Preparation, Characterisation and Properties of Nanocomposites Based on Epoxy Resins – An Overview

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Summary: An overview about the use of nanoparticles in epoxy resins is given. Deaggregated fumed silica, sol gel materials and other spheroidic nanoparticles improved the abrasion resistance and the mechanical properties of filled epoxides, and several properties can be improved by specific particles. Combustion properties, strength and permeation can be improved by organically modified layered silicates. The proper characterisation of the nanocomposites is still an art. TEM analysis of the cured materials and light scattering with 3D cross-correlation for the liquid samples were sufficient methods for the characterisation of filled epoxides.

Keywords: clay; epoxy resin; fumed silica; nanocomposite; particle size

Introduction

Nanofillers used in polymer science are prepared in different ways and have different shapes. Fumed oxides, especially fumed silica, are the most widely used nanofillers. They are characterised by a strongly aggregated and agglomerated structure with more or less round shaped primary particles. With the sol-gel process it is possible to prepare more perfect ball like particles with a minimum of interactions between the particles and very narrow particle size distributions. Furthermore the chemical composition of the particles can be varied in a wide range. Unfortunately the process is difficult to control in big quantities and it is difficult to transfer the particles from the liquid state into a polymer without aggregation.

An other important class of nanofillers used in epoxides are organically modified clay minerals which have a plate-like structure. Most published work[1] is carried out with bentonite as the clay mineral. The organic modification is carried out by the exchange of the sodium ions between the

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layers of alumosilicate. Alkyl ammonium salts with at least one long hydrocarbon chain are commonly used as organic ions. The distance between the single layers and the affinity between the particle surface and the polymer increases due to the modification. Both factors are important to produce nanocomposites instead of the conventional microcomposites obtained by using unmodified clay as a filler.

Another case are nanoporous fillers like zeolites or aerogels based on silicon dioxide. Nanoparticles with several different shapes, e.g. needles or cubes, are known but up to now they are at least of minor practical importance.

The properties of the prepared nanocomposites depend strongly on the particle size distribution and mainly on the interactions between the particles themselves and between the particles and the matrix polymer. Therefore, the processing of the materials is at least as important for the properties of the nanocomposites as their chemical composition.

Determination of Particle Size Distribution and Dispersion Stability

Microscopic and scattering techniques are the main methods to analyse the size and distribution of the particles in a matrix material. From these classes of methods transmission electron microscopy (TEM) and laser light scattering are the most important techniques.

For conventional light scattering the samples of interest need to be nearly transparent which in the majority of cases means strong dilution. This requires scrupulous cleanliness of the samples because the tiniest amounts of dust would lead to malfunctional results. 3D-cross-correlation, a new light scattering method, developed in our laboratories, does overcome these disadvantages: turbid samples are accessible in a wide range of concentration.[2, 3] Therefore, small amounts of dust does not influence the results because of the strong scattering signal of the sample. Furthermore, the new technique offers characterisation of a lot of samples in their original state which would be altered or destroyed by dilution. This means that the measured particle size is not influenced by the preparation of the sample. Due to the ability to measure at higher concentrations the method is additionally able to detect the stability of dispersions, which is not possible with conventional light scattering. Figure 1 shows the way of raw data evaluation. Figure 2 illustrates some causes for the change of particle distribution.

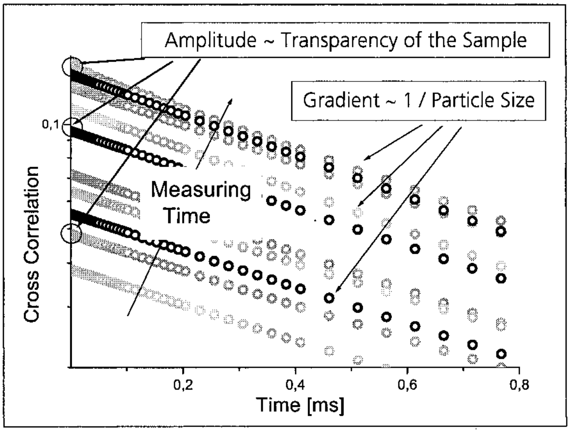

Figure 1. The signal of cross-correlation has two parameters which give information about particle size and stability: With increasing measuring time the sample becomes clearer due to sedimentation. This causes an increase in the amplitude. The gradient gives the particle size which in this case remains unaltered. This means that the sample contains monodisperse particles.

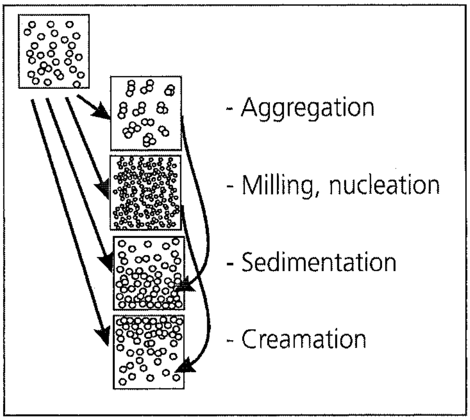

Figure 2. Processes taking place in dispersion leading to a non sufficient stability.

Measured particle size distributions are often a "function of the method used". This might be due to artefacts (e.g. caused by time dependent processes as sedimentation or aggregation as discussed above). Furthermore the different light scattering techniques are sensitive for different ranges of particle sizes. As a rule of thumb instruments based on Fraunhofer and Mie scattering have their strength in characterisation of micro and submicro particles whereas Correlation Spectroscopy is the method of choice for the characterisation of nano particles. It is essential to keep this in mind especially when samples contain particles with a broad or multimodal size distribution. Characterisation of such samples often need an analysation scheme which is a combination of both laser light scattering techniques.[4]

Fumed Oxides and Sol-Gel Particles

Fumed oxides, especially silicon dioxide, have already been used for a long time in polymers, namely in epoxides. It is mainly used to prepare thixotropic formulations and the effects are observed with filler contents in the lower percent range. The achieved changes of the rheological properties are caused by the interaction of the nanoparticles and this is the cause for the restricted maximum amounts of filler in the epoxides.[5] To apply fumed oxides in fields where high amounts of filler or not interacting particles are required, a deaggregation is necessary.

Coatings with high abrasion resistance are required e.g. for parquet, automotive clear coats or the improvement of the scratch resistance of parts made out of transparent polymers like polycarbonate. In recent times the abrasion resistance of coatings was improved by the modification with nanoparticles.[6] The nanoparticles were prepared by the so called sol-gel-process. As the particles are prepared in situ, the applicability is restricted to a limited number of polymers as base material and tailor made products are required for each application. Furthermore the complete filler is synthesised by the hydrolysis of silanes, which is a quite complicated process. To obtain similar results with fumed oxides, a deaggregation and high filler loadings are required. This is obtained by a combination of surface silylation of fumed silica and mechanical processing. In contrast to the sol-gel synthesis of nanoparticles it is not possible to dispense single particles in the organic matrix. TEM examinations (Figure 3) as well as light scattering show that very small agglomerates are formed. The size of theses agglomerates is typically below 100 nm, which is also the reason for the high transparency of the filled polymers. Even at loadings of 50 wt-% the materials are as transparent as the non filled polymers. As the interaction between the particles is reduced, due to the modification, the rheology of the resulting nanocomposites even at filler contents as high as 30 wt-% is only slightly influenced compared to the unfilled resins. Formulations containing the modified nanoparticles and curable resins are applicable as coatings with reduced abrasion. Compared to the non-filled materials the abrasion measured by the Taber abrasion test is reduced by a factor of 2 to 5 for coatings with a filler content of 25 wt-% (Figure 4). The abrasion of an epoxide based coating was reduced from 39 mg to 9 mg (size of the primary particles 12 nm) and 16 mg (size of the primary particles 40 nm) respectively. The much lower abrasion of the material with the 12 nm particles compared to that with the 40 nm particles shows that a real nano-effect is the cause for the improvement.[7]

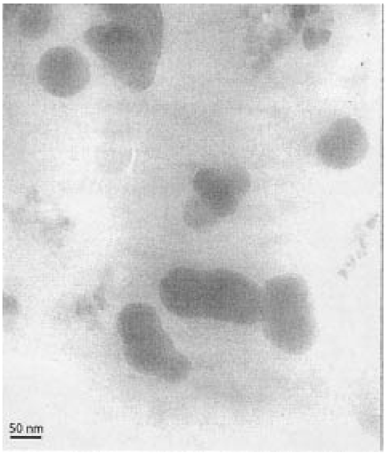

Figure 3. TEM image of a sample with 20 wt-% filler; size of primary particles 40 nm.

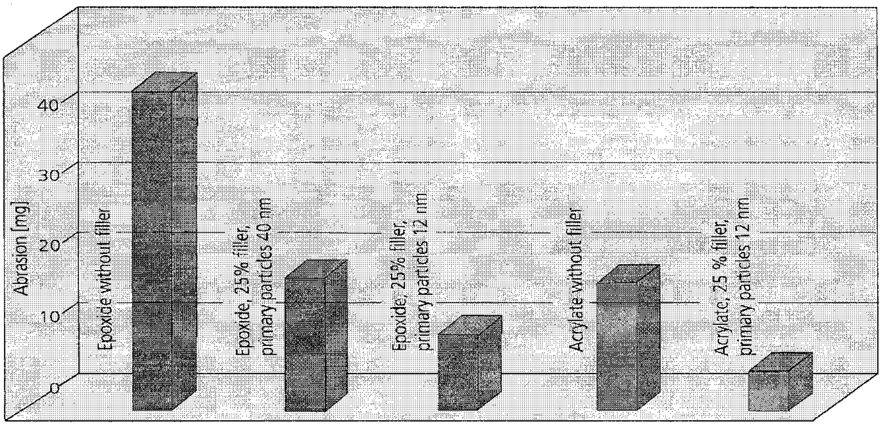

Figure 4. Abrasion properties of nanocomposites

By the incorporation of sol-gel based silica nanoparticles in an epoxy resin the expected increase of the modulus was observed. But interestingly the toughness increases, too. This is in contradiction with the experience made with microparticles in polymer matrices. The bending strength of a glass fibre reinforced epoxide could also be improved with the sol-gel particles. The increase is only observed for particle concentrations up to 10 wt-%, indicating that an interaction between the particles is not the cause for the effect but an interaction between the particle surface and the base polymer.[8] An improvement of the adhesion strength of epoxy resins was also observed for the deaggregated fumed oxides described above.

If additional effects are required beside the improvement of the mechanical properties, other nanoparticles than silicon dioxide are required. An example are indium tin oxide nanoparticles which are suitable to prepare transparent and electrically conductive nanocomposites. These nanocomposites are appropriate heat shielding coatings or can be used for antistatic purposes. Another example are superparamagnetic iron oxide particles. Nanocomposites containing such particles can be heated in a high frequency field, e.g. for curing of epoxides. Conventional electrically conductive adhesives contain silver flakes. Alternatively nanosized silver particles forming aggregates and agglomerates can be used. With this kind of filler the required amount to obtain electrical conductivity could be reduced from about 70 to 55 wt-% and the adhesive connections prepared with filled epoxides have a higher elongation at break and a higher strength if the silver nanopowder is used. At low concentration of silver nanoparticles the polymers, especially the epoxide based adhesives, have a bactericide or bacteriostatic surface depending on the amount of silver used and the polymer composition. The materials filled with micrometer sized silver particles does not show this effect.

Layered Silicates

Layered silicates, namely organically modified bentonites, are used to improve a number of properties of the respective matrix polymers.[9] An optimum improvement is obtained with loadings in the range of 5 wt-% or even lower amounts of bentonite. The most prominent examples are the improvement of the mechanical strength without lowering or even elevating the toughness. The reduction of the permeability of packaging materials, e.g. for the use as bottles or foils, is also an important field of activity. Both kind of effects - reduced permeability and improved mechanical properties - are also important for epoxy resins. Such epoxy resins are for example applicable as adhesives with improved strength and durability. The third important field for the application of organobentonites in polymers is the improvement of the combustion properties. This is shown in more detail for epoxy resins modified with 5 wt-% organobentonite.[10]

A cyloaliphatic and a bisphenol A diglycidylether based epoxy resin were filled with 5 wt-% organobentonite with different organic modifications. The combustion properties of the samples were tested with a horizontal burner test and the reduction of the combustion rate compared to the pure epoxy resin was determined. The results are shown in Figure 5. Although the absolute combustion rate of the cycloaliphatic epoxy resin is much higher than that of the aromatic system, the relative improvement is the same for both systems as long as the same organic modification of the bentonites is used. By a systematic variation of the organic modification of the bentonite it is possible to reduce the combustion rate significantly. The combustion rate of the cycloaliphatic epoxide could be reduced to 12 % of that of the non-filled polymer.

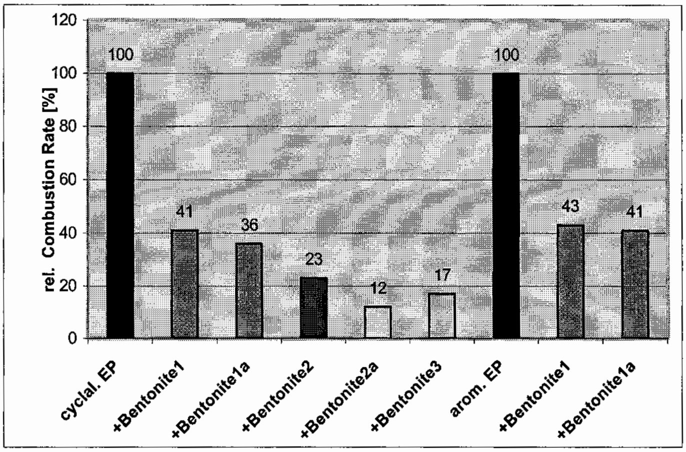

Figure 5. Relative combustion rate of epoxides filled with 5 wt-% organobentonite with different modification.

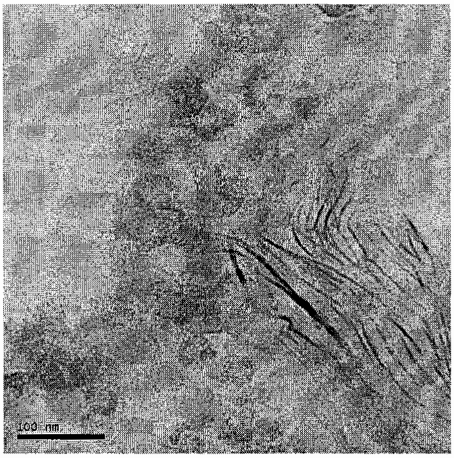

Figure 6. TEM image of the intersection between incinerated and intact area of a nanocomposite consisting of a cycloaliphatic epoxy resin and 5 wt.-% organobentonite (Image taken from the cover page of Macromol. Chem. Phys. **204** (2003), issue 18).

The proposed flame retardation mechanism of bentonite based nanocomposites is the formation of a char like barrier layer. The intersection between the incinerated and the intact area of the samples was examined by TEM (Figure 6). It can be seen that the particles are destroyed during combustion and that the formed barrier layer consists of particles.

Conclusions

A number of properties of epoxy resins can be adjusted by the addition of nanoparticles. To observe the desired effects a reproducible and homogeneous distribution of the particles is important. This is only possible if the particle surface has a high enough affinity to the epoxy resin. If the affinity between the particles is higher compared to the affinity between particles and polymer reaggregation takes place or no homogeneous distribution of the particles is observed. Interestingly the effects are often observed with already small amounts of nanoparticles, indicating the importance of the interaction between particle surface and polymer. Furthermore the use of nanoparticles seems to be a way to combine properties which are in combination not possible with conventional materials, e.g. increasing strength combined with increasing toughness.

Acknowledgements

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