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

AMIRHOSSEIN MAHTABANI1, (Member, IEEE), MINNA NIITTYMÄKI2, (Graduate Student Member, IEEE), RAFAŁ ANYSZKA1, (Member, IEEE), ILKKA RYTÖLUOTO3, XIAOZHEN HE1, (Member, IEEE), EETTA SAARIMÄKI3, KARI LAHTI2, (Member, IEEE), MIKA PAAJANEN3, WILMA DIERKES1, AND ANKE BLUME1

1Chair of Elastomer Technology and Engineering, Department of Mechanics of Solids, Surfaces and Systems (MS3), Faculty of Engineering Technology, University of Twente, 7500 AE Enschede, The Netherlands
2High Voltage Engineering Research Group, Tampere University, 33014 Tampere, Finland
3VTT Technical Research Centre of Finland Ltd., 33014 Tampere, Finland

Corresponding authors: Wilma Dierkes (w.k.dierkes@utwente.nl) and Amirhossein Mahtabani (a.mahtabani@utwente.nl)

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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 nanocomposites, 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) 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].
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).](image-url)
ethanol as the solvent. The latter was done in order to remove any unreacted precursor and reaction by-product from the silica samples.

**B. NANOPIRATE 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 cm⁻¹ and averaged over 128 scans, using a resolution of 4.0 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 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 TMPM\_5 and TMPU\_5 were treated by gold sputtering for a better distinction of the NPs, while Sample 0, TMPM\_1 and TMPU\_1 were measured without gold sputtering to visualize the polymer phases in the blend.
A. Mahtabani et al.: Deposition of Ureido and Methacrylate Functionalities

III. RESULTS AND DISCUSSIONS

A. CHARACTERIZATION OF THE NANOPARTICLES

To further analyze dielectric relaxation processes in the NCs with respect to the frequency of the applied field, the real ($\varepsilon'_r$) and imaginary parts ($\varepsilon''_r$) 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%).

$$\varepsilon^*_r = \varepsilon'_r + i\varepsilon''_r \tag{1}$$

3) BROADBAND DIELECTRIC SPECTROSCOPY (BDS)

To further analyze dielectric relaxation processes in the NCs, samples TMPM_5 and TMPU_5 were treated by gold sputtering for a better distinction of the NPs, while Sample 0, TMPM_1 and TMPU_1 were measured without gold sputtering to visualize the polymer phases in the blend.

To calculate the silane grafting density (GD) from the TGA mass loss according to (2).

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

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 TMPM and TMPU-modified silica, respectively, and $M_W$ is the molecular weight of the silane.

TMPM and TMPU-modified silicas exhibit mass losses of 5.8% and 15%, which account for grafting densities of 0.25 mmol g silica and 0.79 mmol 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 TMPU, however, are generally

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, TMPM_1 and TMPU_1 were measured without gold sputtering to visualize the polymer phases in the blend.
stronger than those of the Si-O-H···O for TMPM, due to the higher electronegativity of nitrogen [36]. This may be a reason for the higher grafting density of TMPU on silica compared to that of TMPM. Furthermore, the stronger hydrogen bond interactions between the silane molecules in TMPU 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 TMPU-modified silica starting from $\sim 300^\circ$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 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 TMPM-modified silica exhibits the characteristic bands of methacrylate groups, C=\(\text{C}\) and C=\(\text{O}\) at 1640 cm$^{-1}$ and 1690 cm$^{-1}$, respectively [37]. The C-H stretching vibration bands, from 2800 cm$^{-1}$ to 3000 cm$^{-1}$, appear in both TMPM and TMPU spectra, which are mostly attributable to the propyl spacer chain in both silanes. The TMPU spectrum contains the characteristic bands related to the ureido groups, C=\(\text{N}\), C=\(\text{O}\) and N-H, appearing at 1560 cm$^{-1}$, 1690 cm$^{-1}$ and 3350 cm$^{-1}$, respectively [38].

FIGURE 5. a) Melting and b) crystallization spectra of the studied NCs.
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.
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 TMPM 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 TMPM. 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 TMPM_5 and TMPU_5 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 TMPM_1 and TMPU_1). This is not visible in the TMPM_5 and TMPU_5 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 (ΔT) 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 ΔT which is another indication of a more efficient nucleation in the modified NCs [44].
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 –NH₂ 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.

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

| Sample   | Onset of Crystallization (°C) | Enthalpy of Melting (J/g) | Degree of Crystallinity (%) | Degree of Supercooling ΔT (°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                          |
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 TMPM_5 and TMPU_5 NCs. The reduction in current density compared to their 1% counterparts is more pronounced in case of TMPU 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 TMPU compared to TMPM.

### 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 TMPM and TMPU-modified NCs compared to the reference samples. In the frequency range above 1Hz, it is clear that with 1% of filler concentration the TMPM modification exhibits lower permittivity values compared to the TMPU-modified NCs and the reference samples. This can be due to the higher grafting density of the TMPU 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, TMPU_5 appears at lower levels of real permittivity compared to TMPM_5. The ureido groups in TMPU 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 TMPU modification results in lower interfacial polarizations compared to the TMPM. This is likely due to two reasons: firstly, the higher grafting density of TMPU 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 (TUMP) 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 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.

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EETTA SAARIMÄKI received the M.Sc.(Tech.) degree in plastics technology from Tampere University of Technology, in 1993. She has been working with VTT Technical Research Center of Finland Ltd., since 1994, where she is currently working as a Senior Scientist. Her research interests include plastic processing technologies, such as extrusion, compounding, and orientation, electromechanical films, plastic nanocomposites, functional polymer composites, electrical insulation materials, and plastics recycling.

KARI LAHTI (Member, IEEE) received the M.Sc. and Ph.D. degrees in electrical engineering from Tampere University of Technology, in 1994 and 2003, respectively. Since 2003, he has been responsible of the High Voltage Laboratory, TUT (since 2019, known as Tampere University (TAU)). Since 2013, he has been the Head of TAU’s Research Group on High Voltage Engineering, focusing mainly on various aspects of high-voltage insulation systems. He currently holds the position of a Senior Scientist or an Adjunct Professor with Tampere University. He has more than 25 years of experience in the field of high-voltage engineering. His research interests include high-voltage metrology and testing techniques, surge arresters, nanocomposite insulation systems, and environmental testing of HV apparatus and dielectric characterization of HV insulation systems.

XIAOZHEN HE (Member, IEEE) was born in Yantai, Shandong, China, in 1990. She received the M.Sc. degree in polymer chemistry and physics from Qingdao University of Science and Technology, China, in 2017. She is currently pursuing the Ph.D. degree with the Chair of Elastomer Technology and Engineering, University of Twente, Enschede, The Netherlands. She is also working on EU Project GRIDABLE. The aim of this project is to develop novel dielectric thermoplastic polymer composite materials for HVDC cable and DC capacitors application. In this project, she is responsible for the nanofiller surface modification via solvent free method and plasma technology. Her research interests include HVDC cable insulation material, nanocomposites, nanofiller surface engineering, and thermoplastic, rubber, and plasma technology.

MIKA PAAJANEN received the M.Sc.(Tech.) and D.Sc.(Tech.) degrees in electrical engineering and technical physics from Tampere University of Technology, in 1995 and 2001, respectively. He has been working with VTT Technical Research Center of Finland Ltd., since 1996, where he is currently working as a Principal Scientist. His research interests include electromechanical films, electrets, plastic nanocomposites, electrical insulation materials, and plastics recycling.

WILMA DIERKES studied chemistry at Technical University, Hanover, Germany. She continued with a postgraduate study in environmental science at Fondation Universitaire Luxembourggoise, Arlon, Belgium. After finishing this study, she started working for Rubber Resources, a rubber recycling company, Maastricht, The Netherlands. She was an in charge of the Research and Development and Technical Service, and developed and introduced short recycling loops for production waste back into the original production process. The next step in her career was the Research and Development Department, Robert Bosch Produktie, Tielen, Belgium, where she developed windshield wipers. Additionally, she was the Head of the Chemical Laboratory and part of the trouble shooting team in the production facility. In 2001, she started to work for the University of Twente, Enschede. From 2009 to 2013, she also held a part-time professorship at Tampere University of Technology, Finland. Since she started her research work at the university, she published more than 100 reviewed articles and 12 book chapters, and holds eight patents. Her research interests include reinforcing filler technology, with emphasis on silica filler systems, and recycling and re-utilization of elastomers. Other research areas are polymer networks and fiber reinforcement. For about ten years, she was a board member of the Dutch Association of Plastics and Rubber Technologists (VKRT), where she was the Chairman of this association, from 2005 to 2014.

ANKE BLUME studied chemistry at the University of Hanover, Germany, from October 1988 to July 1993. In the last year of her study, she came in the first contact with rubber during her master thesis. She received the Ph.D. degree from German Institute for Rubber Technology (DIK), in November 1995. After nine months of postdoctoral time at DIK, she started as a member of the Product Development Group Silica, Applied Technology Department, Degussa A.G. (currently, Evonik Resource Efficiency GmbH), in September 1996. She worked there in different positions, always related to the development of silica and silane for the use in rubber. Since August 2011, she has been holding the position as an IP Manager of silica and silane for rubber applications. In October 2013, she started at the University of Twente, The Netherlands, as the Head of the Chair of Elastomer Technology and Engineering (ETE) Group.