Structure and breakdown property relationship of polyethylene nanocomposites containing laboratory-synthesized alumina, magnesia and magnesium aluminate nanofillers

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ABSTRACT

The emergence of polymer nanocomposites has led to a new field of study in advanced dielectrics. Commonly, a few weight percent of single-metal oxide nanofillers has been added to polymers, and promising dielectric property changes have been found. Nevertheless, contradictory results have also been reported, where the use of single-metal oxide nanofillers has also resulted in degraded breakdown performances. Recently, experimental studies on ceramics showed that multi-element oxide ceramics could have a compact structure with entirely different chemical, mechanical and electrical properties from single-metal oxide ceramics. This approach is, however, less pursued from the perspective of dielectrics. In the current work, the structure and breakdown properties of polyethylene nanocomposites containing laboratory-synthesized single-metal oxide nanofillers, i.e., alumina (Al_2O_3) and magnesia (MgO), and multi-element oxide nanofiller, i.e., magnesium aluminate ($MgAl_2O_4$) nanofiller were compared. The results showed that the use of MgO resulted in higher breakdown strength of the nanocomposites than the use of Al_2O_3. Significantly, the use of $MgAl_2O_4$ resulted in much higher breakdown strength of the nanocomposites than MgO and Al_2O_3, and that the breakdown values could be comparable or even higher than the unfilled polyethylene under DC and AC applied fields. Possible mechanisms governing these property changes are discussed.

1. Introduction

Polymer nanocomposites are commonly defined as polymers containing homogeneously dispersed nanometric-sized fillers (nanofillers) of less than 10 wt% [1]. The addition of nanofillers to polymers has often had positive impacts on the chemical, mechanical, physical and electrical properties of the resulting materials [2–4]. For instance, the presence of nanofillers in polymers has resulted in enhanced thermomechanical efficiency and high degradation resistance of the materials, if properly engineered [5–7]. Meanwhile, the use of polymer nanocomposites as dielectrics – also known as nanodielectrics or nanometric dielectrics [8] – have resulted in enhanced dielectric constant and breakdown performance, when compared with conventional microcomposites [2,9,10]. Significantly, these promising improvements are imperative for addressing the need of advanced electrical insulating materials capable of withstanding higher voltage levels to cater for higher electricity demands [11–13].

To date, many experimental studies have been conducted on the dielectric breakdown strength of polyethylene filled with different types of nanofillers, such as silica (SiO_2) and magnesia (MgO), and enhanced breakdown strength of these nanocomposites has been reported [14,15]. These breakdown enhancements have been attributed to the presence of the interaction zone (interphase) between the polymers and the nanofillers, since the interphase can act as a trapping site for electrons and increase the charge storage capability of the materials [16–18]. In addition, the breakdown strength of nanocomposites under AC and DC stresses greatly depends upon the nanofiller concentration and distribution. In this, homogenously distributed nanofillers within nanocomposites are likely to improve the breakdown strength of the materials, and this effect is particularly noticeable at low nanofiller concentrations.

Although the use of nanocomposites has been shown favorable in breakdown strength improvements, many contradictory results have also demonstrated that the breakdown strength of nanocomposites were

inferior when compared with their unfilled counterparts [19]. Since the interphase of nanocomposites is critical in affecting the breakdown characteristics, various chemical means such as compatibilizers and silane coupling agents have been used to enhance the interfacial bonding between the polymer and the nanofiller. Through the use of different silane coupling agents, different interfacial effects of nanocomposites were expected so that the materials could exhibit entirely different dielectric behaviors for breakdown improvements [20–22]. However, the experimental work of Huang et al. [20] showed that, even with the use of surface-treated alumina nanoparticles, the breakdown strength of polyethylene containing alumina (Al_2O_3) nanofiller was worse than the unfilled polyethylene. Therefore, the use of nanocomposites in improving the breakdown performances of the materials is a challenging topic, as there are many fundamental issues yet to be addressed [19].

Recently, experimental studies on ceramics showed that two different types of inorganic single-metal oxide ceramics can be combined and synthesized in the laboratory scale to result in a multi-element oxide ceramic. Multi-element oxide ceramics can have a compact structure with entirely different chemical, mechanical and electrical properties from the single-metal oxide ceramics [23]. For instance, the work of Clinard et al. [24] suggested that magnesium aluminate ($MgAl_2O_4$) ceramic had different chemical properties and possessed improved mechanical strength over standalone MgO and Al_2O_3 ceramics. Furthermore, due to the strong ionic bonding between cations of Mg and Al and anions of oxygen in the $MgAl_2O_4$ ceramic, the ceramic became highly stable under high temperatures, with improved dielectric strength [25].

As far as the authors are aware, research on nanocomposites' breakdown characteristics has commonly been conducted on polymers containing nanofillers commercially available from the market instead of being synthesized chemically in the laboratory. Synthesized nanofillers, if used, has mainly been based on single-metal oxide nanofillers (e.g., SiO_2, Al_2O_3 and MgO). The effect of adding multi-element oxide nanofillers (e.g., $MgAl_2O_4$) to polymers, from the perspective of dielectrics, has been less explored. Since the properties of a nanofiller can be greatly affected by the way it is synthesized, such as centrifugation, heating and washing processes, these parameter variations were minimized through the laboratory-scale synthesis of Al_2O_3, MgO and $MgAl_2O_4$ nanofillers in the current work, so that any property changes could be associated with the properties of the nanofillers rather than the synthesis parameters. The structure and breakdown properties of these nanofillers when incorporated into low density polyethylene (LDPE) are reported.

2. Experimental

2.1. Materials

Aluminum nitrate nonahydrate ($Al(NO_3)_3 \cdot 9H_2O$) with 98.5% purity and magnesium nitrate hexahydrate ($Mg(NO_3)_2 \cdot 6H_2O$) with 99% purity, both obtained from Sigma-Aldrich, were used to synthesize Al_2O_3 and MgO nanofillers respectively. These reagents were also used in the synthesis of $MgAl_2O_4$ nanofiller. For precipitation purposes, an ammonium hydroxide (NH_4OH) solution with 28.0–30.0% NH_3 basis, obtained from Merck, was used. Meanwhile, the LDPE grade Titanlene LDF200YZ, obtained from Lotte Chemical, was used as the base polymer.

2.1.1. Synthesis of nanofillers

Al_2O_3, MgO and $MgAl_2O_4$ nanofillers were synthesized using a co-precipitation process followed by a hydrothermal method [26,27]. To synthesize the Al_2O_3 and MgO nanofillers, the respective Al($NO_3)_3 \cdot 9H_2O$ and $Mg(NO_3)_2 \cdot 6H_2O$ reagents were added to the required quantity of deionized water to make 0.1 M nitrate solutions. The $MgAl_2O_4$ nanofiller was synthesized using the similar method, but by

mixing the aqueous solutions of $Al(NO_3)_3 \cdot 9H_2O$ and $Mg(NO_3)_2 \cdot 6H_2O$. For this, the molar ratio of the Mg:Al was kept at 1:2. In preparing the Al_2O_3, MgO and $MgAl_2O_4$ nanofillers, the NH_4OH solution, used as a precipitating agent, was added to the respective nitrate solutions dropwise using a pipette and the solutions was continuously stirred and heated at 100 °C. Each solution was then transferred to a stainless-steel autoclave with polytetrafluoroethylene (PTFE) lining (200 ml). The autoclave was placed in a furnace and heated at a temperature of 160 °C for 24 h for the hydrothermal process to take place. The slurry resulted from the hydrothermal process was later divided into flasks of equal weight before subjected to centrifugation and decanting of the supernatant. Distilled water and absolute ethanol were then added to each flask, and the flask was vigorously shaken until the nanofiller was again suspended in the solvent. The washing process was repeated for several times to remove the residuals. The resulting solid was subsequently dried in a vacuum oven at 120 °C for 12 h. The solid (powder) was then calcined at 700 °C for 3 h in a muffle furnace.

2.1.2. Preparation of nanocomposites

The desired amount of the synthesized Al_2O_3, MgO or $MgAl_2O_4$ nanofiller powder (0–3 wt%) was mixed with the LDPE using a laboratory two-roll mill at a temperature of ~140 °C for ~30 min. Thin film samples with an average size of 100 μm were then prepared using a hydraulic laboratory press at a temperature of 160 °C and a load of 3 ton. For the ease of reference, LDPE nanocomposites containing Al_2O_3, MgO and $MgAl_2O_4$ nanofillers are referred to as "PE/Al_2O_3", "PE/MgO" and "PE/$MgAl_2O_4$" respectively while LDPE without nanofiller addition is referred to as "PE/0".

2.2. Characterization

2.2.1. Structure of nanofillers

The structures of the synthesized Al_2O_3, MgO and $MgAl_2O_4$ nanofillers was characterized using the X-ray Powder Diffraction (XRD) technique. The XRD patterns were obtained using the Rigaku Smart Lab X-ray diffractometer using the Cu-kα radiation (40 keV, 40 mA) from 5° to 90° of 2θ at a scan rate of 1.2° min^{-1}. The diffractometer was equipped with a Ni-filtered Cu-kα radiation source (l = 1.54056 Å), operated at 40 kV and 200 mA. The grain size of the samples were estimated from the XRD using the Scherrer equation [28,29].

The field emission scanning electron microscopy (FE-SEM) technique was used to examine the structure of the Al_2O_3, MgO and $MgAl_2O_4$ nanofillers. FE-SEM was conducted using the Hitachi SU8020 SEM integrated with the X-Max^N beam (by Oxford Instrument) at 120 kV. The full control of the probe current from 1 pA to more than 5 nA could be achieved, as reported elsewhere in the literature [30].

2.2.2. Structure of nanocomposites

The chemical structures of the PE/0, PE/Al_2O_3, PE/MgO and PE/$MgAl_2O_4$ samples were investigated using the Fourier transform infrared (FTIR) spectroscopy. The analysis was conducted using the Spectrum Two FT-IR Spectrometer (Perkin Elmer). Furthermore, the dispersion of the synthesized Al_2O_3, MgO and $MgAl_2O_4$ nanofillers within the LDPE was investigated using the JEOL JSM-6390 SEM through secondary electron imaging, with a voltage of 15 kV. The PE/0, PE/Al_2O_3, PE/MgO and PE/$MgAl_2O_4$ samples were fractured in liquid nitrogen, coated and later mounted onto an SEM stub for SEM imaging purposes.

2.2.3. Breakdown testing of nanocomposites

Direct current (DC) and alternating current (AC) breakdown testing was conducted on the thin film samples of PE/Al_2O_3, PE/MgO and PE/$MgAl_2O_4$. Each sample was placed between two opposing steel ball-bearing electrodes, immersed in Hyrax Hypertrans transformer oil to prevent surface flashover. For DC and AC breakdown testing, a DC voltage with a step voltage of 2 kV every 20 s and an AC voltage with a