Functional inorganic nanofillers for transparent polymers

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The integration of inorganic nanoparticles into polymers has been used for the functionalization of polymer materials with great success. Whereas in traditional polymer composites, micron sized particles or agglomerates typically cause significant light scattering hampering optical applications, in nanocomposites the particle dimensions are small enough for the production of highly transparent composites. A challenge for the generation of such materials is to develop an integrated synthesis strategy adapting particle generation, surface modification and integration inside the polymer. Surface grafting using polymerizable surfactants or capping agents allows for linking the particles to the polymer. Novel techniques such as *in situ* polymerization and *in situ* particle processing are beneficial to avoid aggregation of inorganic particles inside the polymer matrix. The functions associated with inorganic fillers are widespread. Layered silicates and related materials are nowadays commercially available for improving mechanical and barrier properties in packaging. With the availability of highly transparent materials, the focus has shifted towards optical functions such as luminescence and UV-protection in transparent polymers. IR-active fillers are used in laser-holography for transparent poly(methyl methacrylate) (PMMA) nanocomposites. Refractive index modulation and ultrahigh refractive index films were developed based on inorganic materials such as PbS. The integration of magnetic nanoparticles has a great potential for applications such as electromagnetic interference shielding and magneto-optical storage.

This *tutorial review* will summarize functions associated with the integration of inorganic nanofillers in polymers with a focus on optical properties.

1. Introduction and scope

The integration of inorganic nanoparticles into polymer based materials allows one to couple properties associated with the inorganic phase to polymers, leading to new functionality of polymer based materials or new processing methods for inorganic materials.[1] Whereas inorganic materials form periodic extended structures leading to important cooperative physical phenomena such as ferromagnetism, ferroelectricity and electron transport, they typically suffer from the high expense necessary for the manufacture of single crystals. Shaping and further processing (cutting, drilling) is often difficult and demanding or impossible. Polymer materials on the other hand allow one to produce spheres and lenses or even complex shapes as well as ultrathin films from only few nm up to several micrometer in thickness with low roughness using

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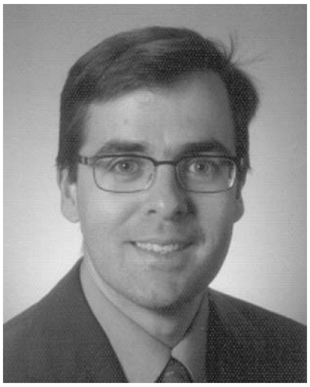
techniques such as dip coating, spin coating, and film casting, or even printing, which are versatile and less expensive.

The integration of inorganic nanoparticles into polymers allows both aspects to be combined and thus new functions in "old" polymers may be generated. New processing techniques can also be achieved for long known inorganic solids. Inorganic fillers have been used as additives for polymers since the earliest developments of polymer based materials for the improvement of mechanical, thermal and chemical stability. However, traditional fillers are often several microns in size and are not on the nanoscale, *i.e.* below 100 nm. In commercially available fillers such as carbon soot and fumed silica (Aersosil, Degussa) the primary particle size is below 100 nm but flame derived powders show a complex aggregate architecture due to aggregation in the secondary hot zone with diameters up to several micron.

Nanoparticles allow one to functionalize transparent polymers if the formation of aggregates or agglomerates is avoided. The particles must be integrated in a way leading to isolated primary particles inside the matrix. For this purpose, traditional preparation methods such as flame pyrolysis or precipitation are problematic even though the powders may have a high accessible specific surface area, because the agglomerates or aggregates formed in the synthesis can not be broken up any more. Additionally, inorganic particles are often hydrophilic and thus the surface has to be functionalized to avoid aggregation when the nanoparticles are integrated in a hydrophobic matrix. Thus a key issue is the development of synthesis methods allowing for particle generation in solution without aggregation (sol formation) and subsequent functionalization and transfer into the hydrophobic matrix without isolation of the particles. The aim of this contribution is to discuss some of the most important methods developed recently such as *in situ generation* and *phase transfer* methods. These techniques are suitable to generate new functions associated with the properties of the inorganic phase into transparent polymers without loss of transparency. The result is a wide range of material properties such as magnetoelasticity, ultrahigh refractive index, color filters but also some applications in the area of energy storage or conductive polymers are discussed, even though transparency is not required in this case but a high degree of dispersion in the nanocomposite. For future developments of bi- and multifunctional hybrid materials, transparent nanocomposites represent a wide open and diverse field benefiting from interdisciplinary cooperation which seems only be limited by a lack of imagination.



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Stefan Kaskel was born in Bonn in 1969. He received a BS in Chemistry at Tübingen University in 1992 and a PhD in Inorganic Chemistry from Tübingen University in 1997. In his thesis work, under the direction of Professor Strähle he investigated solid state reactions using in situ powder diffraction methods. Following his doctoral studies, he was a Postdoctoral Humboldt-Fellow with Professor J. D. Corbett at the Ames Lab (USA). In 2000 he joined the MPI for Coal Research (Mülheim a.d. Ruhr, Germany) as a group leader. Since 2004 he has been a full Professor in Inorganic Chemistry at the Technical University Dresden. His awards include the Feodor Lynen-Award of the Humboldt Foundation, the Reimar Lüst-Award of the Max-Planck Society and the German Ministry Award in Nanotechnology. His main research interests are the design, synthesis, characterization, and applications of porous and nanostructured materials, with an emphasis on MOFs, mesoporous materials and polymer nanocomposites.

2. Synthesis methods and structure

2.1 Particle requirements

The major requirement for nanoparticles to be used as fillers for transparent polymers is a small size. Particle diameters below 40 nm are essential to obtain transparent nanocomposites. The reason is the steeply increasing intensity of scattered light with increasing particle diameter as described by Rayleighs law:

$$\frac{I}{I_0} = \mathrm{e}^{-}\left[\frac{3\phi_\mathrm{p} x r^3}{4\lambda^4}\left(\frac{n_\mathrm{p}}{n_\mathrm{m}} - 1\right)\right] \tag{1}$$

with intensity I of the transmitted and I_0 of the incident light, radius r of the spherical particles, refractive index n_p of the particles and refractive index n_m of the matrix. λ is the wavelength of the light, Φ_p the volume fraction of the particles and x the optical path length. A high scattering intensity of visible light is associated with a turbid appearance of the nanocomposite, limiting optical applications.

However, the exact particle size necessary for a transparent material also depends on the difference of the refractive indices ($n_\mathrm{p} - n_\mathrm{m}$) between the matrix and the particles. If both are equal (so-called index-matching), the scattering intensity is zero and independent on particle sizes.[1]

Decreasing the particle size furthermore allows a much more homogeneous distribution of a material and leads to a drastic increase of the polymer/particle interfacial area. For instance, if the particle size is reduced by a factor of 10, the number of particles has to be increased by a factor of 1000 to achieve the same filler content and the interfacial area increases by a factor of 10 at the same time. The high specific surface area of small

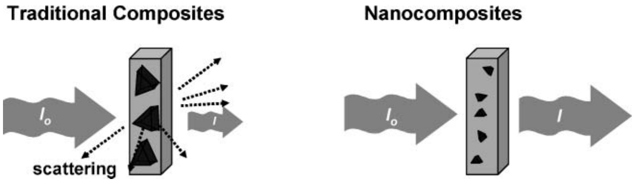


Fig. 1 Decreasing the size of inorganic particles allows for the functionalization of transparent polymers without significant loss of transparency if the particles are isolated from each other inside the polymer matrix.

nanoparticles may induce their aggregation. Aggregates also lower the homogeneity of particle distribution. A homogenous dispersion of the inorganic filler on the nanoscale is important for many applications, especially when it comes to structuring, for example in thin films.

While there are many preparation methods for nanoparticles with a good control over particle size, not all materials are suitable for the use in transparent polymer composites. Large scale industrial processes using gas phase pyrolysis (Aerosil Process) suffer from the formation of aggregates. Even though offering high accessible surface areas, the primary particles can not be dispersed inside the matrix without forming larger aggregates due to the presence of covalent bonds between particles. Thus the development of synthetic methods avoiding the formation of aggregates inside the polymer is the key challenge. For this purpose, nanoparticle syntheses need to be controlled to allow for a generation of the particles and subsequent embedding or stabilization by surface functionalization before aggregation or agglomeration can occur.

2.2 Surface engineering

Due to the enormous interfacial area in nanocomposites, the surface energy is an important contribution for the stabilization energy. In order to minimize interface energies between particles and polymer matrix, several surface functionalization and stabilizing techniques have been developed.

There are two basic requirements for a surface modifier to be used for stabilization of particles in polymer matrices. Anchor groups are needed for adsorption or covalent binding of the modifier on the particle surface, while other parts interact with the polymer and therefore decrease the interface energy. Functional groups like R–NH_2, –SH, –COOH, –SO_2OH, –$PO(OH)_2$ are capable of interacting with inorganic particles by coordinative, electrostatic or hydrogen bonding and act as a reactive anchor. Furthermore covalent binding is viable through silanization chemistry. Silanization is widely applied for silica but can be also used for other oxides. Typically, silanes such as $RSi(OMe)_3$ (R = 3-methacryloxypropyl) not only form a monolayer but a sol–gel coating on the particle and the surface chemistry is not as specific as for thiols binding to metal or chalcogenide surfaces. Thiols on the other hand are rarely suited for industrial applications due to their high toxicity. Amines (R–NH_2) are efficient and easy to use modifiers. They either form coordinative bonds and link directly to metal ions, for example in ZnO, or react with Brønsted acid centers on the particle surface forming very stable ionic bonds. Ammonium salts are also used (see below) for organomodification of clay fillers. A key drawback of amine groups is the low thermal and photochemical stability. The latter is responsible for yellowish products obtained after melt compounding of organoclay composites or pronounced sun light exposure.

The hydrophobic tail of the anchor molecule can either form covalent bonds to the polymer matrix *via in situ* polymerization (below) or interact through van der Waals forces. The mechanisms responsible for a high stability of the resulting particle dispersions are the same as for aqueous colloids. However, a more quantitative description comparable to DLVO (Derjaguin, Landau, Verwey and Overbeek)[2] theory describing electrostatic, steric, or electrosteric stabilization is still needed for particle dispersions in which the matrix is a non-polar monomer, polymer solution or polymer melt, and stable hydrophobic particle dispersions are typically obtained by empirical explorations. A limited degree of estimating forces was achieved by numeric modelling.[3]

For instance, the thiol group (R–SH) was found to tightly bind to gold or II–VI-semiconductor surfaces. Using long alkyl chains as hydrophobic moiety in dodecanethiol, silver nanoparticles were stabilized for the preparation of Ag/HDPE-nanocomposites by solution casting.[4] The same molecule was used as a reactive anchor for CdTe– and HgTe-nanoparticles in poly (lauryl methacrylate) based nanocomposites prepared by *in situ* polymerization.[5] For the preparation of polar nanocomposites from aqueous solutions, polar stabilizers are needed, such as 1-thioglycerol or thioglycolic acid in the case of CdS and CdTe/poly(vinyl acetate-co-crotonic acid) nanocomposite films.[6]

Another method is the modification of particle surfaces by silanization. 3-Methacryloxypropyltrimethoxysilane was used extensively for the functionalization of silica-, alumina- and ZnO-nanoparticles *via* sol–gel processes. The propyl methacrylate residue allows for the homogenous integration in poly(hydroxyethyl methacrylate) in the *in situ* polymerization process. Further grafting techniques are addressed below.

While there is a huge variety of synthesis strategies for nanocomposites, most of them can be grouped into three different types (Scheme 1). The preparation methods are all based on liquid particle dispersions, but differ in the type of the continuous phase. In *melt processing* particles are dispersed into a polymer melt and nanocomposites are obtained by extrusion. *Casting* methods use a polymer solution as dispersant and solvent evaporation yields the composite materials. Particle dispersions in monomers and subsequent polymerization result in nanocomposites in the so called *in situ polymerization* route. A prominent example for *in situ* polymerization in the presence of clay materials is shown in Fig. 3 in which the initiator is linked to the surface *via* ionic interactions and the formation of the polymer in between the silicate layers causes delamination of the layered silicate. In the following chapters, the three methods are discussed in more detail and examples are given.

2.3 Manufacturing approaches

2.3.1 Melt compounding. Direct mixing of particles with the polymer melt in technical polymer processes like extrusion is the classical method for the preparation of composite materials

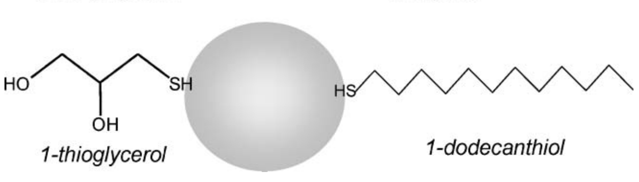
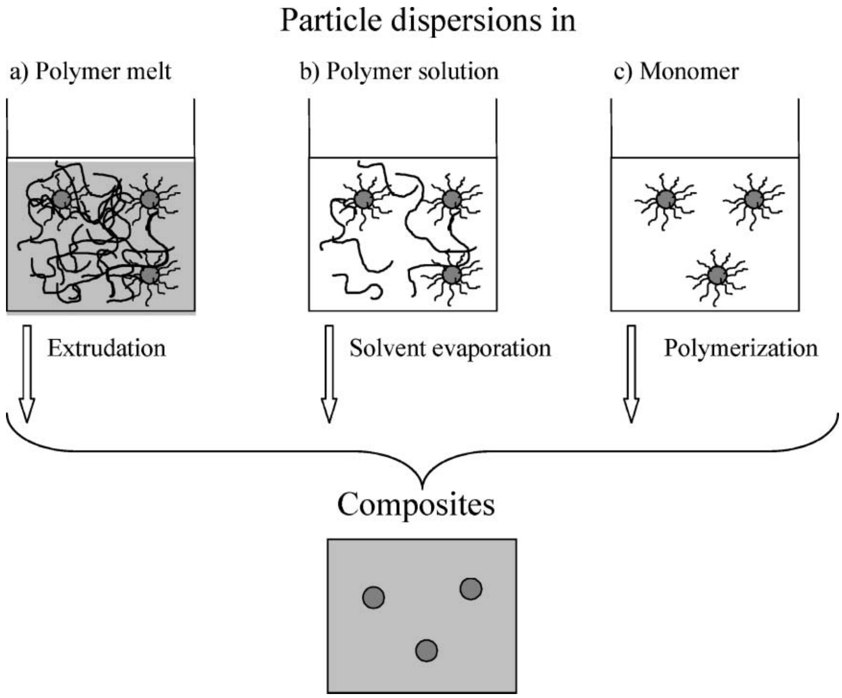


Fig. 2 Reactive anchors used for the functionalization of metal and chalcogenide nanoparticles (ZnS, CdTe *etc.*).



Scheme 1 Preparation methods for nanocomposites in a schematic overview. a) Melt compounding, b) film casting and c) *in situ* polymerization.

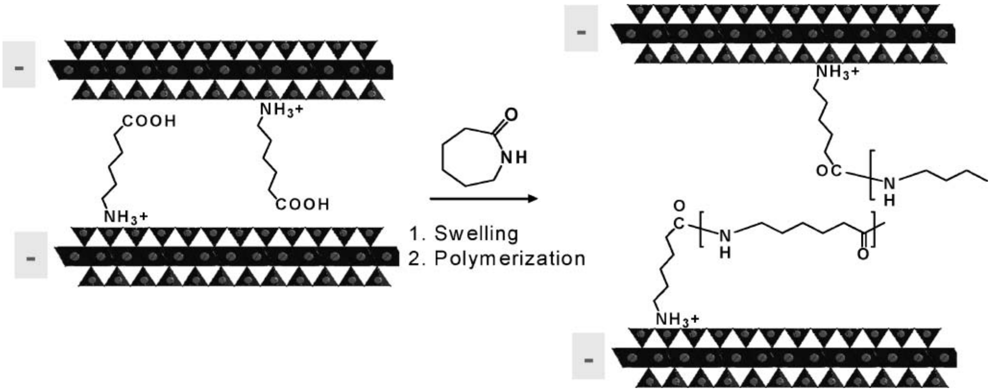


Fig. 3 *In situ* polymerization of ε-caprolactam in the presence of clay fillers.

from thermoplastic polymers. It is widely used for the compounding of clay materials in polyolefins. Cationic modifiers such as organo ammonium salts on the particle surface are used for hydrophobization and production of the so-called organoclays (Nanofil, Südchemie) to achieve a homogenous dispersion during processing and an interfacial adhesion between particles and matrix. Delamination of layered clay materials by polymer intercalation is observed when the clays are modified with alkylamines before mixing with the polymer melt.[7] However, delamination is difficult to control with mechanical forces and often larger aggregates remain in the matrix. For natural clays from commercial producers the lateral extension is ill defined and can vary from 100 nm to several micron with a broad distribution, further reducing the ability to control the dimensions of the clay layers inside the polymer matrix. The high temperatures of melt processing cause degradation of the amines resulting in a yellowish appearance of the products. Long term stability against weathering and UV irradiation of amine containing composites is also one of the major concerns. However, organoclays are already in use as flame retardants in cable isolation and for the production of high strength automotive parts with reduced weight in which optical properties are not a major concern.

Melt compounding is currently explored for a wide range of materials such as oxides, and carbon nanotubes. A strength of melt compounding is the large quantity of material that can be produced by extrusion, since most polymer blends are commercially produced in this way. Surface treated ZnO nanoparticles showed a good dispersion in PP-composites prepared by extrusion.[8] But even if surface modification is applied, breaking aggregates during melt processing is often difficult, especially if the aggregates architecture is a result of the particle manufacturing process.

2.3.2 Film casting. Another approach for the preparation of nanocomposites is to dissolve the hydrophobic nanoparticles in a polymer solution. The mixture may be cast in containers or coated on substrates. Evaporation of the solvent leads to composite sheets or films.

A good solubility of polymer and dispersability of the nanoparticles in the solvent are crucial to get homogenous materials using this method, but the adsorption of the polymer on the surface may also cause flocculation. Due to its simplicity the film casting method is widely used for the preparation of nanocomposite films. Thin films 1–100 nm in thickness are typically prepared by spin coating of the particle/polymer solution. The solvent evaporation takes place during the coating process and homogenous films are obtained.

For the solution casting, the polymer synthesis step can be separated from the particle generation and the nanocomposite processing. Therefore more complex polymer architectures are accessible. Sooklal used this approach for the preparation of CdS/dendrimer nanocomposites.[9] Similarly conjugated polymers were combined with InAs nanocrystals in thin nanocomposite films by film casting for the preparation of light emitting devices.

For the casting of thick polymer sheets the evaporation step is more critical. ZnO/PS nanocomposites were casted from solution in *N*,*N*-dimethylacetamide. The casting and drying step takes several days, followed by hot pressing of the composite to remove solvent residues in order to obtain homogenous nanocomposites.[10]

2.3.3 *In situ* polymerization. While direct mixing and melt processing of particles with polymers often leads to turbid composite materials because of agglomeration of the nanoparticles, miscellaneous methods have been developed to overcome these problems by *in situ* polymerization. The procedure of *in situ* polymerization involves dispersing the inorganic nanoparticles directly in the monomer or monomer solution and subsequent polymerization of the monomer dispersion with standard polymerization techniques. Since the viscosity of monomer dispersions is comparatively low and sedimentation processes can proceed quickly, the main challenge for *in situ* polymerization techniques is to obtain stable dispersions by adequate modification of particle surfaces. Inorganic particles tend to phase separate from the organic polymer, thus specific groups have to be linked to the inorganic surface to stabilize particle dispersions. Unmodified particles can be encapsulated in organic capsules, building inorganic/organic core-shell particles, as described above. In this chapter we will focus on different possibilities to establish coupling agents allowing *in situ* polymerization directly at the surface of inorganic particles. We distinguish three different types of modification.

Amphiphilic molecules, such as stearic acid, oleic acid, oleic amine or long chain alcohols, can adsorb on the particle surface by ionic attractions, hydrogen or coordinative bonding. The surfactant molecules arrange on the mineral surfaces and build a hydrophobic interface protecting the nanoparticles from agglomeration. The surfactant molecules do not participate directly on the polymerization but monomers can solubilize into the hydrophobic surfactant layer and the inorganic particles will be embedded in the growing polymer during the polymerization process (so-called ad-polymerisation).[11]

Avella *et al.* have used $CaCO_3$ particles covered by stearic acid for *in situ* polymerization with PMMA. The presence of the stearic acid increased the compatibility of the inorganic particles with the polymeric matrix and yielded highly transparent bulk composite materials.[12]

Grafting techniques take advantage of monomers being directly adsorbed to the particle surface. In ''grafting to'' techniques, polymer chains modified with anchoring groups are used to bind to the particle surface. By reaction of these anchoring groups with functional sites at the particle surface, the polymer can be grafted *to* the inorganic particle. The polymer can also be grafted *from* the surface by adsorption of monomers at the surface and subsequent growth from the surface.

In case of basic (amines, pyridines *etc.*) or acidic (*e.g.* acrylic acid, methacrylic acid) monomers, the adsorption is provided by acid–base reactions, but also other coordinating mechanisms such as ionic interactions or the use of so-called polymerizable surfactants are possible. Adsorbed functional groups can stabilize monomer dispersions but also participate in the polymerization process encapsulating the inorganic phase in the polymer.

Lü *et al.* have used this method to synthesize bulk ZnS–polymer nanocomposite materials with high inorganic phase content. Taking advantage of the fact that polar organic solvent molecules co-ordinate to the surface of ZnS nanocrystallites, they used *N*,*N*-dimethylacrylamide (DMAA) as coordinating monomer for polymerization with styrene and divinylbenzene as co-monomers.[13] ZnO was embedded in poly(butanediolmonoacrylate) (PBDMA) by *in situ* polymerization of the monomer dispersion with BDMA as stabilizing ligand.[14]

Organic/inorganic nanocomposite materials can also be produced by ''grafting from'' techniques by functionalization of inorganic surfaces with initiating groups, starting the

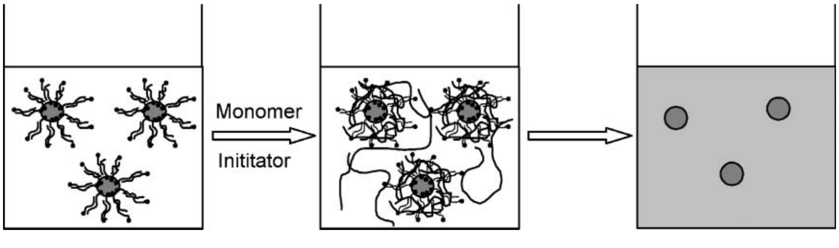


Fig. 4 Ad-polymerization at the surface of inorganic nanoparticles by surfactant adsorption.

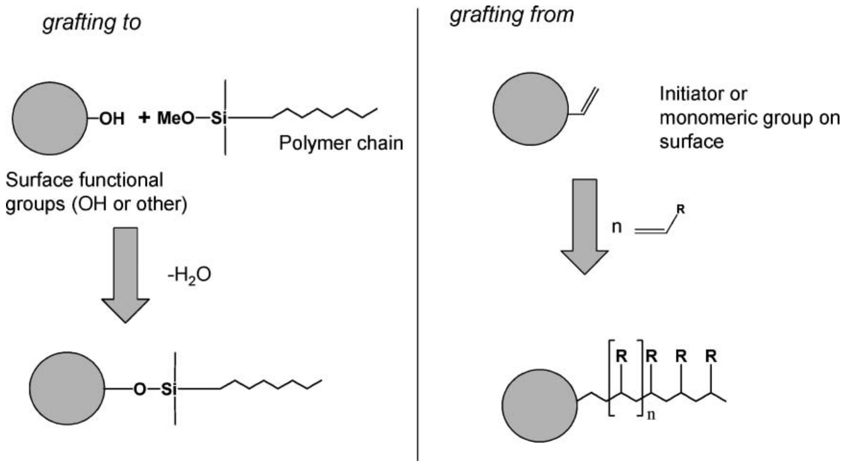


Fig. 5 Grafting techniques for the surface functionalization of inorganic nanoparticles (A = anchoring group, B = reactive group on surface).

polymerization reaction *from* the inorganic surface. Different kinds of functionalization can lead to anionic, cationic or free radical polymerization.[11]

Cationic initiators such as 2,2′-azobis(2-amidinopropane) dihydrochloride (AIBA) are known to form strong ionic interactions with negatively charged surfaces, as found on many oxidic particles. Thus, polystyrene was grafted from TiO_2 particle surfaces by using AIBA as initiator for *in situ* polymerization. Atom transfer radical polymerization is another way allowing for covalent binding of the initiator to the particle surface.

2.3.4 *In situ* particle generation. While *in situ* polymerization techniques as described above always have to deal with the challenge of re-dispersing isolated particles, novel methods already allow single-step synthesis of nanocomposite materials with inorganic nanofillers *in situ generated* in the presence of a polymer or polymer precursor (monomer).

Reverse microemulsions were used for the synthesis of several inorganic materials.[15] They consist of aqueous droplets 2–20 nm in diameter, encapsulated by surfactant molecules and surrounded by an oil phase. Particle formation in reverse micelles can be achieved in different ways. In the single-microemulsion approach, one microemulsion is prepared and subsequently a precursor or reactant is added diffusing through the oil phase to the micelles containing a reactant. A second processing route, a multi-microemulsion route, takes advantage of two or more separately prepared microemulsions of the same water/surfactant/oil ratio, but each microemulsion containing one of the reactants necessary for the particle synthesis in the aqueous core of the reverse micelle. After mixing the microemulsions together, the particle formation occurs by intermicellar exchange of the reactants. A new way of producing nanocomposite materials in a single-step synthesis is the use of microemulsion systems prepared with pure monomer as oil phase, forming a completely polymerizable matrix.[16]

Palkovits *et al.* have used reverse microemulsions containing water/non-ionic surfactant and MMA as the oil phase for the synthesis of SiO_2 nanoparticles by hydrolysis and condensation of an alkoxide precursor tetraethylorthosilicate (TEOS) within the nanosized water droplets (eqn (2)). After several hours of particle formation and growth, the microemulsion system was polymerized using an initiator in the oil phase by radical polymerisation.[17]

By mixing two reverse microemulsions containing Cd^{2+} and S^{2-} in the aqueous phases, Pavel and Mackay have synthesized CdS nanoparticles. CdS/PMMA nanocomposite materials were obtained by microemulsion polymerisation of the MMA oil phase using a polymerisable surfactant as co-monomer.[18]

Template-controlled syntheses of metal or semiconductor nanoparticles in the presence of a polymer allows the control of morphologies. Amphiphilic block copolymers tend to form supramolecular assemblies of different shape in solution, depending on chemical structure, composition, concentration and polarity of the solvent. Spherical or rod-like micelles formed by block copolymers can be used as nano-templates for the controlled synthesis of inorganic particles either within, or in the corona of the micelles.[19] The key to successful control of

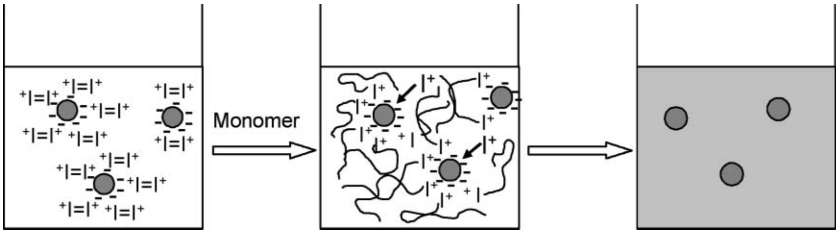


Fig. 6 Polymerization "grafted from" the surface of inorganic nanoparticles by initiator adsorption.

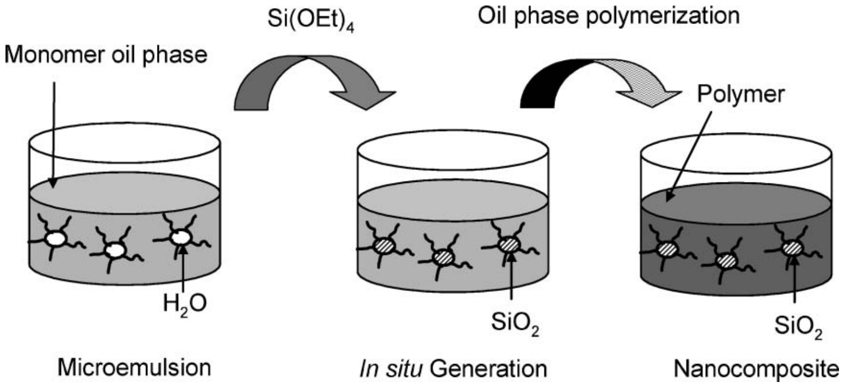


Fig. 7 *In situ* generation of inorganic nanoparticles in reverse microemulsions for the manufacture of transparent polymer nanocomposites.

particle synthesis is the strong interaction between the inorganic precursor and the block copolymer. These interactions can be provided by coulomb attraction, *e.g.* in hybrid systems of block copolymer with cationic surfactants.[20] However, also more complex structures such as dendrimers can be suitable systems for controlled particle synthesis. The synthesis of dendrimers with specific properties is demanding but can be controlled very well providing host molecules adjustable in shape, size and functionality. Soler-Illia *et al.* have used dendrimers to build nanocomposite materials from assemblies of dendrimers and titanium(IV)–oxo-organic clusters cross-linked with each other.[21]

Sol–gel processing of inorganic oxide nanoparticles either in the presence of a preformed polymer or in parallel with the formation of the organic polymer has been a broad field of investigation. The process has been studied extensively with silicon alkoxide molecules leading to SiO_2 nanoparticles, but also other metal precursors have been used.[22,23] The most frequently used precursor, TEOS, undergoes hydrolysis and condensation:

$$Si(OC_2H_5)_4 + \text{excess } H_2O \rightarrow SiO_2 + 4\ C_2H_5OH \qquad (2)$$

In order to avoid phase separation during the sol–gel process caused by the presence of a hydrophobic polymer, the polymers need to be functionalized with groups increasing the compatibility of the organic and inorganic phase. Polymers capable of forming hydrogen bonds can provide interactions with silanol groups embedding the formed silica particles in the polymeric matrix and leading to highly homogenous and optically transparent composite materials.[22] If the organic polymer and the ceramic are formed simultaneously, avoiding phase separation is again crucial to obtain transparent hybrid materials ranging from polymers with only few percent of inorganic phase to continuous interpenetrating networks of silica and organic polymers.[1] Polymers with polar head groups such as HEMA (Fig. 8) can be polymerized simultaneously using sol–gel processing of TEOS leading to homogeneous composite materials with hydrogen bonding between organic and inorganic phases.[24]

Linking inorganic and organic phases is also achieved using covalent bonds. Special bifunctional molecules such as MEMO (Fig. 8), possessing a polymerisable group as well as alkoxy groups are commercially available and can be used to obtain homogeneous hybrid materials with covalent links, either by simultaneous or subsequent polymerization reactions.[25]

A promising method for the *in situ* growth of particles in the presence of a polymer is the thermal decomposition of metal precursors forming metal or metal oxide nanoparticles within the polymeric matrix. However, as for other methods, the metal precursor must exhibit a strong affinity to the polymeric matrix to distribute uniformly in the hybrid material. Interactions can be achieved again by hydrogen bonding to organic polymers, by substitution of a metal ligand by unsaturated groups of the polymer, or by ionic interactions of a basic polymer with an acidic metal precursor such as $HAuCl_4$ (Fig. 9).[1]

3. Functions and properties

3.1 Luminescence in inorganic/polymer nanocomposites

Lighting, screen and display technology have been classical application fields for inorganic luminescent materials. In recent years synthesis routes for the production of several different nanoscale phosphors have been established. While

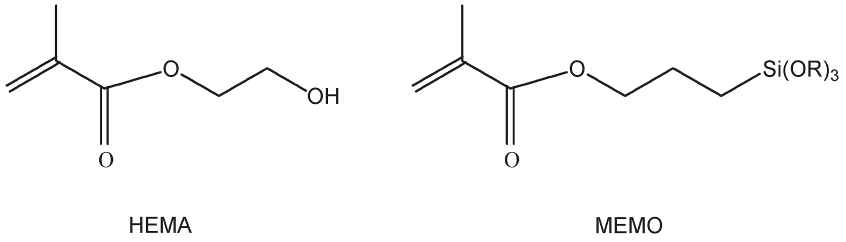


Fig. 8 2-Hydroxyethyl methacrylate (HEMA); 3-methacryloxypropyltrimethoxysilane (MEMO).

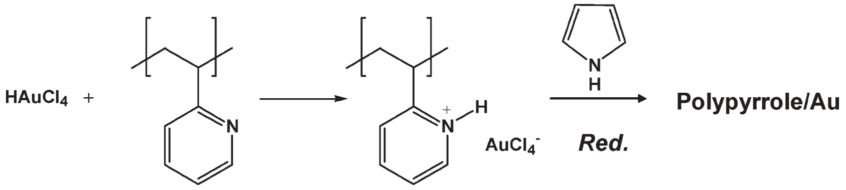


Fig. 9 *In situ* particle generation using specific adsorption of anionic metal precursors and subsequent reduction.

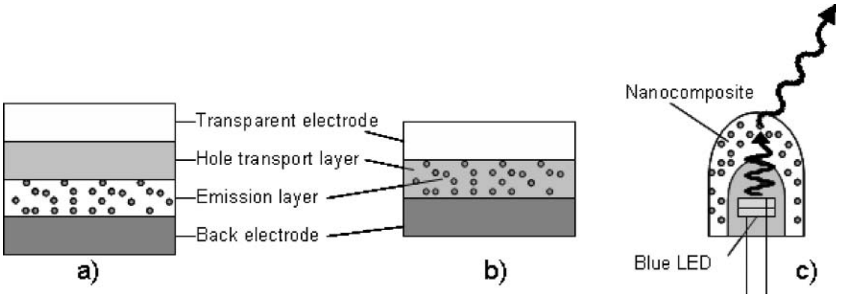


Fig. 10 Schematic device structures for LEDs with separate layers (a), using a nanocomposite layer (b), and a light conversion composite on top of a blue emitting diode (c).

quantum efficiencies are usually lower than for the bulk materials, the nanoscale materials offer a range of interesting, new properties. In semiconducting nanoparticles, emission colors can be tuned by varying the particle size (quantum size effect) or by incorporating dopants and defects. Most prominent examples are clearly the CdSe–Nanodots, prepared by Murray *et al.*[26] Using a coordinating, high-boiling solvent (TOPO = trioctyl phosphine oxide) for the growth of particles and size selective precipitation, the particle sizes can be controlled in a range of 1.2–11.5 nm, leading to emission colors covering the whole visible spectral range. Due to an advanced core-shell system (ZnS shell on CdSe core), quantum efficiencies as high as 50% have been realized.[27]

The integration of luminescent nanoparticles into polymers offers a new range of possible applications. Colvin *et al.* combined CdSe-nanocrystals with semiconducting polymers to construct light emitting diodes with tunable emission colors.[28] Similarly Tessler *et al.* prepared InAs/polymer LEDs with near infrared emission.[29] The general device structure is displayed in Fig. 10. As in OLEDs, semiconducting polymers are used as the hole transport layer, while the emission layer is made from a thin film of inorganic nanoparticles. Alternatively both can be combined in a nanocomposite layer. Nanocomposites of luminescent nanoparticles dispersed in a transparent polymer matrix can also be used for light conversion in a different LED device construction (Fig. 10c). (CdSe)ZnS core-shell nanoparticles were incorporated into lauryl methacrylate and a GaN diode was covered with the resulting nanocomposite material.[30] Under excitation of the blue LED, the particles showed photoluminescence with emission colors depending on the particle size.

However, the toxicity of Cd, Se or As-containing materials may lower their applicability in commercial devices. Doped ZnS nanoparticles on the other hand are an important, non-toxic alternative. Different dopants act as efficient luminescence centers and are used to tune the emission colors in a wide range, with manganese (orange-yellow) and copper (blue-green) being most frequently used. ZnS:Mn nanoparticles with a quantum efficiency of 30% were obtained as a liquid dispersion in acrylic acid. This dispersion is stable for years and is suitable for *in situ* polymerization in combination with other monomers such as MMA, resulting in transparent, luminescent bulk nanocomposites.[31] The liquid can be printed onto transparent plastic sheets by ink-jet printing (Fig. 11). Subsequent UV-hardening affords an invisible, transparent coating with bright orange appearance under UV-excitation.

Yang *et al.* showed the principal applicability of ZnS/polymer nanocomposites in electroluminescent devices.[32] Zinc methacrylate was co-polymerized with styrene and an H_2S-treatment resulted in ZnS-nanoparticles incorporated in a polymer network. The composite was spin-coated as a thin film and a device structure similar to Fig. 10 a) was fabricated, showing electroluminescence with an emission peak at 440 nm.

Due to the unique luminescence properties of inorganic nanophosphors and the good processability of their dispersions in polymer solutions or monomers, inorganic/polymer nanocomposites are promising materials for different lighting and display devices.

Fig. 11 Inkjet printing of transparent, luminescent ZnS:Mn/polymer nanocomposites onto transparent polymer substrates.

Table 1 Band gap energies and corresponding absorption wavelengths of inorganic, UV absorbing materials

Material	Band gap energy ΔE/eV	λ/nm
ZnO	3.2	388
TiO_2 (rutile)	3.03	409
TiO_2 (anatase)	3.18	390
CeO_2	3.15	393

3.2 UV absorption in inorganic/polymer nanocomposites

UV-absorbing pigments are widely used as additives to increase the long term stability of polymers or to prepare UV-protective coatings. While there is a huge range of organic UV-absorbers, they suffer from a low long term stability. Inorganic materials are of great interest due to the high photostability. For most applications a high transparency in the visible and a steep absorption in the near UV range ($\lambda <$ 400 nm) are required. Most promising materials are TiO_2, ZnO and CeO_2, semiconductors with bulk bandgap energies of about 3 eV. The corresponding absorption edges are listed in Table 1. For nanoparticles of small size (below 10 nm), quantum confinement causes an increase of the band gap energy and a blue shift of the absorption edge compared to the bulk material is observed.

Several synthesis methods for nanoparticles of these materials and their surface functionalization have been developed. Nanocomposites based on polyolefins were prepared by melt compounding with nanoscaled ZnO and TiO_2.[8,33,34] Amphiphilic copolymers and surfactants were used to stabilize particles for film casting in polystyrene, polycarbonate and PMMA.[35] *In situ* polymerization of ZnO dispersions in acrylic monomers and epoxy resins[36] resulted in transparent nanocomposite films and bulk materials. A UV-Vis transmission spectrum of a ZnO/PBDMA (PBDMA = poly(butanediol monoacrylate)) nanocomposite is displayed in Fig. 12, showing the high transparency in the visible and the steep UV-absorption band at wavelength below 360 nm.[14] Even low concentrations (<0.1%) of ZnO nanoparticles cause a significant UV-shielding effect.

However, for the protection of substrates with thin UV-absorbing coatings, higher concentrations are needed. To increase the UV resistance of the polymer matrix itself, 1–5 wt% of ZnO or TiO_2 nanoparticles were typically used. Studies on the stability of such nanocomposites against UV-irradiation revealed an enormous effect of the nanoscaled additives. A significant reduction of the carbonyl index, a measure for the photooxidation of polymers, was found for ZnO/PP and ZnO/PE nanocomposites when compared to pure polymers in two different studies.[8,33] Degradation tests with TiO_2/polymer nanocomposites showed the opposite effect.[34] In polyethylene, the nanoparticles show photocatalytic activity leading to a faster and stronger increase of yellowness and carbonyl index compared to pure polyethylene. The surface activity of the TiO_2 also depends on its crystal structure as a lower activity was observed for the rutile modification compared to anatase.[37]

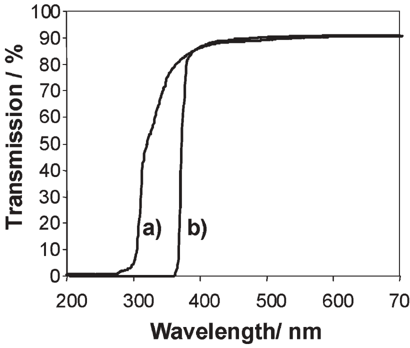


Fig. 12 Transmission spectra of PBDMA (a) and ZnO/PBDMA nanocomposite (b).

Inorganic coatings on the nanoparticle surface, made of Al_2O_3, ZrO_2 or SiO_2, can be applied in order to avoid the photocatalytic degradation of the polymer.[34] In CeO_2-nanoparticles the doping with Ca leads to higher UV-absorption and reduced their catalytic oxidation activity.[38]

In conclusion, inorganic nanofillers based on ZnO, TiO_2 or CeO_2 are efficient UV-shielding pigments. Particle synthesis and surface chemistry play a special role for these materials, not only to avoid particle aggregation but also to reduce photocatalytic oxidation of the polymer matrix.

3.3 Conductivity and isolation

Tailoring the transport properties of polymer based materials is effectively achieved by the incorporation of inorganic nanoparticles. A high electron, thermal or even ionic conductivity may be addressed. But a high static dielectric constant can be a target as well for example in thin film capacitors based on nanocomposite thin layers.

Due to the tremendous interest in carbon nanotubes in recent years, considerable efforts have focused on the integration of single and multi walled carbon nanotubes into polymer materials. Even though chirality of CNTs in principle allows the control of metallic and semiconducting behaviour, in practice the metallic character of CNTs dominates the associated properties of commercially available CNT products consisting of tube mixtures with different chirality. The high aspect ratio renders SWNT as efficient additives introducing electroconductivity at very low critical volume fractions but also a high thermal conductivity is achieved.[39,40] Thus for an aspect ratio of 20, volume fractions of 0.05 were reported whereas for a ratio of 2000, in theory only 0.05 vol% CNTs are necessary to achieve percolation. However, in practice, processing critically affects the experimentally observed percolation threshold and critical volume fractions vary by a factor of 100. The most efficient dispersion methods are *in situ* polymerization, sonication and shear phase separation. The surface chemistry of the CNTs critically affects bonding to the matrix. Whereas covalent bonds are efficient to integrate the tube into the matrix, at the same time the electronic structure of the CNT is disturbed. A promising approach to avoid this disruption is the use of non-covalent functionalization *via* poly(*p*-phenylene ethylene)s.[41] The rigid polymers link to the CNTs *via* π–π interactions so strong that washing, sonication, and filtration cannot remove them from the nanotubes. Adding 2 wt% of such modified CNTs not only causes an increase of the electrical conductivity of greater than twelve orders of magnitudes but also results in 72% increase of tensile strength and 28% increase of Young's modulus.

A promising issue in nanocomposite research is improved ionic conductivity in polymer electrolytes. Especially in lithium batteries, the development of polymer electrolytes with high chemical stability and high ionic conductivity is desired. Oxide nanoparticles of inert materials such as Al_2O_3 and TiO_2 do not enhance the conductivity *per se* but can be used as plasticizers and enhance the ion mobility for example in poly(ethylene oxide) (PEO) at low temperature.[42] Whereas below 60 °C, PEO tends to crystallize causing a drastic reduction of lithium ion mobility, the addition of nanoparticles blocks the crystallization and allows for relatively high ion conductivities (10^{-4} Scm^{-1}) at moderate temperatures (50 °C).

For the design of dielectric composites, ferroelectric ceramics are used as active fillers. A typical example is $BaTiO_3$ incorporated in non-conductive polymers.[43] Nanoparticles are necessary for the manufacture of thin film capacitors, however particles below a critical diameter are not ferroelectric and thus depending on the composition of the inorganic filler, the particle size has to be adjusted in a suitable range. Dielectric constants up to $\varepsilon_r = 150$ were reported and proposed for low cost embedded RF capacitors.[44] Energy storage in supercapacitors was achieved using polyoxometallate–polyaniline nanocomposites. Electrochemical supercapacitors represent a promising energy-storage technology providing higher power density than a battery and higher energy density than a conventional parallel-plate capacitor. With the integration of an electroactive filler such as $H_3PMo_{12}O_{40}$, capacitor cells with a storage capacity of 120 Fg^{-1} were obtained showing good cyclability beyond 1000 cycles.[45]

3.4 IR active fillers

IR absorption and reflection are important functions for the future generation of energy saving windows, heat reflecting shields and security glasses. IR absorption can be also used as a marker. For example, IR absorbing particles in transparent polymers can be addressed using a holographic writing process with an IR Laser. The heat dissipated causes local polymer degradation and a turbid appearance. In this way three dimensional objects can be written inside transparent PMMA blocks. The most prominent IR absorbing pigments are indium tin oxide (ITO) and antimony tin oxide (ATO). ITO nanoparticles are produced *via* flame pyrolysis and commercially available from AdNano (Degussa) for transparent coatings. Near-IR reflective ITO films were also obtained from solution based precipitation processes and spin coating of the resulting 15–30 nm ITO sols.[46] However, documentation in this area of research is dominated by patents whereas only few scientific details are available. Reviews on composition and processing are rare. A common IR absorbing filler is LaB_6 and other rare earth hexaborides. However, often these are micro and not nanoscale materials. IR absorbing inks are used to prevent forgery, which explains the limited degree of information available. IR shielding films are also used in display technology.

3.5 High and low refractive index in polymer nanocomposites

As compared to inorganic solids, optical applications of polymers are often limited due to the relatively narrow range of the refractive indices available. Most of the commercial polymers show refractive indices between 1.3 and 1.7, only few polymers are known with higher refractive indices such as poly(thiophene) with $n = 2.12$. In order to broaden the spectrum of accessible polymer materials, high refractive index composite materials are interesting as well as low refractive index composites. Potential applications range from creating novel composite lenses, optical filters, or reflectors to optical waveguides, optical adhesives, antireflection films or integration into improved efficiency solar cells. The key challenge in preparing transparent high refractive index composite materials is to avoid intensity loss of transmitted light due to Rayleigh scattering. According to eqn (1), this intensity loss is proportional to the difference of refractive indices of the particles and of the matrix. Thus, the size of inorganic particles with high refractive index should be well below 40 nm (one tenth of the wavelength of visible light) in order to reduce Rayleigh scattering.

However, working with nanoparticles of that dimension, quantum size effects have to be considered. Among other optical properties, such as the color dependence of semiconductor nanoparticles on their size, also the absorption coefficient and refractive index show size effects. The size dependence was investigated experimentally for PbS/polymer nanocomposite materials by Suter *et al.*, who reported refractive indices close to that of bulk PbS for PbS particles larger than 25 nm. Smaller particles exhibit a distinct decrease of refractive indices with decreasing particle size.[47]

In order to obtain nanocomposite materials with high and ultrahigh (>2.5) refractive index, different inorganic compounds have been investigated. A variety of inorganic materials with high refractive indices is given in table 2.

PbS with very high refractive index >4 over a broad wavelength range has been in focus for nanocomposite materials. Zimmermann *et al.* have found a linear relationship

Table 2 Inorganic materials with extremely high or low refractive indices

Substance	n (413.3 nm)	n (619.9 nm)	n (826.6 nm)
Os	4.05	3.98	2.84
W	3.35	3.60	3.48
Si crystalline	5.22	3.91	3.67
Si amorphous	4.38	4.23	3.86
Ge	4.08	5.59–5.64	4.65
GaP	4.08	3.33	3.18
GaAs	4.51	3.88	3.67
InP	4.40	3.55	3.46
InAs	3.20	4.00	3.71
InSb	3.37	4.19	4.42
PbS	3.88	4.29	4.5[a]
PbSe	1.25–3.00	3.65–3.90	4.64
PbTe	1.0–1.8	6.40	3.80
Ag	0.17	0.13	0.15
Au	1.64	0.19	0.19
Cu	1.18	0.27	0.26

[a] At 885.6 nm

between refractive index of the nanocomposite materials and the volume fraction of the particles. The relationship is given by eqn (3):

$$n_{\mathrm{comp}} = \phi_{\mathrm{p}} n_{\mathrm{p}} + \phi_{\mathrm{org}} n_{\mathrm{org}} \tag{3}$$

with the refractive indices n_{comp} of the composite material, n_{p} of the inorganic particles and n_{org} of the organic matrix, and the volume fractions Φ_{p} of the particles and Φ_{org} of the organic matrix.[49] According to eqn. (3), the volume fraction of the inorganic filler necessary to obtain a certain refractive index can be calculated. For the preparation of ultrahigh refractive index materials based on gelatin with PbS, the volume fraction of particles needs to be around 0.4 and higher corresponding to a weight fraction of at least 0.8 (using the density of PbS with 7.50 g cm^{-3} and of gelatine with 1.35 g cm^{-3}). Weibel *et al.* also prepared PbS/poly(ethylene oxide) (PEO) nanocomposites with PbS content of 90% w/w (or *ca* 50% v/v) by coprecipitation of lead sulfide and polymer.[50] The materials obtained exhibit extremely high refractive indices of about 3 over a broad wavelength range, higher than any other polymer composite material.

Successful work on high refractive index composites has also been done with other inorganic fillers. Yang *et al.* have used ZnS as high refractive index filler material and integrated ZnS nanoparticles in poly(urethane-methacrylate macromer) (PUMM) nanocomposite films up to 86 wt% of ZnS enhancing the refractive index from 1.645 to 1.796 at 632.8 nm.[48] Only recently they developed a novel route to integrate ZnS in bulk poly(*N*,*N*-dimethylacrylamide) (PDMAA) increasing the refractive index from 1.54 for the polymer matrix to 1.63 for nanocomposite material containing 50 wt% of ZnS.[13]

Crystalline silicon particles have been used to enhance the refractive index of nanocomposite materials, using the advantage of the low density of silicon. This material offers the opportunity to disperse higher volume fractions of silicon but using lower weight fractions at the same time compared to PbS weight fractions for example. By dispersing silicon nanoparticles in gelatine, refractive indices up to 3.2 could be achieved. However, most reports on high refractive index materials use thin films with a thickness of 1–5 micrometer and transparency is achieved with the low thickness, whereas examples of transparent bulk nancomposites with a thickness of 10^{-3} to 10^{-2} m are still rare.

In a similar way as for high refractive index materials, low refractive index composite materials have also been prepared. As suitable filler materials, metals with low refractive indices below 1, such as gold were chosen. Zimmermann *et al.* prepared gold/gelatin nanocomposite films with gold content up to *ca* 90 wt%, lowering the refractive index of the materials down to about 1, offering the lowest refractive indices known for polymer composite materials.[49]

3.6 Magnetic properties

Iron oxides (Fe_3O_4, Fe_2O_3) are most often used to integrate magnetic functions into polymer materials. Nanoscale particles of the ferroelectric metals such as Fe, Co, and alloys on the other hand are easily oxidized and less frequently used. Particle size control is crucial due to the size dependent ferromagnetic–superparamagnetic transition. The transition temperature critically depends on the magnetic anisotropy of the particles and can be controlled with the composition and sometimes with the phase symmetry. For example in nanoscale nickel zinc ferrites, the magnetic anisotropy can be fine tuned by the zinc content.

The elastic properties of a magnetic nanocomposite are field dependent (magnetoelasticity).[51] In a uniform magnetic field a magnetoelast experiences no force but the magnetic particles are aligned. In a magnetic gradient, the particles are attracted by the stronger field and move along with the polymer, causing a macroscopic deformation of the polymer body. Of particular interest is the preparation of composites in which the particles are pre-aligned to form polymers with anisotropic properties. They are obtained if the polymer is prepared in the presence of the magnetic nanoparticles in a uniform magnetic field. The resulting materials show anisotropic elasticity, thus in a magnetic field, the elastic modulus depends on the orientation of the polymer block with respect to the direction of the magnetic field vector. Such magnetoelastic composites are promising materials for the artificial design of sensor and actuator functions. An efficient method for the preparation of magnetic nanocomposites is precipitation of the magnetic phase inside a porous polymer gel (*in situ* generation) or by crosslinking the polymer in the presence of well defined nanoparticle dispersions.

A particular interesting application of magnetic nanocomposites is microwave assisted bonding-debonding developed by SusTech (Germany). In this case, the microwave absorption of spin wave excitations in nickel zinc ferrites in contact with a heat sensitive adhesive is used as a bond/disbond-on-command. However, a limiting disadvantage is the need to focus the microwave radiation on the substrates to be bonded, and thus the shape of the substrate determines the dimensions of the microwave radiator.

4. Summary

For the generation of transparent polymer nanocomposites an integrated understanding of particle formation, colloidal stability, interfacial chemistry and polymer properties are necessary. The creation of stable nanoparticle dispersions in hydrophobic monomers allows for the formation of bulk nanocomposites and thin films with high transparency. A new promising application is printing of inorganic–polymer nanocomposites for display techniques and low cost electronic devices. A wide range of applications has been demonstrated since magnetic, optical and electronic properties may be adjusted or totally changed with the integration of inorganic nanoparticles, setting already standards for promising novel developments of multifunctional nanocomposites.

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