RESEARCH ARTICLE | MAY 05 2023

Influence of prolonged mixing of silicon dioxide nanoparticles on the electrical properties of resin nanocomposites

Ondrej Michal ✉; Václav Mentlik; Jaroslav Hornak

AIP Conference Proceedings 2778, 040018 (2023)
https://doi.org/10.1063/5.0135871

Influence of Prolonged Mixing of Silicon Dioxide Nanoparticles on the Electrical Properties of Resin Nanocomposites

Ondrej Michal[1, a)], Václav Mentlik[1] and Jaroslav Hornak[1]

[1]*Department of Materials and Technology, Faculty of Electrical Engineering, University of West Bohemia, Univerzitní 26, 301 00 Pilsen, Czech Republic.*

[a)] *Corresponding author: mionge@fel.zcu.cz*

Abstract. In today's world, scientists are focusing on developing new materials that provide lower costs, environmental sustainability or increased capabilities. One way to develop new materials is to modify conventional types already established in industry. An example is the development of composite materials with different types of matrices or fillers. In the last two decades, scientific work has mainly focused on the incorporation of nanofillers into conventional and used matrices such as resins, thermoplastics such as polyethylene or others. One of the issues in performing these modifications is the process of incorporation of nanoparticles into matrices, which is problematic in many aspects. This paper focuses on the effect of silica nanoparticles with different incorporation methods into polyester-imide resin (PEI). The main objective of this experiment was to find the optimal way of the process of mixing nanoparticles with the resin. Thus, this optimal process can be used in follow-up experiments to develop a new type of insulating material for high voltage applications. In this experiment, conventional dielectric parameters such as relative permittivity, dissipation factor, volume resistivity and dielectric strength were diagnosed.

INTRODUCTION

In recent decades, nanomaterials have been on the rise and are a frequently discussed topic in scientific publications, not only in the field of electrical engineering. Many nanomaterials have already found practical use in industrial applications. Examples of specific applications are various protective coatings, gas barriers or non-woven nanofibres, which have found applications in medicine as a drug delivery option or as a protective filter layer in modern masks and respirators. In electrical engineering, nanomaterials have been investigated in the context of dielectric materials as a modifier of their properties. [1] In general, nanomaterials, when properly chosen and incorporated, affect polarization processes, reduce local space charge, and thus have an overall positive effect on dielectric parameters such as relative permittivity, loss factor, and others. Therefore, these nanomaterials are used as fillers for composite materials. [2-3] The nanofillers have a positive effect on the properties of the nanocomposite if they are homogeneously dispersed in the matrix without forming agglomerates and overlapping the nanoparticle interfaces. The way to achieve good dispersion is either by mixing the nanoparticles in the matrix or by chemical treatment. Chemical modification or functionalization of the nanoparticle surface is achieved by using binders, which are most commonly silane-based. [4-5]

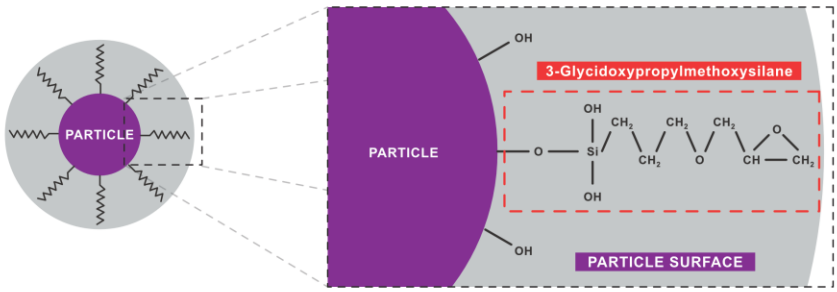

FIGURE 1. Functionalization of nanoparticle surface by silane group GLYMO

Applied Physics of Condensed Matter (APCOM 2022)
AIP Conf. Proc. 2778, 040018-1–040018-6; https://doi.org/10.1063/5.0135871
Published by AIP Publishing. 978-0-7354-4479-9/$30.00

If we do not have modified nanoparticles or the possibility to modify them ourselves, we can use instruments for breaking up agglomerates and their subsequent homogeneous distribution in the matrix. We can simply mechanically mix the agglomerates. However, breaking the agglomerates for a good dispersion is a very time-consuming method (up to tens of hours depending on the material used). However, this long time can be compensated using ultrasound for breaking up the agglomerates and their subsequent dispersion in the matrix. [6]

EXPERIMENT DETAILS

This experiment deals with the process of mixing the silicon dioxide nanoparticles modified by the silane group. Goal was to find the optimal mixing process for two types of polyester-imide resin. Findings from this experiment will be used in the next phase of development of new type of high voltage composite insulating material. Diagnostic method includes dissipation factor and relative permittivity based on frequency, voltage and temperature. Then volume resistivity and dielectric strength. For the purpose of investigating the homogeneity, the SEM images are presented also.

Materials

In general, polyester-based resins are widely used in electrical insulation applications, especially for insulating windings of rotating machinery. Unsaturated polyesters (UP) are used due to their good mechanical and electrical properties and resistance to high temperatures. To achieve thermal stability in particular, functional imide groups are added to conventional polyester resins. [7] UP1 (Elan-Protect UP 142) and UP3 (Elan-Protect UP 343) are newly developed one-component impregnating resins based on polyester-imides. UP3 is a medium viscosity resin which shows good stability, good mechanical and electrical properties even at higher temperatures. It is used for heat class 200. This resin is suitable as impregnant in rotating and non-rotating machines. UP1 is based on a specialized unsaturated polyester-imide resin. It is VOC-free, i.e. it does not contain volatile organic compounds and has low curing emissions. This resin does not contain styrene or vinyltoluene as a reactive diluent. This gives it a low viscosity suitable for impregnation by dipping. Due to its low emissions, there is no need for exhaust during curing. The cured material has good mechanical and electrical properties even at higher temperatures. It is used for 180-200 temperature class of materials.

TABLE 1. Parameters of polyester-imide resins. [8-9]

Parameter	UP1	UP3
Color	Clear yellow	Clear yellow
Viscosity	1000 ± 400 mPa.s	7500 ± 1500 mPa.s
Curing time	160 °C / 1 h	150 °C / 1 h
Volume resistivity	$> 10^{16}$	$> 10^{16}$
Temp. when tgδ=0,1 [50 Hz, 1V]	> 100 °C	> 117 °C
Temperature class	200	220

Based on the previous extensive experiments [11-12], the modified silicon dioxide AEROSIL R974 was used in this experiment. This silicon dioxide is prepared by a pyrogenic process. The pyrogenically produced silicon takes the form of chain-like, branched aggregates resulting in a fluffy powder. Silica prepared in this way has freely accessible silanol groups (Si-OH) on the surface of the particles, which make the particles hydrophilic. For applications in dielectric composite materials, a post-treatment step is required to achieve the hydrophobic nature. The hydrophobic behavior is provided by the reaction of hydrophilic silanol groups with organic groups. These organic groups are then anchored to the surface by a covalent bond. Used AEROSIL nanoparticle is surface treated with dichlorodimethylsilane. Their average size is 10 nm and specific surface size is 150 – 190 m^2/g. [10]

Sample preparation

A set of 5 samples was created for each mixing combination to ensure statistical significance of the results. Mixing was performed with a mechanical magnetic stirrer and 1 wt.% of nanoparticles was used for all sets. The sample preparation process is best described in the Fig. 2, that also includes times and temperatures used in the mixing process. Reference sets of pure resin were also made. All mixed samples were then cured according to the resin details. Sets naming, which is based on the duration of mixing, is presented in Table 2.

TABLE 2. Sets naming and duration of mixing.

Set name	Duration and type of mixing
UP3, UP1	Neat resins without nanoparticles
UP3_4h	Resin with 1 wt.% SiO_2 mechanically mixed for 4 hours
UP3_12h	Resin with 1 wt.% SiO_2 mechanically mixed for 12 hours
UP3_2hU, UP1_2hU	Resins with 1 wt.% SiO_2 mechanically mixed for 2 hours + 30 minutes ultrasonic
UP3_4hU, UP1_4hU	Resins with 1 wt.% SiO_2 mechanically mixed for 4 hours + 30 minutes ultrasonic

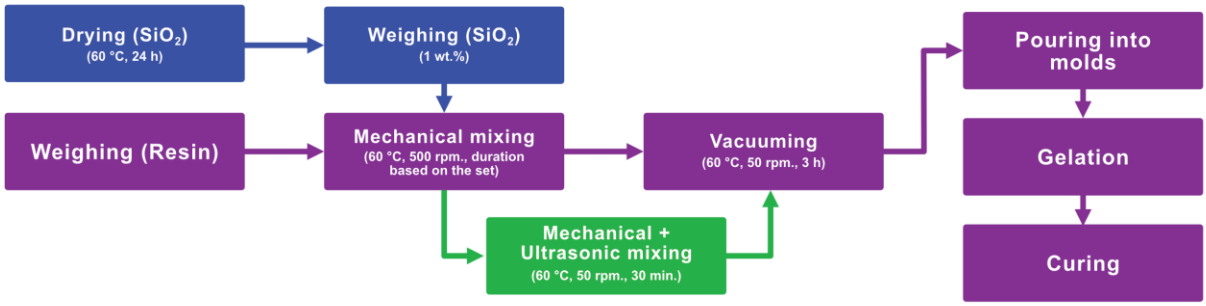

FIGURE 2. Composite manufacturing process including ultrasonic mixing

METHODS, RESULTS AND DISCUSSIONS

In this paper, the frequency and temperature dependence of the relative permittivity and dissipation factor is presented. The frequency dependence was measured by the broadband dielectric spectrometer from Novocontrol Industries when applying 1 V. The frequency spectrum was 0.1 Hz to 10^6 Hz, and temperatures from -50 °C to 90 °C. For the measurement under higher voltage (1 kV, 50 Hz) and higher temperatures (30 – 110 °C) the Tettex automatic dielectric analyzer was used. Absorption and resorption characteristics were also measured according to Standard IEC 62631-3-1:2016. An accurate multimeter Keithley 6517A and 8009 Resistivity Test Fixture was used for this measurement. Dielectric strength was measured according to IEC 60243-1:2013 standard applying a rising voltage (AC, 50 Hz) until breakdown.

Absorption and Resorption Currents

The following conclusions can be drawn from the presented results of the absorption characteristics in Table 3. Incorporation of nanoparticles by mechanical mixing alone resulted in an increase in conduction current and a decrease in volume resistivity. Longer mixing time resulted in a reduction of the deterioration of parameters. Thus, it can be concluded that mechanical mixing alone has a rather negative effect on the parameters obtained from the absorption characteristics. The addition of cavitation by ultrasound, on the other hand, had a clear positive effect. (UP3_4h - 0.71 UP3_4hU - 7.20). We observe that longer mixing gives better results. In terms of the UP1 resin, we can again see a clear positive effect of the nanoparticles on the parameters obtained from the absorption characteristics. Again, a positive effect of longer mixing is seen.

TABLE 3. Absorption and resorption currents results.

Parameter	UP3	UP3 4h	UP3 12h	UP3 2h_U	UP3 4h_U	UP1	UP1 2h_U	UP1 4h_U
Volume resistivity (10^{15} Ω.m)	1.91	0.71	1.44	5.03	**7.2**	0.72	2.57	**3.23**
PI_1	2.9	2.3	2.3	3.1	**3.2**	2.7	2.8	**2.8**
PI_{10}	4.7	3.3	3.3	5.9	**6.9**	3.7	4.2	**4.3**
AURC (10^{-10})	15.04	34.96	34.96	12.75	**12.55**	29.2	10.06	**9.88**

Dissipation factor and Relative permittivity

The combined temperature and frequency dependence of the loss factor was measured in the range -50 °C to 90 °C and in the frequency range 10^{-1} Hz to 10^{6} Hz. 3D plots of these dependencies can be seen in Fig. 3. From the presented dissipation factor results in Fig. 3 a), mechanical mixing alone resulted in increased values. This increase is over the entire measured frequency and temperature range. We can conclude that based on this negative change, there are many agglomerates in the resin. After application of ultrasonic cavitation, we see a visible decrease over the entire measured range. This statement is confirmed by the relative permittivity results in Fig. 3 b), where the most significant decrease was observed for the nanocomposites mixed for 4 hours by mechanical and ultrasonic agitation.

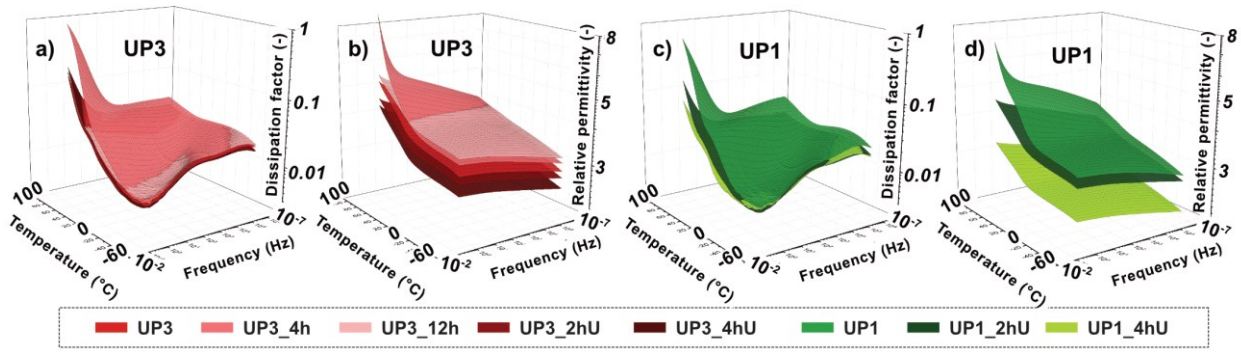

FIGURE 3. Dependences of dissipation factor (a) and relative permittivity (b) on temperature and frequency of nanocomposites with UP3. Dependences of dissipation factor (c) and relative permittivity (d) on temperature and frequency of nanocomposites with UP1.

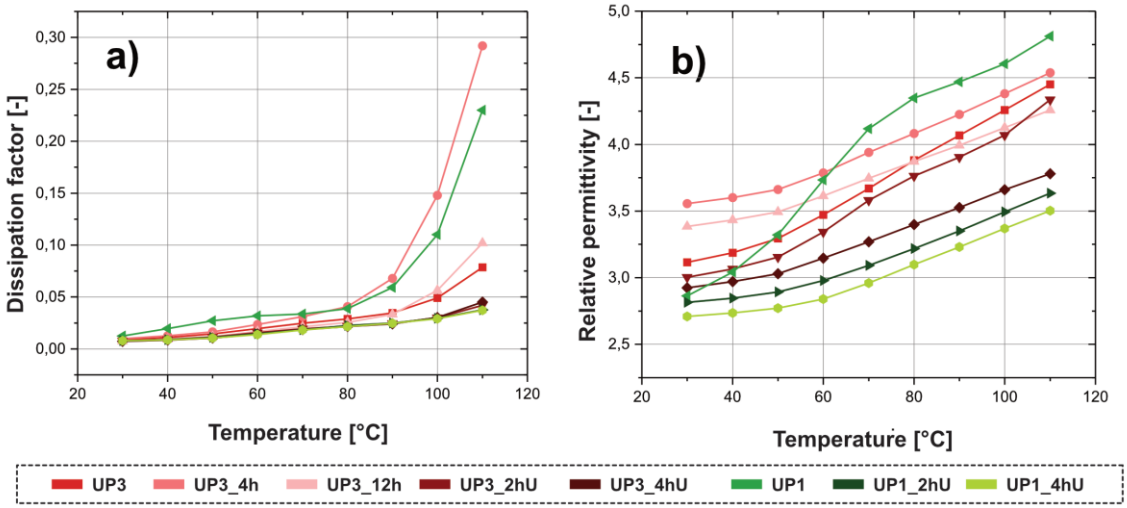

FIGURE 4. Plots of dissipation factor (a) and relative permittivity (b) temperature dependence under 1 kV and 50 Hz voltage.

The measured values of the dissipation factor at higher voltage (1 kV, 50 Hz) correlate with the spectroscopic test results. In terms of the dissipation factor, Fig. 4 a)., the nanocomposites to which ultrasound was applied have a significantly improved thermal stability over the whole range of measured temperatures. Thus, the main disadvantage of the UP1 resin found in the previous experiments (high dependence of parameters on the temperature) has been significantly eliminated. It can be concluded that when ultrasonication is applied, it is advantageous to mechanically stir the mixture longer beforehand. For both resins, a mechanical mixing time of 4 hours followed by ultrasonication works best.

From the observed values of dielectric strength, which can be seen in Fig. 5 and Table 4, we can observe a slight increase in the values for the nanocomposites. This increase is most evident for the UP1_4hU set, where there is an increase in median electrical strength of 2 kV/mm. Further, an increase is seen for the UP3_4hU set, where this increase is 3 kV/mm. This set shows a significantly higher coefficient of variation, 10.2 %. The UP3_4h and UP3_12h sets, which were mixed only mechanically, show a significant decrease in electrical strength, up to 3.8 kV/mm. This is due to the agglomerates, which deform the electric field in the material more significantly and thus more easily conduct the electric discharge through the sample. A statistical analysis of the dielectric strength is presented in Table 4.

TABLE 4. Statistical values of dielectric strength measurements of nanocomposites

Parameter	UP3	UP3 4h	UP3 12h	UP3 2h_U	UP3 4h_U	UP1	UP1 2h_U	UP1 4h_U
Minimum (kV/mm)	31.05	28.28	26.75	30.5	**32.22**	32.07	34.01	**34.12**
Maximum (kV/mm)	**42.03**	33.1	37.44	40.9	41.39	**42.97**	39.34	41.78
Average (kV/mm)	35.85	31.12	31.73	35.05	**36.96**	36.66	36.92	**37.88**
Median (kV/mm)	35.39	31.21	31.7	35.33	**38.34**	35.6	37.02	**37.53**
Standard deviation (kV/mm)	3.85	**1.74**	3.44	3.66	3.77	3.58	**1.81**	2.67
Coefficient of Variation (%)	10.7	**5.6**	10.8	10.4	10.2	9.7	**4.9**	6.7

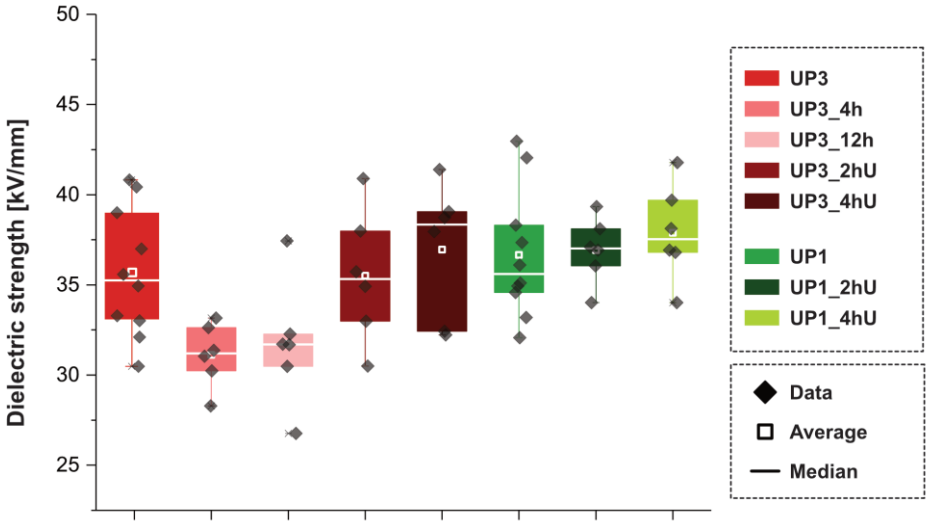

FIGURE 5. Dielectric strength of individual sets of nanocomposites

CONCLUSION

Based on the presented results, it is evident that the process of nanoparticle incorporation was significantly affected by the addition of ultrasound, where the nanoparticle agglomerates were broken down in the resin. This is also evident in the SEM images taken presented in [13]. As a result, it was possible to reduce the sample preparation time by several hours. From the results of the first part, the optimal process for both resins consist of 4 hours of mechanical mixing, 30 minutes of mixing during ultrasound application and approximately 3 hours of vacuuming. During the preparation of samples, it was evident that ultrasound application had also a positive effect on the

removal of air bubbles. This resulted in a further reduction of vacuum time by one hour. For this reason, this process was chosen for the next part of the development of the composite material. It is also evident that nanoparticles significantly modify the properties of UP1 resin, where the thermal dependence of the dissipation factor and relative permittivity are improved. This significant effect of the nanoparticles is probably due to the resin itself, which has a low viscosity. Thus, the internal friction is low, resulting in easier and more homogeneous dispersion of the nanoparticles.

ACKNOWLEDGMENTS

The research was supported by the Student Grant Agency of the University of West Bohemia in Pilsen, grant No. SGS-2021–003 “Materials, technologies and diagnostics in electrical engineering”.

REFERENCES

1. S. Anandhan, and S. Bandyopadhyay, “Polymer Nanocomposites: From Synthesis to Applications” in *Nanocomposites and Polymers with Analytical Methods*, edited by John Cuppoletti, 978-953-307-352-1 (2011).
2. T. Tanaka, "Dielectric nanocomposites with insulating properties", IEEE Transactions on Dielectrics and Electrical Insulation **12**(5), 1070-9878/05/$20.00 2005 IEEE, pp. 914-928 (2005).
3. D. PITSA and M. DANIKAS, “Interfaces features in polymer nanocomposites: A review of proposed models”. Nano Brief Reports and Reviews **6**, 10.1142/S1793292011002949 p. 497 (2011)
4. R. SUBBIAH *et al.,* “Nanoparticles: Functionalization and Multifunctional Applications in Biomedical Sciences “, Current Medicinal Chemistry **17**, 10.2174/092986710794183024, pp. 4559–77 (2010)
5. LI *et al*. “Roles of silanes and silicones in forming superhydrophobic and superoleophobic materials“, J. Mater. Chem. A **4**, 10.1039/C6TA05441B, p. 13677–13725 (2016).
6. HARTMANN *et al*. “Techniques and Protocols for Dispersing Nanoparticle Powders in Aqueous Media - Is there a Rationale for Harmonization?“, Journal of toxicology and environmental health. Part B, Critical reviews, **18**,10.1080/10937404.2015.1074969, p. 1–28 (2015).
7. K. W. LIENERT, “Poly(ester-imide)s for Industrial Use“. in *Progress in Polyimide Chemistry II. Berlin, Heidelberg: Springer Berlin Heidelberg*, 10.1007/3-540-49814-1_2, p. 45–82 (1999)
8. Elantas. Elan-Protect UP 142 product catalogue.
9. Elantas. Elan-Protect UP 343 product catalogue.
10. Evonik Industries. AEROSIL® product catalogue
11. V. Mentlík and O. Michal, “Influence of SiO2 nanoparticles and nanofibrous filler on the dielectric properties of epoxy-based composites”, Materials Letters, 10.1016/j.matlet.2018.04.021 (2018)
12. O. Michal, *et al.*, "Effect of Thermal Stress on the Hybrid Fibre/Particle Nanocomposite," *20th International Scientific Conference on Electric Power Engineering (EPE)*, 10.1109/EPE.2019.8777947 (2019)
13. O. Michal, *et al*. “Impact of ultrasonic mixing on the electrical properties of PEI/SiO2 nanocomposites”. In AIP Conference Proceedings, 10.1063/5.0066867 (2021)