Research Institute for Polymers and Textiles, Ibaraki (Japan)

Viscous properties of calcium carbonate filled polymer melts

T. Kataoka, T. Kitano, Y. Oyanagi, and *M. Sasahara*

With 7 figures and 1 table

1. Introduction

In a previous paper (1) on the viscosity of polyethylene and polystyrene filled with glassy small particles, it was suggested that the relative viscosity η_r of the dispersion in a non-Newtonian medium should be defined as the ratio of the viscosity of the dispersion to that of the medium at the same shear stress. According to this definition, an asymptotic η_r, this is designated as $(\eta_r)_l$ hereafter, was able to be determined in the range of rather low shear stress (or shear rate) such as covered with a cone-plate viscometer. The particles used in the previous srudy were glass beads (GB), glass balloons (GA), and silas balloons. They were spherical and had rather sharp distributions of the particle size except the last ones. Average diameters of the GB and the GA ranged from 36 μm to 100 μm. The relationship between $(\eta_r)_l$ and the volume fraction of the filler ϕ of those systems were able to be represented by a single curve irrespective of the size of the particle as well as the medium polymer. The curve was approximated by equations (2, 3) which proved to be successful for predicting the relative viscosity-concentration relationship of the dispersion of particles in a Newtonian liquid.

If, however, the size of the particles becomes smaller or the surface of these becomes rough, it is considered that the size and the surface-roughness of the filler should affect the $(\eta_r)_l - \phi$ relationship. Calcium carbonate (CC) powder is one of such fillers. Although the rheological properties of CC filled polymer melts have a practical importance, there are rather a few papers on the subject. The paper of *Han* (4) is a prominant one, in which a slit rheometer was used and the viscous and elastic properties

were described. However, this paper did not treat the analytical expression of $\eta_r - \phi$ relationship.

Our paper presents the viscous properties of calcium carbonate filled-polyethylene (CE-series) and -polystyrene (CS-series). The main object of this work is to examine whether an asymptotic value of η_r defined in the previous paper (1) can be determined in the range of shear stress (or shear rate) not so high whether the $(\eta_r)_l - \phi$ relationship of the systems differs from those reported in the previous paper. Furthermore, the yield stress of the CC filled system will be considered.

2. Experimental

2.1. Materials

A low density polyethylene powder ("Flowthene" G 701, Seitetsu Kagaku Ind. Co. Ltd., MFR (190 °C, 2.16 kg) = 7.8) and a polystyrene powder ("Styron" 666, Asahi Dow Co. Ltd., MFR (200 °C, 5 kg) = 9.4)) were used. Both polymers are the same as those used in the previous study (1).

Calcium carbonate (CC) powder (Kanto Kagaku Co. Ltd.) was used after drying in the air oven. The microscopic observation of the powder showed that the particles were approximated by spheres with an average diameter of about 2 μm, though the surface of it was rather rough. – The microscopic photograph of the powder is presented in a separate paper (5).

Weighed amounts of polymer powder and CC powder were mixed thoroughly, and this dry blend was moulded into a plate with 3 mm thickness, from which test pieces for cone-plate viscometer were cut. The samples for the capillary viscometer were prepared by cutting

the plate into the size of about 2 mm × 4 mm. The weight fraction (W) of CC was determined by ignition of the sample after having been tested. The volume fraction ϕ was calculated from densities of both components and W.

Table 1 shows ϕ of the samples together with some of the results.

Table 1. Volume fraction ϕ, shift factor f, limiting relative viscosity $(\eta_r)_l$, and yield stress σ_y

Code	ϕ	f	$(\eta_r)_l$	σ_y (dyne/cm²)
CE-1	0.035	1.1	1.1	9
CE-2	0.069	1.45	1.45	9
CE-3	0.128	1.85	1.85	16
CE-4	0.162	2.2	2.2	120
CE-5	0.228	5.4	5.5	100
CE-6	0.304	10.0	10.0	225
CS-1	0.037	1.1	1.1	
CS-2	0.092	1.9	1.8	
CS-3	0.156	2.1	2.3	
CS-4	0.196	3.4	3.6	
CS-5	0.281	8.0	8.0	

2.2. Viscometry

A cone-plate viscometer ("Rheometer RM-1", Shimazu Seisakusho Co. Ltd.) was used through this work. The cone had a radius of 2.5 cm and an angle of 4°, and was truncated at the tip by 175 μm. The rate of shear ranged from 0.0075 to 30 sec⁻¹; the range was, however, limited to the lower region for CS-series and for highly filled samples. The viscosity measurement was carried out at 200 ± 0.2 °C. The reproducibility of the results was good in the middle but poor in the lower region of shear rate. One data point in the flow curve such as shown in figure 1 was obtained by averaging three data determined on separate test pieces. The corresponding value of ϕ was also the averaged one.

A capillary extrusion viscometer ("Koka Flow Tester", Shimazu Seisakusho Co. Ltd.) was used for CE-series to extend the flow curve to the higher region of shear rate (or shear stress), Three flat dies with the radius of 0.5 mm and l/d of 10, 6, and 2 were used. In the separate paper (5), it is described that the diameter of the die did not affect the flow curve for CC filled polyethylene. The same was reported in the recent paper of *Chan* et al. (6) on the

rheological properties of glass fiber filled polyethylene and polystyrene.

According to the ordinary procedure of the analysis of the capillary extrusion data, the end correction and the Rabinowitsch correction were made, and the relation between the shear stress σ and shear rate $\dot{\gamma}$ in the higher region of shear rate (or shear stress) was determined.

3. Results and discussion

3.1. Flow curves

Figure 1 shows plots of $\log \sigma$ vs. $\log \dot{\gamma}$ of CS-series. The data points of each sample, except several points in the lower shear rate region, can be superimposed on those of the unfilled
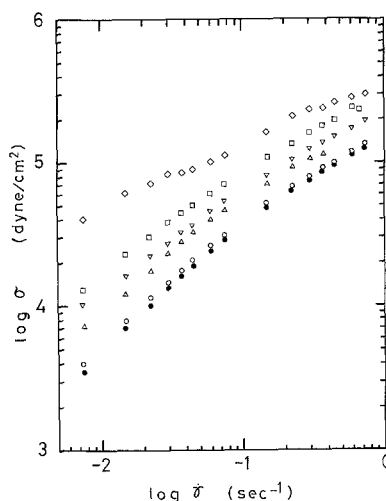
Fig. 1. Relations between $\log \sigma$ and $\log \dot{\gamma}$ for CS series; volume fractions of calcium carbonate are 0 (●), 0.037 (○), 0.092 (△), 0.156 (▽), 0.196 (□), and 0.281 (◊), respectively

polymer by horizontal shift as shown in figure 2. The shift factor f is presented in table 1. With increasing ϕ, the deviation from the reference curve of the points in the lower $f\dot{\gamma}$ region becomes larger and also the occurrence of the deviation shifts to right i.e. to higher stress. These may be attributed to the formation of some aggregates which resist to flow. With increasing ϕ, a larger force is required to separate the aggregates into "bare" particles. The meaning of the "bare" particle will be further considered in the next section.

Figure 3 shows the results for CE-series. In this figure capillary extrusion data are shown as the filled points, each of them denotes an
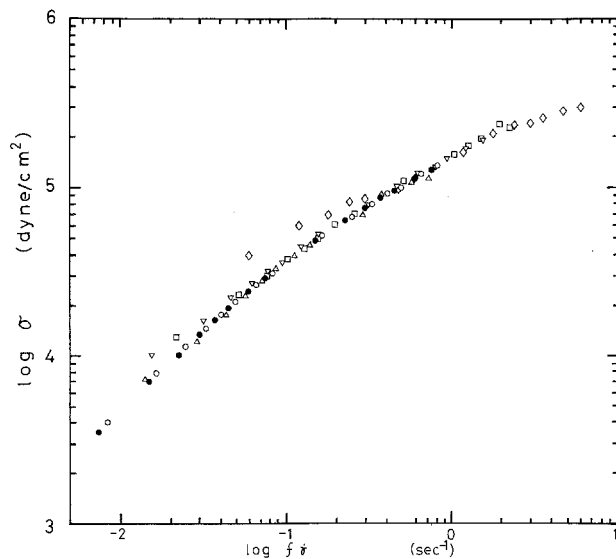
Fig. 2. Master flow curve of CS series; marks are the same as in figure 1
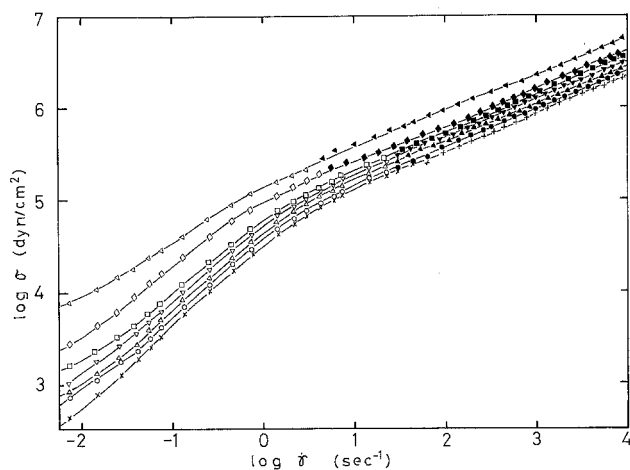

Fig. 3. Flow curves of CE series; volume fractions of calcium carbonate are 0 ($\times$, $+$), 0.035 ($\bigcirc$, $\bullet$), 0.069 ($\triangle$, $\blacktriangle$), 0.128 ($\triangledown$, $\blacktriangledown$), 0.162 ($\square$, $\blacksquare$), 0.228 ($\lozenge$, $\blacklozenge$), and 0.304 ($\triangleleft$, $\blacktriangleleft$), respectively. $\times$ and the open marks denote the data obtained by a cone-plate viscometer and $+$ and the filled marks those obtained by capillary extrusion viscometer

averaged one of several data in the neighbourhood of that point. As is shown in this figure, a few capillary data points, especially for CE-6, deviate rather from the smooth extension of the cone-plate data (open points). This deviation may be attributed to experimental errors, and the curves drawn in figure 3 are used for the calculation of the relative viscosity described in the next section. The flow curve of each sample can be superimposed on that of the

unfilled polyethylene by horizontal shift, though not shown. The shift factors are presented in table 1.

3.2. $(\eta_r)_l - \phi$ relationship

The applicability of the superimposition of the flow curves such as shown in figure 2 suggests the possibility of the superimposition of the relation of $\log \eta$ vs. $\log \sigma$ by vertical shift along the η-axis. Therefore, a constant or, at least, an asymptotic value of the relative viscosity $(\eta_r)_l$ will be obtained, if η_r is defined as the ratio of the viscosity of the filled polymer to that of the unfilled polymer at the same shear stress. Such was acsertained in the previous paper (1).

Figure 4 shows the plots of $\log \eta_r$ vs. $\log \dot{\gamma}$ of the CS-series. Note that the $\log \eta_r$-axis is rather enlarged. Results for CE-series are shown in figure 5, where data obtained from the capillary flow are shown as filled points. Some points of the capillary flow data, especially for CE-6, show irregular deviations. These are considered to be due to experimental errors, and the lines drawn in the figure are used to estimate $(\eta_r)_l$. From figures 4 and 5, it may be concluded that
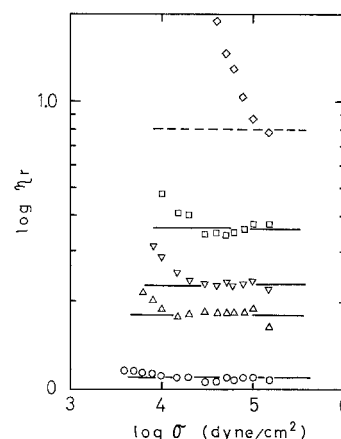

Fig. 4. Relations between $\log \eta_r$ and $\log \sigma$ for CS series; marks are the same as in figure 1

$(\eta_r)_l$ can be determined in the range of shear stresses below 10^5 dyne/cm^2. The value of $(\eta_r)_l$ is listed in table 1. It is a matter of course that $(\eta_r)_l$ is nearly equal to the shift factors described in the preceeding section.

Logarithm of $(\eta_r)_l$ thus obtained are plotted against ϕ as shown in figure 6, where data points in the previous papers (1, 5) are also
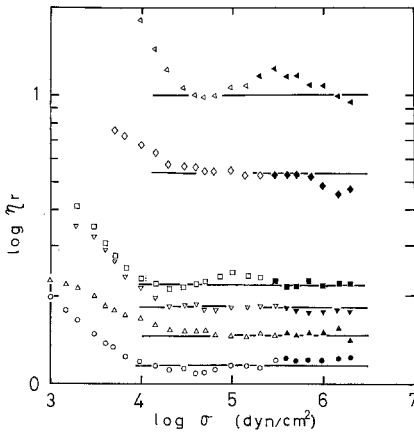
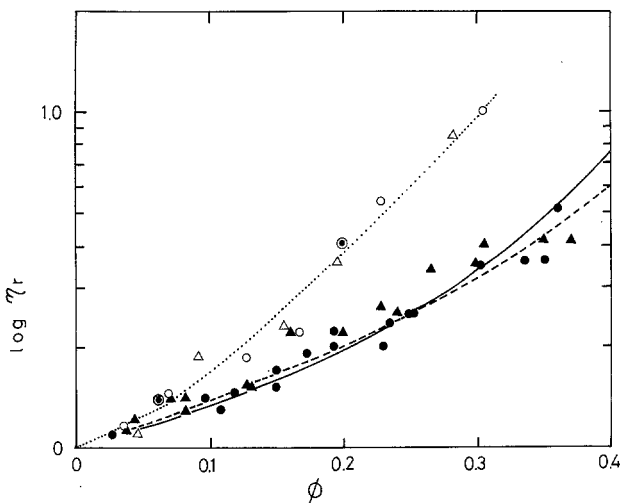Fig. 5. Relations between $\log \eta_r$ and $\log \sigma$ for CE series; marks are the same as in figure 3

Fig. 6. Relations between $\log (\eta_r)_1$ and ϕ for CE series (○) and CS series (△), other marks are results from previous papers (1, 5); calcium carbonate filled polyethylene (5) (◉), glass beads or glass balloons filled-polyethylene (1) (●) and -polystyrene (1) (▲). The solid and the broken lines represent the relations (2, 3); i.e. $\eta_r = (1 - \phi/0.68)^{-2}$ and $\eta_r = \exp(2.5\,\phi/(1 - 1.25\,\phi))$, respectively

shown. The solid line and the broken line, which represent rather well the data points of GB or GA filled-polymer, are those calculated by eqs. [1] (2) and [2] (3), respectively, where ϕ_0 in eq. [1] is set to 0.68 and k in eq. [2] to 1.25:

$$\eta_r = \left(1 - \frac{\phi}{\phi_0}\right)^{-2}, \qquad [1]$$

$$\eta_r = \exp(2.5\,\phi/(1 - k\phi)). \qquad [2]$$

The results of CE and CS series roughly make a single curve (the dotted line) and they are

higher than those of polymer melts filled with glass beads or glass balloons. The higher value of $(\eta_r)_l$ of CC filled polymer melts may be attributed to the small size and rough surface of the CC powder. Eq. [1] can represent roughly the dotted line by setting $\phi_0 = 0.44$, but eq. [2] cannot do even if using various values of k. Thus, eq. [1] seems to have a wider applicability than eq. [2]. However, the value of 0.44 of ϕ_0 seems unrealistic because ϕ_0 is the value (2) of the densest packing fraction of the filler. Thus, it is assumed here that the increase of $(\eta_r)_l$ is due to the increase of the apparent volume of the CC powder and this increase of the volume is attributed to the formation of a fixed layer of the polymer on the rough surface of CC particles. The thickness of the fixed polymer layer was estimated as follows: It is assumed that there are not fixed polymer layers on the GB or GA particles and the solid line in figure 6 (which represents the result of GB or GA filled system) is taken as a reference curve. Then, the value of η_r of CC filled system at $\phi = 0.2$, e.g., corresponds to that of $\phi = 0.32$ on the reference curve. If the thickness of the fixed polymer layer is x μm and the CC particle is approximated as a sphere with diameter of 2 μm, then

$$(2 + 2x)^3 \times 0.2 = 2^3 \times 0.32$$

from which $x = 0.17$ μm is obtained. If the calculation is made with another ϕ, x can be calculated as $0.15 \sim 0.17$ μm. The particle covered with this fixed polymer layer is the "bare" particle described in the preceeding section. This fixed polymer layer resists to separate into pure polymer and CC particle as far as it stays in the range of shear rate investigated here.

3.3. Yield stress

The yield stress σ_y of the CE series was estimated from the Casson's plots. That of the CS series was not estimated because of rather far extrapolation. The logarithm of σ_y is plotted against ϕ in figure 7, where the result of polyethylene filled with GB or GA in the previous paper (1) are also shown. The value of σ_y of CC filled polyethylene is higher than that of GB or GA filled one and seems to increase exponentially with ϕ. However, more data points may be necessary to find an explicit expression of the ϕ dependence of σ_y. This subject will be investi-

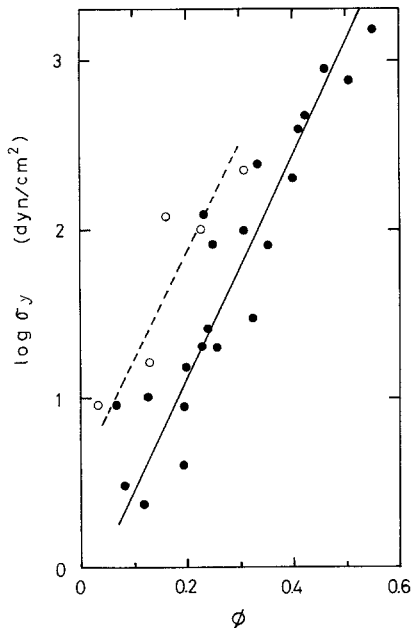Fig. 7. Dependence of σ_y on ϕ for CE series (○); filled points designate σ_y of glass beads or glass balloons filled polyethylene (1)

gated in our laboratory over a wider class of dispersed systems.

Summary

The viscous properties of calcium carbonate filled polyethylene and polystyrene melts were examined. The relative vircosity η_r defined in the previous paper gave an asymtptotic value $(\eta_r)_l$ in the range of the shear stress below 10^5 dyne/cm². $(\eta_r)_l$ of the calcium carbonate filled system was higher than that of the glass beads or glass balloons filled system at the same volume fraction of the filler ϕ. Maron-Pierce equation with $\phi_0 = 0.44$ was able to approximate the $(\eta_r)_l - \phi$ relationship. However, it was deduced here that the high value of $(\eta_r)_l$ of calcium carbonyl filled system was due to the apparent increase of ϕ and this increase was attributed to the fixed polymer layer formed on the powder particle. By assuming the particle as a sphere with a diameter of 2 μm, the thickness of the fixed polymer layer was estimated as about 0.17 μm.

The yield stress estimated from the Casson's plots increased exponentially with ϕ.

Zusammenfassung

Es wurden die viskosen Eigenschaften von Polyäthylen- und Polystyrol-Schmelzen untersucht, die mit Kalziumkarbonat-Teilchen gefüllt waren. Für die relative Viskosität η_r, wie sie in einer vorangegangenen Veröffentlichung definiert worden war, ergab sich bei Schubspannungen unterhalb 10^5 dyn/cm² ein asymptotischer Wert $(\eta_r)_l$. Dieser war bei den mit Kalziumkarbonat gefüllten Schmelzen höher als bei Schmelzen, die bis zur gleichen Volumenkonzentration ϕ mit Glaskugeln oder Glasballons gefüllt waren. Die $(\eta_r)_l - \phi$-Abhängigkeit ließ sich durch eine Gleichung nach *Maron und Pierce* mit $\phi_0 = 0,44$ beschreiben. Es wurde jedoch geschlossen, daß der hohe $(\eta_r)_l$-Wert der mit Kalziumkarbonat gefüllten Schmelzen auf eine scheinbare Zunahme von ϕ zurückzuführen ist, verursacht durch eine feste Polymerschicht auf der Teilchenoberfläche. Unter Annahme kugelförmiger Teilchen mit einem Durchmesser von 2 μm ließ sich die zugeordnete Schichtdicke zu 0,17 μm abschätzen. Die mittels der Casson-Beziehung geschätzte Fließspannung ergab eine exponentielle ϕ-Abhängigkeit.

References

1) *Kataoka, T., T. Kitano, M. Sasahara, K. Nishijima*, Rheol. Acta **17**, 149 (1978).
2) *Maron, S. H., P. E. Pierce*, J. Colloid Sci. **11**, 80 (1956).
3) *Mooney, M.*, J. Colloid Sci. **6**, 162 (1951).
4) *Han, C. D.*, J. Appl. Polym. Sci. **18**, 821 (1974).
5) *Kitano, T., T. Kataoka, M. Sasahara, K. Nishijima*, Senkoken-ho No. 121 (in press).
6) *Chan, Y., J. L. White, Y. Oyanagi*, J. Rheol. **22**, 507 (1978).

Authors' addresses:

Prof. *T. Kataoka*, Dr. *T. Kitano, M. Sasahara*
Research Institute for Polymers and Textiles
1-1-4 Yatabe-Higashi, Tsukuba,
Ibaraki Pref. 300-21 (Japan)

Dr. *Y. Oyanagi*
Kogakuin University
1-24-2, Nishishinjuku, Shinjuku-ku
Tokyo (Japan)