The Sol-Gel Process for Nano-Technologies: New Nanocomposites with Interesting Optical and Mechanical Properties

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Abstract. Various nanocomposite systems have been synthesized by sol-gel routes. For this reason, prefabricated nanoparticles (SiO_2 sols or boehmite powder) have been dispersed after surface modification in sol-gel-derived organically modified or polymeric ligand matrices. In all cases, a significant effect on dispersibility by surface modification could be observed. After curing, the mechanical or optical properties depend strongly on the dispersion and surface modification. Using these results, composites to be used in chip coupling and as hard coatings on polycarbonate and CR 39 have been developed.

Keywords: nanocomposite, surface modification, hard coatings, transparent adhesives

1. Introduction

Sol-gel techniques for a long time have been used for the fabrication of glasses and ceramics [1–6]. The sols used for these investigations are made from alkoxides, and their stability was obtained by controlling the electric charges on the sol particles, which, in general, are in the range of several nanometers in diameter. The formation of these entities either in form of macromolecules or in form of spherical or non-spherical particles follow the established rules for nucleation and growth. For stabilization of the sols, the pH value is established in a range aside from the point of zero charge. The resulting surface charges reduce the particle-to-particle interaction to a level that no aggregation or agglomeration takes place. Thus, gelation can be prevented. Gelation takes place if the surface charges are decreased, for example, by pH change or if the particle-to-particle distance is reduced below the repulsing level [7], for example, by solvent evaporation, and the repulsion turns into attraction. If the particles grow too large, precipitation takes place. In sol-gel systems based on oxides, the particle-to-particle interaction is strong (oxide bridges accompanied by hydrogen bridges) so that, especially after drying, the agglomeration is irreversible.

As described elsewhere, the surface reactivity of the sol particles can be controlled by chemical surface modification. In this case, the concentration of uncontrollable chemically reactive groups can be reduced and substituted by a tailored reactivity, which now depends only on the reactivity of the modifiers (schematically shown in Fig. 1).

This leads to a type of stabilization which, in general, after a "gelation" provides redispersibility [8, 9]. The presence of any type of surface interacting agent during nucleation and growth, of course, interferes with the nucleation and growth process by itself. This has been described in detail elsewhere [9]. Using this approach, it is possible to fabricate sols with specific properties, not only depending on the properties of the core material but also depending on the properties of the surface modifier. This approach has been used meanwhile in many cases for the fabrication of various materials [9–14]. The change of surface properties of the small particles not only governs its chemical properties, but also influences the surrounding matrix when dispersed in liquid or solidified media. In this paper, some examples are investigated showing how sol-gel derived nanoparticles can interact with their environment and how this can be used for the development of the desired material properties.
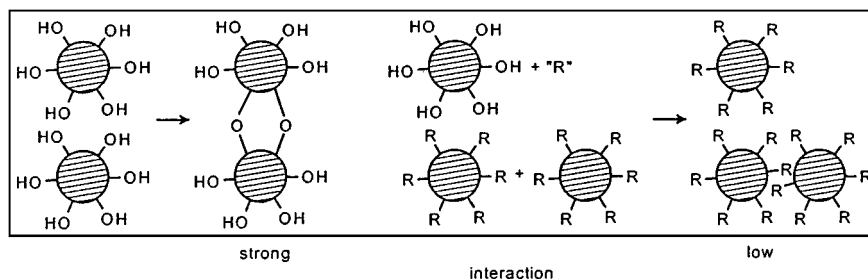
Figure 1.   Effect of surface modification of sol particles on particle-to-particle interaction. "R": chemical groupings linked to oxidic particles, e.g., β-diketones, ether amines, acids.

2.   Surface Modification

The basic principles of surface modification of nanoparticles have been shown elsewhere [9]. In Fig. 2, some selected examples are given [15, 16].

In general, if ceramic particle filled compounds with polymers are produced, the distribution of the particles in the matrix is obtained by mechanical forces, especially by the employment of high shear rates. With decreasing particle size, the effect of shear rate for dispersion is decreasing also, and with nanoparticles, the particle-to-particle interaction becomes the governing force. This is shown schematically in Fig. 3. In addition to this, the dispersion is more or less governed by the interfacial thermodynamics. As soon as the free energy of agglomeration is higher than the interfacial free energy, the system disperses by itself if the activation energy for given temperatures is low enough. This situation can be named as a thermodynamically stabilized dispersion and is schematically shown in Fig. 4.

One can postulate that in the case of (a), due to the strong interaction of the nanoparticles, this type of composite should show a higher viscosity, but should show a low viscosity in the case of (b), see Fig. 4. To demonstrate this phenomenon, composites have been synthesized [17] according to the following experimental route:

1 mole GPTS (glycidyloxypropyltrimethoxysilane) is hydrolyzed with 1.5 mole of water at 120°C for 24 h under reflux. Methanol is eliminated at 70°C at 20 mbar, to prepare a solvent free matrix. Colloidal silica sol (PIA-ST, Nissan Chemicals) with 20 wt% SiO_2 in isopropanol is mixed with 2 mg of tetrahexyl ammonium hydroxide (THAH) per g colloidal silica and stirred for 0.5 h. The solvent free GPTS condensate is mixed with different amounts of this colloidal silica solution and 1.5 wt% of a cationic photocuring catalyst (UVI 6974, UVI 6990) are added. Finally the solvent (isopropanol) is extracted at 50°C under 12 mbar.

These systems show a low viscosity since the crosslinking of the organic groupings has not yet taken place and can be used for photocuring of the composites. In Fig. 5 the viscosities of the surface-modified SiO_2 particle containing system is compared with the unmodified system. Even at low concentrations the unmodified system shows a rather high viscosity compared to the modified system. The effect is attributed to the modification of the SiO_2 surface by THAH, leading to a change in polarity so that no agglomeration takes place. HRTEM investigations showed that in contrast to the untreated SiO_2, the surface-modified composites show a perfect dispersion of the 7-nm particles.
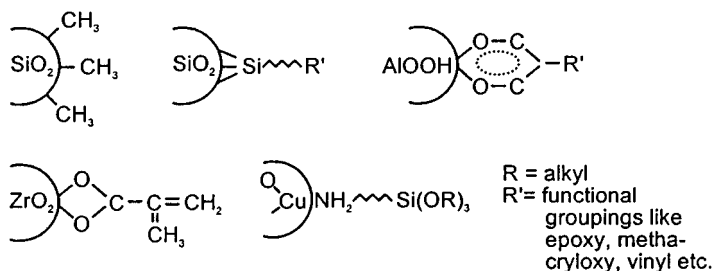

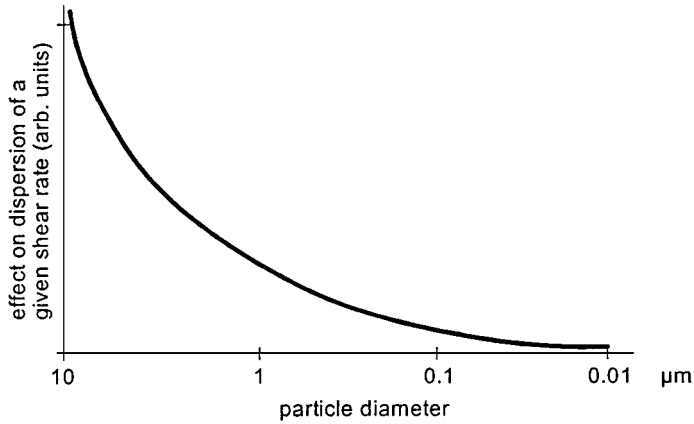*Figure 2.*   Some principles for surface modification of nanoparticles.

Figure 3.   Significance of shear rates for a uniform dispersion of nanoparticles in nanocomposites.
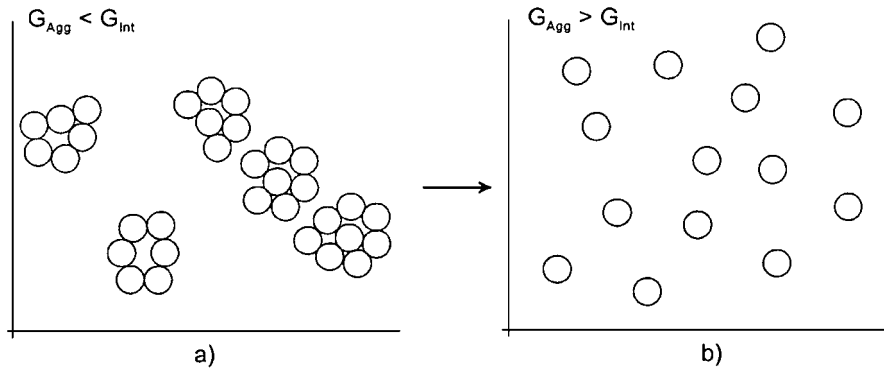

Figure 4.   Effect of free energy levels on the dispersion of small particles in a low viscosity matrix: G_{Agg} = free energy of agglomeration; G_{Int} = interfacial free energy.
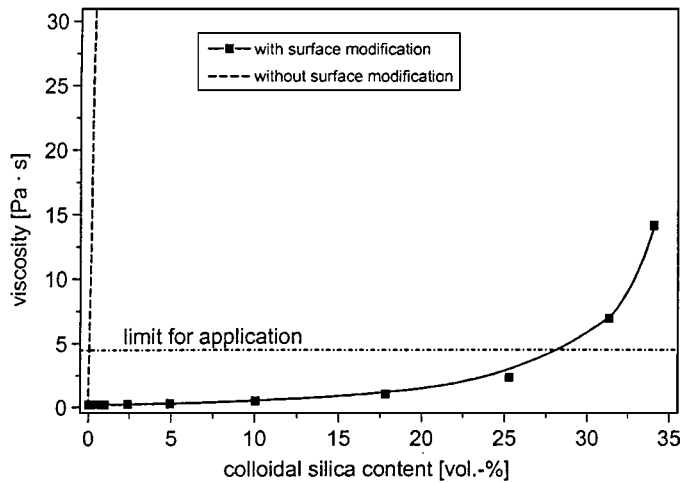

Figure 5.   Viscosity of a nanomer optical glue as a function of colloidal silica content (with and without surface modification by THAH), measured after storage at 25°C for 8 days.
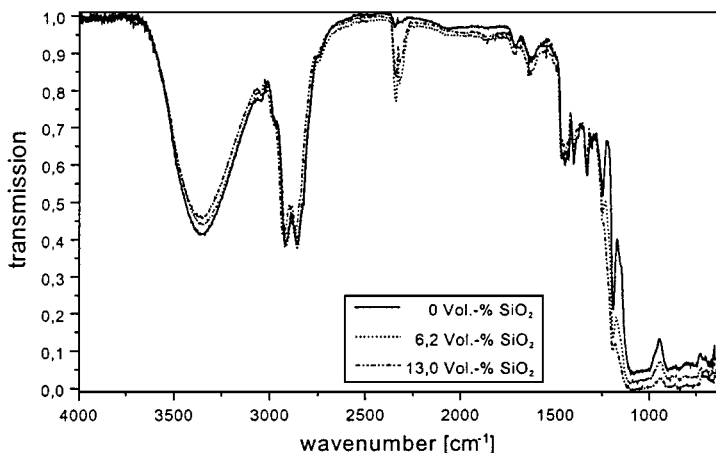
Figure 6.   IR (liquid, ATR) of condensates with different colloidal silica contents.

Due to the residual number of OH groups in the system (Fig. 6), the composite, which is almost independent of the SiO_2 content, shows a very good adhesion on glass surfaces, and in combination with the overall properties of this material, a technology has been developed for using these systems for fiber-to-chip coupling. Compared to conventional sealants mainly based on epoxides or methacrylates, the thermal expansion coefficient is rather low ($30 \cdot 10^{-6}$ K^{-1}), the temperature stability is up to 250°C, and the volume shrinkage during curing is only in the range of 3.6% [18]. One of the surprising findings is that using the surface modification approach, high concentrations of nano-scaled fillers (up to 30 vol%) can be introduced into the systems without affecting the viscosity in an undesired way and without affecting the transparency, due to the perfect distribution. The high transparency is required to use these systems as an optical sealant. The use of fumed silica, for example, leads to unacceptable viscosities even in the range of 1 or 2 wt% filler.

Another example is shown with methacryloxy containing systems using SiO_2 nanoparticles and modifying them with various silanes. The experimental procedure is published elsewhere [19]. SiO_2 sols with a diameter ranging from 1000 to 10 nm were treated with two different silanes: A: Acetoxypropyltrimethoxysilane (a silane with a non-reactive grouping) and M: Methacryloxypropyltrimethoxysilane (polymerizable double bond), and introduced into a matrix consisting of 50% of methylmethacrylate and 50% of hydroxyethylmethacrylate (molar ratios). Stirring the monomer mixture with the SiO_2 sols and subsequent thermal curing including polymerization of the reaction

mixture leads to transparent thermoplastic nanocomposites. Different measurements have been carried out after curing these systems. As shown in Fig. 7 the glass transition temperature T_g of the polymeric matrix obtained from differential scanning calorimetry (DSC) measurements can be varied over a wide range by introducing specially surface coated silica nanoparticles.

Whereas with 1000 nm, 250 nm and 100 nm particles no significant differences could be detected compared to the unmodified matrices; differences could be obtained for the systems with 10 nm particles, especially with those coated with modifier M. It clearly can be seen that only the modifier M, which is polymerized to the matrix shows an effect on T_g as a function of filler content and only in the nano-scale version. Covalent immobilization of matrix molecules on the surface of the M-coated 10 nm silica particles leads to a strong increase of the glass transition temperature of the polymeric matrix. This means that the interface plays an important role for the thermal properties of the composite as far as its volume fraction is large enough to play a sufficiently important role. Again one can see the influence of the particle size and the surface modifier. Modifier A cannot be polymerized and shows a far lower interface effect on the modulus than modifier M.

Information about the reinforcement behavior of nanoparticles with different surface modifications dispersed in the copolymer matrix given above can be obtained by examination of the storage modulus E' from dynamic mechanical thermal analysis (DMTA) in the rubbery plateau region above the glass transition temperature of the polymeric matrix. The dependence of
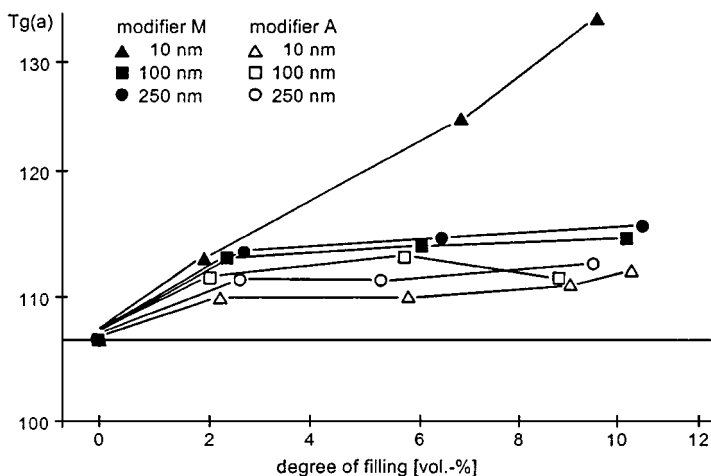
Figure 7. T_g values of SiO$_2$ particle filled composites (10–250 nm in diameter) with the modifiers A and M after polymerization obtained by DSC measurements.

the storage modulus on the filler surface modification and the filler content is shown in Fig. 8.

As shown in Fig. 8, the storage modulus can be increased by a factor 16 compared to the unfilled polymer matrix by introducing 10 vol% M-coated 10 nm SiO$_2$ particles.

Another interesting feature of surface modification is to use the surface modifier as an intermediate in order to make a sol compatible for processing purposes. In this case, the surface modifier should be easily removable so as not to disturb further processes. As shown elsewhere, nanoparticles have been used for reinforcing organic or hybrid matrices in order to increase their scratch resistance. A system based on boehmite and epoxysilanes has been developed to be used as scratch-resistant coatings for eye glass lenses [14, 20]. The detailed experimental process is described elsewhere

[21]. For the preparation of the system, commercially available boehmite powder from Condea (Chemical Company) with 10–17 nm particle size has been used. These powders are stabilized with acetic acid and can be easily redispersed in diluted HCl. However, the viscosity of this system increases with time. This is attributed to the fact that the acetic acid is slowly substituted by electric charges as indicated in Fig. 9.

The viscosity increase of this system is shown in Fig. 10.

Using this type of stabilized sols directly after redispersion, quick hydrolysis and condensation reactions can be started in a mixture of GPTS (γ-glycidyloxypropyltrimethoxysilane) and TEOS (tetra-ethoxysilane) with a molar ratio of 5 : 3 [21]. In this first synthesis step the amount of aqueous boehmite sol corresponds to the theoretical amount of water necessary
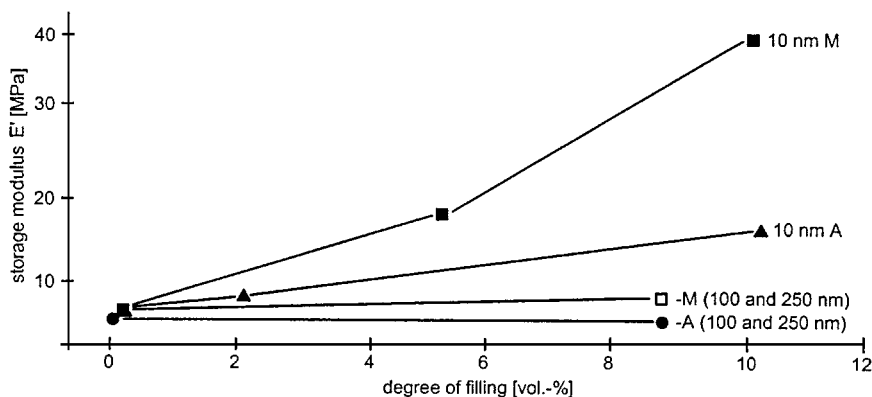

Figure 8.   Storage modulus of filled MMA/HEMA composites with various filler diameters (10, 100 and 250 nm). $T = 170°C$ (rubbery regime).

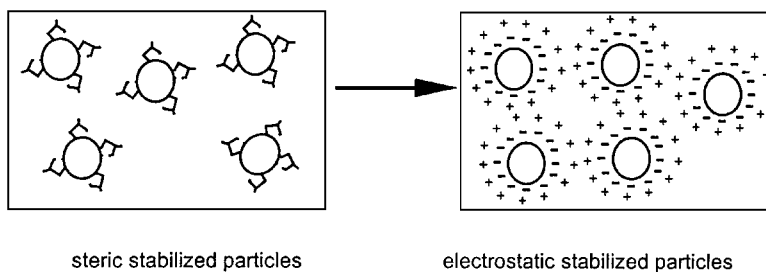steric stabilized particles   electrostatic stabilized particles

Figure 9.   Change of stabilization mechanism of nano-scaled boehmite particles in aqueous media.
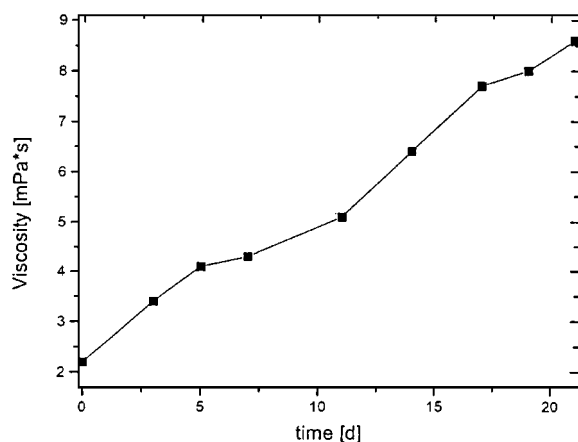

Figure 10.   Changes in viscosity of an aqueous boehmite sol in dependence on the sol age.

for the half-stoichiometric hydrolysis of the silanes. After 2 h reaction time the amount of boehmite can be easily increased up to 10 wt% by a final addition of boehmite sol into the prehyrolyzed silane mixture.

It is assumed that during the mixing of the boehmite with the silanes, the acetic acid is substituted completely by the reaction of silanes to the surface. This can be demonstrated by an aluminum NMR spectroscopy (Fig. 11).

The ^{27}Al-NMR spectrum of a system containing silanes and nano-scaled boehmite particles is shown in Fig. 11. By line shape analysis of the measured spectrum a broad peak at 0 ppm and a smaller peak at 60 ppm can be detected. The peak at 0 ppm can be attributed to aluminium atoms with coordination number VI in Al—O—Al formations of the nanocrystalline boehmite particles, whereas the peak at 60 ppm results from the formation of Al—O—Si bonds, wherein the aluminium atoms show the coordination number IV. This result clearly proves the reactivity of the AlOH groups on the

particle surface in regard to co-condensation reactions with the Si—OH or SiOR groups of the silanes.

If these liquids are used for coating purposes, for example, on polycarbonate, very high scratch resistances can be obtained, as shown in Fig. 12.

The superiority of the boehmite containing nanomer system in comparison to conventional siloxane coatings is demonstrated in taber abrasion and sand fall tests. After 1000 cycles of the taber abrasion test the nanomer coating shows very low haze values similar to those of glass. This result proves the extremely high scratch resistance of the coating material. Comparing the haze values after sand fall tests, it can be shown that the wear resistance of the nanomer system is even higher than the resistance of glass under this very abrasive stress (see Fig. 12).

Other investigations have been carried out to find out the role of the boehmite with respect to the formation of an organic network.

Using ^{13}C-Solid-NMR and NIR spectroscopy it was found that the characteristic signals of epoxide groups disappear during the thermal curing of GPTS-TEOS-boehmite systems (Figs. 13 and 14). In addition to this, new signals can be detected, attributed to the formation of polyethylene oxide chains. In comparison to the composite with boehmite no polymerization reactions of the expoxide groups in analogous GPTS-TEOS systems without boehmite can be detected. It can be supposed that the AlOH groups on the particle surface, which show a Lewis acidity, provoke the polymerization of the epoxides.

The experiments show clearly that an important catalytic activity of the boehmite particles can be detected. This catalytic activity contributes to the formation of an polyethyleneoxide network, which surrounds the boehmite particles (platelets and needles) and which is considered to be an important factor for the extremely high abrasion resistance of these coatings.
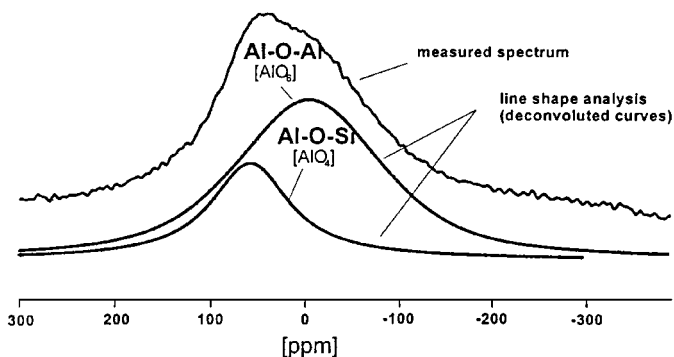
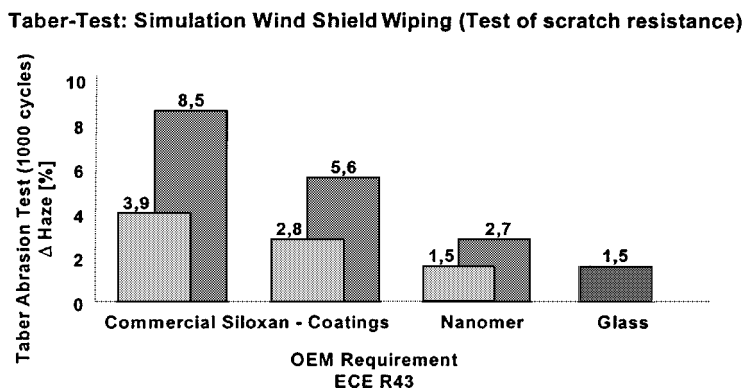*Figure 11.* ^{27}Al-NMR spectra of the GPTS-TEOS-boehmite sol.

Figure 12. Abrasion properties of the boehmite type of hard coatings [21]. The boehmite/epoxysilane coating is indicator as Nanomer (*nano*particle reinforced poly*mer*).
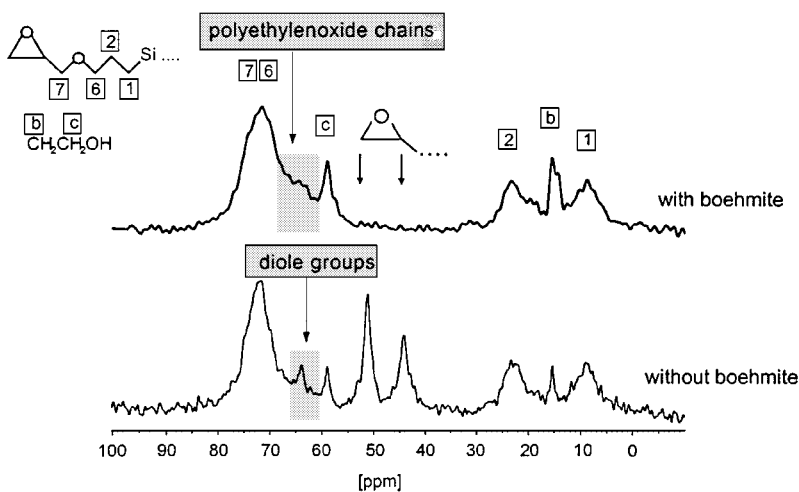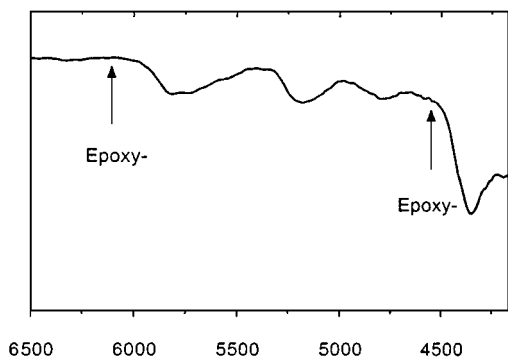

Figure 13.

Figure 14.   NIR spectrum of the boehmite containing nanomer after thermal curing.

3.   Conclusion

As a conclusion it can be stated that the surface chemistry of nano-scaled particles can be considered as a key parameter for processing and properties of the materials produced with nanoparticles. Especially, if organic polymeric networks are present, the surface modifier can influence the surrounding molecular structure in a way that thermal and mechanical properties can be influenced. In addition to this, surface modifiers as intermediates can be used for improvement of the processing properties, and after the removal of the modifiers, other effects of nanoparticles such as catalytic effects can be used, for example, to improve organic cross linking.

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