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UV Effect on the Dielectric Properties of Al_2O_3/TiO_2 Doped PVC

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Abstract. *Poly-vinylchlorid* (PVC) is a material strongly used as cable insulation sheaths. Its dielectric properties are susceptible to be deteriorated under the *Ultraviolet* (UV) radiation effect. In this paper, films of PVC have been doping with alumina and titanium dioxide. The influence of Al_2O_3 and TiO_2, on the dielectric properties of PVC before and after being exposed to 300 h of UV irradiation were studied. FTIR spectroscopy and scanning electron microscopy were used as characterization techniques. Dielectric characteristics were measured using an impedance analyzer. Volume resistivity and average breakdown voltage have been analyzed. Experimental results showed well that Al_2O_3/TiO_2 as nano-fillers improved the dielectric properties of PVC and reduced ageing due to UV irradiation. Volume resistivity decreased and breakdown voltage increased with ceramic content.

Key-words: Al_2O_3/TiO_2 doped PVC; breakdown voltage; UV ageing; volume resistivity.

1. Introduction

In recent years, nanotechnology is more and more used in the synthesis of various types of polymer-nanocomposite [1–4]. The presence of nanoparticles in polymer improves the mechanical, electrical and chemical properties of the materials. For that, the polymers doped with metal oxide nanoparticles have been studied as alternative materials for electrical applications. They have been included as an electrically insulating material in distribution, especially in underground, and transmission cables [5]. Many polymers have proven to be suitable matrices in the development of composite structures due to their ease of production and processing, good adhesion with reinforcing elements, resistance to a corrosive environment, and ductile electrical performances. *PolyVinyl Chloride* (PVC) is a polymer with extensive and well-established use as electrically insulating materials, in both industrial and communication applications. Due to its excellent dielectric strength, low dielectric permittivity, low loss factor and thermo-mechanical behavior, it has been used for several decades, as an electrically insulating material in distribution, especially in underground, and transmission cables [6].

Mastering the ageing of electrical insulation is a key factor to control the reliability of distribution equipment. The ageing due to *Ultraviolet* (UV) radiation is an important parameter that it must be, mastered in the insulating systems. Several researchers have tried to understand this phenomenon implicated in the degradation of the insulating properties of the polymer. Ageing of PVC pure under the UV radiation effect has been studied by John A. *et al.* [7]. It has been found that material oxidation was characterized by a significant increase in the molecular mobility of the amorphous region. The increase in molecular mobility indicates that *Cross-Linked Polyethylene* (XLPE) undergoes chain scission during thermal oxidation.

In P. C. N. Scarpal *et al.*'s works, the ageing study has been made on pure polymers and on that one, doped with carbon black. *Low-density polyethylene* (LDPE) specimens, aged under UV radiation, indicate the presence of relaxation peaks. As the ageing progresses, *Quasi-DC* (QDC) loss processes may be observed in the low-frequency range, for the two different LDPE specimens, without and with carbon black, respectively [8].

Few studies of UV-radiation ageing have been found in the literature. As the works of John A. *et al.* [7], were a comparison of the dielectric response in a frequency range 20Hz – 1GHz of polymeric insulating materials, such as PVC, *polytetrafluoroethylene* (PTFE) and *high-density polyethylene* (HDPE). This comparison was carried out by applying a combined action of UV-radiation and condensation (humidity and heat) in an accelerated weathering tester apparatus [7–9]. Furthermore, the silicone rubber was ageing by gamma-ray radiation. The experimental results obtained in this analysis were consistent with the mechanism that silicone rubber is degraded by forming cross-linked structures via the formation of abundant siloxane bonds [10]. Otherwise, studies on the plasma and UV photochemical processes in low-pressure reactors showed that UV radiation induces polymer cross-linking [11]. However, it is generally recognized that inorganic fillers, such as titanium dioxide (TiO_2), Zinc oxide (ZnO), and alumina (Al_2O_3) particles, can be used as ultraviolet light screening agents in PVC matrix [12–14]. The inorganic fillers can absorb or reflect ultraviolet light and form a barrier between polymer and light sources. This barrier protects, therefore polymer matrix from the sun. Some research showed that inorganic fillers particles could reflect ultraviolet light. It should play a protective role in the photo-degradation of polymers [15].

Other works have been focusing on the Epoxy/Magnesium oxide nanocomposites (Epoxy/nan-MgO) aged under UV effect irradiation. The study concerns the space charges. Specimens with 3wt%$\sim$5 wt% of nano-MgO accumulate less space charge than that only containing 1 wt%. Measurements of dielectric loss factor and volume resistivity have shown that this doping rate contributes to improving the UV ageing resistance in epoxy-based materials [16]. Otherwise, titanium dioxide nanoparticles and their roles in the accelerated ageing of foamed wheat straw fiber/polypropylene composites have been investigated by Lihui Xuan *et al.* [17]. The flexural and tensile properties were improved. A higher *ultraviolet* (UV) stability, of the samples, doped with TiO_2 nanoparticles, was exhibited by using the study of the color change and loss in mechanical properties [17]. Furthermore, the UV shielding of the polymer by Al_2O_3/TiO_2 has been studied in [18]. The samples containing TiO_2. 7 wt.% present a high value of dielectric constant (10.2) and 93% as the value of UV shielding value [18]. These values were larger than those of neat and other of F-Al_2O_3 and F-TiO_2 reinforced composites. Furthermore, the anti-ageing properties, of polymer resins, are also influenced by the dispersion of inorganic fillers in the matrix. The inorganic fillers could effectively absorb or reflect ultraviolet light when they are uniformly dispersed in the matrix. The agglomerated inorganic fillers result in many defects in the polymer matrix [19, 20].

This paper aims to investigate the accelerated UV ageing of the composite Al_2O_3/TiO_2 doped PVC. Doping rates Al_2O_3/TiO_2 have been dispersing and distributed in the PVC matrix in order to slow down ageing due to UV irradiation. For that, the dielectric properties of composites have been studied.

This paper is organized as follows: the experimental procedure is presented in the next Section, the experimental results are given in Section 3, the discussion of the results is conducted in Section 4, and the conclusions are pointed out in Section 5.

2. Experimental Procedure

The composition of the studied samples is given in Table 1. The basic element was the PVC resin used in Algerian industry (H3000 type), mixed with an antioxidant (Barium-Zin), assuring the thermal stability, and with dicumyl peroxide cross as linking agent lubricant and Plasticizer DOP (Di-Octyle Phatalate) from (Zhengzhou P&B Chemical Co., Ltd) (99.5%).

Table 1. Content of PVC/TiO_2/Al_2O_3 composite

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

Two types of samples (standard PVC and Al_2O_3 /TiO_2-doped PVC) have been elaborated in conformity with International Standard [21]. The preparation method is based on two steps:

The first step aims to synthesize the composition of the matrix that is PVC. The latter must be intended for the electrical insulation of the cables. This step is performed by adding additives (antioxidant, lubricant, and plasticizer) to the basic PVC.

The second step consists in preparing our PVC/TiO_2/Al_2O_3 composite. The PVC is dissolved in a solvent and the dopants are added by weight portion to the solution. After a period of mixing, the mixed substrates are subjected to air evaporation.

The formulation has been mixed in a two-roll mixer for 5 minutes at a temperature of 160°C.

The sample was prepared as sheets of predetermined thickness. The sheet is then cut into squares of 10 cm × 10 cm and 0.6 mm as thickness. A certain amount of the composite samples was subject to UV radiation effect for 300 h (Fig. 1). This ageing is carried out using a cubic chamber (80×60×40cm), designed and built, especially for this study. The chamber is fabricated with wood. Inside the cell, the sample irradiation is accomplished using two low-pressure vapour 36-watt fluorescent lamps. The wavelength of the light covers 200nm∼400nm. The specimens were placed 25cm away from the UV source. Only one side of the samples is subjected to radiation. The ageing process was carried out at 30°C, in the ambient environment without controlling the humidity.

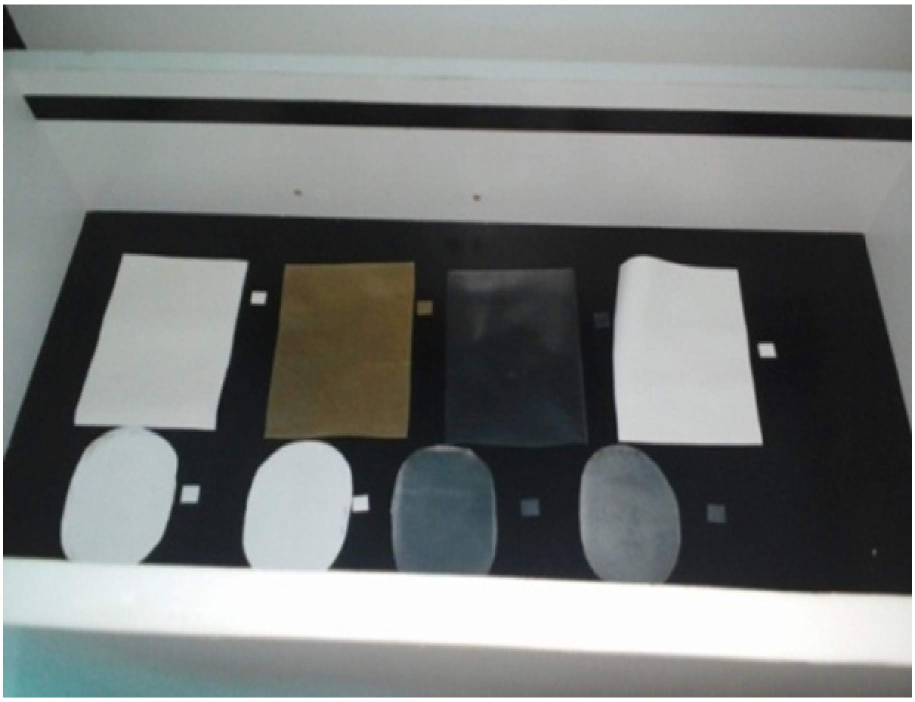


Fig. 1. Samples in UV aging apparatus.

The distribution of additives in the PVC was observed using scanning electron microscopy, of JEOL JSM model 7001F type.

The apparatus used for the dielectric response was an impedance analyzer RLC (WAYNE KERR 6420 type) working in the range frequency up to 10MHz. The samples are then inserted between two plane electrodes made of copper. The capacitor representing the sample is afterwards submitted to an alternating electric field of 1V/m. tgδ, ε_r, and loss index have been measured. The measurement error was ± 0.05%.

For the tracing of changes in the chemical structure of the aged polymers, spectroscopic measurements were performed by a JASC FT/IR 4200 spectrometer.

The volume resistivity, of the PVC nanocomposites, has been measured by the bridge method at room temperature (Fig. 2). Afterwards, some breakdown tests were performed in conformity with International Standard Norm [22] (Fig. 3).

Fig. 2. Measuring circuit of the volume resistivity.

Fig. 3. Circuit of breakdown voltage tests.

Weibull data analysis was used to determine the average breakdown voltage in the 25 samples used in each case for a given combination of dopants. Weibull data analysis is governed by

$$P(U) = 1 - exp\left[-\left(\frac{U}{Ucn}\right)^{\beta}\right], U \succ 0, \tag{1}$$

where: $P(U)$ is the probability of rupture, U is applied electrical voltage, Ucn is the scale parameter and β is the shape parameter.

3. Experimental Results

3.1. Doping effect on permittivity

Fig. 4 represents the evolution of the permittivity as a function of the frequency (0Hz-1KHz) of the samples before and after ageing respectively and for different composites. The dielectric constant varies according to the frequency and the percentage of doping.

Fig. 4.a illustrates that the permittivity of (Al_2O_3, TiO_2) doped PVC increases comparatively with the standard sample. Oxides such as Al_2O_3 and TiO_2 are known for their high permittivity [23]. The permittivity of sample 2 is larger than that of sample 1. ε_r for the sample 3 is larger than that of sample 2, and that of sample 4 is equal to that of sample 3. The results are similar to the results reported in the analysis carried out in [24].

This is clearly seen in Fig. 4, where the permittivity increases gradually (between 3.2 and 7.3 around 50 Hz, and between 2.8 and 6 at 1 kHz) as a function of the type and of additive content. Three zones (I, II and III) were considered in each curve, described as follows:

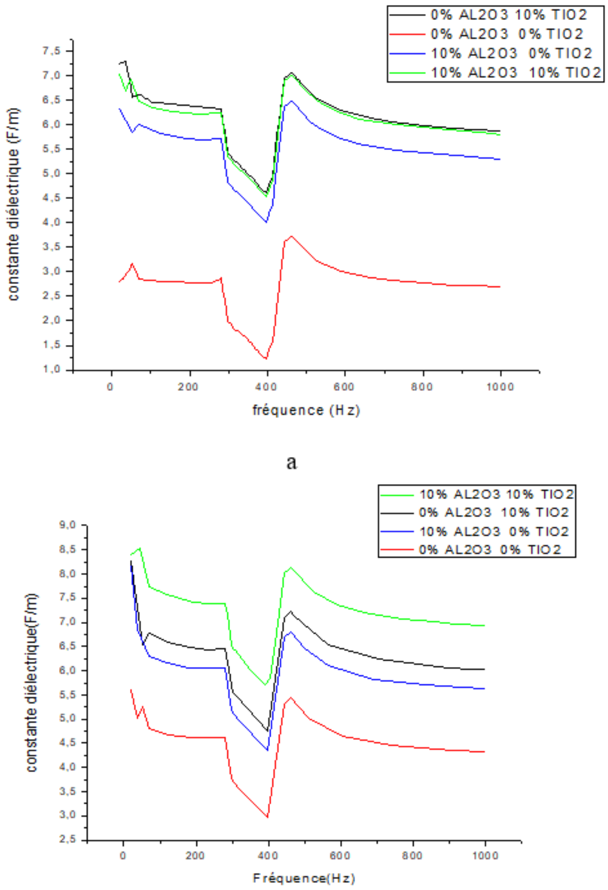
Zone I: Between 0 to 300Hz, it has been found that ε_r reaches a maximum value of 7.2 for samples 3 and 4 and a value of 6.2 for sample number 2. A small peak appeared at a frequency of 47 Hz for the doped samples.

Zone II: Between 300 to 600 Hz, there is relaxation where a minimum at 400 Hz and a maximum at 500 Hz are located respectively. It has been found that all the curves gradually decrease to reach minimum values respectively 1.2, 4 and 4.5 at a frequency of 400Hz. In the range of 400 to 500 Hz, ε_r rises brutally to a maximum value at 500 Hz equals respectively to 3.6, 6.2 and 7.2 for samples 1, 2, 3 and 5.

Finally, beyond 600 Hz, ε_r slowly decreases to reach maximum values of 6.2 for samples 3 and 4 and the values of 5.9 and 2.8 for samples 2 and sample number 1, respectively.

It is to note that for the samples subject to UV ageing Al_2O_3 and TiO_2 as doping (Fig. 4.b) contribute to the ε_r increasing. The time horizon of 250 h of UV ageing seems to have different degree effects on the permittivity of the composite whereas the values of the dielectric constant increase in comparison with that of the pure sample. On the other hand, the gap of ε_r values between that of the doped and virgin samples is reduced. This gap is between 3 and 4 before ageing and 1.5 and 3 after ageing under the UV rays effect. Ageing under the UV radiation effect of the virgin sample was characterized by an increase of 20% of ε_r value (see Fig. 4.b). An increase of about 12% has been recorded for the sample containing 10% TiO_2 and 10% for the sample containing Al_2O_3 10% wt. However, an increase of 22% was obtained for samples number 2, 3 and 4 as compared to the results shown in Fig. 4.a and obtained with the same samples before ageing.

It is pointed out that the greatest value of the dielectric constant is obtained with sample 4, in the two cases before and after UV ageing.



a

b

Fig. 4. ε_r of Al_2O_3/TiO_2 doped PVC and of the standard sample. a) Before UV ageing. b) After UV ageing.

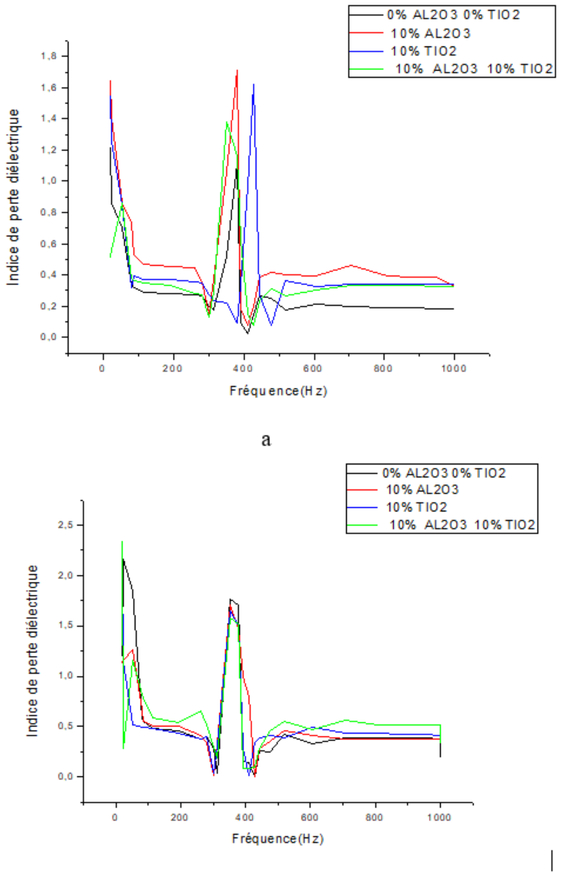
3.2. Doping effect on loss index

Fig. 5 illustrates the evolution of loss index ε_r before and after ageing respectively, as a function of the frequency in the range (0 Hz – 1 kHz). In addition, we can see the obtained results on the standard samples before and after doping. Three parts were considered in each curve (see Fig. 5.a):

i) Between 0 to 300Hz, a broad peak is recorded around 50 Hz for sample 4 and a peak. This one is less broad, at 35Hz for the other samples. After that, the loss index stabilizes between 0.3 and 0.5 until 300 Hz, where it appears a minimum of around 0.15. The smaller index is, recorded for sample 1 and the greater loss index is that one of sample 2.

ii) In the range of 300 to 600 Hz, we can see a broad peak where the loss index varies (according to the type of sample) between 1.1 (sample 1) and 1.7 (sample 2). The peaks of samples 1 and 2 are located at frequencies 380 Hz and 370 Hz respectively. The loss indexes of the samples 3 and 4, are equal to 1.6 and 1.4 respectively. The peaks of these latter are located at frequencies 410 Hz and 350 Hz respectively. Beyond the frequency 410 Hz and until 1 kHz, all the losses stabilize between 0.2 and 0.4.

Under the effect of UV, ageing seems to have different effect degrees on the loss index of the composite. UV ageing of the virgin sample was characterized by an increase of 62% on $\varepsilon_{r''}$, and 216% for sample 3. A reduction of 9% has been, obtained for sample number 4 as compared to the results obtained with the same samples before UV ageing. However, 119% as the increase is the higher loss index measured in sample 2. It is generally observed that the curves of the loss index keep the same shape as well as before than after ageing. In all cases, the peaks appear at frequencies ∼ 50 Hz and 380 Hz respectively.



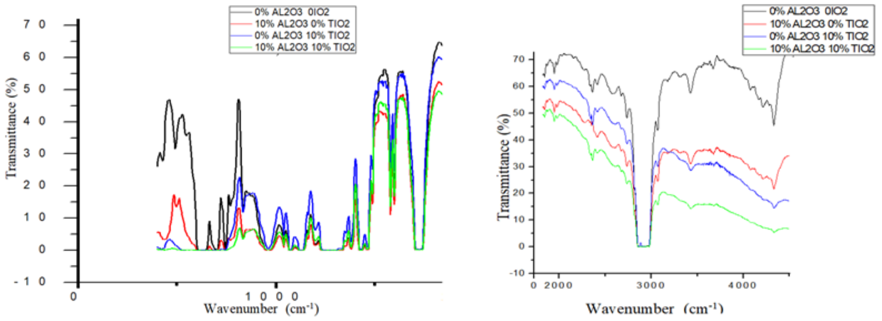
a

b

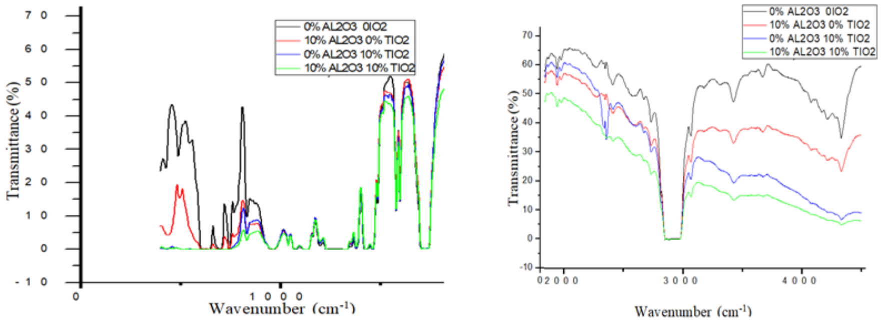
Fig. 5. Loss Index of Al_2O_3/TiO_2 doped PVC and of the standard sample. a) Before UV ageing. b) After UV ageing.

3.3. Fourier Transform Infrared (FT-IR) spectroscopy

The analysis results were obtained from the study of the different samples using JASC FT/IR 4200 spectroscopy which is a single-beam instrument. The infrared spectra of the four samples (before and after ageing) are recorded and next given in Fig. 6.



a (0-2000 cm-1) a (2000-5000 cm-1)



b (0-2000 cm-1) b (2000-5000 cm-1)

Fig. 6. FTIR spectroscopy of pure and Al_2O_3/TiO_2 doped PVC samples. a) Before UV ageing. b) After UV ageing.

A peak characteristic of the C-C bond (sp3) is located at 1000 cm^{-1}. Two wide bands centered at about 1440 and 1370 cm^{-1} respectively characterize the symmetrical and asymmetric deformation vibrations of the PVC CH_3's. The intense band around 700 cm^{-1} is assigned to the swings of $(CH_2)_n$ when $n \geq 4$ whereas that located at 620 cm^{-1} is due to the vibration of the bond C-Cl.

Concerning the virgin PVC, this one reveals between 2970 and 2820 cm^{-1}, three bands assigned to symmetrical and asymmetric elongation vibrations of the C-H bonds CH_2 and CH_3 groups at the end of PVC chains. Adsorption of the -OH groups appear between 3300 and 3665 cm^{-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.

Otherwise, the infrared spectrum of sample 3 showed an intensive and wide band between 430 and 900 cm^{-1} corresponding to a strong Ti-O and Ti linkage elongation vibration Ti-O. The presence of a band at 1630 cm^{-1} has been, attributed to the TiO_2 adsorption on the surface. The peaks appearing at 785 and 586 cm^{-1} represent the Al-O bond.

Aged PVC includes the absence of peaks at 1587 cm^{-1}, 2856 cm^{-1} and 2923 cm^{-1}, which do not match known PVC peaks and sites before [10]. This suggests that ageing has an effect on the plasticizers used (usually phthalates or phosphates) or pigments, rather than on the PVC itself. The FTIR spectra of the PVC/Al_2O_3-TiO_2 composites are, characterized all by peaks located at 1630 cm^{-1} and 1735 cm^{-1}. These indicate that the main degradation processes of photo-degradation of PVC are dehydro-chlorination and simultaneous oxidation reactions.

3.4. Volume resistivity measuring and average breakdown voltage

The measurement results are given in the Table 2 and Table 3.

Table 2. Volume resistivity measuring

Samples N°	1	2	3	4
The standard sample Volume resistivity [10^{14} $\Omega m^2/m$]	8.7975	1.5853	6.11672	1.8370
After UV ageing Volume resistivity [$10^{14}\Omega m^2/m$]	7.9333	8.1088	1.6860	2.178

Table 3. Average breakdown voltage

Samples N°	1	2	3	4
The standard sample [KV]	21,008	24.2	15,2	17.575
After UV ageing [KV]	20.7	27.1	22.4	19.6

Table 2 shows the measurements of the volume resistivity before and after UV ageing respectively for the different samples. It is to note that the maximum value of the resistivity is found in the case of virgin PVC and that the minimum value has been measured in the case of sample 2. In the case of ageing samples, it is noted that sample 2 presents the greater volume resistivity. On the other hand, the smaller resistivity has been measured with sample 3. It can be observed that the volume resistivity decreases for all the samples after UV ageing, except for sample 3, where the resistivity considerable increases.

Table 3 shows the measurements of the average breakdown voltages before and after ageing for the sets of samples. Before UV ageing it should be noted that the maximum value of the average breakdown voltage has been obtained in the case of sample 2. However, the minimum breakdown voltage value has been measured in sample 3. It is lower than the breakdown voltage of the pure PVC samples. In the case of UV ageing, the breakdown voltage of the pure PVC samples decreases. On the other hand, the doped PVC samples show an improvement in the values of this tension. Sample 2 gives the maximum value of the average breakdown voltage. Similarly, there is a slight improvement in the value of the average breakdown voltage in sample 3.

Fig. 7 shows the images obtained by scanning electronic microscopy of the samples before and after being doped, and unaged and aged about 300 h under UV radiation, respectively. Those SEM images generally show that there is a uniform dispersion of nano-particles in the PVC matrix with a small amount of agglomerates especially when PVC is doped with Al_2O_3 and TiO_2 as shown in Fig. 7.d and Fig. 7.h. One can see that the damage occurs after ageing during 300 h under UV radiation. In addition, the surface roughness of the samples has been reduced. Otherwise, micro-cracks are well visible, especially in the SEM images of Fig. 7.f and Fig. 7.h, whereas these ones are less visible in the SEM images of Fig. 7.g. It is resulting from the degradation and evolution of volatile products in the sample surface. In addition, it seems such as carried out in the literature that Al_2O_3 apparently absorbs the incident UV radiation and reduces thus the degradation process. This process can be due to continuous dehydro-chlorination and oxidation reactions in the ageing degradation.

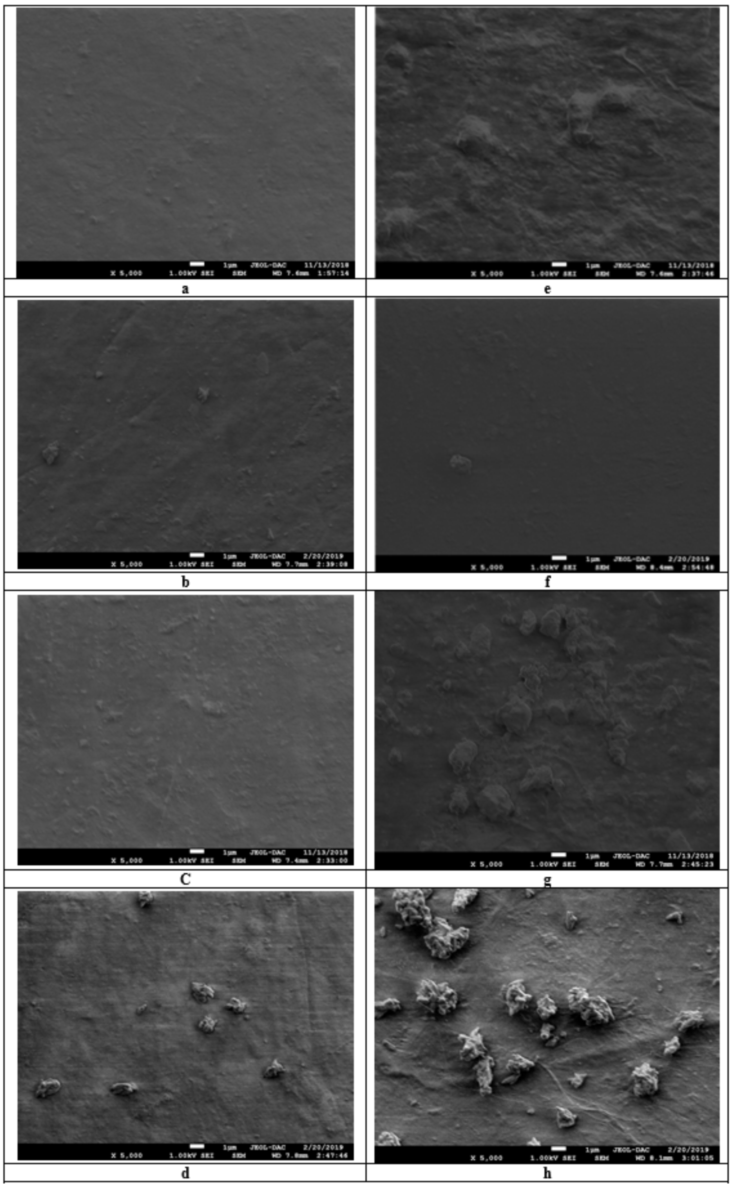


Fig. 7. SEM images of composites before UV ageing: a) PVC b) TiO_2/PVC c) Al_2O_3/PVC d) TiO_2-Al_2O_3/PVC. After UV ageing: e) PVC f) TiO_2/PVC g) Al_2O_3/PVC h) TiO_2-Al_2O_3/PVC.

4. Discussion

The influences of Al_2O_3/TiO_2 as nano-filler and UV radiation as ageing on PVC dielectric properties have been analyzed. Generally, the literature agrees that ε_r and tgδ depend on the physical, chemical, and structural changes of insulators during service. To improve the performances of insulators the novel polymeric composites containing ceramic powder have been elaborated [6], [23–24]. In the electrical engineering area, it is necessary to understand the dielectric behavior of the aged cables or insulator surfaces [26–30].

Ageing of the composite is characterized by a broadening of the peak in the low-frequency region indicated in Fig. 4 and Fig. 5. The same result has been obtained in the $BaTiO_3$ doped PVC [28]. A peak appears in the curve of the dielectric constant around the value of 50 Hz. Otherwise, a second peak, more resolved in the dielectric constant and an inflection in loss index curves, has been recorded around the frequency of 500 Hz. These relaxation frequency values were realized and analyzed in our work [1, 28] and in reference [29], where we find the same relaxation in this work. The first and second relaxation phenomena were at low frequencies around 50 Hz, and 500 Hz as shown in Fig. 4 and Fig. 5. Moreover, the more the content of TiO_2 or Al_2O_3 increases, the more the dielectric constant increases, in the same way, it also varies with the variation of frequency either for the samples with or without an ageing. This variation is consistent with the following equation [1]:

$$\frac{\varepsilon_1 - \varepsilon_c}{\varepsilon_1 - \varepsilon_b}\left(\frac{\varepsilon_b}{\varepsilon_c}\frac{1}{\mu}\right) = 1 - P_{Par}. \tag{2}$$

For example, and according to Table 4, before UV ageing, at f=100 Hz, it is obtained a value of $\varepsilon \mathrm{r}_{\mathrm{Al_2O_3}}$ increase by 230% and $\varepsilon \mathrm{r}_{\mathrm{TIO_2}}$ increase by 250% and at f=400 Hz, a value of $\varepsilon \mathrm{r}_{\mathrm{Al_2O_3}}$ increase by 230% and $\varepsilon \mathrm{r}_{\mathrm{TIO_2}}$ increase by 250% respectively. After UV aging, at f=100 Hz, we have a value of $\varepsilon \mathrm{r}_{\mathrm{Al_2O_3}}$ increases by 131% and $\varepsilon \mathrm{r}_{\mathrm{TIO_2}}$ increases by 141% and at f=400 Hz, a value of $\varepsilon \mathrm{r}_{\mathrm{Al_2O_3}}$ increases by 140% and $\varepsilon \mathrm{r}_{\mathrm{TIO_2}}$ increases by 150% respectively.

Table 4. Dielectric constant

Samples N°		f=100 Hz	f=400 Hz
Before UV ageing	**1**	2.6	1.4
	2	5.8	4.2
	3	6.5	4.7
After UV ageing	**1**	4.6	3.2
	2	6.05	4.5
	3	6.5	4.8

The rate of impact of UV ageing for ε_r values varies between sample differences. We see that for PVC there is an increase in this value of 176% and 228% at f=100 and 400 respectively, on the other hand, for the samples doped in Al_2O_3 the values are 104% and 107% and 400. And for samples doped with TiO_2 there are 100% and 102% where they are more stable.

The peak of the most intense relaxation, occurring in the low-frequency region, seems to be dependent on the content of oxides and on the accumulation of charges at the interface between the sample and electrodes such as those indicated in the references [29–31], because of the *interfacial polarization* (IP) expected at this frequency. Otherwise, there is no change for the values (45 Hz and 500 Hz) of the relaxation frequencies after doping, but the broad peak in the middle frequency region may be due to an enhancement of oxidation products and bond breakage generated by UV radiation and subsequent diffusion of ions such as found in [15].

FTIR spectra in Fig. 6 indicate the presence of ketones and esters located at 1713.6 cm^{-1} and at 1740 cm^{-1}, respectively. The same results have been reported in the literature [18, 23, 30].

On the other hand, we notice that for samples 2 and 3, after ageing time, there is a presence of a narrow peak in the frequency (300Hz-600Hz) range. It is suggested that the presence of ceramic tends to inhibit the oxidation process and bond breakage that can occur by UV radiation. It was verified in the FTIR spectra (Fig. 6.b) that the absorption peak decreased in the 1739.6 cm^{-1} region [33–34].

As well, ageing has few affected the composites. The difference between PVC before and after ageing includes the absence of peaks at 1587cm^{-1}, 2856 cm^{-1} and 2923 cm^{-1} [32] and, the hydroxyl band evolution at 3450 cm^{-1} since the aromatic band at 1610 cm^{-1} is being used as a reference because unaffected by the degradation [7]. This suggests that ageing has an effect on the employed plasticizers (usually phthalates or phosphates) or pigment, rather than on the PVC itself.

In the case of our work, ε_r increases and tgδ decreases when the nano-filler content increases as illustrated in Fig. 4. The volume resistivity is decreasing with increasing ceramic content. This one was explained as reducing space charge (due to the capturing behavior of the ceramics) in the PVC matrix which agrees with the references [16, 35]. The main current carriers were, attributed to free ions from ingredients used in the polymerization reaction of PVC, such as the stabilizer, as well as ingredients in the plastifier itself.

As the samples of this work were elaborated in the same conditions that one reported in [11], one plausible explanation for the increasing of ε_r with nano-filler content (Fig. 4.a) can be the conductivity of the oxide nano-particles incorporated in the inter-granular interfaces of PVC. The UV, therefore, the ionic conduction mechanism of polymers was one of the most studied fields [11, 36]. The electrical conductivity of polymer increases with increasing UV ageing [37]. The electric conductivity is decreasing with increasing ceramic content. The recorded breakdown strength values for nano-composites in sample 2 are higher than this recorded for the pristine PVC as can be clearly seen in Table 2 but the values obtained on samples 3 and 4 are smaller.

Thus, the breakdown strength values increase with the increase of ceramic content and with the type of ceramic. The result is in accordance with that of the references [40, 42]. Here, it's worth mentioning the void defects and electromechanical stress-induced cracks which may be formed during the manufacture of polymer films. This plays an important role to gain to the injected electrons from the electrodes sufficient energy which increases the probability of macromolecules ionization and further initiates the electron avalanche. This leads to accelerating the growth of conducting channels and the final breakdown such as carried out in the literature [38–39, 45]. Moreover, the increasing of interface domain due to the dispersion of nano-particles increases the number of the trapped charge carriers, which play a role in reducing the carrier mobility and delaying the final breakdown [38].

However, Al_2O_3 plays the role of stabilizer in the volume resistivity. This oxide improves the resistance values in the PVC matrix because of alumina particles insertion in the grains boundaries such as reported in [41-44]. On the other hand, TiO_2 has an inverse effect on the PVC matrix. However, UV ageing duration affects greatly the PVC insulation samples. This degradation is observed through the values of the volume resistivity, which experienced a decrease, except the samples 3 and 4. The result agrees with that reported in [11, 46]. Thus, the results obtained in this paper confirm the data presented in the literature [15, 27, 33], [36], where it is reported that TiO_2 plays the role of a screen and a retarder of ageing.

5. Conclusions

Effects of UV ageing, for 300 h, on Al_20_3/TiO_2 doped PVC, were investigated. The results obtained are summarized as follows.

Al_2O_3/TiO_2 improves the dielectric properties of PVC and can be used as ultraviolet light screening agents, therefore, as an anti-ageing agent of PVC matrix for example in Insulated Piercing Connectors or MT Twisted Cable. These oxides can restrain dehydrochlorination and simultaneous oxidation reactions. FTIR results indicated that the presence of Al_2O_3/TiO_2 particles does not exert any effect on the structure of the PVC, but leads to changes in the plasticizer or pigment of PVC.

However, as polar material, PVC exhibits a dielectric relaxation and higher losses in the frequency range 20Hz-1kHz.

Accelerated UV ageing of even a few tens of h leads to a change of color PVC samples; can break the PVC chains and causes dehydrochlorination and simultaneous oxidation reactions. Micro-fissures were observed. Longer-time ageing can lead to water absorption by PVC, which causes an intense dielectric relaxation and high losses, *i.e.*, degradation of the electrical insulating properties of the material. Lower is volume resistivity, and higher is the breakdown voltage.

The results of this article can be exploited in future practical studies such as the realization of new type of Insulated Piercing Connectors.

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