

Supplementary Materials

Epoxy resin nanocomposites: The influence of interface modification on the dispersion structure - A small-angle-X-ray-scattering study

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Synthesis of the coupling agents

The trimethoxysilane- and phosphonic acid coupling agent molecules with diethyleneglycol monomethylether moiety have been prepared as described in a previous paper.[1]

Synthesis of dimethyl 3-(oxiran-2-ylmethoxy)propylphosphonate

The preparation of 3-(2,3-dihydroxypropoxy) propylphosphonic acid dimethyl ester was carried out following a literature procedure [2]. The phosphonic acid ester was prepared by heating 35 mL dimethylphosphite (excess) in a 100 mL one neck round-bottom flask under argon-atmosphere to 120°C. Then, a mixture of 10 g allylglycidylether (87.6 mmol), 685 mg azo-bis-isobutyronitrile (4.17 mmol) and 15 mL dimethylphosphite was added dropwise under stirring. The reaction mixture was further stirred at 120°C for 2h. Then, the excess of dimethylphosphite was removed at 7 mbar / 90°C. The product was yielded as 12.76 g (56.90 mmol, 65%) slightly yellow colored oil.

Characterization:

¹H NMR (CDCl₃): δ(ppm) = 3.65 - 3.56 (m, 1 H, OCH₂-epoxy); 3.62 (s, 6 H, OCH₃); 3.40 - 3.30 (m, 1 H, OCH₂-epoxy); 3.27 - 3.16 (m, 2 H, OCH₂CH₂CH₂P); 2.98 (m, CH epoxide ring); 2.63 (m, 1 H, CH₂ epoxide ring); 2.45 (m, 1 H, CH₂ epoxide ring); 1.72 (m, 2 H, PCH₂); 1.69 (m, 2 H, PCH₂CH₂).

¹³C NMR (CDCl₃): δ(ppm) = 70.7 (OCH₂CH₂CH₂P); 70.4 (OCH₂-epoxy); 52.2 (OCH₃); 50.6 (CH epoxide); 43.9 (CH₂ epoxide); 22.6 (PCH₂); 19.8 (PCH₂CH₂).

³¹P NMR (CDCl₃): δ(ppm) = 46.5.

IR(ATR): ν(cm⁻¹) = 976, 1022 (P-O); 1244 (P=O); 1461 (CH₂ scissoring); 2953 (νCH₂).

Synthesis of 3-(2,3-dihydroxypropoxy) propylphosphonic acid

The hydrolysis step of previously prepared dimethyl 3-(oxiran-2-ylmethoxy)propyl phosphonate, to give the final diol moiety coupling agent by epoxy-ring opening and phosphonic acid ester hydrolysis, was carried out by refluxing 5 g (20.5 mmol) of the phosphonic acid ester with 40 mL HCl conc. for 16 h in a 100 mL one neck round bottom flask. The HCl was then removed in vacuum and the viscous, oily, crude product was recrystallized from chloroform to give 4.0 g (18.7 mmol, 91%) pure product.

Characterization:

¹H NMR (DMSO-d₆): δ(ppm) = 7.62 (s, 2 H, POH); 3.58 (m, 1 H, CH₂OH); 3.56 - 3.20 (m, 7 H, CH₂-O-CH₂-CHOHCH₂OH); 1.65 - 1.35 (m, 4 H, PCH₂CH₂).

^{13}C NMR (DMSO- d_6): $\delta(\text{ppm}) = 71.9$ ($\text{OCH}_2\text{CH}_2\text{CH}_2\text{P}$); 70.9 (OCH_2CHOH); 69.5 (OCH_2CHOH); 63.0 (CHOHCH_2OH); 25.5 (PCH_2); 23.4 (PCH_2CH_2).

^{31}P NMR (DMSO- d_6): $\delta(\text{ppm}) = 39.7$.

IR (ATR): $\nu(\text{cm}^{-1}) = 980, 1112$ (P-O); 1440 (CH_2 scissoring); 2871 (νCH_2).

Preparation of 1-allyl phosphonic acid

The phosphonic acid ester hydrolysis procedure was carried out via the silyl ester method as described in literature [2]. Under argon-atmosphere 2.5 g (14.4 mmol) allylphosphonic acid diethylester were stirred in 10 mL abs. dichloromethane in a 50 mL one neck round bottom flask. Then, 3 mL (23 mmol) trimethylbromosilane were added and the mixture was stirred for 2 h at room temperature. The volatile components were then removed at 1 mbar and 4 mL methanol (99 mmol) mixed with 2 mL water (111 mmol) were added dropwise to the reaction vessel. After stirring for 16 h, again the volatile components were removed at 1 mbar to give 1.7 g (13.8 mmol, 96%) viscous, slightly yellow colored oil.

Characterization:

^1H NMR (CDCl_3): $\delta(\text{ppm}) = 10.84$ (s, 2 H, POH); 5.77 (m, 1 H, CH); 5.23 (m, 2 H, $\text{CH}_2=\text{CH}$); 2.62 (dd, $\text{J}_{\text{HH}} = 7.3$ Hz, $\text{J}_{\text{HP}} = 22$ Hz, 2 H, P- CH_2).

^{13}C NMR (CDCl_3): $\delta(\text{ppm}) = 126.7$ (CH); 120.5 ($\text{CH}_2=\text{CH}$); 62.1 (PCH_2).

^{31}P NMR (CDCl_3): $\delta(\text{ppm}) = 42.9$.

IR (ATR): $\nu(\text{cm}^{-1}) = 918, 983$ (P-O); 1134 (P=O); $1396, 1421$ (CH); 1640 (alkene); 2908 (νCH_2); $2961, 2984$ (CH).

Preparation of oxiran-2-ylmethylphosphonic acid

In a 50 mL one neck round bottom flask 1 g of allylphosphonic acid (6.8 mmol) were dissolved in abs. methylene chloride and 10.2 mmol MCPBA (meta chloro perbenzoic acid) in 15 mL methylene chloride, previously dried over MgSO_4 , were added. The mixture was stirred at room temperature for 20 h. During this time, the product precipitated as white solid, which was then washed with chloroform and dried in vacuum to give 640 mg (68%) white solid.

Characterization:

^1H NMR (DMSO- d_6): $\delta(\text{ppm}) = 6.56$ (s, 2 H, POH); $2.62 - 2.63$ (m, 3 H, epoxide ring); $2.05 - 1.55$ (m, 2H, PCH_2).

^{13}C NMR (DMSO- d_6): $\delta(\text{ppm}) = 53.2$ (CH epoxide); 40.1 (CH_2 epoxide); 36.1 (P- CH_2).

^{31}P NMR (DMSO- d_6): $\delta(\text{ppm}) = 33.8$.

IR (ATR): $\nu(\text{cm}^{-1}) = 925, 979$ (P-O); 1156 (P=O); 2907 (CH); 3083 (epoxide ring).

Elemental analysis: calculated C 26.1, H 5.1, P 22.4; found C 26.9, H 6.0, P 22.7.

Nanoparticle synthesis

Silica nanoparticles. Silica nanoparticles with diameters in the lower nanorange were prepared according to a literature known procedure [3, 4]. 100 mL methanol were mixed with 5.25 mL water and 100 μL of 33 wt% aqueous ammonia solution in a 250 mL round bottom flask. Afterwards 10.5 mL tetraethyl orthosilicate was added dropwise under stirring and the reaction mixture was further stirred at room temperature for three days. At this stage, the particles were either isolated to yield non surface modified nanopowders or the sols were further used in a following in situ-surface modification step. For the isolation of the unmodified particle powder, the solvent was evaporated and the remaining product was washed three times with n-hexane, separated by centrifugation at 6000 rpm and dried over P_2O_5 at 5 mbar to give 2.17 g white powder. Diameter from dynamic light scattering (DLS, in methanol, from mass weighted distribution): 9 ± 2 nm.

Silica nanoparticles with diameters in the upper nanorange were prepared by mixing 50 mL of ethanol with 2 mL water and 3.3 g of 33 wt% aqueous ammonia solutions in a 250 mL round bottom flask [4, 5]. A solution of 50 mL ethanol mixed with 4 mL tetra ethyl orthosilicate was then added slowly under stirring. The reaction mixture was then stirred at room temperature for 16 h. At this

stage, the particles were either isolated to yield non surface modified nanopowders or the sols were further used in a following in-situ-surface modification step. For the isolation of the unmodified particle powder, the solvent was evaporated and the remaining product was washed three times with n-hexane, separated by centrifugation at 6000 rpm and dried over P₂O₅ at 5 mbar resulting in 0.86 g white powder. Diameter from DLS (methanol, from mass weighted distribution): 72 ±10 nm.

Zirconia nanoparticles. Zirconia nanoparticles were synthesized according to a previously published method [6, 7].

Powder-XRD: 100% crystalline ZrO₂, baddeleyite-phase (monoclinic).

Diameter from DLS (methanol, peak from mass weighted distribution): 22 ±7 nm

TEM: single crystals with aspect ratio of ~2.

SBET: 140 m²/g.

Surface modification of nanoparticles

Silica nanoparticles were modified applying an *in situ* approach, directly from the prepared sols. The lower particle diameter sol was used as prepared. From the larger diameter nanoparticle sol, the NH₃ was removed under oil-pump-vacuum and the amount of evaporated solvent was re-added to the mixture, then, 0.1 mL conc. aqueous ammonia solution were added. Furthermore, the coupling agent resulting in a total 7.5 mM solution, was added and the mixture was stirred for 2 days. The particle powders were then isolated by concentrating the dispersion via solvent removal and centrifugation at 6000 rpm. Afterwards they were washed three times with 5 mL of ethanol (centrifugation at 6000 rpm) and dried over P₂O₅ at 5 mbar for 24 h.

The diol-end group modified silica particles were produced indirectly by a heterogeneous hydrolysis reaction of the epoxide end groups of as-prepared glycidoxypropyl modified silica nanoparticles. Therefore, according to a literature known procedure [8], 500 mg nanoparticle powder was dispersed in 3 mL dioxane via treatment in an ultrasonic bath for 15 min. Then 3 mL 0.2M H₂SO₄ in dioxane plus 0.2 mL H₂O were added to give a 0.1 M H₂SO₄ concentration in the reaction mixture. After stirring for 30 min, the particles were separated and washed for 3 times with ethanol via centrifugation at 6000 rpm. The powders were then dried over P₂O₅ in membrane pump vacuum.

Surface-functionalization of the zirconia nanoparticles was carried out applying a post-modification approach following a literature-known approach for titania nanoparticles.[9] 5 mL of an aqueous nanoparticle dispersion (10 g/L) were prepared by dispersing the zirconia nanoparticles in an ultrasonic bath for 30 min. Subsequently HCl conc. was added dropwise to the dispersion to adjust the pH to 2. The phosphonic acid for surface-functionalization, e.g. 18.7 mg dodecylphosphonic acid for a 7.5 mM total coupling agent concentration, was dissolved in 5 mL methanol, added to the particle dispersion, and stirred for 2 days. The target particles were isolated via centrifugation at 6000 rpm, washed three times with ethanol (centrifugation at 6000 rpm), and dried over P₂O₅ at 5 mbar for 24h.

Preparation of epoxy resin nanocomposites

Amine cured bisphenol-F-based epoxy resin was prepared by a literature procedure [1, 10].

In detail, 2.0 g (7.03 mmol) bisphenol-F-diglycidylether were heated to 70°C and the particle powder was added, followed by vigorous magnetic stirring at 750 rpm for 2 h. Afterwards 0.2 g (1.94 mmol) diethylenetetramine were added to the reaction mixture, which was immediately cast on a silicone grease coated stainless steel plate and cured at 120°C for 16 h resulting in sample plates of 1.2 - 1.5 mm thickness and 3 - 5 cm diameter.

UV/VIS spectra

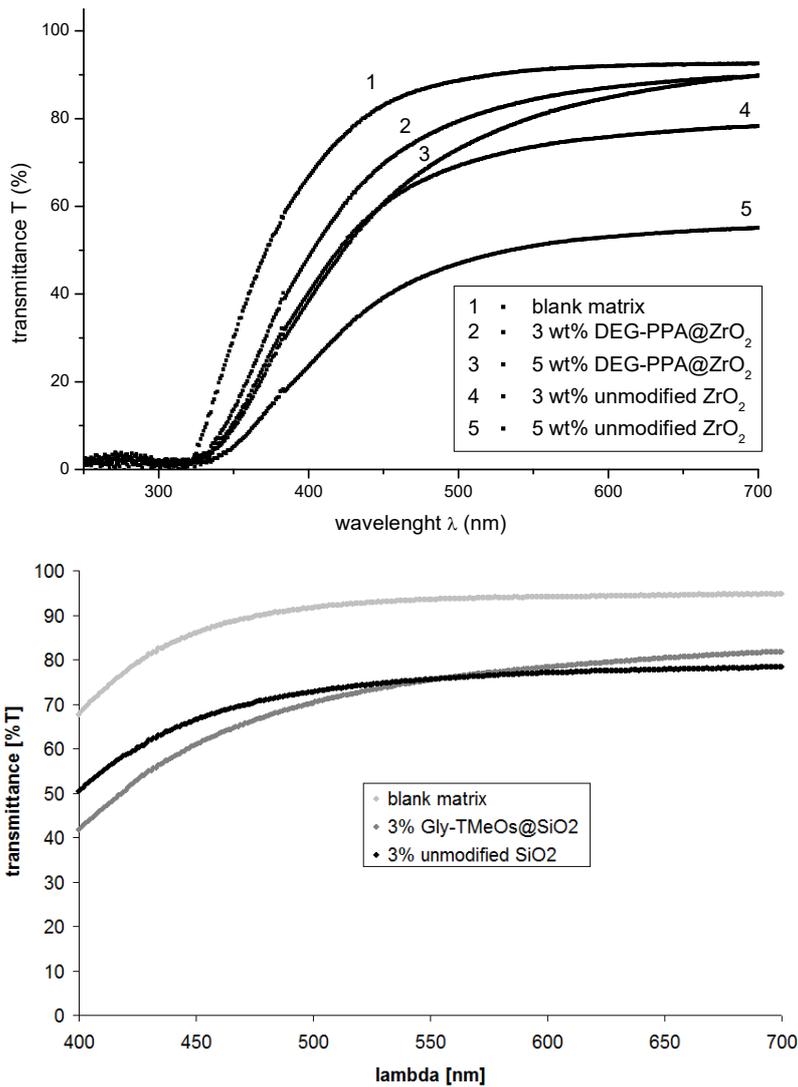


Figure S1. UV/VIS Spectra of 1.4 mm thick epoxy resin plates containing unmodified ZrO₂, DEGPPA@ZrO₂ (upper graph). 5% unmodified larger SiO₂ and 5% Gly-TMeOs@larger SiO₂ nanoparticles (lower graph, zoomed into visible range for better view).

(Thermo)mechanical Tests:

Vickers Hardness tester was used to evaluate hardness with a square-based pyramid diamond indenter with an angle of 136° between the opposite faces at the vertex. The tester was pressed into the surface of the test piece using a small force of 0.98 N; the test force was maintained for 20 s to 30 s. After the force has been removed, the diagonal lengths of the indentation were measured and the arithmetic mean, d , were calculated. The Vickers hardness number, HV , is given by:

$$HV = \text{Constant} \times \text{Test force} / \text{Surface area of indentation} = 0,102 \cdot 2F \frac{\left(\sin \frac{136^\circ}{2}\right)}{d^2} \quad (1)$$

which was then converted to a SI unit (GPa) by multiplication with the numerical factor 0.009807. In order to get precise values, 10 indents were performed on one sample and the average value was then calculated.

Table S1. Vickers Hardness values (GPa) for epoxy resin nanocomposites with diol-end group organically modified silica and zirconia nanoparticles.

Particle type / hardness (GPa)	small SiO ₂	large SiO ₂	ZrO ₂
0 wt%	0.1630	0.1630	0.1630
3 wt%	0.1833	0.1840	0.1650
5 wt%	0.1890	0.1755	0.1756
10 wt%	0.1941	0.1960	0.1863

Table S2. Glass transition temperatures of the epoxy resin nanocomposites from DSC for epoxy resin nanocomposites with diol-end group organically modified silica and zirconia nanoparticles.

Particle type / T_g [°C]	small SiO ₂	large SiO ₂	small ZrO ₂
0 wt%	113	113	113
3 wt%	101	96	107
5 wt%	95	87	104
10 wt%	87	87	104

Table S3. Thermal decomposition onset temperatures of the epoxy resin nanocomposites from TGA for epoxy resin nanocomposites with diol-end group organically modified silica and zirconia nanoparticles.

Particle type / Onset TGA [°C]	small SiO ₂	large SiO ₂	ZrO ₂
0 wt%	354	354	354
3 wt%	359	364	362
5 wt%	363	363	352
10 wt%	362	362	349

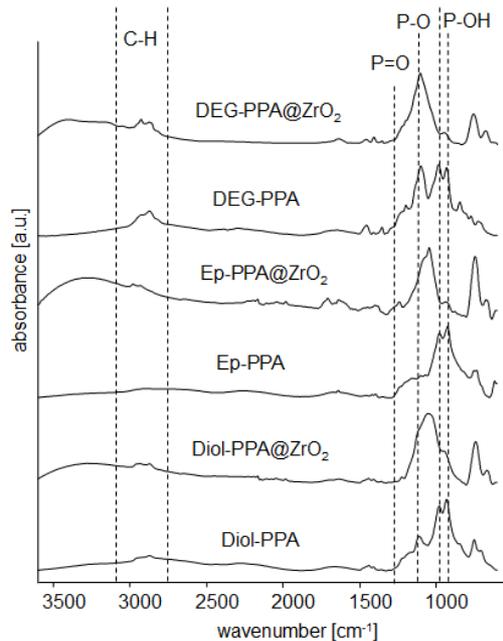


Figure S2. FT-IR spectra of phosphonic acids in pure state and after grafting onto ZrO₂.

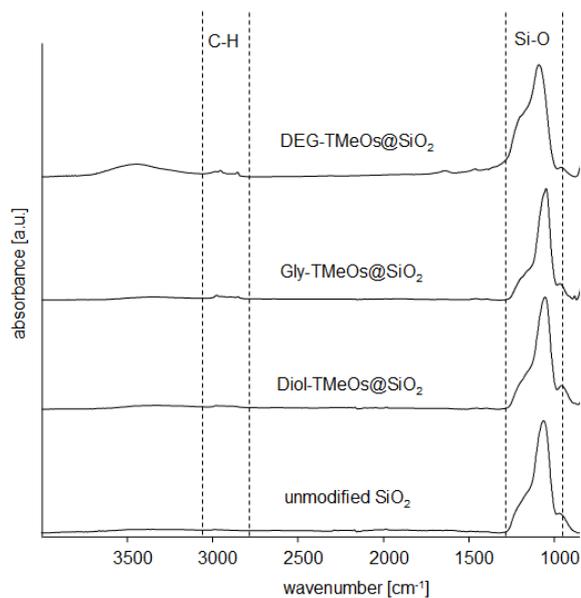


Figure S3. FT-IR spectra of neat and organically surface modified 7.8 nm diameter SiO₂ nanoparticles.

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