Rheological Properties of UV-curable Flexographic Ink

Kyoung-Mo Jeong* and Ken'ichi Koseki

*Graduate School of Science and Technology, Chiba University
1-33, Yayoi-cho, Inage-ku, Chiba, 263-8522, Japan
emos77@graduate.chiba-u.jp

Rheological properties of UV flexographic (flexo) inks were investigated. UV flexo suspensions of carbon black in liquid medium having various binding materials such as acrylate pre-polymer, di-/multi-functional monomer, and diluents, were used as sample inks. Inks were characterized on a rheometer in terms of steady and dynamic behaviors.

In order to understand and to control the rheological property of UV flexo inks, we must determine the specific rheological properties of chemical and/or physical interactions of their components (pigments, functional monomers, and pre-polymers). In particular, we discuss the influence of multi-functional monomers (TMPTA, PO-TMPTA, and GPTA) and the relationship between the rheological property and transient networks formed by carbon black.

Keywords: Rheology, UV flexo inks, Network formation, Multi-functional monomer

1. Introduction

Understanding the pigment blending technique and the photochemical reaction of UV flexographic (flexo) ink in the printing system is very important, and rheological property of UV flexo ink is also one of the most important factors in realizing high-quality flexo printing.

In recent literature, studies have reported on the influence of surface energetic properties on ink transfer in flexo printing¹⁾. Most of them agreed with the fact that the surface energy of the plate exerts little or no influence on ink transfer.

Ludovic et al. reported on the influence of transfer characterization of six/seven kinds of UV flexo inks^{1,2)}. Their study provided an understanding of UV flexo inks having different rheological properties under different conditions of processes such as printing speed, pressing pressure, and cell volume of anilox. Transfer characteristics are probably related to the viscoelastic properties of the ink. The different results emphasize the fact that the ink composition is of prime importance in the transfer phenomena.

In this study, we investigate the interrelationships between rheological properties of UV flexo ink and chemical and/or physical interactions of their components such as pigment, functional monomers (of different chemical structure), and pre-polymers. In this system, the chains of pigment particles form the structure and the formation of polymer bridges by adsorption on adjacent particles, which gives additional power to their viscoelastic interactions.

In general, the decrease in viscosity with increasing shear rate is due to a gradual reduction in the amount of 'structure' in the system. However, 'the structure' is affected by various factors related to the transient forming force/type of network, and when rheological measurements were performed under two testing conditions (steady-state measurements and oscillatory regime).

It is believed that there are two main factors that influence the transient network formation. The first is existence and/or nonexistence of propoxylated parts of the functional monomer, which is probably related to the viscoelastic properties of ink. The second is shaking efficiency and/or time.

Table 1. Formulations of ink suspensions

	wt%
Pigments (Carbon Black)	13.0
Oligomer	14.5
Multi-functional monomer	28.9
Di-functional monomer	30.3
Diluents	12.0
Dispersants	1.3

2. Experimental

2.1 Materials

The pigment powder used was carbon black, which is used for UV flexo inks. Carbon black has a BET surface area of 95[m²/g], a median size of 27[nm], dibutylphthalate (DBP) absorption of 60[cc]/100[g], a chromaticity of 155, and a pH of 3.5. Pre-polymers of polyester acrylate having acrylate group [Oligomer-A (Aronics M-7100, TOAGOSEI Co., LTD., multi-acrylate type, viscosity: 9 [Pa · s] at 25°C), Oligomer-B (Aronics M-6100, TOAGOSEI Co., LTD., di-acrylate type, viscosity: 0.3 [Pa · s] at 25°C)], multi-functional monomer [Trimethylol-propane triacrylate (TMPTA), Trimethylol-propane triacrylate, modified PO (PO-TMPTA), and Glycerol triacrylate, modified PO (GPTA)], and di-functional monomer [Tripropyleneglycol diacrylate (TPGDA)] were used as curing components. Acryloyl morpholine (ACMO) was used as diluting agent. Slosperse3900 (Avecia Co.) was used as dispersing agent.

2.2 Preparation of UV flexo ink suspension

UV flexo ink suspensions were prepared using a paint shaker. The formulations of ink suspensions tested are shown in Table 1. Glass bottles of 100[ml] in volume were used as mill vessels, and as shaking media, ceramic balls (density: 3.60[g/cm³]) of 2[mm] in diameter were used. The materials were mixed in the bottle, and milled with the media for 2 hours.

There are many factors that affect rheological properties of UV flexo ink, such as the following.

1) Shaking Time

2) Chemical Structure

- Number of functional group
(Tri-acrylate, Tetra-acrylate, and Hexa-acrylate)

3) Physical Structure

- Two-dimensional (GPTA), three-dimensional (TMPTA, PETTA)

4) Viscosity of Liquid Mediums (pre-polymer, functional monomer)

5) Shaking Method

6) Density and/or Diameter of Shaking Media

It is also difficult to measure the magnitude of rheological mechanism, and to determine the superiority of the factors affecting chemical/physical interactions and rheological properties. These interactions depend on electric and chemical properties of the pigment particles and the pigment-vehicle interface, such as surface charge, surface potential or the presence of a surfactant layer³⁾.

In order to investigate and determine the superiority of factors affecting rheological properties of UV flexo ink, we carried out three comparative tests.

Fig. 1 Chemical structures of multi-functional monomers

Experiment I

Rheological property was investigated as a function of shaking time (30min, 60min, and 120min); Oligomer-A (pre-polymer) and TMPTA (multi-functional monomer), respectively, were used.

Experiment II

Rheological property of UV flexo ink was investigated as a function of chemical disparity of functional monomers (of different chemical/physical structures); we used three multi-functional monomers (TMPTA, PO-TMPTA, and GPTA) and pre-polymer (Oligomer-A). Chemical structures of multi-functional monomers are shown in Fig. 1.

Experiment III

The influence of viscosity of liquid medium with pre-polymer was investigated using two pre-polymers (Oligomer-A, Oligomer-B). Multi-functional monomer TMPTA was used as well as GPTA, for comparison.

Oligomer-A: $A-(XA-YA)_n-X-A$

A: acrylic acid (functional group)

X: polyhydric alcohol

Y: polybasic acid

Oligomer-B: $A-(M-N)_n-M-A$

M: dihydric alcohol

N: dibasic acid

Fig. 2 Apparent viscosity as a function of shear rate for UV ink suspension (dispersing time: 30min, 60min, and 120min)

2.3 Evaluation of ink sample

In this study, all measurements were carried out using a Rheometrics Fluid Spectrometer (RFS-II, Rheometrics Co.) with couette geometry. Every rheological measurement was performed at 25°C and repeated 3 times for reproducibility. Generally, the three curves were superimposed.

We performed all measurements after applying the steady shear rate of $10[s^{-1}]$ for 600[s] as a pre-shearing. The steady shear measurements were performed at the shear rate ranging from $0.1[s^{-1}]$ to $[100s^{-1}]$.

Fig. 3 Frequency dependence of storage modulus G' for UV ink suspensions at the strain amplitude of 1.0% (dispersing time: 30min, 60min, and 120min).

3. Results and Discussion

3.1 Shaking time

The shear rate dependence of apparent viscosity for UV ink suspension is evident in the shear thinning behavior, as illustrated in Fig. 2.

Carbon black, dispersed in UV curing liquid medium such as pre-polymer and functional monomer, has a thick absorbed layer and structural network⁴⁾. The absorption rate of the layer, which is closely related to the rheological properties of ink, seems to be proportional to the shaking time ($30min < 60min < 120min$).

Fig. 3 shows the frequency dependence of storage modulus G' at the strain amplitude of 1.0%. It is evident that G' correlates to the chemical and physical interactions between pigments and between pigment-liquid medium. These interactions depend on the electric and chemical properties of

the pigment particles and the pigment vehicle interface, such as surface charge, surface potential or the presence of a surfactant layer³⁾.

Results of dynamic viscosity η' in relation to the transient attraction power of ink suspension reveal the internal structure of the system, as shown in Fig. 4.

Fig. 4 Frequency dependence of dynamic viscosity for UV ink suspensions at the strain amplitude of 1.0% (dispersing time: 30min, 60min, 120min).

Fig. 5 Apparent viscosity as a function of shear rate for UV ink suspensions with different multi-functional monomers such as TMPTA, PO-TMPTA, and GPTA, at the strain amplitude of 1.0%.

3.2 Influence of multi-functional monomer

Flow properties of UV flexo ink with different multi-functional monomers are shown in Figs. 5

and 6. Three kinds of UV flexo ink show the shear thinning behavior. Their viscosities are clearly different at a shear rate ranging from $0.1[s^{-1}]$ to $100[s^{-1}]$. At a lower shear rate ranging from $0.1[s^{-1}]$ to $10[s^{-1}]$, the viscosity and shear stress of ink suspension with GPTA are shown to be of higher magnitude, compared with PO-TMPTA. However this tendency of magnitude is reversed at a higher shear rate ranging from $10[s^{-1}]$ to $100[s^{-1}]$.

Fig. 6 Shear stress as a function of shear rate for UV ink suspensions with different multi-functional monomers such as TMPTA, PO-TMPTA, and GPTA.

Fig. 7 Frequency dependence of elastic modulus G' for UV ink suspensions with different multi-functional monomers such as TMPTA, PO-TMPTA, and GPTA, at the strain amplitude of 5.0%.

In Fig. 7 the storage modulus G' of ink suspensions with different kinds of multi-functional monomers, is shown as a function of frequency, at a strain amplitude of 5%. As evident in the figure, for the frequency magnitude ranging from 0.1[rad/s] to 10[rad/s], a non-linear viscoelastic regime is observed, and the internal structure of the system is disrupted as a result of the frequency applied. Different G' results of ink suspensions with different multi-functional monomers seem to be closely related to the transient network formation in the system. Especially, attraction forces dependent on electric and chemical interactions of the pigment-vehicle interface are correlated to the physicochemical differences of multi-functional monomers, as shown in Fig. 1.

It is believed that the existence/nonexistence of propoxylated parts of functional monomers is probably related to the viscoelastic properties of ink suspensions. Two-dimensional structures of GPTA are believed to help in the formation of a transient network structure and polymeric bridges by adsorption on adjacent particles. As a result, G' of ink suspension with GPTA is higher in viscoelastic property than that of others, as shown in Fig. 7.

Fig. 8 Apparent viscosity as a function of shear rate for UV ink suspensions for different liquid mediums.

3.3 Influence of pre-polymer

In this experiment, the decrease in viscosity with increasing shear rate is due to a gradual reduction in

the amount of 'structure' in the system. However, various factors affect the transient network force between pigments, and, as a result, the magnitude of rheological properties between ink samples has shown different tendencies (steady-state measurement and/or oscillatory regime).

It is believed that the viscosity of liquid medium (pre-polymer) is related to the shaking efficiency of UV flexo ink. Thus apparent viscosity of ink suspension with Oligomer-B is higher than that of others, although the apparent viscosity of Oligomer-B is lower than that of Oligomer-A, as shown in Fig 8.

Fig. 9 Frequency dependence of elastic modulus G' for UV ink suspensions with different liquid mediums at the strain amplitude of 1.0%.

On the other hand, dynamic testing results show dissimilar and/or different tendencies for the viscoelastic properties of ink. In this case, elastic modulus G' of ink suspension with GPTA has a higher numerical value than that of others at all frequency ranges, as shown in Figs. 9 and 10.

Donnet et al. explained that the characteristics of viscoelastic properties of ink suspension might be attributed to the internal structure formed by dispersed particles⁵⁾. They referred to this effect as the "chain effect". A third hydrodynamic effect, known as "interaction" occurs when dispersed and continuous phases interact physically, chemically, or mechanically. Such an interaction increases the

effective volume of the dispersed phase, by bonding of part of the continuous phase to the particles.

The ink suspension with Oligomer-B/TMPTA shows a higher elastic modulus G' compared to that with Oligomer-A/TMPTA. Although the apparent viscosity of Oligomer-B/TMPTA is lower than that of Oligomer-A/TMPTA.

Fig. 10 Frequency dependence of elastic modulus G' for UV ink suspensions with different liquid mediums at the strain amplitude of 5.0%.

4. Conclusion

In this study, we investigated the interrelationships between rheological properties of UV flexo ink and chemical and/or physical interactions of their components. In order to

investigate and determine the superiority of factors affecting rheological properties of UV flexo ink, we carried out three comparative tests.

- 1) The shear rate dependence of apparent viscosity for UV ink suspension shows shear thinning behavior.
- 2) The frequency dependency of storage modulus G' at the strain amplitude has an effect on the existence/nonexistence of propoxylated parts. The physical structure (two-dimensional and/or three-dimensional) of multi-functional monomers is another factor affecting the rheological properties of UV flexo ink.
- 3) Viscoelastic properties of UV flexo ink are closely related to the transient cross-linking interaction formed by carbon black, and are mainly affected by the variation of multi-functional monomers and/or pre-polymers.

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