Rheological Properties of UV-curable Ink
- Influence of the Pre-polymer and Colorant -

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In this study, the rheological properties of UV-curable ink were investigated. UV flexo/gravure-type suspension 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. Two types of carbon black, and three kinds of pre-polymer were individually used as ink components. The five kinds of inks were prepared to characterize their rheological properties on a rheometer in terms of steady and dynamic behaviours. In addition, we evaluated the relations between the flocculated structures and nonlinear viscoelastic properties of the inks. We found that because the carbon black particles had extremely high surface activity and absorbed various substances on the particle surface, they easily agglomerated with each other and then conformed to the denser three-dimensional network structure.

Keywords: UV-curable ink, Carbon black, Viscoelastic property, Network structure

1. Introduction

The rheological properties of suspensions greatly depend on the degree of flocculation. The flocculated structure depends on the shape, size, and surface characteristics of the dispersed particles and on the interaction between the dispersed medium and the particles. The structural density is also a function of the volume fraction of the dispersed particles.

The interaction between pigment particles and the continuous phase brings about the formation of a network of particles and aggregates within the ink, which can form a continuous structure over time. Usually in thixotropic materials, this structure is broken down during flow with flocculation and restored once again at rest. The process of network breakdown and build-up is of great importance, because inks should have good flow properties before reaching the blade, although a network structure is required in the final coating layer [1].

To define the rheological features of most printing inks, we use the terms viscoplastic, shear thinning (pseudoplastic), viscoelastic, and thixotropic. Viscoelasticity implies the existence of a yield stress, which is related to a technical characteristic called ‘shortness’: an ink is considered short or long depending on how long a filament can be pulled out on a spatula without breaking [2-6].

Thixotropy has been observed for many years, but the physical mechanisms governing it are still poorly identified. Nevertheless, an understanding of the mechanisms that cause this complex rheological behaviour at the mesoscopic scale is of vital importance when using such materials and in controlling the industrial processes in which they are involved. Indeed, the entities dispersed in the matrix media of such systems form aggregates under the effect of attraction and repulsion forces that may
give rise to continuous aggregated structures [7].

The rheological properties of pigment–polymer matrix systems provide important information on the processing behaviours of composite materials. To understand and control the rheological properties of UV flexo/gravure-type inks, we should be able to accurately analyze the specific rheological properties produced by the chemical and/or physical interactions of the ink components [8-10]. Despite the numerous rheological studies of UV-curable inks carried out over the years, it is still not possible to state precisely the analytical research ensured optimal mechanism of the rheology between variables.

In this study, the relations between flocculated structures and viscoelastic properties were investigated. To investigate the effects of the pre-polymer (oligomer) and colorant (carbon black) on the flocculated structure of UV-curable ink, we carried out rheological tests for UV-curable inks.

2. Experimental
2.1. Materials

The pigment powder used for the two types of UV-curable ink was carbon black. The physical properties of the carbon black are shown in Table 1. Three kinds of the oligomers were used, as shown in Table 2, and the apparent viscosities of the diluted solution (with acryloyl morpholine (ACMO)) of the oligomers are shown in Fig. 1. A multi-functional monomer [Trimethylolpropane triacrylate (TMPTA)] and di-functional monomer [Tripropyleneglycol diacrylate (TPGDA)] were used as curing components. ACMO was used as a diluting agent. Slosperse3900 (Avecia Co.) was used as a dispersing agent.

2.2. Preparation of UV-curable ink

UV-curable inks were prepared using a paint shaker. The base formulations tested are shown in Table 3. Tube-type glass bottles (diameter: 36.0 mm; volume: 110 mL) were used as mill vessels, and ceramic balls (density: 3.60 g/cm²; diameter: 2 mm) were used as shaking media. The materials were mixed in the bottles and milled with the media for 2 hours.

2.2.1. Experimental-I

The UV-curable inks were prepared using the three kinds of oligomers, as shown in Table 2. Pigment I was used only for this group of UV-curable inks.

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Table 1. Properties of pigments (Carbon black).

| Pigment  | Mean particle size (nm) | Specific surface area *1 | DBP absorption *2 | pH |
|----------|-------------------------|--------------------------|-------------------|----|
| I        | 24                      | 115                      | 66                | 3.0|
| II       | 40                      | 56                       | 73                | 3.0|

*1) $\text{N}_2$ absorption method, (m²/g) *2) Dibutyl phthalate (DBP) absorption method, (cm³/100g)

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Table 2. Properties of three kinds of oligomers.

| Oligomer | $M_w$ | Functional group *1 | Viscosity (Pa·s/25°C) | $T_g$ (°C) | Oligomer type          |
|----------|-------|---------------------|-----------------------|------------|------------------------|
| I        | 1000  | 2                   | 150                   | 45         | Polyester acrylate     |
| II       | 1700  | 2                   | 30                    | 65         | Bisphenol-A acrylate   |
| III      | 2500  | 2                   | 65                    | 20         | Urethane acrylate      |

*1) Number of acryloyl groups

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Fig. 1. Apparent viscosity of the diluted solution of the three kinds of oligomers as a function of temperature at the shear rate of 10 s⁻¹ (tested temperature: 40 °C, 50 °C, and 60 °C, ACMO: Oligomer (blending ratio 2:1)).
curable inks.

2.2.2. Experimental-II

The UV-curable inks were prepared using the two kinds of carbon black, as shown in Table 1. Oligomer I was used only for this test to make the ink formulations.

### Table 3. Formulations of ink suspensions.

|                        | wt [%] |
|------------------------|--------|
| Pigments (carbon black)| 10.0   |
| Oligomer               | 10.0   |
| Multi-functional monomer| 32.0  |
| Di-functional monomer  | 32.0   |
| Diluents               | 15.0   |
| Dispersants            | 1.0    |

2.3. Evaluation of ink sample

All measurements were carried out using a Rheometrics Fluid Spectrometer (RFS-II, Rheometrics Co. Ltd., U.S.A.) with Couette-type geometry. We performed all measurements after applying a steady shear stress at 10 s⁻¹ for 600 sec as a pre-shearing step. The steady shear measurements were performed at shear rates ranging from 0.1 to 100 s⁻¹. The frequency dependence of the storage modulus and/or dynamic viscosity was measured in the frequency amplitude region between 0.1 and 100 rad/s at the strain range of 1%. The strain dependence of the storage modulus (\(G'\)) and dynamic viscosity (\(\eta'\)) was examined in the strain region between 0.1% and 100% at an angular frequency of 1 rad/s.

3. Results and discussion

3.1. Influence of oligomers

3.1.1. Flow properties

Oligomer I had the highest viscosity value (150 Pa·s) when compared with oligomer II (30 Pa·s) and oligomer III (65 Pa·s), as shown in Table 1 (oligomer I >> oligomer III ≥ oligomer II). In the case of highly concentrated liquid media, such as oligomer 100 wt%, because the functional group (-OH) existing on the polyester-type acrylate oligomer (oligomer II) increased the shear stress of the polymeric liquid (solution diluted with ACMO) on the rheological measurement, the apparent viscosity of oligomer I showed a higher value when compared with that of oligomers II and III.

Meanwhile, the diluted solutions of the oligomer and ACMO (1:2) showed different behaviours in terms of their fluidic tendencies, as shown in Fig. 1. Oligomer II had the highest viscosity value when compared with oligomers I and III (oligomer II >> oligomer III ≥ oligomer II). In this case, because the polymeric rigidity due to the chemical structure (bisphenol-A) and glass transition temperature increased the shear stress on the polymeric liquid (solution diluted with ACMO) of oligomer II, the diluted solution of the epoxy-type oligomer (oligomer II) showed higher viscosity when compared with the other types of oligomers.

It is believed that because the liquid medium of the UV-curable ink had a decisive effect on the interfacial interaction of the continuous phase, the study of oligomer types and characteristics is very important to understand their rheological behaviour in terms of the interaction between liquid media and colorants (pigments) [10-13].

In this study, we naturally discussed oligomer characteristics, such as molecular weight, glass transition temperature, and functional group content. To investigate the rheological behaviours of UV-curable ink induced by the interfacial interaction between the pigment and the continuous phase, we prepared three types of UV-curable inks with three types of oligomers (oligomers I, II, III).

![Fig. 2. Shear stress and apparent viscosity as function of shear rate for the three kinds of UV-curable inks.](image-url)
phase of the oligomers was not dependent on the shear rate.

![Graph A](image1)

**Fig. 3. Frequency dependence of storage modulus and dynamic viscosity for three kinds of UV-curable inks at strain amplitude of 1.0%.

It seemed that the form of the gel structure obtained depended on the amount of carbon black added in the continuous phase of the liquid medium, because the three-dimensional structure affected the characteristics of carbon black, as shown in Table 1. In addition, it was believed that the structure was formed by a chain of carbon particles, although the formation of polymer bridges by adsorption on adjacent particles was an additional possibility [14].

3.1.2. Frequency dependence of storage modulus ($G'$), dynamic viscosity ($\eta'$)

It is believed that UV-curable inks with different internal structures show differences in their viscosity and shear stress. It was reported that the structural differences based on differences in the interfacial interaction between pigments and liquid media influence the ink properties, such as the frequency dependency of the elastic modulus ($G'$) and overshoot property [10,15]. Meanwhile, the elastic modulus ($G'$) of UV-curable inks greatly affects the ink transfer behaviour (amount of ink transferred) between the rubber roll and print medium [16-18].

The frequency dependence of the storage modulus ($G'$) for UV-curable ink at a strain amplitude of 1.0% in Fig. 3 showed that the dynamic results of UV-curable inks were not dependent on the viscosity of the diluted oligomers, as shown in Fig. 1.

It was considered that the results of the storage modulus ($G'$) and dynamic viscosity $\eta'$ were closely related to the molecular weights of the three kinds of oligomers. In addition, it seemed that glass transition temperature ($T_g$) and functional group content had important roles as additional main factors related to the rheological properties of UV-curable inks [8,13]. To clarify the influence of oligomer characteristics with various values of $T_g$, a newly designed rheological study of UV-curing inks needs to be conducted.

![Graph B](image2)

**Fig. 4. Apparent viscosity of diluted solution of oligomer I as function of shear rate (tested from 40ºC to 60ºC).

3.2. Influence of carbon black

3.2.1. Flow properties

It was found that the liquid medium had a decisive effect on the continuous phase of UV-curable ink. In addition, it was believed that the interfacial interactions between the pigment and continuous phase were one of the most important factors affecting the structural change of the ink [10,19].

To investigate the structural difference of the ink induced by the interfacial interaction between the pigment and the continuous phase, we individually prepared two kinds of UV-curable inks with two types of carbon black, as shown in Table 1.

It was found that the inks showed structural differences induced by the interfacial interaction between the pigment and the continuous phase,
although the viscosity of the diluted solution of oligomer I using ACMO tended to decrease as the temperature increased, as shown in Fig. 4.

3.2.2. Strain dependence of dynamic viscosity ($\eta'$)

It was considered that the strain dependence of the dynamic viscosity ($\eta'$) could be explained by the breakdown and/or build-up of the inter-particle network structure. Two kinds of interfacial interactions existed: 'pigment and pigment' and 'pigment and the continuous phase' [20].

The results of the shear stress and apparent viscosity as a function of shear rate for two kinds of UV-curable inks are shown in Fig. 5. The ink with pigment I exhibited shear thinning behaviour as the shear rate increased. It was found that in the measuring range of the shear rate between $10^{-1}$ s$^{-1}$ and 10 s$^{-1}$, the viscosity of the UV-curable ink with pigment I tended to increase as the temperature increased. It seemed that the interfacial interactions between the pigment and the continuous phase, consisting of a three-dimensional network structure of their components, increased continuously as the testing temperature increased.

In contrast, it was considered that UV-curable ink with pigment II had weak interfacial interactions between the pigment and the continuous phase, although the ink with pigment II exhibited weak shear thinning behaviour at shear rates ranging from $10^{-1}$ s$^{-1}$ to $10^{2}$ s$^{-1}$ (testing temperature: 50 °C and 60 °C).

The testing results of the strain dependence of the dynamic viscosity ($\eta'$) are shown in Figs. 6 and 7. It was found that in the strain region between $10^{-2}$% and 10%, the dynamic viscosity ($\eta'$) of the UV-curable ink with pigment I was gradually increased as the strain amplitude increased and the plot curve was shifted upward as the testing temperature was increased, as shown in Fig. 6.

It was considered that the density of the structural networks was increased as the strain amplitude was increased in the strain region between $10^{-2}$% and 10%, and the structural networks gradually broke down in the strain region ranging from 10% to $10^2$%. On the contrary, it seemed that because the result of the dynamic viscosity ($\eta'$) for UV-curable ink with pigment II had a weak network structure with their component, the interfacial network structure was easily broken down in the strain region ranging from 10% and $10^2$%, as shown in Fig. 7. In addition, the dynamic viscosity ($\eta'$) of the ink with pigment II did not shift upward as the testing temperature was increased in the strain region ranging from 10% to $10^2$%.
4. Conclusions

It was found that the frequency dependence of the storage modulus ($G'$) and dynamic viscosity ($\eta'$) of UV-curable ink was not dependent on the viscosity of the oligomer. It was considered that the results of the elastic modulus ($G'$) and dynamic viscosity ($\eta'$) were closely related to the characteristics of the oligomer (especially molecular weight) and the liquid medium of the UV-curable ink had a decisive effect on the continuous phase of the ink. It was believed that the interfacial interactions between the pigment and continuous phase were one of the most important factors affecting the structural change of the ink.

It was considered that the strain dependence of the dynamic viscosity ($\eta'$) could be explained by the break down and/or build-up of the inter-particle network structure. Two kinds of interfacial interactions existed: 'the pigment and pigment' and 'pigment and the continuous phase'. The dynamic viscosity ($\eta'$) of the UV-curable ink with pigment I was gradually increased as the strain amplitude was increased, as shown in Fig. 6.

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