An Investigation on Printability of Carbon Nanotube (CNTs) Inks by Flexographic onto Various Substrates

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***Abstract*—This paper work will be investigated the printability of carbon nanotubes (CNT) conductive inks by flexographic onto various substrates. Two types CNT which are water and solvent base, and four types of substrates which are silica, biaxially oriented polypropylene (BOPP), 70gms/m^2 white blank office paper and woven had been used. A pattern of multiple solid line of photopolymer printing plate was prepared, with different width but constant gaps width between 2 adjacent of lines. The Printability of printing was checked visually. Simple test of ink functional performance was checked by lighting up led lamp. The roughness of the printed pattern surface was determined by Atomic Force Microscopy (AFM). The result showed that both inks can be printed under different parameter setting. CNTs water base ink is the best ink which can be printed onto many substrates but maintain high electric conductivity.**

***Index Terms*—flexographic, carbon nanotube (CNT), surface morphology**

I. Introduction

Conventional electronic, which with rigid components and circuit boards have been around for decades and served us in many important applications. However, nowadays, printed electronics, which allows even roll to roll (R2R) mass production on several flexible substrates being a new opportunities explored by worldwide researchers [1]-[4]. Components and circuits in printed electronics, is printed by conventional printing methods which familiar in graphic printing processes, like flexographic, ink jet, screen printing, gravure and offset lithographic. The most benefit of printed electronics are enable to be printed onto various flexible substrate (for providing smart or active function), mass production, low cost, high productivity and an environmental friendly, which can utilizes 90 percent of material usage compared to conventional patterning employed in electronics such photolithography or nano imprint lithography [5]. Therefore the main interests in using such printing processes are high productivity and saving raw material.

A. Flexographic

Flexography, the printing form is a relief image produced onto a photopolymer material. The anilox roll is an engraved cylinder that transfers the ink onto the printing form. The surface of the anilox is covered with large numbers of finely engraved cells, which are filled with ink from an enclosed chamber, doctor blades are used to remove excess ink from the non-engraved surface of the anilox.

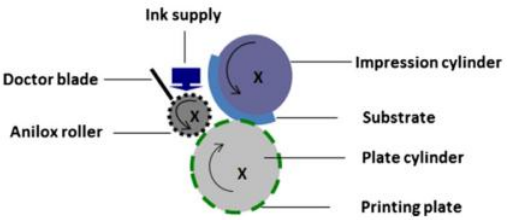

Figure 1. Schematic of flexographic printing processes [6]

The anilox roll is brought into contact with the printing form, also referred to as the plate, thus only allowing transfer of the ink from the anilox roll to the relief areas of the image. The printing form is then brought into contact with the substrate to complete the printing process as Fig. 1.

B. Multiple Solid Lines in Printed Electronics

In electronic manufacturing, patterning issues are crucial. Conventional printing method such as flexographic is dot printing which definitely will affect the electrical performance due to lines width inconsistency with a consequent impact on line conductivity, hence for printed electronic, a solid line is crucial. The comparison of both two pattern line is shown in Fig. 2.

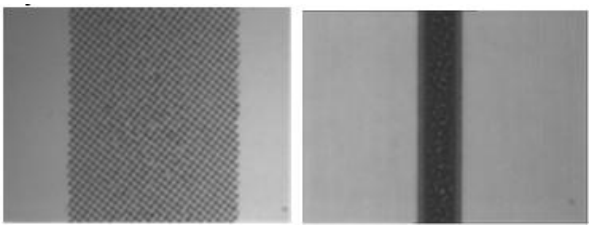

Figure 2. Comparison between solid and dot printed lines by flexographic [7].

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C. Substrates and Inks Effect

In order to achieve best quality and specific requirement of printing both substrates and inks will play a main role. In term of inks properties for example, viscosity, rheological behavior, ink chemistry, solvent evaporation rate, drying and *et al.* [8]. For the substrate properties, smoothness, porosity, wettability, ink receptivity, contact angle compressibility and etc. The additives which normally added in regular ink formulations in order to meet processes requirements such as wettability or viscosity may cause undesired change of electrical properties of the materials and consequently performance of final devices [8].

D. Carbon Nanotube (CNTs)

Carbon nanotubes (CNTs) properties in term of electric conductivity is nearly metallic behavior, in spite of this they are potential candidates for new generation of high performance conductive inks used for printed electronic such as conductive tracks or chip interconnection[9]. However, effective employment of CNTs for these applications need methods to deposit and pattern them over large, areas, higher resolution, while meeting the requirement enforced by the nature of the target substrates. Several other methods of nanotube film fabrication have been reported, including spray coating. The most common method entails the deposition of a colloidal solution of nanotubes onto porous filtration membranes and transferring to other substrates. However, such processes do not scale up easily, require special substrates and are not compatible with standard micro-fabrication processes. Other CNTs patterning techniques often damage the receiving substrate, including either chemical modifications of the substrate or ablations [10]-[12]. Of interest from a technological point of view are processes which are cost effective, scalable to large area with high- throughput fabrication and are flexible enough to be implemented on a large class of substrates including flexible ones, this paper is thus devoted to propose a flexographic for creating CNTs patterns onto a wide range of substrates, with lower cost and mass production for electronic manufacturing.

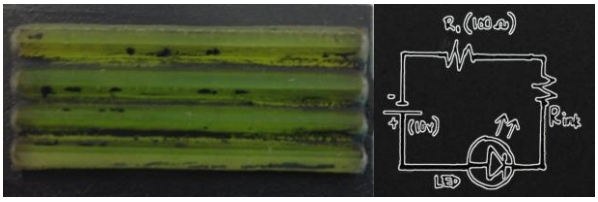
II. Experimental

The two types of samples of CNTs were obtained as test specimen. Water and solvent base CNTs were investigated. The detail composition is shown in Table I.

TABLE I. The Composition of Ink (%)

MATERIAL	CNT-W (water base)	CNT-S (solvent base)
CNTs	1-7	3-5
Water	80-90	0
Polyoxy Propylene Glycol	0	90-95
Resin	1-5	1-3

The inks were printed by flexographic, which the schematically shown in Fig. 1. A pattern of multiple solid line of photopolymer printing plate was prepared, with different width (1.5mm, 1.0mm, 0.8mm and 0.5mm), but constant gaps width(1mm) between 2 adjacent of 25mm length lines showed in Fig. 3(a).



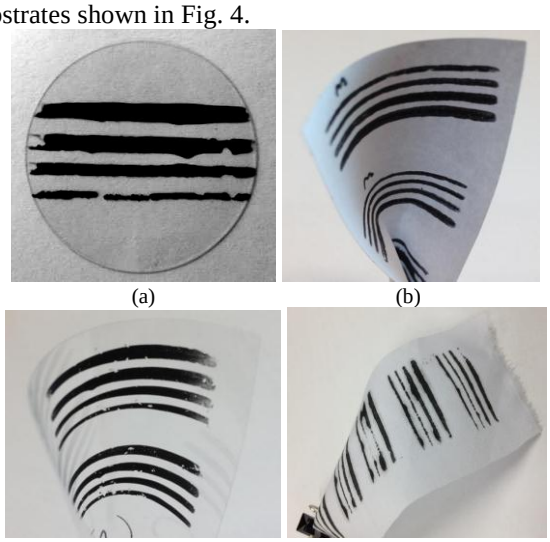
(a) (b)

Figure 3. (a) Printing Plate, (b) Circuit Diagram

The Printability of printing was checked visually by adjusting processes parameters. The four types of substrates which are silica, biaxial oriented polypropylene (BOPP), commercial 70gm/m^2 by Paperone Company, and textile had been used. Simple test of ink functional performance was checked by lighting up led lamp using simple circuit as Fig. 3(b). The roughness of the printed pattern surface was determined by Atomic Force Microscopy (AFM). The analysis result will be considered to most proposed inks and substrates for flexographic.

III. Result and Discussion

The pattern image was successfully printed into substrates shown in Fig. 4.



(a) (b)

(c) (d)

Figure 4. Printed image CNTs (water base) pattern result on (a) silica, (b) BOPP, (c) paper and (d) textile

However, there was some defect such as cut pattern, uneven sharpness and *et al.* From the printed image patterns observation, the factors which influence the defected patterns was including, the ink properties, substrates and machine processes parameters and interfacial phenomena. The inks effects were viscosity, solvent and ink particle size. The substrate effects such as roughness. Interfacial phenomena such as contact angle, cohesion and adhesion that will affect the wettability of printed ink on the substrates.

Adhesion defines the strength of the interface between substrates and printed material, therefore the higher

adhesion is desired. Meanwhile cohesion describes the strength that holds the molecules of printed material together. The effects of processes parameter is including the printing speed, engagement between impression roller and substrates, the deformation of printing plate during printing, the anilox's engraving (lpi-line per inches) and etc.

The printability of CNTs solvent base was poor most likely caused fast drying of the inks on anilox. Dried ink clogged the cells on anilox, reducing ink transfer to printing plate and further to the substrate. The same result was obtained by Tuomas Julin 2011 [13]. The solvent that used in ink printing for flexographic should not be fast dry, otherwise the ink doesn't has enough time to attach onto the substrates from printing plate, or dried in anilox before ink transfer to printing plate. Therefore drying condition is the most important ink properties in flexographic.

Electrical performance test was conducted using simple circuit diagram seen in Fig. 3, the power 10v was supplied, R_1 is 100 ohm and R_{ink} is printed ink which also working as resistor. Table II is shown the brightness level when the others parameters were constant and variable in substrates. Since the high porosity of textile and paper, as mentioned in Fig. 5, significant result can be seen between silica/BOPP and textile/paper, which LED was most bright when R_2 printed onto silica, then BOPP and finally paper because the lower brightness mean conductivity was reduce due to uneven thinner thickness of layer ink. Fig. 6 is shown visually led brightness inspection result which is on silica substrates is most bright.

TABLE II. LED BRIGHTNESS VISUAL CHECK RESULT

SUBSTRATE	CNT-W (water base)
Silica	Very Bright
BOPP	Bright
Textile	Low Bright
Paper	Very low Bright

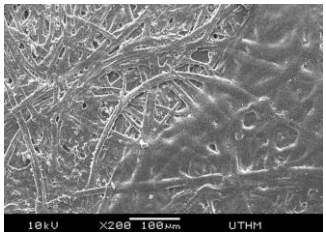
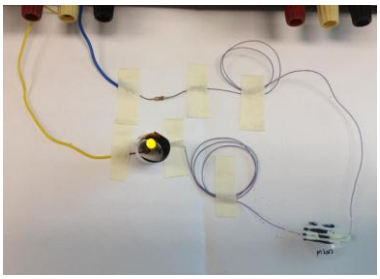
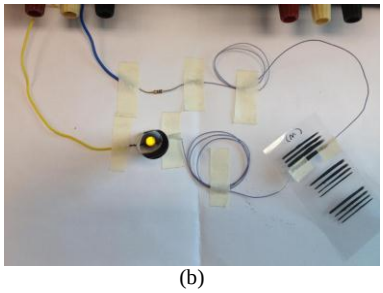


Figure 5. SEM image show the high porosity of paper substrate.



(a)



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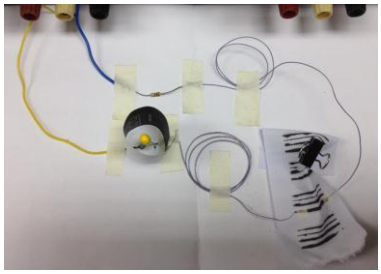

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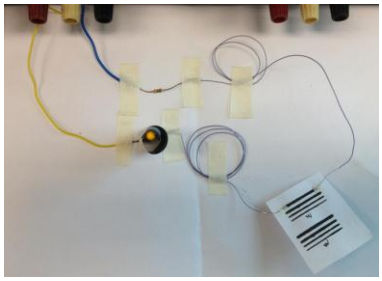
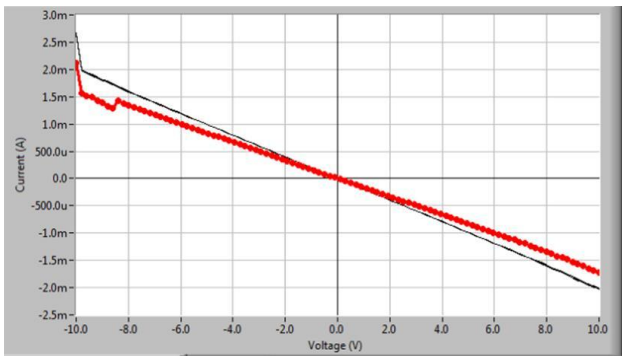
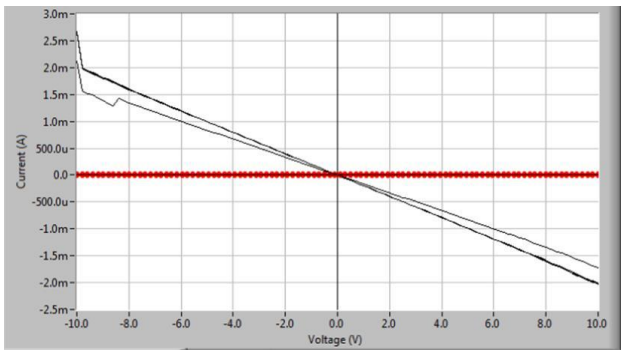


(d)

Figure 6. The conductivity test of CNTs (water base) by lighting up LED. (a) substrates silica, left /bottom photo is LED when off, (b) BOPP, (c) textile and (d) paper



(a)



(b)

Figure 7. IV Graph: (a) CNTs (water base) and (b) CNTs (solvent base) performed by IV station ORIEL Instruments

Current-Voltage (IV) graph Fig. 7 shows that CNTs solvent base (CNT-S) was not conductive since the IV graph indicated zero value (no slope). The caused maybe due to the material (Polyoxy Propylene Glycol) s which normally added in ink formulations in order to meet processes requirements may cause undesired change of electrical properties of the materials and consequently performance of final device. Here the water base maybe good solvent to achieve the low resistivity.

The roughness of printed pattern was investigated. In printed electronic lower roughness is better to have high performance of conductivity. Table III shows the AFM surface image result, solvent base inks was smoother than water base ink whatever type of substrates used. CNTs water base ink had the highest roughness when printed into BOPP and lowest roughness when printed into textile.

However, as shown in Fig. 8, CNTs solvent base ink had the highest roughness when printed to textile and lowest roughness when printed to BOPP. When select a textile or paper as substrates, either solvent base or water base is not have significant different. These phenomena may cause by high permeability of paper and textile. Nevertheless, printed ink surface roughness on BOPP and silica have significant different, when used solvent base ink or water base.

TABLE III. SURFACE ROUGHNESS (MM)

Printed Substrate	CNT-W (water base)	CNT-S (solvent base)
Silica	0.7890	0.1418
BOPP	1.1440	0.0603
Textile	0.3900	0.3310
Paper	0.5010	0.3300

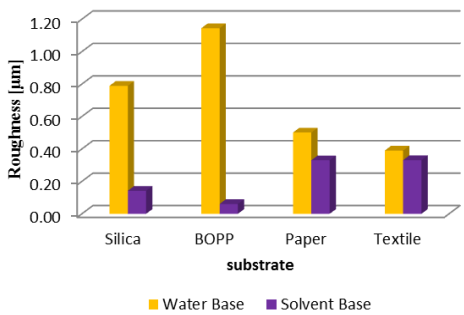
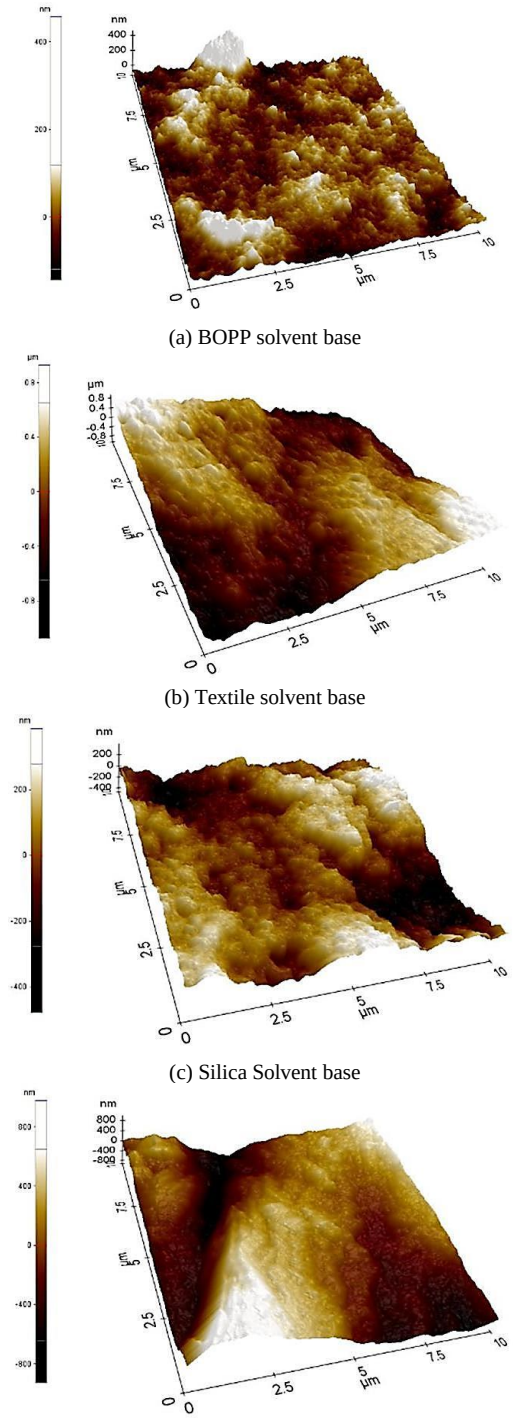


Figure 8. Roughness of surface printed ink comparison between CNTs solvent and water base on various substrates

Fig. 9 and Fig. 10 show the ink surface printed images by AFM which indicate that solvent base inks is smoother compare to water base ink onto all tested substrates.

Fig. 11 and Fig. 12 is comparison between original substrate roughness and printed ink roughness. In Fig. 12 roughness water base ink printing is the highest which is 1.144µm, even though it were printed onto smoother original substrate surface which only 0.0138µm. This is the same result for water base ink printing onto silica. Silica original surface roughness is 0.0028µm, which is the lowest (smoothest) among the tested substrates. However printed water base ink on its, show the higher roughness which is 0.789µm. From this result may conclude chemical reaction does not occur between printed layer and substrate surface. Therefore the roughness is only depended to the ink material itself. This is maybe supported by data from Fig. 11, no significant different for Silica and BOPP when used solvent base ink. Here, the final ink roughness is much affected by the inks properties only not significantly by original substrates surface roughness.



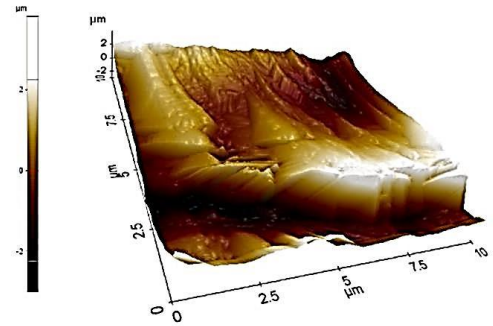
(a) BOPP solvent base

(b) Textile solvent base

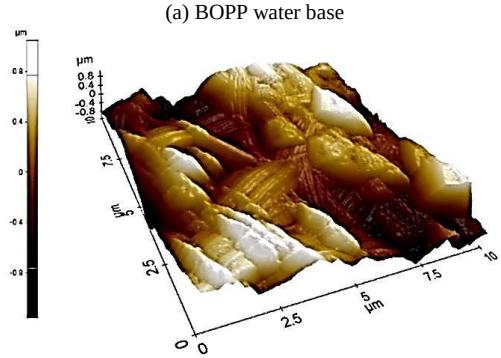
(c) Silica Solvent base

(d) Paper Solvent base

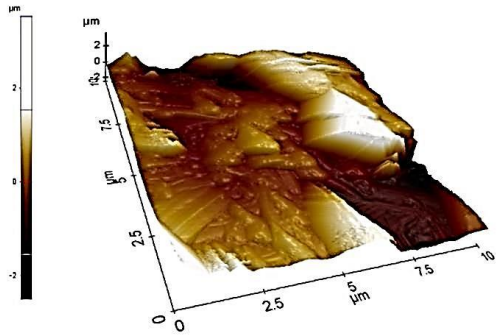
Figure 9. AFM Surface Image of CNTs ASL 0212 (solvent base) Image: (a) BOPP, (b) textile, (c) silica and (d) paper. Scanning area 10µm×10µm



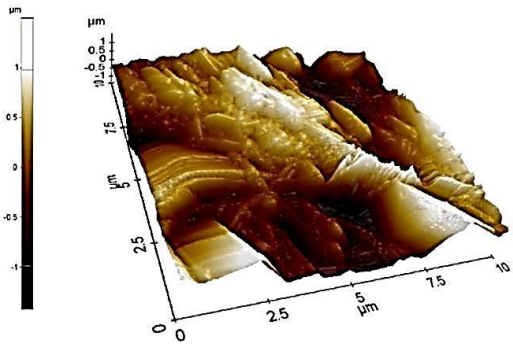
(a) BOPP water base



(b) Textile water base



(c) Silica water base



(d) Paper water base

Figure 10. AFM printed ink surface image of CNTs (water base) on (a) BOPP, (b) textile, (c) silica and (d) paper. Scanning Area 10μm×10μm

Water base inks maybe most suitable for paper textile or other material which having high permeability, those will help to reduce the roughness compared if printed onto lower permeable substrates like silica or BOPP in this study. This is because the roughness is lower which 0.5μm for paper and 0.39μm textile compared to silica which is 0.789μm and 1.144μm for BOPP.

Another finding is solvent base ink suitable for almost substrate, because from Fig. 11, can be seen that lower roughness and no significant different between water and solvent base for each tested material, may cause by cohesion and adhesion of the solvent. Nonetheless, from the Fig. 11 also, solvent base may mostly suitable for less porous material (silica and BOPP). The reason is both silica and BOPP had lowest roughness among the other tested material when used solvent base inks, 0.06μm for BOPP and 0.14μm for silica.

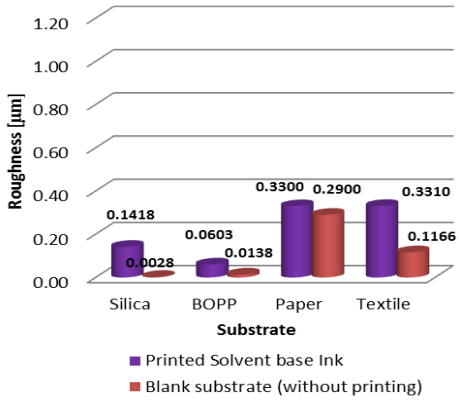


Figure 11. Printed CNT solvent base ink surface roughness comparison with blank surface (without printing)

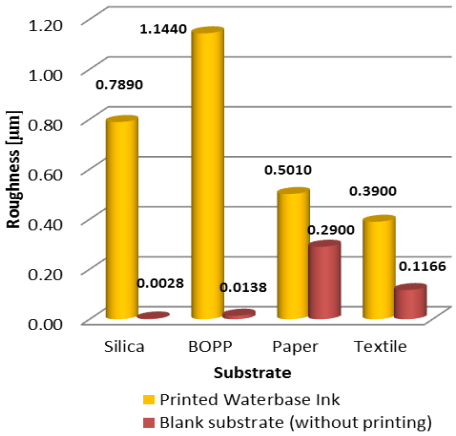


Figure 12. Printed CNT waterbase ink surface roughness comparison with blank surface (without printing)

All the result showed that both substrates and ink properties is playing substantial role in order to get low roughness which is crucial in print functional material for printed electronic. The ink properties like, solvent or water base, drying rate, adhesive, cohesive and etc. The ink itself must be engineered, because not all the inks is suitable for all substrates. Some is suitable to curtain substrates but not to other substrates. Base on this study CNTs water base inks having most brighter led lighting up, although the roughness is highest. It maybe the conductivity is mostly affected by the thickness and length of the printed conductive lines. Very small micron size of roughness may not the important parameter. The thickness of the printed ink lines need to be further investigated. The original surface morphology is shown in Fig. 13. The smoothest surface is silica.

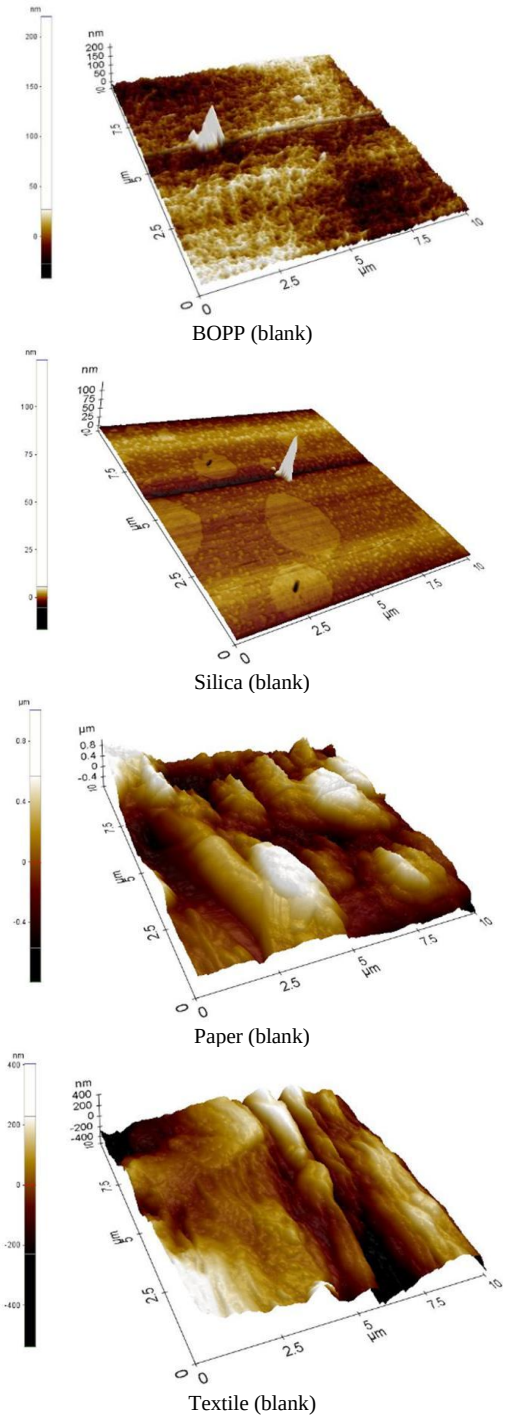


Figure 13. AFM surface image of blank substrates. Scanning area 10μm×10μm

IV. Conclusion

Flexographic is has advantages include high-speed fabrication, low cost manufacturing, and possibility of using flexible substrates, less waste and roll-to-roll capability. On the other hand the printing plate of printed pattern easily can be done by using photopolymer and can be changed follow the desire design. All this factors become a big potential in printed electronics. In this study, CNTs inks were successfully printed onto silica, BOPP, paper and textile. Since, there is very little known about the printability of materials needed for electronic devices, investigation of conductive inks properties and performance have been done. Properties of inks, viscosity, rates of evaporation are very important in the process of evaluating new functional materials for electronics printing. The sample of CNTs ink (CNT-S) solvent base which purchased from market not perform as conductivity, may cause by solvent that used for ink formulation not suitable electrical performance.

Both substrates and inks in an important factor in printed electronic. Properties of inks, viscosity, rate of evaporation and roughness are very important in the process of evaluating new functional materials for electronics printing, however only small roughness will not effect to the conductivity, otherwise if the printed lines in micron-scale size. In this study bigger line (1.5mm×25mm) was performance good conductivity although the roughness is highest among the tested substrates. Water base ink maybe most suitable on paper and textile (porous material), but maybe not much suitable for silica or BOPP due to adhesion matter. Porosity can be defined as a measure of the fluid storage capacity of a porous material. However, solvent base material is almost suitable for Silica, BOPP, textile and paper in term of roughness consideration.

Finally, flexographic is good candidate for printed electronic. Various substrates can be printed by its. The inks properties, substrates and process parameter are main role to success the printed electronic implementation.

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