Full Length Research Paper

Probing of dielectric properties of high density poly-ethylene/calcium carbonate (HDPE/CaCO₃) nano-micro composite

M. A. Al-Eshaikh and M. Iqbal Qureshi*

Research Center, College of Engineering, King Saud University, P. O. Box 800, Riyadh 11421, Saudi Arabia.

In this experimental investigation, high density poly-ethylene/calcium carbonate (HDPE-CaCO₃) micro/nano composite sheets were prepared by melt blending the master batch using twin screw extruder followed by injection molding. The dispersion characteristics were determined by field emission scanning electron microscope (FESEM) and were found to be reasonably uniform. These sheets were then subjected to electrical stresses in order to evaluate their dielectric performance. The dissipation factor (tanδ) and relative permittivity (εᵣ) were evaluated as a function of temperature in a practical range of 23 to 80°C. The composite exhibited decreased εᵣ and tanδ values compared with unfilled HDPE. These results support the multi-layer model proposed in literature for nano-composite. It is also clarified that this nano-micro composite is higher in both ac breakdown strength and partial discharge resistance than for the base polymer.

Key words: High density poly-ethylene/calcium carbonate (HDPE/CaCO₃) nano-micro composite, partial discharge, surface degradation, dielectric properties.

INTRODUCTION

The application of nanotechnologies in the field of electrical insulation for power and high voltage engineering requires extensive research and development of these "advanced" materials. The innovative materials created from the incorporation of nano-particles in a polymer matrix are commonly called nano-dielectrics. It is now accepted that nano-dielectrics insulation performs better in some applications in comparison with conventional insulating materials. These nano-dielectric materials require a detailed electrical, thermal, mechanical and chemical characterization prior to their application in the equipment that undergoes multiple stresses during its life time. Several reviews and original papers have been reported on the electrical properties of such composites (Castellon et al., 2011; Celebrese et al., 2011; Danikas and Tanaka, 2009; Tanaka et al., 2005; Tanaka, 2008; Iyer et al., 2011; Krivda et al., 2012; Nelson, 2010; Park et al., 2011; Wang et al., 2011; Working Group, 2011).

High density poly-ethylene (HDPE) is widely used as a commodity polymer due to its distinctive mechanical and physical properties. However, to improve its performance the HDPE has been reinforced with cheaply available fillers such as calcium carbonate (CaCO₃). Zebarjad and Sajjadi (2008) reported that nano-sized CaCO₃ has significant effect on crystallinity and melting point of HDPE. However, due to its polar nature it is difficult to evenly disperse and stabilize in a polymer matrix. In order to disperse inorganic nano-fillers into organic polymer matrices, the affinity between their surfaces in contact should be taken into consideration. The surface energy is a physical parameter that directly represents the affinity between the two substances. It is necessary to reduce the difference between the two in order to obtain a good composite. In this context, several techniques such as using compatibilizers and coupling agents, high shear force mixing, solution mixing etc. have been adopted to get better dispersion results (Celebrese et al., 2011; Nelson, 2010; Imai et al., 2006; Working Group, 2011). Nano-particles have much higher interfacial area per unit

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*Corresponding author. E-mail: mqureshi1@ksu.edu.sa. Tel: ++966-1-4676963. Fax: ++966-1-4676225.
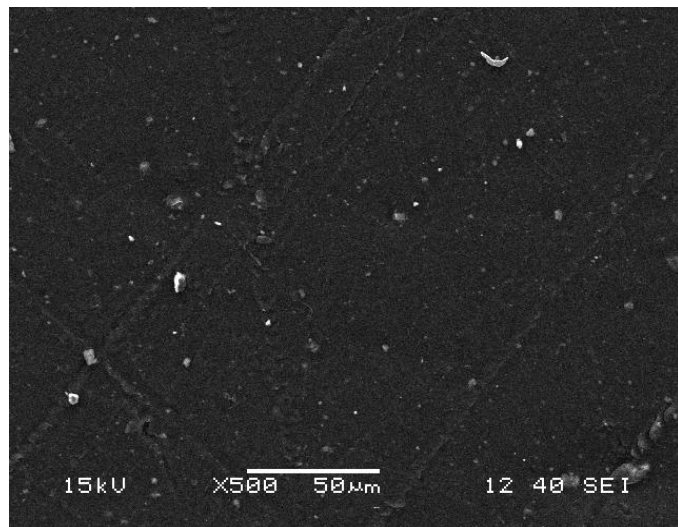
Figure 1. SEM surface micrograph of CaCO$_3$ filled specimen.

volume and in addition the interface between the particle and polymer is thought to have a finite thickness in which the properties of the polymer differ from the original matrix (Tanaka et al., 2008). In such systems the total interfacial volume can be very large and may control the dielectric response of the system (Lewis, 1994). However, there have been conflicting reports in the literature regarding the effect of nano-micro particles on the dielectric properties of polymer composites, since they have been shown to inflict increase and decrease in dielectric properties (Imai et al., 2006; Krivida et al., 2012; Singha and Thomas, 2008). While variations are to be expected in different systems, the effect of processing can also be a determining factor in the final properties. Therefore, it is important to carefully consider and control the processing conditions used when making such composites.

In the present experiments, HDPE composite with CaCO$_3$ was prepared using master batch approach. The master batch contained both the polymer carrier and nano-micro filler. The dispersion and distribution of CaCO$_3$ particles in the composite was characterized by scanning electron microscope (SEM). The impact of CaCO$_3$ filler on the salient electrical properties such as its relative permittivity (ε_r) dissipation factor (tanδ) was compared. Insulating materials used in electrical power apparatus are generally exposed to surface discharges in the course of their normal operation resulting in deterioration of the material's surface that can ultimately lead to their breakdown. In this context, the samples' ac breakdown strength (E$_b$) and partial discharge (PD) resistance were also investigated using the IEC(b) electrode system for several hours. Comparisons were also made for surface roughness observed by precision profilometer and PD resistance was evaluated based on the surface roughness of filled and unfilled specimens.

EXPERIMENTAL METHODS

Preparation of samples

HDPE-54 produced by Saudi Arabian Basic Industry Corporation (SABIC) was used as the base polymer and is of injection molding grade with a narrow molecular weight distribution and high flow ability. The master batch 'Micro Filler-0189' supplied by Wuxi Changhong Master-batches Co., China contained 80 ± 3% micro and ~20% nano CaCO$_3$ on LLDPE as a carrier with granule size of 20 nm to 2 μm. Its surface is not treated. HDPE was dry blended with 5% CaCO$_3$ filler and palletized using an intermeshing and co-rotating twin screw extruder which had both dispersive and distributive mixing elements. The melting was at 235°C under pressure of 7.0 bars. The extrudate was cooled in a water bath, dried and palletized for further use (Elleithy et al., 2010). Flat sheets 100 mm wide, 110 mm long and 1 mm thick were injection molded for the purpose of testing.

The morphological analysis was carried out using field emission scanning electron microscope (FESEM), JOEL model USM-7600F coupled with energy-dispersive X-ray spectroscopy (EDX) elemental analysis tool. To avoid electrostatic charging the surface of the samples was platinum sputter coated imparting thickness of ~10 μm before subjecting them to SEM observations.

The SEM surface profile of CaCO$_3$ filled specimen is shown in Figure 1 which shows a reasonable good distribution with minor tendency of larger particles that have agglomerated. Agglomeration is a well known phenomenon, its probability increases with the decrease in particle size (Celebrese et al., 2011; Park et al., 2011). Nevertheless, the particle size distribution in this molded sample is reasonably homogeneous. Figure 2 exhibits the EDX elemental distribution in the filled sample. It is clear that the presence of calcium is around ~0.63% in this sample, whereas both the filled and unfilled samples are clear of any spurious traces of any other impurities, thus, exhibiting cleanliness of the development process.

Measurements of relative permittivity and dissipation factor

The ε_r and tanδ of the samples was measured as a function of temperature using Tettex precision Schering bridge under electrical stress of 500 V. The samples were placed in test cell Tettex type 2604 in which the temperature was controlled with a precision of ±1°C.

Measurement of dielectric breakdown strength

Dielectric breakdown strength experiments were carried out in a Perspex test cell containing polished sphere to sphere electrode system as shown in Figure 3. In this case, 50 mm wide, 50 mm long and 1.0 mm thick samples were inserted one at a time between the pair of electrodes. Whole electrode system was immersed in transformer oil to enhance the surrounding insulation and suppress occurrence of any surface discharge. High voltage of 60 Hz was ramped at a rate of 1.0 kV/s till breakdown ensued. The power supply was a 90 kV/230 V transformer and the measuring system was microprocessor controlled. The oil was continuously stirred during the measurements to ensure that readings are not affected by the by-products of degradation. Electrodes were replaced after a set of ten measurements.

Measurement of surface erosion due to partial discharge

The IEC(b) electrode system as shown in Figure 4 was used to test these specimens. It consisted of a stainless steel rod and plane electrode. The rod electrode was connected to the high voltage and
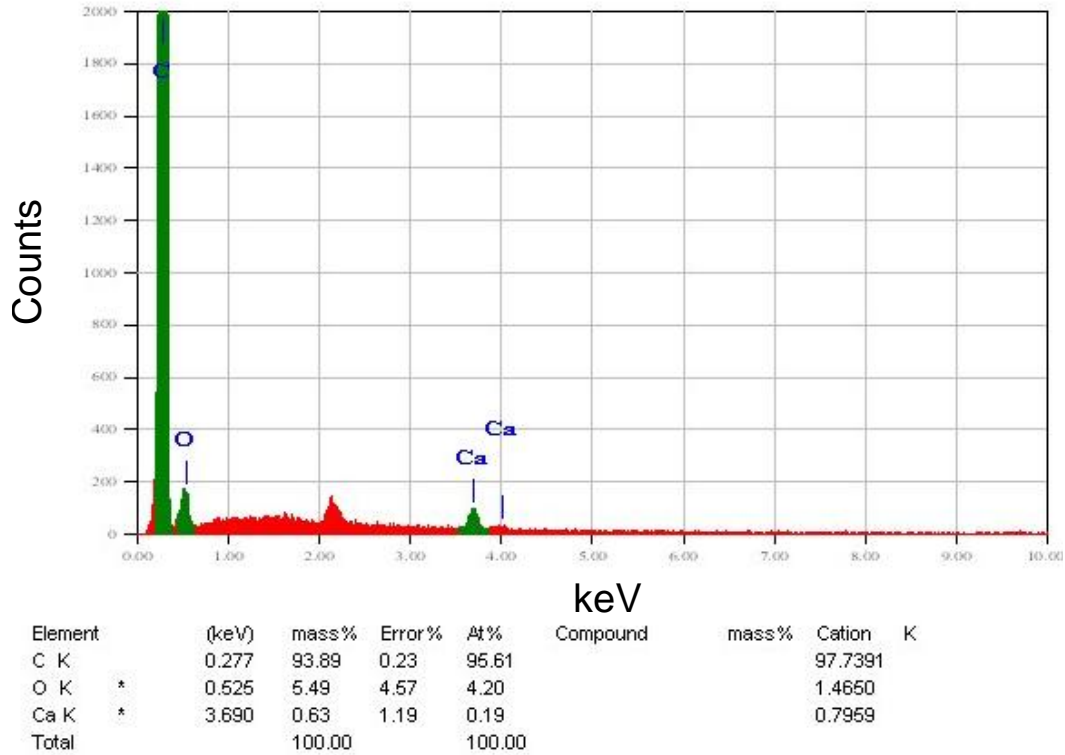
Element		(keV)	mass%	Error%	At%	Compound	mass%	Cation	K
C K		0.277	93.89	0.23	95.61			97.7391	
O K	*	0.525	5.49	4.57	4.20			1.4650	
Ca K	*	3.690	0.63	1.19	0.19			0.7959	
Total			100.00		100.00				

Figure 2. Elemental distribution in $CaCO_3$/HDPE composite.
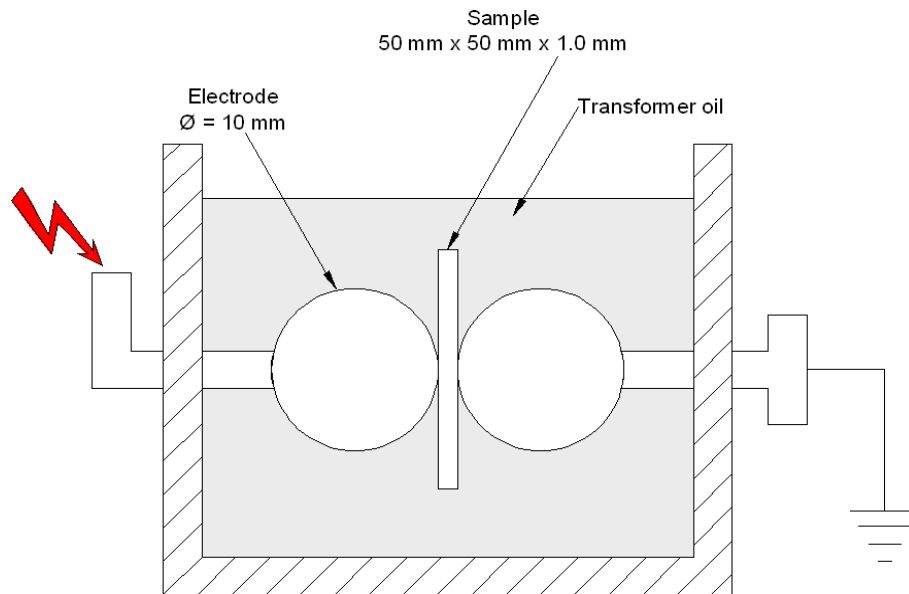
Figure 3. Test cell with sphere to sphere electrodes system for breakdown strength test.

was 6 mm in diameter with end curvature of 1.0 mm radius. The polished plane electrode was grounded. The rod-plane geometry was enclosed in a transparent Perspex cylindrical test cell maintained at room temperature and atmospheric pressure. The specimens, one at a time, were subjected to 60 Hz ac at 15 kV_{rms}

for predetermined fixed times of 6, 19, and 48 h. The resistance towards PD was compared as the depth of the eroded surfaces from adjacent to the electrode edge to the end of the eroded surface using Ultra Surf Inductive Profiler type i-60 from Tylor Hobson, UK.
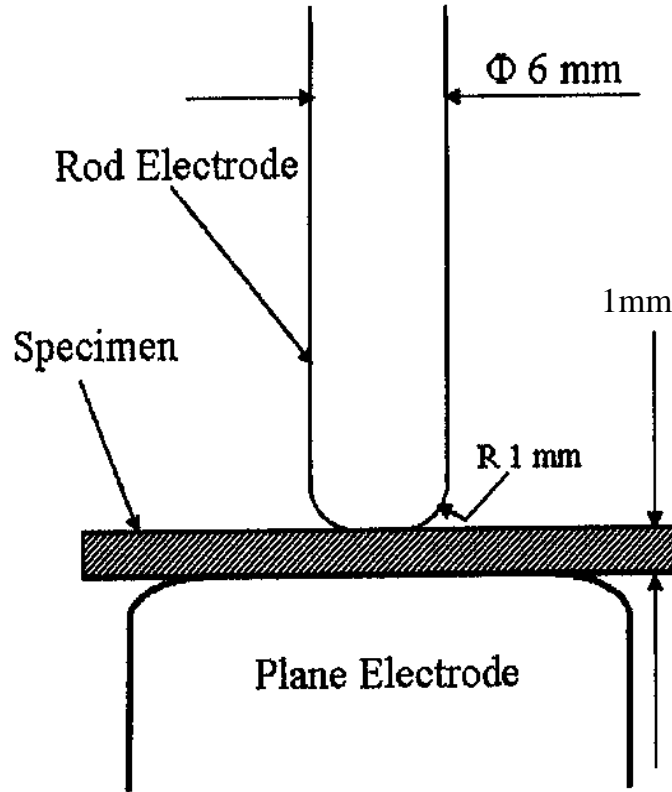
Figure 4. IEC(b) rod-plane electrode assembly.

RESULTS AND DISCUSSION

Higher Values of E_b and PD resistance of a polymer are its important features and pre-requisite for its application as an insulating material. The dielectric ε_r and $\tan\delta$ have influence on the local field distribution and on resistance towards PD erosion of the specimen's surface when these are exposed to high electrical field and temperature. These salient features were, therefore, measured for both types of specimens investigated.

Figure 5 shows variation of ε_r and $\tan\delta$ as a function of temperature. With the increase in temperature, the ε_r decreases slightly in $CaCO_3$ filled sample, while it increases in case of unfilled sample. Similarly, a decrease of almost 45% is observed in $\tan\delta$ value with rise in temperature in filled sample in the measured temperature range. Opposite observations have been reported by Imai et al. (2006) in nano-micro silicate filled epoxy and Hoffmann et al. (2011) in nano-silica filled epoxy at power frequency. The increase in $\tan\delta$ in unfilled samples can be attributed to higher polarization losses, whereas decrease in ε_r in filled HDPE could be due to blocking and trapping of free charge carriers at the filler interfaces. Singha and Thomas (2008) have reported decrease in ε_r depending on the interfacial polarization at particle interlayer; its relaxation mechanism and also due to blocking of dipole mobility. The presence of "free

volume" has also been attributed to the reduction in ε_r. Introduction of nano-particles in the base matrix reduces the free volume (Nelson and Hu, 2004). Tanaka et al. (2005) have proposed a multi-layer model based on the presence of free volume and its interaction with the inter-layers of the nano-composite. Two kinds of players were proposed to be working in this scenario. The first one is the inner inter-layer which acts to block the motion of dipoles originating from some polar radicals, while outer loose layer acts to reduce the free volume. Both of these layers thus contribute in the reduction of ε_r, which is experimentally demonstrated here and thus, substantiates the hypothesis of multi-layer model (Tanaka et al., 2005). Both characters (that is, $\tan\delta$ and ε_r) of $CaCO_3$ filled polymer exhibit here much beneficial dielectric response.

Figure 6 shows successive profiles, representing the progressive erosion of the surface of unfilled HDPE specimen in time lapse of 6, 19, 25 and 48 h, respectively. The surface was scanned on each sample along a radial line starting from the trace of the edge of the electrode up to a distance of 10 mm. Similarly, depth profiles were obtained for the filled specimens. Figure 7 compares the erosion depth profile for filled and unfilled composite samples after 25 h of aging. It is clear that PD erosion in unfilled sample is not only deeper but its pattern is also different. This needs further clarification as to describe the mechanisms that result into this difference. This
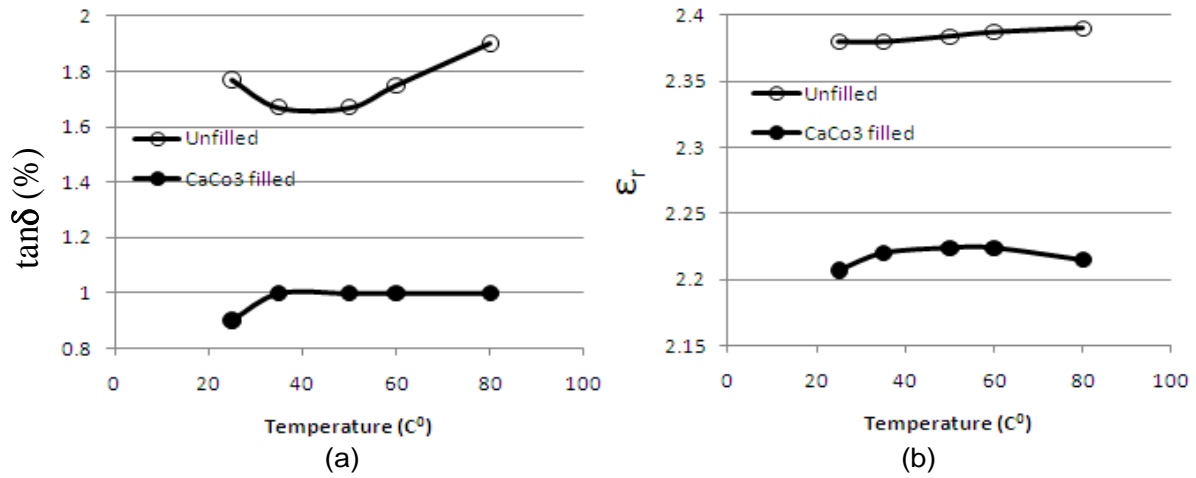
Figure 5. Variation of ε_r and tanδ as a function of temperature for HDPE samples with and without CaCO$_3$ particles.

μm

Distance (mm)
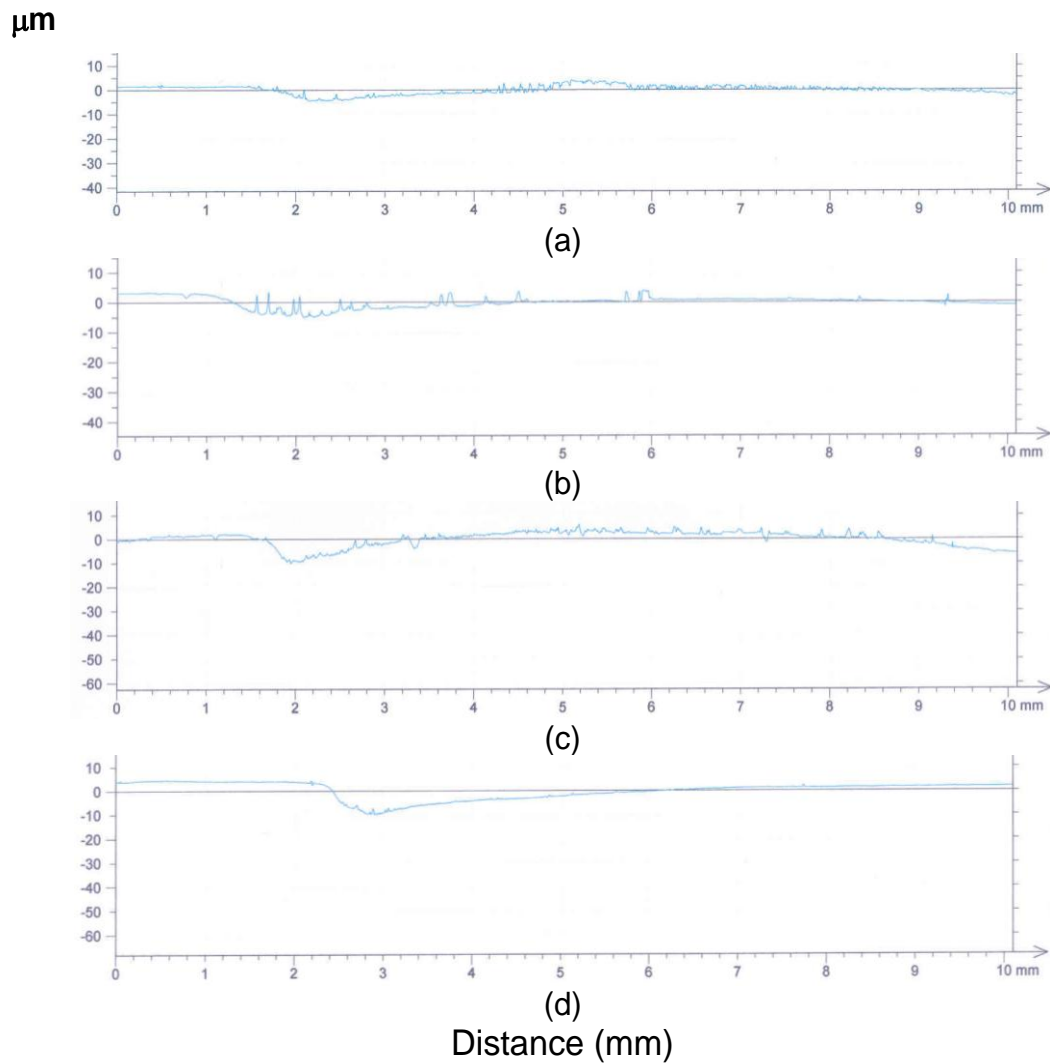
Figure 6. Surface erosion profiles of degraded unfilled specimen after aging of (a) 6 h, (b) 19 h, (c) 25 h, and (d) 48 h.
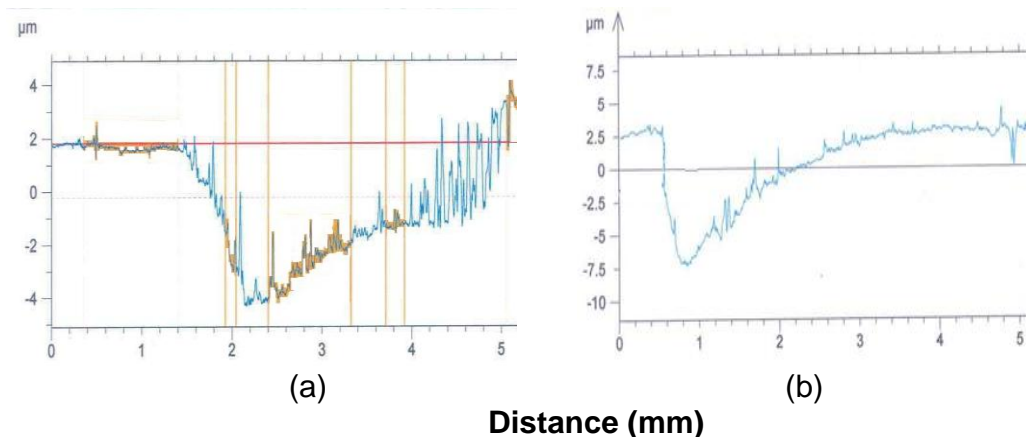
Figure 7. Comparison of erosion on 25 h aged, (a) unfilled, and (b) filled polymer composites.
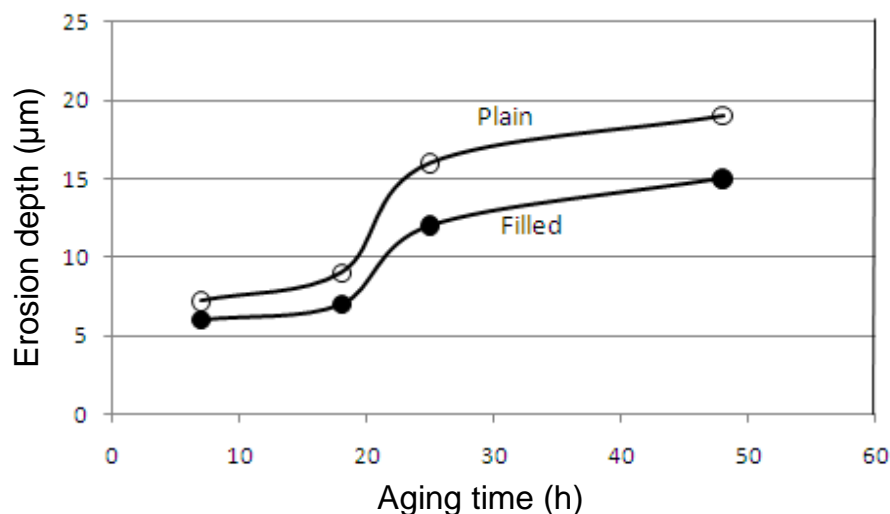

**Figure 8.** Erosion depth as a function of aging duration.

aspect will be further investigated to clarify erosion characteristics in near future. Figure 8 compares the erosion depth as a function of aging time. Here, the point data are the average of three repeated runs on samples of the same type. It is clear that the erosion in time is not linear but tends toward saturation after about 30 h of aging in both samples. However, it is obvious that $CaCO_3$ filled HDPE sample degrades much lesser. Saturation of erosion depth in the long run could be caused by factors such as change in the electric field at the electrode edge caused by the formation of eroded cavity and the physical change in the edge profile of the electrode.

Weibull statistical plots with 90% confidence bounds for E_b of the two compared systems are shown in Figure 9. The shape and scale parameters are summarized in Table 1. In here, the shape parameter could be obtained from the slope meaning the data distribution, and the

scale parameter represented the E_b by which 63.2% (characteristics value) of the cumulative probability was expected to fail. The P_5 value refers to E_b value at which 5% would survive under a given electric field. This value is important for the design engineer. The analysis shows 31% increase in the characteristic value of the E_b of the filled composite, whereas it shows 24% increase in P_5 value, as well. Interestingly, there is not much effect on the shape parameter value which suggests that the filler was evenly dispersed in HDPE which resulted in improved dielectric characteristics.

Conclusion

In this study, HDPE composite was prepared with 5% volume of nano-micro sized $CaCO_3$ by the process of
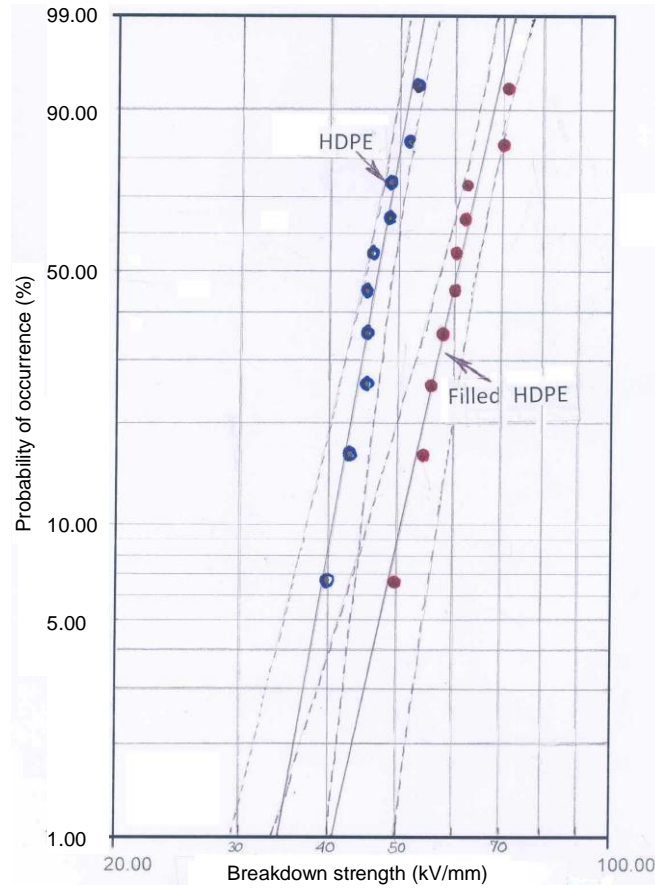
Figure 9. Weibull distribution plot (90% confidence bounds) for the unfilled and filled HDPE composites.

Table 1. Weibull parameters of ac breakdown strength for filled and unfilled HDPE.

Sample type	Scale parameters (kV/mm)	Shape parameter	P$_5$ (kV/mm)
HDPE	48.1	12.3	38.1
Filled HDPE	62.9	11.52	47.2

melt blending from master batch by extrusion and then followed by injection molding.   The morphological analysis revealed a fairly homogeneous dispersion of particles. $CaCO_3$ filled samples exhibit much smaller value of ε_r and almost negligible increase in tanδ as compared to unfilled sample as a function of temperature. HDPE filled with nano-micro $CaCO_3$ is also superior in PD resistance as well as in its ac breakdown strength as compared to unfilled polymer.

ACKNOWLEDGEMENTS

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