NRC Publications Archive
Archives des publications du CNRC

Dielectric measurements on polypropylene nanocomposites filled with natural and synthetic Nanoclay

Hadjadj, Y.; Ghunem, R. A.

This publication could be one of several versions: author's original, accepted manuscript or the publisher's version. / La version de cette publication peut être l'une des suivantes : la version prépublication de l'auteur, la version acceptée du manuscrit ou la version de l'éditeur.
For the publisher's version, please access the DOI link below./ Pour consulter la version de l'éditeur, utilisez le lien DOI ci-dessous.

Publisher's version / Version de l'éditeur:
https://doi.org/10.1109/CEIDP.2017.8257537
2017 IEEE Conference on Electrical Insulation and Dielectric Phenomenon (CEIDP), 2018-01-15

NRC Publications Record / Notice d'Archives des publications de CNRC:
https://nrc-publications.canada.ca/eng/view/object/?id=d1b21faa-b58b-4401-9ca9-1257f7d09418
https://publications-cnrc.canada.ca/fra/voir/objet/?id=d1b21faa-b58b-4401-9ca9-1257f7d09418

Access and use of this website and the material on it are subject to the Terms and Conditions set forth at
https://nrc-publications.canada.ca/eng/copyright
READ THESE TERMS AND CONDITIONS CAREFULLY BEFORE USING THIS WEBSITE.

L'accès à ce site Web et l'utilisation de son contenu sont assujettis aux conditions présentées dans le site
https://publications-cnrc.canada.ca/fra/droits
LISEZ CES CONDITIONS ATTENTIVEMENT AVANT D'UTILISER CE SITE WEB.

Questions? Contact the NRC Publications Archive team at
PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca. If you wish to email the authors directly, please see the first page of the publication for their contact information.

Vous avez des questions? Nous pouvons vous aider. Pour communiquer directement avec un auteur, consultez la première page de la revue dans laquelle son article a été publié afin de trouver ses coordonnées. Si vous n'arrivez pas à les repérer, communiquez avec nous à PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca.

Dielectric Measurements on Polypropylene Nanocomposites Filled with Natural and Synthetic Nanoclay

Y. Hadjadj and R. A. Ghunem
Measurement Sciences and Standards
National Research Council Canada
Ottawa, Ontario, Canada, K1A 0R6

Abstract- **The Effect of the type, size and level of organoclay nanoparticles on the dielectric properties of polypropylene nanocomposites is investigated at different temperatures. Two types of nanoclay, synthetic and natural, are added to polypropylene at different levels. The incorporation of nanoclay into polypropylene is shown to increase the dielectric losses. Unlike the unfilled polypropylene, both real and imaginary part of the permittivity increases at low frequencies with the clay level. Such a finding can be related to the effect of the interface between the nanoclays and the host PP matrix. The effect of compatibilizer added, i.e maleic anhydride, on the losses at very low frequencies is more recognizable at 80°C. This could be due the conductive nature of the maleic anhydride at higher temperatures. Lower losses were measured for the polypropylene filled with 2wt% synthetic nanoclay as compared to polypropylene filled with 2 wt% of natural nano clay. This finding can be attributed to the effect of the size (aspect ratio) of the platelets.**

I. INTRODUCTION

With a growing demand of electrical energy, the need for optimized designs of electrical insulating materials with improved dielectric, mechanical and thermal properties for many applications is important. Polymeric insulating materials such as polypropylene (PP) have been widely used in the high voltage equipment, such as in power capacitors. In recent studies, it has been reported that loading PP with small quantities of nanoclays can enhance the dielectric properties of the composite, such as space charge accumulation, electrical conductivity, dielectric strength and partial discharge resistance [1-4]. It has been reported that the interfacial region or the "interaction zone" between the nanoparticles and the host polymer matrix plays a major role in controlling carrier transport [5]. However, a great care needs to be taken during melt mixing in order to avoid agglomeration of the nano particles into large clusters [6]. The non-uniform distribution of these structures may transform into defects.

Although lower losses were measured for the unfilled as compared to the filled samples, it was found that adding nanoclay to PP increased the dc breakdown strength due to charge trapping at the interface between the nanoparticles and host polymer matrix [2]. The highest breakdown strength was reported for the PP filled with 2 wt% synthetic nanoclay [4]. Higher conductivity was measured for the PP filled with 6wt% natural and PP filled with 8wt% synthetic nanoclays due to the overlapping of the diffused double layer charge clouds [7]. In addition, the PP filled with 2 wt% natural nanoclay was reported as an optimum candidate composite for power capacitor applications as it showed lowest measured quantity of space charge [1]. Overall, the power equipment operates normally at temperatures between 50 and 80°C or more. Therefore, it would be interesting to further investigate these findings at the operating temperature of the power capacitors.

In this paper, the dielectric response of PP filled with natural and synthetic nanoclays is investigated. Dielectric spectroscopy is conducted over a wide frequency range between 0.1 mHz and 1 kHz at different temperatures.

II. BACKGROUND ON DIELECTRIC SPECTROSCOPY

The dielectric frequency response has been widely used as a diagnostic tool for electrical insulating materials [8, 9], as measuring the complex permittivity and the dissipation factor (tanδ) can provide information about the quality of the insulation.

The measured complex permittivity consists of a real part

$$\varepsilon' = 1 + \chi'(\omega) \tag{1}$$

and an imaginary part

$$\varepsilon'' = \frac{\sigma}{\varepsilon_0 \omega} + \chi''(\omega), \tag{2}$$

where χ' and χ'' are the real and inaginary part of the complex susceptibility respectively, σ is the conductivity and ω is the angular frequency.

Jonscher [10] described two different types of dielectric responses, namely the dipolar and the charge carrier processes. The dipolar polarization leaves zeros residual polarization during discharging with an associated loss peak at low frequencies. On the other hand, charge carriers leave a finite residual polarization during discharging with continuous rise of $\chi'(\omega)$ and $\chi''(\omega)$. Such a behavior for charge carriers has been called "low frequency dispersion" (LFD) by Jonscher [11] or "quasi-DC" (QDC) by Dissado and Hill [12]. This low-frequency dispersion or the QDC process is related to the freedom of movement of charge carries (ions, hopping electrons) within tortuous paths through the material. These paths are likely formed by the overlapping of the interaction zones between the nanoparticles and the host PP matrix. In addition, at low frequencies interfacial polarization (Maxwell-Wagner polarization) can be present due to the accumulation of carriers at the interface between the interaction zones between the host polymer and the nanoparticle [13].

The measured dielectric response of solid insulating materials depends on the temperature. In particular, the loss peaks are broader below the glass transition temperature T_g and follow the Vogel-Fulcher law [10] denoted as

$$\omega_p \propto \frac{1}{T-T_0}, \tag{3}$$

where ω_p is the angular frequency of the loss peak and T_0 is the characteristic temperature. Above T_g, the loss peaks is narrower and the response as function of temperature follows Arrhenius process. Arrhenius process can be described as

$$\omega_p \propto \exp\left(-\frac{W}{kT}\right), \tag{4}$$

where W is the activation energy and k is Botzmann's constant. More details about the polarization and depolarization processes of solid insulating materials can be found in [10, 14].

III. EXPERIMENTAL

A. *Nanocomposite samples*

The preparation of the nanocomposite used in the study has gone through steps involving the preparation of the Master Batch (MB), dilution of MB and the preparation of films. A detailed description of these steps can be found in [15]. Two groups of polymer nanocomposite were prepared. The first group containing an isotactic PP filled with 0, 2, 4 and 8 wt% of Topy synthetic tetrasilicic meca, indetified in this paper as PP-S0%, PP-S2%, PP-S4% and PP-S8%. The seccond group is composed of PP with 0, 2 and 4 wt% of Cloisite 20A natural montmorillonite clay, identified in this paper as PP-N0%, PP-N2% and PP-N4%. The difference between the PP-S0% and PP-N0% is the concentration of the compatibilizer. The PP-S0% contains 17.4wt% while the PP0-N0% contains 12.8 wt%. It is important to be noted that the individual platelets aspect ratios were ≤ 6000 for Topy and ≤ 286 for Cloisite 20A.

B. *Dielectric measurements*

The measurements were performed using IDAX™ 300 insulation diagnostic analyzer, over a wide frequency range from 0.1mHz to 1kHz. The measuring equipment was directly connected to a capacitive test cell for solids from Tettex™. The test cell consists of three electrodes; high voltage electrode, low voltage electrode and guard electrode with a circular measurement area of 20 cm^2. The measurements were conducted at temperatures of 30°C, 50°C and 80°C by means of Tettex™ 2966 temperature controller connected to the test cell.

IV. RESULTS AND DISCUSSIONS

Figure 1 presents the real part of the permittivity of the PP filled with synthetic nanoclay. In the frequency range of 1-1000Hz, insignificant difference in the real part of the permittivity was measured for the PP-S0% and the PP-S2%. The real permittivity of PP-S4% and PP-S8% were increased as compared to the PP-S0% and the PP-S2%. The lower permittivity measured for the PP-S8% as compared to the PP-S4% in the frequency range of 1-1000Hz could be obtained as a result of the increased interaction between the nanoparticles and the host polymer matrix, restricting the mobility of the polymer chains [16]. This phenomenon is more pronounced with natural nanoclay, Fig. 2. At lower frequencies, below 1 Hz, the real permittivity shows an increase with decreasing frequency in PP filled with both synthetic and natural nanoclay, Figs. 1 and 2.

The imaginary parts of the permittivity show a linear increase between 0.1Hz and 10 Hz and almost a constant response at very low frequencies (≤ 0.1Hz), Figs. 3 and 4. According to [17] such a behavior could be attributed to the LFD or the QDC processes. However, as the temperature is below T_g, it could be also speculated that the dielectric response of the imaginary part of permittivity at this range might possess a broad peak that typically follows the temperature dependence model of Vogel-Fulcher. This behavior is most likely due to the interfacial polarization in the interaction zone between the nanoclay and the PP host matrix.

The increase in the imaginary part of permittivity in the PP-S0% composite at very low frequencies below 0.01 Hz can be most likely attributed to DC conductivity. The peak appeared in the imaginary part of permittivity of the PP-N0% composite at very low frequencies below 0.01 Hz can be attributed to Maxwell-Wagner polarization at the electrode.

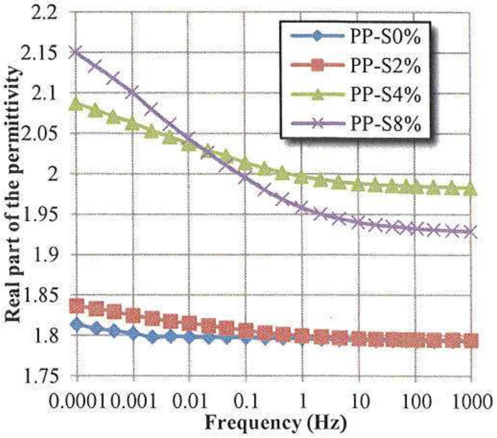

Fig. 1. Real part of permittivity of PP filled synthetic nanoclay versus frequency at 30°C.A semi-log scale is used for clarity

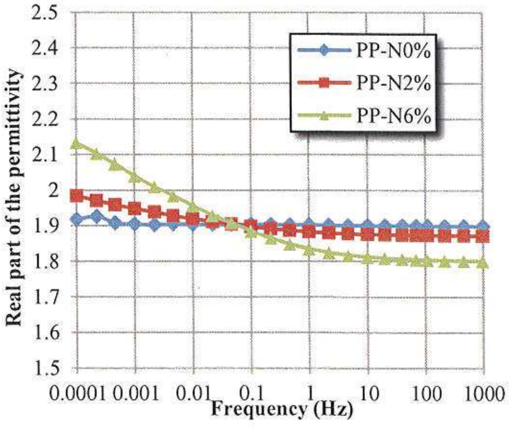

Fig. 2. Real part of permittivity of PP filled natural nanoclay versus frequency at 30°C. A semi-log scale is used for clarity

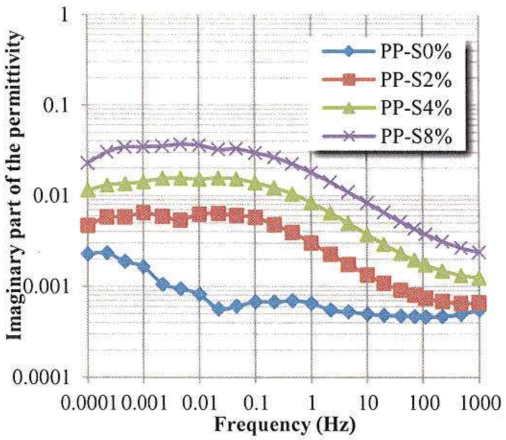

Fig. 3. Imaginary part of permittivity of PP filled Synthetic nanoclay versus frequency at 30°C

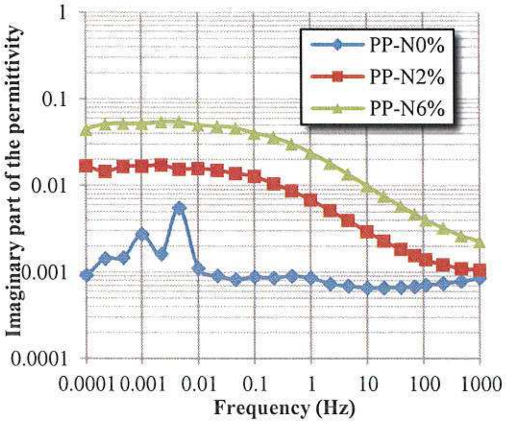

Fig. 4. Imaginary part of permittivity of PP filled natural nanoclay versus frequency at 30°C

Figures 5 to 8 depict the dissipation factor for all the PP composites tested in the study at 50°C and 80°C. Higher losses as indicated by the increase in tanδ were obtained with higher concentration of the nanoclay. Unlike the unfilled PP, all the composites showed a broad loss peak that shifted towards higher frequencies with the increase in temperature. This shift, which can be described using Vogel-Fulcher law, was most likely obtained due to the overlapping of two polarization processes, the long-range motions of the polymer chain and the Maxwell-Wagner polarization.

At very low frequencies (below 0.01 Hz), an increase in tanδ can be observed for the unfilled samples at 50°C (Fig. 5 and Fig. 7); whereas, this increase appeared at 80°C for the filled samples (Fig. 6 and Fig. 8). This increase could be related to ionic conductivity of compatibilizers. Maleic anhydride was added as a compatibilizer to maintain a good dispersion of nanoparticles in the PP. These polar chemicals can be readily hydrolyzed into ionic bi-acids which accordingly affects the conductivity.

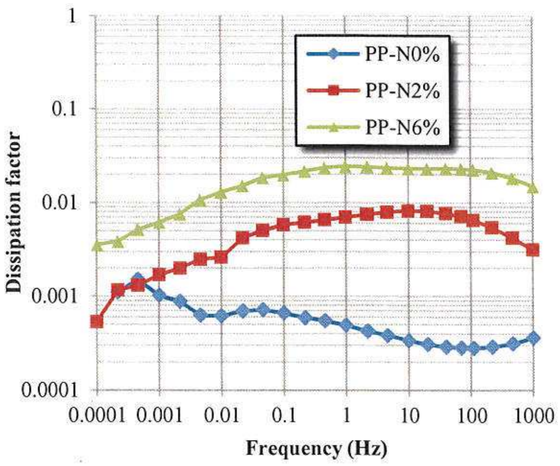

Fig. 5. Dissipation factor of PP filled natural nanoclay versus frequency at 50°C

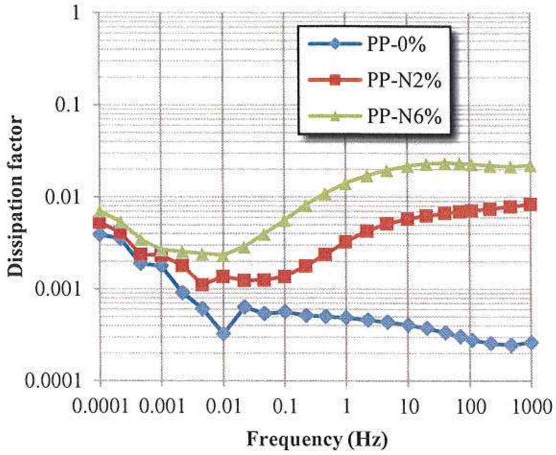

Fig. 6. Dissipation factor of PP filled natural nanoclay versus frequency at 80°C

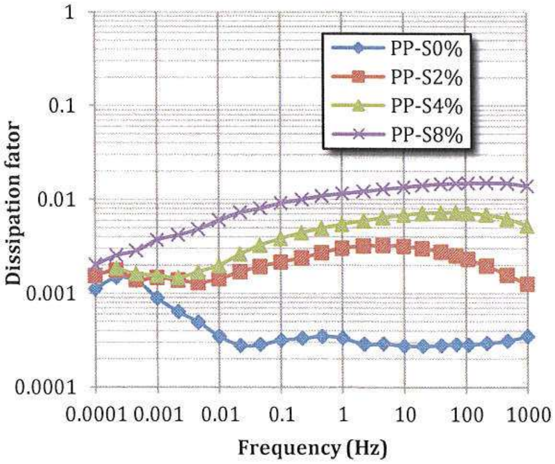

Fig. 7. Dissipation factor of PP filled synthetic nanoclay versus frequency at 50°C

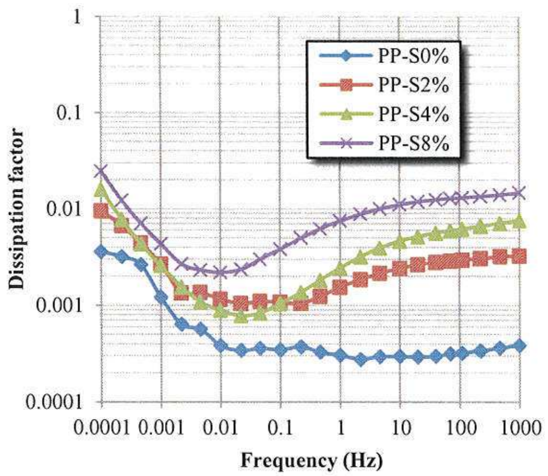

Fig. 8. Dissipation factor of PP filled synthetic nanoclay versus frequency at 80°C

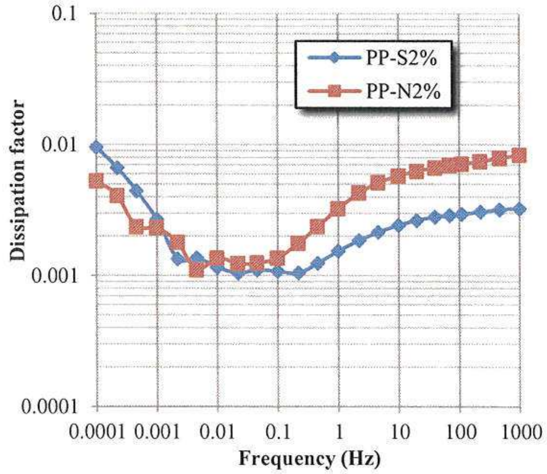

Fig. 9. Dissipation factor measurements of PP-S2% and PP-N2% versus frequency

Fig. 9 presents the dissipation factor measured for the PP-S2% and PP-N2% at 80°C. It is clear that the magnitude of the loss peak is higher for the PP-N2%. This might be related to the lower aspect ratio of the individual natural nanoclay platelets (≤ 286) as compared to the synthetic nanoclay platelets (≤ 6000). The contribution of the interaction zone is more evident with smaller sizes of nano platelet [18]. Bellow 10^{-2} Hz the losses could be attributed to the presence of compatibilizer which is added with higher ratio in the composites with synthetic nanoclay. Table I shows the capacitance and resistivity measurements conducted at power frequency for the tested composites. Unlike the capacitance, a recognizable difference was measured between the PP-S2% and PP-N2% with higher resistivity reported for the PP-S2%. Such a finding suggests that PP-S2% might be still a potential optimum candidate for power capacitor applications.

TABLE I

CAPACITANCE AND RESISTIVITY OF PP-S2% AND PP-N2% AT 60 HZ.

	PP-S2%		PP-N2%	
Temperature	Capacitance (pF)	Resistivity (GΩm)	Capacitance (pF)	Resistivity (GΩm)
30ºC	219	569	249	307
50ºC	220	101	254	35.8
80ºC	222	88.6	261	36.5

V. CONCLUSIONS

The dielectric properties of PP filled with synthetic and natural clays were investigated. It was found that loading the PP with nanoclay increases ε' at very low frequencies while ε'' and tanδ exhibited a broad peak as a result of the Maxwell-Wagner interfacial polarization. Samples containing natural nanoclay showed higher losses as compared to the samples with synthetic nanoclay. Due to the conductive character of the hydrolyzed maleic anhydride, the effect of the added compatibilizer was more pronounced at very low frequencies. However, more work is needed to explore more the effect of concentration of compatibilizers and aging period on the dielectric properties of PP.

REFERENCES

[1] Abou-Dakka, M., R.A. Ghunem, and D. McIntyre. Space charge evolution in polypropylene loaded with synthetic and natural nanoclay aged at 50°C temperature. in 2014 IEEE Conference on Electrical Insulation and Dielectric Phenomena (CEIDP). 2014.

[2] Bulinski, A., S.S. Bamji, M. Abou-Dakka, and Y. Chen. Dielectric properties of polypropylene containing synthetic and natural organoclays. in 2010 IEEE International Symposium on Electrical Insulation. 2010.

[3] Bulinski, A., S.S. Bamji, M. Abou-Dakka, and Y. Chen. Dielectric properties of polypropylene loaded with synthetic organoclay. in 2009 IEEE Conference on Electrical Insulation and Dielectric Phenomena. 2009.

[4] Bamji, S.S., M. Abou-Dakka, A.T. Bulinski, L. Utracki, and K. Cole. Dielectric properties of polypropylene containing nano-particles. in CEIDP '05. 2005 Annual Report Conference on Electrical Insulation and Dielectric Phenomena, 2005. 2005.

[5] Lewis, T.J., Interfaces are the dominant feature of dielectrics at the nanometric level. IEEE Transactions on Dielectrics and Electrical Insulation, 2004. 11(5): p. 739-753.

[6] Frechette, M.F. and C.W. Reed. The role of molecular dielectrics in shaping the interface of polymer nanodielectrics. in 2007 Annual Report - Conference on Electrical Insulation and Dielectric Phenomena. 2007.

[7] Abou-Dakka, M. and L. Cisse. Evolution of some dielectric properties of polypropylene-nanoclay composites with DC poling. in 2011 Annual Report Conference on Electrical Insulation and Dielectric Phenomena. 2011.

[8] Zaengl, W.S., Dielectric spectroscopy in time and frequency domain for HV power equipment. I. Theoretical considerations. IEEE Electrical Insulation Magazine, 2003. 19(5): p. 5-19.

[9] Zaengl, W.S., Applications of dielectric spectroscopy in time and frequency domain for HV power equipment. IEEE Electrical Insulation Magazine, 2003. 19(6): p. 9-22.

[10] Andrew, K.J., Dielectric relaxation in solids. Journal of Physics D: Applied Physics, 1999. 32(14): p. R57.

[11] Jonscher, A.K., A new understanding of the dielectric relaxation of solids. Journal of Materials Science, 1981. 16(8): p. 2037-2060.

[12] Dissado, L.A. and R.M. Hill, Anomalous low-frequency dispersion. Near direct current conductivity in disordered low-dimensional materials. Journal of the Chemical Society, Faraday Transactions 2: Molecular and Chemical Physics, 1984. 80(3): p. 291-319.

[13] Fothergill, J.C., Electrical Properties, in Dielectric Polymer Nanocomposites, J.K. Nelson, Editor. 2010, Springer US: Boston, MA. p. 197-228.

[14] Jonscher, A.K., Universal relaxation law. 1996, London: Chelsea Dielectrics Press.

[15] Bamji, S.S., A. Bulinski, M. Abou-Dakka, and D. McIntyre. Space charge in polypropylene containing synthetic nano particles. in 2009 IEEE Conference on Electrical Insulation and Dielectric Phenomena. 2009.

[16] Singha, S. and M.J. Thomas, Influence of filler loading on dielectric properties of epoxy-ZnO nanocomposites. IEEE Transactions on Dielectrics and Electrical Insulation, 2009. 16(2): p. 531-542.

[17] Nelson, J.K. and C.F. John, Internal charge behaviour of nanocomposites. Nanotechnology, 2004. 15(5): p. 586.

[18] Chen, G., J.T. Sadipe, Y. Zhuang, C. Zhang, and G.C. Stevens. Conduction in linear low density polyethylene nanodielectric materials. in 2009 IEEE 9th International Conference on the Properties and Applications of Dielectric Materials. 2009.