Dielectric properties of SiO₂:PMMA nanocomposites for energy storage

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ABSTRACT

We have made a SiO₂:PMMA hybrid nanocomposite based on 150nm spherical silica nanoparticles synthetized by sol-gel method. A molecule containing a methacrylate group (TPM), was chemically grafted to the silica surface to improve the electrical performance. The filling factor of the nanonanocomposite was up to 20%vol. The ~1um thick nanocomposite films were deposited on polished steel by spin coating. Compared to similarly prepared PMMA films, the dielectric constant, as measured by BDS (proadband dielectric spectroscopy) was enhanced by a factor of two for the nanocomposite, and the disruptive electric field by a factor of 2.5. This eventually yields an overall improvement of the energy density by a factor of 12.5.

Keywords: energy storage, nanocomposite, sol-gel nanoparticles, surface functionalsation, Weibull distribution.

1 MOTIVATION

For energy storage applications requiring quick charging and discharging cycles, capacitors based on hybrid nanocomposites (ceramic fillers in a polymer matrix) have the potential to become a very good choice [1,2]. The stored energy density E_{dens} (J/m³) in a plane capacitor is given by :

$$E_{dens} = \frac{1}{2}\varepsilon_o\varepsilon_r E_d^2 \cdot \qquad (1)$$

where ε_r is the dieclectric constant and E_d is the disruptive electric field ($E_d = V_d/l$, where l is the distance betwee the planes and V_d the disruptive voltage). Therefore, a nanocomposite made of polymeric matrix filled with ceramic nanoparticles appears to be a good solution : in volume, most of the materials is made of ceramics, but the disruptive discharge is largely improved with the polymer which prevent the discharge [3]. This occurs provided the polymer –ceramic interface can sustain large charge polarization. Following this approach, several nanocomposites have already been tested, such as alpha-hematite or ferroelectric embedded in PVDF or PVDF-based polymer.

Although those choices certainly make sense in terms of the final electrical performances of the material, we choose to target a material with the lowest possible production cost, and which can easily be scaled up for production. In this perspective, we then used sol-gel nanoparticles of silica sol gel embedded in PMMA (poly-methylmethacrylate). [4]

2 NANOCOMPOSITE SYNTHESIS

2.1 Sol-gel SiO₂-TPM grafted nanoparticles

Sol-gel SiO₂ nanoparticles have been synthesis by the standard Stöber procedure [5], i.e. with TEOS (tetraethyl ortholicate, Merck 8.00658.1000) as a precursor and NH₃ as a catalyst. We have chosen the synthesis parameters [6,7] in order to have a mean diameter of 150nm, confirmed by DLS (dynamic light scattering) and Atomic Force Microscopy (AFM), as shown in Fig.1. As the nanoparticles are in a closed-packed structure, we can measure the nanoparticules diameter on the AFM image without the artefact coming from the AFM tip radius.
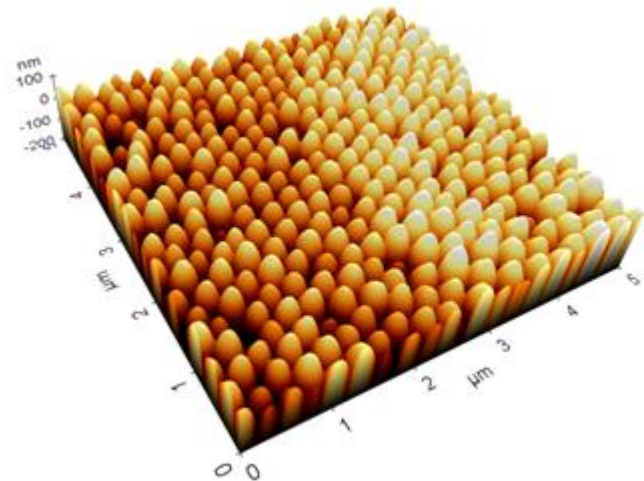

Figure 1: AFM topographic image (5um x 5um FOV) of sol-gel synthetized silica nanoparticles deposited on a silicon wafer.

Silica nanoparticles have been grafted with 3-methacryloxy-propyl-trimethoxysilane (TPM), following the protocole described in [8]. This molecule has a silane group on one side which can covalently bind to the SiO₂ surface of the nanoparticles. The resulting hybrid interface

is expected to improve the electric performance of the nanocomposite, as the chemical group at the other side of TPM is methacrylate, similar to the one found in PMMA.

The grafting procedure has been controlled by ATR-FTIR (Perkin Elmer, model "Spectrum Two FT-IR"). The spectra in the 3000-4000cm^{-1} range is shown in Fig. 2 for the solvent, (cyclohexanone, in blue), for the pristine SiO$_2$ nanoparticles in red and for the TPM grafted SiO$_2$ nanoparticles in green . As we can see, the hydroxyl groups of the pristine SiO$_2$ surface diseapear after the TPM grafting, as expected.
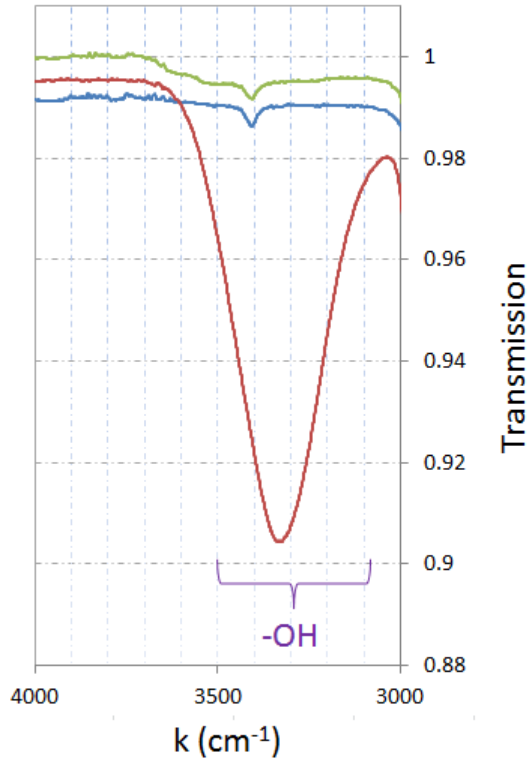

Figure 2: ATR-FTIR spectra of cyclohexanone (blue), SiO$_2$ nanoparticles in cyclohexanone (red) and TPM grafted SiO$_2$ nanoparticles in cyclohexanone (green).

Finally, the SiO$_2$ nanoparticles (either pristine or grafted) were rinsed in EtOH and centifuged at 10'000 rpm during 2 minutes. We repeated this procdedure three times and then we dried the particles at 120°C during 30min.

2.2 Thick film deposition

PMMA with molecular weight of 120'000 g/mol (Sigma-Aldrich 182230) has been dissolved in cyclohexanone, a solvent more convenient for spin coating than THF or chloroform, whose high volatility resulted in large roughness and patterned structures in PMMA films. The SiO$_2$ nanoparticles were then mixed with the PMMA at various %volume (up to 20% vol) with a 100W-30kHz sonicator (Hielschler UP100H).

The nanocomposite films were then deposited by spin coating (2'000 rpm during 1 min) on polished steel substrates and the optical thickness was measured with white-light optical reflectometry. The thickness was typically in the 0.5-3um range. As we did not find significant differences in the elctical properties as a function of the thickness, the electrical data reported below are for an aggregate over several samples with thicknesses in the 0.5-3um range. Most of the samples has a thickness close to 1um.

3   ELECTRICAL CARACTERISATION

3.1   Broadband dielectric spectroscopy

Broadband dielectric spectroscopy (BDS) at temperature ranging from 20°C up to 120°C have been performed in the 100Hz-100kHz range with an Agilent 4294A. At high temperature, the spectra were analyzed with the Havriliask-Negami model :

$$\varepsilon^{*}_{HN}(\omega) = \varepsilon_{\infty} + \frac{\Delta\varepsilon}{(1+(i\omega\tau_{HN})^{\beta})^{\gamma}} \qquad (2)$$

We report here measurement at room temperature, where no relaxation peaks were observed (we are here more interested in the low frequency behaviour).
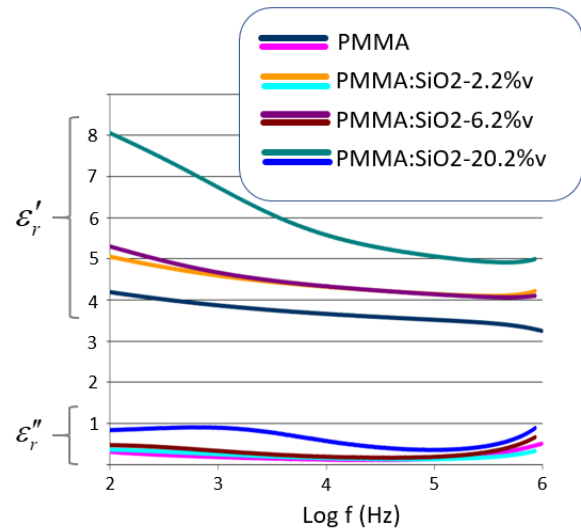

Figure 3: ε'(ω) and ε''(ω) spectra for pure PMMA and PMMA-SiO2(TPM grafted) nanocomposites at room temperature.

Figure 3 shows the BDS spectra from 100Hz to 1MZ for pure PMMA, PMMA-SiO$_2$(TPM) nanocomposite with : 2.2%volume SiO$_2$, 6.2%volume SiO$_2$ and 20.2%volume SiO$_2$ respectively. As we can see, the quasi static dielectric constant is twice larger with the SiO$_2$ nanoparticles

(20.2%vol), compared to pure PMMA. This is due to the large dielectric constant for silica nanoparticles, as reported for example in [9]

3.2 Dielectric strength

The dielectric strength (i.e. E_d, the disrupritve electric field) has been measured with a home-made system shown in Fig 4a). With a high voltage power supply (Stanford Research System, PS-310), we applied voltage ramps up to 1200V at 10V/sec. Fig 4b) is a an example of the damage caused by the electric discharge.
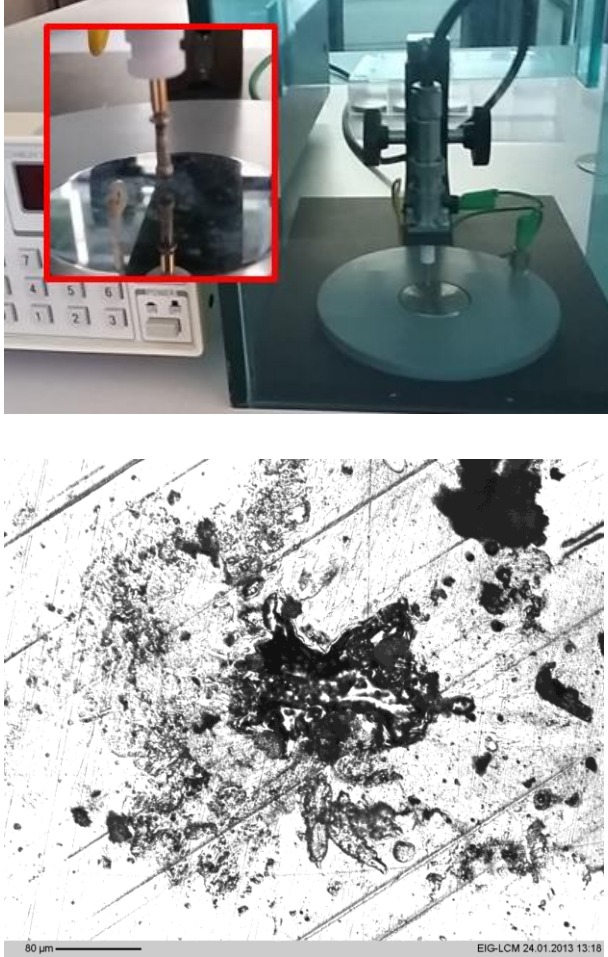

Figure 4: a) Picture of our dielectric strength system (inset : electrode with the 1mm streel ball) b) optical image of the film after the electrical discharge (scale bar : 80um)

The distributions of the disruptive electric field are shown in Fig 5, in blue for the PMMA and in red for the PMMA-SiO$_2$(TPM) nanocomposite. The distribution for the PMMA was best analyzed with the help of the following Weibull distribution :

$$p(x) = \frac{a}{b}\left(\frac{x-m}{b}\right)^{a-1} \exp\left(-\left(\frac{x-m}{b}\right)^{a}\right) \qquad (3)$$

with :   m (position parameter) : 135 V/μm
           a (form parameter) : 1.877
           b (scale parameter) : 756.1 V/μm

The distribution for the nanocomposite (PMMA-SiO$_2$(TPM)) follows a normal (gaussian) distribution with :
           μ (average) : 1300.6 V/μm
           σ (standard deviation) : 113.8 V/μm

It is not clear so far whether this extremely high value of E_d, in the range of MV/um for the nanocomposite, is due to the TPM grafting process or not. Also, the role of the film thickness (about 1 um here) needs further exeriments. Finally, the films have many defects and we observed immediate electric failure for about 50% of the locations. Nevertheles, the improvement of the electric performances of ther nanocomposite over the PMMA is clear from Fig 4 and Fig. 5.
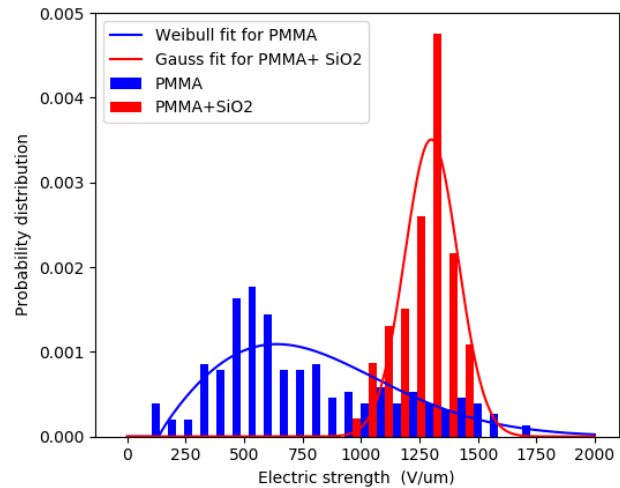

Figure 5: Distribution plots and fits of the disruptive electric field in V/μm for PMMA (blue) and for the nanocomposite (red).

If we combine best results for the dielectric constant (ε_r=8.1) with the most favourable disruptive electric field ($1.3 \cdot 10^9$ (V/m)), we found, according to Equation (1), an energy density of 51 J/cm^3.

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