

Polymers and Nanosized Particles: A Happy Marriage?

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Introduction

The idea to combine polymers with inorganic particles in order to create hybrid materials of properties which cannot be reached – in principle – by a pure material alone exists since decades and finds numerous applications. Examples are pigmented polymers obtained by compounding inorganic particles with polymers to achieve stable coloration, flame-retardancy or UV-light protection. A further example is the blending of polymers with carbon black or metal flakes to achieve certain conductivity characteristics, i.e. to avoid static accumulation of charge. The more recent interest in "nanotechnology" has triggered interest and curiosity as to the question whether novel or even unexpected properties may be achieved decreasing the size of the particles to be embedded or brought in contact with polymers to the nanoscale dimension.

Several aspects may be considered:

- The synthesis of nanosized particles assisted by polymers;
- Stabilization of nanoscale particles against Ostwald-ripening and agglomeration;
- Modification of polymer properties by particle size effects; i.e. colour, transparency, rheology, conductivity, impact strength;
- Synthesis of polymers in presence of nanoscale particles: Controlling the mechanism of chain growth.

Polymer-Particle Interactions

Contrary to public opinion it is not true that all properties change when one approaches the nanoscale dimension. Consider for instance the viscosity of a system composed of a liquid in which solid particles are suspended (Fig. 1). As early as 1906 A. Einstein concluded that the viscosity depends solely on the volume fraction Φ of spherical particles and is independent on their radius r . He applied this equation to determine the dimension of sugar molecules dissolved in water and came out with a very reasonable result, thus demonstrating that the viscosity law holds for large particles to even molecules^[1]. The well known Stokes-Einstein relationship builds on the initial insights of Einstein and is basic to determination of molecular size by dynamic light scattering, again demonstrating that the length scale of the particle size does not contribute to the principal properties. Similarly ionic conductivity is covered by the Nernst-Einstein relationship. While these considerations hold for particles (molecules) in simple low molecular liquids this is not necessarily true for polymers as the matrix. The reason is that polymers are inhomogeneous at the length scale of entanglements^[2,3].

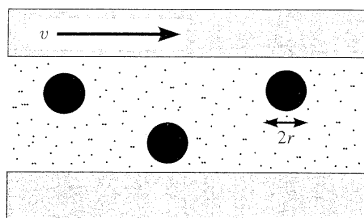


Figure 1

$$\text{Einstein (1906): } \eta = \eta_0(1 + 2.5\Phi)$$

$$\text{Stokes-Einstein: } D = kT/(6\pi\eta r)$$

$$\text{Nernst-Einstein: } \sigma = nq^2(kT)^{-1} D$$

As the particles blended into the polymer become smaller as the "blob" size, that is the characteristic distance between entanglements, one needs to expect significant changes in the motional interaction of the polymer segments with the particle:

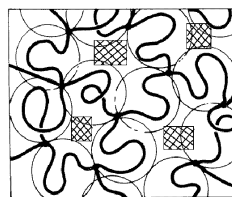


Figure 2

segmental mobility at this length scale is quite different from the global mobility of the macromolecules. Similarly, at high concentration of particles it will be important, if complete wetting of the particle surface can be achieved without disturbing the random trajectory of the

chains (Figure 3a) rather than creating a situation of incompatibility between particles and chains (Figure 3b).



Figure 3 a

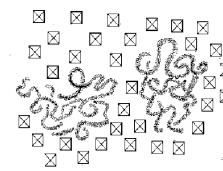


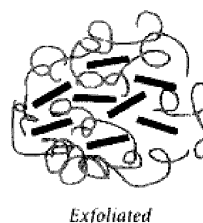
Figure 3b

Such considerations play an important role in optimizing blends of layered silicates ("clays") and polymers where the dimensions of the dispersed clay phase can be varied by controlling the degree of exfoliation (Figure 4)^[4].



Phase separated

Intercalated



Exfoliated

Figure 4

Polymer-assisted Synthesis of Particles

The synthesis of nanoscale particles is a challenge in itself. Nucleation and growth of the particles need to be controlled in order to achieve homogenous size and shape distributions.

The most difficult task is to control the nucleation^[5-7]. A well known example is the application of polyelectrolytes (e.g. polyacrylic acid and derivatives) to control or avoid nucleation of calcite from saturated solutions of calcium carbonate^[7-8]. Thus, all washing powders contain suitable polymers to perform in this way^[9]. Looking into the details of formation of solid calcium carbonate we have succeeded to capture the amorphous form of this material (ACC) as nanosized droplets which undergo rapid glassification^[10]. Polymers are able to protect the initially formed nanosized droplets and protect them against coalescence and coagulation (Figure 5)^[11]. Figure 6 shows such spherical glassy ACC obtained without and in presence of PAA-PEO-bisamphiphilic blockcopolymers. As can be seen from Figure 7, very small amounts of polymers are able to precisely control the particle size distribution^[11]. It is worth noting that such ACC particulate materials are excellently compatible with many polymers.

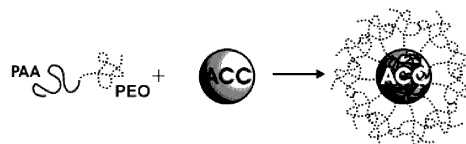


Figure 5

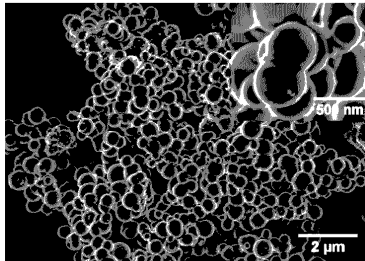
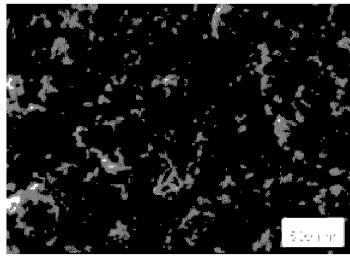


Figure 6 ACC without polymer additive (below) and with Blockcopolymer (above)

The application of polymers in the formation of micro- to nanosized particles finds wide spread application, although the details of the processes are not well understood. It is frequently assumed that the role of the polymer consists in coacervation, that is segregation of a small volume in which nucleation and growth of a precipitate is confined to a small volume within a polymer wall of semipermeable nature (Figure 8) [12].

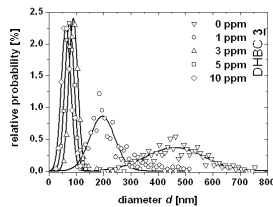


Figure 7 ACC size distribution controlled by PEO-PAA blockcopolymer

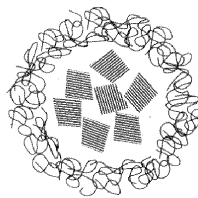
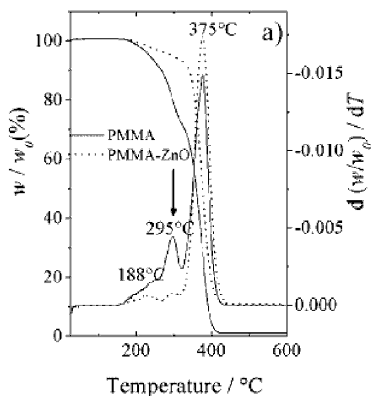


Figure 8 Crystallization inside a polymer coacervate blockcopolymer

Polymerization in presence of particles



Nanosized particles can be dispersed in a monomer and polymerization may be carried out in bulk in order to achieve homogenous blends of particles. We have investigated the bulk polymerization of MMA in presence of zinc oxide (ZnO) as a model case [15]. Suitably surface modified ZnO is totally compatible with the monomer. Bulk polymerization can be carried out quantitatively. Surprisingly, it is found, that ZnO suppresses the gel effect and prevents disproportionation as a termination reaction. The product obtained shows thus a much improved thermal stability due to the absence of vinylidene end groups and head-head links. An electron micrograph demonstrates that ZnO

remains as individual particles in the bulk polymer also it is evident that aggregation to give clusters cannot be prevented on formation of the polymer. This has severe consequences for the optical properties of the material which is dominated by scattering processes. This has to be balanced against the gain in refractive index.

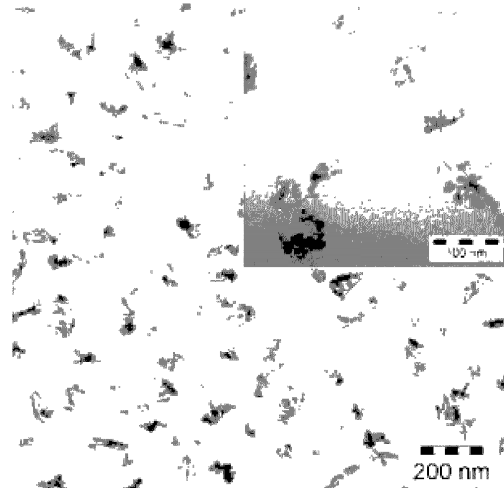


Figure 9 Blend of ZnO nanoparticles with PMMA by bulk polymerization

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