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Measurement of Dielectric Properties of Low-Density Polyethylene Nanocomposites Using "Sub-Hertz" Dielectric Spectroscopy

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Abstract

Recently, many studies have been conducted on the dielectric properties of Low-Density Polyethylene (LDPE) nanocomposites and produced different results. However, the composition of LDPE polymer and boron nitride (BN) as nanofiller has neither been well understood nor producing a convenient result. Similarly, the dielectric spectroscopy measured at "sub–hertz" frequency has been of little interest among researchers since it is often influenced by "conduction-like" effect. This research identified the dielectric properties of LDPE nanocomposites filled with hexagonal boron nitride (h-BN) nanofillers by using dielectric spectroscopy technique. The dielectric loss and relative permittivity for three different filler concentrations were investigated under "sub-hertz" frequency ranges at room temperature. The cylindrical electrode with guard ring configuration was used to conduct the experiment, in accordance to the ASTM D150 standard. The results revealed that 5 wt% filled polymer has lower loss tangent and permittivity compared to the unfilled polymer, due to the strong interaction between nano-particle and the polymer. This strong interaction is believed to limit the movement of the polymer chain. The decrease in loss tangent also indicates lower quasi-DC at low frequency. However, further increase in the filler loading has recorded an increment in the value of permittivity and loss tangent. This higher effective permittivity is mainly due to the influence of the filler permittivity

Keywords*: permittivity, tangent delta, low density polyethylene (LDPE), boron nitride (BN) nanofillers, dielectric spectroscopy*

1. Introduction

Since the 1940s, polymeric insulators had been used instead of glass and ceramic insulators [1]. Many experiments have been conducted in the area of polymer nanocomposites in order to enhance the polymer properties and their utility over the past two decades [2]. In the early 1990, true nylon-6-clay thermoplastic nanocomposite technology had been patented by Toyota research. After one year, Toyota Motor Corporation started to implement the work by using nylon-6-clay nanocomposite to fabricate timing belt covers for their cars. It was the first commercialization of polymer nanocomposites in the industry [3].

Polymer nanocomposites are defined as polymers consist of nanometer size fillers with several weight percentages, which are homogeneously dispersed in the polymer matrix [4]. The key to diversify polymer properties is represented by the conversion of bulk polymer into interfacial polymer. Polymer nanocomposite can be differentiated from microfiller-filled polymer by three major characteristics. The first characteristic is that nanocomposites have very large specific surface area. Secondly, it has smaller filler size, resulting in closer distance between neighboring filler in nanocomposite. Then, the third characteristic is it has a small amount of filler which less than 10 wt%.

In polymer nanocomposite, size of less than 100 nm is defined for nanofiller but for mesoparticle, which is bigger (intermediate size between nano and micro level), the size is larger than 100 nm and less than 1 μm [5]. The role of nanofiller in polymer composite as the main factor to change the dielectric properties of the polymer system were proven from many previous studies. The changes that have been made was significantly affected by the polymer system comparable to traditional polymer. In fact, it has been the reason of polymers having

their unique properties due to the nanofiller-polymer interface area which is called as "Interaction Zone" [6, 7].

Boron nitride is an industrial ceramic material consisting of crystalline compounds of boron nitrogen. There are few characteristics of BN which are a good thermal conductor, low dielectric constant, good breakdown strength (53 kV/mm), high electrical resistivity (1015 Ωcm), non-wetting to molten metal, low dielectric loss, lubricious and low relative permittivity (about 4.0) [1, 2], [8, 9].

In order to identify the dynamical behavior of a sample through the analysis of its frequency dependent dielectric response, a powerful experimental method is used which is dielectric spectroscopy. With this technique, information about dielectric properties can be obtained. The measurement of capacitance as a function of frequency of a sample that had been sandwiched between two electrodes was the foundation for this technique [10]. In this paper, the main objective was to investigate the effects of hexagonal boron nitride (h-BN) nanofiller on the dielectric properties of low-density polyethylene (LDPE). Dielectric properties such as the permittivity and loss tangent of the samples were observed using "sub-hertz" dielectric spectroscopy at room temperature.

2. Experimental
2.1. Sample Preparation
The polymer used in this project was a LDPE, produced by Lotte Chemical Titan Sdn. Bhd. in Malaysia. It has a density of 0.922 g/cm^3 and a melting point of greater than 120 °C. For the h-BN, it was produced by Nanostructured & Amorphous Materials Inc. in USA with a high purity of 99%. It has a density of 2.25 g/cm^3. The polyethylene nanocomposites were fabricated by means of direct mixing method, using two-roll mill machine with rotor speed of 4.8 rpm. The mixing temperature was 160°C and the mixing time was 15 min for each sample [6]. Finally, plane samples of square shape (15 x 15 cm^2) having the thickness of 0.1-0.15 mm were prepared by hot melt pressing at 160°C, for 3 min (after pre-heating for 2 min). Figure 1 shows the fabricated LDPE/BN nanocomposite samples.
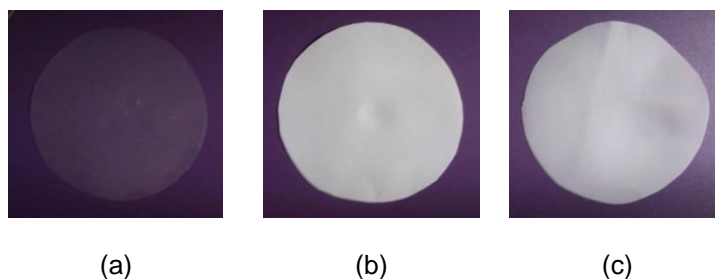

(a)　　　　　　　　(b)　　　　　　　　(c)

Figure 1. Sample of the LDPE/BN nanocomposites: (a) Pure LDPE (b) LDPE/BN 5 wt% (c) LDPE/BN 10 wt%

2.2. Dielectric Spectroscopy
The complex relative permittivity and the loss tangent (tan δ) were measured by dielectric spectroscopy (DS) using a GAMRY Potentiostat Interface 1000^{TM} in conjunction with a 2914 test cell at room temperature. The test cell was equipped with a cylindrical electrode with a guard ring configuration which can prevent the fringing effect. This electrode configuration is in accordance to the ASTM D150 standard. Figure 2 shows the cylindrical electrode configuration which was used in this work. The frequency range under an ac sinusoidal applied voltage of 1 V (rms) was between 10^{-3} Hz and 1 Hz. One disk of 50 mm diameter were cut from one plaque of each sample and tested using the dielectric spectroscopy.

Figure 2. Cylindrical electrode configuration for DS experiment

2.3. Representation of Dielectric Measurements

An equivalent electrical circuit consists of a capacitance, $C(\omega)$ in parallel with a resistance $R(\omega)$ can be assumed similar as the dielectric sample placed between the round plate electrodes of the capacitor. The capacitance and resistance are correlated with impedance, $Z(\omega)$ and dielectric permittivity, $\varepsilon^*(\omega)$ of the sample through the following formula [11]:

$$\frac{1}{Z^*(\omega)} = \frac{1}{R(\omega)} + i\omega.C(\omega) \tag{1}$$

$$\varepsilon^*(w) = \varepsilon' - i\varepsilon'' = \frac{C(\omega)}{C_0} - i\frac{1}{\omega C_0 R(\omega)} = -\frac{i}{\omega C_0 Z^*(\omega)} \tag{2}$$

where $C_0 = \varepsilon_0 \cdot \pi \cdot r^2/d$ is the capacitance of the empty sample cylindrical capacitor, with r=radius, d=thickness of the sample, $\omega = 2\pi f$ and ε_0 = permittivity of the vacuum.

3. Results and Analysis

The experimental works are performed based on ASTM D150 standard setup requirements. The influence of the filler content on the dielectric behavior can be seen in Figure 3 (a) and Figure 4 which show the frequency variations of the real part of the complex relative permittivity (ε_r') and of the loss tangent (tan δ) at room temperature. As seen from Figure 3 (a), ε_r' decrease with frequency for all samples apart from the ε_r' values for 5 wt% sample, which show almost no dependency with frequency as it is changing very lightly compared to the others (from 2.20 to 2.25). Another observation is that the ε_r' values for 5 wt% are less than that of 0 wt% which is the unfilled polymer at all the frequencies. This is probably owing to the fact that the chain movement of the polymer in the nanocomposite is reduced in comparison to the unfilled polymer [12-14]. The same result also being reported for other types of polymer nanocomposites by other researchers [12-15]. Nonetheless, the ε_r' values for 10 wt% from 0.1 Hz to 1 Hz are recorded to be higher than the unfilled polymer. This higher effective permittivity is mainly due to the influence of filler permittivity [16] since BN has a permittivity of about 4 in contrast to 2.3 for LDPE [1]. According to the interface model proposed by Singha et al. [16], polymer-nanoparticle interactions leads to the formation of two nanolayers around the particle where the first nanolayer is tighly bound to the nanoparticle surface, causing the polymer chains to be highly immobile. The second layer, which contains polymer chain and is loosely bound, has a thickness slightly more than that of the first layer. The influence of the chain immobility (due to the first layer interface) and the chain entanglements, will restrict the mobility of the dipolar groups in the nanocomposites, resulting in the effective permittivity to be reduced below the unfilled polymer at BN loading of 5 wt%. At 10 wt%, the effective permittivities of the nanocomposites are determined by the combined interaction of chain immobilization and rate of permittivity enhancement due to the filler loading, where the influence of the latter is slightly more pronounced than the former [16].

Figure 3 (b) depicts the variation of the imaginary part of complex permittivity (ε_r'') over sub-hertz frequency for all sample. Similar observation is found compare to Figure 3 (a) such as ε_r'' decrease with frequency for all samples except that the ε_r'' values for 10 wt% sample are higher than 0 wt% sample at 0.01 Hz and from 0.05 Hz until 1 Hz.

The graph in Figure 4 shows the variation of loss tangent (tan δ) over sub-hertz frequency for all sample. Clearly, 5 wt% sample has the lowest tan δ compared to other samples. In other studies, similar dielectric loss behavior of a lower tan δ in polymer nanocomposite has also been reported [12, 14]. This is probably due to the movement of charge in the material was reduced due to large areas of filler polymer interface and polymer chain restriction in the nanocomposites. Therefore, it may cause a decreasing of electrical conductivity and consequently of the component tan δ [12].

The approximated constant value of tan δ for all samples with the frequency from 0.01 Hz until 0.1 Hz is thought to be related with conductivity which is approximately constant at low frequencies. This typical low frequency dispersion phenomenon is also called as quasi-DC (QDC) behavior as the results have similarity with that of direct current [17].

By analyzing the nanocomposite conduction, the low frequency loss tangent can be more clearly understood. Figure 5 shows the frequency variation of σ' for LDPE/BN nanocomposite that has been constructed by using equation related between σ' and ε_r", σ' = $\omega\varepsilon_0\varepsilon_r$" [17]. It can be seen that σ' changed in LDPE nanocomposites and the 5 wt% sample has lower QDC compared to unfilled polymer. The higher QDC indicated a huge loss tangent of the nanocomposite which anticipated to have a similar function with direct current.

The increasing of nanofiller content such as 10 wt% had little effect on the material QDC and shows a reverse expectation at 0.25 Hz as the QDC continually increasing. The same reverse expectation also occurs for tan δ at the same frequency. This is probably caused by agglomeration of nanoparticles due to poor dispersion in the polyethylene during fabrication. Furthermore, the size of BN nanofiller particles can be considered large which has the size value of 137 nm. With the maximum nanofiller content, 10 wt% and large size of particle, the material would tend to be microcomposite which is not optimum.
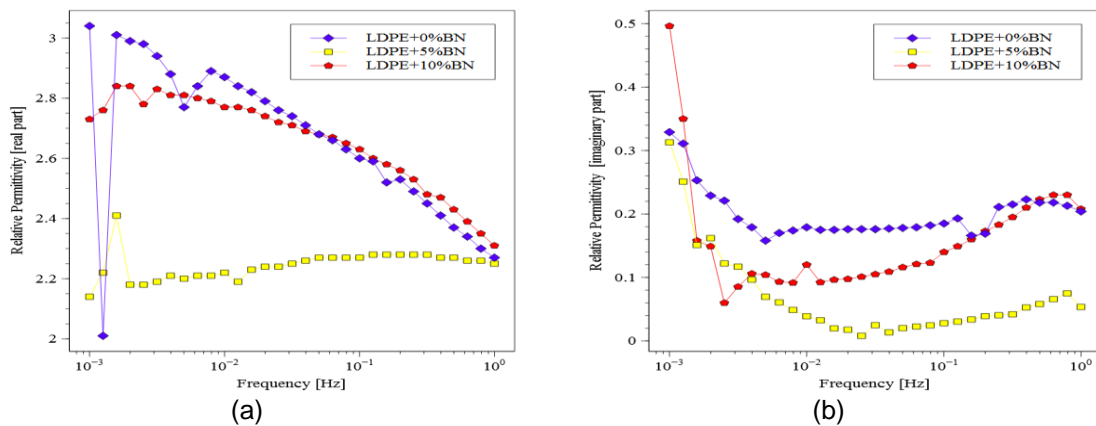

(a)   (b)

Figure 3. Frequency variation of (a) εr' and (b) εr" at room temperature for LDPE/BN nanocomposite with different filler concentration
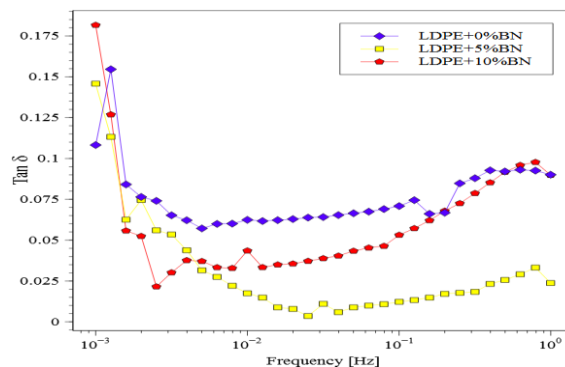

Figure 3. Frequency variation of tan δ at room temperature for LDPE/BN nanocomposite with different filler concentration
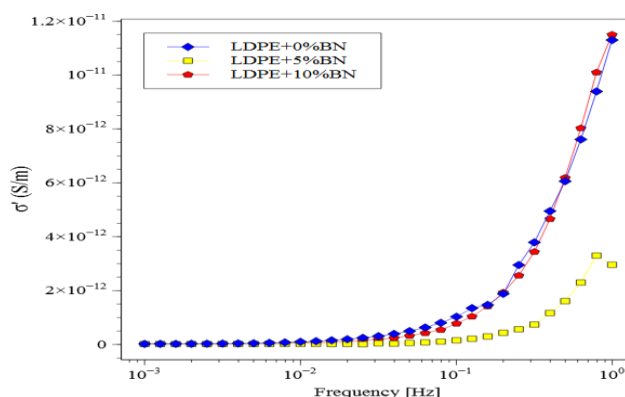
Figure 4. Frequency variation of σ' at room temperature for LDPE/BN nanocomposite with different filler concentration

4. Conclusion

In this paper, the dielectric properties of LDPE nanocomposite are influenced by the filler concentration over the sub-hertz frequency. The results reveal that the addition of 5 wt% BN results in decreasing permittivity as well as the loss tangent while incorporation of 10 wt% nanocomposites results in increasing permittivity and loss tangent. The change in the electrical properties are most probably due to the combined interaction of restriction in the chain movement between nanoparticles and rate of permittivity enhancement due to the filler loading, as enlightened by the interface model. The decrease in permittivity and loss tangent are attributable to the more pronounced effect of the former while the increasing in the permittivity and loss tangent are caused by the second effect being more pronounced. The decrease in the tangent loss at sub-hertz frequency is suggested to be explained by using the QDC of the nanocomposite. This dielectric behavior could lead to an improved polymeric based electrical insulation. To improve the suggested explanation, it is recommended to conduct the morphological analysis of the nanocomposite.

References

[1]   IN Hidayah, M Mariatti, H Ismail, M Kamarol. Electrical Properties of LLDPE/SR with Nano-Silica and Nanoboron Nitride. *Advanced Materials Research*. 2013; 858: 80-87.
[2]   R Ayoob, T Andritsch, AS Vaughan. *The Effect of Material Processing on the Dielectric Properties of Polystyrene Boron Nitride nanocomposites*. Electrical Insulation Conference (EIC). Washington, USA IEEE. 2015: 333-336.
[3]   F Hussain, M Hojjati, M Okamoto, RE Gorga. Polymermatrix Nanocomposites, Processing, Manufacturing and Application. *An overview Journal of Composite Materials*. 2006; 40(17): 1511-1575.
[4]   T Tanaka, GC Montanari, R Mulhaupt. Polymer Nanocomposites as Dielectrics and Electrical Insulation-Perspectives for Processing Technologies, Material Characterization and Future Applications. *Dielectrics and Electrical Insulation, IEEE Transactions*. 2004; 11(5): 763-784.
[5]   R Kochetov, T Andritsch, U Lafont, PHF Morshuis, SJ Picken, JJ Smit. *Preparation and Dielectric Properties of Epoxy-BN and Epoxy-AlN Nanocomposites*. Electrical Insulation Conference, EIC, 2009.
[6]   F Ciuprina, I Plesa, PV Notingher, P Rain, T Zaharescu, D Panaitescu. *Dielectric Properties of LDPE-SiO Nanocomposites*. Solid Dielectrics (ICSD), 10th IEEE International Conference. 2010.

[7]   H Bai, S Zhi, Z Dong, L Lin, W Xuan, L Qingquan. Dielectric Spectra Properties of Low-Density Polyethylene (LDPE)/Zeolite Nanoscale Composite. *Properties and Applications of Dielectric Materials (ICPADM) IEEE.* 2012.

[8]   C Xiaolin, C Yonghong, W Kai, X Xiaojun. Dielectric Spectroscopy Analysis of the h-BN Ceramic. *Journal of Physics D: Applied Physics.* 2007; 40(19): 6034, 2007.

[9]   C Zhang, GC Stevens. Dielectric Properties of Boron Nitride Filled Epoxy Composites. *Electrical Insulation and Dielectric Phenomena IEEE.* 2006.

[10] O Gouda, A Thabet. Thermal Experimental Dielectric Characterization of Cost-Fewer Low-Density Polyethylene Nanocomposites. *Advances in Electrical and Electronic Engineering.* 2014; 12(5): 537-546.

[11] V Saltas, N Lydakis-Simantiris, P Soupios, F Vallianatos. *Complex Dielectric Permittivity and Electrical Conductivity Measurements as a Diagnostic Tool for the Detection of Heavy Metals Adsorbed in Bentonite Samples.* 3rd International Conference on Industrial and Hazardous Waste Management. 2012.

[12] F Ciuprina, I Plesa, PV Notingher, T Tudorache, D Panaitescu. Dielectric Properties of Nanodielectrics with Inorganic Fillers. *Electrical Insulation and Dielectric Phenomena.* CEIDP. 2008.

[13] M Roy, JK Nelson, RK MacCrone, LS Schadler, CW Reed, R Keefe. Polymer Nanocomposite Dielectrics-the Role of the Interface. *IEEE Transactions on Dielectrics and Electrical Insulation.* 2005; 12(4): 629-643.

[14] S Singha, MJ Thomas. Permittivity and Tan Delta Characteristics of Epoxy Nanocomposites in the Frequency Range of 1 MHz-1 GHz. *IEEE Transactions on Dielectrics and Electrical Insulation.* 2008; 15(1): 2-11.

[15] T Tanaka, GC Montanari, R Mulhaupt. Polymer Nanocomposites as Dielectrics and Electrical Insulation-Perspectives for Processing Technologies, Material Characterization and Future Applications. *IEEE Transactions on Dielectrics and Electrical Insulation.* 2004; 11(5): 763-784.

[16] S Singha, MJ Thomas. Influence of Filler Loading on Dielectric Properties of Epoxy-ZnO Nanocomposites. *IEEE Transactions on Dielectrics and Electrical Insulation.* 2009; 16(2).

[17] W Yang, R Yi, S Hui, Y Xu, X Cao. Analysis of the Dielectric Spectroscopy of an Epoxy-ZnO Nanocomposite using the Universal Relaxation Law. *Journal of Applied Polymer Science.* 2013; 127(5): 3891-3897.