EFFECTS OF SHEAR STRESS AND SHEAR TIME ON RHEOLOGICAL PROPERTIES OF ZEOLITES

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RINGKASAN : *Reologi serbuk kering terserak di dalam cecair membolehkan ramalan struktur-mikro dan kemudahserakan ke dalam cecair dilakukan. Kertas kerja ini mengulas perbezaan sifat reologi serbuk zeolite yang mempunyai julat saiz yang hampir iaitu 3.9 - 4.6 µm apabila dikenakan daya ricihan malar iaitu dari 0.85 - 8 Pa dan masa ricihan 720 s. Apabila nilai daya ricihan meningkat, kelikatan zeolite vegabond (ZVXD) berkurangan dengan peningkatan kadar ricihan. Manakala, bagi zeolite doucil (ZDP), daya ricihan kritikal di mana aras kelikatan songsang berlaku pada 7 Pa dan bagi zeolite wessalith (ZWP), tiada penurunan ketara bagi kelikatan seperti yang dilihat dari profil ZVXD dan ZDP. Maklumat kelikatan ini amat berguna untuk formulasi serbuk detergen yang lebih baik memandangkan serbuk zeolite merupakan salah satu daripada bahan aktif yang digunakan. Tambahan pula, pencirian pemecahan struktur boleh dibuat daripada lekuk kelikatan yang terhasil. Kesimpulannya, didapati sifat reologi zeolite yang mempunyai julat saiz yang hampir dapat dibezakan apabila serakannya dikenakan daya ricihan malar dan masa ricihan. Kesan penambahan tekanan ricihan malar dan kesan penambahan masa ricihan ke atas lekuk kelikatan serakan standard telah dikaji menggunakan reometer tekanan terkawal, Carrimed CSL-100.*

ABSTRACT : The rheological properties of dry powders dispersed in liquid enable prediction of microstructure and ease of dispersion of the powders in slurry form. This paper highlights the differences in the rheological properties of various zeolite powder with similar size range of 3.9 - 4.6 µm when subjected to constant shear stress of 0.85 - 8 Pa and shearing time of 720 s. When the value of the imposed shear stress increased, the viscosity of zeolite vegabond ZVXD decreased with increasing shear rate. As for zeolite doucil P, ZDP, the critical shear stress where the viscosity level was inverted, occurred at 7 Pa. In the case of zeollite wessalith P (ZWP), there was no significant reduction of viscosity of ZWP dispersions at low shear stress times as seen in the profiles of ZVXD and ZDP. Knowing viscosity profiles can lead to better formulation of detergents where zeolite powders are the active ingredients. In addition, the characteristics of structural breakdown could be made from the generated viscosity curves. It was found that the rheological properties of zeolites with similar size range differs when subjected to constant shear stress and shearing time. The viscosity curves of standardized dispersion were studied using Carrimed CSL 100, a controlled stress rheometer.

KEYWORDS : Rheology, zeolite, controlled stress rheometer, microstructure

INTRODUCTION

Rheology is the study of the flowability and deformation behaviour of materials. A large number of industries such as the paint, food, oil and coal require the dispersion of powders into liquids at some of its processing stage. A number of problems arise due to the complex flow behaviour of high solid concentration in dispersion of fine powders that commonly have non-Newtonian flow characteristics. This results in difficulties in designing process equipment such as mixers and pumps as well as in obtaining homogeneous products for quality control purposes.

Flow behaviour of liquid can be classified into time independent behaviour that includes Newtonian and Non-Newtonian characteristics (Schramm, 1994 and Benkreira, 1990). The Non-Newtonian are further classified into pseudoplastic liquid, dilatant liquid and pseodoplastic liquid with yield point. These variations in viscosity profiles lead to different resistance imposed by the liquid in relation to structural breakdown within the dispersion. Based on the work of Bossis *et al.* (1984) on concentrated hard-sphere dispersions, the dominant force within the low shear rate region is the hydrodynamic force which results in a flocculated dispersion of particles. As the shear rate increases the particles within the dispersion will orient themselves in the direction of shear in order to reduce resistance to flow. This results in lower viscosity profiles. Liquid that exhibits this behaviour is known as pseudoplastic liquid. For dilatant liquid the viscosity increases with shear rate to give shear thickening behaviour. This behaviour is normally shown by deflocculated dispersions where attraction forces between particles are negligible. Hoffman (1972,1974 and 1982) explained the existence of shear thickening as a two-dimensional layered arrangement of particles at low shear rate. According to Bingham (1922), some particulate dispersions need the imposition of shear stress that exceed the yield stress to initiate their flow. Below this limiting value of shear stress, flow of dispersion stops and the structure reforms due to attraction between particles. This flow of dispersion is known as pseudoplastic liquid with yield point. Some dispersions exhibit time dependent behaviour that can be classified as thixotropic behaviour and rheopectic or anti-thixotropic behaviour. Materials such as high molecular weight polymers, shampoos, shower gels and polymer melts experience "Weissenberg effect". These materials show viscoelastic behaviour (Barnes, 1993). Juszezak and Teresa Fortuna (2006) studied the rheological properties of seven varieties of Polish honeys, among them five nectar varieties, a nectar-honeydew and a honeydew variety, were investigated over temperature range of 10-40°C. The viscosity curves of the samples were obtained using a rotational rheometer. All the honey exhibited Newtonian behaviour. Their viscosity varied between 1.76 and 252.6 Pa s according to the kind of honey and temperature measurement. Jasim Ahmad and Hosahalli S. Ramaswamy (2006) carried out the dynamic mechanical spectroscopy and steady-shear rheological tests to evaluate viscoelastic properties of commercial sweet potato puree infant food using a controlled stress rheometer. The puree behaved like an elastic solid and both the elastic and viscous moduli decreased with an increase in temperature. Their results showed that the steady shear viscometry covering the shear rate range 0.1 to 100s^{-1} indicated the presence of yield stress.

Among the variables that influence the viscosity profiles of dispersions are phase volume, particle size distribution, particle shapes and interaction between the dispersed particles. These variables play a significant part in determining the form and extent of shear thickening and shear thinning of fluids. (Barnes, 1993 and Taylor, 1965). In this study of zeolite dispersions, the onset of shear thickening was observed at high solid concentrations. The study will monitor changes in microstructure within wet dispersions when subjected to various levels of amount shear stress and prolonged shearing time. A knowledge of zeolites dispersion and variation with processing conditions is important for optimum plant operation and detergent production. This work will also confirm the findings of Jung *et al.* (1996) that imposed shearing would result in formation and restructuring of flocs. The effects of shearing on floc structure were monitored using small-angle light scattering technique.

MATERIALS AND METHODS

The instrument used in this study is the Carrimed CSL 100, a controlled stress rheometer that uses the principle to shear any dispersion or liquid under study by the application of a constant torque. The viscosity and shear rate are measured as a function of the applied shear stress that is varied linearly at any specified range of shear stress over a particular time period. The measuring geometry used is cone and plate since it requires a small sample and gave a uniform shear rate across the whole of the sample. The flow and viscosity profiles were monitored at 50 wt/wt of three different grades of zeolites having surface to volume diameter between 3.9-4.20 µm, namely, zeolite doucil P (ZDP), zeolite wessalith P (ZWP) and zeolite vegabond (Z VXD). The physical properties of the materials are given in Table 1. Each measurement was repeated for a minimum of three runs. The maximum standard error of the estimated mean was found to be 0.03 at 95% confidence level. For the effect of constant stress, the values of imposed shear stress was increased from 0.85 to 8 Pa. All the time effect measurements were carried out within a time period of 720 s for increasing and decreasing values of shear stress using the standardised dispersion sample. The schematic representation of cone and plate assembly is shown in Figure 1.

Table 1. Summary of physical properties of zeolites

Material	Surface to volume diameter d_{sv} (µm)[@]	Relative spread σr (-)	Absolute particle density ρ_p(g/cm³)	Porosity within packing E(-)	Hausner ratio HR(-)	Tapped bulk density dt_{180}(g/cm³)
ZVXD	4.20	0.65	1.88	0.78	1.98	0.74
ZWP	4.60	0.69	1.94	0.61	1.91	0.64
ZDP	3.90	0.53	1.85	0.67	2.02	0.69

[@] Dispersed in 1% tetrasodium pyrophosphate solution
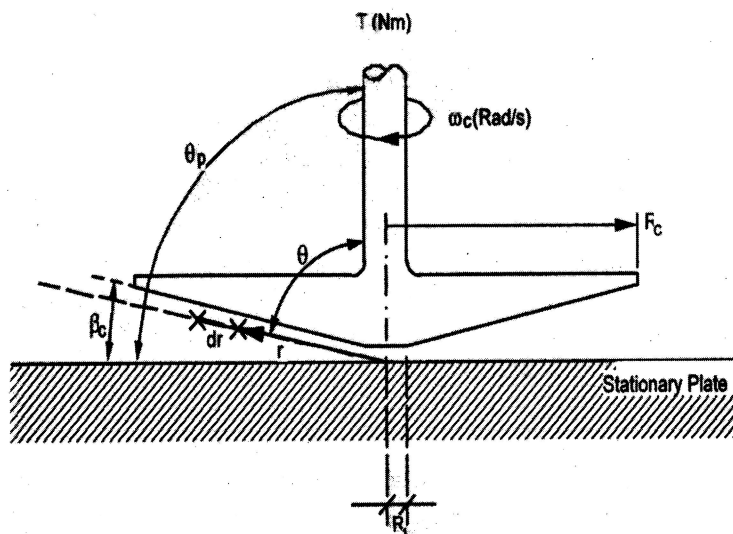
Figure 1. *Schematic representation of cone and plate assembly*

where;

Cone angle (β$_c$): 2° Cone outer radius(R$_c$): 2.5 x 10^{-2}m

Plate angle (θp): π/2 Truncated radius: R$_1$

General radius: r General angle (θ): θ

Increment of radius:dr T = measured torque (Nm).

ω$_c$(θ) = angular velocity of the rotating cone at radius r (rad/s).

RESULTS AND DISCUSSION

Effect of constant shear stress

Figures 2, 3 and 4 show the effect of a series of constant shear stresses on the viscosity curves of 50 % wt/wt concentrations of zeolite dispersions. The holding time is 720 s at each shear stress. In Figure 2, for ZVXD, as the value of the imposed shear stress increases from 0.85 to 8 Pa, the viscosity decreases with increasing shear rate. Above this critical shear stress of 8 Pa the viscosity increases. The alterations in the agglomerate size distributions within the dispersion caused by varying stress conditions resulted in the observed profiles. Below 8Pa, the viscosity decreases as the imposed shear stress increases as a result of a de-agglomeration process. By increasing the shear stress, the ratio of fines within the dispersion is further increased and the process of flocculation is promoted to cause an increase in the dispersion viscosity. Statistically it was found that the viscosity profiles obtained at all five values of constant shear stress were significantly different at the 95% confidence level.
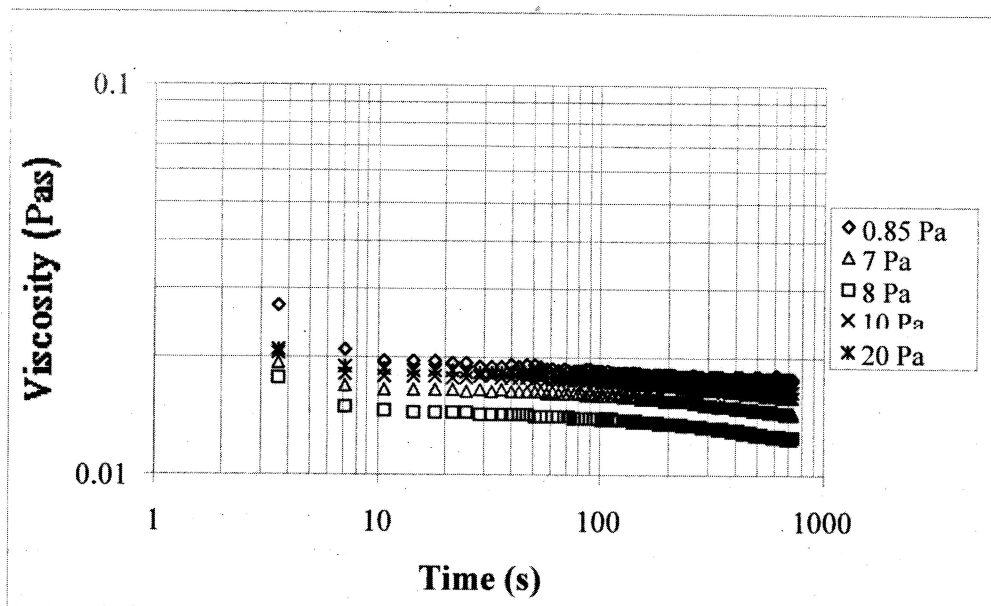

Figure 2. *Effect of constant shear stress on viscosity curves of 50% wt/wt of ZVXD dispersions*

In Figure 3, the critical shear stress where the viscosity level was inverted occurred at 7 Pa. The viscosity profiles of the ZDP dispersions decreased as the applied shear stress increased from 0.85 - 7 Pa. Further reduction of agglomerate size to primary particles within the dispersion occurs above the critical shear stress of 7 Pa as shown by the increase in the dispersion

viscosity. The ZDP dispersion shows a shear thickening behaviour if sheared for a prolonged time at a particular shear stresses. The deviation of the viscosity profile was found to occur at a shear stress of 8 Pa from the general sequential pattern. Hence 8 Pa is the critical value of shear stress where flocculation starts. Beyond this value the imposed shear stress results in formation of flocs.
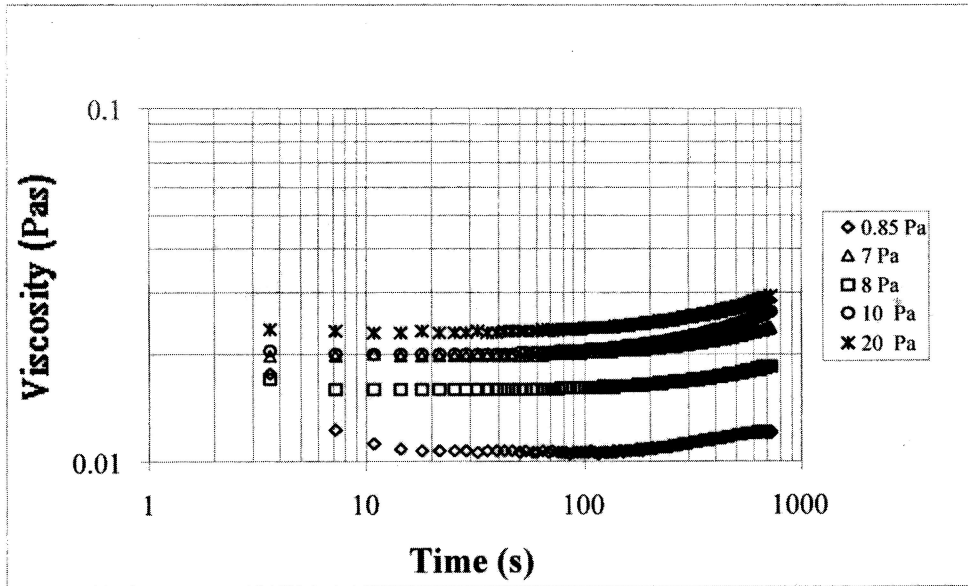

Figure 3. *Effect of constant shear stress on viscosity curves of 50% wt/wt of ZDP dispersions*

The viscosity profiles of the ZWP dispersions when sheared for a prolonged time period could only be obtained at shear stresses up to 7 Pa as shown in Figure 4. The differences between the viscosity profiles at the two values of shear stress were found to be statistically significant. Beyond this value the viscosity could not be measured by the instrument. Figure 4 shows that there is no significant reduction of viscosity for 50% wt/wt ZWP dispersions at low shear times as seen in Figures 2 and 3, respectively. The viscosity of the dispersion is found to increase with shear stress within the shearing period. This probably is due to the presence of strong agglomerates of primary particles within the dispersion that were not broken down further by the imposed shear stress. Shear thickening behaviour is apparent after the ZWP dispersions have been sheared for about 400s at both values of shear stress. The phenomenon is probably due to interlocking of strong agglomerates of ZWP within the dispersion which imposes a resistance to flow resulting in increased viscosities.
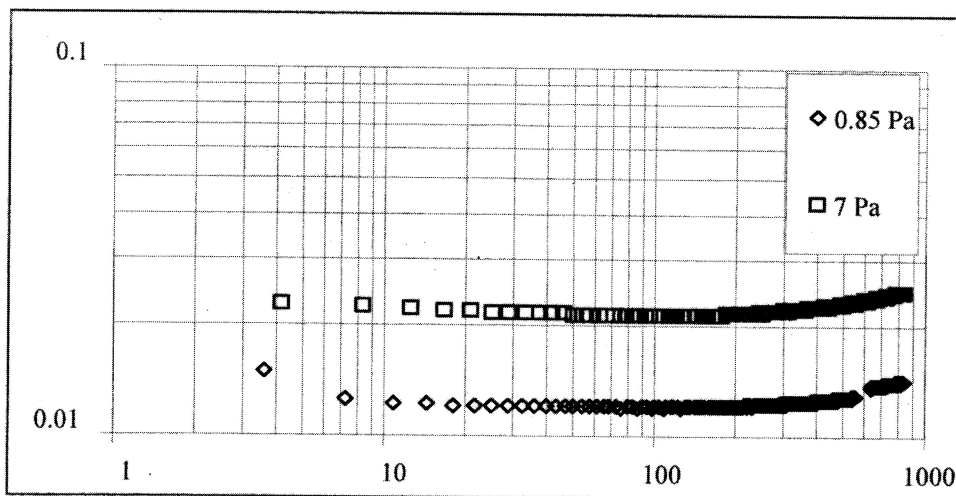
Figure 4. *Effect of constant shear stress on viscosity curves of 50% wt/wt of ZWP dispersions*

Effect of shearing time

Figures 5, 6, 7, 8, 9 and 10 show the time dependency behaviour of the zeolite dispersions when subjected to a cyclic shear rate. All time effect measurements were carried out within a period of 720 s for increasing and decreasing values of shear stress using the standardised dispersion sample and no dispersant. The results clearly demonstrate the time effect for aqueous dispersions of the zeolites and they follow a hysteresis loop. The characteristic of structural breakdown could also be deduced from the viscosity curves of Figures 6, 7 and 8, respectively. For liquids that exhibit a thixotropic behaviour it is expected that as the shear stress increases the viscosity will decrease from the initial value to the equilibrium value after some time, and then increases from an initial low value to a higher value as the shear stress is reduced. Figures 6 and 8 give the impression that initially during run 1, a deflocculation process had taken place with increasing shear stress and that this is followed by a constant viscosity profile when the shear stress is decreased. The viscosity of the dispersion is high during the initial stage of successive runs. This could be due to the flocculation formed at lower shear stresses caused by the dominance of attractive forces over repulsive forces. The subsequent runs also show a thixotropic behaviour at successively lower levels of viscosity. These show an irreversible break down of flocs with time with the ZVXD and ZDP dispersions. The irreversible time dependency effect is also exhibited by the ZWP dispersions as shown in Figure 10. For ZWP, the increase in the viscosity profiles at higher shear stress after successive runs is probably due to the presence of strong agglomerates of primary particles within the dispersion which was not further broken down due to the imposed resistance to flow, resulting in increasing viscosities.
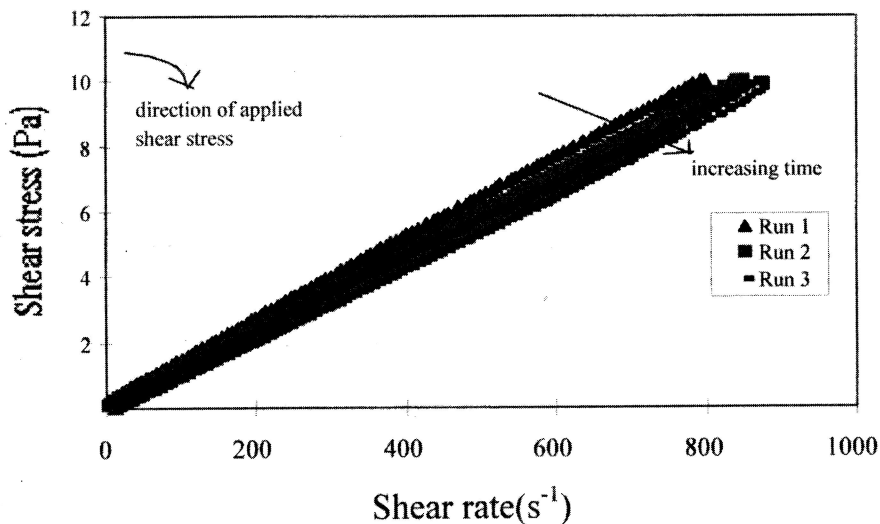
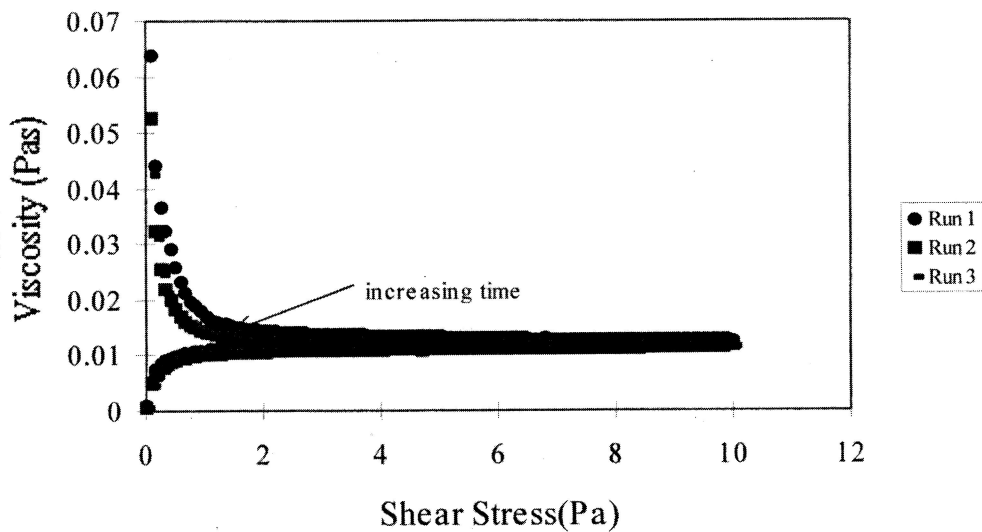**Figure 5.** *Effect of shearing time on flow curves for 50% wt/wt ZVXD dispersions*

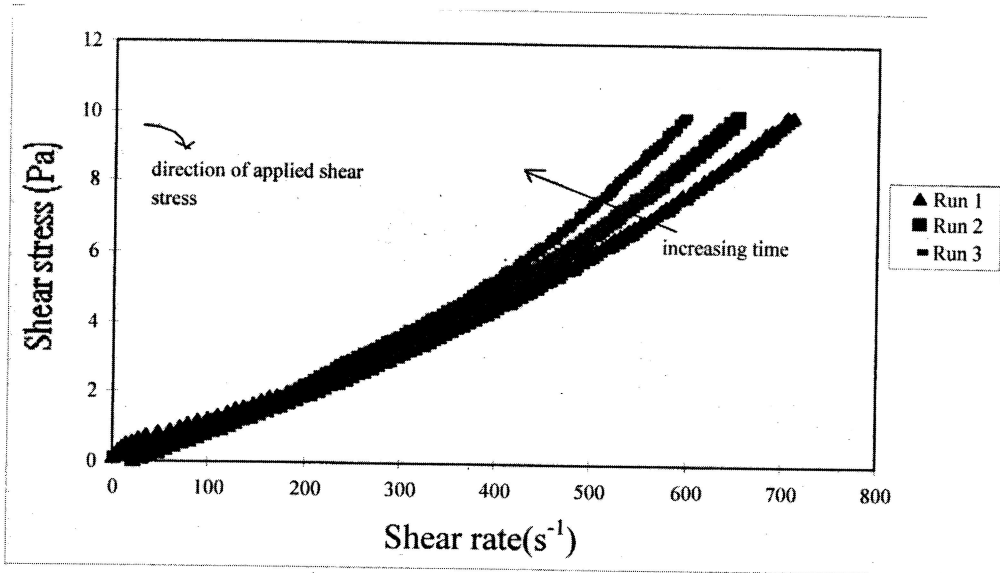**Figure 6.** *Effect of shearing time on viscosity curves for 50% wt/wt ZVXD dispersions*

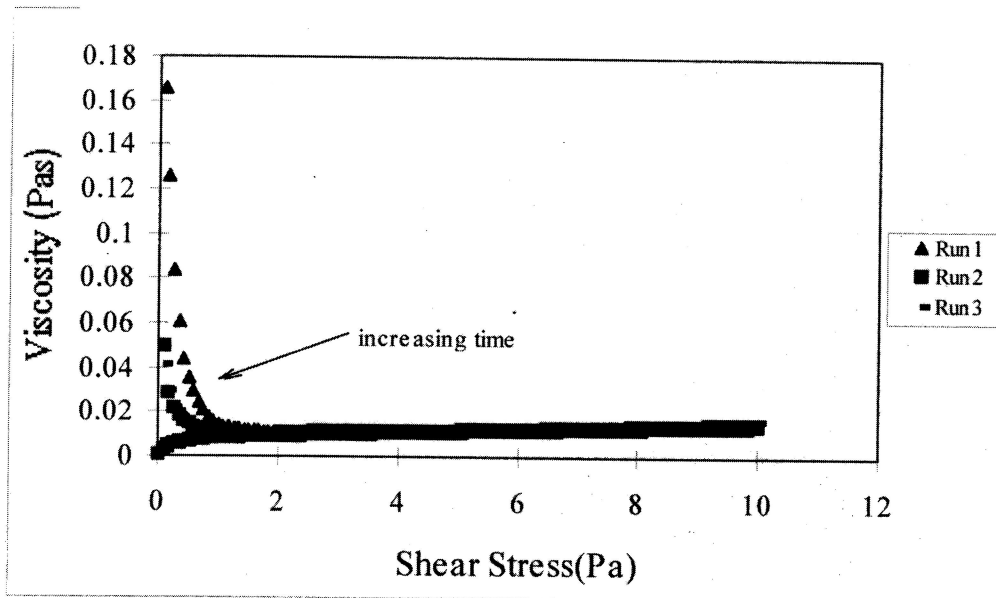**Figure 7.** *Effect of shearing time on flow curves for 50% wt/wt ZDP dispersions*

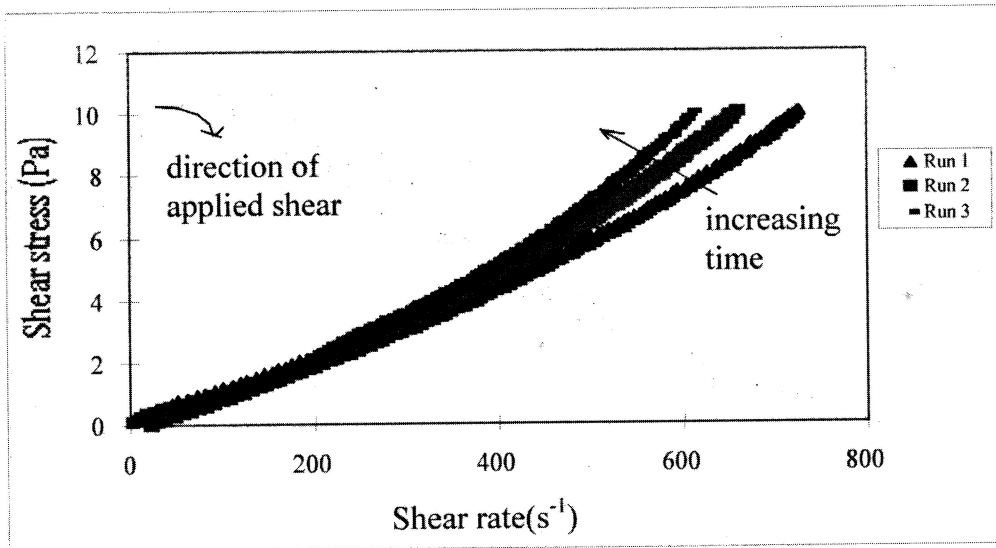**Figure 8.** *Effect of shearing time on viscosity curves for 50% wt/wt ZDP dispersions*

Figure 9. *Effect of shearing time on flow curves for 50% wt/wt ZWP dispersions*

Figure 9 shows hysteresis loops of aqueous dispersions of zeolite at 50% wt/wt concentrations. The ZDP and ZWP dispersions show less marked thixotropic behaviour in the higher shear stress region than the ZVXD dispersion. All three samples show thixotropic behaviour at lower shear stresses. The corresponding viscosity profiles are shown in Figure 10.
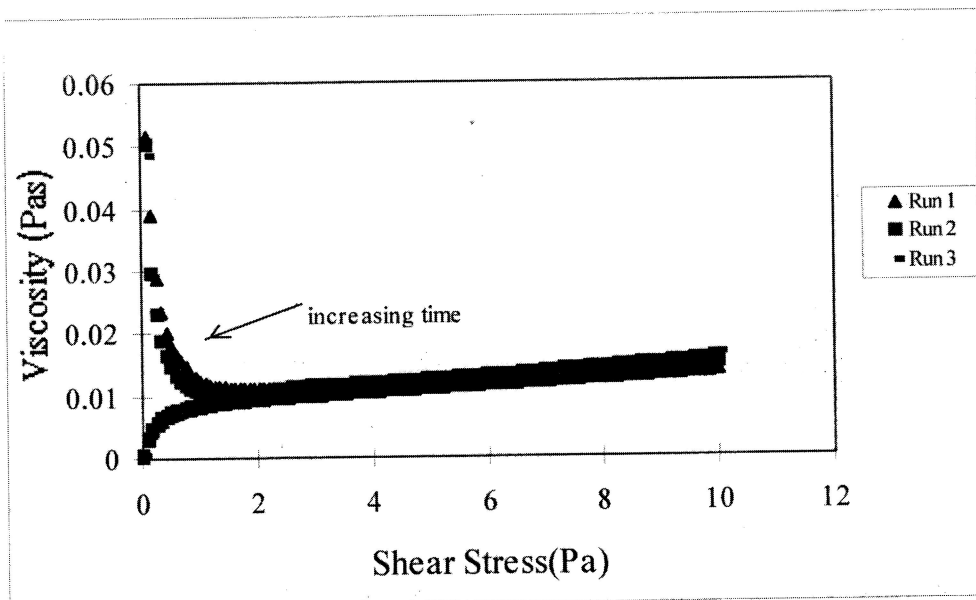

Figure 10. *Effect of shearing time on viscosity curves for 50% wt/wt ZWP dispersions*
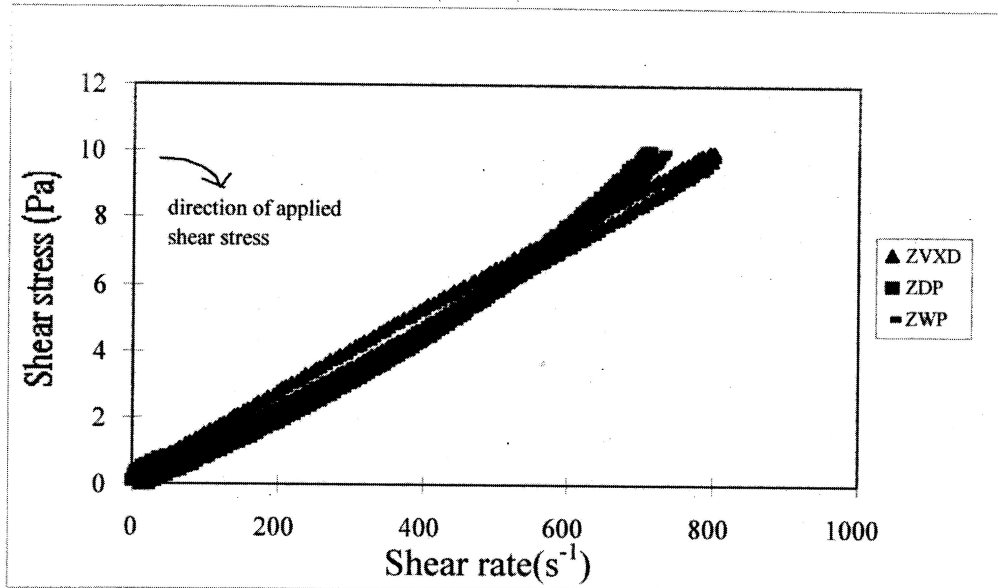
Figure 11. *Effect of shearing on flow curves of 50% wt/wt zeolite dispersions*

Figure 11 shows the hysterisis loops of aqueous dispersions of zeolite at 50% wt/wt concentrations. The ZDP and ZWP dispersions show less marked thixotropic behaviour in the higher shear stress region than the ZVXD dispersion. All the three samples showed thixotropic behaviour at lower shear stress less than 2 Pa. The corresponding viscosity profiles are shown in Figure 12.
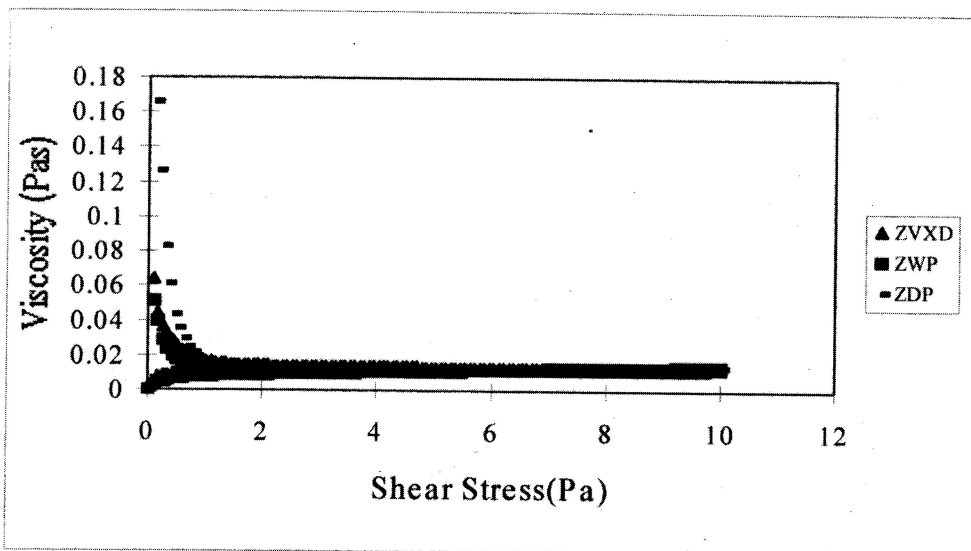

Figure 12. *Effect of shearing time on viscosity curves of 50% wt/wt zeolite dispersions*

CONCLUSION

It was found that the rheological properties of zeolites dispersions with similar size range differ when subjected to constant shear stress and shearing time. These differences in flow behaviour can be attributed to variation in microstucture of the dispersion. It was found that as the value of imposed shear stress increases from 0.85 Pa to 8 Pa, the viscosity of zeolite ZVXD increases within these shear stress values, the viscosity decreases with increasing shear rate. A similar trend was shown by zeolite ZDP but on prolonged shearing time the dispersion showed a shear thickening profile. The viscosity of zeolite ZWP dispersion was found to increase with shear stress within the shearing period. The extent of shear to which flocs are exposed for ZDP and ZVXD grades will affect the structure of the flocs and hence the performance of any mixing and separation processes used for their formulation and subsequent removal. Handling problem is anticipated with ZDP and ZWP. The handling of ZVXD dispersion pose no problem due to its shear thinning behaviour.

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