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$_2$O$_3$/TiO$_2$) on 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 measured. Doping Al$_2$O$_3$/TiO$_2$ into PVC improved its dielectric properties and volume resistivity, while adding more ceramic increased the breakdown strength. Furthermore, the addition of Al$_2$O$_3$/TiO$_2$ caused a significant enhancement in voltage breakdown strength.

Keywords—PVC; composite; alumina; titanium dioxide; Al$_2$O$_3$/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 20Hz–1GHz 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$_2$O$_3$ 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 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$_2$O$_3$/TiO$_2$ composite based PVC. Four PVC samples, a pure sample and three doped with Al$_2$O$_3$/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$_2$O$_3$/TiO$_2$-doped PVC were examined, in conformity with [17].

| TABLE I. CONTENT OF PVC + Al$_2$O$_3$/TiO$_2$ COMPOSITES |
|-------------------|----|----|----|
| Samples          | 1  | 2  | 3  |
| Polymer (PVC)    | 100%| 90%| 90%| 80%|
| Al$_2$O$_3$      | 0% | 0% | 0% | 0% |
| TiO$_2$          | 0% | 10%| 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 $\tan \delta$, relative permittivity $\varepsilon_r$ and loss index ($\varepsilon''$) were measured, with the measurement error being ±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].

III. EXPERIMENTAL RESULTS

A. Doping Effect on Permittivity

Figure 2 shows the permittivity for 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$_2$O$_3$, TiO$_2$) doped PVC rises in comparison with the standard sample. Ferroelectric ceramics, such as Al$_2$O$_3$ 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), $\varepsilon_r$ 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 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, in the third zone, after 600Hz, all curves have little variation.

![Fig. 2. Permittivity ($\varepsilon_r$) of standard and Al$_2$O$_3$/TiO$_2$ doped PVC samples](image)

B. Doping Effect on Loss Index

Figure 3 shows the progress of loss index ($\varepsilon''$), 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. 3. Loss index of standard and Al$_2$O$_3$/TiO$_2$ doped PVC samples](image)

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 (sp3). 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≥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 3665 cm\(^{-1}\), corresponding to the elongation of the chemisorb 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\(_2\)O\(_3\) showed an intensive and wide band at 430-900 cm\(^{-1}\), corresponding to a strong Ti-O and Ti linkage elongation vibration. The presence of a band at 1630 cm\(^{-1}\) is attributed to the adsorption on the surface of TiO\(_2\). The peaks that appeared at 785 and 586 cm\(^{-1}\), and their absence in the FTIR spectrum of pure PVC, represent the Al-O bond.

Moreover, a second peak, more resolved in the dielectric constant and an inflection in loss index curves, has been recorded around 500 Hz as indicated in [24]. However, as the TiO\(_2\) or Al\(_2\)O\(_3\) 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 1713.6 cm\(^{-1}\) and 1740 cm\(^{-1}\) respectively. In this work, \(\varepsilon_r\) increased and \(\delta\) 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 \(\varepsilon_r\) and decreased \(\delta\). 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 \(\varepsilon_r\) 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\(_2\)O\(_3\) 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 Al\(_2\)O\(_3\)/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\(_2\)O\(_3\) 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 20 Hz-1 KHz. FTIR spectroscopy showed changes in the plasticizer or pigment of PVC. Moreover, a change in the transmittance peak with the change in doping Al\(_2\)O\(_3\)/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 Al₂O₃/TiO₂ nano-particles does not exert any influence on the structure of the PVC, and show that ceramics as fillers improved its dielectric properties. Nano-Al₂O₃/TiO₂ 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/Al₂O₃-TiO₂ nanocomposites. This study shows that a well-dispersed ceramic in the nanocomposites results in lower volume resistivity which increases breakdown voltage.

REFERENCES

[1] M. Danikas, A. Bairaktari, R. Sarathi, A. B. B. A. Gani, “A review of two nanocomposite insulating materials models: lewis’ contribution in the development of the models, their differences, their similarities and future challenges”, Engineering, Technology & Applied Science Research, Vol. 4, No. 3, pp. 636-643, 2014

[2] N. Zaman, S. Ahmed, M. Sanuallah, A. U. Rehman, A. R. Shar, M. R. Luhur, “Fabrication and characterization of organoayl reinforced polyester based hybrid nanocomposite materials”, Engineering, Technology & Applied Science Research, Vol. 8, No. 3, pp. 3038-3040, 2018

[3] D. Y. Godovsky, “Device applications of polymer-nanocomposites”, in: Advances in Polymer Science, Vol. 153, Springer, 2000

[4] P. M. Ajayan, L. S. Schadler, P. V. Braun, Nanocomposite science and technology, John Wiley & Sons, 2006

[5] F. A. Kasim, M. A. Mahdi, J. J. Hassan, S. K. J. Al-Ani, S. J. Kasim, “Preparation and optical properties of cds/epoxy nanocomposites”, International Journal Nanoelectronics and Materials, Vol. 5, pp. 57-66, 2012

[6] S. Tachikawa, A. Noguchi, T. Tsuge, M. Hara, O. Odawara, H. Wada, “Optical properties of ZnO nanoparticles capped with polymers”, Materials, Vol. 4, No. 6, pp. 1132-1143, 2011

[7] P. Obreja, D. Cristea, M. Purica, R. Gavrila, F. Comanesucu, “Polymers doped with metal oxide nanoparticles with controlled refractive index”, Polimery, Vol. 52, No. 9, pp. 679-685, 2007

[8] E. D. Owen, Degradation and stabilization of PVC, Elsevier, 1984

[9] J. A. Mergos, M. D. Athanasopoulou, T. G. Argyropoulos, T. C. Dervos, P. Vassiliou, “The effect of accelerated UV-aging on the dielectric properties of PVC, PTFE and HDPE”, 10th IEEE International Conference on Solid Dielectrics, Potsdam, Germany, July 4-9, 2010

[10] C. Neusel, G. A. Schneider, “Size-dependence of the dielectric breakdown strength from nano- to millimeter scale”, Journal of the Mechanics and Physics of Solids, Vol. 63, pp. 201-213, 2014

[11] Y. Gui, S. Li, J. Xu, C. Li, “Study on TiO₂-doped ZnO thick film gas sensors enhanced by UV light at room temperature”, Microelectronics Journal, Vol. 39, No. 9, pp. 1120-1125, 2008

[12] X. Ning, Z. Xiang, Z. Peng, S. Zhang, S. Chen, “Effect of UV ageing on space charge characteristics of epoxy resin and its nanocomposites”, IEEE International Conference on Solid Dielectrics, Bologna, Italy, June 30-July 4, 2013

[13] L. Xuan, G. Han, D. Wang, W. Cheng, X. Gao, F. Chen, Q. Li, “Effect of surface-modified TiO₂ nanoparticles on the anti-ultraviolet aging performance of foamed wheat straw fiber/polypropylene composites”, Materials, Vol. 10, No. 5, pp. 2-13, 2017

[14] Z. Li, K. Okamoto, Y. Ohki, T. Tanaka, “Effects of nano-filler addition on partial discharge resistence and dielectric breakdown strength of micro-Al₂O₃/Epoxy composite”, IEEE Transactions on Dielectrics and Electrical Insulation, Vol. 17, No. 3, pp. 653-661, 2010

[15] V. Dureault, B. Gossé, J. Gatellier, F. Boileau, “UV-induced ageing of epoxy resins: surface conductivity evolution related to chemical modification - application to ageing evaluation related of insulating materials”, IEEE Conference on Electrical Insulation and Dielectric Phenomena, Arlington, USA, October 23-26, 1994

[16] B. Ranby, “Basic reactions in the photodegradation of some important polymers”, Journal of Macromolecular Science, Part A: Pure and Applied Chemistry, Vol. 30, No. 9-10, pp. 583-594, 1993

[17] International Electrotechnical Commission, Common test methods for insulating and sheathing materials of electric cables, IEC 60811-3-2, IEC, 1993

[18] International Electrotechnical Commission, Characteristics of electric infra-red emitters for industrial heating, IEC 60240-1, IEC, 1992

[19] P. Barber, S. Balasubramaniam, Y. Anguchamy, S. Gong, A. Wibowo, H. Gao, H. J. Ploehn, H. C. Zur Loya, “Polymer composite and nanocomposite dielectric materials for pulse power energy storage”, Materials, Vol. 2, No. 4, pp. 1697-1733, 2009

[20] C. Zhang, J. F. Sheng, C. A. Ma, M. Sumita, “Electrical and damping behaviors of CPE/BaTiO₃/VCFC composites”, Materials Letters, Vol. 59, No. 28, pp. 3648-3651, 2005

[21] M. Pandey, G. M. Joshi, A. Mulderjee, P. Thomas, “Electric properties and thermal degradation of poly(vinyl chloride)/polyvinylidene fluoride/ZnO polymer nanocomposites”, Polymer International, Vol. 65, pp. 1098-1106, 2016

[22] C. S. Ramya, S. Selvasekarapandian, G. Hiranakum, T. Savitha, P. C. Anglo, “Investigation on dielectric relaxations of PVP-NH₂SCN polymer electrolyte”, Journal of Non-Crystalline Solids, Vol. 354, No. 14, pp. 1494–1502, 2008

[23] A. Berrag, S. Belkhiat, L. Madani, “Investigation of dielectric behavior of the PVC/BaTiO₃ composite in low-frequencies”, International Journal of Modern Physics B, Vol. 32, No. 9, 2018

[24] A. Patsidis, G. C. Psaras, “Dielectric behaviour and functionality of polymer matrix-ceramic BaTiO₃ composites”, Express Polymer Letters, Vol. 2, No. 10, pp. 718–726, 2008

[25] B. Mailhot, S. Morlat-Therias, P. O. Bussièr, L. Le Pluitt, J. Duchet, H. Sautereau, J. F. Gerard , J. L. Gardette, “Photoageing behaviour of epoxy nanocomposites: comparison between spherical and lamellar nanofillers”, Polymer Degradation and Stability, Vol. 93, No. 10, pp. 1786-1792, 2008

[26] K. Faghhi, M. Soleimani, S. Nezami, M. Shabanian, “Thermal and optical properties of new poly(amide-imide)-nanocomposite reinforced by layer silicate based on chiral n-trimellitliyimido-L-valine”, Macedonian Journal of Chemistry and Chemical Engineering, Vol. 31, No. 1, pp. 79–87, 2012

[27] S. A. Mansour, R. A. Elsad, M. A. Izzularab, “Dielectric properties enhancement of PVC nanodielectrics based on synthesized ZnO nanoparticles”, Journal of Polymer Research, Vol. 23, No. 5, 2016

[28] A. Mohany, V. K. Srivastava, “Dielectric breakdown performance of alumina/epoxy resin nanocomposite under high voltage application”, Materials and Design, Vol. 47, pp. 711-716, 2013

[29] F. Tian, Q. Lei, X. Wang, Y. Wang, “Investigation of electrical properties of LDPE/ZnO nanocomposite dielectrics”, IEEE Transactions on Dielectrics and Electrical Insulation, Vol. 19, No. 3, pp. 763-769, 2012

[30] K. Theodossiou, I. Vitellas, I. Gialas, D. P. Agorits, “Polymer films degradation and breakdown in high voltage AC fields”, Journal Of Electrical Engineering, Vol. 55, No. 9-10, pp. 225–231, 2004

[31] L. Shengtao,, Z. Tuo, H. Qifeng, L. Weiwei, N. Fengyan, L. Jianying, “Vacuum insulation: electric and dielectric behaviors of Al₂O₃-TiO₂ hybrid composites synthesized by in-situ polymerization”, Materials Letters, Vol. 61, No. 7, pp. 1507–1511, 2007