Grafting Polymer from Poly(ethylene terephthalate) Films by Surface-Initiated ATRP

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ABSTRACT: Surface-initiated atom transfer radical polymerization (ATRP) from poly(ethylene terephthalate) (PET) film was studied. Poly(methyl methacrylate) (PMMA), poly(acrylamide) (PAAM), and their diblock copolymer (PMMA/PAAM) on the surface of PET film were successfully prepared by surface-initiated ATRP. The structures and properties of the modified PET film were characterized by FT-IR/ATR, X-ray photoelectron spectroscopy (XPS), measurements of contact angles, and scanning electronic microscopy (SEM). The results indicate that the surface properties of PET film were greatly improved by grafted polymer. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 108: 351–357, 2008

Key words: atom transfer radical polymerization; surface-initiated polymerization; poly(ethylene terephthalate); surface tension

INTRODUCTION

Poly(ethylene terephthalate) (PET) film is widely recognized for its excellent basic properties such as mechanical strength, permeability to gases, transparency, and chemical resistance.[1] However, it possesses strong hydrophobic behavior, low surface energy, and poor wettability of its surface due to the lack of polar groups. The functional surface of PET film is very important in specific applications such as conductive film, biocompatible materials, and packing film.[2–4] A common way to promote surface activation is through modification. Chemical and physical modifications of PET film, therefore, have been extensively studied, especially the grafting of polymer from the surface of PET film as an effective modification.

Polymer grafting from a solid surface is being extensively studied with a range of objectives such as improved wetting, friction, adsorption, and adhesion of substrates. Several living/controlled polymerizations such as ''living'' cationic,[5] anionic,[6] ring-opening,[7] and reversible addition fragmentation chain transfer (RAFT)[8] have been used for grafting polymers from solid surfaces. Recently, the most popular living/controlled polymerization used in grafting polymer brushes from solid surfaces has been atom transfer radical polymerization (ATRP).[9]

An attractive feature of ATRP is its ability to simultaneously grow chains from multifunctional surfaces. Thus, a polymer brush with well-defined structures could be designed and controlled. ATRP has proven to be a powerful tool for synthesis of polymer brushes having variety in composition, toposelectivity, and architectures, while at the same time using easily accessible experimental conditions.[10]

To graft polymers from solid surfaces using surface-initiated polymerization (SIP), the initiator groups must be covalently bound to the substrate surface. With ATRP, it is desirable to limit premature termination of the polymer growing from these surface sites, which is required for the formation of block copolymer. Some research groups have reported successful polymer brush grafting from a variety of solid surfaces such as silicon, carbon fiber, organic latex colloids, emulsions, and carbon black.[9,11] More seldom are reports on the modification of PET film using ATRP, since polyesters usually show a strong hydrophobic behavior and low surface energy. These characteristics make very difficult to introduce the ATRP initiator onto the PET surface. An effective alternative means for surface activation is the use of alkaline hydrolysis, which generates surface-activity groups (carboxyl and hydroxyl) from PET film. From these polar groups, some functional compounds including the ATRP initiator can be introduced onto the surface of PET film. Recently, Roux and Demoustier-Champagne explored different methods of preparing PET surfaces with the aim of carrying out

surface-initiated polymerizations of styrene.[12] Another example of PET and poly(ethylene naphthalate) (PEN) films as reported by Farhan and Huck is that poly(N-isopropyl acrylamide) brush on the surface of those polyester films has been synthesized by combining initiator and ATRP.[13]

In this article, polar groups of carboxyl were produced on the surface of PET film through alkaline hydrolysis and oxidation. Then, the ATRP initiator was immobilized on the surface of PET film. To get different surface properties of PET film, the PMMA, PAAM, and diblock copolymer grafted from PET film were first prepared by surface-initiated ATRP. FT-IR/ATR, X-ray photoelectron spectroscopy (XPS), gel permeation chromatography (GPC), and measurements of contact angles were used to characterize the surface structures, components, and properties of the modified PET film. Scanning electronic microscopy (SEM) shows the surface morphology of PET film and modified PET film. The results indicate that the surface properties of PET film were greatly improved by the grafted polymer. Surface tension of the modified PET film through grafted polymer increased significantly when compared to that of PET film. The surface of modified PET film with PAAM is hydrophilic, while the PET film surface modified with PMMA/PAAM is amphiphilic.

EXPERIMENTAL

Materials and reagents

The PET film supplied by Teijin Techno Products, Japan was washed thrice with acetone/methanol (50/50 vol %) and dried. Methyl methacrylate (analytical reagent) supplied by Kanto Kagaku Co., Japan was washed in a 5% sodium hydroxide solution, stirred over calcium hydroxide for 24 h, and distilled under vacuum and stored at −15°C before use. Acrylamide (A.R.) supplied by Kanto Kagaku Co. was purified through recrystallization with acetone. DL-ethylbromopropionate (99.0%) was provided by ACROS. 2-Bromoisobutyryl bromide (97.0%) was provided by Fluka. CuCl (A.R.) purchased from Kanto Kagaku Co. was purified by stirring in acetic acid, filtered, and then washed with ethanol and dried. 2,2-Bipyridine (bpy) (A.R.) and triethylamine (A.R.) were provided by Kanto Kagaku Co. N,N-dimethylformamide (DMF) and toluene purchased from Kanto Kagaku Co. were distilled before use. All other reagents were used directly without purification.

Analysis and characterization

FT-IR/ATR spectra of PET film and modified PET film were carried out using AVATAR 330 (Thermo Nicolet Co.) with Ge prism. X-ray photoelectron

spectroscopy (XPS) measurements were carried out with ESCALAB 220i-XL (VG CO.). Molecular weights and molecular weight distributions were measured on a SHIMADZU CTO-10A VP GPC system using THF as eluent. The contact angles were directly measured with liquid-drop-shape method at 25°C using an automatic contact angle meter, FACE CA-XP (Kyowa Interface Science Technology Co., Japan). Ion-exchanged water, formamide, and diiodomethane were used as liquids for measurement. The contact angles of samples were decided by θ/2 method. The morphology of PET film and modified PET film was observed by using field mission scanning electron microscopy (JSM-6340 F, Jeol, Japan). The percentage of grafting (PG%) was calculated according to the following relationship:

$$PG\% = (\text{grafted PMMA/PET film charged}) \times 100\%$$

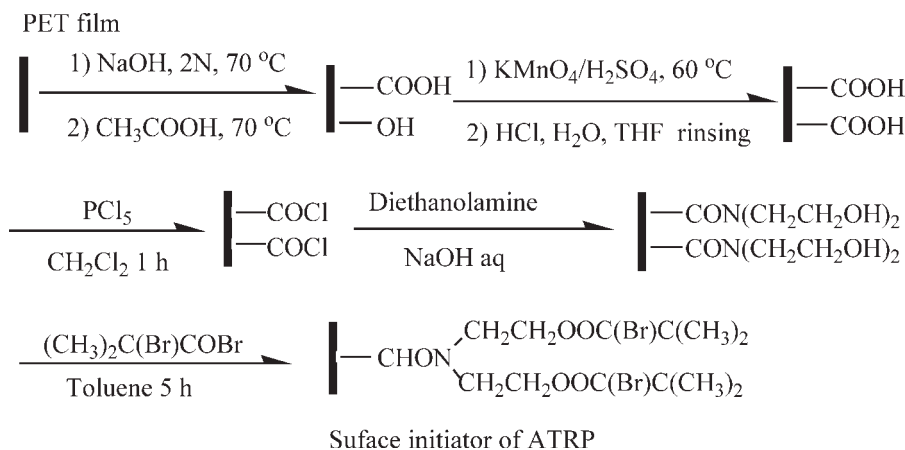### Preparation of surface initiator from PET film

The immobilization process of surface initiators is shown above in Scheme 1. The PET films were hydrolyzed and oxidated to produce carboxyl groups on the surface.[12] The carboxyl was then turned into acid chloride by using PCl_5. To get the initiator densely on the PET film surface, bifurcated structures of diethanolamine were built up on the surface of PET film, followed by esterification with 2-bromoisobutyryl bromide, which was then used as the ATRP surface initiator.[14]

Surface-initiated atom transfer radical polymerization of MMA

A bottom flask was charged with initiator-modified PET film, 0.01 g of CuCl, and 0.047 g of bpy. The flask was sealed and cycled between vacuum and argon, thrice, to remove oxygen. Then, MMA (3.8 mL), DMF (0.4 mL), and DL-ethylbromopropionate (1 μL) were added by syringes. The flask was immersed in a 100°C oil bath. After several hours, the polymerization solution was cooled to room temperature to terminate polymerization. The polymer was diluted with THF. The modified PET film was washed with DMF and acetone to remove the adsorbed free PMMA. The polymer solution was used to measure the molecular weights by GPC.

Surface-initiated atom transfer radical polymerization of AAM

A dry round bottom flask was charged with 0.01 g of CuCl, 0.047 g of bpy, 2.5 g of AAM, and initiator-modified PET film. The polymerization condition of AAM used was the same as described earlier except for the temperature (130°C). After polymerization,

PET film

1) NaOH, 2N, 70 °C

2) CH₃COOH, 70 °C → |—COOH
|—OH

1) KMnO₄/H₂SO₄, 60 °C

2) HCl, H₂O, THF rinsing → |—COOH
|—COOH

PCl₅

CH₂Cl₂ 1 h → |—COCl
|—COCl

Diethanolamine

NaOH aq → |—CON(CH₂CH₂OH)₂
|—CON(CH₂CH₂OH)₂

(CH₃)₂C(Br)COBr

Toluene 5 h → |—CHON ⟨CH₂CH₂OOC(Br)C(CH₃)₂ / CH₂CH₂OOC(Br)C(CH₃)₂

Suface initiator of ATRP

Scheme 1 Synthetic routes of initiator-modified PET film.

the solution was diluted with DMF. The modified PET film was washed with DMF, ion-exchanged water, and acetone to remove the adsorbed free PAAM.

Preparation of diblock copolymer (PMMA/PAAM) from PET film

After the first layer of PMMA formed, the polymer on the PET film surface was used as an anchor initiator for the polymerization of AAM using the same polymerization condition as described earlier.

RESULTS AND DISCUSSION

To prepare polymer layer from the surface of PET film, a uniform and densely packed initiator-modified substrate is indispensable. After surface modification of PET film, XPS was used to confirm the initiator monolayer. The peak of Br 3d was observed around 71 eV (the surface content of Br: 0.4%), indicating the formation of an initiator monolayer (Fig. 1). Besides the Br 3d peak, another peak of N 1s (diethanolamine) was found at 400.1 eV, which is an unambiguous proof of the presence of a grafted organic layer on the PET film surface. These data show that the PET film surface was modified by the ATRP initiator.

ATRP has been successfully used in the polymerization of MMA in solution to yield narrow polydispersity homopolymers.[15] PMMA brush was first prepared by Ejaz et al.,[16] and the PAAM brush was prepared by Huang and Wirth.[17] In this article, MMA and AAM were selected as monomers for the hydrophobic and hydrophilic polymer. Because of the difficulty in obtaining the molecular weights of grafted polymer, we use the "free" polymer formed by a free initiator in solution to monitor the surface-grafted polymerization. The free initiator not only

functions as an indicator of polymerization, but also as a control for ATRP on the PET film surface.[18]

Table I shows the free polymer data. The results of GPC indicate that polymerization was controlled, and polydispersity of the free PMMA was narrow, about 1.1. However, the polydispersity of diblock copolymer was high about 2.17. This might have been due to a side reaction caused by the high temperature.

Wirth and coworkers reported that with polymerization of acrylamide at 130°C, polymer chains grow proportionally to the monomer concentration.[19,20] Although uncontrolled, the ATRP of AAM is useful in modification of the substrate to produce a hydrophilic layer.[18]

To prove the living/controlled nature of polymerization initiated from initiator-modified PET film, the effect of the polymerization time (PMMA) on the PG% was investigated (Fig. 2). It increased linearly with increasing polymerization time, and reached 3.6% after a polymerization time of 16 h, which suggests that ATRP of MMA has the characteristics of living/controlled radical polymerization.

Figure 3 shows the infrared spectra of the initiator-modified PET film and grafted polymer (PMMA, PAAM, and diblock copolymer) on the PET film. In
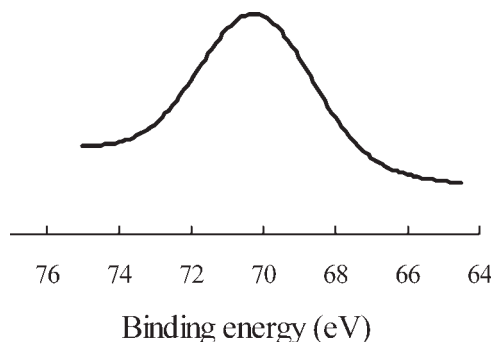

Figure 1 XPS spectra of initiator-modified PET film with self-assemble (the peak of Br 3d).

Binding energy (eV)

Monomer	Solvent	Time (h)	Temperature (°C)	M_n	M_w	M_w/M_n
MMA	DMF	8	100	25311	28342	1.17
MMA	DMF	10	100	52477	61512	1.13
MMA/AAM	DMF	4/10	100/130	20387	44179	2.17

fact, there are almost no differences between the IR spectra of PET film and initiator-modified PET film. In Figure 3(A), the absorption peak at 1343 cm^{-1} was attributed to wagging vibration of —CH$_2$—. The absorption peak at 1248 cm^{-1} was assigned to asymmetric and symmetric stretching of —C—O—C— group of aromatic ester. The absorption peaks at 1126 and 1022 cm^{-1} were attributed to skeletal ring because of 1,4-substitution. The absorption peak at 875 cm^{-1} was assigned to C—H deformation. After surface modification, all those absorption peaks changed little comparing with the absorption peak of ester at 1730 cm^{-1}. In the spectrum of PET film modified by PMMA, the absorption peak at 1730 cm^{-1} (ester group) is stronger than that of initiator-modified PET film. This is because the grafted PMMA introduced many ester groups onto the surface of PET film. In the spectrum of PET film modified by PAAM, a new absorption peak was observed in the region of 1670 cm^{-1} (carbonyl in amide due to the formation of hydrogen bond with amide group). This suggests that the PAAM grew from the surface of the PET film. In the case of PET film modified by diblock copolymer of PMMA/PAAM, the absorption peaks of carbonyl stretching vibration were observed in ester (1730 cm^{-1}) and in amide (1630 cm^{-1}), respectively. It showed that after formation of PMMA layer, as surface macro-initiator for the second polymerization, the diblock polymerization from the first polymer layer was carried out. On the other hand, since the intension of carbonyl absorption peak of grafted polymer is very strong, the surface of PET film was covered by grafted polymer. Absorptive polymers on the surface of modified PET film are unlikely because the modified PET film had been carefully sonicated and cleaned in fresh DMF and acetone for several times.

In the IR spectra of PET film modified by PMMA with different polymerization times, the intensity of the absorption peak at 1730 cm^{-1} of the ester group enhanced as polymerization time increased, which indicates that the thickness of the grafted PMMA from PET film increases because of the living/controlled ATRP. This result was consistent with the testing of PG%.

XPS was used to determine the surface composition and structures of PET film and PET film modified by grafted polymer. In the spectra of PET film and PET film modified by grafted polymer [Fig. 4(A–D)], all the C 1s peaks appeared around 285 eV with a broad shoulder at the higher binding energy. Careful peak fitting on the C 1s peaks resolves three peaks representing different carbons in PET film and PET film modified by PMMA: (A) aliphatic hydrocarbon (C—C/C—H, at a binding energy of 285.0 eV), (B) the methylside ester (C—O at 286.6 eV), and (C) the carboxyl carbon (C=O at 289.2 eV), respectively. Similarly, the PET film modified by PAAM and PMMA/PAAM showed four kinds of carbon: (A) aliphatic hydrocarbon (C—C/C—H, at 285.0 eV), (B) the methylside ester (C—O at 286.3 eV), (C) the amide carbon (CONH$_2$ at 288.1 eV), and (D) the carboxyl carbon (C=O at 289.2 eV) were found, respectively. Comparing with PET film, the peak of C—O increased whereas that of C—C/C—H decreased on the surface of PET film modified by PMMA. This may have resulted from the introduction of many ester groups of the PET film with grafted PMMA. The area ratios of C 1s peaks of the carbonyl between ester and amide in the PET film/PAAM and PET film/PMMA/PAAM were found to be 9 : 13 and 11 : 12, respectively. From these data, the surface of PET film modified by diblock copolymer was not completely covered with the second polymer layer.[21] This result was consistent with the results of the infrared. N can be used as unambiguous elemental marker for the grafted polymer component of the AAM monomer. Both the PET film/PAAM and the PET film/PMMA/PAAM showed
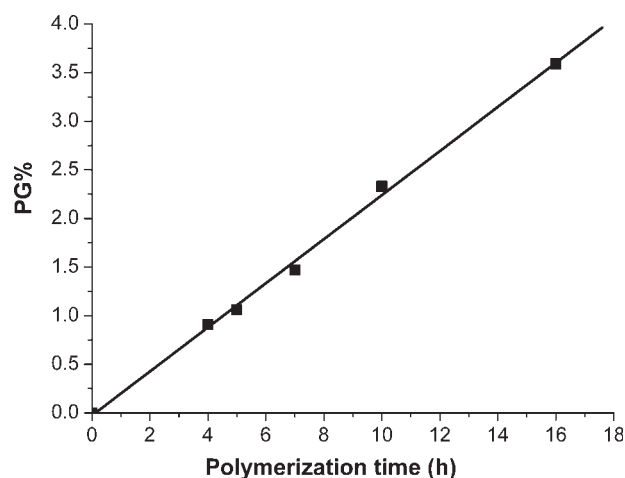

Figure 2 Effect of the polymerization time on PG% of PET film/PMMA.
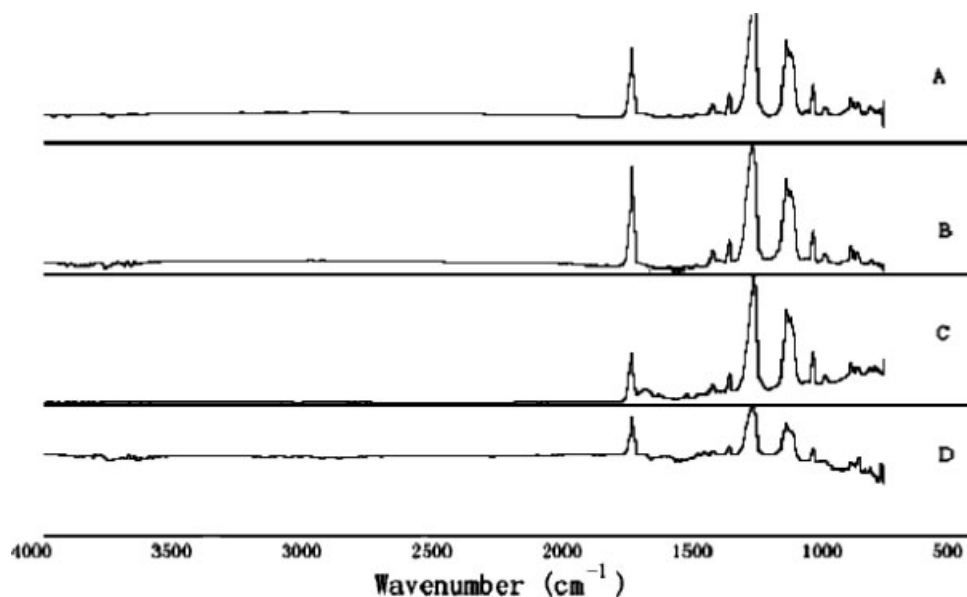
Figure 3 IR spectra of (A) initiator-modified PET film, (B) PET film/PMMA, (C) PET film/PAAM, and (D) PET film/ PMMA/PAAM.

the N 1s peak at 400.1 eV, indicating the formation of PAAM layer on the substrate. The surface of PET film/PAAM is hydrophilic, and the surface of PET film/PMMA/PAAM is amphiphilic, whereas singly, PAAM is hydrophilic but PMMA is hydrophobic. From a contact angle data, we can draw a similar conclusion.

Contact angles were directly measured with liquid-drop-shape method. Ion exchanged water, formamide, and diiodomethane were used as liquids for measurement, from which surface tension and three kinds of contributions to surface tension were obtained. Through contact angles, surface tension and its contributions were calculated as an expanded
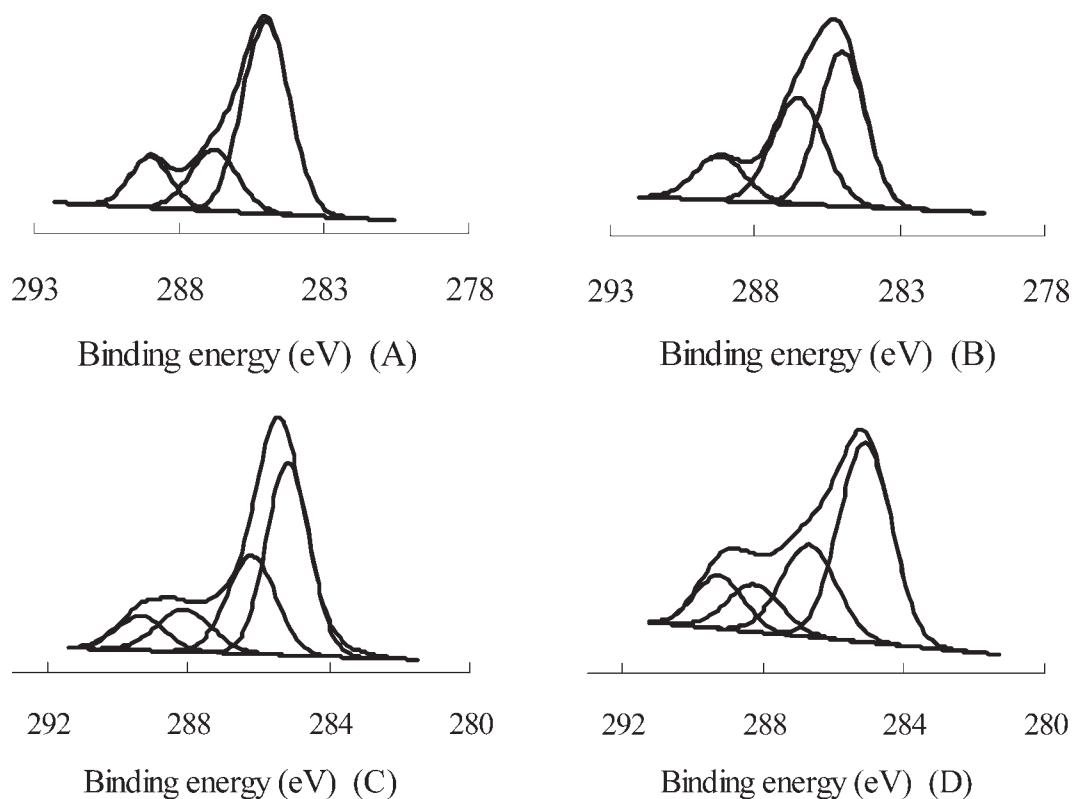

Figure 4 XPS spectra of (A) PET film, (B) PET film/PMMA, (C) PET film/PAAM, and (D) PET film/PMMA/PAAM.

TABLE II
Contact Angle and Surface Tension of Samples

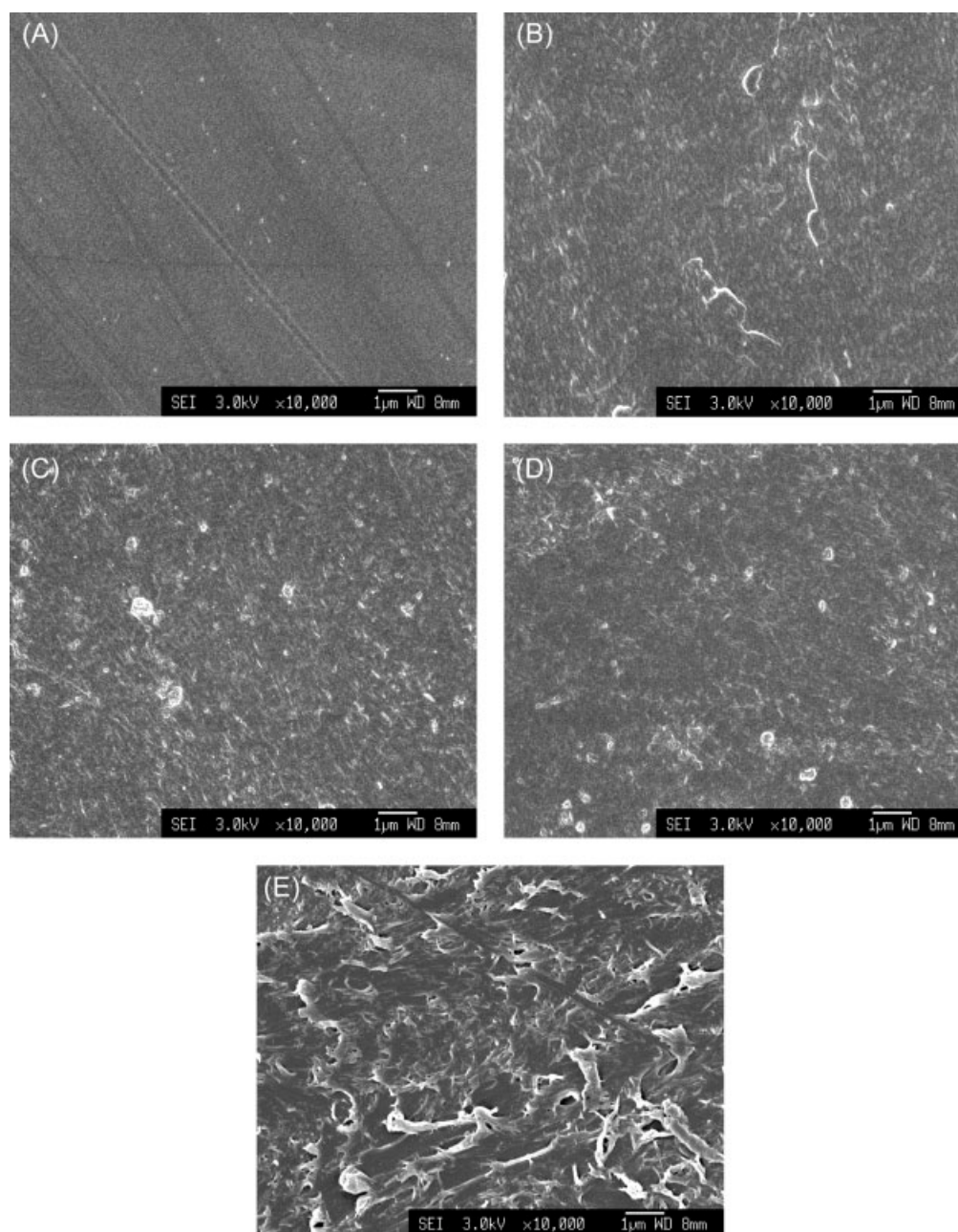| Sample	Contact angle (°)			Surface tension (mN m^{-1})			
	H$_2$O	HCONH$_2$	CH$_2$I$_2$	γ	γ^d	γ^p	γ^h
Water	–	–	–	72.8	29.1	1.3	42.4
Formamide	–	–	–	58.2	35.1	1.6	21.5
Diiodomethane	–	–	–	50.8	46.8	4.0	0.0
PET film	77.7	54.7	30.1	46.0	43.1	1.6	1.3
Initiator-modified PET	67.9	46.8	26.0	64.2	29.5	29.9	4.8
PET/PMMA	70.6	48.0	22.7	58.2	33.4	21.4	3.4
PET/PAAM	40.1	10.2	48.5	76.6	21.0	29.4	26.2
PET/PMMA/PAAM	64.8	44.8	30.1	64.4	28.3	29.0	6.4

Figure 5 SEM micrographs of (A) PET film, (B) initiator-modified PET film, (C) PET film/PMMA, (D) PET film/PAAM, and (E) PET film/PMMA/PAAM.

Fowkes eqs. (1), (2), and (3).[22]

$$\gamma_L(1 + \cos \theta) = 2(\gamma_S^d \times \gamma_L^d)^{1/2} + 2(\gamma_S^p \times \gamma_L^p)^{1/2}$$
$$+ 2(\gamma_S^h \times \gamma_L^h)^{1/2} \quad (1)$$

$$\gamma_S = \gamma_S^d + \gamma_S^p + \gamma_S^h \quad (2)$$

$$\gamma_L = \gamma_L^d + \gamma_L^p + \gamma_L^h \quad (3)$$

γ is the surface tension of liquid (γ_L) or sample (γ_S); γ^d, γ^p, and γ^h are the dispersive, polar, and hydrogen-bonded contributions to surface tension, respectively.

After grafting polymer, a boundary layer formed on the surface of PET film, which contributed some new properties to the matrix.[23,24] Table II details the contact angle and surface tension data of PET film and modified PET film. The surface tensions of modified PET film (PET film/PMMA: 58.2, PET film/PAAM: 76.6, and PET film/PMMA/PAAM: 64.4) are more than that of PET film (46.0). Especially, the surface tension of PET film modified by PAAM is the highest (76.6), which indicates that the surface of modified PET film is active in the chemical interaction. Furthermore, the value of γ_S^p is very small, while the γ_S^d is significantly larger, which suggests that the surface of PET film is hydrophobic, i.e., the surface structure of PET film would be occupied by benzene ring and hydrocarbon from ethylene glycol. However, the value of γ_S^h of PET film modified by PAAM is very high (26.2), which indicates that the surface of modified PET film is hydrophilic ($\theta = 40.1$). This means that the PAAM was grafted from the surface of initiator-modified PET film, and this grafted polymer layer occurred through hydrogen bonding between amides. The contact angles of modified PET film are different (PET film: 77.7, PET film/PMMA: 70.6, PET film/PMMA/PAAM: 64.8, and PET film/PAAM: 40.1), which suggest that different grafted polymers were prepared from PET film, respectively. From data on contact angle and surface tension, the surface of PET film modified by diblock copolymer is amphiphilic, and the surface structures were composed of PAAM and PMMA, which is consistent with the results of XPS and IR also.

Figure 5 shows scanning electron microscopes of PET film and modified PET film. From Figure 5(A), we can see that the surface of PET film is very smooth. Because of hydrolysis and oxidation, the surface of initiator-modified PET film changed very much. It is rougher than that of PET film. After grafting polymer, the formation of the grafted polymer provided a rougher surface morphology of the modified PET film than that of PET film and initiator-modified PET film. Especially, the morphology of PET film modified by diblock copolymer is the roughest, which indicates that the grafting density of PET film modified by diblock copolymer is very high. Furthermore, the surface of modified PET film was covered equably by grafted polymer, which showed some new properties such as hydrophilicity, hydrophobicity, and amphiphilicity.

CONCLUSION

In this article, grafted polymers and diblock copolymer were prepared by surface-initiated ATRP on the surface of PET film. The results of contact angle measurement showed that the surface of PET film modified by PAAM is hydrophilic, and the surface of PET film modified by diblock copolymer is amphiphilic. The surface tension of modified PET film was also greatly increased compared with that of PET film. This novel kind of modified PET film may be widely used in many fields such as biocompatible materials, amphiphilic functional film, and conductive film.

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