Microscopic analysis of polyimide nanocomposites aging mechanism exposed to partial discharges under high frequency voltage stress

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Abstract. For the sake of investigating the influence of nanoparticles on the reduction in structural damage of neat polyimide (PI) and PI nanocomposites, scanning electron microscope (SEM) based microscopic study was conducted on unaged and aged pure PI and PI/TiO\textsubscript{2} nanocomposite samples exposed to partial discharge activity under high frequency ac voltage stress. PI/TiO\textsubscript{2} nanocomposites with 2, 3 and 5 wt.% were fabricated adopting in-situ polymerization technique. Partial discharge (PD) aging measurements were made and PD characteristic parameters were obtained to analyze the electrical performance of both neat PI and PI nanocomposites. Based on microscopic structural analysis, it was found that PI nanocomposite sample experienced less structural damage in contrast with neat PI. Smaller and lesser number of voids were found in PI/TiO\textsubscript{2} nanocomposites than that of neat PI in result of PDs reduction in PI nanocomposite.

Keywords: Polyimide nanocomposites, TiO\textsubscript{2} nanoparticles, polymer interface, PD characteristic parameters, voids, SEM.

1. Introduction

When we talk about the failure and premature aging of solid insulation material, partial discharge (PD) is contemplated as a core cause it which leads insulating material towards its deterioration and performance degradation. In order to get rid of this cause, polymeric nanocomposite materials are being fabricating due to their excellent electrical, mechanical and thermal properties. The nanoparticles are added into known existing polymers for their customization. The nanofillers such as Al\textsubscript{2}O\textsubscript{3}, ZnO, TiO\textsubscript{2} and SiO\textsubscript{2} have been widely used for the fabrication of polymeric nanocomposites in [1], [2], [3], and [4].

It is well known that the addition of nanoparticles into base polymer matrix effectively enhances the partial discharge resistance properties of polymeric insulation material [8- 9]. PD activity under high frequency ac voltage stress brings out high energy space charges species which devastates the structure and polymer organization and leads it towards its degradation and insulation breakdown. Voids are originated by continuous PD activity resulting increase in PD number and amplitude. Furthermore, charge behavior is also considered one the major factors in polymer insulation which influences the PD...
initiated nanocomposites degradation. The high energy electrons and the energy released during charge states change result in chain scissioning and bond cleavage which initiates polymer surface degradation [5-6]. It also has been demonstrated in [7] that incorporation of nanoparticles to polyamides improves the resistance to surface degradation in nanocomposites as compared with neat or unfilled polymer.

In this paper, the microscopic study of interface has been conducted on pure PI and PI nanocomposite (PI/TiO₂) before and after aging for the sake of explaining the influence of TiO₂ nanoparticles on their aging mechanism in detail. And it has been proved that PD is the main cause of insulating material degradation.

2. Relationship between PD and space charges in TiO₂ nanocomposites

The influence of nanoparticles on resultant electric field in air gap which is actually the PD occurrence area is shown in Figure 1, where $E_a$ is representing applied voltage field while $E_q$ is the field produced by space charges. $E_r$ is representing the field actual resultant electric field from $E_a$ and $E_q$. The $E_a$ and $E_q$ act in opposite directions at the time of PD occurrence in both positive and negative half cycles.

![Figure 1. Influence of TiO₂ nanoparticles of space charge behavior and resultant field at discharge air gap](image)

It has been observed from Figure 1(a) that PD activity is depending on the relative direction of space charges field and the applied voltage field, PD is occurring in positive and negative half cycles of applied voltage because the $E_a$ and $E_q$ are in opposite direction and resultant field $E_r$ is being decreased by space charges field, hence higher applied voltage amplitude is needed for PD activity. On the other hand, at the moment of voltage polarity reversal, $E_a$ and $E_q$ both are in the same direction and resultant field towards HV electrode is increased by the space charges accumulation. The influence of nanoparticles
on space charges accumulation can be seen in Figure. 1(b) (c) (d), the space charges field is being increased as compared with pure PI because the nanoparticles generate homogenous charges at the interface and the field of homogenous charges is added into Eq which increases the potential barrier for electron injection by means of repulsion, this phenomenon has also been addressed in [8]. Eq is increasing proportionally with nanoparticles that is why the partial PD number and amplitude are decreased in PI/TiO$_2$ nanocomposites in comparison with pure PI resulting longer life.

3. Material preparation and aging test platform

3.1. Sample preparation

In-situ polymerization technique was taken into account for the preparation of polyimide nanocomposites. KH-550 modified TiO$_2$ nanoparticles were mixed with calculated quantity of DMAC and sonicated in a beaker for an hour. After that, Oxy dianiline (ODA) was added to (DMAC+TiO$_2$) suspension and stirred it for 1 hour until it doesn’t get dissolved into the solvent. The next step was to add pyro mellitic dianhydride (PMDA) into the suspension with weight percentage of 60, 30 and 10, respectively, after every 30 minutes at 40$^\circ$C constant temperature and kept stirred until the yellowish nanocomposite polyamic acid (PAA) obtained. The obtained PAA were put under vacuum in order to remove bubble and other residues. Finally, the PAA solution were poured on glass plate at room temperature to get nanocomposite films of desired thickness. The obtained specimens were 25µm thick.

3.2. Experimental parameters and aging test platform

For the sake of conducting aging test on pure and polyimide nanocomposites, the applied voltage amplitude was set to 1 kV of 15 kHz frequency according with partial discharge inception voltage (PDIV), which was 1.2 times of PDIV. The discharge signal was obtained frequently by means of leakage current during whole life of films.

![Figure 2. Aging test setup including HF & HV source, temperature control module, high frequency electric current transducer and Oscilloscope](image)

The designed electrical aging and partial discharge measurement platform, as shown in Figure 2 comprises of the following parts:

1) Sphere to plane electrode arrangement (copper made); 2) High frequency & high voltage source (voltage and frequency range up to 50 kV, 40 kHz respectively); 3) Protective resistance connected to HV electrode; 4) Temperature control module comprised test chamber (with 220 $^\circ$C tolerable temperature); 5) High frequency electric current transducer, used to capture impulse current, connected.
to ground wire (bandwidth and sensitivity range up to 500 kHz to 120 MHz and 1mA-4.2 mV); 6) A high-speed digital oscilloscope (with 5 GS/s max. sampling frequency.

The obtained signal by means of electric current transducer was too noisy and it was necessary to denoise using signal processing techniques to ensure the actual PD data. The wavelet sym8 signal denoising technique were adopted [9].

4. Results and discussions

4.1. PD aging characteristic parameters and insulation life

In order to investigate the influence of nanoparticles on electrical performance of polyimide nanocomposites under continuous high frequency ac voltage stress, the PD characteristic parameters and insulation lifetime for both pure PI and PI/TiO$_2$ nanocomposites, with different weight percentage, are obtained. The parameters include maximum PD amplitude and total PD number per second, as shown in Figure 3(a) and Figure 3(b).

![Figure 3](image)

**Figure 3.** Contribution of TiO$_2$ nanoparticles on PD Characteristic parameter and insulation life of PI/TiO$_2$ nanocomposites

Figure 3 reveals that nanoparticles play a significant role in electrical performance enhancement in polymer nanocomposites. The maximum PD amplitude and the total PD number per seconds are showing decreasing trend with increase in nanoparticles concentration while insulation life is increasing proportionally with nanoparticles concentration because, as the nanoparticles concentration increases in base polymer matrix, the generation of homogenous charges at the interface increases accordingly which results in increase of repulsive field (field generated by homogenous space charges) against applied field near HV electrode. On the other hand, addition of nanoparticles creates tightly bounded region at interface and provides resistance to degradation. PD characteristic parameter are increasing with increase in nanoparticles above 3wt. %, because of the agglomeration of nanoparticles, can be seen in Figure 4(d).

4.2. SEM measurements

Figure 4 demonstrates SEM images of pure PI and PI/TiO$_2$ nanocomposites before and after aging. For the aged samples, SEM measurements are taken on eroded region around the breakdown point. Figure 4(a) and 4(b) represent unaged PI and PI/TiO$_2$ nanocomposite samples while figure 4 (a’), 4(b’), 4(c’) and 4(d’) are SEM images of aged samples. Nanoparticles are nicely dispersed into base polyimide matrix and small whitish spots are TiO$_2$ nanoparticles. It can be seen in figure 4(a’), 4(b’), 4(c’) and 4(d’) that as the TiO$_2$ nanoparticles with different weight % are being added into base PI matrix, the number of PD initiated voids are decreasing, and pure PI aged sample has experienced most of the voids number. It also can be observed that voids generated in nanocomposites are in smaller size in comparison with the pure PI, this is because of the field produced by homogenous charges present at the interface because of addition of nanoparticles, opposes the applied electric filed resulting a smaller number of
PDs, as shown in Figure 3(a) and 3(b). More weight percentage of nanoparticles will produce a greater number of homogenous charges at interface, which will result in more opposing field, hence lesser and smaller voids. The agglomeration of nanoparticles can be seen in figure 4(d), the reason behind is, nanoparticles start to agglomerate when a certain amount of nanoparticles concentration is increased.

5. Conclusion
In this paper, the influence of nanoparticles on PD initiated structural damage of PI/TiO$_2$ nanocomposites has been investigated. Aging tests were conducted on neat PI and PI/TiO$_2$ nanocomposites at high frequency ac voltage stress until the breakdown occurred. It can be concluded from obtained results and observation that addition of nanoparticles in base polymer (polyimide) matrix
not only offers resistance to PD but also to structural damage, as shown in figure (PD and SEM images). Addition of nanoparticles in PI increase the repulsive field produced by the homogenous charges near electrode which reduces PD amplitude and number, resulting decrease in production of voids at interface, therefore longer insulation life.

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