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 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

<table>
<thead>
<tr>
<th>Type</th>
<th>Density [g/cm³]</th>
<th>Code</th>
<th>Symbol in figs. 11, 12, 13</th>
<th>Average diameter [μm]</th>
<th>Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass bead</td>
<td>2.520</td>
<td>BES</td>
<td>●</td>
<td>36.0</td>
<td>5.47</td>
</tr>
<tr>
<td></td>
<td></td>
<td>BEM</td>
<td>▲</td>
<td>68.2</td>
<td>6.13</td>
</tr>
<tr>
<td></td>
<td></td>
<td>BEL</td>
<td>▼</td>
<td>99.8</td>
<td>7.86</td>
</tr>
<tr>
<td>Glass balloon</td>
<td>0.2782</td>
<td>BAS</td>
<td>○</td>
<td>52.9</td>
<td>7.70</td>
</tr>
<tr>
<td></td>
<td></td>
<td>BAM</td>
<td>△</td>
<td>73.8</td>
<td>8.66</td>
</tr>
<tr>
<td>Silas balloon</td>
<td>0.36</td>
<td>SLB</td>
<td>▽</td>
<td>124.3</td>
<td>34.4</td>
</tr>
</tbody>
</table>
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 x 150 x 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 \( \phi \) 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 \( \phi \) 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 \( \mu \). 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 \( \phi \) 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 \( (\eta) \) 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 \( \phi \). The appearance 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 \( \phi \) 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