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Ceramic Nanoparticles Coated with Polymers Based on Acrylic Derivatives

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Summary: Ceramic nanoparticles are synthesized by a microwave plasma process and coated with a polymer layer generated *in situ* by photopolymerization. Acrylic and methacrylic monomers are the most suitable precursors for polymer coatings. In the case of coatings derived from MMA, only a small quantity of the polymeric material is soluble in organic solvents. GPC analysis of the dissolved part reveals the predominance of oligomers. According to FT-IR spectra, a substantial number of MMA-ester groups is transformed into carboxylates, providing strong adhesion of the polymer to the ceramic core insoluble in THF. Composites with PTFE-analog coating exhibiting enhanced thermal and chemical stability are obtained from the condensation of perfluorinated alkanes on metal oxide nanoparticles.

Introduction

Compounds with particle sizes in the nanometer region are of general scientific and technical interest because of their unique properties such as the superparamagnetism which is observed in nanosized γ-Fe_2O_3.[1, 2] These types of compounds may represent different structural characteristics compared to their macroscopic analogues. An efficient route to prepare ceramic nanoparticles is the microwave plasma process. In this process volatile halides or organometallic precursors (figure 1) are vaporized in an argon stream and introduced into an argon/20 vol% oxygen microwave plasma (plasma zone) where oxide nanoparticles are formed.[3, 4]

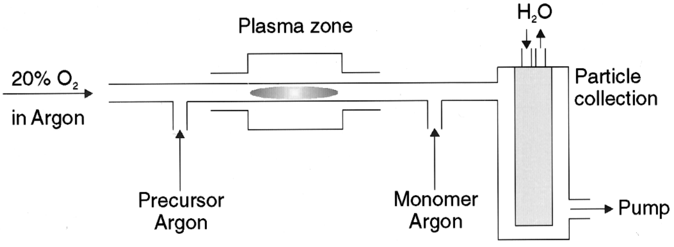

Figure 1. Schematic experimental set-up of the microwave plasma process for the synthesis of nanocomposites.

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In order to prevent the loss of their special size-dependent properties by mutual interaction, the nanoparticles are coated with either a second ceramic layer or with a polymer layer.[4-7] For polymer coating, the vaporized monomer is introduced into the apparatus after the plasma zone. It condenses on the surface of the ceramic nanoparticle and generates the polymer layer under the influence of the UV radiation from the microwave plasma by *in situ* radical polymerization embedding it in a polymer matrix.

Experimental

The microwave plasma syntheses were performed using a frequency of 2.45 GHz. Chemicals were purchased from Sigma-Aldrich, Strem Chemicals, and Lancaster Synthesis (fluorinated compounds) and used without further purification.

GPC analysis was carried out in THF on a ThermoQuest gel permeation chromatograph fitted with MZ-gel SD*plus* columns (MZ-Analysentechnik) and a RI detector. Calibration was made with PMMA standards (Polymer Standards Service).

FT-IR spectra were recorded with a Bruker IFS 28 fourier transform infrared spectrometer using the KBr method.

Results and Discussion

Methacrylic Polymers

Among the photopolymerizable monomers applicable for polymer coating, methyl methacrylate (MMA) and methacrylic acid (MAA) proved to be the most versatile precursors.[5] Pressing of the finely powdered oxide/polymer composites obtained from these systems results in pellets that are usually transparent. The polymer weight fraction of the composites determined by gravimetric combustion analysis normally ranges from 5 to 40 wt% of organic material and is adjustable by variation of the precursor ratio. The characterization of the polymeric material was performed using GPC and FT-IR analysis.

Between 5 and 10 wt% of the MMA-derived polymer (MMAdp) of the nanocomposites are soluble in organic solvents. GPC analysis of these solutions in THF revealed the predominance of low molecular weight oligomers. Depending on the ceramic core, minor differences are observed in the molecular weight distribution. This distribution is independent of the weight fraction of the organic material. Variations of the reaction conditions, such as addition rate of the monomer or gas flow and pressure do not cause significant changes. However, since most of the polymer is not accessible by this method due to its insolubility, these results are hardly representative for the composite.

According to FT-IR spectra, the insolubility of the major amount of organic material is due to a partial loss of the methyl ester functionality. From the IR spectra of different MMAdp coated ceramic nanoparticles it is evident that, in all cases, there are several absorption bands in the typical spectral region of C=O vibrations (figure 2). The spectral features of individual composites exhibit different characteristics with regard to peak position and intensity.

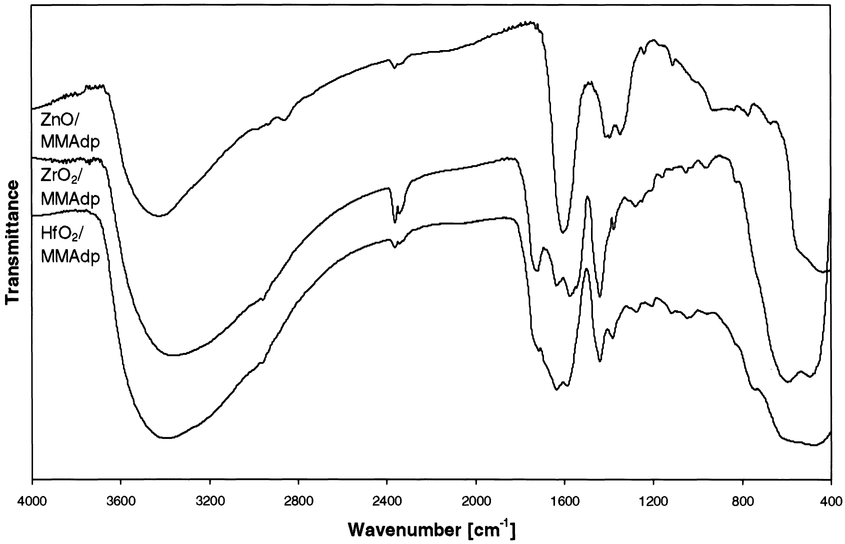

Figure 2. FT-IR Spectra (KBr) of ceramic nanoparticles (ZnO, ZrO_2, and HfO_2) coated with MMAdp.

For conventional bulk PMMA, the C=O vibration of the ester carbonyl group is reported to appear at a wavenumber of 1739 cm^{-1}.[8] In the spectra depicted in figure 2, absorption signals are not observed at this exact position, however, for most composites there are signals near 1715 cm^{-1} (table 1). We suggest their assignment to the ester C=O vibration. The intensity of these peaks is in general low compared to those below 1700 cm^{-1}.

Table 1. FT-IR data of different MMAdp coated ceramic nanoparticles.

	Polymer weight fraction [wt%]	ν(C=O) [cm^{-1}]	ν(COO$^-$) [cm^{-1}]	
Fe_2O_3/MMAdp	8.7		1568	1418
TiO_2•Fe_2O_3/MMAdp	22.5	1711		1422
HfO_2/MMAdp	24.9	1715	1587	1439
Al_2O_3/MMAdp	32.2	1700	1570	1443
ZrO_2/MMAdp	26.6	1718	1574	1437
ZnO/Fe_2O_3/MMAdp	21.0		1558	1418
ZnO/MMAdp	10.2		1605	1412

The comparison of IR spectra of Al_2O_3 nanoparticles coated with MMAdp and the corresponding MAA-derived polymer (MAAdp, figure 3) exhibits almost identical spectral characteristics for both systems. In both spectra, bands or shoulders are observed at 1628, 1587 and 1444 cm^{-1}. The Al_2O_3/MMAdp spectrum contains an additional band at 1700 cm^{-1} due to the ester carbonyl vibration.

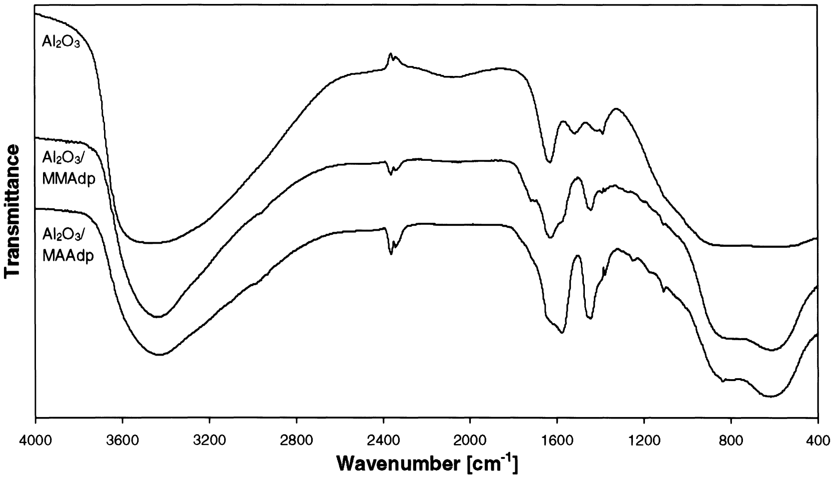

Figure 3. FT-IR Spectra (KBr) of uncoated Al_2O_3 nanoparticles and of Al_2O_3 nanoparticles with polymer coating derived from MAA and MMA.

Considering the chemical composition of these compounds and the relative intensities in the spectra, the signals at 1587 and 1444 cm^{-1} may be assigned to asymmetric and symmetric stretching vibrations of COO$^-$. Obviously, in the course of the formation of ceramic/MMAdp nanocomposites, a substantial number of ester groups is transformed into the corresponding carboxylates. Similar observations were reported for the surface adsorption of PMMA on conventional Al_2O_3.[8, 9] The vibrations near 1630 cm^{-1} can be assigned to molecular water adsorbed on the surface of the ceramic particle. However, in the case of Al_2O_3/MAAdp we consider its origination in the C=O vibration of the carboxylic acid. Signals between 400 and 1000 cm^{-1} are due to metal oxide vibrations of the ceramic core. The increased solubility of metal oxide/MMAdp composites in water compared to organic solvents confirms these results. The main portion of the polymeric material remains insoluble, probably because of chemisorption of the carboxylate anions to the ceramic core.

Fluoropolymers

A restriction in the use of acrylates and methacrylates for the coating of metal oxide nanoparticles is the limited thermal and chemical stability of these compounds. The problems of decomposition occurring from the high temperature in the reaction vessel or the catalytic activity of the ceramic core can be avoided by the use of fluorinated polymers. Additionally, composites with fluoropolymers are of interest because of their very hydrophobic character. In this context, nanocomposites with perfluoroalkyl acrylates and methacrylates were prepared.

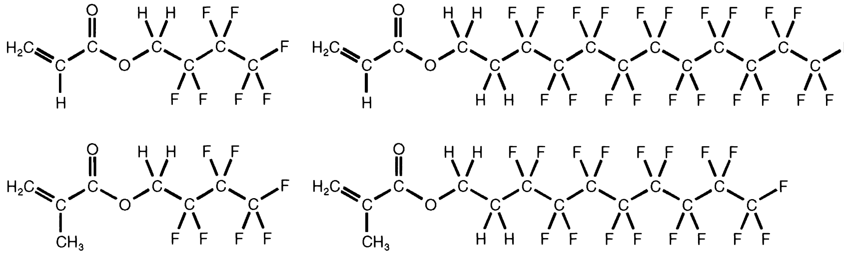

Figure 4. Perfluoroalkyl acrylate and methacrylate monomers used for the coating of ceramic nanoparticles.

Fluorinated methacrylate derivatives are thermally more stable than the corresponding acrylates. Upon prolonged exposition to temperatures above 280 °C these composites show signs of decomposition. In general, perfluoro derivatives are more resistant to high temperatures than MMAdp or MAAdp composites.

Further improved properties should be obtained with nanocomposites coated with polytetrafluoroethylene (PTFE). Since, under the conditions of the microwave plasma process, the plasma synthesis of PTFE or the photopolymerization of TFE is not possible, composites were prepared with commercially available "TFE-oligomers". In this case, perfluorinated alkanes (perfluorododecane, perfluoroeicosane) were vaporized and condensed on the nanoparticle. As expected, this procedure yielded very hydrophobic composites with increased temperature and chemical stability.

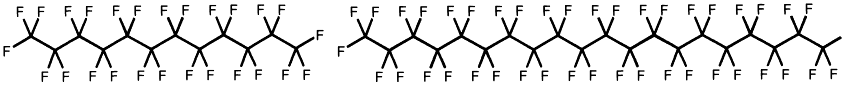

Figure 5. "TFE-oligomers" used for the coating of ceramic nanoparticles.

Conclusion

In the course of the formation of metal oxide/MMAdp nanocomposites *via* microwave plasma synthesis, ester groups of the polymer coating are to some extent transformed into the corresponding carboxylates. The resulting anionic polymer is strongly attached to the ceramic core and insoluble in common solvents. Because of this ionic interaction with metal oxides, methacrylic polymers are particularly well suited as coating for ceramic nanoparticles. Improved thermal and chemical stability of the coating is obtained by employing perfluoroalkyl acrylic or methacrylic monomers. Coating the particles with perfluorinated alkanes leads to very hydrophobic composites with excellent thermal and chemical stability.

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