Full Length Research Paper

Study on the morphology of polyacrylamide – silica fumed nanocomposite thin films

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Silica fumed nanoparticles were dispersed in polyacrylamide thin films by direct mixing. Atomic Force Microscopy study was carried out in order to analyze the surface roughness. Height distribution of surface roughness changes from Gaussian like for polyacrylamide to skew asymmetric when increasing the silica concentration. The length of the distribution tail increases, indicating the formation of multi-scale features that increase in number and size, as the silica increase.

Key words: Polyacrylamide, nanocompsite, surface roughness, AFM.

INTRODUCTION

In recent years, polymeric nanocomposites gained increasing attention in wide range of industrial applica-tions including coatings, electronics, and adhesives (Alexandre and Dubois, 2000; Tsukruk et al., 2002; Karttunen et al., 2008). If properly dispersed, fillers such as silica nano-particles can substantially improve the physical proper-ties of the resulting nanocomposites with respect to mi-crocomposites containing the same amount of filler; the reason for the improvement is the higher inter-facial area between the polymer matrix and filler in the nanocom-posite than in micro-composite, (Alexandre and Dubois, 2000; Lan and Pinnavaia, 1994). But also fillers change the surface morphology and nanoscale rough-ness of the polymer films leading to change in its optical, physical and chemical properties (Richard and Malhotra, 2006; Tjong 2006). Consequently, techniques with high sensiti-vity to the surface physical and chemical properties are required to reveal the nanoscale properties of nano-com-posites. Atomic Force Microscopy (AFM) is a powerful technique that can provide direct spatial mapping of sur-face topography with nanometer resolution (Cleveland et al., 1998). Tapping mode AFM, for example, often re-flects differences in the properties of individual compo-nents of heterogeneous materials deposited on surface,

and is useful for roughness measure-ments and composi-tional mapping of polymer nanocom-posites, copolymers, and coatings. (Raghavan et al., 2000; Raghavan et al., 2001; Gu et al., 2001; Bar et al., 1997; Frisbie et al., 1994). In the present work, the surface morphology and nanoscale roughness of a polymer nanocomposite thin films, namely silica fumed-polyacr-ylamide nanocompo-site used for coating capillary tubes (Alejandro and Jose 1998), prepared by thin film replication method (Sowwan et al., 2008) were studied using AFM.

MATERIALS AND METHODS

Materials

Polyacrylamide (PAam) with Mw 5,000,000 and silica fumed 7nm in diameter were purchased from Sigma-Aldrich Co. and used as received. All solutions were prepared in triple distilled water. Mica sheets (V-5 grade) substrates were purchased from SPI suppliers Co, USA. Glass microscopic slides were purchased from Paul Marienfeld GmbH &Co, Germ. Optical grade silicon window (Nicodom Ltd.).

Instruments

FTIR spectroscopy measurements were performed using a BRUKER IFS66/S spectrophotometer .A scanning atomic force mi-microscope and software designed by Nanotech Electronica com-pany (Madrid , Spain) were used for the surface roughness investigation (Horcas et al., 2007). A SiN tip with a resonance fre-

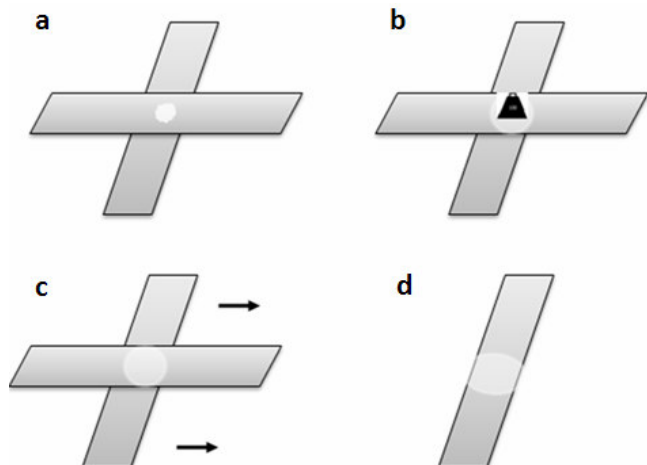*Corresponding authors. E-mail: msowwan@eng.alquds.edu

Figure 1. Schematic representation of the polymer replica preparation procedure (a) A droplet of 5µL of polymer solution were deposited on a pre-cleaned glass substrate surface (b) the substrate and a freshly cleaved mica sheet were pressed (0.5 N/cm^2) together for half minute (c) Sliding the mica sheet horizontally away from the glass surface with a constant speed of 0.5 cm/sec (d) Polymer replica on glass substrate.
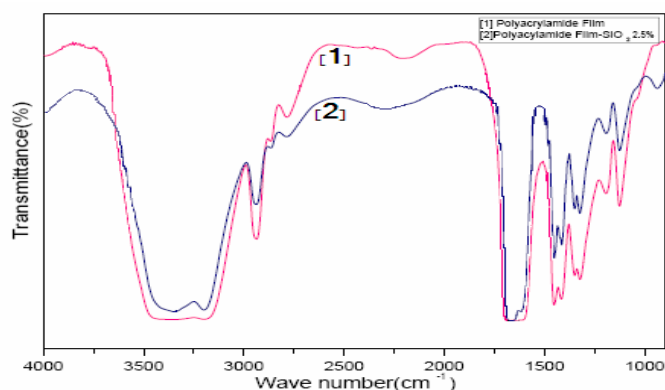

Figure 2. FTIR spectrum of [1] PAam film [2] PAam-Silica 2.5% (wt/wt).

frequency in the range 190-325 KHz and force constant in the range of 5.5-22.5 N/m with tip diameter 10 nm was used as the AFM probe. Tips were purchased from NT-MDT Company (Russia). A set of five frames of equal sizes of certain scale was taken from different areas of each sample surface, four different silica concentrations were tested and three samples of each silica concentration were measured.

Procedure

Preparation of the nanocomposite

To prepare PAam-Silica nanocomposites, 0.710 g of PAam was dissolved in 25 ml of triple distilled water, by gradual addition of silica nanoparticles solution to obtain the adequate concentrations of polyacrylamide – Silica. Different concentrations were prepared 2.5, 7.5, 10 and 15% (wt/wt).

Preparation of thin films

The nanocomposite thin films replicas were prepared in the following way. A droplet of 5 µL of polyacrylamide solution incorporated with silica fumed nanoparticles was deposited on a pre-cleaned glass substrate surface. Afterwards, the substrate and a freshly cleaved Mica sheet were pressed (0.5 N/cm^2) together for half minute, followed by sliding the Mica sheet horizontally away from the glass surface with a constant speed of 0.5 cm/sec, see Figure 1. The prepared replica on the glass substrate was dried in the oven at 40°C for over night. As a result, thin silica- polymer nanocomposite layers of approximately 5 µm thickness, as estimated from the volume of the droplet and the surface area of the compressed polymer (diameter = 2.5cm), were formed between the two surfaces.

RESULTS AND DISCUSSION

FTIR spectroscopy results

FT-IR spectrum of pure PAam film and PAam-Silica nanocomposites (2.5% wt/wt) are shown in Figure 2. The characteristic peaks of PAam and PAam-Silica nanocomposites at different silica concentrations are shown in Table 1, the peaks shift related to the NH$_2$ stretching and C=O, show clear interaction between the silica and the PAam.

AFM results

Figure 3a shows an AFM topography image of polyacrylamide thin film surface with a scan size of 2.5 µm^2. The corresponding surface roughness distribution is shown in Figure 3b. The Y axis represents the number of events (pixels in the image, 1 pixel ~ 5nm) while the X-axis represents the height of these events. For simplicity, Random Gaussian roughness were assumed, the distribution is symmetric Gaussian (blue), this can be seen from the excellent fit.

Figure 4 shows an AFM topography images of fumed silica-polyacrylamide nanocomposite thin films with (a) 2.5% (b) 7.5% (c) 10% (d) 15% (wt/wt) respectively. The corresponding surface roughness distribution is shown in Figure 5. The root mean square roughness (RMS) as a function of silica concentration is shown in Figure 6. The RMS roughness increase as silica increase. However, while the RMS roughness value of a sample surface can be useful, it can be also misleading (Figure 6 -pointers).

Two surfaces can have the same RMS roughness, but different topographies. A study of the surface roughness distribution shape can be effective tool in understanding and characterizing of nano-scale surface roughness. The distribution shape is changing from symmetric, for the pure polyacrylamide, into positively skewed asymmetric when adding the silica nanoparticles. The length of the distribution tail increase, which indicates the formation of multi- scale features that increase in size and number, as the silica increase. This result is consistent with the AFM topography images shown in Figure 4a-d. The Multi-

Table 1. FTIR Characteristic peaks of PAam and PAam – Silica nanocomposite.

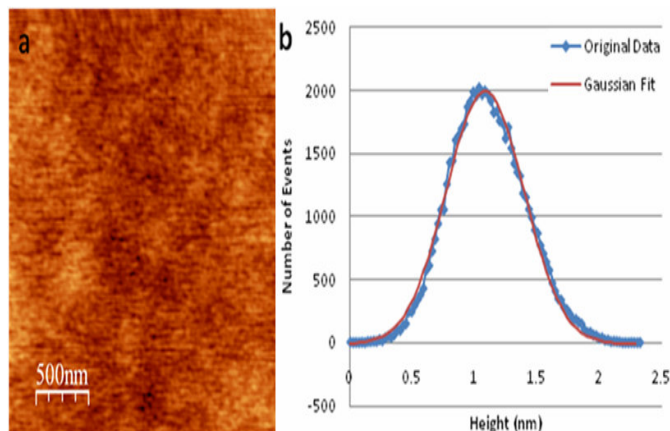| Materials	v_{as} (cm^{-1}) NH$_2$	v_s (cm^{-1}) CH$_2$	v (cm^{-1}) (C=O)	v (cm^{-1}) CH bending	v (cm^{-1}) CH wagging	v (cm^{-1}) NH rocking of NH$_2$
PAam	3353	2936	1658	1452	1324	1125
PAam-Si 2.5%	3347	2948	1676	1451	1323	1124
PAam-Si 7.5%	3344	2945	1665	1451	1323	1124
PAam-Si 10%	3344	2945	1658	1451	1323	1124
PAam-Si 15%	3344	2936	1659	1451	1323	1124

Figure 3a. AFM topography image 2.5 µm^2 scan of pure polyacrylamide thin film on glass substrate (b) Surface roughness height distribution (blue) and the Gaussian fit (Red). The Y axis represents the number of events (pixels in the image, 1 pixel ~ 5nm) while the X-axis represents the height of these events.
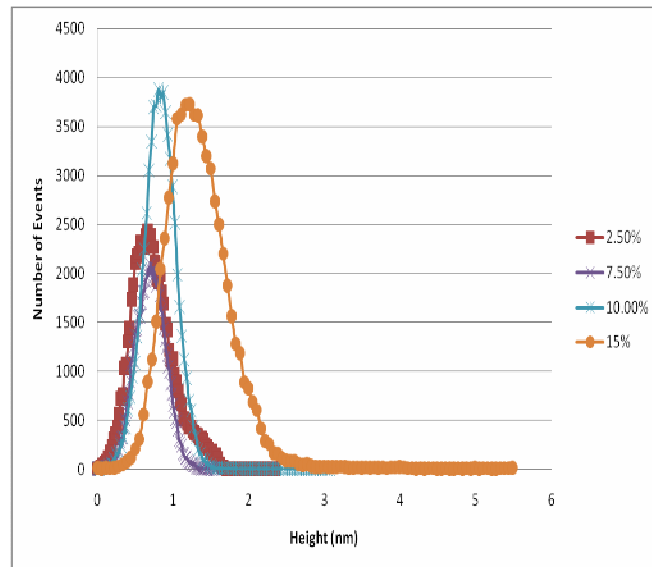

Figure 5. Surface roughness shape distribution of PAam-Silica nanocompsite thin film surface as a function of Silica concentration (wt/wt). The Y axis represents the number of events (pixels in the image, 1 pixel ~ 5nm) while the X-axis represents the height of these events.
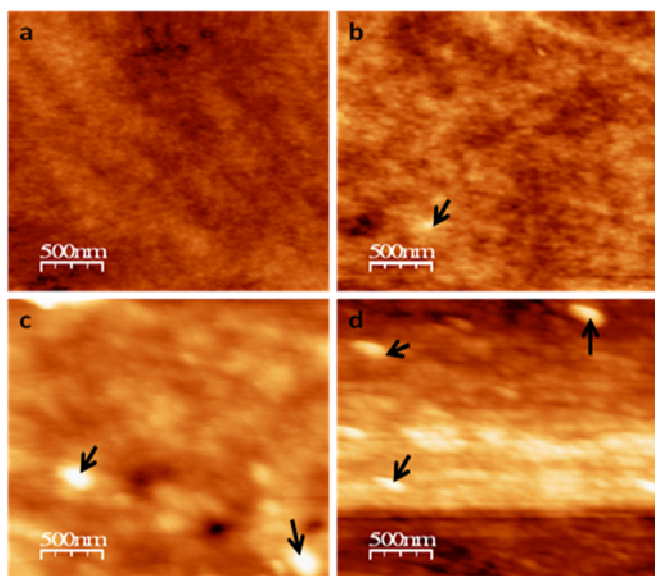

Figure 4. AFM topography images 2.5 µm^2 scan of PAam-Silica nanocomposite thin films surface with different Silica concentrations (wt/wt) (a) 2.5% (b) 7.5% (c) 10% (d) 15%. The Multi-Scale features are marked with small black arrows.
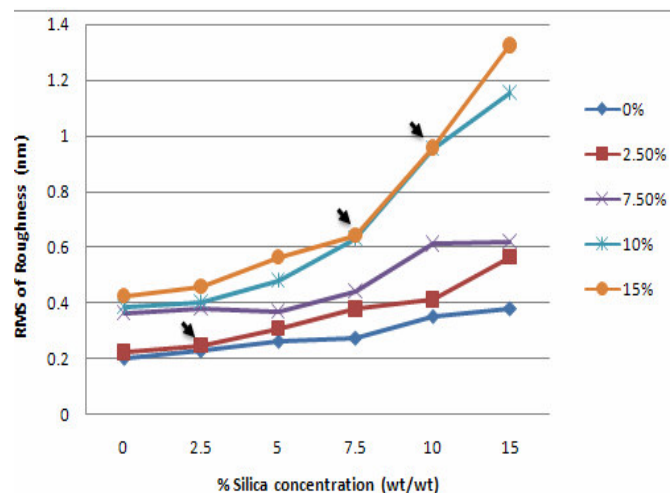

Figure 6. Root Mean Square roughness of PAam-Silica nanocompsite thin film surface as a function of Silica concentration (wt/wt).

Scale features are marked with small black arrows.

Conclusion

AFM study of PAam-Silica nanocomposite thin film replica surfaces on glass substrate showed that the surfaces tend to have a multi scale relief structure. The main component of this structure is the low scale Gaussian roughness. The surface roughness distribution analysis revealed various large-scale features, their size and number increase as a function of silica concentration and hence increase the root-mean-square roughness.

ACKNOWLEDGEMENT

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