

Research Article

High Dielectric Constant Study of TiO₂-Polypyrrole Composites with Low Contents of Filler Prepared by *In Situ* Polymerization

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Received 17 October 2015; Accepted 10 January 2016

Academic Editor: Victor V. Moshchalkov

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TiO₂/polypyrrole composites with high dielectric constant have been synthesized by *in situ* polymerization of pyrrole in an aqueous dispersion of low concentration of TiO₂, in the presence of small amount of HCl. Structural, optical, surface morphological, and thermal properties of the composites were investigated by X-ray diffractometer, Fourier transform infrared spectroscopy, field-emission scanning electron microscopy, and thermogravimetric analysis, respectively. The data obtained from diffractometer and thermal gravimetric analysis confirmed the crystalline nature and thermal stability of the prepared composites. The dielectric constant of 5 wt% TiO₂ increased with filler content up to 4.3×10^3 at 1 kHz and then decreased to 1.25×10^3 at 10 kHz.

1. Introduction

Active (ICs) and passive (capacitors, resistors, and inductors) components have been an integral part of almost all the electronic systems. In an electronic circuit board, the ratio of the passive components is much higher (around 80%) and among these, capacitors are the most important. Functions that capacitors perform include filtering, timing, decoupling, AC and DC conversions, termination, and energy storage. Development of microelectronics requires capacitors with high capacitance but with reduced size. This development is possible only with the use of materials with high dielectric permittivity associated with low dissipation factors. High dielectric constant materials with high dielectric strength, easy to process, and favorable mechanical stability have always been a need for the electronic industry to utilize these materials in energy storage devices [1, 2]. All these properties are hard to exist in a single material. Ceramics have high stiffness, excellent thermal stability with high dielectric constant but due to their high density, brittleness and difficult

processing conditions at very high temperatures [3] are difficult to be used. Polymers, on the other hand, are mechanically flexible, low cost, and easy to process and have high dielectric strength but have very low dielectric permittivity (usually 2 to 5). Considering these facts, polymers have been used as matrix to prepare their composites with high dielectric constant ceramic materials and required properties have been achieved to some extent [4–6]. Such polymer-matrix-composites (PMCs) are easy to process, have good adhesion with the materials reinforced in light weight, and are usually resistant to the corrosive environment.

In most of the cases, the ceramic fillers used are ferroelectric, for instance, titanates of barium, calcium, and lead, with polymer matrix which have high dielectric strength, and are nonconducting one, for example, polyvinylidene fluoride (PVDF) [7, 8], epoxy resins [9, 10], and polyvinyl chloride [11] (PVC). The maximum percentage of the ceramics used was around 40–50%. Conducting polymers such as polyaniline (PANI) [12] and polypyrrole (Ppy) [13, 14] have also been employed. As far as Ppy is concerned, it possesses high air

and thermal stability, and it is easy to process. Its composites with ceramic materials, especially with transition metal oxides, have been under research for potential increase in its conductivity [15, 16]. Concentration [14], shape, and size of the filler particles influence the dielectric properties of the PMCs [4, 17–20]. An unusual high concentration of the filler introduces brittleness, porosity, and low breakdown field.

In the present work, PMC samples have been synthesized using a lower wt% of TiO_2 in Ppy, prepared *in situ* under chemical oxidation environment. Though the electronic band gap of TiO_2 is relatively small (3.3 eV), its dielectric constant can be varied. Depending on the growth process, TiO_2 presents two important phases: anatase and rutile. The last one is a thermally stable phase that presents higher dielectric constant, whereas anatase is thermally unstable with lower dielectric constant. TiO_2 particles were dispersed in low concentrations in the solvent and the composites were obtained by *in situ* polymerization of the monomers. The method adopted to disperse TiO_2 particles resulted in a low concentration of TiO_2 (5 wt%) in the composite which might induce a high dielectric constant near 300 at 1 MHz frequency which was around 80–110 for pure TiO_2 .

2. Experimental

Pyrrole monomer (99%), titanium oxide ($\geq 99.5\%$), HCl (36.5–38.0%, Bio Reagent), NH_4OH (28% NH_3 in H_2O , $\geq 99.99\%$) and double distilled water (molecular biology reagent) from Sigma Aldrich, and ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) from Merck were used to synthesize the samples. 0.067 g of TiO_2 (1 wt% to that of pyrrole) was dispersed in 1 M HCl solution while magnetically being stirred overnight at room temperature (RT). 0.3 M $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ was added and after stirring for 30 minutes, 6.7 g (0.1 moles) of pyrrole was added dropwise. The whole mixture was stirred for 1 hour under inert environment of nitrogen flow at RT. The product was then filtered under vacuum, washed with 1 M NH_4OH ethanol, and then washed again using double distilled water, until the washings were clear. The product thus obtained was labeled as Ppy/ TiO_2 /1 wt% and was dried under vacuum at 60°C for 48 hours.

Following the same procedure, other samples of the composites were prepared adding 0.134 g, 0.20 g, 0.268 g, and 0.335 g of TiO_2 to get Ppy/ TiO_2 /2 wt%, Ppy/ TiO_2 /3 wt%, Ppy/ TiO_2 /4 wt%, and Ppy/ TiO_2 /5 wt%, respectively.

Fourier transform infrared (FTIR) spectra (Bruker Vertex 70, using KBr as a reference material) of the samples were studied in normal IR region of $4000\text{--}400\text{ cm}^{-1}$ obtained at RT. Samples were dispersed in KBr and compressed into pellets. A Rigaku Ultimate IV X-ray diffractometer (XRD) with $\text{CuK}\alpha$ (1.5406 Å) was used to obtain the diffraction patterns at RT, in the 2θ region of 5° to 80° with a scanning speed of $0.02^\circ/\text{min}$. A scanning electron microscope (SEM, JSM-6610) was utilized to investigate the surface morphology of the samples by obtaining images at magnifications of 5k to 100k. Thermal gravimetric analysis (TGA) was performed from 15 to 600°C to determine weight loss at high temperatures. Dielectric constant, dielectric loss, and loss tangent were evaluated using the data obtained from an LCR meter.

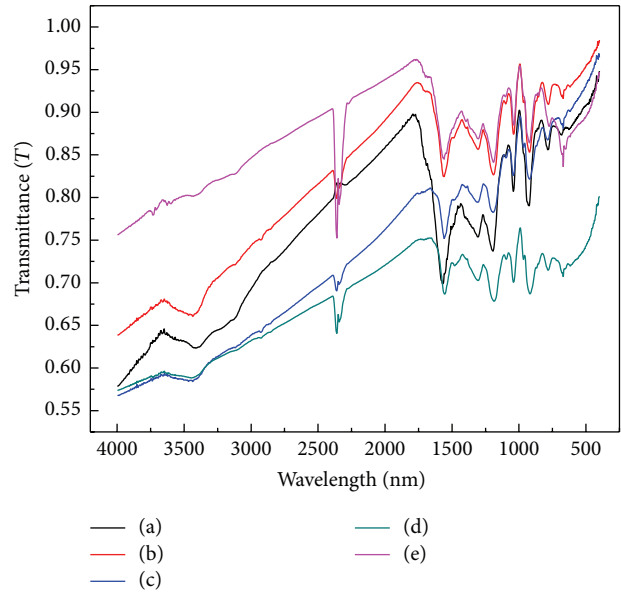


FIGURE 1: FTIR spectra of (a) 1 wt% Ppy/ TiO_2 , (b) 2 wt% Ppy/ TiO_2 , (c) 3 wt% Ppy/ TiO_2 , (d) 4 wt% Ppy/ TiO_2 , and (e) 5 wt% Ppy/ TiO_2 composites.

Compressed pellets of the composites were made under hydraulic pressure of 12 tons and then were placed between the electrodes.

3. Results and Discussion

Figure 1 presents the FTIR spectra of the samples, obtained to confirm the *in situ* formation of Ppy in the composites. The spectra reveal a medium band at $3410\text{--}3440\text{ cm}^{-1}$ corresponding to N–H bond stretching. Absorption observed at 1565 cm^{-1} is due to C=C bond stretching in the pyrrole units of Ppy. A peak of medium intensity at 1314 cm^{-1} may be attributed to C–N in-plane deformation. =C–C stretching vibration in pyrrole ring was observed at 1188 cm^{-1} . Another characteristic absorption peak at 1040 cm^{-1} can also be observed which is due to =C–H and N–H in-plane bending deformation mode. C–H out-of-plane ring deformation is clearly visible at 777 cm^{-1} . C–C out-of-plane ring deformation at 674 cm^{-1} is confirmed from the weak absorption there. The peaks at $2360\text{--}2370\text{ cm}^{-1}$ are attributed to the presence of CO_2 in the ambient moisture present in the samples. In particular, the sample with 5 wt% TiO_2 shows the strongest peak in the region indicating the presence of relatively more moisture.

Figure 2 shows the XRD patterns of the prepared samples. The patterns exhibit strong diffraction peaks at 27° , 36° , and 55° attributed to the rutile phase of TiO_2 . Similarly, the diffraction peaks at 25° and 48° indicate the presence of TiO_2 in anatase phase (Figure 2(a)). All peaks were in good agreement with the standard spectra (JCPDS numbers 88-1175 and 84-1286). From the intensity and broadening of the peaks, it can be inferred that the crystallite size of the Ppy/ TiO_2 composites is in micrometer range [21] and the

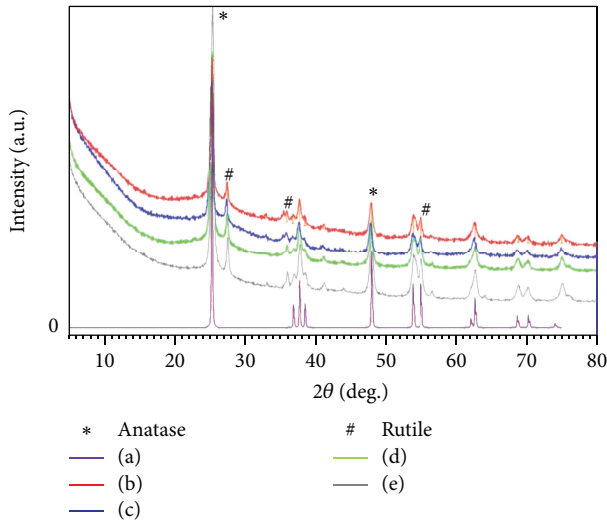


FIGURE 2: XRD patterns of (a) 1 wt% Ppy/TiO₂, (b) 2 wt% Ppy/TiO₂, (c) 3 wt% Ppy/TiO₂, (d) 4 wt% Ppy/TiO₂, and (e) 5 wt% Ppy/TiO₂ composites.

composites have a dominant crystalline nature with TiO₂ particles not much enwrapped by Ppy.

Curves in Figure 3 exhibit TGA of Ppy composite samples obtained in the temperature range of 15°C to 600°C. Sample (a) exhibited a constant weight loss in the whole temperature range whereas a stepwise weight loss was seen in all the other samples. For example, a weight loss of 10% which is attributed to expulsion of water has been observed in the range of 200–250°C for the samples (b–e). This weight loss was higher than that for pure Ppy samples prepared under the same conditions [16]. Further, the degradation process of Ppy matrix in the composites with weight loss of 16–20% was initiated at 280°C after which the decomposition initiated near 300°C and continued until 600°C where the weight loss reached up to 65–80%. The TGA plots also reveal that there is an overall increase in thermal stability of the composites with increase in the content of Ppy. Earlier in the FTIR spectrum, the sample with 5 wt% TiO₂ has shown the strongest peak in the 2360–2370 cm⁻¹ region indicating the presence of relatively more moisture which is also confirmed from the TGA analysis where the expulsion of water from the composite occurs at 200°C with weight loss of 10.8% as shown by Figure 3(e).

Figures 4(a)–4(d) show SEM micrographs of Ppy/TiO₂ composites containing 2 wt%, 3 wt%, 4 wt%, and 5 wt% TiO₂, respectively. The sample prepared with 2 wt% Ppy in TiO₂ matrix reveals the hemispherical Ppy particles engaged in clusters due to the poor compactness and light weight nature of the polymer, as shown in Figure 4(a). Link between the particles has improved after the introduction of TiO₂ particles and porosity of 0.2–1 μm is also much less as compared to that found in pure Ppy sample which is mainly in the range of 2–8 μm [15]. Figures 4(b), 4(c), and 4(d) clearly show the presence of two phases of the composites. The micrograph of the composites containing 2 wt% TiO₂ shows somewhat uniform distribution of the components but in

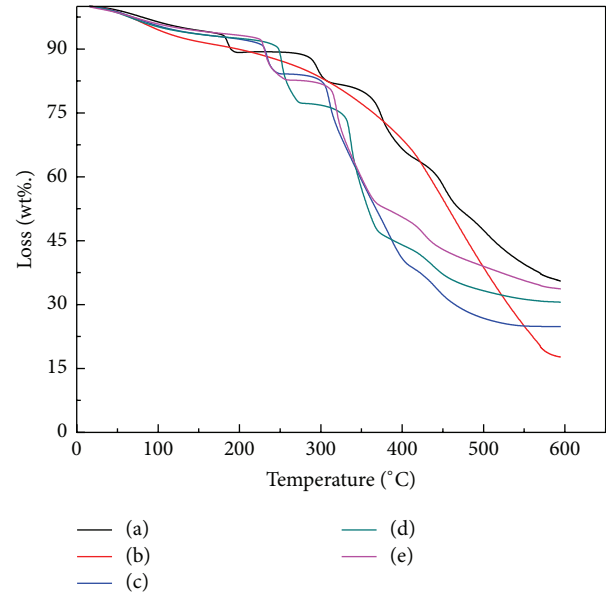


FIGURE 3: TGA curves of (a) 1 wt% Ppy/TiO₂, (b) 2 wt% Ppy/TiO₂, (c) 3 wt% Ppy/TiO₂, (d) 4 wt% Ppy/TiO₂, and (e) 5 wt% Ppy/TiO₂ composites.

the composites from 3 to 5 wt% TiO₂, the particles aggregate and size of aggregates gradually increases up to 0.5–5 μm, accompanied by the reduction in size of grains and decreases in compactness which results in an increase in the dielectric behavior [18, 22].

Effect of AC frequency on the dielectric permittivity (ϵ') of Ppy/TiO₂ composites can be depicted from Figure 5. Ppy/TiO₂ composites having high contents of TiO₂ exhibit large value of ϵ' at lower frequencies while the value of ϵ' decreases at higher frequencies. It is well known that dielectric response of solids is a complicated function of frequency, temperature, and type of solids [23]. At low frequencies, all polarization mechanisms that take account of the interfacial (space charge), dipolar, ionic, and electronic charge displacements can follow the applied electric field. In this case, the highest value of ϵ' is obtained. In the low frequency region, there is an increase in the real permittivity of the composites with increase in TiO₂ contents, especially when it is 3 to 5 wt%. At high frequency, the difference in values of ϵ' for the composites prepared with 4 wt% and 5 wt% TiO₂ goes on decreasing. The data reveals that Ppy/TiO₂ composite with 5 wt% TiO₂ has ϵ' value of 4.3×10^3 at 1 kHz and decreased to $\sim 1.25 \times 10^3$ at 10 kHz. Afterwards, it exponentially decreases to 284 at 1 MHz.

Figure 6 displays variation in dissipation factor ($\tan \delta$) with TiO₂ contents and AC frequency. It shows that $\tan \delta$ increases nearly five times as the wt% of TiO₂ increases from 3 to 4. For 5 wt% TiO₂ contents, the value is somewhat lower in the low frequency range as compared to the sample with 4 wt% TiO₂ contents, but the reverse and usual behavior is observed at higher frequencies. Figure 7 depicts variation in dielectric loss (ϵ'') with TiO₂ contents and frequency. The frequency-dependent behavior of both $\tan \delta$ and ϵ'' can be explained in accordance with Koop's theory by considering

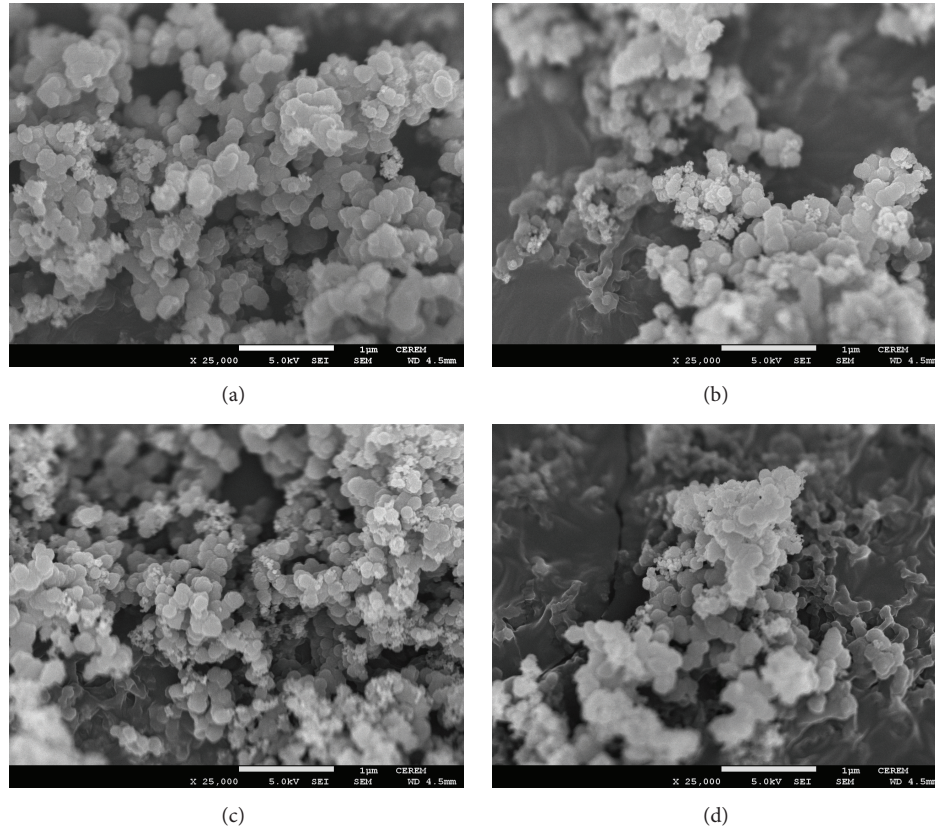


FIGURE 4: SEM micrographs of (a) 2 wt% Ppy/TiO₂, (b) 3 wt% Ppy/TiO₂, (c) 4 wt% Ppy/TiO₂, and (d) 5 wt% Ppy/TiO₂ composites.

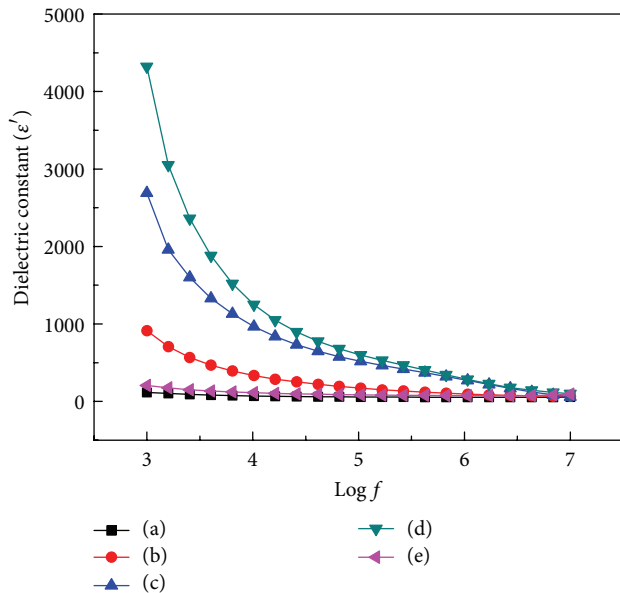


FIGURE 5: Dielectric constant as a function of frequency for (a) 1 wt% Ppy/TiO₂, (b) 2 wt% Ppy/TiO₂, (c) 3 wt% Ppy/TiO₂, (d) 4 wt% Ppy/TiO₂, and (e) 5 wt% Ppy/TiO₂.

dielectric sample as a Maxwell-Wagner type medium, having two inhomogeneous layers. In these layers, the grains act as conducting region as compared to grain boundaries which

behave as relatively less conducting channels. This nonconducting behavior is dominant at low frequencies. When this resistance increases at the grain boundaries, the electrons reaching grain edges via hopping mechanism pile up. In this way, the grains are polarized resulting in high value of permittivity. When the frequency is increased, the probability of electrons reaching the grain boundaries decreases and hence a decrease in permittivity is observed. This in turn decreases the dielectric parameters at high frequencies.

In order to visualize the interfacial polarization relaxation process, a modulus representation of dielectric loss is used [24, 25]. According to the relationship defined by Macedo et al. [26], real and imaginary parts of the electronic modulus M' and modulus M'' can be calculated using ϵ' and ϵ'' [24].

Trends of both these parameters have been plotted in Figures 8 and 9, respectively, as a function of frequency. The plots reveal that real part of electric modulus increases as the frequency increases whereas the imaginary part shows a variable trend. The behavior is in accordance with the previously reported work [24, 26].

4. Conclusion

High dielectric constant composites of TiO₂/polypyrrole have been synthesized by *in situ* polymerization of pyrrole in an aqueous dispersion of low concentration of TiO₂ in the presence of small amount of HCl. FTIR analysis confirmed

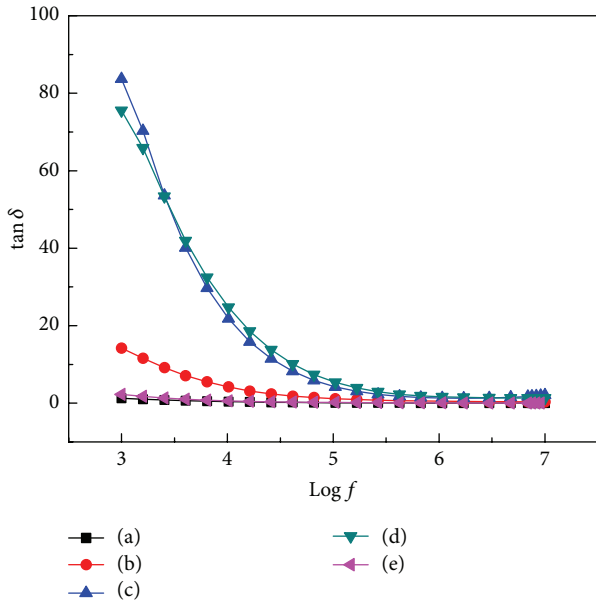


FIGURE 6: Variation of dissipation factor as a function of AC frequency for (a) 1 wt% Ppy/TiO₂, (b) 2 wt% Ppy/TiO₂, (c) 3 wt% Ppy/TiO₂, (d) 4 wt% Ppy/TiO₂, and (e) 5 wt% Ppy/TiO₂ composites.

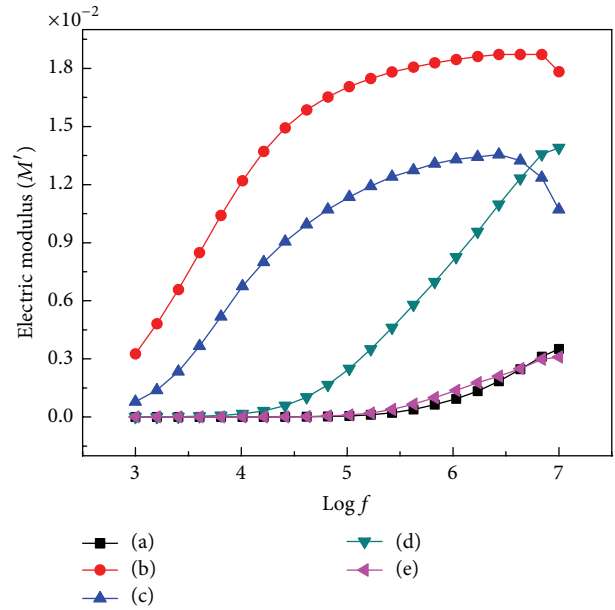


FIGURE 8: Electric modulus of real part versus frequency for various Ppy/TiO₂ composites (a) 1 wt% Ppy/TiO₂, (b) 2 wt% Ppy/TiO₂, (c) 3 wt% Ppy/TiO₂, (d) 4 wt% Ppy/TiO₂, and (e) 5 wt% Ppy/TiO₂ composites.

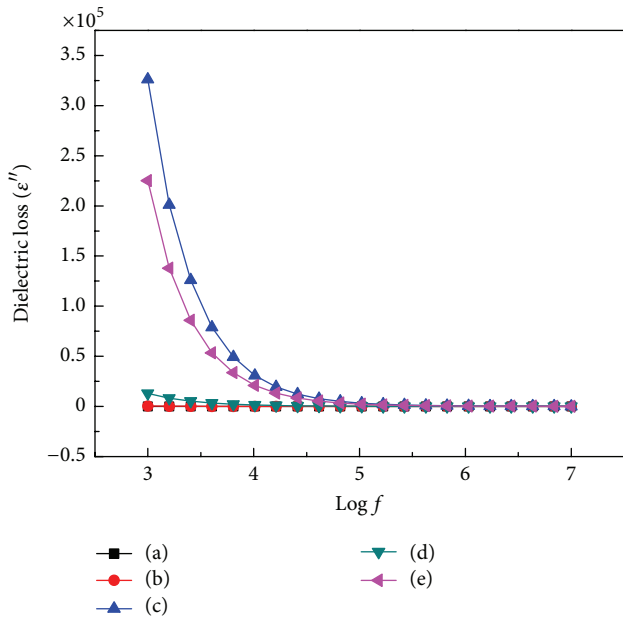


FIGURE 7: Variation of dielectric loss with frequency for (a) 1 wt% Ppy/TiO₂, (b) 2 wt% Ppy/TiO₂, (c) 3 wt% Ppy/TiO₂, (d) 4 wt% Ppy/TiO₂, and (e) 5 wt% Ppy/TiO₂ composites.

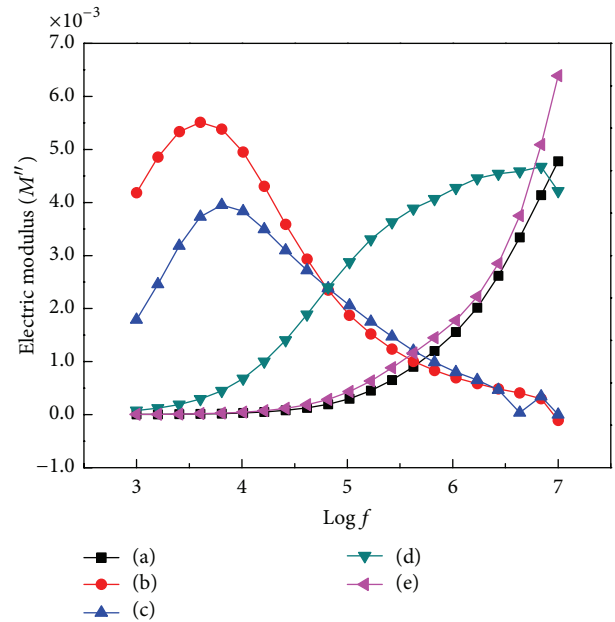


FIGURE 9: Electric modulus of imaginary part versus log f for Ppy/TiO₂ composites: (a) 1 wt% Ppy/TiO₂, (b) 2 wt% Ppy/TiO₂, (c) 3 wt% Ppy/TiO₂, (d) 4 wt% Ppy/TiO₂, and (e) 5 wt% Ppy/TiO₂ composites.

the *in situ* formation of the Ppy in the composites. TGA analysis revealed the expulsion of water from the 5 wt% TiO₂ composite occurs at 200°C with weight loss of 10.8%. Crystal structure of the prepared samples was confirmed as anatase phase of TiO₂. Grains of uniform sizes with homogenous distribution in micrometer range were observed from the microscopic analysis. Dielectric parameters (ϵ' ,

$\tan \delta$, and ϵ'') were found to possess high values at low frequencies which gradually decreased at high frequencies. The dielectric data revealed that Ppy/TiO₂ composite with 5 wt% TiO₂ has ϵ' value of 4.3×10^3 at 1 kHz and decreased to $\sim 1.25 \times 10^3$ at 10 kHz; then it exponentially decreases to 284 at 1 MHz.

Conflict of Interests

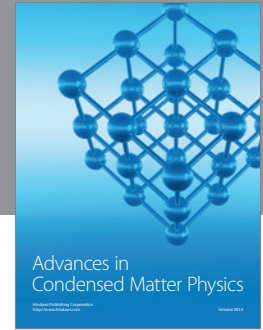
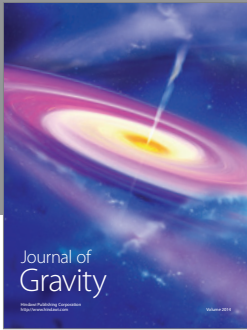
The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgment

The authors extend their appreciation to the Deanship of Scientific Research at King Saud University for funding the work through the Research Group Project no. RGP-VPP-106.

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