

Reactions of Carbon Black. Part I. Nonthixotropic Carbon Black Compositions

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Synopsis

The solution polymerization of butyl acrylate in the presence of a furnace black was found to produce a stable dispersion of carbon black which showed Newtonian flow, while the mixture prepared by mixing the same carbon black into a solution of poly-(butyl acrylate) homopolymer had a large degree of thixotropy. A marked change in the viscosity of the reaction mixture was also observed at an early stage of polymerization when the initial mixture which was a moist mass with no fluidity, turned to a fluid easily stirred. The change in viscosity and the transition in flow behavior were carefully followed with a rotary cylinder type viscometer. The non-Newtonian initial mixture was found to turn to a Newtonian fluid at low conversion of the monomer. Beside the adsorption of the homopolymer onto the surface of carbon black particles, which would occur also in mechanical mixing, the change in the flow behavior was estimated to be caused by the change in the shape and the size of the dispersed carbon black particles due to the change in the condition of the surface of the particles by which growing polymer radicals, as well as initiator radicals, were captured.

INTRODUCTION

The chemical behavior of carbon black has not as yet been fully explored, but, generally, carbon black is recognized as a free-radical scavenger, and its use for the inhibition or retardation of free-radical polymerization of vinyl monomers has been patented.¹

There are various types of oxygen-containing groups assigned to the chemical structure of carbon black, such as phenol, quinone, carboxyl, carboxylic ester, and lactone.² Among those reactive groups, the inhibition of free-radical polymerization is considered to be caused by surface quinone groups.³

The reaction of the free radicals produced by the thermal decomposition of 2,2'-azobisisobutyronitrile^{4,5} and benzoyl peroxide⁶ onto the surface of carbon black has been investigated in order to determine the number of active sites. The formation of bound rubber has also been investigated and interpreted through a free-radical mechanism.⁷

We have been investigating the reaction of free radicals on the surface of carbon black in order to elucidate its unique behavior in the free-radical polymerization of vinyl monomers. According to some reports and pat-

ents,⁸⁻¹¹ the free-radical polymerization of vinyl monomers in the presence of carbon black yielded stable dispersions of carbon black, and a mechanism which was similar to graft copolymerization was proposed.⁸

The free-radical polymerization of vinyl monomers in the presence of carbon black in the form of a solution polymerization produced a carbon black composition in which the dispersion of carbon black was so stable that it was not easily segregated by ordinary means of separation, i.e., filtration or centrifugation. And surprisingly enough, the product mixture prepared by the above-mentioned procedure from a certain combination of carbon black and vinyl monomers showed Newtonian flow, despite high carbon black load rather than the non-Newtonian flow which was common with the carbon black dispersion prepared by mechanical means. The transition from non-Newtonian initial composition to Newtonian final reaction mixture was followed by means of a rotary cylinder type viscometer.

The unique flow behavior of the carbon black composition prepared from the free-radical polymerization of butyl acrylate in ethylene glycol monomethyl ether in the presence of a furnace black is discussed here in this report.

EXPERIMENTAL

Reagents

Carbon Black. The carbon black used for the experiment was a high structure furnace black, Asahi G-2 (Asahi Carbon Manufacturing Company, Ltd.) with the following specifications: oil absorption, 168 cc./100 g.; water content, less than 1%; iodine absorption, 28.7 mg./g.; pH, 8.0; particle size, 70 m μ ; ash content, 0.06%; volatiles, 0.86%.

Butyl Acrylate. Commercially available monomer was used after purification by distillation in a nitrogen atmosphere following the removal of inhibitor by washing with dilute alkali solution, b.p. 52-53°C./22 mm. Hg.

2,2'-Azobisisobutyronitrile. A commercial product was purified by recrystallization from methanol twice.

Ethylene Glycol Monomethyl Ether. A commercial product was purified by distillation. b.p. 124°C.

Preparation of Samples

Polymerization of Butyl Acrylate in the Presence of Asahi G-2 Furnace Black. In the manner of solution polymerization of vinyl monomers, the polymerization of butyl acrylate with 2,2'-azobisisobutyronitrile as initiator was carried out in ethylene glycol monomethyl ether in the presence of Asahi G-2 furnace black.

In a nitrogen atmosphere a mixture of 1000 g. of Asahi G-2 furnace black, 1000 g. of butyl acrylate, 2000 g. of ethylene glycol monomethyl ether, and 0.5 g. of 2,2'-azobisisobutyronitrile was heated at 75°C. with stirring. The initial mixture was almost like a moist mass and difficult to be stirred. Normally this type of free-radical polymerization of vinyl monomers is

TABLE I

Sample number	Conversion, %
a	0
1	4.8
2	5.1
3	12.8
4	25.0
5	42.5
6	63.3
7	78.7
8 ^a	96.9
b	96.9 (control mixture)

^a Sample c in Fig. 1.

retarded very effectively by a furnace black, and the polymerization cannot be brought to high conversion; and further stepwise addition of 2 g. of the initiator in four equal portions brought the polymerization to completion. During the polymerization, samples each weighing about 200 g. were taken out from the reaction mixture, and conversion and viscosity determined. Quenching with hydroquinone was found to be inadequate because of a shift in the flow curve for some unexplained reason, and each sample was quenched by cooling it below 0°C. The conversion in each sample was determined before and after each viscosity measurement by measuring the amount of monomer left by gas chromatography with a Diasolid (a trade name for a modified kieselguhr) column with poly-(diethylene glycol) added with 2% of phosphoric acid. Because of the formation of an inseparable slurry mixture, the conversion of monomer could not be easily determined otherwise. The conversion for each sample is given in Table I.

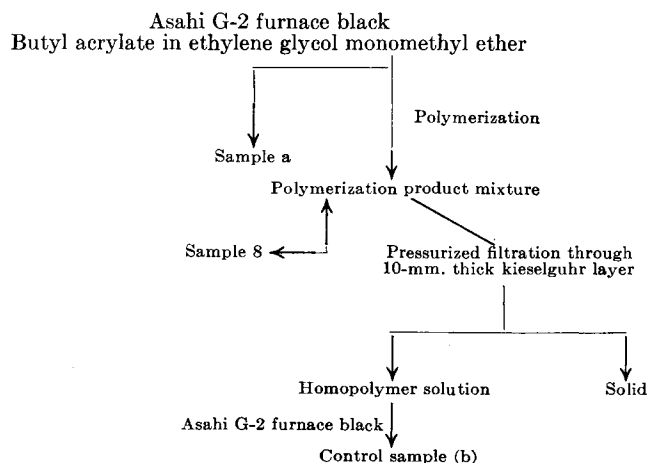


Fig. 1. Preparation of samples.

Preparation of Control Sample for the Viscosity Measurement. The procedure for preparation of the control sample is shown in Figure 1.

As shown in Figure 1, the control sample (b) was prepared by mixing the same carbon black as that used for the reaction mechanically by a roll mill into the homopolymer solution separated from the polymerization product mixture. Its solid content and carbon black/homopolymer ratio were adjusted to the same as that of the original mixture (c). Thus the effect of a possible difference in the molecular weight distribution was minimized. The molecular weight of the homopolymer thus separated was determined by both viscosity and vapor pressure osmometry which gave a low value of 7900 in methyl ethyl ketone.

Measurement of Viscosity

A Couette type rotary viscometer (Shimazu universal rheometer UR-1) with the following specifications was used: cup diameter, 40 mm.; bob diameters, 39, 33, 27, 22 mm.; length of bob, 50 mm.; cup speed, 5–400 rpm.

The flow behavior of the samples was determined at 30°C. at cup speeds of 50, 100, 150, 200, 250, 300, 350, and 400 rpm in a cycle. The viscosity was calculated by the following equations:

$$\eta = \frac{k\theta}{4\pi h\Omega} \left(\frac{1}{R_b^2} - \frac{1}{R_c^2} \right)$$

$$\frac{2}{R_b^2} \left(\frac{\Omega}{\frac{1}{R_b^2} - \frac{1}{R_c^2}} \right) = \frac{1}{\eta} \left(\frac{k\theta}{2\pi h R_b^2} \right)$$

where η is viscosity (poise); k is a wire constant (dyne-cm./radian); θ is the torque acting on the wire (radian); h is the length of the bob in liquid (5.00 cm.); Ω is the angular velocity of the cup (radian/sec.); R_b is the radius of the bob, and R_c is the radius of the cup.

RESULTS AND DISCUSSION

The factors involved in the marked stability of the carbon black dispersions prepared by the free-radical polymerization of vinyl monomers in the presence of carbon black have been the object of our current study. The mixture was examined rheologically during and after the completion of polymerization in comparison with the control mixture.

The dispersion thus prepared from butyl acrylate and a furnace black in ethylene glycol monomethyl ether was so stable that it could not be precipitated completely by centrifugation at 16,000 rpm for 1 hr., while the control sample prepared by mixing the same carbon black with the homopolymer solution mechanically by means of a roll mill was completely precipitated under much milder treatment. Moreover, the dispersion showed Newtonian flow in contrast to the control sample which showed thixotropy.

In Figure 2 the relationships between apparent viscosity and rate of shear for the initial, the control, and the reaction product mixtures are shown. The initial mixture (a) was a nonfluid moist mass, and its viscosity measurement could not be carried out at higher rate of shear. From those

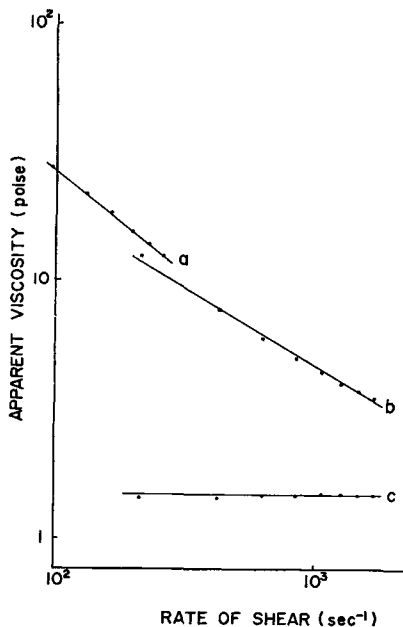


Fig. 2. Dependence of apparent viscosity on rate of shear: (a) initial mixture of Asahi G-2 furnace black and butyl acrylate in ethylene glycol monomethyl ether; (b) control mixture of Asahi G-2 furnace black and poly(butyl acrylate) in ethylene glycol monomethyl ether; (c) dispersion prepared by polymerization of butyl acrylate in the presence of Asahi G-2 furnace black in ethylene glycol monomethyl ether.

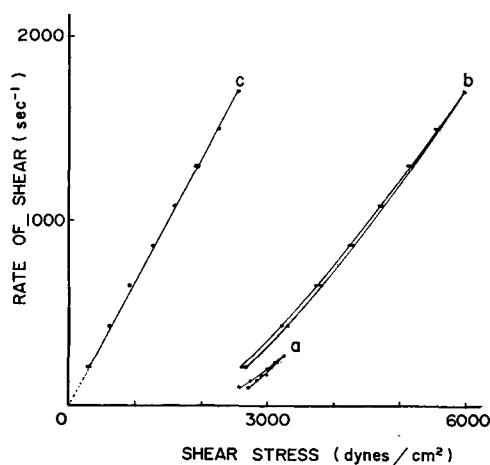


Fig. 3. Rate of shear vs. shear stress plots for the same samples as in Fig. 2.

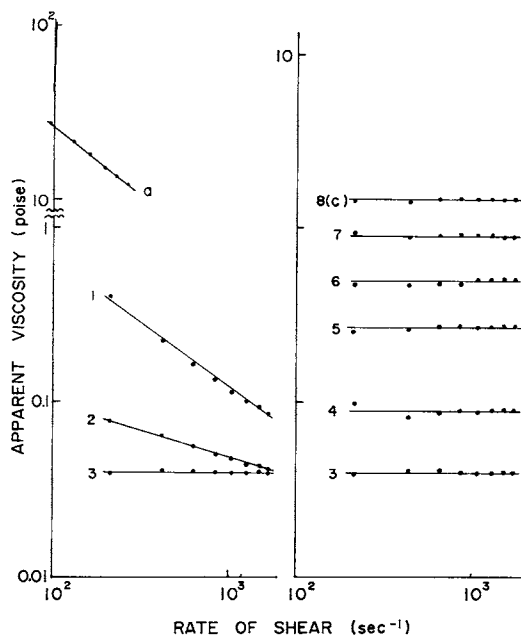


Fig. 4. Dependence of apparent viscosity on rate of shear for the samples listed in Table I.

three slopes indicating the change in apparent viscosity with the change in rate of shear, a radical difference is apparent. The reaction product (c) shows Newtonian flow, while the others are non-Newtonian, and the viscosity of (c) is also lower than that of the control sample (b) with the same solid content and carbon/homopolymer ratio.

Figure 3 shows the relationship between rate of shear and shear stress. As described in the preceding section, the control mixture (b) was prepared from the same carbon black and the poly (butyl acrylate) homopolymer which was separated from the reaction mixture by gradual filtration through a layer of kieselguhr, mixed in ethylene glycol monomethyl ether mechanically, its solid content and carbon black/homopolymer ratio being adjusted to equal original reaction mixture.

As shown in Figure 3, the rate of shear-shear stress curve for the reaction product mixture (c) showed Newtonian flow, being a straight line passing through the origin. On the other hand, the control mixture (b) showed the presence of thixotropy, giving a hysteresis loop with a large yield value. The flow curve of the initial mixture before the polymerization was not too clearly defined because of lack of fluidity due to high solid content, but it was not that of Newtonian fluid.

The change in fluidity of the mixture and the transition from non-Newtonian flow to Newtonian flow of the mixture containing an appreciable amount of carbon black were observed to be rather abrupt and the change in flow behavior was studied in respect to per cent conversion of monomer

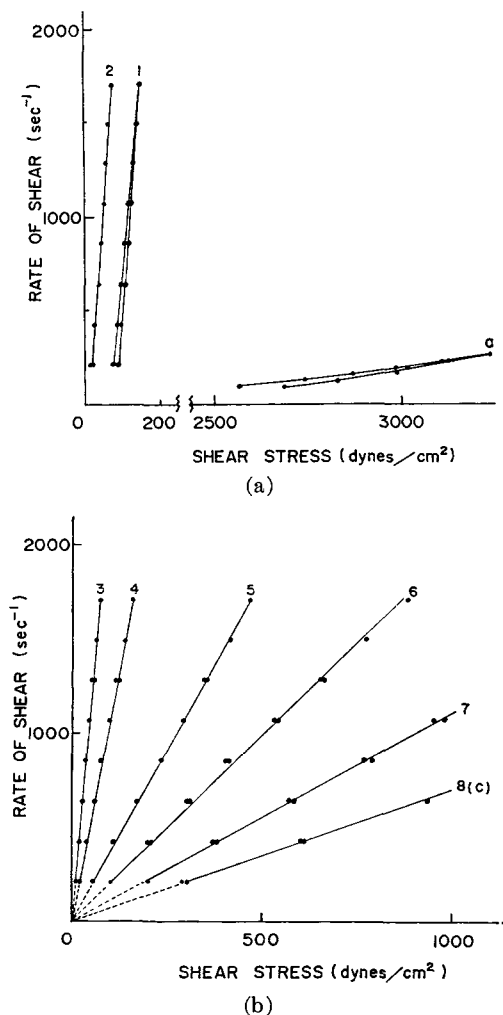


Fig. 5. Rate of shear vs. shear stress plots as a function of conversion for the samples listed in Table I.

to polymer in the mixture of a furnace black and butyl acrylate in ethylene glycol monomethyl ether and the results are shown in Figures 4 and 5, in which the transition in flow behavior is clearly shown.

In Figure 4, the transition is seen to occur at rather low conversion, and after that only viscosity change is observed without loss of Newtonian flow.

The same transition is shown in Figure 5, in which the plots of rate of shear versus shear stress gave hysteresis loops with yield values at low conversion, but with increase in conversion the loops turned to straight lines and their yield value to nil. When apparent viscosity was plotted against conversion, a minimum appeared at about 6.8% conversion, as shown in Figure 6.

The partial disintegration of the so-called structure of carbon black is clearly shown by the electron micrographs in Figures 7-9. Disintegration of the structure to this extent could not be achieved too easily by me-

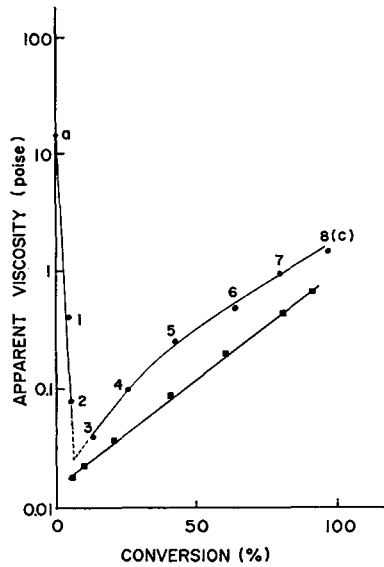


Fig. 6. Dependence of apparent viscosity on conversion for the samples listed in Table I: (●) polymerization mixtures; (■) homopolymer of butyl acrylate separated from the polymerization mixture by the scheme shown in Fig. 1.

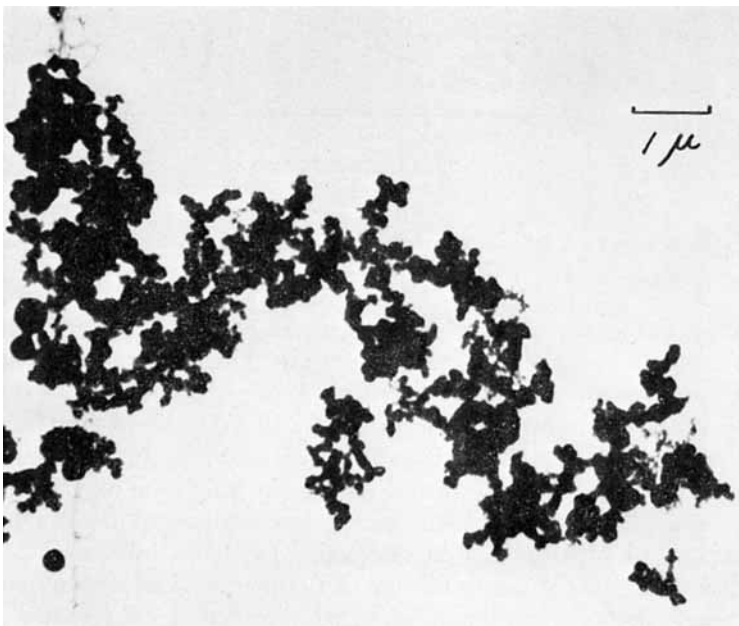


Fig. 7. Electron micrograph of sample a. 14,000X.

chanical means. Beside the adsorption of the homopolymer onto the surface of carbon black particles, which would occur also in mechanical mixing, the change in the flow behavior was estimated to be caused by the

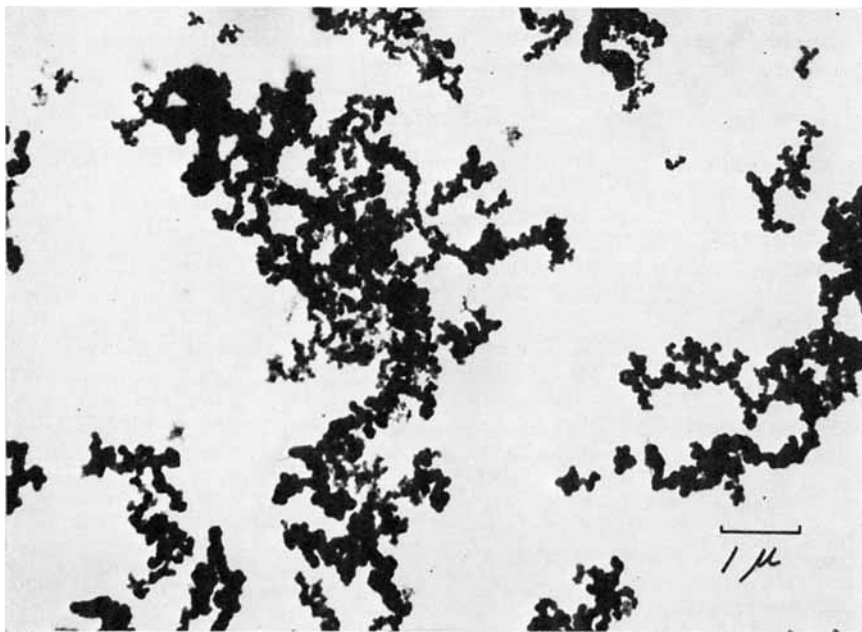


Fig. 8. Electron micrograph of sample b. 14,000 \times .

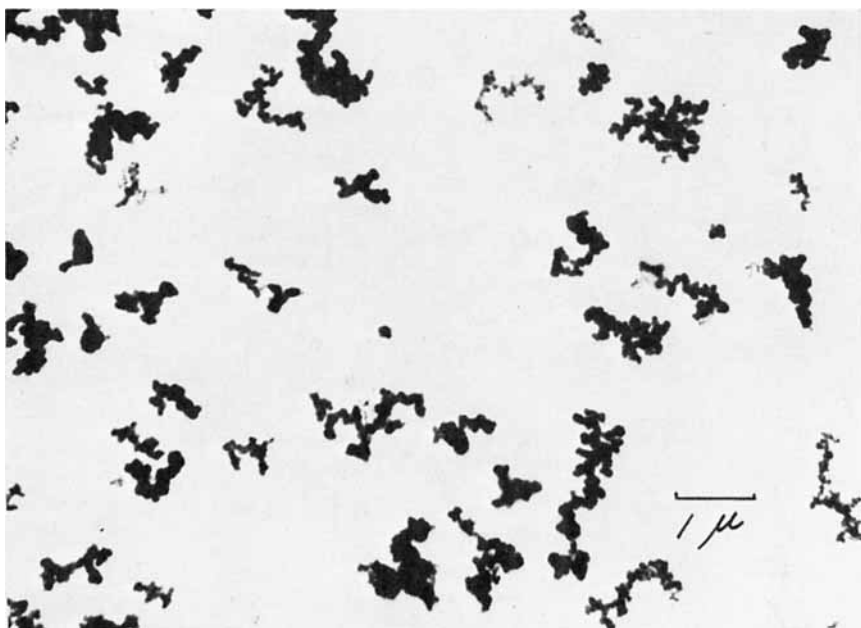


Fig. 9. Electron micrograph of sample c. 14,000 \times .

change in the shape and the size of the dispersed carbon black particles due to the change in the condition of the surface of the particles by which growing polymer radicals, as well as initiator radicals, were captured.

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