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

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Abstract— **Dielectrics are widely used in electrical and high voltage systems. Studies on new dielectric materials, especially polymer nanocomposites, have been extensively carried out in order to investigate the potential improvements of the materials in high voltage insulation. Significantly, the interface between the base material (polymer) and the nanofiller is a vital factor that influences the dielectric performance of the materials. This paper reports on an investigation into the AC and DC breakdown performance of unfilled and polyethylene nanocomposites containing zirconium oxide (ZrO₂) nanofillers at different amounts; 1 wt%, 4 wt%, and 8wt%. The chemical structures of the materials were characterized using Fourier transform infrared (FTIR) spectroscopy. Dielectric spectroscopy was used to measure the dielectric permittivity of the samples. Breakdown testing showed that there were no significant changes on the AC breakdown behaviors of nanocomposites containing both uncalcined and calcined nanofillers. Meanwhile, substantial changes were observed on the materials' DC breakdown strength, even by introducing a small amount of nanofiller (1 wt%); the DC breakdown strength of the nanocomposites enhanced for those containing calcined nanofillers compared to uncalcined nanofillers. The observation is associated with the calcination process of the nanofillers.**

Keywords—nanocomposites; polyethylene; zirconia; breakdown; calcination

I. Introduction

Electrical insulation is important in order to ensure the safety and reliable operations of high voltage equipment. Nowadays, polymers are widely used as insulating materials due to their good dielectric properties, low cost and ease of production. Among many dielectric parameters, electrical breakdown strength is a major factor that measures the insulation capability of the materials [1].

Recently, nanocomposites have become an interesting topic in various disciplines due the unique properties that these materials can exhibit. Nanocomposites can be described as polymers with nanofillers that contain at least one dimension less than 100 nm in size. The combination of polymers with nanofillers are able to achieve desirable dielectric properties. Nanocomposites have much greater interfacial area compared to microcomposites [2], [3] due to the characteristic of nanofiller that have very high surface area-to-volume ratio, such as zirconium dioxide (ZrO₂) nanofiller. This will promote the interactions between the base material and the filler, thus leading to enhanced chemical or heat-resistance properties [4]. ZrO₂ nanofiller is also one of the strongest and toughest ceramic materials.

There have been many studies conducted on the potential improvement of the breakdown strength of dielectrics through nanostructuration, such as the use of polyethylene/silica nanocomposites [5]–[7]. However, there have been limited studies on zirconia nanocomposites, especially on the materials' breakdown strength. Therefore, this study aimed to investigate the AC and DC breakdown characteristics, dielectric permittivity and chemical structures of polyethylene nanocomposites containing ZrO₂ nanofillers. To modify the surface state of the nanofiller, various heat treatment processes via calcination have been applied. The possible mechanisms that govern the breakdown properties of the materials are discussed.

II. Experimental

A. Material

The polyethylene (PE) used in this study was composed of 80% of low density polyethylene (LDPE) grade TITANLENE LDF200YZ and 20% of high density polyethylene (HDPE) grade TITANZEX HI2000 (LOTTE Chemical). The nanoparticle used was ZrO₂, obtained from NanoAmor, with quoted particle size of 20 nm. Three filler concentrations were chosen; 1 wt%, 4 wt% and 8 wt%. The nanofiller was calcined at three different temperature conditions, i.e., 0 ℃ (uncalcined), 600 ℃, and 900 ℃. The nanofiller was calcined at a dwell time of 4 hours and left for 10~12 hours for cooling purposes.

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+ ZrO₂ (uncalcined: 0 °C)	80	20	1	Z/1/0
	80	20	4	Z/4/0
	80	20	8	Z/8/0
LDPE+HDPE+ ZrO₂ (calcined: 600 °C)	80	20	1	Z/1/600
	80	20	4	Z/4/600
	80	20	8	Z/8/600
LDPE+HDPE+ ZrO₂ (calcined: 900 °C)	80	20	1	Z/1/900
	80	20	4	Z/4/900
	80	20	8	Z/8/900

To produce the compound sample of the polyethylene (PE) with the nanoparticle, the Brabender mixer was used. The temperature, rotational speed, and duration of 160 ºC, 55 rpm, and 10 min, respectively, were applied. Each sample was then melt pressed using Carver Hydraulic hot press at a temperature of 160 ºC and 2.5 ton load. Approximately 100 µm thick of a disc-like sample was produced.

Table I shows the PE samples with uncalcined and calcined zirconia nanofiller and their designations.

B. Characterization

The chemical structures of the nanofillers and nanocomposites were characterized using the Perkin Elmer Spectrum One Fourier transform infrared (FTIR) spectroscope. The data spectrum was collected from 400 cm^{-1} to 4000 cm^{-1}.

The dielectric spectroscopy measurement was conducted in order to determine the real relative permittivity ε' of the samples. The measurement was conducted using the Gamry Instruments Interface 1000^{TM} 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.

For electrical testing, the AC and DC breakdown tests were conducted based on the guidelines set out in the ASTM D149 standard solid test method. Each test sample was placed between two 6.3 mm diameter ball bearing electrodes. To avoid surface flashover, the sample was immersed in mineral oil. AC breakdown test was conducted at a step voltage of 1 kV every 20 s while DC breakdown test was conducted at a step voltage of 2 kV every 20 s. For the electrical breakdown testing, fifteen points of breakdown measurements were recorded. All the collected data from the breakdown measurements were analyzed using the two-parameter Weibull distribution analysis [8].

III. RESULTS AND DISCUSSION

A. FTIR analysis

Fig. 1 shows the FTIR spectra for the investigated polyethylene nanocomposite samples. From Fig. 1, it shows that the characteristic absorption bands for U/0/0 were 2800-3000 cm^{-1}, 1460 cm^{-1}, and 720 cm^{-1}, representing C-H bonds of the polyethylene. With the addition of ZrO₂ to the host matrix; two additional characteristic absorption bands can be observed at 800 cm^{-1} and 540 cm^{-1}. These FTIR spectra results were consistent with the past studies [9]–[11].

At 3400 cm^{-1} wavenumber, the broad absorption band could be ascribed to the surface hydroxyl groups of the nanofiller and it is associated with water molecules on the surface of the nanofiller [12]. Of note, for the nanocomposites containing ZrO₂, variations at the 3400 cm^{-1} wavenumber could not be persuasively differentiated.
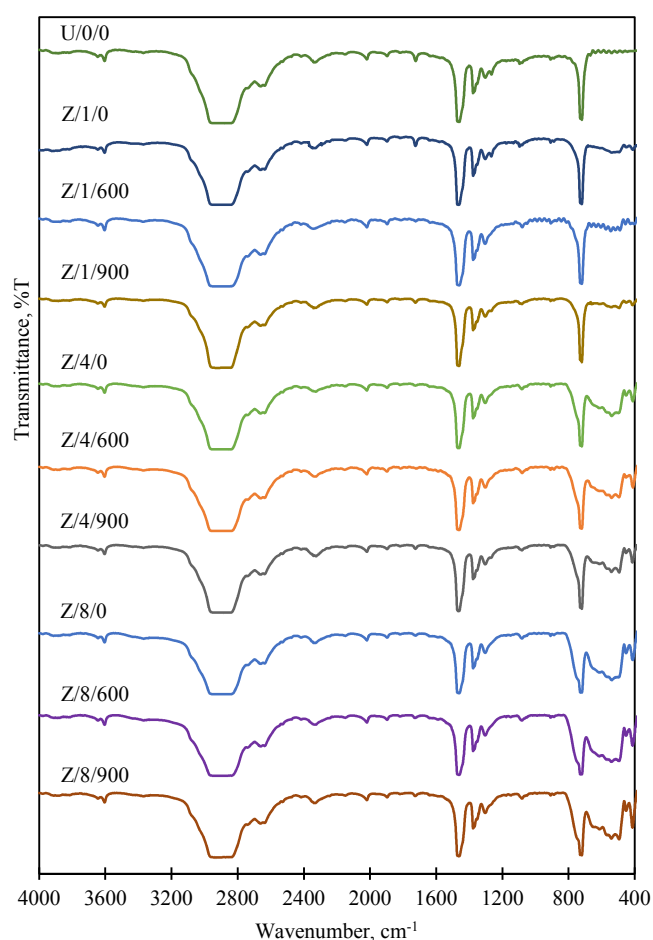

Fig. 1. FTIR spectra comparing unfilled polyethylene with nanocomposites containing uncalcined and calcined nanozirconia

B. Dielectric spectroscopy

Fig. 2 shows the real relative permittivity ε´ for the unfilled polyethylene and zirconia-based polyethylene containing uncalcined and calcined nanozirconia. For U/0/0 sample, it has about 2.3 real relative permittivity. However, for the nanocomposites containing uncalcined nanozirconia, the ε´ is dependent on the content of the nanofiller. As shown in Fig. 2, when the amount of uncalcined nanozirconia increases, an increase in real relative permittivity is observed. For instance, at the highest amount of nanozirconia loading level (8 wt%), Z/8/0 shows an increase in real relative permittivity over Z/1/0 (see Fig. 2).

Upon calcination of nanozirconia at 600 ºC and 900 ºC, the ε´ of calcined nanozirconia decreased compared to uncalcined nanozirconia. Therefore, it can be deduced that, for nanocomposites containing calcined nanozirconia at high calcination temperatures (600 ºC and 900 ºC), the surface hydroxyl content has reduced significantly.

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 nanozirconia. The highest value of AC breakdown strength was recorded for U/0/0. The AC breakdown strength for U/0/0 and Z/1/0 was comparable. The lowest AC breakdown strength was recorded for Z/8/0 which was 122 kV/mm. The inclusion of uncalcined nanofiller up to 4 wt% did not show significant effect on AC breakdown strength when compared with the unfilled polyethylene (see Fig. 3 and Table II). Hence, the inclusion of a low amount of nanozirconia did not affect the AC breakdown strength of the system compared to unfilled polyethylene.
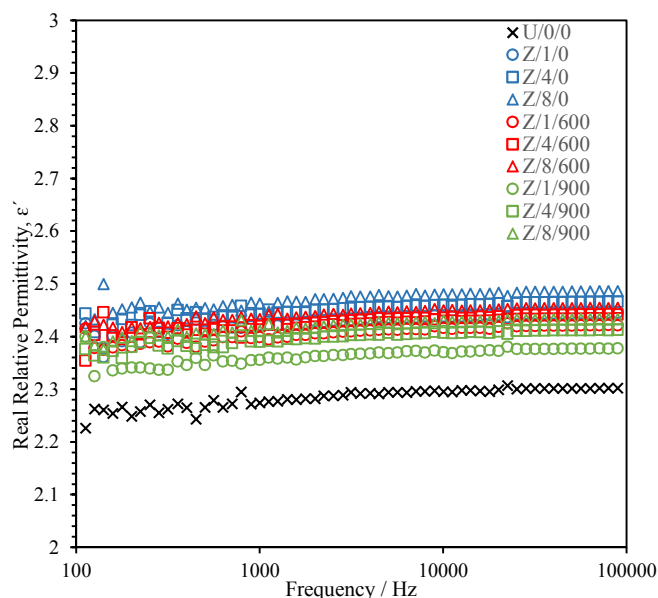

Fig. 2. Real relative permittivity data obtained for uncalcined and calcined samples
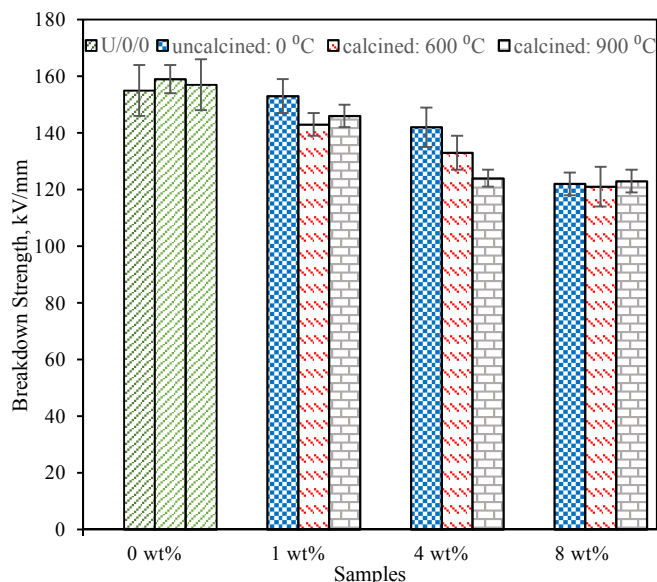

Fig. 3. Comparison of AC breakdown strength for polyethylene nanocomposites containing uncalcined and calcined nanozirconia

TABLE II.   AC BREAKDOWN RESULTS

Blend	Scale Parameter, α (kV/mm)	Shape Parameter, β
U/0/0	155 ± 9	8 ± 3
Z/1/0	153 ± 6	13 ± 5
Z/4/0	142 ± 7	10 ± 4
Z/8/0	122 ± 4	16 ± 7
Z/1/600	132 ± 5	12 ± 5
Z/4/600	133 ± 6	11 ± 4
Z/8/600	121 ± 7	9 ± 3
Z/1/900	146 ± 4	7 ± 3
Z/4/900	124 ± 3	8 ± 4
Z/8/900	123 ± 4	7 ± 2

Upon calcination process at 600 ºC and 900 ºC, no appreciable AC breakdown changes were observed in comparison with their uncalcined counterparts (see Fig. 3). Overall, the breakdown strength of the samples containing ZrO_2 was somehow comparable for all different amounts and calcination conditions. Consequently, for the AC breakdown strength, uncalcined and calcined conditions of the nanofillers have no major effects on the value of breakdown strength. The result is in line with the previous studies [8], [13].

D. DC Breakdown

Fig. 4 shows the comparison of the DC breakdown strength for polyethylene nanocomposites containing uncalcined and calcined nanozirconia. For uncalcined nanozirconia, the nanocomposites experienced much reduced breakdown strength when the amount of nanozirconia was increased. The DC breakdown strength for uncalcined nanozirconia was 262 kV/mm, 226 kV/mm and 167 kV/mm at 1 wt%, 4 wt% and 8 wt% respectively. The highest breakdown value for U/0/0 polyethylene was 332 kV/mm. So, for uncalcined nanozirconia, the DC breakdown strength was sensitive to different amounts of nanofiller loading levels.

Increasing amounts of uncalcined nanofillers reduced the breakdown strength of the materials. This was reported before [14] on the drop of breakdown strength due to increasing amounts of nanofillers.

For nanocomposites containing nanozirconia calcined at 600 ºC and 900 ºC, their DC breakdown strength improved over nanocomposites containing equivalent amounts of uncalcined nanozirconia (see Fig. 4 and Table III). Therefore, upon calcination of the nanozirconia, the DC breakdown strength significantly increased; the value increased around 20 to 60 kV/mm and 70 to 140 kV/mm for nanocomposites containing calcined ZrO_2 at 600 ºC and 900 ºC respectively over their uncalcined counterparts.

Even though the DC breakdown strength reduced upon nanozirconia addition (compared to U/0/0), the breakdown strength increased after increasing the calcination temperature, and the DC breakdown value can even be comparable with U/0/0. For example, by comparing between nanocomposites containing 1 wt % of uncalcined nanozirconia and nanocomposites containing 1 wt% of calcined nanozirconia at 900 ºC, DC breakdown strength showed an increment up to 31%. Meanwhile, at the highest loading level (8 wt %), it shows a significant rise of the DC breakdown strength up to 85 %.

Although the removal of surface hydroxyl groups from ZrO_2 could not be convincingly observed from the FTIR analysis on the samples, the authors believed the surface hydroxyl groups were successfully eliminated from ZrO_2 upon the nanofiller calcination process. This is supported through reduced dielectric permittivity of the materials upon nanofiller calcination. Therefore, the water content on ZrO_2 could be eliminated and the breakdown properties of the materials could be improved.
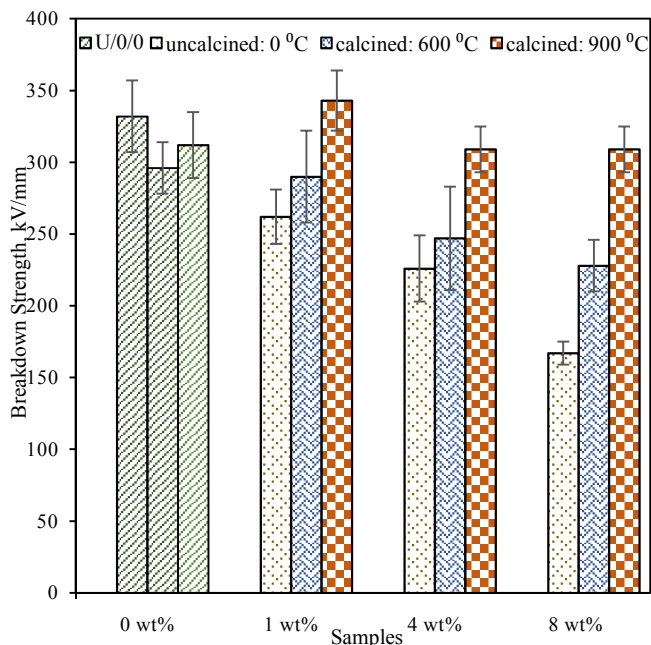
TABLE III.   DC BREAKDOWN RESULTS

Blend	Scale Parameter, α (kV/mm)	Shape Parameter, β
U/0/0	332 ± 25	6 ± 3
Z/1/0	262 ± 19	6 ± 3
Z/4/0	226 ± 23	5 ± 2
Z/8/0	167 ± 8	9 ± 4
Z/1/600	290 ± 32	4 ± 2
Z/4/600	247 ± 36	3 ± 1
Z/8/600	228 ± 18	6 ± 2
Z/1/900	343 ± 21	8 ± 3
Z/4/900	309 ± 16	9 ± 4
Z/8/900	309 ± 16	9 ± 3

IV.   CONCLUSIONS

The AC breakdown strength does not have a major effect when nanozirconia was introduced in the polyethylene host matrix. These results happened for both uncalcined and calcined nanozirconia. Meanwhile, from the DC breakdown results, the addition of 1 wt%, 4 wt% and 8 wt% of nanozirconia resulted in the reduced DC breakdown strength. Nevertheless, the value of the DC breakdown strength for nanocomposites containing calcined nanozirconia increased compared to those containing uncalcined nanozirconia. This indicates that calcination process can be an effective way to improve the DC breakdown strength of nanocomposites. Since the calcination process was also effective in removing the surface hydroxyl groups on the zirconia nanopowder, the improved DC breakdown strength can be attributed to the successful removal of the hydroxyl groups from the surface of the zirconia nanopowder. Therefore, any successful attempt to eliminate water molecules from nanocomposites can promisingly improve the DC breakdown strength of the polyethylene nanocomposites.

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

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