Chinese Journal of Polymer Science Vol. 26, No. 3, (2008), 1–9

Chinese Journal of Polymer Science

CHEMICAL MORPHOLOGY IN GRAFTING ACRYLAMIDE TO POLYETHYLENE*

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Abstract The paper demonstrates the use of scanning force microscopy (SFM)/chemical force microscopy (CFM) to study the growth of grafted polyacrylamide (PAM) chains onto polyethylene (PE)-film with varying grafting time. Results from the CFM reveal reduced interaction between the probe and areas with grafted-PAM on the surface. The topography and the friction trace-minus-retrace (TMR) images are complementary to one another resulting from the reduced interaction of the probe that has specificity to chemical domains.

Keywords: Chemical force microscopy (CFM); Grafted polyacrylamide; PE-film.

INTRODUCTION

In the advancement of polymer materials, it has been essential to modify and tailor-made the properties of a polymer for specific applications. Surface grafting is a method of modification in which only the surface is modified without changing the properties of the bulk. In this way, one reduces the cost of modifying the entire piece of a product when only the surface requires specific function. At the same time, one can also utilize the desirable properties of the bulk. Several surface modification methods can be found in the literature: plasma treatment, chromic acid treatment, and surface grafting[1–14]. Some of the advantages of surface grafting are that it is relatively easy and has controllable grafting process that would yield high density of grafted chains. Because grafting of the surface may only be a small portion, difficult for detection, some of the questionable proof of grafting is yet to be investigated.

In this work, we demonstrate the use of chemical force microscopy (CFM) in studying the surface grafting process of polyacrylamide (PAM) onto polyethylene (PE)-film. CFM is a type of scanning force microscopy (SFM). Ordinary SFM can differentiate the surface chemical properties by sensing the difference in interactions between a sample and a probe tip. Chemical modification of a probe surface can enhance differentiation of the different chemical domains on a sample surface[15, 16]. Probe modifications are mainly carried out using self-assembled monolayers (SAMs) or organosilane with various functional terminal groups. This provides chemical function specificity on the probe surface.

The grafting of PAM onto PE-film is to be investigated because PE is a type of polyolefin that has one of the world largest volume consumption and is of the simplest in terms of composition[17]. However, PE has difficulty in terms of adhesion with applications such as, printing, coating, composites, *etc.* PE surfaces are inert and nonpolar as a result of their long aliphatic chains of hydrocarbon consisting of only carbon and hydrogen[18]. For this reason, there have been several attempts in modifying the PE surfaces so they would be more polar and have better adhesion. PAM is grafted onto PE to improve PE's adhesion properties. Because PAM has amide

* This work was financially supported by the NSTDA for Science and Technology Scholars funding and the MTEC Young Research Group funding MT-NS-45-POL-14-06-G.

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Received March 29, 2007; Revised May 21, 2007; Accepted June 5, 2007

group that can enhance adhesion with various epoxy composites systems or can also enhance adhesion with biological specimen containing proteins.

The paper will demonstrate the use of SFM/CFM to study the growth of grafted PAM chains onto PE-film with varying grafting time. Results from the CFM reveal reduced interaction between the probe and areas with grafted-PAM on the surface. The topography and the friction trace-minus-retrace (TMR) images are complementary to one another resulting from the reduced interaction of the probe that has specificity to chemical domains.

EXPERIMENTAL

Materials

Commercial silicon nitride probe-cantilever assemblies were purchased from Veeco Store, USA. Trichlorooctadecylsilane ($C_{18}H_{37}SiCl_3$) (to be called in short as silane), 30% H_2O_2, 98% H_2SO_4, ethanol, and toluene were purchased from Merck KG, Darmstadt, Germany. Paraffin wax was purchased from Sigma Co., Ltd., U.S.A.

Low-density polyethylene (LDPE) film was purchased commercially. Acrylamide (AAm) monomer, potassium persulfate ($K_2S_2O_8$), and ceric ammonium nitrate [$(NH_4)_2Ce(NO_3)_6$] were purchased from Fluka. Nitric acid (HNO_3) was purchased from Merck KG, Darmstadt, Germany.

Instruments

All image force mapping data collection was performed using a commercial Nanoscope IIIa Multimode scanning force microscope (Veeco Digital Instrument). Commercial silicon nitride tip-cantilever assemblies probes were purchased from Nanosensors. The cantilever has a nominal spring constant of 0.58 N m^{-1}. SFM probe modification was done in a two-liter vacuum chamber equipped with a rotary vacuum pump.

Image Force Mapping Data Collection

The mode of operation for all experiments was done using the contact mode, but scanned laterally to the orientation of the cantilever. The scan size was 15 μm × 15 μm. The scan rate was at 1 Hz.

SFM Probe Silane Modification with —CH_3 Functional Group

The SFM probe was first cleaned in a solution mixture of 7:3 (*V*:*V*) of H_2SO_4 and H_2O_2 for 30 min at 50°C and then rinsed with deionized water. The probes must be kept in deionized water. Probe modification was done in a two-liter vacuum chamber equipped with a rotary vacuum pump.

A Petri dish filled with paraffin wax support was first placed in the vacuum chamber. The chamber was pumped down for 2 h to degas the paraffin support. After 2 h, the vacuum was broke opened and 200 μL of silane was placed on the paraffin support. Selected cleaned SFM probes were attached on a glass slide and placed over the Petri dish. The chamber was closed once again and pumped down for 2 h. The probes were kept under the saturation of silane vapor for 1 week. Then probes were taken out and washed with toluene, ethanol and deionized water then dried with nitrogen gas.

PE-Film Surface Modification

Hydroxylation of PE film

The LDPE film was cut into strips of 2 × 10 cm^2, washed with acetone to remove any adsorbed additives on the surface, and dried at room temperature. Each strip was hydroxylated with a 10% w/v $K_2S_2O_8$ aqueous solution each in an individual test tube. Each tube was de-aerated by bubbling N_2 gas into the solution for 1 min. The reaction was allowed to proceed at 80°C for 3 h and was vigorously shaken every 30 min. At the end of reaction, the samples were removed and washed several times with hot water and dried at room temperature. Hydroxylation was consistent for all films. This process assumed approximately equal grafting sites for all films.

Grafting of hydroxylated film

After hydroxylation, each strip was subjected to the grafting reaction in individual test tube. The solution consists of 3 × 10^{-3} mol/L ceric ammonium nitrate and 7% w/v of AAm in 0.05 mol/L HNO_3. Nitrogen gas was

slowly bubbled through the reaction medium for at least 1 min to remove oxygen gas. The temperature of the reaction was kept at 50°C. The grafting time was varied from 0 to 5 h. After grafting, the grafted films were washed thoroughly with hot water and soaked overnight to remove the residual monomer and homopolymer trapped in the films. It was ascertained that no homopolymer was extracted on further soaking. The films were dried at room temperature and weighed.

RESULTS AND DISCUSSION

Figure 1 shows SFM topography images of hydroxylated PE-*g*-PAM with varying grafting time from 0 to 5 h. The bright spots are expected to be the grafted PAM. With increasing grafting time, the grafted PAM grew bigger. As there are equal number of grafting sites and equal number of acrylamide monomer available, after 3 h, the PAM nodules are almost of the same size as the 5 h shown in Fig. 1(e) and Fig. 1(f), respectively. This indicates that the grafting has approached a plateau after 3 h, a pattern generally observed in surface grafting[19–21]. This results from the depletion of active sites and monomers with increasing grafting time.

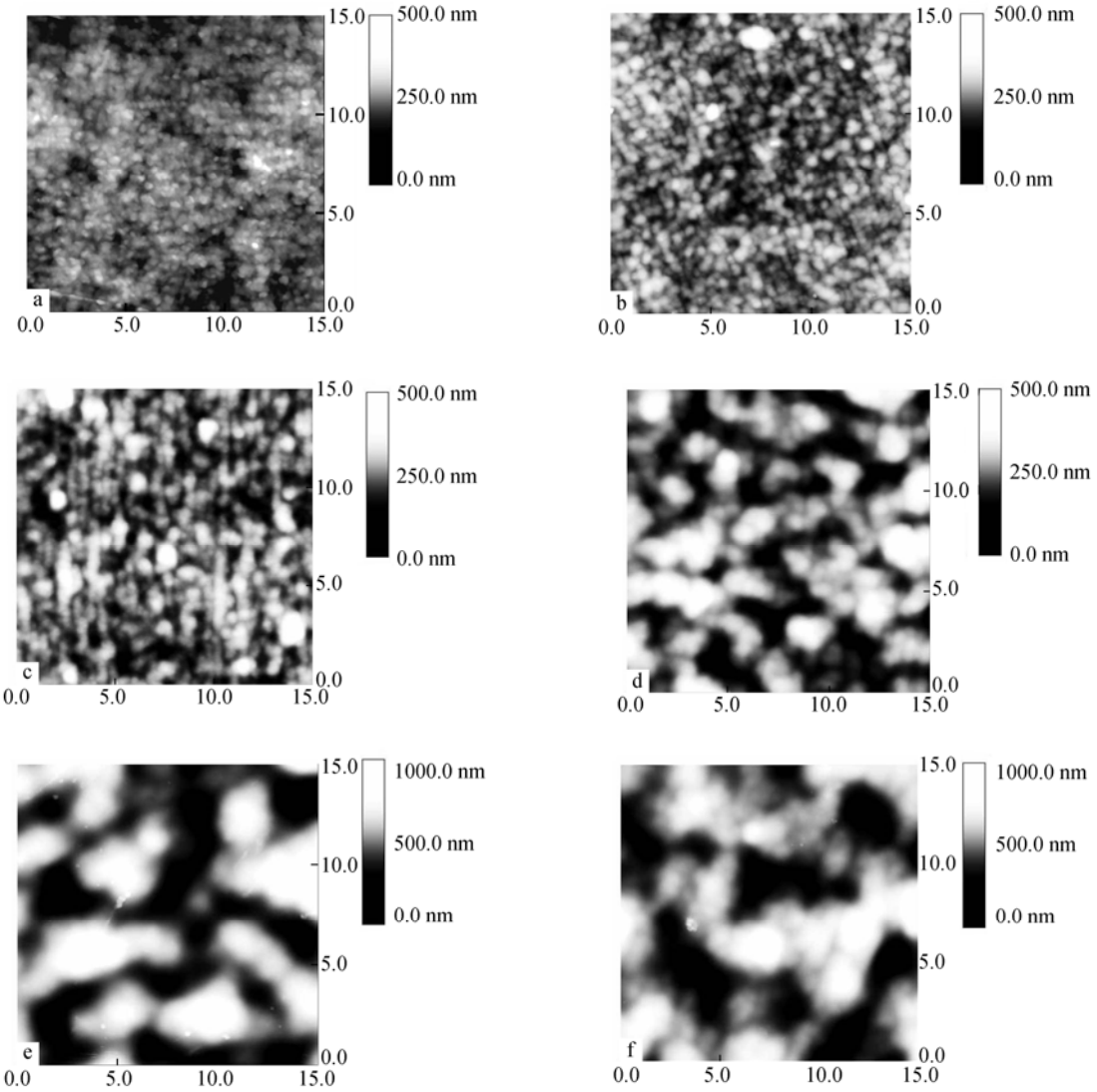

Fig. 1 SFM topography images of PE-*g*-PAM with (a) 0 h, (b) 0.5 h, (c) 1 h, (d) 2 h, (e) 3 h and (f) 5 h grafting time

Figure 2 shows CFM topography images of the same sample as in Fig. 1, but scanned with chemically

modified SFM probe (to be called in short, CFM probe). The probe has been modified to have $-CH_3$ end groups that is nonpolar. Hence, the CFM probe should show higher interaction to PE than PAM, because PE is composed of nonpolar group, *i.e.*, $-CH_2-$ while PAM has $-NH_2$ group that are considered to be polar. This is because nonpolar-nonpolar ($-CH_3-CH_2-$) van der Waals interaction is found to be larger than van der Waals forces for dissimilar pairs (nonpolar-polar), *e.g.* $-CH_3-NH_2$[22]. This result agreed well with Vegte and Hadziioannou detailed study of $-CH_3$ functionalized probe interaction to various substrates including $-NH_2$[23]. Figures 1 and 2, however, show great similarity. This is because they are only topography images. Topography images trace the deflection of the cantilever as the cantilever scans over the surface of the specimen measuring the *z*-axis, *i.e.*, the height variation of the surface not the chemical interaction. The topography and sizes of the nodules being very similar in Figs. 1 and 2, it allows us to claim that in chemically modifying the SFM probe with organosilane does not reduce the xy-resolution of the probe or at least not detectable for the particular scan size.

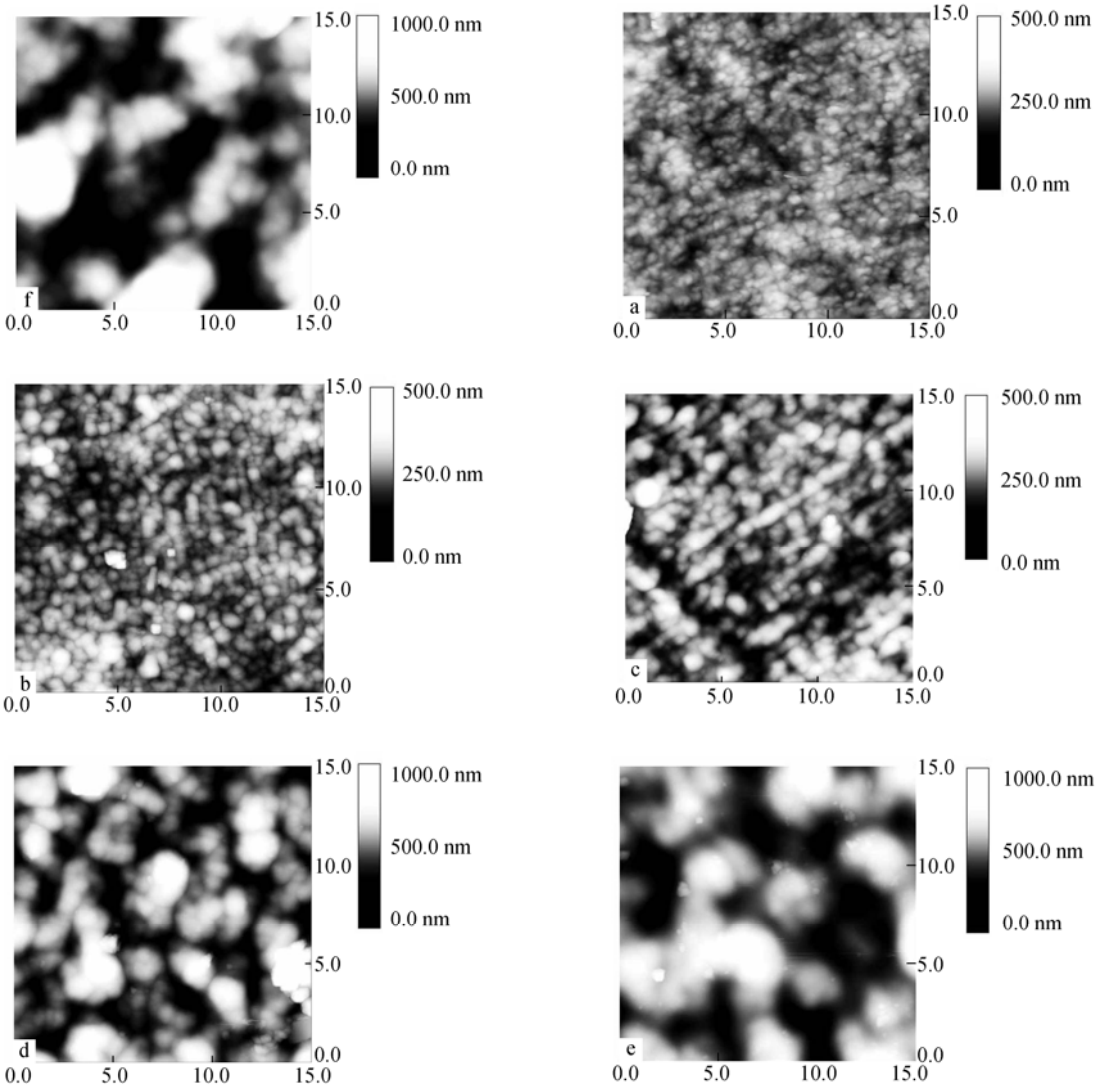

Fig. 2 CFM topography images of PE-*g*-PAM with (a) 0 h, (b) 0.5 h, (c) 1 h, (d) 2 h, (e) 3 h and (f) 5 h grafting time

To detect chemical interaction between the probe and the specimen, a technique known as lateral force

(LFM) or frictional force microscopy (FFM) was performed. This is done by scanning the specimen in a lateral direction to the orientation of the cantilever. In doing so, a post-data processing has also to be performed to correct for imaging that may result from the height difference, this is known as trace-minus-retrace (TMR). In doing LFM, three images are collected simultaneously: the topography image, the friction trace image, and the friction retrace image. Topography image is collected for comparison, giving information regarding the *z*-axis. Subtracting the retrace image from the trace image results in what is known as the TMR image. Figure 3 simulates how doing TMR cancel out the topography information and putting forward only the friction or the chemical interaction information.

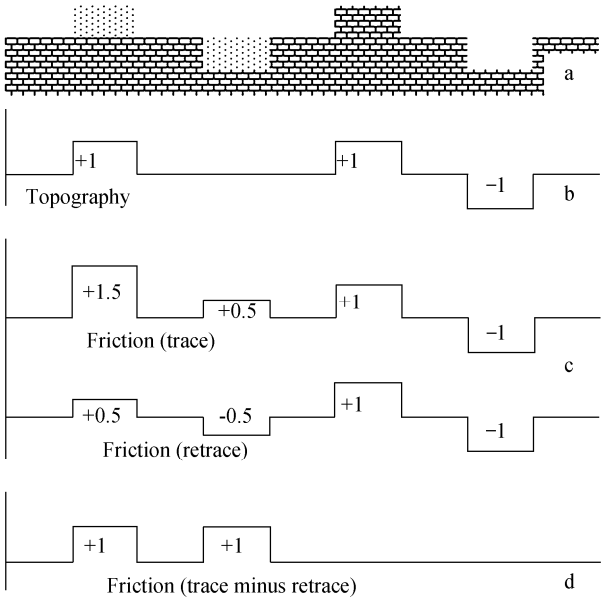

Fig. 3 Illustration of lateral force microscopy trace-minus-retrace (TMR) data processing where only the difference in friction will be reflected in TMR images
a) Simulated surface with two types of materials having different friction and also area with only height differences; b) Topography profile of the simulated surface; c) Friction (trace) and (retrace) profile where both friction and height information are coupled together. But with friction (trace) and (retrace) information, they have opposite signs; d) Result of trace minus retrace profile, leaving only the frictional information

Figures 4(a) and 4(b) are the friction TMR images from SFM and CFM probes, respectively. Figures 1(c) and 2(c) are the topography images collected simultaneously with Figs. 4(a) and 4(b), respectively. Figure 4(a) show similar information as was detected in the topography image, Fig. 1(c). This means that friction TMR image (Fig. 4a) detected little of the chemical domain differences, PE or PAM. But for the friction TMR image from CFM probe, Fig. 4b, a noticeable difference between its topography image can be observed. Figure 4(b) showed grooves complementary to the topography image of Fig. 2(c). Note here, areas that appeared as grooves (dark areas) in friction CFM TMR images are not the physical topography grooves, but correspond to lesser chemical interaction. As mentioned earlier, nonpolar-nonpolar interaction ($-CH_3$ probe and $-CH_2-$ PE-film) is higher than nonpolar-polar interaction ($-CH_3$ probe and $-NH_2$ grafted PAM). The light areas in the friction CFM TMR images resulted from the higher chemical interaction between the $-CH_3$ functional group on the CFM probe to the nonpolar PE-film beneath the grafted PAM. It may also be stated that the complementary grooves have resulted from the lesser interaction of the CFM probe to the grafted PAM. The grafted PAM which dominantly gave rise to topography differences on the specimen surface was observed as dark areas in Fig. 4(b). The PE-film complementary to grooves in Fig. 2(c) were detected by the CFM probe as light areas (stronger interaction) in Fig. 4(b). SFM TMR frictional images were also performed for all grafting time and result in images similar to Fig. 4(a) (not shown here).

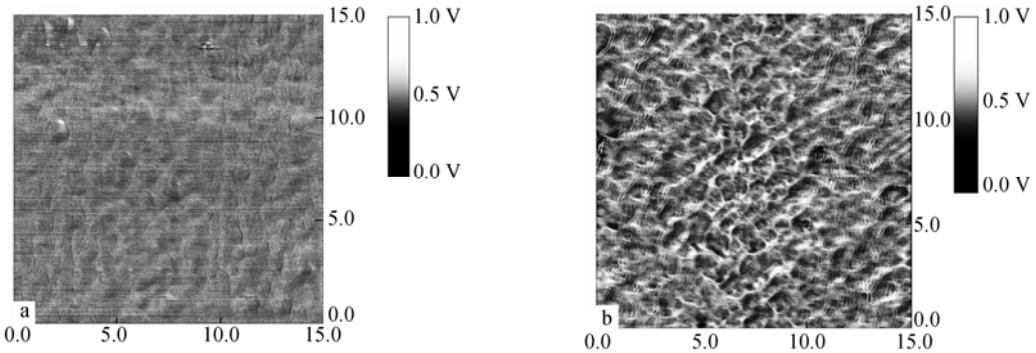

Fig. 4 PE-*g*-PAM images with 1 h grafting time of (a) SFM friction trace-minus-retrace and (b) CFM friction trace-minus-retrace

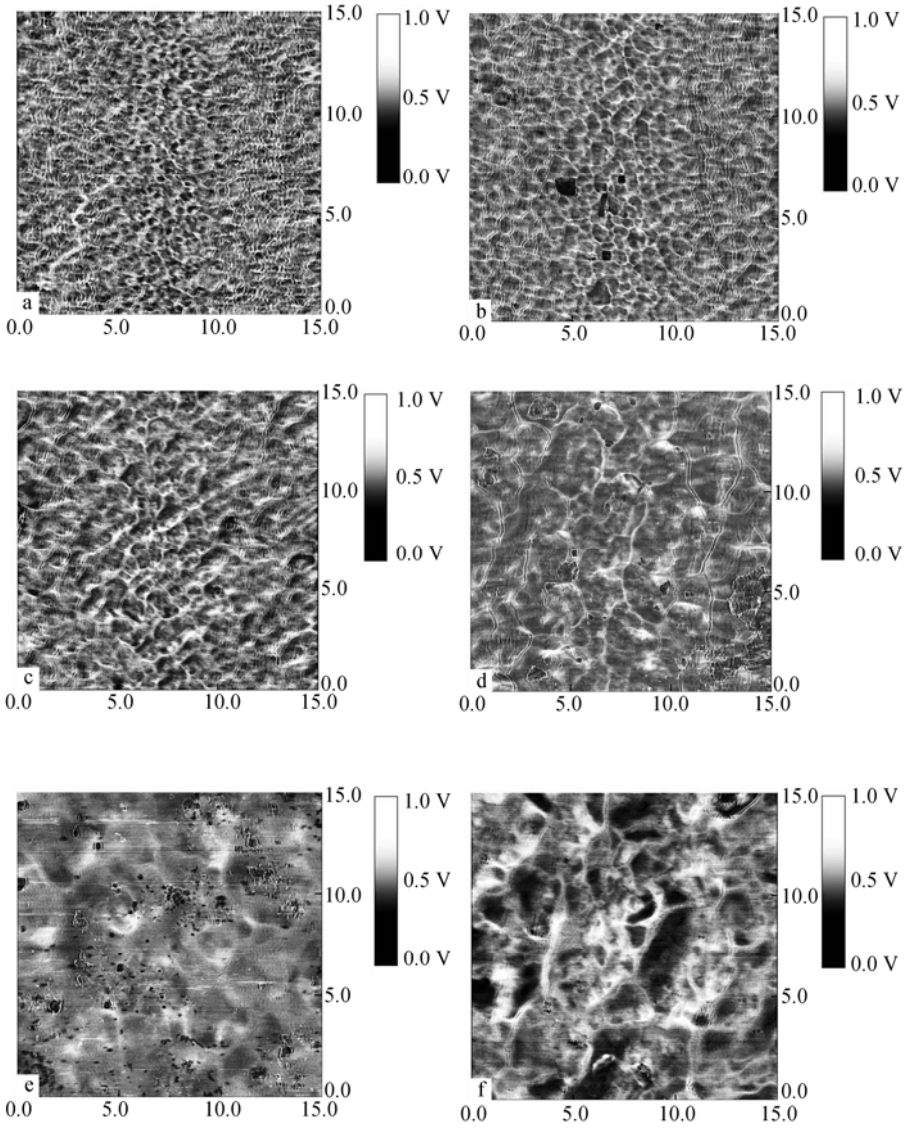

Fig. 5 CFM friction trace-minus-retrace of PE-*g*-PAM images with (a) 0 h, (b) 0.5 h, (c) 1 h, (d) 2 h, (e) 3 h and (f) 5 h grafting time

Figure 5 shows the CFM friction TMR images with the various grafting time. Images in Fig. 5 were collected simultaneously with images in Fig. 2. In Fig. 5, the strong interaction indicated by light areas corresponds to the PE-film. Dark areas (in Fig. 5) are complementary grooves correspond to PAM domains light areas (in Fig. 2). The trend of grafted PAM in Fig. 5 is the same as that of in Figs. 1 and 2. In Fig. 5(a), however, without grafted PAM, complementary grooves to that of Fig. 2(a) is still being observed. This is because the PE-film has been hydroxylated. In the hydroxylation process, the PE-film has been functionalized with —OH group. Therefore, lesser interaction to the $-CH_3$ functionalized probe. Vegte and Hadziioannou had shown that interaction of $-CH_3$ functionalized probe to —OH substrates has equivalent interaction to that of $-NH_2$[23]. At the edges on the topography image (Figs. 1 and 2), higher interaction to the PE-domains (indicated by light areas in Fig. 5) can be explained that during the hydroxylation process, these areas were hydroxylated less. When observed with the CFM TMR frictional image a higher interaction to the PE domains was measured. And with the variation in contrast, in Fig. 5(a), it can be stated that the hydroxylation process is not uniform. Hydroxylation process in solution commonly yielded a non-uniform surface.

Figures 6 and 7 compare unhydroxylate film to hydroxylated one with 0 h grafting time for topography and TMR images, respectively. With the topography images in Fig. 6, it is unidentifiable whether the film had been hydroxylated or not. But in Fig. 7, comparing between the TMR SFM image (Fig. 7a) and the TMR CFM image (Fig. 7b) of the unhydroxylate film, the images showed similar features. But with hydroxylated film, CFM (Fig. 7d) image shows chemical domains of hydroxylated sites being the dark areas (lesser chemical interaction between the —OH substrates to the $-CH_3$ functionalized probe) and lighter areas of higher chemical interaction between the nonpolar-nonpolar ($-CH_3$ probe and $-CH_2-$ substrate) interaction.

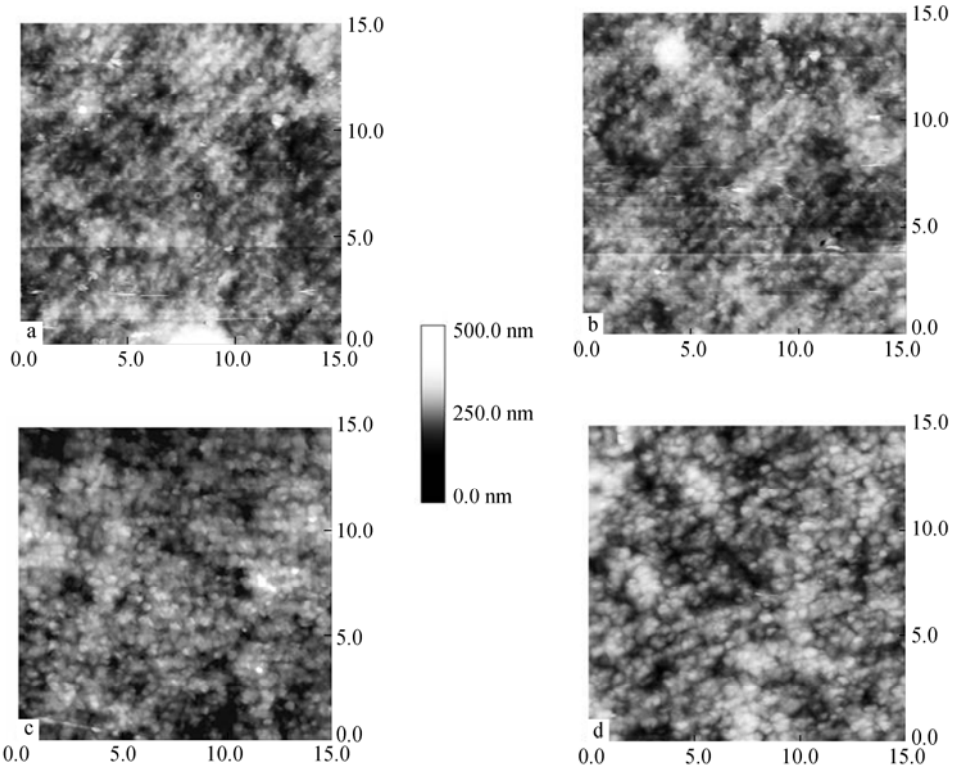

Fig. 6 Topography images of (a) SFM unhydroxylate film, (b) CFM unhydroxylate film, (c) SFM hydroxylated film 0 h grafting and (d) CFM hydroxylated film 0 h grafting

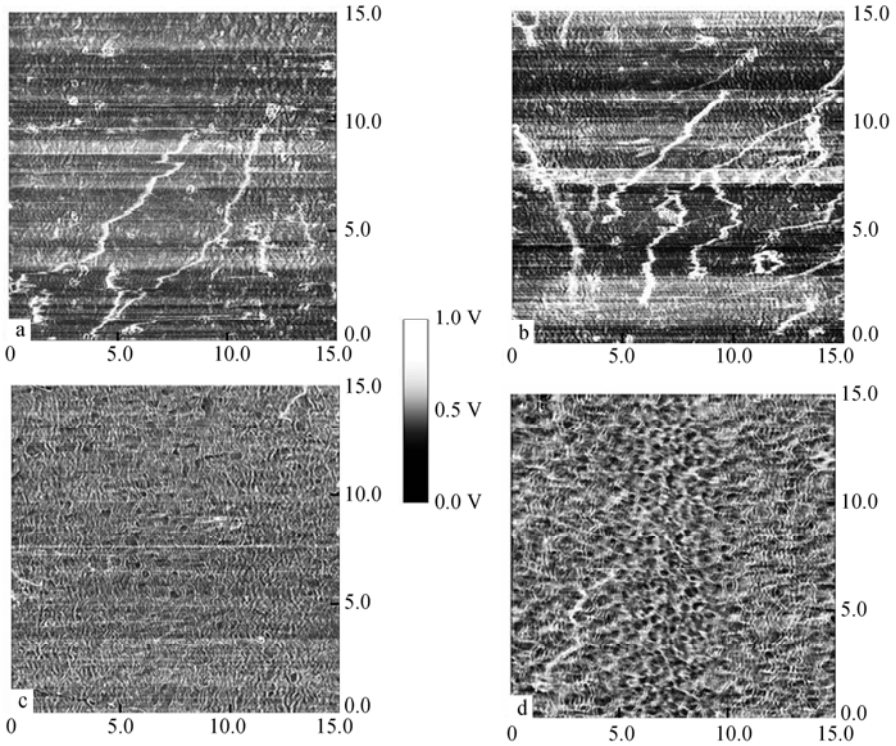

Fig. 7 TMR images of (a) SFM unhydroxylate film, (b) CFM unhydroxylate film, (c) SFM hydroxylated film 0 h grafting and (d) CFM hydroxylated film 0 h grafting

CONCLUSIONS

A few points can be concluded from this work. (1) For a given area with a specific number of grafting sites and monomers available, 3 h would be the maximum grafting time. (2) Topography image does not reveal chemical interaction. The topography and sizes of the PAM nodules being very similar from SFM and CFM probes indicate that in chemically modifying the SFM probe with organosilane does not reduce the xy-resolution of the probe. (3) Using lateral force microscopy (LFM) together with $-CH_3$ functionalized CFM probe, grooves complementary to the topography image indicate specific chemical interaction between the functionalized groups on the CFM probe to the nonpolar PE-film beneath the grafted PAM. (4) In the hydroxylation process, the PE-film is functionalized with $-OH$ group. Lesser interaction with the CFM probe has also been observed with 0 h grafting time. It can also be revealed that hydroxylation process was not uniform. Light areas on the CFM friction TMR images correspond to high PE interaction; indicating no hydroxylation in these areas.

ACKNOWLEDGEMENT The authors wish to acknowledge the facilities provided by the Nano-imaging Unit, Faculty of Science, Mahidol University.

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