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Rheological characterization of carbon black/varnish suspensions

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Abstract

Linear viscoelastic properties of carbon black (CB) suspensions in a rosin-modified phenol resin-type varnish (Varnish-1) were studied as a function of volume fraction (ϕ) of CB and temperature (T) to clarify the effects of the primary particle size and the aggregate structure of CB particles on the rheological properties. All the CB/Varnish-1 suspensions showed a typical sol–gel transition behavior with an increase in ϕ. The critical gel behavior characterized with a power-law relationship between the storage and loss moduli (G' and G'') and frequency (ω), $G' = G''/\tan(n\pi/2) \propto \omega^n$, was observed at a critical gel concentration (ϕ_{crit}). At 30 °C, the critical relaxation exponents (n) were estimated to be 0.72 ± 0.02, irrespective of the primary particle size and aggregate structure of the CB particles. In contrast, the ϕ_{crit} depended strongly on the aggregate structure although it hardly depended on the primary particle size. Both the n and ϕ_{crit} values changed with T. The n values increased from 0.72 at 30 °C to 0.83 at 60 °C and the correspondent ϕ_{crit} values decreased slightly with elevating T for each CB suspension. The increase in n with T indicated that the CB aggregate structures changed from plane-like to more straight with increasing T.

Keywords: Carbon black suspension; Dynamic viscoelasticity; Sol–gel transition; Critical exponent; Critical concentration

1. Introduction

Carbon black (CB) is constituted of carbon particles fused together by covalent bonds to form "*aggregates*" that generally are considered unbreakable during the normal processing of the materials. CB *aggregates* exist in a variety of shape type with higher structure grades containing more branched *aggregates* and lower structure grades containing more compact *aggregates*. The *aggregates* have a strong tendency to agglomerate because of the electronic structure of the CB surface. In contrast to the *aggregates*, these "*agglomerates*" are characterized by weak bonding between the *aggregates* and therefore do not retain their integrity during processing [1]. Suspension systems of CB show peculiar rheological properties due to their network structure of *agglomerates* formed by CB *aggregates* [2,3]. Consequently, the control of the rheological properties plays a major role for pigmentation, electrical conductivity, ink, and coating. Furthermore, rheological properties of CB suspensions are of scientific interest.

Recently, we investigated the dynamic viscoelastic properties of the CB suspensions in various suspending media, and found that the rheological behavior of the CB suspensions changes with the affinity of suspending medium toward the CB particles and is classified into three different types of the behavior as summarized below [4]:

(1) In the medium having a poor affinity toward the CB particles, the CB particles form well-developed network-like agglomerates. This strongly flocculated network structure exhibits highly nonlinear, elasto-plastic features, as reported previously [2,3].
(2) In the medium having a moderate affinity (Varnish-1), the particles form weakly flocculated network-like agglomerates that grow to a self-similar, fractal network as the CB concentration c_{CB} is increased. Correspondingly, a power-law type relaxation similar to that of critical gels, $G' \propto G'' \propto \omega^n$ with $n = 0.71$, is observed at high c_{CB} where this fractal network is formed. Our further study has reported

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a sol–gel transition on an increase in CB volume fraction and its anomalous temperature dependence [5].

(3) In the medium having a high affinity (Varnish-2), the particles are randomly dispersed to form no agglomerates. The slow relaxation observed in this medium is attributable to diffusion of the covalently fused aggregates, just the same as hard sphere suspensions. Another our paper has confirmed this expectation using smaller CB aggregates of an average diameter of 120 nm [6].

Suspensions of weakly attractive particles, exhibiting the type 2 behavior, have been attracting industrial as well as academic interest. Most of the rheological studies for such suspensions were devoted to elastic properties of the gels [7–12] and to gelation processes [13–15]. Rueb and Zukoski [8] investigated the rheology of similar suspensions in decalin and tetradecane and found that the particles interact like hard spheres at high temperature (T) but the gelation due to the interparticle attraction occurred at low T. Trappe and Weitz [10] reported that the G' and G'' versus ω plots for various c_{CB} values can be double-logarithmically shifted to be simultaneously superposed on respective master curves and that the scaling of the dynamic moduli represented by this superposition results from similarity of the agglomerated networks at various c_{CB}. Won et al. [12] studied suspensions of CB in oil, stabilized with adsorbed polyisobutylene succinimide dispersant. They reported that the CB agglomerates changes dramatically with T.

As reported in the previous paper [5], we studied the linear viscoelastic behavior of CB suspensions in the medium having moderate affinity in details and found that the suspensions exhibited a sol–gel transition on an increase in CB volume fraction (ϕ), and the ϕ_{gel} value at the gelation point decreased with increasing T. This T dependence of ϕ_{gel}, being opposite to the dependence seen for usual gelling systems, can be related to a phenol resin-type polymeric component included in the varnish. At high T, the polymeric component should be less solvated, and this less solvated polymeric component possibly is adsorbed on the CB particles, thereby allowing the agglomeration of the particles at small ϕ.

The application of sol–gel transition to the CB suspensions with various types of aggregates should result in a much deeper understanding of the rheology of CB suspensions. Winter and Chambon [16,17] found that the storage modulus $G'(\omega)$ and the loss modulus $G''(\omega)$ follow power laws with the same exponent n at the gel point. The gel point corresponds to the state where $G'(\omega)$ and $G''(\omega)$ parallel each other over the experimentally accessible range of frequencies, and is characterized by a single exponent n which is called the critical relaxation exponent that ranges between 0 and 1:

$$G'(\omega) = A\omega^n \quad \text{and} \quad G''(\omega) = B\omega^n \tag{1}$$

The loss tangent $\tan\delta$ given by

$$\tan\delta = \frac{G''(\omega)}{G'(\omega)} = \tan\left(\frac{n\pi}{2}\right) \tag{2}$$

is independent of the frequency. Eq. (2) is of importance, because Eq. (2) allows the precise value of the gelation point to be determined.

The critical exponent n can be related to the fractal structure of the gelling system [18–25]. When the hydrodynamic interaction is completely screened and the excluded volume effect is dominant, the relation of n to mass fractal dimension d_{f} can be expressed as [22,25]:

$$n = \frac{d}{d_{\mathrm{f}} + 2} \tag{3}$$

where d denotes the space dimension. If the excluded volume effect is screened out near the gel point, the n may decrease as [25]:

$$n = \frac{d(d + 2 - 2d_{\mathrm{f}})}{2(d + 2 - d_{\mathrm{f}})} \tag{4}$$

The mass fractal dimension can be described the structure of an agglomerated structure. The distribution of the particle is the straight line for $d_{\mathrm{f}} = 1$, plane-like for $d_{\mathrm{f}} = 2$, and the three-dimensional space for $d_{\mathrm{f}} = 3$. The agglomerated structure having lower fractal dimension can be described as a more open structure.

Suspensions exhibiting the gelation behavior have been studied extensively [13–15,26]. The experimentally determined relaxation exponent n in the gelation process was reported to be around 0.75 for zirconium alkoxide [13], silica gels [14], and SnO_2 suspensions [15], and 0.13 and 0.15 for TiO_2 suspensions [26]. In the previous papers [4,5], we reported that CB/Varnish-1 suspension showed a sol–gel transition with increasing CB concentration and the critical relaxation exponent n was near 0.7.

Segre et al. [27] showed that gelation of weakly attractive colloids is remarkably similar to the colloidal glass transition. Their results suggested that, like the glass transition, gelation results from kinetic arrest due to crowding of clusters.

Despite these studies, the relationships between the rheology of sol–gel transition of weakly attractive particles and particle morphology have not been fully elucidated. Thus, we have been focusing our attention on CB/Varnish-1 suspensions. Varnish-1, a rosin-modified phenol resin, is a main component in the varnish for printing ink. In this study, we conducted linear viscoelastic measurements of the suspensions of four kinds of CB particles in Varnish-1 as a function of the volume fraction ϕ of CB and temperature T. The critical relaxation exponent n and the critical gel concentration ϕ_{crit} were evaluated and discussed in relation to the CB morphology such as primary particle size and aggregate structure.

2. Experimental

Four kinds of CB samples supplied from Mitsubishi Chemical Corp. were used in this work. The mean particle diameter, the surface area, and di-(butyl phthalate) (DBP) absorption value of the CB particles are shown in Table 1. Surface area is a measure of particle size, and is measured by absorption of nitrogen gas onto the carbon black. DBP adsorption is a measure of aggregate