STUDY OF THE EFFECT OF PVA ON DIELECTRIC CONSTANT AND STRUCTURE OF TiO$_2$-POLYPYRROLECOMPOSITES PREPARED BY IN-SITU POLYMERIZATION

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PVA/TiO$_2$/polypyrrole composites showing high dielectric constant have been synthesized by *in-situ* polymerization of pyrrole in an aqueous dispersion of 5% TiO$_2$ and, 1 wt%, 3 wt% and 5wt%PVA. The structural, chemical and thermal properties of the composites were investigated by X-ray diffractometer, Fourier transform infrared spectroscopy and thermal gravimetric analysis, respectively.The structural morphology of the prepared samples was probed using the images obtained from scanning electron microscopy. An impedance analyzer was utilized to discuss the dielectric parameters. The data obtained from diffractometer confirmed the semi crystalline nature and the thermal gravimetric analysis confirmed the thermal stability of the prepared composites in a wide temperature range. The dielectric constant of 5 wt% PVA increased with filler contents up to 3.2 x 10^{3}at 1 kHz and then decreased to 354 at 1MHz. in this way, an increase in dielectric constant of 5 wt% TiO$_2$/ppy by 70 has been achieved.

1. Introduction

Amazing development in the microelectronic industry has become possible after the formation of micro sized as well as embedded capacitors [1-3] which in turn are produced using thin layers of high dielectric constant materials. These are being used between the charge storing plates of small area obeying the following formula:

$$C = \frac{kt}{A} \tag{1}$$

where *C* is the capacitance of a capacitor, *t* is the thickness of dielectric medium separating the plates, *A* is the area of the plates and *k* is the dielectric constant of the medium between the plates. As the thickness and area cannot be increased beyond certain limits in a microelectronic board so the dielectric constant of the materials, being used has to be increased. The other applications of such materials include active vibration control, aerospace, underwater navigation and surveillance,

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hydrophones, biomedical imaging, non-destructive testing and air imaging microphones[4,5]. In most cases, the dielectric materials required should not possess only a high dielectric constant but it should also exhibit high dielectric strength, thermal stability, mechanical flexibility, easiness in processing, low cost, adhesive and stable under the environment. All these properties are hard to be found in a single material. The only possibility is to combine two or more components in the form of composites to exhibit multiple properties simultaneously. In this context, ceramics are synthesized which possess two of the above mentioned requisite properties, i.e., high dielectric constant and thermal stability. The remaining properties are found in polymers. Most of the research carried out so far includes a high dielectric ceramic filler (5 to 60 wt%) and a non-conducting polymer matrix. The high concentration of the filler in a two phase composite introduces poor flexibility of the composites [6], weak interfacial attraction and pores [7].The other choices are polymer-conducting filler composites based on percolation mechanism, which in turn is an application of scaling theory [8] and three-phase polymer matrix composite[9-11].

The least focused combination is a ceramic filler of high dielectric constant in a conducting polymer matrix. The hurdle is the risk of short circuiting or low percolation threshold of the conducting polymer in spite of the fact that polymers of excellent properties are available such as polyaniline, polypyrrole and polyindole [12], which are thermally stable, easy to process and environment-friendly. Polypyrrole has been found to be less conducting or even non-conducting if prepared at high temperature and under such conditions that the conjugation in its structure is not developed either due to the dominant quinonoid structure or the elimination of what is called polarons by reducing effect of the filler [13]. In a previous work, we have prepared a series of composites using low contents (1% to 5%) 250 nm sized particles of TiO_2 as a filler [14] and polypyrrole by *in-situ* polymerization at 25-30 ℃ [15]. The composites thus obtained were found to possess very low conductivity (1×10^{-6} to 5×10^{-6} Scm^{-1}) and a high dielectric constant of 54 to 284, and low dielectric loss of the order of 0.004 to 1.6 for 1% to 5% of the TiO_2 contents, respectively.

In the present work, a series of composites was prepared using 5% TiO_2 in all the composites and a third component PVA was introduced (1 wt%, 3wt% & 5 wt%) during *in-situ* polymerization of pyrrole. The changes in structural and dielectric properties were then investigated. The addition of large amounts of PVA was not used to avoid film formation of the composites as it could complicate the characterization process and hence, the prospective applications might get limited to certain fields.

2. Experimental

Pyrrole monomers (distilled every time before use) and poly vinyl alcohol from Sigma Aldrich, titanium oxide(TiO_2, Riedel-de Haen, 14027 purity >99.5%) with mean particle size of 0.25 μm having specific surface area of 9.6 m^2g^{-1}, HCl (36.5-38.0%, Bio Reagent), NH_4OH (28% NH_3 in H_2O, purity ≥99.99%), double distilled water and ferric chloride hexahydrate($FeCl_3.6H_2O$) from Merck were used as ingredients in the present work to form the samples.

First of all, a 5wt% PVA/Ppy composite was prepared. For this purpose, 0.335 g PVA was dissolved in 50 mL distilled water at 80℃. This solution was added to 0.3 M $FeCl_3$ solution taken in a three necked flask and stirred for at least 30 min. 6.7 g(0.1 mol) of pre-distilled pyrrole was added drop-wise and the whole mixture was stirred for 1 h under inert environment of N_2 flow at room temperature (RT, 20-25℃). The final product was washed through vacuum filtration apparatus with 1M NH_4OH, ethanol and then double distilled water until the washings were clear. The product thus obtained was labeled as Ppy/TiO_2/PVA (1 wt%) and was dried under vacuum at 60℃ for 48 h.

0.335gof TiO_2 (5 wt% to that of pyrrole) was dispersed in 1M HCl solution while being stirred magnetically overnight at RT. 0.067g of PVA (1 wt% to that of pyrrole) was dissolved in 50 mL of water at 80 ℃. These two solutions were mixed in a three necked flask and stirred for 30 min. Afterward, 0.3 M $FeCl_3$solution was added and after stirring for another 30 min,0.1 mole of pyrrole was added drop-wise. The whole mixture was stirred for 1 h under inert environment of N_2 flow at RT (20 − 25℃). The final product was washed and dried following the same process as

described above. Following the same procedure, other samples of the composites were prepared adding 0.201 g and 0.335g of PVA to get Ppy/TiO$_2$/PVA (3 wt%) and Ppy/TiO$_2$/PVA(5 wt%), respectively.

Fourier transform infrared (FTIR) spectra (BrukerVertex70, using KBr as a reference material) of the samples were obtained in normal IR region of 4000–400 cm^{-1}atRT. A Rigaku Ultimate IV X-ray diffractometer (XRD)with CuK_α (1.5406 Å) was used to obtain the diffraction patterns at RT, in the 2θrange of 10° to 85°with a scanning speed of 0.0.500^o/min. A scanning electron microscope (SEM,JSM-6610) was utilized to investigate the surface morphology of the samples by obtaining images at magnifications of 20kto 100k.Thermal gravimetric analysis (TGA) was performed from 30 to 600 ºC to determine weight loss at high temperatures. Dielectric constant, dielectric loss and loss tangent were evaluated using the data obtained from an impedance analyzer (Wayne Kerr, 6500B). Compressed pellets of the composites were made under hydraulic press by applying a force of 10 – 12tons and then were placed between the electrodes.

3. Results and discussion

Fig. 1 (a) shows the FTIR spectra of all the basic ingredients, i.e., pure PVA, 5%PVA/Ppy composite and pure TiO$_2$, used in this work. Major peaks in all the spectra belong to the characteristic bonds of the respective compounds. For, example, in TiO$_2$ a broad band at 554–792cm^{-1} corresponds to Ti-O-Ti stretching frequencies [13]. In case of 5%PVA/Ppy composite, the broad band observed at 3200–3500cm^{-1}is due to combined effect of hydrogen bonded O-H stretch of PVA and N-H stretch of aromatic amine of Ppy ring. The characteristic C-H stretch of CH$_2$ of PVA was observed at 2945 cm^{-1}. Absorptions due to Ppy at C=C stretching are visible at 1575 cm^{-1}. =C–H and N–H in-plane bending deformation characterizing absorption peak is observed at 1097 cm^{-1}.
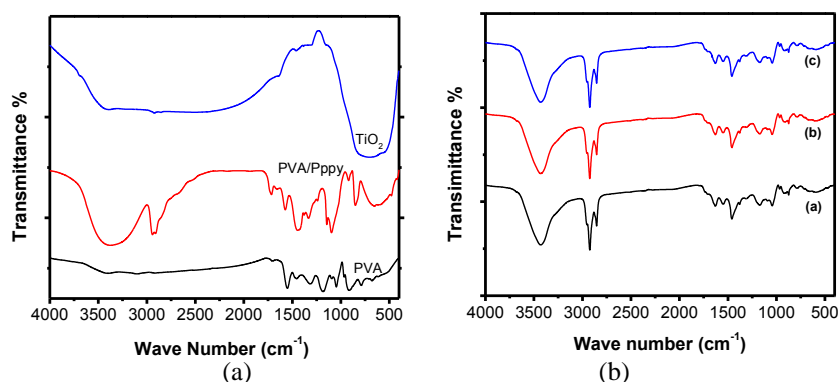

Fig. 1(a). FTIR spectra of pure PVA, 5%PVA/Ppy composite and pure TiO$_2$
(b) FTIR spectra of (a) 1% PVA, (b) 3% PVA and (c) 5%PVA in TiO$_2$ (5%)/Ppy composites

Fig. 1 (b) represents the FTIR spectra of 5% TiO$_2$ +1%, 3% & 5% PVA/Ppy composites, respectively. The characteristic peaks mentioned above seem to be shifted towards comparatively shorter wave number indicating the interactions developed between all the three components combined. For instance, the Ti-O-Ti broad band ends at 785 cm^{-1}. Similarly, N-H stretch of aromatic amine of Ppy ring shifts from 3345 cm^{-1}towards 3410 cm^{-1}. The characteristic C-H stretch of CH$_2$ of PVA shifts from 2945 cm^{-1}towards 2923cm^{-1}. Absorptions due to C=C stretching, visible at 1575 cm^{-1}shifts to 1561 cm^{-1} and .=C–H and N–H in-plane bending deformation, initially present at 1097 cm^{-1} was observed at 1046 cm^{-1}. All these significant changes are attributed to the corresponding chemical interactions between active sites of the components of the prepared composites.
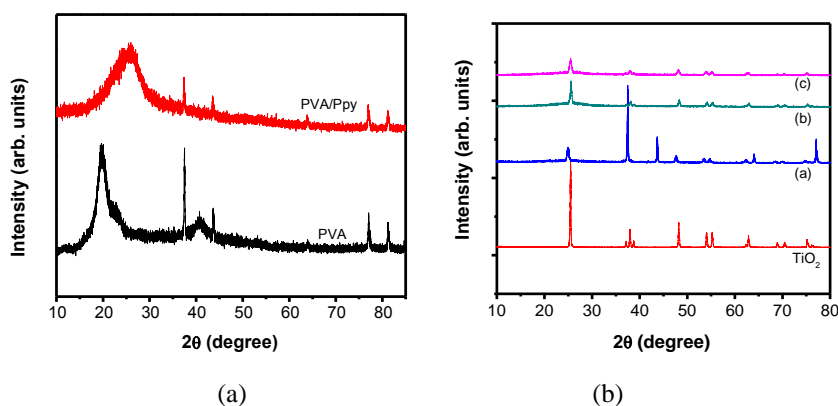
Fig. 2(a): XRD patterns of pure PVA and 5%PVA/Ppy composite,
(b) XRD patterns of pure TiO$_2$& (a) 1% PVA, (b) 3% PVA and (c) 5%PVA
in TiO$_2$ (5%)/Ppy composites

Fig. 2 (a) shows the XRD peaks of pure PVA and its 5 wt% composite with Polypyrrole. In the diffraction pattern of PVA, there is a major peak of medium broadness at $2\theta \approx 19.7^o$ which is characteristic of PVA with its semi-crystalline nature. The introduction of 5% PVA into Ppy caused the disappearance of this peak and a broad peak at $2\theta \approx 25.7^o$ appears due to amorphous Ppy matrix. It can be inferred that PVA particles have been totally encapsulated by Ppy and there is also a change of inter planner spacing [16].

In Fig. 2(b), the XRD pattern of pure TiO$_2$ reveals the diffraction peaks at 2θ values of 25°, 48° for its anatase phase and 37°, 55° for its rutile phase. The same peaks are observed in the composites prepared, with a little broadening of the peaks. The peaks were more prominent in 5 wt% PVA sample, due to the presence of semi-crystalline PVA and amorphous Ppy phases. All the peaks are in good agreement with the standard diffraction patterns available in the literature.
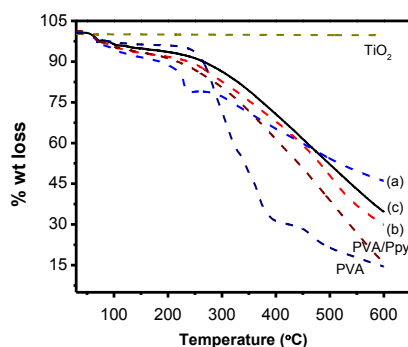

Fig. 3. TGA curves of pure PVA, pure TiO$_2$, 5% PVA/Ppy & (a) 1% PVA, (b) 3% PVA and
(c) 5%PVA in TiO$_2$ (5%)/Ppy composites

Fig. 3 shows the TGA plots of the pure PVA, 5 wt% PVA/Ppy, pure TiO$_2$ employed in this research work and the three phase composites prepared in the temperature range of 30 to 600 ºC. Pure PVA used for all the samples seems to be the least stable component. Pure TiO$_2$ remained unaffected in the whole temperature range. A weight loss of 5% occurred for all the composites even for pure PVA around 100 ºC. 10% weight loss is usually attributed to the expulsion of water from the polymer matrix occurred at 220 ºC for initially prepared 5 wt% PVA/Ppy containing 0% TiO$_2$at around 220 ºC while the introduction of 5 wt% TiO$_2$ enhanced the stability and the temperature reached in the range of 230 to 250 ºC. Pure PVA loses 10% weight at 265 ºC indicating the least moisture in it. The polymer degradation process was initiated in the pure PVA

at 285 ℃ but in the prepared composite samples in the range 300 to 250 ℃. The process continues and at 600 ℃, the weight lost by pure PVA was found 85% while that for 5 wt% PVA/Ppy around 80%. The three phase composites still proved thermally more stable and these lost 55 to 70% of their initial weight. The TGA plots clearly reveal that the introduction of a third component PVA into TiO_2/Ppy composites has increased their thermal stability.
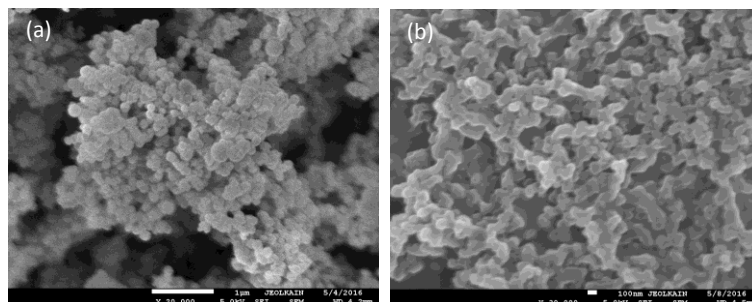

Fig. 4. SEM images of (a) pure TiO_2 and (b) 5%PVA/Ppy composite

Fig. 4 (a) shows the SEM images of pure TiO_2 particles employed. The average particle size of 250 nm as claimed by the supplier company was confirmed. In the Fig. 4 (b), the flakes produced are attributed to the introduction of 5% PVA into Ppy and the single phase impression developed is due to the excess of Ppy which completely encapsulates the PVA particles.
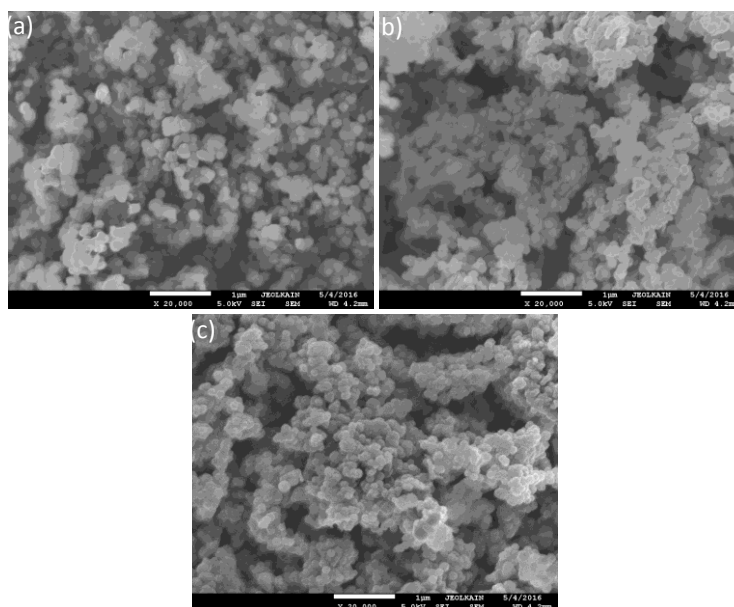

Fig. 5. SEM images of (a) 1% PVA (b) 3% PVA and (c) 5%PVA in TiO_2 (5%)/Ppy composites

Fig. 5(a – c) shows the SEM images of three phase composites containing 5 wt% TiO_2/Ppy with 1wt% , 3 wt% and 5 wt% PVA, respectively. The introduction of smaller amount of PVA has not only produced homogeneity but also an increase in its content has enhanced the formation of hemispherical particles engaged in clusters due to light weight nature of both the polymer components. A decrease in porosity can also be observed which is usually associated with pure Ppy [17]. The cluster formation is also accompanied by the reduction in size of grains providing more grain boundaries which results in the increase in dielectric properties as compared to the TiO_2/Ppy composites.
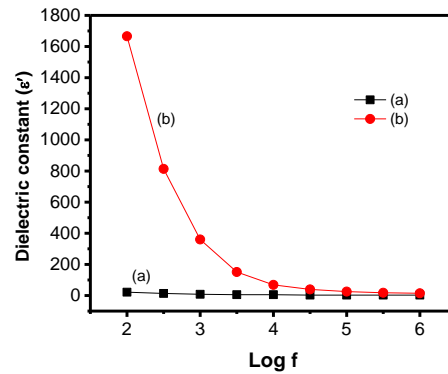
Fig. 6. Dielectric constant as a function of frequency for
(a) pure PVA and (b) 5%PVA/Ppy composite

Fig. 6 shows dielectric constants (ε') and its change with AC frequency for pure PVA and its 5 wt% introduction into the Ppy-matrix. It is evident that this blend has improved the dielectric permittivity of both the polymers as compared to that of the pure components (PVA and Ppy).At 1 kHz the composite exhibitε' value of 360 and it decreases to 14.4 at 1 MHz.
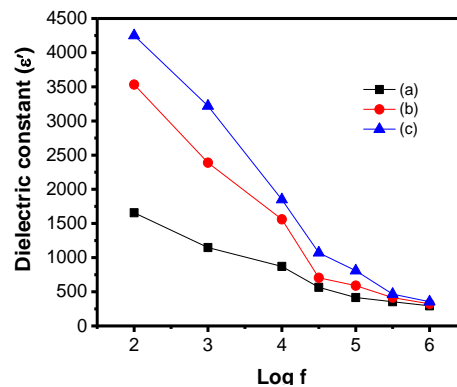

Fig. 7. Dielectric constant as a function of frequency for (a) 1% PVA (b) 3% PVA and
(c) 5%PVA in TiO_2 (5%)/Ppy composites

It can be depicted from Fig. 7 that the introduction of smaller amounts of PVA has increased the dielectric permittivity of 5 wt% TiO_2/ppy composites to a value of 284 at 1 MHz [15]. It is further evident that ε' values become 1.15×10^3, 2.4×10^3 and 3.2×10^3 for 1 wt%, 3 wt% and 5 wt% PVA samples, respectively. However, as the frequency is increased to 1 MHz, the ε' value decreases to 294, 324 and 354, respectively for the above-mentioned composites.
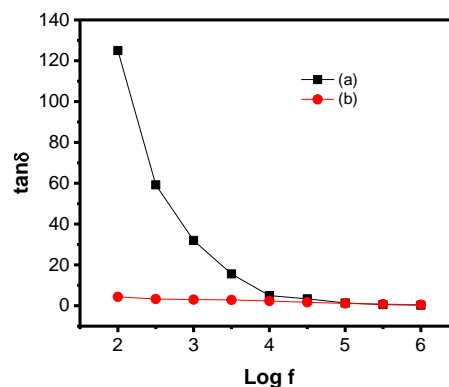

Fig. 8. Variation of dissipation factor as a function of AC frequency
for (a) 5%PVA/Ppy composite and (b) pure PVA

Fig. 8 displays the variation in dissipation factor (tanδ) for pure PVA and 5 wt% PVA /Ppy. The introduction of PVA has increased the dissipation factor appreciably in the low frequency region (1 kHz) with a difference of 47 between the two. This difference becomes negligible to a value of 0.24 at high AC frequency (1 MHz).
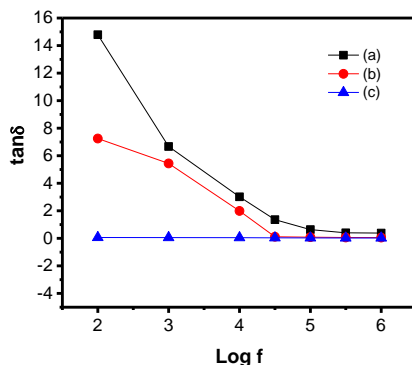

Fig. 9. Variation of dissipation factor as a function of AC frequency for
(a) 1% PVA, (b) 3% PVA and (c) 5%PVA in TiO_2 (5%)/Ppy composites

Fig. 9 shows the values of tan δ for the composites prepared. An increase in the contents of PVA has introduced a decrease in the tan δ, both in the low and high frequency regions. The change is comparatively less prominent probably due to 5 wt% TiO_2.

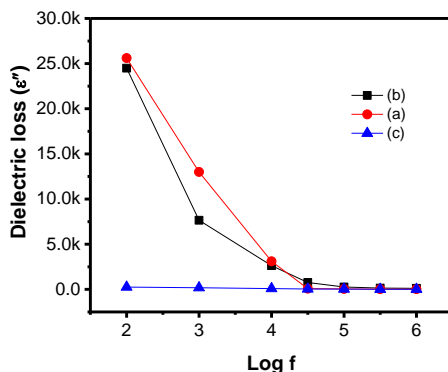*Fig. 10. Variation of dielectric loss as a function of AC frequency for*
(a) 1% PVA, (b) 3% PVA and (c) 5%PVA in TiO_2 (5%)/Ppy composites

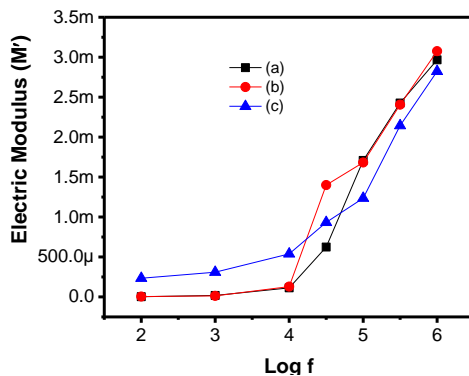*Fig. 11. Electric modulus of real part vs frequency for (a) 1% PVA,*
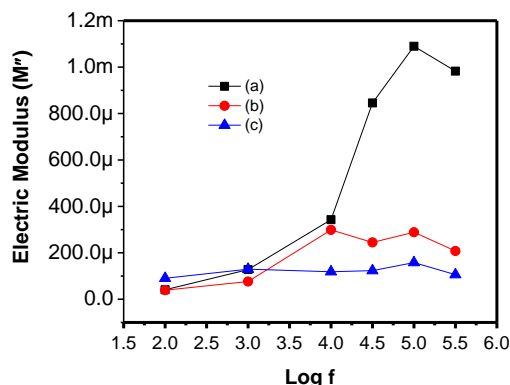*(b) 3% PVA and (c) 5%PVA in TiO_2 (5%)/Ppy composites*

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*Fig. 12. Imaginary part of electric modulus vs frequency for (a) 1% PVA,
(b) 3% PVA and (c) 5%PVA in TiO$_2$(5%)/Ppy composites*

Fig. 10 depicts the variation in dielectric loss (ε'') with frequency for the composites prepared. The introduction of 1 wt% and 3 wt% PVA has surprisingly small values of dielectric loss at higher frequencies. The trend is usual and can be explained with reference to the SEM images of these composites, where the formation of somewhat inhomogeneous layers with less porosity are evident in accordance with Maxwell–Wagner medium.

Interfacial polarization-relaxation processes defined by Macedo et al [18] in terms of real and imaginary parts of the electric modulus (M') and (M''), respectively were calculated using ε' and ε'', and were plotted against log of frequency as shown in Figs. 11 and 12, respectively. Both these parameters have been found to exhibit increasing trend with little exceptions. The behavior is in accordance with the previous work reported in the literature. The resulting improvements in the dielectric behavior of the composites prepared may be attributed to the introduction of PVA into TiO$_2$/Ppy which probably restricted the internal pi-conjugation system of the Ppy whereby, facilitating the availability of most of electrons on nitrogen for polarization phenomena and not for conduction. The possibility of intermolecular hydrogen bonding could also have contributed for binding the three phases.

4. Conclusions

Three phase composites with high dielectric constant were successfully synthesized by *in-situ* polymerization of pyrrole in the presence of PVA and TiO$_2$ particles. FTIR confirmed the formation of Ppy matrix. XRD confirmed the presence of semi crystalline PVA and crystalline TiO$_2$ particles of almost 250 nm size were evident by SEM images. TGA analysis revealed that the introduction of PVA enhanced the thermal stability by increasing the temperature ranges for expulsion of water and degradation processes.

From the microscopic analysis, grains of uniform sizes and their shapes were visualized. Dielectric parameters were found at their higher values in the low frequency regions which gradually decreased at high frequencies. A dielectric constant of 354 was achieved at 1 MHz which was 284 in the absence of PVA under the same circumstances.

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