JOURNAL OF MATERIALS SCIENCE **34** (1999) 1347 – 1352

Particulate size effect on the rheology of SiC-glass composites

S. DAS, V.S.R. MURTHY, G.S. MURTY
Department of Materials and Metallurgical Engineering, Indian Institute of Technology, Kanpur 208 016, India

The rheological behavior of SiC particulate glass composites was investigated in the present study. The nature and extent of flow modifications are addressed with respect to solid content in the suspension, temperature and dispersoid size. A transition from Newtonian to non-Newtonian viscous flow and characteristic shear thinning behavior were observed. With progressive strengthening and deviation from Newtonian flow, a significant loss in rate sensitivity occurred. The apparent viscosity of the composites increased with the concentration and size of reinforcements. The increase in viscosity is explained in terms of hydrodynamic/mechanical interactions between particles in the composites. *© 1999 Kluwer Academic Publishers*

1. Introduction

A wide range of glass and glass-ceramic composites have emerged in the last two decades because of their ease of fabrication and improved mechanical performance. A large number of silicate systems were explored with both continuous (C, SiC and Si_3N_4 fibers) [1, 2] and discontinuous particulate reinforcements (SiC and Si_3N_4 particulates, platelets and whiskers) [3–5]. Although various aspects of these composites were studied in great detail, the rheological behavior of discontinuous particulate reinforced silicate systems remains unexplored. From the composite processing point of view, a clear understanding of the flow behavior of silicate matrix in the presence of reinforcements is essential. Glass generally behaves as a Newtonian viscous material near about its glass transition temperature (T_g). It can also behave as a non-Newtonian material in a certain range of shear rates and temperature [6]. Gadkaree and Chyung [5] observed an increase in processing viscosity when whiskers were dispersed in an aluminosilicate glass matrix. The viscosity increased by two orders of magnitude when compared to aluminosilicate base matrix. Rouxel and Verdier [7] observed non-Newtonian flow in SiC particulate reinforced oxynitride glass composites in the viscoplastic temperature range of 800–900 °C. The effects of reinforcement morphology, SiC particulate volume fraction and temperature were investigated by the authors using SiC-borosilicate glass as a model system [8]. While the flow stress increased with the volume fraction and aspect ratio of reinforcements, the strain rate sensitivity index (m) gradually decreased from unity to 0.4. Further, the flow behavior became non-Newtonian with increasing SiC particulate aspect ratio and volume fraction, showing a sharp increase in viscosity at lower strain rates. A shear thinning behavior of composites was also observed with increasing strain rate. The present work is focussed on the particulate additive size effect of reinforcements on the flow behavior of SiC-borosilicate composites.

2. Experimental

The details of matrix and reinforcements are given in Table I. Initially borosilicate glass powder and SiC particulates were dry ball milled for 24 hours. The admixture was then hot pressed (DPS-6, Dr. Fritsch KG, Germany) at 700 °C at a pressure of 10 MPa by adopting rapid heating and cooling cycles to avoid matrix crystallization [9]. A graphite die assembly coated with BN was used to produce cylindrical composite pellets of 10 mm diameter and 12 mm height. The uniformity of particulate dispersion was examined using an optical microscope. X-ray diffraction was carried out on samples to make sure that there is no crystallization of the matrix. For mechanical testing, both top and bottom surfaces of the pellets were polished to 1 μm finish and care was taken in maintaining the parallelity between them. All the specimens were tested in compression (MTS 810.12) in the temperature range of 625–700 °C. The uniformity in test temperature was monitored with three thermocouples placed at close intervals. Cross head velocity change tests were conducted in the strain rate range of 10^{-2} to 10^{-5} s^{-1}. BN was used as a solid lubricant to minimize the friction between sample and platen surfaces in the compression tests.

3. Results

For each composite a load-displacement plot was obtained from cross head velocity change test in compression. Flow stress (σ) and strain rate ($\dot{\varepsilon}$) were calculated from the load-displacement plot and the data are analyzed in terms of well known power law for strain rate dependent flow:

$$\sigma = K\dot{\varepsilon}^m \tag{1}$$

TABLE I Details of glass matrix and SiC reinforcements

	Material	Shape	Size range (μm)	Density (kg/m^3)	Thermal exp. coeff. (°C^{-1})	Composition (wt %)
Matrix	Borosilicate glass	Powder	<53	2.2×10^3	3.3×10^{-6}	SiO_2: 80
Reinforcement	SiC	Particulate[a]	[b]	3.2×10^3	4.3×10^{-6}	B_2O_3: 14
						Na_2O: 4
						Al_2O_3: 2
						$\alpha + \beta$

[a] Carborundum universal Ltd., India.

[b] Four different size ranges.

1. 44–63 μm
2. 160–210 μm
3. 297–351 μm
4. 500–595 μm

where K is proportionality constant, a function of temperature and microstructure and m is the strain rate sensitivity index. Flow stress-strain rate data are presented in double logarithmic plots to assess the extent and nature of strengthening with respect to particulate filler volume fraction, size and test temperature.

Borosilicate glass behaves as a Newtonian viscous material ($m = 1$) at around its glass transition temperature (T_g). In addition to strengthening, addition of reinforcements leads to non-Newtonian flow especially at higher volume fractions (Fig. 1). The flow becomes increasingly non-Newtonian with decreasing temperature, increase in volume fraction and increase in strain rate. Deviation from linearity also becomes prominent at the higher strain rate regime. Flow behavior of the composites for reinforcements of four different size ranges and volume fraction is found to be strongly dependent on temperature. Fig. 2 shows increasing strengthening effect with drop in temperature. For a given temperature and volume fraction the extent of strengthening depends on reinforcement size. The flow stress is higher for larger particulates (Fig. 3).

While considering the composite flow behavior in terms of flow stress and strain rate, the viscosity of the composites at elevated temperatures is assessed keeping the viscous nature of matrix glass in mind. The following relationship is used for this purpose:

$$\eta = \frac{\sigma}{\dot{\varepsilon}} = \frac{K}{\dot{\varepsilon}^{(1-m)}} \tag{2}$$

It is obvious from Equation 2 that the apparent viscosity is strain rate sensitive, whereas the viscosity remains unchanged with strain rate in Newtonian flow. The results of this study indicate a drop in viscosity at higher strain rates (Fig. 4). A strain rate of 1.0×10^{-4} s^{-1} is selected to calculate the apparent viscosity of each composite using the appropriate m value. For all the composites the apparent viscosity increases with volume fraction of reinforcements and drop in temperature. At a given temperature and volume fraction the

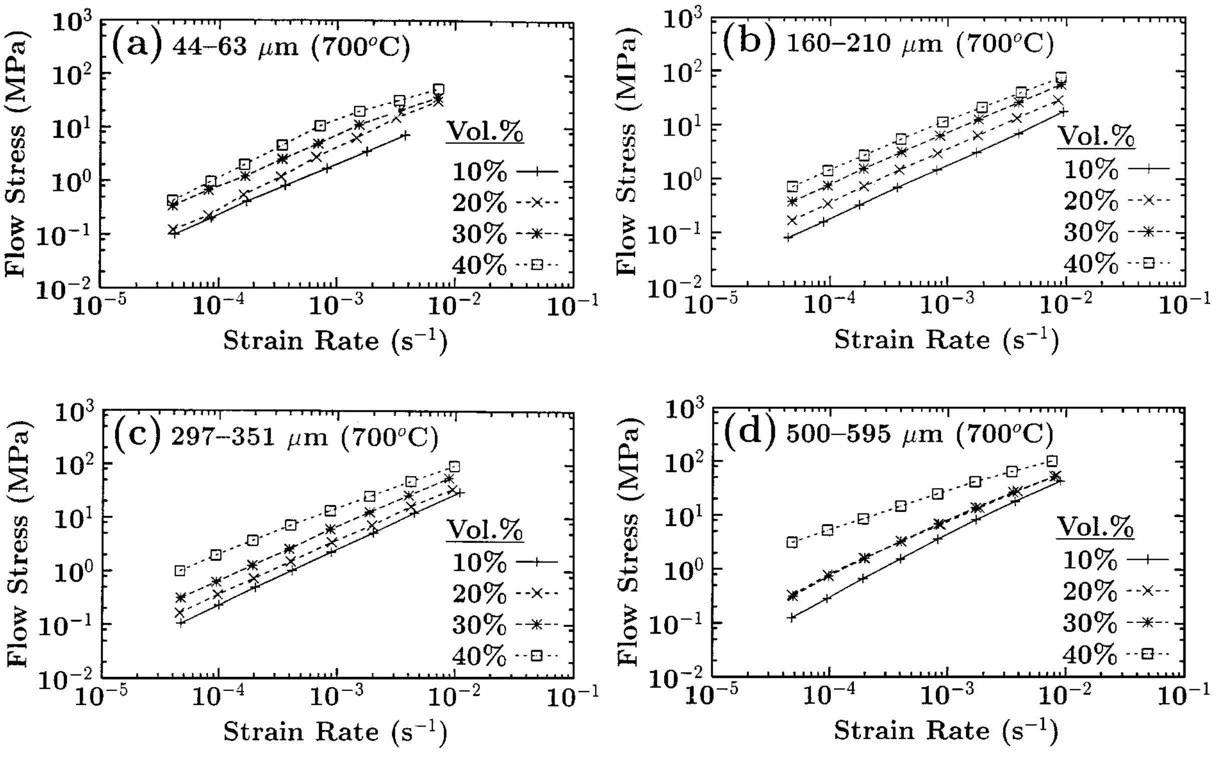

Figure 1 Effect of volume fraction of reinforcements on strengthening of composites for different size ranges of particulates at 700 °C.

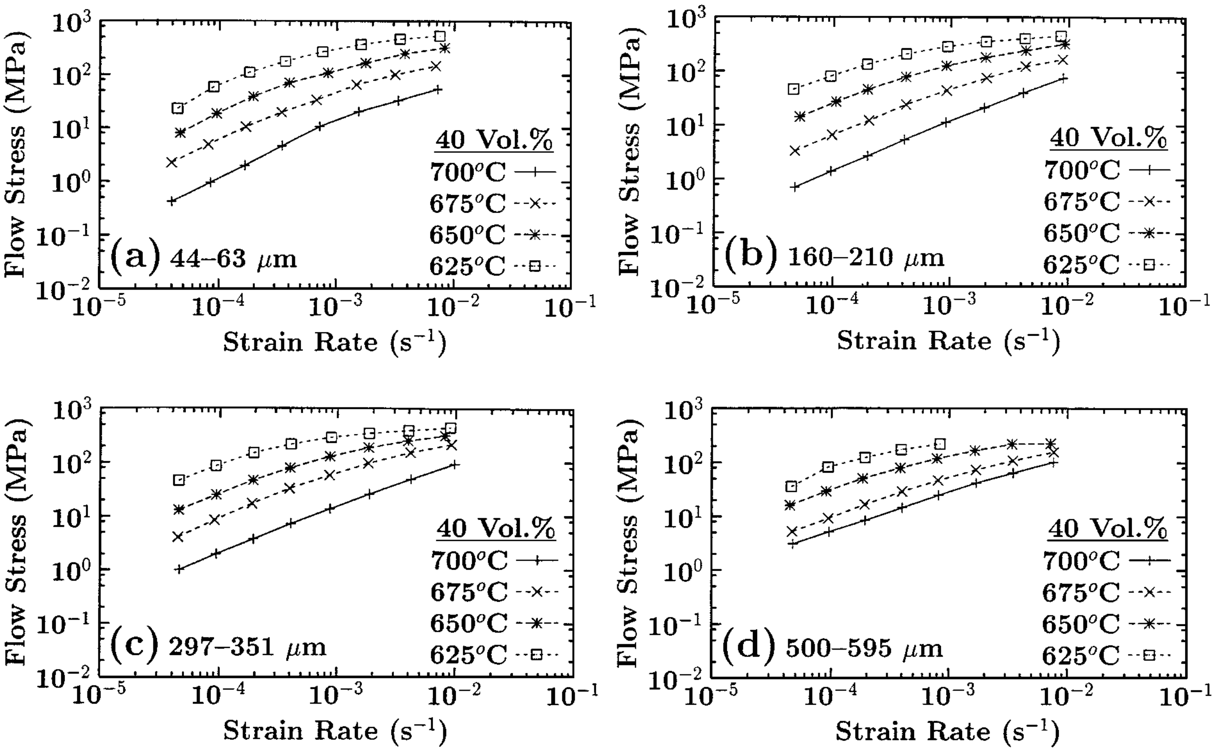

Figure 2 Effect of temperature on strengthening of 40 vol % composites for different size ranges of particulates.

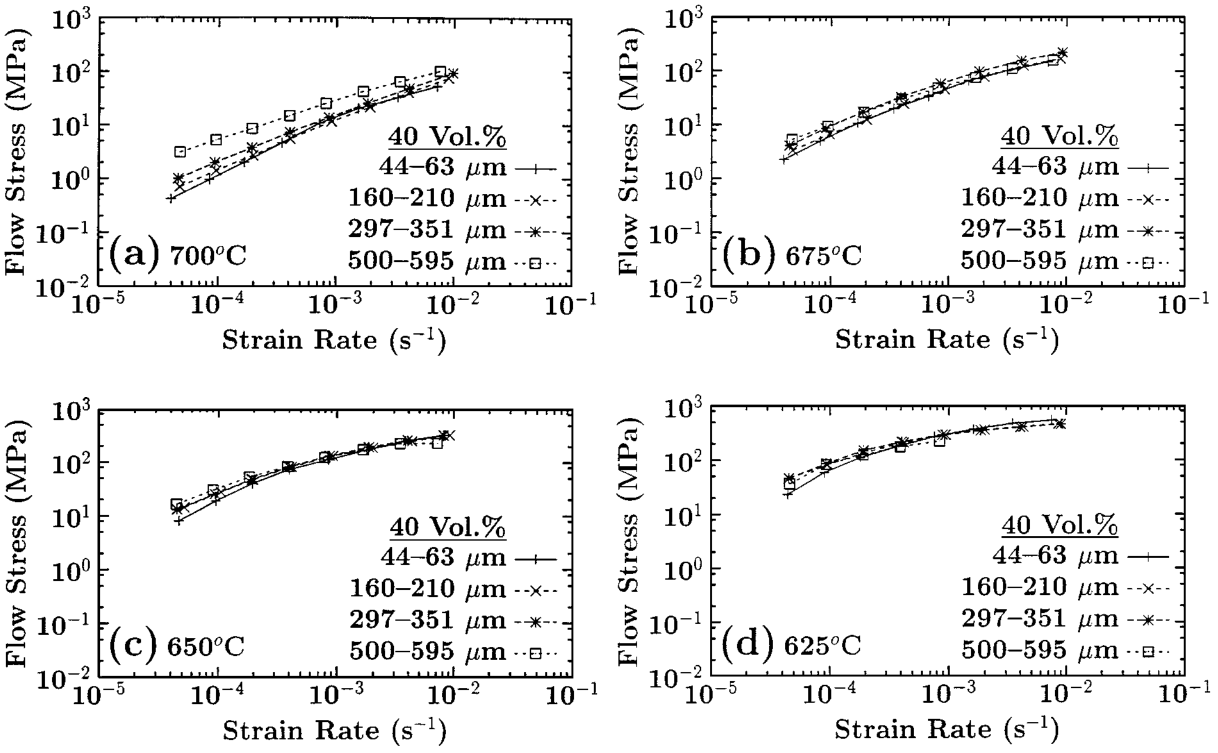

Figure 3 Effect of different size ranges of reinforcements on strengthening of 40 vol % composites at different temperature.

apparent viscosity is observed to increase with reinforcement size. The size range dependence of viscosity is shown in Fig. 5 at two temperatures. An increase in viscosity of nearly five fold is seen for two extremes of particulate size at 40 vol % loading. The activation energy (Q) for flow is calculated using the data available for different temperatures at a constant strain rate of 1.0×10^{-4} s^{-1}. The constitutive relationship used for this case is:

$$\dot{\varepsilon} = A\sigma^{n}\mathrm{e}^{-(Q/RT)} \tag{3}$$

where $n (n = 1/m)$ is the stress exponent, A is a constant and R is the gas constant. From Equation 4 the activation energy (Q) is given by:

$$Q = (R/m)\left[\frac{\delta \ln \sigma}{\delta(1/T)}\right]_{\dot{\varepsilon}} \tag{4}$$

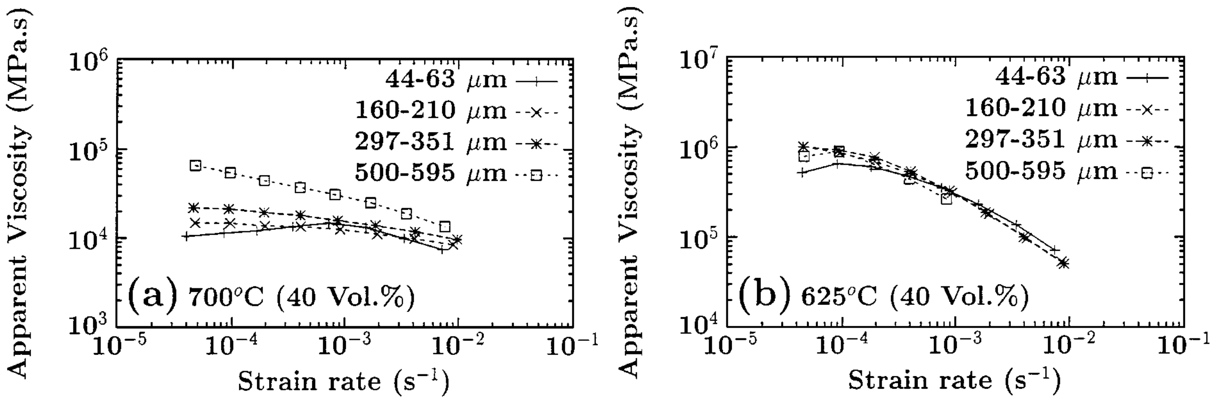

Figure 4 Effect of strain rate on the apparent viscosity of 40 vol % composites for different size ranges of reinforcements at (a) 700 °C and (b) 625 °C.

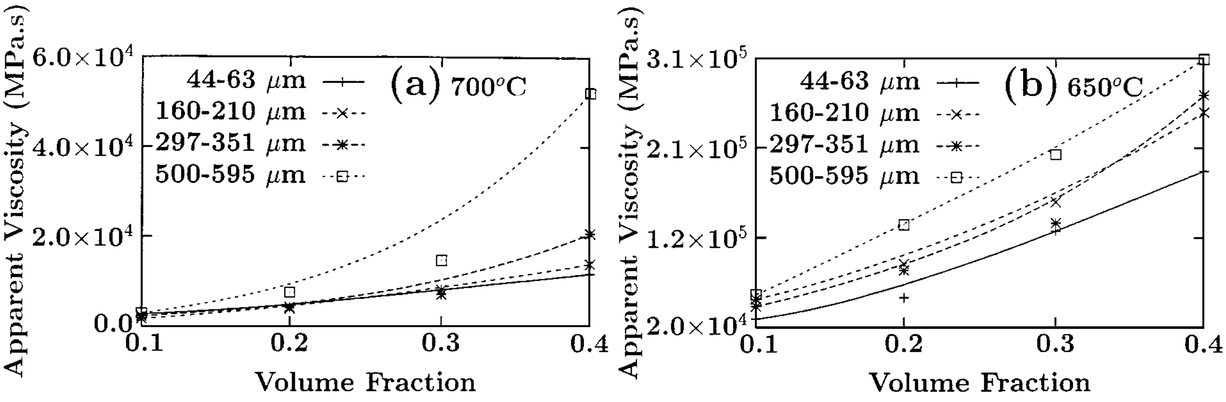

Figure 5 Variation in apparent viscosity for different size ranges of reinforcements at (a) 700 °C and (b) 650 °C.

The activation energy values are found to vary in the range of 335–540 kJ/mol depending on the particle size and volume fraction. The activation energy generally decreased with increasing particle size and volume fraction of particulate.

4. Discussion

At the higher temperatures borosilicate glass exhibits Newtonian viscous flow behavior near its glass transition temperatures. In glasses, transition from Newtonian to non-Newtonian flow is seen with a decrease in working temperature and increase in strain rate [6]. The non-Newtonian behavior is also observed in composite systems with the addition of reinforcements [8]. During non-Newtonian flow, apparent viscosity of the glass increases in the presence of reinforcements. The rise in viscosity mainly depends on particle morphology, silicate chemistry, volume fraction and temperature. In dilute systems, the rise in viscosity is given by well established Einstein [10] relation:

$$\eta = \eta_s(1 + 2.5\phi) \tag{5}$$

where η is the viscosity of the composite, η_s is the viscosity of the suspending medium and ϕ is the volume fraction of the particles. The validity of Einstein relation is verified in a number of dilute systems.

The analysis of concentrated suspensions is more complex. Although several polymeric systems were studied extensively, no work has been reported on silicate-based systems. Further, empirical relations of viscosity developed in polymeric systems may not be valid for glass systems. Neither experimental nor empirical relations are available to calcualte the apparent viscosity in particulate systems as a function of the particle size, shape or volume fraction. While the apparent viscosity in all cases rises with the volume fraction of reinforcements and drop in temperature, the flow studies [11] generally indicate a drop in viscosity as the particle size increases at a given volume fraction of reinforcements. However, the results of the present study indicate the opposite trend of higher viscosity for larger particulates. For example, Sweeny and Geckler [12] observed an increase in viscosity with the decrease in particle size in a glass sphere-zinc bromide aqueous glycerol system. In the same study when non-aqueous medium was used the viscosity was found to be independent of particle size.

The observed particle size effects may be rationalized by considering the colloid-chemical and hydrodynamic/mechanical forces acting on the particles in suspension. For small particle size (<5 μm), colloid-chemical interactions contribute significantly towards an increase in the viscosity [13]. However, the coarser particle size ranges of this study and their inertness to the matrix exclude the possibility of any colloid-chemical activity. Vand [14] has treated the mechanical force produced from interactions among particles in terms of rotation of the particles. Vand's model suggests that particles of adjacent layers sliding past each other form a doublet and rotate in the suspension as a

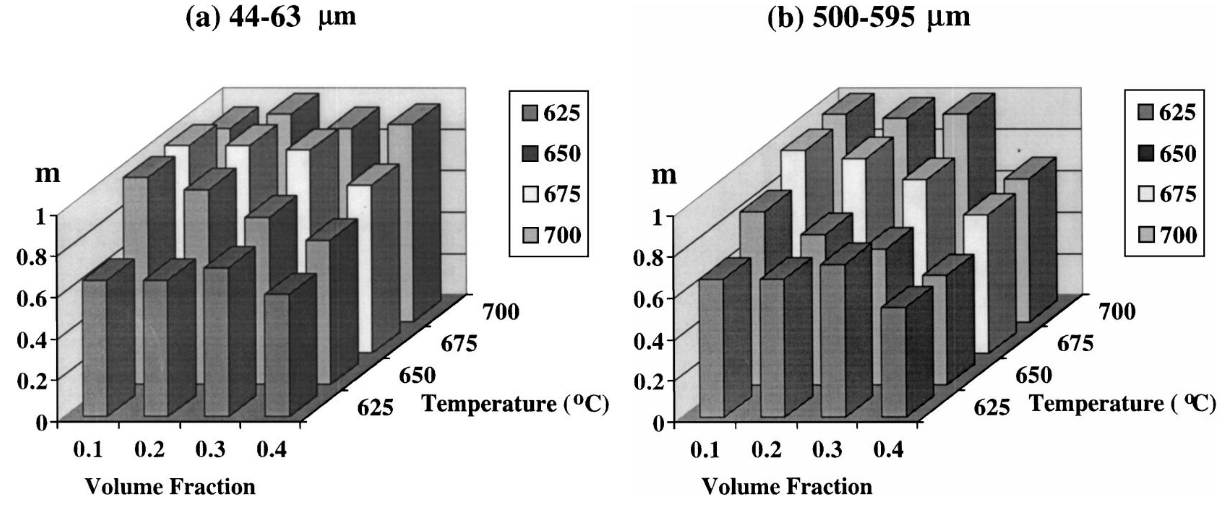

Figure 6 Variation in rate sensitivity index (m) values with volume fraction and temperature for (a) 44–63 μm and (b) 500–595 μm particulate composites.

single entity for a finite period of time. In the process, due to immobilized liquid entrapped in between and around the particles, an effective increase in volume fraction of particles will occur and thereby an increase in viscosity follows. De Bruijn [13] hypothesized the mechanical interaction taking into consideration that every particle would possess a repulsion sphere in opposition to weak attractive forces. The possibility of forming any combined mass of particles is ruled out by the presence of this sphere of repulsion. Instead of forming multiplets, individual particles will rotate until they collide with each other resulting in an energy dissipation which will give rise to an increase in viscosity. The relaxation period associated with restoration of rotation after collision is determined by the inertia of the particles. The angular velocity of spherical particles is proportional to the rate of shear and is independent of size [15]. Hence, the rotational kinetic energy would be higher for larger particles compared to that of the smaller particles. Thus at constant shear rate, the larger particles are expected to release more kinetic energy on collision compared to the smaller particles and hence the viscosity of the former would be higher.

The combined effect of temperature (T), volume fraction (V_f) and average particle size (s) on the apparent viscosity (η) has been analyzed in terms of the following empirical relation:

$$\eta = a \exp(bV_\mathrm{f} + c/T + ds) \qquad (6)$$

where a, b, c and d are constants, T is absolute temperature. From the experimental data, the values of these four constants (a, b, c and d), calculated by regression analysis, are 4.6×10^{-19}, 5.8, 4.8×10^{4} and 1.1×10^{-3} respectively.

The physical phenomena responsible for the rise in viscosity with larger particle and higher degree of particle loading also affect the strengthening behavior of the composites. An increase in flow stress follows from the rise in viscosity.

The rate sensitivity of the composites is another important aspect to be considered, especially, when the change in flow characteristics occur with strain rate. A general observation in this study is a loss in the rate sensitivity with the increase in volume fraction of solids and a drop in temperature. This trend becomes more prominent at higher strain rates. The loss in rate sensitivity indicates a deviation from Newtonian viscous deformation of the composites. Moreover, a gradual loss in rate sensitivity has also been observed for increasing particle size. The loss in rate sensitivity at higher strain rate regime manifests as a linear to non-linear transition in double logarithmic stress-strain rate plots. In an effort to assess this behavior, stress-strain rate plots are assumed to have two m values, one below and the other above a strain rate of 1.0×10^{-3} s^{-1}. The strain rate sensitivity index values calculated below this strain rate are presented in Fig. 6 for two extreme cases of reinforcement size. From the change in rate sensitivity with different parameters, it can be inferred that the factors affecting the strengthening of the composites also affect the rate sensitivity. The alteration of microstructural features as well as load bearing capacity of the material with deformation in progress are responsible for the change in rate sensitivity. In case of crystalline materials the rate sensitivity can be interpreted with respect to several parameters associated with grain structures and deformation process. Non-Newtonian viscous flow in glass has been reported in a number of investigations and the phenomenon is explained through molecular dynamics approach [16]. The value of stress exponent is found to be unity in the case of deformation process of glass-ceramic materials at high temperature [17]. For the particulate reinforced glass composites a gradual loss in rate sensitivity is also probably due to greater frequency of collisions occuring between the particles at higher volume fractions.

5. Summary

The apparent viscosity increases with higher volume fraction and larger size of the particles and with the drop in the temperature. The mechanical/hydrodynamic interactions among the particles are probably responsible for the rise in viscosity in the composites with larger particles. The strengthening behavior of particulate composites at near the glass transition temperature of the matrix is found to be strongly dependent on volume fraction and size of reinforcement, and temperature. The flow stress of the composites increases with increasing volume fraction, drop in temperature and the increase in reinforcement size. A loss in rate sensitivity occurs at higher strain rates. A transition in flow from Newtonian to non-Newtonian is observed along with characteristic shear thinning behavior.

Acknowledgement

The authors are thankful to Prof. R.P. Chhabra for useful discussions. The Financial Assistance from the Department of Science and Technology, India is gratefully acknowledged.

References

1. D. C. PHILLIPS, R. A. J. SAMBELL and D. H. BOWEN, *J. Mater. Sci.* **7** (1972) 1454.
2. K. M. PREWO and J. J. BRENNAN, *J. ibid.* **15** (1980) 463.
3. K. P. GADKAREE, *J. ibid.* **27** (1992) 3827.
4. A. R. B. VERMA, V. S. R. MURTHY and G. S. MURTY, *J. Amer. Ceram. Soc.* **78** (1995) 2732.
5. K. P. GADKAREE and K. CHYUNG, *Amer. Ceram. Soc. Bull.* **65** (1986) 370.
6. J. H. SIMMONS, R. OCHOA, K. D. SIMMONS and J. J. MILLS, *J. Non-Cryst. Solids.* **105** (1988) 313.
7. T. ROUXEL and P. VERDIER, *Acta Mater.* **44** (1996) 2217.
8. S. DAS, V. S. R. MURTHY and G. S. MURTY, *Mater. Sci. Eng.* **A241** (1998) 129.
9. V. S. R. MURTHY, unpublished work.
10. A. EINSTEIN, *Ann. Physik.* **19** (1906) 289.
11. S. G. WARD and R. L. WHITMORE, *Brit. J. Appl. Phys.* **1** (1950) 325.
12. K. H. SWEENY and R. D. GECKLER, *J. Appl. Phys.* **25** (1954) 1135.
13. H. DE BRUIJN, *Discussions Faraday Soc.* **11** (1951) 86.
14. V. VAND, *J. Phys. & Colloid. Chem.* **52** (1948) 277.
15. B. J. TREVELYAN and S. G. MASON, *J. Colloid. Sci.* **6** (1951) 354.
16. J. H. SIMMONS, R. K. MOHR and C. J. MONTROSE, *J. Appl. Phys.* **53** (1982) 4075.
17. J.-G. WANG and R. RAJ, *J. Amer. Ceram. Soc.* **67** (1984) 399.

Received 6 October 1997
and accepted 7 October 1998