Correlation between Structure and Dielectric Breakdown in LDPE/HDPE/Clay Nanocomposites

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Cross-linked polyethylene (XLPE) is commonly used in medium/high voltage insulation due to its excellent dielectric properties and acceptable thermomechanical properties. To improve both electrical and thermal properties to a point that would possibly avoid the need for crosslinking, nanoclay fillers can be added to polymer matrix to form nanocomposites materials. In this paper, PE/clay nanocomposites were processed by mixing a commercially available premixed polyethylene/O-MMT masterbatch into a polyethylene blend matrix containing 80 wt% low density polyethylene LDPE and 20 wt% high density polyethylene HDPE with and without compatibilizer using a corotating twin-screw extruder. Various characterization techniques were employed in this paper, including optical microscopy, AFM, TEM, TGA, DMTA, and dielectric breakdown measurements in order to understand the correlation between structure and short-term dielectric breakdown strength.

1. Introduction

Polyethylene is the insulation dielectric material of choice because of its high dielectric strength coupled with low dielectric loss, in addition to lending itself to easy processing. Furthermore, this polymer can be extensively recycled, making it a suitable candidate for replacing its cross-linked counterpart, which has limited recyclability.

With conventional composite material, the filler is large or micrometric in size. It has been reported that adding microfiller has a negative effect on dielectric breakdown strength [1] due to the enhancement of the electric field around the aggregated filler particles, leading to decreased breakdown strength. To overcome these limitations, nanocomposite was used as an alternative to replace conventional composite [1–15]. Adding a nanoparticle to the polymer matrix resulted in a decrease in the internal electric field due to the reduction in particle size [16]. It has also been suggested that adding nanoclay can significantly decrease charge accumulation, which leads to increase in dielectric breakdown strength [17]. In nanocomposites, the interface between the nanoclay and the polymer matrix is very large, compared to that of composite or microcomposite materials.

Several authors have reported that interface region plays an essential role in improving the insulating performance of nanodielectric materials [18–24].

In this paper, a blend of 80 wt% of LDPE and 20 wt% of HDPE was used as a matrix. The nanocomposite was prepared by melt-compounding the polymer matrix with nanoclay filler using a corotating twin-screw extruder.

Only a few studies have focused on the structure-dielectric breakdown correlation in polyethylene/clay nanocomposites [18]. To understand this relationship, microscopic observation, thermal behavior, and dynamic mechanical thermal analysis, as well as short-term dielectric breakdown, have been studied.

2. Experiment

2.1. Materials. Low density polyethylene LDPE (LF-Y819-A) with a melt flow index of 0.75 g/10 min and a density of 0.919 g/cm³ was supplied by NOVA, Canada, while high density polyethylene HDPE (DGDP-6097 NT 7) with a melt flow index of 10.5 g/10 min and a density of 0.948 g/cm³ was purchased from DOW, USA. The compatibilizer was
Table 1: Sample designation and formulation.

<table>
<thead>
<tr>
<th>Sample designation</th>
<th>LLDPE (wt%)</th>
<th>LDPE/HDPE (wt%)</th>
<th>PE-MA (wt%)</th>
<th>O-MMT (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MB</td>
<td>50</td>
<td>—</td>
<td>—</td>
<td>50</td>
</tr>
<tr>
<td>PE</td>
<td>—</td>
<td>100</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>PE/O-MMT</td>
<td>5</td>
<td>90</td>
<td>0</td>
<td>5</td>
</tr>
<tr>
<td>PE/O-MMT/PE-MA</td>
<td>5</td>
<td>80</td>
<td>10</td>
<td>5</td>
</tr>
</tbody>
</table>

2.2. Preparation of Nanocomposites. The LDPE, HDPE, PE-MA, and the LLDPE/O-MMT masterbatch were dried in a vacuum oven at 40°C for a minimum of 48 hours. Nanocomposites were prepared by melt-compounding using a corotating twin-screw extruder (Haake Polylab Rheomex OS PTW16, D = 16 mm, L/D = 40). The screw speed was set at 140 rpm and the feed rate was at 1 kg/h, while the hopper-to-die temperature profile was 170–180°C. The ingredients were manually premixed before being fed into the twin-screw extruder. After extrusion, the pellets were press-molded to form thin plates with a thickness of 590 μm using an electrically heated hydraulic press. The compositions and sample designations for the prepared nanocomposites are listed in Table 1.

3. Characterization and Measurements

3.1. Optical Microscopy. The morphological properties were carried out using an optical microscope (CE, NMM-800TRF) with a color camera (LEMEX) attached. Observations were realized at a lens magnification of 200x in transmission mode. All samples were prepared as a thin film with a thickness of 200 μm.

3.2. Atomic Force Microscopy (AFM). Microstructures of polyethylene/clay nanocomposites were evaluated using an atomic force microscope (DiNanoScope, Vecco, USA) in tapping mode. The images of the surface topography were then analysed using the Nanoscope (R) III software, version 5.30r3. The nanoclay appeared brighter than the polyethylene matrix. Samples with a thickness of 590 μm were used, and all measurements were carried out at ambient conditions.

3.3. Transmission Electron Microscopy (TEM). The quality of dispersion of the nanoclays in the polymer matrix was examined by transmission electron microscopy (TEM). Ultrathin sections with a thickness of 50–80 nm were cut from the molded plaque of PE/O-MMT and PE/O-MMT/PE-MA nanocomposites at −120°C using an ultramicrotome equipped with a diamond knife. The samples were then examined using a high resolution FEM Tecnai G2 F20 with accelerating voltage of 200 kV.

3.4. TGA Characterization. Thermogravimetric analysis (TGA) of PE and its nanocomposites was performed on a PYRIS Diamond TG-DTA. The heating process was executed from 50 to 700°C at a 10°C/min heating rate. All measurements were carried out under air and nitrogen atmosphere to evaluate the thermal oxidation and the thermal degradation of the materials, respectively. The nanoclay loading of the nanocomposites materials was also evaluated using this technique.

3.5. Dynamic Mechanical Analysis by DMTA. The thermomechanical properties of the neat PE blend and its nanocomposites were obtained using a dynamic mechanical thermal analysis (DMTA).

Dynamic stress $\sigma$ and strain $\varepsilon$ are given by

$$\sigma = \sigma_0 \sin (\omega t + \delta),$$

$$\varepsilon = \varepsilon_0 \sin (\omega t),$$

where $\omega$ is the angular frequency and $\delta$ is the phase angle.

The complex modulus $E^*$ is given by

$$E^* = E' + iE'',$$

where the real part $E'$ reflects the elastic energy stored in the material. The imaginary part $E''$ describes the energy dissipated.

The loss factor $\tan \delta$ is the damping performance and is represented by

$$\tan \delta = \frac{E''}{E'}.$$

Rectangular geometry specimens with a 14 mm length, a 7 mm width, and a 1 mm thickness were used. All the specimens were cut from the compression-molded plaques. The measurements were carried out in dual cantilever mode at a fixed frequency of 1 Hz and a strain of 0.02%. The samples were clamped with a 20 cN-m torque in order to achieve reproducible results and were all cooled down with liquid nitrogen to −30°C and then kept for 10 minutes at that temperature.

Storage modulus $E'$ and loss modulus $E''$ of PE and its nanocomposites were measured from −30 to 100°C at a 5°C/min heating rate. This slow heating rate was chosen in order to avoid having the material moving outside the thermodynamic equilibrium.

3.6. Dielectric Strength. The dielectric breakdown was measured according to the ASTM D 149 standard, using a BAUR...
DTA 100 device to hold both the samples and the surrounding medium. A sample with an average thickness of 590 µm was immersed in a mineral oil (Voltesso 35, ESSO Imperial Oil) and placed between two spherical electrodes 12.5 mm in diameter. A 60 Hz voltage was raised at a rate of 2 kV/s from 0 V until the sample failed.

The dielectric strength $E$ depends on the electrical voltage at breakdown $V$ and thickness of specimen $e$:

$$E = \frac{V}{e}. \quad (4)$$

The dielectric strength data were processed using the two-parameter Weibull statistical distribution (Std-930, 2004). The Weibull statistical distribution in the case of two parameters can be written as

$$P(E) = 1 - \exp\left[-\left(\frac{E}{\alpha}\right)^\beta\right], \quad (5)$$

where $P$ denotes the cumulative probability of electrical failure, $E$ is the experimental dielectric strength, $\alpha$ is the scale parameter which represents the breakdown strength at the cumulative failure probability of 63.2%, and finally $\beta$ is a shape parameter related to the scatter of data. According to the IEEE 930-2004 standard, the probability of failure $P(i,n)$ associated with the $E_i$ data can be approximated by

$$P(i,n) = \frac{i - 0.44}{i + 0.25}. \quad (6)$$

where $i$ is the $i$th result when the breakdown values are sorted in ascending order and $n$ denotes the number of data points. For this work, $n = 20$.

The commonly used 90% confidence intervals were used to compare sets of data by verifying the overlapping of the confidence limits at the 63.2th percentile.

4. Results and Discussion

4.1. Optical Microscopy. Most studies have often used TEM to evaluate the quality of dispersion at high magnifications, while only few works have employed optical microscopy to investigate nanoclay morphologies at low magnifications [25]. The optical microscopy images of the polyethylene blend and its nanocomposites are shown in Figure 1. In the PE/O-MMT nanocomposites, the presence of significant aggregates with varied dimensions was observed (Figure 1(b)) which was not the case in the neat PE (Figure 1(a)). When the compatibilizer was added, the number and size of agglomerates were decreased (Figure 1(c)). This is due to the well-dispersed nanoclay platelet in the polyethylene matrix under the effect of processing conditions and compatibilizer.

4.2. Surface Roughness. In this paper, AFM height images of PE, PE/O-MMT, and PE/O-MMT/PE-MA were used in order to study the dispersion of nanoclay in the polymer matrix. The surface properties of neat PE and its two nanocomposites in 3D height image are shown in Figure 2. It can be seen that the surface of the neat PE (Figure 2(a))
Figure 2: AFM height images of (a) neat PE, (b) PE/O-MMT, and (c) PE/O-MMT/PE-MA.

Table 2: Surface roughness data of PE and its nanocomposites.

<table>
<thead>
<tr>
<th>Nanocomposites</th>
<th>$R_a$ (average surface roughness) (nm)</th>
<th>$R_q$ (root mean squared) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE</td>
<td>11.0</td>
<td>16.3</td>
</tr>
<tr>
<td>PE/O-MMT</td>
<td>13.5</td>
<td>25.4</td>
</tr>
<tr>
<td>PE/O-MMT/PE-MA</td>
<td>11.7</td>
<td>18.0</td>
</tr>
</tbody>
</table>

is relatively smooth in comparison with those of PE/O-MMT (Figure 2(b)) and PE/O-MMT/PE-MA (Figure 2(c)) nanocomposites. From the surface roughness data depicted in Table 2, it is evident that PE/O-MMT/PE-MA shows a decrease in the root mean squared $R_q$ and average surface roughness $R_a$ values when compared with PE/O-MMT. The decrease in surface roughness can be attributed to a decrease in aggregate size [26]. From the images, it can also be seen that, in the compatibilized nanocomposites, the nanoclays are more oriented and structured on the surface. This is due to the good dispersion of nanoclay in PE/O-MMT/PE-MA nanocomposites [27].

4.3. Clay Dispersion by TEM. Because of the small size of the region examined by TEM, the description of the quality of dispersion was qualitative. TEM micrographs of PE/O-MMT and PE/O-MMT/PE-MA are shown in Figure 3. It can be seen that clay is presented as tactoids in the PE/O-MMT nanocomposites (Figure 3(a)). When the compatibilizer was added, the microstructure of the nanocomposites was presented as a combination of intercalated and exfoliated nanoclay layers (Figure 3(b)). A better dispersion of the clay platelets was achieved for PE/O-MMT/PE-MA than for the nanocomposites without a compatibilizer. This result is in agreement with our previous SEM and XRD measurements [28].

4.4. Thermal Properties. Figure 4 shows the TGA curves for neat PE and its nanocomposites PE/O-MMT and PE/O-MMT/PE-MA in air atmosphere. The thermal degradation
parameters derived from these curves are given in Table 3. It is apparent from these results that the initial degradation temperatures for both nanocomposites are higher than for the neat PE. For PE/O-MMT/PE-MA the decomposition temperatures $T_{10\%}$ and $T_{50\%}$ at 10% and 50% weight loss, respectively, of these compatibilized nanocomposites were slightly higher than the PE/O-MMT nanocomposites. This improvement can be due to maleic anhydride polyethylene. It has been reported [29] that, in the presence of this kind of compatibilizer, more intercalation/exfoliated layers can be formed in the polymer matrix and that there is an improvement in the barrier action for diffusion of oxygen into the nanocomposites which can inhibit material decomposition in air.

The thermal scans of PE, PE/O-MMT, and PE/O-MMT/E226 nanocomposites in nitrogen atmosphere are shown in Figure 5, and the degradation temperatures as well as ash content are depicted in Table 4. These results show that the thermal stability of the nanocomposite materials is enhanced when compared to that of the neat PE. On the other hand, it can be seen that the TGA thermogram in

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_{10%}$ ($^\circ$C)</th>
<th>$T_{50%}$ ($^\circ$C)</th>
<th>Loading (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE</td>
<td>389.38</td>
<td>430.00</td>
<td>0</td>
</tr>
<tr>
<td>PE/O-MMT</td>
<td>434.06</td>
<td>468.59</td>
<td>3.88</td>
</tr>
<tr>
<td>PE/O-MMT/PE-MA</td>
<td>440.16</td>
<td>471.63</td>
<td>3.89</td>
</tr>
</tbody>
</table>

Table 3: TGA data of PE and its nanocomposites in air atmosphere.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_{10%}$ ($^\circ$C)</th>
<th>$T_{50%}$ ($^\circ$C)</th>
<th>Loading (wt%)</th>
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<tbody>
<tr>
<td>PE</td>
<td>413.75</td>
<td>456.40</td>
<td>0</td>
</tr>
<tr>
<td>PE/O-MMT</td>
<td>446.25</td>
<td>464.53</td>
<td>3.42</td>
</tr>
<tr>
<td>PE/O-MMT/PE-MA</td>
<td>448.28</td>
<td>466.56</td>
<td>3.40</td>
</tr>
</tbody>
</table>

Table 4: TGA data of PE and its nanocomposites in nitrogen atmosphere.
4.5. Dynamic Mechanical Behaviour. Thermomechanical analysis using DMTA was used to understand the evolution of the viscoelasticity of the nanocomposites over a wide range of temperatures. This technique provides better information on the quality of dispersion of the nanoclay filler in the polymer matrix [30, 31]. The storage modulus $E'$ and loss modulus $E''$ curves of PE and its nanocomposites are depicted in Figures 6 and 7, which show the variation of storage and loss modulus, respectively, as a function of temperature. It is evident that the $E'$ of neat PE and its nanocomposites decreases with an increase in temperature. This is due to the increase in the molecular motion of the polymer chains when the temperature increases. As depicted in Tables 5 and 6, it was found that the incorporated O-MMT improved the storage and loss modulus; at room temperature (25°C), the storage and loss moduli increased from 0.474 GPa and 0.054 GPa, respectively, in the neat PE blend to 0.561 GPa and 0.071 GPa, respectively, in the PE/O-MMT nanocomposites. This noticeable improvement in the thermomechanical stability of these nanocomposites materials from low to high temperatures was caused by the strong interactions between the interface of exfoliated/interacted nanoclay layers and the polymer matrix [32]. On the other hand, compatibilized nanocomposites showed slightly higher storage and loss moduli than nanocomposites without compatibilizers. These results clearly show that the storage modulus value is correlated with the quality of dispersion in nanocomposites materials [33].

4.6. Dielectric Breakdown Measurements. A typical image of a breakdown path for a PE/O-MMT sample in 2D and 3D presentation is shown in Figures 8(a) and 8(b), respectively. Figure 9 shows the Weibull cumulative failure probability plot for the dielectric strength of pure PE and its nanocomposites. As reported in Table 7, for PE, PE/O-MMT, and PE/O-MMT/PE-MA, the scale parameters $\alpha$ were 70.3, 82.4, and 85.7 kV/mm, respectively, and the shape parameters $\beta$ were 18.6, 13.2, and 10.8, respectively. It can clearly be observed from the scale parameter values $\alpha$ and from the confidence intervals that adding O-MMT to the polyethylene matrix...
leads to a noticeable increase in the material dielectric strength. This could be explained by the major role played by the interface between the PE matrix and the nanoclay particles, which could have an impact on the space charge distribution and charge densities. In turn, this probably led to a better distribution of the electrical stress [34]. When the compatibilizer was added to PE/O-MMT nanocomposites, a further improvement of the breakdown strength was noted. A possible explanation relates to the change of microstructure which occurred with the addition of the compatibilizer into the PE/O-MMT' nanocomposites. This change of microstructure was already underlined by the microscopic observation results discussed above.

The shape parameter value $\beta$ decreases when O-MMT is added to the PE matrix. With this parameter being an indication of the data’s scattering, this could indicate either a nonuniform dispersion of the O-MMT or a partial exfoliation of the O-MMT [35].

5. Conclusion

A commercial nanoclay masterbatch was used in this study to prepare PE/clay nanocomposites. The effect of O-MMT clay and compatibilizer on the structure and dielectric breakdown behaviour in PE was investigated. Microstructure characterizations by microscopic observation revealed that nanoclay layers were more intercalated/exfoliated in PE/O-MMT/PE-MA than in PE/O-MMT, thanks to the presence of a compatibilizer. These results are in agreement with TGA and DMTA measurements. Dielectric strength measurements showed that, in PE/O-MMT nanocomposites, significant improvements in dielectric breakdown strength can be reached, as compared to neat PE. When the compatibilizer was added to PE/O-MMT nanocomposites, a further improvement in breakdown strength was noticed. This may suggest a correlation between morphology and breakdown strength.
and that dielectric characterization, especially breakdown strength and dielectric response [28] measurements, can be exploited as an indirect technique for evaluating the degree of dispersion of nanoclay layers in polymer nanocomposites. Further studies will be necessary to confirm the results obtained.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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References


