Conducting polymer–colloidal silica composites

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We describe the preparation of conducting polymer–colloidal silica composites by the *in situ* deposition of a thin coating of chemically synthesized polyaniline or polypyrrole onto monodisperse silica particles (~1 μm diameter). These composite materials have been characterized by thermogravimetric analysis, scanning electron microscopy, four-point probe conductivity measurements, Fourier transform infra-red microscopy and Rutherford back-scattering spectrometry.

(Keywords: conducting polymers; composites; characterization)

INTRODUCTION

Polyaniline is generally recognized to be the only air-stable conducting polymer[1]. Originally it was considered to be an intractable material but in the last few years several groups have reported that both the doped and the undoped forms can be dissolved in various solvents[2–5]. Ring or *N*-substituents such as CH_3–, CH_3O– or SO_3H groups have also been shown to improve the solubility of polyaniline although usually at the cost of reduced conductivity[6–10]. One of us (S.P.A.) has recently described the synthesis of sterically stabilized colloidal dispersions of polyaniline particles[11–15]. In this approach, the submicronic conducting polymer nuclei are stabilized with respect to further aggregation by an outer layer of chemically grafted polymeric surfactant. In 1987 Yassar *et al.* reported that chemically synthesized polypyrrole could be deposited *in situ* onto polystyrene latex particles[16]. The colloidal stability of these composites was not explicitly described by the authors but, in our opinion, the non-solvation of the polypyrrole coating under the reported preparation conditions would inevitably result in the irreversible precipitation of the particles. Furthermore, polypyrrole is insoluble in all known solvents so the redispersion of the coated particles in any medium is unlikely. In this paper we report the preparation and characterization of similar 'inside-out' conducting polymer colloids in which polyaniline or polypyrrole is grown as a thin conducting overlayer on a suspension of ~1 μm diameter colloidal silica particles (*Figure 1*). Unlike the polystyrene–polypyrrole composites described by Yassar *et al.* our polyaniline system can be resuspended in solvent media which are good solvents for the outer layer of polyaniline steric stabilizer.

EXPERIMENTAL

Preparation

The colloidal composites were prepared by a modified chemical synthesis of the conducting polymer using a methodology first described by Gregory and co-workers[17–19].

Polypyrrole-coated silica. Pyrrole (67 μl) was injected into a sample bottle containing a stirred solution of 0.57 g $FeCl_3 \cdot 6H_2O$, 0.15 g salicylic acid and 1.00 g silica (ex. ICI, ~1 μm diameter) in 50 ml deionized water. The reaction mixture was stirred continuously at 25°C for 22 h, filtered under gravity, washed with water and methanol and dried at 65°C for 90 min in air to obtain a fine grey powder.

Polyaniline-coated silica. Aniline (100 μl) was injected into a sample bottle containing a stirred solution of 0.25 g $(NH_4)_2S_2O_8$ and 1.00 g silica in 50 ml 1.2 M HCl. The reaction mixture was stirred continuously at 25°C for 2 h, filtered under gravity, washed with 1.2 M HCl and dried at 95°C for 90 min in air to obtain a fine light green powder.

Characterization

Conductivity measurements were made on compressed pellets of the powder using conventional four-point probe techniques.

Thermogravimetric measurements were made using a Perkin Elmer TGA-7 instrument equipped with a high

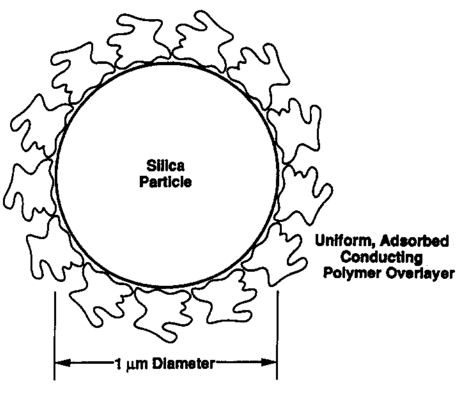

Figure 1 Schematic of conducting polymer-coated silica particles

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temperature furnace. All runs were made under nitrogen at a scan rate of 20°C min^{-1} unless otherwise stated.

Scanning electron microscopy (SEM) studies were carried out using either a Philips SEM 505 or a Camscan 4 instrument. The latter instrument was used for the energy dispersive analytical X-ray (EDAX) measurements. Samples were affixed to aluminium sample holders using a conducting carbon paste.

Fourier transform infra-red (*FT*i.r.) microscopy studies were carried out using a Bio-Rad FTS-40 spectrometer with a Digilab IR-400 microsampling accessory. The spectral resolution was 2 cm^{-1} and 64 scans were averaged for each spectrum. The specimen substrate was a KBr disc.

Rutherford back-scattering experiments[20] were carried out at the Ion Beam Facility at Los Alamos National Laboratory using a previously described instrument set-up[21]. Experimental details: He^+ incident beam energy = 2.2 MeV; ion beam current = 60 nA; total charge focused on sample = 40 μC; single back-scattering detector placed at 13° to the incident He^+ beam. Specimens were affixed to carbon cloth using the same conducting carbon paste used for the preparation of the SEM samples.

The polyaniline–silica composites were redispersed in concentrated sulphuric acid using an ultrasonic bath. If this composite was first dedoped by treatment with 0.1 M $\mathrm{NH_4OH}$ it could be redispersed in dimethyl sulphoxide (DMSO). Redispersal of the doped polypyrrole–silica composites was attempted in $\mathrm{H_2O}$, 1.2 M HCl, methanol and DMSO. Visible absorption spectra of the doped and dedoped polyaniline–silica composites were recorded using a Beckman DU70 spectrophotometer.

RESULTS AND DISCUSSION

Both the pyrrole and aniline polymerizations were carried out at low oxidant and monomer concentrations in order to slow the reaction down and thus promote surface rather than bulk polymerization. This approach was first described by Gregory and co-workers for coating textile substrates[17–19]. This group has suggested that 'Most likely the adsorbing species is either the radical cation, an oligomer thereof, or a metal–monomer complex. As the *in status nascendi* produced intermediate is adsorbed at the solid–liquid interface the concentration of the polymerizing species is increased at the surface'[18].

We were prompted to investigate the coating of colloidal particles with conducting polymer overlayers for two reasons. First, both inorganic and organic colloidal systems of a wide range of particle size and morphology are well-known and, in principle, these could be coated with polypyrrole or polyaniline to provide a rich selection of exotic composite materials. Second, and more specifically, we have recently become interested in preparing larger conducting polymer colloid particles (0.5–1.0 μm diameter) for use as model particles in a research programme focusing on the behaviour of cosmic dust. Such particle dimensions do not seem to be easily accessible by conventional dispersion polymerization/steric stabilization techniques[22].

There are two advantages in using 1 μm diameter silica particles as the colloidal substrate for conducting polymer deposition rather than the 0.13 μm diameter polystyrene latex used by Yassar *et al.*[16]. First, the larger silica particles are visually much easier to unambiguously distinguish from the globular morphology of bulk polypyrrole (typical features 50–250 nm diameter[1]) in SEM studies. The polystyrene latex particles are of very similar dimensions to bulk polypyrrole yet this problem does not seem to have been addressed by Yassar *et al.*

A further advantage of using silica particles rather than polystyrene latex is that the excellent thermal stability of the former system allows the quantitative determination of the adsorbed mass of conducting polymer per unit mass of colloid. Our thermogravimetric analysis data are shown in *Figure 2*. The uncoated silica particles gave a small weight loss of 1.97% which is attributed to dehydration of the hydrophilic silica surface (*Figure 2A*). The polyaniline-coated silica exhibited an overall weight loss of 5.70% which, allowing for the water content of the silica substrate gives a polyaniline layer mass of 3.73% (*Figure 2B*). The remaining silica residue was white, implying complete volatilization of the polyaniline had occurred. The polypyrrole-coated silica particles showed an overall weight loss of 7.70% which suggests the polypyrrole layer comprises 5.73% by mass of the composite. This latter sample was run in an oxygen atmosphere since a preliminary run under a nitrogen atmosphere yielded grey rather than white residues, indicating incomplete combustion of the polypyrrole coating.

Given that the density of amorphous silica is ~2.1 g cm^{-3} and taking the densities of polyaniline and polypyrrole each to be 1.5 g cm^{-3}, if we assume that each silica particle is uniformly coated we may estimate the average thickness of the conducting polymer overlayer from the thermogravimetry data[1]. These layer thicknesses are ~9 and ~14 nm for polyaniline and polypyrrole, respectively.

Scanning electron micrographs of the polyaniline- and polypyrrole-coated silica particles are shown in *Figure 3*. The samples were not sputter-coated with a metal overlayer for these studies (a technique used to prevent electrostatic charging of the sample), so the observed high image resolution is good evidence for the conductive nature of the specimens. The SEM micrographs confirm that the silica particles are not uniformly coated with polyaniline or polypyrrole. Indeed, in the latter sample a considerable fraction of particles appear to be almost completely uncoated. This suggests that the assumptions we made in estimating an average conducting polymer

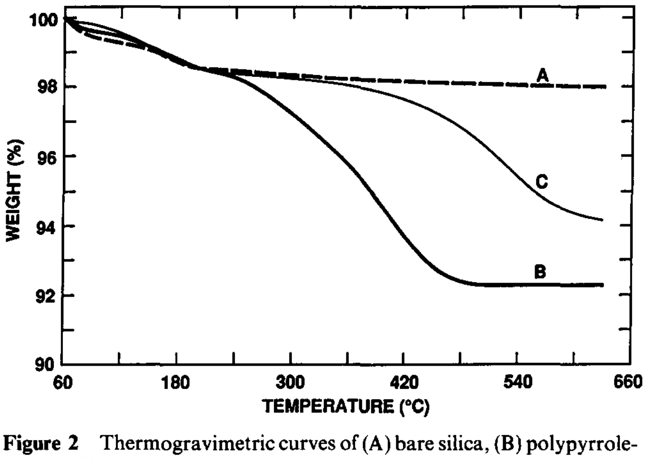

Figure 2 Thermogravimetric curves of (A) bare silica, (B) polypyrrole-coated silica and (C) polyaniline-coated silica

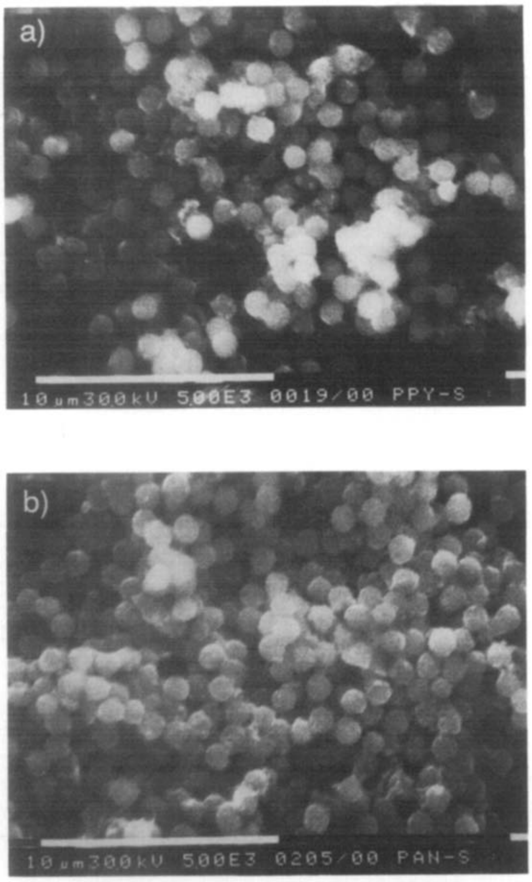

Figure 3 Scanning electron micrographs of (a) polypyrrole-coated silica particles and (b) polyaniline-coated silica particles

coating thickness are not valid. Clearly, for optimum conductivity all the particles should be coated with conducting polymer and work is currently in progress to investigate and hopefully improve the uniformity of the electroactive overlayer. High magnification micrographs of the polypyrrole–silica composites (*Figure 4*) suggest that the polypyrrole coating is somewhat globular, with feature dimensions of the order of 100–150 nm. This morphology is similar to that previously reported for chemically synthesized bulk polypyrrole[23].

The four-point probe conductivities of the polyaniline–silica and polypyrrole–silica composites were 4×10^{-3} and 2×10^{-5} S cm^{-1} respectively. The measurements were difficult to make due to the extreme brittleness of the pellets. It is difficult to reconcile this conductivity data with the thermogravimetry results. One would naively expect the polypyrrole–silica composite to be the more conductive sample since it contains a higher proportion of conducting polymer by mass. Its lower conductivity compared to the polyaniline–silica sample could be due to the polypyrrole overlayer being more inhomogeneously distributed between the silica particles. Alternatively, the lower conductivity could be an intrinsic property of the polypyrrole since carboxylate dopant anions similar to the salicylate anion have been reported to adversely affect the conductivity of electrochemically synthesized polypyrrole films[24].

It is interesting to compare our results with those reported by Yassar *et al.* for polypyrrole–polystyrene latex composites[16]. Yassar *et al.* claim a remarkably homogeneous coating of polypyrrole on the polystyrene colloidal substrate (original particle diameter 130 nm) with a quoted coating thickness of 70 nm. Such a thick and uniform overlayer would perhaps explain their higher compressed pellet conductivities (0.25 S cm^{-1} for the sample in question). Their preparation conditions are different from the conditions we used; in particular we calculate that their colloidal substrate surface area is much higher ($\sim$110 *versus* 2.8 m^2 for the same liquor volume). This could possibly explain the surprising uniformity of the polypyrrole coating. We also note that the surface of the polystyrene latices contain SO_3^- or CO_2^- groups which the authors suggest could act as dopant anions for the deposited polypyrrole overlayer. These groups might conceivably promote a more homogeneous coating of the particles, at least for the first monolayer. However, we are puzzled by other aspects of their work. For example, it is stated that the mean particle diameter is observed to increase from 130 to 200 nm by SEM and then it is claimed that the thickness of the polypyrrole overlayer is equal to the difference between these diameters, 70 nm when clearly this coating thickness must be equal to half this difference, or 35 nm. Furthermore, we estimate that the maximum theoretical coating thickness of polypyrrole is only $\sim$1.3 nm based on the initial $FeCl_3$ and pyrrole concentrations given by the authors (assuming that 1 mol of pyrrole monomer is polymerized by 2.33 mol of $FeCl_3$ oxidant, that the densities of polystyrene and polypyrrole are 1.05 and 1.50 g cm^{-3}, respectively, and that the pyrrole polymerization goes to completion).

Our *FT*i.r. microscopy studies confirmed the presence of polypyrrole and polyaniline, respectively, in the two composites. The bare silica powder spectrum had two major peaks at 804 (scissor deformation) and 1105 cm^{-1} (three superimposed bands due to the Si–O stretch mode). The polypyrrole–silica composite had additional bands at 1566 and 1484 cm^{-1}, whilst the polyaniline–silica composite had additional bands at 1593, 1498 and 1310 cm^{-1}. All these bands are characteristic of polypyrrole[1] and polyaniline[1,15]. The low water content of the silica particles was confirmed by the small absorption peak at $\sim$3450 cm^{-1} and is consistent with the thermogravimetric results.

The EDAX studies confirmed only the presence of

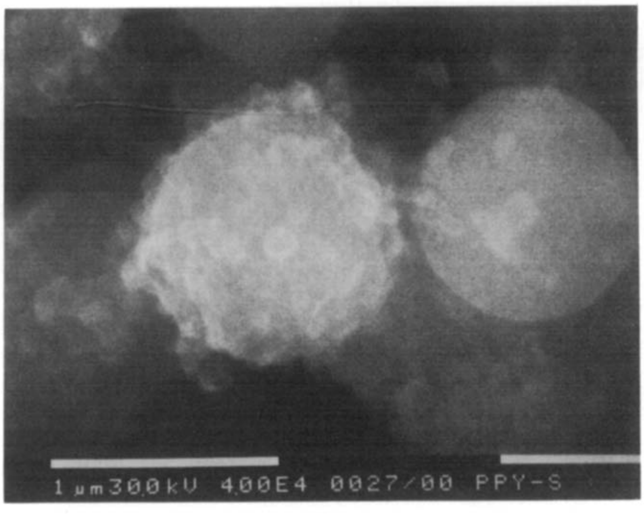

Figure 4 High magnification SEM micrograph of a polypyrrole-coated silica particle

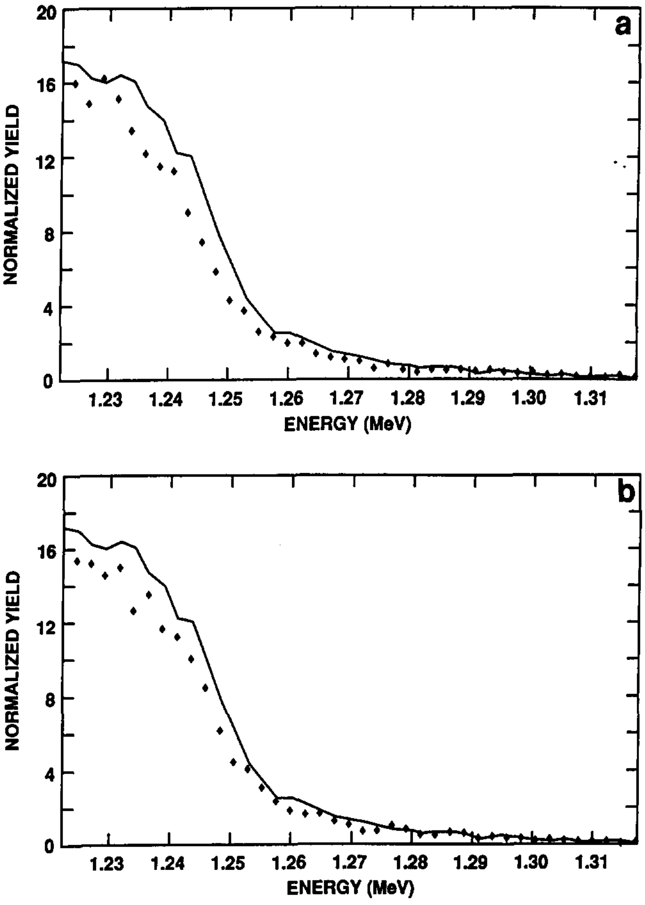

Figure 5 Rutherford back-scattering spectra for (a) polyaniline–silica (◆) and bare silica (—) and (b) polypyrrole–silica (◆) and bare silica(—)

chlorine and tin as well as the main silicon peak in both conducting polymer–silica composites. The former element is presumably present as the chloride anion, the recognized dopant counterion for both polypyrrole and polyaniline prepared in aqueous media[1,25,26]. The origin of the tin species is not known but is possibly an impurity in the silica particles. The complete absence of sulphur and iron is consistent with the observations of Kuhn and co-workers for conducting polymer-coated textiles[27], and suggests that neither the $FeCl_3$ nor the $(NH_4)_2S_2O_8$ oxidant is adsorbed at the silica surface prior to or during the polymerization reactions.

In our Rutherford back-scattering studies we examined the energy shift in the silicon edge for the thinly coated conducting polymer–silica composites relative to the bare silica particles. It is known that the size and shape of this shift can, in principle, be quantitatively related to the thickness of the conducting polymer overlayer. However, in our experiments we were working near the resolution limits of the instrument and were restricted to a more qualitative interpretation of the results (*Figure 5*). It is apparent that the polyaniline–silica composite gives rise to a curve which is shifted slightly further from and is more parallel to the silicon edge than the corresponding polypyrrole–silica curve. Although neither overlayer can be described as truly uniform, the polyaniline overlayer is probably of more uniform thickness than the rather inhomogeneous polypyrrole overlayer. This result is consistent with our SEM observations.

We found that the polyaniline-coated silica particles could be redispersed in media which exhibited good solvency for the polyaniline overlayer. Thus the dry, light-green polyaniline–silica composite could be easily redispersed in concentrated sulphuric acid, which is known to be a good solvent for doped polyaniline[4]. The dedoped, blue polyaniline–silica composite could be similarly redispersed in DMSO, which has been reported to be a good solvent for dedoped polyaniline by various groups[1,3,6]. In both cases we observed coloured sediments settling out under gravity on prolonged standing, which suggests that at least some of the polyaniline overlayer remains physically adsorbed to the surface of the silica particles in each system. Visible absorption spectra of both the doped polyaniline–silica dispersion in concentrated sulphuric acid and the dedoped polyaniline–silica dispersion in DMSO are shown in *Figure 6*. They are identical to spectra previously reported for solutions of doped and dedoped polyaniline in the same media[4,28].

In contrast the polypyrrole–silica composites could not be redispersed in H_2O, 1.2 M HCl, methanol or DMSO (concentrated sulphuric acid was not used as a dispersion medium since it is known to degrade polypyrrole). This is not surprising since no solvent has been reported for bulk polypyrrole, which is believed to be a crosslinked and hence intrinsically insoluble material[29].

We have made some preliminary attempts to increase the conducting polymer loading on the silica colloids using a modified experimental procedure[30]. In one polypyrrole–silica sample, our thermogravimetric results indicated that the composite consisted of ~39.5% by mass of conducting polymer, which corresponds to an average coating thickness of ~120 nm. However, our SEM studies clearly showed that this thicker polypyrrole coating was predominantly non-uniform with a globular morphology (*Figure 7*). A Rutherford back-scattering characterization suggested that most, if not all, of the silica particles were coated with relatively thin, uniform polypyrrole overlayer of ~40 nm. In addition, a large fraction of these particles seemed to be coated with a thicker, non-uniform overlayer (*Figure 8*). The precipitated powder was black rather than grey and the compressed pellet conductivity was 5.0 S cm^{-1}.

We anticipate that such conducting polymer–silica

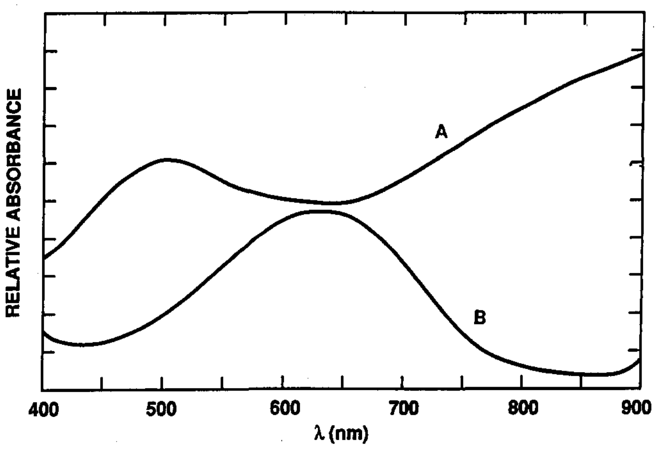

Figure 6 Visible absorption spectra of (A) doped polyaniline–silica in concentrated sulphuric acid and (B) dedoped polyaniline–silica in DMSO

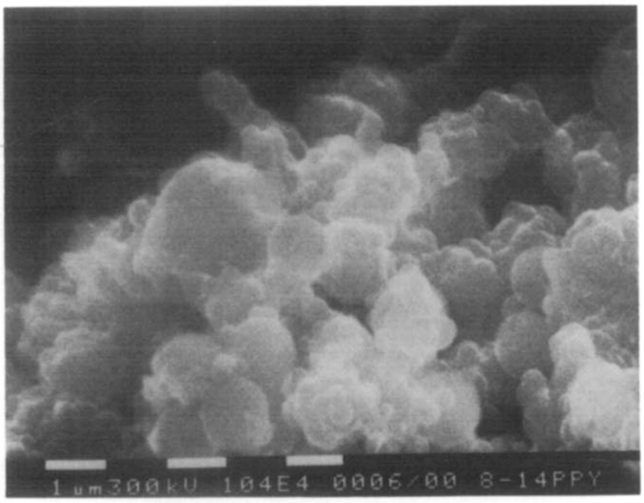

Figure 7 Scanning electron micrograph of a thickly coated polypyrrole–silica composite (polypyrrole content 39.5% by mass)

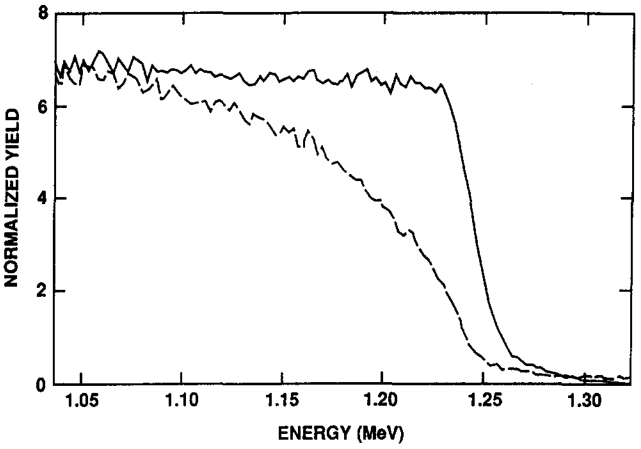

Figure 8 Rutherford back-scattering spectra of (—) bare silica and (---) thickly coated polypyrrole–silica composite (polypyrrole content 39.5% by mass)

composites will prove interesting model systems for mimicking the behaviour of cosmic dust particles[31]. Charge–velocity analysis experiments are currently in progress to investigate the charging efficiency and particle size distribution of these composites[22].

CONCLUSIONS

We have described the preparation of conducting polymer–colloidal composites by the *in situ* polymerization of pyrrole or aniline in the presence of a colloidal dispersion of monodisperse silica particles (~1 μm diameter). By carrying out the polymerizations at low concentration the surface deposition of the conducting polymer is favoured over conventional bulk precipitation. Thermogravimetric analyses suggest that our thinly coated polypyrrole– and polyaniline–silica composites contain, respectively, 5.73 and 3.73% conducting polymer by mass. Scanning electron microscopy studies show that the conducting polymer deposition is a non-uniform process with some silica particles being thickly coated whilst the majority remain uncoated. This observation is contrary to that claimed by Yassar *et al.*[16] for polystyrene latex. Fourier transform infra-red microscopy and EDAX studies confirm the presence of chloride-doped polypyrrole and polyaniline on the coated silica particles. Four-point probe conductivity measurements on compressed pellets give values of 2×10^{-5} and 4×10^{-3} S cm^{-1} for the thinly coated polypyrrole– and polyaniline–silica composites, respectively.

The Rutherford back-scattering results show that the silica particles are coated with conducting polymer overlayers. Qualitatively it appears that the polyaniline overlayer may be more uniform in thickness than the polypyrrole layer.

Our redispersion experiments show that the polyaniline–silica composites can be redispersed in media which are good solvents for the polyaniline overlayer. Thus doped polyaniline–silica can be redispersed in concentrated sulphuric acid and dedoped polyaniline–silica can be suspended in DMSO. The polyaniline appears to remain adsorbed to the silica surface (i.e. acts as a steric stabilizer) in both cases. No solvent system is known for polypyrrole (either doped or dedoped) so we believe that the polypyrrole–silica composites cannot be redispersed in any media and are therefore intrinsically less processable than the polyaniline–silica particles. Our preliminary results suggest it is possible to obtain thicker, albeit non-uniform, conducting polymer coatings which result in improved conductivities (up to 5 S cm^{-1} for 39.5% by mass polypyrrole).

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