

Custom Engineered Nanoparticles for Superior Nanocomposite Materials

Prof A.S. Vaughan, Prof P.G.R. Smith, Dr J.C. Gates, Dr M. Praeger, Dr S. T. H. Virtanen, Dr L.G. Carpenter

Aims

Energy security and mitigation against climate change are two of the major problems faced by all economies, consequently, a vast amount of investment is being undertaken to “green” our electrical power systems. So-called nanodielectrics have attracted growing interest over the last 20 years, due to the highly desirable combinations of properties that they *can* exhibit. However, the field is plagued by poor reproducibility, which stems from the use of poorly characterised components. This project set out to explore the potential of **flame hydrolysis deposition** (FHD) (see Fig.1) as a novel means of producing a new generation of nanoparticles for use in nanodielectrics. This approach has the potential to produce electrically novel systems, by doping silica glass nanoparticles with carefully controlled quantities of elements such as boron, germanium, and phosphorus in order to modify the local electronic states within the system. This completely new approach will provide novel insights into aggregation processes and charge transport dynamics and could be the disruptive technology that facilitates the adoption of nanodielectrics on a large scale.

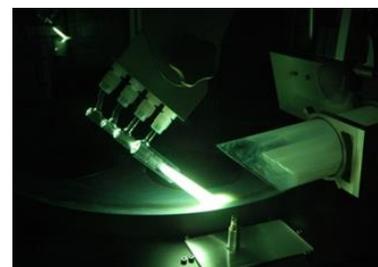


Fig.1: The flame hydrolysis deposition system shown with the distinctive green flame caused by boron doping.

Results

Nanoparticle Production Phase 1: Direct Deposition. It is generally believed that the process of FHD is initiated by the production of nanoparticles within the flame. Initial attempts to exploit this (with the flame directed onto the platter as in Fig.1) resulted in agglomeration and fusing of these particles to varying degrees, as determined by the precise conditions; Fig.2a shows a range of typical particle morphologies obtained. Viewing the particles at higher magnification (Fig.2b) reveals evidence of primary nanoparticle formation indicating that FHD equipment does indeed produce nanoparticles. Despite this, the inevitable conclusion from these studies is that deposition onto a solid substrate close to the flame results primarily in material that is dominated by thermal reorganisation/annealing/agglomeration effects. A very different procedure is therefore required.

Nanoparticle Production Phase 2: Electrostatic Collection. The production of particles of nanometric scale inevitably results in these being charged and, therefore, a potential alternative approach is to exploit electrostatic fields as a means of sweeping the charged particles from the flame into a ‘cold’ collection vessel; thereby prevent thermal reorganisation (Fig.3a). In the present implementation, particle collection efficiency is low and the system cannot be run for extended periods due to overheating of the gas extract. Although it yields only small quantities of material; this method was used to produce samples of several particle types (taking the form of a thin crust of powder deposited on the inner edge of the collection vessel).

Nanoparticle Initial analysis. If present in sufficient quantity, dry powders were extracted from the collection vessel; where this was not possible a small quantity of methanol was used to wash the material out of the container. The particles in methanol remained suspended for many days with minimal sedimentation; however, during this time there was a progressively change in colour; although the origins of this effect could not be fully explored, we suggest that it may be indicative of incomplete reaction during FHD. Immediately after collection, samples were prepared for SEM inspection. In the case of the PCl_3 based material nanoparticles could be observed but appeared to be embedded within another substance (possibly residue from incomplete hydrolysis or the result of a subsequent chemical reaction). For BCl_3 and SiCl_4 based deposits particles were observed in various states of agglomeration with isolated nanoparticles clearly present (see Fig.3b).

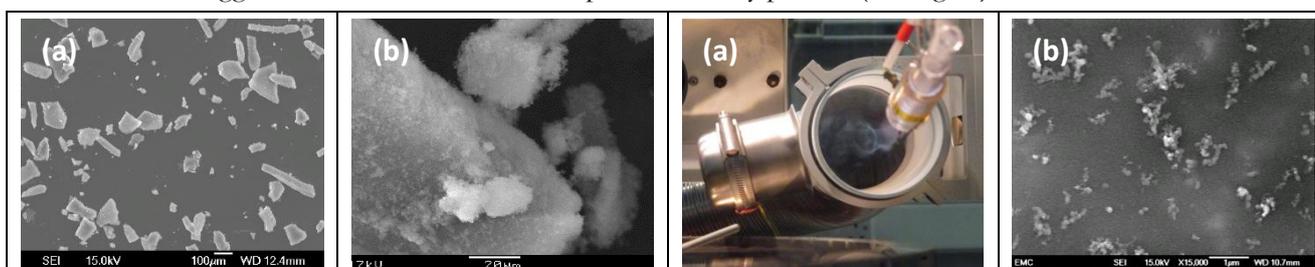


Fig.2: Particles produced under standard FHD conditions: (a) Shards of sample NB120 (Ge P). (b) Material NB130 (Si) produced with the lower gas flow rate and the flame further from the plate shows evidence of its nanoparticulate origins.

Fig.3: The electrostatic collection process: (a) Photograph of the FHD apparatus with particle stream visible. (b) Sample V6 (Electrostatically collected nanoparticles from a SiCl_4 flame) dispersed in methanol then dripped onto carbon tape for SEM imaging.

Sample Preparation. The various inorganic systems were combined with a matrix polymer to produce composite materials. Polystyrene was chosen as the matrix since it is readily dissolved in a range of solvents, and can be processed in small volumes. Also, being a thermoplastic, specimens can, to some degree, be recycled with the same material being used a number of times. The amorphous nature of polystyrene allows permanganate etching to be used as a highly effective means of revealing the particle distribution within the matrix (well separated, isolated nanoparticles can clearly be seen in Fig.4).

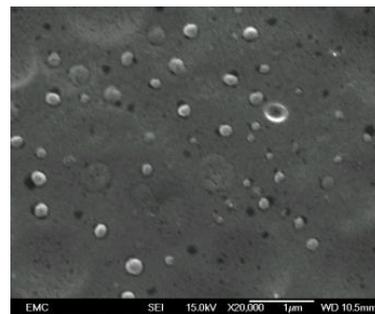


Fig.4: Sample V9 (Electrostatically collected nanoparticles from a BCl_3 flame) dispersed within a polystyrene matrix.

Material Analysis. The quantity of nanofiller material entrained within the polymer during solvent blending was measured using *thermal gravimetric analysis* (TGA). Despite producing very low-volume samples the filler loading was only in the range 0.2 – 2.0 %w.t. The minimal sample volume meant that measurement of the electrical breakdown strength was not possible. **DC conductivity** for nanocomposites produced from the electrostatically collected particles was found to be 5 times lower than that of the reference polymer at an applied voltage of 3 kV (this could be a very significant finding). For the majority of samples produced **Dielectric spectroscopy** was unable to distinguish any significant differences relative to the reference polymer. Only samples which contained large agglomerates of particles and had high filler loading differed from the reference; exhibiting increased relative permittivity (real and imaginary) at low frequencies. Surprisingly, this remained the case even after soaking the samples in water (water uptake is very effective as a probe of the particle surface). Undoubtedly the very low filler loading plays a part; however, this is also an indication that the nanoparticles that are present, are well dispersed and integrated into the polymer (i.e.: moisture is prevented from accumulating at the nanoparticle surface). These results are encouraging since the dielectric properties of the base polymer are excellent (low dielectric losses in the frequency range of electrical power) and yet the nanoparticles reduce DC conductivity and are also likely to improve thermal and mechanical properties.

Impact of the Stimulus Fund in Enabling the Research

The concept underpinning this proposal was generated as a result of the ZI Away Afternoon in July 2013. However, with no resources (consumables or researcher time), the concept was discussed but remained dormant until the announcement of the ZI Stimulus Fund. As such, the ZI Stimulus Fund was instrumental in facilitating the work and in initiating a new dialogue between the ORC and workers in the Tony Davies HV Laboratory.

Impact of the Scientific Outputs

This funding has enabled us to demonstrate that FHD is indeed a potential route to the production of a unique range of nanoparticle systems and, as such, the project has fulfilled its primary aim. The main outstanding issue concerns increasing the efficiency of nanoparticle capture in the electrostatic collection system. The work has demonstrated that the existing FHD equipment is well suited to its primary aim, namely, the production of consolidated planar materials. Critical reliance on thermal effects for the generation of chemically stable material is entirely contrary to the requirements for discrete nanoparticle production and thus poses a significant challenge.

Publications, Patents and Outputs

This project was based upon no prior history of either work in this area or of collaboration between the two groups involved. It represented a totally novel and high risk undertaking and, as such, the work has not progressed thus far to the point where it could be reported yet alone exploited. While this project has demonstrated the potential of the approach, a significant development programme will be required to realise the potential. We propose to undertake this as part of WP2.1 in the **Advanced Polymer Materials for Energy Security (POLYMAT)** EPSRC proposal, which is nearing completion (case attached). We are currently in the process of collecting statements of support and this will be refined to reflect these and then submitted in September/October 2014.

Expenditure against the Allocated Budget

The requested funds were to cover salary costs and consumables, notably the adaption of the FHD system to capture the nanoparticles.

Salary Costs. The resignation of a key post doc (Dr Alex Holt in February 2014) affected the projected spend pattern but as a result of successfully appointing a replacement, expenditure under this heading has amounted to £4552.08, compared with the budget of £5015.

Consumables etc. The dominant consumable expenditure was in the reconfiguration of the FHD system including components for the extract system, gas handling, speciality pre-cursors and cleaning equipment. £4458.84 was spent against a budget of £4,500.