

Influence of polar and unpolar silica functionalization on the dielectric properties of PP/POE nanocomposites

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Abstract- This study focuses on the influence of polar and unpolar surface functionalization of silica on the dielectric performance of PP/POE (polypropylene/poly(ethylene-co-octene)) nanocomposites. The silica fillers were surface-modified with unpolar trimethylethoxysilane (TMES) or polar 3-aminopropyl triethoxysilane (APTES). Fourier-Transform Infrared Spectroscopy and Thermogravimetric analysis were performed and confirmed qualitatively and quantitatively the successful silica-silane modification. Silica/PP/POE nanocomposite films were prepared using a mini-extruder. Scanning Electron Microscope images showed good dispersion of the modified silica in the PP/POE matrix. However, the polar silica cluster size (300 nm) is slightly larger than the one of the unpolar silica (100 nm). Thermally Stimulated Depolarization Current (TSDC) characterization data showed that the polar silica introduced deeper charge traps than the unpolar one, which also showed higher trap density. The apparent conductivity measured during the TSDC poling phase indicated that the polar silica filled nanocomposites featured very fast polarization to reach the saturation state, while the unpolar silica had a rather slow polarization rate. From Pulsed Electroacoustic Analysis it was obvious that the space charge is suppressed by addition of the polar silica, but increased by the presence of the unpolar silica.

I. INTRODUCTION

Nanodielectrics have drawn a lot of attention in the High Voltage Direct Current (HVDC) field [1,2,3]. It is reported that adding a nanofiller to dielectrics can suppress space charge accumulation [1,2] and improve the breakdown strength [3]. However, the dispersion of a nanofiller in a polymer matrix is a major challenge. Polyethylene or polypropylene feature an unpolar nature; hence, in order to increase the compatibility and dispersibility of a polar filler with the polymer matrix, an unpolar functionalization is needed [1]. However, it is also reported [2] that the introduction of various polar functional groups into nanocomposites results in an improvement of dielectric

properties. In this study, we are comparing the effect of polar and unpolar silica functionalization on the dielectric properties of PP/POE/silica nanocomposites, with the goal to find the best balance in terms of polarity and dielectric performance.

II. MATERIALS AND CHARACTERIZATION

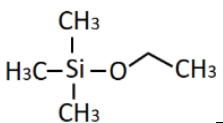
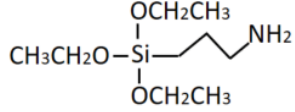
A. Materials

Fumed silica (Aerosil 200 from Evonic, Germany) is selected as the reference silica in this study. Trimethylethoxysilane (TMES) and 3-aminopropyl triethoxysilane (APTES) – the chemical structures are shown in TABLE I - were supplied by abcr, Germany.

Functionalization of silica was performed as follows: The silica was placed in a glass reactor, mixed with the chosen silane and the catalysts (trifluoroacetic acid and water) for 24 hours at room temperature and put into a vacuum oven for 24 hours at 80 °C to remove volatiles.

The reference and modified silicas were incorporated into the PP/POE (50:50) compound together with an antioxidant in a twin screw extrusion process. A thin film was obtained from cast extrusion with the thickness of around 350 μm.

TABLE I. Chemical structure of the silanes used in this study

Silane	Chemical Structure
TMES	
APTES	

B. Characterization

The Thermogravimetric Analysis (TGA) and Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) were performed in order to control the presence of the silane on the silica surface. For the DRIFTS spectrum, KBr was used for diluting the silicas and the background record. In the TGA test, the samples were heated up from 30 °C to 850 °C in a synthetic air atmosphere with a heating rate of 20 °C/min. Compound micromorphology and silica dispersion were studied by Scanning Electronic Microscopy (SEM). The cast film compounds were broken in liquid nitrogen in order to get the cross section surface. The trap distribution behavior was studied by Thermal Stimulated Depolarization Current (TSDC). The compound samples were coated with gold electrodes. During the test the samples were firstly heated up to 70 °C for 5 min stabilization at 70 °C. Afterwards, an electrical field (3 kV/mm) was applied for 20 min and then the sample was quickly cooled down to -50 °C. Finally, the samples were short-circuited and heated to 140 °C with a heating rate of 3 °C/min to record the thermally stimulated current. The space charge accumulation behavior was studied by the Pulsed Electro-Acoustic (PEA) technique involving a 3 hours polarization phase and 1 hour depolarization at 70 °C.

II. RESULTS AND DISCUSSION

Fig.1 shows the TGA curves of the modified silicas. In case of the unmodified reference silica, 2.6 % weight loss is measured stemming from the removal the adsorbed water and silanol group condensation on the silica surface. After modification with TMES and APTES, the weight loss of the modified silica increased to 4.7 % and 12.2 %, respectively. This indicates that both silanes were attached to the silica surface. The difference in weight loss is resulting from the different number of alkoxy groups of TMES (1 alkoxy group) and APTES (3 alkoxy groups). Therefore, APTES not only reacts with silanol groups on the silica surface, but also with itself via condensation of the alkoxy groups. As a result, the APTES modified silica shows a higher weight loss than TMES modified silica due to the self-condensation of APTES and thus a higher number of silane molecules attached to the silica surface.

Fig. 2 shows the DRIFTS spectra of the silicas. The isolated silanol group of the reference silica with a band at 3747 cm^{-1} [4] is used to indicate the silica modification. In case of modified silicas, the isolated silanol group band did completely vanish on the APTES modified silica, while there is still a small amount of isolated silanol groups detected on TMES modified silica. This indicates that both silanes reacted with the silica, but that APTES completely covered the silica surface while TMES did not fully cover the silica surface, as shown in Fig. 3. This is due to the self-condensation reaction of APTES forming a layer and covering the silica surface. Furthermore, the CH stretching at 2979 cm^{-1} also proves that

TMES reacted with the silica, and the CH stretching at 2979 cm^{-1} , the NH deformation at 1679 cm^{-1} , the CN stretching at 1405 cm^{-1} [5] all together prove that APTES reacted with the silica surface.

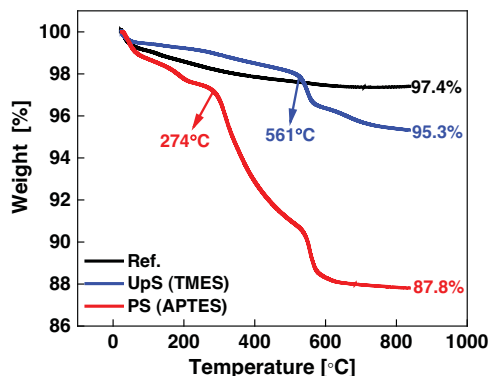


Fig. 1. TGA curve of the unmodified and modified silicas: UpS (TMES) represents the unpolar silica modified with the TMES silane. PS (APTES) represents the polar silica modified with the APTES silane.

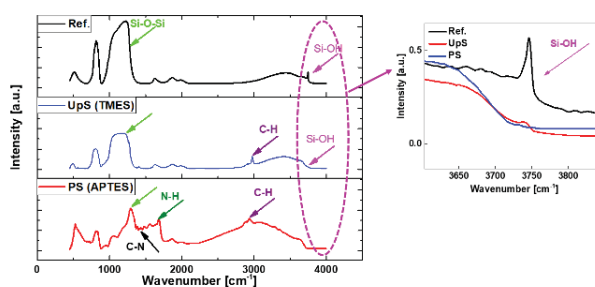


Fig. 2. DRIFTS spectra of reference and modified silica.

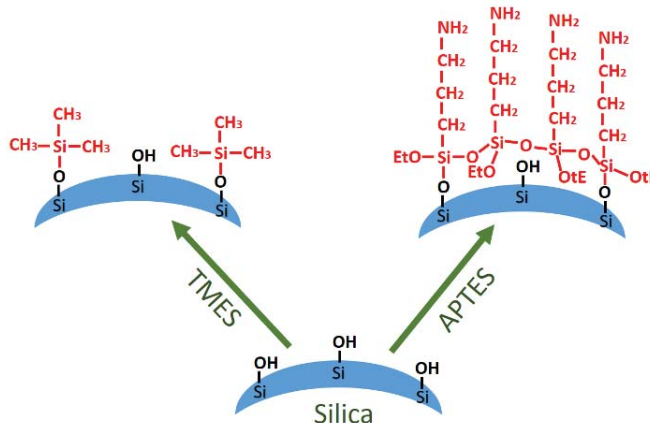


Fig. 3. Reaction scheme of the reference and modified silicas.

One of the challenges of nanodielectrics is the dispersion of the nanofiller in the polymeric matrix. Fig. 4 shows the micromorphology of the unfilled PP/POE blend and the nanocomposites filled with unpolar or polar silica. It is clearly seen that two phases separation is present in the unfilled PP/POE blend resulting from the difference in viscosity of PP and POE. This indicates that the PP and POE exhibit low miscibility based on the viscosity-difference. In gen. In the

nanocomposites, the different silicas are located mainly in the PP phase, which is consistent with the outcome of an earlier study [6]. Both, unpolar and polar silica, exhibited good dispersion and there are no large clusters (1 μm) of nanosilica found. However, the average size of unpolar silica clusters (less than 100 nm) is lower than the ones of the polar silica (around 300 nm). There are two possible reasons for it: (i) PP and POE are both unpolar, which will result in a better compatibility with unpolar silica; (ii) due to condensation of the APTES silane, a condensed silane-oligomer bridge might be formed between silica primary particles during the modification process, which leads to formation of bigger size nanosilica clusters.

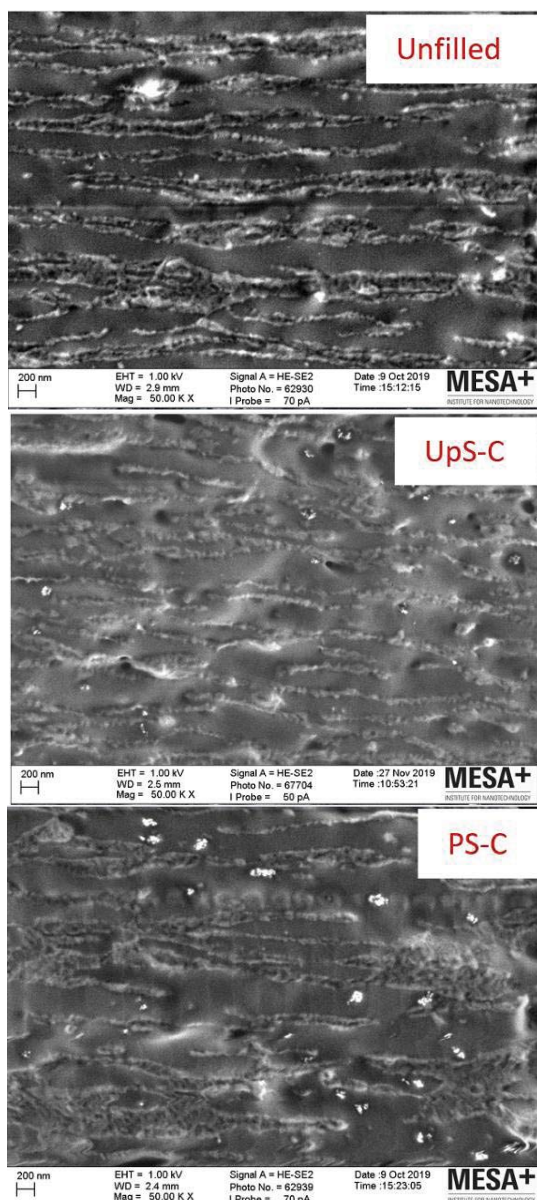


Fig. 4. SEM images of the unfilled PP/POE blend and the nanocomposites: Unfilled represents the unfilled PP/POE blend. UpS-C represents the PP/POE nanocomposite filled with the unpolar silica. PS represents the PP/POE nanocomposite filled with the polar silica.

In order to study the effect of silica modification on the charge trapping properties, TSDC was performed on the unfilled PP/POE blend and the nanocomposites filled with the unpolar or polar silica. The depolarization curves of the studied samples are shown in Fig.5. In case of the unfilled PP/POE blend, there are two peaks visible: one complete peak with a position at 69 $^{\circ}\text{C}$, and the second uncompleted peak with a position around 140 $^{\circ}\text{C}$. The incorporation of the unpolar or polar silica suppresses the deepest traps around 140 $^{\circ}\text{C}$, but introduced another deep trap. Addition of the unpolar silica introduced a deep trap at 76 $^{\circ}\text{C}$ with higher trap density than the unfilled PP/POE, and another deep trap at 100 $^{\circ}\text{C}$ with very low trap density. The latter one might be due to the unreacted silanol groups in the interface between silica and polymeric matrix. The addition of the polar silica introduced the deep charge traps at 100 $^{\circ}\text{C}$ with relatively low trap density, which might result from the polar amine moiety introduced by APTES modified silica.

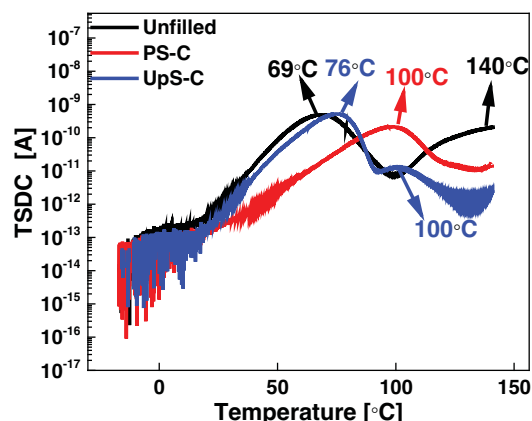


Fig. 5. The depolarization curve of the unfilled PP/POE blend and of the nanocomposites filled with unpolar (UpS-C) or polar silica (PS-C).

In order to get an insight into the dielectric properties of the studied samples, the conductivity versus time curve under polarization in the TSDC test is also plotted in Fig. 6. The initial conductivity of the polar silica filled nanocomposite is much lower than the one of the unpolar silica filled nanocomposite and the unfilled blend, which indicates that the initial injected charge is much lower in the polar silica filled nanocomposite, probably resulting from the low trap density. The unpolar silica filled nanocomposite with the highest initial conductivity value showed a slow polarization behavior with a gradually decreasing current, which is similar to the unfilled compound. The gradual decrease might be caused by the high amount of trap sites and the high mobility of charge carriers at 70 $^{\circ}\text{C}$, which contributes to the formation of the internal current and space charge accumulation, and, as a result, leading to the decreased conductivity. In case of the polar silica filled nanocomposite, the composite showed very fast polarization to reach saturation. This might be due to the low trap site and low mobility of the charge carrier at 70 $^{\circ}\text{C}$ in polar

silica filled nanocomposite. For the long term, the continuously decreasing conductivity of the unpolar silica filled nanocomposite will result in a better dielectric performance than the polar silica filled nanocomposite.

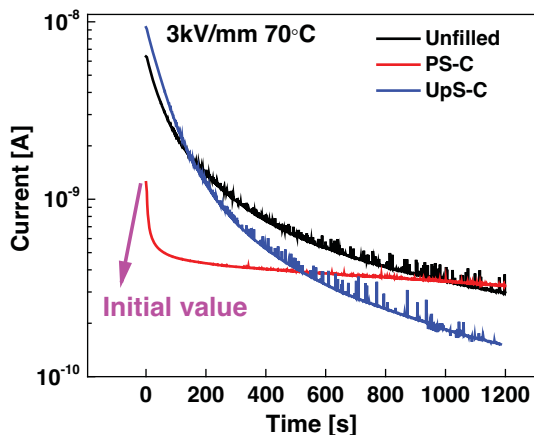


Fig. 6. The apparent conductivity curves of the unfilled PP/POE blend and the nanocomposites filled with unpolar or polar silica during the poling phase of the TSDC test.

Space charge accumulation is a big concern for HVDC cable application, since a high amount of space charge can distort the local electrical field, causing breakdown. The amount of space charge after volt off of the studied samples is shown in Fig. 7. It is clearly shown that unpolar silica increased the amount of space charge, while it is decreased in the polar silica filled nanocomposite. This showed a connection with the trap density. Unpolar silica filled nanocomposites with the highest trap density presented the highest amount of space charge, and the polar silica filled nanocomposites with the lowest trap density exhibited the lowest amount of space charge.

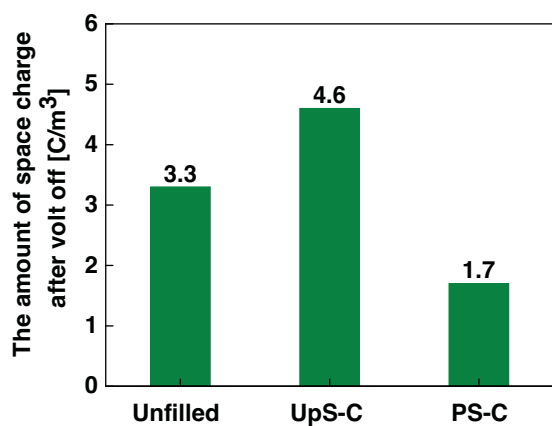


Fig.7. The amount of space charge of the unfilled blend and the nanocomposites filled with unpolar or polar silicas after volt off.

III. CONCLUSION

In order to compare the effect of polar and unpolar silica on the dielectric properties of a PP/POE blend, trimethylethoxysilane (TMES) and 3-aminopropyl triethoxysilane (APTES) were selected for silica modification. DRIFTS and TGA results showed that TMES and APTES are both successfully grafted onto the silica surface. In the thermoplastic matrix, the unpolar silica resulted in a smaller cluster size than the polar silica. The polarity of the silica filler surface also influenced the dielectric properties of the nanocomposites in terms of space charge accumulation and conductivity. Unpolar silica caused a higher trap density than the polar silica, and the latter introduced a higher amount of deeper traps than the unpolar silica. The polar silica filled nanocomposite showed a much lower initial conductivity, but higher final conductivity in the steady state. Furthermore, the polar silica resulted in the lowest space charge accumulation among the studied samples.

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REFERENCES

- [1] J. S. Park, et al, Polyethylene/Graphene Nanoplatelet Nanocomposite-Based Insulating Materials for Effective Reduction of Space Charge Accumulation in High-Voltage Direct-Current Cables. *Journal of Nanomaterials*, vol. 2019, 2019.
- [2] X. Huang, P. Jiang, and Y. Yin, Nanoparticle surface modification induced space charge suppression in linear low density polyethylene. *Applied Physics Letters*, 95(24), pp. 242905, 2009.
- [3] D. Ma, Influence of nanoparticle surface modification on the electrical behavior of polyethylene nanocomposites. *Nanotechnology*, 16(6), pp. 724, 2005.
- [4] B. McCool, L. Murphy, and C.P. Tripp, A simple FTIR technique for estimating the surface area of silica powders and films. *Journal of colloid and interface science*, 295(1), pp. 294-298, 2006.
- [5] Wilfong, Walter Christopher, Chakravartula S. Srikanth, and Steven SC Chuang. In situ ATR and DRIFTSS studies of the nature of adsorbed CO₂ on tetraethylenepentamine films. *ACS Applied Materials & Interfaces*, 6(16), pp. 13617-13626, 2014.
- [6] X. He, et al. Surface Modification of Fumed Silica by Plasma Polymerization of Acetylene for PP/POE Blends Dielectric Nanocomposites. *Polymers* 11(12), pp. 1957, 2019.