# Properties of Epoxy/SiO<sub>2</sub> - and Epoxy/ZrO<sub>2</sub> - Nanocomposites

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#### Abstract

The synthesis, structure and mechanical properties of inorganic organic nanocomposites are investigated: The systems consist of an aliphatic amine cured Bisphenol-F-based epoxy resin as organic matrix and SiO<sub>2</sub> and ZrO<sub>2</sub> nanoparticles as inorganic fillers. Silica and zirconia nanoparticles have been prepared in two different size ranges, one in the upper nano range (30-60 nm) and other in the lower nano range (5 – 15 nm). Zirconia particles were synthesized via a hydrothermal approach and silica particles were prepared via Stoeber-process. Both nanoparticles have been surface functionalized with novel diethyleneglycol (DEG) where the organic moiety is immobilized via phosphonic acid and trialkoxysilane anchor group to enhance the interfacial compatibility. The structure was characterized by MAS-NMR, SAXS and TEM to determine the influence of the capping agents on the dispersion of the particles within the resin. Thermomechanical properties were determined by TGA, DMA and hardness tests to quantify the influence of different amounts of nanoparticles. An improvement in hardness and elastic modulus has been reported while thermal degradation behaviour of the materials are almost unaffected by the incorporation of surface modified nanoparticles.

#### Motivation

 $SiO_2$ -*Stoeber*-particles were chosen as model systems because they are widespread in nanocomposite research and allow a good comparison to reported work<sup>1,2</sup>. The major motivation for the use of zirconia in nanocomposite research is the enhancement of hardness and other mechanical properties.

### Experimental

Silica nanoparticles were prepared using a literature known procedure<sup>3,4</sup>, zirconia nanoparticle powder was also prepared by literature known procedure.<sup>5,6</sup> The capping agents were attached to the nanoparticle surface by covalent bonds consisting of diethyleneglycol-monomethylether-chains, which enable excellent interaction with the epoxy resin. The formulae of the prepared capping agents are given below.

| capping agent formula | capping agent  | abbreviation |
|-----------------------|--|--------------|
|                       | Diethylene glycol<br>monomethyl ether-<br>phosphonic acid  | DEGPPA       |
|                       | Diethylene glycol<br>monomethyl ether-<br>trimethoxysilane | DEGTMS       |

Chart 1: Capping agents used for nanoparticle surface modification

Structural Characterization

TEM on different ultra microtome thin cuts of the nanocomposite samples are shown below (Figure 1). Zirconia particles (Figure 1a and 1c) are obviously better dispersed than silica nanoparticles (Figure 1b and 1d).



*Figure 1:* Representative TEM micrographs of ultra microtome-thin-cuts of epoxy resin nanocomposites containing 5 wt % inorganic fractions each sample: a) unmodified ZrO<sub>2</sub> small; b) modified SiO<sub>2</sub> big; c) DEGPPA@ZrO<sub>2</sub> small; d) DEGTMS@SiO<sub>2</sub> big.

The structural properties, in particular the aggregation behavior described by the so-called hard sphere volume fraction from SAXS measurements, is shown in Figure 2a for  $SiO_2$  and in Figure 2b for  $ZrO_2$  particles, respectively. Neither the surface-functionalization of  $SiO_2$  particles nor the amount of nanoparticles affects the agglomeration significantly. Only the size of the particles is decisive: The higher values for  $\eta$  of larger nanoparticles are explained by the higher possibility to interact with a neighbour particle as with the polymer chains.



*Figure 2:* Hard-sphere volume fraction  $\eta$  for a) unmodified and modified SiO<sub>2</sub> and b) ZrO<sub>2</sub> particles for different amount of particles embedded in epoxy-resin.

## **Thermomechanical Properties**

 $T_{\rm g}$ , measured by temperature modulated DSC, decreased with increasing amount of nanoparticles. The very probable explanations are entropic reasons: Whereas very small

nanoparticles can easily be incorporated into the polymer, larger nanoparticles lead to a polymer chain expansion and a loss of entropy, a so-called "stretching free energy cost"<sup>7</sup>.



*Figure 3:* Glass transition temperature  $T_g$  of modified epoxy nanocomposites with different filler content.

At room temperature there is an increase of the storage modulus for the  $SiO_2$  nanocomposites with increasing particle content. This effect is more pronounced in the case of the big particles. The glass transition is shifted to lower temperatures with increasing particle content; the effect is only slightly in the  $ZrO_2$  system. But, in both systems the decrease is stronger for the big particles as it was already shown by the DSC results. The plateau modulus increases with increasing particle loading whereas the increase is more pronounced if small particles are incorporated. There should be several reasons for that behaviour. First, the degree of chemical cross-linking of the matrix polymer is higher in the case of small particles. Second, due to the much higher number of small particles distributed in the matrix the amount of physical crosslinking points is higher for that kind of nanocomposites. Assuming a reduced degree of chemical cross-linking by adding nanoparticles, especially in the case of  $SiO_2$ , it can be seen how influential the effect of this obstacles is at temperatures above glass transition, where the difference in chain mobility between the matrix chains and the interphase chains is reduced.



*Figure 4:* DMA results of epoxy with different contents of modified (a) silica and (b) zirconia. (s.): small particles, (b.): big particles

The hardness increases significantly with increasing nanoparticle content as shown in Fig. 5.



*Figure 5:*a) The effect of modified  $SiO_2$  and b) of modified  $ZrO_2$  nanoparticles on the hardness of epoxy nanocomposites.

#### Conclusions

Improved mechanical properties were evidenced by significantly increased hardness in the case of the bigger nanoparticles as well as by an increased storage modulus from DMA analysis for the epoxy-silica system. The thermal stability of the epoxy composite was nearly unaffected, which suggests that even after surface functionalization no chemical reaction has taken place between epoxy and nanoparticles.

#### References

<sup>2</sup> Rittigstein, P.; Priestley, R. D.; Broadbelt, L. J.; Torkelson, J. M., *Model polymer nanocomposites provide an understanding of confinement effects in real nanocomposites*, Nat. Mater. 2007, 6, (4), 278-282

<sup>3</sup> Litschauer, M.; Neouze, M.-A., *Nanoparticles connected through an ionic liquid-like network*, J. Mater. Chem. 2008, 18, (6), 640-646

<sup>4</sup> Stoeber, W.; Fink, A.; Bohn, E., *Controlled growth of monodisperse silica spheres in micron size range*, J. Colloid Interface Sci. 1968, 26, (1), 62-69

<sup>5</sup> Murase, Y.; Kato, E., *Preparation of Zirconia Whiskers from Zirconium Hydroxide in Sulfuric Acid Solutions under Hydrothermal Conditions at 200°C*, J. Am. Ceram. Soc. 2001, 84, (11), 2705-2706

<sup>6</sup> Carriere, D.; Moreau, M.; Barboux, P.; Boilot, J.-P.; Spalla, O., *Modification of the Surface Properties of Porous Nanometric Zirconia Particles by Covalent Grafting*, Langmuir 2004, 20, (8), 3449-3455

<sup>7</sup> Mackay, M. E.; Tuteja, A.; Duxbury, P. M.; Hawker, C. J.; Van Horn, B.; Guan, Z.; Chen, G.; Krishnan, R. S., *A General Strategy for Nanoparticle Dispersion*, Science 2006, 311,(5768), 1740-1743

<sup>&</sup>lt;sup>1</sup> Holzinger, D.; Kickelbick, G., *Organically Functionalized Silica Nanoparticles*, Chem. Mater. 2003, 15, (26), 4944-4948