Surface study of graphene ink for fine solid lines printed on BOPP Substrate in micro-flexographic printing using XPS analysis technique

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Abstract. Micro-flexographic printing is a combination of flexography and micro-contact printing technique. It is a new printing method for fine solid lines printing purpose. Graphene material has been used as depositing agent or printing ink in other printing technique like inkjet printing. This graphene ink is printed on biaxially oriented polypropylene (BOPP) by using Micro-flexographic printing technique. The choose of graphene as a printing ink is due to its wide application in producing electronic and micro-electronic devices such as Radio-frequency identification (RFID) and printed circuit board. The graphene printed on the surface of BOPP substrate was analyzed using X-Ray Photoelectron Spectroscopy (XPS). The positions for each synthetic component in the narrow scan are referred to the electron binding energy (eV). This research is focused on two narrow scan regions which are C 1s and O 1s. Further discussion of the narrow scan spectrum will be explained in detail. From the narrow scan analysis, it is proposed that from the surface adhesive properties of graphene, it is suitable as an alternative printing ink medium for Micro-flexographic printing technique in printing multiple fine solid lines at micro to nano scale feature.

1. Introduction

Surface adhesion could be described as the molecular force of attraction between dissimilar materials for example graphene with plastic substrate and lanthanum with glass substrate. The attraction strength of the surface adhesive was determined by the surface energy of the material which known as binding energy (eV). The higher surface binding energy, the molecular attraction will be greater [1]. A simple particle intercalation method was reported to characterize graphene adhesion which was essential in designing graphene based electronic devices and in gauging its realibility [2].
Micro-flexographic printing technique was the combination of flexography and micro-contact printing (µCP) techniques. It was a new printing technique in roll to roll flexography printing group. The combination of both printing techniques were expanded in the new era of high speed printing machine that could print fine solid lines image in micro to nano scale feature [3]. The achievement was very useful in printing industry especially in micro-electronics industry [4]. By using micro-flexographic printing technique, the authors managed to print fine solid lines in micro measurement which was 3 µm line width and 3 µm line gaps. The achievement was the lowest fine solid lines printed by a flexography printing technique. Graphene ink was used as printing ink medium in this research which was printed on biaxially oriented polypropylene (BOPP) thin film surface as substrate.

From the latest printing development process, the printing components played important roles in producing micro to nano scale printing image with a good surface adhesive property. Examples of printing components were ink, printing plate, substrate, roller engagement and others. Ink and substrate properties which constitute some of the main components in printing also played the main role in achieving the best quality of image or fine solid lines printing. The ink properties could be ink chemistry, viscosity, rheological behavior, solvent evaporation rate and drying [5].

Previous research had indicated that the higher electricity generation with graphene particle type was attributed to higher electrical conductivity in thickness direction, large surface area, catalytic activities of oxygen reduction and the open structure into that facilitates mass transfer of fuels and ions [6]. Graphene material also exhibited better electrochemical performance and lower impedance compared with activated carbon (C) or unmodified electrode [6]. The study had investigated two types of graphene which were regular graphene sheet and crumpled graphene particle in modifying anode and cathode electrodes in microbial fuel cell (MFC). In particular, the regular graphene particle performed even better than regular graphene sheet.

The attraction and chemical bonding between graphene metal printed and surface was due to a chemisorption and physisorption process. On previous research, the study of graphene attraction could be referred to the example of Lanthanum Oxide (La$_2$O$_3$) adhesion property on Silica, Si substrate which had been successful when O 1s binding energy could be seen from La$_2$O$_3$ and SiO$_2$ components. There were four components that contributed to O 1s photoelectron which were La$_2$O$_3$, SiO$_2$, O bulk and water vapour [1].

In fine solid lines printing, Yusof [7] managed to print out 50 µm line width and 50 µm line gap by using carbon graphic inks as printing inks. The author used web press industrial machine as a printing method. This technique used photopolymer as a mold to transfer the ink from plate roller to substrate. While, in micro-contact printing (µCP), Perl [8] showed that µCP could produce fine solid lines below 1 µm [8] which was smaller than flexography printing technique. This research used heavy-weight dendritic thioethers as printing inks and octadecanethiol as backfilling agent.

By combining both printing techniques, it was clearly seen that with the advantages and disadvantages of these techniques, a new era of printing technology could be explored in producing micro to nano scale printing image [3]. The knowledge gap in contact mechanism, printing plate deformation, ink spreading mechanism and other important factors were still under further development.

Graphene was the example of material that could be used as printing ink for Micro-flexographic printing process. Graphene ink was a step to move forward in order to achieve high speed printing in electronic with simple, rapid, low cost method, less waste and roll-to-roll capability. This type of ink was practically used in electronic printing industries that aimed on printing multiple micro to nano fine solid lines feature [9].

Graphene characteristics were the most important thing that must be understood whether it was suitable to be used as a printing ink for combination of flexography printing and µCP which known as Micro-flexographic. This study was investigated on the surface adhesion analysis of using graphene ink in Micro-flexographic printing technique to achieve the printed fine solid lines image with good surface adhesion on BOPP substrate.
2. Research Methodology
The Micro-flexographic printing process was initiated from the preparation of printing plate [10]. A pattern of fine solid lines image was produced on printing plate [11] which it was attached at plate cylinder. Micro-flexographic printing process was almost same as flexography printing process [12]. Ink was transferred to the printing plate by using an engraved cylinder known as an anilox roll as shown in figure 1. The anilox roll was the primary control of the quantity of ink transferred to the plate and subsequently the print. The ink characteristic was studied by referring to its morphology, size and depth of engrave cells. Here, the thin film analysis of printed graphene ink had been performed the surface characterization using X-ray Photoelectron Spectroscopy (XPS).

Figure 1. Schematic of the Micro-flexographic processing

2.1. Graphene Characteristics: In General
Generally, graphene had chemical and electronic properties that meet the requirements for applications in various fields such as transistor channel, printed circuit board and etc. The base material for the samples used in this area was normally commercially available graphene ink. Graphene was a pure carbon in the form of a very thin in micro to nano range. It was nearly transparent sheet and one atom thick. The average thickness of the graphene sheet with four layers was approximately 1.3 nm [13]. It was also remarkably strong for its very low weight and it conducts heat and electricity with a great efficiency. The material had high thermal conductivity too and because it was a two-dimensional (2D) material that was almost transparent, it interacted in other interesting and useful ways with light and with other materials. Graphene could be used in many applications but it stilled not commercially used.

Graphene material consisted of a two-dimensional (2D) sheet of covalently bonded carbon atoms, forms the basis of both 3D graphite and 1D carbon nanotubes. Previous experiment established graphene as the strongest material ever measured and showed that atomically perfect nanoscale materials could be mechanically tested to deform well beyond the linear regime [14].

2.2. Surface Analysis Using XPS Study
X-ray Photoelectron Spectroscopy (XPS) was an advanced surface analytical technique that was used to characterize the elemental composition of the graphene printing ink. The method was favourable for several nanometer thickness oxide or deposition [15][16]. XPS can be used to detect elements present within approximately the outermost 1 to 3 nm of the nano particle surface. XPS analysis technique also capable to perform surface chemical composition [17]. XPS spectrum were obtained using Thermo Scientific K-Alpha equipped X-ray source energy from monochromated aluminium Kα at 1486.7 eV and operated under vacuum chamber condition as low as 1 x 10⁻⁹ mbar. The XPS system
was equipped with a flood gun that will allow for surface sputtering etched. Etching could be performed using an Ar$^+$ ion gun.

XPS spectrum analysis was deconvoluted using commercial software known as Casa XPS. This software was capable to manipulate the spectrum iteration for photoelectron and background signal. The synthetic spectrum for the photoelectron peaks and its background signal was optimized using a specific model such as linear, Shirley and Tougaard method. In this work Shirley method had been used for background model, while the synthetic photoelectron signal was assigned using mixed of Gaussian-Lorentzian method. The ratio for both Gaussian and Lorentzian had been assigned using area in the ratio of 70% and 30% respectively. In this work, the data deconvolution was performed for element of interest on the substrate by referring to the narrow scan. There were two regions of interest which were carbon, C 1s and oxygen, O1s. Further discussion for this narrow scan deconvolution will be discussed in the result and analysis section.

3. Result and Analysis

The Micro-flexographic experimental printing trial had be done successfully on biaxially oriented polypropylene (BOPP) substrate by using graphene ink. The result from Scanning Electron Microscope (SEM) analysis was shown in figure 2. The printed lines contained narrow and wider. The narrow line showed the BOPP substrate with 1 µm gap while the wider line showed the graphene ink with 3 µm width.

The printed fine solid lines image of graphene ink on the top surface of BOPP substrate was analyzed by using X-ray Photoelectron Spectroscopy (XPS).

The position for each synthetic component in the narrow scan of C 1s and O 1s were referred to the electron binding energy (eV). The spectrum analysis was deconvoluted by Casa XPS software.

![Figure 2. Printed fine solid lines image of graphene ink on BOPP substrate](image)

The deconvolution of Carbon, C 1s photoelectron spectrum for graphene were involved by C-O, C sp$^3$ and C sp$^2$ species with binding energy position of 286.1, 284.4 and 283.4 eV respectively as shown in figure 3. The deconvolution of oxygen, O 1s photoelectron spectrum for graphene indicated that the oxygen species was contributed by photoelectron peaks at 530.3, 532.3 and 533.8 eV associated with O (Graphene), O (Graphite) and OH$^-$ as illustrated in figure 4. As shown in figure 4, it is obviously seen that the surface mainly dominated by three species of oxide which were came from the bulk of the carbon. On the other hand, there existence of hydroxyl component, OH$^-$ could be due to water vapour that covers the sample surface and its came from the ambient environment.
Figure 3. XPS spectrum deconvolution for C 1s for graphene on BOPP substrate

Figure 4. XPS spectrum deconvolution for O 1s for graphene on BOPP substrate

Graphene functionalized had a complex C 1s spectrum contained with sp\(^2\) component. While sp\(^3\) component came from graphite, the C sp\(^3\) peaks must be 1 eV to the higher binding energy side of C sp\(^2\) component. From the analysis result, Carbon sp\(^2\) in fine solid lines graphene ink was seen at 283.4 eV which was 1 eV lower than Carbon sp\(^3\) binding energy. This indicated the surface may be dominated by two types of carbon species which were graphene and graphite. The XPS analysis result has proven the graphene ink functionality in fine solid lines printed by Micro-flexographic printing method.

Overall result indicated that the graphene C 1s and O 1s narrow scan revealed the carbon and oxygen species of this particular ink printed that were associated with BOPP substrate. The carbon species, C from C 1s narrow scan indicated there were three species of carbon bonding with the C 1s signal which were contributed by C-O, C sp\(^3\) and C sp\(^2\). The information of oxygen species, O\(^2-\) component from O 1s narrow scan indicated there was three species of oxygen associated with the O 1s signal which was contributed by oxygen (Graphene), O (Graphite) and OH\(^-\) components. The photoelectron signal from both species had become a clear evidence to support this finding. It means that most of the graphene printed was residual at the top layer of the substrate surface.

Therefore, it could be concluded that the surface adhesion property of the graphene ink fine solid lines printed was influenced by the biaxially oriented polypropylene (BOPP) substrate. The formation of these fine solid lines printed or bonding was respected to a good adhesion between ink printed and substrate due to the anion and cation interaction under a thermodynamic influenced.

4. Conclusions
Surface adhesion study of graphene ink prints on BOPP substrate is successfully done. From this work, several conclusions can be summarised as follows:

- There are two types of species on the substrate which are carbon and oxygen.
- The components that contribute to O 1s photoelectron are oxygen (Graphene), O (Graphite) and OH\(^-\) (water vapour).
- The components that contribute to C 1s photoelectron are C-O, C sp\(^3\) and C sp\(^2\).
- The chemical bonding formation between the fine solid lines graphene ink printed and the BOPP substrate surface is due to a chemisorption and physisorption process.
- A successful observation of graphene fine solid lines adhesion property on BOPP substrate is clearly seen from the C 1s binding energy from C-O, C sp\(^3\) and C sp\(^2\) component.
- Micro-flexographic printing process is good candidate for printing electronic with graphene ink property, substrates and process parameters are main role to success the implementation.
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Acknowledgments

This project was supported by ‘Skim Latihan Akademik Bumiputera’ (SLAB) from Ministry of Education Malaysia.