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Printing Properties of Water-based Pigmented Inkjet Inks on the Oxygen-plasma Modified Polylactide Sheets

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Abstract

Oxygen plasma pretreatment on pure polylactide (PLA) sheet and associate printing properties by a set of water-based inkjet ink was investigated. Surface property of the sheet was controlled by power and exposure time of the plasma. Contact angle measurement was employed to observe wetting and calculate the total surface free energy. Surface morphology and surface roughness were observed by atomic force microscopy. Tone reproduction of the sheets printed with the inks indicated that the oxygen plasma treatment is capable of improving wettability, increased surface roughness, and color sharpness. The longer exposure time of the sheets improved more color qualities than did the irradiation power of the plasma and the optimum surface roughness produced the better printed color quality.

Key words: Polylactide sheet, Oxygen plasma, Water-based inkjet ink, Color qualities

Introduction

Presently, utilization of petroleum-based plastic products increases continuously worldwide at approximately 200 billion tons per annual which is equivalent to an average consumption of 80-100 Kg per capita per year [1]. To compare with the leading countries, like the Americans, their recycle is just 7 percent of 48 billion tons of plastics annually. The recycling of the plastic products is only at 30% in Thailand. Thailand's plastic consumption is increasing steadily to make the plastic waste accumulation up to 2 million tons per year. This amount of plastic waste has threatening the well being of Thai people and destroying the environment and ecological sustainability.

Bioplastic has slowly replaced the functions of petroleum-based plastics in packaging sectors which led to a demanding growth at a rate of 30% while the production capacity of bioplastic is only at 360,000 tons per year with a market share of only 1% [1]. Bioplastic is a green product obtained from fermentation of naturally derived feed stock which needs low energy to run its production [2]. More importantly, it can be degraded by heat, sunlight and soil compostable to carbon dioxide and water [3]. Therefore, better quality printing on the bioplastic surface should conform to those high qualities so obtained from the petroleum-based plastics. One way to improve good printed image qualities is to give corona discharge, flame treatment or plasma treatment on bioplastics surface before printing. These treatments increase the surface energy of plastic sheets, foils, paper and polymer objects to improve wettability and adhesion of inks, coatings and adhesives. Plasma treatment only modifies the outermost thin layer of the surface, while the bulk properties will be kept and do not generate waste water [4, 5]. The treatment produces new functional groups on the surface. Like many gas pretreatments, plasma has an ageing effect. Surface roughness is another parameter which can be correlated with the amount of coating adhered to surface and can be altered by the plasma treatment [6]. Junkar et al. [7] investigated the effects of oxygen and nitrogen gas plasma on PET [poly(ethylene terephthalate)] surface for fucoidan coating. They investigated the extent of plasma treatment with surface roughness and fucoidan coating. The oxygen plasma treatment produced the rougher surface (Ra = 9.9 nm) and fucoidan could wet the treated PET surface much better than that of nitrogen plasma treated surface. Kim and Masuoka [8] studied the carbon dioxide plasma treatment on degradation of PLA and PHBV sheets. The plasma treatment increased hydrophilicity of the sheets as the contact angles decreased from 80^o to 45^o. XPS (X-ray photoelectron microscopy) results indicated the presence of C and O as a ratio of O/C; and PLA sheet had a high ratio than that of the PHBV sheet. Both treated sheets degraded at a higher rate in acidic, neutral and basic conditions. Chen et al. [9] used oxygen plasma to treat PBO [poly(p-phenyl benzobisoxazole)] for characterization of surface functional groups and roughness as a function of the treater power.

In the present research, a commercially available polylactide plastic was treated with oxygen plasma. The freshly treated plastics were characterized for surface wettability via contact angle measurement, infrared spectroscopic and AFM microscopic analyses. The sheets were printed with a set of commercially available pigmented inkjet inks. The printed sheets were analyzed for the effect of oxygen plasma treatment on color reproduction and ink adhesion.

Experimental

Plasma treater

A diagram of the radio-frequency plasma generation and treatment (RF, CESAR 1310, Dressler HF-Technik GMbH, Germany) is shown in Figure 1. The main components of system are the reactor chamber, the RF generator, the gas supply system and the impedance matching network. A base pressure at 4×10^{-3} Pa was achieved using a turbo molecular pump backed by a rotary vane pump. After the base pressure was reached, a specified gas was allowed to enter the chamber via a mass flow controller.

Procedure

PLA sheet

Polylactide sheet with a thickness of 300 µm (Biogreen World) was used a printing substrate. The sheet size 17.8 × 12.2 cm were cleaned with 2% solution of a dish washing detergent (Teepool) and rinsed with de-ionized water until a clear sheet was obtained. The sheets were air-dried in a clean room. The clean sheets were exposed with the oxygen plasma at 30, 50, 70 and 100 W for 30 s in the chamber. Another set of sheets was irradiated with the oxygen plasma at 30 W for 10, 15, 20, 25, 30 and 40 min. All the untreated sheets and the treated sheets were measured for surface energies by contact angle measurement (FACE contact angle, CA-A, Kyowa Interface Science, Japan) with deionized water and methylene iodide. Surface energies of the plastic sheets are calculated based on the geometric mean theory [10],

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$$\gamma_l(1+\cos\theta_1) = 2[(\gamma_s^d\gamma_l^d)^{\frac{1}{2}} + (\gamma_s^p\gamma_l^p)^{\frac{1}{2}}] \quad (1)$$

$$\gamma_s = \gamma_s^d + \gamma_s^p \quad (2)$$

where γ_l = surface tension of test liquid,

γ_s = total surface energy of printing substrate,

γ_s^d = dispersion contribution of surface energy

γ_s^p = polar contribution of surface energy,

γ_l^d = dispersion contribution of test liquid,

γ_l^p = polar contribution of test liquid, and

θ = contact angle of test liquid.

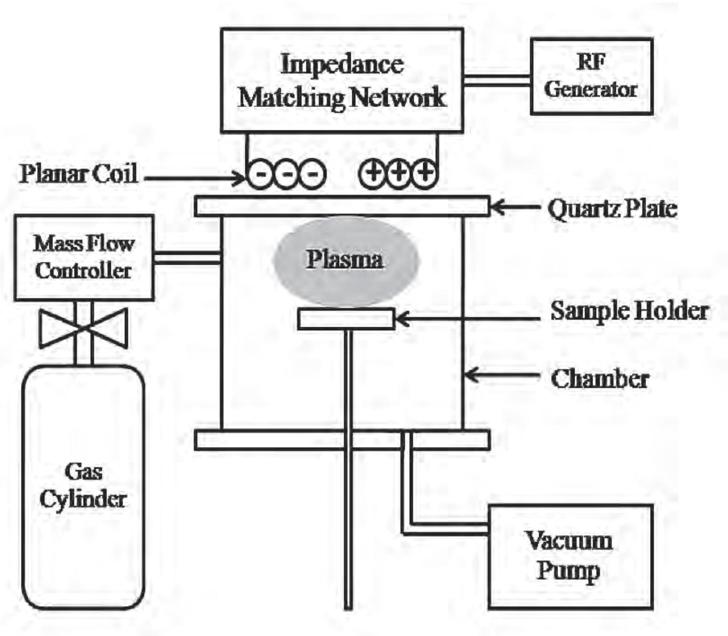

Figure 1 *Diagram of the radio-frequency (RF) inductively coupled oxygen plasma reactor.*

IR spectroscopy and AFM of the sheets

The untreated sheet and treated sheets were subjected to IR spectroscopy (FT-IR Spectrometer, Nicolet iS 10, Thermo Fischer Scientific, U.S.A.) for changes in functional groups. The surface roughness was obtained using atomic force microscopy (NanoScope-IV, Veeco, USA), operated in a tapping mode and presented in terms of Ra distance and root mean square roughness as follows:

$$RMS_{xy} = \sqrt{\sum_{x,y=1}^{N} \frac{(Z_{x,y} - Z_{average})^2}{N^2}} \qquad (3)$$

Where $Z_{average}$ is the average Z value within the examined area, $Z_{x,y}$ is the local Z value, and N indicates the number of points within the area [11].

Printing

The water-based pigmented inkjet inks (cyan, magenta, yellow and black) were measured for their surface tension with an Interfacial Tensiometer (Kruss 6, KRÜSS GmbH, Hamburg, Germany). The sheets were printed by an ink-jet printer (Stylus T13, Seiko Epson Corporation, China) with a conventional set of water-based pigmented ink (Inkman, Thailand).

The continuous tone reproduction chart in the QEA Test Chart was extracted by Illustrator software for printing the plastic sheets with the inkjet inks in the print at the highest printing quality and without color management. Duplication of each experiment was done. Comparison of the printing qualities between the untreated and treated plastic sheets was performed.

Results and discussion

Based on the structure of PLA as shown in Figure 1, the IR spectra of the PLA pellets and the PLA sheet, identical peaks are found as follows: the medium peaks at 2997 and 2941 cm^{-1} for C-H stretch, the strong peak at 1741 cm^{-1} for the carbonyl ester (-C=O) stretch, the medium peak at 1446 cm^{-1} for C-H bending, at 1381 and 1357 cm^{-1} medium peaks for the ‒ C-H scissoring, two strong peaks at 1180 and 1080 cm^{-1} for O‒C=O ester stretch and two medium peaks of C-H bending at 869 and 754 cm^{-1}. All the exposed PLA films by 30 W RF oxygen plasma for 30 s, 10, 15, 20, 25, 30, and 40 min did not give any degraded products because the IR spectra are identical.

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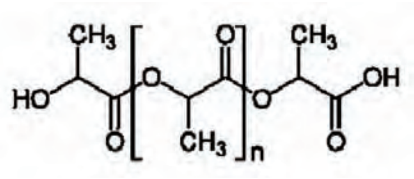

Figure 1 structure of PLA

The above data indicate that the PLA sheets were not degraded after the PLA pellets were processed to become the sheets.

Surface tension of the ink and surface energy of PLA sheets

Surface tensions of 26±1, 32±0.5, 30±0.5 and 28±0.5 mN m^{-1} were found for the yellow, cyan, magenta and black pigmented inks, respectively. The standard deviation values are within ± 0.5. The surface tensions of all inks are within the standard range and it is acceptable for ink performance, i.e., droplet formation and spreading on printing substrates. Therefore, surface energy of the printing substrate is very important. The contact angles and surface energies of the PLA sheets for the untreated and treated sheets with the set condition are presented in Table 1.

Table 1 indicates that the untreated PLA sheet (0 W and 0 s) has a relatively low polar contribution component of surface energy. With a fixed exposure time of 30 s and varied power, one can see that the polar contribution component of surface energy increased when compared with that of the untreated sheet. However, increasing the treater power did not increase the polar contribution component because the exposure time was too short to allow the reaction to take place although there were abundant amount of electron to functionalize the surface. One can also see that the dispersion contribution component of the exposed area remained constant as that of the untreated sheet. The polar/dispersion contribution ratio at various plasma powers and a constant exposure time is found approximately 1:1 and the total surface energy of the sheets is between 47 - 50 mN m^{-1}.

Table 2 exhibits the effects of increasing exposure time on the extent of polar contribution component. The similar trend as those exhibited in Table 1 was found. Increases in exposure time to expose the oxygen gas plasma cannot increase the extent of polar contribution component. An increase of 11-14 mN m^{-1} of polar contribution component was obtained when subjecting the PLA sheets to the RF treater at 30 W for 30 s or longer exposure times.

Likewise, the ratios of polar-to-dispersion contribution at all exposure times are approximately 1:1 and the total surface energy of the sheets is between 45-51 mN m^{-1}. No matter many longer exposure times of the oxygen gas plasma are given, the dispersion contribution component of surface energy could not be increased at all as expected due to the following reasons.

Table 1 Surface energies of PLA sheets at varied power of the oxygen gas plasma treater

Treatment		Contact angle (°)		Surface energy (mN m^{-1})		
Power (W)	Exposure time (s)	Deionized Water	Methylene iodide	γ_S^p	γ_S^d	γ_S
0	0	68.1±1.6	47.8±2.6	14	26	40
30	30	51.6±2.6	41.7±1.6	25	26	51
50	30	53.8±2.2	42.8±1.5	23	25	48
70	30	56.2±2.7	42.7±1.2	21	26	4

When oxygen gas is ionized, electrons collide with polymer surfaces to break molecular bonds, creating free radicals which react in the presence of reactive oxygen species (ROS) to form high polarity functional groups such as carbonyl, carboxyl, hydroxyl, or amine. The ionized oxygen gas contains ions and electrons; the oxygen gas can be split to give monoatomic oxygen, O^- or O^+ to attack the H atom on the polymer backbone. The surface energy of PLA is increased by hydrogen abstraction at the methyl groups (Figure 1) to become ions, radicals, or photon, followed by passivation by O atom, may be forming peroxy groups. The degree of functionalization depends upon on the gas plasma and energy density. The increase of the polar contribution portion takes place at the expense of the C-H and the C-C bonds to become the oxygen containing portions. In the present case, with the high amount of energy density (through the long time exposure), the increases in the polar contribution component is negligible as shown in Table 2. Two possible reasons can be postulated: first, a limited number of methyl groups are present in the polymer chain and, second, aging effect of the oxygen plasma treated surfaces at the longer exposure times.

Effect of exposure time on surface physical property

According to the results presented in Tables 1 and 2, a limit amount of increased polar contribution component of surface energy was found at 30 W at various exposure times. Interaction of the etching oxygen plasma and the PLA surface can be observed via the 3-D images shown in Figure 2. Figure 2 shows the 3-D surface structure of PLA sheets in which Figure 2(a) is the untreated sheet in

Figure 2 with a flat and smooth layer (Ra value = 7.1 nm). When exposing to the oxygen plasma of 30 W for (b) 30 s, some small roughness was seen on the surface (Ra = 10.4 nm). With the longer exposure times from 20 min exposure in Figure 2(c) to 40 min exposure in Figure 2(d), the heights of surface roughness increased markedly from 53.8 nm to 85.5 nm, respectively. Likewise, the root-mean-square roughness (RMS) was increased from 10, 13, 67, and 105 nm for the untreated sheet and the treated sheets at 30 s, 20 min and 40 nm exposures, respectively.

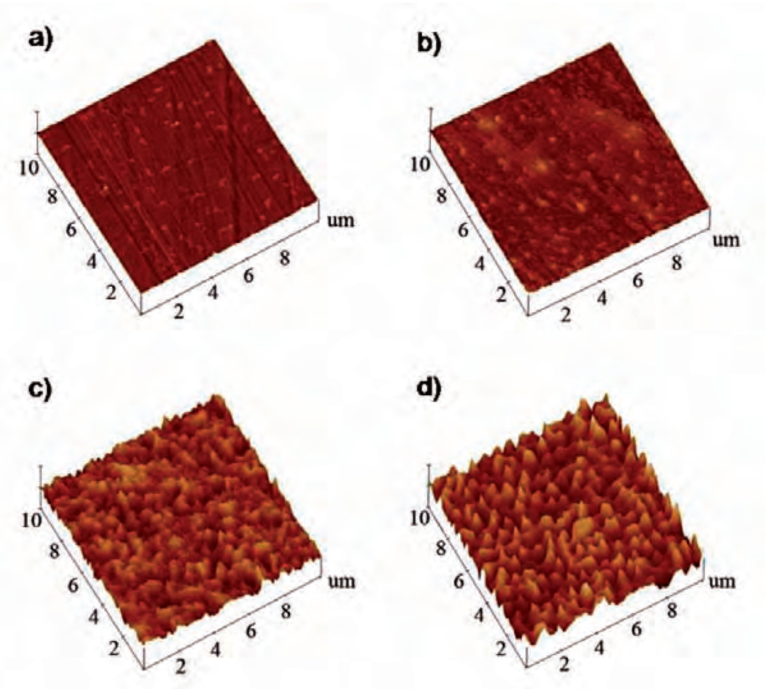

Figure 2 *Surface roughnesses of PLA sheets: (a) the untreated surface, and the treated surfaces with the oxygen gas plasma of 30 W at (b) 30 s, (c) 20 min and (d) 40 min.*

Table 2 Surface energies of PLA sheets at various exposure times to the oxygen plasma

Treatment		Contact angle (°)		Surface energy (mN m^{-1})		
Power (W)	Exposure time	Deionized Water	Methylene iodide	γ_S^p	γ_S^d	γ_S
0	0	68.1±1.6	47.8±2.6	14	26	40
30	30 s	61.6±2.6	41.7±1.6	25	26	51
30	10 min	54.7±3.0	44.2±1.3	25	23	48
30	15 min	57.3±0.9	48.1±1.1	23	22	45
30	20 min	50.3±1.3	46.3±1.3	28	22	50
30	25 min	50.8±0.9	45.5±0.7	27	23	50
30	30 min	55.1±0.7	46.1±0.9	26	23	49
30	40 min	51.9±0.9	45.2±0.6	26	23	49

Printing quality

As shown in Figure 3, the quality of the printed sheets depends largely on the oxygen plasma treatment, i.e., the power and exposure. The higher power of the treater, 70 W and 100 W, produced low printing qualities [Figure 3 (b) and Figure 3 (c)] when compare with the lower treater power, 30 W, with the longer exposure time, 20 and 30 min [Figure 3 (d) and Figure 3 (e)]. More details are given below.

Effect of plasma power

Although the surface energy of the untreated PLA sheet is about 10 mN m^{-1} higher than those of the inks, the inks cannot spread evenly on the areas of high tonal density [Figure 3(a)]. The maximum tonal density to achieve the even ink spreading was found at 40% tone (Figure 4). Color bleeding was also found in the red to green and black colors [Figure 3(a)]. The better print qualities were found in the treated areas where increasing the treating power increased to give a higher tonal density up to 70% and with a little smooth leveling.

When increasing the exposure times, all the color inks printed on the tone reproduction wedges became smoothly spread. The optimal exposure time for the good leveling quality was found with the exposure times of 20 to 25 min (Figures 3-5); afterwards, a slightly poor leveling or spreading was seen in the printed strips. Less color bleeding was observed when a longer exposure time was given to the PLA sheet [Figure 3(d) and 3(e)].

The exposure time has a marked effect on the exposed surface roughness (Ra distance) and RMS as shown in Figure 6. As presented in Figure 2(c) and Figure 2(d), one can see that the number of pikes was reduced but their heights were sharply increased. The number of pikes and grooves are then proposed to give good ink adhesion to the PLA surface. The effect of exposure time on surface roughness indicated that longer exposure times produced the higher RMS values (more roughness). It is inevitable to note that the higher exposure times at 30 and 40 min cannot print the inks to the full tonal density with good quality.

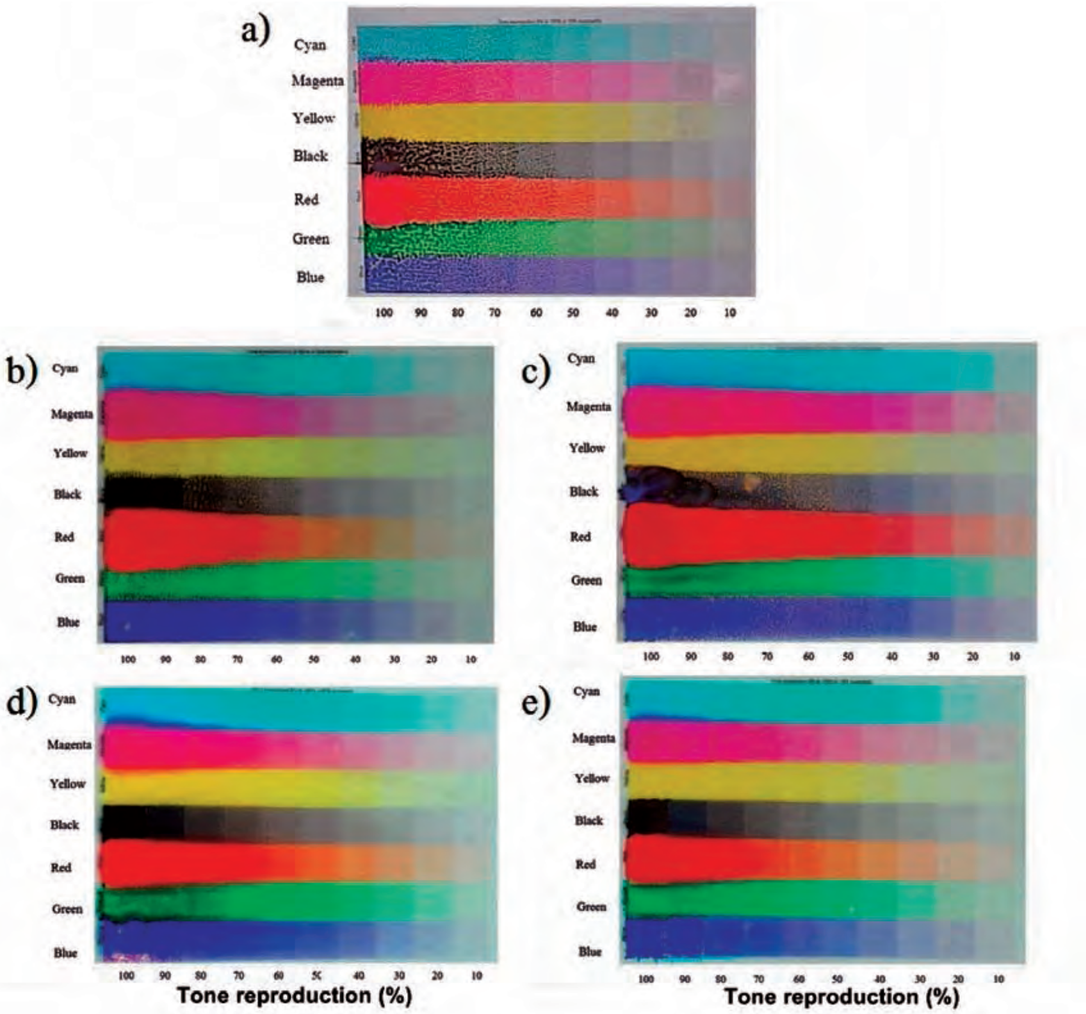

Figure 3 *Printing quality of the continuous tone reproduction of PLA sheets (a) the untreated and treated sheets at (b) 70 W, 30 s; (c) 100 W, 30 s; (d) 30 W, 20 min and (e) 30 W, 25 min*

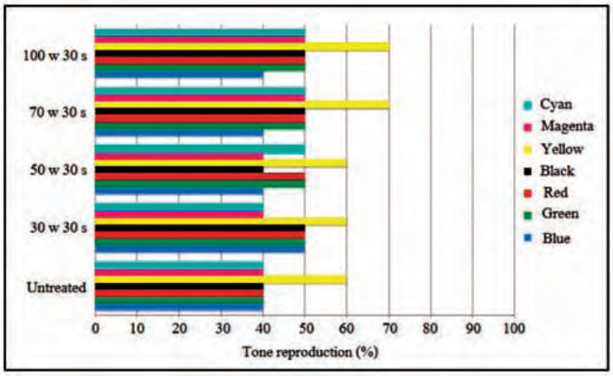

Figure 4 *The tone reproduction level in the test chart printed with the untreated and treated PLA sheets at a constant exposure time and varied RF powers*

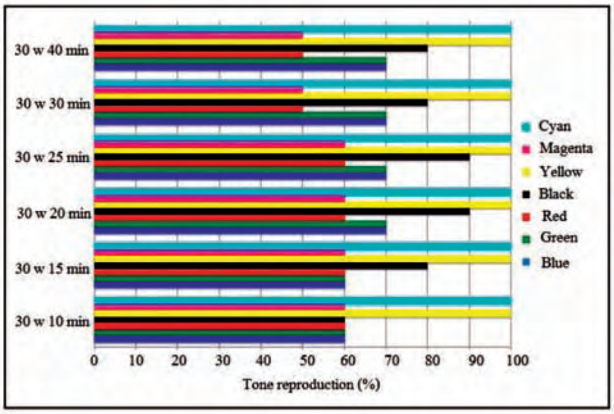

Figure 5 *The tone reproduction level in the test chart printed on the untreated and treated PLA sheets at a constant RF power and varied exposure times*

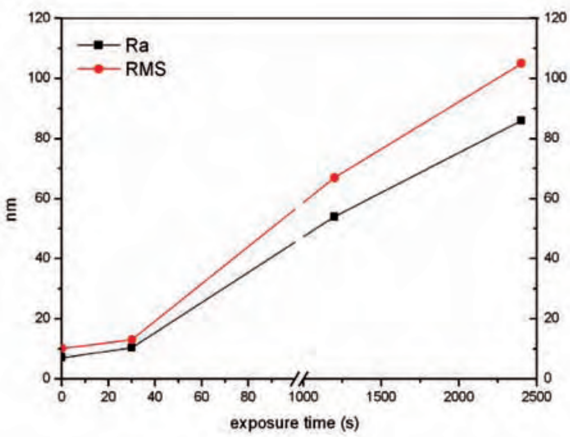

Figure 6 *Effect of exposure time for surface treatment of PLA sheets on surface area and root mean square roughness*

However, the better quality prints are not observed with the exposure times longer than 25 min; i.e., an optimum roughness can better accommodate the applied ink film with leveling and fuller toner reproduction range. Adhesion impediments can be resulted from surface abnormalities such as roughness, one general property for good adhesion. Improved adhesion of the interfaces between the PLA surface and the ink film could be due to physical interaction and chemical bonds. It is suspected that the long-lived oxygen ions or radicals may etch the pigment density due to its etching power and ion interaction between the PLA surface and the pigmented ink.

Conclusion

The oxygen plasma can be used a pretreatment gas for increasing surface energy of the PLA surface by increasing the polar contribution component by 10–12 mN m^{-1} which exceeds the surface tension of the inks used by more than 10 mN m^{-1}. Increases in the polar contribution component of the surface energy reached a maximum limit depending on the RF power and exposure time from which the longer exposure time of the oxygen plasma imposed the effective wetting, leveling, surface roughness and better adhesion of the printing ink. It is found that primary adhesion impediments depended on low surface tension of the printing ink, a higher surface polarity, better wettability and medium RMS of the printing substrate.

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Biography

Warinpong Jittiwattanapong works presently as a Quality Assurance at CCL Label, Wellgrow Industrial Estate, Chachoengsao, Thailand. He graduated his B.S. degrees in Imaging and Printing Technology, Faculty of Science, Chulalongkorn University, Bangkok, Thailand. His research involves with printing properties of substrate and biodegradable plastic. Printing properties of polylactide in inkjet with water based ink is his senior project topic and has been published and presented in Chiba-CU Student Workshop#1, 2011.

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