

## 충진제 입도가 현탁계의 점도에 미치는 영향: 2. 유리구-PVA 수용액계

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### Effect of Filler Particle Size on the Rheological Properties of Suspension: 2. Glass Bead Suspended in Aqueous PVA Solution

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**요 약 :** 수용성 폴리비닐 알콜(PVA)에 유리구를 현탁시킨 계의 점도 거동을 유리구의 농도, 입자 크기 및 입자크기분포를 변화시켜 조사하였다. PVA 수용액은 거의 뉴턴성을 나타내었으나 유리구의 함량이 증가할 수록 점차 비뉴턴성이 더 강하게 나타났다. 그리고 유리구의 함량이 높을 때 PVA-유리구 현탁계는 뚜렷한 항복응력을 나타내었다. 단일 분포 또는 다상분포에 상관없이 입자분포가 넓어짐에 따라 비점도는 낮아졌다. 즉 입자분포가 넓어짐에 따라 입자의 최대 충전률은 높아졌다.

**Abstract :** The viscosity behavior of polyvinyl alcohol (PVA) aqueous solution suspended with glass bead was examined in terms of glass bead concentration, particle size, and particle size distribution. Almost Newtonian viscosity behavior of PVA aqueous solution became more non-Newtonian with increasing glass bead content. At the high glass bead loadings, there was a clear evidence of yield stress for PVA-glass bead suspensions. The relative viscosity became lower for the wider particle size distribution for both monomodal and multimodal systems. In other words, the maximum packing fraction became higher for the wider particle size distribution.

## INTRODUCTION

Beginning with the classic work of Einstein,<sup>1</sup> for dilute suspension system there have been numerous rheological studies of suspensions contain-

ing rigid particles.<sup>2~33</sup> These studies include flow behavior of suspending medium (e. g., Newtonian vs. non-Newtonian), flow situation (shearing vs. elongational),<sup>11~13</sup> viscoelasticity,<sup>11,14,15</sup> particle size,<sup>16,17</sup> particle size distribution,<sup>17~21</sup> particle

shape and geometry,<sup>11, 22~28</sup> and interactions between particles and matrix.<sup>15, 29~33</sup> Despite of these many reports, there are very few rigorous theories for predicting the bulk rheological properties of suspensions. Nevertheless, we can draw several general conclusions from data published in the literatures including filled molten polymers.

(1) There appears to be no effect of particle size or the viscosity of suspension medium. In other words, for the monodispersed system, the relative viscosity (ratio of viscosity of suspension to that of suspending medium) is independent of particle size and fluid viscosity.

(2) The volumetric concentration of solid particles ( $\phi$ ) controls the viscosity of suspension.

(3) At very low range of solid concentration (less than  $\phi=0.04$ ), the Einstein equation may be an accurate representation of viscosity behavior of suspension.<sup>1</sup>

$$\eta_r = \frac{\eta}{\eta_s} = 1 + 2.5 \phi \quad (1)$$

In eq.(1),  $\eta_r$  is the relative viscosity,  $\eta$  the viscosity of suspension, and  $\eta_s$  the viscosity of suspending medium.

(4) As the solid concentration becomes higher, the particles are approached closer each other. At the densest packing of particles, the maximum packing fraction ( $\phi_m$ ), the viscosity rises to infinity.

(5) The particle size distribution has a big influence to the viscosity by allowing smaller particles fill-in between bigger particles. Therefore, the wider particle size distribution yields the lower viscosity at the same volume fraction and the higher maximum volume fraction.

There are many equations suggested to describe the viscosity-concentration relationship of suspension (refer to 34 for example). Among these, two equations are of particular interest; the Mooney equation<sup>2</sup> and the Brinkman-Roscoe equation.<sup>35,36</sup>

$$\text{Mooney}^2 \quad \log \eta_r = \frac{A\phi}{1-B\phi} \quad (2)$$

$$\text{Brinkman-Roscoe}^{35,36} \quad \eta_r = (1-\phi/B')^{-2.5} \quad (3)$$

The original form of eq.(2) gave  $A=2.50$  and  $1.33 \leq B \leq 1.91$ . The value of  $A$  is the Einstein constant and  $B$  is a reciprocal value between the simple cubic packing ( $\phi_m=0.524$ ) and the tetrahedral (body-centered cubic) packing ( $\phi_m=0.74$ ) for the monodispersed particles. However, treating the  $A$  value as unknown, one can determine  $A$  and  $B$  from the rearranged form of eq.(2).

$$\frac{\phi}{\log \eta_r} = \frac{1}{A} - \frac{B}{A} \phi \quad (4)$$

In other words, plot of  $\phi/\log \eta_r$  vs.  $\phi$  may be a straight line, from which  $A$  and  $B$  can be determined from intercept and slope, respectively. In fact, several workers<sup>37~39</sup> found that the Einstein constant varied with the particle size and particle size distribution. Another interesting point of eq.(2) or (4) is that the so-called "crowding factor"  $B$  is the reciprocal of maximum packing fraction,  $\phi_m$ , from which one can estimate the packing pattern of the known solid particles.

The simple eq.(3), the Brinkman-Roscoe equation,<sup>35,36</sup> was derived by extending the Einstein theory using a mean field approach. Eq.(3) in its exact form with a constant value of  $B'$  has found a limited use. A modified expression, with an exponent of 2 instead of 2.5, has been more useful in empirical correlations to suspensions.<sup>40,41</sup>

$$\eta_r = (1-\phi/B')^{-2} \quad (5)$$

Originally,  $B'$  in eq.(5) was reported to be 0.68 for suspensions of smooth spheres in a liquid. As with the  $B$  value ( $\equiv 1/\phi_m$ ) in eq.(2), however,  $B'$  in eq.(5) can also be varied.<sup>42,43</sup> In the limit of  $\phi \rightarrow 0$ , its contribution become minimal ( $B'=1$ ). But as  $\phi$  approaches to  $\phi_m$ ,  $B' \rightarrow \phi_m$ .

This obvious discrepancy in exponent and  $B'$  value was first understood by Robinson,<sup>44</sup> caused by the fractional increase of the effective volume of the rigid phase due to liquid entrapment between solid particles. Thus, for intermediate concentration, Tsenoglou<sup>45</sup> proposed the concentration dependent  $B'$  value as

$$B'(\phi) = 1 - (1-\phi_m) \frac{\phi}{\phi_m} \quad (6)$$

Variation of  $B$  in eq.(2) and  $B'$  in eq.(5) is attributable to particle packing pattern and particle size distribution as demonstrated by Farris<sup>19</sup> and others.<sup>17,20,21,43</sup> In fact, the relative viscosity of bimodal system (size ratio=10) is less than  $10^3$  at 75%  $\phi$  with 60~70% coarse particles. This 75%  $\phi$  is higher than  $\phi_m=0.74$  for the most tight packing (tetrahedral packing) of monodispersed system at which  $\eta_r$  becomes infinite.

In this continuous study, the viscosity behavior of glass bead filled aqueous polyvinyl alcohol solutions was examined in terms of glass bead size and size distribution.

## EXPERIMENT

### Materials

Polyvinyl alcohol(PVA) used in this study was manufactured by Denka Co. (Japan) having molecular weight ( $\bar{M}_w$ ) of 22,000 (B05, DP=500), 74,800 (B17, DP=1,700), and 105,000 (B24T, DP=2,400) with 87~89% hydrolysis. The glass bead (Union Co., Japan) had the specific gravity 2.5. Formulations and particle size distributions are given in Tables 1 and 2, respectively.

In Tables 1 and 2, three systems are monomodal (G-1, 5 and 6) with relatively narrow particle size distribution, one bimodal (G-2), and two trimodal (G-3 and 4). Further, G-2 to 5 have similar weight average particle size but different size distribution.

### Equipments

Particle size and size distribution were measured

**Table 1.** Experimental Formulations of Glass Bead Systems

Code	Coarse (88 $\mu$ m)	Medium (65 $\mu$ m)	Fine (28 $\mu$ m)	Weight Average Size $\bar{D}_w$ ( $\mu$ m)
G-1	100			88.0
G-2	61.5		38.5	69.9
G-3	43.1	30	26.9	66.5
G-4	24.6	60	15.4	65.4
G-5		100		65.0
G-6			100	28.1

by Granulometer 715 (Cilas Alcatel Ltd., France) equipped with a stirrer and a sonicator to prevent any agglomeration during the measurement. Haake Rotovisco RV-II (Haake Mess-Technik GmbH Co., West Germany) was employed to measure the viscosity.

## RESULTS AND DISCUSSION

### Viscosity of Aqueous Solutions

Fig. 1 shows viscosity behavior of three aqueous PVA solutions of 15 wt.% at 25°C. All three PVAs exhibit nearly Newtonian behavior within the range of shear rates tested. This nearly Newtonian behavior does not change with temperature and concentration as shown in Figs. 2 and 3. In Figs. 2 and 3, the highest molecular weight sample (DP=2,400) was used.

### Effect of Particle Size

Various glass fiber systems (Tables 1 and 2) were suspended in an aqueous solution (15 wt.%) of PVA (DP=2,400) with 40~60 volume % range. Fig. 4 shows viscosity of G-1 suspended systems at various loadings. As the glass bead content increases, the viscosity of suspension is increased and

**Table 2.** Particle Size Distribution of Glass Bead Systems

Size( $\mu$ m)	G-1	G-2	G-3	G-4	G-5	G-6
4-6	0.0	0.0	0.0	0.0	0.0	0.0
6-8	0.0	0.2	0.2	0.1	0.0	0.5
8-12	0.0	0.5	0.5	0.4	0.0	1.9
12-16	0.0	1.7	1.8	0.8	0.0	5.1
16-24	0.0	9.4	5.8	1.6	0.0	24.3
24-32	0.0	8.4	3.7	2.4	1.5	37.5
32-48	0.2	0.0	4.3	12.9	1.4	23.6
48-64	3.1	3.6	15.0	26.4	41.4	2.7
64-96	60.4	47.4	46.3	46.8	49.3	0.0
96-128	34.9	26.1	20.0	9.4	4.5	0.0
128-192	0.0	0.0	0.0	0.0	0.0	0.0
Mean( $\bar{D}_w$ )	88.0	69.9	66.5	65.4	65.0	28.1
Mean( $\bar{D}_n$ )	69.84	25.60	18.63	17.26	56.52	26.02
$\bar{D}_w/\bar{D}_n$	1.26	2.73	3.57	3.79	1.15	1.08

\* Numbers are weight fractions.

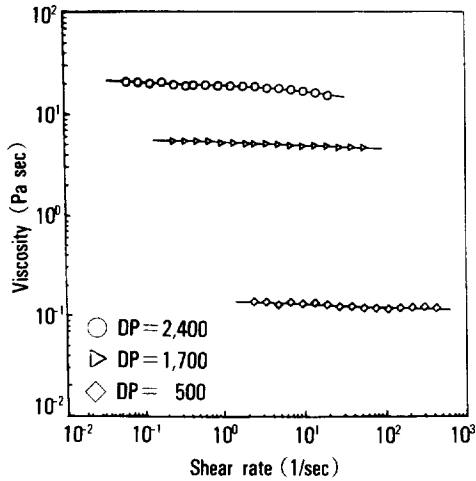


Fig. 1. Viscosity vs. shear rate for three polyvinyl alcohols in 15 wt.% aqueous solution at 25°C.

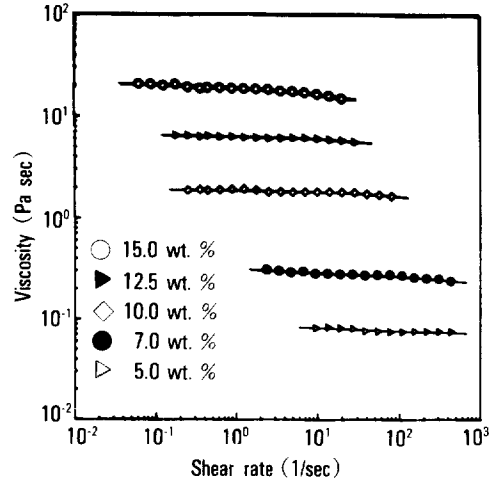


Fig. 3. Viscosity vs. shear rate for PVA (DP=2,400) aqueous solutions in various concentration at 25°C.

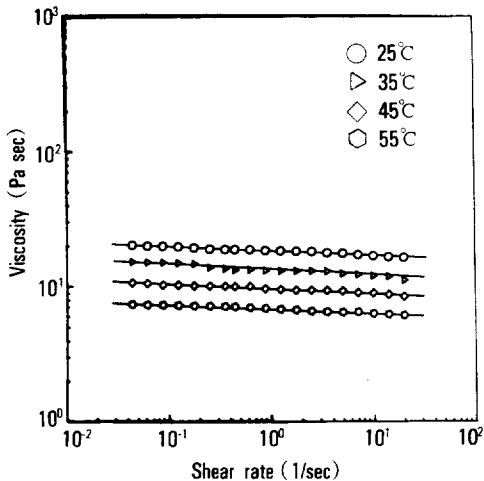


Fig. 2. Viscosity vs. shear rate for a PVA (DP=2,400) aqueous solution (15 wt.%) at four different temperatures.

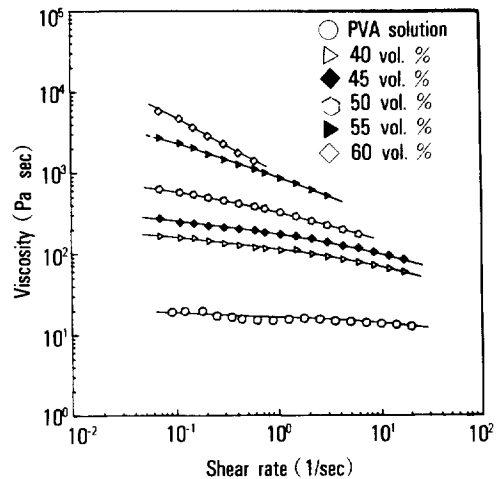


Fig. 4. Viscosity vs. shear rate for the glass bead (G-1) suspended in a PVA (DP=2,400) aqueous solution (15 wt. %) at various glass bead contents and 25°C.

becomes more non-Newtonian. When G-5 and G-6, two other monomodal, are used, similar viscosity behaviors are observed. However, at same glass fiber content, the larger particle gives the lower viscosity.

Fig. 5 shows plot of viscosity against shear stress instead of shear rate for G-6 suspension, the smallest particle size ( $28.1 \mu\text{m}$ ). One may see from

Figs. 4 and 5 that G-6 suspension gives higher viscosity than G-1 suspension, the largest particle size ( $88 \mu\text{m}$ ). However, the main advantage of Fig. 5 over Fig. 4 is that one can easily recognize the existence of yield stress. In other words, the near vertical line in Fig. 5 at 60 vol.% glass bead loading implies that there is yield stress of about  $10^3$  Pa for the suspension system. The lower contents

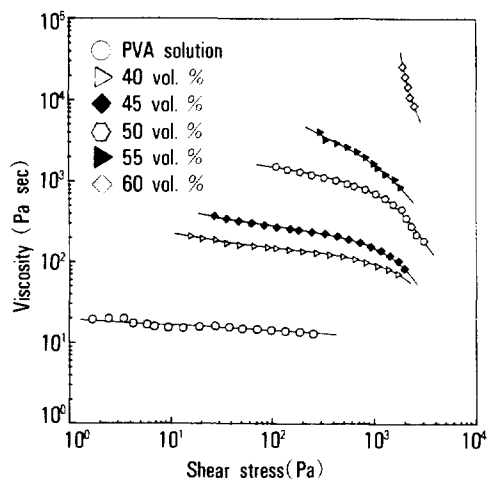


Fig. 5. Viscosity vs. shear stress for the glass bead (G-6) suspended in a PVA (DP=2,400) aqueous solution (15 wt.%) at various glass bead contents and 25°C.

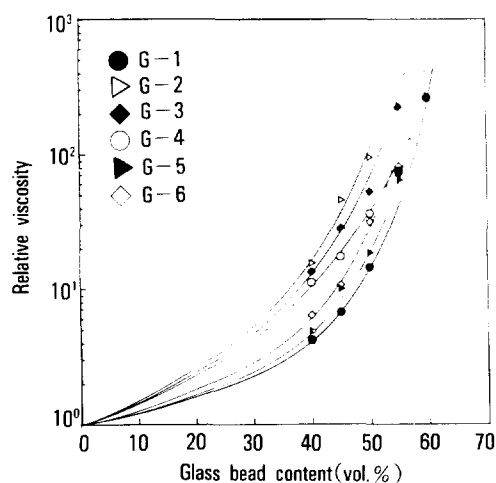


Fig. 6. Relative viscosity vs. glass bead content for PVA (DP=2,400)-glass bead suspension systems at 500 Pa shear stress.

of glass bead also shows some tendency of yield stress. As demonstrated with Fig. 4, however, the yield stress from plot of viscosity vs. shear rate can be seen by negative 45°. Detailed discussion on yield stress will be given elsewhere.<sup>46</sup>

#### Effect of Particle Size Distribution

The relative viscosity of various glass bead sus-

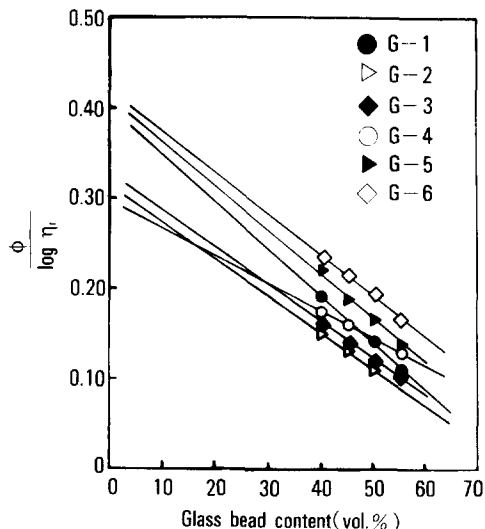


Fig. 7.  $\phi / \log \eta_r$  vs.  $\phi$  for PVA (DP=2,400)-glass bead suspension systems at 500 Pa shear stress.

pension systems is shown in Fig. 6. Fig. 6 contains three monomodal (G-1, 5 and 6), one bimodal (G-2), and two trimodal (G-3 and 4). A general conclusion from Fig. 6 is that the monomodal suspensions give lower relative viscosity at low concentration range (< 50 vol.%) than the multimodals. At high concentration range (> 50 vol.%), however, the viscosity of monomodals rapidly increases. In fact, as will be seen later (Table 3), the maximum volume fraction of monomodals is lower than multimodals.

Comparing G-2, 3 and 4, one may see the effect of particle size distribution with about same particle size ( $\bar{D}_w$ ). The relative viscosity of suspension is in order of G-2 > G-3 > G-4, the exact same order with polydispersity ( $\bar{D}_w/\bar{D}_n$ ), 2.73, 3.57, and 3.79. In other words, the wider particle size distribution gives the lower suspension viscosity.

#### Evaluation of Eqs. (2) and (5)

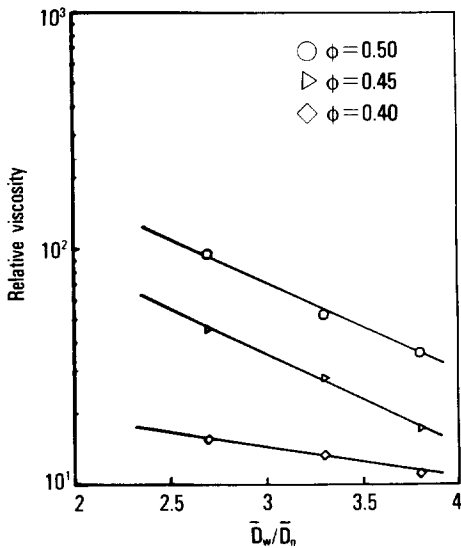
Fig. 7 shows plot of  $\phi / \log \eta_r$  vs.  $\phi$  at 500 Pa shear stress, from which one can determine constants of the Mooney eq. (2) as shown in Table 3.

There are several observations to make from Fig. 7 and Table 3.

(1) The A value for G-1 is same as the Einstein

**Table 3.** Constants of the Mooney Equation for PVA-Glass Bead Suspension Systems from Fig. 7

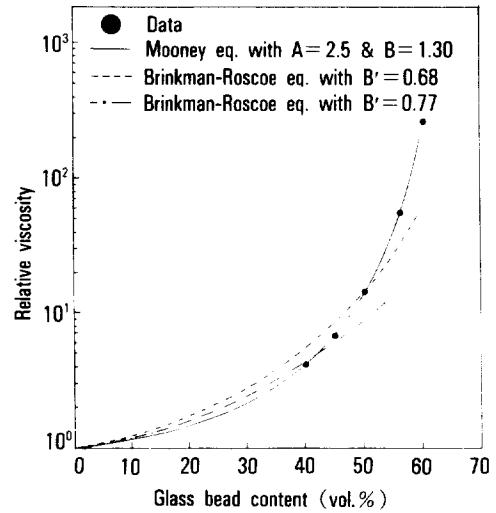
Code	A	B	$\phi_m$	$\bar{D}_w/\bar{D}_n$
G-1	2.50	1.30	0.77	1.26
G-2	3.18	1.30	0.77	2.73
G-3	3.03	1.27	0.79	3.57
G-4	3.33	1.20	0.83	3.79
G-5	2.44	1.35	0.74	1.15
G-6	2.40	1.39	0.72	1.08

**Fig. 8.** Relative viscosity vs. particle size distribution for PVA (DP=2,400)-glass bead suspension systems at three glass bead contents.

constant 2.50. Two other monomodal (G-5 and 6) gives lower values than 2.50 while three multimodal (G-2, 3, and 4) show much higher values. There is no clear explanation for this large difference for the multimodal in A value. However, an increase of particle interaction for the smaller particles and limited numbers of data are contributed, at least partially, to the large deviation.

(2) For monomodal systems, the wider particle size distribution gives the higher  $\phi_m$ , the reciprocal of B.

(3) The multimodal (G-2, 3, and 4) have higher  $\phi_m$  than monomodal. Again, the wider distribution yields the higher  $\phi_m$ , resulting in

**Fig. 9.** Relative viscosity vs. volume fraction of glass bead (G-1) for comparison of the Mooney equation and the Brinkman-Roscoe equation.

lower relative viscosity at the same glass bead loading as shown in Fig. 8.

Fig. 9 compares the Mooney eq. (2) and the Brinkman-Roscoe eq. (5) with experimental data for G-1 system.

The Mooney eq. (2) describes experimental data well while the Brinkman-Roscoe eq. (5) is not. Obviously, eq. (5) is not suitable for the PVA-glass bead system in this study.

## CONCLUSION

(1) Almost Newtonian viscosity behavior of aqueous polyvinyl alcohol solution became more non-Newtonian as glass bead content increased in PVA-glass bead suspensions.

(2) There was a clear evidence of yield stress at higher content of glass bead, which was clearer with the plot of viscosity vs. shear stress instead of shear rate.

(3) For both monomodal and multimodal, the wider particle size distribution gave the lower viscosity.

(4) The maximum packing fraction was increased with the increase of particle size distribution.

For monomodals  $\phi_m$  was in the range of 0.72~0.77 and for multimodals 0.77~0.83.

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