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# Deposition of Ureido and Methacrylate Functionalities onto Silica Nanoparticles and Its Effect on the Properties of Polypropylene-Based Nanodielectrics

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**ABSTRACT** Surface modification of nanoparticles is often utilized to tailor the interfacial properties in dielectric nanocomposites. Introducing different functional groups to the nanoparticles' surface may induce localized states (traps) that can enhance the dielectric performance of the material depending on their density and energy levels. Furthermore, surface modification of the filler can affect the dispersion quality and crystallization of the nanocomposites which can ultimately alter the dielectric response of the material. In this study, functionalization of silica nanoparticles is demonstrated using 3-(trimethoxysilyl)propyl methacrylate (TMPM) and 1-[3-(trimethoxysilyl)propyl]urea (TMPU) as modifying agents. The effect of such modifications on the crystallization behavior, dispersion quality of the nanoparticles, as well as charge trapping and transport under a medium DC field is studied in nanocomposites based on polypropylene (PP)/ethylene-octene-copolymer (EOC) blends at 1% and 5% of filler concentrations. The results show that both ureido and methacrylate functional groups introduce localized states, but with different energy levels. Nitrogen containing ureido groups in TMPU tend to introduce deeper traps to the filler-polymer interfaces, compared to the methacrylate silane modification. Comparing the two types of surface functionalization, the ureido-functionalized silica resulted in a suppression of space charge formation at the interfaces under a medium DC electric field, despite the relatively larger mean cluster size of nanoparticles.

**INDEX TERMS** Surface functionalization, silica nanoparticles, dielectrics, nanocomposites, HVDC, electrical properties, insulation materials.

## I. INTRODUCTION

Nanodielectric materials attracted immense attention in the past few decades, being studied in a wide range of applications such as insulating materials, electronics, sensors etc [1]–[5]. Nanodielectrics, based on polypropylene (PP)

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blended with thermoplastic elastomers have shown not only promising electrical properties, but also undeniable potential in addressing the shortcomings of the conventional high voltage insulating material i.e. crosslinked polyethylene (XLPE) [6]. The absence of crosslinking by-products in PP-based nanodielectrics results in an improved space charge accumulation, and their thermoplastic nature allows for a more sustainable end-of-life for these materials [6]–[9]. This

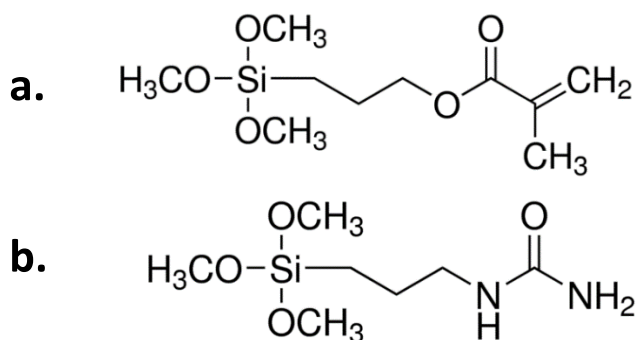
class of dielectric nanocomposites also exhibit good mechanical properties, comparable to XLPE, which makes them a reliable candidate for high voltage direct current (HVDC) cable insulation systems [10]–[12]. Recent studies have been focusing on different types of thermoplastic elastomers to be blended with PP for HVDC applications. In this regard, polypropylene/ethylene-octene copolymer (PP/EOC) blends are among the best candidates, due to their susceptibility to reduce space charge accumulation under high DC electric fields [13]–[15]. The improved properties of nanodielectrics are known to be a result of large interfacial zones introduced by the addition of nanoparticles (NPs) to the polymeric matrix [16]. Therefore, altering interfacial interactions within nanocomposites (NCs) is of crucial value in order to control their macroscopic dielectric properties [17], [18]. In case of insulating NCs, properties including conductivity, permittivity, breakdown strength, tracking resistance and space charge accumulation are shown to be highly influenced by the properties of the interfacial areas [19], [20]. Accordingly, engineering the surface properties of NPs, and consequently the interfacial zones within NCs, is a promising way for designing high performance nanodielectrics for insulation applications.

The addition of NPs results in electrical defects in the dielectric NCs [21], therefore, improving their dispersion in the polymer matrix can lead to improvements of the dielectric properties such as breakdown strength [22]. Several studies have reported the significance of filler dispersion in determining the properties of nanodielectrics [23]–[26]. Surface treatment of nanofillers is a promising way to improve dispersion qualities in NCs, and benefit from their large interfacial areas [27]. Accordingly, NPs dispersion can be influenced by the type of functional groups in the structure of the modifying agent. Moreover, altering the chemistry of the NPs surface can affect the morphological properties of the NCs, particularly in case of semi-crystalline polymers [28], [29]. Therefore, studying the morphological aspects of nanodielectrics is of great importance for tailoring their macroscopic dielectric properties.

Tailoring the chemical composition of the NPs surface can result in improvement of the dielectric properties of the NCs, not only by influencing their morphological aspects, but also by introducing electrically active functional groups to the filler-polymer interfaces [20], [22]. Filler functionalization can introduce new localized states into the nanodielectric, and consequently affect the charge trapping and transport as well as space charge phenomena in the system. In our previous studies [30]–[32], for instance, it was shown that grafting polar amino functional groups to the surface of silica NPs would hinder the interfacial polarization and formation of space charge at the interfaces in the corresponding NCs. These observations imply that the presence of nitrogen containing functional groups at the surface of NPs can induce such effect. Therefore, it is of interest to investigate the above hypothesis with a different type of nitrogen containing

functionality, and compare the properties to other types of modification.

In this study, the functionalization of silica NPs is demonstrated using 3-(trimethoxysilyl)propyl methacrylate (TMPM) and 1-[3-(trimethoxysilyl)propyl]urea (TMPU) as modifying agents (see Figure 1). Subsequently, the effect of such modifications on the crystallization behavior and dispersion quality of the NPs is studied in NCs based on polypropylene (PP)/ethylene-octene-copolymer (EOC) blends. The studied NCs are then subjected to dielectric measurements. Broadband dielectric spectroscopy (BDS) and thermally stimulated depolarization current (TSDC) tests are performed to analyze the alterations in charge trapping and transport as well as space charge formation in the aforementioned NCs, upon introducing methacrylate and ureido functional groups to the filler-polymer interfaces. Since the effective grafting density of the silanes is limited by their reactivity and the specific surface area of the NPs, higher concentrations of these functional groups in the system is only possible by increasing the filler content. Therefore, two different filler concentrations are studied for the modified samples, in order to further investigate the effect of these functional groups on the dielectric properties of the NCs.



**FIGURE 1.** Chemical structures of a) 3-(trimethoxysilyl)propyl methacrylate (TMPM) and b) 1-[3-(trimethoxysilyl)propyl]urea (TMPU).

## II. EXPERIMENTAL WORK

### A. SILICA MODIFICATION

AEROSIL 200 silica NPs were provided by Evonik Industries (Germany). The silica NPs were treated in liquid phase in a glass round bottom flask immersed in an oil heating bath equipped with a mechanical stirrer, cooler and thermometer. 3-(trimethoxysilyl)propyl methacrylate (TMPM) and 1-[3-(trimethoxysilyl)propyl]urea (TMPU) were purchased from Sigma-Aldrich (Germany), and used as the modifying agent without further purification. Toluene (Boom Chemicals, the Netherlands) was used as the reaction medium, and a stoichiometric amount of water was added to the reactor to hydrolyze the added amount of silane. The modification reaction took place at 80 °C for 24h. The silica NPs were stored in an oven at 120 °C overnight prior to modification, and cleaned after modification via Soxhlet extraction using

ethanol as the solvent. The latter was done in order to remove any unreacted precursor and reaction by-product from the silica samples.

### B. NANOPARTICLE CHARACTERIZATION

Thermogravimetric Analysis (TGA) was performed to quantify the level of modification in terms of grafting density by TGA 550 (TA Instruments, USA). 2-3 mg of the silica NPs were heated from room temperature to 850 °C with a rate of 20 °C/min under air atmosphere, while measuring the mass of the sample. Diffuse reflectance Fourier transform infrared spectroscopy (DRIFTS) was utilized using a Perkin Elmer (USA) Spectrum 100 with a diffuse reflectance accessory. The samples were prepared by mixing the NPs with potassium bromide (KBr; 99+%, FTIR grade, Harrick Scientific Corporation, USA) as background. The spectra were recorded from 4000-400  $\text{cm}^{-1}$  and averaged over 128 scans, using a resolution of 4.0  $\text{cm}^{-1}$ .

### C. PREPARATION OF THE NANOCOMPOSITES

Nanocomposites based on polypropylene (PP, 3 w% ethylene)/ ethylene-octene copolymer (EOC, 17 w% octene) blends were prepared by the addition 1 w% and 5 w% of the silica NPs as well as a phenolic/phosphite antioxidant package to the polymer matrix in a twin-screw micro extruder (Haake MiniLab Rheomix CTW5, Thermo Fisher Scientific, USA) at 230 °C and 100 rpm, and subsequently injected into a square mold with dimensions of 26×26 × 0.5 mm, using a Haake MiniJet Pro Piston Injection Molding System (Thermo Fisher Scientific, USA).

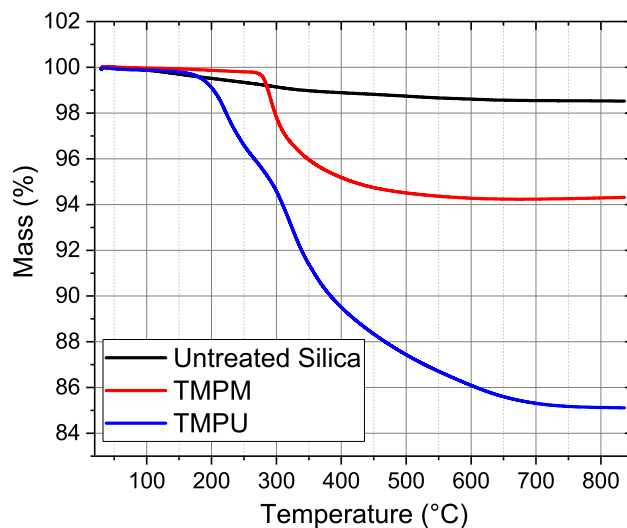
### D. CHARACTERIZATION OF NANOCOMPOSITES

#### 1) MORPHOLOGY AND CRYSTALLINITY ANALYSIS

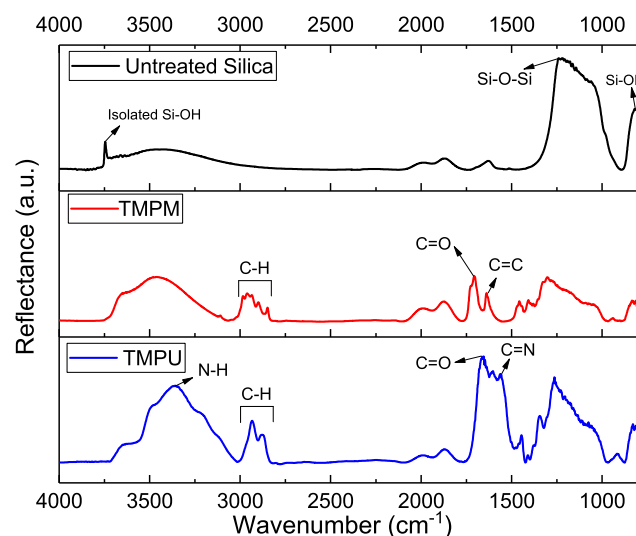
Scanning Electron Microscopy (SEM) was performed on the dielectric NCs using a Jeol (Japan) JSM-6400 to study the NP dispersion and polymer blend morphology. Sample preparation was done both with and without gold sputtering in order to visualize the particles and the polymer phases in more detail. The silica cluster size distribution in the studied NCs was analyzed using open-source ImageJ software with Trainable Weka Segmentation plugin [33]. Differential Scanning Calorimetry (DSC) was done by means of a Netzsch (Germany) DSC 214 Polyma. Specimens were subjected to two heating/cooling cycles from -50 °C to 200 °C. The rate of heating/cooling was set at 3 °C/min, to be comparable to the heating rate in TSDC measurements.

#### 2) THERMALLY STIMULATED DEPolarization CURRENT (TSDC)

Thermally Stimulated Depolarization Current (TSDC) was utilized to analyze the charge trapping and transport phenomena and space charge formation in the NCs under a high direct current (DC) field. The samples were prepared by depositing circular gold (Au) electrodes (100 nm in thickness) on

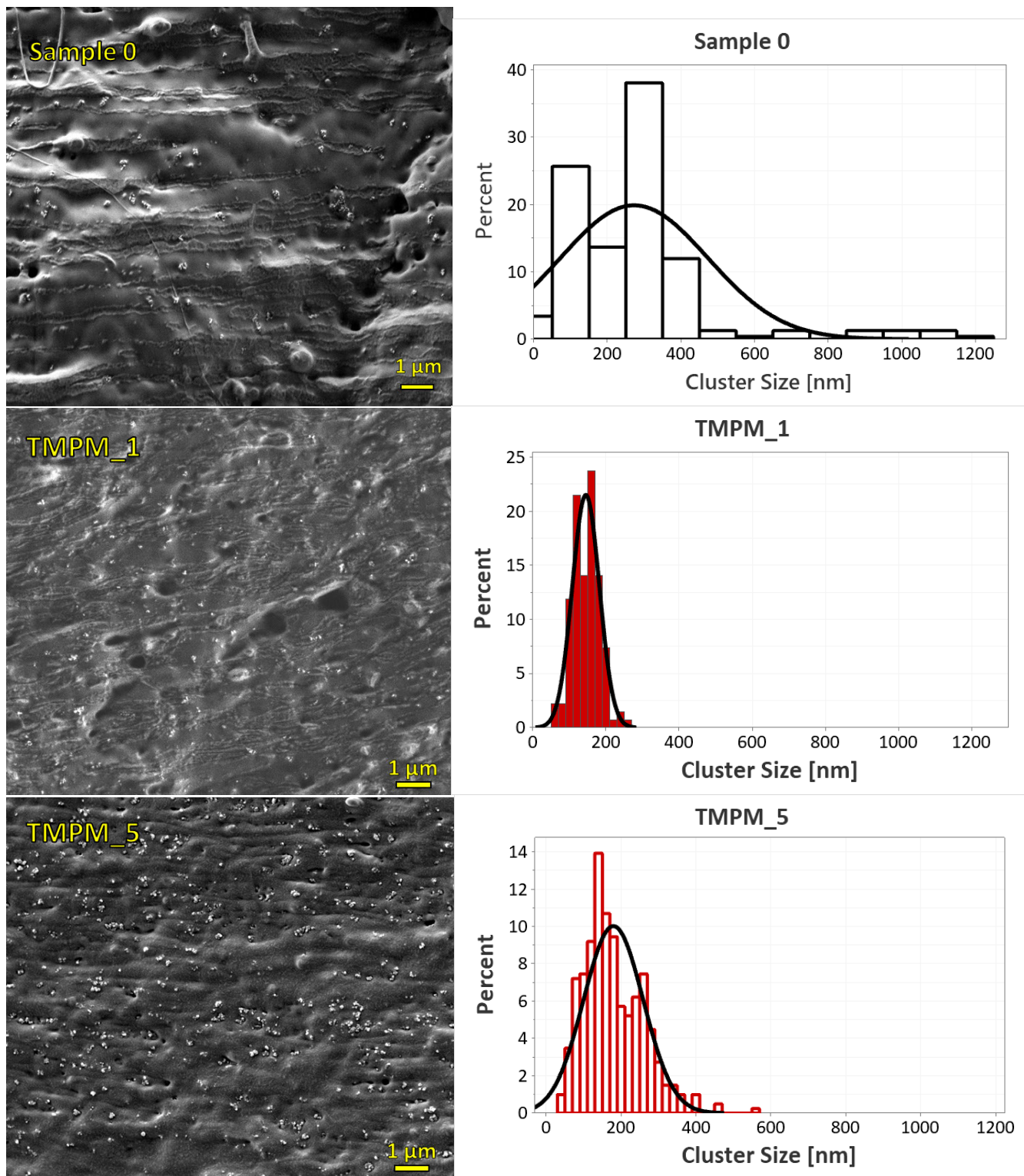


**FIGURE 2.** TGA thermograms of the unmodified and modified silica NPs. The main mass loss step is related to the release of the grafted precursor.

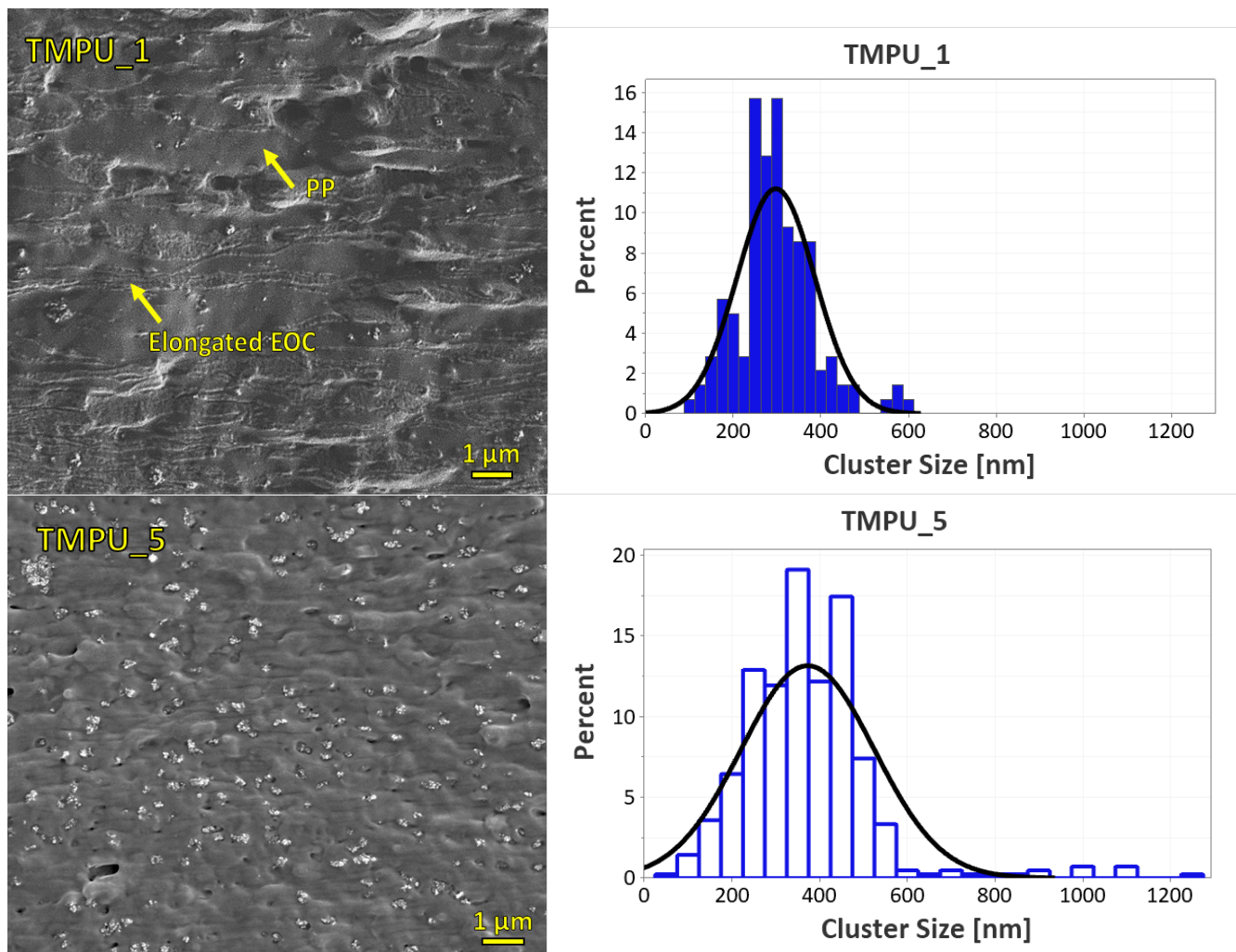


**FIGURE 3.** DRIFTS spectra for the modified and unmodified NPs.

both sides of each NC specimen by e-beam evaporation under high vacuum. Subsequently, the samples were short circuited and kept in a vacuum desiccator overnight prior to the measurements to remove any stored charge during evaporation. The TSDC tests were performed by rapidly heating up the NCs to the poling temperature of 70 °C, and then a 3 kV/mm DC electric field was applied for 20 minutes under isothermal conditions. After the poling step, the samples were cooled down to -50 °C while the electric field was still on. This would force the polarized species and injected charges to remain in the specimen. The samples were then short-circuited and linearly heated up to 140 °C at 3 °C/min, while the depolarization current being measured by an electrometer 6517B (Keithley Instruments, USA).



**FIGURE 4.** SEM images of the NCs' cross section to visualize the silica dispersion and blend morphology, samples TPM\_5 and TPMU\_5 were treated by gold sputtering for a better distinction of the NPs, while Sample 0, TPM\_1 and TPMU\_1 were measured without gold sputtering to visualize the polymer phases in the blend.



**FIGURE 4.** (Continued.) SEM images of the NCs' cross section to visualize the silica dispersion and blend morphology, samples TMPM\_5 and TMPU\_5 were treated by gold sputtering for a better distinction of the NPs, while Sample 0, TPM\_1 and TMPU\_1 were measured without gold sputtering to visualize the polymer phases in the blend.

### 3) BROADBAND DIELECTRIC SPECTROSCOPY (BDS)

To further analyze dielectric relaxation processes in the NCs with respect to the frequency of the applied field, the real ( $\epsilon'_r$ ) and imaginary parts ( $\epsilon''_r$ ) of permittivity (as in (1)) were measured directly after the TSDC measurements, using a Novocontrol (Germany) Alpha-A dielectric analyzer in a broad frequency range of 10-2-106 Hz and under an applied voltage of 1 V. All the measurements were conducted at the ambient environment (23 °C, RH ~ 35%).

$$\epsilon_r^* = \epsilon'_r + i\epsilon''_r \quad (1)$$

## III. RESULTS AND DISCUSSIONS

### A. CHARACTERIZATION OF THE NANOPARTICLES

Figure 2 presents the TGA thermograms of both modified samples along with the untreated silica. The 1.5% mass loss of the untreated silica is due to the release of physisorbed and chemisorbed water. The latter occurs via siloxanation of silanol groups on the silica surface, and accounts for a

density of 4 SiOH/nm<sup>2</sup> [34]. Silane modification results in the consumption of physisorbed and chemisorbed water on the silica surface. Regarding the modified silica, one can calculate the silane grafting density (GD) from the TGA mass loss according to (2).

$$GD\left(\frac{\text{mmol}}{\text{g silica}}\right) = \frac{\Delta W \times 100}{M_W \times (100 - \Delta W)} \quad (2)$$

where  $\Delta W$  is the mass loss of the thermogram in the temperature ranges of 270 °C to 850 °C, and 200 °C to 850 °C for the TPM and TPU-modified silica, respectively, and  $M_W$  is the molecular weight of the silane.

TPM and TPU-modified silicas exhibit mass losses of 5.8% and 15%, which account for grafting densities of 0.25  $\frac{\text{mmol}}{\text{g silica}}$  and 0.79  $\frac{\text{mmol}}{\text{g silica}}$ , respectively. Due to the hydrogen bond interactions between both silanes and the silanol groups on the silica surface, both reactions are expected to proceed in a self-catalyzing manner [35]. The Si-O-H...N hydrogen bonds in the case of TPU, however, are generally

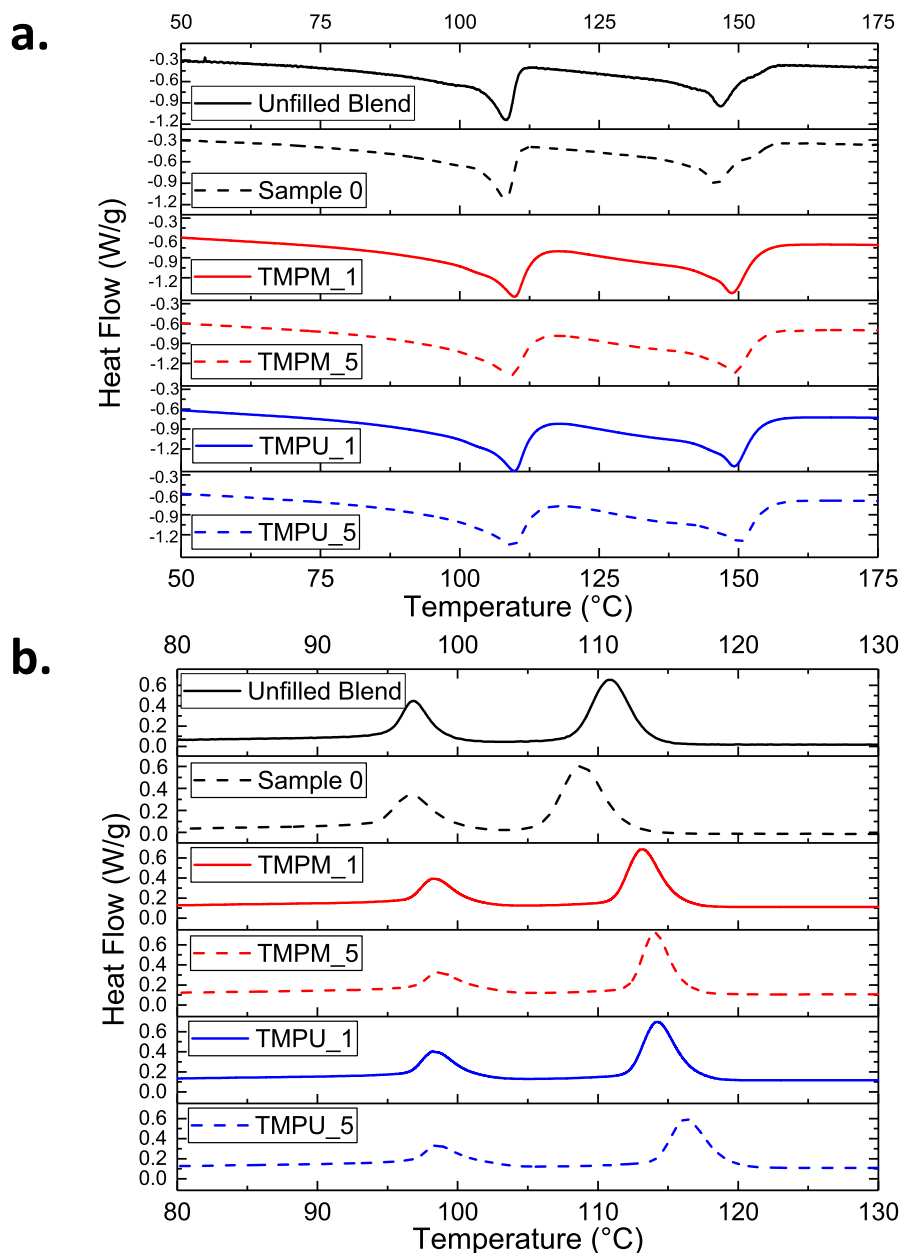
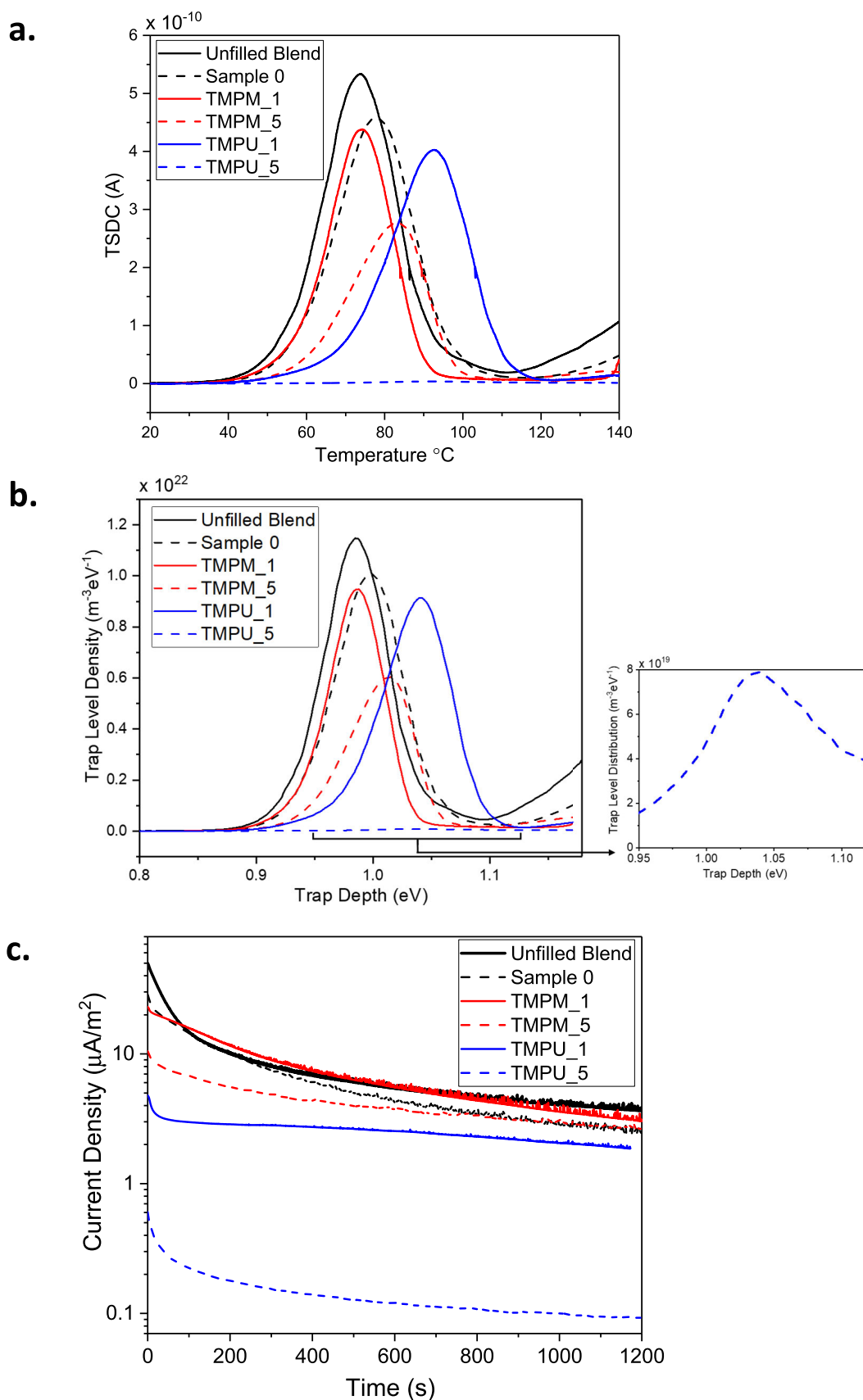


FIGURE 5. a) Melting and b) crystallization spectra of the studied NCs.

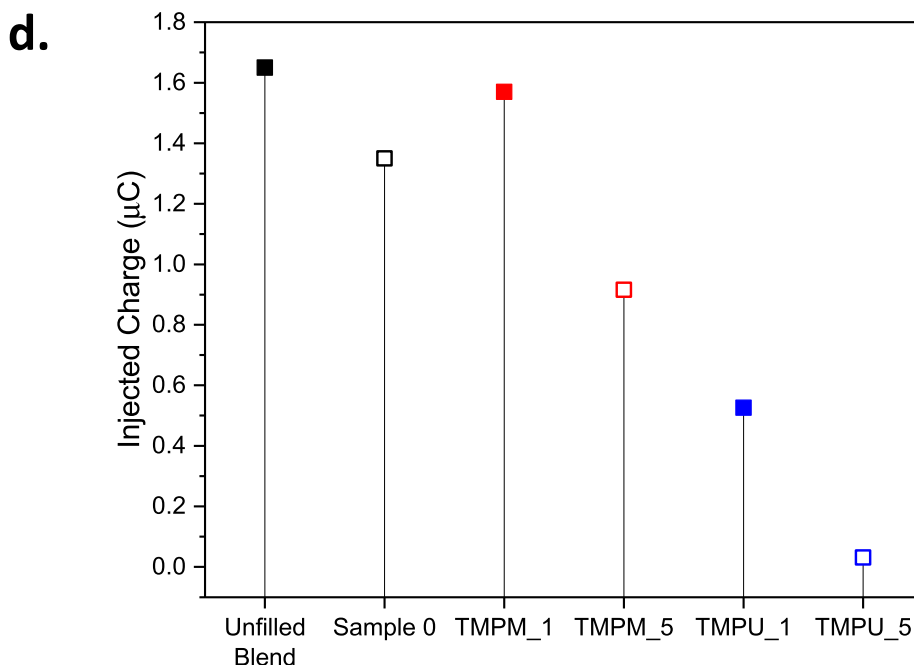
stronger than those of the Si-O-H...O for TPM, due to the higher electronegativity of nitrogen [36]. This may be a reason for the higher grafting density of TPU on silica compared to that of TPM. Furthermore, the stronger hydrogen bond interactions between the silane molecules in TPU may lead to oligomerization of this silane and formation of longer chains. This can manifest itself as multiple steps in the TGA thermograms. The second mass loss step in case of TPU-modified silica starting from  $\sim 300$  °C may be due to this reason.

The DRIFTS spectra in Figure 3 represent the chemistry of the surface before and after modification, and confirm the successful deposition of each silane onto the nanoparticles.

It is clear that the band at  $3750\text{ cm}^{-1}$  corresponding to the isolated silanol groups disappears upon modification of the silica. This is indicative of effective coverage of nanoparticles upon deposition of the silane. The TPM-modified silica exhibits the characteristic bands of methacrylate groups, C=C and C=O at  $1640\text{ cm}^{-1}$  and  $1690\text{ cm}^{-1}$ , respectively [37]. The C-H stretching vibration bands, from  $2800\text{ cm}^{-1}$  to  $3000\text{ cm}^{-1}$ , appear in both TPM and TPU spectra, which are mostly attributable to the propyl spacer chain in both silanes. The TPU spectrum contains the characteristic bands related to the ureido groups, C=N, C=O and N-H, appearing at  $1560\text{ cm}^{-1}$ ,  $1690\text{ cm}^{-1}$  and  $3350\text{ cm}^{-1}$ , respectively [38].



**FIGURE 6.** a) TSDC spectra, b) occupied trap level distribution and density, c) current density during poling and d) amount of injected charge during poling for all NCs and the unfilled reference.



**FIGURE 6.** (Continued.) a) TSDC spectra, b) occupied trap level distribution and density, c) current density during poling and d) amount of injected charge during poling for all NCs and the unfilled reference.

### B. DISPERSION AND CRYSTALLINITY ANALYSIS

Dispersion of the filler in nanocomposite systems is one of the key factors that determines some of their electrical properties, e.g. space charge accumulation and breakdown strength [39]. Besides, it has been shown that the introduction of nanoparticles with poor dispersion can result in a drastic reduction of some mechanical properties, such as elongation at break [12]. Therefore, filler dispersion of the NCs under study are analyzed using SEM. Cross-sectional SEM images along with histograms of particle size distributions are presented in Figure 4. The mean silica cluster size for untreated silica in the PP/EOC matrix (Sample 0) with 1% filler concentration is approximately 300 nm. With the same silica concentration, a mean cluster size around 160 nm is achieved with the TPM modification, indicating a relatively better NPs dispersion with this type of treatment. Whereas, TMPU-modified silica exhibits a mean cluster size of 300 nm. This can be due to the nitrogen containing ureido groups deposited on the NPs surface interacting strongly via hydrogen bonds resulting in relatively larger clusters compared to TPM. Another reason can be the oligomerization of the ureido silane, binding the particles by strong covalent bonds. The much higher grafting density of TMPU shown in Figure 2 is an evidence for this oligomerization. Increasing the filler content to 5% results in relatively bigger clusters for both types of modification as TPM<sub>5</sub> and TMPU<sub>5</sub> exhibit mean aggregate sizes of around 200 nm and 400 nm, respectively. The polymer blend exhibits a well dispersed two-phase morphology, with the EOC domains elongated along the direction of the flow in the mold (see TPM<sub>1</sub> and TMPU<sub>1</sub>). This is not visible in the TPM<sub>5</sub> and TMPU<sub>5</sub> images

since these samples were gold sputtered to achieve higher resolutions.

The melting and crystallization behavior of the studied NCs, characterized by DSC, are presented in Figure 5. The melting spectra exhibit two distinct peaks at 108 °C and 147 °C, corresponding to melting temperatures of EOC and PP components of the blend, respectively. While there is no significant differences between the melting curves of all samples (Figure 5a), the non-isothermal crystallization of the NCs undergoes meaningful changes upon incorporation of the NPs and their modification (Figure 5b). Two crystallization peaks are observed in the unfilled blend spectrum, at 110 °C and 97 °C, related to the PP and EOC crystalline domains. Table 1 presents the DSC parameters calculated from the plots. It is evident that upon incorporation of the unmodified NPs, the onset of crystallization decreases despite the expected nucleating effect of NPs [40], [41]. This is likely due to the adsorption of the polar antioxidant particles onto the silica surface, resulting in fewer nucleating sites in the matrix [42], [43]. For the same reason, the degree of crystallinity is not affected by the addition of the untreated silica. Nevertheless, the modification of NPs results in a significant increase of the onset of crystallization by 4 to 7 °C, as well as of the degree of crystallization, which indicates the higher nucleating effect of the silica upon modification. The degree of supercooling ( $\Delta T$ ) can be defined as the difference between the melting and crystallization peak temperatures at a given cooling rate. This is calculated for the PP domains and presented in Table 1. It is evident that the modification of silica results in lower  $\Delta T$  which is another indication of a more efficient nucleation in the modified NCs [44].



**TABLE 1.** DSC parameters calculated for different NC samples; significant differences are observed upon addition and modification of the silica NPs.

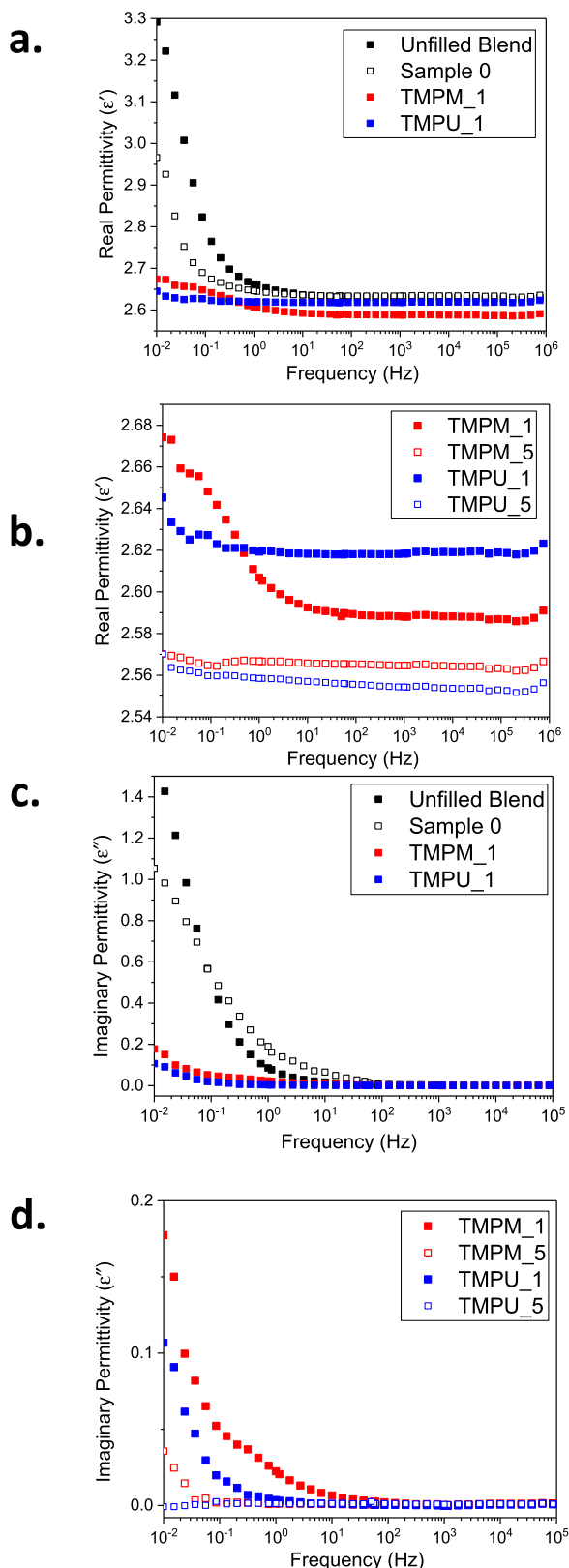
	Onset of Crystallization (°C)	Enthalpy of Melting (J/g)	Degree of Crystallinity (%)	Degree of Supercooling $\Delta T$ (°C)
Unfilled Blend	114	77.3	31	36.2
Sample 0	112	74.9	30	37.4
TMPM_1	116	109.7	44	35.9
TMPM_5	117	104.1	42	34.9
TMPU_1	117	110.9	44	34.7
TMPU_5	119	104.3	42	33.8

Moreover, increasing the filler content from 1% to 5% in both, TMPM and TMPU cases, results in a decrease in the degree of crystallization by 2%. This can be due to the slight increase in cluster size when increasing the filler content, which can result in a lower degree of crystallization [40].

### C. THERMALLY STIMULATED DEPolarization CURRENT (TSDC)

The TSDC spectra of all studied NCs are presented in Figure 6a. In principle, TSDC is able to detect low-frequency relaxations in the material by thermal stimulation of a charged sample and monitoring the discharge current [45]. The discharge current at elevated temperatures, generally above the glass transition temperature of the polymer, can be attributed to the relaxation of space charge accumulated at the interfaces within the NC. Accordingly, the temperature of the peak and the corresponding current can be respectively correlated to the depth and the density of occupied charge traps in the NC using a numerical method based on a model where a continuous distribution of (electron) traps is considered [46]. This is presented in Figure 6b. It can be seen that the unfilled blend exhibits a space charge relaxation peak at 75 °C corresponding to a trap depth distribution around 0.98 eV. These are the localized states resulting from the structural defects in the polymer matrix as well as the defects related to the introduction of antioxidant particles. The addition of untreated silica (Sample 0) slightly shifts the traps to higher energy levels indicating new localized states existing in the NPs lattice structure and at the filler-polymer interfaces. With 1% of filler concentration, TMPM-modified silica introduces shallower traps compared to the untreated NPs. Evidently, the methacrylate groups on the NP surface induce relatively shallow trapping states, whereas the ureido functionality in TMPU-modified silica creates deep traps with energies around 1.05 eV. The deepening of the trapping states in case of TMPU is very similar to the effect of

amino functionalized NPs in our previous studies [31], [32]. This can lead to a similar conclusion that nitrogen containing functional groups can induce deep traps at the filler-polymer interfaces. Moreover, a lower density of occupied traps is observed for the TMPU-modified silica compared to TMPM. This indicates that with the presence of ureido groups at the interfaces, the net amount of charge injected to the NC is reduced which is better visualized in Figure 6d. This is also in-line with our previous observations and indicates the hampering of space charge formation (under relatively low fields) in the presence of nitrogen containing functional groups at the filler-polymer interfaces which were attributed to the large density of valence states around the  $-NH_2$  moiety [31], [32], [47]. This suggests that the space charge phenomena in nanodielectrics can significantly be affected by the change in the electronic structure of the filler surface. This would enable to tailor the filler-polymer interfaces in the nanodielectric without inducing chemical bonds between the filler and the polymer. Increasing the filler concentration to 5% results in a reduction of occupied trap densities compared to the 1% NCs. This reduction is most significant in case of TMPU\_5, where the trap density is three orders of magnitude smaller compared to TMPU\_1 (Figure 6b). As was shown in the SEM analysis, the TMPM modification resulted in a better dispersion of the NPs compared to TMPU. Nevertheless, the TMPU-modified NCs exhibit less susceptibility for space charge formation under electric fields. This suggests that the charge transport and space charge phenomena in these systems are more significantly affected by the chemical composition of the NPs' surface, rather than their dispersion quality. Figure 6c presents the charging current densities measured for all the studied samples during the poling step of the TSDC test. In general, increasing the filler concentration results in an increased number of conduction pathways due to the overlapping of the interfacial areas [48] which would potentially result in an increased current density.



**FIGURE 7.** a), b) real and c), d) imaginary parts of permittivity for the modified samples compared to the unfilled and untreated references.

However, in our case, due to the surface functionalization and the introduction of relatively deep localized states at the filler-polymer interfaces, the current density is reduced upon

increasing the filler content. This suggests that at higher filler concentrations, even though more conduction pathways are likely accessible to the charge carriers, the trapping processes prevail. This results in a lower mobility of the charge carriers and a reduced current density in the NCs, as can be seen in Figure 6c. This effect is more clearly observed in comparing TPM\_5 and TPMU\_5 NCs. The reduction in current density compared to their 1% counterparts is more pronounced in case of TPMU modification. This is due to the presence of deeper localized states which results in a lower mobility of charge carriers, and hence, lower current density for TPMU compared to TPM.

**D. BROADBAND DIELECTRIC SPECTROSCOPY (BDS)**

Broadband dielectric spectroscopy (BDS) is a powerful method to study the permittivity and frequency-dependent relaxations in a nanodielectric, and can provide information about interfacial polarizations and space charge formation in the material. Figure 7a and 7b present the variations in the real part of permittivity for the TPM and TPMU-modified NCs compared to the reference samples. In the frequency range above 1Hz, it is clear that with 1% of filler concentration the TPM modification exhibits lower permittivity values compared to the TPMU-modified NCs and the reference samples. This can be due to the higher grafting density of the TPMU silane on the NPs which results in a higher number of polarizable species in the system, and hence, higher permittivity. Increasing the filler content to 5%, on the one hand, decreases the permittivity of the NCs, compared to their 1% counterparts. On the other hand, TPMU\_5 appears at lower levels of real permittivity compared to TPM\_5. The ureido groups in TPMU can interact strongly with each other and with other polar species in the system (e.g. antioxidant particles) via hydrogen bonds, and when incorporated at higher concentrations, can hinder the polarization mechanisms in the NC.

At the lower range of frequencies (below 1 Hz), a significant rise is observed in both parts of permittivity for the unfilled blend and Sample 0. This phenomenon is generally related to the occurrence of interfacial polarizations or Maxwell-Wagner (space charge) relaxations which can lead to breakdown under high fields [49], [50]. It is clear that while the reference samples exhibit a significant amount of these relaxations, the introduction of either modifying agent to the NPs results in a decrease in this low frequency rise, suggesting lower susceptibility to space charge formation as a result of filler surface modification. This effect is pronounced when increasing the filler concentration to 5%, when only a marginal increase is observed in the low frequency range for both modified samples. It can be noted that the TPMU modification results in lower interfacial polarizations compared to the TPM. This is likely due to two reasons: firstly, the higher grafting density of TPMU results in a higher number of functional groups at the filler-polymer interface, which induces a pronounced effect in suppressing the space charge relaxations. Secondly, it has been shown that the nitrogen

containing functional groups are prone to suppress space charge formation in NCs [22], [31], [32]. Therefore, it can be assumed that the ureido groups in the TMPU structure can induce the same effect.

#### IV. CONCLUSION

Successful modification of silica NPs was demonstrated using 3-(trimethoxysilyl)propyl methacrylate (TMPM) and 1-[3-(trimethoxysilyl)propyl]urea (TMPU) as modifying agents. Subsequently, nanodielectrics based on polypropylene (PP)/ethylene-octene-copolymer (EOC) blends were analyzed. A two-phase morphology, typical for this polymer blend, was observed. Filler dispersion was shown to be improved when TMPM-modified NPs were incorporated into the polymer matrix. The ureido and methacrylate functional groups introduced localized states with different energy levels. Nitrogen containing ureido groups in TMPU tend to induce deeper traps to the filler-polymer interfaces with a lower density, compared to the methacrylate silane modification. Furthermore, the TMPU modification hindered the formation of space charge at the interfaces more effectively than TMPM, even though the latter resulted in a relatively better dispersion of NPs. This suggests that nitrogen containing functional groups are more beneficial for modification of NPs, in order to reduce interfacial polarizations in NCs. Increasing the filler concentration resulted in further reduction of occupied trap densities, and hence a reduced space charge formation for both types of modification.

#### REFERENCES

- [1] L. S. Schadler and J. K. Nelson, "Polymer nanodielectrics—Short history and future perspective," *J. Appl. Phys.*, vol. 128, no. 12, Sep. 2020, Art. no. 120902.
- [2] T. Tanaka and T. Imai, "Advances in nanodielectric materials over the past 50 years," *IEEE Elect. Insul. Mag.*, vol. 29, no. 1, pp. 10–23, Jan. 2013.
- [3] M. F. Frechette, M. L. Trudeau, H. D. Alamdari, and S. Boily, "Introductory remarks on nanodielectrics," *IEEE Trans. Dielectr. Electr. Insul.*, vol. 11, no. 5, pp. 808–818, Oct. 2004.
- [4] A. Lahav, "Surface plasmon sensor with enhanced sensitivity using top nano dielectric layer," *J. Nanophoton.*, vol. 3, no. 1, Jan. 2009, Art. no. 031501.
- [5] S. Ju, K. Lee, M.-H. Yoon, A. Facchetti, T. J. Marks, and D. B. Janes, "High performance ZnO nanowire field effect transistors with organic gate nanodielectrics: Effects of metal contacts and ozone treatment," *Nanotechnology*, vol. 18, no. 15, Apr. 2007, Art. no. 155201.
- [6] B. Dang, Q. Li, Y. Zhou, J. Hu, and J. He, "Suppression of elevated temperature space charge accumulation in polypropylene/elastomer blends by deep traps induced by surface-modified ZnO nanoparticles," *Compos. Sci. Technol.*, vol. 153, pp. 103–110, Dec. 2017.
- [7] B. X. Du, H. Xu, J. Li, and Z. Li, "Space charge behaviors of PP/POE/ZnO nanocomposites for HVDC cables," *IEEE Trans. Dielectr. Electr. Insul.*, vol. 23, no. 5, pp. 3165–3174, Oct. 2016.
- [8] N. Tortorella and C. L. Beatty, "Morphology and crystalline properties of impact-modified polypropylene blends," *Polym. Eng. Sci.*, vol. 48, no. 8, pp. 1476–1486, Aug. 2008.
- [9] J. Ying, X. Xie, S. Peng, H. Zhou, and D. Li, "Morphology and rheology of PP/POE blends in high shear stress field," *J. Thermoplastic Compos. Mater.*, vol. 31, no. 9, pp. 1263–1280, Sep. 2018.
- [10] Y. Gao, J. Li, G. Chen, T. Han, and B. Du, "Compatibility dependent space charge accumulation behavior of polypropylene/elastomer blend for HVDC cable insulation," *IEEE Trans. Dielectr. Electr. Insul.*, vol. 27, no. 3, pp. 947–955, Jun. 2020.
- [11] Y. Zhou, J. He, J. Hu, X. Huang, and P. Jiang, "Evaluation of polypropylene/polyolefin elastomer blends for potential recyclable HVDC cable insulation applications," *IEEE Trans. Dielectr. Electr. Insul.*, vol. 22, no. 2, pp. 673–681, Apr. 2015.
- [12] J. Diao, X. Huang, Q. Jia, F. Liu, and P. Jiang, "Thermoplastic isotactic polypropylene/ethylene-octene polyolefin copolymer nanocomposite for recyclable HVDC cable insulation," *IEEE Trans. Dielectr. Electr. Insul.*, vol. 24, no. 3, pp. 1416–1429, Jun. 2017.
- [13] B. Dang, J. He, J. Hu, and Y. Zhou, "Large improvement in trap level and space charge distribution of polypropylene by enhancing the crystalline–amorphous interface effect in blends," *Polym. Int.*, vol. 65, no. 4, pp. 371–379, Apr. 2016.
- [14] S. Hölzer, M. Menzel, Q. Zia, U. S. Schubert, M. Beiner, and R. Weidisch, "Blends of ethylene–octene copolymers with different chain architectures—morphology, thermal and mechanical behavior," *Polymer*, vol. 54, no. 19, pp. 5207–5213, Aug. 2013.
- [15] X. He, P. Seri, I. Rytoluoto, R. Anyszka, A. Mahtabani, H. Naderiallaf, M. Niittymäki, E. Saarimäki, C. Mazel, G. Perego, K. Lahti, M. Paajanen, W. Dierkes, and A. Blume, "Dielectric performance of silica-filled nanocomposites based on miscible (PP/PP-HI) and immiscible (PP/EOC) polymer blends," *IEEE Access*, vol. 9, pp. 15847–15859, 2021.
- [16] J. K. Nelson, *Dielectric Polymer Nanocomposites*. USA: Springer, 2010.
- [17] T. J. Lewis, "Nanometric dielectrics," *IEEE Trans. Dielectr. Electr. Insul.*, vol. 1, no. 5, pp. 812–825, Oct. 1994.
- [18] T. Tanaka, M. Kozako, N. Fuse, and Y. Ohki, "Proposal of a multi-core model for polymer nanocomposite dielectrics," *IEEE Trans. Dielectr. Electr. Insul.*, vol. 12, no. 4, pp. 669–681, Aug. 2005.
- [19] L. Zhang, M. M. Khani, T. M. Krentz, Y. Huang, Y. Zhou, B. C. Benicewicz, J. K. Nelson, and L. S. Schadler, "Suppression of space charge in crosslinked polyethylene filled with poly(stearyl methacrylate)-grafted SiO<sub>2</sub> nanoparticles," *Appl. Phys. Lett.*, vol. 110, no. 13, Mar. 2017, Art. no. 132903.
- [20] M. Roy, J. K. Nelson, R. K. MacCrone, and L. S. Schadler, "Candidate mechanisms controlling the electrical characteristics of silica/XLPE nanodielectrics," *J. Mater. Sci.*, vol. 42, no. 11, pp. 3789–3799, Jun. 2007.
- [21] V. Kasperovich, K. Wong, G. Tikhonov, and V. V. Kresin, "Electron capture by the image charge of a metal nanoparticle," *Phys. Rev. Lett.*, vol. 85, no. 13, pp. 2729–2732, Sep. 2000.
- [22] D. Ma, T. A. Hugener, R. W. Siegel, A. Christerson, E. Mårtensson, C. Önnby, and L. S. Schadler, "Influence of nanoparticle surface modification on the electrical behaviour of polyethylene nanocomposites," *Nanotechnology*, vol. 16, no. 6, pp. 724–731, Jun. 2005.
- [23] S. Singha and M. J. Thomas, "Influence of filler loading on dielectric properties of epoxy-ZnO nanocomposites," *IEEE Trans. Dielectr. Electr. Insul.*, vol. 16, no. 2, pp. 531–542, Apr. 2009.
- [24] M. Kozako, S. Yamano, R. Kido, Y. Ohki, M. Kohtoh, S. Okabe, and T. Tanaka, "Preparation and preliminary characteristic evaluation of epoxy/alumina nanocomposites," in *Proc. Int. Symp. Electr. Insulating Mater. (ISEIM)*, Jun. 2005, pp. 231–234.
- [25] C. Calebrese, L. Hui, L. Schadler, and J. Nelson, "A review on the importance of nanocomposite processing to enhance electrical insulation," *IEEE Trans. Dielectr. Electr. Insul.*, vol. 18, no. 4, pp. 938–945, Aug. 2011.
- [26] D. Tan, E. Tuncer, Y. Cao, and P. Irwin, "Nanofiller dispersion in polymer dielectrics," in *Proc. Annu. Rep. Conf. Electr. Insul. Dielectric Phenomena*, Oct. 2012, pp. 916–918.
- [27] T. Tanaka, G. C. Montanari, and R. Mulhaupt, "Polymer nanocomposites as dielectrics and electrical insulation—perspectives for processing technologies, material characterization and future applications," *IEEE Trans. Dielectr. Electr. Insul.*, vol. 11, no. 5, pp. 763–784, Oct. 2004.
- [28] D. Malec, V. H. Truong, R. Essolbi, and T. G. Hoang, "Carrier mobility in LDPE at high temperature and pressure," *IEEE Trans. Dielectr. Electr. Insul.*, vol. 5, no. 2, pp. 301–303, Apr. 1998.
- [29] D. Ma, Y. A. Akpalu, Y. Li, R. W. Siegel, and L. S. Schadler, "Effect of Titania nanoparticles on the morphology of low density polyethylene," *J. Polym. Sci. B, Polym. Phys.*, vol. 43, no. 5, pp. 488–497, 2005.
- [30] R. Anyszka, X. He, A. Mahtabani, W. K. Dierkes, and A. Blume, "Effective surface functionalization of fumed silica with NBR telechelic oligomer for high-voltage polyolefin-based dielectric composites," in *Proc. Nordic Insul. Symp.*, no. 26, 2019, pp. 118–122.

- [31] A. Mahtabani, I. Rytöluoto, R. Anyszka, X. He, E. Saarimäki, K. Lahti, M. Paajanen, W. Dierkes, and A. Blume, "On the silica surface modification and its effect on charge trapping and transport in PP-based dielectric nanocomposites," *ACS Appl. Polym. Mater.*, vol. 2, no. 8, pp. 3148–3160, Aug. 2020.
- [32] X. He, I. Rytöluoto, R. Anyszka, A. Mahtabani, E. Saarimäki, K. Lahti, M. Paajanen, W. Dierkes, and A. Blume, "Silica surface-modification for tailoring the charge trapping properties of PP/POE based dielectric nanocomposites for HVDC cable application," *IEEE Access*, vol. 8, pp. 87719–87734, 2020.
- [33] I. Arganda-Carreras, V. Kaynig, C. Rueden, K. W. Eliceiri, J. Schindelin, A. Cardona, and H. S. Seung, "Trainable weka segmentation: A machine learning tool for microscopy pixel classification," *Bioinformatics*, vol. 33, no. 15, pp. 2424–2426, Aug. 2017.
- [34] A. Mahtabani, D. La Zara, R. Anyszka, X. He, M. Paajanen, J. R. van Ommen, W. Dierkes, and A. Blume, "Gas phase modification of silica nanoparticles in a fluidized bed: Tailored deposition of amino-propylsiloxane," *Langmuir*, vol. 37, no. 15, pp. 4481–4492, Apr. 2021.
- [35] M.-C. B. Salon, P.-A. Bayle, M. Abdelmouleh, S. Boufi, and M. N. Belgacem, "Kinetics of hydrolysis and self condensation reactions of silanes by NMR spectroscopy," *Colloids Surf. A, Physicochemical Eng. Aspects*, vol. 312, nos. 2–3, pp. 83–91, Jan. 2008.
- [36] S. J. Grabowski, "Ab initio calculations on conventional and unconventional hydrogen bonds study of the hydrogen bond strength," *J. Phys. Chem. A*, vol. 105, no. 47, pp. 10739–10746, Nov. 2001.
- [37] R. H. Halvorson, R. L. Erickson, and C. L. Davidson, "The effect of filler and silane content on conversion of resin-based composite," *Dental Mater.*, vol. 19, no. 4, pp. 327–333, Jun. 2003.
- [38] C. Xie, X. Zeng, W. Fang, X. Lai, and H. Li, "Effect of alkyl-disubstituted ureido silanes with different alkyl chain structures on tracking resistance property of addition-cure liquid silicone rubber," *Polym. Degradation Stability*, vol. 142, pp. 263–272, Aug. 2017.
- [39] Y. Zhou, J. He, J. Hu, and B. Dang, "Surface-modified MgO nanoparticle enhances the mechanical and direct-current electrical characteristics of polypropylene/polyolefin elastomer nanodielectrics," *J. Appl. Polym. Sci.*, vol. 133, no. 1, pp. 42863–42873, Jan. 2016.
- [40] C. Saujanya and S. Radhakrishnan, "Structure development and crystallization behaviour of PP/nanoparticulate composite," *Polymer*, vol. 42, no. 16, pp. 6723–6731, Jul. 2001.
- [41] V. Vladimirov, C. Betchev, A. Vassiliou, G. Papageorgiou, and D. Bikaris, "Dynamic mechanical and morphological studies of isotactic polypropylene/fumed silica nanocomposites with enhanced gas barrier properties," *Compos. Sci. Technol.*, vol. 66, no. 15, pp. 2935–2944, Dec. 2006.
- [42] A. Mahtabani, X. He, I. Rytöluoto, K. Lahti, M. Paajanen, E. Saarimäki, R. Anyszka, W. Dierkes, and A. Blume, "Effect of silica modification on charge trapping behavior of PP blend/silica nanocomposites," in *Proc. 2nd Int. Conf. Electr. Mater. Power Equip. (ICEMPE)*, Apr. 2019, pp. 241–245.
- [43] F. L. Binsbergen, "Heterogeneous nucleation in the crystallization of polyolefins: Part 1. Chemical and physical nature of nucleating agents," *Polymer*, vol. 11, no. 5, pp. 253–267, May 1970.
- [44] S. Jain, H. Goossens, M. van Duin, and P. Lemstra, "Effect of *in situ* prepared silica nano-particles on non-isothermal crystallization of polypropylene," *Polymer*, vol. 46, no. 20, pp. 8805–8818, Sep. 2005.
- [45] T. J. van, "Thermally stimulated discharge of polymer electrets," *Polym. J.*, vol. 2, no. 2, pp. 173–191, 1971.
- [46] F. Tian, W. Bu, L. Shi, C. Yang, Y. Wang, and Q. Lei, "Theory of modified thermally stimulated current and direct determination of trap level distribution," *J. Electrostatics*, vol. 69, no. 1, pp. 7–10, Feb. 2011.
- [47] X. He, P. Seri, I. Rytöluoto, R. Anyszka, A. Mahtabani, H. Naderiallaf, E. Saarimäki, M. Niittymäki, C. Mazel, G. Perego, K. Lahti, M. Paajanen, W. Dierkes, and A. Blume, "Influence of polar and unpolar silica functionalization on the dielectric properties of PP/POE nanocomposites," in *Proc. IEEE 3rd Int. Conf. Dielectrics (ICD)*, Jul. 2020, pp. 229–232.
- [48] X. Yang, J. Hu, S. Chen, and J. He, "Understanding the percolation characteristics of nonlinear composite dielectrics," *Sci. Rep.*, vol. 6, no. 1, p. 30597, Nov. 2016.
- [49] J. K. Nelson and J. C. Fothergill, "Internal charge behaviour of nanocomposites," *Nanotechnology*, vol. 15, no. 5, p. 586, 2004.
- [50] R. Guffond, A. Combessis, and S. Hole, "Contribution of polymer microstructure to space charge, dielectric properties and electrical conduction," in *Proc. IEEE Conf. Electr. Insul. Dielectric Phenomena (CEIDP)*, Oct. 2016, pp. 141–144.



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