

*Full Length Research Paper*

# Analysis, characterization and some properties of polyacrylamide-Ni(II) complexes

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The complexation of polyarylamide (PAam) with Ni(II) metal ions at different concentrations was investigated. The metal complexes were characterized by fourier transform infrared spectroscopy (FTIR), UV-visible, differential scanning calorimeter (DSC) and atomic force microscope (AFM). FTIR spectroscopy was used to study the characteristic shifts of the absorbance bands of C=O and N-H<sub>2</sub>. UV-visible spectroscopy was used to follow the complex formation of PAam-Ni(II) and showed the appearance of a new band that was absent both in PAam and Ni(II) salt solutions. Thermal parameters, such as the glass transition temperature (T<sub>g</sub>) and the melting point (T<sub>m</sub>) of the polymer-metal complex have been measured by DSC. The variation of T<sub>g</sub> and T<sub>m</sub> with different Ni(II) concentrations was attributed to the complexation of the native polymer during the increasing of Ni(II) concentration. AFM was used to study the surface morphology of PAam films and its complexation with Ni(II) at different concentrations. The root mean square roughness increased as the Ni(II) concentration increases.

**Key words:** Polyacrylamide, polymer metal complex, thermal properties, surface roughness, AFM.

## INTRODUCTION

Over the last two decades, extensive studies have been devoted to the study of polymer metal complexes. Coordination of water soluble polymers such as polyacrylamide (PAam) and poly acrylic acid (PAA) with metal salts have found wide applications in pollution control (Orazzhanova et al., 2003), waste water treatment (Mizuta et al., 2000), hydrometallurgy (Varvara et al., 2004), hydrogels (Varghese et al., 2001), and other applications (Fenger and Le Drian, 1998; Ahmed et al., 2004). Mathew et al. (1992) investigated the thermal properties of mixture of PAam and dithiocarbamate and synthesized its complexes using Cu(II), Zn(II), Co(II), Ni(II) and

and Hg(II). Diab and El-Sonbati have investigated the thermal properties of poly (ethylene glycol)-metal complexes with Co(II), Cu(II), Ni(II) and Cd(II) (Diab and El-Sonbati, 1990).

Gupta and Sutar (2007) have studied polymer-metal complexes and their catalytic activities in the oxidation of phenol. Poly (vinyl alcohol) with Cu(II) was investigated by means of Nuclear magnetic resonance (NMR) techniques (Yasuyoshi et al., 1995). In this study, the characterization and analysis of the coordination polymer of PAam-Ni(II) were investigated using fourier transform infrared spectroscopy (FTIR), UV-visible spectroscopy, differential scanning calorimeter (DSC) and atomic force microscopy (AFM).

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**Abbreviations:** PAam, Polyarylamide; FTIR, fourier transform infrared spectroscopy; DSC, differential scanning calorimeter; AFM, atomic force microscopy; TDW, triple distilled water; DSC, differential scanning calorimeter.

## MATERIALS AND METHODS

PAam and Ni(II) sulfate hexahydrate (NiSO<sub>4</sub>.6H<sub>2</sub>O) were obtained from Sigma-Aldrich Co. The average molecular weight of the polymer was  $5 \times 10^6$  Dalton. Mica sheets (V-5 grade) substrates

**Table 1.** The heating and cooling program used in the DSC measurements.

Ramp	20°C
Thermal equilibrium	1 min
Jump	- 40°C
Ramp	20 to 250°C (1st heating)
Ramp	20 to -40°C (Cooling)
Ramp	To 250°C (2nd heating)

**Table 2.** FTIR spectral data of PAam and PAam-Ni(II) complexes.

Materials	$\nu_{as}$ (cm <sup>-1</sup> )	$\nu$ (cm <sup>-1</sup> )	$\nu$ (cm <sup>-1</sup> )	$\nu$ (cm <sup>-1</sup> )
	NH <sub>2</sub>	C=O	CH <sub>2</sub> (s)	NH wagging
PAam	3353	1658	2936	1322
PAam-Ni(II) 5%	3347	1659	2946	1326
PAam-Ni(II) 7.5%	3347	1659	2950	1326
PAam-Ni(II) 10%	3347	1659	2946	1326

were supplied from SPI supplies Co, USA. All solutions were prepared in triple distilled water (TDW). All glasses used in sample preparations were scrupulously cleaned with chromic acid solution and rinsed with TDW.

#### Preparation of the PAam-Ni(II) complex

PAam was dissolved in TDW. Different concentrations of NiSO<sub>4</sub>·6H<sub>2</sub>O were prepared by dissolving in TDW. The aqueous solutions of Ni(II) were added gradually to the polymer solution with constant stirring to obtain polymer-metal complexes.

#### Instruments and measurements

For the FTIR measurements, 50  $\mu$ L of the sample solution was deposited on optical grade silicon window "NICODOM Ltd" and placed in an incubator at 40°C overnight to get a transparent film after complete evaporation of water. FTIR spectra were collected at room temperature on a BRUKER IFS66/S spectrophotometer in the wave number range of 400 to 4000 cm<sup>-1</sup> at a resolution of 4 cm<sup>-1</sup>. UV-visible spectra of the PAam-Ni complexes were studied in the form of transparent films prepared by pouring the solution into a glass Petridishes and then incubated overnight at 40°C for complete evaporation of water molecules. The measurements were taken at room temperature on a Perkin-Elmer lambda 5 UV- visible spectrophotometer with a variable wavelength between 200 to 800 nm. For DSC measurements, sealed aluminum cells were used with 10 mg mass sample and empty aluminum cell was used as a reference. Experiments were carried out in dry nitrogen atmosphere with a 40 ml/min flux. A heating and cooling program was used at a heating rate of 10°C/min as shown in Table 1. The measurements were performed using DSC 2920 modulated DSC (TA instruments).

AFM and software designed by Nanotech Electronics Company (Madrid, Spain) were used for the surface roughness investigation (Horcas et al., 2007). A SiN tip with a resonance frequency in the range 190 to 325 KHz and force constant in the range of 5.5 to 22.5 N/m with tip diameter < 20 nm was used as the AFM probe. Tips were purchased from NT-MDT Company (Russia). For the AFM measurements, 5  $\mu$ L of the sample solution at different Ni(II) concentrations was deposited on a freshly cleaved mica substrate and dried with nitrogen gas.

## RESULTS AND DISCUSSION

### FTIR measurements

In this study, different vibrational modes of pure PAam and PAam doped with Ni(II) at a concentration of 5, 7.5 and 10% wt/wt as shown in Table 2 were focused on. The FTIR results were shown in Figure 1, the peaks at 1658 cm<sup>-1</sup> and 3353 cm<sup>-1</sup> are strong peaks which are the characteristic band of the C=O and NH<sub>2</sub> stretching respectively.

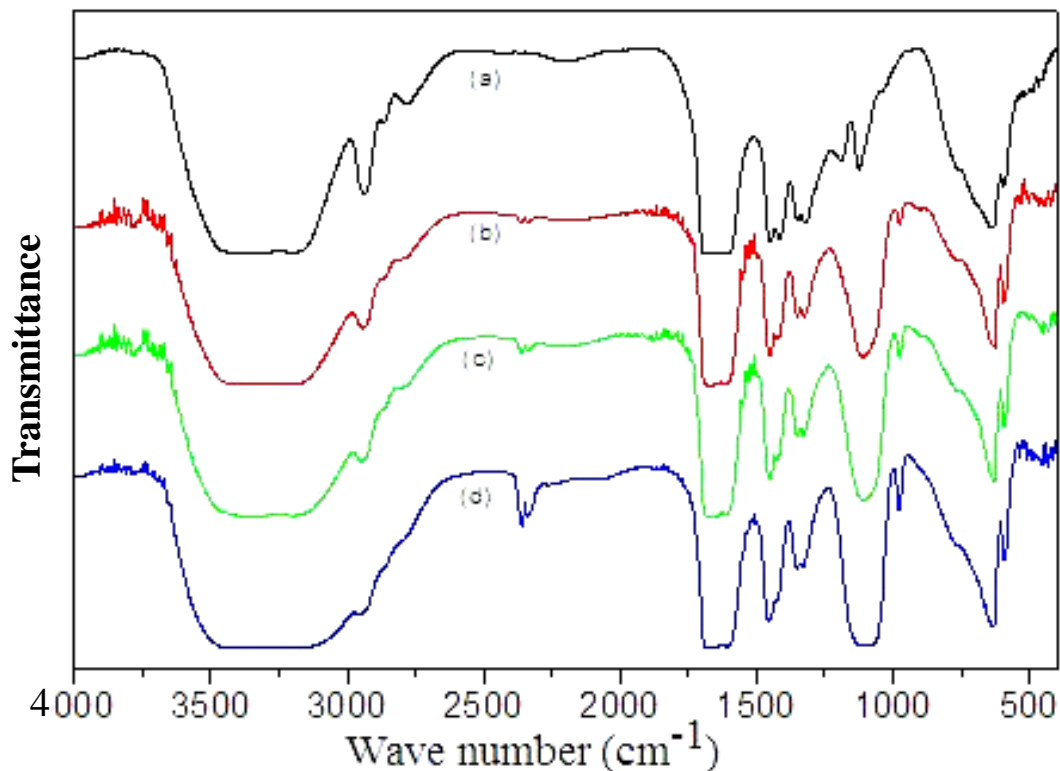
While the NH<sub>2</sub> band of pure PAam was shifted by 6 cm<sup>-1</sup> in the presence of Ni(II), the C=O band of pure PAam showed no change due to doping with Ni(II), which indicated that the coordination was to NH<sub>2</sub> groups as monodentate, as illustrated in Figure 2.

### DSC measurements

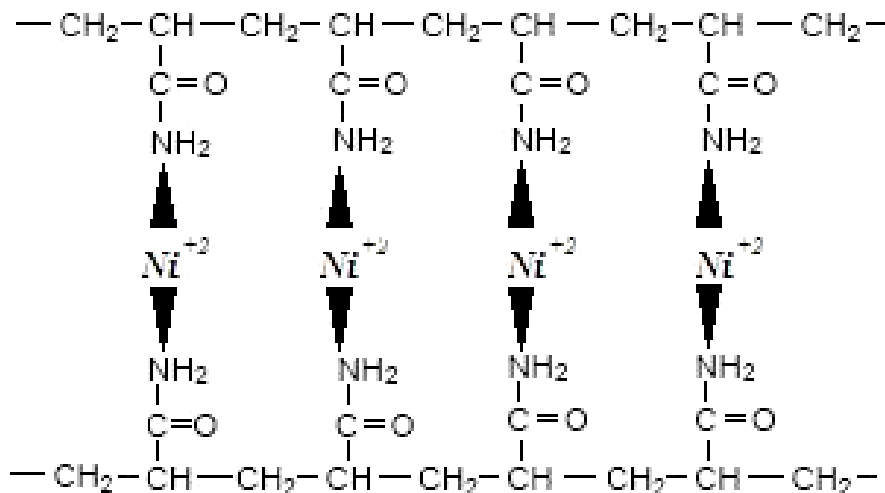
The thermogram of pure PAam was shown in Figure 3, the glass transition temperature ( $T_g$ ) and melting point ( $T_m$ ) of PAam were found at 161.4°C and 237°C respectively. The  $T_g$  and  $T_m$  of PAam-Ni(II) were shifted from that of pure PAam to 167.8°C and 255°C respectively as shown in Figure 4 for Ni(II) concentration of (5% wt/wt). This shift was due to the interaction that occurred between the hydrophilic part of PAam and Ni(II) metal ions.

### UV-visible spectroscopy measurements

The wavelength spectra were measured in the range of 200 to 800 nm. The UV-visible spectrum of pure PAam showed only one characteristic band at  $\lambda_{max} = 230$  nm as



**Figure 1.** FTIR spectrum of (a) PAam film (b) PAam-Ni<sup>2+</sup> 5% (c) PAam-Ni<sup>2+</sup> 7.5% (d) PAam-Ni<sup>2+</sup> 10%. NH<sub>2</sub> stretching vibrations of PAam and PAam-Ni(II) complexes were observed at 3353 cm<sup>-1</sup> and 3347 cm<sup>-1</sup> respectively. The carbonyl group (C=O) stretching vibrations of PAam and PAam-Ni(II) complex films were at 1658 cm<sup>-1</sup> and 1659 cm<sup>-1</sup> respectively.

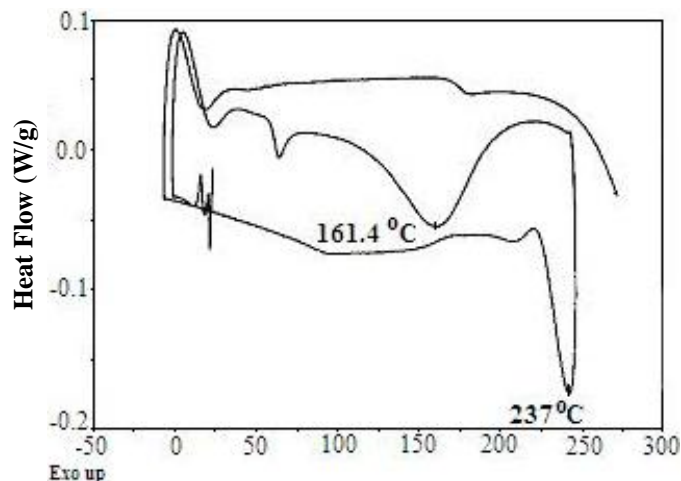


**Figure 2.** Schematic representation of the complex formation of PAam-Ni(II).

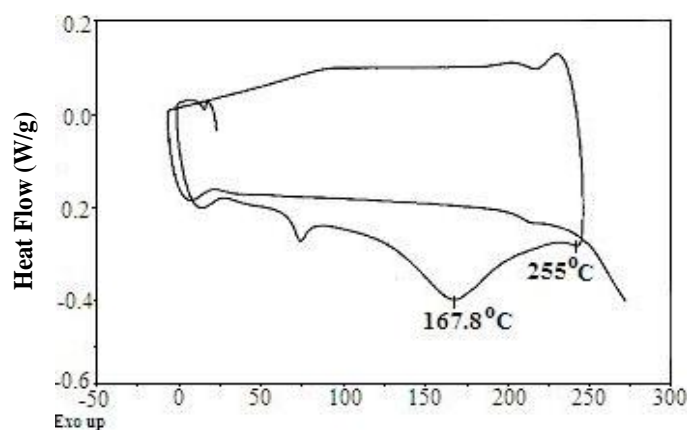
shown in Figure 5. The spectrum of Ni(II) ions solution was presented in Figure 6. The main bands appeared at  $\lambda_{\max}$  393.2 nm and 721.4 nm. The influence of the addition of Ni(II) was negligible on the characteristic band of PAam, however, a new band was observed at  $\lambda_{\max}$  = 285 nm PAam-Ni(II) as shown in Figures 7 and 8.

### AFM measurements

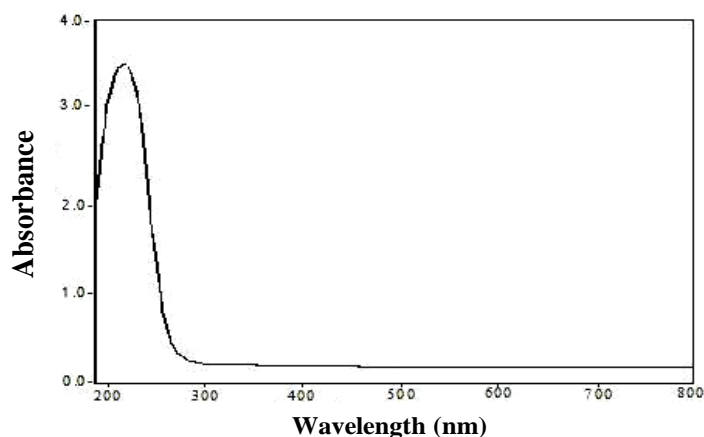
Tapping mode AFM was used to characterize the topographical features of the polymer film surface. The topographical surface of PAam film on cleaved mica surface was shown in Figure 9. AFM images of PAam-Ni(II)



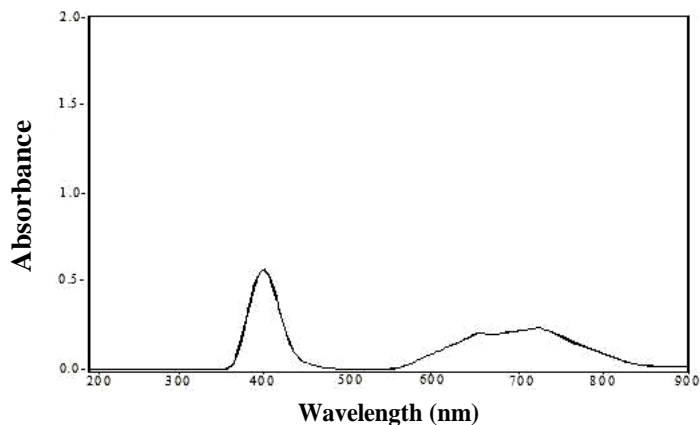
**Figure 3.** DSC thermogram of pure film polyacrylamide; the glass transition temperature ( $T_g$ ) and melting point ( $T_m$ ) were performed at 161.4 and 237°C, respectively.



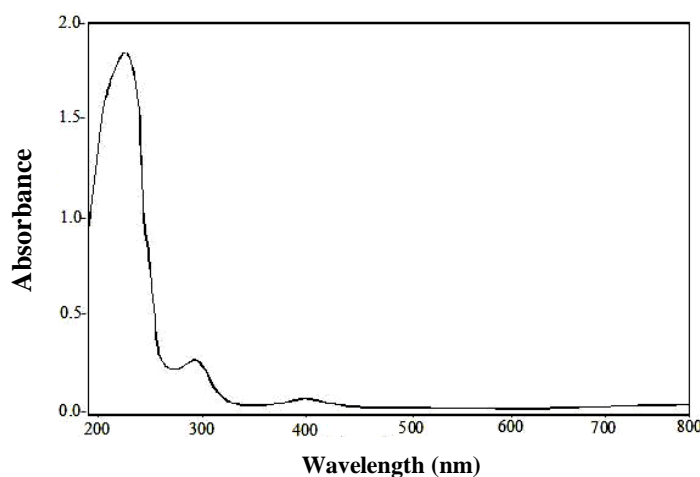
**Figure 4.** DSC thermogram of PAam-Ni(II) at 5% concentration; The glass transition temperature ( $T_g$ ) and melting point ( $T_m$ ) were performed at 167.8 and 255°C respectively.



**Figure 5.** UV-visible spectroscopy of Pure PAam; the characteristic band of PAam was observed at  $\lambda_{max} = 230$  nm.



**Figure 6.** UV-visible spectroscopy of Ni(II) solutions. The major bands of Ni (II) solution were appeared at  $\lambda_{max}$  393.2nm and 721.4nm.

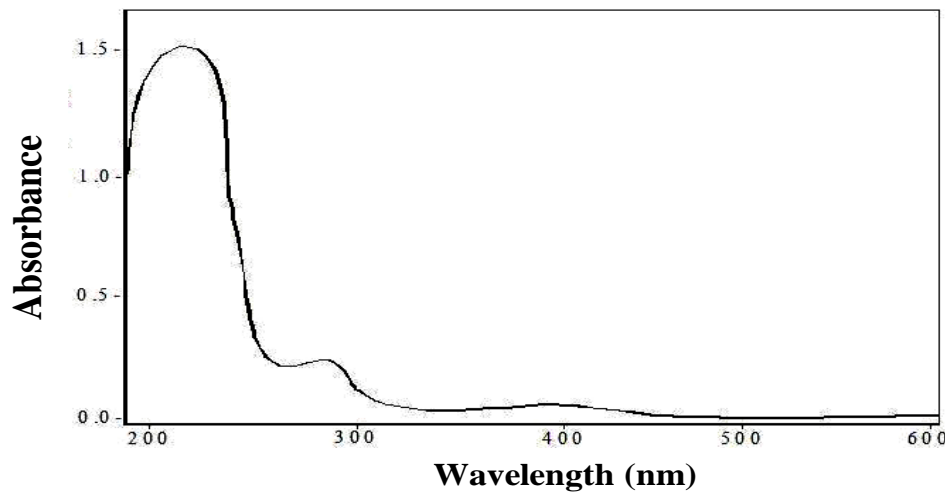


**Figure 7.** UV-visible spectroscopy of PAam-Ni(II) (5%). A new band transition was appeared at  $\lambda_{max} = 285$  nm due to the complexation with Ni (II) metal ions.

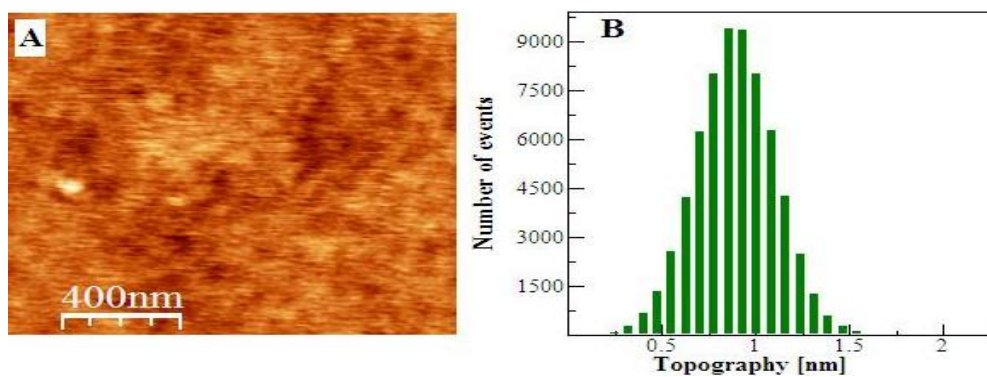
complexes based films at 2.5, 5, 10, and 15% respectively were shown in Figure 10. Addition of Ni(II) to a PAam solution was found to be effective in increasing the root mean square (RMS) roughness of the surface as shown in Figure 11. The increase was from 0.22 to 0.44 nm.

## Conclusion

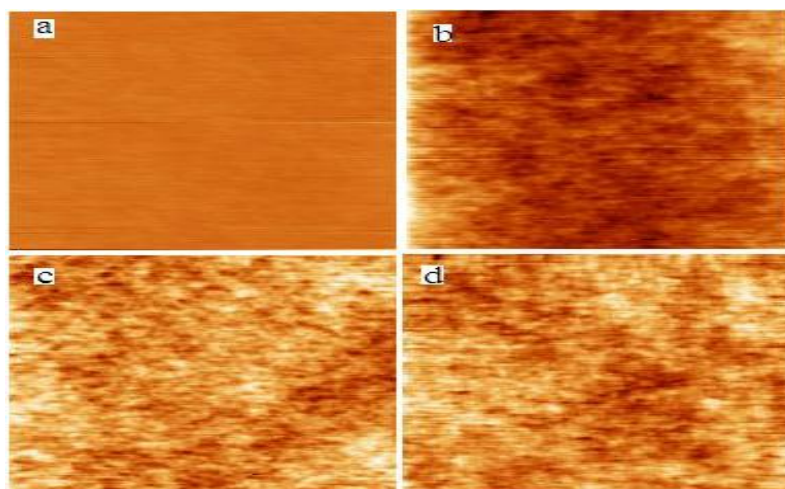
In this study, the complexation of the hydrophilic side-groups in PAam with Ni(II) ions using FTIR, UV-visible spectroscopy, DSC and AFM techniques were investigated. The FTIR spectrum of PAam-Ni(II) complexes showed characteristic absorption bands which are different from the spectra of pure PAam particularly in  $NH_2$  stretching vibration regions which indicated that the coordination was monodentate. In addition the UV-visible spectroscopy of PAam-Ni(II) showed the appearance of a



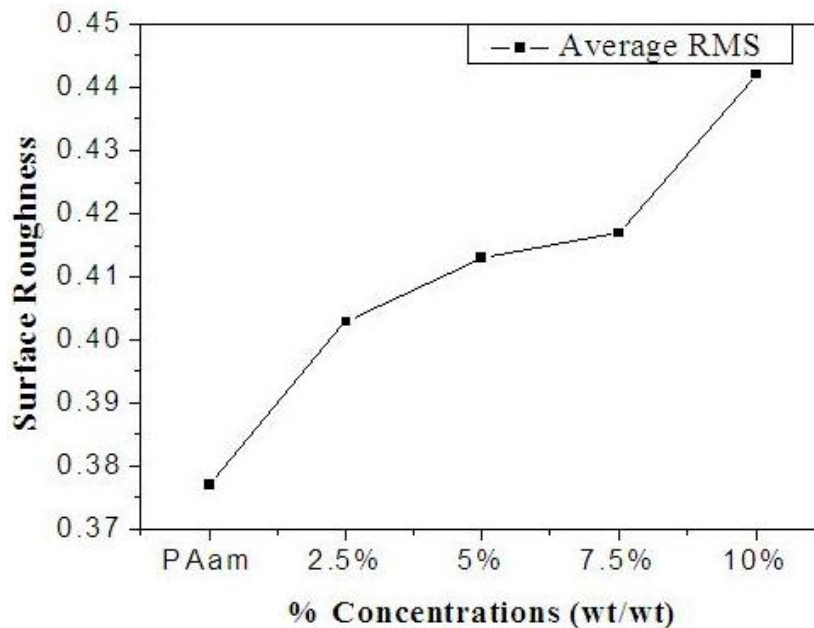
**Figure 8.** UV-visible spectroscopy of PAam-Ni(II) (10%). A new band transition was appeared at  $\lambda_{\text{max}} = 285$  nm due to the complexation with Ni (II) metal ions.



**Figure 9.** (a) AFM topography image  $2.5 \mu\text{m}^2$  scan size of pure PAam film on mica substrate (b) surface roughness height distribution. The Y axis represents the number of events (pixels in the image, 1 pixel  $\sim 5$  nm) while the X-axis represents the height of these events in nm.



**Figure 10.** AFM topography images ( $2.5 \times 2.5 \mu\text{m}$ ) scan of PAam-Ni(II) complex thin films surface with different Ni(II) concentrations (wt/wt) (a) 2.5% (b) 5% (c) 10% (d) 15%.



**Figure 11.** Root mean square roughness of PAam-Ni(II) complexes thin film surface as a function of Ni(II) concentration (wt/wt).

new peak around 285 nm which was absent in both polymer and metal salt solution.

$T_g$  of PAam appeared at 161.4°C, while the  $T_g$  of PAam-Ni(II) was shifted to 167.8°C. This meant that the polymer became more rigid after complexation. The melting temperature ( $T_m$ ) of PAam appeared at 237°C which was shifted to 255°C in the PAam-Ni(II) complex due to intermolecular complex formation between polymer and Ni(II).

Finally, AFM study of PAam-Ni(II) complex films surfaces on mica substrate showed that the root mean square (RMS) roughness of the film surfaces increased as Ni(II) concentration increases.

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