometrically by means of the iodide method. The grafted PET surfaces were characterized by attenuated total reflectance infrared spectroscopy, scanning electron microscopy, and contact angle measurements. The electron micrographs showed that the grafting changed the surface morphology of the PET film, which is consistent with the infrared spectra of the grafted films. To evaluate the surface hydrophilicity, water drop contact angle was determined. The contact angle decreased as a result of graft polymerization. It was also found that the hydrophilicity is related to the surface morphology and grafting level. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 76: 401–407, 2000

Key words: CO_2 laser; graft copolymerization; surface modification; polyethylene terephthalate; acrylamide

INTRODUCTION

The increasing demand for providing surface functional properties such as adhesivity, wettability, or biocompatibility has led to the development of numerous methods of polymer surface modifications with minimum deterioration of the bulk properties. Radiation-induced graft copolymerization is a well-known method for modification of the chemical and physical properties of polymer materials and has attracted considerable attention because it imparts desirable surface properties.[1,2] Among various radiation techniques for grafting, laser irradiation is highly suitable for this purpose. This technique is applicable to surface modification of any polymeric material, even if they are chemically inert like silicone and polytetrafluoroethylene.[3,4] However, very few works have been reported on graft copolymerization with laser[5–8] compared with those of the laser structuring and laser polymerization.[9–14] Although the excimer lasers are mainly used for ablation and surface modification of polymers,[15,16] the use of CO_2 pulsed laser provides certain advantages such as large beam sizes, large pulse energy, the use of nontoxic gases, high laser efficiency, and finally, cheap and easy operation in comparison with the excimer laser.[17]

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Polyethylene terephthalate (PET) has proven to have the most excellent mechanical properties among the commodity polymers, especially when utilized as film and fiber.[18] However, a few problems have been shown to exist with regard to the surface properties, mainly originating from its low water wettability.

In the present study, we are concerned with the graft polymerization of acrylamide onto the PET surface using a CO_2 pulsed laser to improve water wettability. The technique used for graft polymerization is preirradiation of the films in the presence of air without using a sensitizer. The changes in the surface properties of PET attributed to graft polymerization of acrylamide will be described also.

EXPERIMENTAL

Materials

The substrate used was PET film (Dupont Mylar; thickness, 70 μm). The surfaces of all samples were ultrasonically cleaned with ethanol and dried at 40°C in a vacuum oven before irradiation. The acrylamide (AAm) monomer from Aldrich was recrystallized from an aqueous solution. Other reagents of extra-pure grade were used without further purification.

Laser Treatment

Laser-induced graft copolymerization was performed by preirradiation technique. The film samples were irradiated using a line tunable pulsed transverse excitation atmospheric (TEA) CO_2 laser (Lumonics 103-2) which provides laser beams of wavelengths from 9–11 μm and a pulse fluence between 0.4–2.0 J/cm^2. The laser was operated at 0.5 Hz pulse repetition frequency to avoid cumulative heating of the film. The strips of PET film were placed on a belt of a special step motor and the irradiation was carried out in air with desired pulses at a wavelength of 9.25 μm (1081 cm^{-1}), which is a relatively strongly absorbed line in PET. The film strips were moved for irradiation to the other area of the film by the step motor.

Graft Polymerization

After irradiation with the CO_2 pulsed laser, the PET samples were immersed in the aqueous solution of monomer with various concentrations and heated under nitrogen atmosphere at 60°C for 4 h to decompose the polymeric peroxides thermally. To minimize homopolymerization, ferrous ammonium sulfate (Mohr's salt) was added to the monomer solution. The AAm homopolymer formed was removed from the grafted film by extraction with distilled water at 70°C for >15 h under continuous stirring. The density of PAAm grafted was determined gravimetrically using the following equation:

$$\text{Graft density } (\mu\text{g/cm}^2) = W_g - W_o/S$$

where W_g and W_o represent the weights of the grafted and ungrafted film, respectively, and S is the original surface area of the samples.

Peroxide Determination

The concentration of peroxides generated onto the irradiated PET film surfaces was determined spectrophotometrically by means of the iodide method.[19] Peroxides on the surface of the PET film were quantitatively reacted with sodium iodide in a mixture of isopropyl alcohol and benzene (6:1 v/v) containing a trace of ferric chloride (1 ppm) at 60°C for 10 min to obtain iodine. From the absorption intensity (at 360 nm) of the iodine as triiodide anion in the mixture solution, the concentration of peroxide on the PET surface was determined. The absorption intensity was measured using a Pharmacia Biotech spectrophotometer (model Novaspec II).

Infrared Spectroscopy

To characterize the surface of modified samples, attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) with a ZnSe prism and an incident angle of 45° was performed using an FTIR instrument (BOMEM Model BM-102). Spectra were collected as 50 scans at 2 wave number resolution.

Scanning Electron Microscopy (SEM)

The surface morphology was observed with an SEM (Philips model XL30) after sputter gold coating of the samples.

Contact Angle Measurement

Static contact angles were measured using the sessile drop method by contact angle measurement equipment (Krüss G10). All water drop contact angles are the minimum value of five measurements on different parts of the film. Dynamic contact angle analysis was performed with the Wilhelmly plate technique using a tensiometer (Krüss model K12).

Staining

The cross section of the grafted film was stained with 2.5% eosin in a 3:1 water methanol solution for 48 h. After staining, samples were washed in distilled water for 2 h to remove excess stain, and then dried before optical microscope examination.

RESULTS AND DISCUSSION

Surface Oxidation

Laser irradiation forms various radicals on the PET film surface.[20] The formed radicals, when contacted with air, are rapidly modified into corresponding peroxides. The concentration of peroxides formed in the surface layer of irradiated PET film is shown as a function of laser pulses in Figure 1. The peroxide density was determined by means of the iodide method. As can be seen in Figure 1, peroxides are formed increasingly with increases in the laser pulses. A maximum concentration of 1.8×10^{-8} mol/cm^2 was obtained when laser treatment of PET film was performed with three pulses. Further treatment with laser seems to result in less peroxide formation. It might be attributed to the decomposition of the peroxide groups upon further laser pulses delivered to the PET surface. Although the radiation with higher laser pulses may induce higher radical concentration, simultaneous fragmentation may occur, inducing surface ablation or facilitating the recombination reaction of radicals, both of which are responsible for the reduction of peroxide density. On the other hand, Figure 1 shows that the water drop contact angle with irradiated PET surfaces decreased with increasing the laser pulses. The decrease in contact angle is ascribed to the formation of various kinds of oxidized groups such as hydroxyl and carbonyl functions in addition to hydroperoxides.[21] A similar trend was obtained also for ultraviolet irradiation of PET surface.[22]

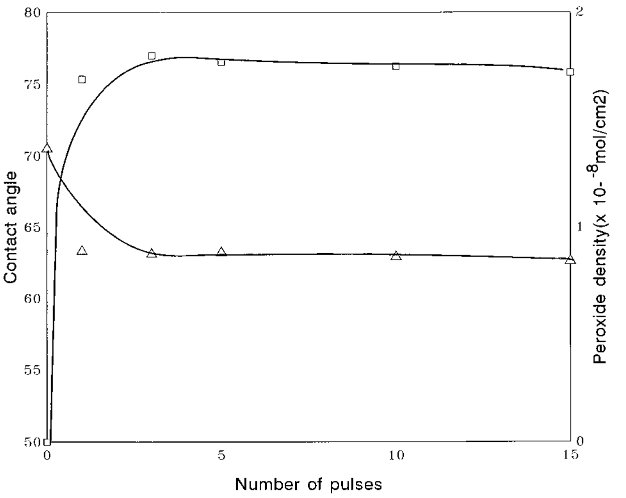


Figure 1 Variation of peroxide density and contact angle as a function of pulse number: (□) peroxide density (△) contact angle.

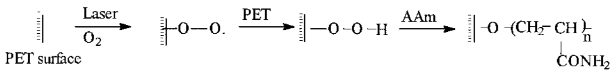


Figure 2 Schematic illustration of laser-induced graft polymerization.

Graft Polymerization

Laser treatment of PET film was first performed to introduce peroxides on the PET surface. Then the peroxidized film was immersed in aqueous monomer solution and heated to decompose polymer peroxides, which are capable of initiating the monomer polymerization. Laser-induced graft polymerization of AAm onto the PET was performed according to the scheme briefly illustrated in Figure 2.

Figure 3 shows IR spectra of the virgin and AAm grafted PET film. The film was irradiated using CO_2 pulsed laser and followed by graft polymerization of AAm at 60°C for 4 h in the presence of Mohr's salt to give a graft density of 230 μg/cm^2. The absorption band at 1717 cm^{-1} which corresponds to the C=O stretching vibration in PET almost disappeared under formation of amide bond in the grafted films. The spectrum of AAm grafted PET revealed the characteristic bands of primary amide at 1650 and 1601 cm^{-1} corresponding to C=O stretching and N—H bending vibrations, respectively. This finding gives evidence of graft polymerization of AAm onto the PET film surface.

Figure 4 shows an optical microscopic photograph of the cross section of the AAm grafted

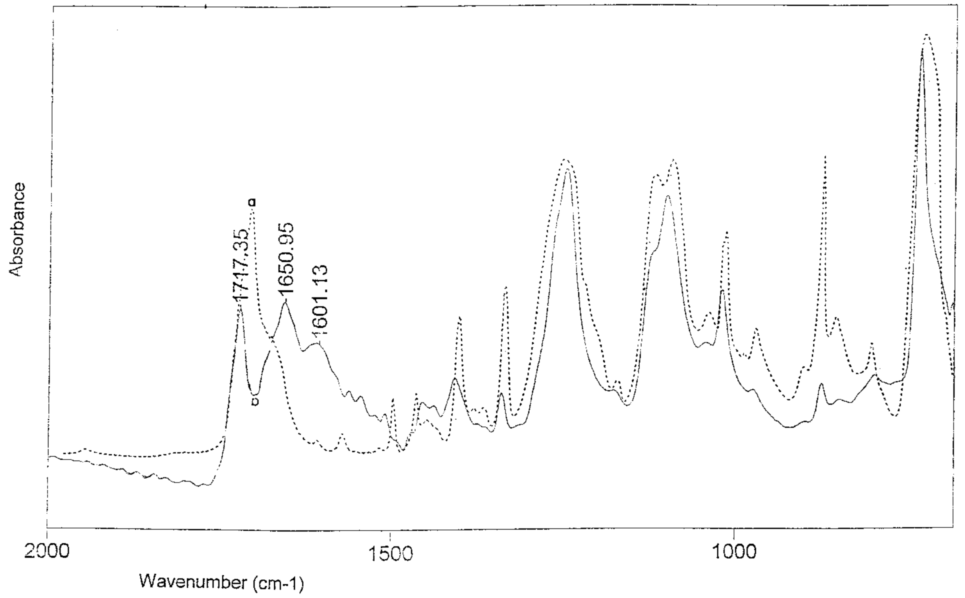


Figure 3 ATR-FTIR spectra of (a) the original PET film and (b) AAm grafted PET film (graft density 230 μg/cm^2).

PET film with a graft density of 359 μg/cm^2 after staining with eosin. As shown in the photograph, location of the grafted layer is restricted to the film surface region. The thickness of the grafted layer is estimated from this photograph to be approximately 15 μm. There are at least two reasons for the graft layer to be limited to the film surface region. One is the limited polymer radical formation owing to low penetration of the laser beam, and the other is the limited monomer penetration along the direction of the film thickness.

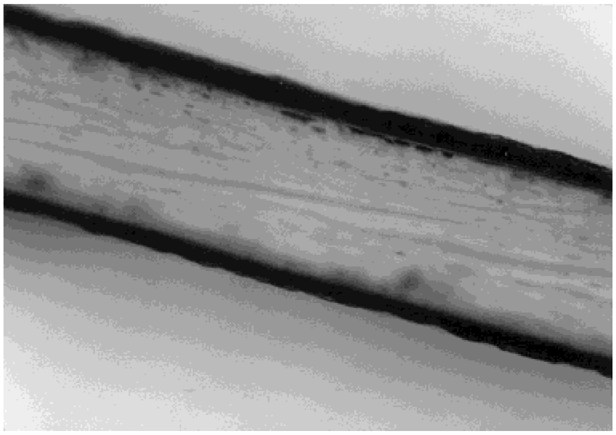
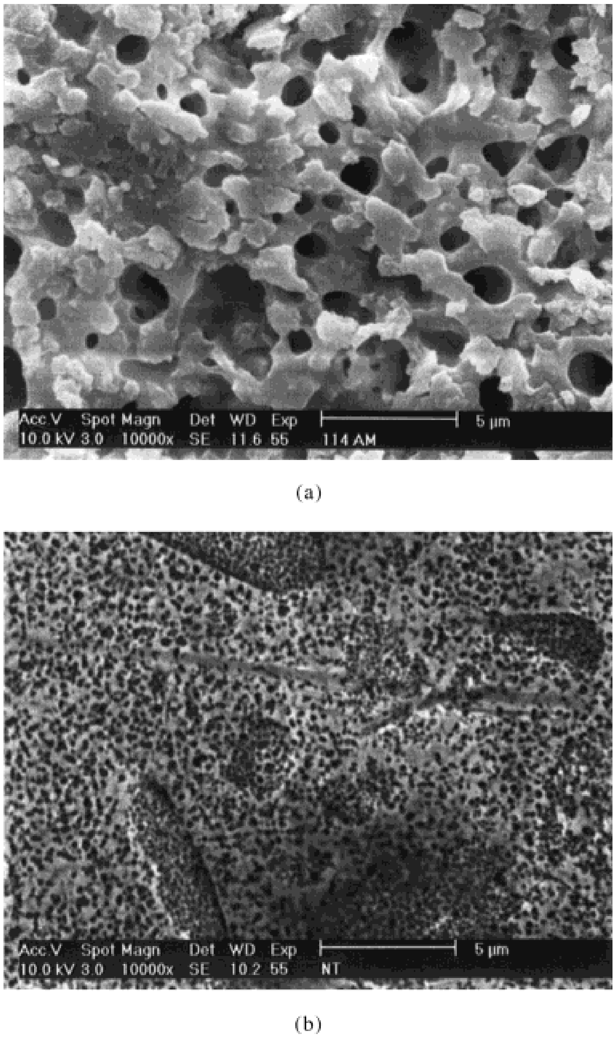


Figure 4 Optical microscopic photograph of the stained cross section of an AAm grafted PET film (graft density 359 μg/cm^2).

Figure 5 shows SEM micrographs of AAm grafted PET and the original PET surfaces. As can be seen, the grafted PET surface is highly rough and porous in comparison with the original PET film surface. Such porosity and roughness is attributed to a high graft density (230 μg/cm^2). Therefore, from the SEM micrographs and increasing the weight of grafted samples, we can conclude that the AAm have been graft polymerized onto the PET film surfaces.

The effect of monomer concentration on the grafting process was studied using various AAm concentrations (wt %) in distilled water in the presence of 0.05 wt % Mohr's salt and a prior CO_2 laser irradiation with 10 pulses. As shown in Figure 6, at low AAm concentrations, grafting begins very slowly and the graft density increases remarkably with increases of the monomer concentration. Therefore, the graft density can be controlled by varying the concentrations of AAm.

Although the CO_2 laser irradiation itself causes a decrease of the contact angle as shown in Figure 7, the surface of PET film became more hydrophilic upon graft polymerization of AAm. As can be seen in Figure 7, the original



(a)

(b)

Figure 5 SEM micrographs of (a) the grafted PET with acrylamide (graft density 230 $\mu g/cm^2$) and (b) the original PET. Original magnifications ×10,000.

PET film has 89.0 and 66.7° as the advancing and the receding contact angle, respectively. The CO_2 laser treatment of the PET films without any graft polymerization decreased the contact angles to 80.4° for advancing and 52.5° for receding. It seems the decrease in contact angle is caused by the formation of polar groups onto the surface of irradiated PET film. The receding contact angle further decreases to 43.6° because of AAm graft polymerization, whereas the advancing contact angle decreases to 72.2° as shown in Figure 8. The decrease in contact angle strongly confirms the graft polymerization of AAm on the PET surface.

As far as the water wettability of the PET film is concerned, excellent wettability with a static contact angle as low as 27.6 will be attained upon CO_2 laser-induced graft polymerization of AAm at approximately 10 wt % aqueous solution. As can be seen in Figure 9, the contact angle of AAm grafted PET samples decreased with increasing the graft density up to a definite level and then increased, probably because of a thick hydrated layer existing at the interface between the grafted surface and water.[23] The same trend is also observed in Figure 8. This could be due to the increase of the steric hindrance effect and the repulsion between the

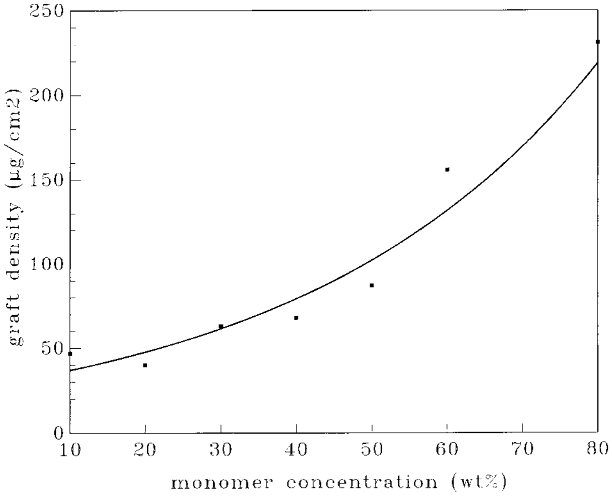


Figure 6 Effect of monomer concentration on the CO_2 laser-induced graft polymerization of AAm onto PET film.

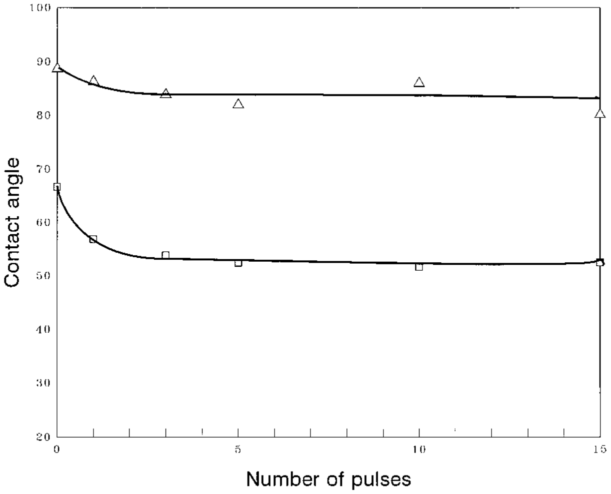


Figure 7 Dependence of the contact angle of irradiated PET film at 9.25 μm. (□) advancing, (△) receding.

condensed grafted hydrophilic groups and water molecules, at high graft degree.[23,24]

CONCLUSIONS

The surface of PET film can be graft polymerized when preirradiated using a CO_2 pulsed laser in air without a sensitizer. The graft polymerization was initiated by peroxide formation upon laser treatment. The maximum peroxide density was 1.8×10^{-8} mol/cm^2 when the PET film was treated with three pulses. The peroxides are produced in the surface region. The concentration of the PAAm grafted on the PET surfaces using CO_2 laser was dependent on the concentration of monomer and increased remarkably with increasing the concentration of monomer solution under the same polymerization conditions. The contact angle of PET surface decreased with increasing laser pulses without grafting. Subsequently, it reached 27.6° owing to AAm graft polymerization and then somewhat increased with increasing the graft density. ATR-IR spectra showed the characteristic bands of primary amide at 1650 and 1601 cm^{-1}. This is consistent with the SEM micrograph and optical microscopic picture showing surface graft polymerization of AAm onto the PET surface.

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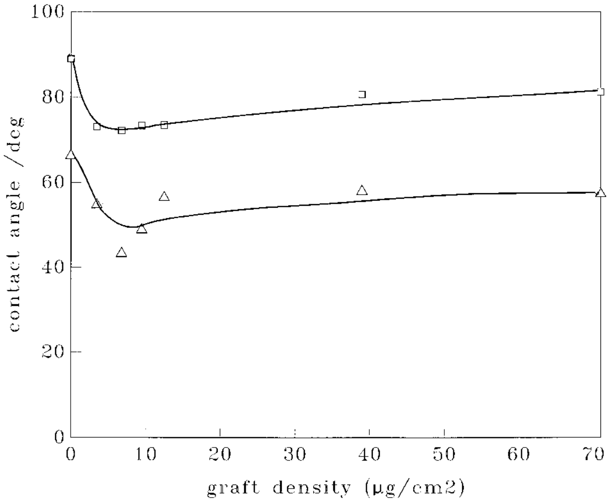

Figure 8 Contact angles value of AAm grafted PET film as a function of graft density: (△) receding (□) advancing.

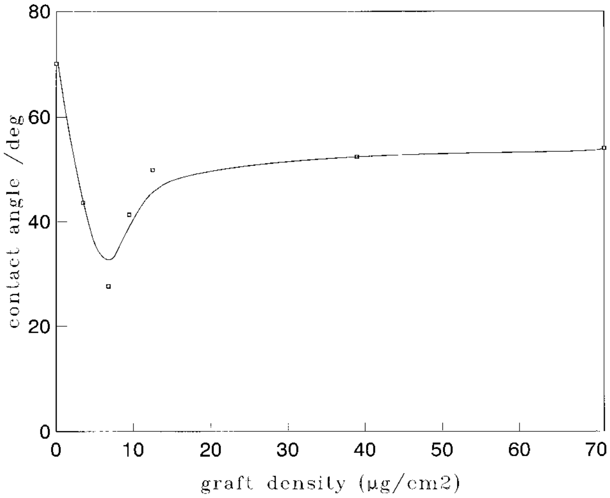

Figure 9 Static contact angle values of AAm grafted PET film as a function of graft density.

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