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Surface modification of polystyrene and poly(ethylene terephtalate) by grafting poly(N-isopropylacrylamide)

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In this work, poly(N-isopropylacrylamide) (PNIPAAm) was incorporated into previously oxidized PS and PET surfaces by grafting using two photo-initiation pathways. The incorporation of PNIPAAm was observed by drop water contact angle measurements, dyeing with Methylene Blue and AFM images analysis of the virgin and modified polymers. It was verified that the grafting process depends on the chemical surface environment. The grafted surfaces are hydrophilic below 32 °C and hydrophobic above this temperature. The transition is due to the incorporated PNIPAAm. This characteristic gives to the grafted materials potential to be applied as biomaterials.
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1. Introdution

The major polymers used in industrial purposes are, in general, hydrophobic [1], thus are not useful for many biotechnological process like substrates for adherent cell growth [2, 3] and others. Due to this, the incorporation of functional groups to the polymer surface to obtain more hydrophilic character, without altering the mechanical properties of the bulk, is widely studied.

Nowadays, a lot of technologies concerning the polymer surface modification are available. For instance, irradiation techniques may use different sources such as UV or plasma beams and others [4–6]. The surface exposure to the ozone beam is also an easy way to create hydrophilic groups [7]. In this sense, surface modifications using wet chemistry (persulfates, etc.) and posterior grafting were investigated by several authors [7, 8]. This field of investigations is based on the consensus that the biocompatibility is closely related to a balance among hydrophobic and hydrophilic groups at the surface [3].

The grafting of vinyl monomers into surface of polyethylene (PE), poly(ethylene therephtalate) (PET), polypropylene (PP) and polystyrene (PS) may be achieved by the use of photo-initiation using aromatic ketones, quinones or by the use of thermal initiation using peroxides [9].

The poly(N-isopropylacrylamide), (PNIPPAm), that presents LCST (Lower Critical Solution Temperature) phase diagram, have been grafted into polymers [4, 9–11] and the resultant materials show hydrophilic behavior at temperatures below 32 °C (the LCST of PNIPAAm in water) [12, 13] and more hydrophobic character above [2, 14, 15]. In short, when the temperature is lower than 32 °C, the PNIPAAm chains present affinity to water and are hydrated and expand in aqueous media. When slightly warmed to above 32 °C the water affinity decreases and the collapsing of the PNIPAAm chains is observed leading to a more compact morphology [10]. Photografting of PNIPAAm into cellulose may be performed through the use of cerium(IV) in acidic medium and exposure to high pressure Hg lamp (254–580 nm) in N_2 atmosphere [16]. It is well known that sodium-2-sulfonate antraquinone may be used as sensibilizer for UV (360 nm) photo-initiated polymerization of vinyl monomers, but the degassing is crucial [4]. One reliable method for graft vinyl or ionic monomers into PET was developed by Uchida and co-workers, where sodium periodate ($NaIO_4$) is used as sensibilizer and further exposure to Hg lamp, without the need of degassing [17–19].

Several works have been performed to show that the collapsing of PNIPAAm chains may be used in the biotechnology allowing the detachment of adherent cells [20]. At 37 °C cells adhere and grow easily on PNIPAAm-grafted surfaces and detach just by cooling to 10 °C [21]. It should be highlighted that the detachment of cells by the introduction of chemicals like EDTA or proteolytic enzymes could, sometimes, damage the cells [14, 22].

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TABLE I Some used conditions for the grafting on PS and PET surfaces, through the two-stepped method

		PS	PET
Step 1	DMAAm % wt	30	20
	Immersion time (min)	90	15 ($Na_2S_2O_8$) 90 (Hg lamp)
Step 2	AAm % wt	7.4	0.5
	NIPAAm % wt	11.3	2.5
	DMAAm % wt	5.0	—
	MBAAm % wt	0.3	—
	KIO_4 % wt	1.0	0.1
	Exposure time (min) to Hg lamp	60	240

TABLE II Some used conditions for the grafting on PS and PET surfaces, through the one-step method

	PS	PET
AAm % wt	7.4	2.8
NIPAAm % wt	11.3	9.0
MBAAm % wt	0.3	—
AQS % wt	3.2	0.5
Exposure time (h) UV lamp (360 nm)	24	24

Modifications of PS surface, just by absorbing PNIPAAm from aqueous solution, have been performed in our group [22]. It was verified that cells like CHOK1 (Cell Hamster Ovary, type K1) grow and adhere in the PS-PNIPAAm absorbed surface at 37 °C and detach by cooling to 10 °C.

In this work, PNIPAAm was incorporated into previously oxidized PS and PET surfaces by grafting using two photo-initiation pathways. The incorporation was observed by drop water contact angle measurements, dyeing of Methylene Blue and AFM images analysis of virgin and modified polymers.

2. Materials and methods

2.1. Materials

Acrylamide (AAm) 99% (14 866-0), N-isopropylacrylamide (NIPAAm) 97% (41 532-4), N,N′-dimethylacrylamide (DMAAm) 97% (27 413-5) and sodium persulfate ($Na_2S_2O_8$) 98% (21 623-2) were purchased from Aldrich. The N,N′-methylenebisacrylamide (MBAAm) 97% (17-1304-02) was purchased from Plusone. Potassium periodate (KIO_4) 99.5% (700) was purchased from Vetec, Brazil. Sodium-2-sulfonate antraquinone (AQS) 98% (10 670) was purchased from Fluka. They were used as received, except NIPAAm that was purified by re-crystallization from hexane.

2.2. Methods

2.2.1. Oxidation

Commercial PET and PS, both in film form, were cleaned using methanol and ethanol, respectively, during 24 h at least. The cleaned surfaces were submitted to oxidation process through two different ways:

1. Using UV source of high pressure Hg lamp ($\lambda =$ 254–580 nm, 215 W), in air and at room temperature. The exposure time was fixed in 40 min for PS and 25 min for PET.

2. Using $Na_2S_2O_8$ 10 wt % aqueous solution at 70 °C. The films were kept in the solution during 90 min for PS and 60 min for PET.

2.2.2. Grafting

After the oxidation process, the PS and PET oxidized were cleaned by washing with distilled and deionized water in abundance. Two graft methods were used: in the first one the PS or PET was immersed in an aqueous solution of DMAAm at 70 °C, during 90 min for PS and 15 min, for PET previously oxidized with sodium persulfate, or 90 min, for PET previously oxidized with Hg lamp. In step 2, after step 1, the materials were immersed in an aqueous solution of DMAAm, NIPAAm, MBAAm, and AAm as monomers and KIO_4 as sensibilizer and exposed to the Hg lamp. To compare the influence of the oxidation process (Hg lamp and $Na_2S_2O_8$) on the grafting process, steps 1 and 2 were performed in the virgin PS and virgin PET. Table I describes the conditions used in steps 1 and 2. The second graft method is made up of only one step. The previously oxidized materials were immersed in a solution having NIPPAm, AAm, MBAAm, AQS and some drops of isopropanol. The system was deoxygenated by N_2 bubbling (15 min) and exposed to a UV lamp (black light, $\lambda = 360$ nm, 8 W). For PET the used solvent was water and for PS the solvent was DMSO. The conditions used in this method of grafting are described in Table II. After the grafting process, the materials were exhaustively washed with water and immersed in methanol (30 min) to remove the adsorbed chemicals.

2.2.3. Characterization

2.2.3.1. Drop water contact angle measurements. The contact angle of a drop water (Mili-Q®) deposited in the surface of virgin, oxidized and grafted materials were measured in temperatures from 25 to 45 °C, using a Tantec Contact Angle Meter.

2.2.3.2. Dyeing. Virgin, oxidized and grafted (PS and PET) films were immersed in a 10^{-4} mol l^{-1} concentration aqueous solution of Methylene Blue dye at 25 °C and at 70 °C. The intensity of dyeing in each case was qualitatively evaluated by the final color of the materials. Pictures of died films were taken using a SONY digital camera model CCDMVC-FD73.

2.2.3.3. Atomic force microscopy. The microscopy images of virgin and modified PET film were determined by non-contact topographic mode AFM (Topometrics, TMX-2010) with Nanoprobe of 200 µm length, and a pyramidal oxide-sharpened silicon nitride cantilever with a spring constant of 0.12 Nm^{-1}. The images were processed only by flattening to remove background slope.

3. Results and discussion

3.1. Oxidation

The oxidation of PS and PET was performed to enhance the reactivity of the surfaces and thus, to raise the grafting yield. In Figs. 1 and 2 the dependence of drop water contact angle (DWCA) of the oxidized PS and PET by Hg lamp and sodium persulfate, as a function of time, are respectively shown. The change in the wetability of the surfaces, due to the oxidation process, may be observed by the decrease of the contact angle from 84°, in the virgin PS, to 50°, in the oxidized PS surface using Hg lamp after 90 min exposure, and to 59° after 90 min treatment using sodium persulfate, as shown in Fig. 1. The DWCA for the virgin PET is ca. 90° and decreases to ca. 25° after 60 min exposure to the Hg lamp and to 60° after treatment using sodium persulfate during 60 min. The exposure to Hg lamp is more effective in the PS and PET oxidation than the sodium persulfate aqueous solution treatment at 70 °C. Also, the presence of oxygen is important to the oxidation process, because lower DWCA values are obtained in air than in vacuum, as shown in Fig. 2.

3.2. Grafting

The grafting of PNIPAAm into previous oxidized surfaces of PS and PET was evaluated by measurement of DWCA as a function of temperature. The dependence of DWAC as a function of temperature for PS and PET, grafted through the two-stepped method, are presented in Figs. 3 and 4, respectively. The grafting process leads to a subsequent decreasing in the DWCA. This indicates an enhancing on the hydrophilic character as compared to the oxidized surfaces. But, the hydrophilicity is significantly changed by slightly warming the grafted materials to above the LCST of the PNIPAAm, as it may be observed in Figs. 3 and 4. The DWCA of PET surface grafted through the two-stepped method, without previous oxidation, changes from 55° (at 25 °C) to 65° (at 45 °C). The DWAC of PET surfaces grafted using the same conditions but after Hg lamp or sodium persulfate oxidation changes from 22° (at 25 °C) to 55° (at 45 °C).

The DWCA values for PS and PET grafted using the one step method are presented in Figs. 5 and 6, respectively. Comparing the curves of Figs. 5 and 6 to those presented in Figs. 3 and 4, it can be seen that analogous results were obtained weather the graft process in PET is performed through the one step method or the two-step method. However, the grafting performed directly in the virgin PS gives the same DWAC values than those observed when the grafting is done in the previously oxidized PS surfaces. It means that the previous oxidation of PS is not so important to graft through the one step method, as observed in the two-step method. Also, the type of the oxidant used does not influence in the DWAC values of the PS-grafted surface. Different behavior was observed for PET. For instance, in the one-step grafting done directly in virgin PET the DWAC changes from 48° (at 25 °C) to 54° (at 45 °C), and after the oxidation, using the sodium persulfate, the DWAC changes from 35° (at 25 °C) to 49° (at 45 °C).

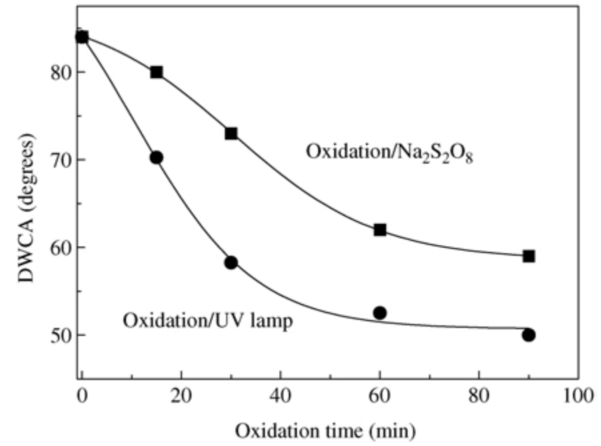

Figure 1 DWCA of PS surface as a function of oxidation time, using sodium persulfate and UV lamp.

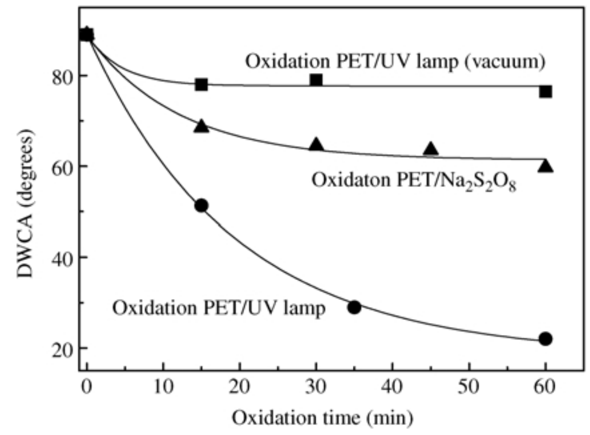

Figure 2 DWCA of PET surface as a function of oxidation time, using sodium persulfate and UV lamp.

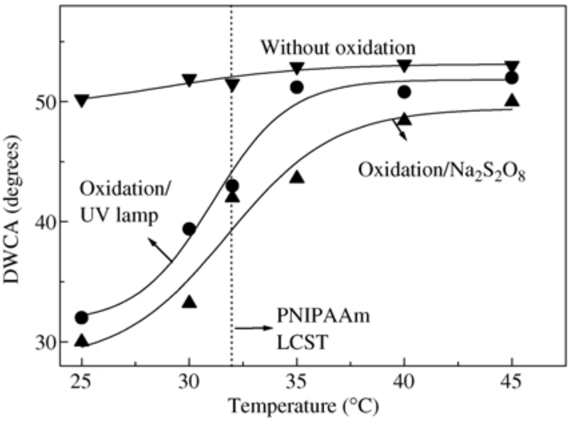

Figure 3 DWCA of grafted PS using the two-step method as a function of temperature.

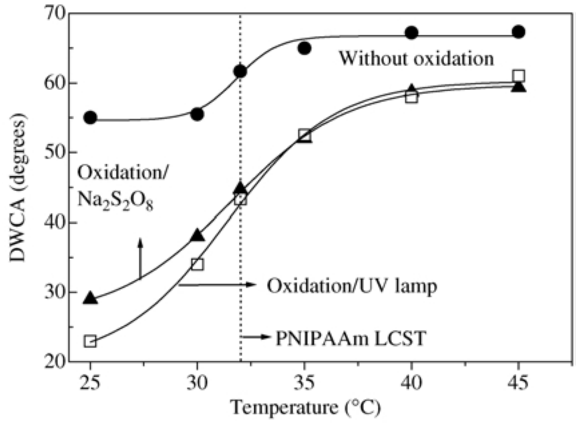

Figure 4 DWCA of grafted PET using the two-step method as a function of temperature.

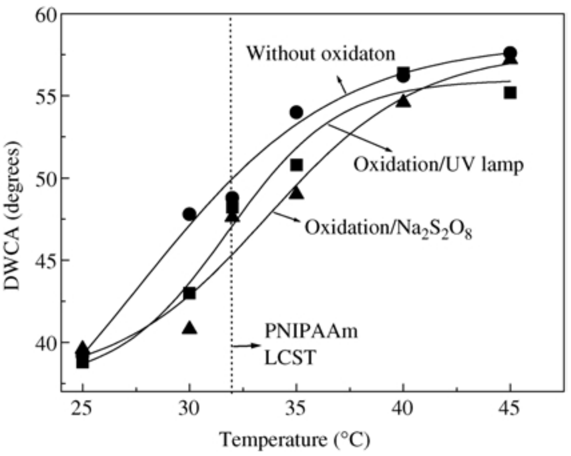

Figure 5 DWCA of grafted PS surface using the one-step method as a function of temperature.

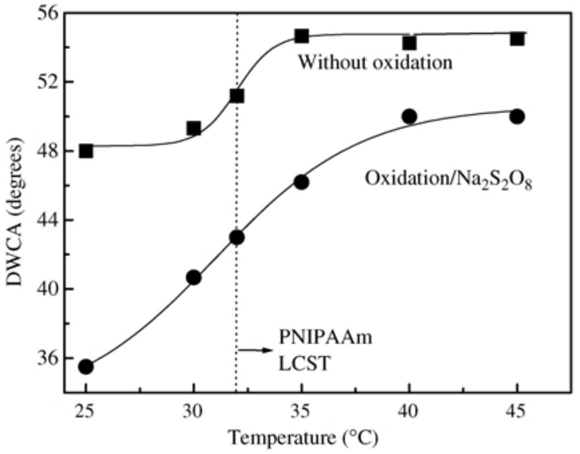

Figure 6 DWCA of grafted PET surface using the one-step method as a function of temperature.

This means that the grafting is more effective when the PET surface is previously oxidized: using the one step or two steps the graft of PNIPAAm is more intense if the surface is previously oxidized. It should be highlighted that the DWAC values of PS and PET, virgin and oxidized, do not change significantly with the temperature.

The results described here indicate that the oxidation creates more reactive groups on polymeric surface and also that the graft process is dependent of surface environment. The grafting process by exposure the virgin films of PET or PS immersed in aqueous NIPAAm solution to the Hg lamp, was not successful: no grafting was verified. It may be attributed to the low reactivity of NIPAAm and to the absence of reactive groups in the virgin polymer surface. In the two-step method, the previous oxidation, the immersion of DMAAm, in the first step of grafting, and the presence of more reactive monomers DMAAm and AAm mixed to the NIPAAm, in the second step, overcame these problems.

The use of one-step method to graft NIPAAm into PE surface is well known [4], but not many works have been published using this method for grafting PNIPAAm into PS or PET surfaces. It is suggested [4] that the presence of isopropanol enhances the sensibility of AQS to the UV ($\lambda = 360\,\text{nm}$) irradiation. It is easy but low yield was verified. The inconvenience of this method, for industrial purpose, is the need of deoxygenation step and the use of the AQS solution. Despite the method using Hg lamp constitutes in the oxidation and further grafting in two steps, it is more suitable to be used in large scale.

3.3. Dyeing

Pictures of films (virgin, oxidized, and grafted) dyed in Methylene Blue aqueous solution at 25 °C and 70 °C may be observed in Figs. 7 and 8, for PS and PET, respectively. The virgin and the oxidized PS or PET films dye in lower intensity than the respective grafted polymers. In the dyeing the Methtylene Blue could be trapped into the grafted material surface (PNIPAAm or PAAm chains, etc.) and this leads to a higher dyeing intensity. The trapped dye may be removed from the surface just by dipping the dyed material in pure water for 5 h at 40 °C. As it will be shown in Section 3.4, the surface of grafted PET presents higher roughness than the virgin or the oxidized ones. Virgin and oxidized (PET and PS) surfaces present low roughness, which is not enough to promote some visual detectable dyeing, despite the virgin ones to be hydrophobic. In addition,

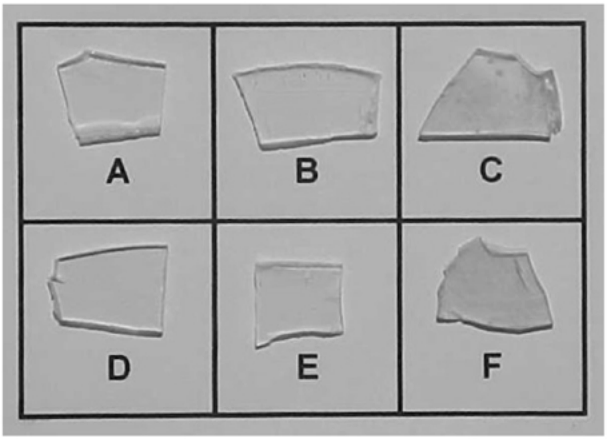

Figure 7 Pictures of PS submitted to dyeing in Methylene Blue aqueous solution: A and D: virgin; B and E: oxidized; C and F: grafted. A, B and C: dyed at 25 °C; D, E and F: dyed at 70 °C.

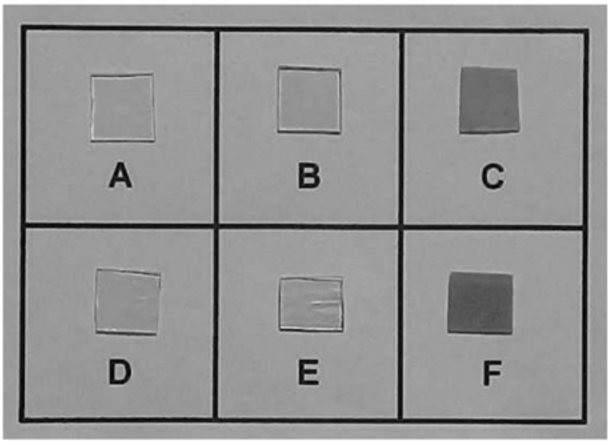

Figure 8 Pictures of PET submitted to dyeing in Methylene Blue aqueous solution: A and D: virgin; B and E: oxidized; C and F: grafted. A, B and C: dyed at 25 °C; D, E and F: dyed at 70 °C.

as it may be seen in Figs. 7 and 8, the dyeing done at 70 °C is slightly more intense than the dyeing done at 25 °C for PS and for PET as well.

3.4. AFM images

AFM images of virgin and modified PET are presented in Fig. 9. Comparing the AFM images of virgin (Fig. 9(a)), oxidized using sodium persulfate (Fig. 9(b)) and grafted PET through the two step method (Fig. 9(c)), significant difference may be achieved in the morphologies and in the roughness as well. In the virgin PET, flatter surface may be observed in contrast to the oxidized and grafted ones. In the PET oxidized surface the topography tends to be less flat and some points show roughness spots. The points are isolated and no connection between can be observed. They could be correlated to the oxidation sites. The image of the grafted PET surface consists of undulations, large holes and projections on the order of few micrometers. The roughness is higher in the grafted PET surface than in the virgin or oxidized ones. This characteristic morphology was already observed in other work [20, 21, 23] where the hydrophilic–hydrophobic transition on the surface of PNIPAAm was observed by AFM. The morphologies of oxidized and grafted PET surfaces observed in this work by AFM images match very well to the contact angle values and to the dyeing intensity. The contact angle decreases from ca. 90° on virgin PET to 50–60° on oxidized PET and to 30–60° on grafted PET. The hydrophilic–hydrophobic transition on the contact angle observed by increase of the temperature correlates to the roughness of PNIPAAm grafted surface observed by AFM. In addition, the dyeing intensity of Methylene Blue observed on the grafted PET surface is significantly higher than the observed in virgin or oxidized surface PET and PS, even at ambient temperature.

It is known that to enhance bio-interactions the surface should not be extremely hydrophobic or hydrophilic [3]. The best situation is a co-existence of the two conditions or an amphiphilic surface. For instance, adherent cells grow easily in a surface with DWCA between 45° and 60° [3, 24].

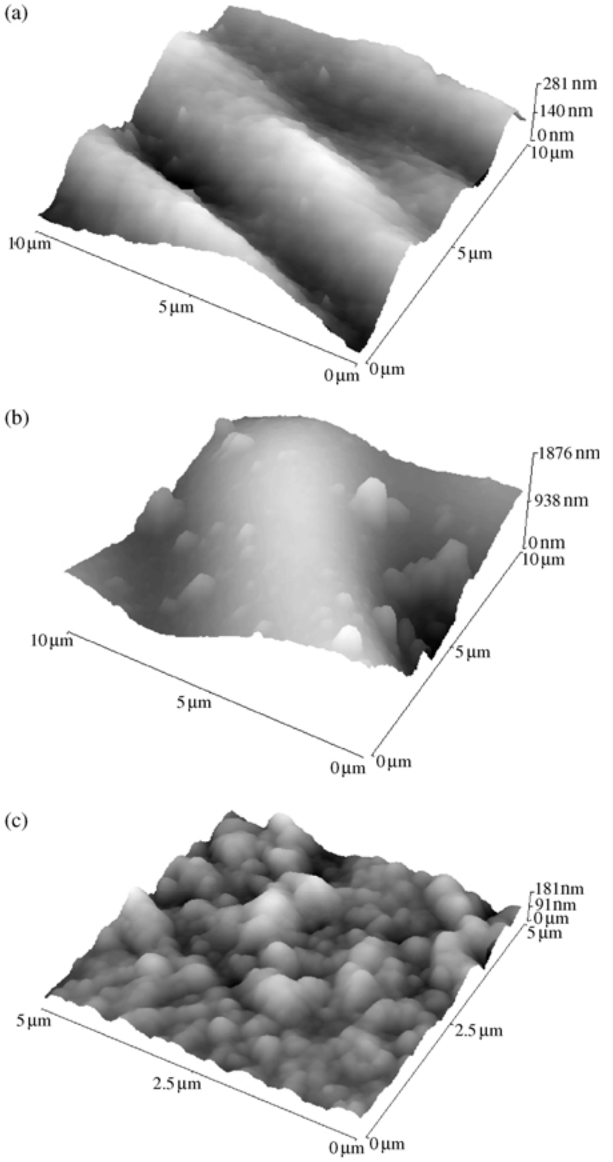

Figure 9 AFM images of PET: (A) virgin; (B) oxidized, and (C) grafted by two-step method.

4. Conclusions

In this work, PNIPAAm was incorporated into previously oxidized PS and PET surfaces by grafting using two photo-initiation pathways: one-step method, using AQS as sensibilizer and further exposure to a UV lamp (360 nm, 8 W) as light source; two-step method, using the incorporation of DMAAm in the first step and in second step KIO_4 was used as sensibilizer and further exposure to Hg lamp (254–580 nm, 215 W). The incorporation was observed by drop water contact angle measurements, dyeing with Methylene Blue and AFM images analysis of the virgin and modified polymers. It was verified that the grafting process depends on the chemical surface environment. Previous oxidation of PS and PET is essential to graft PNIPAAm using the Hg lamp. This is not necessary for graft into PS if the one-step method is used. For the PET, the oxidation is necessary to graft using the one-step or the two-step methods. The grafted surfaces are hydrophilic below 32 °C and hydrophobic above this temperature. The transition is due to the PNIPAAm incorporated. This characteristic gives to the grafted materials potential to be applied as biomaterials.

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