

Reviews

Polymers and Inorganics: A Happy Marriage?

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Abstract: The most recent developments in two areas: (a) synthesis of inorganic particles with control over size and shape by polymer additives, and (b) synthesis of inorganic-polymer hybrid materials by bulk polymerization of blends of monomers with nanosized crystals are reviewed. The precipitations of inorganics, such as zinc oxide or calcium carbonate, in presence and under the control of bishydrophilic block or comb copolymers, are relevant to the field of Biomineralization. The application of surface modified latex particles, used as controlling agents, and the formation of hybrid crystals in which the latex is embedded in otherwise perfect crystals, are discussed. The formation of nano sized spheres of amorphous calcium carbonate, stabilized by surfactant-like polymers, is also discussed. Another method for the preparation of nanosized inorganic functional particles is the controlled pyrolysis of metal salt complexes of poly(acrylic acid), as demonstrated by the syntheses of lithium cobalt oxide and zinc/magnesium oxide. Bulk polymerization of methyl methacrylate blends, with for example, nanosized zinc oxide, revealed that the mechanisms of free radical polymerization respond to the presence of these particles. The termination by radical-radical interaction and the gel effect are suppressed in favor of degenerative transfer, resulting in a polymer with enhanced thermal stability. The optical properties of the resulting polymer-particle blends are addressed based on the basic discussion of the miscibility of polymers and nanosized particles.

Keywords: nanoparticles, mineralization, polymer hybrids, bishydrophilic polymers, optical properties.

Introduction

Nature controls the formation of inorganic structures by biogenic macromolecules, mostly specific proteins. Calcium carbonate or hydroxyapatite are better known examples, and their formation under bioinspired or biomimetic conditions is the subject of Biomineralization studies.¹⁻³ However, the studies of mineralization, nucleation and growth mechanisms of small inorganic particles as products or intermediates are also of large industrial interest since long. The application of pigments is a key issue. Control of particle size and shape and adjusting surface properties for applications as components in more complex systems (e.g. pigmented and filled polymers, cosmetics, as catalysts) are issues of current research. How to obtain materials with homogeneity and specificity of both crystal shape and size distribution is a key aspect of general concern.^{4,5} This is also true for organic pigments and organic functional materials (e.g. in food and

pharmaceutical applications). Important research in this direction proceeds in industry for which recent work by D. Horn and J. Rieger serves as example.⁶ A key application of inorganic powder particles concerns their blends with polymers where they act as pigments, extenders, modifiers, fire retardants, just to mention a few targets. The recent interest in Nanotechnology has raised principal questions as to the miscibility of nanosized particles with polymer melts or glasses.

Besides theoretical interest in how to deal with the thermodynamics of mixtures of polymers and particles as the particle size approaches the intrinsic length scale of the polymers⁷ experimental observations on particle accumulation and specific aggregations in block-copolymers⁸⁻¹¹ have found their way in the most recent literature. The intensive research activity devoted to optimising the mechanical and thermal properties of polymers by blending with clay minerals falls also into this category.^{12,13} Among others the question how and if at all the optical properties of polymers can be modified or tuned by blending with nanosized inorganic particles plays an increasing role¹⁴⁻¹⁷ with regard to applica-

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tions in optical communication technology and attempts to replace classical inorganic glasses.

The second topic, namely blends of inorganic and polymer materials with enhanced functional properties cannot be properly approached without having the synthetic and physico-chemical tools to reproducibly prepare and handle the inorganic nanosized powders. These powders need to be prepared at least on a multigram scale and in such a way that spontaneous agglomeration can be prevented. In consequence, mineralization of nanoscale particles needs to be developed targeted towards forming blends with polymers.

Recent activities of our laboratory devoted to synthesis of inorganic particles with the aim to obtain hybrid polymer/inorganic materials will be reviewed in the following.

Controlled Mineralization

Water soluble polymers composed of acidic (e.g. carboxylic, sulfonic acid etc.) moieties and polar, non ionogenic moieties (e.g. oxyethylene, *N*-substituted pyrrolidone etc.) have the potential to control nucleation and crystal growth in the course of precipitation of inorganic materials from aqueous media. This was first demonstrated using bishydrophilic blockcopolymers (DHBC) of PEO and PMAA for mineralization of CaCO_3 by Marentette, Wegner *et al.*¹⁸ It was shown that synthetic polymers are able to give identical effects as previously only known from biogenic polymers. The general importance of DHBC's for the control of mineralization under non-biomimetic conditions was first seen by M. Oner *et al.*¹⁹ They were able to control size and shape of zinc oxide microcrystals as precipitated from aqueous solution in presence of minute amounts of DHBC's. They also demonstrated the first structure-properties relationships concerning the activity of the DHBC's. It was hinted that adsorption of the polymer to growth centers at the surface of the growing crystals is responsible for shape control.

The potential to control particle growth features in mineralization of zinc oxide was further extended to comb copolymers prepared by copolymerization of a PEO-macromonomer and acrylic acid.²⁰ It was shown that graft or comb copolymers are much more active compared to block copolymers. A model explaining the effect of shape control was given which also explains that a large fraction of the polymer additive becomes embedded in the final precipitate. This is shown in Figure 1.

Finally, it was shown for the first time that latex particles prepared by miniemulsion polymerization in such a manner that their surface exposes a corona of acidic chain segments diluted by short chains of PEO have the same effect. The remarkable effect is that such particles become eventually embedded into the crystals during growth. This results in novel hybrid materials ("swiss cheese" morphology of the microcrystals). An example for the case of calcium carbonate is shown in Figure 2.

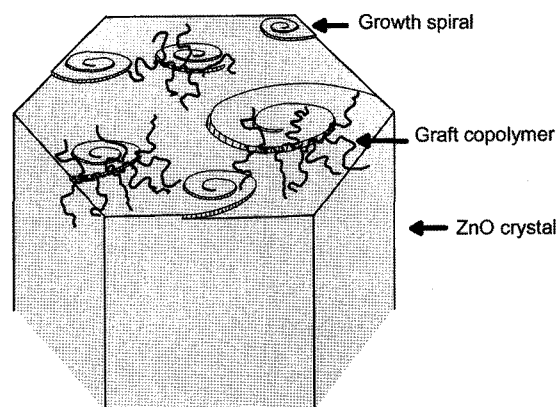


Figure 1. Adsorption/desorption equilibrium of polymer to growth sites determines the growth rate of crystals. The adsorbed polymer becomes engulfed into the crystals.

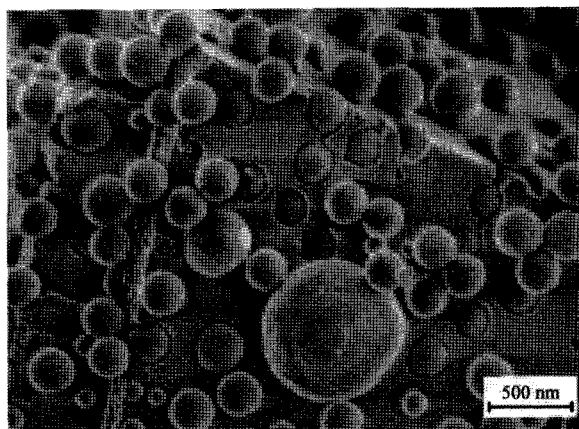


Figure 2. Miniemulsion prepared latex particles in contact with the growth surface of calcite crystals; note the engulfment of the particles.

More details relating the structure of the DHBC's to the growth features of ZnO were worked out by A. Taubert,^{21,22} and a quantitative description of the kinetics of crystal growth of zinc oxide in the presence of miniemulsion prepared latex was presented recently by R. Munoz-Espi, Y. Qi, and coworkers.²³ The latter authors emphasized that the surface functionalized latex particles may be considered as biomimetic models of certain proteins which are known to control the mineralization of calcium carbonate in living systems.

The question whether amorphous, glassy calcium carbonate is a precursor in the formation of calcite or aragonite structures (skeletons, egg shells etc.) in nature²⁴ has triggered research whether this material can also be prepared *in vitro*.

In our laboratory, M. Faatz and coworkers^{25,26} have found conditions to prepare submicron to nanosized spherical particles of glassy amorphous calcium carbonate. The thermal

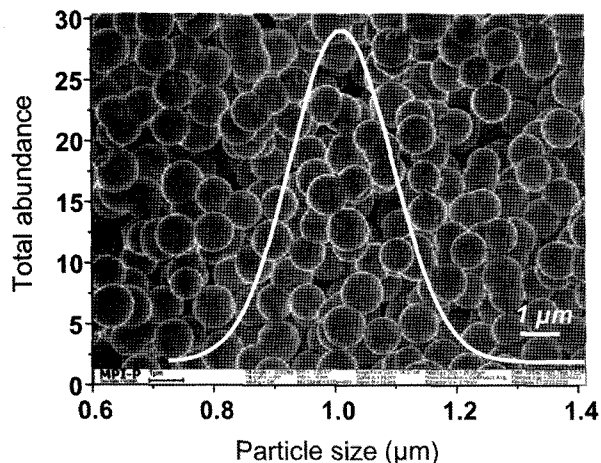


Figure 3. Amorphous, glassy CaCO_3 particles and their size distribution.

stability of this material and its physical properties²⁷ make it worthwhile to be considered as pigment in the paper industry or filler in polymers. In consequence, the synthesis of this material has been stepped up to reach the kilogram level per batch.²⁸ Typical particle morphologies and particle size distribution are shown in Figure 3.

Amorphous calcium carbonate is formed as result of a liquid-liquid phase separation when CO_2 is created in situ by decomposition of an alkyl carbonate in aqueous alkaline solutions of calcium salts. Once again, presence of DHBC's allows to control the size of the particles. Very small concentrations of DHBC's of 1-5 ppm give nanoscale non-aggregated spheres of less than 100 nm diameter.²⁸

Controlled Pyrolysis

While the term mineralization describes the precipitation of an inorganic material from an aqueous medium - frequently as consequence of a hydrolytic reaction - particle formation may also occur by controlled pyrolysis of a polymer precursor. The production of preceramic powders by pyrolysis of labil organic salts of metals with or without a polymer binder has a long history in materials science.^{29,30} We have developed the controlled pyrolysis of mixed metal salt complexes of low molecular weight polyacrylic acid into a versatile method to prepare mixed metal oxides in form of 20-50 nm sized crystalline particles which are only loosely aggregated and can be readily dispersed into organic media. Actual examples are lithium cobalt oxide (Li Co O_2)³¹ to be applied in lithium batteries, zinc oxide and the substitutional alloy zinc/magnesium oxide³² to be applied for blending with polymers. The desired stoichiometry of the product is pre-defined by the composition of the soluble polymer precursor material in all of these cases. This method is therefore uniquely suited to prepare non-stoichiometric or precisely doped ceramic powders in a rational way.

Composites of PMMA and Nanoparticles

Composites which show visible light transmittance but UV absorption and display a refractive index comparable to optical glasses are in high demand. Unfortunately it is not straightforward to achieve situations in which inorganic particles are homogeneously dispersed in a bulk polymer matrix and agglomeration is suppressed. It may be remembered that transparency requires that the particles have diameters

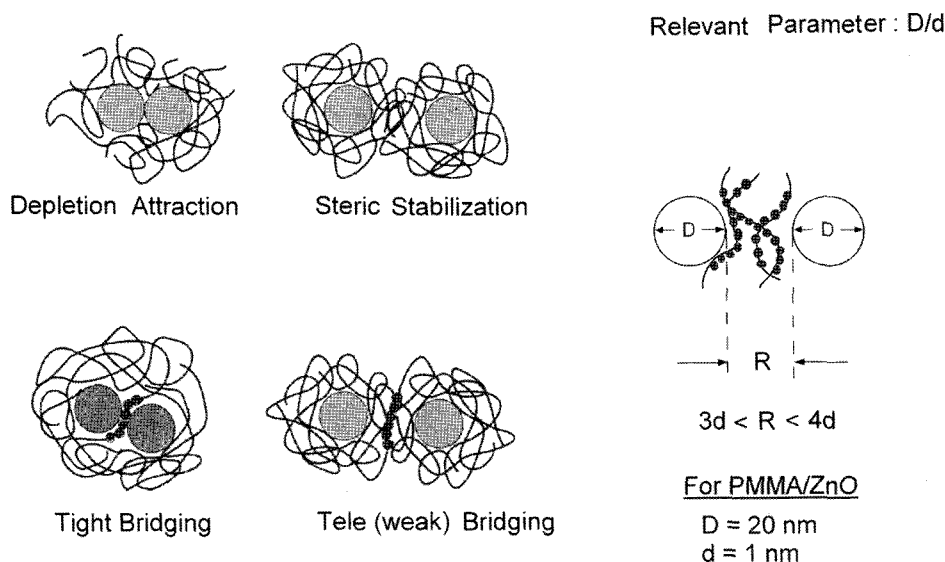


Figure 4. Various scenarios of particle-polymer interaction following K. Schweizer *et al.*⁷ and chain particle packing for PMMA/ZnO at the limit of compatibility.³³

$D \leq 20$ nm (that is $\lambda/20$), if λ is the wavelength of light to be transmitted. In fact and considering recent theory by K. Schweizer *et al.*⁷ it may be questionable whether particles are compatible at all with polymers even if the particles approach dimensions comparable to the intrinsic length scale of bulk polymers (see Figure 4). The relevant dimensions d (cross section of polymer chain) and D (diameter of particles) are such that segregation is highly probable for $D \leq 20$ nm.

M. Demir *et al.* have tried to verify this in our laboratory by blending surface modified zinc oxide particles of $D \leq 20$ nm with bulk PMMA.³³ While a homogeneous dispersion in the monomer MMA was readily achieved, polymerization gave rise to weak agglomeration of the particles as their concentration was increased beyond 2 wt%. This is to be expected on the basis of the aforementioned theory.⁷ The volume fraction of the particles could be varied from 0.1 to 8% (0.5–30 wt%). Although the particles were homogeneously dispersed in the monomer, clouds of weakly agglomerated particles were observed at increasing concentration giving reason for strong turbidity. Optical constants of thin wave guiding films of 2.0 μm thickness were determined. The absorption coefficient at 350 nm follows Beer's law only at low concentrations levelling off at 5 vol% towards a value of ca. 5000 cm^{-1} . Waveguide loss coefficients increased strongly with a slope of 52 dB $\text{cm}^{-1}\text{vol}\%$. Refractive index depends linearly on volume fraction and varies between 1.487 (pure PMMA) to 1.507 (7.7 vol%) at 633 nm. It is worth mentioning that morphological investigation indicated that the clouds of weakly aggregated particles were nevertheless homogeneously distributed throughout the bulk of the material indicating that the particle density fluctuation was driven by thermodynamic constraints. These findings do not only corroborate theory but also exemplify that it will be very difficult if not impossible to create transparent materials of optical quality by blending of nanoscale particles with polymers for intrinsic reasons of polymer physics. However, it was found³⁴ that the presence of nanosized ceramic powders has remarkable and unexpected effects on the free radical bulk polymerization: bulk polymerization of blends of methyl methacrylate with e.g. nanosized zinc oxide reveals that the mechanisms of free radical polymerization responds to the presence of the particles. Termination by radical-radical interaction and gel effect are suppressed in favour of degenerative transfer giving the resulting polymer with enhanced thermal stability.

Conclusions

The control of nucleation and growth of inorganic particles as they precipitate from aqueous solution is a field in which polymers play an ever increasing role. Hybrid materials can be obtained in which the polymer additive becomes embedded into the bulk of the crystals under suitable conditions. These are new classes of materials which may rapidly find

their way into active technology wherever porous or surface modified materials are required. Similarly, controlled pyrolysis of well defined polymer-metal salt complexes is a useful and versatile method to create functional pigments and pre-ceramic powders. While polymers are combined in a successful manner with inorganics in these two cases, the seemingly simple blending of nanosized particles with polymers to create novel bulk materials meets with principal obstacles. It seems impossible to create transparent bulk polymer blends the optical properties of which approach those of high refractive index glasses for reasons deeply imbedded in polymer physics.

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