Effect of Nano-Clay Filler on the Thermal Breakdown Mechanism and Lifespan of Polypropylene Film Under AC Fields

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ABSTRACT The wide application of nanocomposites in the insulation system has greatly contributed to the performance improvement of power equipment. However, nano fillers are not omnipotent for improving the properties of composite dielectrics. In some situations, nano-modified materials are in fact a compromise of improving some performance features while sacrificing others. In this work, the breakdown characteristics and time-to-failure of polypropylene film with nano-clay fillers have been evaluated under combined thermal stress and AC electric fields. Experiments on plain polypropylene (PP) samples have also been carried out under the same test conditions as control. Test results indicated that the time-to-failure of the samples with nano-clay filler was shorter than those without nano filler, which is different from the previous experience. SEM and EDS analyses were conducted to study how the failure mechanism had taken place in both plain polypropylene and the nano-clay filled polypropylene. The failure phenomenon in these materials can be explained by molecular thermodynamics. The main reason for the premature thermal breakdown of PP nanocomposite is essentially due to the weak coupling between nano-clay filler and polymer matrix. Finally, suggestions are proposed for nano modification methods and lifespan prediction models of composite dielectrics.

INDEX TERMS Electrical insulation, thermal breakdown, polypropylene film, nanocomposites, dielectrics, time-to-failure, aging.

I. INTRODUCTION

In recent years, the application of polymer as dielectric materials in power grid has effectively improved the performance of power equipment, such as energy storage characteristics [1], [2], mechanical properties [3], electrical strength [4], [5] and so on. Many studies have shown that, on the basis of ensuring the original properties of the above polymeric dielectric materials, nano-fillers can further improve the properties of the materials through effective combination with the polymer matrix [6]–[8]. Considering the advantages of nanocomposite dielectrics, however, attention still needs to be paid to the degradation of material properties in practical applications. One of the most noticeable problems is the aging under the comprehensive effect of multiple factors [9]–[11], which will affect the service lifespan of power equipment and may bring additional operation and maintenance costs.

Polypropylene (PP) is a common dielectric material usually used in radio frequency, thin-film capacitors [12], [13] as well as cables as insulating material [14]. In our previous research [15], it was found that the electrical strength of PP film could be improved by mixing with natural nano-clay at room temperature. However, in this work, a much lower electric field than the breakdown electric field is applied to the same sample at elevated temperature, an unexpected result is obtained. The time-to-failure of PP film loaded with nano-clay is found to be shorter than that of plain PP.

Previous studies have shown that space charge has a great influence on the breakdown characteristics of nanocomposite dielectrics [16], [17]. However, it seems not much research
has been conducted with respect to the influence of nano fillers on the molecular structure of the matrix in the process of breakdown.

In this paper, the breakdown characteristics and time-to-failure of PP film under the combined thermal stress and electric fields are studied experimentally. Moreover, theoretical analysis is carried out to explore the mechanism of the experimental results. The conclusion of this work can be used for evaluating the service lifespan of PP film and a recommendation for the nano modification of polymer dielectric is provided.

II. EXPERIMENTAL ARRANGEMENT AND METHODS

A. TEST SAMPLES

In order to carry out the comparative experiment, two groups of samples were prepared in this paper. The first group was plain isotactic PP film as control group; the other group, on the other hand, was PP film, filled with 2 wt% natural nano-clay. The composition of natural nano-clay is montmorillonite, also known as epidote or Cloisite® 20A, [Al1.67 Mg0.33 (Na0.33)Si4 O10 (OH)2. The details of the material preparation were presented in the previous study [15]. In the experiment, the thickness of each PP film sample is 135 µm with a variation within ±10% and prepared as 50 mm x 50 mm square.

B. EXPERIMENTAL METHODS

In order to assure that there were no impurities the sample surfaces and the circular aluminum electrodes were cleaned using ethanol. After the cleaning process the test sample was placed between the electrodes. The diameter of the aluminum electrodes was 32 mm with curved edges so that the fringing effect was minimized to ensure almost a uniform electric field distribution in the test sample to avoid corona discharges [18].

The electrode-film assembly was inserted in a 1 L beaker which was placed on a hotplate to provide the temperature required by the experiment. The top of the beaker was covered by a 15 mm thick PTFE (Teflon®) lid to enhance thermal insulation and avoid heat leakage.

High voltage was applied to one of the electrodes through a bushing, while the other electrode was grounded. The ground current from the grounded electrode was continuously monitored in order to detect the moment of breakdown in the test sample. The experimental layout and the schematic of the test circuit are shown in Figure 1. More experimental details have been introduced in our previous research [19].

After the hotplate was energized at a certain level the temperature was continuously monitored on the sample using a thermocouple gauge in order to maintain the desired temperature. When the temperature was fixed at the desired level, then the thermocouple gauge was removed and the high-voltage was applied to reach the prespecified electric field intensity. The setup was not touched until the sample breaks down. The sample failure was detected when the continuously monitored ground current suddenly jumps to a high level caused by breakdown.

The time-to-breakdown of each sample was recorded at a distinct temperature and electric field.

III. TEST RESULTS

Figure 2 presents the comparison of time-to-failure between plain PP film and its nanocomposites under the electric field of 60kV/mm at temperatures of 58°C, 72°C and 92°C.

Experimental results showed that with the increase of electric field intensity or temperature, the time-to-failure of...
PP film would decrease. Moreover, the time-to-failure of nanocomposites was found to be shorter than that of plain PP film. This phenomenon seems to be different from our expectation of the experiment. In a previous research, nano-fillers have a significant effect on improving the electrical strength of PP films [15]. In the present study the applied electric field intensity was set to a much lower level than the breakdown strength of plain PP and the PP nanocomposite. Also, the temperature on the materials was elevated well above the room temperature. Whereas, the study in [15] was done at room temperature to find the breakdown strength of the material when subjected to a voltage with fixed ramp rate.

In this work, the experimental conditions are closer to the actual operating state of composite dielectric materials. In addition to the long-term effect of electric field, the materials will also face the impact of elevated temperatures. In the temperature elevating process of PP film, there is also heat leakage around the electrode. When the heat gain exceeds heat loss, the temperature of dielectric materials will continue to rise, resulting in the decomposition and carbonization of the material as well as breakdown. Consequently, the failure of PP film is thermal breakdown under thermal-electric coupled fields. Without thermal stress, the failure of PP film is electric breakdown. Due to the different thermal properties of the nanoparticles and the polymeric matrix, the mixed nano-clay may bring new defects to the materials in the continuous high temperature environment. As a result, the time-to-failure is reduced.

IV. DISCUSSIONS

A. BREAKDOWN MECHANISM

Although the electric field intensity exerted on the samples was far less than the breakdown strength in this experiment, the long-term effect of the electric field coupled with thermal stress may be the cause of the above phenomenon.

Figure 3 presents the breakdown phenomenon of samples (2 wt %) under two different experimental conditions. A small microscope (Nurugo Micro) was also used to take micrographs of the sample that was magnified 400 times. In electrical breakdown at room temperature, the size of the breakdown point is small, and the appearance of the materials around the breakdown point have no obvious change. On the contrary, size of the thermal breakdown point under low electric field intensity and higher than room temperature is large and the carbonization of the surrounding material is significant.

Figure 4 shows microscope (× 400) and SEM micrographs of the surface structure of the film before and after thermal breakdown. In the process of thermal breakdown, nanoparticles separated from the polymer matrix and agglomerated under long-term thermoelectric field.

The nano-clay fillers in the samples have different physical and chemical properties from the polymer matrix. The natural nano-clay used in this work is known as Cloisite® 20A (MMT) [20] with an internal structure of laminated layer of clay flakes. The flakes will peel off from the substrate in water or aqueous systems and dissolve in water. However, the polymer matrix in the PP film is hydrophobic hydrocarbon macromolecule, which is mutually incompatible with hydrophilic silicates. Therefore, when using natural nano-clay to modify the PP film, Cloisite® 20A should be intercalated first. During the intercalation process, the Na+ in Cloisite® 20A will be replaced by organic functional groups. Afterwards, the compatibilizer Polybond® 3150 (PP-MA) [21] was used to make the organic modified MMT and PP miscible.
The intercalation not only changed the properties of the nano-clay (from hydrophilic to hydrophobic), but also expanded the interval between clay flakes by 2 to 3 times. The expansion of the clay flake spacing effectively promotes the diffusion of macromolecular chains between clay flakes. During this process, a diffuse ionic layer is formed around the clay flakes, and additional ion clusters are dispersed in the polymer matrix. Consequently, the modified nano-clay particles and the polymer matrix are only connected by electrostatic adsorption in the test samples.

Obviously, the internal structure of isotactic PP is changed by mixing with natural nano-clays. At room temperature, the electrical properties of the materials were improved for the following reasons. Firstly, nano-clay particles fill the unoccupied holes in PP and thus improve the breakdown strength. Secondly, nano fillers form new chemical bonds and bring new components to the material. As a result, the polarization of the dielectric in the AC electric field becomes more complex, and the dielectric constant of PP film with nanocomposites will be different from plain PP materials. To some extent, the breakdown strength would be enhanced.

**B. THERMAL PROPERTY AND LIFESPANS**

Whereas the temperature of nanocomposites increased under the long-term AC field, the situation changes. The thermal motion of all molecules in the PP film will be enhanced with the elevated temperature, which will destroy the diffused ionic layer between the clay flakes and the polymer matrix. As a result, a large number of clay flakes would peel off from the polymer matrix. Therefore, the natural nano-clays and polypropylene could no longer be treated as a whole. On the other hand, they have different physical and chemical properties, respectively.

The thermal motion of natural nano-clays is more intense than that of polymer matrix due to lighter weight and smaller size. The clay pieces fall off from the matrix would accumulate and collide with the polymer molecules. Accelerated by AC field which provides further energy for these pieces, such structural damage will be enhanced. This situation will eventually lead to the destruction of the original molecular structure of the PP film loaded with nano-clay. Figure 5 shows the failure process of PP film mixed with nano-clay in a thermoelectric coupled field.

In conclusion, the aging and failure of dielectric materials in the long-term thermoelectric field is a process of thermal breakdown, which is accelerated by nano fillers, resulting in the shortening of lifespan.

According to kinetic nature of strength [22], the failure of a dielectric is a time-dependent phenomenon. The time-to-failure, \( \tau \), decreases if the absolute temperature, \( T \), increases at constant electrical field intensity, or if the field intensity increases within a range of fixed temperatures during each test. Equation (1) and Equation (2) describes this relationship:

\[
\tau(E, T) = \tau_0 e^{\frac{Q(E)}{kT}} \quad (1)
\]

and

\[
Q(E) = Q_0 - \alpha E \quad (2)
\]

where, \( Q(E) \) Being the activation energy at electrical destruction. \( \tau_0 \approx (10^{-12} - 10^{-14}) \) s is the atomic vibration period in solids, \( k \) is the Boltzmann constant, \( Q_0 \) is the value of the initial barrier of electrical destruction, \( E \) is the electric field intensity and \( \alpha \) is a coefficient which depends on the local increase in the electrical field intensity and intermolecular cavities.

In this research, the coupling between nano filler and polymer matrix is proved to be not strong enough. When the structure of the nanocomposite-modified PP film changes, the existence of nano filler reduces the value of \( Q_0 \), which leads to the decrease of the lifespan.

**V. CONCLUSION AND RECOMMENDATION**

In this paper, the effect of nano fillers on the properties of polypropylene film under AC electric field combined with thermal stress is investigated through experiments. One of the important conclusions of this work is, PP loaded with 2 wt % natural nano clay indicated a reduced lifespan compared to the unfilled isotactic PP under thermoelectric field. This result may overturn the conventional expectations of nano modification of composite materials.

The main reason for this result is that the coupling between nano fillers and polymer matrix is not strong enough, which leads to the dissociation of nano fillers under long-term electric field and relatively high temperature. The nanoparticles separated from the matrix will aggregate and become the weak point of the material. Compared with the plain PP film, the life of the nanocomposite film is shorter in this case due to aging.

Polypropylene is often used as dielectric in power grid equipment. According to the conclusion of this work, it is recommended that, appropriate nano modification could improve the performance of insulation material under normal operation environment. However, better coupling agent has to be used to enhance the chemical bond between the nano filler and the matrix should the material utilized at elevated temperature.
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