Supplementary Information – Further Experimental Details:

Hydroxyapatite Nanoparticles as Novel Low-Refractive Index Additives for the Long-Term UV-Photoprotection of Transparent Composite Materials

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Photocatalytic Activity Tests

The photo-catalytic activity of the nanoparticles was assessed and compared by measuring the degradation-rate of an organic substrate molecule under UV-irradiation. To avoid interpretation problems arising from direct photolysis of the substrate, which is sometimes the case with commonly applied tests using coloured dye molecules as an indicator for the determination of photocatalytic activity [*], a colourless organic molecule (perchloroethylene, PER, C_2Cl_4) was used as a test substrate. Instead of the typically used dyes (e.g. methylene blue), which absorb light in the region of the semiconductor bandgap, the organic substance PER (absorbance < 280 nm) was not directly irradiated in our tests. Depending on the type of catalyst and the duration of the UV-light exposure, different values of hydrochloric acid were built according to the following idealized stoichiometry:

$$C_2Cl_4 + O_2 + 6\,H_2O \xrightarrow{h*\upsilon,Kat.} 2\,CO_2 + 4\,HCl \quad (1)$$

Therefore, the consumed Volume of 0.01M NaOH, for the titration of the HCl was recorded. To figure out the activity of the different nanoparticles it was necessary to draw a graph (see Fig. S1 below) with $-\ln\left(\frac{c_{0,PER} - c_{PER}}{c_{0,PER}}\right)$ versus the duration of the UV- light exposure.

From the slope of the plots, the half-life-times of the substrates were calculated, which is a direct measure for evaluating destructive processes under irradiation. Furthermore, the amount of degraded PER is an indication of the photocatalic activity of the additive materials:

Material	$\tau_{1/2}$ ***[min]***	***Degraded PER [%]***
Degussa P-25	248	21.05
Hydroxyapatite	$7*10^{15}$	0.19
DLS 210	1250	2.88

This test figured out, that there is no undesired photocatalytic effect caused by hydroxyapatite.

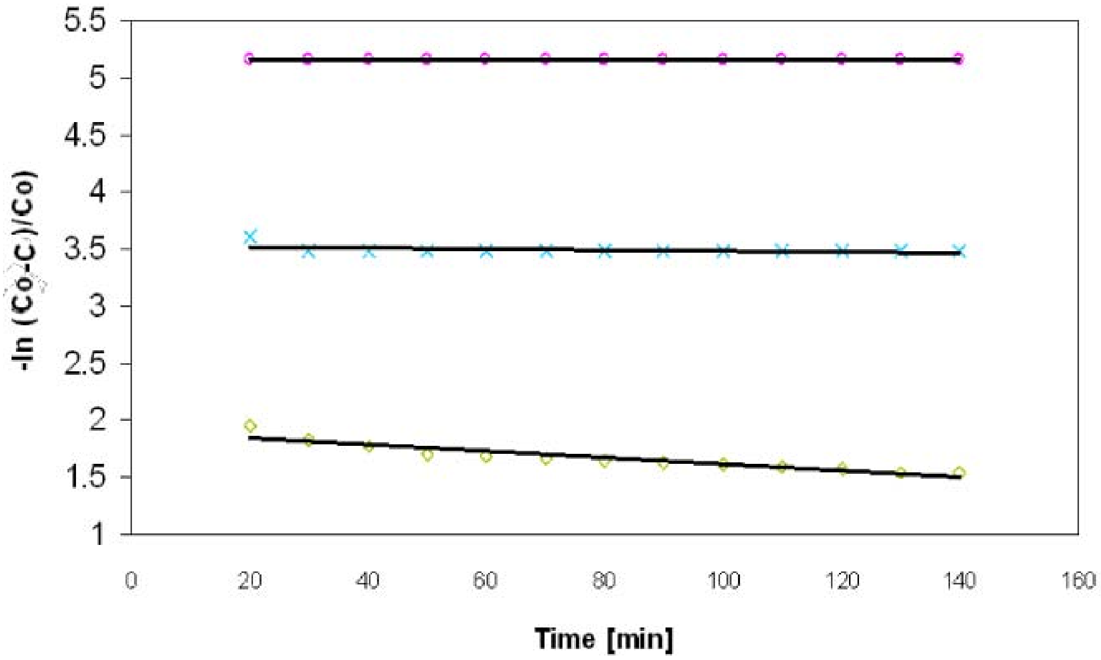
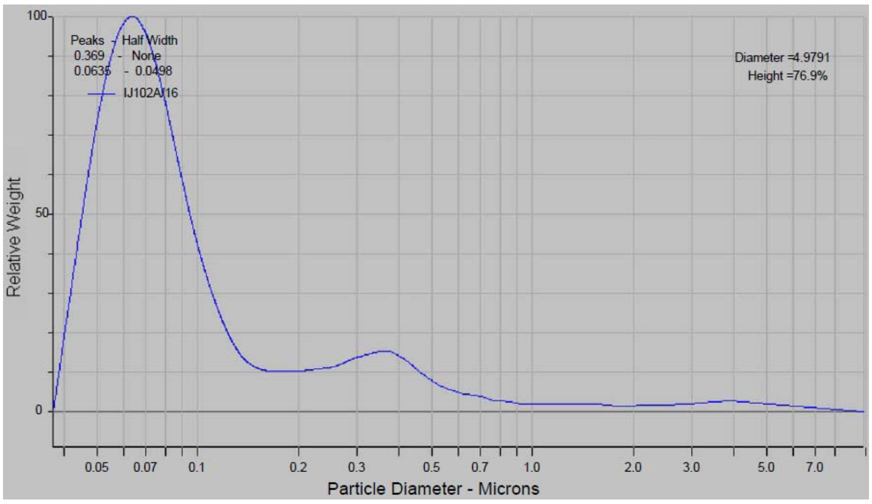


Figure S1. Photocatalytic degradation of perchlorethylene (PER) in the presence of inorganic UV-absorbers. The plot at the bottom shows Degussa P-25 (reference-substance, 25% Rutile, 75% Anatase). The graph above shows DLS 210-particles (a Rutile-based UV-light-stabilizer from DuPont) and the graph on the top the Hydroxyapatite-nanoparticles.

[*] X. Yan, T. Ohno, K. Nishijima, R. Abe, B. Ohtani, "Is methylene blue an appropriate substrate for a photocatalytic activity test? A study with visible-light responsive titania", *Chemical Physics Letters*, **2006,** *429*, 606.

Particle Distribution Curve

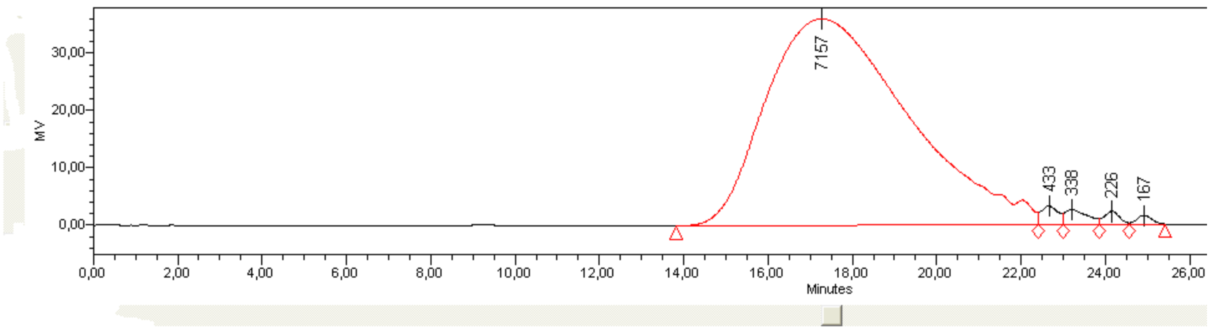
The size distribution profile of the hydroxyapatite particles obtained from high-speed disk-centrifuge measurements is shown in the plot below (Peaks at 64nm and 369 nm):



Molecular Weight and T_G of the Polyester Samples

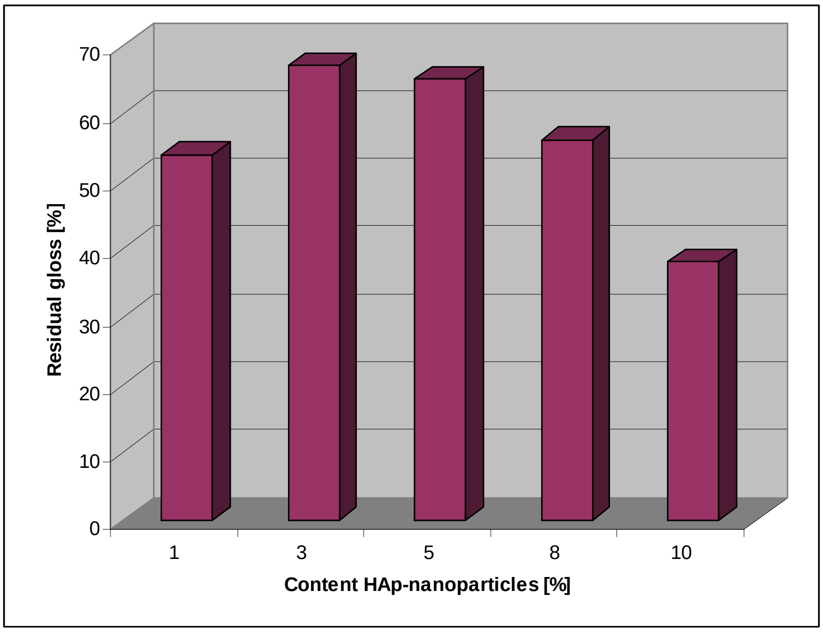
For a hydroxyapatite content of 3-5%, the T_G-values of the materialls were measured as 68 ºC (see table below). For materials with the optimum content of 3% of additives, a molecular weight distribution plot (GPC-measurement indicating a MW of 7160 Daltons for polyester with 3% nanoparticle content) is also shown below:

Particle	*Particle content [%]*	*SZ*	*OHZ*	*η_{200} [Pa.s]*	*T_G [°C]*
Reference	-	33.7	2.3	3.23	66.0
Hydroxyapatite	3	33.4	2.6	3.17	67.7
Hydroxyapatite	5	28.7	3.2	3.79	67.7



	Name	Retention Time (min)	Area (µV*sec)	Mn (Daltons)	Mw (Daltons)	MP (Daltons)	Mv (Daltons)	Mz (Daltons)	Mz+1 (Daltons)	Polydispersity
1	Peak3	17,274	8435232	3369	7061	7157		11506	15637	2,095715
2		22,663	90111			433				
3	Peak2	23,210	92993	315	319	338		322	325	1,010091
4		24,156	57115			226				
5		24,912	37436			167				

Effect of nanoparticle content on photostability:



Optimum range of protection (maximum residual gloss after exposure) in the range of 3-5% of hydroxyapatite added.