

Metal Fluoride Based Transparent PMMA and Fluoropolymer-Composites with High Transparency and Exceptional Mechanical Stability

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Abstract

The synthesis and modification of magnesium fluoride nanoparticles used in the preparation of transparent nanocomposites based on fluoropolymers and PMMA accessing materials with superior properties was investigated. Nanoscopic magnesium fluoride obtained via the fluorolytic sol gel synthesis was surface modified by adsorption and reaction with different acids and introduced into the copolymer THV221 GZ and PMMA. Stress tests were recorded to show improved thermal and mechanical properties. By incorporation of nanoscopic magnesium fluoride as filler mechanical strength improvement was achieved while the transparency of the fluoropolymer was maintained.

1. Introduction

Fluoropolymers are interesting materials for high-technology applications and life sciences as well. Since the discovery of fluoropolymers in the 1930 ties and their first industrial application in the 1940ties they found applications in many different areas because of their exceptional properties. Thus, high chemical resistance and repulsion of polar liquids like water are of interest in many application fields. Treating textiles or cookware by fluoropolymers makes them water proof and resistant against pollutants. Laboratory equipment made of fluoropolymers is inert against highly corrosive liquids or gases like hydrogen fluoride [1]. Besides all these advantages there is a crucial problem in the use of most fluoropolymers: mechanical as well as thermal stability are often poor.

Thermal and mechanical properties of non-fluorine polymers like polycarbonate or poly(methyl methacrylate) are often improved by the incorporation of metal oxide nanoparticles [2, 3, 4]. Different synthesis routes for nanoparticles are described in the literature [5, 6, 7]. Homogeneous distribution of nanoparticles inside a polymer is a crucial point, since heterogeneous dispersion leads to deviating properties throughout the bulk material. To overcome this problem it is often recommended to modify surfaces, e.g. by organic materials [8]. Unfortunately, most

of the synthesis routes are not suitable to prepare modified nanoparticles, especially vapour deposition techniques usually fail due to harsh processing parameters. Thus, sol-gel based processes usually overcome all these drawbacks, and hence, are favoured [9].

Although mechanical and thermal properties of fluoropolymers are often not exciting, they exhibit a great advantage compared to non-fluorine polymers. Their refractive index is very low (1.5 and often lower) and high UV- and IR-transmission rates are observed [10]. If metal oxide fillers are used for their modification, which is state of the art, their optical properties are worsened

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by increasing refractive index or reducing transmission abilities [11].

Metal fluoride nanoparticles are excellent alternatives to overcome all these problems. They exhibit a significantly lower refractive index in comparison with their corresponding metal oxides and can be prepared similarly easy via the fluorolytic sol-gel process developed by our group some years ago [12, 13]. Different nanoscopic metal fluorides have already been synthesized under mild conditions via this route [14-16]. Modification of metal fluoride nanoparticles can be easily realized by adding acids [17]. We report here a new approach to overcome the problems in mechanical and thermal instability of fluoropolymers under preservation of optical properties by employing modified metal fluoride nanoparticles (MF-NPs).

2. Experimental

Sols were synthesized under dry conditions using Schlenk techniques. Solvents were dried by refluxing methanol with magnesium turnings for at least six hours followed by leaving it over night over molecular sieve (3 Å).

Alcoholic HF solutions were prepared asap by dissolving anhydrous HF (provided by Solvay Fluor Hannover) in methanol yielded 10 molar HF solutions. The exact HF concentration was determined by titration with 0.1 M NaOH solution. For the preparation of magnesium fluoride sols, 1.95 g of magnesium turnings (ChemPur, 99.5%) were dissolved in dry methanol. After complete dissolution a methanolic solution of hydrogen fluoride (16.04 M; 8.5 ml for 1.7 eq or 9.5 ml for 1.9 eq respectively) was added to the solution of magnesium methoxide under stirring. Ten minutes later the corresponding amount of acid (0.3 eq or 0.1 eq) was added. The solvent of the sols was evaporated by spray drying (80 °C nozzle temperature), which yielded a fine fluent xerogel.

The xerogel was mixed with the fluoropolymer granular (THV 221, provided by Dyneon, 3M® Company; PMMA 7H, provided by Evonik Industries). The following extrusion was carried out at a Thermo Scientific Haake PolyLab System (consisting of Haake Rheocord 6300 and Haake Rheomex 5501). Sheets were produced by a hydraulic squeezer.

XRD patterns were measured using a Seifert XRD 3003 TT (Cu K_{α1,2}-Rays with λ=0.154 nm; 40 kV, 40 mA). Nuclear magnetic resonance was determined with a Bruker Avance II 300 (7T), MAS-NMR with a Bruker

Avance 400 (9.4 T). SAXS measurements were performed using an Anton Paar SAXSess mc² (Cu K_{α1,2}-Rays with λ=0.154 nm; 40 kV, 50 mA). IR-spectra were obtained from Digilab Varian FTS 3000 Excalibur Series using MKII Golden Gate with crystal KRS-5. Thermal analysis was measured using a STA 409 C/CD (Netzsch Gerätebau GmbH) coupled with quadrupol mass spectrometry tool Balzers QMG 422 with a platinum sample crucible against a Pt/PtRh10 thermal element. Transmission measurements were carried out at a F10-RT from Filmetrics Company with wavelength range from 380-1050 nm.

3. Results and Discussion

3.1 Nanoparticles Synthesis

The reaction of magnesium with dried methanol to magnesium methoxide followed by fluorolysis to hydrogen fluoride in dried methanol via the fluorolytic sol-gel route yields magnesium fluoride nanoparticles [18].



Agglomeration can be suppressed by addition of different acids, thus transparent MgF₂-sols can be obtained [19]. Characteristic chemical shifts of ¹⁹F-NMR spectra of nanoscopic MgF₂-particles appear at -198 ppm, whereas the particles size derived from X-ray diffraction pattern according the Scherrer equation [20] ranges from 8 to 10 nm. The addition of acids as modifier does not significantly affect the crystallinity of the nanoparticles [21].

The MgF₂-nanoparticles synthesized this way correspond to the XRD and NMR data published before (see Figure 1). The particle size of nanoparticles can be usually investigated by dynamic light scattering (DLS), but in case of the MgF₂-sols investigated here, DLS measurements gave no reliable results due to high polydispersity of the sample. Therefore SAXS measurements were performed, which indicate low particle size (see Figure S1). As mentioned above, the ¹⁹F-NMR spectrum shows a peak with a shift at -198 ppm corresponding to magnesium octahedrally coordinated by fluoride ions. However, there is a shoulder at lower field indicating minor parts of Mg-species that are partially coordinated by oxygen from OR-groups (indicating the presence of MgF_{6-x}(OR)_x moities), too [22].

Figure 1: ^{19}F -NMR-Spectrum of the Sol (a) and XRD-Pattern (b) of the Corresponding Magnesium Fluoride Xerogel

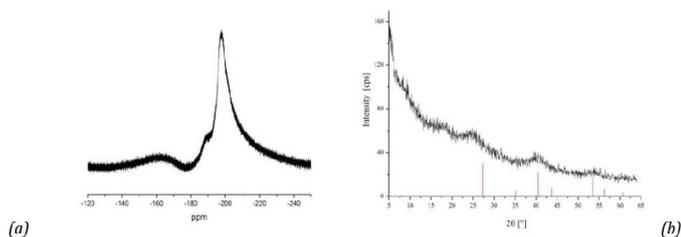


Figure S1: SAXS Measurements of Modified Magnesium Fluoride Nanoparticles

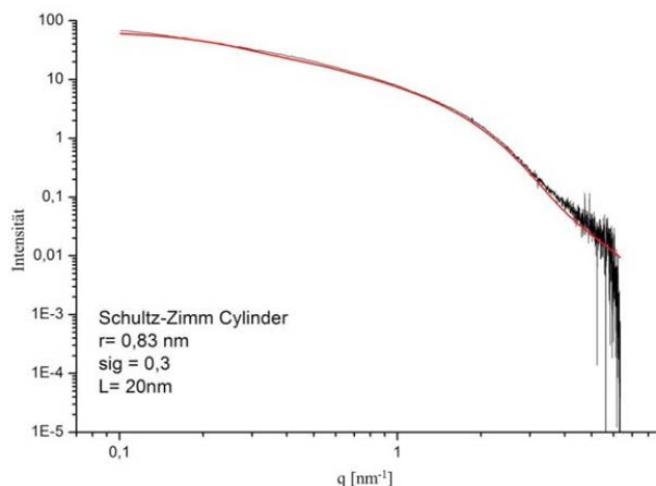


Figure 2: ^{19}F -MAS-NMR-Spectrum (a) and ATR-IR-Spectrum (b) of Unmodified Magnesium Fluoride Xerogel

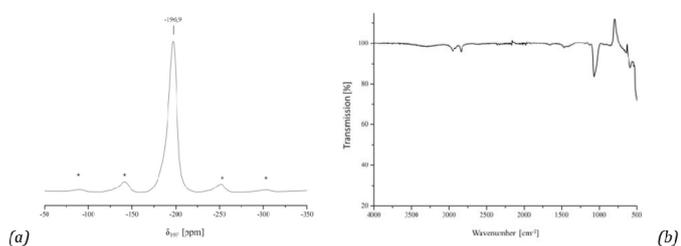
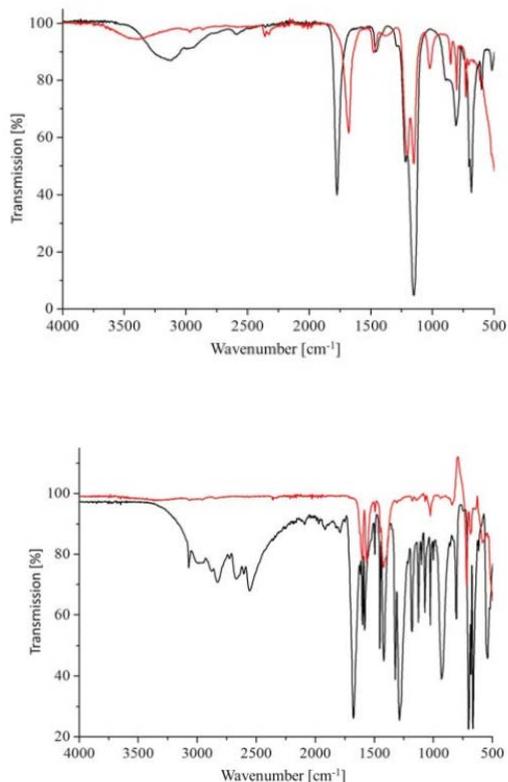


Figure 3: (a) ATR-IR-Spectra of Trifluoroacetic Acid (black) and TFA-Modified Magnesium Fluoride (red).

(b) ATR-IR-Spectra of Benzoic Acid (black) Versus BzOH-Modified Magnesium Fluoride (black)



MgF_2 -nanoparticles were modified by trifluoroacetic acid (TFA) for better miscibility in fluoropolymers and benzoic acid (BzOH) for their use in poly methyl methacrylate. Thus, the nanoparticle surfaces were made compatible to the properties of the corresponding polymer. The respective ATR-IR-spectra are shown in figure 3. For better comparison, the respective NMR and IR-data for unmodified MgF_2 -xerogels are given in figure 2. Comparing pure TFA (black) and modified nanoparticles (red) in (3a) a significant shift of the vas vibration of the carbonyl group (1830 cm^{-1} to 1682 cm^{-1}) indicates covalent binding of the trifluoroacetate group onto MgF_2 -NPs. Besides, there is also a shift in the carbonyl deformation (1194 cm^{-1} to 1203 cm^{-1}) and valence vibrations (1122 cm^{-1} to 1152 cm^{-1}). In the ATR-IR-spectrum of pure benzoic acid versus modified MgF_2 -nanoparticles (3b) the total extinction of the OH valence vibrations indicates covalent binding of benzoic acid. In addition the valence vibrations of the carbons in the phenyl group shift considerably. All these observations clearly evidence the reaction of trifluoroacetic acid and benzoic acid with the MgF_2 -nanoparticles resulting in a surface modification.

The spray-dried MgF_2 -xerogel was investigated by thermal analysis in order to gain information about the thermal stability of the modified MgF_2 -nanoparticles. In extrusion process thermal stability is crucial, since the polymer is melted and mixed directly inside the

extruder with the MgF_2 -nanoparticles. The observed mass loss in figure 4 shows, that the solvent methanol and water, which represents about 11% of the whole mass are removed until about 180 °C, while the covalently bound acid persists at the MgF_2 -particles up to 230 °C. This clearly indicates that these modified particles should be thermally stable enough to be used for extrusion procedure with fluoropolymers. That means, the organic solvent can be removed but the surface bound modifying organic acid needed for compatibility of the MgF_2 -nanoparticles to the polymer melt, remains intact at the particle's surface. Similar results were obtained for benzoic acid modified MgF_2 -nanoparticles, where thermal stability is even higher and the material can be used until about 350 °C without any decomposition (see Figure S2, supporting information).

Figure 4: Thermal Analysis of Magnesium Fluoride Nanoparticles Modified by TFA

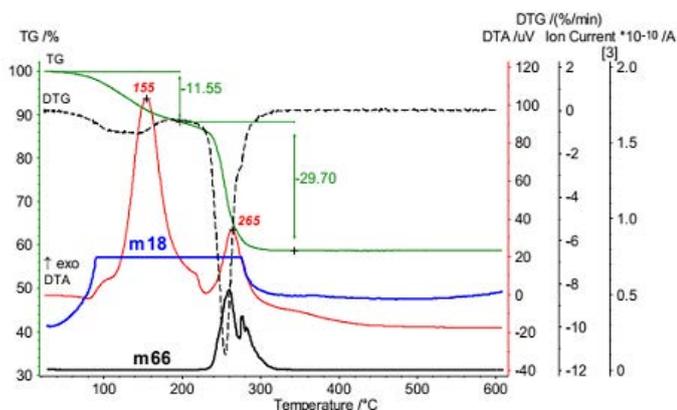
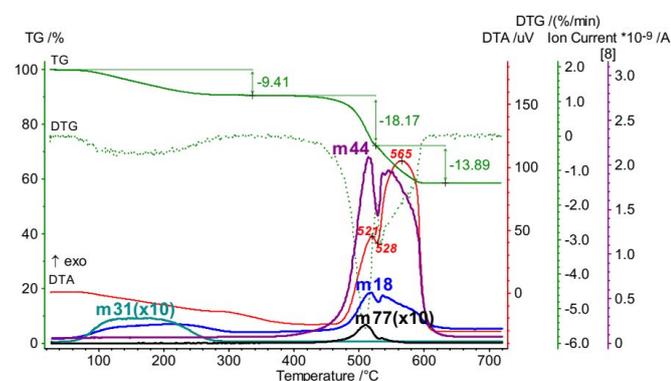


Figure S2: Thermal Analysis of Benzoic Acid Modified Magnesium Fluoride Nanoparticles



3.2 Composite Materials Preparation

The trifluoroacetic acid modified nanoparticles were mixed with the granulate THV221 GZ provided by Dyneon, 3M® Company, which is a co-polymer consisting of polytetrafluoroethylene, polyhexafluoropropylene and polyvinylidene fluoride. Consequently, the surface of this polymer is composed of fluoride and a smaller amount of hydrogen atoms, all bound to carbon backbone. The trifluoroacetic acid modified nanoparticles exhibit a similar surface composition, and hence, can be easily introduced into the fluoro-co-polymer. Likewise considerations can be figured out with benzoic acid and poly methyl methacrylate where the organic modifier imitates an organic surface on the MgF_2 -nanoparticles.

Different acid loadings of the MgF_2 -nanoparticles go in hand with their dispersibility in the copolymer. While nanoparticles with 0.3 equivalents of acid are easily dispersed inside the polymer (low viscosity of the melt), particles with 0.1 equivalents behave tough and exhibit significantly higher viscosity of the mixture, what can be observed by comparing rotational velocity (see figure S3, supporting information). Obviously the acids act like lubricants and enable a homogenous dispersion of the nanoparticles. However, transparent granulates can be obtained with both additive amounts.

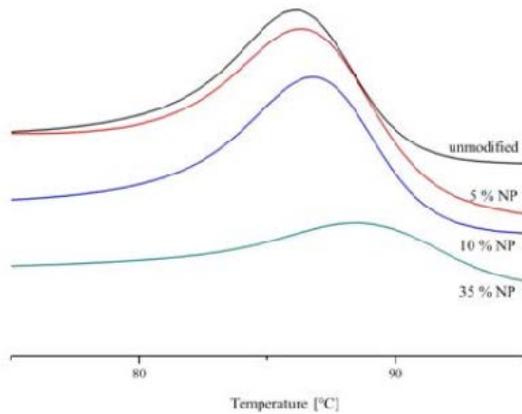
The main aim in this work is improving thermal and mechanical stability of fluoropolymers and optical properties of poly methyl methacrylate or likewise polymers. Different investigations to monitor these changes were carried out. First of all, differential scanning calorimetry (DSC) showed a slight increase in the glass transition temperature. The corresponding cooling curves are shown in Figure 5.

The peak maximum is shifted to higher temperatures from 86.38 °C to 88.80 °C. Since the crystallization temperature measured here is directly linked to the glass transition temperature, the result of the DSC measurements evidences a slight increase in thermal stability.

Besides thermal stability, mechanical properties of the composite materials were also of interest. Elongation and development of the elasticity modulus can be measured according to DIN EN ISO 527-3, which shows an overwhelming change in the mechanical properties of

the fluoropolymer. The elongation of the polymer and the composite are very similar (502 % without nanoparticles against 482 % with nanoparticles; see Figure 6). Notably, the elasticity modulus changes dramatically. As shown in figure 7, the value for the modulus rises by a factor of up to three as compared with the unmodified reference sample.

Figure 5: DSC Cooling Curve of Pure (black) and MgF₂-Nanocomposites with Different Amounts of NPs



S3: Change of Turning Moment with Increasing Rotational Velocity (red: 1, 9 eq HF, black: 1, 7 eq HF)

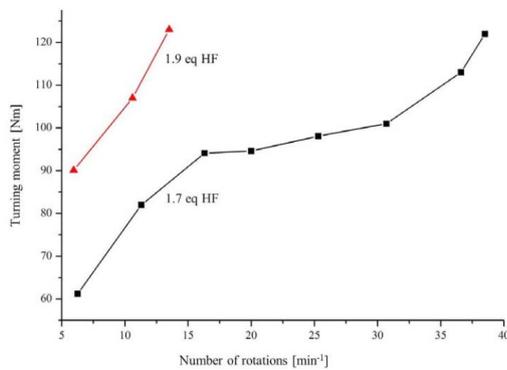


Figure 8: a) EDX of THV 221 GZ Foil Filled with Magnesium Fluoride Nanoparticles. b) Reflectance Spectra of THV-Sheets with Different Amounts of Nanoparticles (black: none; red: 5% NP, blue: 10% NP, magenta: 35 %)

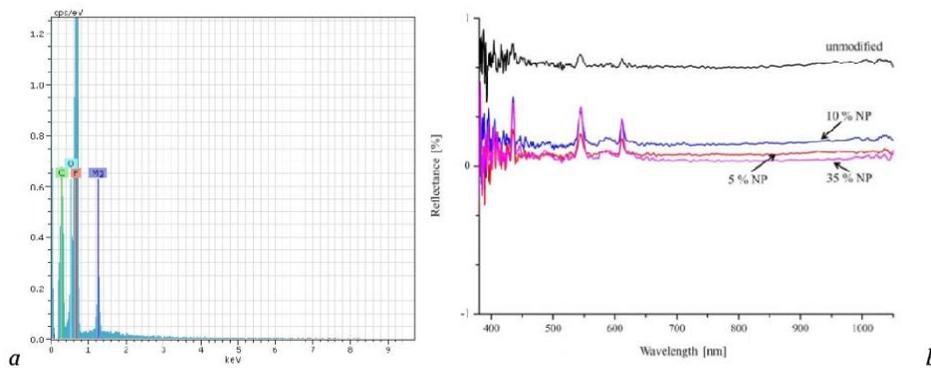


Figure 6: Elongation of Polymer and Composite

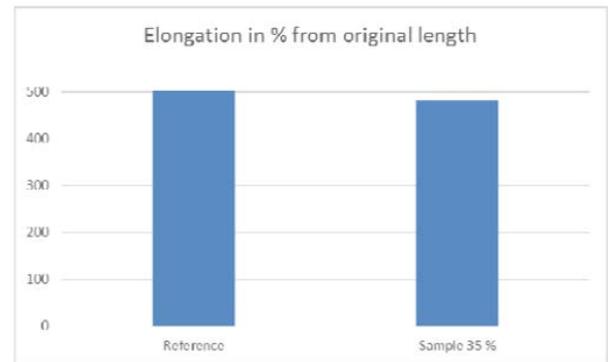
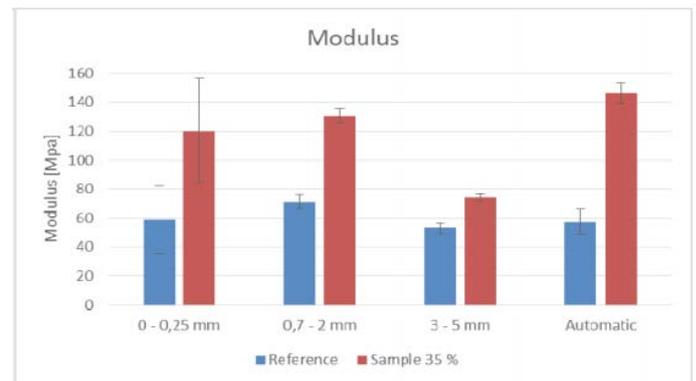
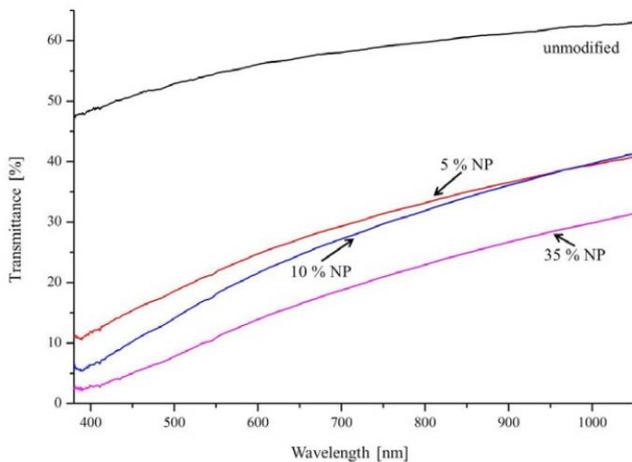


Figure 7: Change of the Modulus by the Nanoparticles



A homogeneous distribution of the nanoparticles inside the polymer was evidenced by measuring EDX at various spots of the foils giving all the same distribution pattern (see figure 8a). Transmission measurements show a decrease of transmitted light (see figure S4 supporting information) due to process colouring, though reflectance also decreases (see Figure 8b).

S4: Transmittance of Pure (black) and Modified (red: 5%, blue: 10%, magenta: 35%) THV Sheets



4. Summary

Magnesium fluoride nanoparticles accessible via the fluorolytic sol gel-synthesis can be modified by chemically bound trifluoroacetic acid (TFA) for better miscibility in fluoropolymers and benzoic acid (BzOH) for their use in poly methyl methacrylate. The MgF_2 nanoparticles were investigated by XRD, SAXS, MAS-NMR and IR. Thermal stability of the modifying acids has increased due to covalent binding to the particle surface as has been proven by thermal analysis. Thus, these thermally stable, modified nanoparticles allow for preparation of transparent metal fluoride/fluoropolymer composite materials. DSC and mechanical tests demonstrate an improvement of the mechanical and thermal properties as compared to the pure fluoropolymer. Homogeneous distribution of the inorganic filler MgF_2 , has been evidenced by EDX. Thus, organically modified nanoscopic magnesium fluoride is an excellent filler for fluoropolymers improving the mechanical properties of the resulting composite material while the optical transparency remains preserved.

Further improvement is related to the optimization of the thermal stability of the modifying acid in order to achieve an even better durability during the extrusion process which is topic of further investigations.

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