Rheological Properties of UV-curable Flexographic Ink (II) 
Influence of Interfacial Interactions in Relation to 
Rheological Variables of Ink and its Printability

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The rheological properties of UV flexographic (flexo) inks were investigated. UV flexo suspensions of carbon black in liquid medium containing various binding materials, such as acrylate pre-polymers, di-/multi-functional monomers, and diluents, were used as sample inks. The inks were characterized on a rheometer in terms of steady and dynamic behaviors. The rheological properties of polymer-pigment systems are a function of some interfacial parameters that characterize the degree of “affinity” of pigment surfaces to the polymer medium. The addition of pigments into liquid medium introduces polymer-pigment junctions besides the polymer-polymer junctions due to entanglement. These newly created junctions arise from the sorption of pigments to the polymer chains. In this study, we found that the frequency dependence of storage modulus G’ at a certain strain amplitude is proportional to the number of acryloyl groups in the multi-functional monomer (TMPTA<PETTA<<DPHA). The chemical difference due to chain length (TMPTA<GPTA) is another factor affecting the rheological properties of UV flexo ink. In addition, we surmise that a transient network structure is formed by mechanical interactions that are induced by the addition of high concentrations of small solid particles such as carbon black to a polymer or a multi-phase solution. In such a system, the particle chains form the network structure, although the formation of polymer bridges by adsorbing to adjacent particles is another possibility.

Keywords: Rheology, UV flexo ink, Interfacial interaction, Transient structure

1. Introduction

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 [1, 2].

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 [3].

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 [4].

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 [3].

The characteristic shear thinning behavior is

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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.

The breakage rate $\beta_t$ of a pigment strand between a polymer entanglement and a polymer-pigment adsorption site is given by

$$\beta_t = \frac{1}{\tau_p} + \frac{1}{\tau_s} \quad [1]$$

$\tau_p$: Relaxation time of pigment-polymer junctions
$\tau_s$: Lifetime of polymer-polymer junctions

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 [3].

The results were compared with those of printing tests to determine the relationship between printability and the rheological properties of UV flexo inks.

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 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 °C], multi-functional monomer [Trimethylol-propane triacrylate (TMPTA), Pentaerythritol tetraacrylate (PETTA), Glicerol triacrylate, modified PO (GPTA), and Dipeptenthiol hexaacrylate (DPHA)], and di-functional monomer [Tripropyleneglycol decyrate (TPGD)] 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
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$^3$) of 2 mm in diameter were used. The materials were mixed in the bottle, and milled generally with the media at 2 hours.

![Chemical structures](image)

(A) TMPTA

(B) PETTA
Fig. 1 Chemical structures of multi-functional monomers.

Experiment I
Rheological property was investigated as a function of mixing time (2 hours, 4 hours, and 6 hours); Oligomer-A (pre-polymer) and DPHA (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: we used four multi-functional monomers; (TMPTA, PETTA, GPTA, and DPHA) and pre-polymer (Oligomer-A). Chemical structures of multi-functional monomers are shown in Fig. 1.

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 type 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 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 \(t_{p}^{1/2}\). \(\sigma_{max}\) is the peak value of stress. A. de Waele proposed a logarithmical plot of \(\Delta \sigma\) against rest time, \(t_p\). \(\Delta \sigma\) (\(\sigma_{max} - \sigma_{eq}\)) 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 [5-7].

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 \(t_{p}^{1/2}\) [8]. However, experimental results are plotted by the value of \((\Delta \sigma)\) and \(t_p\). Because the peak value of the stress of flexo ink is shown lower scale of the stress than that of offset one.

2.4 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 (PET

**Fig. 2** Apparent viscosity as a function of shear rate for UV flexo ink suspensions (mixing time: 2 hours, 4 hours, and 6 hours).

**Fig. 3** Apparent viscosity as a function of shear rate for UV flexo ink suspensions (different kinds of multi-functional monomers).

**Fig. 4** Frequency dependence of storage modulus G' for UV flexo ink suspension with DPHA (mixing time: (A) 2 hours, (B) 4 hours, and (C) 6 hours).
film was used) was evaluated with an image analyzer.

3. Results and Discussion
3.1 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 [4].

The shear rate dependence of the apparent viscosity for UV flexo ink suspensions exhibits the shear thinning behavior, as shown in Fig. 2. 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.

At high deformation rates, the stress is dominated by inter-particle hydrodynamics, which is dependent on the rheological behavior of the suspending fluid (apparent viscosity of multi-functional monomers: GPTA<TMPTA <PETTA << DPHA) and the arrangement of the particles [4]. At the region influenced by the hydrodynamic interaction, The four types of UV flexo ink suspensions exhibit a difference in the apparent viscosity in the shear rate range of $10^1$ s$^{-1}$ to $10^2$ s$^{-1}$, although they have similar apparent viscosities of ink suspensions in the shear rate range of $10^{-1}$ s$^{-1}$ to $10^0$ s$^{-1}$, as shown in Fig. 3.

Therefore, the formation of the thick adsorption layer between pigments and the increase in the elastic rigidity of the structural network, which are closely related to the interaction force of non-hydrodynamic regimes, with the increase of the mixing time of the ink suspension, seem to be correlated to the variation of the storage modulus (G’) of the ink suspensions over the frequency range of $10^1$ rad/s to $10^6$ rad/s, as shown in Fig. 4.

![Graph showing frequency dependence of storage modulus G' for UV ink suspension at strain amplitudes ranging from 1% to 40%](image)

**Fig. 6** Frequency dependence of storage modulus G’ for UV ink suspension at strain amplitudes ranging from 1% to 40%.

3.2 Frequency Dependence of Storage Modulus G’
The frequency dependence of G’ at the strain amplitude of 1.0 % in Fig. 5 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 [9, 10]. 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 [11].

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 [1].

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. 6.

3.3 Strain dependence of storage modulus $G'$

Figure 7 shows the strain dependence of $G'$ at two frequency amplitudes: (A) 0.1 rad/s and (B) 10 rad/s. We found that structural interruption between ink components against flowing occurs up to the certain point (a critical strain point) of strain existing between $10^{-1}$ % and $10^{0}$ %, after that of critical point elastic rigidity of $G'$ is decreased markedly with increasing strain. This means that the structural networks are going to be gradually breakdown with increasing strain.

Pigment-pigment attraction forces are non-hydrodynamic in nature [4], and 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 [11]. The hydrodynamic forces applied to the particles by the stress in the fluid do not influence them [12].

The rheology of pigment-polymer matrix systems depends, in a very complex way, on the structural states of the particles and the fluid. However, there seem to be limiting flow regimes for which the flow behavior might be expressed in a simplified form. 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 depends on the rheological behavior of the suspending fluid and the arrangement of the particles [4].

In pigment-polymer matrix systems, the non-hydrodynamic interactions relax very slowly and seem to give rise to the flow-induced structure over the very low strain range (from $10^{-1}$ % to $10^{0}$ %), whereas the hydrodynamic interactions relax quickly and seem to give rise to the structural breakdown over the high strain range (from $10^{0}$ % to $10^{2}$ %). It is believed that this flow dynamics is correlated with the strain dependence of $G'$.

It is evident that the difference in the results of $G'$ is closely related to the different deformation tensors of the filled polymer matrix, the properties of which seem to be related to the attraction force expressed by such terms as $\tau_{p}$ and $\tau_{s}$, between ink suspensions with DPHA and those with GPTA. As a result, the magnitudes of $G'$ of the ink suspensions with DPHA and GPTA show reversed tendencies at frequencies of 0.1 and 10 rad/s.

In this experiment, we found that this tendency of $G'$ is also closely related to the transient cross-linking interaction formed by pigment-pigment attraction forces. In particular, the attraction forces that depend on the electric and chemical properties of the pigment-vehicle interface are related to the properties of the multi-functional monomer (TMPTA, PETTA, GPTA, and DPHA).

3.4 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
results in Figs. 8 and 9, we surmise that the rebuilding speed of ink suspension is related to the ink transferring rate of anilox.

Roll transference involves transfer from plate cylinder to printing medium. We assume that this property is correlated with the viscoelastic properties of the ink suspension. As shown in Table 2, roll transference (transferring weight of ink, %) is proportional to G' of the ink suspension shown in Fig. 5.

Table 2 Results of roll transference tested by C1

<table>
<thead>
<tr>
<th></th>
<th>Transferring weight of ink, g/m²</th>
<th>Transferring rate of ink, wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td>DPHA</td>
<td>3.024</td>
<td>50.1</td>
</tr>
<tr>
<td>GPTA</td>
<td>2.734</td>
<td>44.1</td>
</tr>
<tr>
<td>TMPTA</td>
<td>2.375</td>
<td>41.8</td>
</tr>
<tr>
<td>PETTA</td>
<td>2.513</td>
<td>39.6</td>
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</tbody>
</table>

4. Conclusions

We investigated the rheological properties of UV flexo inks from the viewpoint of the relaxation mechanisms existing between the particles and the particle-fluid interface.

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 elastic rigidity of the structural network with the increase of the mixing time of the ink suspension. Thus, the three types of UV ink suspensions exhibit a clear difference in apparent viscosity, although they have the same chemical composition of the dispersing liquid medium.

2) The existence of propoxylated parts in GPTA is 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 TMPTA, PETTA, and DPHA.

3) The magnitudes of G' of the ink suspensions with DPHA and GPTA show reversed tendencies at frequency amplitudes of 0.1 and 10 rad/s, as observed in Fig. 7. It is evident that ink suspensions with DPHA and GPTA have different deformation tensors in their internal structures. Consequently, an in-depth understanding of interfacial attraction, which could be expressed by such terms as τ₁ and τ₂, is of fundamental importance for the design and/or preparation of UV
curing ink.

4) 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.

5) We hypothesize that the two types of transferring behaviors, anilox and roll transference, are correlated with the rheological properties of UV flexo ink.

References