Research Institute for Polymers and Textiles, Yokohama (Japan)

Viscosity of particle filled polymer melts

T. Kataoka, T. Kitano, M. Sasahara, and *K. Nishijima*

With 13 figures and 2 tables

1. Introduction

The rheological behavior of concentrated suspensions in polymer melts has recently been a subject of large interest owing to the increasing use of composite materials. To search for the application of "silas balloons" (glassy micro balloons developed by National Industrial Research Institute of *Kyushu* (1)) to composite materials, we made, several years ago, studies (2, 3) on viscous properties of silas balloon filled polystyrene. It was concluded that the flow curves could be superimposed with respect to temperature (2) and concentration of filler (3). However, viscosity-concentration relationship was treated only qualitatively and was not determined as a unique function.

The shear rate dependence of the viscosity of a suspension of particles in a non-Newtonian medium is complicated because the non-Newtonian property of the medium is superimposed on the non-Newtonian effect due to the suspended particles. While many studies (4–8) have been made on rheological properties of such suspensions and succeeded in clarifying some behaviors characteristic of the systems,

there remained some uncertainty about the relative viscosity-concentration relationship, because the relative viscosity is not constant but decreases with shear rate.

This paper presents experimental results of the viscosity of particles filled-polymer melts. Main object of this study is to correlate relative viscosity with concentration of filler and to test the applicability of equations (9, 10) which proved to be successful for predicting the relative viscosity-concentration relationship of suspensions of particles in a Newtonian liquid, to the present results.

2. Experimental

2.1. Polymers

A low density polyethylene powder ("Flowthene" G 701 N, 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, 5.0 kg) = 9.4) were used.

2.2. Fillers

Fillers used were glass beads, glass balloons and silas balloons listed in table 1. Glass beads and glass balloons were sieved and silas balloons were used

Table 1. Fillers

Type	Density [g/cm³]	Code	Symbol in figs. 11, 12, 13	Average diameter [μ]	Standard deviation
Glass bead	2.520	BES	●	36.0	5.47
		BEM	▲	68.2	6.13
		BEL	▼	99.8	7.86
Glass balloon	0.2782	BAS	○	52.9	7.70
		BAM	△	73.8	8.66
Silas balloon	0.36	SLB	▽	124.3	34.4

10*

without sieving. Fractions listed in table 1 were chosen in this study. The glass beads and glass balloons were spherical but silas balloon deviated slightly from spherical shape. Estimations of particle size distribution were made by measuring the size of particles on enlarged photographs. Results are shown in table 1 and figure 1. The size distribution was somewhat broader for glass balloons than for glass beads. This was attributed to the light sieving to avoid the break of balloons.
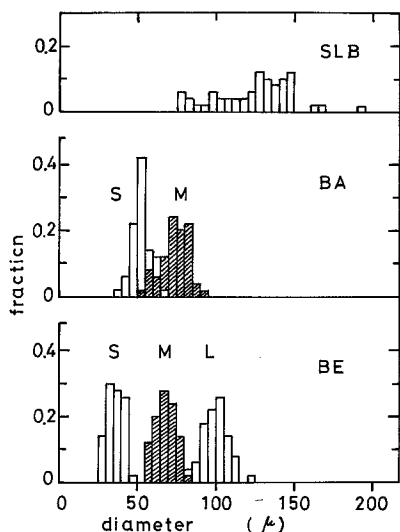

Fig. 1. Histogram of particle size of glass beads (BE), glass balloons (BA), and silas balloons (SLB)

2.3. Samples

Weighed amounts of filler and polymer powder were mixed thoroughly, and then this dry blend was moulded into a plate (150 × 150 × 0.5 mm), from which test pieces were cut. The content of filler was determined by ignition of the sample after having been tested. The volume fraction ϕ of the filler in the sample was calculated from densities of both components. By suspending the ignition-residue in water, it was found that the balloons in the test piece did not break during test as long as ϕ was smaller than about 0.4.

2.4. Viscometry

A cone-plate viscometer (Rheometer RM-1, Shimazu Seisakusho Co. Ltd.) was used. The cone had a radius of 2.5 cm and an angle of 4°, and was truncated at the tip by 175 μ. Viscosity measurements were carried out at 200 ± 0.2 °C. The rate of shear ranged from 0.0075 s^{-1} to 30 s^{-1}. The range was, however, limited to the lower region for polystyrene series and highly filled-samples. The reproducibility of results was good in the middle but poor in the lower region of shear rate. One data point in the flow curve such as in figure 2 was obtained by averaging three points determined on separate test pieces. The corresponding value of ϕ was also the averaged one.

3. Results and discussion

3.1. Superposition of flow curves

Figures 2 and 3 are doubly logarithmic plots of viscosity (η) vs. shear rate ($\dot{\gamma}$) for some of BEM/PE and BAS/PE series, respectively (for codes see table 2). Smooth curves are drawn in these figures. Figures 2 and 3 show typical features characteristic of suspensions in which a non-Newtonian liquid is the medium. A sharp increase in viscosity with decreasing $\dot{\gamma}$ in the lowermost region of $\dot{\gamma}$ is due to the suspended particles (4, 6). This feature is more evident for balloon filled systems than for bead filled systems and diminishes with decreasing ϕ. The appearence of an inflection point in a flow curve is attributed to the superposition of the non-Newtonian property due to suspended particles on that of the medium. Figure 4 shows results of BAS/PS series. In contrast to filled polyethylene, the sharp viscosity increase with decreasing ϕ is not clear even for the highest filled sample. This may be attributed to the shear rate being too high to let this feature appear.
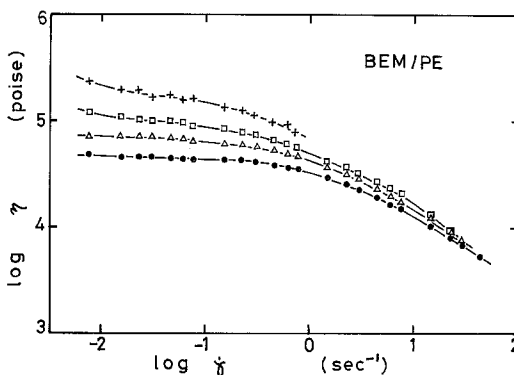

Fig. 2. Flow curves of BEM/PE series, symbols (●) represent polyethylene, all others are listed in table 2
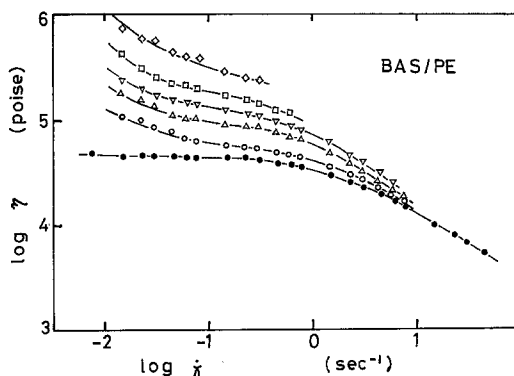

Fig. 3. Flow curves of BAS/PE series, symbols (●) represent polyethylene, all others are listed in table 2
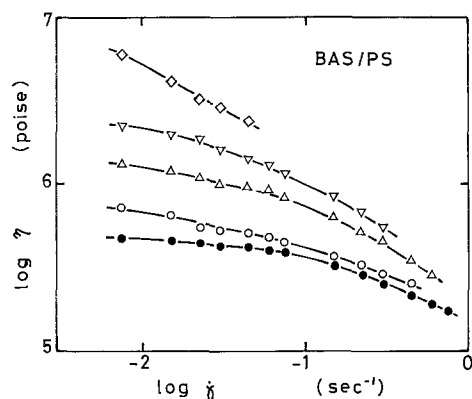
Fig. 4. Flow curves of BAS/PS series, symbols (●) represent polystyrene, all others are listed in table 2

To show all data in a condensed form, the superposition procedure (3) is applied, i.e., logarithm of reduced viscosity $(\sigma_s / f \dot{\gamma})$, ratio of shear stress to reduced shear rate, f: shift factor) is plotted against logarithm of reduced shear rate $(f \dot{\gamma})$. This has been done in figures 5, 6, 7 and 8, where results of all series are presented. To avoid confusion, data of unfilled-polymers are not shown. Shift factors are listed in table 2. The superposition of data in the middle range of $f \dot{\gamma}$ is fairly good for all series. The deviation of points from the master curve in the lower $f \dot{\gamma}$ region, which is striking for highly filled polyethylene, is attributed to the non-Newtonian effect due to the suspended particles.

Table 2. Volume fractions of samples

| Sample designation	Symbol in figs. 2–10	Volume fraction (%)	Shift factor f	Sample designation	Symbol in figs. 2–10	Volume fraction (%)	Shift factor f
PE series				PS series			
BES/PE-1	○	3.4	1.12	BES/PS-1	○	3.6	1.1
BES/PE-2	△	6.0	1.2	BES/PE-2	△	8.2	1.25
BES/PE-3	▽	11.8	1.4	BES/PS-3	▽	13.0	1.45
BES/PE-4	□	19.2	2.1	BES/PS-4	□	20.0	2.0
BES/PE-5	◇	23.5	2.2	BES/PS-5	◇	30.5	3.6
				BES/PS-6	+	35.0	4.4
BEM/PE-1	○	2.6	1.1	BEM/PS-1	○	4.3	1.1
BEM/PE-2	△	9.6	1.45	BEM/PS-2	△	8.1	1.3
BEM/PE-3	▽	15.0	1.6	BEM/PS-3	▽	13.0	1.4
BEM/PE-4	□	19.2	2.0	BEM/PS-4	□	22.8	2.7
BEM/PE-5	◇	25.2	2.6	BEM/PS-5	◇	30.0	3.2
BEM/PE-6	+	33.5	4.0	BEM/PS-6	+	42.0	6.2
				BEL/PS-1	○	3.4	1.12
				BEL/PS-2	△	7.0	1.3
				BEL/PS-3	▽	16.0	1.9
				BEL/PS-4	□	24.0	2.3
				BEL/PS-5	◇	26.5	3.3
				BEL/PS-6	+	37.0	4.0
BAS/PE-1	○	10.8	1.35	BAS/PS-1	○	13.0	1.22
BAS/PE-2	△	25.0	2.5	BAS/PS-2	△	26.5	2.9
BAS/PE-3	▽	30.2	3.6	BAS/PS-3	▽	45.0	5.0
BAS/PE-4	□	36.0	5.0	BAS/PS-4	□	44.0	6.0
BAS/PE-5	◇	45.2	11.0	BAS/PS-5	◇	50.8	12.0
BAM/PE-1	○	15.0	1.6	BAM/PS-1	○	8.4	1.6
BAM/PE-2	△	23.0	2.2	BAM/PS-2	△	27.5	2.9
BAM/PE-3	▽	35.0	4.0	BAM/PS-3	▽	43.3	6.8
BAM/PE-4	□	42.0	7.0				
SLB/PE-1	○	8.4	1.3	SLB/PS-1	○	8.4	1.1
SLB/PE-2	△	14.0	1.6	SLB/PS-2	△	27.5	2.4
SLB/PE-3	▽	36.0	3.2	SLB/PS-3	▽	38.5	4.6
SLB/PE-4	□	41.0	4.6	SLB/PS-4	□	47.5	7.7
SLB/PE-5	◇	50.0	7.4				
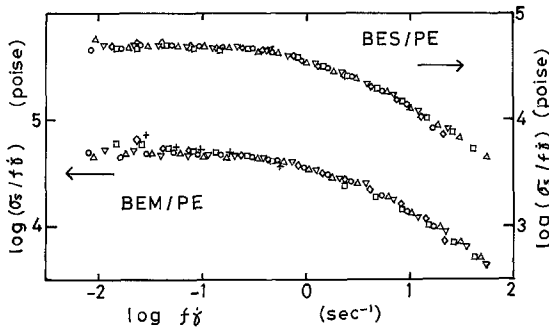
Fig. 5. Master flow curve of polyethylenes: filled with beads. See table 2 for symbols
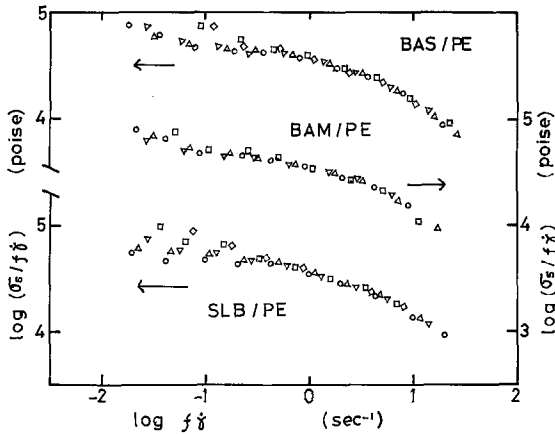

Fig. 6. Master flow curve of polyethylenes filled with balloons. See table 2 for symbols
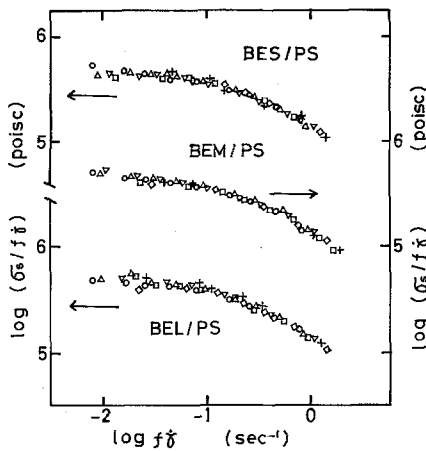

Fig. 7. Master flow curve of polystyrenes filled with beads. See table 2 for symbols
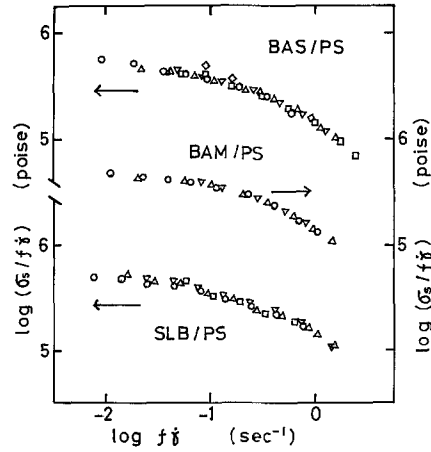

Fig. 8. Master flow curve of polystyrenes filled with balloons. See table 2 for symbols

relative viscosity η_r and volume fraction ϕ of filler up to $\phi \approx 0.5$. For suspensions in which a non-Newtonian liquid is the medium, it is said (11, 12) that η_r should be taken as the value at infinite shear rate, $(\eta_\infty)_r$. However, the use of $(\eta_\infty)_r$ is not realistic since the estimation of η_∞ (viscosity at infinite shear rate) is difficult especially for polymer melts.

Figure 9 shows relative viscosities as functions of shear rate for four series, where η_r is taken as the ratio of viscosity of filled polymer to that of unfilled polymer at the same shear rate.

3.2. Relative viscosity-concentration relationship

For suspensions in which a Newtonian liquid is the medium, several equations (9–11) were successful to represent the relation between
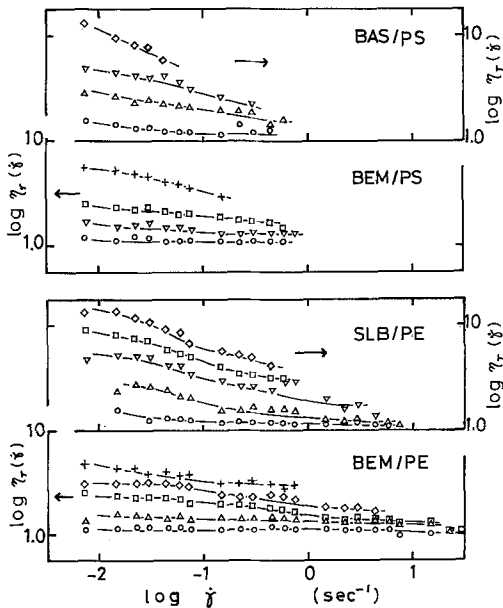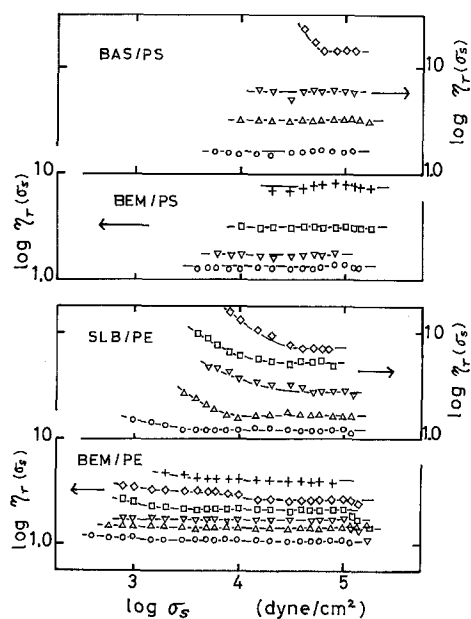

Fig. 9. Relations between log η_r and log $\dot{\gamma}$; η_r is defined as viscosity ratio of filled to unfilled polymer at the same $\dot{\gamma}$.

Fig. 10. Relations between $\log \eta_r$ and $\log \sigma_s$; η_r is defined as viscosity ratio of filled to unfilled polymer at the same σ_s

With increasing $\dot{\gamma}$, η_r decreases rapidly in the lower region of $\dot{\gamma}$ and gradually in the middle range of $\dot{\gamma}$; an asymptotic value is not obtained for highly filled samples.

On the other hand, the applicability of superposition of flow curves such as in figure 5 shows the possibility of the superposition of the relation of log (viscosity) vs. log (shear stress) by vertical shift along the viscosity axes. Therefore, a constant or, at least, an asymptotic value of relative viscosity will be obtained, if a relative viscosity is defined as the ratio of viscosity of filled sample to that of unfilled sample at the same shear stress. Hereafter, this definition of η_r is used. In figure 10, logarithms of relative viscosity are plotted against logarithm of shear stress for the same systems as in figure 9. Nearly constant or asymptotic values of η_r are obtained even for highly filled samples, as expected. Thus, η_r of a sample with a definite ϕ is determined as a unique value. The value η_r thus obtained is, of course, nearly the same as the shift factor in table 2.

In figure 11, logarithm of relative viscosity is plotted against ϕ. Data except SLB series can be roughly approximated by a curve, and there seems no tendency which reflects the difference of the particle size, particle rigidity (or mass), or suspending medium. The low value at each ϕ

for the SLB filled-sample may be attributed to the broad distribution of particle size. The solid lines and broken lines in this figure are drawn according to eq. [1] (9) with $\phi_0 = 0.68$ and eq. [2] (10) with $k = 1.25$, respectively, where ϕ_0 and k are constants relating to packing geometry:

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

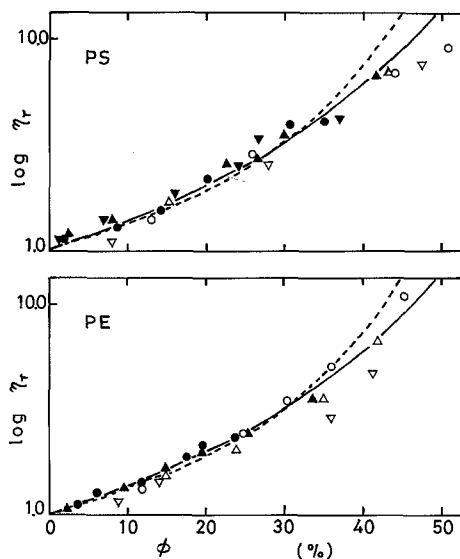$$\eta_r = \exp\left(\frac{2.5\,\phi}{1 - k\,\phi}\right). \qquad [2]$$

Fig. 11. Relations between $\log \eta_r$ and $\log \phi$; η_r is estimated from plots such as in figure 10. The solid line represents the relation $\eta_r = (1 - \phi/\phi)^{-2}$ and the broken line $\eta_r = \exp[2.5\,\phi/(1 - 1.25\,\phi)]$

If constants (in those equations) corresponding to broad size distribution are used, the calculated lines shift to lower positions than in figure 11.

Thus, we find that eq. [1] or eq. [2] predict the η_r vs. ϕ relationship fairly well, at least in the region of ϕ below 0.4 or so. Data at high ϕ are not precise enough to decide which equation fits better. Both eqs. [1] and [2] seem to be superior to others such as those derived by *Thomas* (11) since they include only one constant relating to the packing geometry.

3.3. Yield stress

While there are some uncertainties about the presence of a true yield stress for suspension in which the suspended particles are not small enough for colloidal interaction, an apparent

yield stress σ_y is, in most cases, present with highly filled material, if Casson plots (13) are made. Figure 12 shows plots according to *Casson*'s equation for four series of data of filled polyethylene. Data of BES/PE with $\phi = 0.034$ give a line with intercept nearly zero, which means the yield stress of the sample is nearly zero. With increasing ϕ, σ_y increases. There were some series of data in which Casson plots did not give a straight line. Such data were omitted
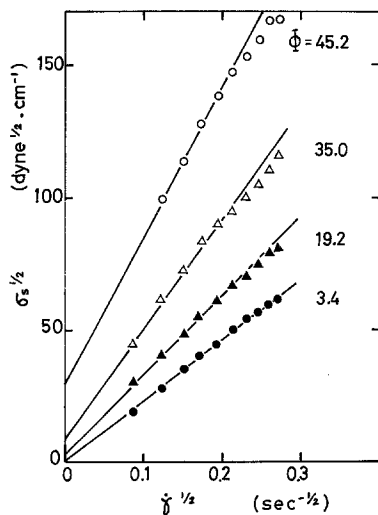

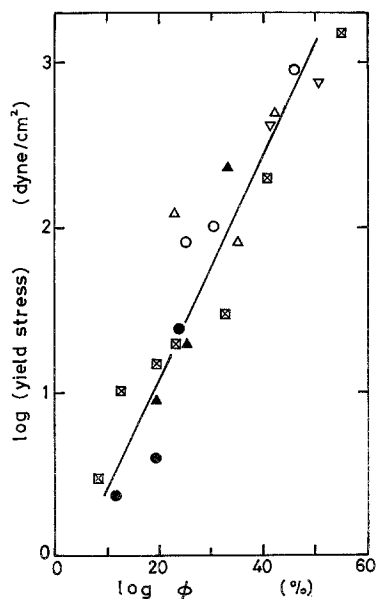Fig. 12. Casson plots for BES/PE — / (○), BEM-4 (▲), BAS/PE-5 (○), and BAM/PE-3 (△).

Fig. 13. Dependence of σ_y on ϕ. ⊠ represent earlier data (SLB/PS). Other symbols are those in table 2

here without further consideration. Data for filled polystyrenes were also not treated because the shear stress was too high to allow a reasonable extrapolation.

Figure 13 shows the plots of $\log \sigma_y$ against ϕ. In this figure, earlier data (2) for SLB/PS are also shown. The line calculated by the least square method is applied to points in the range of $0.1 \le \phi \le 0.5$. It may be mentioned that σ_y increases exponentially with ϕ in the range of $0.1 \le \phi \le 0.5$, although the functionality should break at $\phi = 0$ and $\phi = \phi_0$. Approximate values of σ_y are $10\,\mathrm{dynes/cm^2}$ at $\phi = 0.2$ and $1000\,\mathrm{dynes/cm^2}$ at $\phi = 0.5$. These values seem to hold for filled polymer melts in which the particle diameter ranges from several tens up to a few hundred microns.

4. Conclusion

This paper presents the viscosity of dispersions of various particles in polyethylene and polystyrene melts. To correlate the relative viscosity η_r with the volume fraction ϕ of the particles, it was suggested to take the relative viscosity as a ratio of viscosity of filled polymer to that of unfilled polymer at the same shear stress. According to this definition, an asymptotic η_r is determined. The η_r vs. ϕ relationship for these dispersions can be predicted well by the equations derived by *Maron* and *Pierce* or by *Mooney*. It is mentioned that only the particle size-distribution had an effect on η_r, within a particle size range from several tens to a few hundreds microns.

An apparent yield stress σ_y was estimated and it could be shown that σ_y increased exponentially with ϕ in the range of $0.1 \le \phi \le 0.5$.

Summary

Viscosities of particle filled polymer melts were measured at fairly low shear rate. Particles were glass beads, glass balloons, and silas balloons. Polymers were polyethylene and polystyrene. Flow curves were superimposed with respect to concentration of filler. The relative viscosity defined as the ratio of viscosity of filled polymer to that of unfilled polymer at the same shear stress is obtained as an asymptotic value even for highly filled material. The relation between relative viscosity and volume fraction of filler was represented by the equations derived by *Maron* and *Pierce* or *Mooney*. Only the distribution of particle size had influence on relative viscosity at a defined filler concentration. Yield stresses were estimated, and found to increase exponentially in the range of volume fraction from 0.1 to 0.5.

Zusammenfassung

Viskositäten von Polymerschmelzen, die mit Teilchen gefüllt worden waren, wurden bei mittleren Schergeschwindigkeiten bestimmt. Als Teilchen wurden Voll- und Hohlkugeln aus Glas, sowie sog. „silas balloons", als Polymere Polyäthylen und Polystyrol verwendet. Die Fließkurven für verschiedene Füllstoffkonzentrationen wurden überlagert. Die relative Viskosität, definiert als das Verhältnis der Viskositäten von gefülltem und ungefülltem Polymer bei gleicher Schubspannung, besitzt einen asymptotischen Wert selbst für hoch gefülltes Material. Die Beziehung zwischen relativer Viskosität und Füllstoff-Volumenkonzentration läßt sich durch eine von *Maron* und *Pierce* oder eine von *Mooney* abgeleitete Gleichung beschreiben. Nur die Teilchengrößenverteilung hat bei einer definierten Füllstoffkonzentration einen Einfluß auf die relative Viskosität. Fließspannungen werden abgeschätzt und dafür in einem Konzentrationsbereich zwischen 0,1 und 0,5 ein exponentieller Anstieg gefunden.

References

1) *Isahaya, Y., K. Kimura, K. Jinnai*, Kogyo Zairyo **19**, 84 (1971).

2) *Kataoka, T., S. Ueda, R. Onooka, K. Nishijima*, Kobunshi Kagaku ("Chemistry of High Polymer" in Japan) **30**, 260 (1973).

3) *Kataoka, T., K. Nishijima*, Kobunshi Ronbunshu **32**, 501 (1975).

4) *Matsumoto, T., A. Takashima, T. Masuda, S. Onogi*, Trans. Soc. Rheology **14**, 617 (1970).

5) *Mills, N. J.*, J. Appl. Polym. Sci. **15**, 2791 (1971).

6) *Nicodemo, L., L. Nicolais*, J. Appl. Polym. Sci. **18**, 2809 (1974).

7) *Dubois, D., D. Dubos, G. Evrard*, Rheol. Acta **13**, 658 (1974).

8) *Angerer, G., D. Wolff*, Rheol. Acta **15**, 57 (1976).

9) *Maron, S. H., P. E. Pierce*, J. Colloid Sci. **11**, 80 (1956).

10) *Mooney, M.*, J. Colloid Sci. **6**, 162 (1951).

11) *Thomas, D. G.*, J. Colloid Sci. **20**, 267 (1965).

12) *Cross, M. M.*, Rheol. Acta **14**, 402 (1975).

13) *Casson, N.*, in: *C. C. Mill* (ed.), Rheology of Disperse Systems, p. 84 (Pergamon Press, London 1959).

Authors' address:

Prof. *T. Kataoka* et al.
Research Institute for Polymers and Textiles
Sawatari 4, Kanagawa-ku
Yokohama 221 (Japan)