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Biomaterials 21 (2000) 1387–1392

Biomaterials

Characterisation of the rheological properties and zeta potential of a range of hydroxyapatite powders

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Received 27 October 1999; accepted 17 January 2000

Abstract

The effect of precipitation temperature, i.e. particle morphology on the rheological properties of a hydroxyapatite (HA) slip was investigated and compared to a commercial HA (batch P120 supplied by Plasma Biotal, Tideswell, Derbyshire, UK). The commercial HA was highly crystalline and had a particle size much larger than the HA precipitated at 60 and 80°C. With no deflocculant addition, the commercial HA had a viscosity much higher compared to the precipitated HA as expected. The commercial HA and the HA precipitated at 60°C showed similar pseudoplastic behaviour, but the HA precipitated at 80°C showed Newtonian behaviour. This was explained by the HA precipitated at 80°C having mean particle size of 82.24 nm, but a much wider particle size distribution. This is confirmed by the electrophoretic mobility measurements which show that the HA precipitated at 80°C has a much lower zeta potential at a 0 wt% addition of deflocculant. Because of the wider particle size distribution, the need to add deflocculant is much reduced.

Keywords: Hydroxyapatite; Rheology; Zeta potential

1. Introduction

Hydroxyapatite has been used extensively as a material for implant use and bone regeneration [1–3] due to its bioactivity [2]. It has been used in various forms, such as monolithic block [4], porous foam [5,6] coatings [7,8] and granules [9].

To produce more complex implant designs there are various processing methods and one that is available for producing porous HA implants is reticulated foam technology [10], which makes use of a polyurethane foam, which is coated with an HA slip and then fired to burn off the polyurethane. However, in order to optimise this processing method, an understanding of the rheological properties must be acquired, in order to optimise the slip to coat the foam. The work presented in this paper is an in depth study of the rheology and zeta potential measurements of various HA slips compared to a commercially available HA and a study of the effect of precipitation temperature and hence particle morphology on the rheology and zeta potential of the HA slips. Work was also carried out to optimise the deflocculation of the slip and this is also presented.

2. Materials and methods

2.1. Precipitation

HA was prepared from solutions of calcium nitrate tetrahydrate (118.06 g in 900 ml of double-distilled water (DDW)) and diammonium hydrogen phosphate (39.64 g, 1600 ml DDW), both solutions were adjusted to approximately pH11 with ammonium hydroxide. The diammonuim solution was then added drop wise to the calcium solution (held at either 60 or 80°C) and then left to mature at that temperature for 24 h. The remaining suspension was then rinsed five times with DDW (5 × 1 l), filtered via a Buchner funnel and then dried in a drying cabinet at 70°C.

The commercial HA was supplied by Plasma Biotal (Plasma Biotal, Tideswell, Derbyshire, UK) and had a batch code P120.

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0142-9612/00/$ - see front matter
PII: S0142-9612(00)00032-6

2.2. X-ray diffraction (XRD)

XRD of the samples was carried out on a Philips PW1050/1082 powder diffractometer, in flat plate geometry using Ni filtered Cu K_α radiation (wavelength 1.5406 Å). Samples were ground to a fine powder and mounted in the holder of the diffractometer. Data were collected from 10 to 100° 2θ with a step size of 0.02° and a count time of 12 s. Particle size was determined using the following equation [11].

$$B = \frac{0.9\lambda}{t \cos\theta}$$

where B is the broadening of the diffraction line measured at half its maximum intensity (radians) and t is the diameter of the crystal particle. Corrections for instrument broadening were made using powdered silicon. Full width a half maximum (FWHM) measurements were made on the 0 0 2 peak for HA and on the 1 1 1 peak for silicon.

2.3. Transmission electron microscopy (TEM)

An HA solution was prepared by dispersing 1 g of HA in 50 ml of water. This was placed in an ultrasonic bath for 30 min, to ensure thorough dispersion. A drop of the solution was placed on a Formvar carbon-coated copper 200 grid and left for 1 min. Excess liquid was removed with filter paper and the grid was allowed to dry for about 10 min. The HA particles were then viewed with a JEOL 100CX TEM at an accelerating voltage of 80 kV.

2.4. Flow curves

HA (20 g) was suspended in DDW (30 ml) to produce slips containing 40 wt% solids. The rheological properties of these suspensions were then investigated using a Brookfield Rotating Rheometer DVIII+. The HA slips were stirred at a constant rate on a magnetic stirrer for 5 min to break down any aggregates within. The slip was then transferred to the rheometer. The shear rate was started at 0.13 s^{-1} (the lowest shear rate obtainable with this rheometer) and then varied between 2.5 and 55 s^{-1} at intervals of 2.5 s^{-1}. Each shear rate was given a time lag of 1 min to establish an equilibrium before proceeding to the next shear rate step. Measurements of shear rate vs. viscosity were taken to produce flow curves. The standard deviation was calculated from at least two repeat measurements. The method was repeated with deflocculant additions at 0, 0.03, 0.06, 0.13 and 0.19 wt%.

2.5. Thixotropic properties

The slips were stirred at a constant rate on a magnetic stirrer for 5 min and then were transferred to the rheometer. Their viscosity and shear stress were measured at a constant shear rate (the variation of velocity with distance) of 50 s^{-1} for 60 min with data being collected at 1 min intervals, the data for these 60 points were averaged and the standard deviation calculated. The method was repeated for deflocculant additions of 0, 0.03, 0.06, 0.13 and 0.19 wt%.

2.6. Zeta potential

Zeta potential measurements were performed on the HA P120 and the precipitated HA particles using the Rank Brothers electrophoresis apparatus. The HA particles were suspended in a 0.001 mol% potassium chloride (KCl) solution so as to maintain a constant electrical double-layer thickness. 0.05 wt% solutions were used so a good contrast could be achieved when viewing the particles through the microscope. Measurements were taken after each deflocculant addition of 0, 0.06, 0.13 and 0.19 wt% and the mean was calculated from measurements on 20 particles, for each deflocculant addition.

3. Results

3.1. X-ray diffration

The X-ray diffraction (Fig. 1) shows that the P120 is significantly more crystalline compared to the HA precipitated at both 60 and 80°C. From the particle size measurements, the P120 has a significantly larger particle size with a values of 129.99 nm compared to the HA precipitated at 60 and 80°C, which had a particle size of 61.06 and 82.24 nm, respectively.

3.2. Transmission electron microscopy

Fig. 2a–c shows the morphology of the HA powders after precipitation. Measurement of particle size from the TEM images, is difficult, due to the high aspect ratio of the particles, for all three HA's, however, Fig. 2a is concurrent with the X-ray diffraction measurements, in

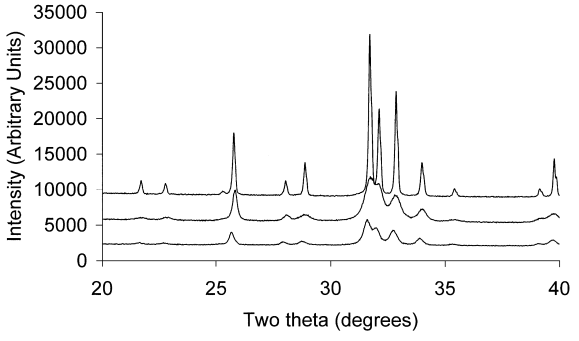

Fig. 1. X-ray diffraction traces for P120 (upper), HA precipitated at 60°C (middle) and 80°C (lower).

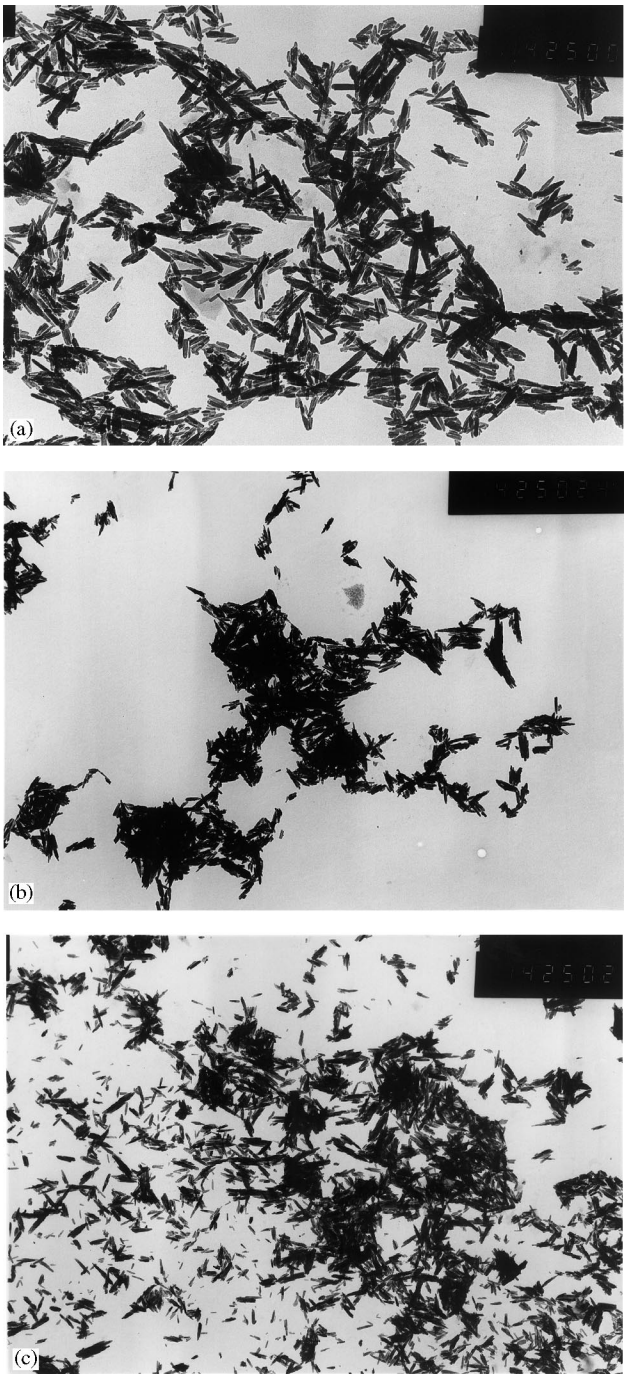

Fig. 2. TEM of HA for: (a) P120 (original magnification ×23 000) (b) HA precipitated at 60°C (original magnification ×14 000) and (c) HA precipitated at 80°C (original magnification ×14 000).

that the P120 has a much greater particle size compared to the two precipitated HA's. The HA precipitated at 60°C (Fig. 2b) shows a relatively narrow particle size distribution like the P120, but the HA precipitated at 80°C (Fig. 2c) shows evidence for the presence of some fine particles. All three HA's showed an acicular morphology.

3.3. Flow curves

It can be seen from Fig. 3 that at a 0 ml addition the HA precipitated at 80°C acts as a Newtonian system whereas the HA precipitated at 60°C and the HA P120 behave as pseudoplastic systems. Also the viscosity for the P120 is very much higher compared to the precipitated HA's. When a small amount of deflocculant is added, for the P120, the viscosity increases slightly. For the HA precipitated at 80°C, there is no effect on the rheology. The HA precipitated at 60°C shows a change to Newtonian behaviour with a 0.06 wt% addition of deflocculant (Fig. 4). The HA P120 starts to deflocculate at a 0.13 wt% addition (Fig. 5) and is fully dispersed and Newtonian in character at a 0.19 wt% addition (Fig. 6), the HA precipitated at 60°C exhibits dilatant behaviour at a 0.19 wt% addition (Fig. 5). The change in behaviour with deflocculant addition for the three different types of HA is summarised in Table 1.

3.4. Thixotropic properties

Fig. 7 shows the effect of Dispex N40 on the viscosity of the systems when subject to constant shearing at 50 s^{-1}. It can be seen that the HA precipitated at 80°C is at a constant low value of less than 50 MPa throughout all Dispex additions. The HA precipitated at 60°C also stays at constant level of approximately 300 MPa even though its rheological behaviour is changing. The HA P120, however, starts off as a highly viscous system with a viscosity of 1000 MPa and when deflocculated comes down to a viscosity of 70 MPa.

No thixotropic properties were found in any of the systems.

3.5. Zeta potential

The zeta potential of each of the systems at a 0 wt% addition are negative (Fig. 8) with HA precipitated at 80 being the most negative then the HA precipitated at 60°C and then the HA P120. On addition of Dispex N40 the zeta potential rises. All systems have a maximum around the 0.06 wt% addition.

4. Discussion

The P120 HA is produced via a hydrothermal method and has a significantly larger particle size compared to the precipitated HA samples. For the precipitated HA samples, it is known that temperature significantly affects the precipitate morphology [12] and our findings are concurrent. The HA precipitated at 60°C has a particle size of 61.06 nm and at 80°C, a particle size of 82.24 nm, measured by line broadening effects. This does not explain the deflocculant effects. However, the TEM may

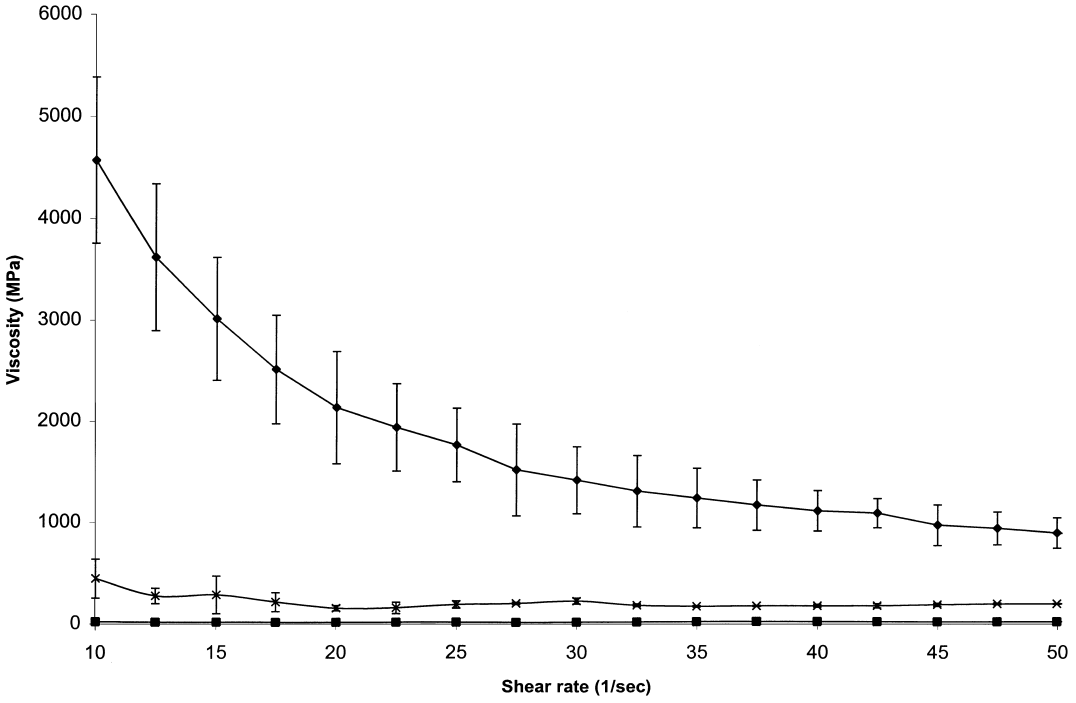

Fig. 3. Viscosity against shear rate for the 3 HA's with 0 wt% deflocculant (◆—HA P120, ■—HA precipitated at 80°C, ×—HA precipitated at 60°C).

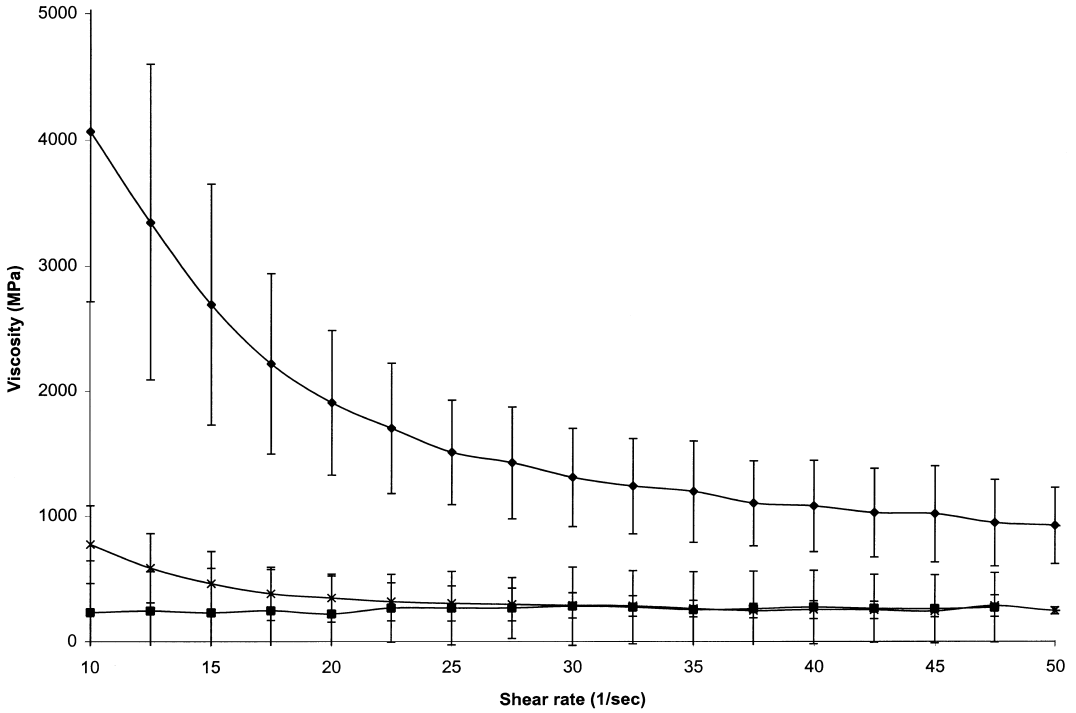

Fig. 4. Viscosity against shear rate for the 3 HA's with 0.06 wt% deflocculant (◆—HA P120, ■—HA precipitated at 80°C, ×—HA precipitated at 60°C).

help to explain this. Whilst the mean particle size for the HA precipitated at 80°C is larger, there appears in the TEM to be some fine particulate, which would stay in suspension more easily, hence the findings for the viscosity at 0 ml addition and the effect of deflocculant additions.

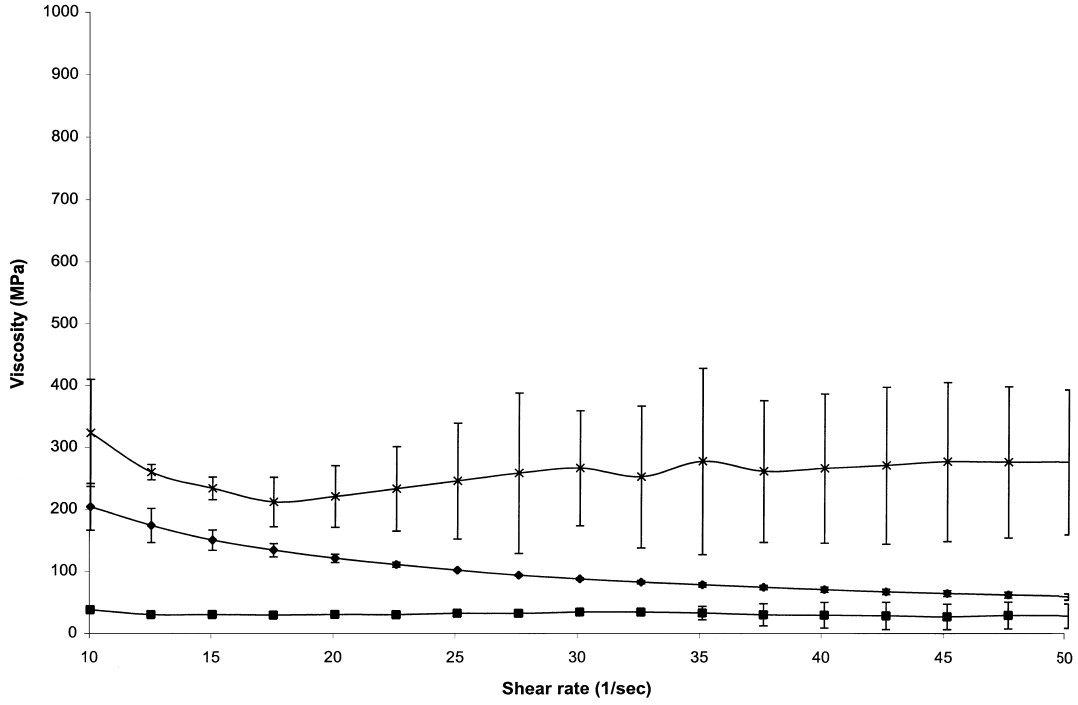

Fig. 5. Viscosity against shear rate for the 3 HA's with 0.13 wt% deflocculant (◆—HA P120, ■—HA precipitated at 80°C, ×—HA precipitated at 60°C).

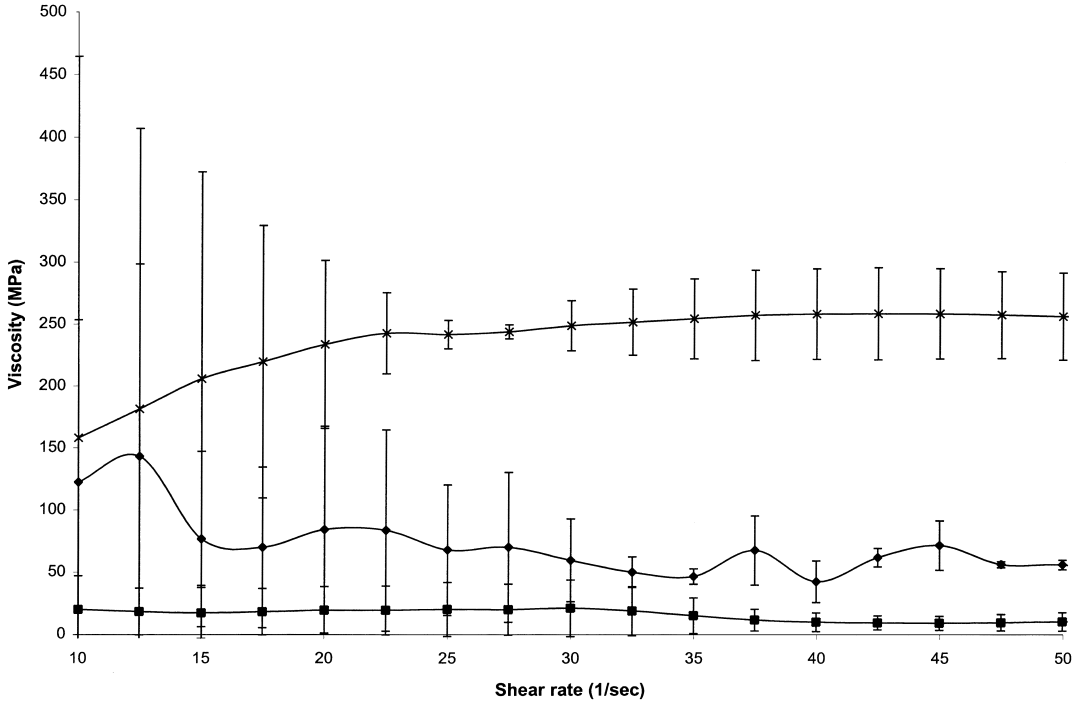

Fig. 6. Viscosity against shear rate for the 3 HA's with 0.19 wt% deflocculant (◆—HA P120, ■—HA precipitated at 80°C, ×—HA precipitated at 60°C).

At a 0 ml addition the HA precipitated at 80°C acts as a Newtonian system indicating that all the particles are already in suspension and are fully deflocculated without the need for any addition of Dispex N40. The HA precipitated at 60°C and the P120 both behave as pseudoplastic systems with no Deflocculant added. The HA P120 requires more Dispex N40 to fully deflocculate the system because of its larger particle size. Once the systems have been fully deflocculated a further addition of deflocculant to any of the systems does not have a large effect on the viscosity but their behaviour changes from Newtonian to dilatant.

Table 1
Summary of change in rheological properties with deflocculant addition for the three hydroxyapatites

wt%	HA P120	HA @ 60	HA @ 80
0	Pseudoplastic	Pseudoplastic	Newtonian
0.03	Pseudoplastic	Pseudoplastic	Newtonian
0.06	Pseudoplastic	Newtonian	Newtonian
0.13	Almost Newtonian	Newtonian	Newtonian
0.19	Newtonian	Dilatant	Newtonian

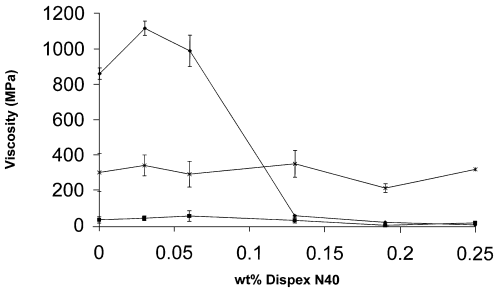

Fig. 7. Effect of deflocculant addition on viscosity for the three HA's with a shear rate of 50 s^{-1} (◆—HA P120, ■—HA precipitated at 80°C, ×—HA precipitated at 60°C).

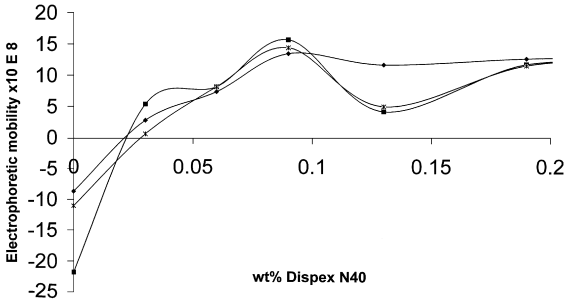

Fig. 8. Effect of deflocculant addition on the electrophoretic mobility of the 3 HA's (◆—HA P120, ■—HA precipitated at 80°C, ✳—HA precipitated at 60°C).

No thixotropic properties were noticeable in any of the suspensions, this was because of the low solids content that was used in these experiments.

All the systems begin with a negative zeta potential indicating that they all start with a positive charge. When the Dispex N40 is added to the systems the zeta potential increases slowly until it is positive indicating that the particles have a net negative charge. This is because Dispex N40 dissociates in water to produce a sodium cation and a polymeric anion. Since the HA particles have an overall positive charge, the polymeric anion is attracted to the surface of the particle and interacts. This happens many times over the particle surface. The particle is effectively stabilised by the neutralising effects of the positive to negative interaction and the particle is now overall negatively charged. When the maximum adsorption of the potential determining ion on the surface of the HA particles has been reached, further addition of this potential determining ion only increases the charge in the liquid phase therefore reducing the potential difference between the surface and the liquid. This reduction in surface potential leads to a reduction in the zeta potential.

5. Conclusions

HA precipitated at 80°C is suspended in solution without the need for any deflocculants this is due to the particle size distribution. HA P120 and HA precipitated at 60°C both act as pseudoplastic materials with the HA precipitated at 60°C being the first to deflocculate and show Newtonian behaviour with the addition of Dispex N40. This is because the HA precipitated at 60°C has a smaller particle size than the HA P120. If an excess of deflocculant was added in any of the systems they would exhibit dilatant behaviour.

Zeta potential measurements show that all the particles start off with a positive charge. When deflocculation has occurred, the overall charge becomes negative. This is due to the negative part of the dissociated deflocculant attaching itself to the HA particles.

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