NON LINEAR RHEOLOGICAL PROPERTIES OF CARMINE 6B / POLYBUTADIENE SUSPENSION

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Key Words: Rheology, Viscoelasticity, Network Structure, Dispersibility

ABSTRACT

Non-linear viscoelastic properties of suspensions of Carmine 6B in polybutadiene were investigate. The pigment particles of brilliant carmine 6B have a scaly shape and form denser network structure in disperse medium and show complicated rheological properties depending on flow history. In this study suspensions of carmine 6B in polybutadiene having different molecular weight were used as sample suspensions. Dynamic viscoelastic properties under various flow histories were mainly investigated and we discussed about the relations between the rheological properties and network structure formed by carmine 6B pigments. The followings are concluded.

The anisotropic shape carmine 6B pigments in lower viscosity disperse medium tends to stack together which results in rupturing the network structure and this phenomenon is accelerated with applying moderate amplitude of oscillatory shear. The peculiar non-linear viscoelastic behavior in suspension of carmine 6B can be explained by the competition between formation and breaking down of the network structure of flocculated particles.

INTRODUCTION

Rheological properties of printing inks affect the ink transfer on a printing press and the printability which governs the print quality. In order to control the printability of inks on printing processes, we have to know the specific rheological properties of the inks. On a printing press, printing inks are supplied from ink duct. They transfer to and pass through the rollers, and then reach to a substrate. During these processes, printing inks have been subjected to by various kinds of deformation and wide range of

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rate of shear, repeatedly. These behavior can be investigated scientifically from a view point of non-linear viscoelasticity.

Normally, commercial printing inks are composed with pigments, resin varnishes, and several kinds of additives. These materials influence the rheological properties of printing inks, and it makes rheological analysis complicated.

In order to investigate the basic relationship between printability and rheological properties of printing inks, simple suspensions are often used for sample printing inks. .

On the other hand brilliant carmine 6B (C6B) is common magenta pigment for the four color process printing inks. However, the magenta ink of C6B is not always working well and some problems are pointed out on their flow properties and dispersibility. It is well known that the viscoelastic properties of the suspension of C6B show remarkable concentration dependence and they behave as typical non-linear rheological materials.

Then, in this study, we have used as sample inks the simple suspensions of brilliant carmine 6B in polybutadiene having different viscosity. Dynamic viscoelastic properties under various flow histories were mainly investigated and the relations between the rheological properties and flocculated structure formed by dispersed particles were discussed. The goal in this study is to clarify the mechanism of remarkable non-linear rheological properties of the magenta inks of C6B.


EXPERIMENTAL

Sample

In this study, we have used following materials.
As a pigment, we have used brilliant carmine 6B(C.l.Pigment No.Red 57:1), which is a magenta pigment of the mono-azo-calcium lake. The particle size distribution determined by X-ray diffraction analysis has two main peaks at 19 and 35 nm . The surface area is 120 m^2/g and pH is 7.0. The pigment particles of brilliant carmine 6B have scaly shape. The characteristics of the pigment are shown in Table 1.

Table 1 Characteristics of Carmin 6B

• Carmine 6B [C. I. Pigment No. Red 57:1]
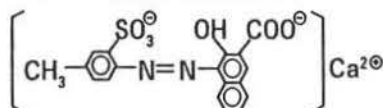
Product Name	Particle Size (X-ray diffraction)	Surface Area (BET)	pH
Carmine 6BC−487A •	19~35 (nm)	120 (m^2/g)	7. 0

• Sumika Color Co. , Ltd.

Disperse mediums used in this study are fluid polybutadienes, B-1000, B-2000, and B-3000 (Nippon Petrochemicals Co.,Ltd.) which have different viscosity. Each polybutadiene has alkyl group at the terminal of the chain, and constituent of a butadiene unit is approximately 60-70% of vinyl bond, 15% of cis bond and 15% of trans bond. The number average molecular weight of polybutadienes are 930, 2000 and 2930, respectively.(Table 2)

Table 2　Characteristics of Disperse medium.

· Polybutadiene

$$R-CH_2-(CH_2-CH=CH-CH_2)_n-(CH_2-CH)_m-H$$
$$|$$
$$CH$$
$$\|$$
$$CH_2$$
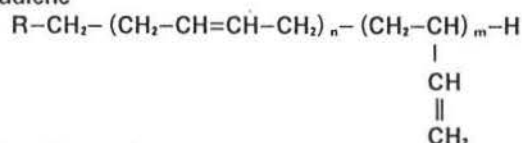
Polybutadiene	$\overline{M}n$	Viscosity (Pa · s)	Specific gravity	Constituent (%)		
				Vinyl	Trans	Cis
B－1000　·	930	1. 32	0. 89	58	16	17
B－2000　·	2000	13. 4	0. 89	65	14	16
B－3000　·	2930	39. 4	0. 89	67	13	15

· Nippon Petrochemicals Co. ,Ltd.

In our study, three kinds of suspensions were prepared by flushing method have dispersed 20 wt% of brilliant carmine 6B presscake to plybutadienes which have different molecular weight in a flusher. The disperse medium for Ink 1 is B-1000 for Ink 2 is B-2000 and for Ink 3 is B-3000, respectively. The flushed out water was poured off and the residual water in the suspensions was removed by heating under vacuum. After taking out from the flusher, each suspension was grounded by a three roll mill to make it homogeneous.

Measurements

In this study, all measurements were carried out using a Rheometrics Fluid spectrometer (RFS- II) with a cone and plate geometry. A angle between cone and plate was 0.04 radian and a diameter of cone was 25 mm. We performed all measurements after applying the steady shear at 10 s^{-1} for 300 seconds as a pre-shearing.
The steady shear measurements were performed at the rate of shear ranging from 0.1 s^{-1} to 50 s^{-1}. The strain dependence of storage modulus , G' was measured in strain region between 0.2 and 200% at an angular frequency of 1 rad/sec. These measurement were done after holding samples for 1800 seconds after cessation of pre-shearing.
The changes in storage modulus, G' as a function of elapsed time after cessation of 10 s^{-1} of the steady shear were observed at the strain amplitude of 0.2 and 1.0% for 7200 sec.

RESULTS AND DISCUSSION

Flow Properties

Figure 1 shows the flow curves of each polybutadiene. Each sample shows the Characteristics of Newtonian flow and any viscoelastic behavior is not observed. The viscosity for each polybutadiene was calculated from each slope, the values of viscosity of B-1000, B-2000, and B-3000 are 1.32 Pa.s, 13.4 Pa.s, and 39.4, respectively.

Figure 2 shows the plots of shear stress against rate of shear for each suspension. They show a typical pseudo-plastic flow behavior. The plastic viscosity(PV) and yield stress(YV) shown in Figure 3 were calculated by Casson's equation in the shear rate region between 1 and 10 s⁻¹. Comparing with another suspensions of pigments, the values of yield stress are extremely large.
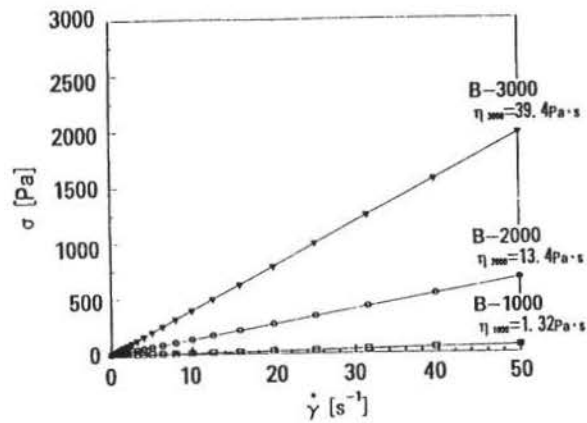

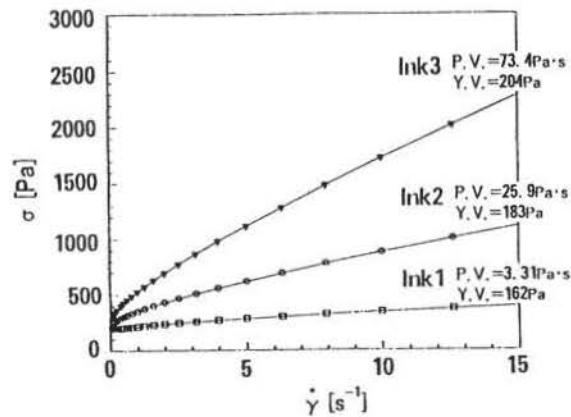Fig. 1 Plots of shear stress against rate of shear for polybutadienes.

Fig.2 Plots of shear stress against rate of shear for sample inks.

Dependence of Viscoelastic Properties on Strain Amplitude

Figure 3 shows the logarithmic plots of storage modulus against strain amplitude for each suspension measured in the strain region between 0.2 and 200% at an angular frequency of 1 rad/sec. The values of G' are far larger than that estimated from their contents of pigment. Even in rather low strain amplitude, the values of G' decrease with increasing strain amplitude and this tendency is remarkable in Ink 1. In the lower strain region, the values of G' for Ink 1 are larger than those of the other inks, in spite of the
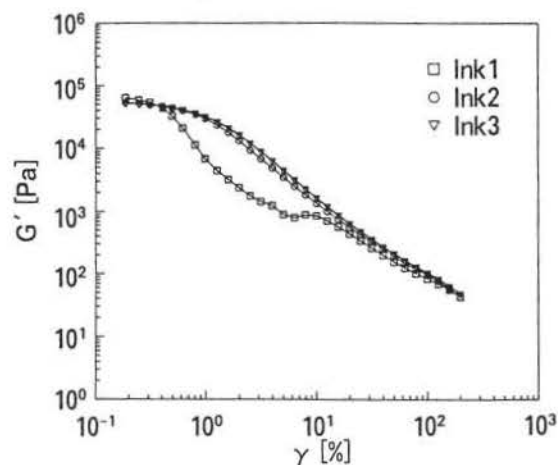

Fig 3. Logarithmic plots of G' measured at 1 rad/sec against strain amplitude for various inks.

viscosity of polybutadiene 1000 is the smallest of all. In the strain region between 0.5 and 10 %, G' for Ink 1 shows peculiar strain dependence; the value of G' for Ink 1 starts to decrease at smaller strain amplitude and shows the smaller value, and a quasi-equilibrium portion is observed in the strain region between 5 and 10 %. However at the strain around 10% they get to the same level of value as that for the other inks and then decrease again with increasing strain amplitude . The dependence of storage modulus on strain amplitude can be explained by the process of structural change such as breaking down of the structural networks formed by dispersed particles. From the difference in the strain dependence of G', we can deduce the process of formation and breaking down of the network structure of dispersed particles in Ink 1 differs from that in the other inks, namely the structural networks in Ink 1 are the most strain sensitive and reduce the structural density with increasing strain amplitude. The disruption of the structural network of Ink 1 seems to be caused with the following two steps. The first step is the disruption of weak portion of the network strands and the second step is the disruption of relatively strong space-filling networks. The former, partially disruption is induced by moderate amplitude of oscillation and the latter, wide range of disruption is induced by large amplitude of oscillation and/or disruptive shear flow.
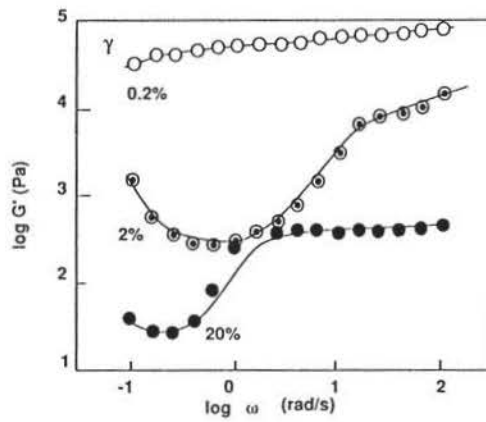
Fig.4 Frequency dependence of G' at various strain amplitudes as indicated for Ink 1.
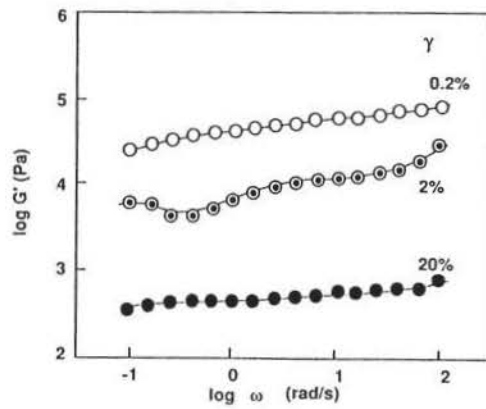
Fig.5 Frequency dependence of G' at various strain amplitudes as indicated for Ink 2.
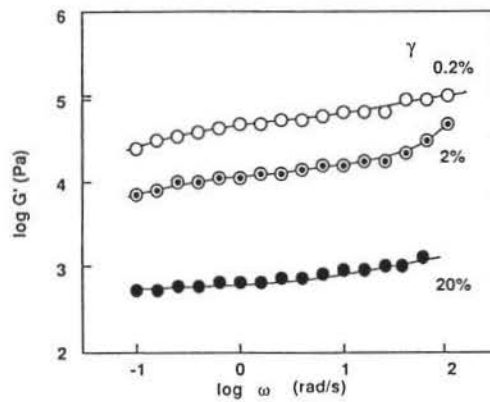
Fig.6 Frequency dependence of G' at various strain amplitudes as indicated for Ink 3.

Frequency Dependence of Storage Modulus at Various Strain Amplitudes

Figures 4, 5, and 6 show the logarithmic plots of G' against angular frequency at various strain amplitudes for Ink 1, Ink 2, and Ink 3, respectively. At small strain amplitude, the values of G' for Ink 1 seem to be slightly higher than the other inks and almost constant irrespective of frequency. Same frequency dependences of G' are observed for the other inks. In the concentrated suspension having three dimensional structural networks formed by dispersed particles the equilibrium value of G' which independent of frequency is observed in very low frequency region and this phenomenon can be attributed to the relaxation processes in some internal structure formed by dispersed particles.

With increasing strain amplitude the values of G' for Ink 2 and Ink 3 decrease holding the same frequency dependence, however, for Ink 1 G' shows a peculiar frequency dependence; in the very low frequency region the value of G' decreases with increasing frequency and after reaching the minimum the value increases again. This phenomenon suggests that relaxation mechanisms having longer relaxation time are destroyed with applying large amplitude of oscillatory shear and this tendency is pronounced in the disperse system of low viscosity disperse medium. For Ink 2 and Ink 3, the frequency dependence of G' shows characteristics for suspension even though at large amplitude of oscillatory strain. Therefore, by the application of large shear strain, the density of structural networks may be reduced, while the structural networks themselves have not been completely destroyed.

Structural Change After Cessation of Steady Shear Flow

Figure 7 shows the logarithmic plots of G' measured at a frequency of 1 rad/sec at the strain amplitude of 0.2% against the elapsed time after the
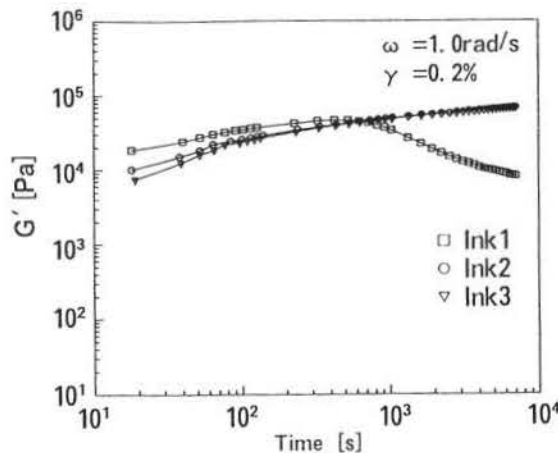

Fig. 7 Logarithmic plots of G' measured at 0.2 % of strain amplitude against the elapsed time after cessation of 10 s^{-1} of steady shear flow for various inks.

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cessation of 10 s^{-1} of steady shear flow for 300 sec. The values of G' for each suspension increase with the elapsed time. The values of G' for Ink 1 are larger than those for Ink 2 and Ink 3 in the initial time region. We can deduce the structural networks of dispersed particles which have been broken down by the applying steady shear flow are gradually recovering. However, the values of G' for Ink 1 becomes to decrease at around 700 sec, on the contrary the values of G' for the other inks are still increasing within the observed period.

Figure 8 shows the same results measured at the strain amplitude of 1% at the frequency of 1 rad/sec.

In this case, we can also observe the value of G' for Ink 1 take larger values than the others in the initial region. Ink 1 attains the maximum at around 40 sec and then take an equilibrium value in a longer elapsed time region. This equilibrium value seems to relate with the quasi-equilibrium portion which is observed in Figure 3. Ink 2 also attain the maximum at around 200 sec. For Ink 3, the maximum is not clear within the observed period.
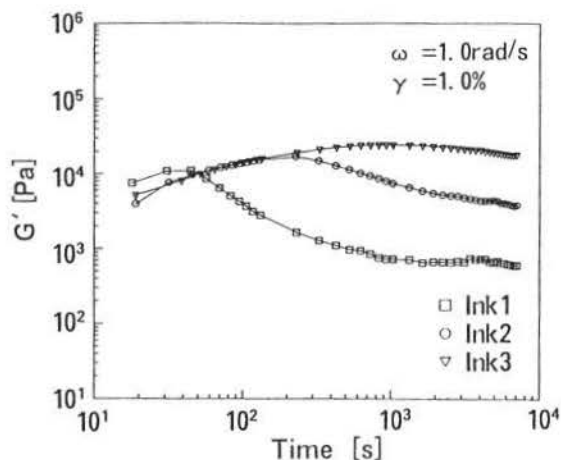

Fig. 8 Logarithmic plots of G' measured at 1 % of strain amplitude against the elapsed time after cessation of 10 s^{-1} of steady shear flow for various inks.

These phenomena can be explained by the competition between formation of three dimensional network structure and alteration of the networks under oscillatory shear. In the steady shear flow the network structures are ruptured depending on the rate of shear and become to reconstruct the structure after cessation of the shear flow. The process of reformation of the network structure depends on particle size, viscosity of disperse medium, the shear rate preceding cessation of flow, and measuring condition. The smaller particles in lower viscosity medium are apt to form denser network structure within comparatively shorter time. When the shear rate preceding cessation of flow is higher, the balky and widely expanded network structures are expected. The used pigment of carmine 6B have a scaly shape and tend to stack together. The structures formed by the anisotropic shape pigments are extremely affected by the mechanically

applied shear. If the dispersed particles are easy to move, an appropriate oscillatory shear seems to accelerate the stacking structure. The whole network structure may be ruptured with growing the partially stacked network elements.

Figure 9 shows the effect of standing time for formation of the stacking structure. After applying 10 sec^{-1} of steady shearing, the sample ink was left for stand for predetermined periods ranging from 0 to 1000 sec. The dynamic measurements were performed at the frequency of 1 rad/sec and the strain amplitude of 1% after various standing times. The initial values of G' after various standing times seem to be the same level and decreases rapidly to the equilibrium value with time . This results shows that the alteration of network structure does not proceed for the standing period, however with applying oscillatory shear the network structure converges rapidly upon the equilibrium state corresponding to the strain amplitude of 1%.
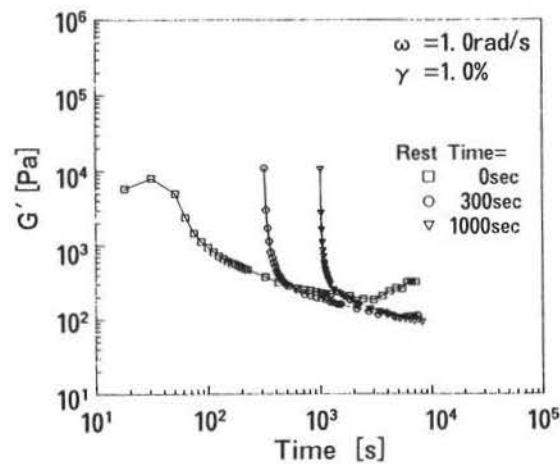

Fig.9 Logarithmic plots of G' for Ink 1 against elapsed time after various rest periods as indicated.

Effects of Strain Amplitude and Steady Shearing on the Structural Change

In order to investigate the effect of oscillatory shear on the network structure, dynamic measurements were carried out depending on the experimental sequence as shown in Figure 10 :
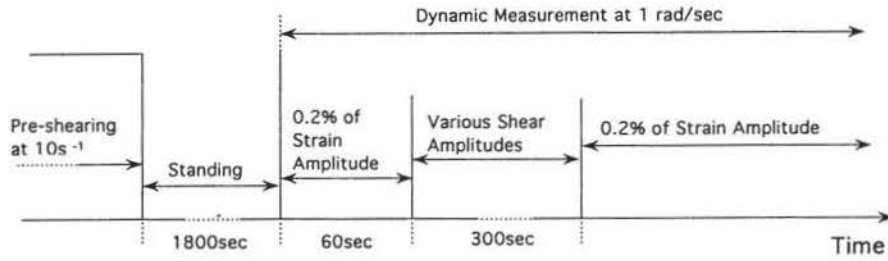
Fig.10 Experimental sequence for the dynamic measurements.

After cessation of pre-shearing, sample inks were left for stand for 1800 sec, and dynamic measurements were performed. At first 0.2% strain amplitude of oscillatory shear at 1 rad/sec was applied for 60 sec, next the oscillatory shear was increased to large amplitude ranging from 1 to 100% for 300 sec, and the strain amplitude was returned to the original amplitude of 0.2%. Storage modulus was measured as a function of elapsed time.

Figure 11 shows the results of the dynamic measurement for Ink 1. Initially, the values of G' are about 4×10^4 Pa at the strain amplitude of 0.2%, however with increasing strain amplitude the values of G' are decreased rapidly and attain the equilibrium state. For ordinary concentrated
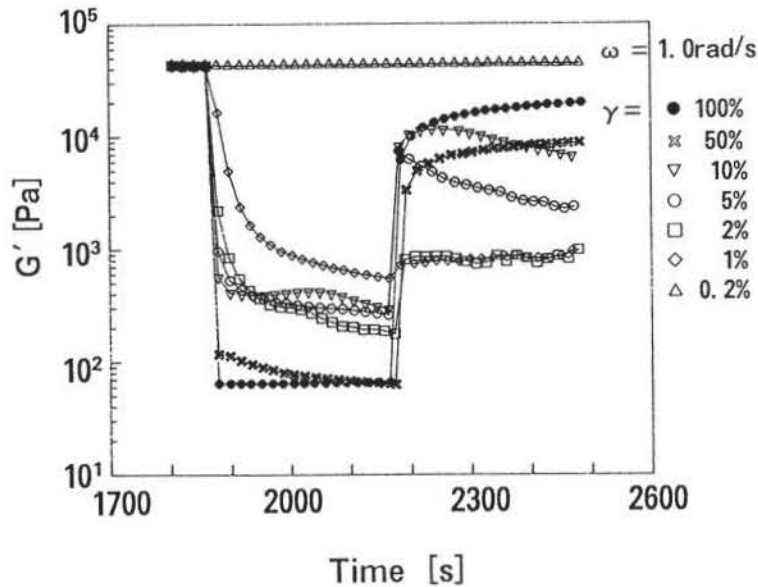

Fig.11 Change of G' on the dynamic measurements for Ink 1.

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suspensions, the value of G' decreases with increasing strain amplitude, but in Ink 1 the dependence of G' on strain amplitude is really complicated, especially at the strain amplitude below 10%. Under the moderate amplitude of oscillatory shear, rupturing of the network structure proceeds complex manner with strain amplitude. After applying large strain amplitude, the dynamic measurement was continued at 0.2 % of strain amplitude, however the value of G' did not recover to the initial value. This tendency was pronounced in the case of applying the small amplitude of oscillatory shear. This phenomenon suggests that an irreversible structural change occurs with applying the moderate amplitude of oscillatory shear.

Figure 12 shows the same results for Ink 3. Initially, the same order of G' as Ink 1 was observed at the strain amplitude of 0.2%, and the value of G' was reduced with increasing strain amplitude in order of the magnitude of strain. After returning the strain amplitude to the original state, 0.2%, the value of G' seemed to approach to the initial value, however G' did not recover completely. This tendency was pronounced in the case of which larger oscillatory shear strain was applied in advance.

These phenomena can be explained by the process of formation and breaking down of flocculated structure formed by the C6B pigment and the structural change affected by shape and movability of pigments. The pigment in low viscosity disperse medium seems to be easy to move and
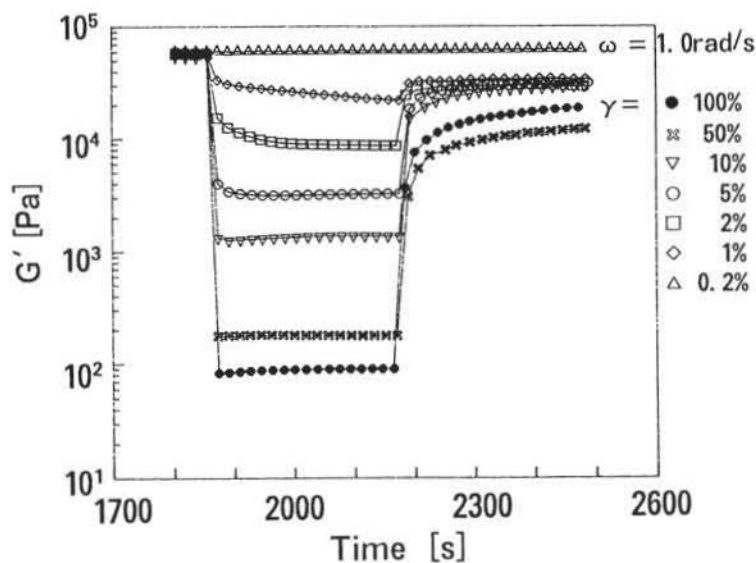

Fig.12 Change of G' on the dynamic measurements for Ink 3.

construct a effective network structure rapidly, however the quickly growth network structure is sensitive to change in applied shear and apt to be ruptured. The growth of stacking structure of C6B pigments results in breaking down of the network structure. Since the stacking structure is hard to recover under small amplitude of oscillatory shear, the broken down network structure cannot be reconstructed and the small values of G' are observed. On the other hand, in higher viscosity disperse medium, the pigments are not so easy to move and difficult to stack together. Therefore, in Ink 3 the process of network formation is not so fast but the network structure is rather durable comparing with that in Ink 1.

Effects of steady shear on the structural formation was examined according to the experimental sequence described in Figure 13.
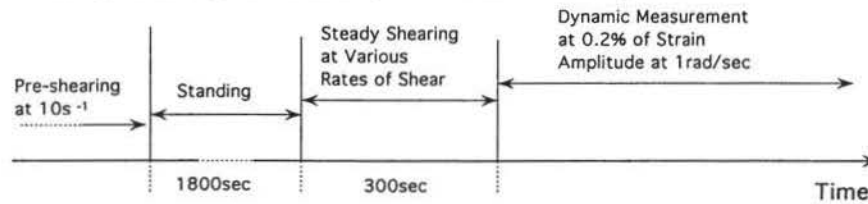
Fig.13 Experimental sequence of the transient measurements.

After cessation of pre-shearing, sample inks were left for stand for 1800 sec, and subject to steady shear at various rates of shear for 300 sec. After cessation of the steady shear, dynamic measurements were performed at 1 rad/sec at the strain amplitude of 0.2%.
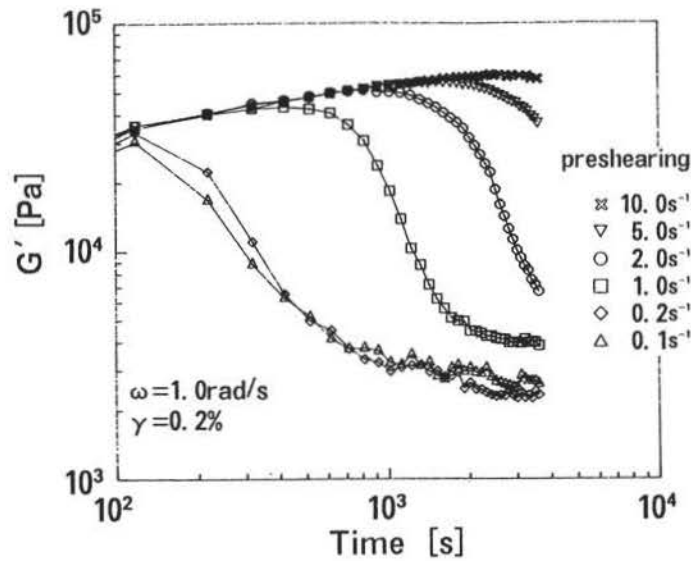
Fig. 14 Logarithmic plots of G' for Ink 1 against elapsed time after cessation of steady shear at various shear rates as indicated.

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Figure 14 shows the time dependence of storage modulus on the elapsed time after cessation of steady shear flow at various rates of shear. For the sample ink after applied sufficiently high rate of shear, the value of G' increases with elapsed time, however the value becomes to decrease at longer time region depending on the rate of shear precedently applied. The time when G' becomes to decrease sift to shorter time with decreasing the shear rate. For the case of applying shear at 0.2 sec^{-1} G' decreases monotonously with elapsed time and attain the equilibrium state. Flocculated pigment cluster under low shear rate seems to be convenient to form stacking structure under small amplitude of oscillatory shear. The same experiments were performed for Ink 3 and it was observed that the value of G' after cessation of steady shear flow increased monotonously irrespective of the shear rate precedently applied. The interesting behavior shown in Figure 14 may be associated with the formation of the stacking structure of C6B pigments.

Figure 15 shows the schematic diagram of the interparticle structures of the dispersed pigments under various situations. C6B pigments are well dispersed under shear flow like ordinary suspensions. With applying the higher rate of shear the flocculated structure of pigments breaks down into their smaller size. After cessation of steady shear, a space-filling network structure develops with elapsed time. The process of formation of the network structure depends on the initial dispersing state and the movability of pigments. Well dispersed fine cluster of pigments form a denser network structure and the pigment cluster in a lower viscosity disperse medium builds up the network structure over the whole system during short time.
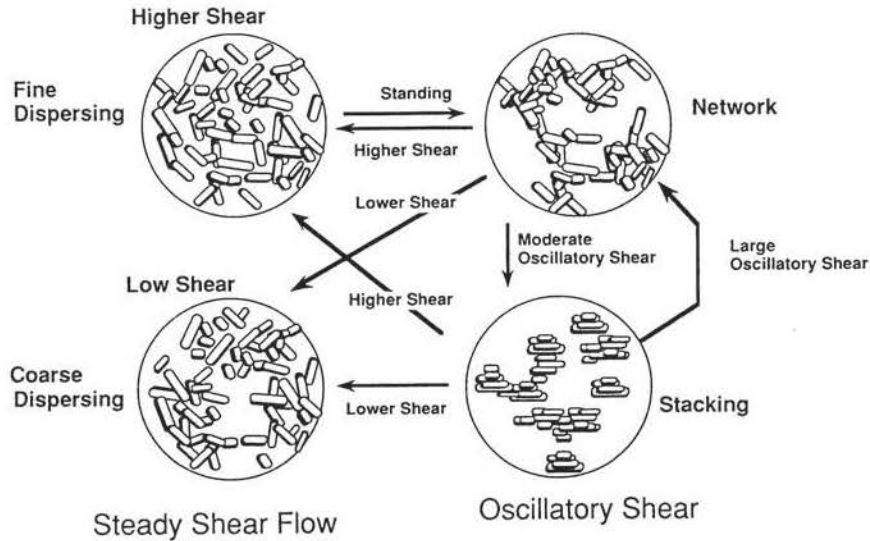

Fig.15 Schematic diagram of the structural change in the suspension of carmine 6B in polybutadiene.

On the other hand, the stacking structure is formed under moderate oscillatory shear, especially in the suspension of lower viscosity medium. A contraction of the network strands is induced by stacking of pigments and the space-filling networks are ruptured here and there. However the isolated stacking structure is released with applying a large amplitude of oscillatory shear or a disruptive steady shear. It is interesting the stacking structure of C6B pigments is formed only with applying oscillatory shear and the formation of stacking structure is associated with the movability of pigments in the disperse system. The structural changes associated with strain history govern the rheological properties of the C6B magenta inks.

CONCLUSIONS

The non-linear viscoelastic properties of suspensions of brilliant carmine 6B in polybutadiene having different viscosity were investigated and the following conclusions were obtained.

1. Fine particles of carmine 6B form a denser network structure in disperse medium and the suspension show a typical pseudo plastic behavior and remarkable non-linear viscoelastic properties.

2. Carmine 6B pigments in low viscosity disperse medium construct a space-filling network structure rapidly, however the quickly growth network structure is sensitive to change in applied shear and apt to be ruptured.

3. The anisotropic shape carmine 6B pigments in lower viscosity disperse medium tends to stack together which results in rupturing the network structure and this phenomenon is accelerated with applying moderate amplitude of oscillatory shear.

4. The non-linear viscoelastic behavior in suspension of carmine 6B can be explained by the competition between formation and breaking down of the network structure of flocculated particles.