

# *The Effect of Water Absorption on the Dielectric Response of Calcined Zirconia-based Polyethylene Nanocomposites*

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# The Effect of Water Absorption on the Dielectric Response of Calcined Zirconia-based Polyethylene Nanocomposites

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**Abstract**— Polymer nanocomposites have become one of the attractive research areas in exploring new dielectric materials. This is due to their potential dielectric property enhancements as a consequence of nanostructuration. However, the degradation of the dielectric performance of nanocomposites has also been reported and this is can be related to the presence of water within the materials. The main objective of the current work was to investigate the effects of water absorption on the mass change and dielectric response of polyethylene (PE) nanocomposites containing uncalcined and calcined zirconia ( $ZrO_2$ ) nanofillers. The results show that nanocomposites containing uncalcined  $ZrO_2$  exhibited a marginal increase in the real permittivity after water immersion. Under similar water immersion periods, nanocomposites containing calcined  $ZrO_2$  also demonstrated a marginal increase in the real permittivity. Factors influencing the dielectric response of the nanocomposites after  $ZrO_2$  calcination and water immersion are discussed.

**Keywords**—nanocomposites; zirconia; dielectric response; calcination; water absorption

## I. INTRODUCTION

Polymer nanocomposites have attracted many researchers' attention in dielectrics and electrical insulation since 2003 [1]. This is due to the unique dielectric property changes associated with the addition of nanofillers at low weight percentages (usually less than 10 wt%), which cannot be achieved with conventional or microscale fillers [2]. However, many fundamental challenges have yet to be addressed for using polymer nanocomposites practically in the field of electrical insulating materials [3].

In 2013, Lau et al. [4] demonstrated that the presence of water in nanocomposites, especially those containing oxide-based nanofillers, was critical and required significant attention. This is because oxide-based nanofillers commonly contain hydroxyl groups on their surface and the presence of such functional groups promotes water absorption [5]. The water absorption issue, if not addressed appropriately, could detrimentally affect nanocomposites' electrical properties [4]. In [6], the increase in water content within polymer nanocomposites was demonstrated to increase the dielectric loss tangent of the materials and negatively affect the dielectric properties of the materials [6].

Calcination of nanofillers has been proposed as an effective method to eliminate adsorbed water on the surface of nanofillers [7]. Recently, the DC breakdown performance of nanocomposites containing calcined nanofillers, such as  $ZrO_2$ , have been shown to improve compared to nanocomposites containing uncalcined  $ZrO_2$  [8]. However, the effects of nanofiller calcination on the water absorption behavior and hence the dielectric properties of nanocomposites have been scarcely reported. This paper therefore expands our previous work on  $ZrO_2$  calcination [8] by comparing the water absorption behavior of polyethylene (PE) nanocomposites containing uncalcined and calcined  $ZrO_2$ . Mass changes of the materials under different water immersion intervals were monitored and the dielectric response of the materials after water immersion was determined, to understand the effect of water absorption on the nanocomposites after  $ZrO_2$  calcination.

## II. EXPERIMENTAL

### A. Materials

The base polymer used was a polyethylene blend composed of 80% of low density polyethylene (LDPE) grade TITANLENE LDF200YZ and 20% high density polyethylene (HDPE) grade TITANZEX HI2000 (LOTTE Chemical Titan). The nanofiller used was zirconia ( $ZrO_2$ ) with a quoted particle size of 20 nm, sourced from NanoAmor. Different loading levels of 1, 4, and 8 wt% of  $ZrO_2$  were used. Before being added to the PE blend, the  $ZrO_2$  was calcined at 600 °C and 900 °C. The  $ZrO_2$  was calcined in a furnace for 4 h and left to cool down naturally. Details of the calcination process can be found elsewhere [9].

A Brabender mixer was used to produce a nanocomposite compound of PE with the aforementioned  $ZrO_2$  nanoparticles. The materials were compounded at a temperature, rotational speed, and duration of 160 °C, 55 rpm, and 10 min, respectively. In order to produce disc-like samples nominally 100  $\mu\text{m}$  in thickness, each material was melt pressed using a hydraulic laboratory press at a temperature of 160 °C. Table I shows the produced test samples and their designations.

TABLE I  
DESIGNATIONS OF TEST SAMPLES

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

### B. Characterization

To examine the effect of nanofiller calcination on the water absorption behavior of PE nanocomposites, nanocomposite samples were immersed in 200 ml of distilled water in separate beakers for up to 15 days for different time intervals (0 day, 1 day, 2 days, 4 days, 10 days, and 15 days) under laboratory ambient conditions. The mass of the water-immersed samples was monitored continuously. Before weighing, the samples were placed on filter papers and dried carefully using tissue paper. Equation 1 shows the formula used to calculate the percent changes (mass increment).

$$\% \text{ Mass} = \left| \frac{M_w - M_d}{M_d} \right| \times 100\% \quad (1)$$

where  $M_w$  is the mass of the sample after water immersion and  $M_d$  is the mass of the dry sample.

To determine the real part of the relative permittivity,  $\epsilon'$ , and imaginary part,  $\epsilon''$ , dielectric spectroscopy measurements were conducted using the Gamry Instruments Interface 1000™ with Tettex's 2914 Test Cell for Solid Insulants (with 25 mm radius inner guarded electrode). A 1 V<sub>rms</sub> AC signal was used with a frequency range of 10 Hz to 100 kHz, averaged over 20 cycles.

## III. RESULTS AND ANALYSIS

### A. Mass Changes

Fig. 1a presents plots of the water absorption behavior of nanocomposites comprising uncalcined ZrO<sub>2</sub> initially and after, 1 day, 2 days, 4 days, 10 days, and 15 days; the unfilled PE serves as a reference sample. The variation in the mass of the unfilled PE was comparable to measurement uncertainties and, as such, these changes are insignificant. Referring to Fig. 1a for nanocomposites containing uncalcined ZrO<sub>2</sub>, the mass marginally increased with increasing amounts of ZrO<sub>2</sub> (compare Z/1/0, Z/4/0, and Z/8/0), and with increasing period of water immersion duration up to 15 days.

Similar trends were observed for nanocomposites containing ZrO<sub>2</sub> calcined at 600 °C (Fig. 1b) and nanocomposites containing ZrO<sub>2</sub> calcined at 900 °C (Fig. 1c), where marginal changes in mass were recorded with increasing water immersion periods. Although the absorbed water content for ZrO<sub>2</sub> nanocomposite samples for uncalcined and calcined conditions is less than 0.04%, the

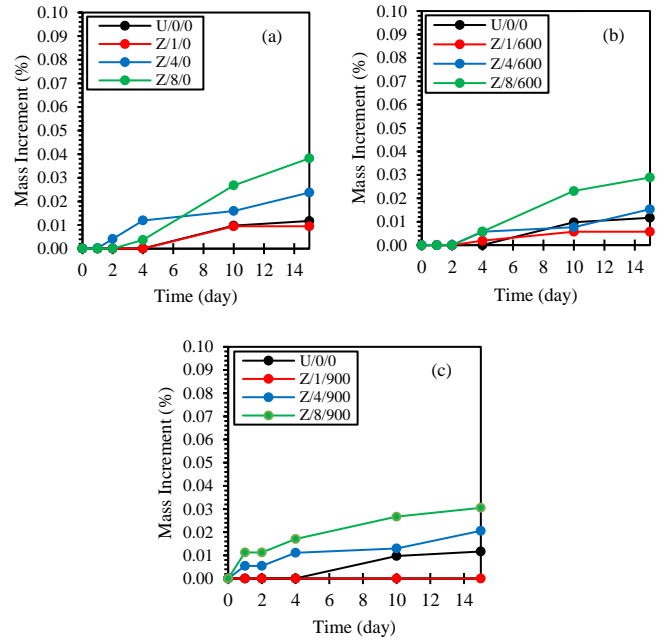


Fig. 1 Water absorption capability of ZrO<sub>2</sub> nanocomposites containing (a) uncalcined ZrO<sub>2</sub>, (b) ZrO<sub>2</sub> calcined at 600 °C, (c) ZrO<sub>2</sub> calcined at 900 °C, normalized with reference to unfilled PE

results show that the absorbed water content for nanocomposites containing uncalcined ZrO<sub>2</sub>, ZrO<sub>2</sub> calcined at 600 °C, and ZrO<sub>2</sub> calcined at 900 °C was altered systematically in accordance with the amount of ZrO<sub>2</sub>. This reinforces our previous assertion that water-related effects can be influential in affecting the dielectric properties of PE/ZrO<sub>2</sub> nanocomposites [8].

### B. Dielectric Spectroscopy

Results from dielectric spectroscopy show that the real and imaginary parts of the relative permittivity of the nanocomposites containing uncalcined ZrO<sub>2</sub> increased slightly with increasing time of water immersion (see Fig. 2). Similarly, the real and imaginary permittivities of nanocomposites containing ZrO<sub>2</sub> calcined at 600 °C (see Fig. 3), and 900 °C (see Fig. 4) also increased slightly upon immersion in water for up to 15 days. For nanocomposites containing 8 wt% of ZrO<sub>2</sub> calcined at 600 °C and 900 °C, the real part of the relative permittivity of the nanocomposite samples increased notably with increasing water immersion periods across the whole frequency range studied (see Fig. 3b and Fig. 4b). In our previous work [8], the permittivity values obtained from nanocomposites containing calcined ZrO<sub>2</sub> were less than those obtained from nanocomposites containing uncalcined ZrO<sub>2</sub>, a result we asserted as being a direct consequence of the effectiveness of the calcination process in removing water-related species. In addition, the associated changes in the structure of ZrO<sub>2</sub> may lead to enhanced interactions between calcined ZrO<sub>2</sub> and PE, which may also serve to lower the effective permittivity of nanocomposites containing calcined ZrO<sub>2</sub> compared to those containing uncalcined ZrO<sub>2</sub>. In the current work, water immersion resulted in a marginal increase in the permittivity values with increasing amounts of uncalcined and calcined ZrO<sub>2</sub>, and with increasing period of water immersion up to 15 days. We therefore suggest that water-related interactions are influential in ZrO<sub>2</sub>-based nanocomposites and that

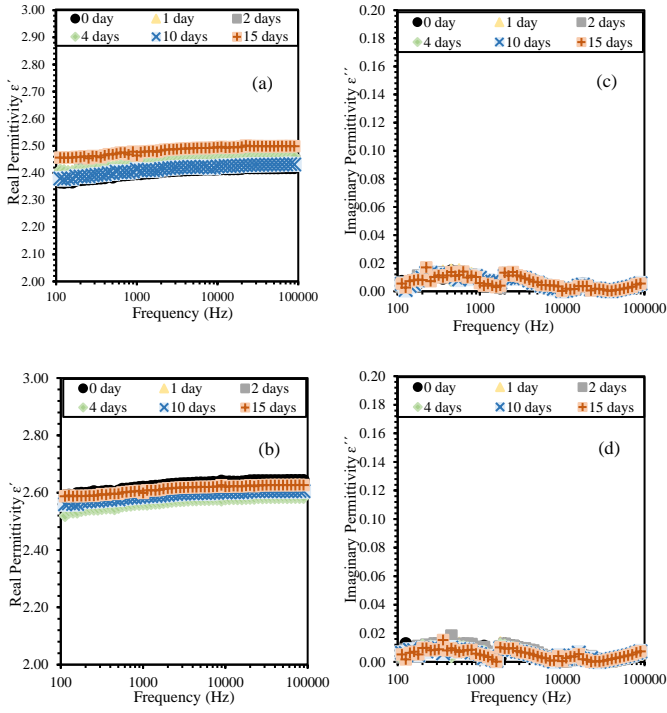


Fig. 2 Real permittivity of  $ZrO_2$  nanocomposites comprising (a) 1 wt%, (b) 8 wt % of uncalcined  $ZrO_2$  and imaginary permittivity of  $ZrO_2$  nanocomposites comprising (c) 1 wt%, (d) 8 wt% of uncalcined  $ZrO_2$  upon water immersion at different time intervals

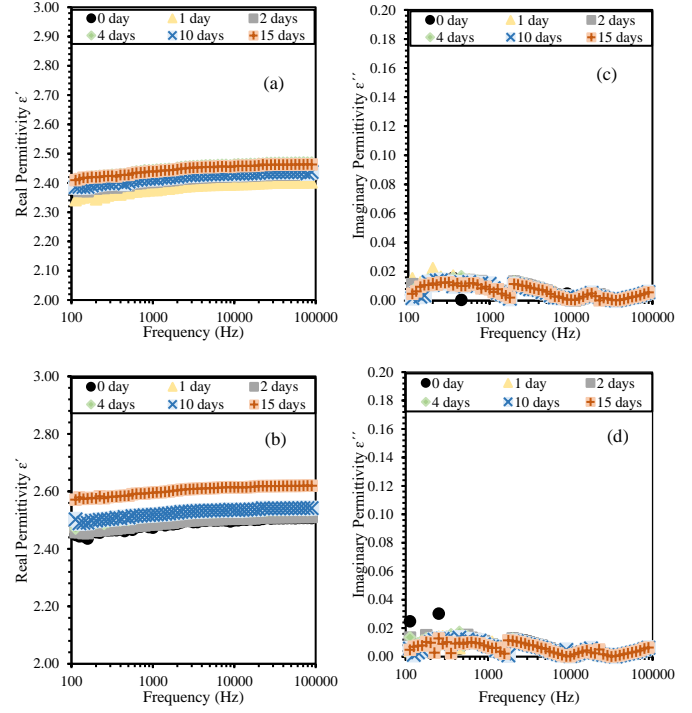


Fig. 4 Real permittivity of  $ZrO_2$  nanocomposites comprising (a) 1 wt%, (b) 8 wt % of calcined  $ZrO_2$  at 900 °C and imaginary permittivity of  $ZrO_2$  nanocomposites comprising (c) 1 wt%, (d) 8 wt% of calcined  $ZrO_2$  at 900 °C upon water immersion at different time intervals

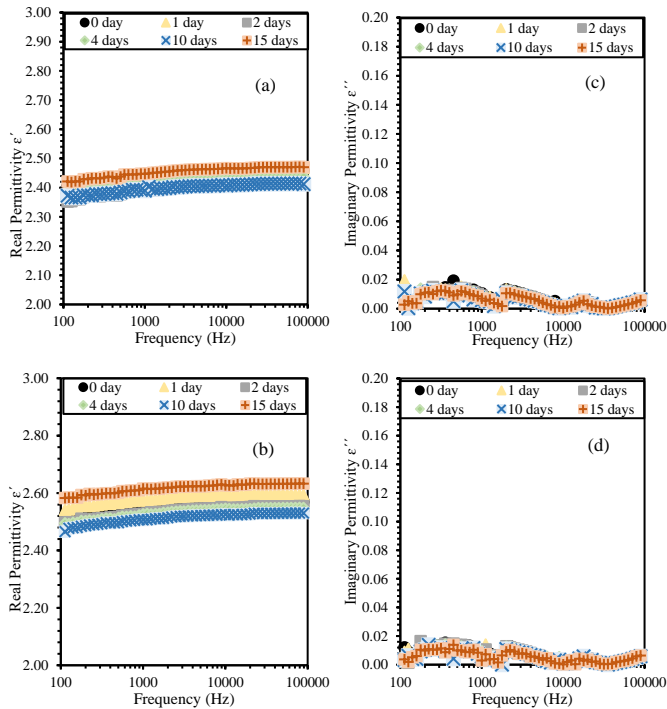


Fig. 3 Real permittivity of  $ZrO_2$  nanocomposites comprising (a) 1 wt%, (b) 8 wt % of calcined  $ZrO_2$  and imaginary permittivity of  $ZrO_2$  nanocomposites comprising (c) 1 wt%, (d) 8 wt% of calcined  $ZrO_2$  at 600 °C upon water immersion at different time intervals

rehydroxylation of  $ZrO_2$ -based nanocomposites can happen during water immersion. This, again, reinforces our previous assertion that water-related effects can be influential in affecting the dielectric properties of PE/ $ZrO_2$

nanocomposites, albeit that associated changes in the structure of  $ZrO_2$  are more relevant in affecting dielectric interactions between calcined  $ZrO_2$  and PE. Since structural changes of  $ZrO_2$  dominate over changes in the water-related surface chemistry of  $ZrO_2$ , any effects associated with water absorption after  $ZrO_2$  calcination is marginal through changes in mass or changes in the dielectric response of the materials, as demonstrated in the current work.

#### IV. CONCLUSIONS

The current work investigates the effect of water immersion for different time intervals on the mass changes and dielectric response of nanocomposites based upon  $ZrO_2$  and PE. From the water immersion tests, the absorbed water content was marginally affected for nanocomposites containing uncalcined  $ZrO_2$ . Similar effects were seen with the addition of  $ZrO_2$  calcined at 600 °C and 900 °C to PE. Nevertheless, the absorbed water content for nanocomposites containing uncalcined  $ZrO_2$ ,  $ZrO_2$  calcined at 600 °C, and  $ZrO_2$  calcined at 900 °C was altered systematically in accordance with the amount of  $ZrO_2$ . Meanwhile, the real and imaginary permittivities of nanocomposites containing uncalcined  $ZrO_2$ , nanocomposites containing  $ZrO_2$  calcined at 600 °C, and nanocomposites containing  $ZrO_2$  calcined at 900 °C, immersed in water for different time intervals up to 15 days, increased slightly with increasing time of water immersion. For nanocomposites containing 8 wt% of  $ZrO_2$  calcined at 600 °C and 900 °C, the real part of the relative permittivity of the nanocomposite samples increased notably with increasing water immersion periods across the whole frequency range studied. These results reinforce our previous assertion that water-related effects can be influential in affecting the dielectric properties of PE/ $ZrO_2$  nanocomposites, albeit that associated changes in the structure of  $ZrO_2$  are more relevant

in affecting dielectric interactions between calcined  $ZrO_2$  and PE, where structural changes of  $ZrO_2$  dominates over changes in the water-related surface chemistry of  $ZrO_2$ . It is noteworthy that the interpretation of the current experimental results is limited up to 15 days of water immersion duration without considering the water uptake of the samples reaching a plateau. A longer water immersion period, by considering the water uptake of the samples reaching a plateau, would therefore provide a better insight into the water absorption behavior of the investigated samples.

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