RSC Advances

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

Surface Modification of Poly(p-phenylene terephthalamide) Fibers with HDI Assisted by Surpercritical Carbon Dioxide

Kong Haijuan, Yang Peng, Teng Cuiqing, Yu Muhuo*

State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, Donghua University, Shanghai 201620, P.R.China,

College of Material Science and Engineering, Donghua University, Shanghai 201620, P.R.China

Abstract

A process of surface modification of poly(p-phenylene terephthalaramide) fibers was reported to improve the adhesion to epoxy, that the fibers were treated in supercritical carbon dioxide ($ScCO_2$) with hexmethylene diisocyanate (HDI). After the modification, the surface chemical composition of the fibers was identified by X-ray photoelectron spectroscope (XPS), and the results showed Ph-NH_2 groups are formed on fibers after treated in $ScCO_2$ with HDI. From the scanning electron microscope (SEM) and atomic force microscope (AFM) results, we can find the surface of fibers treated with HDI in $ScCO_2$ became much rougher. The interfacial properties of aramid/epoxy composites were investigated by microdebond test, the results showed that the interfacial shear strength (IFSS) was improved by 22%. It is beneficial for the application of the fiber material as reinforcement in an epoxy system that can improve the interfacial property of PPTA fibers with epoxy.

Key words: surface modification, poly (p-phenylene terephthalaramide) fibers, surpercritical carbon dioxide, interfacial properties.

1. Introduction

Aramid or poly p-phenylene terephthalamide (PPTA) fibers have high tensile strength and tensile modulus, high thermal resistance, and low density, make aramid fiber fabrics ideal reinforcing materials in the advanced composites fields, such as aviation, aerospace, automobile and shipbuilding application[1]. However, aramid fibers have poor interfacial bonding with most of the commercially available resins used in composites. These limitations lead to poor out-of-plane (off axial) strength of the composites. In order to enhance the aramid/matrix interfacial strength, various fiber surface modification techniques have been investigated such as oxidation treatment[2], coatings[3-4], ultrasonic processing[5], chemical modifications[6-10], plasma-aided grafting and low-pressure plasma treatments[11-13]. Although these methods for surface modification increased aramid/matrix interfacial strength, they often had negative effects on tensile strength of aramid fibers as the damage of fiber surface, it may bee caused by the damage at the skin division as the aramid fiber was the Skin-Core structure[14-15] .

Super critical carbon dioxide has been frequently employed as an extraction medium due to its combination of low viscosity and negligible surface tension[15]. Zhao et.al[16] designed a new pretreatment process, in which the organometallic complex was impregnated into Kevlar® fabrics/fibers by using $ScCO_2$ to electro conductive composite fabrics/fibers and metalizing aramid fibers using supercritical by copper Plating of aramid film[17].

In an early study, we have reported a new method by infiltrating polymeric materials into aramid filament networks to improve their mechanical properties with the aid of $ScCO_2$[18]. In this study, the surface and the adhesion properties of aramid fibers were further researched. The results showed that surface of the fiber treated in $ScCO_2$ with

HDI became much rougher and their interfacial shear strength (IFSS) with resin increased evidently. Surface morphology, surface chemical composition and interfacial bond strength of the fibers before and after treated in $ScCO_2$ to epoxy resin were investigated by the XPS, SEM, AFM and IFSS.

2. Materials and Characterization

2.1 Materials

PPTA fibers were supplied by Hebei Silicon Valley Chemical Co., Ltd. China. The yarn is made of 1000 filaments with average single filament 12.7μm diameter and the specific linear density is 1111dtex. Carbon dioxide (purity: +99.99%) was purchased from Shanghai Chenggong Gases Co., Ltd. (China) and used as received. Hexa-methylene diisocyanate (purity: 99%) was purchased from J&k chemical Ltd (Shanghai, China) and used without further purification. Acetone (chemically pure grade) was bought from the Shanghai Ling Feng Chemical Reagent Co., Ltd. (China). The matrix used in this paper was epoxy resin prepared with E-56 (A type of epoxy), epoxy curing agent (YS5618) and acetone at the ratio of 10:3:2, all provided by Shanghai resin Co. Ltd., China

2.2 Treatment in $ScCO_2$

The process in treatment in $ScCO_2$ was stated[18], PPTA fibers were cleaned in the Soxhlet extractor with acetone at the temperature of 75^{o}C (20 h), and dried in an air oven (110 ^{o}C/3h) to remove acetone thoroughly prior to proceeding the $ScCO_2$ pretreatment. The reactions were carried out in high-pressure stainless steel vessels. All parts of the vessels were washed with clean acetone, acid bathed (2.0 M aqueous sulfuric acid), then thoroughly rinsed in clean water, and finally dried at 120 °C. The $ScCO_2$ impregnation process was carried out in a 2 L vessel. Samples were rolled, tied

on a stainless steel formwork with controlled tension. An amount of 10 wt% of HDI solvent related to the weight of the fibers was placed on a glass filter. When the vessel reached the set temperature, the cartridge was introduced. Then, carbon dioxide gas was supplied via a high-pressure syringe pump, and maintained at a preset pressure. Subsequently, the system was kept stable during a certain time to allow the HDI to dissolve into $ScCO_2$ and to react with the aramid fibers. Finally, decompression was slowly conducted. The impregnation processes were carried out under static conditions.

2.3 SEM

The JSM-5600 LV model SEM was employed to analyze the surface morphology change of PPTA fibers untreated and treated. Before SEM experiment, all samples were coated with a vapor deposited thin conducting layer of gold to minimize charge.

2.4 AFM analysis

The surface morphology of PPTA fibers were examined using atomic force microscope (AFM). The AFM used in this study was SPM Nan scope IV provided by America Veeco. Scanning was carried out in tapping mode operation. A scan size of up to 4 μm and a scan rate of 1.0 Hz were chosen for analyzing the surface morphology and roughness of the untreated and treated aramid fibers.

2.5 XPS analysis

The surface elemental composition of PPTA fibers was carried out on a RBD upgraded PHI-5000C ESCA system (Perkin Elmer) with MgKα radiation (h=1253.6 eV) power 250W, high voltage 14.0 kV with a detection angle at 54^{o}. The pass energy was fixed at 23.5 eV and the base pressure of the analyzer chamber was about 5×10^{-8} Pa. The sample was directly pressed to a self-supported disk (10×10 m) and mounted on a sample holder, then transferred into the analyzer chamber. The whole spectra

(0~1100 (1200) eV) and the narrow spectra of all the elements with much high resolution were both recorded by using RBD 147 interface (RBD Enterprises, USA) through the Auger Scan 3.21 software.

2.6 Interfacial shear strength

The interfacial shear strength (IFSS) of fiber/epoxy interfacial adhesion was measured based on the micro-bond technique, epoxy resin was dropped on the PPTA fiber and the fiber length imbedded in epoxy resin was controlled within 1mm. Then specimens were cured at 80^{o}C for 2 hours in a vacuum oven. And microscope was used to measure the diameters of the fibers and the length of the epoxy beads. The micro-bond tests were carried out using tensile strength tester 0-100 cN (XQ-1A) with a speed of 10 mm/min at gauge length of 10 mm. The value of IFSS was cacaulated according to Eq.(1).

$$IFSS = \frac{F}{\pi DL} \quad (1)$$

where F is the value of maximum load, D is the average diameter of aramid fiber,L is the embedded length of PPTA fiber in epoxy resin. The average values were calculated from at least 50 samples.

3. Results and discussion

3.1 Surface chemical composition of PPTA fibers

Figure 1 shows the XPS survey spectra for PPTA fibers before and after treated in $ScCO_2$. The chemical composition of PPTA fiber surfaces is shown in Table 1. Compared with the results from untreated fiber and only treated in $ScCO_2$, there is a slight difference. But when HDI was introduced, the carbon element concentration of fiber was decreased and it was also noticed that the oxygen level for the fibers was increased, which has been reported to be good for bonding of the resin. Further,

nitrogen element concentration was improved and nitrogen to carbon atoms was also improved, meanwhile the oxygen to carbon atoms was almost increased.

More chemical interaction information about fibers could be obtained by deconvolution of N_{1s} peaks. Fig.2 (a-c) shows N_{1s} spectras of the untreated and treated PPTA fibers. There are three kinds of carbon states, -NH- at 399.2ev, -N-C=O at 399.8ev and NH_2- at 401.2ev. The most significant differences between the spectra of treated and untreated fibers are the increase of -PhNH_2 and -N-C=O components and decrease of -NH-. These changes suggest that the $ScCO_2$ with HDI treatment involves both the reaction of the -C-NH- bond in the amide group, creating -NH_2 functional groups. These changes can be corresponding to the increase in N/C reported in **Table 1**.

3.2 Surface morphology

The surface morphology of PPTA fibers was investigated by SEM. Fig.3 (a-c) shows the SEM and AFM images of untreated PPTA fiber, treated in $ScCO_2$ and treated in $ScCO_2$ with HDI. The surface of the untreated fibers (Fig.3a) is relatively smooth and clean, which means that the interfacial adhesion between the fibers and expoxy resin is rather poor. When fibers were treated in $ScCO_2$ without HDI as seen in Fig.3b, there are some spots on the surface and the surface of fibers becomes rougher than untreated fibers. And the fibers treated in $ScCO_2$ with HDI, there are remarkable differences on the surfaces can be seen (Fig.3c), comparing to the untreated and only treated in $ScCO_2$, the cracks and defects on the fiber were reduced and some mild grooves were generated on the surface, which made the surface rougher.

AFM was used to further observe the surface morphology of PPTA fibers. Fig.4 (a-c) showed the three-dimensional and two dimensional topographies AFM images of

untreated fiber, treated in $ScCO_2$ and treated in $ScCO_2$ with HDI. The AFM results are consistent with the SEM analysis. Especially for PPTA fiber treated in ScCO2 with HDI, clear spots and flaws could be observed on the fiber surface. The results of surface roughness, the arithmetic mean roughness (R_g) and root mean square roughness (R_q) of the PPTA fibers obtained by AFM measurement are shown in table 2. And the results also suggest that the roughness was improved when treated in $ScCO_2$.

The results of surface topography as indicated by SEM and AFM observations suggest that a polymer layer might have been formed on the treated aramid fiber, which was significantly roughened by the HDI treated in $ScCO_2$. The polymer layer may be caused by surface crosslinking and grafting reactions of HDI with the amide agent group on the surface. These results show that fibers treated in $ScCO_2$ with HDI could enhance the surface roughness and provide much larger surface area for stronger interfacial bonding. With the increase of the surface roughness, the interfacial adhesion of the fiber material as reinforcement in a composite system was improved.

3.3 Adhesion of epoxy resin to PPTA fiber

The interface properties of PPTA fiber and epoxy composites were studied using microdebond test, the numbers of pull-out fibers numbers and the IFSS results are shown in the table 3. The untreated fibers exhibited an IFSS of 9.1 MPa and the fibers treated with HDI in $ScCO_2$ showed an increase by 25.2%. This because the fibers were treated with HDI in $ScCO_2$ leading more active functional groups on the surface of fiber that contributed to the improvement of fiber adhesion performance. In addition, the formed polymer layer makes the surface roughness increased. Both polar functional groups and roughness make the interfacial bonding enhanced resulting in an improved IFSS. The results suggest that PPTA fiber/epoxy composites with

superior interfacial properties could be developed when fibers treated in $ScCO_2$ with HDI.

4. Conclusions

The surface modification of PPTA fibers treated in $ScCO_2$ with HDI could make the fiber surface much rougher and formed a polymer layer that might be caused by surface crosslinking and grafting reactions of HDI with the amide agent group on the surface. SEM, AFM, XPS results showed fibers treated in $ScCO_2$ with HDI could enhance the surface roughness and provide much larger surface area for stronger interfacial bonding. The fiber surface after treated in ScCO2 with HDI became much rougher and their interfacial shear strength (IFSS) with resin increased evidently. Moreover, it is beneficial for the application of the fiber material as reinforcement in an epoxy system, which can improve the interfacial property of PPTA fibers with epoxy.

Acknowledgements

This work was supported by National Basic Research Program of China (973 Program) (2011CB606101).

Reference

1. J. W. S, Hearle.., High-performance fibres. Woodhead Publishing Ltd, Cambridge: 2001.
2. S. Hussain,., C. Yorucu,., I. Ahmed, R.Hussain, , B. Chen, M.Bilal Khan, , N. A.Siddique, , I. U.Rehman, Surface and Coatings Technology **2014,** 258, 458-466.
3. J.R.Chen, J. Y.F. Zhu, Q.Q.Ni, Y.Q.Fu, X. Fu, Appl Surf Sci., **2014,** 321, 103-108.
4. Y.Zhang, J. Zou, H.Wu and Y.Qiu, ICAFPM 2009 - Proceedings of 2009 International Conference on Advanced Fibers and Polymer Materials., 2009, 1229-1231.
5. L. Liu, Y. D. Huang, Z. Q. Zhang, Z. X. Jiang and L. N.Wu, Appl Surf Sci., **2008,** 254 (9), 2594-2599.
6. A. Castro-Muniz , F. Suarez-Garcia, A. Martinez-Alonso and J. M. Tascon, J Colloid Interface Sci., 2011, 361 (1), 307-15.
7. F. Suárez-García , A.Martínez-Alonso and J. M. D. Tascón, Carbon., **2004,** 42 (8-9), 1419-1426.
8. S. R.Wu, G. S.Sheu, S. S. Shyu, J Appl Polym Sci.,**1996,** 62 (9), 1347-1360.
9. C. Y. Yue and K. Padmanabhan , Compos Part B-En., **1999,** 30 (2), 205-217.
10. T. M.Liu , Y.-S. Zheng and J. Hu, Polym Bull. , **2010,** 66 (2), 259-275.
11. M. Xi, Y. L. Li, S. Y. Shang, D. H. Li, Y. X. Yin and X. Y. Dai, Surface and Coatings Technology.,

2008, 202 (24), 6029-6033.
12. C. Jia, P. Chen, W. Liu, B. Li and Q. Wang, Appl Surf Sci **2011.,** 257 (9), 4165-4170.
13. R.X.Gu, J. R. Yu, C.C.Hu, L.Chen, J.Zhu and Z.M. Hu, Appl Surf Sci., **2012,** 258 (24), 10168-10174.
14. Z.Jia, Y.G..Yang, In Advanced Materials Research, 2012. 548, 29-33.
15. T. Matsuoka, S.Kazuhiko, S.Yotsu, In FRC 2000–Composites for the Millennium, Gibson, A. G., Ed. Woodhead Publishing: 2000; pp 159-166.
16. A. I.Cooper, J Mater Chem ., **2000,** 10 (2), 207-234.
17. X. Zhao, K. Hirogaki, I.Tabata, S.Okubayashi and T.Hori, Surf Coat Tech., **2006,** 201 (3-4), 628-636.
18. M.Belmas, I.Tabata, K. Hisada and T. Hori, Sen-I Gakkaishi., **2010,** 66 (9), 215-221.
19. H.J. Kong, C.Q.Teng, X.D. Liu, J.J. Zhou, H.P.Zhong, Y. Zhang,K.Q. Han and M.H.Yu, Rsc Advances **2014,** 4 (39), 20599-20604.

Table .1 Surface element analysis of PPTA fibers before and after treatment

Sample	Chemical composition (at. mol%)			Atomic ratio	
	C	N	O	O/C	N/C
a	79.31	4.35	16.34	0.206	0.055
b	79.53	4.62	15.85	0.199	0.058
c	74.02	9.63	16.35	0.22	0.130

Table 2. The arithmetic mean roughness (Rg) and root mean square roughness (Ra) of the PPTA fibers

Samples	Ra（nm）	Rq（nm）
As received fibers	93.8	110.2
$ScCO_2$ treated without HDI	124.5	145.0
$ScCO_2$ treated with HDI	137.9	161.0

Table 3. IFSS of PPTA fibers

Sample	IFSS (MPa)
untreated PPTA fibers	9.1
$ScCO_2$ treated fibers without HDI	9.2
$ScCO_2$ treated fibers with HDI	11.4

Figures

Fig.1 Figure 1. XPS survey spectra showing the results for PPTA fiber (a) untreated PPTA fiber, (b) PPTA fiber treated in $ScCO_2$ without HDI, and (c) PPTA fiber treated in $ScCO_2$ with HDI

Fig.2 Nitrogen (1s) spectra and Concentrations of correlative functional groups of fiber samples: (a) untreated PPTA fibers, (b) ScCO2 treated fibers without HDI, and (c) $ScCO_2$ treated fibers with HDI

Fig.3 SEM images of PPTA fibers (a) untreated PPTA fibers, (b) ScCO2 treated fibers without HDI, and (c) ScCO2 treated fibers with HDI

Fig.4 AFM images of PPTA fiber (5μm*5μm) (a) untreated PPTA fibers, (b) ScCO2 treated fibers without HDI, and (c) $ScCO_2$ treated fibers with HDI

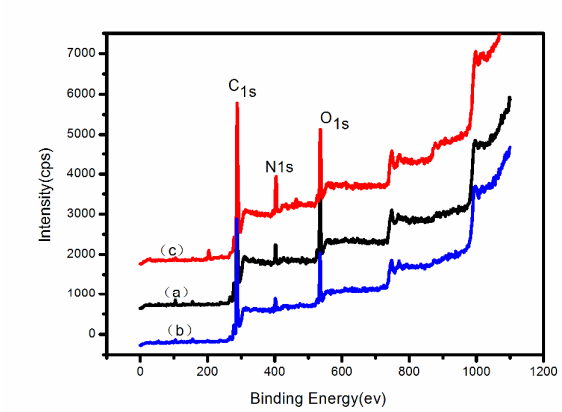
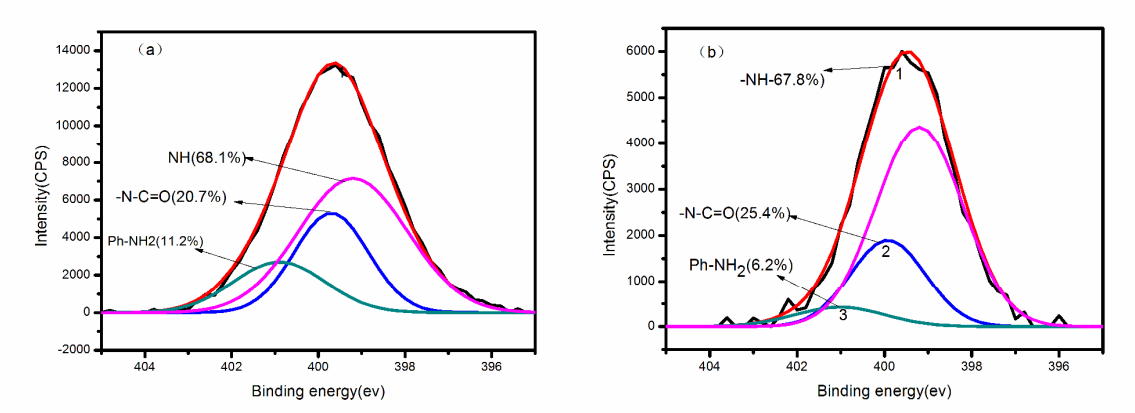


Fig.1



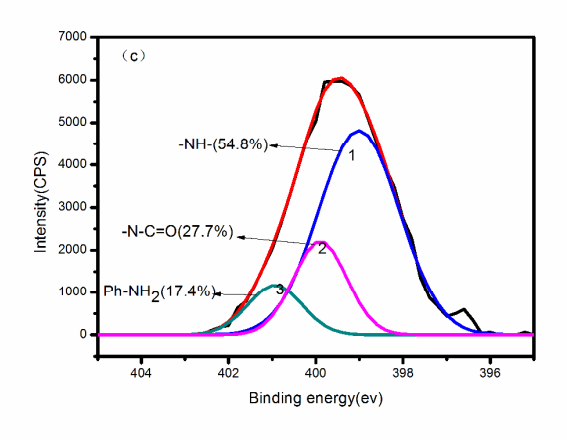


Fig.2

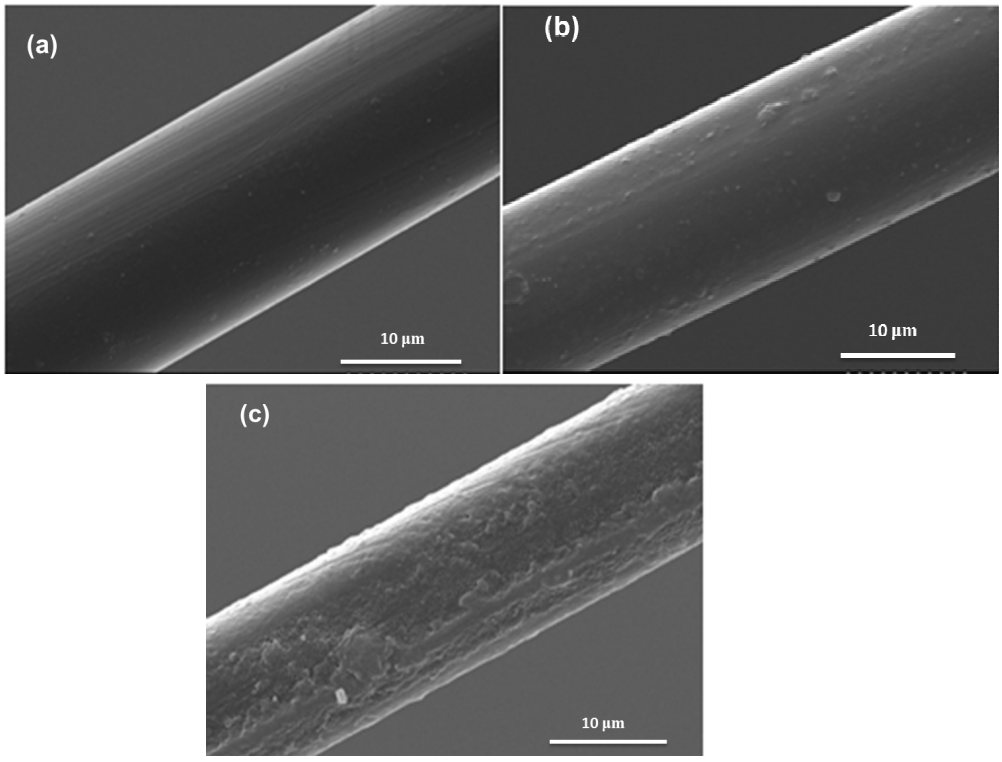


Fig. 3

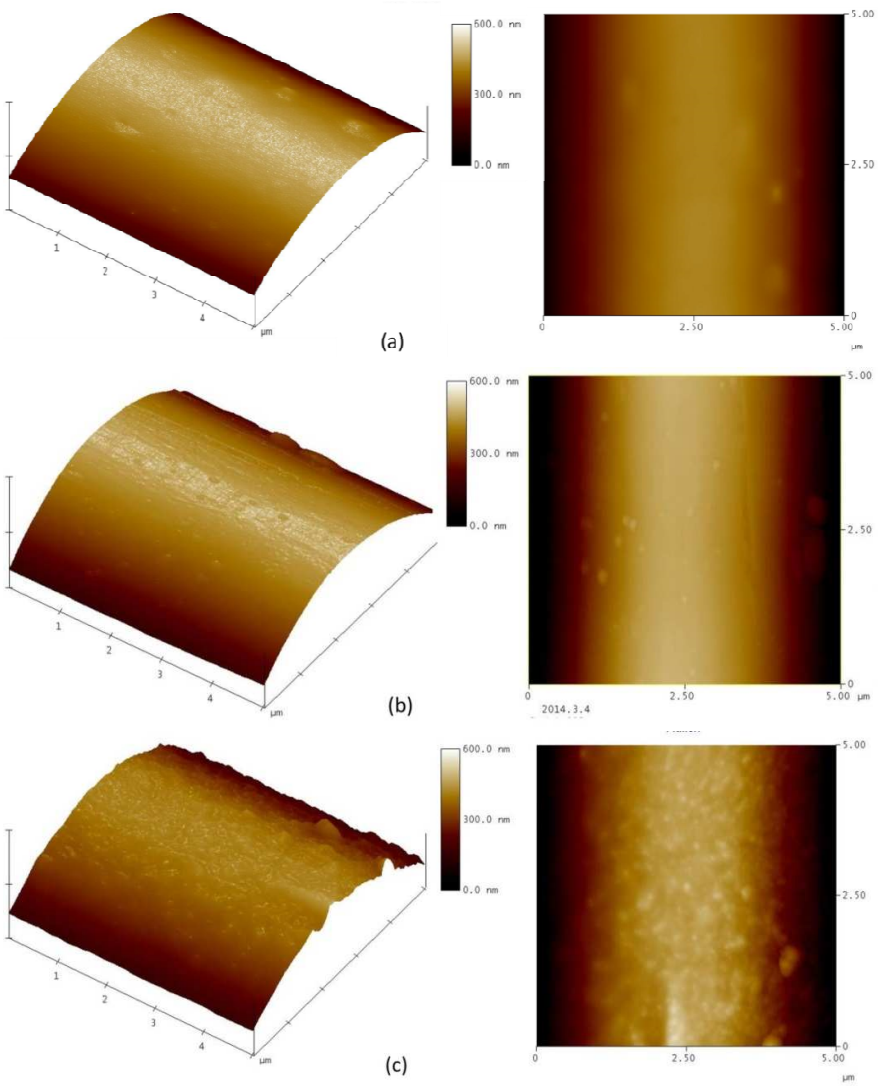


Fig. 4