One-pot, *in situ* synthesis of ZnO-carbon nanotube-epoxy resin hybrid nanocomposites†

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⁵ Received (in XXX, XXX) Xth XXXXXXXXX 200X, Accepted Xth XXXXXXXXX 200X

First published on the web Xth XXXXXXXXX 200X

DOI: 10.1039/b000000x

This paper presents a clean and efficient *in situ* method for the preparation of thermoset composites containing ZnO nanoparticles and/or ZnO-coated carbon nanotubes.

Polymer nanocomposites combine the flexibility and processibility of polymers with the thermal, electrical, optical, magnetic and/or materials properties of inorganic nanoparticles.¹ Control of the nanoparticle size, shape, crystallinity, dispersion, homogeneity and the loading fraction are essential for optimising the properties of the resulting material. Nanocomposites are usually prepared by *ex situ* routes, mixing pre-synthesised nanoparticles into a polymer. Although rarer, *in situ* synthesis of nanoparticles in the presence of a (pre)polymer, often based on sol-gel alkoxide chemistry, provides advantages including greater loading fractions and processibility.² A recent commercial example successfully introduces silica into cross-linking resins, but, is limited to amorphous and symmetric particles.^{3–5}

This manuscript explores a relatively new concept in polymer nanocomposite preparation: the use of organometallic dialkyl metal precursor reagents to effect the chemically-tolerant synthesis of well-dispersed oxide nanoparticles, by hydrolysis *in situ* within the polymer. Dialkyl zincs are classic organometallic compounds, long-handled under rigorously anhydrous conditions. Although accidental hydrolysis has no doubt often yielded zinc oxide nanoparticles, attempts to study and exploit these products deliberately have not been reported until very recently.⁶ Our synthesis applies the hydrolysis of diethyl zinc in chemically-active thermosetting resins, allowing the production of zinc oxide nanoparticles dispersed in an epoxy resin matrix. Epoxy systems are widely used as adhesives, coatings, and composite matrices; modification with *ex situ* nanoparticles is well-known, but often suffers from agglomeration and processing difficulties. Zinc oxide is a useful filler material, chosen for its optical, electronic, mechanical, and thermal characteristics; it is usually prepared *ex situ* either by high temperature, physical methods,⁷ or by metathesis reactions of zinc salts with alkaline hydroxides,⁸ followed by condensation and dehydration. There are a small number of reports describing the conversion of dialkyl zinc and alkyl zinc alkoxide precursors, *ex situ*, to ZnO using both low-moderate temperature thermolysis⁹ and hydrolysis.^{6, 10}

Only a very few examples of *in situ* synthesis of ZnO nanoparticle composites are known. The standard zinc acetate metathesis route has been used to synthesise nanoparticles within thermoplastic matrices,¹¹ however, as will be shown, the conditions required for nanoparticle synthesis are incompatible with reactive thermosetting systems, such as epoxies (*vide infra*),

Fig. 1 *In situ* synthesis of the ZnO epoxy resin nanocomposite (solid line represents the cross-linked epoxy resin and black circles the ZnO nanoparticles).

generating undesirable alkaline salt by-products.¹² Alkyl zinc precursors have also been exploited, *in situ*, in unreactive thermoplastic thin films of ethylene-vinyl acetate copolymers (EVA), polyphenylene vinylene (PPV) and poly(3-hexylthiophene) (P3HT).^{13–15} The thermoplastic nature of these matrices, and the need to remove solvents and/or reaction byproducts, severely limits the thickness of the films produced. In contrast, our *in situ* process is compatible with a range of cross-linking resin chemistry, and yields bulk nanocomposites with high ZnO loading fractions.

Diethylzinc is commonly available either as neat liquid or a solution in hexane, both of which are miscible with the epoxy prepolymer (Araldite), based on bisphenol-A. Due to the pyrophoric nature of diethylzinc, the solution was handled under inert atmosphere until after the nanoparticle synthesis was complete. The diethylzinc/ prepolymer solution was reacted with a slight excess of water, diluted in acetone, at room temperature to yield a ZnO prepolymer nanocomposite (Fig. 1). The only by-product of the hydrolysis is ethane, which is unreactive towards the matrix and volatile, and therefore bubbles out of the reaction mixture. The prepolymer was subsequently cured at 120 °C with a diamine hardener to yield a dense, epoxy resin nanocomposite (Fig. 1). The *in situ* hydrolysis reaction occurs readily but, despite the high reactivity of diethyl zinc, the resin chemistry is unaffected. In contrast, when conventional conditions for ZnO nanoparticle synthesis were applied (zinc dichloride, NaOH and MeOH solvent), the epoxy prepolymer was destroyed. Methoxide anions (generated by reaction between the base and the solvent) or hydroxide anions (from the base) attack the epoxide end-groups on the Araldite prepolymer and prevent the curing cross-linking reaction (see Fig. S1, Supporting Information).

By increasing the molar ratio of diethylzinc:Araldite, the loading of ZnO in the final composite was increased from 5 to 40 wt%, as confirmed by thermal gravimetric analysis (TGA) in air (Fig. S2, Supporting Information). The thermal stability

of the ZnO

Fig. 2 X-ray diffraction pattern (a) of 20 wt% nanocomposite confirming the formation of ZnO (conventional peaks indicated). At low resolution (b), TEM images show small clusters of ZnO particles; at higher resolution (c), the average primary particle diameter was found to be 5 nm, with lattice fringes indicating a high degree of crystallinity. One particle is highlighted though contrast is low due to the epoxy matrix.

nanocomposites matched that of the pure epoxy resin, with a degradation onset at around 400 °C. The combustion is complete by 750 °C, at which point the loading of ZnO in the original nanocomposite can be easily assessed, assuming that no other solid oxides are generated. The shape of the thermal degradation profile (Fig S2) of each nanocomposite is comparable to that of the pure epoxy resin, ruling out phase segregation in the polymeric component.

The presence of zinc oxide was confirmed by UV-Vis spectroscopy, X-ray Diffraction, and Transmission Electron Microscopy (TEM). The UV-Vis spectrum shows a broad band at 350 nm characteristic of ZnO and highlights the potential to use ZnO nanoparticles as UV-filters in polymers and resins (see Fig. S3, Supporting Information). The X-ray data (Fig. 2a) indicated the presence of crystalline zinc oxide, with a characteristic size, estimated from broadening of the (110) peak ($2\theta = 56^\circ$), of 3.9 nm. TEM confirmed the presence of individual, single-crystal nanoparticles of similar dimensions and small agglomerates of up to 100 nm in diameter (Fig. 2b and 2c). Energy dispersive X-ray data confirmed that the only elements present are Zn, O and C (Fig. S4, Supporting Information) [H is not detected]. Although the thermal curing of the matrix will ensure full crystallinity, *ex situ* experiments indicate significant crystallinity even after the room temperature reaction. The approach may thus be particularly useful for temperature sensitive or low-temperature curing systems.

Dramatic increases in viscosity often impose a practical limit on the loading fraction of nanoparticles that can be incorporated within a resin. The viscosity of the ZnO nanocomposite system

was therefore examined. Cone and plate shear rheometry, before the addition of hardener but after the synthesis of ZnO and

Fig. 3 (a) Shear viscosity of *in situ* ZnO-loaded epoxy resins (before the addition of hardener), at a shear rate of 100 s⁻¹, as a function of loading. Note the minimal increase in viscosity at up to 30 wt% nano-ZnO; (b) Thermal-conductivity of the epoxy resin-ZnO nanocomposites

removal of volatiles, showed a negligible increase in viscosity (Fig. 3a), which remained Newtonian even at high loading fractions of up to 30 wt%. Only at 40 wt% ZnO does the system begin to gel, as evidenced also by a strong shear thinning and unstable stick-slip behaviour (not shown). The low viscosity confirms that the nanocomposite resin system remains highly processable, despite a high solid content, as indeed observed during the preparation of the nanocomposite samples. The benefit of low viscosity is particularly relevant to situations where infiltration is required, for example in potting or fibre composite matrix applications. The low viscosity is perhaps surprising but has been observed previously for the *in situ* synthesis of amorphous silica particles in epoxy, although the mechanism is uncertain.³

The presence of the ZnO within the matrix modifies the properties of the resin. Although a full characterisation remains to be performed, the stiffness of the nanocomposites was found to increase by a factor of two at 40 wt% ZnO, using dynamic thermal mechanical analysis in bending (not shown). The thermal conductivity, similarly, shows a linear correlation with ZnO loading (Fig. 3b). The increase in thermal conductivity is modest, given that the expected conductivity of ZnO is around 60 Wm⁻¹K⁻¹, more than two orders of magnitude higher than the matrix. However, unfunctionalised nanoparticles are known to be relatively ineffective at increasing thermal conductivity due to the large surface area, and high interfacial thermal resistance.¹⁶ Improvements could be anticipated by varying the organometallic precursors to favour direct bonding to the resin, as has been developed with silica systems.^{4, 5} In addition, a stronger interfacial interaction would simultaneously improve dispersion, transparency, and mechanical properties.

Fig. 4 TEM images of ZnO nanoparticles coated onto CNTs, *ex situ* (a, c, d) and *in situ* in epoxy (c). Note the smaller ZnO on oxidised (a,d) than base-washed (b) CNTs. Contrast is poorer in (c) due to the remaining epoxy matrix

In addition, the *in situ* approach is able to generate more complicated, higher order structures directly within the resin. The growth of the ZnO nanoparticles can be nucleated at the surface of another filler, in order to generate a hierarchical or hybrid, structure. To illustrate the effect, we have used the diethyl zinc chemistry to coat multi-walled carbon nanotubes (CNTs), which are, in themselves, an important class of nanocomposite filler.¹⁷ In a first experiment, the nanotubes were coated *ex situ* by slowly adding a diethyl zinc solution to a suspension of carboxylic acid functionalised CNTs, in acetone. After work-up, the CNTs were observed to be coated with small, crystalline ZnO nanoparticles (Fig. 4a & d). When the CNTs were base-washed to reduce the concentration of surface groups¹⁸, ZnO nucleation was suppressed, leading to larger nanoparticles (Fig. 4b). On adding the diethyl zinc to a suspension of acid-functionalised CNTs in Araldite, the same coating behaviour was observed *in situ* (Fig. 4c), after curing the matrix. ZnO can be coated onto CNTs using standard acetate chemistry,¹⁹ but only our new approach is compatible with the epoxy resin.

In summary, we have developed an efficient, single pot method to prepare bulk ZnO-epoxy resin nanocomposites. The controlled hydrolysis of diethylzinc generates ZnO nanoparticles at room temperature within the epoxy prepolymer, evolving gaseous ethane as the only by-product. Once the ethane and any residual water are removed, the curing agent can be added and the bulk nanocomposite resin processed and studied using standard procedures. The same one-pot approach allows the preparation of more complex hierarchical structures, by nucleating ZnO on the surface of other fillers. We believe that that method could be generalised to any metal oxide system for which a suitable, moisture sensitive metal precursor exists, and also to zinc chalcogenides for which a suitable H₂E reagent exists, for

example ZnS (from H₂S) and ZnSe (from H₂Se). A variety of more functional nanoparticles could thus be produced on CNT networks *in situ*. The mild synthesis conditions and simple processing, suggest that the current approach may be usefully extended to a range of polymer systems.

Notes and references

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- † Electronic Supplementary Information (ESI) available: Full experimental details, NMR spectrum, TGA and representative EDXS of the nanocomposites. See DOI: 10.1039/b000000x/
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Graphical and textual abstract for table of contents:

This simple, efficient method generates zinc oxide nanoparticle-polymer composites, by hydrolysis of an organometallic zinc precursor *in situ* within the prepolymer matrix. The same, one-pot strategy generates hybrid, hierarchical structures when combined with carbon nanotubes.