

Egyptian Journal of Chemistry

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High -k Green Polymer Nanocomposites Based on Polyvinyl Alcohol for Electrostatic Dissipation Applications

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Abstract

Polyvinyl alcohol (PVA) as a green biodegradable polymeric matrix was chosen to fabricate high-k (high permittivity) polymer nanocomposites with good magnetic and electric properties to be used for electrostatic dissipation applications. PVA was doped with different concentration of magnetite (Fe₃O₄) nanoparticles and barium titanate (BaTiO₃) nanoparticles before and after treatment with ionic liquid (IL). The magnetic properties were investigated by vibrating sample magnetometer (VSM) and the obtained results revealed an improvement in such properties by the ionic liquid treatment of BaTiO₃. This finding widens the application scope of PVA nanocomposites to include electromagnetic purposes. Moreover, electrical properties including permittivity ε' , dielectric loss ε'' in addition to electrical conductivity σ were also studied. The dielectric properties were also enhanced after ionic liquid treatment. In addition, the values of conductivity σ was in the order ~ 10⁻⁷ S/cm which endorse using such nanocomposites for electrostatic dissipation applications.

Keywords; Poly vinyl alcohol (PVA). Magnetic nanoparticles (MNPs). Magnetic properties. Dielectric properties. Electrical conductivity.

1. Introduction

Magnetic nanoparticles (MNPs) have attracted great interest in many life applications because of its magnetic properties as well as size in nanoscale, biocompatibility, crystallinity and surface modification potential. Although there have been numerous notable advancements in the manufacturing of magnetic nanoparticles. maintaining their stability for extended periods of time without agglomeration or precipitation remains a challenge [1]. To overcome agglomeration and provide homogenous distribution as usual, layers of MNPs were coated with polymeric materials such as polyethylene glycol (PEG), poly methyl methacrylate (PMMA) and polyvinyl alcohol (PVA), in order to retain magnetic properties required for high potential application in multi fields [2]. Among the various

types of synthetic polymers that can be used for coating MNPs, PVA has potential applications, due to its thermal stability, high mechanical performance, and excellent biocompatibility. So a novel approach was made to dielectric composite materials is the combination of polymer materials with fillers and forming capabilities with a ceramic material, characterized by a high dielectric constant to generate a tailor built composite [1-3]. The selection of suitable polymer matrix and the proper filler can lead to the fabrication of excellent composites with variable dielectric characteristics. Polymer and ceramic compounds / ferroelectric particles can typically be manufactured using the casting method techniques. Composite films are prepared by mixing an insulating polymer solution and nano-sized ferroelectric particles, and evaporating the polymer solution solvent. Many efforts have been done in the last years to investigate alternative high-permittivity (high-k) dielectrics that could replace SiO2 and SiON

*Corresponding author e-mail: <u>khairysh53@gmail.com</u> Receive Date: 5 June 2022, Revise Date: 22 June 2022, Accept Date: 29 June 2022 DOI: 10.21608/EJCHEM.2022.142955.6242

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as gate insulators in the metal-oxide-semiconductor (MOS) transistors. The higher dielectric constant provides higher gate capacitances with moderated thickness layers. In addition, high-k dielectrics as novel metal electrodes are demanded to replace the traditional polysilicon gate electrode that is to avoid the polysilicon depletion, boron penetration, and compatibility issues with high-k dielectrics [4]. The most common process to enhance the dielectric permittivity of a polymer is the dispersion of a high electrical permittivity ceramic powder such as barium titanate (BaTiO₃) or lead titanate (PbTiO₃) in the polymer to form a composite. In order to obtain a high value of dielectric permittivity, a large amount of fillers must be loaded. Another way to obtain high dielectric permittivity composites is to use conductive filler such as magnetite (Fe₃O₄) near its percolation threshold to produce the composites [5]. These composites are versatile could simply processed and shaped to be readily treated and molded into any shape to be utilized for wide range of electrical and electronic applications [5-6]. Many investigations on polymer dielectrics with good processing qualities have been conducted, and it has been discovered that low-polarity covalent dipoles yield a comparatively low dielectric constant [6]. Composites made by dispersing inorganic filler particles in a polymer binder have a wide range of applications due to the combination of specific properties of two classes of compounds and the possibility of a wide range of property adjustment due to changes in component ratio and inorganic filler size [7]. This research focused on the preparation and characterization of a multifunctional PVA nanocomposite. PVA was simply mixed via casting method with different concentrations of magnetite and barium titanate nanoparticles in addition to barium titanate treated with ionic liquid as well. The physical properties of the prepared nanocomposites such as electrical, magnetic properties were reported.

2. Experimental

2.1 Materials and Methods

The samples were prepared by casting method to form three different nanocomposites (NCPs). **Materials**

Poly vinyl alcohol (PVA) with M.Wt about 1.15,000 was provided from Loba Chemie and used as received. Fe_3O_4 nanoparticles (NPs) were prepared as mentioned before [8]. Barium titnate BaTiO₃ (M.Wt 233.24) was supplied from Merck KGaA (Germany).

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The ionic liquid was prepared as mentioned before [9] . After that, The reactive surface of BaTiO₃ NPs has been treated with Ionic liquid as mentioned before [9,10]. Then 1 gm of PVA was dissolved in 30 mL of distilled water and stirred continuously at 30°C for 3 h using a magnetic stirrer. Then set a constant as 10 wt% Fe₃O₄ and different content at (2.5, 5, 7, 10, 15 and 20) wt% of IL treated BaTiO₃, then follow the same steps to get NCPs.

1- Preparation of PVA / Fe₃O₄ NCPs

1 gm of PVA was dissolved in 30 mL of

distilled water by stirring continuously at

30°C for 3 h using a magnetic stirrer. Then

contents varying at (2.5, 5, 7, 10, 15 and 20)

wt% of Fe₃O₄ (NPs) were added to the PVA

suspension and mixed using ultrasonic path

for 1 h and mechanical stirred for 24 h to

reach a homogeneous distribution. Finally,

the solution was poured onto glass plates

and dried at 60 °C in an oven for 24 h to

2- Preparation of PVA / 10 wt% Fe₃O₄ /

1 gm of PVA was dissolved 30 mL of

distilled water and stirred continuously at

30°C for 3 h using a magnetic stirrer. Then

different content at (2.5, 5, 7, 10, 15 and 20)

wt% of BaTiO₃ then follow the steps above

3- Preparation of PVA / 10 wt% Fe₃O₄ /

Fe₃O₄ and

3. Techniques

form films.

BaTiO₃ NCPs

to form NCPs films.

set a constant as 10 wt%

IL treated BaTiO₃ NCPs.

Vibrating sample magnetometer (VSM) model Lake Shore Model 7410, USA was used for the magnetic properties measurements. The system is equipped with a 10-inch electromagnet providing magnetic fields up to 3.1 T, accuracy = +/- 1%, maximum sample size = 1 in and variable temperature (CCR) = ~ 20 K to 450 K. measurements including the Dielectric permittivity (dielectric constant) ɛ', loss factor tan δ and ac-resistance $R_{\rm ac}$ were measured at room temperature ~ 25 °C in a broad frequency range (0.1 Hz - 1 MHz). The measurement was computerized by interfacing the impedance analyzer with a personal PC through a cable type GPIB IEE488. A commercial interfacing and automation software program "Lab VIEW" was used for data acquisition. The error in ε' and tan δ amounts to ± 1 % and ± 3 %, respectively.

The temperature of the samples was controlled by a temperature regulator with (Pt 100) sensor. The error in temperature measurements amounts ± 0.5 °C.

4. Results and Discussion

4.1 VSM Measurements

The magnetic properties of the prepared novel nanocomposites that consist of PVA polymer as a matrix and Fe₃O₄, BaTiO₃, IL treated BaTiO₃ as dopants are characterized by using VSM technique at room temperature. The VSM analysis was carried out at room temperature and hysteresis loops are shown in Figure (1) and Figure (2). Figure (1) shows the hysteresis loop of the PVA / Fe₃O₄ NCPs at different concentration (5, 10, 15 and 20) wt% of Fe₃O₄ NPs. Besides, the values of saturation magnetization (M_S), remanent magnetization (Mr) and coercivity force (H_c) are tabulated in Table1. From the Table it is shown that Ms increases from 1.85 to 8.24 emu/g with increasing Fe₃O₄ content but beyond a certain point the value of magnetization saturates and attains a maximum value of magnetization and domain grows. The samples show super paramagnetic nature with increasing NCPs loading which implies the ability of the sample to retain a large fraction of the magnetic field when the driving field was removed. However, an overdose of NPs content may lead to agglomeration, which may impede its dispersion in the matrix and uniform distribution of its magnetic moment. The values of H_c decreased when the content of NPs increased, this is due to the presence of nonmagnetic components with magnetite but the coercivity value at higher concentration of nanoparticles increased, this is due to the presence of surface roughness of nanoparticles at high content and also with the formation of ferromagnetic clusters in the polymer matrix [11,12]. It is clear from the discussion that adding Fe₃O₄ to nanocomposites improves magnetic behavior and increases the material's sensitivity to changes in the external magnetic field, resulting in an increase in magnetic values [13,14]. The property of super paramagnetic behavior of the nanocomposite suggest that it can be responsive to alternating current magnetic fields of magnetic separation, particle adsorption, and design of smart magnetic devices.



Figure (1): Hysteresis loop of PVA doped with (5, 10, 15 and 20) wt% of Fe₃O₄ NPs loading respectively.

Table1: Magnetic parameters of different content of ${\rm Fe_3O_4}$ nanoparticles and copolymer nanocomposites

PVA / Fe ₃ O ₄	Ms	M _r	H _c
Content (wt%)	(emu/g)	(emu/g)	(G)
5	1.85	0.29	108.94
10	2.37	0.36	102.90
15	2.84	0.44	103.88
20	8.24	1.35	104.85

Figure (2) shows the hysteresis loop of the nanocomposites consisted of PVA / 10 wt% Fe₃O₄ / (5, 10, 15, 20) wt% BaTiO₃ and PVA / 10 wt% Fe₃O₄ / (5, 10, 15, 20) wt% IL treated BaTiO₃, the values of M_s, M_r and H_c with and without ionic liquid are tabulated in Table2. Figure (2) a, represents the hysteresis loops for PVA / 10 wt% Fe₃O₄ / BaTiO₃ NCPs at (5, 10, 15 and 20) wt% different content of BatiO₃, it showed that increase in M_s with increasing content of BaTiO₃ and also due to appearance of Fe₃O₄ with constant percent in NCPs. It showed that the composite material exhibits the typical ferromagnetic loops with super paramagnetic properties, also in the zoom curve that appear more broad hysteresis loop for high saturation indicate the NCP is more magnet [15]. Figure (2) b, represents the hysteresis loops for PVA /10 wt% Fe₃O₄ / IL treated BaTiO₃ NCPs at (5, 10, 15 and 20) wt% different content of treated, also clarified that the increment in M_s with increase content of IL treated BaTiO₃, may be due to the presence of a fixed ratio of Fe₃O₄ in NCPs, which helps the appearance of the super paramagnetic property. Also, the presence of IL with different content in NCPs improved the hysteresis loop shape, making it more regular and broader. So, we can explain that the presence of IL in the NCPs led to the improvement of magnetic properties and can be used in many electromagnetic applications [16].



Figure (2): Hysteresis loop for (a) PVA / 10 wt% Fe₃O₄ doped with (5, 10, 15 and 20) wt% BaTiO₃ loading and (b) PVA /10 wt% Fe₃O₄ doped with (5, 10, 15 and 20) wt% IL treated BaTiO₃ loading .

Table 2: Magnetic parameters of different content of $BaTiO_3$ and IL treated $BaTiO_3$ nanoparticles and copolymer nanocomposites

	Without treatment			Treated with ionic liquid		
PVA / 10 wt%	Ms	Mr	Hc	Ms	Mr	Hc
Fe3O4 / BaTiO3	(emu/g	(emu/g)	(G)	(emu/g)	(emu/g	(G)
Content (wt%)))	
5	0.62	0.11	112.	0.69	0.12	118.1
			93			8
10	1.06	0.18	111.	2.03	0.33	110.7
			22			6
15	1.92	0.31	104.	2.27	0.35	107.6
			98			0
20	2.11	0.34	107.	3.61	0.61	105.8
			63			2

4.2 Dielectric Measurements

The ability of polymers to store/ dissipate energy described by the terms permittivity (ε') and dielectric loss (ε''). Both parameters are significantly affected by the polymer polarity, kind of filler, and loading amount. Figure (3) presents the variation of both ε' and ε'' versus *f*, the applied frequency (10⁻¹ -10⁶ Hz) at room temperature (RT) \cong 25°C. The permittivity ε' of the NCPs was found to increase by increasing Fe₃O₄ and decrease shapely by increasing the applied frequency. The presence of Fe₃O₄ with its ionic dipoles masses could be the reason of the increase in ε' values [17]. So a pronounced increase in ε' values was detected as the result of increasing the content of the semiconductor Fe₃O₄ particles in the NCPs [18]. The high values of ε' which were detected at low frequency could be owing to the compatibility of the interfacial electric dipoles and the electrical field at that range frequency so that the dipoles at the interface has strong ability to ordination at that low frequency [17].

The dielectric loss ε'' dependence upon the frequency, f, of PVA / Fe_3O_4 NCPs shown in Figure (3) reveals sharp decrease in ε'' by increasing the applied frequency up till $\cong 10^3$ Hz after which an increase in ε'' values was detected. The dielectric loss ε'' is closely connected to the NCPs relaxation phenomena that measure the exponential decay of polarization with respect to time. The reduction in dielectric loss with increasing frequency is attributed to a variety of losses, including losses owing to dielectric nonuniformity, losses related to electrical conductivity, and Fe₃O₄ / PVA structure development [19]. The greater ε'' value in the low frequency range is due to free charge mobility inside the materials. In both instances, ϵ'' values increase by increasing Fe₃O₄ in the matrix. Anyway, the curves ε'' versus f are very complicated reflecting more than one relaxation manner [20,21]. These relaxation peaks are caused by the flexible side group or, in certain cases, by the mobility of the main chains and its correlated motions. For high performance energy storage application, the balance between high ε' and low ε'' was demanded [22]. Curves relating both ε' and ε'' at fixed f = 100 versus Fe₃O₄, Figure (3) can reflect the feature of both ε' and ε'' . From this figure it is notable that the optimum content suitable for such application was 10 wt% of Fe₃O₄ after that concentration a dramatic increase in ε'' was detected.



Figure (3): (a) ε' and ε'' versus f for PVA/Fe₃O₄ and both values versus Fe₃O₄ at fixed f = 100 Hz presented in (b) at room temperature (RT).

Cole–Cole plots aim to analyze the contribution of the relaxation mechanisms. The Nyquist diagram in Figure (4) shows the electric modulus complex smooth plots (Cole–Cole plots), M'' vs. M' (imaginary part vs. real part of the electric modulus) for PVA / Fe₃O₄. At this temperature, the Cole–Cole plots reveal two arcs. The first one relates to lower frequency, i.e., left side semicircle, is a result of crankshaft types of motion of the main polymeric chain in which a few segments are involved ($\alpha\beta$). Whereas, the second relaxation mechanism is attributed to β -relaxation this may be due to the orientation of the side chains and/or attached groups in the polymer. Clearly, the semicircles nature changed by incorporating Fe₃O₄ as depicted by the changes of the semicircles radius. This means that the relaxation mechanisms are affected by its incorporation. Moreover, the semicircle nature reduced and becomes more skewed at higher Fe₃O₄ content. The start of semicircles matched with the graph origin is a definite sign that no supplementary relaxation process is existed at lower frequencies in all investigated concentrations.



Figure (4): Cole–Cole plots of M" vs. M' for PVA doped with $Fe_3O_4 \mbox{ at RT}.$

Figure (5) depicts the change of AC conductivity with frequency for various Fe_3O_4 loading in PVA. According to the graph, for all loading conductivity rises as both frequency and content of Fe_3O_4 increases following power law function;

$\sigma = A \omega^{s}$ Eq (1)

Where ω is angular frequency, A is a parameter independent upon the frequency whiles is a power value and are found to be $s \leq 1$, it is governed by the electronic hopping processes [23,24]. It was discovered that the ac conductivity at room temperature remained constant. Conductivity rises regardless of frequency at low and high frequencies [25]. The electronic and ionic mobility rises as the concentration of Fe₃O₄ increases. As a result, as the hopping electron charge carrier interacts with the defects produced in the polymer chain, the conductivity rises [26]. DC conductivity σ_{dc} was calculated from power law fitting as declared in Figure (5) a and the obtained values are presented in Figure (5) b. The observer could clearly see that σ_{dc} values increases pronouncedly after 10 wt% loading of Fe₃O₄. From the dielectric as well as conductivity data it is concluded that 10 wt% loading of Fe₃O₄ is the much more promising composite for further investigations. For this reason BaTiO₃ in various concentrations was doped with host PVA / 10wt% Fe₃O₄ matrix to form ternary PVA composite for enhancing the electrical / magnetic properties.



Figure (5): (a) σ vs. *f* for PVA doped with different Fe₃O₄ loadings at RT. The fit lines in according to power law Eq. (1). (b)Variation of DC conductivity with Fe₃O₄ content.

The effect of various concentrations of BaTiO₃ on real part of ε' and ε'' in the frequency range $(10^{-1} 10^{6}$ Hz) and their respective graphs are given in the Fig.6. ε' measures the energy stored while ε'' is a measure of energy dissipated due to molecular collisions as the composite dipoles do work and lag for aligning themselves parallel to the applied electric field [27]. At low frequency, it is notable that both ε' and ε'' are high, this is because of the charge polarization close to the electrode – electrolyte border due to the free mobile charges in the back bone of PVA [28-30]. The increase in ε' with increasing BaTiO₃ loading is related to the fact that microcapacitors are constructed by particles near to each other and ultra-thin PVA separated in the centre under electric field [31-33]. Both ε' and ε'' decreases by increasing *f*, this is because of fact that the dipoles of composite molecules are not capable to rotate parallel with respect to speedy periodic phase turnaround of electric field and the result is time lag between the frequency of dipole and that of electric field [34], this finding means that there is no ion dissemination and charge build up. As seen in Figure (6), the ε'' of the NCPs reduced fast at low *f* values and subsequently increased somewhat at high f as the testing frequency increased. The increase in BaTiO₃ concentration resulted in a significant rise in ε'' of the NCPs at low f, which was attributed to the high leakage conductance [35] caused by the PVA /

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BaTiO₃ interface areas. At higher *f*, the values of ε'' for all NCPs changed slightly and remained low. Figure (6) b illustrates the relationship between both ε' and ε'' and BaTiO₃ loading in the nanocomposites. The general trend noticed was the abrupt increase in both values after 10% of BaTiO₃. This finding suggests that concentration to be the most promising one for energy storage applications.



Figure (6): (a) ε' and the $\varepsilon'' vs f$ for PVA / 10 wt% Fe₃O₄ / BaTiO₃ nanocomposites and both values versus BaTiO₃ at fixed f = 100 Hz presented in (b) at RT.

The Nyquist diagram in Figure (7) shows the electric modulus complex plane plots (Cole–Cole plots) drawn as M" vs. M' (imaginary part of electric modulus vs. real part of electric modulus) for PVA / 10 wt% Fe₃O₄ / BaTiO₃ nanocomposites. As in Figure (4), the Cole–Cole plots disclose two arcs corresponding to $\alpha\beta$ and β -relaxation respectively. The semicircle radius influenced by incorporating BaTiO₃ and becomes more skewed at than those in Figure (4). This a clear sign that the relaxation mechanisms are affected by BaTiO₃ incorporation.



Figure (7): M" vs. M' (imaginary part of electric modulus vs. real part of electric modulus) for PVA / 10 wt% Fe_3O_4 / $BaTiO_3$ nanocomposites at RT.

Figure (8) a, presents the variation of σ vs. frequency f for PVA / 10 wt% Fe₃O₄ doped with different BaTiO₃ loadings at RT. At low f, conductivity of all NCPs was kept at low levels, indicating low border leakage conduction in composite system [36]. At high f, σ values increase. As the concentration of BaTiO₃ increases, the electronic and ionic mobility increases. So the conductivity increases as hopping electron charge carrier interacts with the defects formed in PVA chain [26]. DC conductivity σ_{dc} was calculated as explained previously and illustrated versus BaTiO₃



in Figure (8) b. The observer could clearly see that σ_{dc} values increases pronouncedly or with loading of BaTiO₃.

Figure (8): (a) σ vs. *f* for PVA / 10 wt% Fe₃O₄ doped with different BaTiO₃ loadings (b) Variation of DC conductivity with BaTiO₃ content at RT.

However the effect of BaTiO₃ treatment with ionic liquid as mentioned before were also investigated [9]. In this investigation 10wt% Fe₃O₄ was added to the various content of treated BaTiO3 to form hybrid nanocomposites. The obtained dielectric data are presented in Figure (9). Further increase in both ε' and ε'' was detected after IL treatment see Figure (9). The permittivity ε' of hybrid NCP contain IL treated BaTiO₃ are significantly greater than that of untreated ones Figure (6). The increase in ε' with increasing IL treated BaTiO₃ content is related to the construction of the micro-capacitors by particles near to each other and ultra-thin PVA separated in the centre under electric field [37,38]. In addition, the increase in ε' values for NCPs containing IL treated BaTiO₃ when compared with those untreated Figure (6) is attributed to the presence of the low molecular weight ionic liquid which is characterized by its high ε' . This ionic liquid physically interacts with PVA and the result is decrease in the viscosity and consequently forms higher number of charge carriers [39]. Figure (9) shows also the variation of ε'' versus the frequency. Values of ε'' are directly correlated to the relaxation phenomenon of composites and considered to be the events of the exponential decay of polarization with respect to time [19]. It is also seen that the ε'' values of the NCPs increased fast at low frequencies and subsequently reduced somewhat at high frequencies as the testing frequency increased. The increase in IL treated BaTiO₃ content resulted in a significant rise in ε'' values of the nano composites at low frequencies, which was attributed to the high leakage conductance caused by the hybrid NCPs interface areas. The ε'' values reduced quicker in the NCPs with increasing IL treated BaTiO₃ percentage in the low frequency range of 10^{-1} - 10^{3} Hz. The comparatively high ε'' values of the hybrid NCPs at low frequencies should be attributed to the impeded orientation of ionic dipoles in it as a result of a strong coupling effect between the high-polarity ionic dipoles due to the presence of ionic liquid [17]. At 10^4 – 10^7 Hz, the ε'' values of all NCPs changed slightly. Overall, the ε'' values of hybrid NCP contain IL treated BaTiO3 are significantly greater than that of untreated ones. At a 10 wt% loading ε " of the film contain BaTiO₃ before treatment was about 40 at 100 Hz but it can reach up to 100 at the same frequency for NCP containing 10 wt% of IL treated BaTiO₃, approximately two times greater than the untreated one. This finding suggests such composite to be our optimum concentration recommended for energy storage applications.



Figure (9): (a) ε' and ε'' versus f for PVA / 10 wt% Fe₃O₄ / IL treated BaTiO₃ and (b) both values versus IL treated BaTiO₃ at fixed f = 100 Hz at RT.

Surprisingly the addition of untreated and IL treated BaTiO₃ to PVA / 10wt% Fe₃O₄ has a good impact on loss factor tan δ as shown in Figure (10) as it decreased upon increasing the loading of both of them. These finding suggest these composites to be recommended for high k applications.



Figure (10): The loss factor tan δ at RT versus frequency for f for the three investigated systems.

On the other hand Figure (11) a, presents the variation of σ vs. frequency *f* for PVA /10 wt% Fe₃O₄ doped with different IL treated BaTiO₃ loadings at RT. From which σ_{dc} was calculated as mentioned above and given in Figure (11) b. From this figure it is clear that the values of σ_{dc} lies in the order of 10⁻⁷ S/cm this finding highly recommend such NCPs to be used as anti dissipation composites as the demanded range for such application was 10⁻⁵ –10⁻⁹ S/cm [40].



Figure (11): (a) σ vs. f for PVA / 10 wt% Fe_3O_4 doped with different IL treated BaTiO_3 loadings at room temperature. (b) Variation of DC conductivity with IL treated BaTiO_3 content at RT.

5. Conclusion

All composites under investigations were prepared by using casting technique. Magnetic investigations led to the conclusion that the presence of ionic liquid in the nanocomposites improved the magnetic properties which recommend such composites to be used in many electromagnetic applications. The permittivity ε' and dielectric loss ε'' values of composites are found to be the optimum in case of Fe₃O₄ and treated BaTiO₃ with ionic liquid particles. The percolation threshold is defined as the stage that electrical conductivity reaches the values 10⁻⁷ S/cm. In fact the highest values of the σ_{dc} values were detected in case of IL treated BaTiO₃ / Fe₃O₄ composites. This finding recommend the using of composites for electrostatic such dissipation applications because the range needed for such

6. Acknowledgment

application is 10^{-5} – 10^{-9} S/ cm.

The authors also Acknowledge the in-house projects in National Research Centre, Dokki, Giza, Egypt for funding support of this work through the in-house project no 12020225.

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