

Characterization of Multiphase Polypyrrole/Vanadium Oxide Nano Composites for a.c. Conductivity and Dielectric Properties

Harshitha R*, Nihal B Kottan†, Purnachandra Ganesh K M‡, Prajwal M Laxmeesha§, Chalugaraju B V** and Murugendrappa M V††

Abstract

Vanadium oxide:Phase-1 and Phase-2 nano powders were synthesized from vanadium pentoxide in the presence of glucose using the hydrothermal technique. The polypyrrole/vanadium oxide (PV P-1 and PV P-2) nano composites were synthesized with 15, 30, 45 and 60 weight percents of vanadium oxide: Phase-1 and Phase-2 pyrrole, by the chemical polymerization (oxidation) method. The SEM micrographs of vanadium oxide: Phase-1 and Phase-2 nano powders have shown mixture of nano belts & rods

* Department of Physics, Bangalore Institute of Technology, Bengaluru, India; harshithagowda13@gmail.com

† B.E., Department of Mechanical Engineering, Bangalore Institute of Technology, Bengaluru, India; nihalkottan@gmail.com

‡ B.E., Department of Mechanical Engineering, Bangalore Institute of Technology, Bengaluru, India; purnachandra.feb26@gmail.com

§ M.S. Student, Department of Materials Science and Engineering, College of Engineering, Drexel University, Philadelphia, PA 19104, USA; prajwal.ml714@gmail.com

** Department of Physics, Bangalore Institute of Technology, Bengaluru, India; chalugaraju@bit-bangalore.edu.in; bvcgowda@gmail.com

†† Department of Physics and Center of Excellence in Advanced Materials Research, BMS College of Engineering, Bengaluru, India; murugendrappam.v.phy@bmsce.ac.in

and PV P-1 & PV P-2 nano composites indicate that the composites have cluster formation with almost spherical nature particles and form elongated chains at some places. Conductivity versus frequency plots have shown exponential increase in conductivity. The value of σ increases to 1.13×10^{-3} S/cm for 15 wt.% of VO₂ P-1 in polypyrrole & to 2.43×10^{-3} S/cm for 30wt. % of VO₂ P-2 in polypyrrole at 1 MHz. The higher VO₂ concentration may have increased the chain length of PPy facilitating the bouncing of charge carriers. $\sigma_{a.c.}$ and dielectric studies revealed that the nano composites may be a good a.c. conductor and low-value dielectric materials. The composites may also find applications in humidity and gas sensors, micro power generator, thermo cooling and EMI shielding.

Keywords: Polypyrrole; Vanadium Oxide; Nano Composites; Conductivity; Dielectrics.

1. Introduction

Curiosity in the growth of intrinsic conducting polymers (ICP) has increased tremendously because of their electro-chromic properties suitable for applications in batteries, functional electrodes, electrochromic devices, optical switching devices, electronic devices, sensors such as gas, bio, solid-state, humidity, microwave, electromagnetic interference shielding [1-5] and thermo-electric power [6-8]. The conducting polymers have two major groups of applications. The first group utilizes their conductivity as its main property, while the second group utilizes the electro-activity [9].

ICPs are synthesized from techniques such as electrochemical or chemical polymerization [10]. Monomers can be oxidized by oxidizing agents, such as ammonium persulphate, ferric chloride, etc., to produce conducting polymers by using the chemical polymerization process [11]. Chemical synthesis has the benefit that it facilitates bulk production at a moderate cost.

The conducting polymer polypyrrole is derived from the pyrrole monomer. It accentuates the progress that has been made to understand, characterize complex systems and also highlight the

improvement made in their physical properties [12-20]. Polypyrrole is one of the best conducting polymers [21].

Polypyrrole has found applications in Plastic LEDs, Micro-motors, Batteries, Optical-storage, Photocopiers, Transducers, Lithography, Conductivity, Photo-conducting, Piezoelectric, Photochemical reactions, Harmonic generators, Display devices, Magnetic recording, Sensors, Super-capacitors, etc. [19-22].

Vanadium pentoxide (V_2O_5) is a brown/yellow solid; it has an amphoteric oxide and an oxidizing agent due to its high oxidation state. During the preceding few years, materials, which are synthesized based on vanadium oxides, have fascinated considerable responsiveness due to their attractive structures, properties such as electronic property, optical property and magnetic property. These are significant to such diverse domains as lubrication, chemical sensor, catalysis, cathode materials in batteries, minerals, self-lubricating applications, production of ferrovanadium and sulfuric acid [23-29], as a detector material in bolometers and micro-bolometer arrays for thermal imaging due to its high coefficient of thermal resistance, active electrode in a rechargeable lithium battery as well as solid-state micro-battery applications. Vanadium redox batteries are used for energy storage, wind farms, thermal switching and sensing [30-31].

VO_2 (metastable phase oxide) is made up of distorted VO_6 octahedra, which shared edges and corners [32]. Also, it is found to be of thought-provoking cathode properties in batteries like lithium-ion batteries [33-34]. VO_2 synthesis is normally attained through low-temperature chemical methods [32, 35-37]. VO_2 nanostructures may be synthesized using a nontoxic reducing agent. VO_2 nanowires, nanobelts, nanoribbons, nanoneedles and nanorods were respectively synthesized [38-44]. VO_2 nanobelts are synthesized using nontoxic glucose as a reducing agent.

2. Experimental Details

2.1. Synthesis

2.1.1. Synthesis of the Pure Polypyrrole (PPy)

A. R. grade pyrrole (Sisco Laboratories Pvt. Ltd., Mumbai, India) [6-8] was used. 0.3 M pyrrole solution [6-8] was taken in a beaker. 0.6 M [6-8] ammonium persulphate (APS) (Sisco Laboratories Pvt. Ltd., Mumbai, India) solution was prepared and added dropwise to pyrrole solution for polymerization. The reaction was continued for 4 hours with continuous stirring. The precipitated polypyrrole was obtained. It was filtered and dehydrated using a hot air oven at 100°C. PPy was measured, and the yield was 1.8 g [6-8].

2.1.2. Synthesis of Vanadium Oxide: Phase-1 and Phase-2 (VO₂ P-1 & VO₂ P-2) Nano Powders

In a usual technique, 1 mmol V₂O₅ (NR CHEM Pvt. Ltd., Mumbai, India) and 0.5 mmol glucose (Thomas Baker Chemicals Pvt. Ltd., Mumbai, India) were dissolved in 30 ml distilled water. 0.5 g sodium sulfate was added to the solution later. Homogeneous yellow suspension was obtained after 20 minutes of stirring. It was transferred into a 50 ml teflon-lined autoclave, and distilled water was successively added up to 80 % of its measurements. The autoclave was sealed, and it was placed in an oven for heating at 160°C for 24 hours. The precipitate was centrifuged with distilled water and ethanol (Thomas Baker Chemicals Pvt. Ltd., Mumbai, India) for 4 times. The final sample was dried in an oven at 60°C for 24 hours at Phase-1. The obtained nano *black* powder is named VO₂ Phase-1 (VO₂ P-1) [43].

Similarly, VO₂ is again synthesized at Phase-2, and the obtained precipitated sample was dried in an oven at 100°C for 24 hours. The obtained nano *pale blue* powder is named VO₂ Phase-2 (VO₂ P-2) [43].

2.1.3. Synthesis of the Polypyrrole/Vanadium Oxide: Phase-1 and Phase-2 (PV P-1 and PV P-2) Nano Composites

0.27 g (15 weight percent) of synthesized vanadium oxide Phase-1 (VO₂ P-1) nanopowder was added to the 0.3 M pyrrole solution and mixed thoroughly. Further, 0.6 MAPS was added dropwise, with the

help of a burette, continuously to the above solution, to get a polypyrrole/vanadium oxide (15 wt. %) Phase - 1 (PV P-1 15%) nanocomposite. Similarly, for 30, 45 and 60 wt. %, 0.54 g, 0.81 g and 1.08 g of VO₂ P-1 powders were taken and the above procedure repeated to get the PV P-1 nanocomposites. The nano composites yields were 3.6 g, 2.8 g, 3.2 g and 3.8 g, respectively [6-8].

Similarly, polypyrrole/vanadium oxide Phase-2 (PV P-2) nanocomposites were synthesized using the same above mentioned procedure. The yields of the nanocomposites were 3.9 g, 4.8 g, 5.11 g and 5.78 g, respectively [6-8].

A hydraulic press was used to compress the PV P-1 and PV P-2 nanocomposites powders into pellets which have a thickness between 1 mm and 3 mm and diameter 1 cm by applying 10-13 tons pressure (Shimadzu, Japan) [13]. The compacted pellets were coated with Silver paste on both flat surfaces for the physical properties measurements. a.c. conductivity and parameters of dielectric properties were measured using the 6500B series of Precision Impedance Analyzers (Wayne Kerr Electronics Pvt. Ltd., India), in the frequency range from 20 Hz to 1 MHz, at room temperature for the composites [6-8].

2.2. Characterization

PPy, PV P-1 and P-2 composites and VO₂ samples spectra were recorded on an FTIR (Shimadzu, Japan) spectrometer, in a medium of potassium bromide, at normal temperature. The XRD patterns of the samples were recorded on an X-ray Diffractometer (Bruker AXS D8 Advance, India), using Cu K_α radiation ($\lambda=1.5418 \text{ \AA}$), in the 2 θ range of 5°-90°. A Scanning Electron Microscope (Jeol 6390 LV, India) was used to obtain the SEM micrographs.

3. Results and Discussion

3.1. SEM Analysis

Figures 1.a-g show the SEM micrographs of the pure polypyrrole, VO₂ P-1, PV P-1 & P-2 composites and VO₂ P-2, respectively. Fig 1.a shows an image with spherical clusters and few chains, which is typical of PPy monomer. The SEM micrograph (Figure 1.b) of VO₂

P-1 shown that the mixture of nanobelts and nanorods particles of VO_2 at Phase-1 (60°C). The SEM micrographs of PV P-1 composites (Figure 1.c-f) show the formation of spherical clusters around the vanadium oxide nanorods. The SEM micrograph (Figure 1.h) of the vanadium oxide nanopowder at Phase-2 (100°C) revealed nanorods intact. Similarly, as PV P-1 composites, the SEM micrographs of PV P-2 composites (Figure 1.h-k) are revealing of a spherical nature and clusters formation in the composites except for the PV P-2 (15 %) nanocomposites which show agglomeration of spherical particles around rod-like structures [45-53].

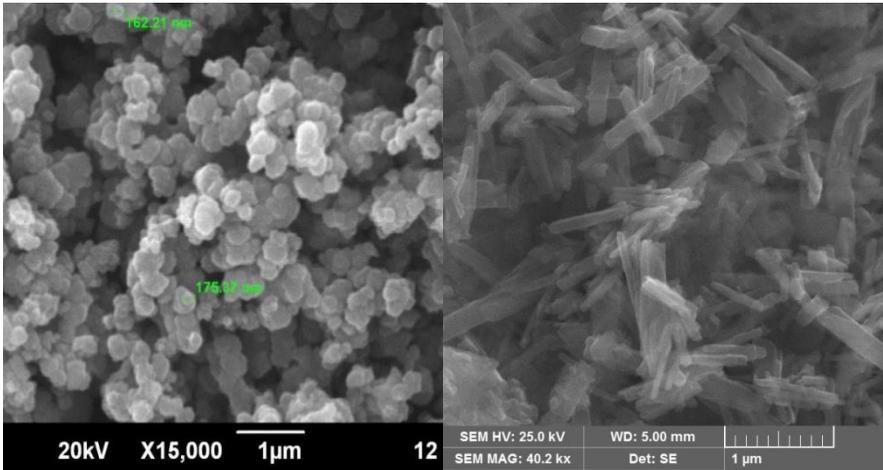


Figure 1.a:SEM micrograph of the pure PPy powder

Figure 1.b:SEM micrograph of the VO_2 nano powder Phase-1

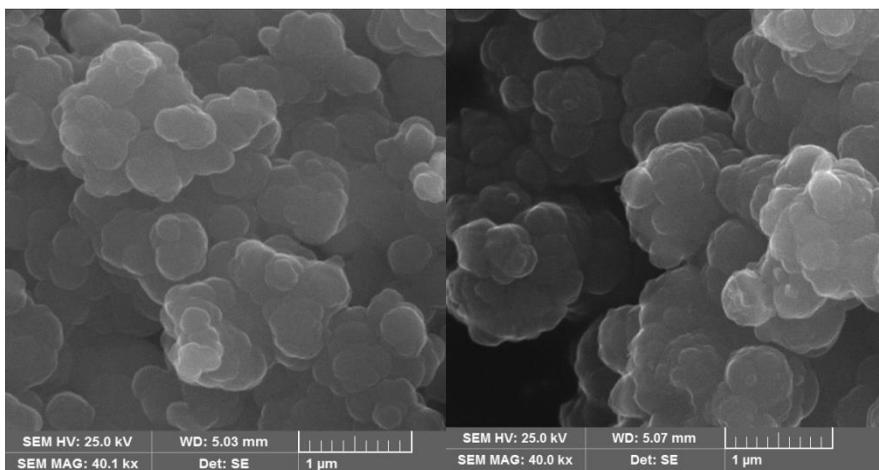


Figure 1.c: SEM micrograph of the PV P-1 (15%) nano composites

Figure 1.d: SEM micrograph of the PV P-1 (30%) nano composites

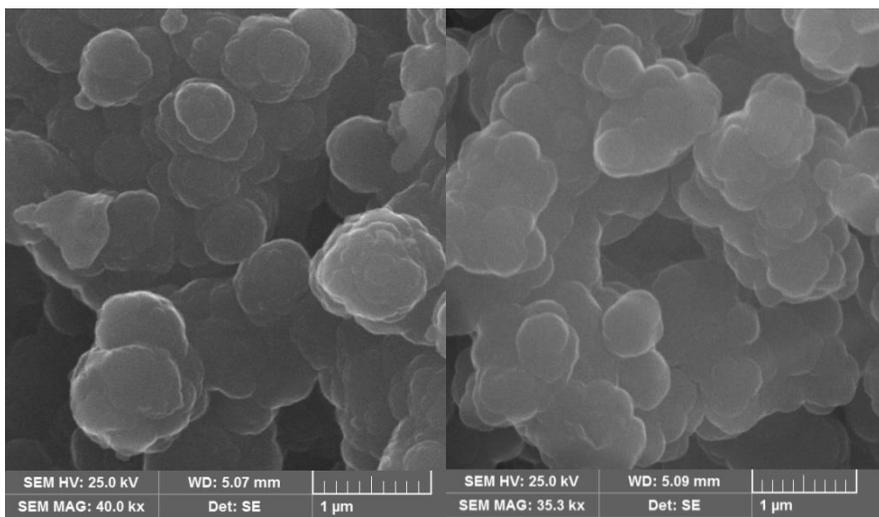


Figure 1.e: SEM micrograph of the PV P-1 (45%) nano composites

Figure 1.f: SEM micrograph of the PV P-1 (60%) nano composites

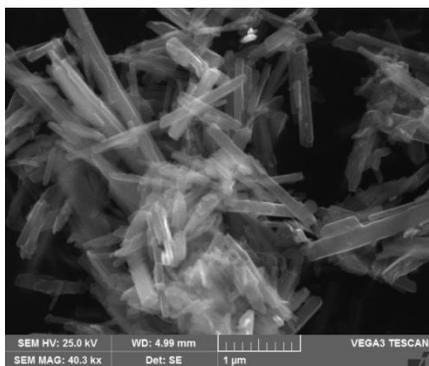


Figure 1.g: SEM micrograph of the vanadium oxide nano powder Phase-2

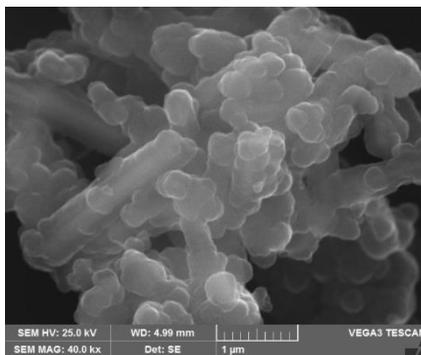


Figure 1.h: SEM micrograph of the PV P-2 (15%) nano composites

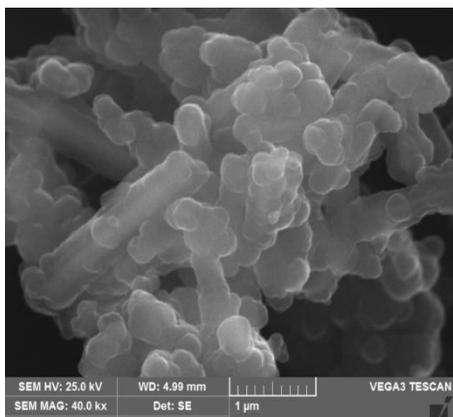


Figure 1.h: SEM micrograph of the PV P-2 (15%) nano composites

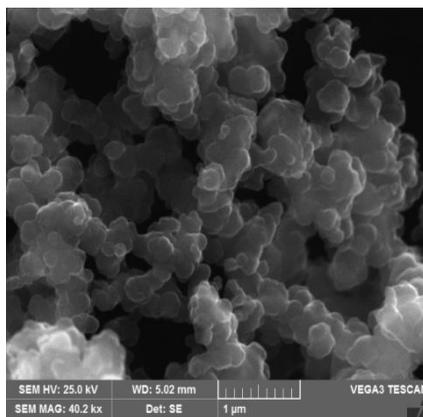


Figure 1.i: SEM micrograph of the PV P-2 (30%) nano composites

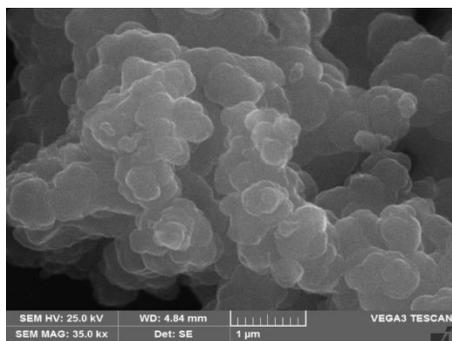


Figure 1.j: SEM micrograph of the PV P-2 (45%) nano composites

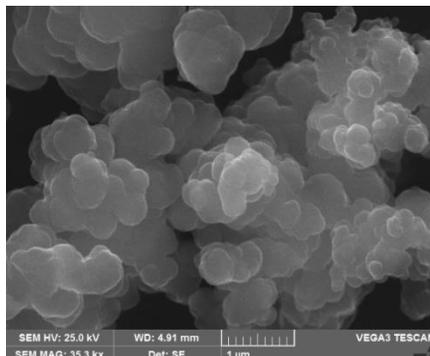


Figure 1.k: SEM micrograph of the PV P-2 (60%) nano composites

3.2. Study of a.c. Conductivity

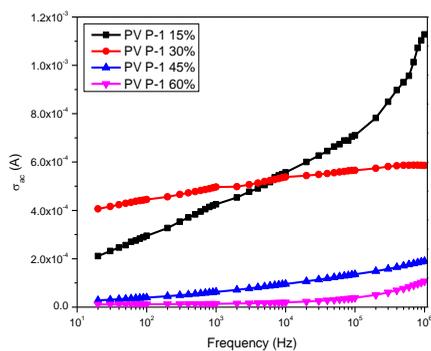


Fig. 5.a: σ_{ac} versus f of PV P-1 composites

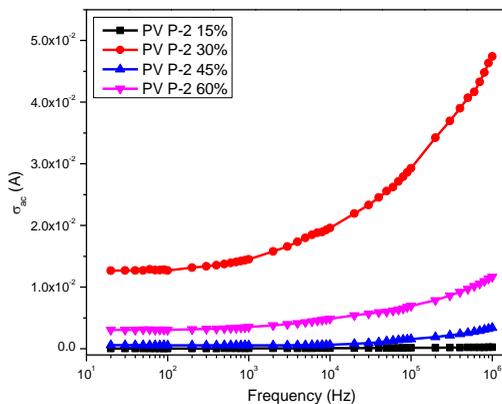


Fig. 5.b: σ_{ac} versus f of PV P-2 composites

a.c. conductivity rises with an increase of frequency at a given temperature for the composites. This phenomenon is a common response for intrinsically conducting polymer-based composites [54-55]. Variation of the a.c. conductivity versus frequency for the PVP-1 and P-2 composites was shown in Figures 5.a and 5.b. It was observed that the conductivity increases exponentially as frequency increases at high-frequency region. It can also be seen that the value of conductivity increases for $1.13 \times 10^{-3} \text{ S/cm}$ for 15% weight percent of VO_2 P-1 in polypyrrole & for $2.43 \times 10^{-3} \text{ S/cm}$ for 30% weight percent of VO_2 P-2 in polypyrrole at 1 MHz. This may be due to the extended chain length of polypyrrole, which facilitates the hopping of charge carriers when the content of VO_2 particles was increased for composites. The increase in conductivity for the PPy/ VO_2 P-1 (15%) composite and the PV P-2 (30%) composite was due to the variation in the distribution of VO_2 P-1 and P-2 particles, respectively, which may be supported for more number of charge carriers to hop between favourable localized sites causing an increase in conductivity. The decrease in conductivity for the rest of PV P-1 and P-2 composites may be attributed to the trapping of charge carriers in the polymer chain. Charge trapping in PPy and blends was a general universal feature of these materials. 5.85 , 1.90 , and $1.06 \times 10^{-4} \text{ S/cm}$ were conductivity values at 1 MHz for the PV P-1 (30% 45% and 60%) composites, respectively as well as 0.0474 , 0.0034 and

0.01167x10⁻³S/cm were conductivity values at 1 MHz for the PV P-2 (15%, 45% and 60%) composites respectively.

Studies reveal that the PV P-2 (30%) composite has the highest conductivity among all. Hence, VO₂ P-2 particles concentration influenced the PPy in the synthesis of the above composite[56-64].

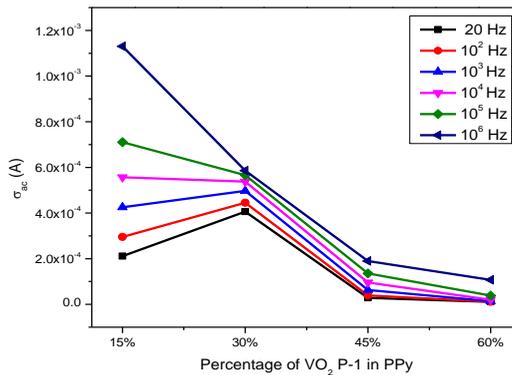


Fig. 5.c: σ_{ac} versus weight percent of PPy for PV P-1 composites

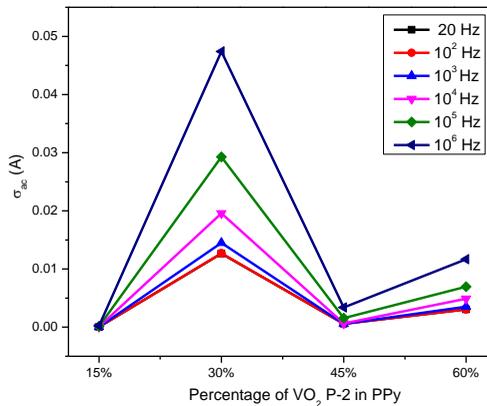


Fig.5.d: σ_{ac} versus weight percent of PPy for PV P-2 composites

Figures 5.c and 5.d were shown the variation of ac conductivity as a function of the weight percentage of VO₂ P-1 and P-2 in PPy at different frequencies. The values of the conductivity increased for 15 weight percent VO₂P-1 in PPy for PV P-1 composite as well as for 30 weight percent VO₂ P-2 in PPy for PV P-2 composite. These points were percolation thresholds, respectively, and the composites are shown to obey percolation theory. Furthermore, a decrease in the conductivity, which could be attributed to the blocking of hopping charge carriers by the presence of larger grain size vanadium oxide particles, can be observed in some composites. [56-64].

3.3 Dielectric Constant and Dielectric Loss Studies

The interactions between the dispersant and matrix along with the physical properties of the matrix, influence the agglomeration of particles during polymerization. Cross-linking between polymer chains plays a major role in the way transport properties are exhibited [65]. The effect of dopant concentration on the dielectric constant, dielectric loss, and tangent loss of polypyrrole based composites was studied by varying vanadium oxide content.

3.3.1 Dielectric Constant Studies

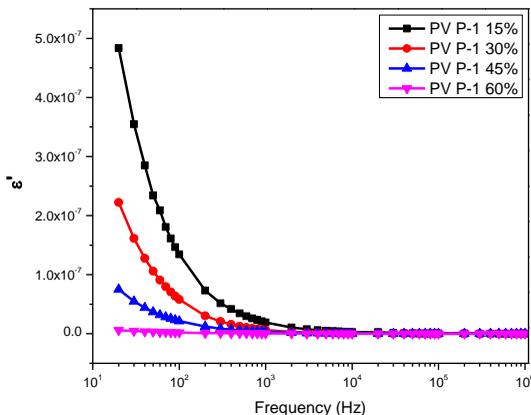


Fig. 6.a: ε' versus f of PV P-1 composites

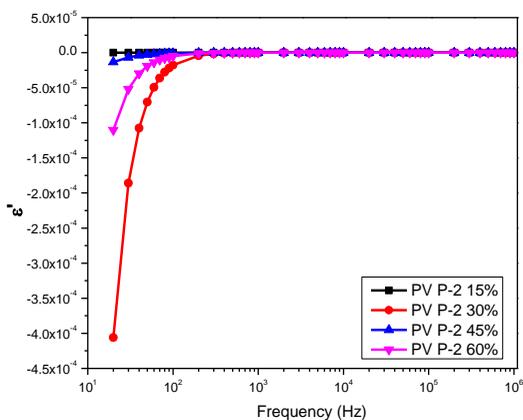


Fig. 6.b: ϵ' versus f of PV P-2 composites

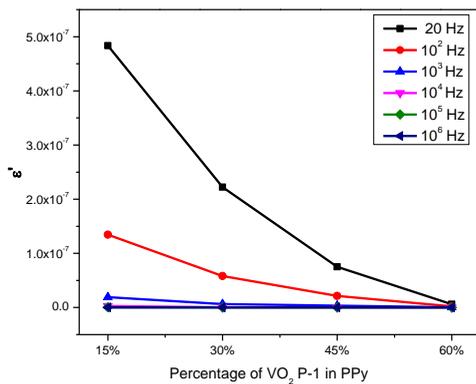


Fig. 6.c: ϵ' versus weight percent of PPy for PV P-1 composites

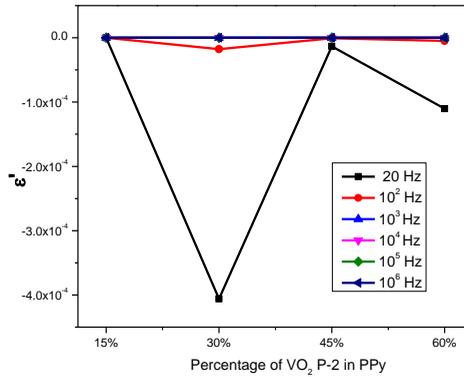


Fig.6 d: ε' versus weight percent of PPy for PV P-2 composites

The positive dielectric constant and negative dielectric constant (Fig.6.a and Fig.6.b) decreases with increasing frequency for PV P-1 and P-2 composites. The PV P-1 (15%) and V P-2 (30%) composite have shown high dielectric constant values. The negative dielectric constant is due to the increase in ac conductivity. The tendency of dipoles in composite to orient themselves in the direction of applied field may cause this. Electrode and interfacial effects of the composite could be a cause for the high values of ε' at low frequency. On the other hand, the value remained a constant at the high-frequency range with respect to frequency. A similar trend is seen after observing the behaviour of all composite from the graph and this could be due to hindrance of rotation of the dipoles at higher frequencies which leads to difficulty in reorientation [66-74].

Variations of dielectric constants with weight percents of VO₂ P-1 and P-2 particles in PPy of PV P-1 and P-2 composites as shown in Fig. 6.c and Fig. 6.d. Figures revealed that the percolation points at respective positions for all composites like in the case of ac conductivity studies [66-74].

3.3.2 Dielectric Loss Studies

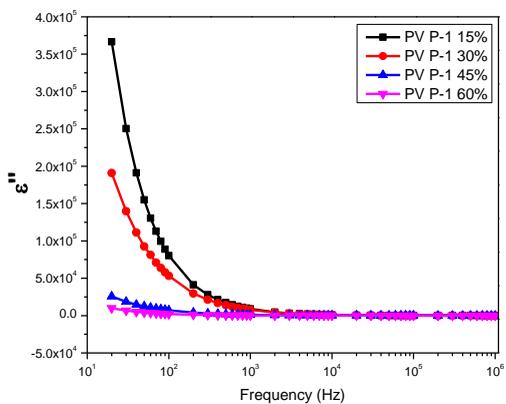


Fig. 6.e: ϵ'' versus f of PV P-1 composites

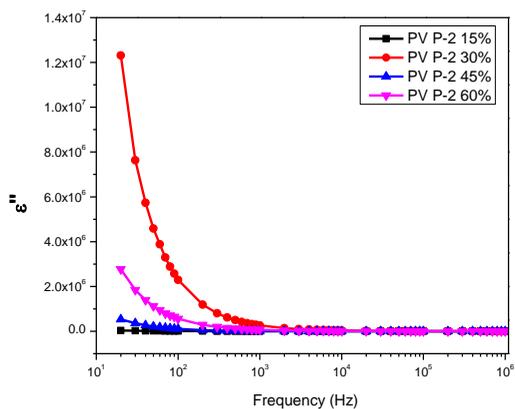


Fig. 6.f: ϵ'' versus f of PV P-2 composites

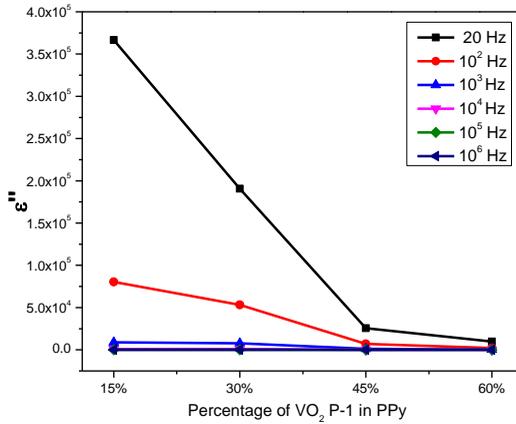


Fig. 6.g: ϵ'' versus weight percent of PPy for PV P-1 composites

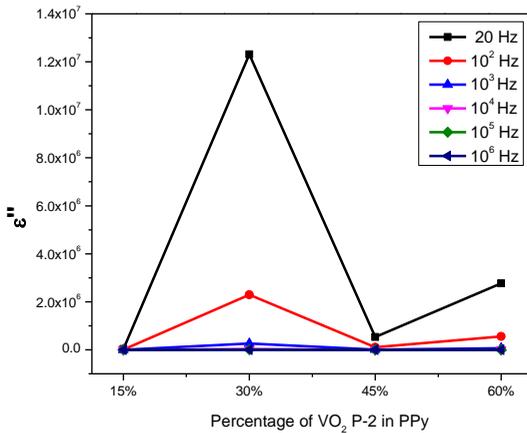


Fig.6.h: ϵ'' versus weight percent of PPy for PV P-2 composites

The constant dielectric loss (Fig.6.e and Fig.6.f) decreases with increasing frequency for PV P-1 and P-2 composites. The PV P-1 (15%) and V P-2 (30%) composites have shown high dielectric loss values. Mobile charges present within the polymer backbone may explain the larger value of the dielectric loss at a lower frequency.

On the other hand, the mobile charges of PPY could be held accountable for the lower value of ϵ'' at high frequency [66-74].

Variations of dielectric losses with weight percents of VO₂ P-1 and P-2 particles in PPY of PV P-1 and P-2 composites are shown in Fig. 6.g and Fig. 6.h. Figures revealed that the percolation points at respective positions for all composites, like in the case of constant dielectric studies [66-74].

4. Conclusion

Vandium oxide: Phase-1 & Phase-2 and multiphase polypyrrole/vandium oxide nanocomposites were synthesized. The obtained samples were analyzed using SEM technique. a.c. conductivity and dielectric properties studies were done successfully, which revealed in all plots. a.c. conductivity and dielectric properties studies revealed that the nanocomposites might be good ac conductor and low-value dielectric materials. The composites may also find applications in micropower generator, thermo cooling, EMI shielding, humidity and gas sensors.

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Conflict of Interest statement

No Conflict of Interest

Author contribution statement

All authors are equally contributed at different levels.