Preparation of stable polymeric grafted layers on poly(ethylene terephthalate) by thermal annealing

Peerasak Paoprasert[a,*]**, Warisara Boonthong**[a]**, Chanatip Kookarinrat**[a]**, Nuanphun Chantarasiri**[b]

[a] Department of Chemistry, Faculty of Science and Technology, Thammasat University, Pathumthani 12121 Thailand

[b] Supramolecular Chemistry Research Unit, Department of Chemistry, Faculty of Science, Chulalongkorn University, Bangkok 10330 Thailand

*Corresponding author, e-mail: peerasak@tu.ac.th

ABSTRACT: This work presents a simple and versatile grafting method to prepare stable polymer layers on poly(ethylene terephthalate) (PET). Poly(styrene-*co*-2-hydroxyethyl methacrylate) was synthesized by free radical polymerization. The copolymer was grafted onto poly(ethylene terephthalate) via the hydroxyl groups upon thermal annealing. The percentage of copolymer grafting was studied as a function of copolymer composition, PET surface treatment, annealing time, and annealing temperature. The grafted polymer layer on PET remained stable when immersed in an organic solvent whereas the non-grafted polymer layers were completely desorbed within two weeks. In addition, poly(4-vinylpyridine-*co*-2-hydroxyethyl methacrylate) was grafted onto PET to test the versatility of this grafting method. Control experiments were carried out to demonstrate that the grafting occurs through the available hydroxyl groups on the polymers and the surfaces. Based on these results, this grafting method offers a simple and versatile strategy to prepare stable polymeric layers on polymeric surfaces, and therefore, expands the tool box for functionalizing polymer surfaces.

KEYWORDS: coatings, adhesion, polymer grafting, hydroxyl linker

INTRODUCTION

The modification of polymeric substrates by grafting is an important route to modify a polymer surface properties and to introduce new functions, for example, biocompatibility[1], adhesion[2], friction[3], lubrication[4], hydrophobicity[5], or hydrophilicity[6], to the substrates. There are two main approaches to graft polymers onto solid surfaces: grafting-from and grafting-to[7,8]. In the grafting-from method, the monomers react with a surface activated by high energy irradiation or a chemical initiator forming polymer chains tethered to the surface. In the grafting-to approach, the pre-synthesized polymer chains are anchored onto the solid surface through linker groups. The grafting-from method often yields high-density polymer layers, but has poor control over polymer molecular weight and distribution. In addition, it uses a large amount of starting materials, including the monomer and initiator (in the case of chemical grafting). Since the samples must be totally immersed in a solution, the grafting-from method produces abundant chemical waste and a relatively small amounts of polymers grafted to the surface. In contrast, in the grafting-to method, the polymer is pre-synthesized so that the desired molecular weight and distribution can be obtained

prior to grafting. Less chemical waste is generated as a thin layer of polymer can be directly transferred to the substrate before the grafting step. The linker groups however must be installed in the polymer chains and therefore the proper linkers must be chosen and the polymerization conditions must be compatible.

There are several linker groups for grafting organic materials onto inorganic substrates. For example, silanes[9], carboxylic acids[10], phosphonic acids[11], and catechols[12] are linkers for oxide surfaces whereas thiols are linkers for gold[13]. However, unlike the inorganic substrates, the polymeric substrates are more difficult to graft because most commodity polymers are inert or lack active groups such as surface hydroxyls or metal atoms, to react with those linkers. There are only a few reports on grafting polymers on polymeric substrates, for example, fluorinated silane grafted poly(vinylidene fluoride)[14], hydrophilic polymer-coated polydimethylsiloxane through silane linker[15], and hepamine-coated polyurethane through catechol linker[16]. Grafting such polymers is difficult as the synthesis of these polymers requires several steps and the grafted polymeric layers may be unstable. There is a need therefore to develop new grafting methods for the preparation of stable polymeric layers on polymer surfaces.
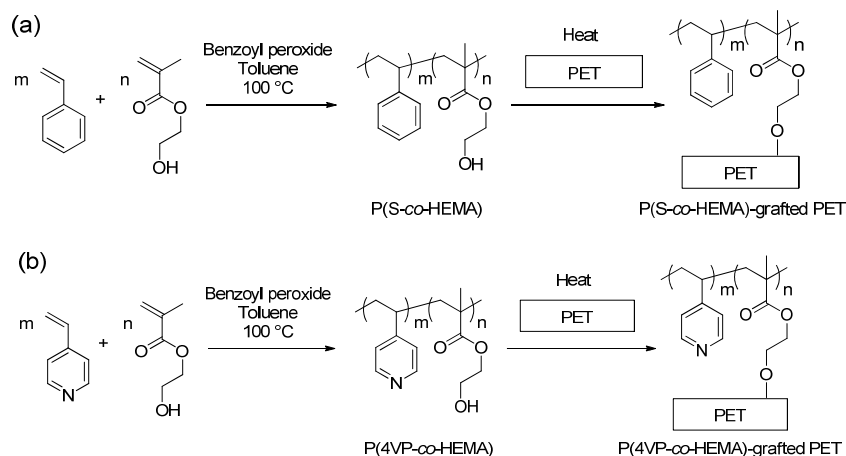
Fig. 1 Synthesis and grafting on PET surface of (a) P(S-*co*-HEMA) and (b) P(4VP-*co*-HEMA).

Recently, hydroxyl groups have been used as surface linker to graft polymers[17] and rhenium-bipyridine dyes[18] onto oxide substrates by thermal annealing. By simple heating at 140–160 °C, the hydroxyl groups of an organic material and oxide surface condense to form an ether linkage resulting in organic layers chemically bonded onto the surface. The organic layers show good stability against desorption in aqueous and organic solutions.

In this study, poly(ethylene terephthalate) (PET) was chosen as the polymeric substrate because it is a cheap, non-toxic, and chemically stable semicrystalline thermoplastic polymer[19] widely used to fabricate several kinds of commercial articles. In addition, PET has been used for a variety of advanced technological applications ranging from electronic[20] to biological devices[21]. Polymers based on styrene and 4-vinylpyridine were used to graft onto PET surfaces. The copolymers were characterized by nuclear magnetic resonance spectroscopy (NMR), Fourier transform infrared spectroscopy (FTIR), and gel permeation chromatography (GPC). The surface topography and composition of the grafted samples were characterized using atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS), respectively. The stability of the grafted polymer layers in organic solvent was investigated.

MATERIALS AND METHODS

Materials

All chemicals were purchased from Sigma-Aldrich. Styrene, 2-hydroxyethyl methacrylate, and 4-vinyl-pyridine were purified by passing through silica gel columns. Benzoyl peroxide was recrystallized in methanol and dried at room temperature.

Synthesis of copolymers

The copolymers used in this work were synthesized using a conventional free radical polymerization method as follows (Fig. 1). To prepare poly(styrene-*co*-2-hydroxyethyl methacrylate) (P(S-*co*-HEMA)), styrene (8 g), 2-hydroxyethyl methacrylate (1 g for 10 mol% and 4 g for 40 mol%), toluene (10 ml), and benzoyl peroxide (30 mg) were added to a round-bottom flask. The reaction mixture was heated at 100 °C for 16 h. Then the solution was cooled down, diluted with toluene, and precipitated in methanol twice. To prepare poly(4-vinylpyridine-*co*-2-hydrox-yethyl methacrylate) (P(4VP-*co*-HEMA)), 4-vinyl-pyridine (8 g), 2-hydroxyethyl methacrylate (4 g), toluene (10 ml), and benzoyl peroxide (30 mg) were added to a round-bottom flask. The reaction mixture was heated at 100 °C for 16 h. Then the solution was cooled down, diluted with toluene, and precipitated in methanol twice.

Grafting procedure

PET samples were obtained as a thin sheet and cut into 0.5×0.5 cm^2 pieces. The average thickness of PET samples measured by a micrometre was 0.240 ± 0.001 mm. Prior to grafting, the PET samples were cleaned by ultrasonication in acetone, hexane, and deionized water (10 min each), and then dried at 70 °C overnight in an oven. The PET samples were dipped in an ethyl acetate solution of copolymer (0.2 mg/ml) and air-dried. Then they were thermally annealed at temperatures from 100 °C to 160 °C for times from 6 h to 96 h. After that the samples were ultrasonicated in dichloromethane (3×10 ml
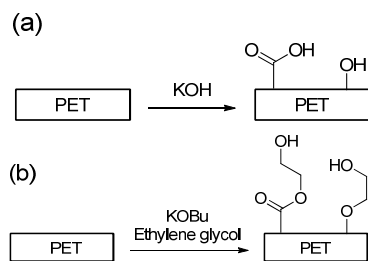
Fig. 2 Preparation of (a) KOH-treated PET and (b) KOBu-treated PET.

for 10 min each) and dried overnight at 70 °C until the weight was constant. A confirmation test was carried out by subjecting the sample to soxhlet extraction in chloroform overnight. It was found that the weight of the sample did not change. This test confirms that the ultrasonication in dichloromethane (3x10 ml for 10 min each) is sufficient to clean the samples. The percentage of grafting was determined as $(w_2 - w_1)/w_1$, where w_2 is the weight of sample after grafting and w_1 is the weight of PET sample before grafting. The average percentage of grafting was calculated from at least five samples in each condition.

Surface treatment procedures

Two surface treatment methods, KOH and potassium tert-butoxide (KOBu), were employed on PET samples following standard procedures from the literature[22] as follows (Fig. 2). Cleaned PET samples were heated in 1 M KOH solution at 80 °C for 90 min. The samples were then ultrasonicated in deionized water three times (10 min each) and rinsed with acetone. The samples were then dried overnight at 70 °C. To treat with KOBu, cleaned PET samples were immersed into 25 ml of 0.60 M KOBu solution in ethylene glycol. After 4 h of reaction at room temperature, the film was rinsed sequentially with ethylene glycol (two aliquots), water, 0.1 M HCl, water (two aliquots), methanol, and hexane and then dried overnight at 80 °C.

Stability test

Three different PET samples were prepared for the stability test in organic solvent as follows. To prepare P(S-*co*-HEMA)-grafted PET, the cleaned PET samples were dipped in an ethyl acetate solution of P(S-*co*-HEMA) (0.2 mg/ml) and for thermally annealed at 130 °C for 48 h (Fig. 3a). The samples were then ultrasonicated in dichloromethane (3×10 ml for 10 min each) and dried overnight at 70 °C. To
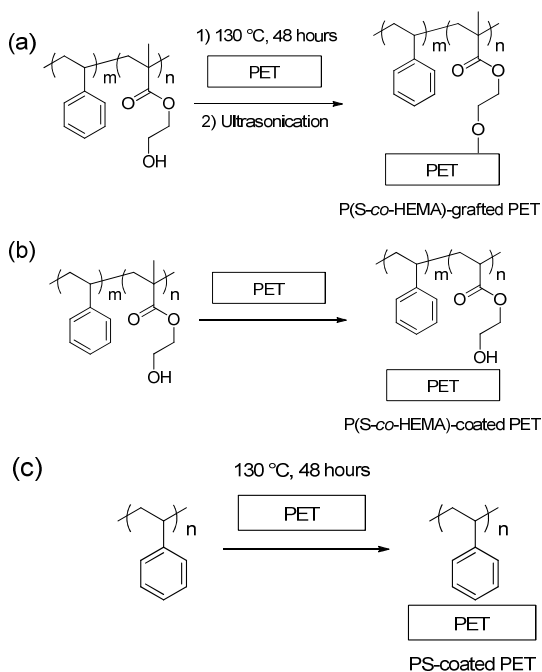
Fig. 3 Preparation of (a) P(S-*co*-HEMA)-grafted PET, (b) P(S-*co*-HEMA)-coated PET, and (c) PS-coated PET.

prepare P(S-*co*-HEMA)-coated PET, the cleaned PET samples were dipped in an ethyl acetate solution of P(S-*co*-HEMA) (0.2 mg/ml) and air-dried (Fig. 3b). To prepare PS-coated PET, the cleaned PET samples were dipped in an ethyl acetate solution of polystyrene (0.2 mg/ml) and air-dried. They were then thermally annealed at 130 °C for 48 h (Fig. 3c).

Instruments and measurements

^{1}H (500 MHz) NMR spectra were recorded on an AVANCE[III] Digital NMR Spectrometer (Bruker Biospin; AV-500) using chloroform-d as solvent. Polymer molecular weights and polydispersities were obtained using a Waters e2695 gel permeation chromatograph equipped with a Viscotek 3580 refractive index detector. Tetrahydrofuran was used as eluent with a flow rate of 1.0 ml/min. The polymers were dissolved in tetrahydrofuran (2 mg/ml) and the solutions were filtered through 0.45 μm membrane filters. The relative molecular weights and polydispersities of the polymers were calculated using polystyrene standards. The FTIR spectra were obtained using a Perkin Elmer FTIR (Spectrum 2000 model) and NaCl salt windows. Atomic force microscopy (AFM) images were recorded using a Seiko atomic force microscope (Model SPI 4000). The scan speed was 1 Hz. Silicon tips with resonance frequency of 140 kHz and force

constant of 3.5 N/m were used. The chemical composition of the sample surface was investigated using an X-ray photoelectron spectrometer (AXIS ULTRA[DLD], Kratos analytical, Manchester UK). The base pressure in the XPS analysis chamber was about 5×10^{-9} torr. The samples were excited with X-ray hybrid mode at 700×300 μm spot area with a monochromatic Al $K_{\alpha1,2}$ radiation at 1.4 keV. The X-ray anode was run at 15 kV, 10 mA, and 150 W. The photoelectrons were detected with a hemispherical analyser positioned at an angle of 45° with respect to the sample surface.

RESULTS AND DISCUSSION

Synthesis of P(S-*co*-HEMA)

First, we demonstrated the surface grafting of styrene-based polymers on PET. Styrene was chosen as it is a common monomer for a variety of polymer-related applications. To graft styrene-based polymers onto PET surfaces through the hydroxyl groups, 2-hydroxyethyl methacrylate (HEMA) was used as hydroxyl-containing monomer to provide the linker group in the polymer chain. The copolymer, P(S-*co*-HEMA), was synthesized by free radical polymerization using benzoyl peroxide as initiator (Fig. 1). To study the effect of copolymer composition on grafting percentage, two copolymers were synthesized. From the integration of peak areas in the NMR spectra, it was found that the two copolymers contained 11 mol% and 17 mol% of HEMA with respect to styrene contents. By comparing with the FTIR spectra of polystyrene and poly(2-hydroxyethyl methacrylate), the FTIR spectrum of P(S-*co*-HEMA) showed characteristic peaks that belong to a combination of two homopolymers, for example peaks at 3480, 1729, and 1455 cm^{-1} corresponding to the O−H, C=O, C=C stretches. Hence the FTIR results confirm the structure of the copolymer. From GPC characterization, the number-average molecular weights of 11 mol% and 17 mol% of HEMA-containing copolymers are 15 994 g/mol and 41 492 g/mol, respectively. The molecular weight distributions of the copolymers are 1.86 and 2.04, respectively. Although these two copolymers possess different molecular weights and polydispersities, previous studies showed that the grafting efficiency does not depend on the polymer's molecular weight or polydispersity[17]. Hence these two copolymers were used for grafting studies as follows.

Effect of surface treatment and copolymer composition

The PET samples were dipped in an ethyl acetate solution of copolymers and then air-dried for a few min-
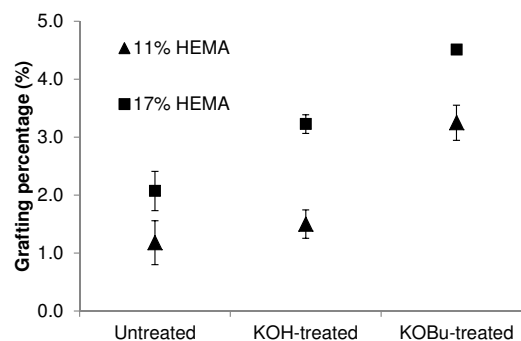
Fig. 4 Grafting percentages of 11% and 17% HEMA-containing copolymers grafted on untreated, KOH-treated, and KOBu-treated PET surfaces.

utes. The copolymer-coated PET samples were then annealed at 130 °C for 48 h. This annealing condition was first selected because it was similar to that of previous work where HEMA-containing copolymers were grafted on oxide substrates[17]. According to the literature, the grafting process occurs through the condensation reaction between surface hydroxyl groups and hydroxyl groups of the copolymer. The grafting efficiency depends on the hydroxyl contents[18]. Hence the effects of surface treatments and HEMA contents in the copolymer on grafting efficiency were simultaneously investigated. Two copolymers were synthesized as discussed above and three different PET surfaces were prepared: untreated, KOH-treated, and KOBu-treated. The KOH solution will hydrolyse the ester bonds in the PET chain to create carboxyl and hydroxyl groups whereas the KOBu/ethylene glycol solution generates only the hydroxyl groups on the surface (Fig. 2)[22]. The untreated PET samples theoretically contain the carboxyl and hydroxyl groups only at polymer chain ends. The amount of hydroxyl and carboxyl groups on these surfaces cannot be accurately quantified using routine surface characterization techniques, such as X-ray photoelectron spectroscopy, because the oxygen atoms are also present in the PET polymer chains. The PET surfaces can be, however, qualitatively analysed by contact angle measurement. The water contact angles of untreated, KOH-treated, and KOBu-treated PET samples are 87°, 74°, and 75°, respectively. An approximately 12°–13° decrease in water contact angle upon KOH and KOBu treatments is consistent with literature results[22].

The grafting percentage of copolymers on PET was measured (Fig. 4). The results show that both HEMA percentages in the copolymer and the surface treatment used affect the grafting percentage. For both

copolymers, the KOBu-treated PET samples gave the highest grafting percentage followed by the KOH-treated samples and untreated samples. These results are expected because the KOBu/ethylene glycol cleaves the ester bonds in PET and converts them into hydroxyl groups whereas the KOH cleaves the ester bonds into hydroxyl and carboxyl groups. In contrast, the untreated samples have the hydroxyl groups only at polymer chain ends. As a result, the surface hydroxyl contents can be ranked as follows: KOBu-treated > KOH-treated > untreated, which agrees with the grafting percentages. The greater the density of surface hydroxyl groups, the higher the grafting percentage of the copolymers that are grafted on the PET surfaces. The grafting percentage also depends on the HEMA contents in the copolymers. The 17% HEMA-containing copolymer gave higher grafting percentages than the 11% HEMA-containing copolymer for all types of PET samples. The higher the number of polymer hydroxyl groups, the higher the grafting percentage of the polymers that are grafted on the surface. These results confirm that the grafting occurs through the hydroxyl groups.

A control experiment was carried out to confirm that the grafting of the copolymers occur through the hydroxyl groups. In this study, polystyrene homopolymer (without HEMA units) was coated and annealed on KOBu-treated PET substrates at 130 °C for 48 h. The samples were then cleaned using the same procedure as for the copolymers. Since polystyrene does not contain the hydroxyl groups as surface linker, it should be completely removed upon ultrasonication as it is only physically absorbed on the surface. Indeed, after ultrasonication in organic solvent, the grafting percentage was zero, confirming that no polystyrene layer was formed on the PET surface. This result indicates that the hydroxyl groups in the copolymer are the surface linkers necessary for forming chemical bonds with the PET surface.

Effect of annealing temperature

The effect of annealing temperature on grafting percentage of the copolymer on KOBu-treated PET was investigated. In this study, 17% HEMA-containing copolymer and KOBu-treated PET substrates were used. The samples were annealed in a hot air oven at temperatures ranging from 100 °C to 160 °C for 48 h. As the annealing temperature increased from 100 °C to 130 °C, the average grafting percentages increased from 1% to 4% and then dropped to 2% when the temperature increased further to 160 °C (Fig. 5). The thickness of the grafted layer on top and bottom surfaces of the sample was obtained by subtracting
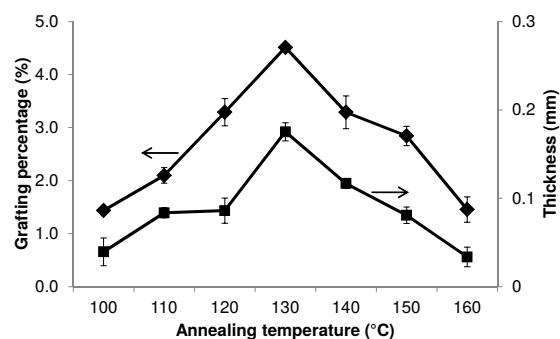
Fig. 5 Grafting percentages (diamonds) and thicknesses (squares) of P(S-*co*-HEMA) (17 mol% HEMA content) grafted on KOBu-treated PET samples as a function of annealing temperature.

the thickness of the bare PET sample from the sample thickness after grafting. The thicknesses of the grafted layers correlate well with grafting percentages and reach 0.175 mm at 130 °C grafting. High temperatures may decompose the polymer samples resulting in lower grafting percentages. These results suggested that an annealing temperature of 130 °C is optimal to achieve the highest grafting percentage. A vacuum oven or thermal annealing under inert atmosphere will reduce polymer degradation. However, the aim of this report is to demonstrate the simplicity of this grafting method in which even a home baking oven can be used.
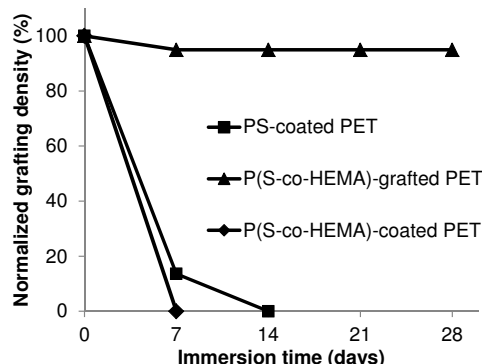
Effect of annealing time

The effect of annealing time on grafting of the copolymer on PET was studied. Again, 17% HEMA-containing copolymer and KOBu-treated PET substrates were used. The samples were annealed at 130 °C, the optimum annealing temperature derived from the previous experiment. The annealing time was varied from 6 h to 96 h. It was found that an annealing time of 48 h gave the highest grafting percentage (Fig. 6). The thicknesses of the grafted layers also correlate well with grafting percentages. The shorter annealing times may not be enough to complete the grafting process whereas the longer annealing times may start to decompose the polymer samples.
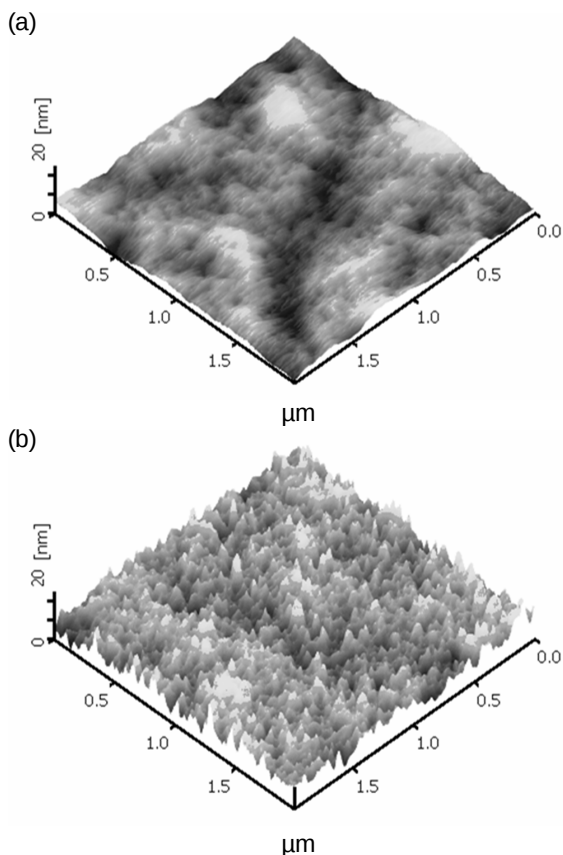
Surface topography

The surface topography of KOBu-treated PET and P(S-*co*-HEMA)-grafted PET samples was measured using atomic force microscopy (AFM). From the AFM images (Fig. 7), it can be observed that the KOBu-treated PET sample was smoother than the P(S-*co*-HEMA)-grafted PET sample. The root mean-
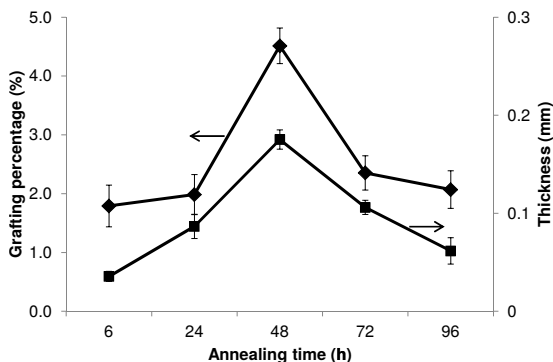
Fig. 6 Grafting percentages (diamonds) and thicknesses (squares) of P(S-*co*-HEMA) (17 mol% HEMA content) grafted on KOBu-treated PET samples as a function of annealing time.

(a)

(b)

Fig. 7 AFM images of (a) KOBu-treated PET and (b) P(S-*co*-HEMA)-grafted PET.

square roughness of KOBu-treated PET sample was 1.43 nm whereas that of the P(S-*co*-HEMA)-grafted PET sample was 2.98 nm, or about twice as much. The increase in surface roughness of the grafted sample was due to the presence of grafted layer indicating


Fig. 8 Plot of normalized grafting percentages of P(S-*co*-HEMA)-grafted PET, P(S-*co*-HEMA)-coated PET, and PS-coated PET samples in toluene as a function of immersion time.

that the P(S-*co*-HEMA) chains were anchored on the PET surface.

Stability of the polymer layers on PET surface

The stability of the polymer layers on PET substrates in organic solvent was investigated. In this study, the P(S-*co*-HEMA)-grafted PET was prepared by annealing 17% HEMA-containing copolymer on KOBu-treated PET at 130 °C for 48 h. Then the samples were immersed in toluene and compared with the PS-coated PET and P(S-*co*-HEMA)-coated PET. Toluene was chosen because it is a good solvent for these polymers. The PS-coated PET was prepared by coating polystyrene on KOBu-treated PET samples and then annealed at 130 °C for 48 h. The samples were then directly immersed in toluene without cleaning. The P(S-*co*-HEMA)-coated PET samples were prepared by coating 17% HEMA-containing copolymer on KOBu-treated PET, but they were not annealed prior to immersion in toluene. The grafting percentages of all samples were monitored overtime and normalized (Fig. 8). It was found that the P(S-*co*-HEMA)-coated PET and PS-coated PET samples were completely desorbed within 7 and 14 days, respectively, whereas the P(S-*co*-HEMA) grafted layer was stable against desorption over 28 days. These results confirm that the presence of HEMA monomer and thermal annealing are necessary for the formation of chemical linkage between the hydroxyl groups which improves the stability of the polymeric layer against desorption in organic solvent.

Synthesis and grafting of P(4VP-*co*-HEMA)

One more experiment to demonstrate the scope of this grafting approach was carried out. In this study,
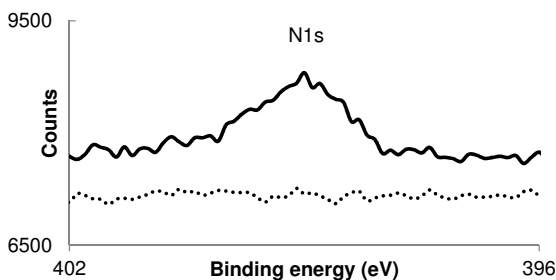
Fig. 9 XPS spectra of N1s peak of P(4VP-*co*-HEMA)-grafted PET (solid) and KOBu-treated PET (dotted).

P(4VP-*co*-HEMA) was synthesized using benzoyl peroxide initiator. The copolymer was confirmed using FTIR and NMR characterizations (not shown). Compared with the FTIR spectra of poly(2-hydroxy-ethyl methacrylate) and poly(4-vinylpyridine), it was found that the copolymer spectrum had characteristic peaks from both homopolymers, for instance, C=O at 1725 cm^{-1} and C=C at 1600 cm^{-1}, confirming the formation of the copolymer and consistent with the NMR result.

The KOBu-treated PET samples were dipped in *N*,*N*-dimethylformamide solution of P(4VP-*co*-HEMA) and then annealed at 130 °C for 48 h. After annealing, the samples were ultrasonicated in chloroform. It was found that the grafting percentage of P(4VP-*co*-HEMA) was 3%, which is comparable to P(S-*co*-HEMA).

The XPS spectra of P(4VP-*co*-HEMA)-grafted PET and KOBu-treated PET were taken (Fig. 9). The N1s peak at 399 eV binding energy was observed whereas the KOBu-treated PET sample did not contain nitrogen. The XPS results confirm the presence of the copolymer layer on the PET surface after thermal annealing.

CONCLUSIONS

In this work, a simple grafting-to method to prepare thin polymeric layer on PET substrate using thermal annealing was demonstrated. It is a novel result demonstrating that thermal annealing can be used to graft polymers onto polymeric surfaces. Two copolymers, P(S-*co*-HEMA) and P(4VP-*co*-HEMA) were synthesized and grafted onto PET substrates. The grafting percentage of P(S-*co*-HEMA) on PET was affected by surface treatment methods, copolymer composition, annealing temperature, and annealing time. The method offers a number of advantages such as (i) it can be applied to a variety of polymers as long as they contain the hydroxyl linkers and (ii) the

grafted polymeric layer shows much improved stability against desorption in organic solvent compared to the physisorbed ones. Based on these results, the grafting method, which can be achieved simply by heating, provides another means for grafting stable polymeric layers onto polymeric substrates. Applications for this grafting strategy include the preparation of functional surfaces, such as superhydrophobic and responsive surfaces. This grafting method is not limited to PET, but is envisioned to be applicable to other polymeric substrates as long as they contain or are prepared to have surface hydroxyl groups.

REFERENCES

1. Solouk A, Cousins BG, Mirzadeh H, Seifalian AM (2011) Application of plasma surface modification techniques to improve hemocompatibility of vascular grafts: A review. *Biotechnol Appl Biochem* **58**, 311–27.
2. Gustafsson Y, Haag J, Jungebluth P, Lundin V, Lim ML, Baiguera S, Ajalloueian F, Del Gaudio C, et al (2012) Viability and proliferation of rat MSCs on adhesion protein-modified PET and PU scaffolds. *Biomaterials* **33**, 8094–103.
3. Mizote N, Katakai A, Tamada M, Matsuoka H (2010) Surface modification of vulcanized rubber by radiation grafting, part 1: Improvement in friction behavior. *J Appl Polymer Sci* **117**, 2825–30.
4. Michielsen S (1999) The effect of grafted polymeric lubricant molecular weight on the frictional characteristics of nylon 6,6 fibers. *J Appl Polymer Sci* **73**, 129–36.
5. Nyström D, Lindqvist J, Östmark E, Hult A, Malmström E (2006) Superhydrophobic bio-fibre surfaces via tailored grafting architecture. *Chem Comm* **34**, 3594–6.
6. Wang Y, Kim JH, Choo KH, Lee YS, Lee CH (2000) Hydrophilic modification of polypropylene microfiltration membranes by ozone-induced graft polymerization. *J Membr Sci* **169**, 269–76.
7. Zdyrko B, Luzinov I (2011) Polymer brushes by the "grafting to" method. *Macromol Rapid Comm* **32**, 859–69.
8. Bao Z, Zheng Y, Baker GL, Bruening ML (2011)

Preparation of Polymer Brushes Using "Grafting-from" Techniques. Wiley-VCH, Weinheim, Germany.

9. Onclin S, Ravoo BJ, Reinhoudt DN (2005) Engineering silicon oxide surfaces using self-assembled monolayers. *Angew Chem Int Ed* **44**, 6282–304.

10. Chiba Y, Islam A, Watanabe Y, Komiya R, Koide N, Han LY (2006) Dye-sensitized solar cells with conversion efficiency of 11.1%. *Jpn J Appl Phys* **45**, L638.

11. Hofer R, Textor M, Spencer ND (2001) Alkyl phosphate monolayers, self-assembled from aqueous solution onto metal oxide surfaces. *Langmuir* **17**, 4014–20.

12. Marczak R, Werner F, Gnichwitz JF, Hirsch A, Guldi DM, Peukert W (2009) Communication via electron and energy transfer between zinc oxide nanoparticles and organic adsorbates. *J Phys Chem C* **113**, 4669–78.

13. Vericat C, Vela ME, Benitez G, Carro P, Salvarezza RC (2010) Self-assembled monolayers of thiols and dithiols on gold: new challenges for a well-known system. *Chem Soc Rev* **39**, 1805–34.

14. Chen Y, Kim H (2009) Preparation of superhydrophobic membranes by electrospinning of fluorinated silane functionalized poly(vinylidene fluoride). *Appl Surf Sci* **255**, 7073–7.

15. Cordeiro AL, Zschoche S, Janke A, Nitschke M, Werner C (2009) Functionalization of poly(dimethylsiloxane) surfaces with maleic anhydride copolymer films. *Langmuir* **25**, 1509–17.

16. You I, Kang SM, Byun Y, Lee H (2011) Enhancement of blood compatibility of poly(urethane) substrates by mussel-inspired adhesive heparin coating. *Bioconjugate Chem* **22**, 1264–9.

17. In I, La YH, Park SM, Nealey PF, Gopalan P (2006) Side-chain grafted random copolymer brushes as neutral surfaces for controlling the orientation of block copolymer microdomains in thin films. *Langmuir* **22**, 7855–60.

18. Paoprasert P, Kandala S, Sweat DP, Ruther R, Gopalan P (2012) Versatile grafting chemistry for creation of stable molecular layers on oxides. *J Mater Chem* **22**, 1046–53.

19. Paszun D, Spychaj T (1997) Chemical recycling of poly(ethylene terephthalate). *Ind Eng Chem Res* **36**, 1373–83.

20. Hota K, Hota MK, Bera MK, Maiti CK (2012) Flexible metal-insulator-metal capacitors on polyethylene terephthalate plastic substrates. *Semicond Sci Tech* **27**, 105001.

21. Dhahri M, Abed A, Lajimi RH, Mansour MB, Gueguen V, Abdesselem SB, Chaubet F, Letourneur D, et al (2011) Grafting of dermatan sulfate on polyethylene terephtalate to enhance biointegration. *J Biomed Mater Res* **98A**, 114–21.

22. Chen W, McCarthy TJ (1998) Chemical surface modification of poly(ethylene terephthalate). *Macromolecules* **31**, 3648–55.