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Effects of Thermal Aging on Structure and Dielectric Properties of Polypropylene/Calcium Carbonate Nanocomposites

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Abstract- This paper reports on an investigation of the effect of thermal aging on the structure and dielectric properties of unfilled polypropylene (PP) and PP nanocomposites containing 1 wt%, 2 wt%, and 5 wt% of calcium carbonate (CaCO_3) nanofiller. Three different aging temperatures were considered, i.e., 20 °C (unaged), 110 °C, and 140 °C. After aging, the dielectric strength of the samples was tested by means of DC breakdown testing. The results showed that, although the breakdown strength of PP nanocomposites was lower than that of unfilled PP before aging, the reduction in DC breakdown strength of PP nanocomposites was less pronounced compared with unfilled PP after aging. This indicated that the DC breakdown property of PP nanocomposites was less susceptible to thermal aging.

Keywords—nanocomposites; polypropylene; calcium carbonate; breakdown; aging

I. INTRODUCTION

In general, polymeric insulation materials are exposed to many environmental impacts during their service lifetime. It has been reported that the physicochemical characteristics of polymers change due to exposure to heat over a long period of time. This causes property modifications of the materials and can result in the degradation of the materials. For example, the maximum allowable operating temperature of crosslinked polyethylene (XLPE) cable insulation is commonly 90 °C. Above that operating temperature, the dielectric properties of the insulation material will become severely compromised [1, 2].

To date, various research studies have demonstrated that the electrical and mechanical properties of polymers are significantly affected by accelerated thermal aging. For instance, Brzozowska-Stanuch [3] pointed out that chemical bonding in polypropylene (PP) could be degraded due to exposure to temperatures above 100 °C. During aging, oxidation occurred at the carbon centers of the PP chain, which led to chain breaking by reaction with oxygen. This is because oxygen can promote the formation of free radicals, which subsequently changes the molecular structure.

Meanwhile, Fiebig et al. [4] and Ferhoum et al. [5] showed that thermal aging changed the amorphous regions of polymers. This led to an increase in the density and modulus of the

materials. Ghasemzadeh-Barvarz et al. [6] found that the tensile strength of polymer nanocomposites increased with increasing thermal aging duration. Ghasemzadeh-Barvarz et al. [6] claimed that the improvement of tensile strength after thermal aging was due to the enhancement of interfacial adhesion between the nanofiller and the polymer matrix. However, Liu et al. [7] demonstrated that the breakdown strength of nanocomposites reduced after thermal aging.

Although PP nanocomposites have recently been highlighted as a potential alternative to replace XLPE in cable applications, due to the base PP possessing a high melting temperature (commonly above 150 °C), high mechanical strength, low dielectric constant, reduced space charge accumulation, and high volume resistivity compared with XLPE [8], the effects of elevated temperatures on PP nanocomposites are not well understood from the perspective of dielectrics. Therefore, the work reported here set out to consider the effects of different thermal aging temperatures, i.e., 20 °C (unaged), 110 °C, and 140 °C, on the structure and dielectric properties of unfilled PP and PP nanocomposites containing calcium carbonate (CaCO_3) nanofiller. The prepared samples were characterized by means of differential scanning calorimetry (DSC) and DC breakdown testing to evaluate the effects of thermal aging on the structure and electrical properties of the unaged and aged insulation materials.

II. EXPERIMENTAL

A. Sample Preparation

The polymer matrix used in this study was a PP blend (PPb) composed of 50% of PP homopolymer (isotactic, grade TITANPRO 6531M) and 50% of PP impact copolymer (grade TITANPRO SM340), obtained from Lotte Chemical Titan. CaCO_3 (with a manufacturer-quoted particle size of 15-40 nm, obtained from SkySpring Nanomaterials), was used as a nanofiller. Three nanofiller loading levels were chosen, i.e., 1 wt%, 2 wt%, and 5 wt%. PP nanocomposites containing CaCO_3 were prepared by using a Brabender melt mixer. The rotational speed, temperature, and duration were set at 50 rpm, 180 °C, and 10 min, respectively. To produce thin film samples of approximately 100 μm in thickness, the samples were melt-

TABLE I
Sample Designation.

Samples (P/F/T)	Polymer (P)	Filler and amount (F)	Thermal aging (T)
PPb/0/0	PP blend	No filler	Unaged
PPb/CaCO ₃ -1/0	PP blend	1 wt% CaCO ₃	Unaged
PPb/CaCO ₃ -2/0	PP blend	2 wt% CaCO ₃	Unaged
PPb/CaCO ₃ -5/0	PP blend	5 wt% CaCO ₃	Unaged
PPb/0/110	PP blend	No filler	110 °C
PPb/CaCO ₃ -1/110	PP blend	1 wt% CaCO ₃	110 °C
PPb/CaCO ₃ -2/110	PP blend	2 wt% CaCO ₃	110 °C
PPb/CaCO ₃ -5/110	PP blend	5 wt% CaCO ₃	110 °C
PPb/0/140	PP blend	No filler	140 °C
PPb/CaCO ₃ -1/140	PP blend	1 wt% CaCO ₃	140 °C
PPb/CaCO ₃ -2/140	PP blend	2 wt% CaCO ₃	140 °C
PPb/CaCO ₃ -5/140	PP blend	5 wt% CaCO ₃	140 °C

pressed using a hydraulic laboratory press at a temperature of 180 °C. The melt pressed samples were then left to cool down naturally under laboratory ambient conditions. For convenience, all prepared samples were denoted using the general notation “P/F/T”. In this, P refers to the polymers, F signifies the nanofiller type and amount, and T represents the thermal aging, as indicated in Table I.

B. Thermal Aging

Thermal aging was carried out by means of a vacuum oven. The duration of thermal aging was 360 h. Three levels of aging temperature were considered, i.e., 20 °C (unaged), 110 °C, and 140 °C. After completing the thermal aging, the samples were left to cool down naturally under laboratory ambient conditions.

C. Characterization

The thermal behavior of the prepared samples was obtained using a Perkin Elmer differential scanning calorimeter (DSC) 6 under the nitrogen atmosphere. For each measurement, 5 mg of the sample was prepared and was sealed in an aluminum pan. During each DSC scan, the sample was heated from 60 °C to 180 °C at a scan rate of 10 °C/min to characterize its melting behavior. The sample was then cooled from 180 °C to 60 °C at 10 °C/min to determine its crystallization behavior. Perkin Elmer’s Pyris software was used to analyze the resulting data.

DC breakdown tests were performed using a dielectric strength tester. The tests were carried out based on the guidelines set out in ASTM D149. The thickness of each test sample was approximately 100 µm. The sample was sandwiched between two 6.3 mm diameter steel ball electrodes and immersed in mineral oil to prevent surface flashover. A DC step voltage of 2 kV every 20 s was applied until breakdown. 15 breakdown points were recorded for each sample type, and the breakdown data were analyzed using the two-parameter Weibull distribution.

III. RESULTS AND DISCUSSION

A. Thermal Properties

The DSC melting and cooling traces comparing unfilled PP with nanocomposites containing CaCO₃ under unaged and aged conditions are shown in Fig. 1a and Fig. 1b, respectively. The peak melting temperature for unaged samples was ~162 °C,

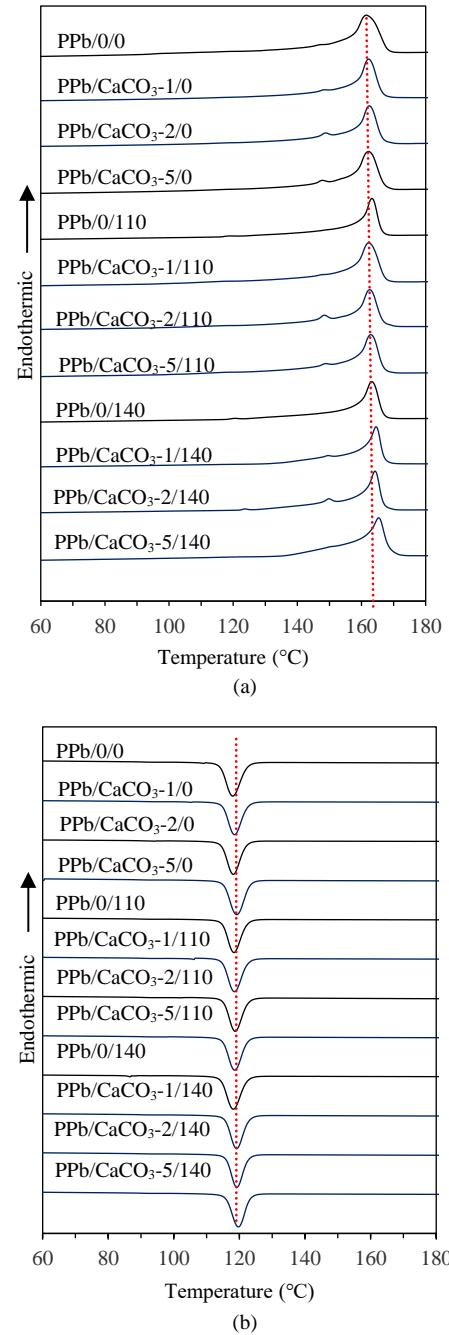


Fig. 1. DSC (a) melting traces, (b) cooling traces comparing unfilled PP with nanocomposites containing CaCO₃ under unaged and aged conditions.

which corresponds to the fusion of α -crystals of PP [9]. In addition, a secondary melting peak at 148 °C is indicative of a fusion peak of β -crystals [9]. Significantly, the melting peak increased with thermal aging temperatures as a result of crystal annealing, in line with reports in the literature [2, 10]. Meanwhile, the samples’ peak cooling temperature (T_c) were similar, at about 119 °C. Thermal aging had no appreciable effects on T_c of all samples.

Of note, thermal aging also increased the degree of crystallinity for all samples (see Fig. 2). This suggests that thermal aging modified the materials’ morphology. Table II

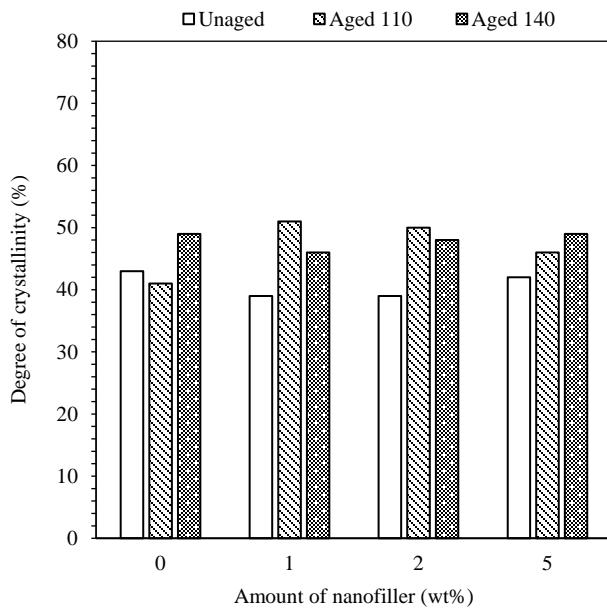


Fig. 2. Degree of crystallinity comparing unfilled PP with PP nanocomposites containing CaCO_3 under unaged and aged conditions.

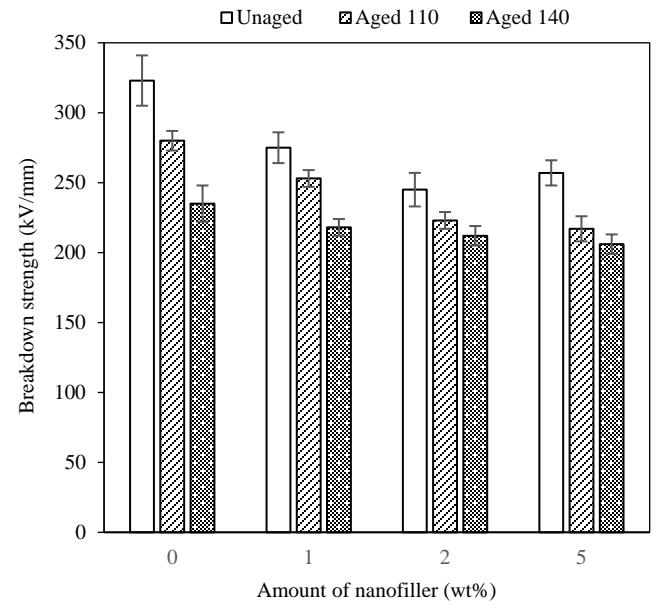


Fig. 3. DC breakdown strength comparing unfilled PP with nanocomposites containing CaCO_3 for unaged and aged samples.

TABLE II

Peak melting temperature, peak cooling temperature, and crystallinity of unfilled PP and PP nanocomposites under unaged and aged conditions.

Samples	T_m (°C)	T_c (°C)	Crystallinity (%)
PPb/0/0	161	118	43
PPb/ CaCO_3 -1/0	162	119	39
PPb/ CaCO_3 -2/0	162	119	39
PPb/ CaCO_3 -5/0	162	119	42
PPb/0/110	163	118	41
PPb/ CaCO_3 -1/110	162	118	51
PPb/ CaCO_3 -2/110	163	119	50
PPb/ CaCO_3 -5/110	163	119	46
PPb/0/140	163	118	49
PPb/ CaCO_3 -1/140	165	119	46
PPb/ CaCO_3 -2/140	164	119	48
PPb/ CaCO_3 -5/140	165	120	49

summarizes the peak melting temperature, peak cooling temperature, and crystallinity obtained from DSC under unaged and aged conditions for unfilled PP and PP nanocomposites.

B. Electrical Breakdown

Figure 3 compares the DC breakdown strength of unfilled PP and PP nanocomposites containing CaCO_3 under unaged and aged conditions; derived Weibull parameters are listed in Table III. The DC breakdown strength of unaged, unfilled PP was 323 ± 18 kV/mm. By adding 1 wt%, 2 wt%, and 5 wt% of CaCO_3 to PP, the DC breakdown strength reduced to 275 ± 11 kV/mm, 245 ± 12 kV/mm, and 257 ± 9 kV/mm, respectively.

Significantly, the DC breakdown strength of all samples, when aged at 110°C , reduced compared with unaged condition. A further reduction in DC breakdown can be observed when all the samples were aged at 140°C . These obtained results are in line with the research in [10].

Fig. 4 shows the breakdown strength of each material, normalized with respect to the breakdown strength of unaged,

TABLE III
DC breakdown parameters.

Sample	α (kVmm ⁻¹)	β
PPb/0/0	323 ± 18	8 ± 3
PPb/ CaCO_3 -1/0	275 ± 11	11 ± 4
PPb/ CaCO_3 -2/0	245 ± 12	9 ± 3
PPb/ CaCO_3 -5/0	257 ± 9	14 ± 5
PPb/0/110	280 ± 7	18 ± 6
PPb/ CaCO_3 -1/110	253 ± 6	20 ± 7
PPb/ CaCO_3 -2/110	223 ± 6	16 ± 6
PPb/ CaCO_3 -5/110	217 ± 9	10 ± 4
PPb/0/140	235 ± 13	8 ± 3
PPb/ CaCO_3 -1/140	218 ± 6	16 ± 7
PPb/ CaCO_3 -2/140	212 ± 7	15 ± 6
PPb/ CaCO_3 -5/140	206 ± 7	14 ± 5

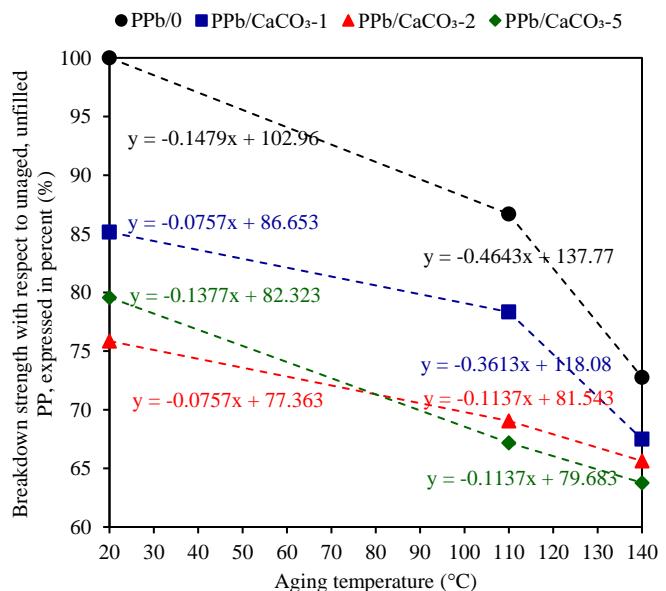


Fig. 4. Breakdown strength of each material with respect to the breakdown strength of unaged, unfilled PP, expressed in percent.

unfilled PP (323 kV/mm); that is 323 kV/mm is equivalent to 100% in the graph. Information pertaining to the percent reduction in the DC breakdown of PP nanocomposites under different aging temperatures with respect to unfilled PP can be extracted from Fig. 4; the breakdown strength of PP nanocomposites reduced with increasing amounts of CaCO_3 .

In addition, the percentage reduction in the DC breakdown strength of each material before and after aging can also be interpreted from Fig. 4 through a linear interpolation across the plotted data. Of note, the percent reduction in the DC breakdown strength of PP nanocomposites was less pronounced compared with unfilled PP after aging, and the effects of aging on DC breakdown can be discussed in 2 phases – from 20 °C to 110 °C and from 110 °C to 140 °C. Clearly, the reduction in the DC breakdown strength of unfilled PP was more significant than all the investigated nanocomposites, where the slope representing the degree of reduction in DC breakdown was steeper for unfilled PP (~0.15) between 20 °C and 110 °C. Furthermore, the slope became much steeper for unfilled PP (~0.46) from 110 °C to 140 °C, suggesting that unfilled PP suffered from much reduced DC breakdown strength under elevated temperatures.

The DC breakdown trend of nanocomposites containing 1 wt% of CaCO_3 appeared similar to that of unfilled PP, suggesting that the breakdown behavior of the nanocomposites was largely determined by property of the base PP. However, the percentage changes in the DC breakdown strength of nanocomposites containing 1 wt% of CaCO_3 were less pronounced compared with the unfilled PP after aging. This suggests that the CaCO_3 somehow hinder the breakdown process after aging, albeit that this was not prevalent at 1 wt% loading level. By adding 2 wt% and 5 wt% of CaCO_3 to PP, the hindrance of the nanocomposites' DC breakdown property against aging became more prevalent, especially at elevated temperatures. Specifically, the slope characterizing the DC breakdown reduction between 110 °C and 140 °C became 0.11 for both nanocomposites containing 2 wt% and 5 wt% of CaCO_3 , in contrast to 0.46 for unfilled PP. This shows that thermal aging has less detrimental effect on PP nanocomposites' DC breakdown strength compared with unfilled PP.

IV. CONCLUSIONS

The current work reports on the effects of thermal aging on the structure and dielectric properties of unfilled PP and PP/ CaCO_3 nanocomposites. Although all the investigated nanocomposites possess lower DC breakdown strength than unfilled PP, the nanocomposites show less reduction in DC breakdown strength after being subjected to aging at elevated temperatures. This indicates that the DC breakdown property of PP nanocomposites is less susceptible to thermal aging than unfilled PP. More experimental work is currently ongoing to understand the possible mechanisms associated with the observed DC breakdown difference between PP nanocomposites and unfilled PP with regard to aging.

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