

Effect of Nanofiller Calcination on Breakdown Performance of Silica Based Polyethylene Nanocomposites

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Abstract— Polymer nanocomposites have become one of the main research studies in investigating the potential use of new dielectric materials especially in high voltage insulation. Many promising results, especially on the use of polyethylene nanocomposites as dielectric materials, have been reported in the literature. Significantly, the main factor that affects the dielectric performance of the materials was attributed to the interface between the host matrix and the nanofiller. This paper reports on an investigation into the AC and DC breakdown performance of unfilled and polyethylene nanocomposites containing silicon dioxide (SiO₂) nanofillers at different loading levels (1 wt%, 4 wt%, and 8wt%). By using the Fourier transform infrared (FTIR) spectroscopy, the chemical structures of the materials were characterized. The dielectric permittivity of the samples was analyzed using dielectric spectroscopy. From the breakdown results, it showed that AC breakdown testing did not result in significant changes on the breakdown strength between uncalcined and calcined nanofillers. Meanwhile, for DC breakdown testing, introducing a small number of nanofillers could have a major impact on the DC breakdown strength. These results were correlated with the calcination process of nanofiller; the DC breakdown strength improved for calcined nanofiller compared to uncalcined nanofiller.

Keywords—nanocomposites; polyethylene; silica; breakdown; calcination

I. INTRODUCTION

Recently, researchers from various field are working on the hybrid approach on micro and nanofiller. Research on the hybrid fillers can be as a new alternative filler in the materials technologies. For instance, rubber composite-filled hybrid fillers showed that the improvements on tensile strength and modulus [1]. Filler and additive agents are currently used in electrical insulating materials in order to improve the mechanical and electrical performance of the materials [2]. Lately, the use of nanodielectrics or nanocomposites has become an interesting topic for researchers to develop an innovative class of dielectric materials for high voltage engineering applications. Polymer nanocomposites can be

defined as polymers with nanometre-sized (just few weight percentage, wt %) fillers homogeneously distributed and dispersed within the polymer matrices [3]. Normally, less than 10 wt% of nanofiller is used in nanocomposites in order to demonstrate its unique properties, in contrast to the conventional or microscale fillers [4].

There have been many previous studies reporting on the enhancements of the dielectric breakdown strength of polymer nanocomposites, such as polyethylene/silica nanocomposites [5]–[7]. The studies showed positive results on the breakdown strength of the nanocomposites. Therefore, the promise to develop a new class of electrical insulation technology for dielectric applications based on nanocomposite materials could be achieved. The presence of low dielectric constant surfactants may result in better electric potential distribution, which then improves the breakdown strength and electrical stress distribution [8].

With nanotechnology, beneficial discovery on the interfacial technology governing the nanofillers and the base polymers is expected. The role of the interface has been expected to be an important reason for the improved breakdown strength of many nanodielectrics [9]. Therefore, in an attempt to improve the interaction between the host matrix and nanofiller, various heat treatment processes, including calcining nanofillers at different temperatures, have been used [10], [11]. This paper investigates the AC and DC breakdown characteristics, dielectric permittivity and chemical structures of polyethylene nanocomposites containing uncalcined and calcined silicon dioxide (SiO₂) nanofillers, in determining potential interfacial factors that affect the breakdown behaviors of the materials.

II. EXPERIMENTAL

A. Material

A blend of polyethylene (PE) with 80% of low density polyethylene (LDPE) grade TITANLENE LDF200YZ and 20%

TABLE I. Test samples and their designations

Test Sample	Polymer		Filler (wt%)	Designation
	LDPE (%)	HDPE (%)		
Unfilled: LDPE+HDPE	80	20	0	U/0/0
LDPE+HDPE+	80	20	1	S/1/0
SiO ₂	80	20	4	S/4/0
(uncalcined: 0 °C)	80	20	8	S/8/0
LDPE+HDPE+	80	20	1	S/1/600
SiO ₂	80	20	4	S/4/600
(calcined: 600 °C)	80	20	8	S/8/600
LDPE+HDPE+	80	20	1	S/1/900
SiO ₂	80	20	4	S/4/900
(calcined: 900 °C)	80	20	8	S/8/900

of high density polyethylene (HDPE) grade TITANZEX HI2000 (LOTTE Chemical) was used. Nanosilica with a quoted particle size of 20 nm was obtained from NanoAmor. The amounts of nanoparticles added to the polyethylene were chosen to be 1 wt%, 4 wt%, and 8 wt%.

Three different conditions of calcination were applied, i.e., 0 °C (uncalcined), 600 °C, and 900 °C. The nanofiller was subjected to calcination in a furnace at a dwell time of 4 hours and the cooling process was about 10–12 hours.

The Brabender mixer was used to produce the compound of the polyethylene (PE) with the nanoparticles. This was prepared at a temperature, rotational speed, and duration of 160 °C, 55 rpm, and 10 min, respectively. To produce a disc-like sample, each sample was then melt pressed at a temperature and load of 160 °C and 2.5 ton, respectively. An approximately 100 μm thick sample was produced.

Table I shows the produced test samples of polyethylene with uncalcined and calcined nanofiller and their designations.

B. Characterization

To characterize the chemical structures of the nanoparticles and nanocomposites, the Perkin Elmer Spectrum One Fourier transform infrared (FTIR) spectroscope was used. The data for each spectrum was collected from 400 cm^{-1} to 4000 cm^{-1} .

To determine the real relative permittivity, ϵ' of the samples, the dielectric spectroscopy measurement was conducted using the Gamry Instruments Interface 1000TM with Tettex's 2914 Test Cell for Solid Insulants (with 25 mm radius inner guarded electrode). A 1 V_{rms} AC signal was applied with a frequency range of 10 Hz to 100 kHz, averaged over 20 cycles.

AC and DC breakdown tests were conducted based on the guidelines set out in the ASTM D149 standard solid test method. The nanocomposite sample was placed between two 6.3 mm diameter ball bearing electrodes, immersed in mineral oil to avoid surface flashover. For an AC test breakdown, a step voltage of 1 kV every 20 s was applied. The DC breakdown testing was conducted in a similar way to the AC breakdown testing, but with 2 kV every 20 s was applied. Fifteen points of breakdown measurements were recorded for each type of samples. By using the two-parameter Weibull

distribution analysis [12], all collected data from the breakdown measurements were then analyzed.

III. RESULTS AND DISCUSSION

A. FTIR analysis

Fig. 1 shows the FTIR spectra for the investigated polyethylene nanocomposite samples. The characteristic absorption bands for the U/0/0 were 2800–3000 cm^{-1} , 1460 cm^{-1} , and 720 cm^{-1} , representing C-H bonds of the polyethylene. Three additional characteristic absorption bands can be observed with the addition of SiO₂ to the host matrix; 1100 cm^{-1} , 800 cm^{-1} , and 470 cm^{-1} . These spectral bands indicate the Si-O-Si bonds. These FTIR spectra results were consistent with the previous findings [12]–[15].

Of note, at 3400 cm^{-1} wavenumber, the broad absorption band could be ascribed to the surface hydroxyl groups of the nanofiller and it is related to water molecules on the surface of the nanofiller [16]. In this regard, the surface hydroxyl groups and related water molecules on the surface of SiO₂ became more apparent with an increasing amount of SiO₂. Upon nanofiller calcination, the intensity at 3400 cm^{-1} OH was reduced, indicating that the surface hydroxyls groups were reduced.

B. Dielectric spectroscopy

Fig. 2 shows the real relative permittivity ϵ' for the unfilled polyethylene and silica-based polyethylene containing

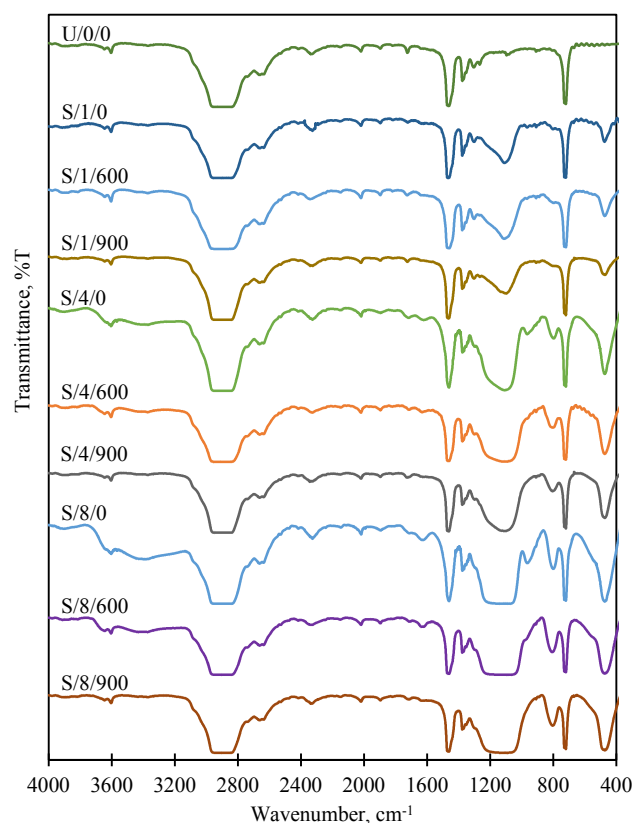


Fig. 1. FTIR spectra comparing unfilled polyethylene with nanocomposites containing uncalcined and calcined nanosilica

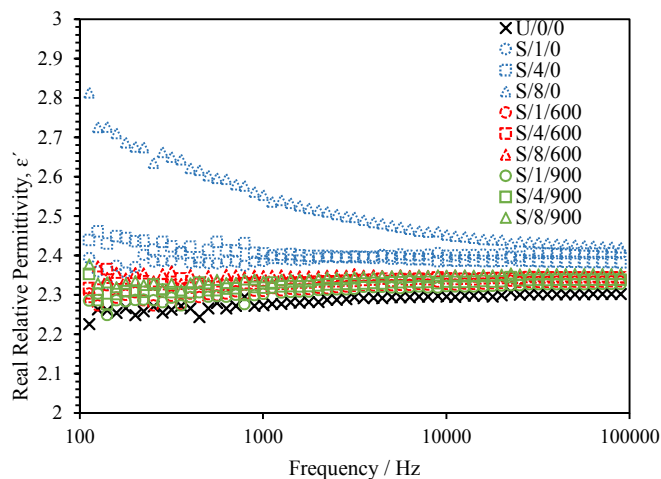


Fig. 2. Real relative permittivity data obtained for uncalcined and calcined samples

uncalcined and calcined nanosilica. For U/0/0 sample, it has 2.3 real relative permittivity. Meanwhile, for the nanocomposites containing uncalcined nanosilica, the ϵ' is dependent on the amount of nanofiller loading level. As the amount of uncalcined nanosilica increases, some seeming increases in real relative permittivity can be observed. For example, at the highest amount of nanosilica loading level (8 wt%), S/8/0 shows an increase in real relative permittivity over S/1/0 (see Fig. 2).

Upon calcination of nanosilica at 600 °C and 900 °C, it shows that the ϵ' of calcined nanosilica decreased compared to uncalcined nanosilica. Since Fig. 2 shows the reduction of real relative permittivity for both calcined nanosilica compared to uncalcined nanosilica, it can be deduced that, for nanocomposites containing calcined nanosilica at 600 °C and 900 °C, the surface hydroxyl content has reduced considerably [17].

C. AC Breakdown

Fig. 3 compares the AC breakdown strength of polyethylene nanocomposites containing 0 wt%, 1 wt%, 4 wt%, and 8 wt % of uncalcined and calcined nanosilica. The addition of uncalcined nanofiller up to 1 wt% did not show a significant effect on AC breakdown strength when compared with the unfilled polyethylene (see Table I). Therefore, it shows that a low amount of nanofiller does not alter the AC breakdown strength of the system compared to unfilled polyethylene. The addition of nanofiller up to 4 wt % of uncalcined nanosilica into polyethylene showed a slightly reduced AC breakdown strength. At 8 wt % of nanosilica loading level, the AC breakdown strength slightly decreased but the value still commensurate with 4 wt% of nanosilica loading level when taking into account the uncertainties in Weibull analysis.

Upon calcination process at 600 °C and 900 °C, there are no significant changes for both uncalcined and calcined nanosilica. Overall, the breakdown strength of the samples containing SiO₂ was somehow similar for all different amounts and calcination conditions. Therefore, for AC breakdown strength, uncalcined and calcined conditions of the

nanofillers do not significantly affect the value of breakdown strength. This is in line with the previous studies [12], [18].

D. DC Breakdown

Fig. 4 shows the comparison of the DC breakdown strength for polyethylene nanocomposites containing uncalcined and calcined nanosilica. The highest DC breakdown strength was recorded for U/0/0 with 332 kV/mm (see Table II). The DC breakdown strength for uncalcined nanosilica was 183 kV/mm, 101 kV/mm and 75 kV/mm at 1 wt%, 4 wt%, and 8 wt% respectively. From the trend, it shows a dramatically reduced DC breakdown strength with increasing amounts of uncalcined nanosilica. Hence, the addition of even a small amount of SiO₂ to polyethylene can give a major negative impact on the DC breakdown strength of the polyethylene nanocomposites [6].

For nanocomposites containing nanosilica calcined at 600 °C and 900 °C, their DC breakdown strength improved over nanocomposites containing equivalent amounts of uncalcined nanosilica (see Fig. 5 and Table III). Clearly, upon calcination of the nanosilica, the DC breakdown strength significantly increased; the value increased around 40 kV/mm and 60 kV/mm for nanocomposites containing calcined SiO₂ at 600 °C and 900 °C respectively over their uncalcined counterparts.

At low nanofiller loading level (1 wt %), the breakdown strength has increased after increasing the calcination temperature. By comparing between nanocomposites containing 1 wt % of uncalcined nanosilica and nanocomposites containing 1 wt% of calcined nanosilica at 900 °C, the breakdown strength showed an increment up to 35 %. Meanwhile, at 8 wt %, it shows a substantial rise of the DC breakdown strength up to 96 %. Consequently, calcination of nanosilica at high temperature up to 900 °C resulted in a major effect on the DC breakdown strength.

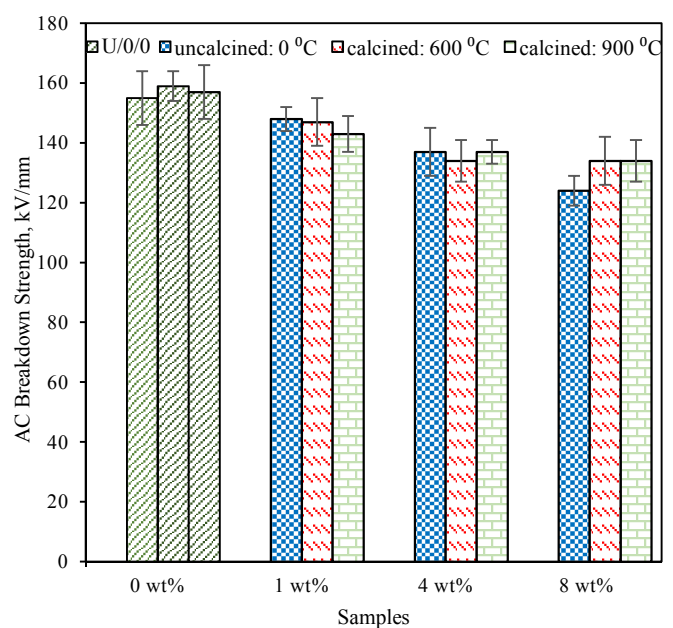


Fig. 3. Comparison of AC breakdown strength for polyethylene nanocomposites containing uncalcined and calcined nanosilica

TABLE II. AC BREAKDOWN RESULTS

Blend	Scale Parameter, α (kV/mm)	Shape Parameter, β
U/0/0	155 \pm 9	8 \pm 3
S/1/0	148 \pm 4	19 \pm 7
S/4/0	137 \pm 8	8 \pm 3
S/8/0	124 \pm 5	13 \pm 4
S/1/600	147 \pm 8	9 \pm 3
S/4/600	134 \pm 7	9 \pm 4
S/8/600	134 \pm 8	8 \pm 3
S/1/900	143 \pm 6	11 \pm 4
S/4/900	137 \pm 4	15 \pm 5
S/8/900	134 \pm 7	9 \pm 4

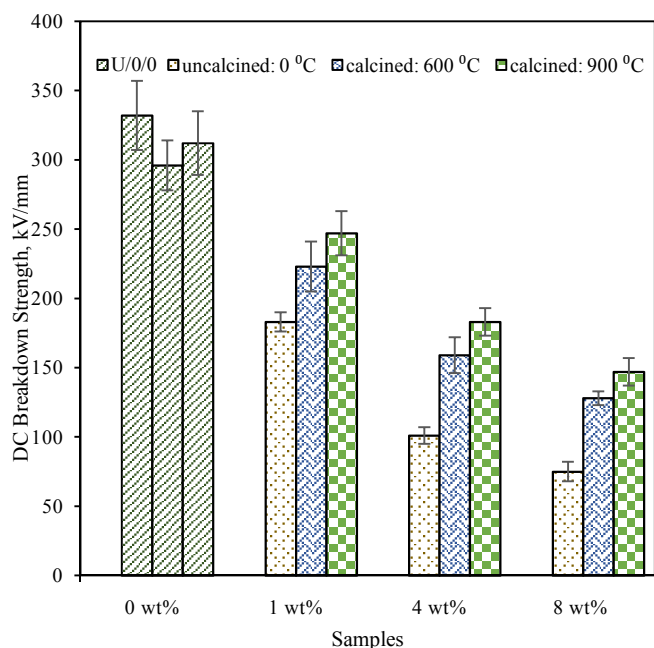


Fig. 4. Comparison of DC breakdown strength for polyethylene nanocomposites containing uncalcined and calcined nanosilica

TABLE III. DC BREAKDOWN RESULTS

Blend	Scale Parameter, α (kV/mm)	Shape Parameter, β
U/0/0	332 \pm 25	6 \pm 3
S/1/0	183 \pm 7	12 \pm 5
S/4/0	101 \pm 6	8 \pm 2
S/8/0	75 \pm 7	5 \pm 2
S/1/600	223 \pm 18	6 \pm 2
S/4/600	159 \pm 13	6 \pm 2
S/8/600	128 \pm 5	11 \pm 4
S/1/900	247 \pm 16	7 \pm 3
S/4/900	183 \pm 10	8 \pm 4
S/8/900	147 \pm 10	7 \pm 2

IV. CONCLUSIONS

The AC breakdown strength currently did not have a significant effect when nanosilica was introduced in the based polyethylene. These results occurred for both uncalcined and calcined nanosilica. Conversely, with the the addition of 1 wt%, 4 wt% and 8 wt% nanosilica, surprisingly the DC breakdown strength was reduced. However, compared with uncalcined and calcined nanosilica, the value of the DC breakdown strength for calcined nanosilica was increased. Although the addition of nanosilica reduces the value of the DC breakdown strength, upon calcination process the value

of calcined nanocomposites could be higher compared to uncalcined nanocomposites. Therefore, this research works could underline the potential of further investigation on dielectric materials. From the research, it is predicted that the presence of surface hydroxyl groups within the nanocomposites (as shown through the FTIR spectra) gave a dominant role too. This is because the presence of water would negatively affect the breakdown strength of any dielectrics. While these effects could be associated with the real relative permittivity (as shown through the dielectric spectroscopy). Consequently, the considerations of the mechanisms in nanocomposite water absorption or nanofiller water adsorption are critical in dielectric materials technology. Calcination can be one of the technique to eliminates the water content in nanofiller itself. Consequently, a positive attempt to eliminate water molecules from nanocomposites can promisingly improve the DC breakdown strength of the polyethylene nanocomposites.

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REFERENCES

- [1] Z. A. S. Abdul Salim, A. Hassan, and H. Ismail, "A Review on Hybrid Fillers in Rubber Composites," *Polym. - Plast. Technol. Eng.*, vol. 57, no. 6, pp. 523–539, 2018.
- [2] E. Watanabe, Y. Takeda, M. Yoshizawa, T. Moriya, and M. Nakajima, "The effect of filler particle size on ultrasonic image of electrical breakdown region in filler-added insulating materials," in *Electrical Insulation and Dielectric Phenomena, 1996. IEEE 1996 Annual Report of the Conference on*, 1996, vol. 2, pp. 697–700.
- [3] T. Tanaka, "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, 2004.
- [4] M. A. Lopez-Manchado, J. L. Valentinn, J. Carretero, F. Barroso, and M. Arroyo, "Rubber network in elastomer nanocomposites," *Eur. Polym. J.*, vol. 43, no. 10, pp. 4143–4150, 2007.
- [5] W. Wang, S. Li, F. Tang, and J. Li, "Characteristics on breakdown performance of polyethylene/silica dioxide nanocomposites," in *Annual Report - Conference on Electrical Insulation and Dielectric Phenomena, CEIDP*, 2012, pp. 521–524.
- [6] K. Y. Lau, A. S. Vaughan, and G. Chen, "Nanodielectrics: Opportunities and challenges," *IEEE Electr. Insul. Mag.*, vol. 31, no. 4, pp. 45–54, 2015.
- [7] K. Y. Lau, M. A. M. Piah, and K. Y. Ching, "Correlating the breakdown strength with electric field analysis for polyethylene/silica nanocomposites," *J. Electrostat.*, vol. 86, pp. 1–11, 2017.
- [8] E. Tuncer, A. J. Rondinone, J. Woodward, I. Sauer, D. R. James, and A. R. Ellis, "Cobalt iron-oxide nanoparticle modified poly(methyl methacrylate) nanodielectrics : DDDDielectric and

- electrical insulation properties,” *Appl. Phys. A Mater. Sci. Process.*, vol. 94, no. 4, pp. 843–852, 2009.
- [9] M. Roy, J. K. Nelson, R. K. MacCrone, L. S. Schadler, C. W. Reed, and R. Keefe, “Polymer nanocomposite dielectrics—the role of the interface,” *Dielectr. Electr. Insul. IEEE Trans.*, vol. 12, no. 4, pp. 629–643, 2005.
- [10] M. Praeger, I. L. Hosier, A. S. Vaughan, and S. G. Swingler, “The effects of surface hydroxyl groups in polyethylene-silica nanocomposites,” in *33rd Electrical Insulation Conference, EIC 2015*, 2015, pp. 201–204.
- [11] A. Krivda *et al.*, “Characterization of epoxy microcomposite and nanocomposite materials for power engineering applications,” *IEEE Electr. Insul. Mag.*, vol. 28, no. 2, pp. 38–51, 2012.
- [12] K. Y. Lau, A. S. Vaughan, G. Chen, and I. L. Hosier, “Polyethylene nanodielectrics: The effect of nanosilica and its surface treatment on electrical breakdown strength,” in *Annual Report - Conference on Electrical Insulation and Dielectric Phenomena, CEIDP*, 2012, pp. 21–24.
- [13] Ziyi Huang, “Rating Methodology of High Voltage Mass Impregnated DC Cable Circuits,” 2014.
- [14] W. Cheng, W. Miao, L. Zhang, and J. Peng, “Covalently Bonded Pe/Sio₂ Nanocomposites Synthesized By Reactive Extrusion,” *Iran. Polym. J.*, vol. 20, no. 8, pp. 681–687, 2011.
- [15] L. Peng, W. Qisui, L. Xi, and Z. Chaocan, “Investigation of the states of water and OH groups on the surface of silica,” *Colloids Surfaces A Physicochem. Eng. Asp.*, vol. 334, no. 1–3, pp. 112–115, 2009.
- [16] M. Parvinzadeh, S. Moradian, A. Rashidi, and M. E. Yazdanshenas, “Surface characterization of polyethylene terephthalate/silica nanocomposites,” *Appl. Surf. Sci.*, vol. 256, no. 9, pp. 2792–2802, 2010.
- [17] M. G. Todd and F. G. Shi, “Characterizing the interphase dielectric constant of polymer composite materials: Effect of chemical coupling agents,” *J. Appl. Phys.*, vol. 94, no. 7, pp. 4551–4557, 2003.
- [18] G. Iyer, R. Gorur, R. Richert, A. Krivda, and L. Schmidt, “Dielectric Properties of Epoxy Based Nanocomposites for High Voltage Insulation,” *IEEE Trans. Dielectr. Electr. Insul.*, vol. 18, no. 3, pp. 659–666, 2011.