

Experimental Study of Electric and Dielectric Behavior of PVC Composites

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Abstract—Polyvinyl chloride (PVC) is usually used as insulation in electrical engineering, mainly as cable insulation sheaths. A method for improving PVC's dielectric properties, reducing the effects of UV ageing, is the use of PVC films doped in alumina and titanium dioxide. This research investigated the influence of alumina and titanium dioxide (Al_2O_3/TiO_2) to the dielectric properties of PVC. Four PVC samples were examined using an RLC impedance analyzer. Fourier Transform Infrared (FTIR) spectroscopy was utilized on the sample's surfaces, exploring the chemical stability of the tested materials. In addition, the volume resistivity and average breakdown voltage of each sample was examined. Doping Al_2O_3/TiO_2 into PVC improved its dielectric properties and volume resistivity, while adding more ceramic decreased volume resistivity. Furthermore, the addition of Al_2O_3/TiO_2 caused a significant enhancement in voltage breakdown strength.

Keywords-PVC; composite; alumina; titanium dioxide; Al_2O_3/TiO_2 doped PVC; breakdown voltage

I. INTRODUCTION

In recent years, nanotechnology has been used in the synthesis of various types of polymer nanocomposites and in understanding their physical and chemical properties [1-5]. The presence of nanoparticles in polymers improves their mechanical, electrical and chemical properties. Polymers doped with metal oxide nanoparticles have been studied as alternative materials for electrical applications, especially in underground and transmission cables [6-7]. Many polymers have been proved as suitable matrices in the development of composite structures, due to their ease of production and processing, good adhesion with reinforcing elements, resistance to corrosive environment, and occasionally ductile electrical performance. Polyvinyl chlorides (PVCs) are polymers used as electrical insulating materials in both industrial and communication applications. Due to its excellent dielectric strength, low dielectric permittivity, low loss factor and thermomechanical behavior, PVC has been used for a long time as an electrical insulator in distribution [8]. Its compression behavior was studied in [9], where the dielectric reaction in the frequency range of 20Hz–1 GHz of polymeric insulating materials, such as PVC, polytetrafluoroethylene (PTFE) and high-density polyethylene (HDPE) was evaluated. Furthermore, it is

recognized that inorganic fillers, such as TiO_2 , ZnO, and Al_2O_3 particles, can be used as ultraviolet (UV) light screening agents in a PVC matrix [10, 11]. The inorganic fillers can absorb or reflect UV light, forming a barrier between the polymer and the light source. Researchers in [12] focused on the space charge characteristics of epoxy resin and its nano-MgO composites. It was found that specimens with 3wt%~5wt% nano-MgO accumulate less space charge, while the 1wt% nanocomposites accumulate the most. Surface modification and characterization of TiO_2 nanoparticles and their roles in thermal, mechanical, and accelerated aging behavior of foamed wheat straw fiber/polypropylene composites were studied in [13]. The anti-aging properties of polymer resins are influenced by the dispersion of inorganic fillers in the matrix. The inorganic fillers can effectively absorb or reflect UV light when they are uniformly dispersed in the polymer matrix, while agglomerated inorganic fillers result in many defects [15, 16].

This paper studies the dielectric properties of the Al_2O_3/TiO_2 composite based PVC. Four PVC samples, a pure sample and three doped with Al_2O_3/TiO_2 , were examined, studying the effect of doping in permittivity, loss index, chemical stability, volume resistivity and average breakdown voltage.

II. EXPERIMENTAL METHOD

The structure of the studied samples is given in Table I. The basic component was the PVC resin used in the Algerian industry (type H3000), mixed with an antioxidant (Barium-Zinc) to assure thermal stability, Dicumyl peroxide as linking agent lubricant, and DOP (Di-Octyle Phthalate-99.5%) plasticizer from Zhengzhou P&B Chemical Co Ltd. Four types of samples, standard PVC without additives and Al_2O_3/TiO_2 -doped PVC were examined, in conformity with [17].

TABLE I. CONTENT OF PVC - Al_2O_3/TiO_2 COMPOSITES

Samples	1	2	3	4
Polymer (PVC)	100%	90%	90%	80%
Al_2O_3	0%	10%	0%	10%
TiO_2	0%	0%	10%	10%

The preparation was mixed in a two-roll mixer for 5 minutes at 160°C. The samples were prepared as sheets of

predetermined thickness. The sheets were cut into 10cm×10cm squares with 0.6mm thickness. The apparatus used for the dielectric response was an RLC (Wayne Kerr, type 6420), using a range up to 10MHz. The samples were then introduced between two plane copper electrodes. Afterwards, the capacitor representing the sample was submitted to an alternating electric field of 1V/m. Dielectric loss factor $tg\delta$, relative permittivity ϵ_r and loss index (ϵ'') were measured, with the measurement error being $\pm 0.05\%$. The volume resistivity of the PVC nanocomposites was measured using the bridge method, at room temperature (Figure 1). Tests on the voltage breakdown of the samples were performed, using Weibull's method, in conformity with [18].



Fig. 1. Measuring circuit of the volume resistivity

III. EXPERIMENTAL RESULTS

A. Doping Effect on Permittivity

Figure 2 shows the permittivity for different frequencies in the range 0-1KHz on the four samples of different doping types and rates. It was noticed that the dielectric constant varies, depending on the frequency and the percentage of doping and that the permittivity of the ferroelectric ceramic (Al_2O_3 , TiO_2) doped PVC rises in comparison with the standard sample. Ferroelectric ceramics, such as Al_2O_3 and TiO_2 , are known for their high permittivity [19-20]. In Figure 2 permittivity increases gradually, between 3.2-7.3 at 50Hz and between 2.8-6 at 1KHz) as a function of the type of additive content. Three zones were observed in each curve. In the first zone (0-300Hz), ϵ_r reaches a local maximum value of 7.2 for samples 3 and 4 and 6.2 for sample 2. Moreover, doped samples have a small peak at 47Hz. The second zone, in the range of 300-600Hz, is turbulent and has two peaks, and all curves gradually decrease to minimum values at 400Hz, while in the range of 400-500Hz ϵ_r rises rapidly, reaching a maximum value at 500Hz. Finally, in the third zone, at frequencies greater than 600Hz, ϵ_r slowly decreases and stabilizes.

B. Doping Effect on Loss Index

Figure 3 shows the progress of loss index (ϵ''), for doped and standard samples as a function of frequency. It is observed that there are also three zones in each curve. In the first zone,

between 0 and 300Hz, an important peak appears at around 50Hz for sample 4 and at 35Hz for the other samples. After that, all curves vary slowly until 300Hz. The second zone, (300-600Hz), is turbulent as after the minimum at 300Hz a new peak is appearing at 350, 370, 380 and 410 Hz for samples 4, 2, 1 and 3 respectively. Finally, at the third zone, after 600Hz, all curves have little variation.

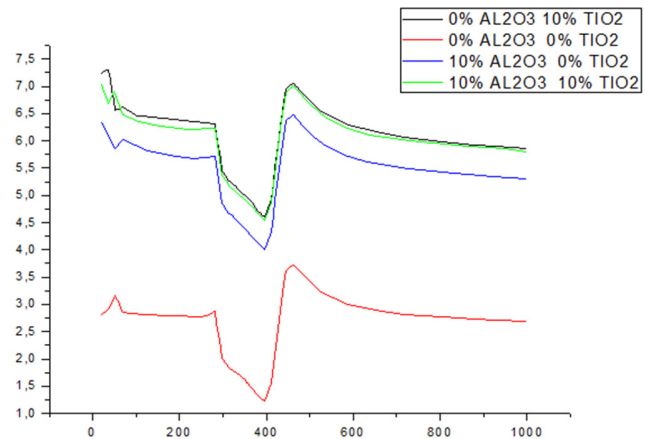


Fig. 2. Permittivity (ϵ_r) of standard and Al_2O_3/TiO_2 doped PVC samples

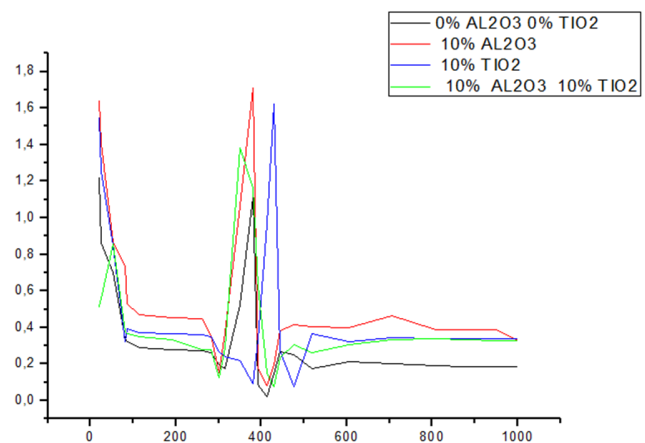


Fig. 3. Loss index of standard and Al_2O_3/TiO_2 doped PVC samples

C. Fourier Transform Infrared (FTIR) Spectroscopy

FTIR spectroscopy results are shown in Figure 4. At first, it is noted that the infrared spectrum of the four samples with and without doping have slight variation and broad resemblance on the following characteristic bands: A peak at the area of $1000cm^{-1}$ shows the existence of the C-C bond (sp^3). Two wide bands centered at about 1440 and $1370cm^{-1}$ respectively characterize the symmetrical and CH_3 asymmetric deformation vibrations. The intense band around $700cm^{-1}$ is assigned to the swings of $(CH_2)_n$, when $n \geq 4$ whereas that noted to $620cm^{-1}$ is due to the vibration of the C-Cl bond. Concerning the standard PVC sample, three bands are revealed, between 2970 and $2820cm^{-1}$, assigned to the symmetric and asymmetric elongation vibrations of the C-H bonds, CH_2 and CH_3 groups at the end of PVC chains. An adsorption of -OH groups appears

between 3300 and 3665cm^{-1} , corresponding to the elongation of the chemisorbed hydroxyl groups at the level of the surface adsorption sites, as well as to the contribution of the dissociated and molecularly adsorbed hydroxyl groups. In addition, the infrared spectrum of the PVC sample doped with 10% TiO_2 and 0% Al_2O_3 showed an intensive and wide band at 430 - 900cm^{-1} , corresponding to a strong Ti-O and Ti linkage elongation vibration. The presence of a band at 1630cm^{-1} is attributed to the adsorption on the surface of TiO_2 . The peaks that appeared at 785 and 586cm^{-1} , and their absence in the FTIR spectrum of pure PVC, represent the Al-O bond.

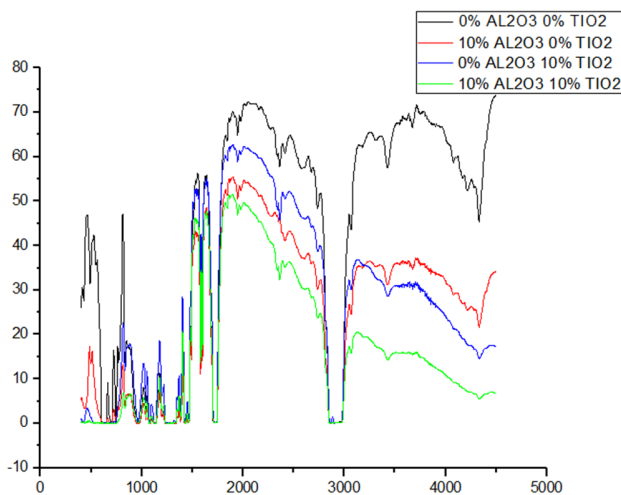


Fig. 4. FTIR results for standard and $\text{Al}_2\text{O}_3/\text{TiO}_2$ doped PVC samples

D. Volume Resistivity and Average Breakdown Voltage

Table II shows the measurements of volume resistivity and average breakdown with and without doping. Standard PVC had the maximum resistivity. The TiO_2 doped samples, had much smaller resistivity values than the other samples. On the other hand, the TiO_2 doped samples had the minimum average breakdown voltages, which was lower than the breakdown voltage in standard PVC samples.

TABLE II. VOLUME RESISTIVITY AND AVERAGE BREAKDOWN VOLTAGE

Sample number	1	2	3	4
Volume resistivity ($10^{14}\Omega\text{m}^2/\text{m}$)	8.7975	6.11672	1.5853	1.8370
Average breakdown voltage (KV)	21.008	24.2	15.2	17.575

IV. DISCUSSION

Usually, ϵ_r and $\text{tg}\delta$ depend on the physical, chemical and structural variations of insulators during service. Novel polymeric composites containing ceramic powders have been utilized in order to improve insulators' performance [8, 19-22]. After the doping process in the samples a broadening of the peak in the BF region occurs [23] (Figures 2 and 3). A peak appears in the curve of the dielectric constant and in parallel an inflection in the curve of the loss index under around 50Hz .

Moreover, a second peak, more resolved in the dielectric constant and an inflection in loss index curves, has been recorded around 500Hz as indicated in [24]. However, as the TiO_2 or Al_2O_3 content increases the dielectric constant increases. The peak of the most intense relaxation, occurring in the low-frequency region, seems to be depending on the content of ceramics and on the accumulation of charges at the interface between the sample and electrodes, such as those indicated in [22, 24], because of the interfacial polarization (IP) expected at this frequency. FTIR spectroscopy indicates the presence of ketones and esters [19, 22] in the 1713.6cm^{-1} and 1740cm^{-1} respectively. In this work, ϵ_r increased and $\text{tg}\delta$ decreased when the nano-filler content increased. The volume resistivity decreased with increasing ceramic content. Comparing the ceramic doped samples, increasing the nano-filler content increased ϵ_r and decreased $\text{tg}\delta$. This is explained as reducing of space charge, due to the capturing behavior of the ceramics, in the PVC matrix [25]. The main carriers present were attributed to free ions from the ingredients used in the polymerization reaction of PVC, such as the stabilizer, as well as the ingredients in the plasticizer itself. As the samples of this work were elaborated in the same conditions as in [5], one plausible explanation for the increase of ϵ_r with nano-filler content can be the conductivity of BaTiO_3 nano-particles incorporated in the inter-granular interfaces of PVC. The electric conductivity decreased as ceramic content increased. This can be explained as reducing of space charge, due to the capturing behavior of the ceramics, in the PVC matrix [26].

The recorded breakdown strength value of sample 2 is higher than standard PVC's, but samples 3 and 4 fall short. The variation of the breakdown strength values depends on the ceramic content, as they tend to decrease by increasing ceramic content up to some practical limit [27-28]. It was well shown that, void defects and electromechanical stress produced cracks, which play an important role in the injected electrons from the electrodes gaining sufficient energy which increases the probability of macromolecule ionization and further initiation of electron avalanche. This process accelerates the rising of conducting channels and the final breakdown [29-31]. Furthermore, the increasing interface domains, due to the dispersion of NPs, increase the number of the trapped charge carriers, which plays a role in reducing carrier mobility and delays the final breakdown [29]. Al_2O_3 makes possible to stabilize the volume values and to improve the resistance values in the PVC matrix, on the basis of the insertion of the alumina [12, 27-28, 32]. On the other hand, TiO_2 has an inverse effect on the PVC matrix.

V. CONCLUSION

This study investigated the effects of $\text{Al}_2\text{O}_3/\text{TiO}_2$ doping in PVC's dielectric properties. Moreover, electrical breakdown tests were carried out on standard and doped PVC samples, in order to examine the influence of TiO_2 and Al_2O_3 on the behavior of these insulators. The results showed that PVC reveals a degree of dielectric relaxation and higher losses in the frequency range of 20Hz - 1KHz . FTIR spectroscopy showed changes in the plasticizer or pigment of PVC. Moreover, a change in the transmittance peak with the change in doping Al_2O_3 - TiO_2 in the polymer nanocomposites was revealed. This

explains the increased compatibility, in chemical composition, between polymer and nanoparticles. These results indicate that the presence of $\text{Al}_2\text{O}_3/\text{TiO}_2$ nano-particles does not exert any influence on the structure of the PVC, and show that ceramics as fillers improved its dielectric properties. Nano- $\text{Al}_2\text{O}_3/\text{TiO}_2$ particles reflect UV light, which can destroy the PVC chain, restraining dehydrochlorination and the simultaneous oxidation reactions. Additionally, the segmental motion of polymer chains and a hopping mechanism is revealed, which contributes equally in coupled form for ion transportation in the PVC/ Al_2O_3 - TiO_2 nanocomposites. This study shows that a well dispersed ceramic in the nanocomposites results in lower volume resistivity which increases breakdown voltage.

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