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Rheological Behavior of Polybutadiene/Carbon Black Ink

Tsutomu HAYASHI*, Kotaro MORITA**, Minoru TATEIRI**
and Takeshi AMARI*

1. Abstract

Rheological properties of printing inks were investigated. Simple suspensions of carbon black in polybutadiene having different molecular weight were used as sample inks, and rheological properties, stress growth in steady flow, dynamic viscoelastic properties, and creep, were measured using two types of rheometer.

The effects of viscosity of disperse medium on the rheological properties of the disperse system were mainly discussed. In the disperse medium with lower molecular weight, pigment particles constructed a denser network structure in a comparatively short time. Therefore, in spite of lower viscosity of the system, higher value of storage modulus and remarkable strain dependence were observed in the disperse system with lower molecular weight disperse medium. Creep and recovery were measured at various magnitudes of shear stress and various rest periods. Creep compliance decreased with increasing rest period and decreasing viscosity of the disperse medium. The elastic modulus of network structure formed by dispersed particles in the disperse medium with lowest viscosity was determined as 159 Pa from the dependence of recoverable strain on stress and decreased with increasing viscosity of the disperse medium.

Key-words : Carbon Black, Polybutadiene, Structural Network, Creep, Stress Overshoot

2. Introduction

Rheological properties of printing inks govern the ink transfer on printing press and affect the printing quality. In order to get good results on printing quality, we have to understand the peculiar rheological properties of printing inks. Concentrated suspensions such as printing inks show peculiar rheological properties due to their denser structural networks formed by pigment particles. Furthermore commercial printing inks contain resin, pigment, and some kinds of additives, and the rheological behavior of printing inks is influenced by those materials. Therefore precise analysis seems to be very difficult. Since these materials may complicate the rheological properties of printing inks, it is reasonable to use a simple suspension consisting of only pigment and vehicle for the good understanding of basic rheological properties of printing inks.

Some rheological studies have been performed using simple suspension from a view

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* Graduate School of Science and Technology, Chiba University
1-33 Yayoi-cho Inage-ku Chiba 263, JAPAN

** SAKATA INX CORP. 2291 Makinouchi Ozaki Noda-shi Chiba 270-02, JAPAN

point of the formation and breaking down of network structure of dispersed particles^{1~4)}. The process of the formation and breaking down of network structure depends on kinetics of particles in continuous disperse medium. However the effect of the time dependence of structural recovery on rheological properties has not been clear.

In this study, the suspensions of carbon black in polybutadiene having different molecular weight were used for samples. Dynamic viscoelasticity and creep were measured, and the effect of the formation and breaking down of network structure of carbon black particles on the rheological properties were mainly discussed from a view point of time dependence.

3. Experimental

3.1 Samples

In this study, the following three kinds of disperse systems were used as ink samples. Twenty wt% of carbon black was dispersed in polybutadiene having different molecular weight as shown in **Table 1**. Inks 1, 2, and 3, are referred to ink samples using polybutadiene with the molecular weight of 1000, 2000, and 3000, respectively. The rheological behavior of polybutadiene shows only viscous behavior, and polybutadiene has no polar radicals in its structure of molecule. So, the viscoelastic behavior which depend on the wetting phenomenon between carbon black and polybutadiene is not need to take into consideration and we can discuss the effects of viscosity of disperse medium on the rheological properties of the disperse system.

3.2 Measurements

In this study, two types of rheometer were used. The flow property and the dynamic viscoelasticity were measured by a Rheometrics fluid spectrometer (RFS-II). The steady shear measurements can be performed at the rates of shear ranging from 0.1 to 40 s⁻¹. The stress overshoot was measured after various rest periods; ts ranging from 30 to 7200 s after applying the 10 s⁻¹ of the steady shear for 5 min.

The dynamic elasticity G' and viscosity η' were measured by strain sweep mode in the strain region between 10⁻¹ and 10% at an angular frequency of 10 rad/s.

The creep behavior was measured by a Rheometrics dynamic stress rheometer (DSR). The creep experiment was performed at the stress of 20 Pa at various rest periods between 30 to 7200 s after applying the steady shear. The recoverable strain following creep

Table 1 Characteristics of polybutadiene

Polybutadiene	$\overline{M}_n$	Viscosity (Pa·s)	Specific gravity	Constituent (%)		
				Vinyl	Trans	Cis
B-1000	1000	1.3	0.89	58	16	17
B-2000	2000	13.5	0.89	65	14	16
B-3000	3000	39.6	0.89	67	13	15

Table 2 Plastic viscosity and yield value for each ink

	Plastic viscosity (Pa·s)	Yield value (Pa)
Ink 1	4.6	84.2
Ink 2	33.7	139.8
Ink 3	87.8	156.9

Fig. 1 Flow property of each polybutadiene **Fig. 2** Plots of shear stress against rate of shear for each ink **Fig. 3** Plots of shear stress against rate of shear for each ink

deformation at various magnitudes of stress ranging from 2 and 100 Pa was also measured.

4. Results and Discussion

4.1 Flow Properties

Figure 1 shows the plots of shear stress against rate of shear for each polybutadiene. Each sample shows only viscous flow and pronounced viscoelastic behavior can not be expected. **Figures 2** and **3** show the plots of shear stress against rate of shear, and the plastic viscosity of the ink is dominated by molecular weight of disperse medium. The plastic viscosity and yield value which were determined by Bingham's equation are shown in **Table 2**. We can deduce the degree of flocculation from the magnitude of the yield value.

4.2 Stress Overshoot

The flocculated structure and their networks can also be discussed by the stress growth experiment after various rest periods. **Figures 4, 5** and **6** show the stress growth curves for sample Inks 1, 2 and 3, respectively, at various rest periods as indicated after applying steady shear. For Ink 1 stress overshoot phenomenon can be observed even at

Fig. 4 Time dependence of stress overshoot for Ink 1 at various rest periods

Fig. 5 Time dependence of stress overshoot for Ink 2 at various rest periods

the rest period shorter than 30 s and becomes pronounced with increasing rest period. On the other hand, stress overshoot cannot be observed at the rest period up to 120 s for Ink 2 and 600 s for Ink 3. Stress overshoot phenomenon can be attributed to three dimensional network structure formed by dispersed particles in the system. These results suggest that the velocity of structural recovery for Ink 1 having low molecular weight disperse medium is faster comparing with Inks 2 and 3. The pigment particles in the lower viscosity disperse medium may form the network structure for comparatively short period.

This velocity of structural recovery can be evaluated by the Cartwright's thixotropic index⁵⁾ and the de Waele's equation⁶⁾. **Figure 7** shows the logarithmic plots of maximum

Fig. 6 Time dependence of stress overshoot for Ink 3 at various rest periods

Fig. 7 Logarithmic plots of maximum stress against rest period for each ink

Fig. 8 Logarithmic plots of G' against strain for each ink

Fig. 9 Logarithmic plots of η' against strain for each ink

stress ($\sigma_{\max}$) against rest period (t_s) for each ink. The maximum stress value increases with increasing the molecular weight of disperse medium. The dependence of $\sigma_{\max}$ on t_s in Ink 3 is smaller than that in Inks 1 and 2. It is thought that formation of structural network in Ink 3 is not so remarkable comparing with that in the other inks. The velocity of structural formation may be dominated by the viscosity of disperse medium.

4.3 Dynamic Viscoelasticity

Figures 8 and 9 show the strain dependence of the dynamic elasticity G' and viscosity η' , respectively, measured in the strain region between 10^{-1} and 10% at an angular frequency of 10 rad/s. The strain dependence of viscoelastic properties is most pronounced in Ink 1. In the lower strain region, the values of G' and η' seem to be constant irrespective of strain amplitude. In this strain region, the structural networks are not destroyed by the applying oscillatory shear. In Ink 1 the value of G' is larger than that in the other inks although the value of η' is the smallest of all. Therefore, we can deduce that the structural networks formed by dispersed particles affect the elastic

Fig. 10 Time dependence of creep at various rest periods for Ink 1

Fig. 11 Time dependence of creep at various rest periods for Ink 2

properties of the system. On the other hand, η' of the system is dominated by the viscosity of the disperse medium. The network structure is very sensitive to change magnitude of applying shear. With increasing strain amplitude, the values of G' and η' decrease and the strain dependences of G' and η' are pronounced in Ink 1. The strain dependence of viscoelastic properties can be attributed to the breaking down of the flocculated network structure. Therefore, we can deduce that the density of network structure for Ink 1 is higher than that of the other inks and is reduced with increasing strain amplitude.

4.4 Creep (Rest period dependence)

The carbon black particles in disperse medium can easily move and form the structural networks in a short period. **Figures 10, 11, and 12** show the creep curves at various rest periods on applying 20 Pa stress for 60 min. The creep curve shifts to downwards with increasing rest period and this tendency is pronounced in Ink 1 and in longer time region. This phenomenon shows that the structural networks of carbon black in Ink 1 are constructed in a comparably short time. With proceeding the formation of the network structure in the creep measurement, the increment of strain seems to be suppressed. The magnitude of strain after a long rest period of Ink 1 is the smallest of all. In Ink 3, creep curves are located upward comparing with those at the same rest period in other inks, and the dependence of creep curve on rest period is rather small. These phenomena can be explained by the process of formation of the network structure.

4.5 Creep (Recoverable strain)

In order to investigate the elastic properties of flocculated structure, the recoverable strain was measured after short-period creep experiment. **Figure 13** shows an example of creep and recovery at various magnitudes of stress. Obvious creep recovery was observed, and magnitude of strain and recoverable strain increase with increasing stress.

Figure 14 shows the relation between recoverable strain and stress for each ink. The experiments were carried out at the stress ranging from 2 and 100 Pa. There is an

Fig. 12 Time dependence of creep at various rest periods for Ink 3

Fig. 13 Results of creep experiment at various stresses

evident inflection point in each plot. Up to this critical point, the recoverable strain increases linearly with increasing the stress. For each ink, the inflection point is appeared at about 30 Pa, and this stress value seems to correspond to the true yield value for each ink. The elastic modulus can be calculated from the initial linear portion of each curve. The values of modulus are determined 159 Pa for Ink 1, 110 Pa for Ink 2, and 123 Pa for Ink 3. We can deduce the elastic modulus of flocculated structure from those values. The magnitudes of recoverable strain for Inks 1, 2 and 3, are 20, 35, and 26%, respectively. These results can be explained by the formation and breaking down of structural networks in each ink during creep experiments. Namely, in Ink 1 the density of the structural network seems to be the highest, but the network structure itself can be broken down easily during creep experiment. Therefore the highest modulus and the smallest recoverable strain are observed in Ink 1. On the other hand, with increasing viscosity of disperse medium the formation of the network structure seems to be depressed, but the network structure itself cannot be broken down easily. The rate of the formation of the network structure in Ink 2 is faster than that in Ink 3. After creep experiment, however, the density of residual network structure in Ink 3 is slightly higher than that in Ink 2.

From these results, following consideration could be obtained. For the rheological study of concentrated suspensions such as printing ink, molecular weight and viscosity of disperse medium are among the most important factor. That is, the carbon black particles can move easily in the disperse medium having low molecular weight and form the network structure in a comparatively shorter time, and the network structure seems to be denser compared with the suspension of high molecular weight disperse medium.

5. Conclusions

Rheological properties of suspension which is composed by carbon black in polybutadiene having different molecular weight are investigated, and following conclusions are obtained ;

1. The carbon black particles in the disperse medium having lower molecular weight form a denser network structure comparably in a short time scale.
2. The suspension of carbon black in the low molecular weight disperse medium shows the most pronounced strain dependence of viscoelastic properties comparing with

Fig. 14 Relation between recoverable strain and stress for each ink

that of high molecular weight.

3. With increasing viscosity of disperse medium, the formation of network structure seems to be depressed, but network structure itself cannot be broken down easily.

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