

Surface Modification of Fumed Silica by Dry Silanization for PP-based Dielectric Nanocomposites

Xiaozhen He¹, Amirhossein Mahtabani¹, Ilkka Rytöluoto², Eetta Saarimäki³, Kari Lahti², Mika Paajanen³,
Rafal Anyszka¹, Wilma Dierkes¹, Anke Blume¹

¹ University of Twente, Faculty of Engineering Technology, Department of Mechanics of Solids, Surfaces & Systems (MS3),
Chair of Elastomer Technology and Engineering, Enschede, The Netherlands

² Tampere University of Technology, Electrical Engineering, P.O. Box 692, FI-33101 Tampere, Finland

³ VTT Technical Research Centre of Finland Ltd, Tampere, Finland

Abstract- Novel nanocomposites for dielectric applications based on a polypropylene (PP) blend filled with nanosilica are developed in the frame of the European ‘GRIDABLE’ project.

A systematic study of the influence of surface modification of the nanosilica on the dielectric properties of the PP/silica blend was performed. The main goal of this investigation was to modify the chemical composition of the silica surface, which is expected to improve the charge trapping properties of the nanocomposites. For the modification of the silica surface, a “green” approach was utilized: a dry silanization method, which is performed without the need of a solvent.

Eight different silanes were investigated in this study, which are categorized into three different groups:

- I) Aliphatic silanes with a different number of alkoxy groups
- II) Hydrocarbon silanes containing delocalized electron clouds
- III) Polar silanes containing hetero elements (nitrogen, sulfur or oxygen)

The results of the thermogravimetric analysis (TGA) show higher weight loss of the modified silicas in comparison to the unmodified one. This indicates that the dry process is an effective method to perform silica surface modification using alkoxysilanes.

The charge trapping properties were studied by Thermally Stimulated Depolarization Current (TSDC) measurements. The obtained TSDC results show that the trap density peak is not significantly shifted in temperature when the silica is modified with functional groups elementally similar to the polymer matrix. However, their incorporation influences the traps density and suppress the deeper traps occurring near the range of the melting temperature of PP. When the silica surface is modified with a precursor containing a hetero element, it has an effect on both, trap level depth as well as density. Depending on the type of the hetero element (sulfur, nitrogen, oxygen), the trap depth shifted to higher temperatures, and the trap density decreased to significantly lower levels. Nitrogen appears to have the strongest effect on the charge trap properties.

All these first stage of results show that incorporation of modified nanosilica into a PP matrix seems to be a promising approach to tailor its electric properties. Further development of these composites would lead to benefits for high-voltage cable and capacitors applications.

Keywords: Silica surface modification, Dry silanization, Polypropylene dielectric nanocomposites, Charge trapping properties, TSDC, High voltage cable.

I. Introduction

GRIDABLE is a European project funded by the European Union’s Horizon 2020 research program. It aims to develop optimized polypropylene/silica insulation nanocomposites on laboratory scale and further up-scale the production of these composites for applications in the next generation of high-voltage direct current (HVDC) cables and DC film capacitors.

Applying the dielectric polymer nanocomposites (PNCs) in high voltage insulation attracts not only academic researchers attention but also industries globally [1-4]. For instance, the nanoparticle filled polymers are reported to exhibit better resistance to partial discharge degradation [5], and enhanced thermomechanical properties in comparison to the micro-particle filled polymers [6]. The improved insulating properties (dielectric strength and voltage endurance) of the nanoparticle filled polymers were investigated and reported [7, 8]. The high performance dielectric property of PNCs is mainly due to the evenly scattered large interface area of the filled nanoparticles, which can lead to changes of the space charge accumulation and trap level density [9, 10]. The space charge accumulation in PNCs is the key issue for the insulation material, especially for HVDC applications [11]. Doping nanoparticles can suppress the space charge accumulation of PNCs, as reported in several publications [2, 8, 10].

Further dielectric improvement of PNCs can be achieved by changing the surface polarity of nanoparticles. One of the basic principles is changing the surface polarity of the nanoparticles in order to get higher compatibility with a polymer matrix. This can improve the filler dispersion and distribution [12]. Another approach is based on introducing functional groups onto the surface of nanoparticles, which can result in alteration of charge trapping and transport locally in the particle–polymer interface and hence modification of bulk dielectric properties [13].

Based on the literature, one can see how the different dielectric properties of PP filled with silica modified by polar or non-polar agents change. In this paper, a systematic investigation on the dielectric properties of the PP/modified-silica blends were performed by means of thermally stimulated direct current (TSDC) measurements.

In addition, a novel approach of dry modification was used in this study. Compared to the solvent-based chemical modification, dry modification is much more environmentally friendly because barely any waste is produced. This is also an effective way to change the silica surface properties and to reach a high level of surface modification.

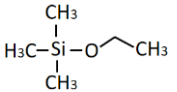
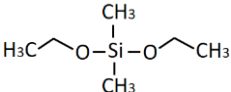
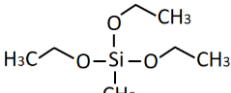
II. Experimental

1. Silica Dry Modification

The dry modification method was performed on fumed silica by 8 different silane agents. The investigated silanes were divided into three groups:

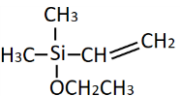
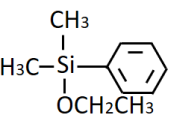
I. Aliphatic silanes with a different number of alkoxy groups (Table 1).

Table 1 Silanes from the group I

| Silane | Full name | Structure |
|--------|-------------------------|---|
| TMES | Trimethylethoxy silane |  |
| DMES | Dimethyldiethoxy silane |  |
| TEMS | Triethoxymethyl silane |  |

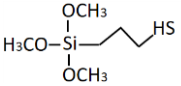
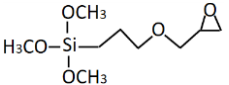
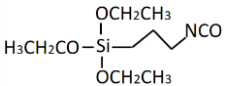
II. Hydrocarbon silanes containing delocalized electron clouds (Table 2).

Table 2 Silanes from the group II

| Silane | Full name | Structure |
|---------------|----------------------------|---|
| Vinyl-silane | Vinyldimethylethoxysilane |  |
| Phenyl-silane | Phenyldimethylethoxysilane |  |

III. Polar silanes containing hetero elements (nitrogen, sulfur or oxygen) (Table 3).

Table 3 Silanes from the group III

| Silane | Full name | Structure |
|--------------|--------------------------------------|---|
| HS-silane | Mercaptopropyltrimethoxy silane |  |
| Epoxy-silane | 3-Glycidyloxypropyl trimethoxysilane |  |
| NCO-silane | Isocyanatepropyltriethoxy Silane |  |

The Epoxy-silane and NCO-silane were bought from Sigma-Aldrich. The rest of all the silanes were bought from Aber GmbH.

The above classification aims at systemically studying the influence of surface modification of the nanosilica on the charge trapping properties of the PP/silica composites. This new approach of dry modification was carried in a sealed glass jar in an anhydrous environment at room temperature for 24 hours. No solvent waste was generated during the process. This makes the silica dry modification much more environmentally friendly than solution methods. All the modifications were performed with the same amount of fumed silica (10 g), catalyst-1 (0.6 g), catalyst-2 (0.2 g) and various amounts of silane. The amount of the different silanes used for the dry modification reaction are shown in Table 4. After the modification, the product was placed in a vacuum oven at elevated temperature 80°C for 24 hours to remove unreacted agents volatiles.

Table 4 Amount of silane used during the modification

| Silane | Amount/g | Silane | Amount/g |
|--------------|----------|---------------|----------|
| TMES | 2.00 | Phenyl-silane | 3.00 |
| DMES | 2.50 | HS-silane | 3.19 |
| TEMS | 2.94 | Epoxy-silane | 3.84 |
| Vinyl-silane | 2.15 | NCO-silane | 4.03 |

2. Thermogravimetric analysis (TGA)

Thermogravimetric analysis was performed for the reference silica sample and all dry-modified silica samples. This characterization was done in a synthetic air atmosphere with a heating rate of 20 °C/min. The temperature range was from ambient temperature up to 850 °C.

3. Polypropylene/silica composites preparation

The different nanocomposite samples were prepared by melt-blending the reference silica (unmodified) or the modified silica with polypropylene-based blend intended for

cable applications in a twin-screw micro extruder at a temperature of 230 °C with a screw speed of 100 rpm. Afterwards the mixed samples were immediately injection-molded into thin sheets with a size of 260 x 260 x 0.5 mm.

4. Thermally Stimulated Depolarization Current (TSDC)

The charge trapping properties were studied by Thermally Stimulated Depolarization Current (TSDC) measurements. Circular Au electrodes (100 nm in thickness) were deposited on both sides of the sample films by e-beam evaporation under high vacuum. The measurement procedure consisted of the following steps:

- 1) The samples were heated up to 70 °C.
- 2) DC poling field of 3 kV/mm was applied for 20 min under isothermal conditions at 70 °C.
- 3) The samples were rapidly cooled down to -50 °C with the voltage still applied, and kept at this temperature for 5 min for stabilization.
- 4) Poling field was removed and the samples were short-circuited through an electrometer. The short-circuited samples were maintained at -50 °C for 3 min to allow fast polarization to decay.
- 5) The samples were linearly heated up to 130 °C with a heating rate of 3 °C/min. Meanwhile, the depolarization current was recorded.

III. Results and Discussion

The modified silica particles were firstly characterized by TGA, as shown in Figures 1, 3 and 5. The modified samples show a higher weight loss in comparison to the reference unmodified silica. This indicates that the dry process is an effective method to perform silica-silane surface modification.

Based on literature [14], the evaporation of water physically adsorbed on the surface of silica particles is the main cause of the weight loss at low-temperatures (<200 °C). The weight loss in the temperature range of 200–850 °C results from the chemically bonded silane and the condensation of silanol groups present on the silica surface.

The charge-trapping properties of the injection-moulded compounds were characterized by the TSDC method. The data obtained from the neat PP matrix and unmodified silica filled PP were compared with the nanocomposites filled with differently modified silica, as is shown in Figures 2, 4 and 6. In principle, when a sample with frozen-in polarization/space charge is heated linearly under short-circuit conditions, gradual relaxation of (dipolar) polarization and trapped charge occurs, giving rise to a thermally stimulated current in the external circuit. Typically, for non-polar polymers, the TSDC above the glass transition temperature is mostly attributable to space charge relaxation, with the temperature at peak maximum and the peak intensity being related to the depth and density of the charge traps, respectively.

Figure 1 presents the weight loss of the silicas modified with the silanes containing a different number of alkoxy-functional groups. The level of deposition increases with an increase of the number of ethoxy groups in the silane molecule. This can be explained by a possible condensation of alkoxy groups leading to formation of complex oligomeric structures on the silica surface. TMES silane contains only one alkoxy group, therefore it is not able to initiate the condensation reaction resulting in the lowest deposition. However, the morphology of the TMES surface mono-layer is the most uniform because of the lack of the side-condensation reactions. This seems to be associated with a shift of the TSDC peak to higher temperatures, hence indicating trap depth becoming deeper (Figure 2). DMES and TEMS introduce two and one methyl group respectively to the silica surface, whereas TMES contains three methyl groups. When attached to the silica surface, the latter provides the most effective compatibilization with the PP matrix. Therefore, even though the modification level of silica is lower for TMES, the hydrophobization effect is higher, hence promoting better dispersion of the silica in the PP matrix. Consequently, the silica/PP interfacial volume fraction increases, providing potentially more effective modification of the charge trapping and transport properties of the bulk nanocomposite.

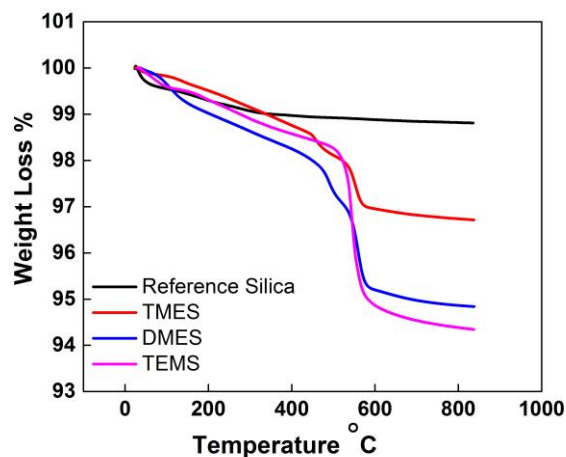


Figure 1 TGA results of reference silica and silicas modified with silanes from group I).

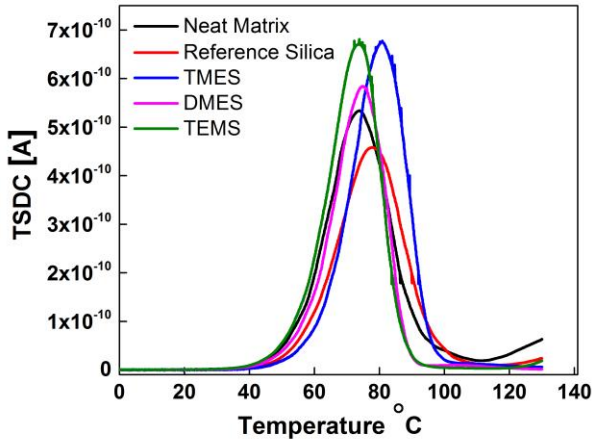


Figure 2 The TSDC results for the neat PP matrix, and the PP composites filled with reference silica and the silicas modified with the silanes from group I)

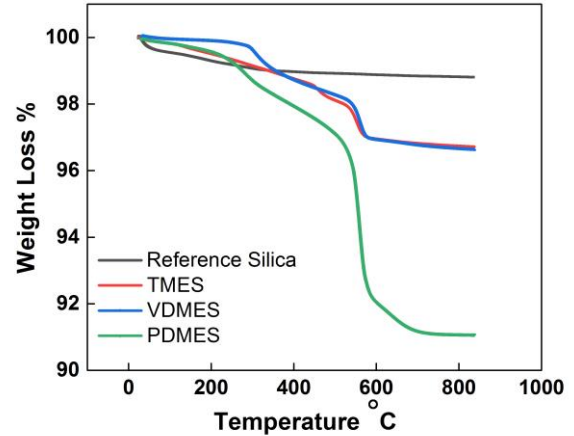


Figure 3 TGA results of reference silica and silicas modified with silanes from group II).

Figure 3 depicts the weight loss of silica samples modified with the silanes from group II in order to investigate the influence of chemical groups containing conjugated p-orbitals with delocalized electron clouds (aromatic rings and C=C double bonds) on the electrical performance of PP based composites (Figure 4). The chemical groups containing delocalized electron clouds were reported to improve the dielectric properties of polymer composites via an electron withdrawing effect [15]. The level of surface modification is the highest for the silica treated with PDMES because of much higher molecular weight of the phenyl ring-containing silane.

The charge-trapping characteristics of the PP based composites containing silicas modified by the silanes from group II measured by TSDC are consistent with the results obtained for the TMES sample. The maximum of the depolarization current curve is shifted to higher temperatures in comparison to the neat PP matrix, again suggesting the trap level becoming deeper. This is most probably caused by a regular mono-layer silane deposition similar to the TMES sample. However, the TSDC peak intensity is seen to vary in these samples; this may be due to differences in compatibility with the PP matrix, resulting in overall differences in trap density. The samples containing silica modified with phenyl or vinyl-functionalized silanes exhibit lower compatibility with the PP matrix than the silica modified with TMES, presumably reducing the interfacial volume fraction; consequently, this could be associated with lower trap density for these compounds.

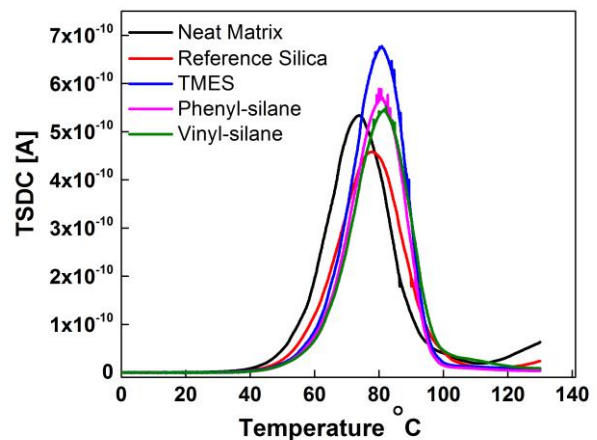


Figure 4 The TSDC results of the neat PP matrix, and the PP composite filled with reference silica and the silicas modified with the silanes from group II)

Application of tri-functional silanes for silica modification results in a significant degree of chemical deposition on the silica surface. This is an effect of condensation and oligomerization of the silane molecules (Figure 5). Utilization of 3-glycidyloxypropyltrimethoxy silane for the modification resulted in a deposition exceeding 15 % of the treated silica mass. This is an exceptional result in comparison to the state of the art presented in literature, in which the deposition usually does not exceed 10 % [16], unless there is a complex, multi-step procedure involved allowing higher deposition rates [17].

Introduction of polar groups containing hetero-elements alters the charge trapping characteristics significantly (Figure 6). The TSDC peak intensity starts to decrease slightly for the HS-silane, and this is much more pronounced for epoxy- and NCO-silanes. Moreover, a significant shift of the TSDC peak maximum towards higher temperatures, is observed especially for the samples containing functional isocyanate groups containing nitrogen

and oxygen. These observations may be related to changes in trap depth and density distributions.

In general, incorporation of unmodified as well as modified silica suppress the very deep traps present in the PP blend, which is observed by suppression of the a growing peak over 110 °C (Figures 2, 4 and 6).

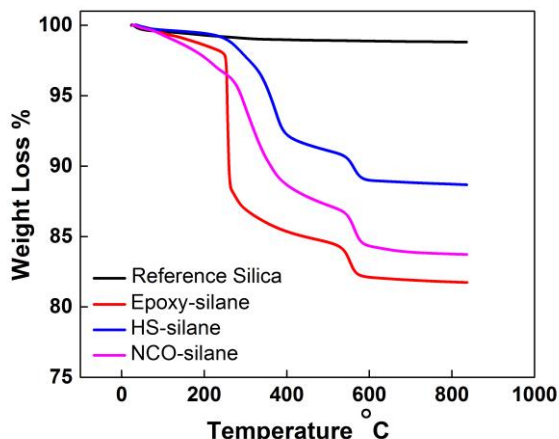


Figure 5 TGA results of reference silica and silica modified with silane from group III).

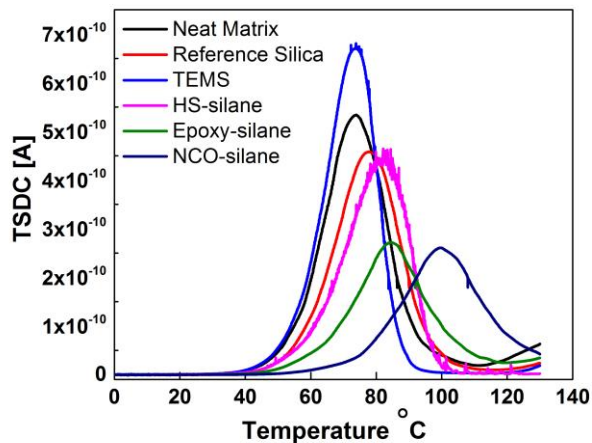


Figure 6 The TSDC results of the neat PP matrix, and the PP composites filled with reference silica and the silicas modified with the silanes from group III)

IV. Conclusions

The dry modification with silane results in a successful modification of fumed nano-silica reaching a very high deposition level for the silanes containing three ethoxy-functional groups. This is caused by condensation and oligomerization of the silane on the surface of the silica. The first stage of TSDC studies indicate that surface modification of silica with hydrocarbon-based silanes does not influence the depth of the charge traps significantly. However, the composites containing the silica modified with polar

silanes containing hetero elements show a significant shift of the TSDC peak to higher temperatures, indicating deeper trap levels. Moreover, this modification also suppresses the apparent trap density.

ACKNOWLEDGEMENTS:

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 720858. The authors also would like to thank the ECIU Researcher Mobility Fund for supporting this research work.

REFERENCES:

- [1] Tanaka, T. (2005). Dielectric nanocomposites with insulating properties. *IEEE Transactions on Dielectrics and Electrical Insulation*, 12(5), 914-928.
- [2] Wu, C., Yan, W., & Phung, B. T. (2013, October). Influence of plasma-treated nanoparticles on space charge accumulation in epoxy resin insulation. In *Electrical Insulation and Dielectric Phenomena (CEIDP)*, 2013 IEEE Conference on (pp. 784-787). IEEE.
- [3] Pourrahimi, A. M., Pallon, L. K., Liu, D., Hoang, T. A., Gubanski, S., Hedenqvist, M. S., ... & Gedde, U. W. (2016). Polyethylene nanocomposites for the next generation of ultralow-transmission-loss HVDC cables: Insulation containing moisture-resistant MgO nanoparticles. *ACS applied materials & interfaces*, 8(23), 14824-14835.
- [4] Rytöluoto, I., Ritamäki, M., Lahti, K., Paajanen, M., Karttunen, M., Montanari, G. C., ... & Naderiallaf, H. (2018, July). Compounding, Structure and Dielectric Properties of Silica-BOPP Nanocomposite Films. In *2018 IEEE 2nd International Conference on Dielectrics (ICD)* (pp. 1-4). IEEE.
- [5] Kozako, M., Kido, R., Fuse, N., Ohki, Y., Okamoto, T., & Tanaka, T. (2004, October). Difference in surface degradation due to partial discharges between polyamide nanocomposite and microcomposite [electrical insulation applications]. In *Electrical Insulation and Dielectric Phenomena, 2004. CEIDP'04. 2004 Annual Report Conference on* (pp. 398-401). IEEE.
- [6] Kango, S., Kalia, S., Celli, A., Njuguna, J., Habibi, Y., & Kumar, R. (2013). Surface modification of inorganic nanoparticles for development of organic-inorganic nanocomposites—a review. *Progress in Polymer Science*, 38(8), 1232-1261.
- [7] Wang, S. J., Zha, J. W., Wu, Y. H., Ren, L., Dang, Z. M., & Wu, J. (2015). Preparation, microstructure and properties of polyethylene/alumina nanocomposites for HVDC insulation. *IEEE Transactions on Dielectrics and Electrical Insulation*, 22(6), 3350-3356.
- [8] Han, B., Wang, X., Sun, Z., Yang, J., & Lei, Q. (2013). Space charge suppression induced by deep traps in polyethylene/zeolite nanocomposite. *Applied physics letters*, 102(1), 012902.
- [9] Roy, M., Nelson, J. K., MacCrone, R. K., Schadler, L. S., Reed, C. W., & Keefe, R. (2005). Polymer nanocomposite dielectrics-the role of the interface. *IEEE transactions on dielectrics and electrical insulation*, 12(4), 629-643
- [10] Zhou, Y., Hu, J., Dang, B., & He, J. (2016). Titanium oxide nanoparticle increases shallow traps to suppress space charge accumulation in polypropylene dielectrics. *RSC Advances*, 6(54), 48720-48727.

- [11] Hampton, R. N. (2008). Some of the considerations for materials operating under high-voltage, direct-current stresses. *IEEE Electrical Insulation Magazine*, 24(1), 5-13.
- [12] Zhang, L., Zhou, Y., Cui, X., Sha, Y., Le, T. H., Ye, Q., & Tian, J. (2014). Effect of nanoparticle surface modification on breakdown and space charge behavior of XLPE/SiO₂ nanocomposites. *IEEE Transactions on Dielectrics and Electrical Insulation*, 21(4), 1554-1564.
- [13] Siddabattuni, S., Schuman, T. P., & Dogan, F. (2013). Dielectric properties of polymer-particle nanocomposites influenced by electronic nature of filler surfaces. *ACS applied materials & interfaces*, 5(6), 1917-1927.
- [14] Chen, G., Zhou, S., Gu, G., & Wu, L. (2007). Modification of colloidal silica on the mechanical properties of acrylic based polyurethane/silica composites. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 296(1-3), 29-36.
- [15] S. Siddabattuni, T. P. Schuman, and F. Dogan, "Dielectric Properties of Polymer-Particle Nanocomposites Influenced by Electronic Nature of Filler Surfaces," *ACS Applied Materials & Interfaces*, vol. 5, no. 6, pp. 1917-1927, 2013/03/27 2013.
- [16] Tang, Z., Huang, J., Wu, X., Guo, B., Zhang, L., & Liu, F. (2015). Interface engineering toward promoting silanization by ionic liquid for high-performance rubber/silica composites. *Industrial & Engineering Chemistry Research*, 54(43), 10747-10756.
- [17] Qiao, B., Wang, T. J., Gao, H., & Jin, Y. (2015). High density silanization of nano-silica particles using γ -aminopropyltriethoxysilane (APTES). *Applied Surface Science*, 351, 646-654.