Relationship between Printability and 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

ABSTRACT

Relationship between printability and rheological properties of UV flexographic (flexo) inks were investigated. UV flexo suspensions of carbon black in liquid medium having various binding materials such as acylate 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. To understand the rheological properties 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 discussed the influence of multi-functional monomers and the relationship between the rheological properties and transient networks formed by carbon black.

In this study, we investigated the interrelationships between rheological properties of UV flexo inks and chemical and/or physical interactions of their components. To investigate correlations between the printability and the rheological behaviors induced by interfacial interactions between ink compositions, we carried out rheological tests of UV ink suspensions. The results were compared with printing tests so as to find out the relationship between printability and rheological properties of ink.

INTRODUCTION

In spites of rheological studies carried out over many years, it is still not possible to state precisely the characteristics that will ensure good printing qualities of UV flexo ink. The printability has, however, a close relationship to the rheological properties of UV flexo ink [1].

The rheological properties of pigment-polymer matrix systems provide important information on the processing behaviors of composite materials. In order to understand and control the rheological properties of UV flexo inks, we must determine the specific rheological properties produced by the chemical and/or physical interactions of the ink components [2, 3].

In recent literature, studies have reported on the influence of surface energetic properties on ink transfer in flexo printing [4, 6, 7]. 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 [4, 5]. 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 recent study, to investigate the rheological behaviors induced by interfacial interactions between ink compositions, we carried out three comparative tests by means of rheological measurement. The results were compared with printing tests so as to find out the relationship between printability and rheological properties of inks [1].

Also, It was assumed that two types of transferring behaviors, anilox and roll transference, are correlated to the rheological properties of UV flexo ink. One is anilox transference (transfer from anilox roll to plate cylinder). On the basis of the results, it can therefore be presumed that the rebuilding speed of ink suspension seems to be probably related to the ink-transferring rate of anilox. The other is roll transference (transfer from plate cylinder to printing medium). From the result, it was assumed that this property seems to be correlated to the viscoelastic properties of ink suspension. Results of roll transference (transferring weight of ink, (%)) is proportion to the elastic modulus G' of ink suspension. [1].

Inn and Wang reported on the transient network model for a multiphase polymeric fluid. The interactions between pigment particles and the continuous phase bring about the formation of a network of particles and aggregates within the ink, which can form a continuous structure with time [8].

Pigment-pigment attraction forces are non-

hydrodynamic in nature. These non-hydrodynamic interactions depend on the electrical and chemical properties of the particles and the particle-fluid interface, such as surface charge, surface potential, or the presence of a surfactant layer [9].

There are two types of strands in the network: the **p-strands** are the chains between polymer-polymer junctions and the **f-strands** are the chains bridging a polymer-polymer junction and a polymer-filler (pigment) junction. The interfacial interactions between polymer matrix and undeformable pigments control the level of pigment contribution to the stress increment by influencing the flow deformation of the polymer melts [8].

The characteristic shear thinning behavior is phenomenologically incorporated into the network model by assuming that the lifetime of a strand is shortened upon flow deformation. When solid pigments are dispersed in the polymer matrix, a second type of strand, called filler strand (f-strand), is created, with one end connecting to an entanglement point and the other end terminating at a pigment surface [8].

It is argued that the interfacial characteristics depend not only on the strength of the direct adhesive interaction at pigment-polymer interfaces, but also on the strength of the polymer-polymer interaction in the bulk. The calculations by Inn and Wang indicate that at a fixed volume fraction of pigments, the viscosity increment may differ depending on the interfacial strength and that interfacial interactions can be modified by either pigment surface treatment or change of molecular weight of the polymer matrix [8].

EXPERIMENTAL
Materials

The pigment powder used was carbon black, which is used for UV flexo inks. Carbon black has a BET surface area of 95 m^2/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 ℃), multi-functional monomer [Trimethylol- propane triacrylate (TMPTA), Pentaerythritol tetraacrylate (PETTA), Glicerol triacrylate, modified PO (GPTA), and Dipentaerythritol hexaacrylate (DPHA)], 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.

Preparation of UV flexo ink suspension

Four types of UV flexo ink suspensions are prepared using a paint shaker. The base formulations tested are shown in Table 1. Glass bottles of tube type (diameter: 360 mm) of 110 ml in volume were used as mill vessels to gain high mixing efficiency, and as shaking media;

ceramic balls (density: 3.60 g/cm^2) of 2 mm in diameter were used. The materials were mixed in the bottle, and milled generally with the media at 2 hours.

Table 1. Formulations of Ink suspensions

	wt [%]
Pigments (Carbon Black)	13.0
Oligomer	14.5
Multi-functional monomer (4 types)	28.9
Di-functional monomer	30.3
Diluents	12.0
Dispersants	1.3

Rheological property of UV flexo ink was investigated as a function of chemical disparity of functional monomers: we used four multi-functional monomers; (TMPTA, PETTA, GPTA, and DPHA) and pre-polymer (Oligomer-A).

Evaluation of ink sample

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

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

The strain dependence of the storage modulus, G' was examined in strain region between 0.1 % and 100 % at an angular frequency 0.1 and 10 rad/s, respectively. The frequency dependence of storage modulus and/or dynamic viscosity was measured in the frequency amplitude region between 0.1 and 100 rad/s at the strain of 1 % and 5 %.

The stress overshoot (structural recovery) measurements were performed at 10 s^{-1} of the steady shear after various rest periods ranging from 4 to 2500 sec after 10 s^{-1} of the steady shear for 600 sec.

There are several methods to evaluate the velocity of structural recovery. R.F.S Cartright proposed a thixotropic index defined by the slope in the relation between ($\sigma_{max})^{1/2}$ and $t_s^{1/2}$. σ_{max} is the peak value of stress. A. de Waele proposed a logarithmical plot of $\Delta\sigma$ against rest time, t_s. $\Delta\sigma(\sigma_{max} - \sigma_{eq.})$is the stress growth and is given by the difference between a maximum value and equilibrium value before the rest period. On the slope of curve, the velocity of structural recovery can be discussed [14-15].

In this study, we have made the R.F.S Cartright plots for our experimental results. The value of $(\Delta\sigma)^{1/2}$ is calculated by subtracting the equilibrium value of stress

from the peak value of the stress. With increasing standing time, the flocculated structure becomes denser with increasing $t_s^{1/2}$ [16]. However, experimental results are plotted by the value of $(\Delta\sigma)$ and t_s. Because the peak value of the stress of flexo ink is shown lower scale of the stress than that of offset one.

Transfer tests

Two types of behaviors, ink transfer phenomena, which seem to be related to the rheological properties of UV flexo ink. One is anilox transference; transfer from anilox roll to plate cylinder, the other is roll transference; transfer from plate cylinder to printing medium. Which seem to be required to different transferring properties of ink, rheologically.

Printing experiments were carried out on two types of IGT tests: C1 usually dedicated to offset tests and F1, specifically dedicated to flexography.

Every measurement was performed at 25 °C and repeated 10 times for reproducibility. Generally, the data were superimposed. The reproducibility of the experiments was very good.

C1 tester

Tester description
The major elements of this tester are a printing cylinder, an inking unit with elastomer distribution roller, and the printing unit. The printing pressure can be gradually adjusted from 100 to 1000 (N). The printing speed is constant on this tester (0.3 m/s).

Test procedure
☐Inking of the distribution roller (2 minute)
☐Weighing of the printing cylinder (without ink)
☐Inking of the printing cylinder (1 minute)
☐Weighing of the printing cylinder after inking and before printing
☐Printing on substrate
☐Weighing of the printing cylinder after printing

The printing pressure selected for our experiments was 300 N. Transferring rate of the ink measured with an electrical balance.

F1 tester

Tester description
The tester composed of a ceramic anilox roller (70 line/cm and 0.83 ml/m² cell volume), a doctor blade with an angle of 60°, a printing cylinder covered by the photopolymer plate, a rubber printing cylinder and a substrate carrier.

The following parameters are adjusted on the tester
☐The printing speed: 0.3 m/s.
☐The inking pressure (between the anilox and the plate): 200 N.
☐The printing pressure (between the plate and the substrate): 300 N

The printing quality of the printed samples (office paper, inkjet paper, and PET film) was evaluated with an image analyzer.

RESULTS AND DISCUSSION
Flow properties

At low deformation rates, the stress is dominated by the non-hydrodynamic interactions of the particles. At high deformation rates, the stress is dominated by inter-particle hydrodynamics, which is dependent on the rheological behavior of the suspending fluid and the arrangement of the particles [9].

The shear rate dependence of the apparent viscosity for UV flexo ink suspensions exhibits the shear thinning behavior [1]. Carbon black, dispersed in UV curing liquid medium containing oligomers and functional monomers, seems to induce the formation of a thick adsorption layer and increase the rigidity of the structural network with the increase of the mixing time of the ink suspension from 2 h to 6 h. The three types of UV flexo ink suspensions show a clear difference in the apparent viscosity in the shear rate range of $10^{-1}\,s^{-1}$ to $10^0\,s^{-1}$, although they have the same chemical composition of the dispersing liquid medium.
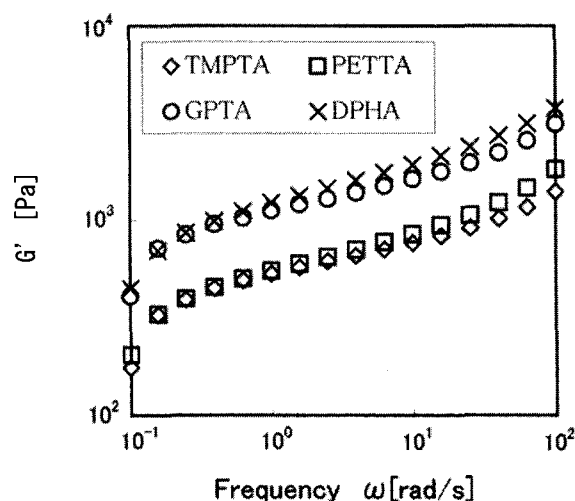

Fig 1. Frequency dependence of storage modulus G' for UV ink suspension at the strain amplitude of 1.0%.

Frequency Dependence of Storage Modulus G'

The frequency dependence of G' at the strain amplitude of 1.0 (%) in Fig. 1 shows that G' is proportional to the number of acryloyl groups in the multi-functional monomer (TMPTA < PETTA << DPHA). It seems that the acryloyl groups function as absorption points in the system [14, 15]. 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 layer [16].

In addition, we found that the chemical difference caused by chain length (propoxylated parts) is another factor affecting the rheological properties of UV flexo ink [2].

GPTA, a tri-functional monomer, has three acryloyl groups, similar to TMPTA. However, G' of the ink suspension with GPTA is higher than that of the ink suspension with TMPTA. It is speculated that the propoxylated parts in GPTA are useful for the formation of a transient network structure that function as polymeric bridges by adsorbing to adjacent particles. However, its interfacial interaction is weaker than those of the other monomers, as shown in Fig. 2.
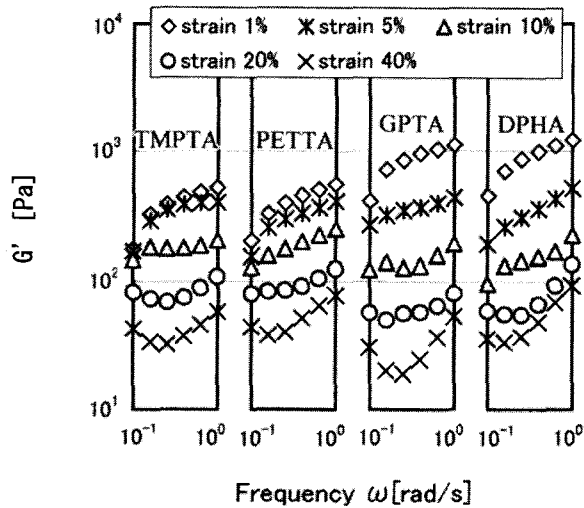

Fig. 2 Frequency dependence of storage modulus G' for UV ink suspension at strain amplitudes ranging from 1% to 40%.

Measurement of thixotropy

The occurrence of thixotropy implies that the flow history must be taken into account in predicting flow behavior. This property of ink has been the subject of many studies for several decades. The ultimate goal of such tests as the gradual recovery of structure test is to predict the performance of ink in the printing process.

In the case of the recovery of flocculated structures, the rebuilding speed of network structures, the properties of which are closely related to the number of acryloyl groups in the multi-functional monomer, is very important, because their disparity of chemical structure seems to play an important role between components. The rebuilding speeds of TMPTA, PETTA and DPHA (TMPTA<PETTA<<DPHA) are higher than that of GPTA, which are influenced by the existence and/or chemical entanglement of the propoxylated parts, as shown in Fig. 3.
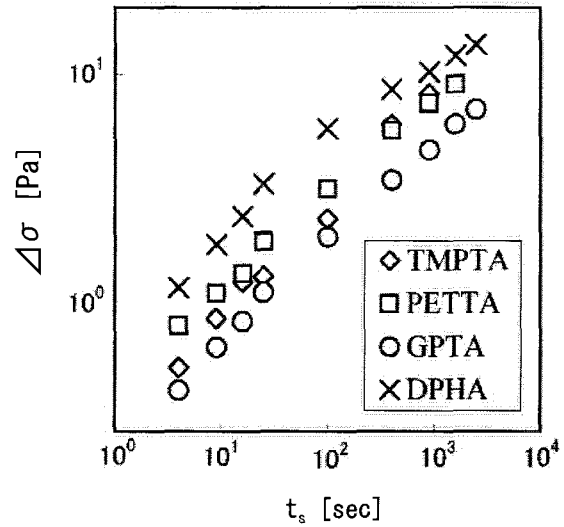

t_s [sec]

Fig 3. Plots of $\Delta\sigma$ vs. t_s for UV flexo ink suspensions with different multi-functional monomers (TMPTA, PETTA, GPTA, and DPHA).

Printability

In this study, we assumed that two types of transferring behaviors, anilox and roll transference, are correlated with the rheological properties of UV flexo ink [1].

Transfer modeling between anilox roll and plate cylinder (anilox transference)

Anilox transference involves transfer from anilox roll to plate cylinder. On the basis of the results, in Figs. 3 and 4, we surmise that the rebuilding speed of ink suspension is related to the ink transferring rate from anilox roll to plate cylinder.
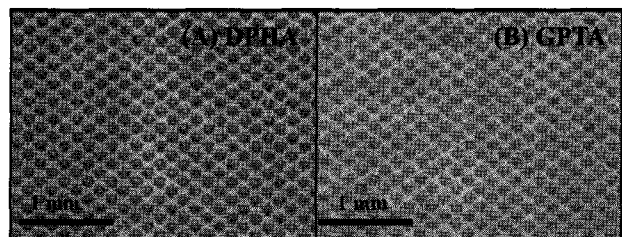

Fig. 4 Anilox transference of UV flexo ink suspension tested by IGT printability tester F1 (anilox cell: 70lines/cm, 0.83ml/cm² cell volume, printing medium: inkjet paper).

Transfer modeling between plate cylinder and printing medium (roll transference)

Roll transference involves transfer from plate cylinder to printing medium. We assume that this property is correlated with the viscoelastic properties of the ink

212

suspension. As shown in Table 2, roll transference (transferring weight of ink, %) is proportional to G' of the ink suspension shown in Fig. 1.

Table 2 Results of roll transference tested by C1

	Transferring weight of ink, g/m²	Transferring rate of ink, wt %
DPHA	3.024	50.1
GPTA	2.734	44.1
TMPTA	2.375	41.8
PETTA	2.513	39.6

Influence of printing speed

There are many factors that affect the transfer rate of UV flexo ink with various printing speeds, such as the following.

1) Rheological properties of ink:
   Elastic modulus G' and structural recovery
2) Properties of anilox cell:
   Cell volume, Channel, and Cell depth

It is believed that anilox transference of ink suspension is influenced by cell volume of anilox, as shown in Fig. 5. In addition, influence of the valuable at various different speeds may prove to be very complicated.
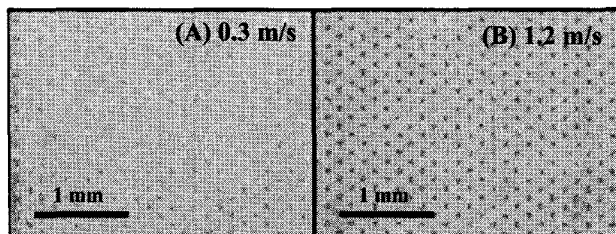

Fig. 5 Anilox transference of UV flexo ink suspension with GPTA tested by IGT printability tester F1 (anilox cell: 70lines/cm, 0.14ml/cm² cell volume, printing medium: office paper).

CONCLUSIONS

We investigated the rheological properties of UV flexo inks from the viewpoint of correlations between the printability and the rheological behaviors induced by interfacial interactions between ink compositions.

1) It is believed that roll transference of UV flexo ink is correlated with the elastic modulus G' of ink suspensions.
2) The rebuilding speed of network structures is very important. We surmise that this property is closely related to the chemical composition of the liquid medium, such

as the number of acryloyl groups in the multi-functional monomer.

3) We hypothesize that the two types of transferring behaviors, anilox and roll transference, are correlated with the rheological properties of UV flexo ink. And we believe that this possibility would be very useful to understand and control the printability of UV flexo ink.

REFERENCE

1. Jeong, K.M. and Koseki K., Rheological Properties of UV-curable Flexographic Ink (II) - Influence of interfacial interactions in relation to rheological variables of ink and its printability, J. Photopolym. Sci. Tech., 18 (6): 691 (2005)
2. Jeong, K.M. and Koseki K., Rheological Properties of UV-curable Flexographic Ink, J. Photopolym. Sci. Tech., 18 (1): 165(2005)
3. Branes, H.A., Hutton, J.F, and Walters, K., An Introduction to Rheology, 4th Ed., 115-139 ELSEVIER SCIENCE B.V. (1996)
4. Fouché, L. and Blayo, A., Transfer Characterization of UV Flexo Inks, TAGA Proceeding 2001, p.426 (2001)
5. Fouché, L., Rheological Characteristics of UV Flexo Inks, TAGA Proceeding 2000, p.774 (2000)
6. Lagerstedt, P., Kolseth, P., Influence of Surface Energetics on Ink Transfer in Flexo Printing, Advances in Printing Science and Technology, p.23 (1995)
7. Lavelle, J.S., et al., Measurement of flexographic ink transfer on a modified Prufbau, International printing and graphic arts conference, Tappi Press, p.199 (1996)
8. Inn, Y.W. and Wang, S.Q., Transient network model for multiphase polymeric fluid, Rheol. Acta, 32 (6): 581 (1993)
9. Stephens, T.S., Winter, H.H., and Gottlieb M., The steady shear viscosity of filled polymeric liquids described by a linear superposition of two relaxation mechanisms, Rheol. Acta, 27 (3): 263(1998)
10. R.F.S. Cartright, Measurement of Thixotropy in Lithographic Printing Inks, The British Ink Maker, 8(2): 83 (1966)
11. A. de Waele: J. Oil Color Chem: Assoc., 44( ): 377 (1961)
12. Morita, K., Tateiri, M., and Amari, T., Rheological Properties of Suspension of Brilliant Carmine 6B in Polybutadiene, J. Jpn. Soc. Colour Mater., 68(11), 682 (1995)
13. Wei, X. and Amari, T., Rheological Properties and Thermal Conductivity of Suspension of Metal Powder, J. Jpn. Soc. Colour Mater., 65(9): 535 (1992)
14. Tanaka, F. and Edwards, S.F., Viscoelastic Properties of Physically Cross-Linked Networks. Transient Network Theory, Macromolecules, 25 (5): 1516(1992)
15. Wang, S.Q., Transient Network Theory for Shear-Thickening Fluids and Physically Cross-Linked Systems, Macromolecules, 25(25): 7003 (1992)
16. Sherman P., Industrial Rheology, 97-184, Academic Press (1970)