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นายบุญชัย นันทพิเชษฐกุล

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EFFECTS OF PROPYLENE-ETHYLENE COPOLYMER ON GRAVURE PRINTING OF CORONA-TREATED BOPP FILMS

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บุญชัย นันทพิเชษฐกุล : ผลของโพรพิลีน-เอทิลีนโคพอลิเมอร์ต่อการพิมพ์กราวัวร์ของฟิล์มบีโอพีพีที่ปรับผิวด้วยคอโรนา. (EFFECTS OF PROPYLENE-ETHYLENE COPOLYMER ON GRAVURE PRINTING OF CORONA-TREATED BOPP FILMS) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: รศ.ดร.ศุภวรรณ ตันตยานนท์, 59 หน้า.

งานวิจัยนี้เตรียมฟิล์มบีโอพีพีตัวอย่างโดยใช้เอกซ์ทรูเดอร์แบบ 3 ชั้น ความหนาของชั้นผิว 1 ไมครอน ชั้นผิวของฟิล์มบีโอพีพีปรับเปลี่ยนโดยใส่โพรพิลีน-เอทิลีนโคพอลิเมอร์ 3-6 % โดยน้ำหนัก พื้นผิวของฟิล์มบีโอพีพีผ่านการปรับผิวด้วยคอโรนาทันทีหลังการดึงยืดสองทิศทางเสร็จสมบูรณ์ ต่อจากนั้นทำการตรวจวัดค่ามุมสัมผัสและค่าพลังงานผิวอิสระของฟิล์มบีโอพีพี ยิ่งไปกว่านั้นตรวจวัดผลกระทบของแอนติ-สแตติคเอเจนท์ และสลิปเอเจนท์ ในชั้นในของฟิล์มบีโอพีพีต่อค่าพลังงานผิวอิสระ ผลแสดงค่าพลังงานผิวอิสระของฟิล์มบีโอพีพีเพิ่มขึ้นเมื่อเพิ่มปริมาณโพรพิลีน-เอทิลีนโคพอลิเมอร์และแอนติ-สแตติคเอเจนท์ ที่ 6% ของโพรพิลีน-เอทิลีนโคพอลิเมอร์ในชั้นผิว, พลังงานผิวอิสระของฟิล์มบีโอพีพีเพิ่มประมาณ 20% ซึ่งมากกว่าฟิล์มบีโอพีพีปกติ ข้อมูลฟูเรียทรานซ์ฟอร์มอินฟราเรดสเปคโทรสโคปีของฟิล์มมีโอพีพีที่ 6% แสดงแถบการดูดกลืนคาร์บอนิลสูงสุด ตรวจวัดประสิทธิภาพการพิมพ์ของฟิล์มบีโอพีพีโดยใช้เครื่องกราวัวร์พรูฟกับหมึกสีนำเงินและสีแดงชมพู ภาพพิมพ์ของฟิล์มบีโอพีพีสังเกตุด้วยกล้องไมโครสโคปซึ่งแสดงภาพพิมพ์ดีสุดเนื่องจากการหายของหน่วยเซลล์บนเม็ดสกรีนน้อย

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BOONCHAI NUNTAPICHEDKUL: EFFECTS OF PROPYLENE-ETHYLENE COPOLYMER ON GRAVURE PRINTING OF CORONA-TREATED BOPP FILMS. ADVISOR : ASSOC. PROF. SUPAWAN TANTAYANON, Ph.D., 59 pp.

In this study, the BOPP film samples were prepared using the 3-layers co-extruder, with 1.0 μm thickness of skin layer. The skin layer of BOPP film was modified by adding propylene-ethylene copolymer at various amount of 3-6% by weight. The film surface was subjected to corona treatment which was in line of production after the film was completely biaxially oriented. The contact angle of these BOPP films was subsequently measured and their surface free energy (SFE) was calculated. In addition, the effect of antistatic agent and slip agent in the major layer of BOPP film to SFE were also investigated. The results exhibited that the SFE of BOPP films was higher with the increasing content of propylene-ethylene copolymer and the presence of the antistatic agent. At 6% of propylene-ethylene copolymer in the skin layer, the SFE of BOPP film was approximately 20% higher than the original BOPP film. Its FTIR spectrum of BOPP film at 6% showed the carbonyl absorption band with highest intensity compare to the others. The printability of BOPP films was also investigated using Gravure proof machine with magenta and cyan inks. The printing images of BOPP films were visually observed with a microscope. It was found that exhibited the best printing image due to the least disappearance of the unit cell on the dot screen.

Field of Study : ..Petrochemistry and Polymer Science…Student's Signature…………….
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LIST OF ABBREVIATIONS

°C : Degree Celsius
BOPP : Biaxially-oriented polypropylene
CA : Contact angle
CO : Propylene-ethylene copolymer
COF : Coefficient of Friction
d : Dispersion component
DBD : Dielectric barrier discharge
DC : Direct current
EVA : Ethylene vinyl acetate
FTIR : Fourier-Transform Infrared Spectroscopy
γ^d : Dispersion component
γ^p : Polar component
LDPE : Low-denstity polyethylene
MD : Machine Direction
MDO : Machine Direction Oriented
mJ/m^2 : milliJoule per square metre
p : Polar component
PE : Polyethylene
PP : Polypropylene
sec : Second
SFE : Surface Free Energy
SR : Silicone rubber
TD : Transverse Direction
TDO : Transverse Direction Oriented

CHAPTER I

INTRODUCTION

1.1 Introduction

Biaxially-oriented polypropylene (BOPP) is a polypropylene (PP) film that made from extruded PP and stretched in both the machine direction and transverse machine direction. BOPP film is available in a wide range of film variations targeting the packaging, protective coating, pressure sensitive tape, label, printing, metallizing and decorative markets [1-5].

However, the BOPP films have limitation to their adhesion properties owing to their non-polar nature and low surface energy. It is necessary to modify their surfaces to increase the surface energy without change in their bulk properties for many commercial applications. Several surface modification methods are employed to modify the polymer surface, such as chemical treatment, thermal treatment, corona discharge, flame treatment, plasma treatment and U.V. treatment, etc [1, 3, 6-10] All methods create polar groups on the polymer surface such as –OH, C=O, COOH and COO- and lead to increase the surface free energy and wettability of polymer [4, 11-16].

The corona discharge treatment is one of the processes that are widely used to improve the wettability, surface free energy and printability of polymers [16-20]. The main advantages of corona treatment result in its high ease of handling and integration into production lines, its relatively low induced running costs and its efficiency in several applications [20]. Corona treatment is based on an electrical discharge in air which activates oxygen producing electrons, ions, radicals, photons and ozone. As a result, the surface of the film is activated by ions and photons to give carbon radicals. These radicals react with the surrounded gaseous species, leading to the formation of mainly oxygen based functional groups, such as alcohol, ether, ketone, acid or ester [2, 3, 21-26].

In the flexible packaging industry, the BOPP is one of the most common polymers that used in printing process because it shows excellent mechanical properties, light weight, good barrier to water vapor, good dimensional stability, high gloss, good puncture and a high adaptability to complicated structures [1, 3, 27].

Product packaging is an important marketing instrument. It also indicates a specific entrepreneur as the origin of the products. Printing design can be protected trade mark and copyright. The designs of printing image which is complicated are concerned with the appearance of part or of the whole products. It may consist of two dimensional features, such as patterns, lines or color or of three-dimensional features, such as shape, texture or surface of an article.

In printing process such as offset, flexo and gravure printing, the gravure printing is one of most common printing process because it can be used for printing on almost any type of substrates including plastic, metallic films, cellophane and paper. Gravure printing is a well established printing technique which is mainly used for high quality and long run printing of magazine, catalogues etc. In addition, gravure printing process has been widely used to print inexpensive high-volume printed matter [27-31].

1.2 Objectives of research

The purpose of this work is to investigate the surface modification of BOPP films using propylene-ethylene copolymer and observe the ink transfer and printing characteristics in gravure printing of the surface modified BOPP films.

1.3 Scope of research

- Literature survey; author compared the advantage and disadvantage of several techniques that used to modify surface of polymer such as flame treatment, corona treatment and plasma treatment.
- Investigation the surface free energy (SFE) of BOPP surface using the contact angle measurement.
- Investigation of migratory additive which migrated to BOPP surface using the universal testing machine.
- Characterization of chemical functional group on treated BOPP surface using FTIR.
- Printability on BOPP film using the gravure proofer machine and microscope.
- Investigation of haze property of BOPP film using haze machine.
- Investigation of tensile strength and elongation using the universal testing machine.
- Summary of result and conclusion

CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Biaxially oriented polypropylene

Polypropylene is found in a wide variety of films and multilayer film structures as a result of its strength, toughness and high melting point. The homopolymer chemical structure is rather simple, a methyl group located on every other methylene unit.

When polypropylene film is extruded and stretched in both the machine direction (MD) and transverse machine direction (TD) it is called Biaxially Oriented Polypropylene (BOPP). Among oriented films, the biaxial orientation is the most preferred technology as it leads to improved properties in both MD and TD directions.

BOPP film is one of the most popular raw materials of flexible packaging industry in the world. Lower costs and convenience has added to the growth of BOPP in the past few years, along with other flexible packaging materials.

2.2 Corona treatment [26, 32]

Corona treatment (sometimes referred to as air plasma) is a surface modification technique that uses low temperature corona treatment to impart changes in the properties of a surface. The corona treatment is generated by the application of high voltage to sharp electrode tips, as revealed in Figure 2.1. Materials such as plastics, cloth, or paper may be passed through the corona treatment curtain in order to change the surface free energy of the material. Corona treatment is a widely used surface treatment method in the plastic film, extrusion, and converting industries.

The basic mechanism of treatment starts with the generation of a free radical on the polymer chain. A free radical is a very reactive chemical species it reacts with an oxygen molecule, O_2, which forms peroxide. The peroxide then decomposes by various routes to form ethers, alcohols, aldehydes, ketones, or carboxylic acid groups on a material surface.

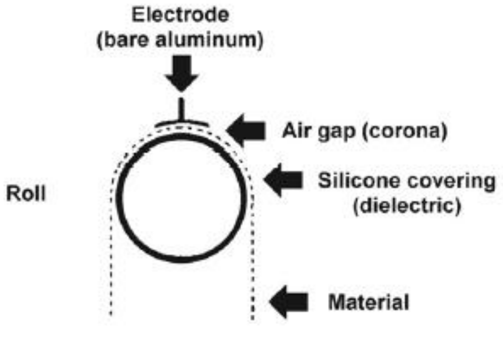

Figure2.1 Configurations of corona treatment equipment.

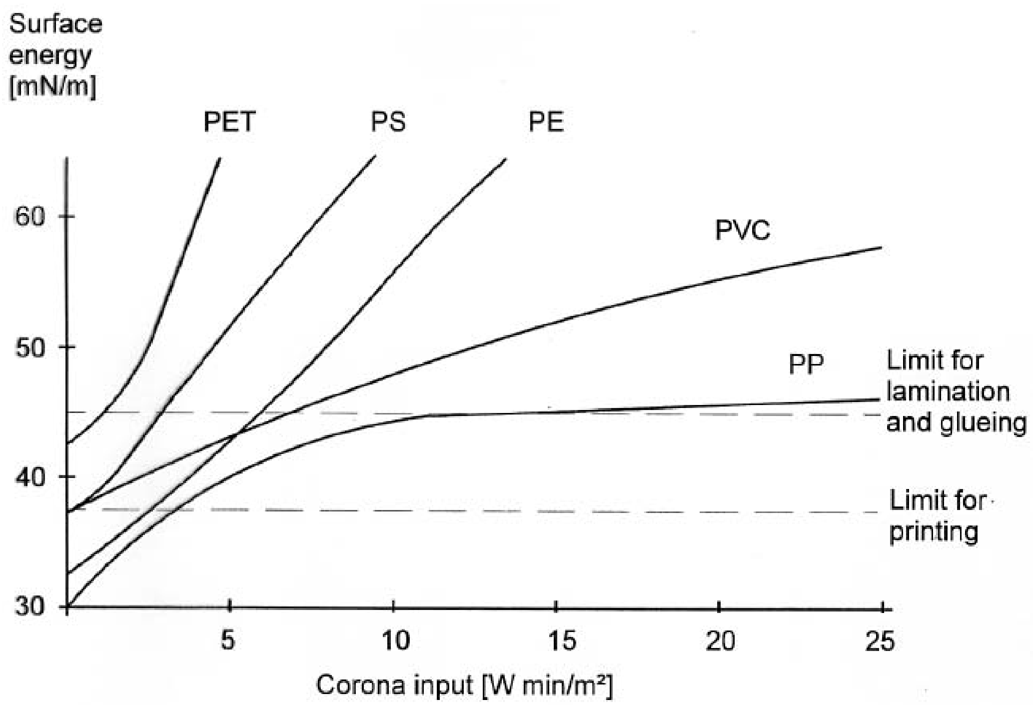

Figure 2.2 Treatability of different polymer films.

Generally, plastics have chemically inert and nonporous surfaces with low surface tensions causing them to be nonreceptive to bonding with substrates, printing inks, coatings, and adhesives. A corona treatment system is designed to increase the surface energy of plastic films. Figure 2.2 exhibited the treatability of difference polymer films. PP film is lowest surface free energy although to increase the corona input while PET, PS, PE and PVC are increasing with increase of corona input.

For the PET film, usually does not need to be treated for printing due to the level of the surface free energy in the untreated state lies clearly over the value needed for printing.

2.3 Contact angle measurement [33]

The contact angle is defined as the angle between the solid surface and a tangent, drawn on the drop surface, passing through the triple point atmosphere-liquid-solid. For this purpose, liquid was continuously added to the droplet by means of a syringe. During the measurement, the tip of the syringe remained within the center of the drop, as revealed in Figure2.3. An image analysis system calculated the contour of the drop from an image captured by means of a video camera.

The contact angle is a measurement of a liquid that spread on a surface. It quantifies the wettability of the solid surface by the liquid. If the molecules of a liquid are strongly attracted to the molecules of a solid then a drop of the liquid will completely spread out on the solid surface, corresponding to a contact angle of 0°. Weaker attractions between liquid and solid molecules will result in higher contact angles. In this study, water is representative the polar component and diiodomethane is representative the dispersion component.

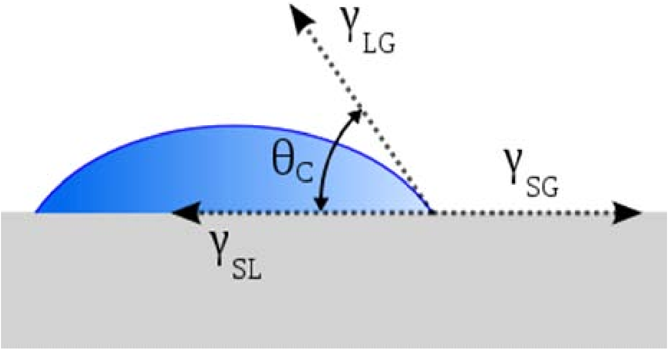

Figure 2.3 Contact angle of a liquid sample.

2.4 Calculation of surface free energy [7, 33, 34]

It is generally agreed that the measurement of contact angle on a given solid surface is the most practical way to obtain surface energies. The theory of the contact angle of pure liquids on a solid was developed nearly 200 years ago in terms of the Young equation:

$$\gamma_L COS\theta = \gamma_S - \gamma_{SL} \qquad (1)$$

Where γ_L is the experimentally determined surface energy (surface tension) of the liquid, θ is the contact angle, γ_S is the surface energy of the solid and γ_{SL} is the solid/liquid interfacial energy.

2.4.1 One component theories [33, 35]

- The Zisman Theory

The Zisman theory is the simplest commonly used theory, as it is a one component theory, and is best used for non-polar surfaces. The SFE of solids assumes that the contact angle of a liquid on a solid becomes zero when the surface free energy of the solid and the surface tension of the liquid are equal, and the interfacial solid–liquid energy is reduced to zero.

However, the shortcoming of this method is a result of the fact that Zisman theory treats the surface energy as one single parameter, rather than accounting for the fact that, for example, polar interactions are much stronger than dispersive ones, and thus the degree to which one is happening versus the other greatly affects the necessary calculations. As such, it is a simple but not particularly robust theory. Since the premise of this procedure is to determine the hypothetical properties of a liquid, the precision of the result depends on the precision to which the surface energy values of the probe liquids are known.

2.4.2 Two component theories

- The Owens-Wendt Theory [34]

The Owens-Wendt method divides the surface energy into two components: surface energy due to dispersive interactions and surface energy due to polar interactions. Interactions between molecules of two substances, present in their surface layer, are equal to the geometric mean of intermolecular interactions within each sub- stance. The polar component is understood as the sum of polar, hydrogen, inductive and acid–base interactions. The following equation allows one to determine the SFE. The accuracy and precision of this method is supported largely by the confidence level of the results for appropriate liquid-solid combinations. The Owens-Wendt theory is typically applicable to surfaces with low charge and moderate polarity.

- The Wu Theory [33]

The Wu theory is also essentially similar to the Owens-Wendt. It divides surface energy into a polar and a dispersive component. The primary difference is that Wu uses the harmonic means rather than the geometric mean known surface tensions, and subsequently the use of more exacting mathematics is employed. Wu theory provides more accurate results than do the other two component theories, particularly for high surface energies. However, suffer from one complication, because of the mathematics implicated, the Wu theory is accepted widely that the intermolecular energy between two materials results from the summation of a dispersion component (γ^d) and a polar component (γ^p).

2.5 Gravure printing technique [27-29]

Gravure printing has been widely used to print inexpensive high-volume printed matter. Gravure printing technique, the recessed printing image is formed by a raster of gravure groove which is chemically etched or mechanically engraved (diamond, laser) into the surface of a metallic printing cylinder, as reveal in Figure2.4.

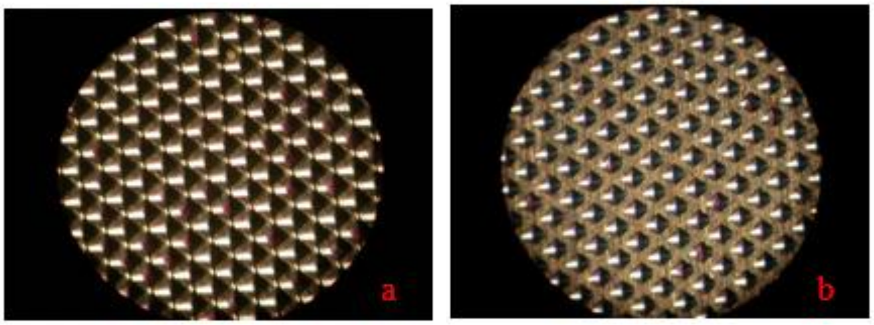

Figure2.4 A quadrangular gravure grooves; (a) is 100 and (b) 50 dot%.

During printing, the gravure grooves are continuously filled with ink while the excess ink is removed by a doctor blade. A defined amount of ink from inside the gravure groove is then transferred reproducibly to the substrate when the printing cylinder is brought into direct contact with the substrate resulting in an image raster. Subsequent to printing, the wet image has to be dried to remove the solvents and potentially also has to be cured. Figure2.5 presents a picture of the principle of gravure printing.

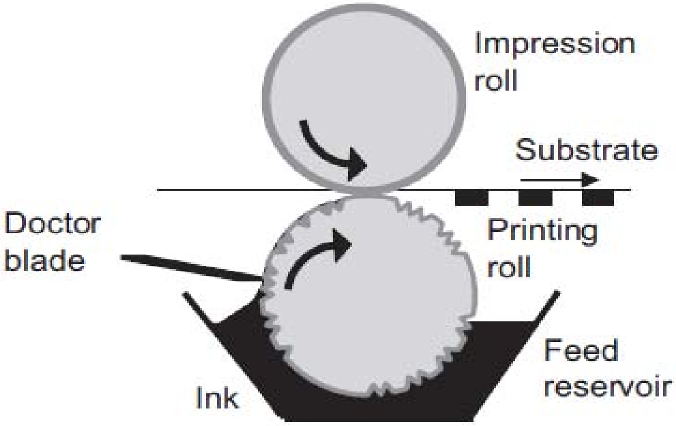

Figure2.5 Schematic illustration of gravure printing process.

2.6 Literature review

Polymer surface properties are related closely to the applications of polymeric materials like polypropylene (PP), polyethylene (PE) etc, especially in areas of gluing and printing technology. Adhesion is one of the basic physical properties which are significant for many industrial processes. Contact angle (CA) and surface free energy (SFE) are used to characterize and predict adhesion properties of polymeric materials.

In 2001 S.J. Park et al. [22] studied the surface functionality and surface free energy of low-density polyethylene (LDPE) film that surface was treated by corona discharge. Electron spectroscopy for chemical analysis (ESCA) was used to investigate

LDPE surface. It was found acidic polar groups, i.e., O=C-O, C=O, and C-O. These functional groups lead to increase surface free energy of LDPE surface.

In 2001 A.P. Pijpers et al. [14] studied the adhesion property of polypropylenes after treated by flame treatment. The results are presented on the characterization of flame treated PP compounds by XPS, as well as the predictive information obtained from the XPS study concerning the paint adhesion behaviour of the modified PP surfaces. The oxygen concentration on the PP surface is increasing after treated by flame treatment and lead to increasing the paint adhesion. However, flame treatment is possible to damage PP surface.

In 2002 L. Carrino et al. [5] studied the wettability and adhesion properties of polypropylene that treated by cold plasma treatment. The experimental results revealed the plasma process may increase polypropylene wettability and adhesion properties. The best results in terms of wettability are obtained for condition 10 kV, 30 s, 20 dm^3/h and the corresponding contact angle is equal to about 60°. The contact angle of non-treated polypropylene material is about 86°.

In 2002 N.Y. Cui et al. [11] studied PP surfaces that modified by an air dielectric barrier discharge treatment. They believed the CH_3 groups present on the polymer backbone in PP are preferred oxidation during the air-discharge plasma treatment with the backbone carbons relatively unaffected. As the oxidation progresses the surface wettability is improved and is attributed to the increase of surface free energy caused by growing presence of oxygen containing polar groups introduced to the sample surface during plasma exposure.

In 2004 S. Bhowmik et al. [9] studied the wettability and physicochemical characteristics of Polypropylene (PP) sheet when exposed to a DC glow discharge, through air across different electrodes such as copper, nickel and stainless steel at 13 W power level of DC glow discharge under an electrode size of 64 cm^2. The stainless steel electrode is best to increasing the surface free energy of PP sheet.

In 2006 Y. Zhu et al. [24] studied the degradation of silicone rubber (SR) and ethylene vinyl acetate (EVA) copolymer after corona discharge treatment. FTIR results show that hydrophilic OH groups, which are byproducts of aging, are formed instead of hydrophobic C–H bonds on the surface of SR and EVA specimens aged by corona discharges due to the reduction of the hydrophobicity of polymeric materials.

In 2007 M. Zenkiewicz [7] studied the SFE values of a solid that calculated by different methods such as, Owens–Wendt (OW), van Oss–Chaudhury–Good (vOCG) and Neumann. Three measuring liquids that are water, formamide and diiodomethane are used to determine the contact angle. They found the SFE values are different in each the calculation method due to objective existing differences in the mathematical formulae used. In addition, the differences in the SFE values, calculated with various methods, depend also on the kind of measuring liquids used in the contact angle measurements.

In 2007 T.A. Yovcheva et al. [21] studied the surfaces of polypropylene (PP) after treated by corona discharge using positive and negative corona polarities at -20 and 75 °C temperatures. The result indicated oxygen content in negative corona charged samples is approximately 2.4 times higher than that of positive corona charged samples. This correlation is the same for samples charged at both -20 and 75 °C.

In 2007 S.M. Mirabedini et al. [3] studied wettability of BOPP films that treated by low-pressure plasma treatment. Exposing BOPP films to low-pressure plasma is a simple and effective way for modifying and improving the wettability. The BOPP films become highly hydrophilic when exposed, even for a very short time. FTIR spectra revealed the two peaks at 1800–1591 and 1590–1490 cm^{-1} in the spectra of both O_2 and Ar plasma treated BOPP is an evidence of chemical changes in the BOPP surface. The peak in the area of 1800–1591 cm^{-1} is related to the C=O stretching bond and the other peak located at 1590–1490 cm^{-1} concerns the C=C stretching vibration.

In 2008 F. Leroux et al. [2] studied surface of polypropylene film after treated by dielectric barrier discharge plasma treatments at atmospheric pressure using air as a plasma gas give a permanent oxidation of the polypropylene surface. This oxidation increases the polymer surface free energy from 33.6 to 47.7 nN/m by adding polar groups such as hydroxyl, carbonyl and carboxyl depending of the treatment power.

In 2009 K. Navaneetha Pandiyaraj et al. [1] studied polypropylene film which surface is modified by DC glow discharge plasma. The results show that the surface hydrophilicity has been improved due to the increase in the roughness and the introduction of oxygen-containing polar groups. The AFM observation on PP film shows that the roughness of the surface increased due to plasma treatment. Analysis of chemical binding states and surface chemical composition by XPS showed an increase in the formation of polar functional groups and the concentration of oxygen content on the plasma-processed PP film surfaces.

In 2009 K. Navaneetha Pandiyaraj et al. [6] studied the adhesive properties of polypropylene film that is modified by plasma treatment. All the literature researches exhibited several treatment techniques were correlated to the surface oxidation which leaded to increases the polymer surface free energy, wettability and adhesive properties by adding polar groups, such as C-O, C=O, COOH.

In 2009 J.W. Lee et al. [27] studied the ink transfer efficiency and printing characteristics in high speed gravure printing on poly(ethylene terephthalate) (PET) and biaxial-oriented polypropylene (BOPP). The flexible substrates were printed in an aqueous ink diluted with ethanol under various machine factors such as printing speed, nip force, and groove size. The chromaticity of the printed ink layer is decreased with the addition of ethanol as diluent into the ink due to the decrease in the ratio of pigment in the ink and increasing of gravure groove size (dot %) is leading to increasing the chromaticity of the printed ink layer.

CHAPTER III

EXPERIMENTAL

3.1 Material

- Polypropylene homopolymer (HP525J grade, HMC Polymers Company limited)
- Propylene-ethylene copolymer (FS5612L grade, The Polyolefin Company (Singapore) Pte. Ltd.)
- 30% of Amides, coco, N,N-bis(hydroxyethyl) in polypropylene homo polymer
- 6% of erucamide in polypropylene homopolymer

3.2 Chemicals

3.2.1 Chemicals for contact angle measurement

- Distilled water (Merck KGaA, Germany)
- Diiodomethane (CH_2I_2, 98%, Merck Schuchardt OHG, Germany)

3.2.2 Chemicals for printing

- Ethyl acetate ($CH_3COOC_2H_5$, 99.5%, Merck KGaA, Germany)
- Cyan ink (code C39, Toyo Ink (Thailand) Co., Ltd)
- Magenta ink (code M17, Toyo Ink (Thailand) Co.,Ltd)

3.3 Apparatus

- BOPP machine (“Bruckner Group” Model AJP-1327)
- Corona discharge system (Electronic Industrial Equipment MR\B 35K-IGBT\CU, me.ro S.R.L.Ponte a Morinao-LUCCA-ITALY)
- FTIR spectrometer (“PerkinElmer” Frontier-FTIR)
- Universal Testing Machine (“Instron” model 2300/3300, Series IX Automated Materials Testing System, 500 N of load cell capacities)
- Haze meter (“BYK Gardner” model Haze-gard *Plus*)
- Contact angles machine (“Kyowa” Model DM500)
- COF testing machine (“Lloyd Instruments” Model LRX Plus, 50 N of load cell capacities)
- Gravure proof machine (“PK Print Coat Instrument”, Model K Printing Proofer)
- Measuring microscope with light (model TS-7LE, Sugitoh Co., Ltd, Japan)
- Light microscope (model Axioskop 40, Carl Zeiss Microscopy)

- Flow Cub (Zahn Cup No.4, ASTM D4212); one can convert efflux time to kinematic viscosity by using an equation for each cup specification number, where *t* is the efflux time and is the kinematic viscosity in centistokes.

  Conversion:
    - Zahn Cup#1: $= 1.1(t - 29)$
    - Zahn Cup#2: $= 3.5(t - 14)$
    - Zahn Cup#3: $= 11.7(t - 7.5)$
    - Zahn Cup#4: $= 14.8(t - 5)$
    - Zahn Cup#5: $= 23t$

3.4 Experimental procedures

3.4.1 Preparation of BOPP film samples

In this study, 3-layers co-extruder ("Bruckner Group" Model 1327AJP, Germany) was used for producing the BOPP film samples, containing different components. Twin screw is used in the co-extruder for mixing, compounding, or reacting polymeric materials. In addition, thickness gauge that is gamma-rays type is used to control thickness of BOPP film. It will send the signal to die lip when the film thickness is over range. The three layers were extruded through the top, core and bottom dies and named skin (1.0 μm), major layer (18 μm) and inner layer (1.0 μm), respectively. The as-prepared BOPP film had the total of 20 micron thickness and 8.75 meter width. The skin layer was composed of propylene-ethylene copolymer and polypropylene, the core layer contained the antistatic masterbatch and the slip agent, and the inner layer was only polypropylene, as shown in Table 3.1.

The BOPP film begins with the extrusion casting of a primary film from a slot die. This film is then oriented by stretching two-stage drawing process. During the Sequential Stretching process, the film is first stretched in machine (longitudinal) direction. This is accomplished in the Machine Direction Orienter (MDO). The film is warmed-up to 150 °C an optimum stretching temperature in the pre-heating zone, and stretched ratio is 4.6X by rolls which run different speeds in the stretching zone.

In the second step of Sequential Stretching, the longitudinally oriented film is stretched in a Transverse Direction Orienter (TDO) that stretching ratio is 9.0X. The film is clipped-in on both sides and then a diverting chain track system stretches the film. The chain track system is covered by an oven (170 ± 5 °C) to supply the necessary heat to accomplish the stretch. Finally thickness of BOPP film is 20 microns and 8.75 M of film width.

Table 3.1: Components in BOPP films

Sample No.	Skin layer (1.0 µm)		Major layer (18 µm)			Inner layer (1.0 µm)
	PP	CO	PP	AS	SA	PP
1	100	0	100	0	0	100
2	0	100	100	0	0	100
3	100	0	99.5	0.5	0	100
4	97	3	99.5	0.5	0	100
5	95	5	99.5	0.5	0	100
6	94	6	99.5	0.5	0	100
7	100	0	99	0.5	0.5	100
8	97	3	99	0.5	0.5	100
9	95	5	99	0.5	0.5	100
10	94	6	99	0.5	0.5	100

PP = Polypropylene, CO = Propylene-ethylene copolymer, AS=Antistatic masterbatch and SA= Slip agent

After stretched in a Transverse Direction, BOPP films were immediately treated by corona using three electrodes system consisting of a grounded roll electrode, a 34 W.min/m of power value, 450 m/min speed line and 2 mm of corona gap. After the corona treatment, the contact angles of all BOPP films were measured.

3.4.2 Physical and mechanical measurements of BOPP films

- Contact angle measurements

Surface free energy of the BOPP films were evaluated as static contact angles using a "Kyowa" Model DM500 contact angle measuring system. The procedure used to measure the contact angle was based on the ASTM5725 standard. The contact angles were determined using the following liquids: double distilled water (Merck KGaA, Germany) and diiodomethane (CH_2I_2, 98%, Merck Schuchardt OHG, Germany). The liquids were chosen to cover the broadest possible spectrum from highly polar and disperse component. Ten droplets of each liquid were tested on the surface of each BOPP film samples in order to ensure the statistical validity of the results.

- Surface free energy calculation

The surface free energy was determined by using the Wu theory that represents the contact angle data in the Wu equation.

$$\gamma_{SL} = \gamma_S + \gamma_L - \frac{4\gamma_S^d \gamma_L^d}{\gamma_S^d + \gamma_L^d} - \frac{4\gamma_S^p \gamma_L^p}{\gamma_S^p + \gamma_L^p} \qquad (2)$$

- Haze measurements

The haze-gard *Plus* from BYK Gardner, is used to evaluation of specific light-transmitting and wide-angle-light-scattering properties of BOPP films. Cut each test specimen to a size large enough to cover the entrance port of the sphere. A disk 50 mm (2 in.) in diameter, or a square with sides of the same dimensions, is suggested. The specimen shall have substantially plane-parallel surfaces free of dust, grease, scratches and blemishes. The procedure used to measure the haze was based on the ASTM D 1003.

- Coefficient of Friction (COF) measurements

The COF testing can be carried out using a "Lloyd Instruments" Model LRX Plus, 50 N of load cell capacities. The test specimen that is to be attached to the plane shall be cut approximately 250 mm (10 in.) in the machine direction and 130 mm (5 in.) in the transverse direction. A film specimen that is to be attached to the sled shall be cut approximately 120 mm (4 ½ in.) square. A sled is specified weight 200 g. The sled is pulled across a second surface at a speed of 150 mm/minute. The force to get the sled started (static) and to maintain motion (kinetic) is measured. The procedure used to measure the COF was based on the ASTM D 1894.

- Surface analysis by FTIR-ATR technique

FTIR-ATR spectra of treated BOPP substrates were recorded on a Perkinelmer Frontier-FTIR spectrometer with measurement conditions as follows: a horizontally mounted internal reflection element (IRE) (Diamond crystal); angle of incidence on IRE (45 °); accumulations 4 scans and spectral resolutions of 4 cm^{-1}.

3.4.3 Mechanical properties of BOPP films

- Tensile and elongation measurements

The procedure used to measure the tensile strength and elongation at break was based on the ASTM D 882 standard. The tensile strength and elongation at break was carried out using Universal Testing Machine ("Instron" model 2300/3300, Series IX Automated Materials Testing System, 500 N of load cell capacities) at a rate of 300 mm/min at room temperature, sample width 15mm and 100 mm of grip range.

3.4.4 Printability measurements

Ink transfer and printing characteristics in gravure printing were investigated on BOPP films. The flexible substrates were printed in a solvent ink diluted with ethyl acetate. Viscosity of ink solution is maintained at 18 – 20 sec by Zahn cup#4 (192 – 222 centistokes). The printability testing can be carried out using a "PK Print Coat Instrument" Model K Printing Proofer, as presented in Figure 3.1. A quadrangular gravure grooves of 100, 90, 70, 50, 30, 10 and 5 % of densities (dot %) were engraved on a gravure plate via a laser engraving process. The gravure plate KS 5611 which sizes of unit cells were 175 line/ inch are used. The depths of the engraved gravure grooves were observed to deepen with increasing dot% and were in the range of 2-40 μm. The test specimen should be cut approximately 250 mm in the machine direction and 130 mm in the transverse direction. The printed images and ink transfer efficiency were examined using an optical microscope.

Figure 3.1 Gravure proof machine, RK Print Coat Instruments Ltd.

CHAPTER IV

RESULTS AND DISCUSSION

BOPP films were prepared using biaxial-oriented machine “Bruckner Group” Model AJP-1327, which was for the industrial scale manufacture. The machine was the three layer co-extrusion with a twin screw mixer for each layer, and had the IR-Gauge for the clear film thickness control. Both functions cannot be found in the pilot scale or lab scale machine. By using this industrial scale machine, it could be ensured that the skin layer of BOPP film samples could be maintained to be 1.0 micron in this study. In addition, the corona treatment system was installed in-line process after the biaxial-oriented machine.

In this research, the BOPP film samples are composing of three layers. The top layer for further printing would be referred to the skin layer which contained the various amount of propylene-ethylene copolymer in polypropylene with 1.0 micron thickness. The second layer, as referred to the major layer, contained 0.5% antistatic agent and slip agent thickness 18.0 microns. The third layer, as referred to the inner layer, was plain polypropylene. The total thickness of each BOPP film sample was 20.0 microns.

4.1 Physical properties of modified BOPP film

4.1.1Contact angle and surface free energy of modified BOPP film

The contact angle of water with Sample No.2 is lowest due to the treated surface is generated the polar group such as –OH, C=O, -COOH and –COO [22, 24, 25] and lead to increasing SFE. In contrast, contact angle of Sample No.11 that non-corona treatment is highest because surface of BOPP film is non-polar, as revealed in Table 4.1.

The SFE of non-corona-treated BOPP, Samples No.1, was 39.5 mJ/m^2 which was much lower than treated propylene-ethylene copolymer, 68.7 mJ/m^2. These results were due to the existence of the polar group at the film surface. For Sample No. 1, the tertiary radicals formed in polypropylene generally decayed via β–scission or disproportionation faster than combination with oxygen. In case of Sample No. 2, the secondary radicals were formed in the ethylene moieties and then the combination with oxygen was likely to occur [10, 36]. Therefore Sample No. 2 had more polar groups than Sample No. 1. This observation was confirmed by the IR spectroscopic study as described in Section 4.1.4. In all places radical formation in the polymer chain caused by the corona treatment, This species can combine with oxygen from air and lead to the increase in the amount of polar group, such as –OH, C=O, -COOH and –COO [22, 24, 25] and thus increase in the polar component.

Table 4.1 : contact angle and surface free energy of BOPP films

Sample No.	Contact angle (deg)		SFE (mJ/m^2)		
	Water	Diiodomethane	d	p	total
No.1	60.0	46.0	28.7	10.8	39.5
No.2	19.6	55.9	20.4	48.3	68.7
No.3	68.6	55.2	22.8	18.6	41.4
No.4	63.3	60.1	20.2	23.1	43.1
No.5	56.3	60.6	19.5	27.7	47.2
No.6	55.1	60.2	19.7	28.4	48.1
No.7	72.7	58.8	21.6	16.9	38.5
No.8	65.0	58.0	21.2	21.4	42.6
No.9	61.0	55.3	22.1	23.3	45.4
No.10	59.1	55.5	21.9	24.6	46.5
No.11 (non treatment)	100.3	59.3	28.4	2.6	31.0

d= dispersion component, p = polar component and total = total surface free energy

In high speed gravure printing process, it is necessary to add antistatic masterbatch and slip agent in BOPP film to prevent the fire which might initiate from the ink solution and to support high speed printing, respectively. However, both antistatic masterbatch and slip agent are migratory additives and may affect to the surface free energy. Therefore the surface free energy of the modified BOPP film with antistatic masterbatch and slip agent in the major layer was studied.

The SFE is 41.4 mJ/m^2 and 39.5 mJ/m^2 for Sample No. 3 that 0.5% of antistatic masterbatch is introduced in major layer and Sample No.1 that without antistatic masterbatch, respectively. These results may be explained as follows; the antistatic masterbatch migrated to BOPP surface after treated by corona treatment and led to increase the polar component on the BOPP surface owing to the chemical structure of antistatic masterbatch has polar group.

On the other hand, SFE is 38.5 mJ/m^2 for Sample No.7 which is lower than Sample No.1. These results may be explained as follows; the slip agent that is introduced in the major layer of Sample No.7 is migrating to BOPP surface and leads to reduce the surface free energy owing to more hydrophobic nature of chemical structure.

The SFE of BOPP film is increasing when propylene-ethylene copolymer is introduced in skin layer. Figure 4.1 is exhibited the SFE of BOPP films that various 3-6% propylene-ethylene copolymers are introduced in the skin layer (Samples No. 4 to 6 and Samples No.8 to 10). SFE of Sample No.6 and Sample No.10 is 48.1 and 46.5 mJ/m^2, respectively; while the SFE of Sample No.1 is 39.5 mJ/m^2. The result indicated SFE can increase after using propylene-ethylene copolymer in skin layer before corona treatment. In this experiment, SFE is approximately 20% higher when 6% of propylene-ethylene copolymer is introduced on the skin layer before corona treatment, as revealed in Figure 4.1.

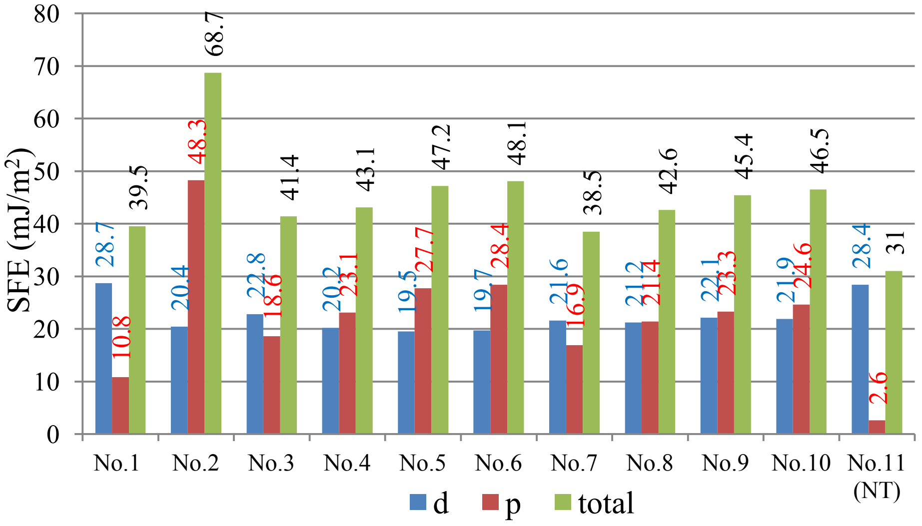

Figure 4.1 Surface free energy of BOPP film samples, (d= dispersion component, p = polar component and total =sum of polar and dispersion components), NT = non corona-treatment.

4.1.2 Haze of modified BOPP film

The optical properties of BOPP, such as clarity haze and transparency, is help producers of film or packagers to create gloss high-transparency film that enhances the appearance of packaging or other products. In this experiment, a haze property of BOPP films is investigated, as revealed in Figure 4.2

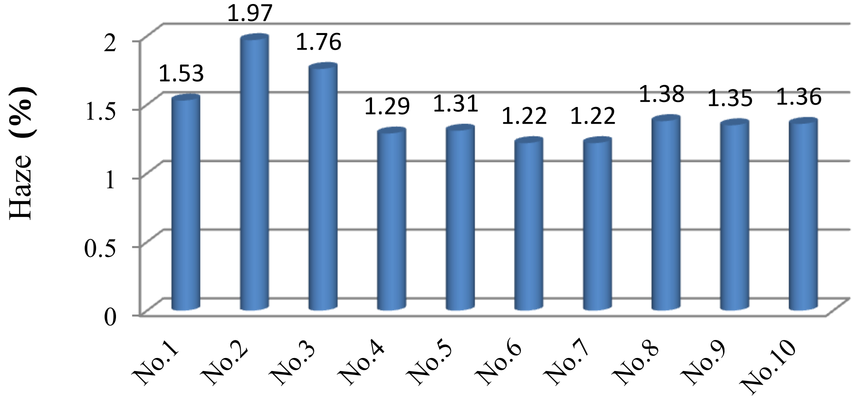

Figure 4.2 Haze properties of modified BOPP films with various amount of propylene-ethylene copolymer in skin layer.

The haze property is 1.5 and 2.0% for Sample No.1 that without propylene-ethylene copolymer and Sample No.2 with 100% of propylene-ethylene copolymer is introduced in skin layer, respectively. The haze of Sample No.2 is higher than Sample No.1 owing to propylene-ethylene copolymer can form crystallinity more than polypropylene because the structure of polypropylene have methyl group which reduce create crystalline region. However, the haze result of BOPP films that 3-6% of propylene-ethylene copolymer is introduced in skin layer is less than 1.5 % which it is suitable for printing application.

4.1.3 Coefficient of Friction (COF) of modified BOPP film

COF is one properties of flexible packaging that user request to reduce owing to the user want to increase the output of packing machine. The migratory additive such as antistatic and slip agent is migrated to surface of BOPP film and lead to change the slip property of BOPP surface.

The effectiveness of slip agent and antistatic masterbatch are normally determined by the coefficient of friction (COF) it allows, which is measured using ASTM D-1894, “Standard Method of Test for Coefficient of Friction of Plastic Film”.

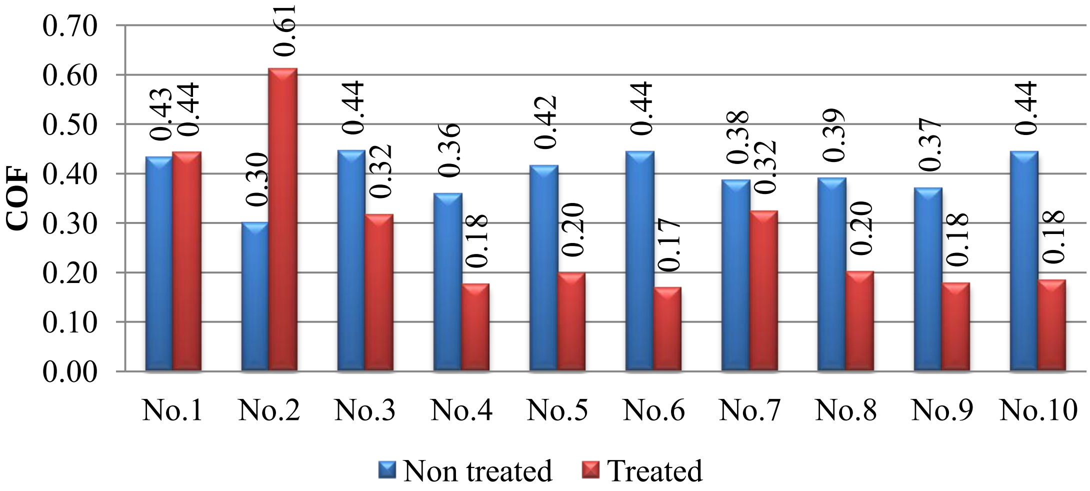

Figure 4.3 Coefficient of friction (COF) of modified BOPP films; blue color is non-corona treated side and red color is corona treated side.

Both Sample No.1 and Sample No.2 presented the COF that is more than 0.40 for treated side and other side is approximately 0.30 – 0.40, as revealed in Figure 4.3. This result indicated the surface roughness on the treated side is more rough than surface of the non-treated side because the corona treatment damages film surface. In addition, migratory additive such as antistatic masterbatch and slip agent, are presented in Sample No.3 and Sample No.7. Both antistatic masterbatch and slip agent reduce the COF the on treated side, as revealed in Figure 4.3.

COF of the treated side in Sample No.3 is 0.32 while COF of Samples No.4, No.5 and No.6 is approximately 0.20 which indicated the propylene-ethylene copolymer supported the migration of antistatic masterbatch that present in major layer of BOPP films. Also the COF of Samples No. 8, No.9 and No.10 is approximately 0.20 due to the influence of propylene-ethylene copolymer is supporting the migration of slip and antistatic masterbatch that used in major layer of BOPP films.

On the other hand, COF of the non-treated side is more than 0.30 that indicated the migratory additive cannot migrate to non-treated side.

4.1.4 Surface analysis by FTIR-ATR technique

When observing the ATR-FTIR spectra of untreated and corona-treated film, one recognizes in the differential spectrum that somewhere around wave number 1700 cm^{-1} a new peak emerges which is typical for a carbon-oxygen double bond. This leads to the existence of this C=O group (named carbonyl or carboxylic group) is responsible for the wettability.

BOPP film that 100% propylene-ethylene copolymer is introduced in the skin layer of corona treated BOPP film which is Sample No.2, ATR-FTIR spectra presented one peak at 1738.01 cm^{-1} which was an evidence of chemical changes in the BOPP surface, perhaps due to the oxidation. The peak in 1800-1591 cm^{-1} is related to the C=O stretching bond [2]. The result indicated propylene-ethylene copolymer which is introduced in the skin layer when treated with corona treatment generated the polar functional group more than the BOPP film that polypropylene homopolymer introduced in skin layer. Sample No. 11 which is non corona treated BOPP film possesses, the surface without the polar functional group, as revealed in Figure 4.4.

ATR-FTIR spectra of the corona-treated BOPP films that used propylene-ethylene copolymer in the skin layer were studied, 3-6%, are illustrated in appendices B-2 and B-3. The appearance one weak peak centered around 1737-1738 cm^{-1} can be assigned to carboxylic and ester groups [3].

Oxygen being reactive in nature, contributes mainly to incorporation groups such as –OH, O=C and –COO [3, 22, 24, 25]. This is indicated as an increase in surface energy to an equilibrium value, for corona treatment. Also, it appears that oxygen created the activated species with sufficient energy to create radicals having a long lifetime to interact within BOPP surface.

It should be noted that corona functionalization occurs by inclusion of active species (oxygen containing species) in the free radicals generated during the treatment and some functionalization can be achieved after corona treatment; when corona treated samples are exposed to ambient atmosphere, O_2 from the air can rapidly react with some free radicals and this contributes to intensify surface functionalization phenomenon. [6]

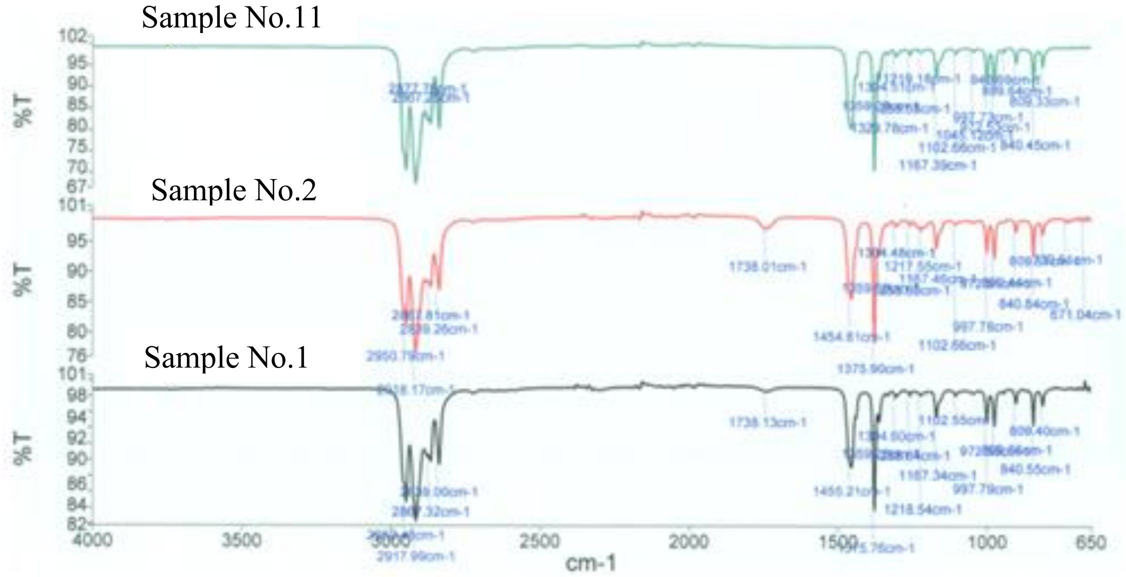

Figure 4.4 ATR-FTIR spectra of Sample No.11 is non-corona-treated BOPP film, Sample No. 2 corona-treated BOPP film with skin layer used propylene-ethylene copolymer and Sample No.1 is corona-treated BOPP film with skin layer of polypropylene.

4.2 Mechanical properties of modified BOPP film

4.2.1Tensile strength of modified BOPP film

Tensile strength is the maximum stress that a material can withstand while being stretched in printing and lamination process. The flexible substrate that low tensile strength is generating the overlap printing problem due to substrate is expand while apply the high tension. In this case, both TD and MD direction of BOPP film are investigated the tensile strength properties. The tensile strength in TD direction of Sample No.2 is 29.43 kgf/mm^2 while other BOPP films higher 30 kgf/mm^2. This behavior is influence of propylene-ethylene copolymer that introduced in skin layer, as revealed in Figure 4.5. This result indicated the tensile strength is not change when propylene-ethylene copolymer is introduced in skin layer, 3-6% by weight.

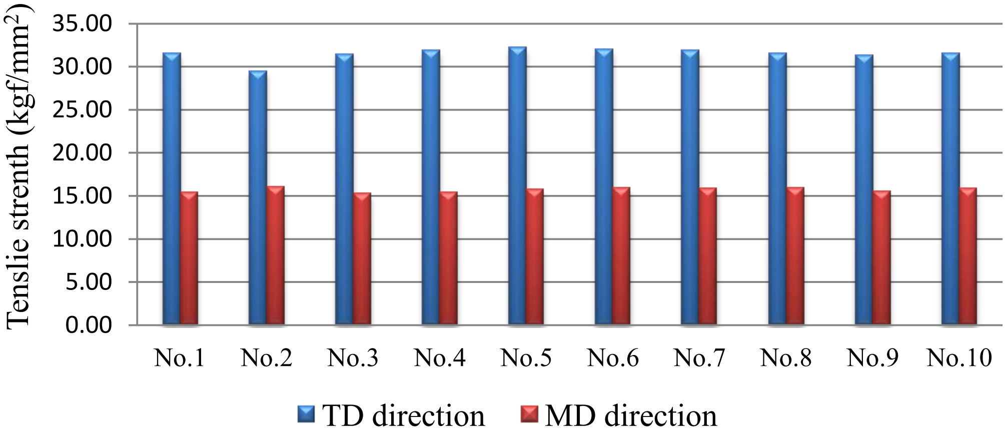

Figure 4.5 Tensile strength of modified BOPP films; red color is MD direction and blue color is TD direction.

4.2.2 Elongation at break of modified BOPP film

The ultimate elongation of a flexible material is the percentage increase in length that occurs before it breaks under tension. Absolute elongation values of several hundred percent are common for elastomers and packaging polyolefin film. In the gravure printing process, it request high tension for spread out film surface and elongation is another one that request. The flexible substrate which is high elongation is stretched due to apply high tension during printing and lead to generated overlap printing problem. In this case, elongation at break of modified BOPP films is investigated. The elongation in MD direction of Sample No.2 is highest due to the skin layer used only the propylene-ethylene copolymer. For the other BOPP films, elongation in MD and TD direction are less difference, as revealed in Figure 4.6. This result indicated amount of propylene-ethylene copolymer that used 3-6% in one side of skin layer cannot change the elongation properties of BOPP films.

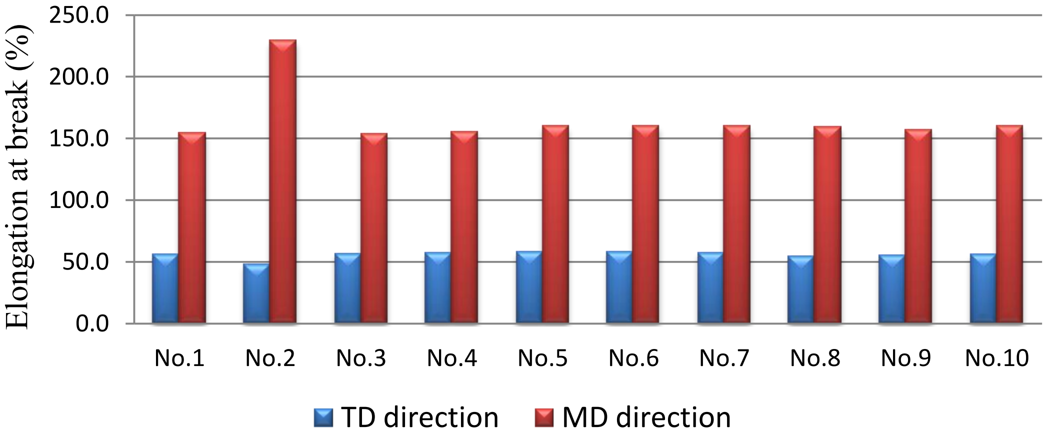

Figure 4.6 Elongation of modified BOPP films; red color is MD direction and blue color is TD direction.

4.3 Printability and ink transfer efficiency of modified BOPP film

The chromaticity of printed BOPP film obtained with gravure proof machine. The quadrangular gravure grooves of 100, 90, 70, 50, 30, 10 and 5 dot% were used. Commonly of printed image of BOPP films are without the problem if a size of gravure groove is more than 30 dot%. In contrast, printed image of BOPP films are not completely with gravure groove is reduced. In this case, printed image of BOPP films at 10 and 5 dot% of gravure grooves size are investigated.

Ink transfer efficiency of Sample No.2 that 100% of propylene-ethylene copolymer is introduced in skin layer, is better than Sample No.1 that skin without propylene-ethylene copolymer. The SFE of Sample No.2 is 68.6 mJ/m^2 but printing image is not complete. These results may be explained as follows; it is possible influence of static effect on BOPP surface. It pushes the ink drop reverse to gravure groove and led to ink repeal on the BOPP surface. This behavior believes the polar component of Sample No.2 which is 48.3 mJ/m^2. It generated the static effect on BOPP surface and leads to push the ink drop which reverses to inside of gravure groove. Figure 4.8 is exhibited the static mark around the unit cell of gravure printing on BOPP surface.

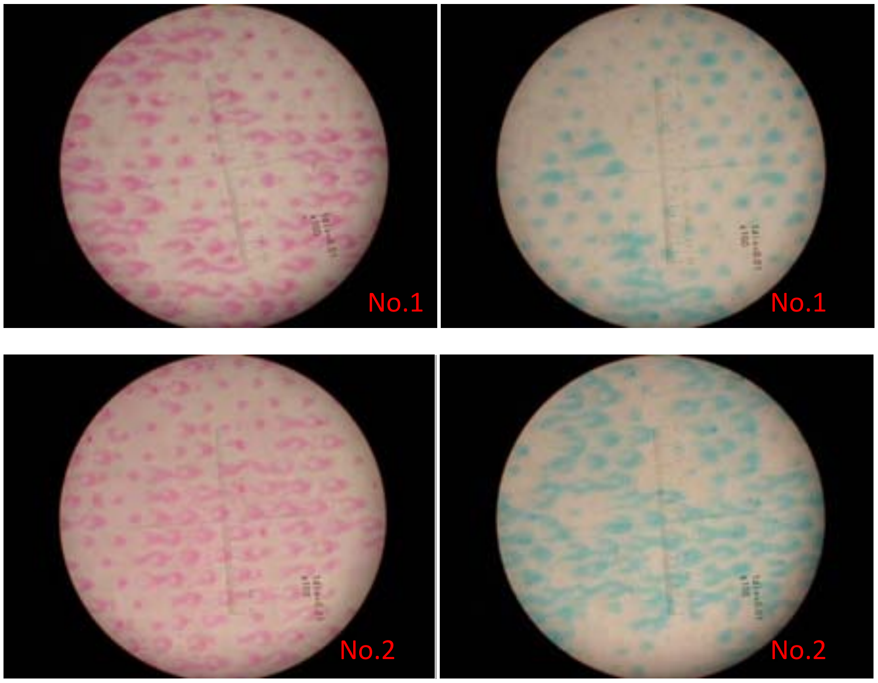

Figure 4.7 Ink transfer efficiency of BOPP film that difference modified surface with M17-magenta and C39-cyan is used, 10% of quadrangular gravure grooves size, the image were taken at a magnification of 100X.

In this case, static mark on BOPP surface is investigated by using the static mark powder. It revealed the static mark on the BOPP surface that red mark presents positive charge on BOPP surface and blue mark presents negative charge on BOPP surface. This result indicated treated BOPP film is generating the static effect on the surface, as revealed in Figure 4.9. Antistatic materbatch and slip agent are used in major layer of BOPP film as presented in Table 3.1

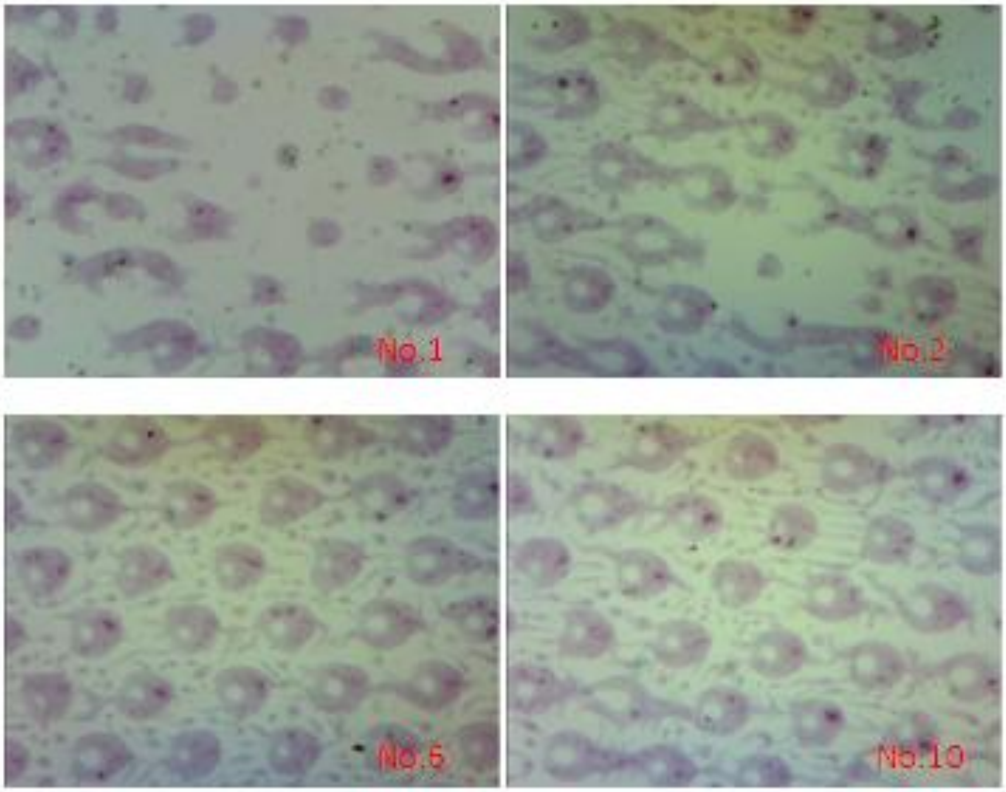

Figure 4.8 Static marks of printed BOPP films which M17-Magenta and 10% of quadrangular gravure grooves are used. The images were taken at a magnification of 100X by Light Microscope (model Axioskop 40, Carl Zeiss Microscopy).

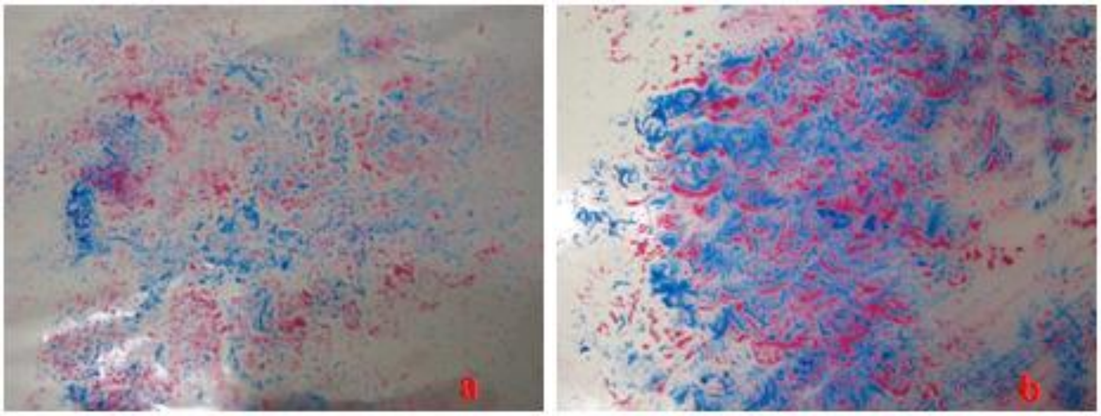

Figure 4.9 Static marks on BOPP surface, (a) is Sample No.1 and (b) is Sample No.2.

Figure 4.10 and Figure 4.11 are exhibited the ink transfer efficiency of BOPP films at 10 dot% of gravure groove size. Ink transfer efficiency of Sample No. 1, Sample No.3 and Sample No.7 are very poor but ink transfer efficiency of Sample No.6 is best when 6% of propylene-ethylene copolymer is introduced in skin layer.

Sample No.6 and Sample No.10 are using 6% of propylene-ethylene copolymer but the ink transfer efficiency of Sample No.6 is better than Sample No.10 due to slip agent that used in major layer of Sample No.10 migrated to the surface and generated hydrophobic properties on the surface of BOPP. The influence of hydrophobic properties reduced the printability and ink transfer efficiency of BOPP film. However, propylene-ethylene copolymer that introduced in skin layer of BOPP increased the ink transfer efficiency when comparing with BOPP film that skin layer without propylene-ethylene copolymer.

Ink transfer efficiency at 5 dot% of gravure groove is revealed in Figure 4.12 and Figure 4.13, the tendency of ink transfer efficiency of BOPP film that propylene-ethylene copolymer is introduced in skin layer like a result of 10 dot% of gravure groove. Although, the quality of printing image at 5 dot% is not perfect owing to shape of unit cell is not complete and dot screen is lost. This result complies with J.W. Lee et al. [27] that studied the ink transfer efficiency and printing characteristics in high speed gravure printing on BOPP film.

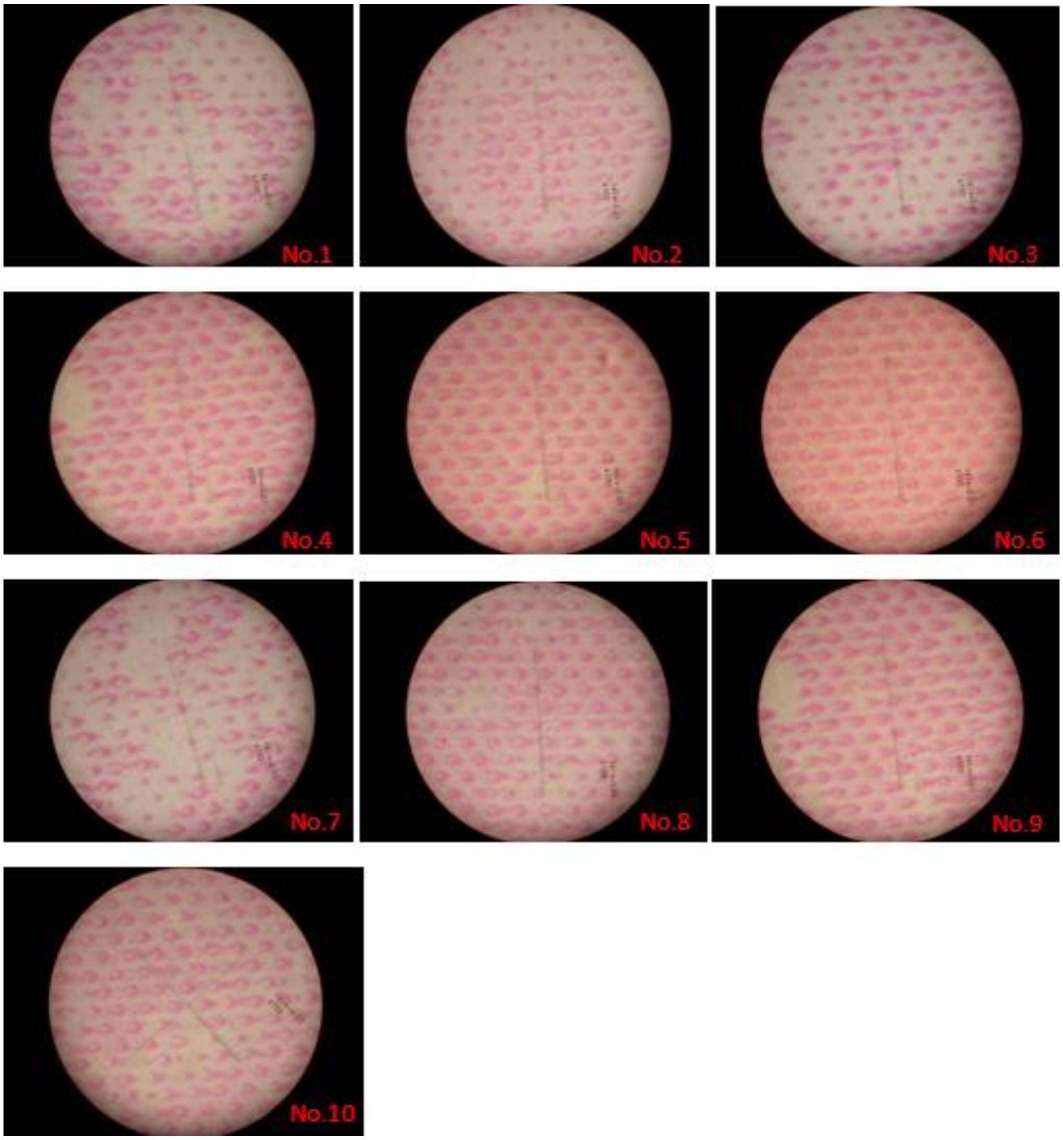

Figure 4.10 Printing images of BOPP film with M17-Magenta ink and 10% of quadrangular gravure grooves. The images were taken at a magnification of 100X.

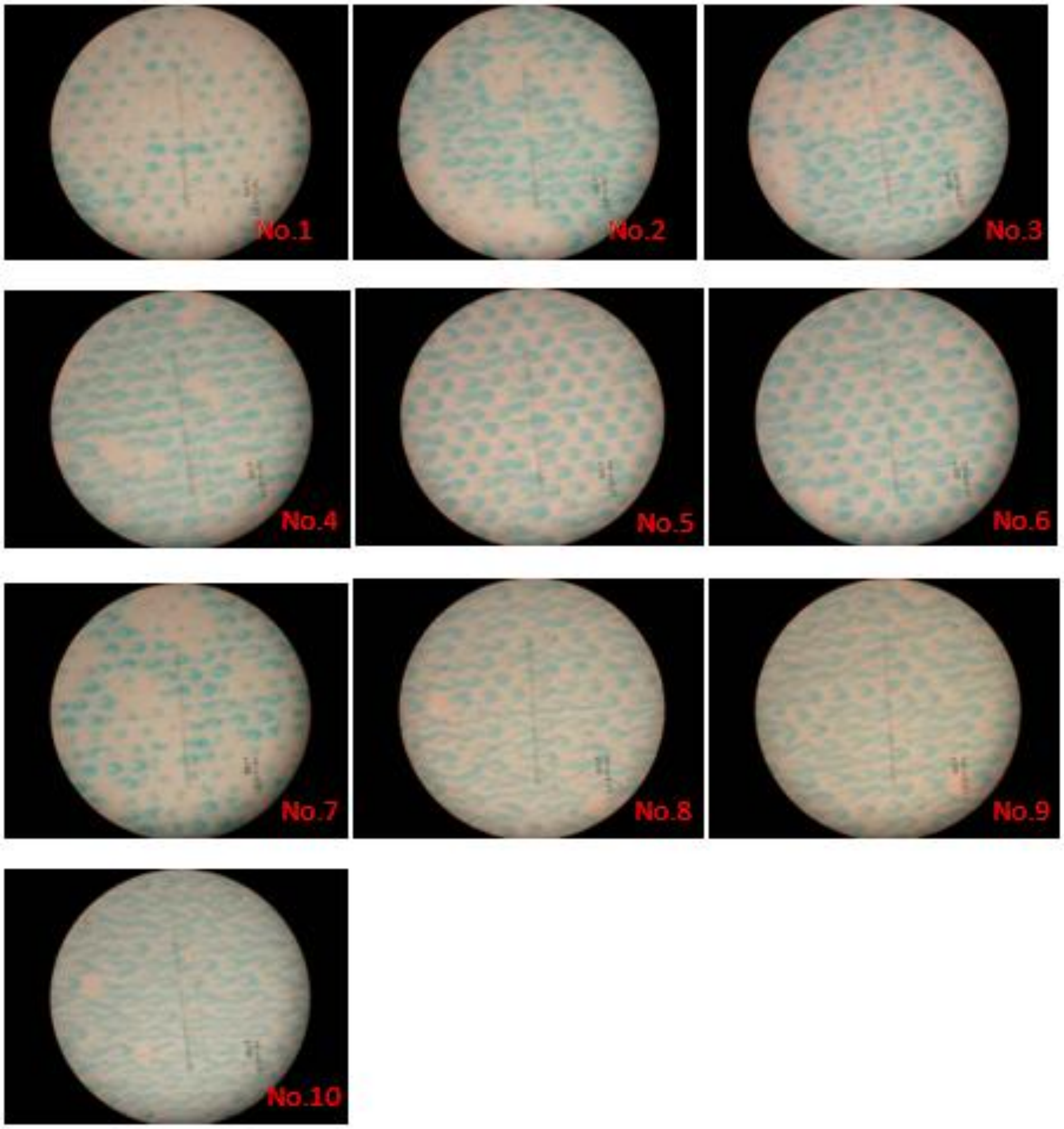

Figure 4.11 Printing images of BOPP film with C39-Cyan ink and 10% of quadrangular gravure grooves. The images were taken at a magnification of 100X.

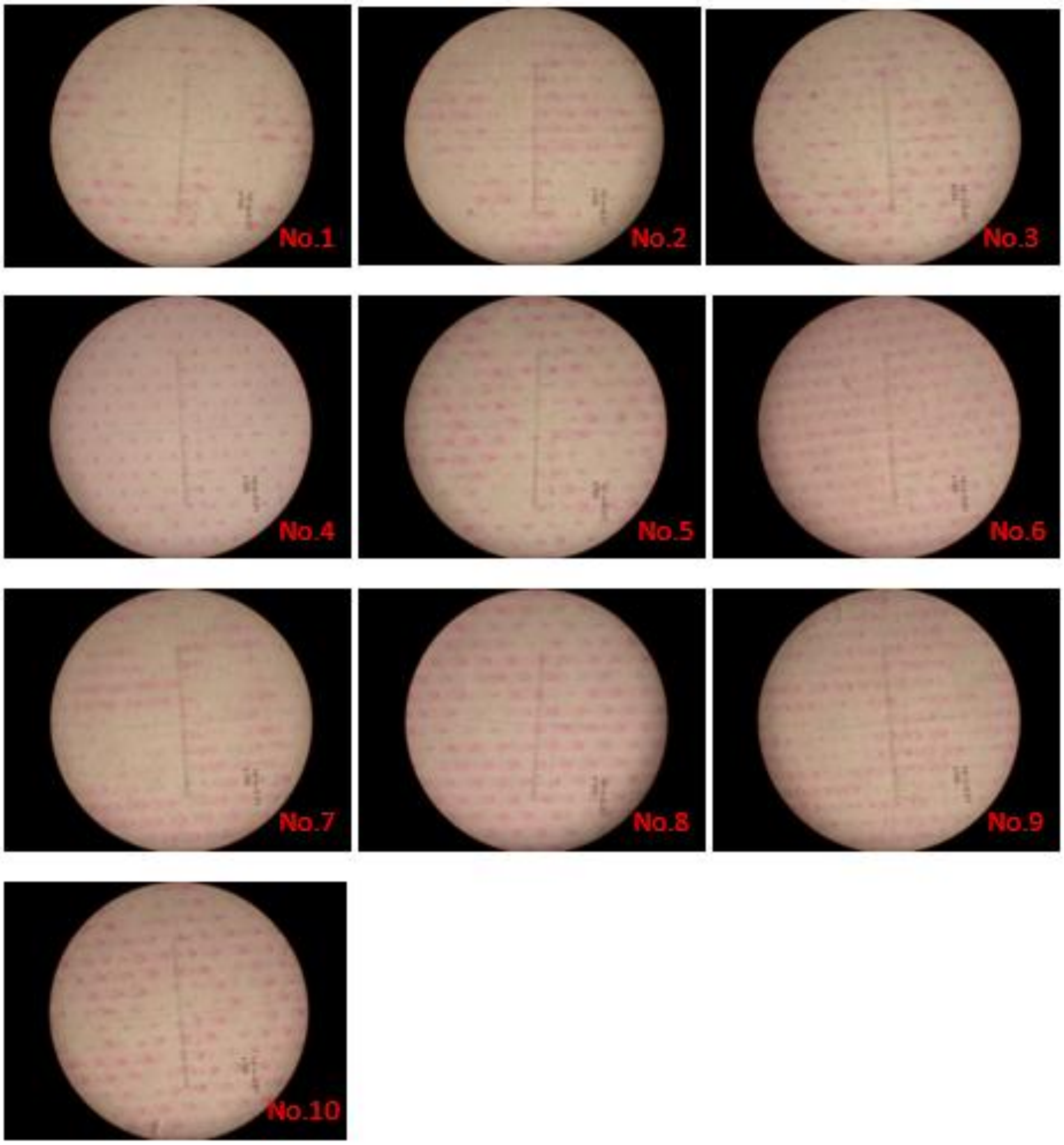

Figure 4.12 Printing images of BOPP film with M17-Magenta ink and 5% of quadrangular gravure grooves. The images were taken at a magnification of 100X.

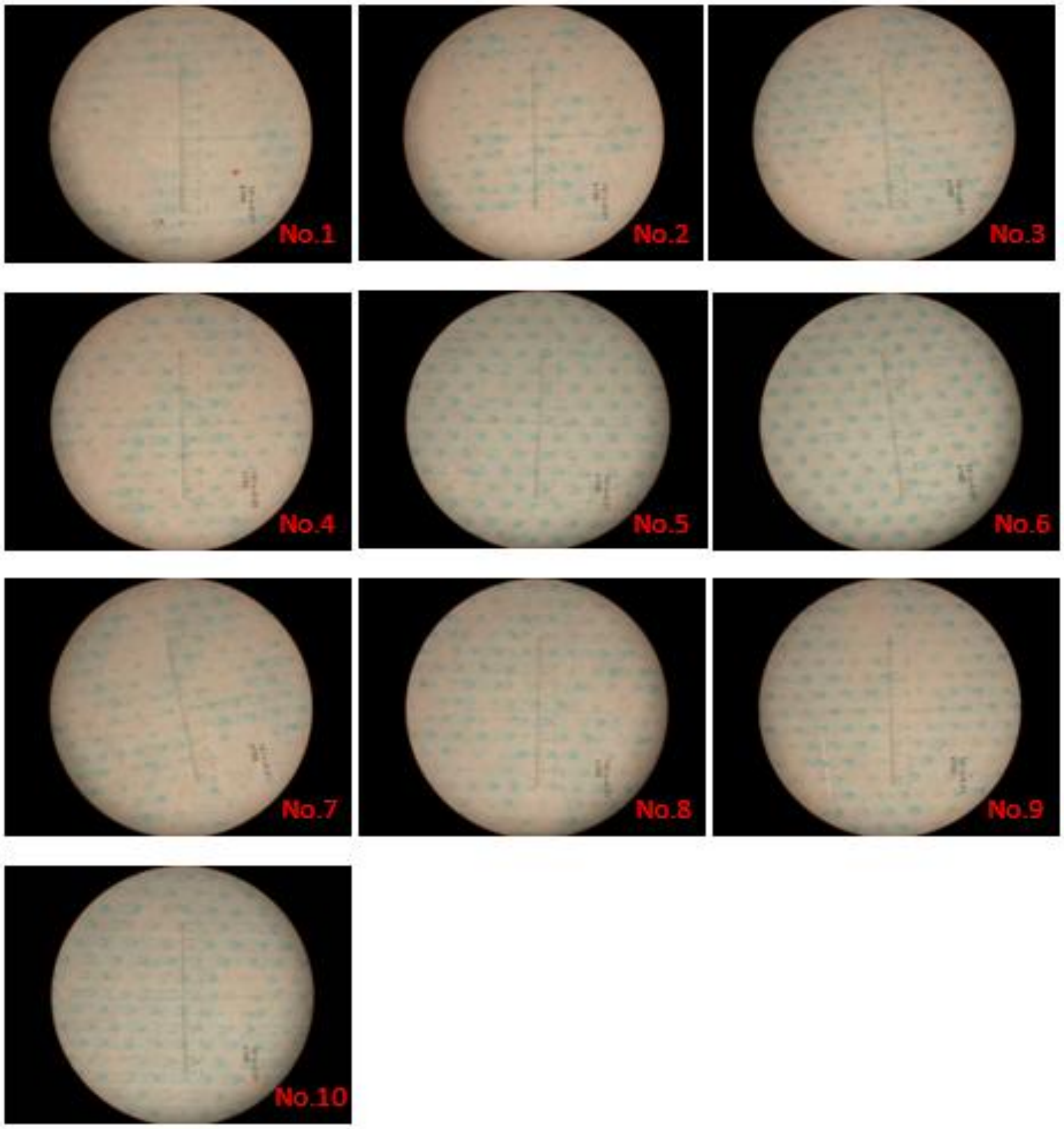

Figure 4.13 Printing images of BOPP film with C39-Cyan ink and 5% of quadrangular gravure grooves. The images were taken at a magnification of 100X.

CHAPTER V

CONCLUSIONS

5.1 Conclusions

The surface free energy of BOPP film that modified by propylene-ethylene copolymer with corona treated is significantly increasing. Its SFE is approximately 20% higher when 6% of propylene-ethylene copolymer is introduced on skin layer. This behavior is believed to reflect the oxidation reaction on the corona treated BOPP film. It is mainly due to the formation of polar groups such as C-O, O=C-O, C=O and COOH were introduced onto the BOPP surface. The CH_3 groups present on the polymer backbone in PP are believed to generate tertiary radicals which normally are formed in polypropylene material generally decay via β-scission or disproportionation. In contrast, the secondary radicals which are formed such as in polyethylene combination is likely to occur and react with the surrounded gaseous species, leading to the formation of mainly oxygen based functional groups, such as alcohol, ether, ketone, acid or ester.

The corona treatment usually accelerates the migration of the antistatic masterbatch to that side, by increasing the concentration gradient and also by making that surface more polar. This behavior is effect of antistatic masterbatch structure which has a hydrophobic organic end and a hydrophilic end. The strongly polar hydrophilic end which is reduced the contact angle lead to increasing the surface free energy. In contrast, the slip agent that migated to treated side of BOPP films, it has the effect to increase contact angle on BOPP surface, lead to reducing surface free energy. This behavior is believed the chemical structure of slip agent that hyprophobic is dominant.

Ink transfer efficiency on corona treated BOPP films that propylene-ethylene copolymer is introduced on the skin layer, is better than BOPP film that skin layer without propylene-ethylene copolymer. Increaseing the surface free energy of BOPP fims that 6% of propylene-ethylene copolymer is introduced on skin layer and treated by corona treatment , these is key to support ink transfer on BOPP surface and lead to good image of printing.

5.2 Suggestion for the future work

Future work should be study the effects of static charge on treated BOPP surface with ink transfer efficiency from gravure plate to BOPP film. Ink ingredients should be investigated. In addition, printing image should be investigated under various printing factors, such as printing speed, size of gravure groove, viscosity and ingredient of ink.

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APPENDICES

Appendix A

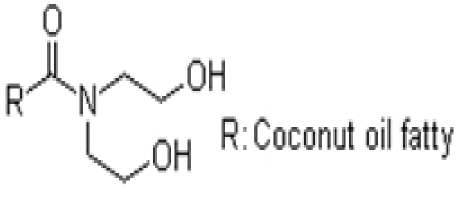


Figure A-1 Molecular structure of amides, coco, N,N-bis(hydroxyethyl), CAS No. 68603-42-9, boiling point 168.274 °C, water solubility 5-10 g/100 mL at 18 °C.

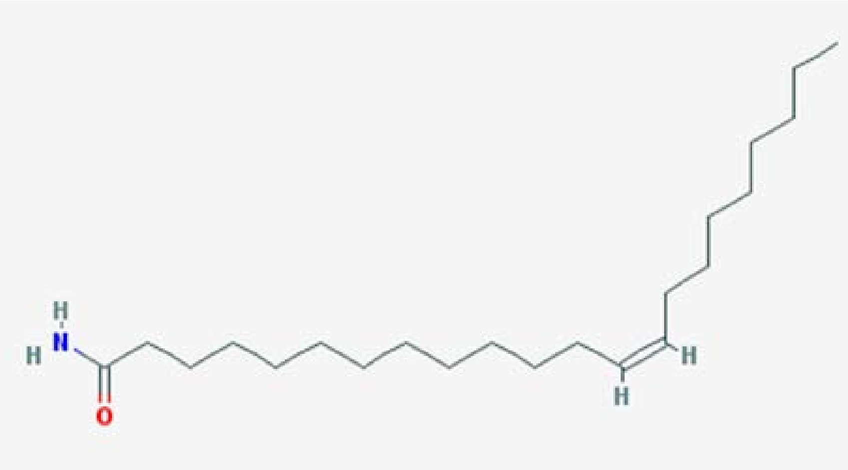


Figure A-2 Molecular structure of erucamide, CAS No. 93050-58-9, molecular Weight: 337.58292 [g/mol], water solubility < 50 ug/ml at 25.0 °C.

Appendix B

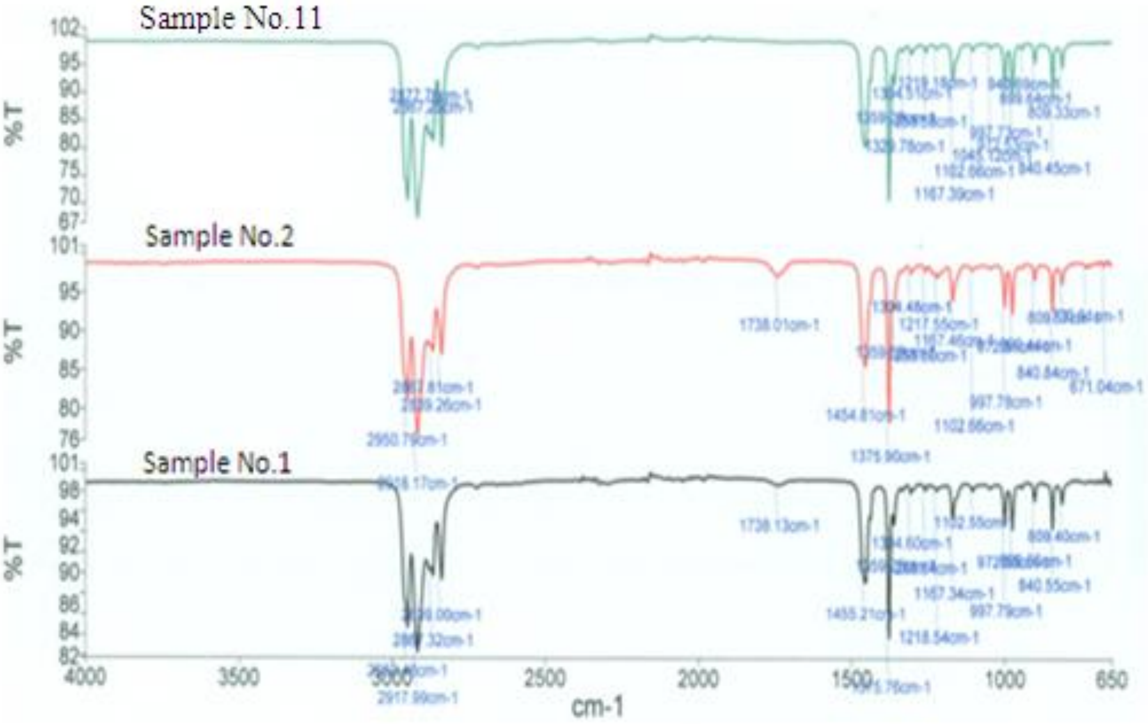


Figure B-1 ATR-FTIR spectra of Sample No.1 that is treated BOPP film with skin layer used only homopolypropylene, Sample No. 2 that is treated BOPP film with skin layer used only propylene-ethylene copolymer and Sample No.11 that is non-treated BOPP film.

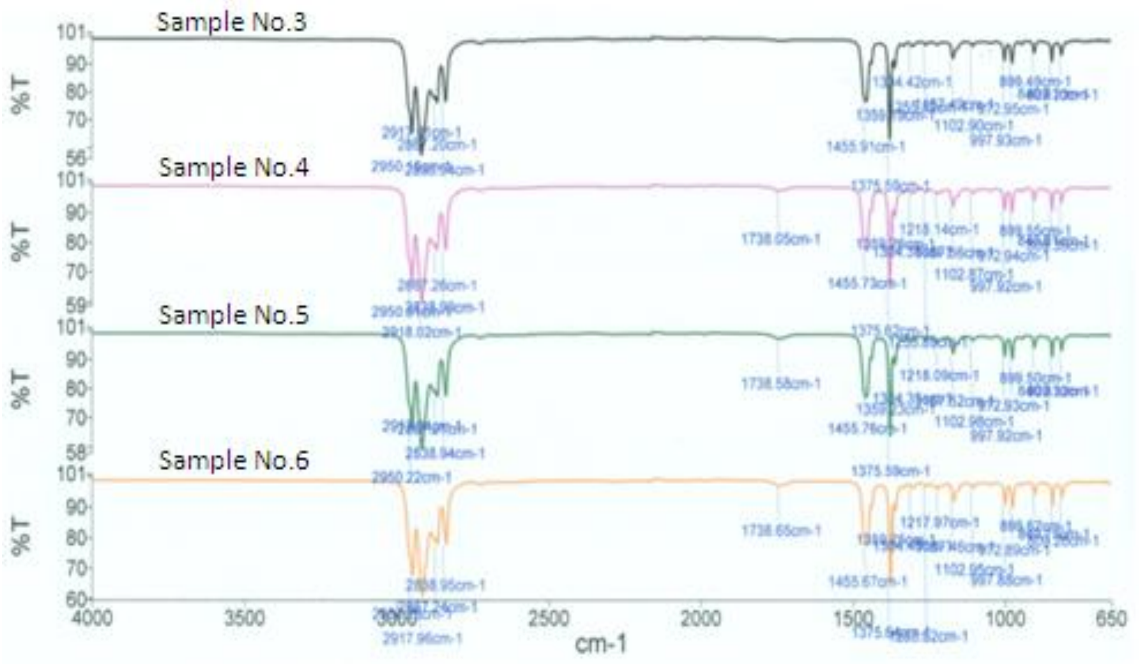


Figure B-2 ATR-FTIR spectra of Sample No.3 is treated BOPP film that skin layer used only polypropylene with 0.5% antistatic masterbatch in major layer, Sample No. 4 is treated BOPP film that 3% propylene-ethylene copolymer is introduced in skin layer with 0.5% antistatic masterbatch in major layer, Sample No.5 is treated BOPP film that 5% propylene-ethylene copolymer is introduced in skin layer with 0.5% antistatic masterbatch in major layer and Sample No.6 is treated BOPP film that 6% propylene-ethylene copolymer is introduced in skin layer with 0.5% antistatic masterbatch in major layer.

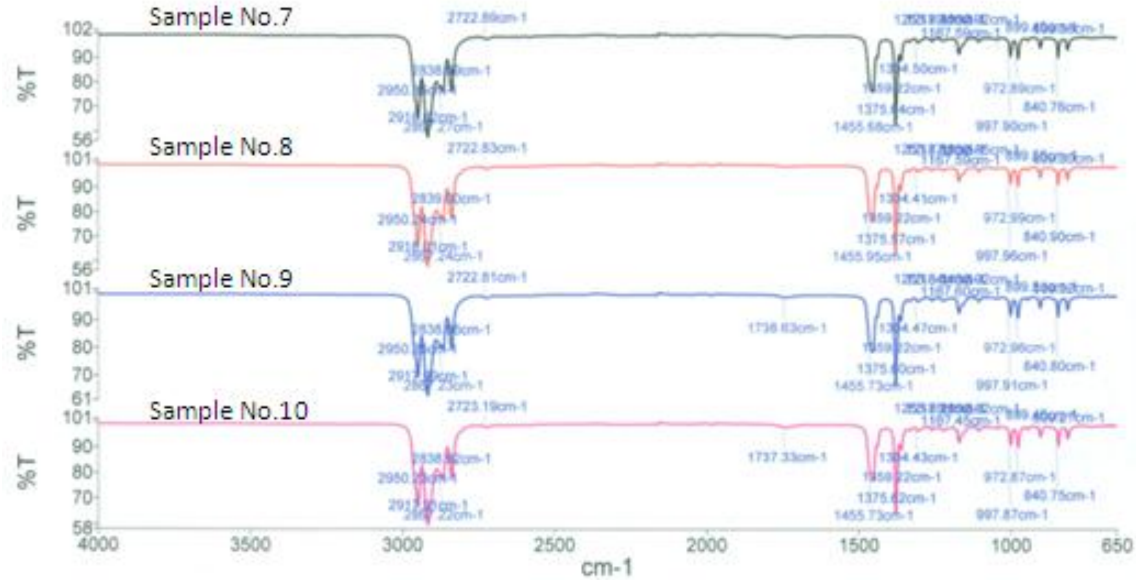
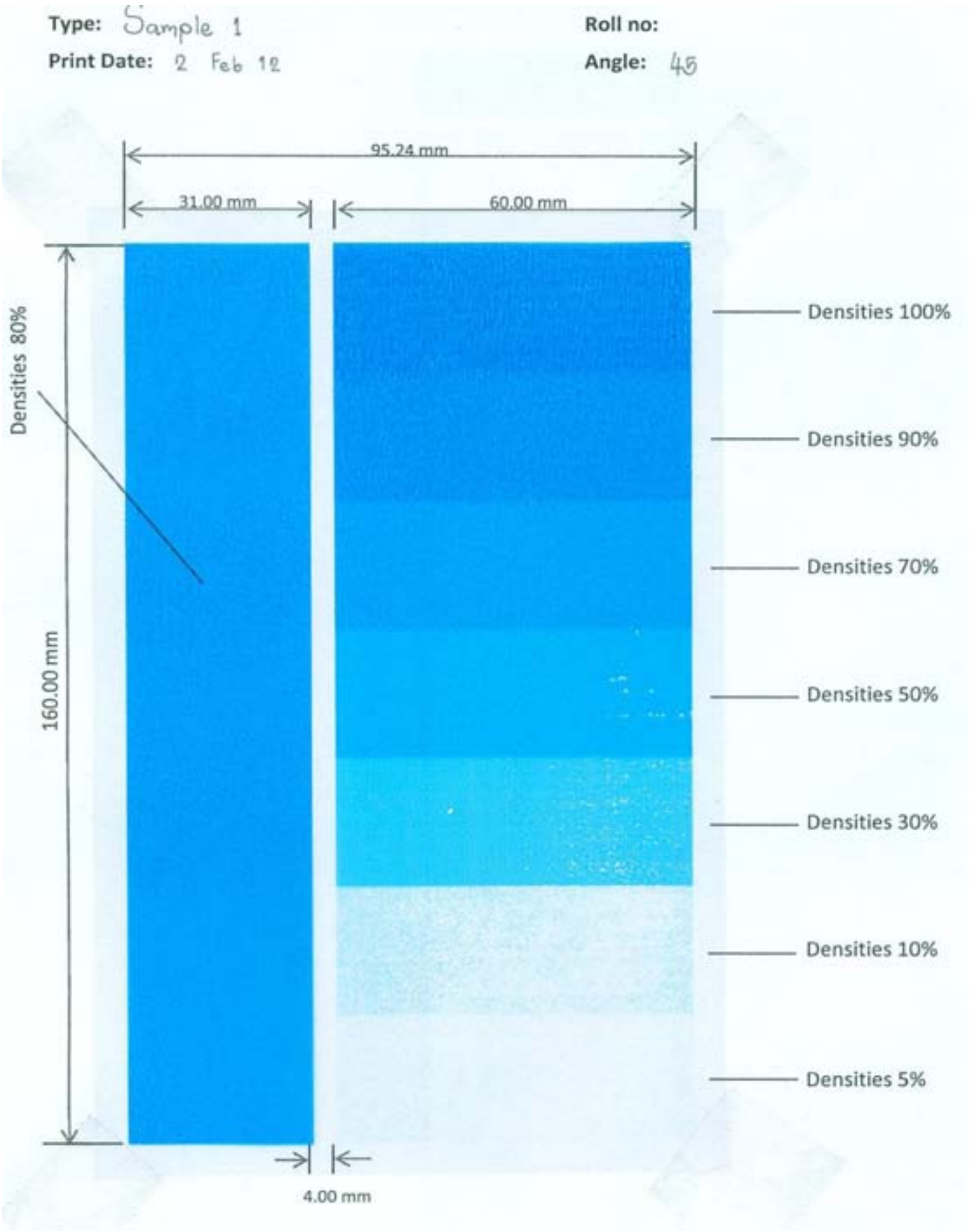


Figure B-3 ATR-FTIR spectra of Sample No.7 is treated BOPP film that skin layer used only polypropylene with 0.5% each antistatic masterbatch and slip agent introduced in major layer, Sample No. 8 is treated BOPP film that 3% propylene-ethylene copolymer is introduced in skin layer with 0.5% each antistatic masterbatch and slip agent introduced in major layer, Sample No.9 is treated BOPP film that 5% propylene-ethylene copolymer is introduced in skin layer with 0.5% each antistatic masterbatch and slip agent introduced in major layer and Sample No.10 is treated BOPP film that 6% propylene-ethylene copolymer is introduced in skin layer with 0.5% each antistatic masterbatch and slip agent introduced in major layer.

Appendix C



Type: Sample 1

Print Date: 2 Feb 12

Roll no:

Angle: 45

Figure C-1 Printability of Sample No.1 that can be carried out using a "PK Print Coat Instrument" Model K Printing Proofer, quadrangular gravure grooves of 100, 90, 70, 50, 30, 10 and 5 % of densities (dot %). Cyan ink (code C39, Toyo Ink (Thailand) Co., Ltd) is used.

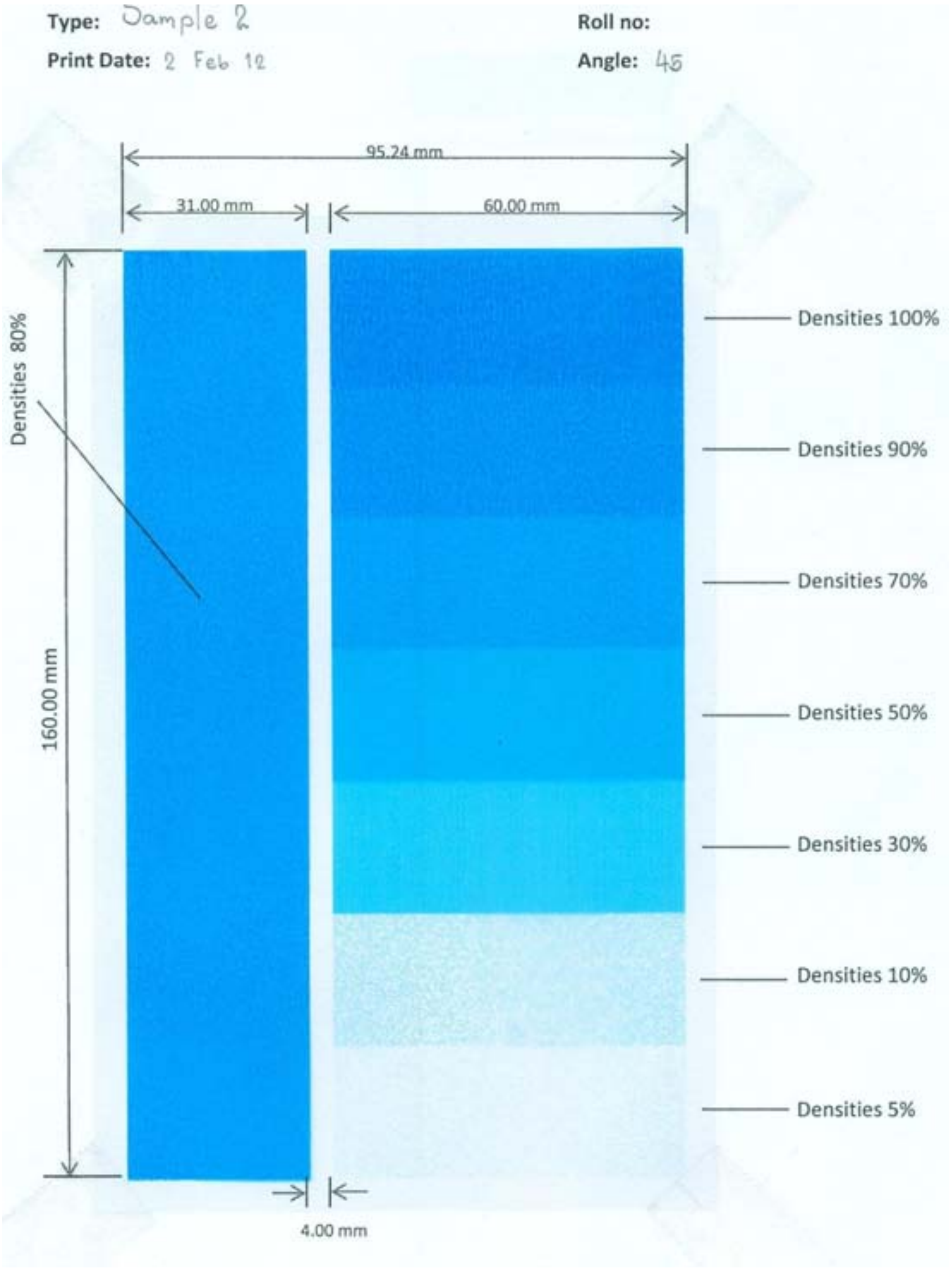
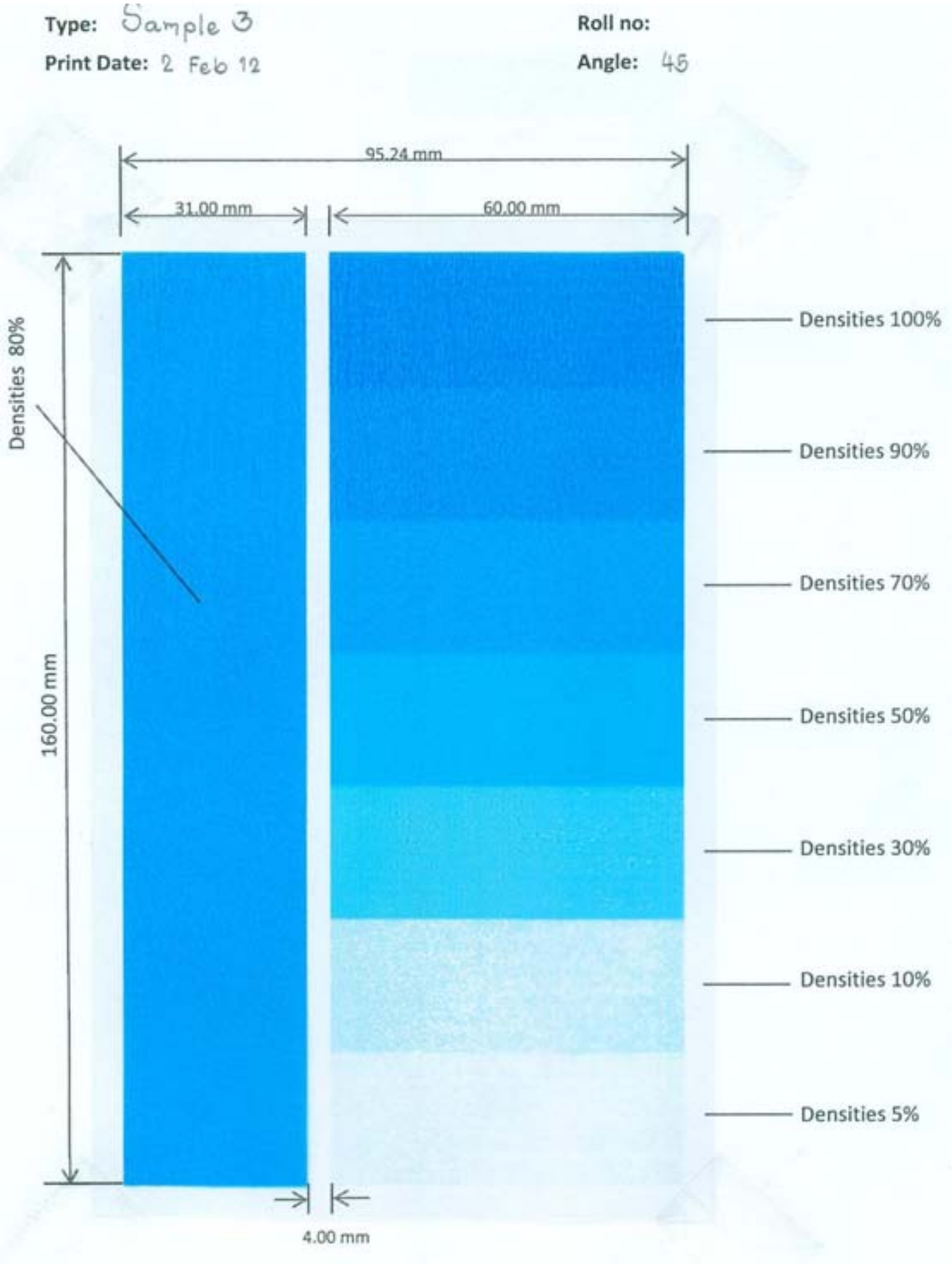


Figure C-2 Printability of Sample No.2 that can be carried out using a "PK Print Coat Instrument" Model K Printing Proofer, quadrangular gravure grooves of 100, 90, 70, 50, 30, 10 and 5 % of densities (dot %). Cyan ink (code C39, Toyo Ink (Thailand) Co., Ltd) is used.



Type: Sample 3
Print Date: 2 Feb 12
Roll no:
Angle: 45

Figure C-3 Printability of Sample No.3 that can be carried out using a "PK Print Coat Instrument" Model K Printing Proofer, quadrangular gravure grooves of 100, 90, 70, 50, 30, 10 and 5 % of densities (dot %). Cyan ink (code C39, Toyo Ink (Thailand) Co., Ltd) is used.

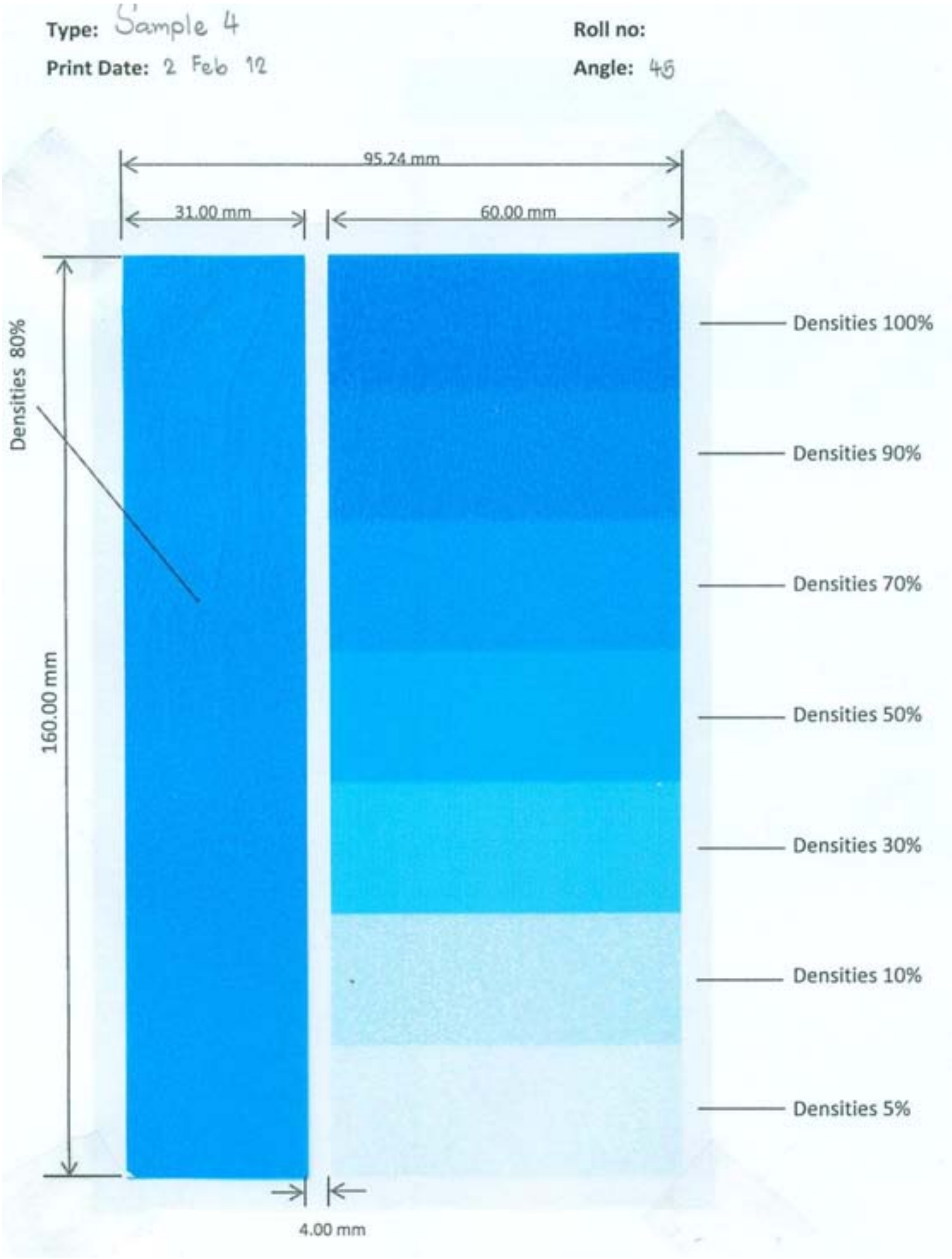


Figure C-4 Printability of Sample No.4 that can be carried out using a "PK Print Coat Instrument" Model K Printing Proofer, quadrangular gravure grooves of 100, 90, 70, 50, 30, 10 and 5 % of densities (dot %). Cyan ink (code C39, Toyo Ink (Thailand) Co., Ltd) is used.

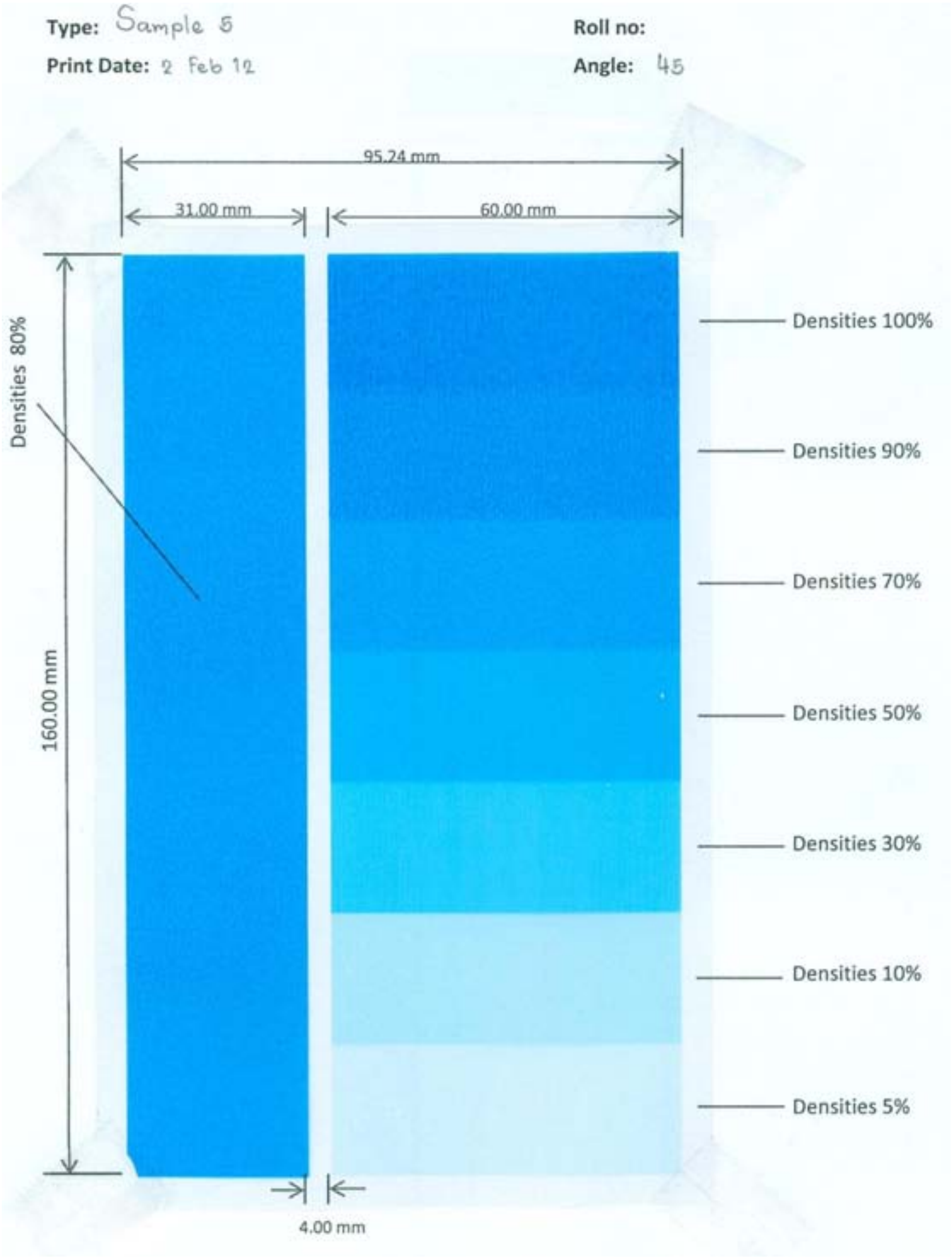


Figure C-5 Printability of Sample No.5 that can be carried out using a "PK Print Coat Instrument" Model K Printing Proofer, quadrangular gravure grooves of 100, 90, 70, 50, 30, 10 and 5 % of densities (dot %). Cyan ink (code C39, Toyo Ink (Thailand) Co., Ltd) is used.

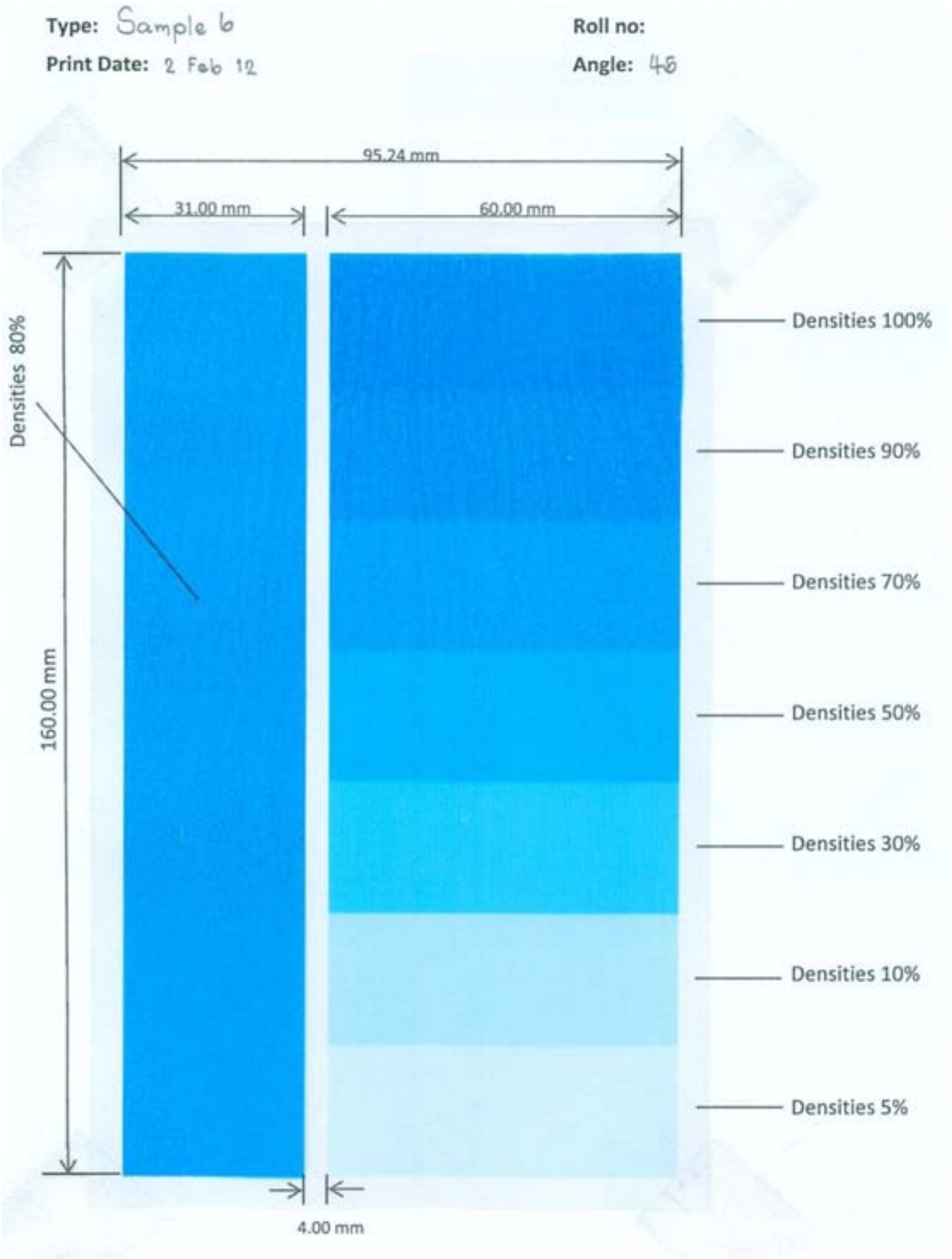


Figure C-6 Printability of Sample No.6 that can be carried out using a "PK Print Coat Instrument" Model K Printing Proofer, quadrangular gravure grooves of 100, 90, 70, 50, 30, 10 and 5 % of densities (dot %). Cyan ink (code C39, Toyo Ink (Thailand) Co., Ltd) is used.

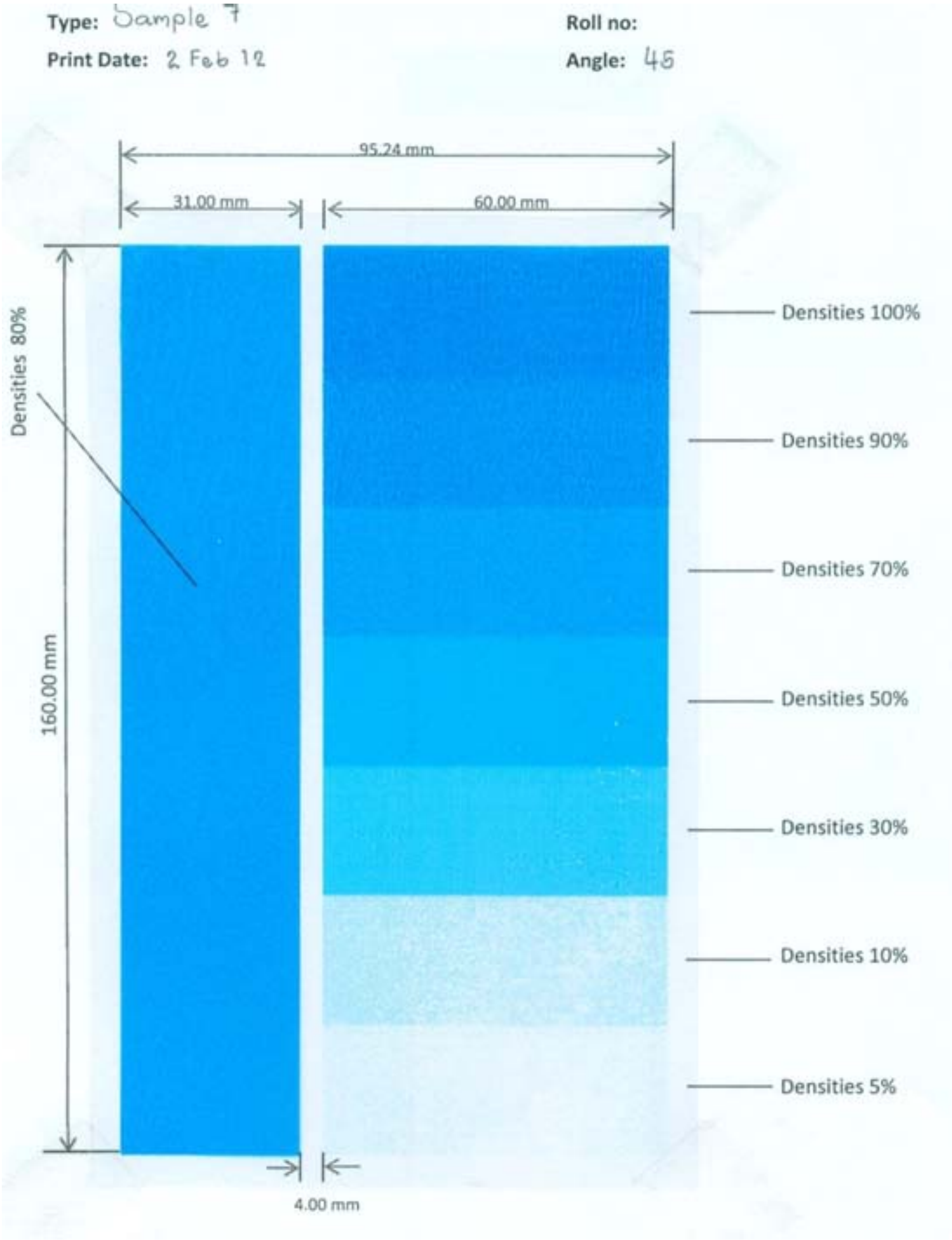
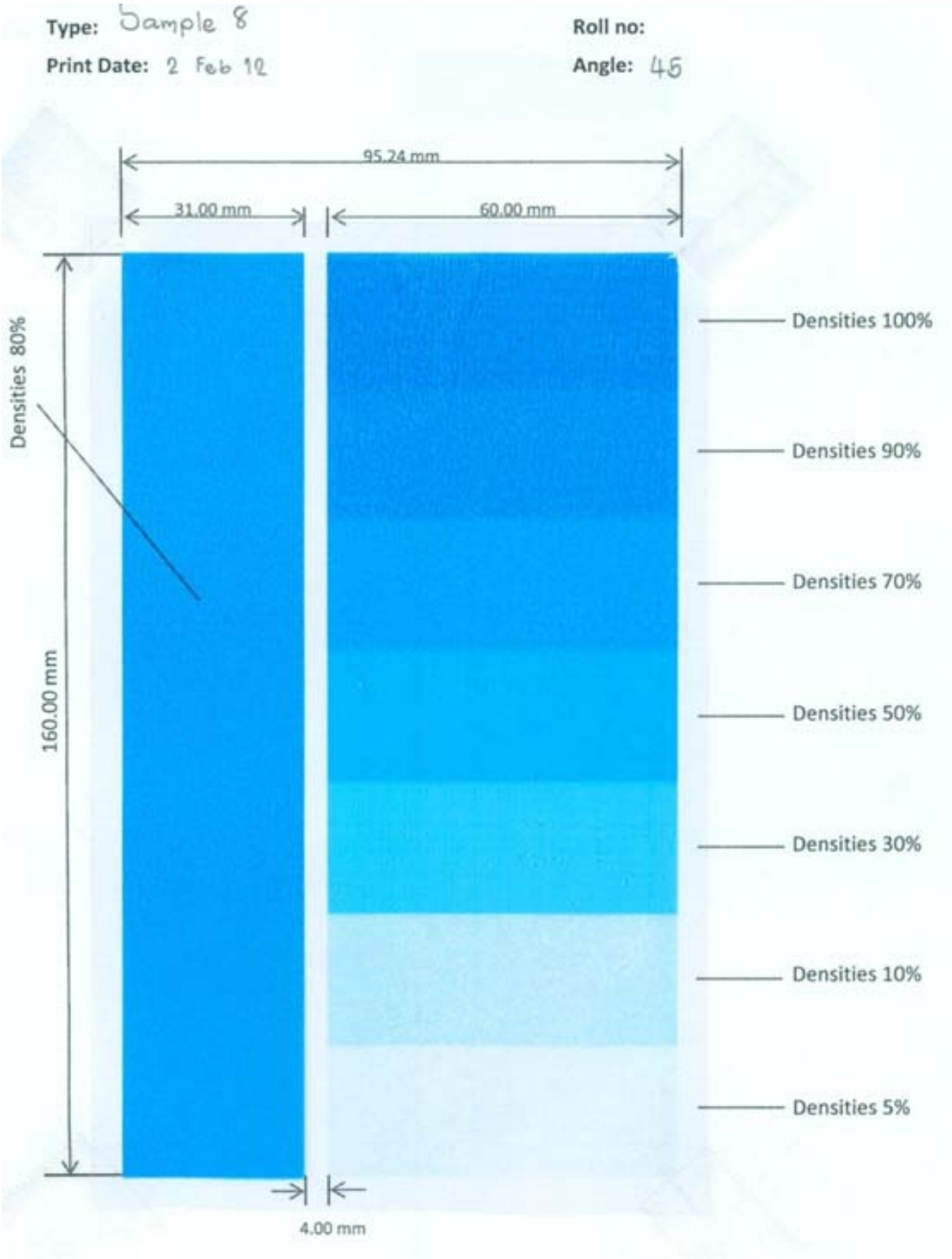


Figure C-7 Printability of Sample No.7 that can be carried out using a "PK Print Coat Instrument" Model K Printing Proofer, quadrangular gravure grooves of 100, 90, 70, 50, 30, 10 and 5 % of densities (dot %). Cyan ink (code C39, Toyo Ink (Thailand) Co., Ltd) is used.



Type: Sample 8
Roll no:
Print Date: 2 Feb 12
Angle: 45

Figure C-8 Printability of Sample No.8 that can be carried out using a "PK Print Coat Instrument" Model K Printing Proofer, quadrangular gravure grooves of 100, 90, 70, 50, 30, 10 and 5 % of densities (dot %). Cyan ink (code C39, Toyo Ink (Thailand) Co., Ltd) is used.

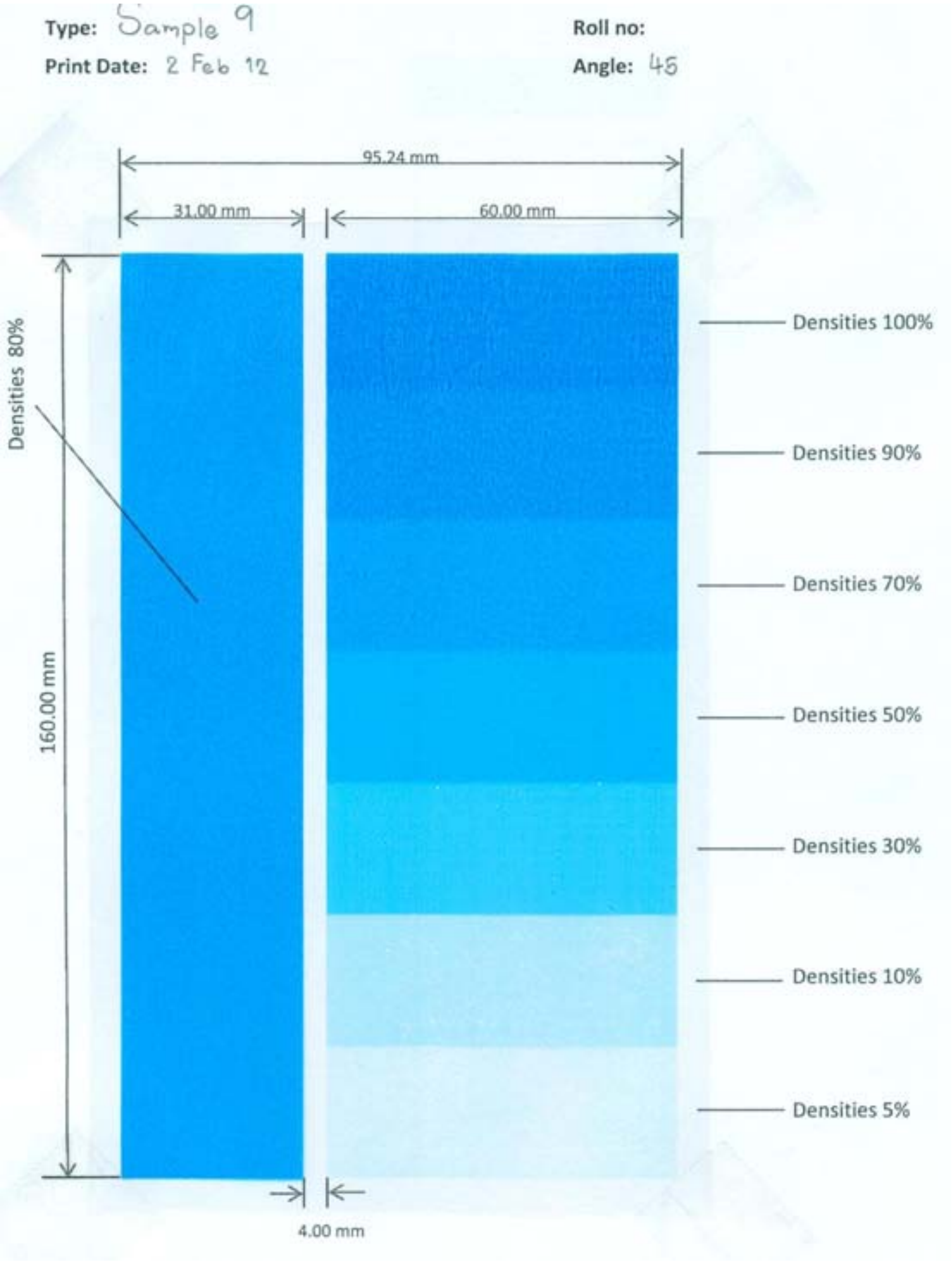


Figure C-9 Printability of Sample No.9 that can be carried out using a "PK Print Coat Instrument" Model K Printing Proofer, quadrangular gravure grooves of 100, 90, 70, 50, 30, 10 and 5 % of densities (dot %). Cyan ink (code C39, Toyo Ink (Thailand) Co., Ltd) is used.

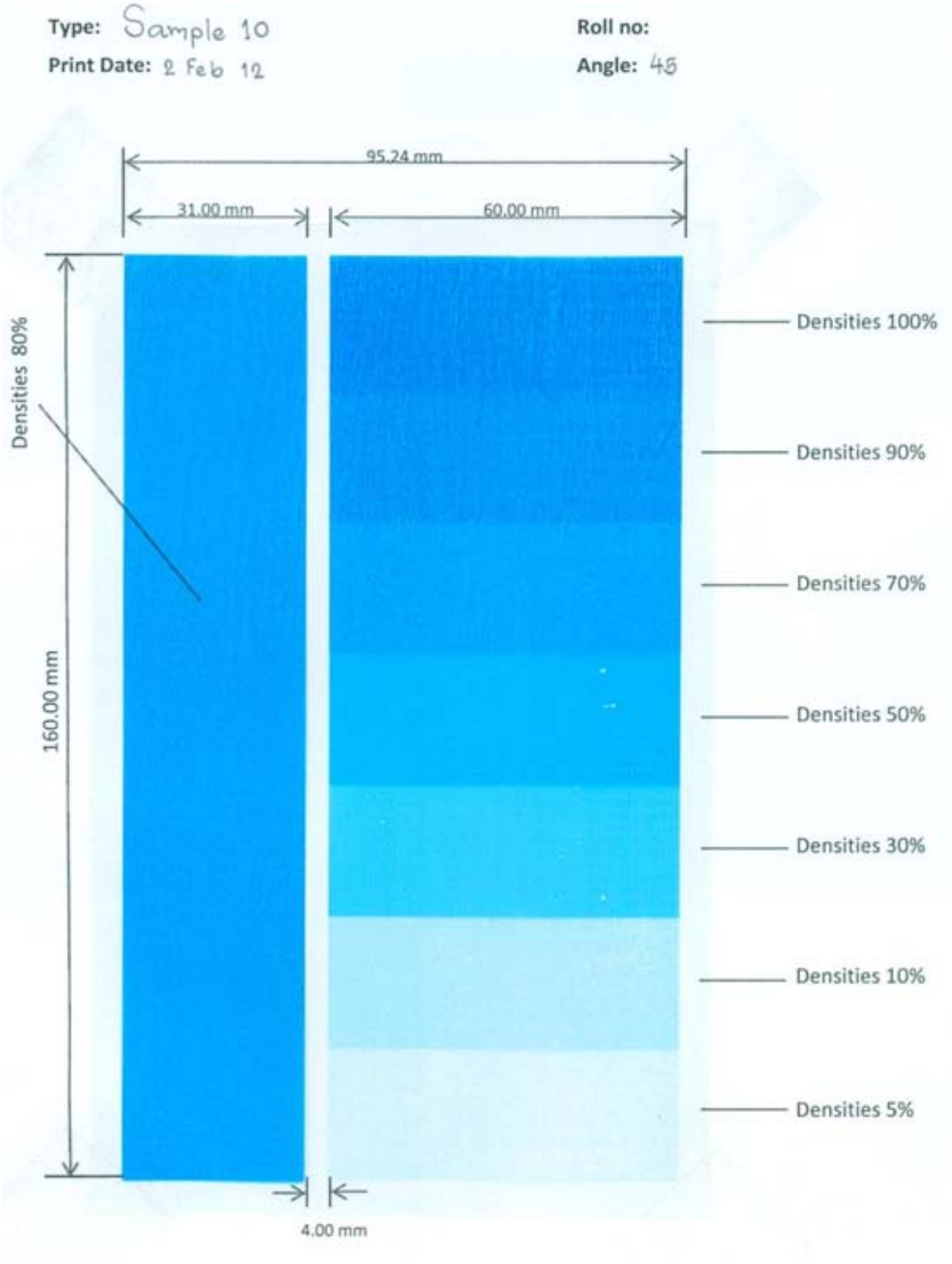


Figure C-10 Printability of Sample No.10 that can be carried out using a "PK Print Coat Instrument" Model K Printing Proofer, quadrangular gravure grooves of 100, 90, 70, 50, 30, 10 and 5 % of densities (dot %). Cyan ink (code C39, Toyo Ink (Thailand) Co., Ltd) is used.

Appendix D

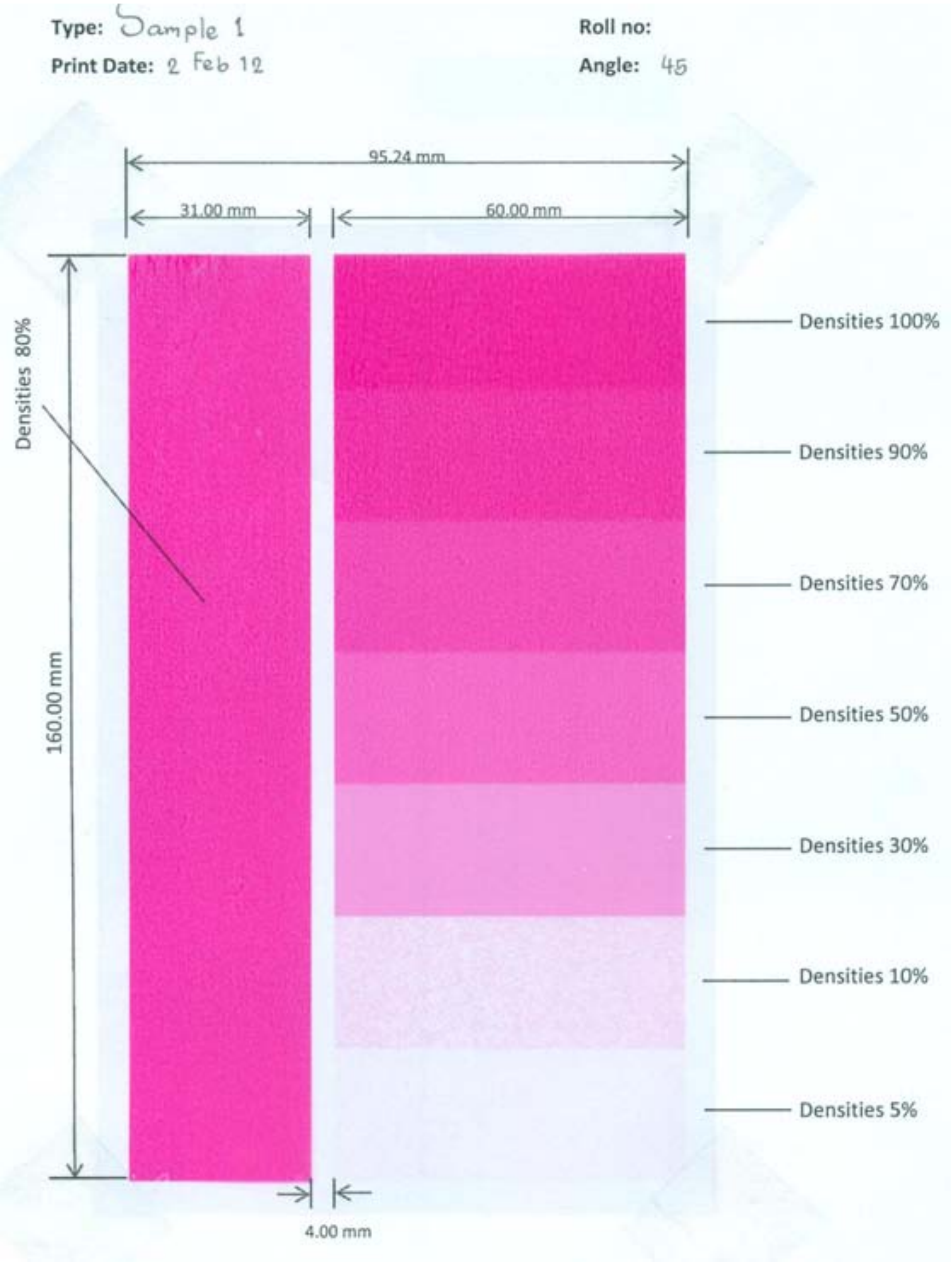


Figure D-1 Printability of Sample No.1 that can be carried out using a "PK Print Coat Instrument" Model K Printing Proofer, quadrangular gravure grooves of 100, 90, 70, 50, 30, 10 and 5 % of densities (dot %). Magenta ink (code M17, Toyo Ink (Thailand) Co., Ltd) is used.

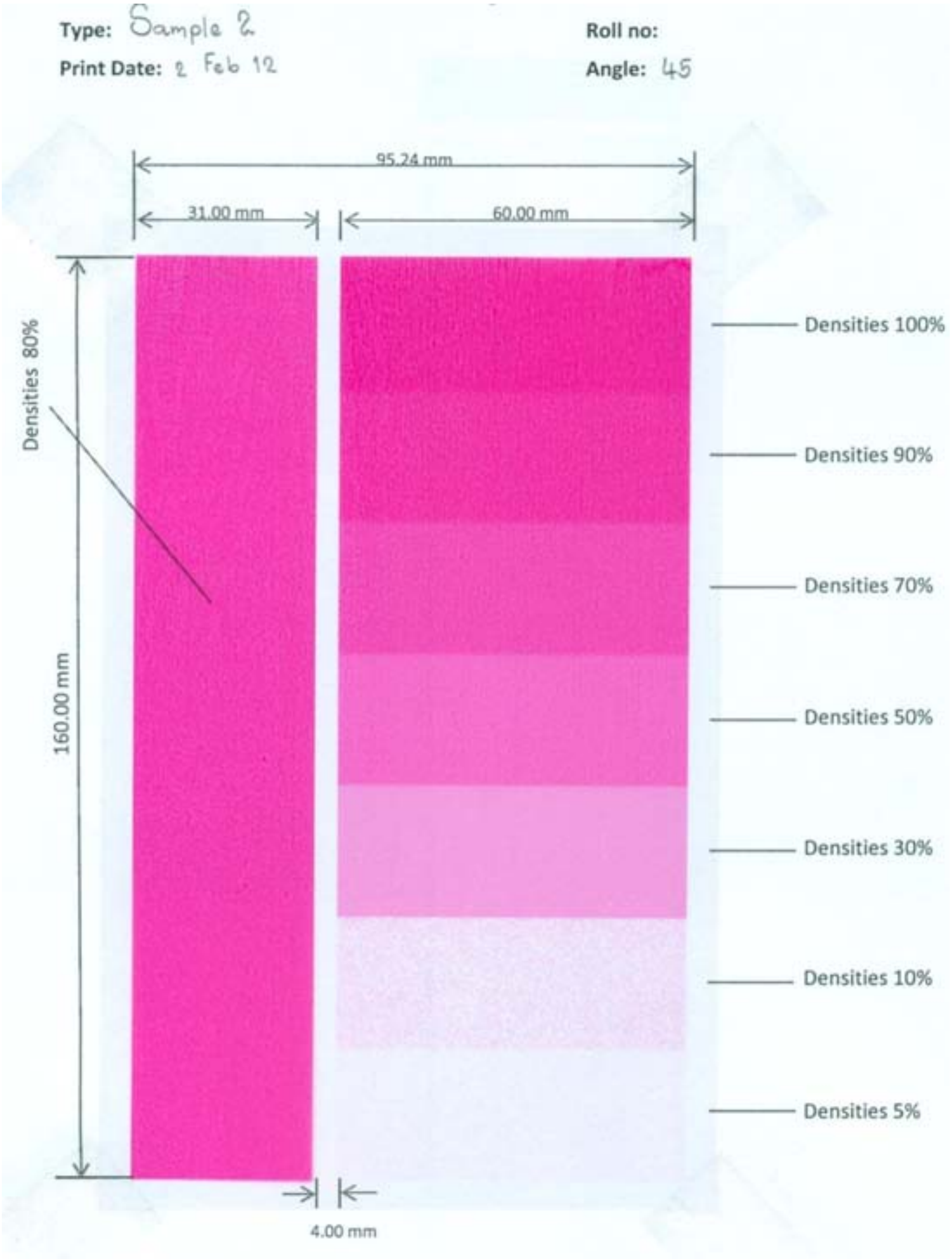
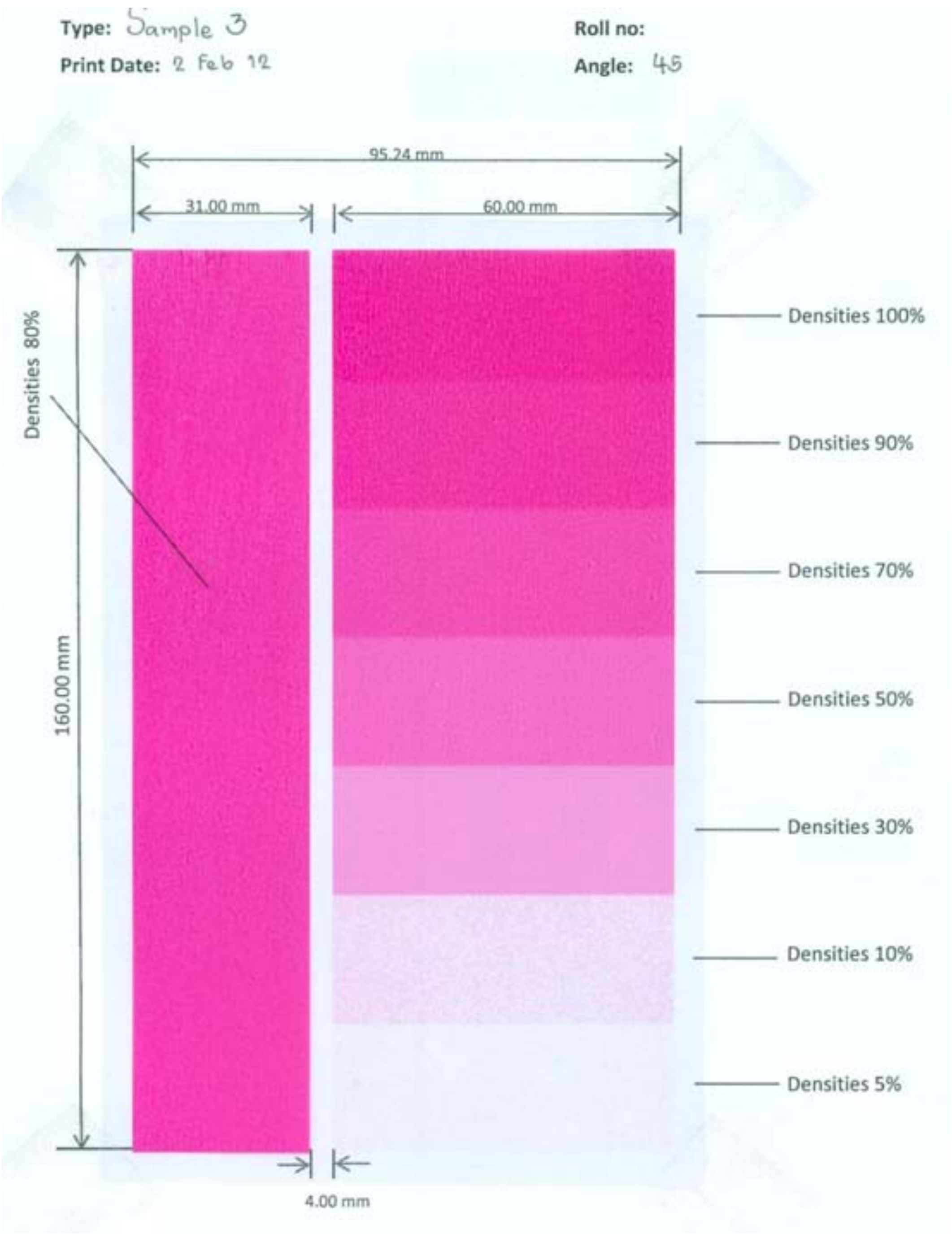


Figure D-2 Printability of Sample No.2 that can be carried out using a "PK Print Coat Instrument" Model K Printing Proofer, quadrangular gravure grooves of 100, 90, 70, 50, 30, 10 and 5 % of densities (dot %). Magenta ink (code M17, Toyo Ink (Thailand) Co., Ltd) is used.



Type: Sample 3

Roll no:

Print Date: 2 Feb 12

Angle: 45

Figure D-3 Printability of Sample No.3 that can be carried out using a "PK Print Coat Instrument" Model K Printing Proofer, quadrangular gravure grooves of 100, 90, 70, 50, 30, 10 and 5 % of densities (dot %). Magenta ink (code M17, Toyo Ink (Thailand) Co., Ltd) is used.

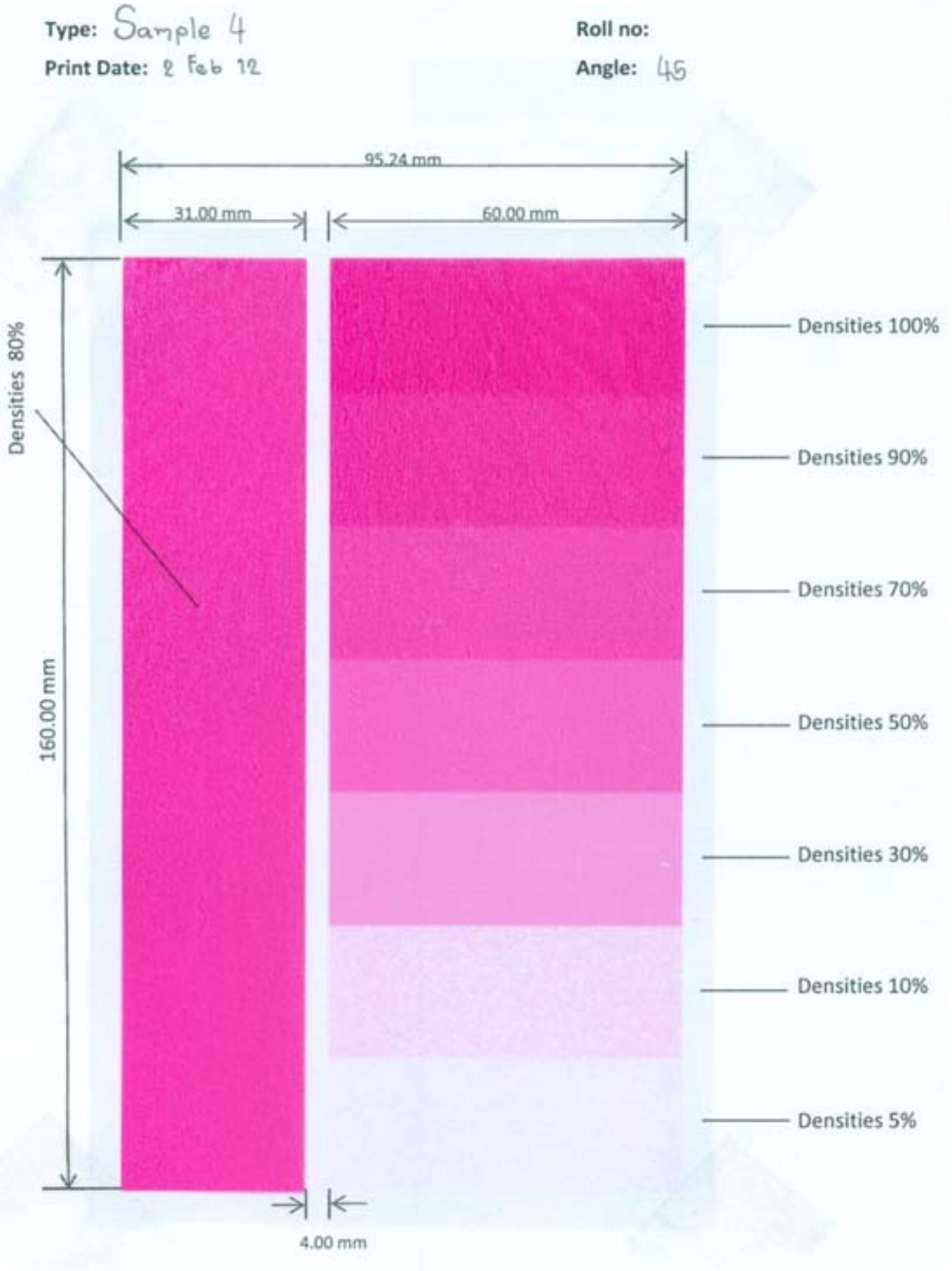


Figure D-4 Printability of Sample No.4 that can be carried out using a "PK Print Coat Instrument" Model K Printing Proofer, quadrangular gravure grooves of 100, 90, 70, 50, 30, 10 and 5 % of densities (dot %). Magenta ink (code M17, Toyo Ink (Thailand) Co., Ltd) is used.

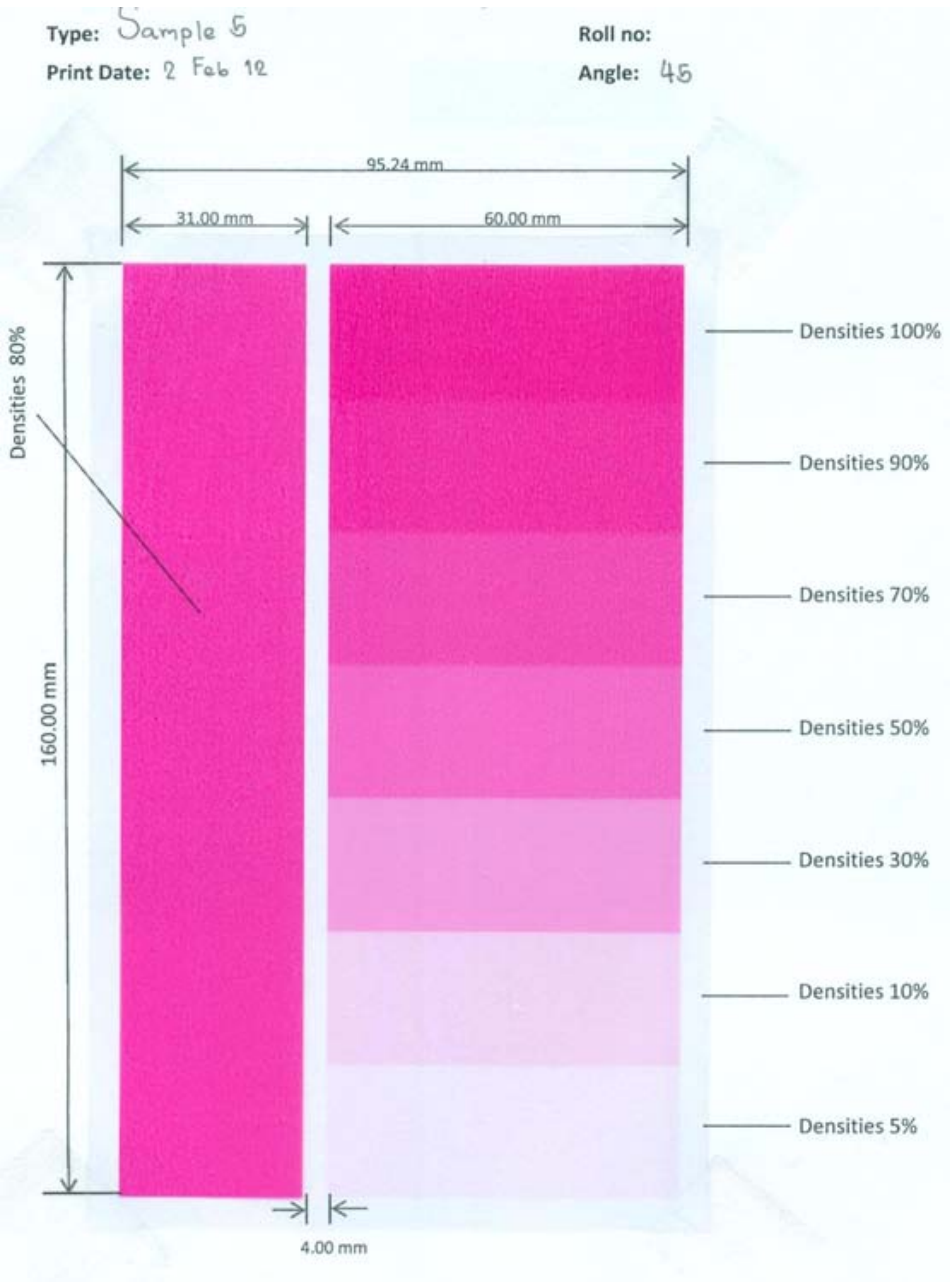


Figure D-5 Printability of Sample No.5 that can be carried out using a "PK Print Coat Instrument" Model K Printing Proofer, quadrangular gravure grooves of 100, 90, 70, 50, 30, 10 and 5 % of densities (dot %). Magenta ink (code M17, Toyo Ink (Thailand) Co., Ltd) is used.

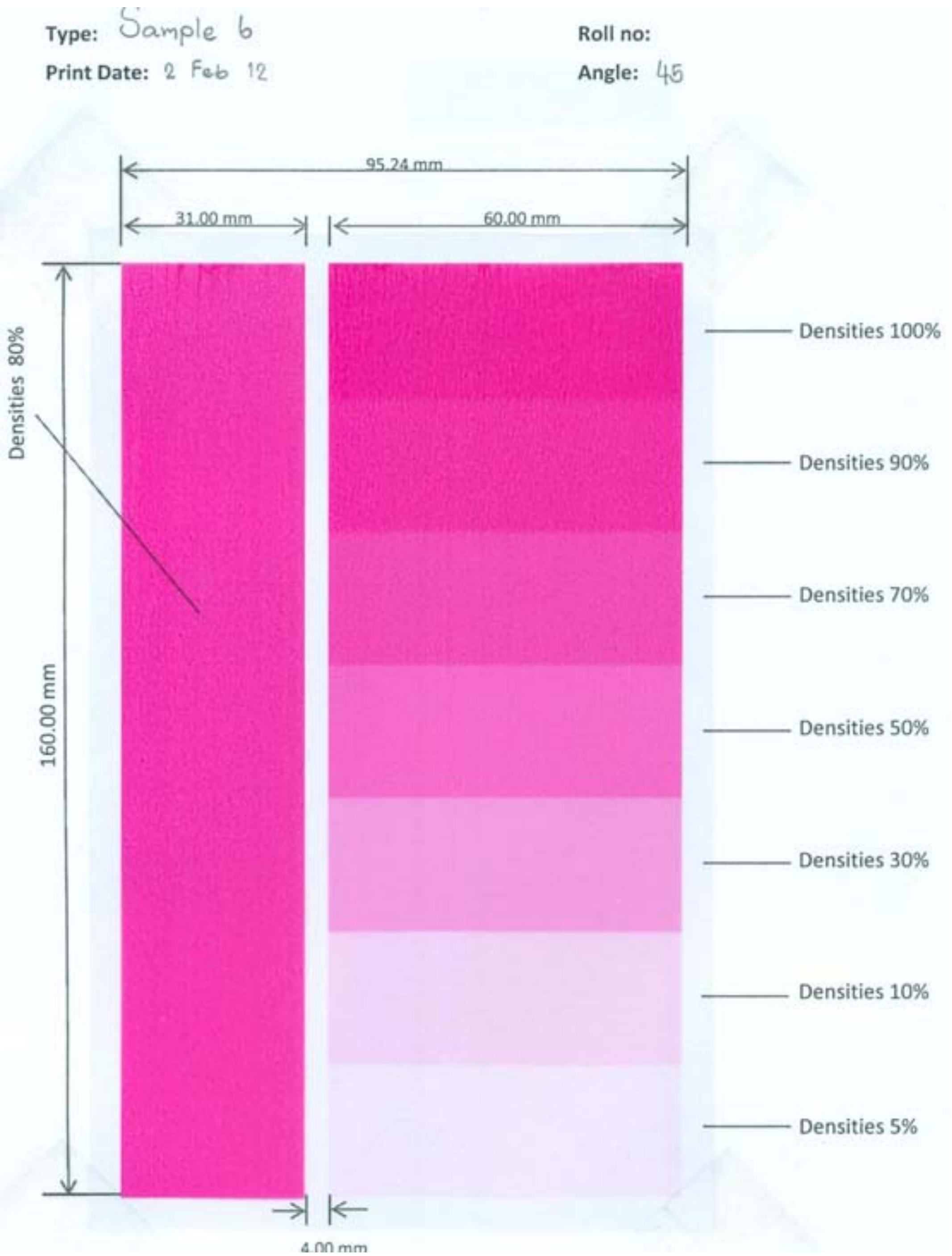


Figure D-6 Printability of Sample No.6 that can be carried out using a "PK Print Coat Instrument" Model K Printing Proofer, quadrangular gravure grooves of 100, 90, 70, 50, 30, 10 and 5 % of densities (dot %). Magenta ink (code M17, Toyo Ink (Thailand) Co., Ltd) is used.

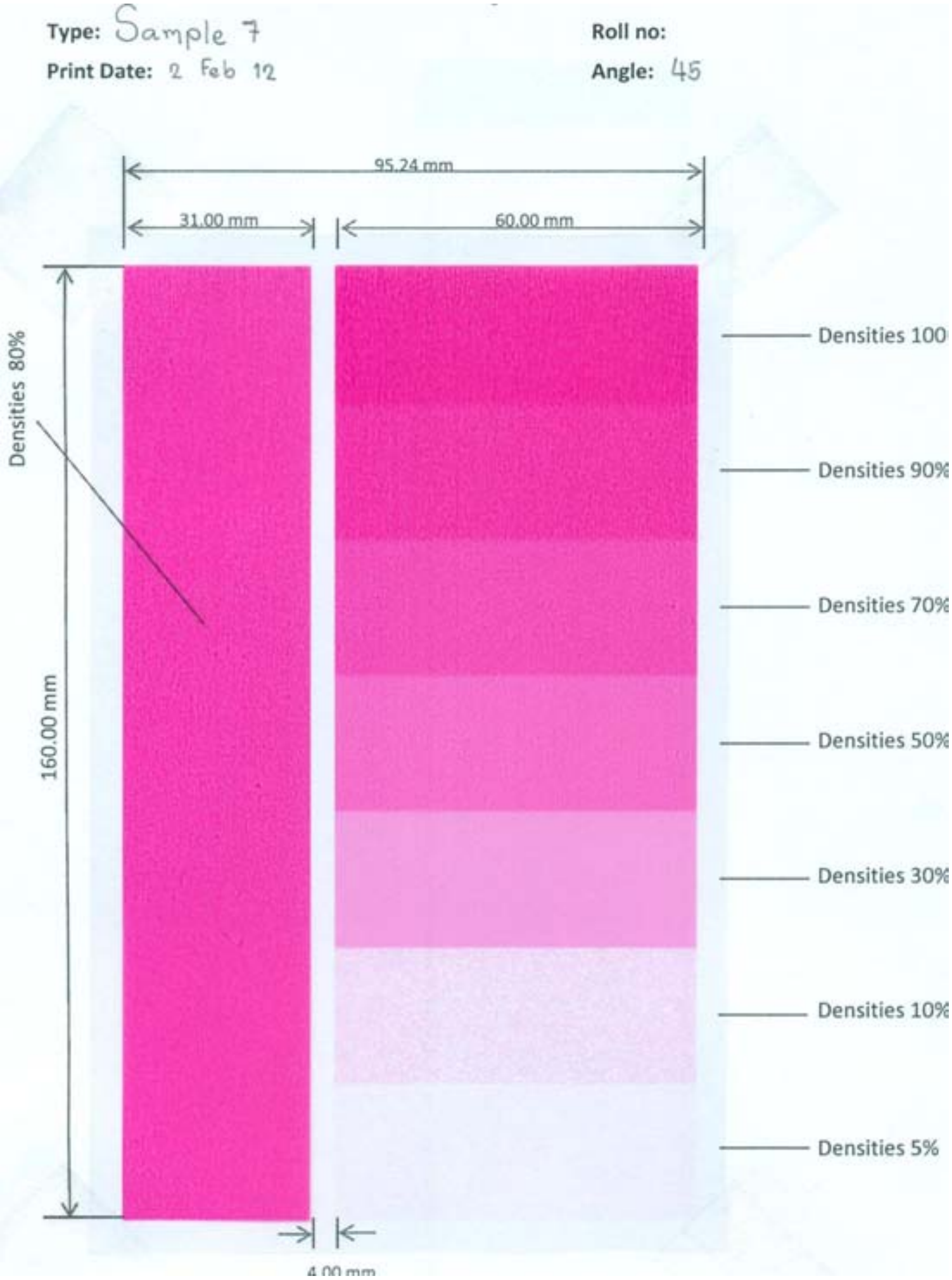
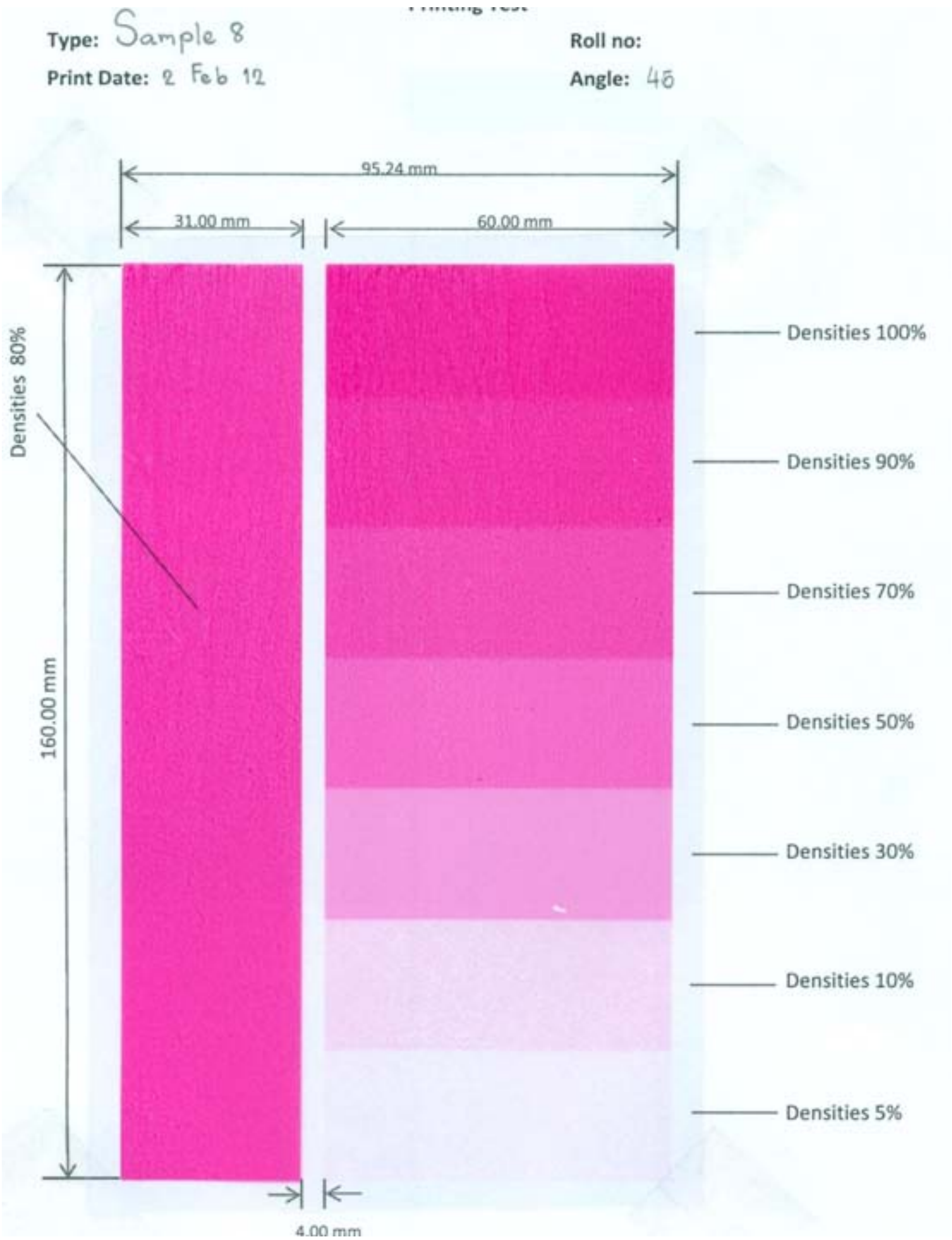


Figure D-7 Printability of Sample No.7 that can be carried out using a "PK Print Coat Instrument" Model K Printing Proofer, quadrangular gravure grooves of 100, 90, 70, 50, 30, 10 and 5 % of densities (dot %). Magenta ink (code M17, Toyo Ink (Thailand) Co., Ltd) is used.



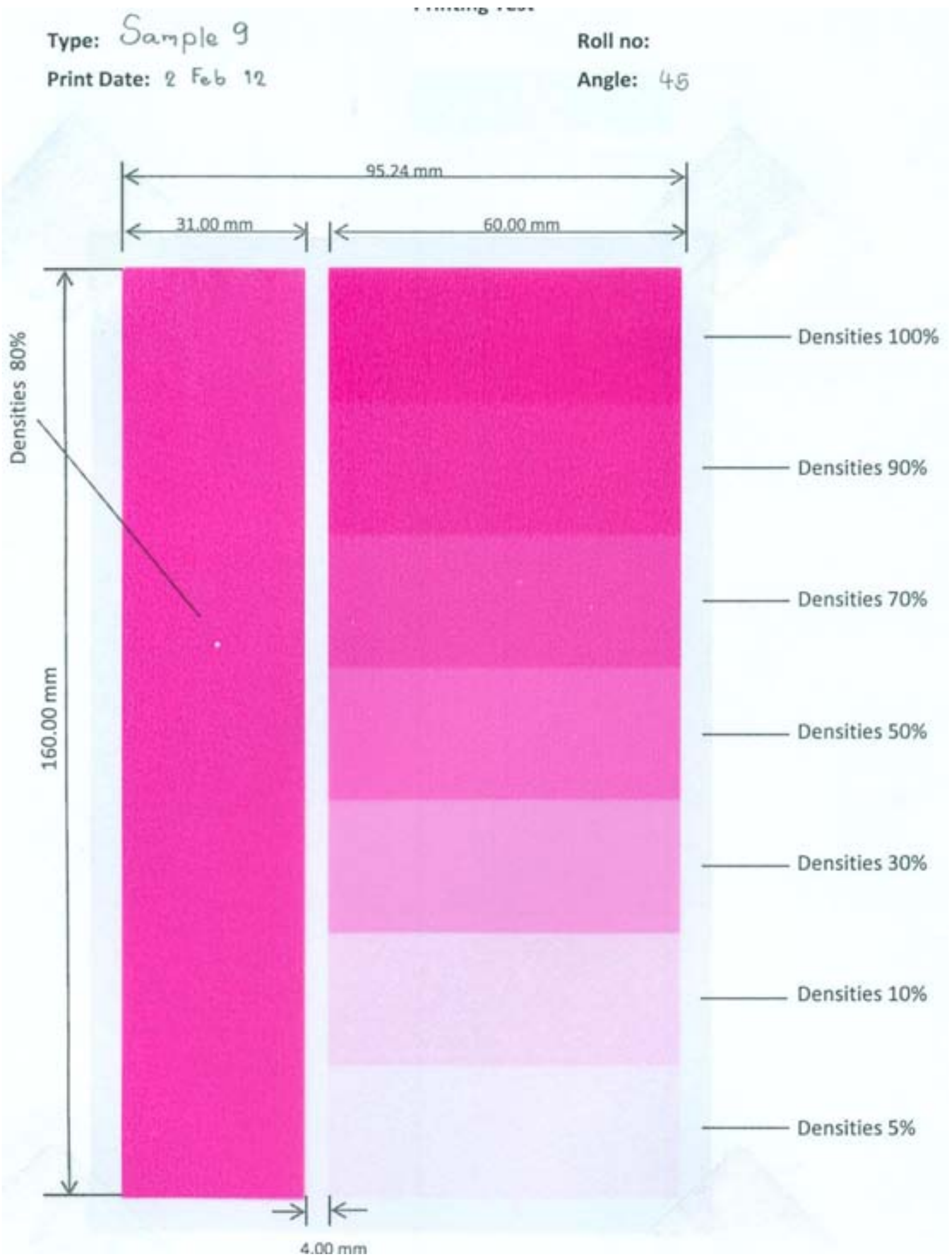
Type: Sample 8

Print Date: 2 Feb 12

Roll no:

Angle: 45

Figure D-8 Printability of Sample No.8 that can be carried out using a "PK Print Coat Instrument" Model K Printing Proofer, quadrangular gravure grooves of 100, 90, 70, 50, 30, 10 and 5 % of densities (dot %). Magenta ink (code M17, Toyo Ink (Thailand) Co., Ltd) is used.



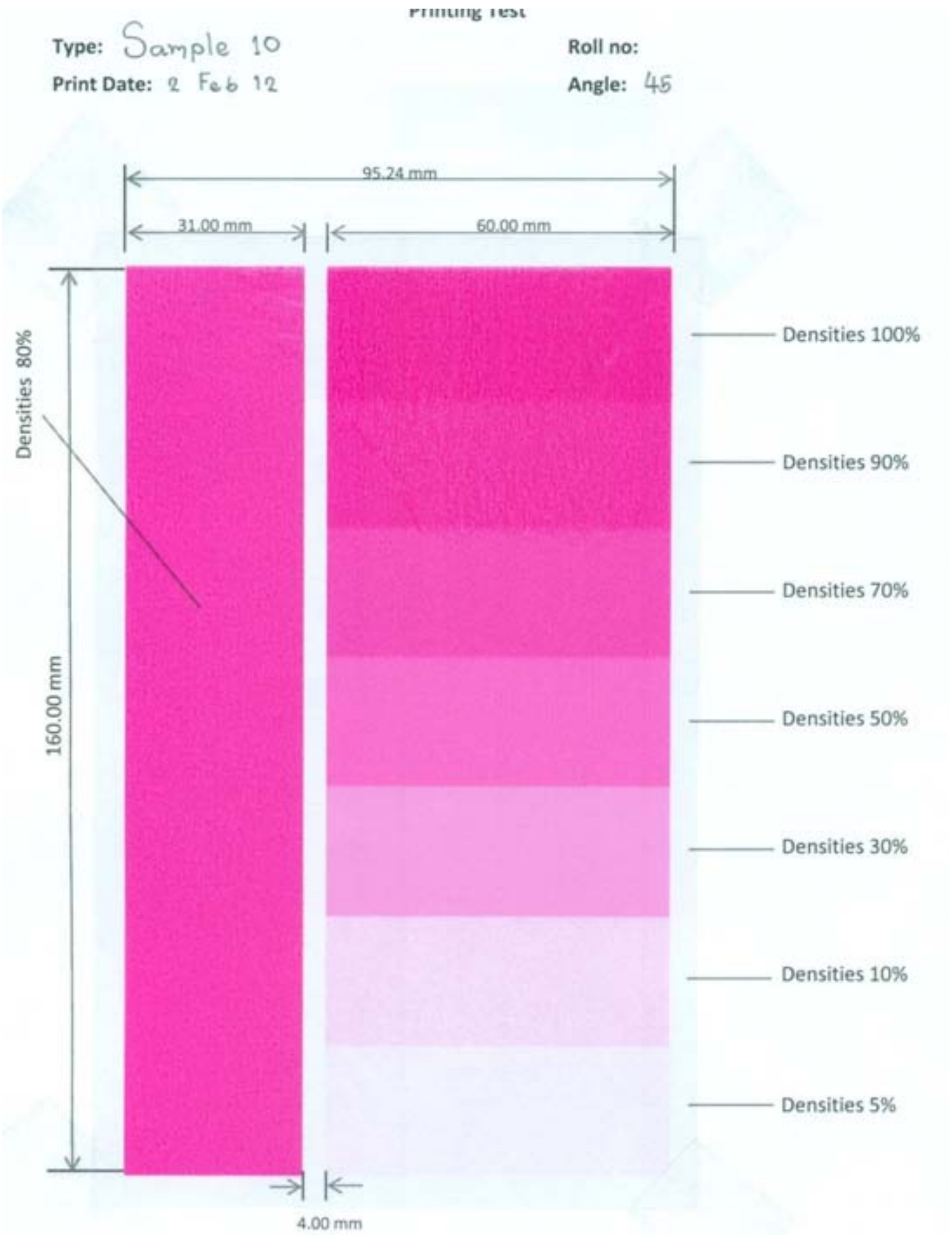
Type: Sample 9

Print Date: 2 Feb 12

Roll no:

Angle: 45

Figure D-9 Printability of Sample No.9 that can be carried out using a "PK Print Coat Instrument" Model K Printing Proofer, quadrangular gravure grooves of 100, 90, 70, 50, 30, 10 and 5 % of densities (dot %). Magenta ink (code M17, Toyo Ink (Thailand) Co., Ltd) is used.



Printing Test

Type: Sample 10

Print Date: 2 Feb 12

Roll no:

Angle: 45

Figure D-10 Printability of Sample No.10 that can be carried out using a "PK Print Coat Instrument" Model K Printing Proofer, quadrangular gravure grooves of 100, 90, 70, 50, 30, 10 and 5 % of densities (dot %). Magenta ink (code M17, Toyo Ink (Thailand) Co., Ltd) is used.

VITA

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