Bioglycerol from biodiesel production used as plasticizer in flexographic printing ink

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***Abstract*—This research aimed to study bioglycerol byproduct of biodiesel making process as the function of plasticizer in a water based flexographic printing ink. The four-color flexographic printing inks: cyan, magenta, yellow and black, were studied viscosity, surface tension, and end-use properties. The results were found that the bioglycerol did not have adverse effect to ink viscosity, flowing, and surface tension. Regression analysis was used to determine influence of bioglycerol to the ink property. The optimum content of the bioglycerol in printing ink was between 2 to 6 % by weight of ink that the end-use properties exhibited excellent flexibility on a printing substrate of polyethylene flexible film.**

Keywords— bioglycerol; flexography; printing ink; plasticizer

I. INTRODUCTION

It has been reported by Thai government that Thailand has planning to raise biodiesel production target to 7.3 million litres per day by 2021. Curren production capacity is about 2.8 million litres per day, growing from 1 million litres per day in 2007. Several biodiesel plants are operating in Thailand using the excess palm oil, palm stearin and waste vegetable oil as raw materials. Biodiesel is fatty acid esters made from vegetable oil, or from animal fat. Typically, biodiesel production uses chemical process to convert vegetable oil into biodiesel via esterification reaction with an alcohol, e.g. methanol. There are 2 chemical processes for obtaining Ester: 1) using acid as catalyst, and 2) using alkaline as catalyst. An example of tranesterification reaction to obtain biodiesel is as follows: [1]

$$\text{Vegetable oil + Alcohol} \xrightarrow[\text{[Acid, or biodiesel alkaline catalyst]}]{\text{Esterification}} \text{Esters + Glycerol}$$

Glycerol is by-product of biodiesel production; it is called bioglycerol in this paper. There is for 100 kg of glycerol produced from 1000 kg of biodiesel that is cause of waste glycerol from the biodiesel production process. However, glycerol has many commercial and industrial uses, and is generally considered a relatively valuable product. The glycerol can be utilized directly, or converted into other products, e.g. ethanol, propylene glycol, and epichlorohydrin. Glycerol can be used as a plasticizer, directly, in many applications, plastic, adhesive, food and pharmaceutical products, etc. [2]

Flexographic printing technology is growing in packaging printing, and advanced technology of flexographic printing ink is aiming to produce green water-based printing ink for flexible packaging film, e.g. polyethylene (PE), polypropylene (PP), Polyethylene terephthalate (PET). [3]

A printing ink is typically composed of pigment, vehicle, and additives. Pigments are composed in printing ink formulation to give colors to the printing ink. Pigment isn't soluble, but is particle dispersion in ink medium, or vehicle. In printing ink making process, grinding is a step to reduce particle size of pigment agglomerate and disperse pigment in vehicle composed of polymeric resin, solvents, and addtives. After grinding stage, letdown is adding to decrease viscosity of the printing ink discharged from grinding, more additives might be added. Color pigment used in printing ink is organic pigment, which cyan, magenta, yellow process color printing inks made from Pigment blue – PB 15; Copper Phthalocyanine blue, Pigment red – PR57:1; lithol rubine red, Pigment yellow – PY12; diarylide yellow. Black pigment is carbon black prepared from burning natural gas or petroleum oil. [4]

Viscosity and flow behavior of the printing ink are important for distributing and transferring from ink fountain to printing plate, onto printing substrate, and print quality. Since a printing ink has complex structure blended with many of compositions: solid particle, polymer resin, solvents and other agents, it causes the printing ink possess viscoelastic property, non-newtonian flow with yield stress value, which exhibits more significant with high pigmented and binder type. Flow behavior of the printing ink is needed to response on shear force as shear thinning flow for printability well driven by printing machine. Rheology of the printing ink depends on pigmentation, polymeric binders, solvents and other ingredients.[5,6,7]

Plasticizer might be used as an additive of the printing ink for flexible plastic film printing to prevent inkfilm cracking onto plastic surface after drying. However, caution is migration of plasticizer that causes blocking, and food contamination. The plasticizer which typically used in printing ink for plastic film is phthalate chemical, which has toxicity. There has been report that phthalate is a common contaminant from printing ink for PE film. [8] Consequently, it is a challenge to apply bioglycerol using for printing ink formulation. Aim of this study was to use bioglycerol, a byproduct received from chemical reaction of palm oil biodiesel. The bioglycerol was used as plasticizer in water based flexographic printing ink.

II. Experimental

A. *Materials*

Materials and chemicals used for preparing water based flexographic printing ink. The printing ink ingredients and formulation were supported by the Inter-ink Co., Ltd., Bangkok, Thailand, as shown in Table I. Bioglycerol used in this study was a byproduct of biodiesel process from Krabi Palm oil Community Cooperative, Ltd., Krabi Province, Thailand. The bioglycerol was purified to have 94%wt of purity. Physical properties of bioglycerol in Table II were measured before mixing in the printing ink.

TABLE I. Formulation of the water based Flexographic printing ink

Ingredients	Amount (%wt)	Ink preparing stages
Pigment	20	Milling Pasted
Acrylic resin	20	
Water	15	
Isopropyl alcohol	4.5	
Wax	1.5	
Dispersing agent	0.5	
Antifoaming agent	0.5	
Acrylic resin	9.5	Let Down
Water	8.5	
Water Resistance	15	
Bioglycerol	5	
Total	100	

TABLE II. Physical properties of bioglycerol

Physical properties	
Density	1.24 g/ml
Viscosity	1, 258 mPa s
Flowing time (Zahn cup no. 4)	25 Sec
Surface tension	62.4 mN/m

B. *Methods and apparatus*

- Preparation of the bioglycerol added flexo-graphic printing inks

Ingredients of the water based flexographic ink as shown in Table I was grinded in a laboratory shaker, Red Devil Vibro Shaker, milling by steel grinding balls with a diameter of 2.5 mm for 2 hrs. Next step of milling was adding letdown to lower viscosity for 35% of the paste viscous; ink additives was composed in the letdown. The bioglycerol was incorporated in the letdown. Four process color flexographic printing inks: cyan, magenta, yellow, and black, were measured properties, which were fineness of grind using a grind-o-meter, flowing time using Zhan cup no. 4, dynamic viscosity using a Brookfield rotational viscometer, and ink surface tension using Dunoy-ring tensi-o-meter.

The prepared flexographic printing inks were test drying time as following; firstly, the testing ink was drawdown on sheets of corona treated flexible polyethylene film using a 4-sided applicator, ZFR 20 ZEHNTNER, an uniform thickness of 30 µm. The drawdown samples were dried in a horizontal position without an oven.

- Viscosity measurement

Viscosity and viscosity dependency of the flexo ink was measured and studied, respectively, via Brookfield viscometer: LV-E model. The measuring method was using spindles no. 61-64 as well as adjusting spindle speed in order to control %torque reading to be close to 100% or not below 10%; under room temperature 25°C. The viscosities were measured at shear rates of 10, 20, 30, 50, 60, 100 RPM..

- Ink surface tension

Surface tension of the flexo ink was measured via Du Nouy ring tensiometer, TD2, Lauda. Du Nouy ring method widely used for surface, or interfacial tension measurement of liquids. This method used a platinum ring which was submersed in the flexographic ink below the air/ink interface for 3 mm. The surface tension of the ink was determined as the tension of pulling force required to lift the ring out of the ink's surface. Prior submerging into the ink, the Du Nouy ring was heated on a flame shortly; and it was followed by methanol rinsing.

- Inkfilm cracking test

This method was modified for understanding influence of bioglycerol as a plasticizer, which had capability of cracking resistance of the dried inkfilm. Firstly, the prepared flexographic printing ink was drawdowns on a sheet of corona treated flexible polyethylene film using four-sided applicator, ZEHNTNER GmbH, at an uniform thickness of 30 µm; cut the film into a piece of 120x15 mm, the printing ink was let to dry in laboratory room. The dried inkfilm adhered on the polyethylene film were brought to test cracking by elongating the film using a tensile tester, HSK-S, Hounsfield, pulling at a low speed. A length in millimeter of elongating PE film at cracking point of inkfilm was recorded.

- Dry/wet rub test

For dry rub test, the test printing inks were drawdown onto a sheet of white cardboard paper via anilox handproofer, let the printing ink dried completely prior it was brought to rub test using Digital ink rub tester 10-18-01, TMI. Rubbing pad was covered with a small dry sheet of white uncoated paper, then rubbing onto the sample sheet for 80 cycles with a rubbing pressure of 586 g. Rub resistance were determined by rating scale of stain, 1 to 5 scales by measuring a density value (D) of the rubbing pad.

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Scale 5, D	=	0.0	Excellent
Scale 4, D	=	0.12-0.20	Good
Scale 3, D	=	0.13-0.24	Fair
Scale 2, D	=	0.25 – 0.52	Poor
Scale 1, D	=	0.53 – 0.75	Very poor

Wet rub test was done by rubbing onto the ink drawdown cardboard sheets with dampen white thin fabric with a loose, open weave for 2 cycles with a rubbing pressure of 586 g. Determination of wet rub resistance by rating scale of stain, 1 to 5 scales.

- Lightfastness

Samples were brought to be exposed with sunlight for 1-3 weeks. CIE-Lab* color values of the drawdowns were measured using a spectrophotometer, SpectroEye, X-Rite. Color different values (ΔE) between color values on dark exposed area, and light exposed area were calculated to find color changing, or color fading.

- Blocking test

Blocking test was to check bonding of the printing ink onto backside of film plastic when heat and pressure were supplied. The method was that surface of inkfilm printed onto plastic film (polyethylene) was covered with a sheet of polyethylene film, then put 1.8 kg weigh onto the sheet of polyethylene film for 24 hrs at 40°C, and then blocking tendency was observed.

III. Results and Discussion

A. Flexographic printing ink properties

In ink making process, it was found that adding bioglycerol into letdown showed better spreading onto polyethylene film than that of mixing in grinding stage. Fineness of grind was about 5 to 7.5 µm. Viscosity and flowing of the printing inks was being dependent on pigments used in the inks. Because of pigment characteristic such as shape, surface structure, chemical property and so on, which differed among the pigments, resulted in different pigment-vehicle interaction as well as rheology behavior. Fig. 1 shows viscosity against shear force rate of the water based flexographic printing inks that had shear thinning non-newtonian and pseudoplastic behavior. It was showed that the black ink had strong pseudoplastic behavior having higher viscosity and higher yield stress than those of cyan, magenta, and yellow inks. Fig. 2-4 show that shear thinning pseudoplastic behavior of the printing inks was decreased when adding more bioglycerol content since it was a Newtonian liquid. Figure 5, the black ink had pseudoplastic behavior from the bioglycerol contents of 0-10%wt because it possed high yield stress pseudoplastic behavior. Fig. 6-8 was plotted between ink viscosity and contents of bioglycerol mixed in the inks for 2-10%wt, it was described that the ink viscosity linearly decreased against the content increasing. It was possible that bioglycerol mixing into the flexographic printing inks didn't have strong intermolecular interaction or chemical reaction between molecules of the bioglycerol and ink compositions such as pigment and other additives. The bioglycerol effected to flowing time via Zahn efflex cup reduction, proportionally, as shown in Fig. 9.

Fig. 10 shows surface tension of the printing inks, the different surface tensions of the different cyan, magenta, yellow and black inks were effect of pigment types which had differences of particle shape, particle size, physical properties and chemical compositions. Because the bioglycerol had high surface tension of 62.4 mN/m as shown in Table II, so the addition of bioglycerol into the printing inks effected to raise up the surface tension of the inks.

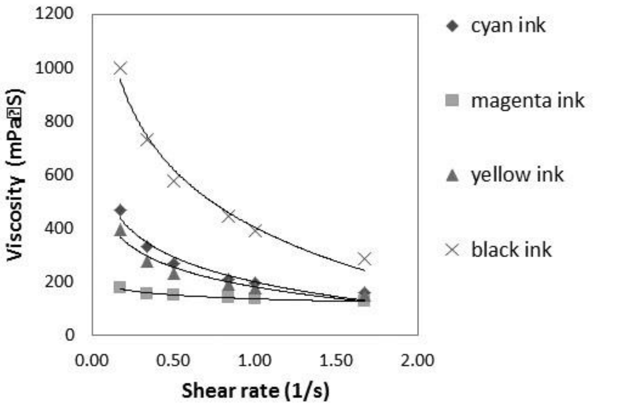

Fig. 1 *Dependency of viscosity on shear rates of water based flexographic printing inks; at 0%wt of bioglycerol.*

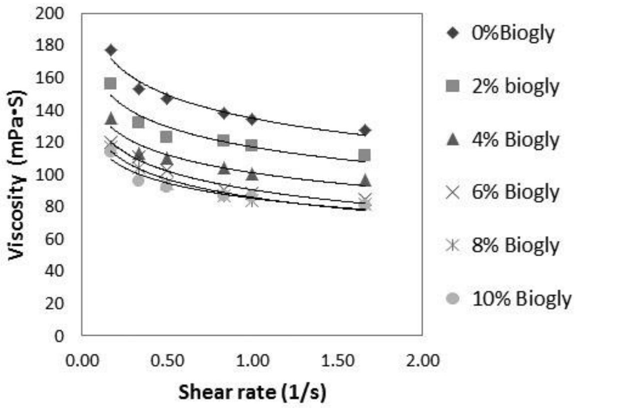

Fig. 2 *Dependence of viscosity on shear rates with bioglycerol contents for magenta ink.*

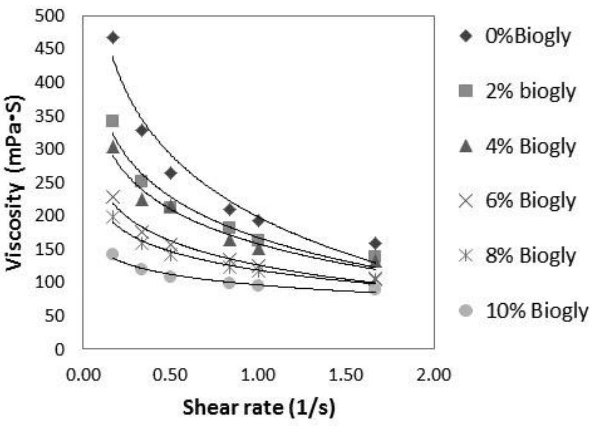

Fig. 3 *Dependence of viscosity on shear rates with bioglycerol contents for cyan ink.*

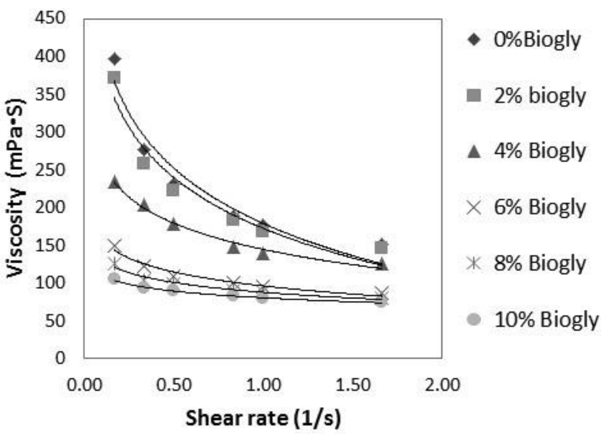

Fig. 4 *Dependence of viscosity on shear rates with bioglycerol contents for yellow ink.*

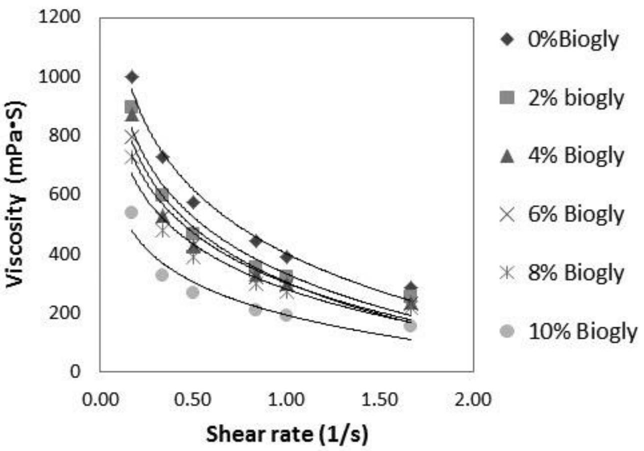

Fig. 5 *Dependence of viscosity on shear rates with bioglycerol contents for black ink.*

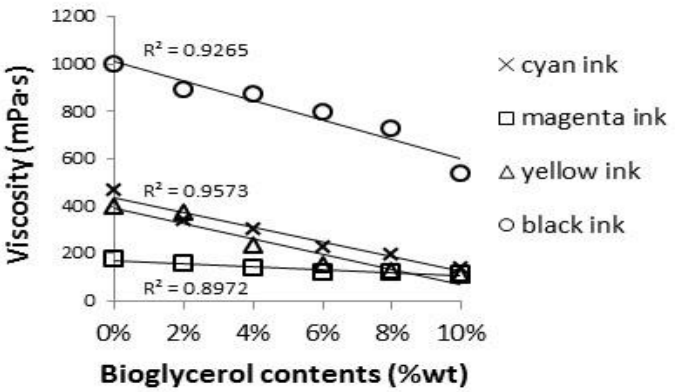

Fig. 6 *Dependence of viscosity on bioglycerol contents in cyan, magenta, yellow, black flexographic printing inks at a shear rate of 10 RPM.*

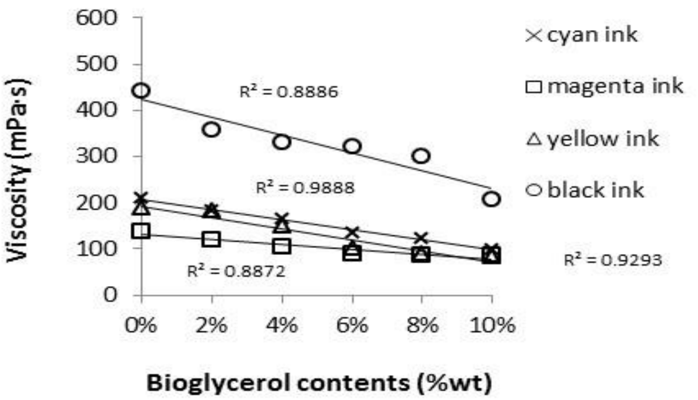

Fig. 7 *Dependence of viscosity on bioglycerol contents in cyan, magenta, yellow, black flexographic printing inks at a shear rate of 50 RPM.*

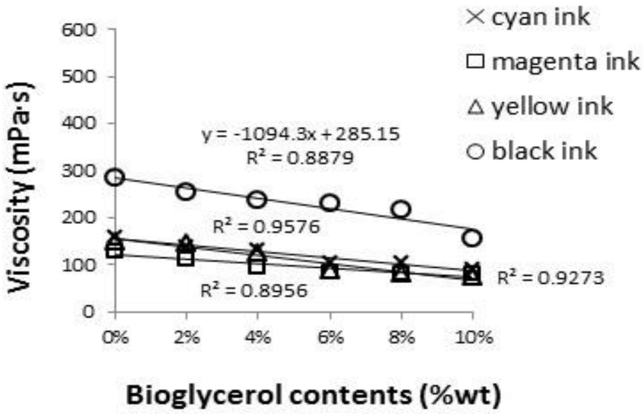

Fig. 8 *Dependence of viscosity on bioglycerol contents in cyan, magenta, yellow, black flexographic printing inks at a shear rate of 100 RPM.*

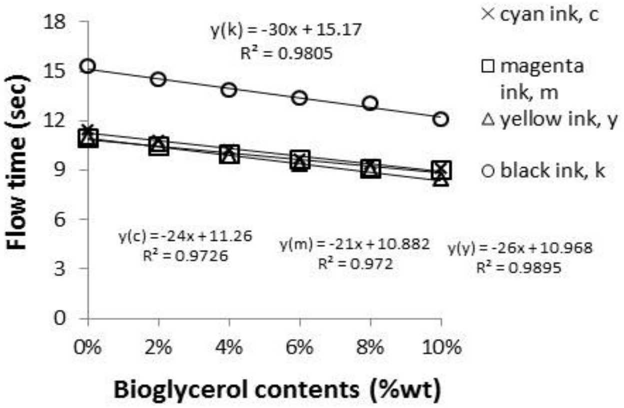

Fig. 9 *Dependence of flowing time through Zahn efflux cup (#4) on bioglycerol contents in the cyan, magenta, yellow, black flexographic printing inks*

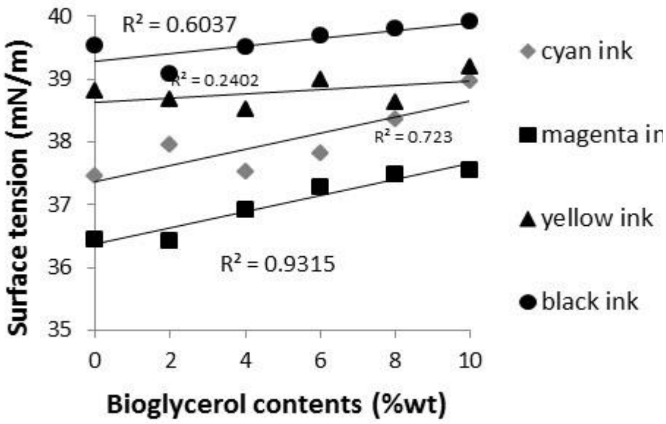

Fig. 10 *Dependence of surface tension on bioglycerol contents in cyan, magenta, yellow, black flexographic printing inks.*

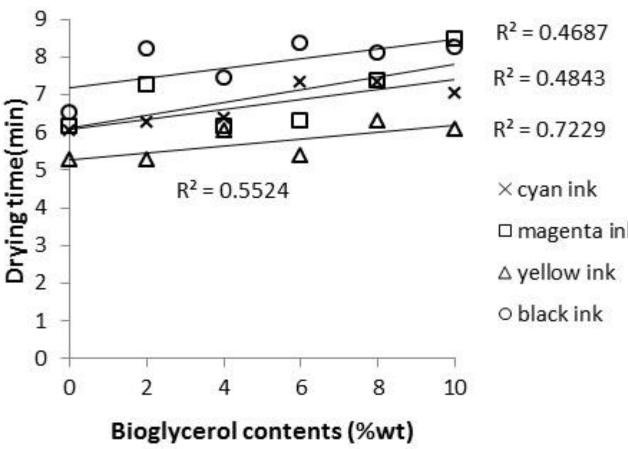

Fig. 11 *Dependence of drying time on bioglycerol contents in cyan, magenta, yellow, black flexographic printing inks.*

B. Testing for end-use properties

The drying time of the ink was retarded for 1-2 min from 0-10 %wt adding of bioglycerol, but proportion between the drying time and %wt of bioglycerol in the ink was not perspicuous (Fig. 11). As same as glycerol, bioglycerol had had higher boiling point,

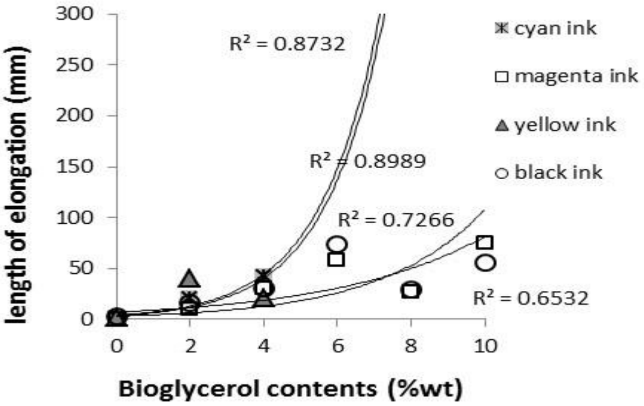

Fig. 12 *Dependence of length of elongated film on inkfilm cracking on bioglycerol contents in cyan, magenta, yellow, black flexographic printing inks.*

TABLE III Blocking test of the bioglycerol added flexographic printing inks on polyethylene film

Inks	%wt of bioglycerol in the ink					
	0	2	4	6	8	10
Cyan	no	no	no	yes	yes	yes
Magenta	no	no	no	no	yes	yes
Yellow	no	no	yes	yes	yes	yes
Black	no	no	no	yes	yes	yes

TABLE IV Dry rub test of the bioglycerol added flexographic printing inks on a cardboard carton paper

Color Inks	%wt of bioglycerol in the ink					
	0	2	4	6	8	10
Cyan	5	5	5	5	5	5
Magenta	5	5	5	5	5	5
Yellow	5	5	5	5	5	5
Black	5	5	5	5	5	5

1- very poor, 2-poor, 3-fair, 4-good, 5-excellent

TABLE V Wet rub test of the bioglycerol added flexographic printing inks on a cardboard carton paper

Color Inks	%wt of bioglycerol in the ink					
	0	2	4	6	8	10
Cyan	3	3	2	2	2	2
Magenta	3	3	3	3	3	2
Yellow	3	3	3	2	2	2
Black	2	2	2	2	2	2

1- very poor, 2-poor, 3-fair, 4-good, 5-excellent

lower evaporation than water had, so that the evaporation, or drying time of the printing ink was retarded.

Flexibility of dried inkfilm was definitely improved by bioglycerol. At 0%wt content of bioglycerol, it showed cracking inkfilm whenever it was dried. Length of elongation of the dried inkfilm before cracking was extended for more than 10 times of 0%wt bioglycerol. Fig. 12 represents the non-linear increasing of the elongation length on bioglycerol contents. Consequently, flexibility of the inkfilm was advanced with a small amount of bioglycerol. Yellow and cyan pigmented inks gave much improvement without inkfilm cracking by adding for 6%wt of bioglycerol. It might be understood that bioglycerol had small size molecule; acted as plasticizer that lubricated dried binder molecule allowing polymer chains sliding past each other.

Blocking commonly is a problem of printing on plastic that printing ink adhered on a printed sheet had sticking inside plastic roll, or stack of plastic sheets when degree of temperature and pressure increase. Because a printing ink for plastic composed of plasticizer to avoid cracking of dried inkfilm onto plastic surface. Plasticizer such as glycerol was a small molecule for passing in polymer chain; it also migrated onto surface of inkfilm when ink drying was completed. Bioglycerol used in the ink having low molecular weight that could migrate onto the ink surface. Dried inkfilm surface was soften so that blocking was occurred when the printed plastic sheets was kept in higher degree of temperature with pressure, or weight. Result of blocking test was shown in Table III that there was difference among color inks; the reason was possible that there was interaction of the bioglycerol onto the pigment surface; different pigments had different chemical groups.[9] Table IV shows result of dry rub testing on all printed samples, it was clear that dry rub resistance of the water based flexographic printing ink was not lost when the bioglycerol was mixed into the ink formulation. Since the water based printing ink had not good property of waterfastness as well as hydrophilicity of glycerol molecule having OH groups attracting to water molecules by hydrogen bonding. The bioglycerol mixing into flexographic printing ink consequently gave lower wet rub.

IV. Conclusions

Using of bioglycerol into water based flexographic printing ink as plasticizer showed that the bioglycerol had high capability to improve flexibility of the inkfilm. Type of pigment used into the printing ink formulation was a factor to effect on ink properties. However, bioglycerol had physical property that could be caused adverse effects of blocking, slow drying, and poor water resistance to the printing ink. A suitable content of bioglycerol mixing into the printing ink formulation was suggested to consider on what color of the printing ink will be made. The limitation of content loading into the ink formulation was at content between 2-4 %wt, or for 6%wt for the magenta printing ink. It was recommended that bioglycerol had good capability to be used and be modified to develop ink formulation further.

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