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Effect of nanoTiO₂ dopant on electrical properties of SR8100/nanoTiO₂ PMNC



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Introduction

During the recent decade polymer doped with ceramic oxide nano filler composite has received a great attention due to their interesting electrical and electronic properties [1–3]. Nano particle ceramic oxide fillers including TiO₂, SiO₂, and Al₂O₃ have previously been shown to have a significant effect on the electrical properties of polymers [4,5]. In some cases conductivity increases of more than one order of magnitude have been reported in several cases such as in crystalline PEO-based complexes. Ceramic oxide nano filler contributes to these enhancements by promoting the polymer structure [2,6-8]. In addition, most ceramic-polymer nanocomposites are easily fabricated and are usually of reduced weight compared to all-ceramic materials. These factors are of tremendous attractions in energy storage application. However, most ceramic nano fillers are difficult to distribute homogeneously in the polymer matrix and it results in the agglomeration, especially when the concentration of the ceramic nano fillers is high. The inhomogeneity has negative influences on the electric properties of the nanocomposites [9,10]. So far, much work has been made to improve the dispersion of ceramic nano fillers in the polymer matrix [11–17]. SR8100 is a promising polymer with good

ABSTRACT

SR 8100 epoxy was doped with nTiO₂ nano filler to produce a semiconducting PMNC. The specimen made of SR8100/nanoTiO₂ PMNC with nanoTiO₂ content ranges from 1 to 5 wt% with 1% step prepared by hot vibrate dispersion (HVD). Morphology changes in polymer were detected by XRD and it has been found that SR8100 begins to have a crystalline nature when nanoTiO₂ concentration was 3%, 4% and 5%. Electrical resistivity increases from $1*10^{-9} \Omega$ m for SR8100 up to $2.3*10^{-4} \Omega$ m for SR8100/5% nanoTiO₂ PMNC which means that the material turns from an insulator to a semiconductor. © 2015 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY license (http://

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mechanical properties and low cost produced by Sicomen company in USA, electrical resistivity of this polymer is $1*10^{-9} \Omega$ m [18]. Nano titania nanoTiO₂ on the other hand is one of the most widely nano ceramic oxide fillers used with an electrical resistivity of $1^*10^{13} \Omega$ m [19–22]. Modification effect of m-TiO₂/silicon rubber composite on electrical properties was investigated. It was found that this addition leads to a decrease in both dielectric loss and resistivity of the composites. This can be taken charge by the much uniform dispersion state of m-TiO₂ as well as an enhanced interaction with SR matrix [23]. Aim of this research is to prepare a new PMNC made of SR8100 matrix, and nanoTiO₂ dopant with five different weight percent. PMNC was prepared using hot vibration dispersion method to ensure a good dispersion for the nanoTiO₂ through the SR8100 matrix, the effect of this dopant on morphology, electrical resistivity, and electrical conductivity of the SR8100/nanoTiO₂ PMNC was studied.

Experimental

Materials

SR8100 polymer containing resin and hardener was purchased from SICOMEN, USA (99.9%) and 10 nm TiO₂ from HORIBA, Germany.

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Fig. 1. XRD of SR8100/nanoTiO₂ PMNCs.

Table 1

Lattice parameters of nanoTiO2 rutile, nanoTiO2 anatase.

-	iiiio ₂ iutile	$nTiO_2$ anatase
Lattice	Cubic	Cubic
S.G	Pn3m (224)	Fm3m (225)
a = b = c	4.26960 Å	5.64020 Å
a/b = a/c	1.00000	1.00000
$\alpha = \beta = \gamma$	90°	90°
Ζ	2	4
Mol. weight	143.09	58.44
Volum [CD]	77.83	179.4
Dx	6.106	2.163
Dm	-	2
l/lcor	-	4.40

Method of preparation

Polymer matrix discs were prepared using mould with 1 cm diameter, and 1 cm height, resin and hardener was mixed by 1:3, stirred by a magnetic stirrer for 5 min, then it was poured into the mould leaving for 24 h. After solidification the polymer discs put in 1^{*1} cm cylindrical mould with a moving base, on the base the TiO₂ nano powder was spread, the mould then was heated

up to 120 °C and vibrated ultrasonically for 1hr to ensure a uniform dispersion of TiO_2 nano particles in the SR8100 polymer matrix, then it was left to cool down to room temperature. The specimen was tested by XRD to detect their properties.

Results and discussion

Among all the ceramic oxide nano fillers nanoTiO₂ exerted the highest effect on the PMNCs especially on the electrical properties, this improvement in electrical properties was observed for nanoTiO₂. Filled polymers could be due to one and/or more of the following factors (i) the large surface area of nano particles which creates a large interaction zone or region of altered polymer behaviour, (ii) change in the polymer morphology due to the surfaces of nano particles, (iii) a reduction in the internal field caused by the decrease in the size of the particles, (iv) change in the space charge distribution, (v) scattering mechanism [23–25]. This brief introduction will be very useful all over our discussion.

SR8100/nanoTiO₂ PMNCs morphology

X-ray diffraction (XRD) was used to investigate changes in SR8100 polymer matrix after the addition of 1-5% weight percent of nanoTiO₂ ceramic oxide nano filler, results are shown in Fig. 1.

Fig. 1 illustrates XRD of SR8100 and SR8100/nanoTiO₂ PMNCs with nanoTiO₂ weight percent from 1% to 5%, respectively. It is obvious that the starting material is amorphous with no peaks on XRD. Peaks begin to appear when nanoTiO₂ concentration exceeds 3% weight and become very clear at the top three specimens where nanoTiO₂ is equal to 3%, 4% and 5% weight . XRD also indicates that these peaks are related to the presence of nanoTiO₂ rutile, and nanoTiO₂ anatase. The last may be found as an impurity in the starting material, or it may be produced by the action of fabrication method due to the vibrating and heating of SR8100 polymer leading to release of some internal energy causing this phase transition. Never the less nanoTiO₂ anatase presence leads us to expect some unusual changes in the properties of the SR8100/nanoTiO₂ PMNCs [23,24].

Table 1 shows lattice parameters of nanoTiO₂ rutile, and anatase respectively. From data given in Table 1 we clearly see that the cubic shape of nanoTiO₂ rutile, and anatase is reserved where a = b = c and this equal to 4.2696 Å for rutile, and 5.6402 Å for anatase, according to this fact we must consider an important fact that there will be different stretching values in the polymer structure caused by the difference in the dimension of cubic nanoTiO₂



Fig. 2. FTIR of SR8100/nTiO2 PMNC.

Table 2Electrical resistivity of SR8100, nTiO2, and SR8100/nTiO2 PMNC.

Specimen Number	Specimen composition	Resistivity (Ωm)
1	SR8100	1*10 ⁻⁹
2	nTiO ₂	1*10 ⁻¹³
3	SR8100 + 1% nTiO ₂	8.21*10 ⁻⁸
4	SR8100 + 2% n TiO ₂	3*10 ⁻⁷
5	SR8100 + 3% n TiO ₂	$4.65^{*}10^{-5}$
6	SR8100 + 4% n TiO ₂	$5.71^{*}10^{-4}$
7	SR8100 + 5% n TiO ₂	$2.30^{*}10^{-4}$

Table 3

Electrical resistivity of Ti-O system.

Ti-O system	Chemical formula	Resistivity (Ωm)
1	TiO ₂	1*10 ⁻¹³
2	Ti ₈ O ₅	4*10 ⁻²
3	Ti ₆ O ₁₁	$1.6^{*}10^{-2}$
4	$Ti_5O_9 + Ti_6O_{11}$	$2^{*}10^{-3}$
5	Ti ₅ O ₉	1.6*10 ⁻³
6	$Ti_4O_7 + Ti_5O_9$	3*10 ⁻³
7	Ti ₄ O ₇	$9.7^{*}10^{-4}$
8	$Ti_{3}O_{5} + Ti_{4}O_{7}$	$2.4^{*}10^{-3}$
9	Ti ₃ O ₅	1.6*10 ⁻³

rutile and anatase leading to a high changes in energy levels within the $SR8100/nanoTiO_2$ PMNCs which will have an effect on the resultant electrical properties of the specimen.

Fig. 2 illustrates FTIR of $SR8100/TiO_2$ PMNC. Peaks at 1427, 1635 refer to phases where SR8100 epoxy is dominant, while peaks at 3587, 3525, and 3464 are places where $nTiO_2$ concentrate [28].

Electrical resistivity

Electrical resistivity of SR8100/nanoTiO2 PMNCs was measured using meager device; the results are listed in Table 2.

In the present work electrical resistivity of SR8100/nanoTiO₂ PMNCs increased from $1*10^{-9} \Omega$ m for pure SR8100 polymer matrix up to $2.3*10^{-4} \Omega$ m to SR8100/5%nanoTiO₂ PMNC. This means that the material turns from being an insulator to a semiconductor, where the limit of semiconductors is $10^{-6} < 6 < 10^5 \Omega$ m [27–33]. This can be explained through two point views.

1st quantum theory

This huge enhance in conductivity of the SR8100/nanoTiO₂ PMNC can be related to the presence of electrons near HOMO, and LUMO regions which means more excited electrons in LUMO region, and this can be seen from resistivity values in Table 1 where we can see a huge transition in conductivity values due to the decrease in resistivity. This result was also certified by peaks in XRD (see Fig. 1) where PMNC reaches a stable crystalline structure. Crystallinity came from oxygen voids within the polymer due to the vibration during specimen preparation by hot vibrate dispersion and this leads to formation of a bend in energy levels creating several new energy sublevels in the material as we mentioned earlier in the introduction of our discussion. These new energy levels make electron transition more easy and hence increase electrical conductivity. So far this is a very interesting result and very important in several applications which we shall work on in the future.

2nd Ti-O system

The Ti–O system has several forms beside TiO₂, each form has a different electrical resistivity. These forms are illustrated in Table 3 [25].

As it is clear from the table above there are nine values for electrical resistivity within the Ti–O system range from 10^{13} for nanoTiO₂ to 7.9*10⁻⁴, this means that several forms of Ti–O system lie in the region of semiconductor material and this may explain resistivity values in Table 2. Oxygen concentration will also increase due to the hot vibrate dispersion technique of SR8100/nanoTiO₂ PMNC because of the combined action of ultrasonic, heating, and extra low particle size and very high surface area of nanoTiO₂ all these factors together will lead to form one or more of Ti–O system components, and this will decrease electrical resistivity of the produced PMNC. In addition to these two point views, this behaviour can be taken charge by the much uniform dispersion state of nTiO₂ as well as an enhanced interaction with SR matrix [23].

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Further reading

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