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Fabrication and Properties of Film Nanocomposites (PVA–PAA)_{1-x}/TiN_x for Energy Storage and Release Application

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Nanocomposites are actually promising materials in many modern industrial or medical applications, which are attributed to their good properties such as light weight, high flexibility, resistance to oxidation, cheap price, good electrical, optical, and mechanical properties. In this paper, fabrication of polyvinyl alcohol (PVA)–polyacrylic acid (PAA)–titanium nitride (TiN) nanocomposites with low weight, low cost, high corrosion resistance and high efficiency for thermal energy storage and release is investigated. The structural and dielectric properties of (PVA–PAA–TiN) nanocomposites are studied. The experimental results show that the dielectric constant and dielectric loss of (PVA–PAA–TiN) nanocomposites decrease with increase in frequency, while the electrical conductivity increases as frequency increases. The dielectric parameters of polymer blend increase with increase in TiN-nanoparticles' concentration. The results of solar energy storage and release show the decrease in melting and solidification times as the TiN-nanoparticles' concentration increases.

Нанокомпозити насправді є перспективними матеріалами в багатьох сучасних промислових або медичних застосуваннях, які приписуються їхнім хорошим властивостям, таким як невелика вага, висока гнучкість, стійкість до окиснення, дешева ціна, хороші електричні, оптичні та механічні властивості. У цій роботі досліджено виготовлення нанокомпозитів полівінілалкоголь (ПВА)–поліакрилова кислота (ПАК)–нітрид титану (TiN) з низькою вагою, низькою вартістю, високою корозійною стійкістю та високою ефективністю для зберігання та вивільнення теплової енергії. Досліджено структурні та діелектричні властивості нанокомпозитів (ПВА–ПАК–TiN). Експериментальні результати показують, що діелектрична проникність та діелектричні втрати нанокомпозитів (ПВА–ПАК–TiN) зменшуються зі збільшенням частоти, в той час як електропровідність збільшується зі збільшенням частоти. Діелектричні параметри полімерної суміші збільшуються зі збільшен-

ням концентрації TiN-наночастинок. Результати зберігання та вивільнення сонячної енергії показують зменшення часу топлення та затвердіння, оскільки концентрація наночастинок TiN збільшується.

Key words: titanium nitride, nanocomposites, dielectric properties, conductivity, solar energy.

Ключові слова: нітрид титану, нанокомпозити, діелектричні властивості, провідність, сонячна енергія.

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1. INTRODUCTION

Recently, there has been a constant search for new materials that possess good dielectric permittivity and good mechanical properties for important technological applications. Polymers are materials with low-density flexible, easy to synthesized, superior in dielectric breakdown strength and mechanically more compliant than the ceramics; but its dielectric values are much lower than those of the ceramics. On the other hand, ferroelectric ceramics possess high values of dielectric permittivity, but with poor mechanical properties and lower dielectric breakdown strength. By integrating high values of dielectric permittivity of the ceramic powder with superior dielectric strength of the polymer, it is possible to develop a composite with high dielectric permittivity and high breakdown strength. This type of composites has high capability of energy storage and can be used in capacitors and energy storage devices. The easiness of composite synthesis allows producing thin film capacitors, which are difficult to achieve with ceramics due to complicated fabrication routes.

Polyvinyl alcohol (PVA) is a good insulating material with low conductivity; hence, it is very useful in industry of microelectronics. Its electrical conductivity depends on the thermally generated carriers and with the addition of suitable dopants. Moreover, the polyvinyl alcohol extends the industrial applications in pharmaceutical, membrane medical and optical fields. Polyvinyl alcohol is a semi-crystalline material with several interesting physical properties, which are very useful in technical applications. Different additives have been added into polyvinyl alcohol to modify and improve its dielectric properties. Inorganic additives, such as transition metal salts, have a considerable effect on the optical and electrical properties of polyvinyl alcohol [1].

Polyacrylic acid (PAA) is a non-toxic, hydrophilic and biocompatible superabsorbent polymer with a three dimensional (3D) network. PAA was chosen as a host polymer in this research due to its fasci-

nating behaviours, such as excellent stability in acidic and basic media, high ionic conductivity, strong adhesive properties, superior selectivity and permeability, and high ability to associate with a variety of multivalent metal ions in solution [2].

Transition metal nitrides, especially titanium nitride (TiN), have been studied for the last three decades due to the unique combination of their material properties. Metallic behaviour of TiN combined with its hardness and chemical stability has attracted attention in microelectronics research [3].

Abundance of renewable energies available in nature should be harnessed and utilized to meet the growing power demand for sustained future. Renewable energy systems play a vital role in energy savings and reduction of global gas emission to have a pollution free environment for future generations. Solar energy claims to be the primary source among various renewable energy sources, which is intermittent and uncertain by its nature. Henceforth, a need arises to develop thermal storage systems to store the available excess energy for later use. Thermal energy storage system should possess good storage capacity, high efficiency, quick charging-discharging, cost effective, and hazard free.

Phase change materials (PCMs) with their heat storage and releasing behaviour have found suitable for latent heat storage systems that can be operated at wide range of temperatures. High-energy process of PCMs (latent heat of vaporization) is not preferred due to their large density changes, which are need in additional support equipment. Hence, latent heat of fusion of PCMs is utilized for thermal applications. Incorporation of nanomaterials could possibly increase the thermal conductivity of the PCMs with their high surface area to volume ratio.

Aluminium oxide (Al₂O₃), copper (Cu), copper oxide (CuO), gold (Au), silver (Ag), silicon carbide (SiC), titanium carbide (TiC), titanium oxide (TiO₂), and carbon nanotubes were some of the nanoparticles used for thermal applications [4].

The low heat flux achieved due to the low thermal conductivity of most phase change materials, which drastically affects the melting and solidification performance of the system, widespread use of latent heat stores has not yet been realised. A larger heat flux can be achieved by enhancing the effective thermal conductivity. Different approaches have been proposed to overcome this problem; use of metal thin strips, porous metals, porous graphite, metal foam matrix and carbon fibres are among the common techniques used to enhance the effective thermal conductivity of PCMs. The presence of the nanoparticles in the PCMs increases significantly the effective thermal conductivity of fluid and consequently enhances the heat transfer characteristics [5].

Polymeric nanocomposites consisting of organic polymers and inorganic nanoparticles represent a class of materials, which have motivated considerable interest in recent years. The nanocomposites' applications are rather promising in the fields of medicine, injection moulded products, automobiles, optical integrated circuits, aerospace, packaging materials, coatings, microelectronics, packaging drug delivery, sensors, membranes, fire-retardants, adhesives, consumer goods, *etc.* [6–11].

2. MATERIALS AND METHODS

The (PVA–PAA–TiN) nanocomposites are fabricated by dissolving 1 gm of polyvinyl alcohol and polyacrylic acid in 30 ml of distilled water with weight percentage of 85 wt.% PVA and 15 wt.% PAA by using magnetic stirrer to mix the polymers for 1 hour to obtain solution that is more homogeneous. The titanium-nitride nanoparticles (TiN NPs) were added to (PVA–PAA) blend with different concentrations (1.5, 3, 4.5 and 6 wt.%). The casting method is used to prepare the nanocomposite samples in the template (Petri dish has diameter of 10 cm).

The dielectric properties of samples tested with frequency range from 100 Hz to $5 \cdot 10^6$ Hz by using LCR metre type (HIOKI 3532-50 LCR HI TESTER). The thermal energy storage and release applications include analysing the melting and solidification characteristics of nanofluids during heating and cooling processes. The water and nanofluids were used as the heat-transfer fluid, whose temperature can be varied from 20°C to 90°C, with stirrer and measuring the temperature of nanofluids during the heating and cooling processes by digital device.

The dielectric constant (ϵ') of nanocomposites is given by the equation [12]:

$$\epsilon' = C_p / C_o, \quad (1)$$

where C_p is parallel capacitance and C_o is vacuum capacitor. The dielectric loss (ϵ'') is calculated by the following equation [13]:

$$\epsilon'' = \epsilon' D, \quad (2)$$

where D is dispersion factor. The A.C. electrical conductivity of (PVA–PAA–TiN) is calculated by the following equation [14]:

$$\sigma_{A.C.} = w \epsilon'' \epsilon_o, \quad (3)$$

where w is the angular frequency.

3. RESULTS AND DISCUSSION

Figures 1 and 2 show the variation of the dielectric constant of the (PVA-PAA-TiN) nanocomposites with TiN-nanoparticles' concentration and frequency, respectively, within the frequency range $100-5 \cdot 10^6$ Hz.

It is observed that the dielectric constant of the (PVA-PAA-TiN) nanocomposites decreases as the frequency increases, *i.e.*, the dielectric constant has higher values in the low-frequency range, and then it decreases as the frequency increases. This behaviour has

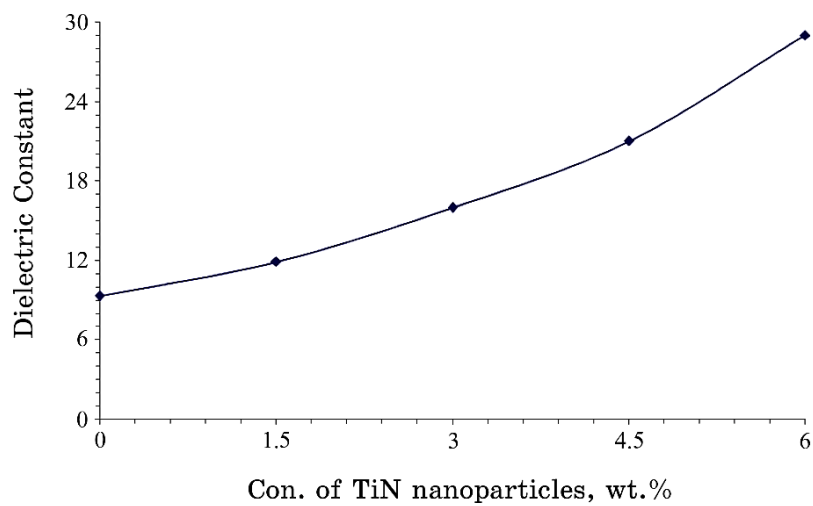


Fig. 1. Effect of TiN-nanoparticles' concentration on dielectric constant for (PVA-PAA) blend at 100 Hz.

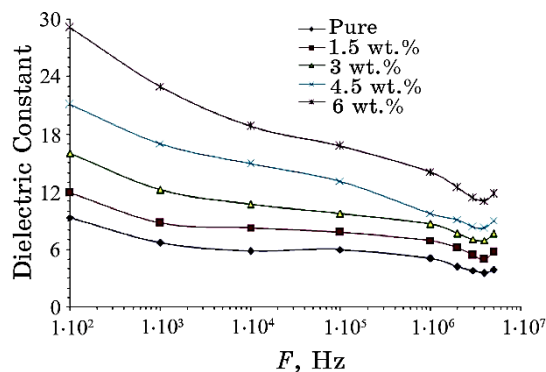


Fig. 2. Variation of dielectric constant for (PVA-PAA-TiN) nanocomposites with frequency at room temperature.

been attributed to the fact that there are all types of polarizations: electronic, ionic, dipolar, and space-charge polarization (Maxwell–Wagner polarization) in the low-frequency range. The behaviour in the high-frequency range is quite different because the electric dipoles cannot follow up the frequency of the applied electric field [15–19].

Figures 3 and 4 show the variation of the dielectric loss of the (PVA–PAA–TiN) nanocomposites with TiN-nanoparticles' concentration and frequency, respectively. It is clear that the values of the

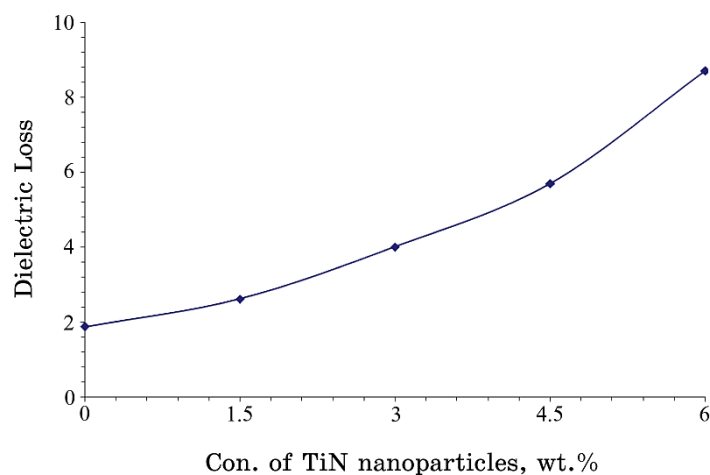


Fig. 3. Effect of TiN-nanoparticles' concentration on dielectrics loss for (PVA–PAA) blend at 100 Hz.

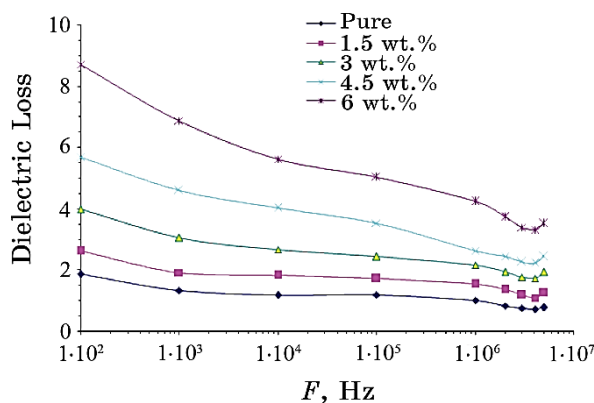


Fig. 4. Variation of dielectrics loss for (PVA–PAA–TiN) nanocomposites with frequency at room temperature.

dielectric loss of the (PVA-PAA-TiN) nanocomposites are very high at low frequencies. Such a high value of dielectric loss at low frequencies has been explained by the presence of space-charge effects, which is contributed by the accumulation of charge carriers near the electrodes. At higher frequencies, dielectric loss values of the (PVA-PAA-TiN) nanocomposites have been found to be relatively constant with frequency. This is because periodical reversal of field takes place so rapidly that the charge carriers will hardly be able to orient themselves in the field direction resulting in the decrease in dielectric loss.

At low titanium-nitride nanoparticles' concentration, the dielec-

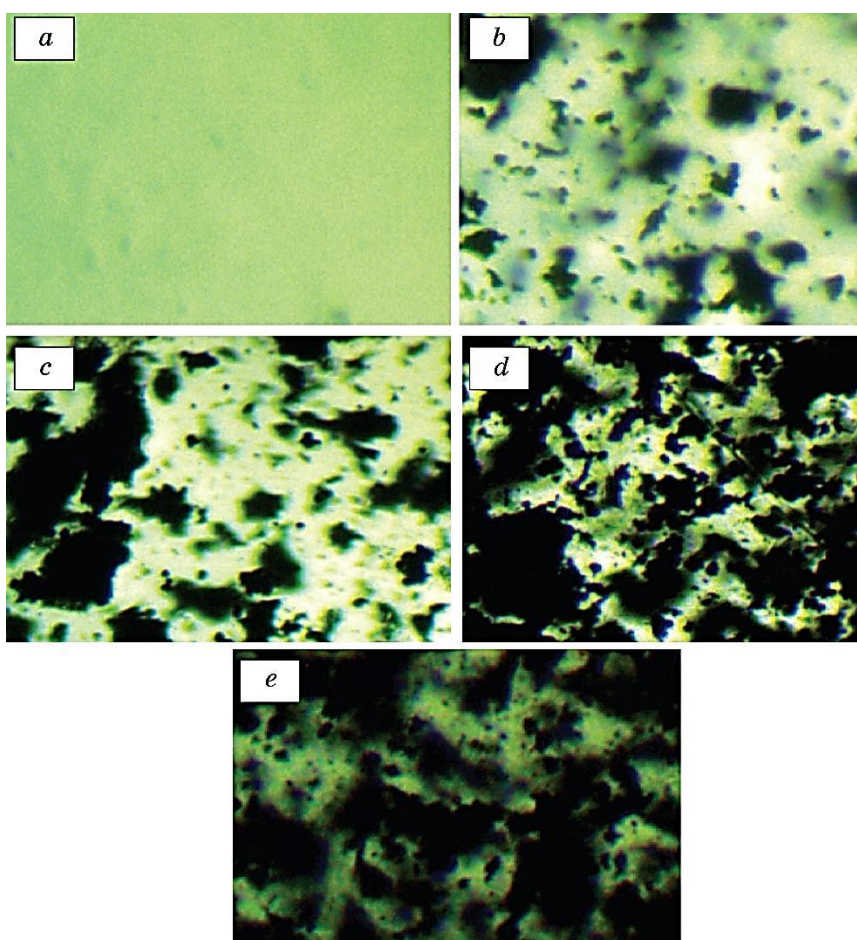


Fig. 5. Photomicrographs ($\times 10$) for (PVA-PAA-TiN) nanocomposites: (a) for (PVA-PVA) blend; (b) for 1.5 wt.% TiN; (c) for 3 wt.% TiN; (d) for 4.5 wt.% TiN; (e) for 6 wt.% TiN.

tric constant and dielectric loss values of the (PVA-PAA-TiN) nanocomposites are low. The increase of titanium-nitride nanoparticles' concentration caused an increase in the average number of concentrations among the titanium-nitride nanoparticles. At high concentrations of titanium-nitride nanoparticles, the dielectric constant and dielectric loss of the (PVA-PAA-TiN) nanocomposites are due to formation of a continuous network of nanoparticles through the nanocomposites [20], as shown in Fig. 5.

The variation of electrical conductivity for (PVA-PAA-TiN) nanocomposites with TiN nanoparticles' weight percentages is shown in Fig. 6 at 100 Hz. From this figure, the electrical conductivity increases as the TiN-nanoparticles' concentration increases. This increase of the conductivity is caused by the increase the number of charge carriers due to dopant TiN-nanoparticles' composition, which reduces the resistance of (PVA-PAA-TiN) nanocomposite and increase the conductivity. At high concentrations of TiN nanoparticles, the nanoparticles form a network in the (PVA-PAA-TiN) nanocomposite.

Figure 7 shows the variation of electrical conductivity of (PVA-PAA-TiN) nanocomposites with frequency. The conductivity increases with frequency of electric field increasing; this behaviour is attributed to the mobility of charge carriers and the hopping of ions from the cluster.

In the low-frequency range, more charge accumulation is occurred at the electrode and electrolyte interface, leading to the number of mobile ions and electrical conductivity decrease. The

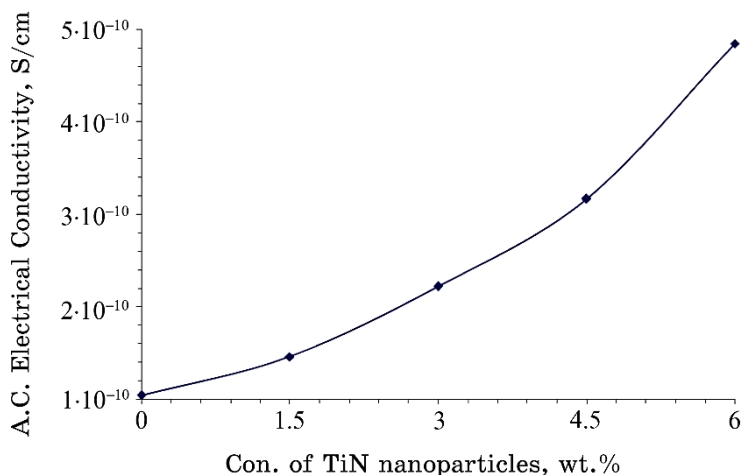


Fig. 6. Effect of TiN-nanoparticles' concentration on A.C. electrical conductivity for (PVA-PAA) blend at 100 Hz.

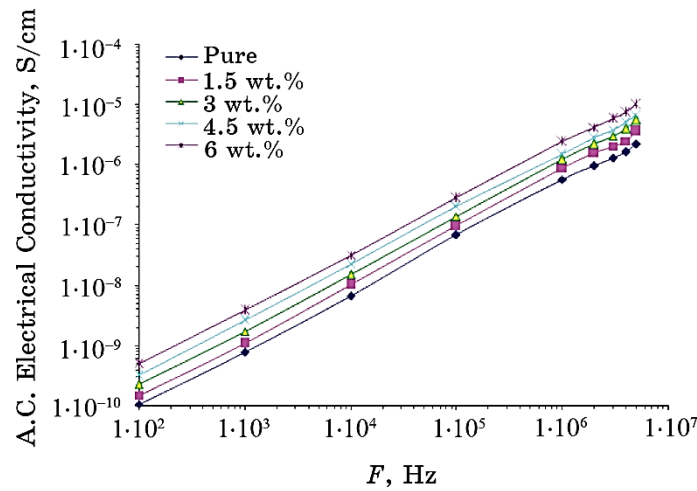


Fig. 7. Variation of A.C. electrical conductivity for (PVA-PAA-TiN) nanocomposites with frequency at room temperature.

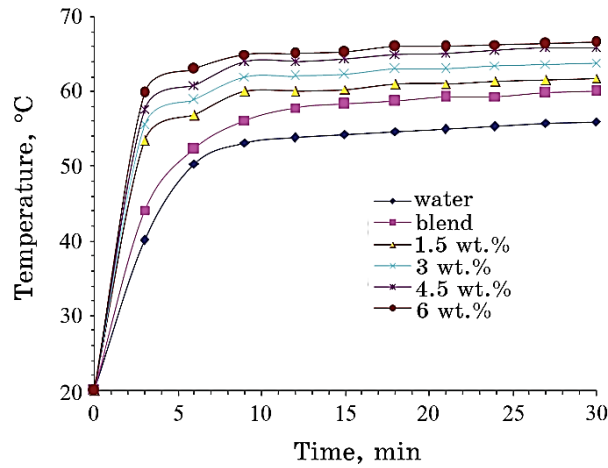


Fig. 8. Melting curves of (PVA-PAA-TiN) nanocomposites.

charge carriers' mobility was higher in the high-frequency region; hence, the conductivity increases with frequency [21–25].

Figures 8 and 9 display the melting and solidification curves for (PVA-PAA-TiN) nanocomposites, respectively. The times of melting and solidification decrease with inserting TiN-nanoparticles' concentration.

This is a good criterion to evolve the entire thermal conductivity of (PVA-PAA) nanofluid. Energy storage and release average are substantial signals to increase the efficiency of heat transfer. The

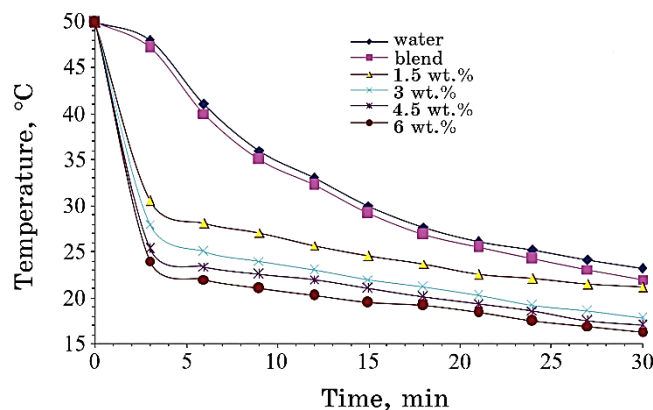


Fig. 9. Solidification curves of (PVA-PAA-TiN) nanocomposites.

decrease of melting and solidification times is related to improve the thermal conductivity [26–31].

4. CONCLUSIONS

The dielectric parameters (dielectric constant, dielectric loss, and electrical conductivity) of (PVA-PAA) blend increase as the titanium-nitride nanoparticles' concentration increases.

The dielectric constant and dielectric loss of (PVA-PAA-TiN) nanocomposites decrease, while the conductivity increases with increase in frequency.

The (PVA-PAA-TiN) nanocomposites have high efficiency for solar energy storage and release with low weight, high corrosion resistance and low cost. The melting and solidification times decrease with increase in TiN-nanoparticles' concentration.

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