論 文

Flocculated Structure and Flow Properties of Suspensions of Brilliant Carmine 6B in Polybutadiene.

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The flocculated structure and flow properties of suspensions of brilliant carmine 6B (C6B) in polybutadiene were investigated. In this study, we have used simple suspensions of C6B in polybutadiene having different viscosity. Stress overshoot phenomenon after various rest periods and double-step shearing test were examined for the suspensions. In the double-step shearing test, a transient stress overshoot was observed in the suspension of C6B in lower viscosity disperse medium, when the shearing was switched suddenly from higher to lower. This peculiar phenomenon was discussed in comparison with the other kinds of suspensions and was explained from the view point of the alteration of dispersing state and formation of flocculated network structure of C6B.

Key words: Brilliant carmine 6B / Polybutadiene / Flocculated structure / Stress overshoot / Transient network structure

1. INTRODUCTION

Brilliant carmine 6B (C6B) is a common magenta pigment in printing ink industry. The particle of C6B is very fine and has scaly shape. The particles of C6B form denser network structure and the flocculated structure shows remarkable

strain sensitive viscoelastic behavior. It has been reported in our previous paper¹⁾ that the anisotropic shape C6B pigments in low viscosity disperse medium tend to stack together which results in rupturing the network structure and this phenomenon is accelerated with applying moderate amplitude of oscillatory shear.

Generally, commercial printing inks are composed with pigments, resin varnishes, and several kinds of additives. These materials influence the rheological properties of printing inks and lead to complicate the rheological analysis. It is reasonable to use a simple suspension consisting of only pigment and medium for the good understanding of rheological properties of a printing ink. Some rheological studies have been performed with simple suspension and have discussed the formation and breaking down of network structure formed by dispersed particles²⁾⁻⁵⁾. In this study, we have used the simple suspensions of C6B in polybutadiene having different viscosity.

Stress overshoot phenomenon after various rest periods were examined and the variation of network structure was investigated. Double-step shearing test⁶⁾ was performed and the structural changes when the shearing was switched suddenly from higher to lower were discussed. The goal of this study is to clarify the mechanism of formation and breaking down of network structure formed by C6B pigments.

2. EXPERIMENTAL

2-1 Experimental materials

C6B (Sumika Color Co., Ltd.) used in this study is as follows. The particle size distribution determined by X-ray diffraction analysis has two main peaks in 19 and 35 nm. The surface area is 120m²/g. Generally, pH value of pigment is determined as follows: 5g of pigment is boiled with 100g of distilled water for 15 min, and pH value of the filtrate is measured using a pH meter. The pH value for this C6B pigment was 7.0.

Disperse mediums used in this study are fluid polybutadiene, B-1000, B-2000 and B-3000 (Nippon Petrochemical Co., Ltd.), which are of different viscosity. The number average molecular weight of each polybutadiene are 930, 2000 and 2930, and the values of viscosity of them are 1.02, 9.90, and 25.2 Pa.s at 30°C, respectively.

The suspensions were prepared by flushing method as follows: we have dispersed 20wt% of C6B presscake to each polybutadiene in a flusher. After taking out from the flusher, each suspension was ground by three-roll-mill to make it homogeneous.

The suspensions were referred as Ink 1, Ink 2 and Ink 3, of which disperse medium were B-1000, B-2000 and B-3000, respectively. The suspensions of lower pigment concentration were prepared by letting down 20wt% suspensions with each medium.

Details of the experimental materials and the suspension preparation were described in the previous paper⁷⁾.

Fig.1 Cryo-SEM picture of 20wt% suspension of C6B in polybutadiene, B-1000 (Ink 1).

In Fig.1, Cryo-SEM picture of 20wt% suspension of C6B in B-1000 (Ink 1) is shown. We can find the scaly shaped C6B particles are dispersed and connecting and/or stacking together in the disperse medium.

We also used, as references, some suspensions. Carbon black (Furnace black #50, mean particle size is 28 nm, pH is 6.0, Mitsubishi Chemical Corp.) was dispersed in linseed oil varnish #4. Carbon black (Furnace black MA-7, mean particle size is 24 nm, pH is 3.0, Mitsubishi Chemical Corp.) was dispersed in polybutadiene, B-1000, which is the same medium as Ink 1. Barium ferrite (mean particle size is 48 nm, Toshiba) was dispersed in silicon oil (TSF-451-1000, Toshiba silicon).

2-2 Measurements

In this study, all measurements were carried out using a rheometer (Rheometrics RFS-II) with a cone and plate geometry. The angle between cone and plate was 0.04 radians and the diameter of cone was 25 mm. All measurements were performed at 30°C. The steady shear at 10 sec⁻¹ for 300 sec was applied prior to measurements.

Dependence of apparent viscosity on shear rate

were examined at the rate of shear ranging from 0.03 to 50 sec^{-1} .

The stress overshoot was examined under the steady shear at 5 sec^{-1} after various rest periods, t_s ranging from 10 to 3600 sec which followed the pre-shearing.

Double-step shearing test were performed as shown in Fig. 2. After a rest period for 600 sec which followed the pre-shearing, the steady shear ranging from 0.1 to 10 sec^{-1} for 600 sec was applied as a first step and then suddenly switched to another steady shear ranging at 0.1 or 0.03 sec^{-1} for 600 sec as a second step, and the shear stress was observed as a function of elapsed time.

Fig. 2 Schematic diagrams representing the profiles of shear rate and stress of "double-step shearing test".

3. RESULTS

3.1 Steady shear flow

Fig. 3 shows the shear rate dependence of apparent viscosity for suspensions of C6B in polybutadiene, B-1000 at various concentrations. Dependence of viscosity on shear rate for the medium, B-1000 shows a characteristic of Newtonian fluid. With increasing the concentration of pigments, the viscosity of the suspension increases and shear-thinning behavior becomes pronounce. The same tendency was observed in the suspensions of C6B in B-2000 or B-3000. From these results, we can deduce that the concentrated suspensions form the denser flocculated network structures, and these network structures are broken down gradually with shearing.

Fig. 4 shows the logarithmic plots of yield value against pigment concentration for suspensions of C6B in the mediums of different molecular weight. The yield values were determined from Casson's plots for each suspension. In Fig. 4, linear relationship is observed and the slopes in suspensions of B-1000, B-2000 and B-3000 were 4.03, 3.60 and 3.47, respectively. It means that the yield value for the suspension in lower viscosity medium shows remarkable concentration dependence.

Fig. 3 Shear rate dependence of apparent viscosity for suspensions of C6B in polybutadiene, B-1000 at various concentrations.

Concentration (wt%):
20% (●); 15% (○); 10% (▲); 5% (△); 0% (+).

Fig. 4 Logarithmic plots of yield value, σ_y , against pigment concentration, C, for suspensions of C6B in polybutadiene of various viscosity.

Disperse medium: B-1000 (○); B-2000 (×); B-3000 (△).

3.2 Stress overshoot

In concentrated suspensions, dispersed particles form a flocculated network structure and the formation and breaking down of the structure in shear field characterize the flow properties of the suspension. The structural networks destroyed by

shearing are formed again depending on a rest period after cessation of shearing. The structural recovery can be examined by the experiment of stress overshoot after the various rest periods. The stress overshoot curves at various rest periods (t_s) from 10 to 3600 sec for the sample suspensions are shown in Figs. 5. Figs. 5(a), 5(b) and 5(c) are the stress growth curves for Ink 1, Ink 2 and Ink 3, respectively. We can observe stress overshoot phenomenon in stress growth curve for each suspension. After sudden initiation of shear flow following various rest periods, the stress increases abruptly, and attains a peak value within a short time. After attaining the peak, the stress decreases and takes an equilibrium value. The longer the suspensions are rested, the higher the peak values are observed. We can find that Ink 1 takes the stress peaks in shorter time than Ink 3, the time when the stress peak appears is 0.08 sec in Ink 1 and that is 0.15 sec in Ink 3. From these results, we can deduce that the network structure in B-1000 is broken down with applying 40% of strain and that in B-3000 is broken down with 75% of strain.

In Fig. 5(d), the stress growth curves for 20wt% suspension of carbon black in linseed oil varnish #4 is shown. We can find that the peak value is observed at a longer elapsed time comparing with the suspensions of C6B. This means that larger strain is required to break down the network structure in the carbon black suspension, in other words, the network structure formed by carbon black is more durable than that formed by C6B.

3・3 Double-step shearing test

The double-step shearing test were performed after a rest period for 600 sec which followed the pre-shearing at 10 sec^{-1} for 300 sec. The higher steady shears ranging from 0.1 to 10 sec^{-1} were applied as a first step shearing and then suddenly switched to the lower steady shear as a second step shearing. (Fig. 2)

Fig. 6 shows the time dependence of stress at 0.1 sec^{-1} in the second shearing after switching from several shear rates of first shearing for Ink 1.

In Fig. 6, we can observe the stress overshoot phenomenon right after the switching of the shearing

Fig. 5 Stress overshoot curves at various rest periods (t_s) from 10 to 3600sec for the several suspensions. (a) Ink 1; (b) Ink 2; (c) Ink 3; (d) 20wt% suspension of carbon black in linseed oil varnish #4.

rate from higher to lower. The values of stress increase and attain peaks and then take equilibrium values like the stress overshoot experiments. In the stress overshoot experiments (Fig.5), we observed that the higher stress growth followed the longer rest period. However, in the case of Fig.6, even though the suspensions are not rested between the first shearing and the second shearing, we can observe

Fig. 6 Time dependence of stress at 0.1 sec^{-1} in the second shearing after switching from several shear rates of the first shearing for Ink 1.

First shearing (sec^{-1}): 10 (●); 5 (△); 1 (□); 0.5 (▲); 0.2 (◇); 0.1 (+).

the stress growth phenomenon depending on shear rates of first shearing. The difference between the peak and the equilibrium value ($\Delta \sigma$) increases with increasing the first shearing rate.

4. DISCUSSION

4.1 Rest time dependence of the stress growth

In Fig.5, we examined the stress growth phenomenon for the suspensions of 20wt% of C6B in various polybutadienes having different viscosity. In the initial time region, the stress overshoot were observed in the suspensions. Figs.7(a), 7(b) and 7(c) shows the logarithmic plots of stress growth, $\Delta \sigma$, against t_s for the suspensions of C6B in B-1000, 2000 and 3000 at various pigment concentrations from 5 to 20wt%, respectively. A.de Waele reported the linear relationship between $\Delta \sigma$ and t_s for several suspensions and discussed the rate of structural recovery from the slope of the linear portion⁸⁾. We can confirm the linear relationship between $\Delta \sigma$ and t_s for the suspensions of C6B in B-1000, and the lines for different concentrations are parallel each other. However, the plots for the suspensions of C6B in B-2000 or B-3000 do not

Fig.7 Logarithmic plots of $\Delta \sigma$ against t_s for the suspensions of C6B at various pigment concentrations from 5 to 20wt%.

Disperse medium:

(a) :B-1000, (b) :B-2000, (c) :B-3000.

show the linear relationship. The stress growths, $\Delta \sigma$, increase rapidly with rest periods in the initial time region, and then they have leveled off after longer rest periods. During the rest period, the particles of C6B start to aggregate again, and then they form the flocs. The diameter of these flocs becomes larger with time and the flocs cannot move easily, especially in the higher viscosity medium. Therefore the formation of network structure is gradually depressed with rest time in the higher viscosity medium. These results support our previous results⁷⁾.

4·2 Effective factors for the stress overshoot phenomenon on the double-step shearing test

4·2·1 Pigment concentration of suspension

In Fig. 6, we observed the stress overshoot phenomenon, when the steady shearing was switched suddenly from the first shearing to the second shearing. Figs. 8 and 9 show the same experimental results for 15wt% and 10wt% suspension of C6B in B-1000, respectively. We can find the stress overshoot phenomenon in 15wt% suspension, but not almost in 10wt% suspension. We can deduce that 15wt% suspension forms the tentative three dimensional network structure while even in a very short transient period, but 10wt% suspension does not. It is too thin to form the network structure in a very short transient period.

4·2·2 Comparison with the other kinds of suspensions

Figs. 10(a), 10(b) and 11 show the same experimental results for various kinds of suspensions after cessation of several kinds of higher rates of shear. Figs. 10(a) and 10(b) are for 20wt% suspensions of carbon black (Furnace black #50) in linseed oil varnish #4 and carbon black (Furnace black MA-7) in B-1000, respectively, at 0.1 sec^{-1} in the second shearing.

Fig. 11 is for 20wt% suspension of barium ferrite in silicon oil at 0.03 sec^{-1} of the second step shearing.

The particle of carbon black has a spherical shape and connects together and forms a "structure". The mean particle size of Furnace black #50 is 28 nm and that of Furnace black MA-7 is 24 nm. The

Fig. 8 Time dependence of stress at 0.1 sec^{-1} in the second shearing after switching from several shear rates of the first shearing for 15wt% suspension of C6B in B-1000.

First shearing (sec^{-1}):

10 (●); 5 (△); 1 (□); 0.3 (▲); 0.2 (◇); 0.1 (+).

Fig. 9 Time dependence of stress at 0.1 sec^{-1} in the second shearing after switching from several shear rates of the first shearing for 10wt% suspension of C6B in B-1000.

First shearing (sec^{-1}):

10 (●); 5 (△); 1 (□); 0.3 (■); 0.2 (◇); 0.1 (+).

particle of barium ferrite has a hexagonal plate shape and its mean particle size is 48 nm. We do not observe any stress overshoot phenomena in Figs. 10(a), 10(b) or 11. The lower level of stress value recovers to the equilibrium value in the shear field. This tendency becomes pronounced with increasing the shear rate of the first shearing.

It seems that the stress overshoot phenomenon on the double step shearing test is a peculiar phenomenon for C6B suspension in polybutadiene, especially in lower viscosity medium.

On the other hand, similar phenomenon of a transient stress overshoot has been reported for 33wt% suspension of acicular magnetic ($\gamma\text{-Fe}_2\text{O}_3$) powder in mineral oil⁹⁾. It has been presumed that

Fig. 10(a) Time dependence of stress at 0.1 sec^{-1} in the second shearing after switching from several shear rates of the first shearing for 20wt% suspension of carbon black, #50, in linseed oil varnish #4.

First shearing (sec^{-1}): 5 (Δ); 1 ($\square$); 0.5 ($\blacksquare$); 0.2 ($\diamond$); 0.1 (+).

Fig. 10(b) Time dependence of stress at 0.1 sec^{-1} in the second shearing after switching from several shear rates of the first shearing for 20wt% suspension of carbon black, MA-7, in polybutadiene, B-1000.

First shearing (sec^{-1}): 10 ($\diamond$); 5 ($\square$); 1 ($\circ$); 0.5 (∇); 0.2 ($\times$); 0.1 ($\triangle$).

Fig. 11 Time dependence of stress at 0.03 sec^{-1} in the second shearing after switching from several shear rates of the first shearing for 20wt% suspension of barium ferrite in silicon oil.

First shearing (sec^{-1}): 2 ($\diamond$); 1 ($\square$); 0.5 ($\blacktriangle$); 0.1 (+); 0.05 ($\blacklozenge$); 0.03 ($\times$).

the overshoot phenomenon depends on the volumetric change of floc phase in suspensions of acicular ferric-oxide particles under shear. Therefore the transient stress overshoot phenomenon seems to be different from the case of C6B suspension.

4.2.3 Effect of changing the steady shear rate of the second step shearing

Fig. 12 shows the time dependence of stress for Ink 1 at several shear rates of the second shearing from 0.03 to 5 sec^{-1} after switching from the first shearing at 10 sec^{-1} . We can find that the stress overshoot phenomenon becomes pronounced with decreasing the rate of the second shearing.

Fig. 12 Time dependence of stress for Ink 1 at several shear rates of the second shearing from 0.03 to 5 sec^{-1} after switching from the first shearing at 10 sec^{-1} .

Second shearing (sec^{-1}): 5 (Δ); 2 ($\diamond$); 1 ($\square$); 0.5 ($\blacktriangle$); 0.3 ($\blacksquare$); 0.1 (+); 0.05 ($\blacklozenge$); 0.03 ($\times$).

Fig. 13 Time dependence of stress at 0.03 sec^{-1} in the second shearing after switching from several shear rates of the first shearing for Ink 1.

First shearing (sec^{-1}): 10 ($\bullet$); 5 (Δ); 3 ($\circ$); 2 ($\diamond$); 1 ($\square$); 0.5 ($\blacktriangle$); 0.3 ($\blacksquare$); 0.1 (+); 0.05

Fig. 13 shows the time dependence of stress at 0.03 sec^{-1} in the second shearing after switching from several shear rates of the first shearing for Ink 1. The same experiments as shown in Fig. 6 were performed at lower shear rate of the second shearing, 0.03 sec^{-1} . We observe that the stress overshoot phenomenon is more remarkable in Fig. 13 than that in Fig. 6. We also observe that the value of $\Delta \sigma$ increases and the time when the peak appears shifts to longer time region with increasing the rate of the first shearing.

4・2・4 Viscosity of disperse medium

Figs. 14 and 15 show the time dependence of stress for Ink 2 and Ink 3, respectively, which are the same experimental results as Fig. 6. The measurements were performed at 0.1 sec^{-1} in the second shearing after cessation of various shear

Fig. 14 Time dependence of stress at 0.1 sec^{-1} in the second shearing after switching from several shear rates of the first shearing for Ink 2.
First shearing (sec^{-1}):
10 (●); 5 (△); 1 (□); 0.5 (▲); 0.2 (◇); 0.1 (+).

Fig. 15 Time dependence of stress at 0.1 sec^{-1} in the second shearing after switching from several shear rates of the first shearing for Ink 3.
First shearing (sec^{-1}):
10 (●); 5 (△); 1 (□); 0.5 (▲); 0.2 (◇); 0.1 (+).

rates of the first shearing. We can not find any stress overshoot phenomena observed in Fig. 6 in both Figs. 13 and 14. However, we can find that the equilibrium values of the second step stress increase with increasing the rate of first shearing. It seems that the well broken down suspension make a bulky structure and shows higher equilibrium values.

Figs. 16 and 17 show the time dependence of stress for Ink 2 and Ink 3, respectively, at various temperatures ranging from 30°C to 70°C , as indicated in each figure. The measurements were performed at 0.1 sec^{-1} in the second shearing after cessation of 10 sec^{-1} of the first shearing. In these cases, we observe the stress overshoot phenomenon at higher temperature. In Fig. 16 (for Ink 2), the stress overshoot phenomenon can be observed from 40°C , and in Fig. 17 (for Ink 3), it can be observed from 50°C . These results can be explained from the view point of the viscosity of disperse medium.

Based on Einstein equation of Brownian motion, the moving distance, $\bar{x}$, per time, t , of the pigment particle whose diameter is r can describe as equation (1);

$$\bar{x} = \sqrt{RTt / 3\pi\eta rN_A} \dots\dots (1)$$

where R is gas constant, T is absolute temperature, η is viscosity of disperse medium and N_A is Avogadro's number. From the equation (1), we can understand that the pigment particle dispersed in B-1000 move about 5 times faster than that dispersed in B-3000.

Fig. 16 Time dependence of stress for Ink 2 at 0.1 sec^{-1} in the second shearing after switching from 10 sec^{-1} of the first shearing at various temperature.
Temperature ($^\circ\text{C}$):
30 (●); 40 (△); 50 (□); 60 (○); 70 (+).

Fig. 17 Time dependence of stress for Ink 3 at 0.1 sec^{-1} in the second shearing after switching from 10 sec^{-1} of the first shearing at various temperature.

Temperature ($^{\circ}\text{C}$):

30 (●); 40 (△); 50 (□); 60 (○); 70 (+).

Fig. 18 shows the relationship between the plots of moving distance ($\bar{x}$) and difference of stress ($\Delta\sigma$) against viscosity of disperse medium. The viscosity dependence curve of moving distance seems to be close to that of $\Delta\sigma$. In the suspension of C6B in polybutadiene, the rate of formation of flocculated network structure depends on Brownian motion of dispersed particles.

Fig. 18 Relationship of plots of moving distance (○) and difference of stress (△) against viscosity of medium.

Fig. 19 shows the schematic diagram of interparticle structures of dispersed pigments under different situations. C6B pigments are well dispersed under higher shear flow like ordinary suspensions. In the suspension composed with larger particles, after switching a higher shearing to a lower shearing, the flocculated structures recover gradually to a dynamic equilibrium state with time. However, in the suspension of C6B in

polybutadiene, especially in lower disperse medium, the pigment particles form a expanded network structure at the transient situation, because the C6B particles move quickly in the medium. The peculiar stress overshoot phenomenon on the C6B suspension in the double-step shearing test can be explained by the competition between formation and breaking down of the network structure of flocculated particles at the transient situation.

Fig. 19 Schematic diagram of interparticle structures of dispersed C6B pigments under different situations.

5. CONCLUSIONS

We have investigated the flocculated structure and flow properties of suspensions of C6B in polybutadiene having different viscosity. The following conclusions are obtained;

1. Fine particles of C6B pigment form a denser network structure in disperse medium and the viscosity of disperse medium affect formation and breaking down of the network structure.
2. The suspension in lower viscosity medium recovers the network structure in a shorter period after cessation of shearing than that in higher viscosity medium.
3. The colloidal fine particles of C6B move quickly especially in lower viscosity medium in comparison with the other ordinary

pigment particles, and show transient stress overshoot phenomenon in the double-step shearing test when the shearing was switched from higher to lower.

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