Structure of Polypropylene-based Nanocomposites containing Calcium Zirconate

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Abstract— Polypropylene (PP) has recently been proposed as a good alternative to cross-linked polyethylene (XLPE) in the field of dielectrics due to PP's beneficial properties to withstand higher thermal endurance of up to 150 °C along with its ability to be recycled with ease, when compared with XLPE. However, PP is much stiffer than XLPE, making it unsuitable to be extruded as a high voltage cable insulation. Furthermore, PP has poor thermal conductivity under room temperature when compared with XLPE, which will otherwise result in inferior dielectric performances. Therefore, PP needs to be modified to alter its physical as well as electrical properties. In the current work, ethylene-propylene-diene monomer (EPDM) was proposed to be combined with PP to produce a PP blend with reduced overall stiffness. To increase the thermal conductivity of the PP blend, nanofillers were proposed to be added to the PP blend. For these reasons, the structure of the proposed materials was investigated by Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC).

Keywords—polypropylene, EPDM, XLPE, nanofiller structure

1 INTRODUCTION

Progressive development in high voltage direct current (HVDC) transmission projects has raised concerns regarding the problems faced by the use of high voltages cross-linked polyethylene (XLPE) cables. The concern arises from the use of XLPE include the presence of chemical by-products produced from the cross-linking process and its limited operating temperature, which is at 90°C [1]. Since the production of XLPE involves the uses of crosslinking agents, this produces by-products mainly polar in nature and to some degree, affect the dielectric performance of XLPE cables [2]. Inefficient reproducibility and inconvenient recyclability have also raised the environmental concerns. This led to the need to develop a novel type of insulation medium. Therefore, large-scale research on production and environmental friendly HVDC cables is aggressively ongoing. The mainly focus has thus to be on polyethylene (PE) blend and polypropylene (PP) blend based insulation medium, as well as nanocomposites.

Specifically, a thermoplastic polymer, like PP has a high melting temperature, which is very applicable in high temperature operation cables. The breakdown strength, volume resistivity, and leakage current of the material can also be improved [3]. By improving all these criteria, the operating voltage level of the cable and the line ampacity increases, which is great for a cable performance. Howbeit, the properties of PP are rigid and brittle [4]. The fundamental properties of PP have been further studied and the modification has been made by incorporating a thermoplastic elastomer, such as ethylene-propylene-diene monomer (EPDM). The high melting temperature of PP showing it is a good heat resistant substance. Therefore, by using PP/EPDM nanocomposites, the breakdown strength of this insulation material is expected to be better. The translucent property of PP makes the electrical forensic easy to identified when the breakdown occurs.

Doping a nano-scale material within polymer matrix has been shown to be able to improve electrical insulation properties such as DC volume resistivity, space charge, breakdown strength, and dielectric response [5]. In commercial cable applications, such as low density polyethylene (LDPE) and XLPE, nanoparticles such as silica (SiO_2), magnesia (MgO), alumina (Al_2O_3), zinc oxide (ZnO), zirconia (ZrO_2), titania (TiO_2), montmorillonite clay, and zeolite had been widely added and investigated from the perspective of improving AC and DC dielectrics [6]. In the field of nanoparticles technology, hybrid nanoparticles have also been highlighted since previously, multi-element metal oxide nanoparticles (such as magnesium aluminate, ($MgAl_2O_4$)) has shown much higher breakdown strength than single-element metal oxide nanoparticles (such as magnesium oxide (MgO) and aluminum oxide (Al_2O_3)) [7]. Calcium zirconate ($CaZrO_3$) is a multi-element oxide that is grouped in perovskite family. The chemical stability of the compound is very high, thus making it a stable chemical quasi-binary system. Although modifications of the electrical properties of XLPE has been well known, there is still few numbers of researches about the effect of nanoparticles on the properties of PP/EPDM [8].

In this study, the use of PP/EPDM nanocomposites with different amounts of $CaZrO_3$ was proposed. To realize uniformity and well dispersion, a compatibilizer was used to disperse the nanofillers well into the polymer thermoplastic/elastomer matrix [9]. The morphology, structure, and electrical properties of the resulted nanocomposites will be investigated. The influence of $CaZrO_3$ nanofiller on the properties of PP/EPDM matrix will be investigated in detail, and the optimal content of nanofillers will be determined experimentally. The objective of this study was to develop the optimised insulation configuration of PP nanocomposites for power cables.

2 EXPERIMENTAL PROCEDURES

2.1 MATERIALS

The host polymer used for this study was a thermoplastic (PP) homopolymer with melt flow index (MFI) of 0.9 g/cm^3, supplied by LOTTE Chemical Titan. The thermoplastic elastomer, namely ethylene-propylene-diene monomer (EPDM) was proposed to be blended with the PP homopolymer. Nano-CaZrO$_3$, with relative density of 5.11 g/mL at 25°C, was obtained from Sigma-Aldrich.

2.2 CHARACTERIZATION

Thermogravimetric (TGA) analysis was be performed to analyze a material's thermal stability. The material's differences in weight, as a function of increasing temperature can be monitored. The PP pellets, EPDM pellets, and as-received CaZrO$_3$ nanopowder were tested using a Perkin Elmer Pyris 1 TGA equipment to study their thermal profile before mixing them. 20 mg of each material was placed in an aluminum crucible pan for each of the measurement. The temperature ranges for conducting the test was from 30°C until 950°C (the maximum temperature of the TGA equipment), and the temperature was increased by 10°C/min under 20 ml/min of nitrogen flow rate.

Calorimetry experiments were performed by using a Perkin Elmer differential scanning calorimetry (DSC) 7 and the data were analyzed by Pyris software. DSC was used to gather the data of the thermal behavior, melting and crystallization peaks of the test samples. 5 mg of each material was weighed and placed into a sealed aluminum crucible pan and heated from 30°C until 200°C for PP and 30°C until 250°C for EPDM. The heating session was operated at a scan rate of 10°C/min and the test was performed in an atmosphere of nitrogen gas.

For the purpose of calibration, high purity indium, with having a known melting temperature of 156.6°C and melting enthalpy of 28.45 J/g was used. It should be noted that the calibration values are dependent on the temperature scan rate used. Therefore, for each temperature scan rate, the calibration needed to be conducted accordingly.

Fourier Transform Infrared (FTIR) spectrometer was used to characterize the CaZrO$_3$ nanoparticle and PP homopolymer. A Perkin Elmer Spectrum One was employed, of which the data were collected at wave numbers ranging from 370 cm^{-1} to 4000 cm^{-1} over 32 scans at a resolution of 4 cm^{-1}. The standard detector used was the mid-infrared triglycine sulphate (MIRTGS). A solid sample with a thickness of about ~100μm was used.

3 RESULTS AND DISCUSSION

3.1 THERMOGRAVIMETRIC ANALYSIS

Figure 1 shows the weight reduction of PP started at 360°C. A noticeable weight decrement (%) occurred from 360°C to 470°C. Subsequently, the mass of PP was completely loss even heated up to 950°C. The decomposition temperature of PP occurred at a very high temperature, an indicator that PP is a thermally stable compound [10].

For EPDM, as shown in Figure 2, the weight changes started to experience loss when subjected to TGA heating. The weight of EPDM was constant until it reached a temperature of 350°C. A total of 100% weight loss was

reached fully within the temperature range from 350°C to 500°C [11]. The decomposition temperature of EPDM was similar to the decomposition temperature of PP although EPDM is an elastomer rubber type material. This indicates that EPDM is also a thermally stable material to be used as a matrix in the cable insulation medium.

Figure 3 shows magnified TGA curves of the reduction of weight of CaZrO$_3$ nanopowder. It can be seen that the slight loss occurred in two stages. First, a weight reduction of about 4% happened in the first stage when heated up to 600°C. Second, the weight continued decrease drastically
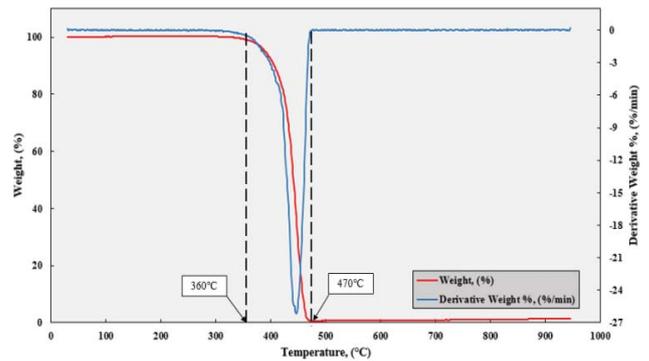
Figure 1. TGA curves for PP.
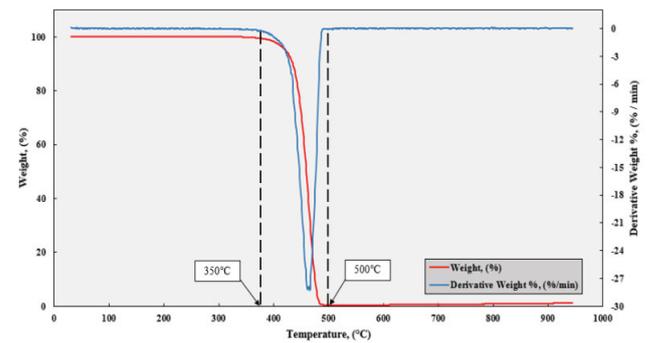
Figure 2. TGA curves for EPDM.
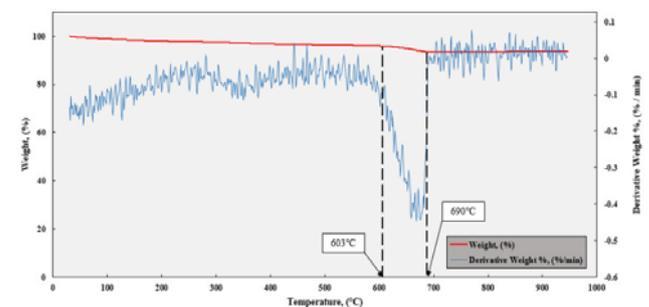
Figure 3. TGA curves for CaZrO$_3$.

about 2.5% from 600°C to 690°C. Therefore, a total reduction weight of 6.5% happened within in the overall temperature range studied [12].

3.2 FOURIER TRANSFORM INFRARED SPECTROSCOPY

The FTIR spectra of PP is shown in Figure 4. The absorption stretching band between 2840-3000 cm^{-1} indicates C-H bonds as a representation of alkane functional group. Broad and sharp peak at 2916.37 cm^1 and 2951.09 cm^{-1} is related to the molecular structure of PP (i.e.[C$_3$H$_6$]$_n$) that contains C-H bonds. The sharp bending of

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absorption band at 972.12 cm^{-1} corresponded to the C=C bond. This bond represents the existence of alkene functional group, which has the characteristics of strong covalent bond [10].

Figure 5 shows the spectra of EPDM at about 1465 cm^{-1} representing the C-H bending that is from the methylene group. The strong covalent bond of C=C bonds that have been found at the peak of 721.38 cm^{-1} portrayed dissubstituted chain, in which it exhibited the identity of alkene functional group in EPDM molecular structure. The
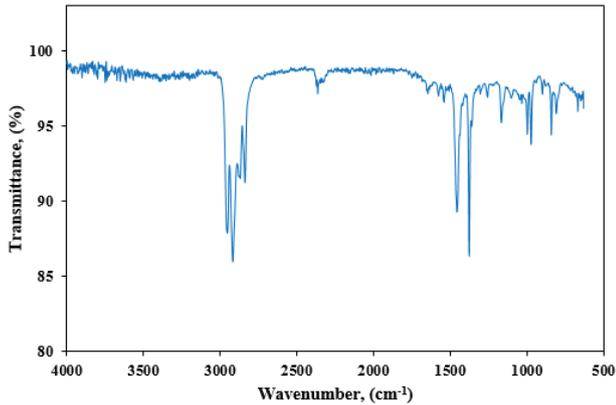
Figure 4. FTIR spectra of PP.
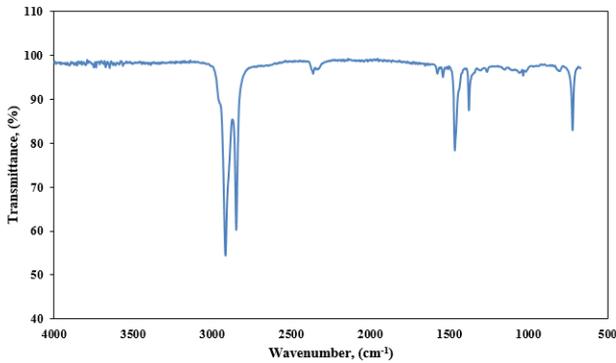
Figure 5. FTIR spectra of EPDM.
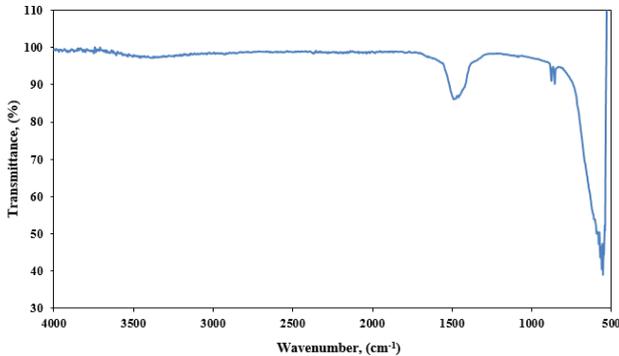
Figure 6. FTIR spectra of CaZrO$_3$.

sharp and broad stretching vibrations of C-H bonds at 2848.86 cm^{-1} and 2916.37 cm^{-1} are attributed to the

characteristics of alkane group. The peak at 1377.17 cm^{-1} originated from the bending of hydroxyl functional group. Next, the peak of 1261.45 cm^{-1} indicates that C-O bond was depicted from the group of aromatic ester and alkyl aryl ether [13]. These adsorption band represents EDPM molecular structure.

Figure 6 shows the molecular structure of CaZrO$_3$. The adsorption band of CaZrO$_3$ the spectra that validated the mechanism of CaO and ZrO$_2$ had present in the chemical compound [10]. The absorption band at 400-800 cm^{-1} was as the representation of zirconium dioxide (ZrO$_2$). While the chemical compound of calcium oxide (CaO) was observed to be present at the broad absorption band of 1360-1600 cm^{-1}.

3.3 DIFFERENTIAL SCANNING CALORIMETRY

The DSC curves in Figure 7 shows the peak temperature (T_m) of PP, at 165°C which compatible with the previous literature [14]. This melting point would be an indicator to the melting temperature of resulted PP nanocomposites. Meanwhile, figure 8 shows the crystallization temperature (T_c) of PP is 115°C [15].
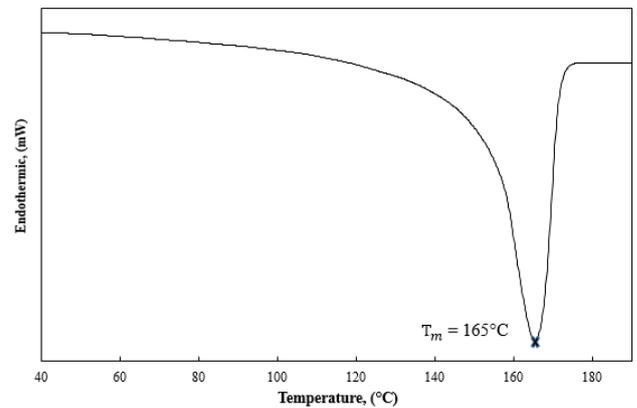
Figure 7. DSC melting peak of PP
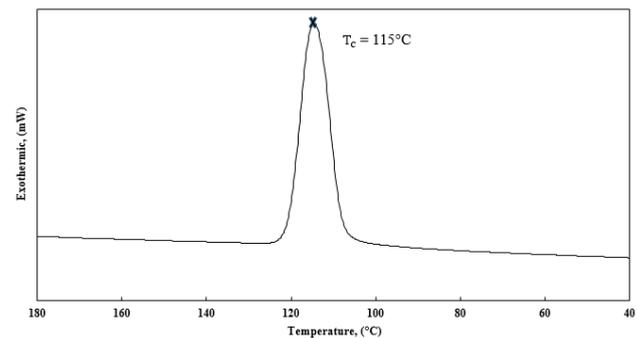
Figure 8. DSC crystallization peak of PP

4 CONCLUSIONS

In current work, the raw materials of PP, EPDM, and CaZrO$_3$ were characterized in order to proceed with sample preparation and electrical testing towards PP/EPDM nanocomposites. The TGA results of all the materials show thermally stable compounds. From these results, the differences in weight were also monitored as a function of increasing temperature. The DSC data show the melting

temperature and crystallization temperature of PP were similar with the previous literature. The FTIR results validated the chemical compounds present in the raw materials. From the results, PP, EPDM, and $CaZrO_3$ displayed a desirable characteristic. In future work, PP/EPDM blends and PP/EPDM nanocomposites with 0.5 wt%, 1 wt%, and 3 wt% of $CaZrO_3$ will be prepared and characterized to identify the structure and morphology. The optimal content of nanofiller will be determined by testing all the samples with electrical tests such as AC and DC breakdown strength.

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