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ORIGINAL ARTICLE

The effect of hot DMSO treatment on the γ-ray-induced grafting of acrylamide onto PET films

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In the present study, the γ-ray induced grafting of acrylamide (AAm) onto poly(ethylene terephthalate) (PET) films and the resulting changes in properties, including the Hg(II)-capturing functionality, were investigated. No grafting was observed on pristine PET films. Therefore, the films were treated with dimethyl sulfoxide (DMSO) before the γ-ray grafting with the goal of facilitating grafting; some of the samples were pretreated at high temperature (100–160 °C) and showed a considerable increase in the adsorption of AAm from solution. The highest graft yield obtained in the present study was 15.5% for the DMSO specimens pretreated at 140 °C and γ-ray irradiated with a 100-kGy total dose (1-kGy h^{-1} dose rate) in 50 wt% AAm-monomer solutions in the presence of 1 wt% $FeCl_3$ (polymerization inhibitor). In addition to the promotion of the graft yield, the formation of micropores in the DMSO-pretreated specimens was found during the optical microscopy investigations. This structural change is hypothesized to assist the adsorption and γ-ray grafting of AAm to PET. The AAm-grafted PET films prepared using DMSO pretreatment showed high removal efficiency for Hg(II) ions, whereas the pristine PET film showed no uptake, reflecting these changes.
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Keywords: acrylamide; Poly(ethylene terephthalate); radiation grafting; swelling agent

INTRODUCTION

Poly(ethylene terephthalate) (PET) is a thermoplastic polyester with excellent properties, such as mechanical strength, chemical and thermal resistance, and insolubility in the majority of solvents.[1] Owing to these useful properties and the low production costs, PET is extensively used in packaging, fiber and engineering applications. In addition to these conventional applications, PET has been used as a functional material by attaching amino, carboxylic or other reactive groups to its surface to expand its applications to many fields, such as conductive films, biocompatible materials and recovery agents for heavy metals.[1–6] To fabricate such highly functional PET, graft copolymerization is a useful technique that causes the covalent bonding of functional monomers onto the polymer surface while maintaining the properties of parent polymer.[7–12]

In the present study, we attempted to bind acrylamide ($CH_2=CH$-CO-NH_2, AAm), a highly water-soluble vinyl monomer well known as the monomer of polyacrylamide (PAAm), to the surface of PET. PAAm has been widely used as a water-soluble thickener in waste-water treatment, gel electrophoresis, papermaking, ore-processing, tertiary oil recovery and the manufacture of permanent press fabrics. In addition to its usage as the starting material for PAAm, AAm has been known to functionalize the surfaces of many polymers by grafting and as an environmental purifying material.[13–18] A reactive fibrous adsorbent prepared using graft copolymerization of AAm onto PET fibers has been studied for the adsorption of Pb(II) ions from aqueous solution, and the capacity of the adsorbent has been reported to be 39.57 mg g^{-1} of fiber for a graft yield of 15.7%.[13] The graft copolymerization of the AAm monomer onto the non-woven, polyethylene-coated polypropylene fabric was carried out using an irradiation method and the uptake of Cu(II), Co(II) and Ni(II) by the grafted fabrics was evaluated.[14] Ion-exchange membranes have been prepared via the alkaline hydrolysis of radiation-grafted polyethylene-grafted AAm membranes and an excellent binding capacity of the membranes for mercury ions has been reported.[15] AAm has been grafted onto poly(vinyl chloride) using γ-ray irradiation to prepare ion exchange membranes with a strong tendency to remove ^{60}Co from radioactive liquid waste containing both ^{60}Co and ^{137}Cs.[16] AAm-grafted sawdust, converted to anion exchanger via treatment with ethylenediamine followed by HCl, has been used effectively for the removal of Cr(VI) from aqueous solutions.[17] AAm-based chelating resins prepared using *N*,*N*'-methylene-bis-acrylamide as the crosslinking agent has been studied for the adsorption of Fe(III), Fe(II), Ni(II) and Cu(II).[18]

As mentioned in the preceding paragraphs, the grafting of AAm on PET has been performed through various methods to combine the excellent properties of PET and the characteristic functionality of AAm. Most of the earlier studies used chemical methods of initiation for the grafting of AAm[11,13,19,20] or other vinyl

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monomers[4–6,8–10,12,21–25] on PET. Although the chemical method produced AAm-grafted PET with high graft yield, it is known that the chemical initiation method is not free from contamination and also that chemical initiation often brings about problems arising from the local heating of the initiator.[26] Toxic chemical initiators also have the risk of environmental pollution. Therefore, the grafting of AAm through methods other than chemical initiation, such as photografting,[2,27,28] CO_2-laser-induced graft copolymerization[29] or surface-initiated atom transfer radical polymerization[3,30] has also been investigated. However, the low graft yield obtained using these methods is not suitable for the application of grafted products in the field of heavy metal adsorption or other uses described in the preceding paragraph.

From this point of view, the radiation-induced grafting can be the most suitable method for the grafting of AAm on PET films. The major advantages of radiation grafting are as follows. (a) In a radiation technique, no initiator is required; as free radicals are formed on the polymer/monomer backbone, the purity of the processed products may be maintained. (b) The widespread penetration of ionizing radiation through the polymer matrix ensures rapid and uniform formation of radicals to initiate the grafting process throughout the entire polymer matrix. (c) The reactions can be conducted at room temperatures. (d) The radiation technique generates less environmental pollution than chemical methods.[26,31] The radiation-induced graft copolymerization of various vinyl monomers, such as acrylic acid,[32] acrylic acid/acrylonitrile,[33] acrylic acid/*N*-vinyl pyrrolidone,[34] acrylic acid/*N*-isopropyl AAm[35] and *N*-vinyl pyrrolidone[36] onto PET fibers and acrylic acid,[37] styrene,[31] *n*-butyl acrylate[38] and *n*-butyl acrylate/styrene[39] on the PET films demonstrated the high quality of the product generated using radiation-induced grafting for different applications.

However, to the best of the authors' knowledge, no previous studies have reported on the powerful γ-ray-induced graft copolymerization of AAm onto PET films or fibers. This lack of study is due to serious difficulties in grafting of AAm onto PET films:

(1) the strong propensity of AAm to homopolymerize,
(2) the low diffusion of AAm through PET.

Although homopolymerization (condition 1) is known to be suppressed by some transition metal salts,[32] condition 2 has been difficult to overcome because the origins lie in the nature of the PET: the high degree of crystallization and ordering of the amorphous regions retard the AAm monomer permeation into the interior of the PET.

Under these conditions, the authors used γ-ray-induced grafting assisted by *dimethyl sulfoxide* (DMSO) pretreatment in the present study to attain a higher graft yield of AAm on PET while maintaining the product purity. The effects of grafting on the surface structures and on the mercury (Hg(II)) adsorption properties of the AAm-grafted PET were comparatively investigated to examine their relationship. Hg(II) is a well-known toxic material classified as a priority pollutant in spite of being commonly used in many industries;[40] therefore, the Hg(II)-capturing property is important from the view point of environmental protection.

MATERIALS AND METHODS

Materials

Commercial PET films (Teijin DuPont films, G2) with thicknesses of 50 μm were kindly provided by Teijin Co. Ltd (Osaka, Japan). These films were cut into small pieces (2 cm × 2 cm), washed with acetone and dried in a vacuum oven before use. AAm and $FeCl_3$ were procured from Sigma-Aldrich (St Louis, MO, USA). DMSO and KOH were supplied by Wako pure chemical industries Ltd. (Osaka, Japan). Hg(II) acetate (anhydrous, Chameleon Reagent) and Hg(II) standard solution (Merck, Darmstadt, Germany) were used as the source of the adsorbate and for the calibration of the metal concentrations, respectively.

Sorption of AAm solution to the DMSO-pretreated PET films

Dry PET films (weighing W_{pristine}) were soaked in DMSO for 0.5 h at different temperatures (from 60 to 160 °C). After withdrawing the PET films from the DMSO, the excess liquid on the PET surface was removed by blotting between filter papers and the weights of the films (W_{DMSO}) were recorded. Then, the films were kept in the AAm aqueous solution (50 wt%) for 24 h. Moreover, after withdrawing the PET films from the AAm solution, the surface fluid was absorbed using filter paper, and the film weights ($W_{\text{AAm sol}}$) were recorded. Following the previous study,[41] the ratios of the adsorbed DMSO (δW_{DMSO}) and AAm ($\delta W_{\text{AAm sol}}$) to PET were calculated using the equations below:for the DMSO absorption ratio,

$$\delta W_{\text{DMSO}}(\%) = \left(W_{\text{DMSO}} - W_{\text{pristine}}\right)/W_{\text{pristine}} \times 100 \quad (1)$$

for the AAm absorption ratio,

$$\delta W_{\text{AAm sol}}(\%) = \left(W_{\text{AAm sol}} - W_{\text{pristine}}\right)/W_{\text{pristine}} \times 100. \quad (2)$$

Grafting of AAm onto DMSO-pretreated PET films

The DMSO-pretreated PET films were put into several glass bottles containing aqueous AAm solutions with different concentrations (25, 40, 50 and 70 wt%). After 24 h, $FeCl_3$ was added to the bottles at a constant concentration (1 wt%) to minimize homopolymer formation. Then, the bottles with specimens were γ-ray-irradiated for different periods in a 1.0-kGy h^{-1} field (the total doses were 20, 50, 70 or 100 kGy) in the ^{60}Co γ-ray irradiation facility at the Research Reactor Institute, Kyoto University (the grafting reactions were conducted without deoxygenating the AAm aqueous solutions following previous studies[42–44] to keep the process convenient and economical). The PET films were removed from the bottles after the irradiation and, then, soaked in 60 °C distilled water for 24 h to remove the AAm homopolymers from the films. The rinsed films were dried in a 60 °C vacuum oven for 24 h and, finally, the weights of the PET films were measured ($W_{\text{AAm grafted}}$).

The graft yields of the specimens were calculated from the percentage increase in weight ($\delta W_{\text{AAm grafted}}$) as in the previous study[41] using the equation,

$$\delta W_{\text{AAm grafted}}(\%) = \left(W_{\text{AAm grafted}} - W_{\text{pristine}}\right)/W_{\text{pristine}} \times 100. \quad (3)$$

Moreover, following[Ref. 24] the AAm graft densities (D) were derived using the equation,

$$D(\mu\text{g cm}^{-2}) = \left(W_{\text{AAm grafted}} - W_{\text{pristine}}\right)/S \quad (4)$$

where S is the surface area of the pristine PET sample.

Optical micrograph

The optical micrographs of the wet and dry PET films after different pretreatments were observed using an optical microscope (Nikon, Tokyo, Japan, Inverted microscope, Eclipse TE 300) with a magnification of × 40.

X-ray diffraction

X-ray diffraction (XRD) measurements were performed using a SmartLab X-ray diffractometer (Rigaku. ID no: FKOD 12-001). The diffractograms were measured over 2θ in the range of 5–60° using Cu-K_α radiation monochromated with a nickel filter.

Infrared (IR) spectroscopy

The vibrational spectroscopic analyses of the specimens were performed using a Fourier transform infrared (FTIR) spectrophotometer (Jasco FTIR 620) over a wavenumber range from 400 to 4000 cm^{-1} to investigate the interactions between the PET matrix and the grafted AAm and, also, to estimate the amount of AAm grafted to PET.

Scanning electron microscopy

In addition to the optical microscopic observations over a 100-μm range, the minute surface morphologies of the pristine and AAm-grafted PET films were observed using a scanning electron microscope (SEM, Zeiss Ultra55) operated at 10 KeV after carbon coating.

Water uptake measurements

After weighing (W_O), each of the pristine and dried AAm-grafted PET films was kept in a beaker filled with distilled water at 25 °C for 24 h. After this period, the specimens were removed from the containers, and their weights (W_S) were measured immediately after blotting their surfaces. From the measured weights, the water-uptake percentage was calculated using the equation,

$$\text{Water uptake}\,(\%) = (W_S - W_O)/W_O \times 100. \quad (5)$$

Hydrolysis of AAm-grafted PET film and Hg(II) uptake measurements

The films with a 14% graft yield were hydrolyzed by 10% KOH at 60 °C for 1 h. Then, each of the 20-mg hydrolyzed AAm-grafted PET films was soaked in 5 ml of an aqueous 100.0 mg l^{-1}-Hg(II) solution (pH ~ 4.5) for 40 min at room temperature (25 °C) to examine the Hg(II) uptake ability of the hydrolyzed AAm-grafted PET.

Determination of the hydrolysis percentage of AAm. Following the previous study,[45] the hydrolysis percentage of the amide groups to carboxylate groups was calculated from the IR absorbance using the equation,

$$\text{Hydrolysis}\,(\%) = (B - C)/(B - A) \times 100 \quad (6)$$

where A, B and C are the absorbance ratios of (3200 cm^{-1} (assigned to –NH_2 groups of AAm)/3054 cm^{-1} (aromatic –CH stretching vibration of PET)) of the non-grafted, AAm-grafted and hydrolyzed AAm-grafted PET films, respectively.

Determination of the Hg(II) uptake efficiency. Before and after the adsorption, the Hg(II) concentrations of the aqueous solutions were analyzed using an inductively coupled plasma mass spectrometer (ICP-MS, Agilent7700 Series). The Hg(II) uptake efficiencies of the films were calculated using the equation,

$$\text{Uptake efficiency}\,(\%) = (C_1 - C_2)/C_1 \times 100 \quad (7)$$

where C_1 and C_2 are the Hg(II) concentrations (mg l^{-1}) before and after the adsorption, respectively.

RESULTS

DMSO-assisted grafting of AAm onto PET films by γ-ray irradiation

The pristine PET films showed no AAm-grafting, despite the fact that those films had been γ-ray-irradiated in the AAm solution in the usual manner. In this situation, the authors attempted to investigate the AAm grafting onto DMSO-pretreated PET films under various conditions: at several DMSO pretreatment temperatures, in the presence and absence of a polymerization inhibitor, at several AAm-monomer concentrations and at several γ-ray total doses and dose rates.

Effect of the DMSO pretreatment temperature on the grafting of AAm. Before the AAm-solution adsorption, the PET films were pretreated with DMSO at temperatures over the range 60–160 °C. It was found that the specimens pretreated with DMSO over the temperature range 60–140 °C showed increases in both the DMSO and AAm adsorption (Figure 1), whereas the samples pretreated at 160 °C showed lower AAm adsorption than that at 140 °C despite the greater DMSO adsorption. It should also be noted that no significant weight loss was observed for the DMSO-pretreated PET films over the range 60–140 °C.

The γ-ray grafting of AAm was performed on the DMSO-pretreated PET films at 100, 140 and 160 °C, which showed significant amounts of DMSO and AAm adsorption. The graft yield was observed to increase as the DMSO-pretreatment temperature increased up to 140 °C (Figure 1): 5% at 100 °C and 14% at 140 °C and decreased to 8% at 160 °C.

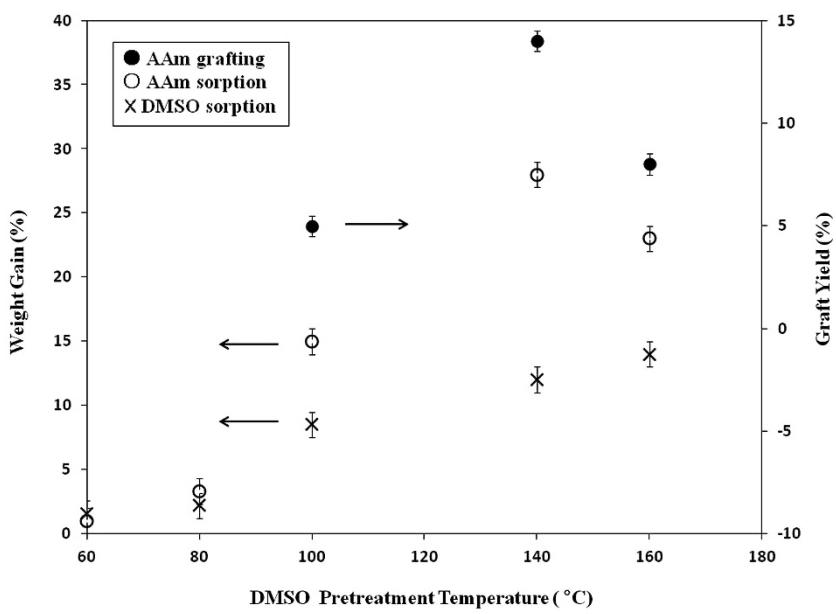

Figure 1 Weight gain (× after soaking in DMSO for 0.5 h, ○ after soaking in 50 wt% AAm solution for 24 h) and graft yield (● after grafting at 50 wt% AAm monomer concentration, with a 50-kGy dose at a dose rate of 1 kGy h^{-1}, and at 1 wt% $FeCl_3$) as a function of the DMSO pretreatment temperature.

On the basis of these results for graft yields, the subsequent investigations were performed on the PET films pretreated with DMSO at 140 °C.

Effect of $FeCl_3$ on AAm grafting. To examine the effect of a polymerization inhibitor ($FeCl_3$), the AAm graft yields derived after γ-ray-grafting process in the presence and absence of $FeCl_3$ were compared while keeping the other conditions the same (140 °C DMSO-pretreated PET films, grafting at 50 wt% AAm concentration and 50-kGy radiation dose at a 1-kGy h^{-1} dose rate). The obtained graft yield was 11% without $FeCl_3$, which increased to 14% in the presence of $FeCl_3$. It was also observed that the AAm solution surrounding the AAm-grafted PET film in the absence of $FeCl_3$ formed a hard gel of homopolymerized PAAms during irradiation, whereas the AAm solution formed a soft gel (for high AAm concentration) or remained liquid (for low AAm concentration) in presence of $FeCl_3$.

Effect of the monomer concentration on the grafting of AAm. To investigate the dependence of the graft yields on the AAm-monomer concentration, the yields obtained after grafting with different monomer concentrations from 25 to 50 wt% were investigated with the other conditions kept the same (140 °C DMSO-pretreated PET films, γ-ray grafting with a 50-kGy radiation dose at a 1-kGy h^{-1} dose rate in the presence of 1 wt% $FeCl_3$).

The graft yield increased as the monomer concentration increased from 25 to 50 wt% (Figure 2): 8% graft yield at 25 wt% AAm and 14% for 50 wt%, whereas the graft yield slightly decreased at 70 wt% of monomer (Figure 2).

Effect of the dose and dose rate on the grafting of AAm. To study the total γ-ray dose dependence of the graft yield, the graft yields acquired using total doses that varied from 20 to 100 kGy were obtained under the same conditions (140 °C DMSO-pretreated PET films, γ-ray grafting at 50 wt% of AAm and a 1-kGy h^{-1} dose rate in the presence of 1 wt% $FeCl_3$; Figure 3).

The graft yield increased as the total dose increased, whereas the rate of increase decreased as the total dose increased (Figure 3).

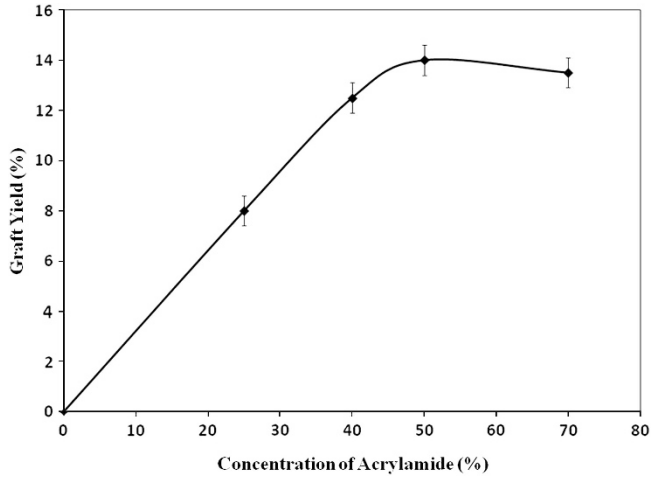

Figure 2 The AAm monomer concentration dependence of the AAm-graft yield onto the 140 °C DMSO-pretreated PET films while maintaining the other grafting conditions: a 50-kGy total dose, a 1-kGy h^{-1} dose rate and the presence of 1 wt% $FeCl_3$.

In addition to the total γ-ray dose dependence, the graft yields obtained using two dose rates, 1.02 and 2.40 kGy h^{-1}, were investigated while keeping the other conditions same (140 °C DMSO-pretreated PET films, γ-ray grafting at 50 wt% of AAm and a 50-kGy total dose in the presence of 1 wt% $FeCl_3$); however, the graft yield was found to be almost unchanged.

The highest graft yield obtained was 15.5% for the 140 °C DMSO-pretreated PET films under the following grafting conditions: 50 wt% AAm monomer, a 100-kGy total dose at a rate of 1 kGy h^{-1}, and 1 wt% $FeCl_3$.

In Table 1, the γ-ray graft yield and/or graft density derived in the present study is compared with those obtained from some other methods.[3,28–30]

Optical micrographs of PET films

The optical micrographs of the surface of the pristine PET films after the different pretreatments are shown in Figure 4. More pores are observed in the micrograph of wet DMSO-pretreated films (Figure 4b) than the pristine PET films (Figure 4a), indicating the formation of micropores on the PET surface by the DMSO pretreatment. The pore structure of the DMSO-pretreated film changed after soaking in an AAm solution, which became more significant in the

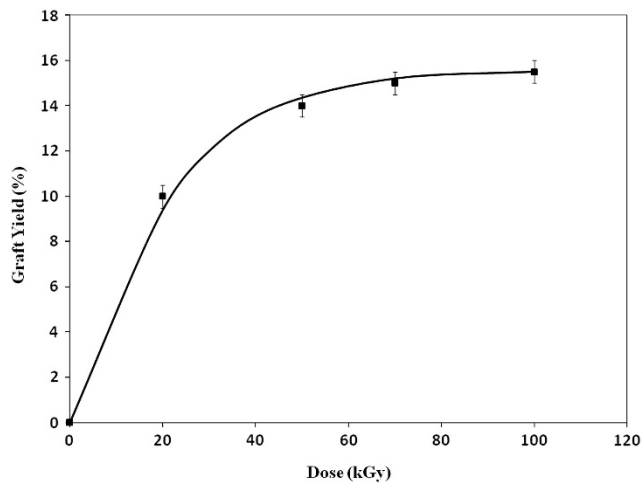

Figure 3 The total γ-ray dose dependence of the AAm-graft yield on the 140 °C DMSO-pretreated PET films with all other grafting conditions held constant: 50 wt% AAm, a 1-kGy h^{-1} dose rate and the presence of 1 wt% $FeCl_3$.

Table 1 A comparison of graft yield and/or graft density derived in the present study (γ-ray) with the results obtained using other methods

Grafting method	*Graft yield (%)*	*Graft density ($\mu g\,cm^{-2}$)*
UV radiation[24]	0.3[a]	—
UV radiation[22]	—	10[a]
CO_2 laser[23]	—	359[a]
SI-ATRP[24]	1.37[a]	—
SI-ATRP[3]	2.52[a]	—
γ-ray irradiation (present study)	15.5 (±0.5)	1125 (±25)

Abbreviations: SI-ATRP, surface-initiated atom transfer radical polymerization; UV, ultraviolet.
[a]The values are described as they appear in the references.

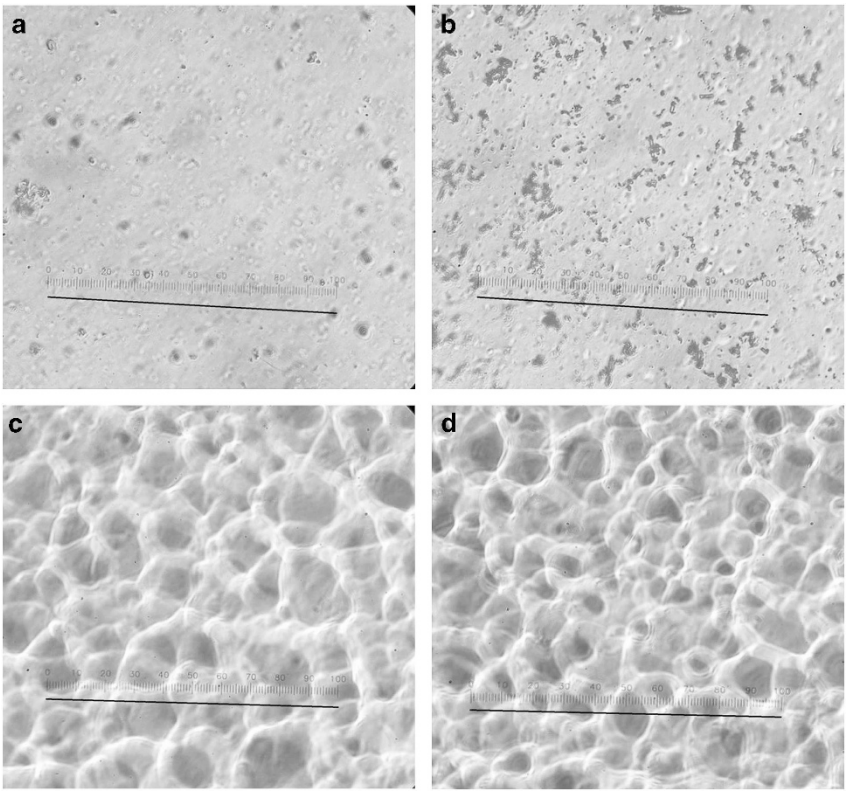

Figure 4 Optical micrographs of (**a**) the pristine PET film, (**b**) the DMSO-pretreated (at 140 °C) wet film, (**c**) the wet AAm-solution-soaked DMSO-pretreated film (DMSO pretreated at 140 °C and soaked in 50 wt% AAm solution) and (**d**) AAm-grafted PET film (DMSO pretreated at 140 °C and γ-ray irradiated with a 50-kGy dose at a 1-kGy h^{-1} dose rate in the presence of 1 wt% $FeCl_3$ after soaking in 50 wt% AAm solution) (The black line inside each figure represents 100 mm). A full color version of this figure is available at *Polymer Journal* online.

wet AAm-solution-soaked PET film (Figure 4c). The surface structure of the AAm-grafted film resembled that of the wet AAm-solution-soaked DMSO-pretreated film (Figure 4d).

The optical micrographs of the PET films were also studied to investigate the effect of the DMSO-pretreatment temperatures on the surface structure. Figure 5 shows the optical micrographs of the PET films after DMSO pretreatment at 100 °C (Figure 5a), 140 °C (Figure 5c) and 160 °C (Figure 5e) as well as the samples soaked in AAm solution after the DMSO treatment (Figures 5b, d and f), respectively.

As shown in Figure 5, the number of pores and their diameters increased with increasing pretreatment temperature, which promoted monomer diffusion into the polymer matrix.

XRD analysis of PET films

XRD analyses were performed on the pristine PET film, the DMSO-pretreated wet PET film (pretreated at 140 °C), the AAm-soaked (50 wt% AAm solution) wet film (after DMSO pretreatment at 140 °C) and the AAm-grafted PET film (DMSO-pretreated at 140 °C and γ-ray-irradiated with a 50-kGy dose at a 1-kGy h^{-1} dose rate in the presence of 1 wt% $FeCl_3$ after soaking in 50 wt% AAm solution). The investigation showed that the amount of the crystalline phase in the PET film increased significantly after the treatment with DMSO (Figure 6b). The AAm-soaked wet film showed little increase in the degree of crystallinity compared with the DMSO-treated film (Figure 6c). However, the AAm-grafted film showed a significant decrease in the degree of crystallinity compared with the AAm-soaked wet film (Figure 6d).

FTIR spectroscopic analysis of PET films

To investigate the effects of the AAm grafting, the IR spectra of pristine PET and the AAm-grafted PET films were investigated and compared over the wavenumber ranges from 3800 to 2400 cm^{-1} (Figure 7a) and 1700–1450 cm^{-1} (Figure 7b). The grafted films used for the IR analyses were DMSO-pretreated at 140 °C and immersed in 25, 40 and 50 wt% AAm solutions. They were γ-ray-irradiated with a 50-kGy total dose at a 1-kGy h^{-1} dose rate in the presence of 1 wt% $FeCl_3$. New peaks appeared, which indicated grafting onto PET and were assigned to the AAm groups, whereas the other characteristic peaks of PET remained almost unchanged. Specifically, in the spectra of the AAm-grafted PET films, the newly observed peaks at 3350 and 3200 cm^{-1} were assigned to the asymmetric and symmetric stretching vibrations of the $-NH_2$ groups of AAm, respectively. The intensity of the peaks related to the $-NH_2$ groups increased with the graft-yield percentage as shown in Figure 7a; in addition, a new shoulder peak also appeared at 1672 cm^{-1}, which was assigned to the vibration of carbonyl amide (Figure 7b). The characteristic peaks of PET and AAm observed in the present study agreed well with the values reported in the literature.[3,4]

As shown in Figure 7c, the ratio of the IR absorption intensity of the 3200-cm^{-1} peak (assigned to the NH_2 symmetric stretching of AAm) to the 3054-cm^{-1} peak (assigned to the aromatic CH

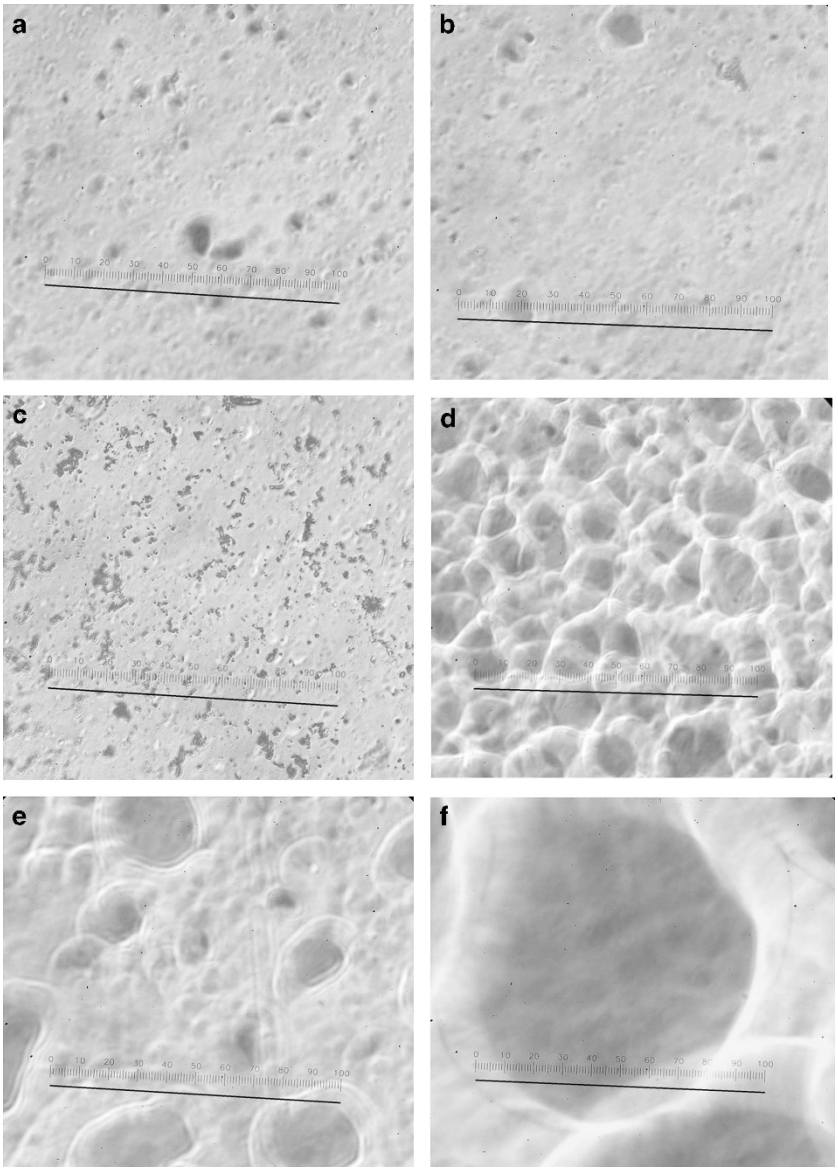

Figure 5 Optical micrographs of the wet PET films with (**a**) DMSO pretreatment at 100 °C, (**b**) AAm sorption (50 wt% AAm solution) after (**a**), (**c**) DMSO pretreatment at 140 °C, (**d**) AAm sorption (50 wt% AAm solution) after (**c**), (**e**) DMSO pretreatment 160 °C, and (**f**) AAm sorption (50 wt% AAm solution) after (**e**) (The black line inside each figure represents 100 mm). A full color version of this figure is available at *Polymer Journal* online.

stretching of PET) showed a linear dependence on the AAm-graft yield (calculated from the gravimetric data).

Scanning electron microscopic analysis of PET films

The surface textures of the pristine PET and AAm-grafted-PET films were observed using SEM to probe the morphological changes after AAm grafting at a smaller scale than the optical microscopy. The grafted films used for the SEM analyses were DMSO-pretreated at 140 °C and γ-ray-irradiated with a 50-kGy dose at a 1-kGy h^{-1} dose rate in the presence of 1 wt% $FeCl_3$ after soaking in a 50 wt% AAm solution. An SEM micrograph of the pristine PET film is shown in Figure 8a and an image of the AAm-grafted PET film and its contrast-enhanced image are shown in Figure 8b and c and, respectively. From the micrographs, it is clear that the AAm grafting caused significant changes in the surface morphologies of the PET films.

Water-uptake measurements

AAm-grafted PET films with different yields (from 0 to 14%) were prepared for experiments that measured the water uptake (after DMSO pretreatment at 100 or 140 °C, immersion in a 25 or 50 wt% AAm solution, and γ-ray irradiation with a 50-kGy total dose at a 1-kGy h^{-1} dose rate in the presence or absence of 1 wt% $FeCl_3$). The water uptake percentages of the AAm-grafted PET films in distilled water are shown in Figure 9. The water uptake percentage simply increased with the graft yield, despite the various preparation conditions.

Hg(II) uptake

The pristine PET film showed no Hg(II) adsorption. To increase the accessibility of the metal ions to the amide groups, the AAm-grafted films (DMSO-pretreated at 140 °C, γ-ray-irradiated with a 50-kGy dose at a 1-kGy h^{-1} dose rate in the presence of 1 wt% $FeCl_3$ after

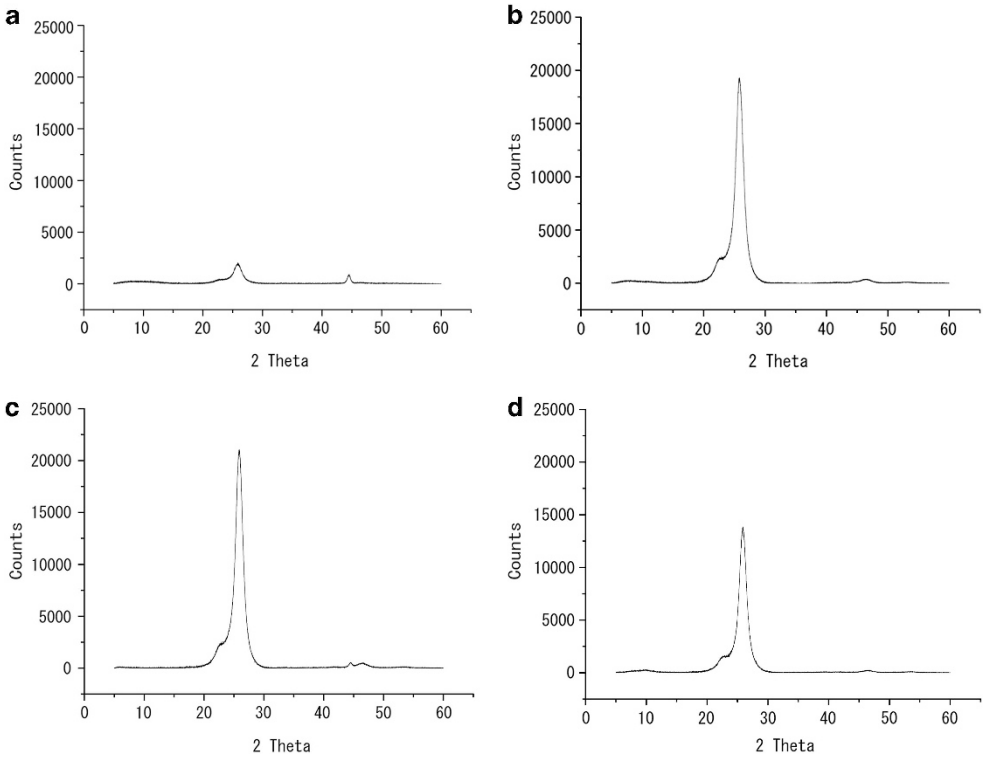

Figure 6 X-ray diffractograms of (**a**) pristine PET film, (**b**) wet PET films with DMSO pretreatment at 140 °C, (**c**) AAm-soaked (50 wt % AAm solution) wet film after DMSO pretreatment at 140 °C, (**d**) AAm-grafted PET film (DMSO-pretreated at 140 °C and γ-ray irradiated with a 50-kGy dose at a 1-kGy h^{-1} dose rate in the presence of 1 wt % $FeCl_3$ after soaking in 50 wt % AAm solution).

soaking in 50 wt% AAm solution) with a 14% graft yield were partially hydrolyzed by KOH (the hydrolysis percentage was ~30%),[15] and the hydrolyzed films were used to examine the Hg(II) adsorption capacity. The hydrolyzed, AAm-grafted PET films showed high removal efficiency for Hg(II) ions (Table 2).

DISCUSSION

In the present study, the authors investigated the γ-ray-induced grafting of AAm onto PET films. During the AAm grafting, the SEM photographs demonstrated changes in the morphology of the PET surface, indicating the emergence of graft chains on its surface. This observation is the most fundamental condition necessary for water and Hg(II) uptake because the water uptake is related to the hydrophilicity of the AAm group, and the Hg(II) uptake is expected to come from the ability of the AAm amide groups to form covalent bonds with Hg(II) ions. In addition to the SEM images, the FTIR spectra of the AAm-grafted PET films also showed peaks that were not observed in the pristine PET film, which were assigned to the symmetric and asymmetric stretching of the AAm NH_2 group. The authors confirmed a linear relationship between the graft yield (obtained using the gravimetric method) and the normalized absorbance at 3200 cm^{-1} (assigned to the NH_2 symmetric stretching of AAm) divided by the absorbance at 3054 cm^{-1} (assigned to the aromatic CH stretching of PET). These features demonstrate the evolution of the AAm graft in the PET matrix. It is very difficult to distinguish between PAAms covalently bonded to PET or firmly entangled in PET; however, by taking into account the water solubility of the monomeric AAm or homopolymerized PAAms, it is expected that almost all of the non-bonded PAAms were partitioned into the water after a 24-h washing of the AAm-grafted PET films at high temperature, as described in Materials and methods section. Actually, the water- and Hg(II)-uptake capacities of the grafted films were considerably larger than those of the pristine PET film, reflecting the emergence of grafted AAm chains in the PET matrix.

During the investigations, the authors found that the graft yield and, correspondingly, the adsorption capabilities were increased considerably by the DMSO treatments of the PET surfaces at high temperatures (100–140 °C) before the grafting procedure. The highest graft yield obtained in the present work was 15.5% under conditions of 140 °C for the DMSO-pretreatment temperature, 50 wt% of the AAm monomer and a 100-kGy total dose (dose rate: 1 kGy h^{-1}) in 1 wt% of $FeCl_3$ solution, which is much higher than that achieved using other non-chemical grafting techniques, such as UV irradiation, a CO_2 laser or the surface-initiated atom transfer radical polymerization method (Table 1). In addition to the increase in the graft yield, the optical micrographs observed after the high-temperature DMSO pretreatments demonstrated the formation of micropores on the PET surfaces. These pores are hypothesized to facilitate the permeation of the AAm monomers into the PET matrix and to assist the subsequent AAm grafting as well as increase the graft-possible surface area. As no significant weight losses were measured in the PET specimens after the DMSO pretreatments, the pore formation is not believed to occur via the dissolution or extraction of PET but due to the dislocation of PET polymer chains caused by the interaction between DMSO and PET. The details on this phenomenon are described in the following paragraphs.

As is often experienced, AAm grafting on the pristine PET film was not successful, which might be due to the high degree of crystallization and ordering of the amorphous regions of PET that retards monomer diffusion. In the present work, the authors attempted to

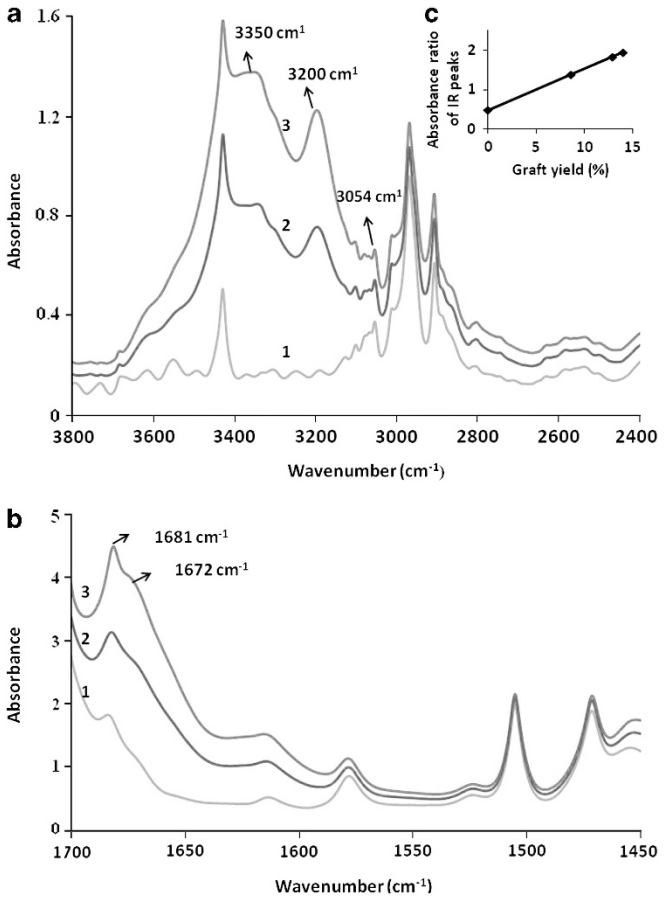

Figure 7 FTIR spectra in the (**a**) higher and (**b**) lower wavenumber regions for (1) pristine PET, (2) the AAm-grafted PET with an 8.6% graft yield, and (3) with a 12.9% graft yield. (**c**) The graft yield dependence of the absorbance ratio of the IR peak at 3200 cm^{-1} to that at 3054 cm^{-1}. A full color version of this figure is available at *Polymer Journal* online.

treat the PET films with DMSO before the AAm-γ-induced grafting, which considerably increased the graft yield. The reasons for adopting DMSO is hypothesized as follows: solvents with similar solubility parameters to PET will swell the PET's surface, which will provide enough energy to disrupt the intermolecular cohesive forces between the polymer chains and will permit chain mobility.[46,47] During this process, surface pore formation can occur, depending on the interaction degree between the solvent and the polymer.[48] PET is an (AB) alternating copolymer, where A is the semirigid aromatic segment -CO-C_6H_4- with 9.5 as the solubility parameter (δ), and B is a flexible aliphatic ester -CO-O-CH_2-CH_2- with $\delta = 12.0$. As the δ of the aliphatic ester portion is very close to that of DMSO ($\delta = 12.9$), the situation is favorable for AAm diffusion into PET and the subsequent grafting onto it.[20]

The pretreatment of the PET film with DMSO at high temperatures may increase the interaction between PET and DMSO and, consequently, this interaction can promote pore formation on the PET surface, which facilitates the diffusion of AAm into the polymer matrix. Although negligible for the pristine PET film, the AAm solution adsorption increased with increasing DMSO pretreatment temperature over the range from 60 to 140 °C and reached a maximum value, 28%, for a film treated at a temperature of 140 °C (Figure 1). Although this trend can be explained by the preceding discussion, there were also different features observed for the specimen pretreated at 160 °C (Figure 1): the AAm solution adsorption decreased, which is most likely due to the extraction of the low-molecular-weight PET and partial dissolution of PET in DMSO at 160 °C.[7,49] The DMSO pretreatment temperature dependence of the AAm-grafting degree agrees with the AAm adsorption, which indicates a close relationship between the AAm absorption amount and the grafting yield.

The effect of the DMSO pretreatment on the structure of the PET film that aids the diffusion of AAm is further revealed via XRD analysis of the films. The XRD results show an increase in the crystalline phase after DMSO treatment. It is hypothesized that DMSO penetration into the PET matrix enhanced the segmental mobility of the macromolecules in the amorphous phase, which made the diffusion of the AAm monomer into the PET matrix easier. As a result of the enhancement of the segmental mobility of the macromolecules in the amorphous phase induced by DMSO, the volume of the crystallites that existed in PET before the DMSO treatment increased.[44] Moreover, the reduction in the degree of crystallinity after AAm grafting might be due to the disordering of the chain structures of the PET matrix caused by the amorphous AAm grafts. Dilution of the crystalline structure of PET after graft co-polymerization is also reported in previous studies.[31,37]

As for the homopolymerization inhibitor, the AAm grafting was investigated in the presence and absence of a homopolymerization inhibitor, $FeCl_3$: the $FeCl_3$ addition enabled a significant reduction in the AAm homopolymerization. The formation of a hard gel of homopolymerized PAAm in the AAm solution surrounding the AAm-grafted PET film in absence of $FeCl_3$ made the separation of the AAm-grafted PET surface from the ungrafted AAm monomers laborious. Conversely, in the presence of $FeCl_3$, the surrounding AAm solution formed a soft gel (for high AAm concentration) or remained liquid (for low AAm concentration) and, consequently, the separation between the AAm-grafted PET surface and the ungrafted AAm monomers became easier. The facile separation of the grafted product from the monomers is an important consideration for practical application of the graft copolymerization method. Owing to the reduction of the homopolymerization, larger amounts of AAm monomers are estimated to be available for the AAm grafting on PET and the graft yield is thought to increase. In the present study, the graft yield increased over the AAm-monomer concentration ranging from 25 to 50 wt% without homopolymerization, whereas the yield decreased above 50 wt% where noticeable homopolymerization was observed.

The authors also investigated the total-γ-ray-dose dependence of the graft yield over the range from 20 to 100 kGy. The graft yield increased linearly in the lower dose region and showed saturation at higher doses. This saturation feature could be due to an increase in the obstruction of the AAm-monomer permeation during the γ-ray irradiation due to the growing and extending mass of γ-grafted AAm on the PET surface. In addition to this saturation feature of the dose dependence, the graft yield also showed a similar behavior in the dependence on the γ-ray dose rate from 1.02 to 2.40 kGy h^{-1}. One might think that the phenomenon also originates from the above-mentioned homopolymerization: the graft yield could become lower in the above mentioned homopolymerizing system because the dose-rate increase would promote the AAm homopolymerization, which would increase the solution viscosity and restrict monomer diffusion. However, such an adverse effect was not expected in the present case because the AAm solution was incorporated into the DMSO-pretreated PET films before irradiation. Additionally, the $FeCl_3$ should reduce the homopolymerization during the γ-ray irradiation.

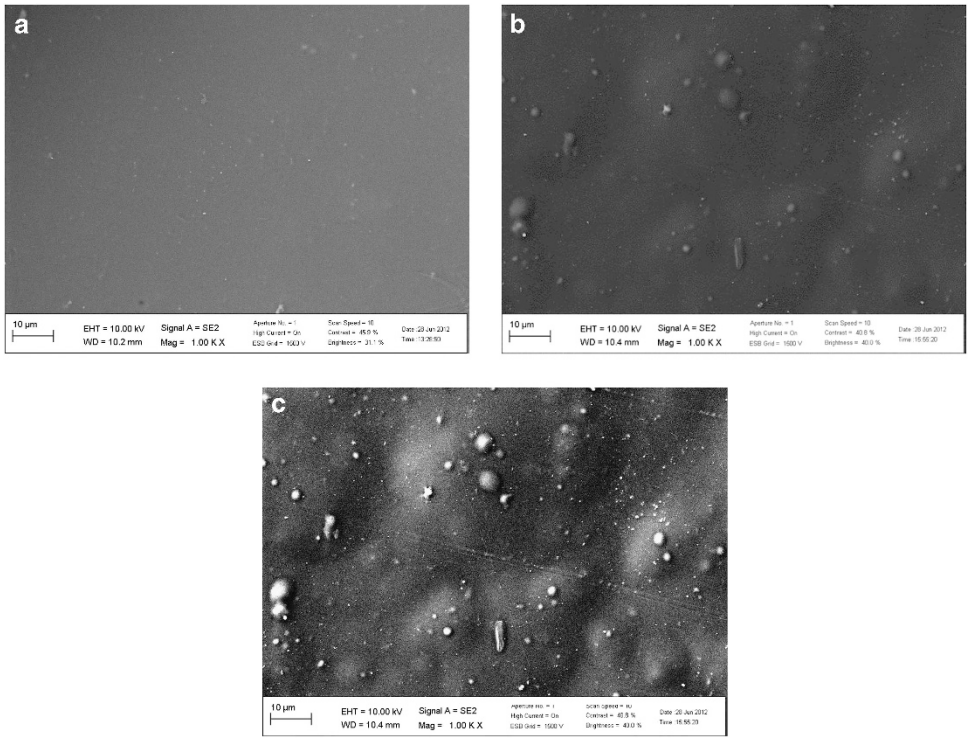

Figure 8 (**a**) SEM micrographs of pristine PET film surfaces, (**b**) SEM micrographs of the AAm-grafted PET film, (**c**) the contrast-enhanced image of (**b**).

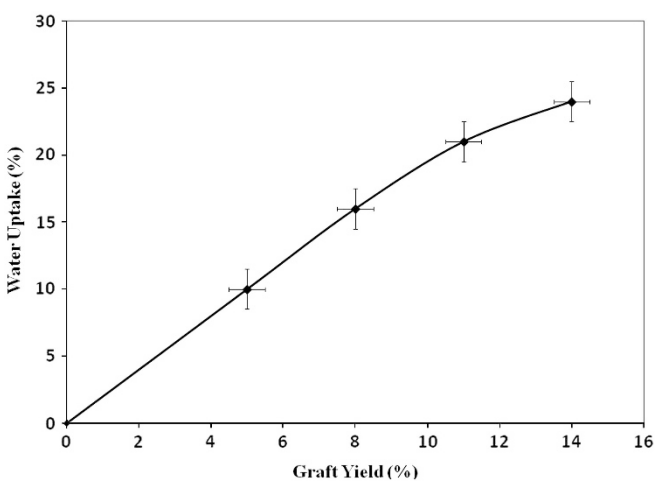

Figure 9 The graft yield dependence of the water uptake in the AAm-grafted PET films.

Table 2 The removal of Hg(II) ions by the pristine PET and the hydrolyzed, AAm-grafted PET filmsAbbreviations: AAm, acrylamide; PET, poly(ethylene terephthalate)

Initial Hg(II) concentration (mg l^{-1})	*Sample adsorbent*	*Hg(II) removal (%)*
100.0 (±0.5)	Pristine PET film	0
	Hydrolyzed AAm-grafted PET film	96 (±1)

CONFLICT OF INTEREST

The authors declare no conflict of interest.

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