Largely enhanced dielectric properties of TiO2-nanorods/poly(vinylidene fluoride) nanocomposites driven by enhanced interfacial areas

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ABSTRACT

In this work, nanocomposites consisting of TiO2-nanorods (TiO2-NRs) with less than 100 nm in size and poly(vinylidene fluoride) (PVDF) were prepared using a liquid-phase assisted dispersion and hot-pressing methods. At 1 kHz and 25°C, the high dielectric permittivity of ~66 and loss tangent of ~0.03 can be obtained in the nanocomposite with a filler volume fraction of 0.5, which was higher than that of a neat PVDF matrix by a factor of 6. Dielectric permittivity of TiO2-NRs/PVDF nanocomposites not only highly increased with TiO2-NRs, but also almost independent of the frequency range of 10^2–10^6 Hz. The significant enhancement in dielectric permittivity is mainly attributed to the interfacial polarization at the interfaces of TiO2-NRs and PVDF, and semiconducting properties of TiO2-NRs. Among the various models used for rationalizing the dielectric behavior, the experimental dielectric data is in close agreement with EMT ($n = 0.11$) and Yamada models ($n = 8$).

1. Introduction

High dielectric performance materials have attracted intensive attention in the fields of electronics and energy storage. In the last decade, dielectric polymer composites have been made for preparing embedded capacitors, gate dielectrics, and electric energy storage devices to meet the requirement of miniaturization trend of integrated circuits [1–9]. This is because common polymers are lightweight, flexible, have excellent mechanical strength, and are easily integrated. However, most pure polymers show low dielectric permittivity ($\varepsilon'$) in the range of 2–5 [2,10]. Poly(vinylidene fluoride) (PVDF) is well known for having piezo-ferroelectricity characteristics and has enormous potential for use in industrial applications [2]. With the advantages, outstanding properties, and high dielectric performance of PVDF, dielectric composites based on the PVDF matrix have drawn considerable attraction in potential electronic applications. The strategy to obtain dielectric composites is to combine high dielectric ceramics and polymers to form ceramic/polymer composites. Many works had widely reported composites with various kinds of ceramic fillers into the polymer.
matrix to enhance their high dielectric such as Pb(Zr,Ti)O₃ (PZT) [11], Pb(Mg₁/₃Nb₂/₃)O₃–PbTiO₃
(PMN–PT) [12], Ba(Zn₁/₃Ta₂/₃)O₃ (BZN) [13], CaCu₃Ti₄O₁₂ (CCTO) [14–16], Na₀.₅Bi₀.₅Cu₃Ti₄O₁₂
(NBTCO) [17], Na₀.₅Y₀.₅Cu₃Ti₄O₁₂ (NYCTO) [18], BaTiO₃ (BT) [19–21], and Ba₀.₆Sr₀.₄TiO₃ (BST)
[9,22,23]. However, fillers contain lead (e.g. PZT and PMN–PT) which is not environmentally
friendly. Therefore, lead-free fillers such as ACTO and their family (A = Na₀.₅Bi₀.₅, Na₀.₅Y₀.₅, Na₁/₃
Ca₁/₃Bi₁/₃) have yet to attain satisfactory performance. Although ACTO is a lead-free fillers and can
lead to the formation of composites with high ε’ (by a factor of 10³–10⁵), their loss tangent (tanδ) is also
high (>0.1) at 1 kHz [17,18,24]. High tanδ is one of the most serious factors for the use of the dielectric
polymer composites, which is necessary to solve this problem to harness their dielectric performance.
Besides, it was found that the tanδ value was usually remained low (~0.04) for polymer composites con-
taining ferroelectric BT [25], which is lower than that of ACTO compounds. Unfortunately, ε’ of BT is
strongly dependent on the temperature near Curie temperature (Tc), resulting in mechanical res-
sonance in the device during charging and discharging [26]. This is unsuitable for developing for use in electrical devices.

To meet the requirement of high ε’, low tanδ, ε’ stable ability and environmental friendly, TiO₂ has
received much attention thanks to its stability, abundant, environmental friendly, and low toxicity char-
acter [27–30]. Therefore, it is widely used in many applications such as sensors, catalysis, and photocata-
ylist battery. It is worth noting that high ε’ were found in rutile-TiO₂ ceramic bulks due to the exist-
ence of polaron-like electron hopping between Ti⁵⁺ and Ti⁴⁺ ions and oxygen vacancies in bulk ceramic
by pentavalent ions [29,30]. Hence, rutile-TiO₂ particles have been used as fillers in a polymer matrix
to create composites (e,g. TiO₂/PVDF [31], TiO₂/PENs [32], (Er + Nb) co-doped TiO₂/P(VDF-TrFE)
[33], and TiO₂/PDMS [34]). One of the most significant effects that enhanced the dielectric properties of these TiO₂/polymer composites is interfacial polarization. Accordingly, the interfacial area is one of the most important factors contributing to the intensity of interfacial polarization. The surface area of any filler nanoparticle with a spherical shape (aspect ratio = 1) can be increased by using this filler material in other shapes with an aspect ratio of more than 1 such as in nanorods or nanofibers. It was also reported that the dielectric properties of the TiO₂ nanorod array/PVDF composites could be improved. However, the ε’ value was ~32.5 at 1 kHz
[35]. Furthermore, the TiO₂ nanorod array/PVDF composite system was fabricated by a complex
method using multistage processing. To the best of our knowledge, there is no report on the fabrication
and dielectric properties of TiO₂ nanorod/PVDF composites with random dispersion of TiO₂ nano-
rods. Thus, the aim of this work is to improve the dielectric properties of the TiO₂/PVDF composite system using TiO₂ nanorods as a filler. It is expected that the dielectric response in the composite can be enhanced due to the increased interfacial areas of the filler.

In this work, we prepared two-phase polymer nanocomposites comprising a new rutile-TiO₂ with
nanorod shape and PVDF polymer. TiO₂-nanorods (TiO₂-NR)/PVDF nanocomposites were fabricated
using liquid-phase assisted dispersion and hot-pressing methods. The phase composition, morphologies,
microstructures, oxidation stages, and dielectric properties of nanocomposite are investigated. Various theoretical models, including the Maxwell – Garnett model, logarithmic model, effect-
ive medium theory model, and Yamada model, were used to predict the dielectric behavior of the TiO₂-
NRs/PVDF nanocomposite.

2. Experimental details

2.1. Preparation of heat treatment of TiO₂-NRs

TiO₂-NRs with particle size <100 nm (99.5%, Sigma-Aldrich) were heat treatment at 500 °C for
3 h in air to evaporate the moisture. After that, TiO₂-NRs were obtained to cool down at 25 °C.

2.2. Preparation of TiO₂-NRs/PVDF nanocomposites

TiO₂-NRs were used as filler into commercial PVDF powder (Mw ~ 534,000, Sigma-Aldrich) were heat treatment at 200 °C for 30 mins with a pressure of 10 MPa. Finally, the sample of polymer nanocomposites with a diameter of about 12 mm and a thickness of about 0.6–1 mm was obtained. Note that, for a pure PVDF polymer sample, a PVDF powder was mixed by ball milling with ZrO₂ balls in absolute ethanol for 3 h. Second, the mixture was dried at 80 °C for 24 h to evaporate the absolute ethanol. Then, the dry mixed powder was molded by hot-pressing at 200 °C for 30 mins with a pressure of 10 MPa. Then, the dried powder of PVDF particles was molded by hot-pressing
at 200 °C for 30 mins with a pressure of 10 MPa.
2.3. Characterization

The phase structures and crystal composition of fillers, PVDF, and polymer nanocomposites were characterized by an X-ray diffractometer (XRd, PANalytical, EMPYREAN, Netherlands). Surface morphologies of TiO2-NRs were revealed using transmission electron microscopy (TEM, FEI Tecnai G², Netherlands). The oxidation stages of TiO2-NRs/PVDF nanocomposites were analyzed by X-ray photoelectron spectroscopy (XPS, PHI5000 VersaProbe II, ULVAC – PHI, Japan) at the SUT-NANOTEC – SLRI Joint Research Facility, Synchrotron Light Research Institute (SLRI), Thailand. The crystalline phase of PVDF and nanocomposites was determined using Fourier transform infrared spectroscopy (FTIR, Bruker, TENSOR27, Germany) in the range of wave number 600–2000 cm⁻¹. The fractured microstructure of the nanocomposites was characterized using a focus ion beam-field emission scanning electron microscope (FIB – FESEM, FEI Helios Nanolab G3 CX, USA). Before FESEM characterization, nanocomposite samples were fractured by liquid N₂, and then their surfaces were coated using gold using the sputtering technique. Capacitance (Cp) and tanδ (D) were measured using an Impedance analyzer (KEYSIGHT E4990A, USA) over the frequency range of 10²–10⁶ Hz with an oscillation voltage of 0.5 volts. Before dielectric measurements, the top and bottom surfaces of the samples were painted with an Ag paste as the electrodes and dried at 150 °C for 2 h.

3. Results and discussion

Figure 1 displays the XRD pattern of TiO2-NRs. The result shows that the sample exhibits diffraction peaks at 2θ of 20°–80° corresponding to the planes of (110), (101), (200), (111), (210), (211), (220), (002), (310), (301) and (112). It is confirmed that the main phases can be indexed to the rutile phase of TiO₂ with a tetragonal structure (JCPDS 21-1276). In this case, the characteristic peaks were observed at the same position compared to the rutile-TiO₂ standard data, which indicates the temperature of heat treatment at 500°C has no effect on the phase and crystallinity of the TiO₂-NRs. The impurity phase was not observed in TiO₂-NRs. Surface morphologies of TiO₂-NRs were revealed by TEM technique, as illustrated in the inset of Figure 1. The size of submicron TiO₂-NRs is less than approximately 100 nm with rod shape and smooth surface.

XRD patterns of PVDF, TiO₂-NRs, and TiO₂-NR/PVDF nanocomposites with various content loading of TiO₂-NRs are presented in Figure 2. The diffraction peaks of PVDF corresponding to the (100), (020), (110), and (021) planes were observed, which were assigned to the α-phase [10]. The nanocomposites show high diffraction intensity of PVDF at only low f̃ (TiO₂-NRs). With increasing f̃ (TiO₂-NRs), the intensity of PVDF decreased while the intensity of TiO₂-NRs increased. It is due to the crystalline structure of TiO₂-NRs more dominant than the semi-crystalline structure of PVDF. All nanocomposites show intensity peaks of TiO₂ and no impurity was observed.

Among the five known crystalline forms of PVDF, namely α-, γ-, ε-, δ-, and β [31], the β-phase results in good piezoelectric, ferroelectric and dielectric properties. Unfortunately, the β-phase cannot be observed by XRD. To further investigate the β-phase, FTIR characterization was collected. Figure 3 shows the FTIR spectra of PVDF and TiO₂-NR/ PVDF nanocomposites with different f̃ (TiO₂-NRs) of PVDF and nanocomposites exhibit the characteristic bands at 840 cm⁻¹, corresponding to the polar γ- and β-phases [10] at the same time the characteristic band at 1279 cm⁻¹, assigned to the only polar β-phase [10]. The transmittance bands at 614, 766, 795 and 976 cm⁻¹, are attributed to the non-polar α-phase [10]. This result demonstrated that the TiO₂-NRs/PVDF consist of the polar phase of γ-, β-PVDF and nonpolar phase of α-PVDF. Importantly, β-phase of PVDF has dielectric, piezoelectric, and ferroelectric properties, leading to enhancement of ε’ of nanocomposites [36]. When the volume fraction of TiO₂-NRs increased, the transmittance band became very weak because of the reducing PVDF, corresponding to the result shown in the XRD of Figure 2. It is important to note that the observed β-phase of PVDF in the FTIR spectra may be associated with effect of hot-press process, giving rise to very well oriented crystallites in the perpendicular direction of the applied pressure. Thus, it can be sensitive by the FTIR technique due to the vibration of the β-PVDF.
molecules. The \( \beta \)-phase of PVDF was not sensitive by the XRD technique.

Figure 4 presents the FESEM images of the fracture surface of TiO\textsubscript{2}-NRs/PVDF with \( f_{\text{TiO}_2\text{-NRs}} = 0, 0.3, \) and 0.5. It can be clearly observed that the \( f_{\text{TiO}_2\text{-NRs}} = 0 \) (pure PVDF) is smooth and self-connected into a continuous network (see Figure 4(a)).

The slightly partial aggregation of TiO\textsubscript{2}-NRs can be seen in the nanocomposites at high content of filler, as shown in Figure 4(b,c). The overall results indicated that homogeneous TiO\textsubscript{2}-NR/PVDF nanocomposites were achieved by using a liquid-phase assisted dispersion method. TiO\textsubscript{2}-NRs were found to become connected to form a continuous cluster, but only a small number of pores were observed in the nanocomposites.

X-ray photoelectron spectroscopy (XPS) analysis was collected to investigate the chemical states and compositions. Figure 5 shows XPS results of TiO\textsubscript{2}-NR/PVDF nanocomposites with \( f_{\text{TiO}_2\text{-NRs}} = 0.5 \) using Gaussian-Lorentzian profile fitting. As was shown in Figure 5(a), the peak positions of the Ti 2\( p_{3/2} \) were observed at 457.50 and 458.82 eV, corresponding to the presence of Ti\textsuperscript{3+} and Ti\textsuperscript{4+}, respectively [29,30]. The Ti\textsuperscript{3+}/Ti\textsuperscript{4+} ratio was found to be 3.9%. This result demonstrated the existence of Ti\textsuperscript{3+} in the samples by electron hopping (Ti\textsuperscript{4+} $\rightarrow$ Ti\textsuperscript{3+}). The XPS spectra of O 1s profiles were measured and shown in Figure 5(b). Three prominent peaks were ascribed to an oxygen lattice (Ti-O), oxygen vacancies, and hydroxyl group [29,30]. The result confirmed the semiconducting properties of TiO\textsubscript{2}-NRs, leading to enhancement of the \( \varepsilon' \) TiO\textsubscript{2}-NRs.

Figure 6 illustrates the frequency dependence of \( \varepsilon' \) and tan\( \delta \) at 25°C for TiO\textsubscript{2}-NRs/PVDF nanocomposites various content loading of TiO\textsubscript{2}-NRs. As can be seen from Figure 6(a), it was observed that \( \varepsilon' \) of the nanocomposites increased with increasing concentrations of TiO\textsubscript{2}-NRs fillers. The \( \varepsilon' \) showed a relatively stable frequency dependence for all samples in the wide range from 10\textsuperscript{2} Hz to 10\textsuperscript{6} Hz. The \( \varepsilon' \) values of nanocomposites were achieved to be 81.9, 65.9, and 63.1 at the frequency of 10\textsuperscript{2}, 10\textsuperscript{3}, and 10\textsuperscript{4} Hz, respectively, with \( f_{\text{TiO}_2\text{-NRs}} = 0.5 \). Interestingly, it shows that the tan\( \delta \) remained very low with increasing TiO\textsubscript{2}-NRs, even though the volume fraction of filler was as high as 50 vol\% (\( f_{\text{TiO}_2\text{-NRs}} = 0.5 \)), as illustrated in Figure 6(b). The tan\( \delta \) value remained 0.029 at 1 kHz, which value is
similar to tanδ of pure PVDF [2]. Especially in the high-frequency range of $10^5$–$10^6$ Hz, the tanδ of TiO$_2$-NR/PVDF increased with the increase of TiO$_2$-NRs loading. The tanδ of nanocomposites at low frequency was relatively low, indicating that the contribution of the interface was rather low, and then the tanδ greatly increased at high frequency, mainly determined by the PVDF polymer matrix. It is important to note that tanδ increases with decreasing the frequency from $10^3$ to $10^2$ Hz. Nevertheless, tanδ values at $10^2$ Hz of the TiO$_2$-NR/PVDF composites were lower than those reported in CaCu$_3$Ti$_4$O$_{12}$/PVDF and Ba(Fe$_{0.5}$Nb$_{0.5}$)O$_3$/PVDF composites [37,38]. The significant enhancement in $\varepsilon'$ of TiO$_2$-NR/PVDF nanocomposites are influenced by the inherent semiconducting properties of TiO$_2$-NRs, the polar $\beta$-phase, and the interfacial polarization. Generally, interfacial polarization induced by the interface between semiconducting TiO$_2$-NRs and insulating PVDF, would lead to an improvement of electron mobility and Maxwell-Wagner-Sillars (MWS) effect [3], resulting in larger $\varepsilon'$ of the TiO$_2$-NR/PVDF nanocomposites.

Figure 7 shows the dependence of $\varepsilon'$ and tanδ at 25°C for PVDF and TiO$_2$-NR/PVDF with varying $f_{\text{TiO}_2\text{-NRs}}$. The $\varepsilon'$ and tanδ values of TiO$_2$-NR/PVDF nanocomposites as a function of $f_{\text{TiO}_2\text{-NRs}}$ at 1 kHz and 25°C.
shows that most of all composites exhibit an increased at 0.5.

It indicates that both satisfactory high $\varepsilon'$ and very low tan$\delta$ are accomplished in the PVDF-based polymer composites incorporating TiO$_2$-NPs. Polymer nanocomposites are a key material in energy harvesting and storage devices due to their fast charge-discharge capability [35,42,43]. The energy storage performance is influenced by the $\varepsilon'$ and tan$\delta$ values. Although the TiO$_2$-NR/PVDF nanocomposites can exhibit a high $\varepsilon'$ with low tan$\delta$, the energy density of the nanocomposites cannot be obtained due to the limitations of the dielectric data in this current study, which was measured at a low electric field. Thus, the high field properties such as dielectric displacement, ferroelectric hysteresis loops, and breakdown strength of the TiO$_2$-NR/PVDF nanocomposites need to be tested before consideration for application in energy storage devices [42,43].

Various models, including the effective medium theory (EMT) model, Yamada model, the logarithmic model, and the Maxwell–Garnett (M–G) model, were put forward to predict the $\varepsilon'$ of the TiO$_2$-NR/PVDF nanocomposites [38,44–46]. These four models can be expressed as follows:

**Effective medium theory (EMT) model:**

$$\varepsilon' = \varepsilon_p \left[ 1 + \frac{f_T (\varepsilon_T - \varepsilon_p)}{\varepsilon_p + n (\varepsilon_T - \varepsilon_p) (1 - f_T)} \right], \quad (1)$$

**Yamada model:**

$$\varepsilon' = \varepsilon_p \left[ 1 + \frac{n f_T (\varepsilon_T - \varepsilon_p)}{n \varepsilon_p + (\varepsilon_T - \varepsilon_p) (1 - f_T)} \right], \quad (2)$$

**Logarithmic model:**

$$\ln \varepsilon' = (1 - f_T) \ln \varepsilon_p + f_T \ln \varepsilon_T, \quad (3)$$

**Maxwell–Garnett model:**

$$\varepsilon' = \varepsilon_p \left[ 1 + \frac{3 f_T (\varepsilon_T - \varepsilon_p)}{2 \varepsilon_p + \varepsilon_T + (\varepsilon_T - \varepsilon_p) f_T} \right], \quad (4)$$

As followed in Equations (1)–(4), $\varepsilon'$ is the effective dielectric permittivity of the TiO$_2$-NR/PVDF nanocomposite. $f_T$ is the volume fraction of TiO$_2$-NRs ($f_{\text{TiO}_2\text{-NRs}}$). $f_p$ is the volume fraction of PVDF. $\varepsilon_T$ and $\varepsilon_p$ are dielectric permittivities of the rutile-TiO$_2$ and PVDF were found to be 150 [29] and 10.78 (an experimental value), respectively. The $\varepsilon'$ data was measured at 1 kHz and $\sim 25^\circ C$. $n$ is a ceramic morphology fitting factor. Figure 9 presents the experimental $\varepsilon'$ of TiO$_2$-NR/PVDF nanocomposite and the $\varepsilon'$ calculated based on various models for different volume fractions of TiO$_2$-NPs. All models fitted well with the experimental $\varepsilon'$ values at lower filler loading ($f_{\text{TiO}_2\text{-NRs}} < 0.3$). Large deviations from the experimentally observed values in the Logarithmic and Maxwell–Garnett models indicate that these two models are not suitable to describe...
the dielectric properties of TiO$_2$-NR/PVDF composites. Both Logarithmic and Maxwell–Garnet models assume a two-phase dielectric component with spherical-shaped inclusions ideally dispersed in the matrix [47]. Hence, it might be that the size, geometry, and imperfect dispersion of TiO$_2$-NRs have not correlated in the Logarithmic and Maxwell–Garnet models. On the other hand, the experimental data were found to fit well with the EMT model. Using EMT model, the morphology factor $n$ was found to be 0.11, which is closer to the results reported for ceramic/PVDF composites ($n=0.11$) [17,37] and ($n=0.15$) [18]. Using the Yamada model, the experimental value fitted well with the morphology parameter $n=8$, similarly to that of reported (9.3) [37]. However, the experimental dielectric data of nanocomposites at a high concentration of filler ($f_{TiO_2-NRs}=0.5$) deviated from all models. The possible reason is that interfacial physical and chemical properties of composites have not been taken into consideration in the models [33]. The deviation of the experimental data at $f_{TiO_2-NRs}=0.5$ is due to the dominant effect of the interfacial polarization. As the filler loading increased, the interparticle distance is very short, giving rise to the strong interfacial polarization.

4. Conclusion

Dielectric nanocomposites were successfully prepared by introducing the semiconducting TiO$_2$-NRs fillers into a PVDF matrix. It was clearly demonstrated that TiO$_2$-NRs can cause a significant increase in $\varepsilon'$, while a very low tan$\delta$ was suppressed. The high $\varepsilon'$ of TiO$_2$-NR/PVDF nanocomposites is mainly attributed to the formation of interfacial polarization at the interface between TiO$_2$-NRs and PVDF. The variation in $\varepsilon'$ of TiO$_2$-NR/PVDF nanocomposites was well described by the EMT and Yamada models. To further study the possible application of the TiO$_2$-NR/PVDF nanocomposites in energy harvesting and storage devices, ferroelectric hysteresis loop and breakdown strength that are used to calculate the energy density in dielectric capacitor need be studied.

Disclosure statement

No potential conflict of interest was reported by the authors.

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