

Solution Modified Fumed Silica and Its Effect on Charge Trapping Behavior of PP/POE/Silica Nanodielectrics

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Abstract

Various dielectric nanocomposite materials are studied in the frame of the European Commission funded project GRIDABLE. This project has the aim to develop DC cable extruded insulation and medium and low voltage DC capacitor films exhibiting enhanced performance with respect to presently used materials. The nanocomposites intended for cable applications are polypropylene (PP)/polyolefin elastomer (POE) blends filled with surface modified nano-silica particles. The surface modification is carried out via the state-of-the-art solution method using a polar silane as the modifying agent. Thermally Stimulated Depolarization Current (TSDC) measurements were carried out in order to study the charge trapping behavior of the nanocomposite samples. TSDC results indicate that the addition of the treated nano-silica, for most cases, reduces the density of the deep traps significantly. The effect of the addition of silica nanoparticles - both modified and unmodified - on the crystallinity of the samples was studied using X-ray Diffraction (XRD). This is important as the charge trapping properties of the nanodielectrics can be affected by the degree of crystallinity. While more detailed studies are necessary, these results imply that the depth and the density of the deep trap states is profoundly influenced by the level of the silica modification i.e. the amount of the grafted silane on the silica surface.

1. Introduction

A European project called GRIDABLE (Polymer Nanocomposite Insulation Material Enabling Integration of Renewables and DC Storage Technologies in the AC Energy Grid) was inaugurated under the HORIZON 2020 framework co-funded by the European Community. Various partners, both academic and industrial, are working together within this project, aiming to develop novel nanostructured polymer-based materials suitable for high voltage DC (HVDC) cable insulators and capacitors. The goal of GRIDABLE is to develop polypropylene-based nanocomposites with proper nanoparticle functionalization and dispersion quality. This novel material can bring about significant improvements for the state of the art DC cable insulations and film capacitors.

Incorporating nanoparticles in dielectric materials, in order to improve their insulating properties, was studied extensively in

the recent years [1-4]. Nanodielectric composites containing filler particles of size lower than 100 nm in one dimension, may exhibit significant enhancements in e.g. dielectric strength and voltage endurance [5]. These improvements can be due to various phenomena, which mainly stem from the high interfacial area implemented by nanofillers incorporated to the polymer matrix [6] as well as the alteration of the features of the polymer/filler interphase [5]. Changing the type and surface characteristics of the filler leads to alteration of the polymer/filler interphase region. This can influence crystallinity [7], molecular mobility [8] and entanglement density [9, 10]. These changes in the nanoparticles' surface properties can contribute to further improvements of the dielectric properties of the nanocomposites filled with them. Changing the surface properties of the nanoparticles is possible through surface modification that is substituting the existing chemical structure on the particles' surface with a certain functionality tailored for a specific application.

Surface modification of nanofillers may improve the dielectric properties of the nanocomposites by enhancing their dispersion in the polymer matrix. Since the nanofiller particles act as electrical defect centers in polymers [11], they can distort and enhance the local electric field in their vicinity, leading to a decrease in the dielectric breakdown strength as compared to the neat polymer. The extent of this local field distortion and enhancement is not only a factor of the difference in permittivity or conductivity between the particles and the polymer matrix, but also of the particle size, their aggregation and agglomeration [1]. Therefore, improving the dispersion of the nanofillers in a nanodielectric material can result in improvement of the dielectric breakdown strength.

Another parameter that can lead to early electrical breakdown of a nanocomposite, is poor polymer/filler adhesion due to chemical incompatibility [12]. Chemical incompatibility could result in formation of small voids at the polymer/filler interface and thus decrease the dielectric breakdown strength. Hence, particle surface modification in order to bond/bind the nanofiller to the polymer matrix, can increase the breakdown strength and reduce the dielectric losses [13].

Another way in which surface modification of the nanoparticles can influence the dielectric properties of the nanodielectrics is alteration of the electronic features of the

interface between the coated particles and the polymer matrix [1]. Siddabattuni et al. [14], observed a significant reduction in leakage currents and dielectric losses and an improvement in dielectric breakdown strengths, electron-withdrawing phenyl groups were located at the polymer–particle interface. Accordingly, it can be speculated that introduction of a polar moiety to the surface of the nanoparticles can induce this sort of electronic behavior as the dipoles at the particle/polymer interface may affect charge carrier transport and trapping [4].

Space charge distribution is a direct outcome of combined trapping/de-trapping and transport behavior of charges in insulating polymers and varies with trap density, trap depth distribution, and charge carrier mobility [15]. While the space charge phenomena can possibly be controlled by changing the morphology and crystallinity of the polymer, space charge distribution can be influenced by grafting functional groups onto the nanofiller particle surface, influencing charge mobility through the introduction of shallow trap sites [16] or reducing the number of charges trapped in deep traps [1] in the filler/polymer interaction zones.

In this study, silica nanoparticles were modified with a polar modifying agent, and compounded with PP/POE polymer blends. The aim of surface modification was to improve the trapping/de-trapping behavior of the PP/POE/silica nanocomposites. Firstly, the modification was proven using Thermogravimetry Analysis (TGA). Subsequently, the influence of silica modification on the charge trapping properties of the aforementioned nanocomposites was studied via Thermally Stimulated Depolarization Current (TSDC). Since the charge trapping behavior can be significantly influenced by differences in the crystalline phase structure, crystallite size and overall degree of crystallinity, XRD analysis was performed on certain samples to study the crystalline structure in detail. Nevertheless, this paper is based on preliminary results of the study, and further elaborations are planned to be done in future publications.

2. Experimental Section

2.1 Silica Modification

A fumed silica grade with high purity and low moisture content was selected for this study. The silica surface modification was carried out via the state-of-the-art solution method using a polar silane as the modifying agent under different reaction conditions. Further specification of these materials is at this moment not possible due to intellectual property reasons. The details of each modification reaction for each modified silica sample is depicted in Table 1. The modification was carried out in a glass round bottom flask, immersed in an oil heating bath, equipped with a mechanical stirrer, cooler and thermometer. The silica, silane and additional water were mixed with toluene, which was the liquid medium of the reaction.

The polar silane used in this study is prone to alter the silica-polymer interphase which, as a consequence, can change the dielectric behavior of the nanocomposites. It is assumed that by the introduction of this polar functionality to the silica surface, charge trapping properties of the dielectric material undergo

meaningful changes, which might induce beneficial influences on the ultimate insulation characteristics of the nanocomposite materials.

Table 1. Reaction conditions utilized for modification of the silica nanoparticles

Sample Number	Temperature (°C)	Time (hour)	Added Water (gram)
0	Untreated Silica		
1	80	24	1.8
2	20	1	1.8
3	80	1	0.0
4	20	24	1.8
5	80	1	1.8

2.2 Preparation of the Nanocomposites

The nanocomposites studied in this work are based on PP/POE blends filled with surface modified nano-silica particles. The specimens were prepared by addition of 1 w% of different silica samples to the polymer matrix in a twin-screw micro extruder and mixed at 230°C. Subsequently, the compound was injected into a square mold using a mini-injection molding machine. The dimensions of the mold were 260x260x0.5 mm. The resulting nanocomposite (NC) samples were named according to the silica sample used. For instance, NC_1 is nanocomposite filled with silica sample number 1. There was also an unfilled sample which was named UP.

2.3 Thermogravimetry Analysis (TGA)

Thermogravimetry analysis was performed on the modified silica samples as well as the unmodified silica in order to quantify the level to which the modification process is successful. This method involves heating up the silica powder from room temperature to 850 °C with a rate of 20 °C/min while measuring the weight loss of the sample. The weight loss between 300–850 °C can be attributed to the thermal decomposition of this silane coupling agent chemically bonded to the silica surface [17]. Figure 1 demonstrates the results of this measurement as the weight loss percentage over temperature.

2.4 Thermally Stimulated Depolarization Current (TSDC)

Thermally Stimulated Depolarization Current (TSDC) measurements were carried out in order to study the charge trapping behaviour of the nanocomposites. Circular gold (Au) electrodes (100 nm in thickness) were deposited on both sides of the sample films by e-beam evaporation under high vacuum. The samples were first heated up to 70 °C, and subjected to a 3 kV/mm DC electric field for 20 minutes under isothermal conditions. The samples were then cooled down to –50 °C while the poling voltage was still on. Subsequently, the samples were short-circuited and linearly heated up to 140 °C at 3 °C/min, while the depolarization current was monitored by a highly sensitive ammeter.

2.5 X-Ray Diffraction (XRD)

X-Ray Diffraction (XRD) analysis was done to study the crystallinity of the nanocomposites. The samples were scanned

with the 2θ value varying from 8° to 37° at a scanning rate of $0.05^\circ/8\text{ s}$ using a Philips X'Pert 1 X-ray diffractometer. The samples for XRD analysis were taken from the injection-molded thin sheets.

3. Results and Discussion

TGA results, depicted in Figure 1, show a higher weight loss for the modified silicas compared to the untreated one, which is an indication of the successful modification of the silica surface. Different reaction conditions were utilized to achieve different levels of silane modification. The values of weight loss above 300°C are listed in Table 2. It can be seen that a range of weight losses, from ca. 3% to 6%, is achieved by altering the reaction conditions.

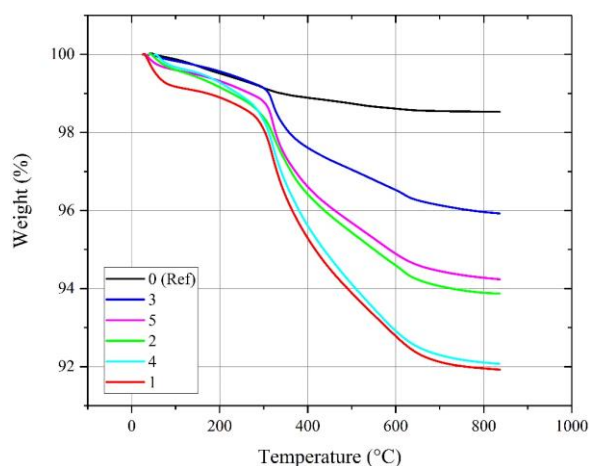


Figure 1. TGA results for the modified silica samples compared to the untreated silica.

Nevertheless, altering the modification reaction conditions can change not only the thickness of the deposited layer, but also its morphology, wettability and extent of silane hydrolysis. Each of the aforementioned factors can affect the interfacial properties between the fillers and the polymer chains which can lead to different dielectric behavior of the nanocomposites.

Table 2. TGA Weight Loss Values at Temperatures above 300°C .

Sample Number	TGA Weight Loss (%)
0	0.61
1	6.16
2	4.52
3	3.21
4	6.23
5	4.55

Figure 2 shows the TSDC plots of all the silica filled samples as well as of the unfilled polymer as a secondary reference. In principle, the TSDC spectra are attributable to the relaxation of (dipolar) polarization and accumulated space charge formed during the isothermal polarization phase. It is remarked that the short-circuit TSDC is a net sum of both, homo- and heteropolar discharge current components, and hence, the integrated charge represents the net charge. For most semi-crystalline and non-polar polymers, such as PP, the high-temperature TSDC

spectrum above the glass transition temperature is mainly associated with the relaxation of trapped space charge. It is also remarked that this high-temperature space charge relaxation can be influenced by thermal transitions (such as softening/melting) of a single phase in heterophase polymer blend systems. To a first approximation, the TSDC peak temperature and intensity can be attributed to the depth and density of charge traps, respectively, as is done in the following analysis.

The results in Fig. 2 indicate that upon incorporation of the treated nanosilica the TSDC spectra become more complex and a significant shift of the main TSDC peak towards higher temperatures occurs, being indicative of the trap becoming deeper. For the samples with the polar functionality on the filler surface, a new (deep) trap emerges in the $93\text{--}97^\circ\text{C}$ range, while a smaller side peak is observed around the same temperature ($\sim 78^\circ\text{C}$) as the intrinsic TSDC peaks of the two reference samples (UP and NC_0). Comparing NC_3 and NC_4 with the lowest and the highest levels of silica modification, respectively, it can be observed that the location of the new deep trap peak is shifted to higher temperatures. Moreover, the intensity of the TSDC peak is seen to vary significantly depending on the type of treated silica, with some of the samples exhibiting (apparent) reduction in the main peak current intensity; this may be related to (i) reduction of the density of the trap states or (ii) more uniform distribution of the space charge in the specimen (hence leading to smaller measurable external current in the TSDC experiment). While more detailed studies are necessary, these results imply that the depth and the density of the newly introduced trap is profoundly influenced by the level of the modification i.e. the amount of the grafted silane on the silica surface.

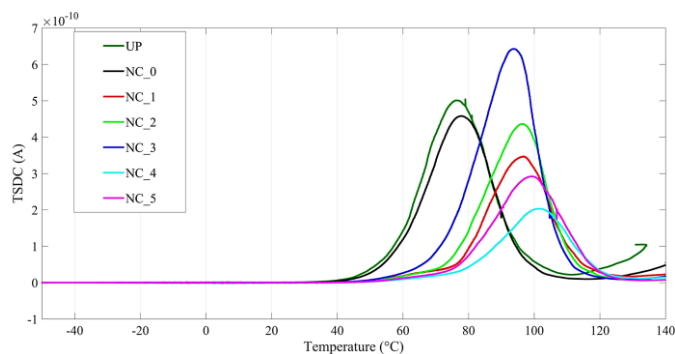


Figure 2. TSDC spectra of injection molded PP blend samples.

The above trend is however not entirely dominant as there are some repeatable exceptions. For instance, samples NC_1 and NC_4 contain silica samples number 1 and 4, respectively, which have more or less equal TGA weight losses. However, for NC_4, the deep trap peak is more suppressed compared to NC_1. It is the same for samples NC_2 and NC_5. A possible explanation is that the depth and density of the traps are not only a function of the thickness of the silane layer, but also of other parameters such as filler dispersion, silane layer morphology, micro-structure and crystallization characteristics of the compound.

In order to gain more insight into the results above, the areas under current versus time curves during polarization and

depolarization were calculated, providing an indication of how much charge was injected into or released from the sample, respectively. Figure 3 demonstrates the calculated amount of charges for each sample during isothermal polarization and depolarization. It can be seen that the amount of the charges injected during the polarization phase is significantly reduced upon modification of the filler. Figure 4 shows the values of released charges relative to the amount of the injected charges for these samples: for the reference samples UP and NC_0, only 19% and 17% of the injected charges are released during depolarization, whereas, in case of samples with highly modified silica e.g. NC_1, this value increases to 55%. These observations can indicate that there is a lower remaining accumulated space charge for the samples with modified silica.

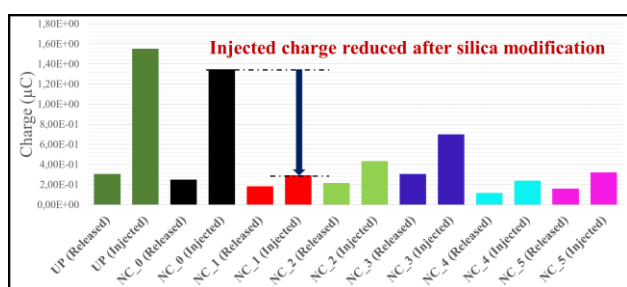


Figure 4. Amount of charge released during thermally stimulated depolarization versus the amount of injected charge during the polarization phase

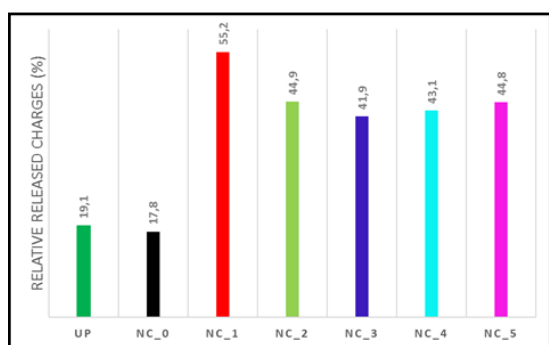


Figure 5. Values of released charges relative to the amount of the injected charges

Morphological variations arising from differences in the crystalline phase structure, crystallite size and overall degree of crystallinity are expected to influence the dielectric properties of nanocomposites. Therefore, XRD analysis was performed on certain samples to study the crystalline structure in detail. As shown in Figure 5, the diffraction peaks at 2θ angles of 14.1° , 16.8° , 18.2° and 25.4° are characteristic of the thermodynamically stable α -form of PP and respectively correspond to (110), (040), (130), and (060) crystallographic planes. There is also a small (300) diffraction peak at 16.1° which can be addressed to β -form PP crystallites [18]. In addition to the PP crystalline phase, orthorhombic PE crystals corresponding to (110) and (200) crystallographic planes were detected at 2θ angles of 21.4° and 23.4° , respectively. These are attributable to the POE component of the polymer matrix [19]. The degree of crystallinity (X_c) as well as the apparent average

size of the crystallites were calculated. As presented in Table 3, there is no significant change in X_c and the crystallites size after the incorporation of the silica nanoparticles or upon surface modification. Moreover, the level of silica modification has no significant effect on the degree of crystallinity and the apparent average size of the crystallites. This observation indicates that the difference in the charge trapping behavior of these nanodielectrics is not stemming from the difference in their crystallinity, but from the different electronic characteristics of

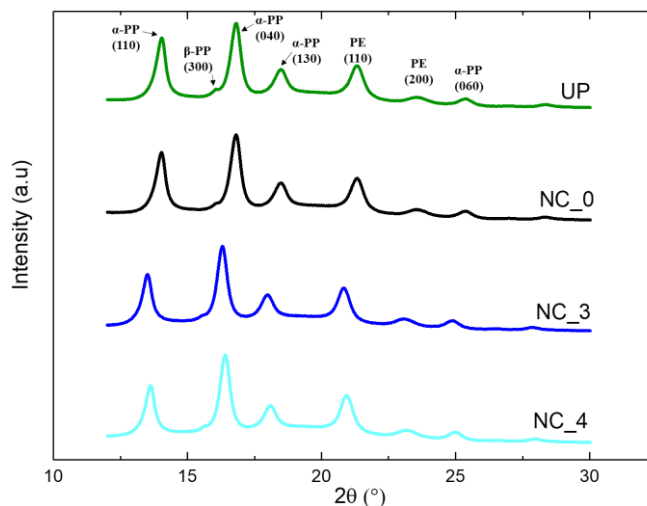


Figure 3. X-ray diffraction patterns of the unfilled PP/POE blend (UP), nanocomposites filled with unmodified silica nanoparticles (NC_0) and nanocomposites with the lowest (NC_3) and the highest (NC_4) levels of filler modification the filler/polymer interphase induced upon silica modification.

Table 3.

Sample	X_c [%]	Apparent average crystallite size (nm) [*]
UP	32.3 ± 2.2	16.86
NC_0	33.5 ± 2.1	16.89
NC_3	31.2 ± 2.1	16.59
NC_4	30.4 ± 2.1	16.76

^{*}The apparent average crystallite sizes are calculated using Scherrer's equation [20]

4. Conclusions

Based on the results presented in this report, modifying the surface of the silica nanoparticles has a profound effect on the charge trapping properties of the PP/POE/silica nanocomposites without altering the crystalline structure of the nanocomposites. This shows that upon modification, the polar functional groups added to the silica surface, alter the electronic features of the nanoparticles in such a way that the deep charge traps are suppressed and new and deeper traps are introduced. Moreover, there is an indication that modifying the filler surface can lead to lower accumulation of space charge. It also can be seen that increasing the amount of the grafted silane on the silica surface results in more pronounced suppression of the deep traps. However, there are exceptions. Some of the samples with the same modification levels behave differently during the TSDC measurement. This could be due to the fact that altering the

modification reaction conditions changes not only the amount of grafted silane, but also the grafted layer morphology, accessible surface area, wettability and extent of silane hydrolysis, each of which can affect the interfacial properties between fillers and the polymer chains leading to different dielectric behavior of the nanocomposites. In order to get a clearer image of the functionalization of the silica and its effect on the charge trapping behavior of dielectric nanocomposites, studying the aforementioned factors seems to be interesting for future studies.

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