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Manufacture of colloidal polymer ellipsoids for anisotropic conducting nano-composites

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This project aimed to make anisotropic conducting nano-composites based on a segregated system of 20 nm gold particles and deformed polyethylene spheres of colloidal size. Two methods for achieving the deformation of the colloidal polyethylene spheres were attempted, namely to exploit the elongational flow field at the entrance to a capillary and alternatively to make cast films of a water soluble polymer containing the colloidal particles and draw them in the solid state. In the latter method, sections of film were elongated at an elevated temperature using a tensile testing machine. The drawn films were dissolved in water and the deformed particles were extracted and concentrated by ultracentrifugation. This method was successful in producing ellipsoids of a prescribed aspect ratio. Further successful deformation was carried out using PMMA particles and monodisperse polystyrene particles. Polystyrene spheres containing 20 nm diameter magnetite particles could not be deformed using this process. A range of experimental techniques were exploited to characterise the ellipsoidal particles, including transmission electron microscopy and photocorrelation spectroscopy. Subsequent addition of metal oxide particles to the polymer ellipsoids resulted in some success in that a small number of 20 nm diameter magnetite particles was observed to be attached to the surfaces of the much larger (1 μm) polystyrene ellipsoids. The mechanism of attachment has not yet been elucidated but this has significant potential for future composite device production. © *2001 Kluwer Academic Publishers*

1. Introduction

Earlier work on conduction mechanisms in metal-filled composites with polymer matrices [1] was found to produce novel materials because of a segregated network of interconnecting particles which enhanced the anticipated electrical conductivity of the material. As the metal particles were segregated, the measured conductivity was higher than that expected for a system in which the metallic particles are uniformly distributed. The electrical conductivity was isotropic as the particles had spherical geometries. The actual segregated system used consisted of 100 nm diameter polyethylene particles and 20 nm diameter gold particles. The segregation arose because the gold particles were added to the colloidal polyethylene particles in aqueous media. The gold particles were attracted to the surfaces of the polyethylene particles and the colloid was destabilised using an acid. The polyethylene/gold precipitate was filtered, dried and carefully pressed into discs to retain the segregation. The system is shown schematically in Fig. 1a and b.

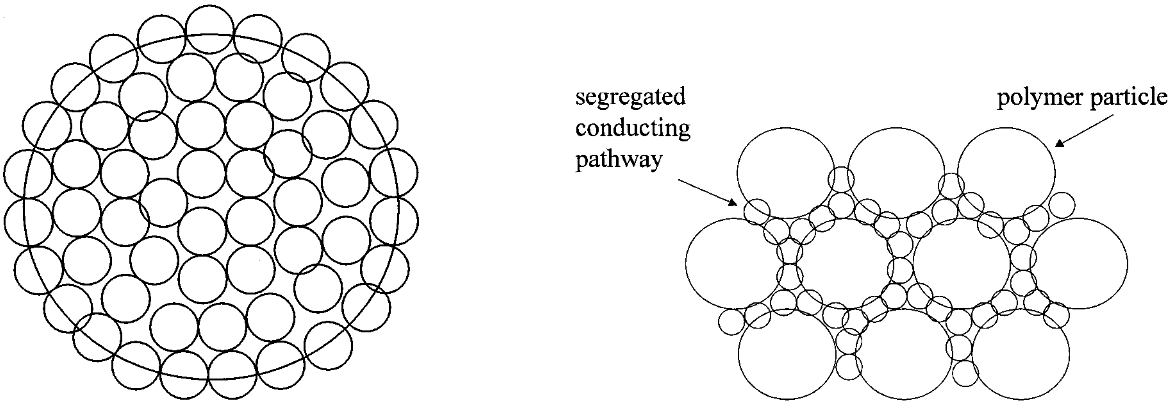
In our current work, it was intended to extend the above ideas to the case where the polymer particles have an ellipsoidal shape, as shown in Fig. 2a and b. This will require a method for deforming the initially spherical particles into ellipsoids having a specified ellipticity ratio. Once the ellipsoidal particles have been prepared, metal particles can be added to produce a segregated system, as described above. If the ellipsoidal particles can be aligned, then a composite having an anisotropic conductivity should result. This alignment may occur naturally due to mutual self-aggregation of the polymer particles, as in liquid crystals [2], or may be induced by the application of an external electric field. In the latter case, there is the prospect of producing a useful optical switch.

Ellipsoidal polymer particles have previously been made [3, 4] but none as small as these proposed here. The source materials will be a range of polymer latex particles with diameters of the order of nanometres. The effects of flow on the deformation of viscous particles has long been investigated [5–8]. Preliminary investigations at Brunel University into a new method which exploited the extensional flow field at the entrance to a capillary have been carried out and was shown to have potential. It was intended that this method will be investigated further, alongside established solid state deformation processes.

2. Materials and process methods

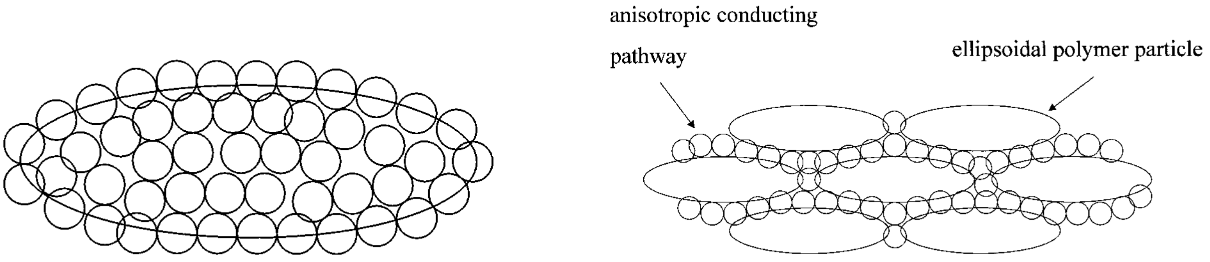
2.1. Materials

The aqueous colloids used were PolyEM40, a polyethylene (PE) latex, and Primal-B85, a polymethylmethacrylate (PMMA) latex supplied by Rohm



(a) (b)

Figure 1 (a) Colloidal polymer sphere coated with smaller metal particles; (b) idealised section through the composite structure showing segregation of polymer and metal components and also the conducting pathway.



(a) (b)

Figure 2 (a) Colloidal ellipsoidal polymer particle coated with smaller metal particles; (b) idealised section through the composite structure again showing component segregation and the anisoptropic conducting pathway.

and Haas. Also used were two monodisperse polystyrene (PS) latices 1.0 μm and 0.1 μm diameter and two superparamagnetic polystyrene latices (SPPS) with average diameters of 0.8 μm and 0.9 μm containing magnetite (67% of solids and 24% of solids respectively) supplied by Sigma Chemicals. Selected materials were further characterised by photon correlation spectroscopy (PCS), scanning and transmission electron microscopy (SEM, TEM) to look at particle size and morphology. Differential scanning calorimetry (DSC) measurements were used to aid the selection of processing temperatures. PolyEM40 and Primal-B85 colloidal systems in the "as received" state were stabilised by surfactant molecules. The surfactants were extracted from the system and identified by infra-red analysis.

2.2. Capillary deformation

A capillary deformation method [1] had previously been investigated. The aim was to see if heated PE latex particles could be deformed in the elongational and shearing flow fields generated in the capillary. The vessel containing the hot latex was pressurised to a level where the latex was just observed to flow through the capillary. Several cycles of the latex were made through the capillary. Initial results had suggested that the process produced a few deformed particles but this was later thought to be contamination of some kind. Repeating the same processing procedure in this study did not produce any deformed particles but it was thought that the process still had some potential.

The system was improved to work at higher, more controllable pressures and temperatures. Sampling techniques were improved, so that instead of sampling the latex from the whole run, smaller aliquots were taken when the pressure was steady and the temperature in the equipment had had time to equilibrate. The hot latex was chilled on exit from the flow cell. A computer generated set of experiments using the maxima and minima of each variable were carried out using PolyEM40 latex, as shown in Table I. The variables were: deformation temperature, pressure and number of passes through the flow cell. The number of passes through the flow cell may have an advantageous or deleterious effect on the number of particles produced. Any deformed particles produced may relax back on reheating for the next pass though the flow cell or they may behave differently at temperature and remain in the deformed state.

Further to this, PE latex particles were added to glycerol and poly(vinyl alcohol) solutions to look at the effect of increasing the viscosity ratio between the bulk phase and the particle phase. The elongational flow field at the capillary entrance was exploited to its limits, but ultimately did not produce individual ellipsoidal particles. The process did produce some necklace type structures of adjoined spheres, most likely due to collisions in the capillary. The necklaces were between two and nine particles long and their overall external shape was rod-like. These may be of interest at a future stage.

TABLE I Computer designed randomised experiment set for capillary deformation

Experiment no.	Temperature (°C)	Pressure (kPa)	Number of Passes
11	100	70	4
2	100	48	2
15	93	48	2
1	93	70	8
4	93	28	8
7	93	48	4
3	93	70	2
1	93	70	8
13	97	28	2
3	93	70	2
2	100	48	2
12	97	70	2
10	100	28	4
9	93	28	2
5	100	70	8
14	100	48	8
6	97	70	4
4	93	28	8
8	97	48	8
5	100	70	8

2.3. Solid state deformation

The latex particles were stirred into a 7.5 wt% aqueous polyvinyl alcohol solution and a film was cast. The polyvinyl alcohol needed to be added to the water quickly and with stirring to get a uniform solution. Small gels formed otherwise which affected the uniformity of the drawing process. The films were cast onto a carefully levelled glass plate to ensure an even thickness. After drying, the films were cut into strips and drawn in an Instron Tensile Testing machine using special film holders. An oven attachment was used to achieve the temperature required. The drawn films were redissolved directly into clean water to avoid possible relaxation effects and the particles were separated using an ultracentrifuge. The ellipsoidal particles from the ultracentrifuge were re-suspended in water. The particles were examined using SEM, TEM and laser particle sizing.

Drawing temperatures and % elongation required for a specified particle aspect ratio were established for each material, except for the SPPS which did not deform. For PE, temperatures between 65°C and 105°C and strains between 80% and 195% were used. Particle aspect ratios (length/diameter) between 2 and 6 were achieved. Only one set of PMMA films were made and these were drawn at 115°C and a strain of 115 ± 5%. PS films were drawn between 130°C and 190°C and strains between 85% and 160%. As the temperature increased, film relaxation became a problem and at 190°C, the films showed signs of degradation. Particle aspect ratios achieved were between 2.1 and 5.7. A combination of the highest temperature and highest strain rate did not always produce the highest aspect ratio.

This deformation technique was an improvement over the existing method [3] in that a uniform draw ratio in the cast film was achieved and much cleaner particles were obtained. PMMA, PE, 1.0 μm PS, 0.1 μm PS and the filled SPPS particles were subjected to this process.

2.4. Re-suspension of the ellipsoids and addition of conducting particles

Scanning electron microscopy and laser particle sizing of the PolyEM40 particles after ultracentrifugation showed that they had aggregated as shown in Fig. 3. During the process of being mixed into the polyvinylalcohol film and the ultracentrifugation, the original

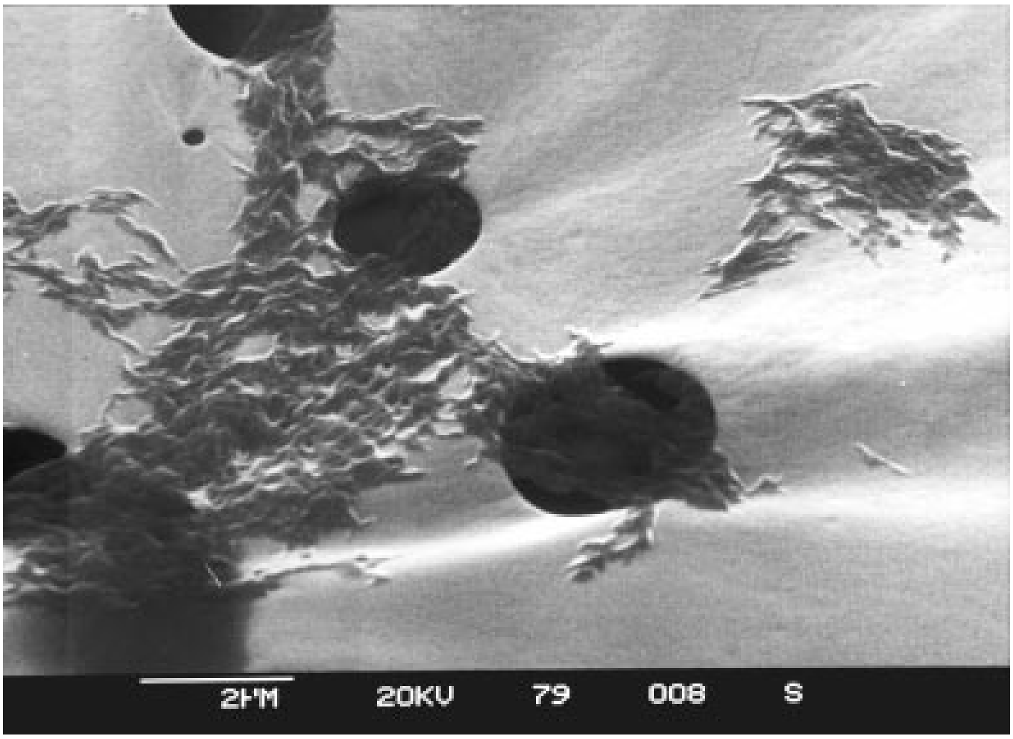


Figure 3 Scanning electron micrograph of PolyEM40 ellipsoidal particles after ultracentrifugation from the redissolved film.

surfactant stabiliser had been lost. As the surfactants in the as-received Poly EM40 and the Primal 85 had been identified by Infra-red Spectroscopy, suitable surfactant molecules were able to be re-introduced to the particle/water suspension after particle recovery from the ultracentrifuge to aid floc break up. Gold particles and magnetite particles were added to the suspensions to see if there was any attraction between them and the polymer ellipsoids.

3. Results

3.1. Materials characterisation

Electron microscopy indicated that the various as-received latex particles had a spherical morphology. Particle size analysis by photon correlation spectroscopy agreed well with the manufacturer's specifications. The TEM, even under low dose viewing conditions, gave differing results, with some particles appearing larger and some smaller than specified. The TEM was useful for comparing the shapes of the deformed particles with the starting spheres, although size measurements were not absolute. The TEM had been fully calibrated using a grating.

3.2. Capillary deformation

Even after optimising the equipment, this technique did not produce any permanently deformed particles. Under transmission electron microscopy, the process was shown to produce necklaces of joined spherical particles. The longest necklace seen consisted of 9 particles but the diluting and sampling technique for transmission electron microscopy would not have favoured longer chains. Most necklaces were 3–6 particles long. The glass flow cell allowed for the flow to be observed under crossed polarisers. Birefringence was seen but was due to "necklace" formation rather than actual deformed particles.

The glycerol/PE experiment produced large PE particles of 2–3 μm diameter. Some flocculation of the particles may have occurred during mixing and the flocs coalesced on heating. The polyvinyl alcohol/PE experiment did not produce the characteristic necklaces and the PE particles did not flocculate. The particles looked the same before processing as afterwards. Polyvinyl alcohol acts as a steric surfactant which may have prevented the PE particles approaching each other and hence prevented necklace formation.

3.3. Solid state deformation

The drawing of cast films was the most successful technique, as shown in Figs 4–10. The maximum aspect ratio achievable depended on the material being deformed but prescribed aspect ratios could be produced by controlling the draw ratio of the cast film.

The SPPS particles could not be deformed. The polyvinyl alcohol/SPPS film was heated to 200°C. At this temperature, the film showed signs of degradation. A batch of films was crosslinked using an ion beam to see if the shear stress transfer to the particles could be increased but the magnetite loaded particles remained spherical as shown in Fig. 11.

Figure 4 Transmission electron micrograph of 0.1 μm polystyrene ellipsoids.

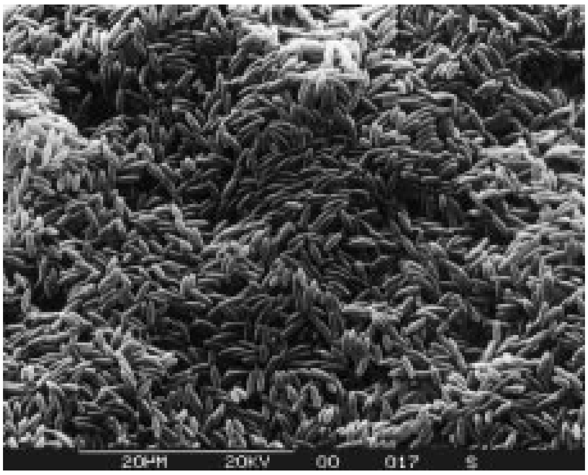


Figure 5 Scanning electron micrograph of 1.0 μm polystyrene ellipsoids.

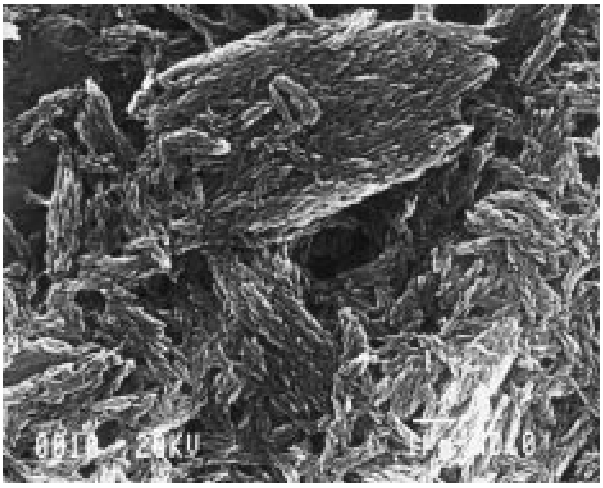


Figure 6 Scanning electron micrograph of 0.1 μm polystyrene ellipsoids.

3.4. Re-suspension and addition of conducting particles

Laser particle sizing indicated that adding new surfactants did help to break up the flocs that had formed when the particles had been extracted from the polyvinyl alcohol and water mix in the ultracentrifuge. The 20 nm gold particles did not show a preference for the polymer

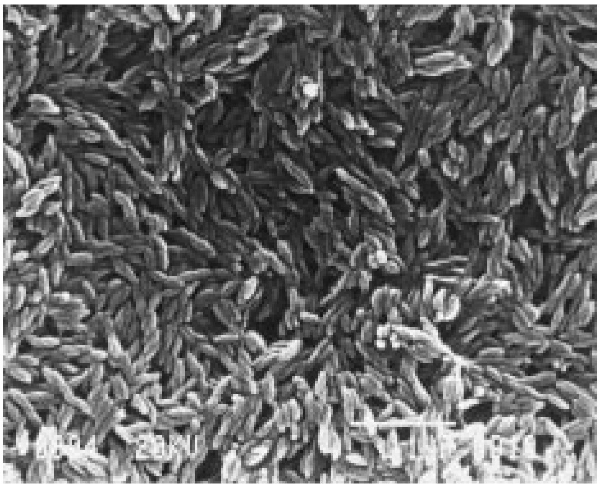


Figure 7 Scanning electron micrograph of 0.1 μm polystyrene ellipsoids.

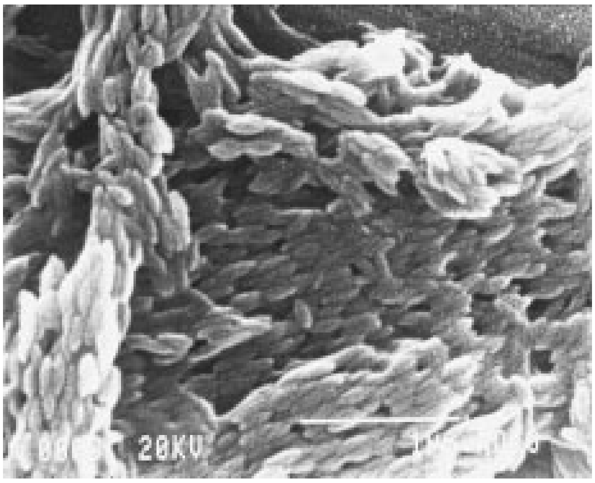


Figure 8 Scanning electron micrograph of 0.1 μm polystyrene ellipsoids.

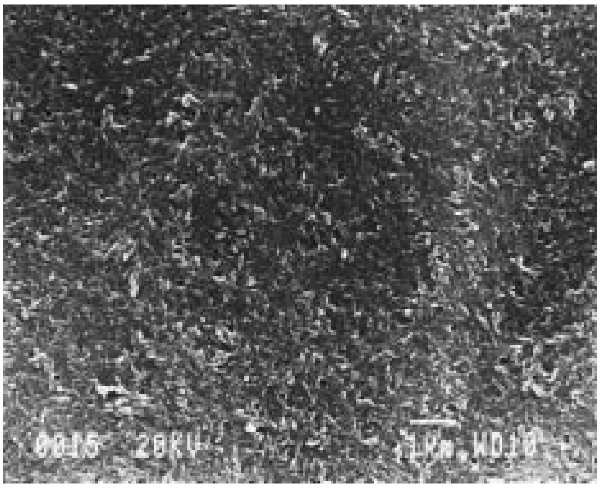


Figure 9 Scanning electron micrograph of 0.1 μm PolyEM40 ellipsoids.

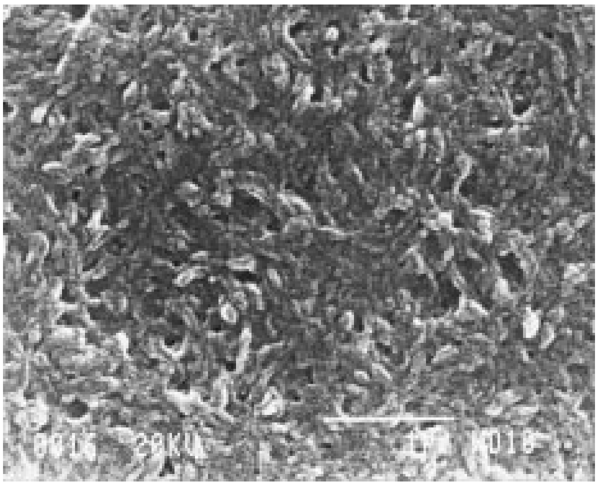


Figure 10 Scanning electron micrograph of 0.1 μm PolyEM40 ellipsoids.

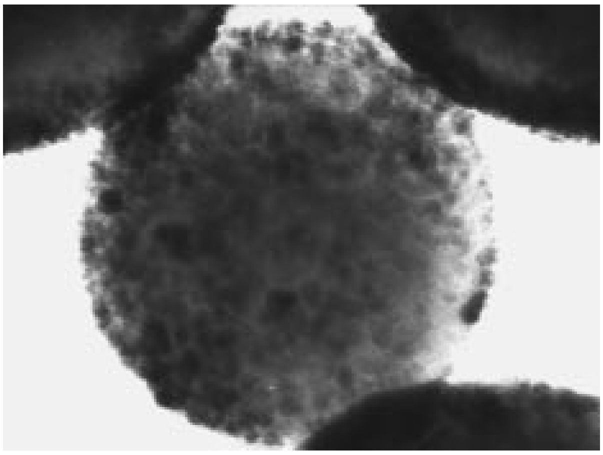


Figure 11 Transmission electron micrograph of 250 nm diameter magnetite loaded polystyrene particle.

Figure 12 Transmission electron micrograph of 1 μm polystyrene ellipsoids and magnetite particles.

particles but some magnetite particles were attracted to the polystyrene particles as shown in Fig. 12.

4. Discussion

4.1. Capillary deformation

This process was taken to its limits to try to get it to work. It is still possible some deformation was happening but relaxation processes were occurring. The range of temperatures used meant that the PolyEM40 particles had a range of viscosities. A lower viscosity favours deformation but the higher temperature used to obtain it favours relaxation. Increasing the viscosity of the deforming matrix did not produce any permanent particle deformation.

4.2. Solid state deformation

This process was successful in producing ellipsoidal particles once some initial problems had been overcome. The concentration of polyvinyl alcohol is important. Films with 10 wt % polyvinyl alcohol in water could not easily be redissolved after drawing. The drawing temperature increased the crystallinity of the film and made it less soluble. 7.5 wt % was found to be the optimum level. The SPPS particles could not be deformed at the limits of the process. The addition of even small amounts of material to a polymer is known to increase its viscosity substantially and it was thought that these particles were just too viscous.

4.3. Re-suspension and addition of conducting particles

Flocs forming after ultracentrifugation needed to be broken up to expose the surface area of the ellipsoids to the metal particles. This meant adding a surfactant which was likely to be detrimental to the approach of metal particles. Non-ionic, anionic and cationic surfactants were tried but were not successful in attracting the metal particles to the small polymer particles. The larger PS particles did show some attraction for the magnetite but a surfactant was not needed in this system to redisperse the PS ellipsoids, because of their size. The lack of surfactant would have allowed the metal particles to approach the surface of the PS ellipsoids.

5. Conclusion

The project produced very small ellipsoidal particles of polyethylene, polystyrene and polymethylmethacrylate. The ellipsoids showed promising behaviour in terms of their aggregation. Using a combination of temperature and strain in the drawing process, any particle aspect ratio can be achieved within limits. Deformation of filled particles of the type used proved unsuccessful using this technique. Deformation of different particles with lower solids content may be successful.

Some natural affinity was demonstrated between magnetite particles and the polystyrene particles. This aspect of the work needs investigating further to achieve a conductive coating (made up of discrete colloidal metal particles) on the polymer particles, prior to the formation of conducting composite systems.

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