Preparation and Characterization of PANI/PVA Blends as Electrolyte Materials

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Abstract

This work presents a detailed study on the preparation and performance of polyaniline (PANI)/Polyvinyl alcohol (PVA) blend. The blends are prepared by the casting method at different weight ratios (1, 2, 3, 4, and 5 wt%). The structural morphology was characterized using scanning electron microscope SEM. The morphological analysis showed a uniform blend of PANI with PVA matrix. PVA exhibits lamellae structure of different shapes and dimensions. For 1% PANI, the results showed homogeneous blending, which decreases with an increase of the PANI ratio. Phase separation and semispherical region formation in the PVA matrix were seen. It was found that incompatibilities increase with increasing the PANI ratio. Also, the results proved in the blends scanning electron microscope anilinium cation – radical surfaces for an aggregate of different dimension and spherical shapes, which induced by surface tension. The electrical conductivity study of PANI/PVA blends and PVA reveals that PANI/PVA gives the conductivity of 10^{-4} $(cm.\Omega)^{-1}$, while PVA presented the lowest conductivity with the value of 10^{-12} $(cm.\Omega)^{-1}$. The results also showed an increase in ionic conductivity with temperature and PANI weight ratio. The increase in electrical conduction with increasing temperatures is due to the negative thermal coefficient, this result is attributed to the polymer chains that act as traps for charge carriers, and when the temperature rises, the transfer mechanism will be reigned by the hopping process.

1. Introduction

Although polymers are mostly known for their use in electrical and thermal insulation [1, 2] industry, they have very strong footsteps in an electronic industry where they are used as conducting materials [3, 4]. For example, conducting a form of polymers is very useful in helping dissipate and shield off any electrostatic charge from rubber and plastic parts of any electronic instrument. There are many types of conductive polymer coatings such as Polyaniline, polyvinyl alcohol/polyvinyl pyrrolidone, and polypyrrole. Polyaniline is the most popular conductive polymer due to its high conductivity properties among polymers and it also has reversible acid/base characteristics. However, PANI is very harmful to the environment, hard to produce, and expensive. Thus, PVA/PVP is used as a cheaper alternative. In addition, it has good stability, is environmentally friendly, easy to

process, and rich in charge transport mechanism [5]. PVA/PVP combination will improve the conductivity properties of the polymer due to the conductivity of polyvinyl alcohol. For example, conducting a form of polymers is very useful in helping dissipate and shield off an electrostatic charge from rubber and plastic parts of any electronic instrument. The basic approach to convert polymers from insulating to conducting form is by using conducting fillers, such as metallic powders and fibres, carbon nanotube, graphene, and conducting polymer [5, 6]. Among all conducting polymers conducting filler has received a great deal of attention for advanced applications including field-effect transistors corrosion protection actuators, and sensors [7-9]. Polyaniline PANI is found in one of the three idealized oxidation states during the polymerization of aniline monomer: leucoemeraldine (white/clear), emeraldine (salt-green/base blue), and pernigraniline (blue/violet). Fully oxidized PANI is known as pemigraniline base, half of the oxidized PANI is reduced as the emerald base, and PANI is completely reduced as the emeraldine base [10]. PANI is quite suitable for its distinguished characteristics such as environmental stability in the conducting form, ease and low-cost synthesis, high yield, and relatively, high conductivity [10-11]. Electrical conductivity is achieved in the conjugated polymers using delocalization of the π-electrons that allow charge mobility along the backbone of the polymer chain. Various applications of conducting polymers in diverse fields have been proposed as transducers for biosensors [12], electrodes of rechargeable batteries [13], artificial nerves and muscles [14], gas sensors [15], solid electrolytic capacitor, diodes, and transistors [16], anti-static electromagnetic shielding [17], and biomedical applications [18]. Through the combination of conventional polymers with conductive polymers, the mechanical properties of conducting polymers can be improved. The insulating polymer removes the brittleness and lack of process ability that are the main drawbacks hindering conducting polymers. In composites applications, it requires that conductivity is achieved at a small weight fraction of conducting polymer [19]. There is also an increased requirement for polymeric materials whose electrical conductivity can be tailored. The combination of conventional polymers with conductive polymers or fillers is an important alternative to obtain new polymeric materials with designed properties [20-22]. In this work, an attempt has been made to improve conductivity by PANI addition, and PANI/PVA preparation with good conductivity, which is suitable for electrolyte materials application.

2. Materials
In this research, PVA as white powder was supported by Barcelona (DIDACTC) company and PANI in the form of a black powder (Panichem Co) (PA-W35) Water-dispersible polyaniline –solid type.

2.1. Film Casting for Purified PVA
10 g of PVA was dissolved in (100 ml) of distilled water, put the solution in a water bath with the heat increasing up to 90°C by using a magnetic stirrer till getting a homogenous solution. Then leave the solution to cool to room temperature, with continuous stirring. The solution was put into the clean flat glass to dry at room temperature for (24h).

2.2. Film Casting for PANI/ PVA
10 g of PVA was dissolved in (100 ml) of distilled water, put the solution in a water bath with the heat increasing up to 90°C by using magnetic stirrer till getting homogenous solution of PVA. Then PANI was added at different weight ratios of (1, 2, 3, 4, and 5 wt%). Keep on stirring without heating until getting a homogenous solution. Put the solution on a magnetic stirrer until getting the homogeneous solutions and the temperature solution reach room temperature. The solution was cast in clean flat glass to dry at room temperature for (24h).

3. Results and Discussion
3.1. SEM Analysis
Figure 1 shows SEM results of PVA before and after PANI addition at different concentrations and weight ratios (1, 2, 3, 4, and 5 wt%). For PVA, it was seen grain structure of different shapes and dimensions. For 1% PANI, the results proved homogeneous distribution, which decreased with the PANI ratio increase. It was seen as phase separation and semi-spherical region in the PVA matrix. It was found that incompatibilities increase with the PANI ratio increase [21, 22]. By the PANI weight ratio increased, bubbles, pores, PANI agglomeration increased, which were caused by inhomogeneous PANI distribution. The results proved that the blends SEM anilinium cation–radical surfaces for an aggregate of different dimensions and spherical shapes, which was

induced by surface tension. By PANI ratio increase caused in rode's formation from AlKyl of PVA after bonding with PANI, that was in good agreement with [23].
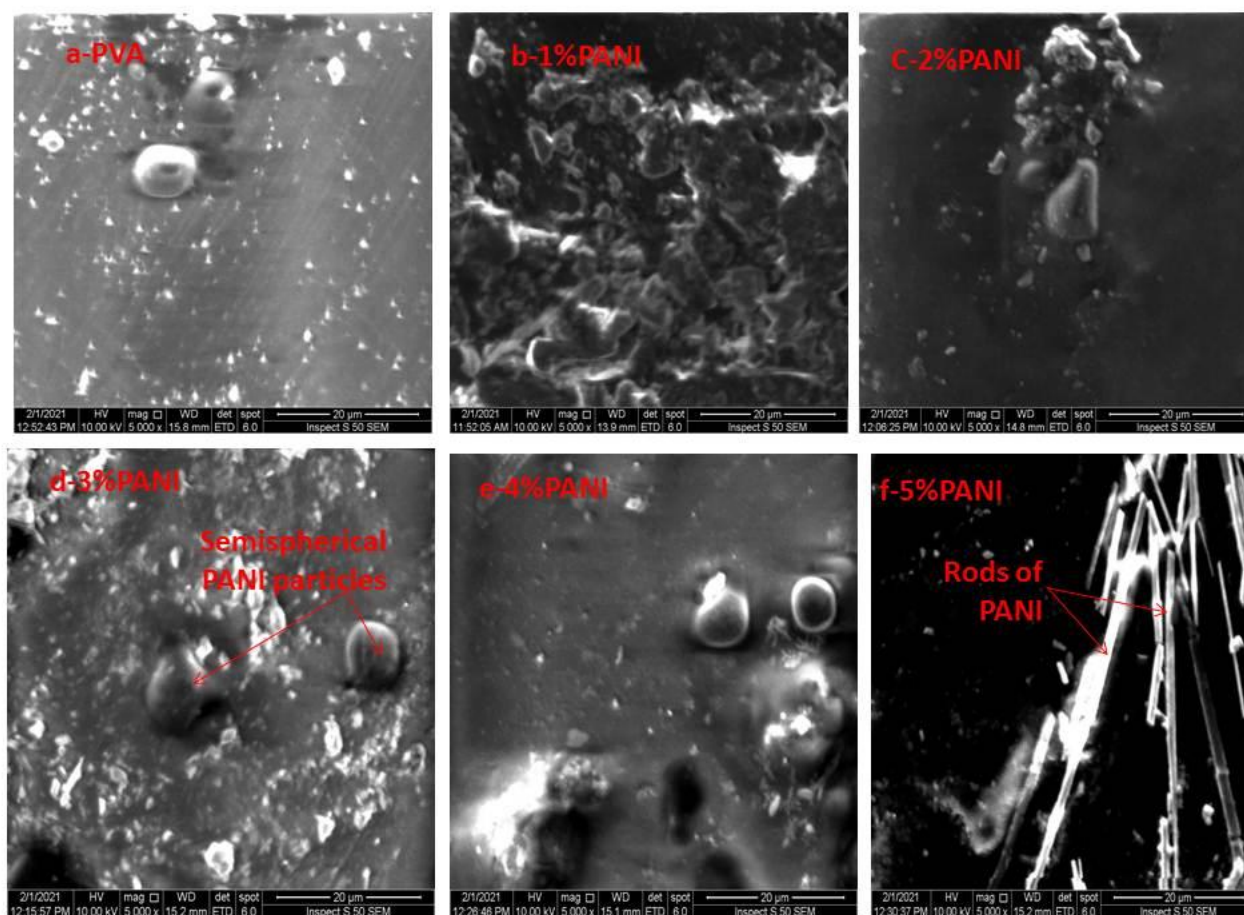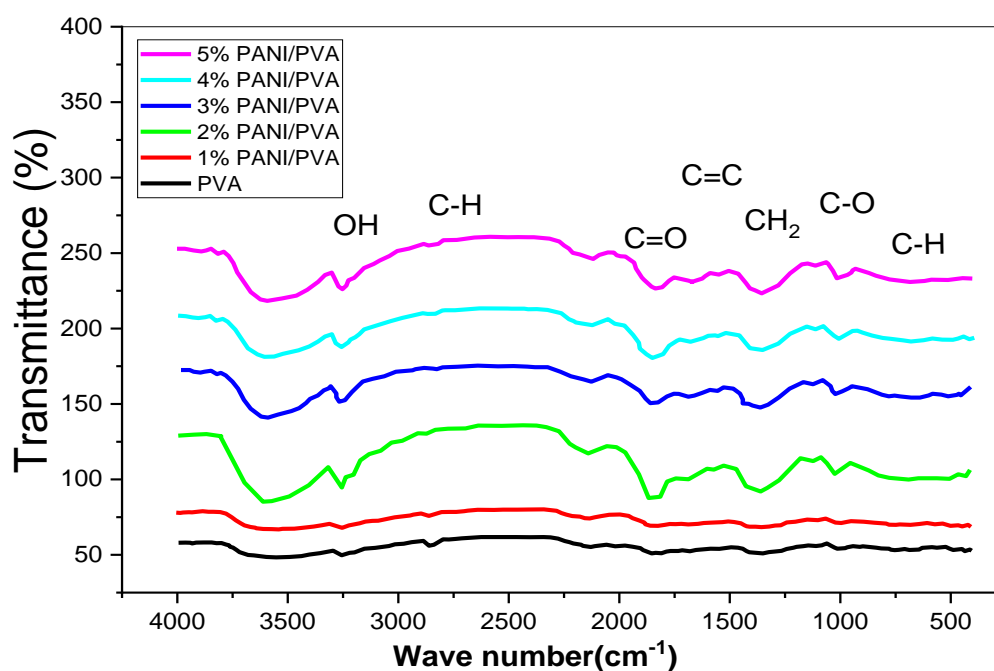

Figure 1: SEM images of PVA before and after PANI additions at different weight ratios (X5000M(20µm)).

3.2. FTIR Analysis

FTIR spectra are very sensitive to hydrogen bond formation [24]. Figure 2 shows the FTIR specters for (PVA) before and after PANI addition at different weight ratios (1-5 wt/wt%). Table 1 summarizes the FTIR characteristic of PVA before and after PANI addition at different ratios. For the (PVA) spectrum, it was found two bands at (659.75 cm^{-1}) and (918.16 cm^{-1}), which were attributed (C-H) bond out of phase bending, and (C-O) bond stretching in respectively. Band appearance at (1332.80 cm^{-1}) was due to (CH$_2$) bond bending. The band at (1579.75 cm^{-1}) was attributed to (CH$_2$) wagging and (C=C) bond stretching. The band (2926.11 cm^{-1}) was due to (C-H) bond stretching, and the bond at (3342.75 cm^{-1}) was due to (OH) bond stretching. There were two characteristic bands in the (PVA) spectrum, was due to the hydroxyl group of (PVA), and the second which was induced by (C-H) bond stretching. For PANI/PVA FTIR spectra it was seen band shift at the (3100-3600 cm^{-1}) range, which was attributed to (N-H) bond stretching, by PANI ratio increase. The appearance of new bands at (2800-3000 cm^{-1}), was due to the methyl group in PVA aliphatic chain, its intensity decreased with the PANI increase. The band at (1550.1610 cm^{-1}), was attributed to (C-N) bond stretching of the benzene ring, which was induced by PVA and PANI crosslinking, its intensity increased with PANI ratio increase. The band at (8.46) cm^{-1} was attributed to (C-H) bond bending in the benzene ring [25].

Table 1: FTIR characteristic of PVA before and after PANI addition at different ratios.

P.S	C-H out phase Bending 625-970 cm⁻¹	C-O Stretch 880-1000 cm⁻¹	CH2 Bending 1300-1380 cm⁻¹	CH2 Wagging C=C Stretch 1550-1610 cm⁻¹	C=O Stretch 1550-1750 cm⁻¹	C-H Stretch Aliphatic 2800-3000 cm⁻¹	C-H Stretch 2800-3050 cm⁻¹	OH Stretch 3100-3600 cm⁻¹
PVA	659.75 918.16	918.16	1332.56	1579.75	1649.19	2926.11		3342.75
1% PANI	667.39 833.28 920.08	920.08	1327.07		1654.98	2922.26	2922.26	3342.75 3387.11 3402.54
2% PANI	846.78	922.00	1330.93		1651.12	2862.46 2918.40	2862.46 2918.410	
3% PANI	846.78	918.15	1325.14	1564.32	1564.32 1651.12 1707.06	2916.47 2935.76	2916.47 2938.76	3416.65
4% PANI	700.18 846.78 920.08	700.18 846.78 920.08	1327.07		1647.25 1707.06	2860.53 2918.40	2860.53 2918.4	3394.83 3431.48
5% PANI	676.74 673.18 846.78 922.00	922.00	1327.07	1564.32 1646.33	1564.32 1646.33	2916.47 2936.76	2916.47 2936.76	3408.33

Figure 2: FTIR Spectra of PVA before and after PANI addition at different weight ratios.

3.3. Electrical Properties

Electrical properties of PVA before and after PANI addition at different weight ratios were determined by measuring the dielectric constant, loss factor, and A.c conductivity ($\sigma_{a.c}$) at room temperature within the frequency range of (100Hz to 1MHz) by using (impedance analyzer 429A). In which provided data and Win Fit software for experimental data visualization and treatment. Calculate the electrical conductivity from the resistance, length, and area of the current. The resistivity is given as p = RA/l where p is the resistivity, R is the resistance, A is the area and l is the length. The conductivity is s = 1/p where s is the conductivity.

3.3.1. A.C. Conductivity

Figure 3 shows the A.C conductivity changes with frequencies for PVA before and after PANI addition with different weight ratios (1-5 Wt%). The conductivity depends on temperature and frequency in polar polymers [23]. The hopping term refers to the charge carrier in a localized state, which was induced by charge carriers' excitation in the localized state and transferred to the conduction band, which was in good agreement with [26, 27]. The hopping term refers to the sudden displacement of charge carriers from one site to another. In general, it includes a process to transit potential barrier and mechanical quantum tunnels, which was in good agreement with [28]. The A.C conductivity was attributed to delocalized electron movements, and at the same time, it was due to electron hopping among redox sites in the polymer chain. The results proved a significant increase in conductivity with a frequency increase of more than (10^2 Hz). The sudden increase in A.C conductivity was induced by the process of the hopping electron, which was increased at high frequencies, and the PANI weight ratio increased. Figure 3 shows ($\sigma_{a.c}$ conductivity) changes with frequency, it was seen that the changes depend on the two relaxation process, which changes with frequency. The first relaxation process was (α-relaxation), which was induced by the micro-Brownion motion of polymer chains in the amorphous and crystalline regions of the PVA, and the second was attributed to the side group motions or the changes inside a group of the polymer matrix [29, 30].
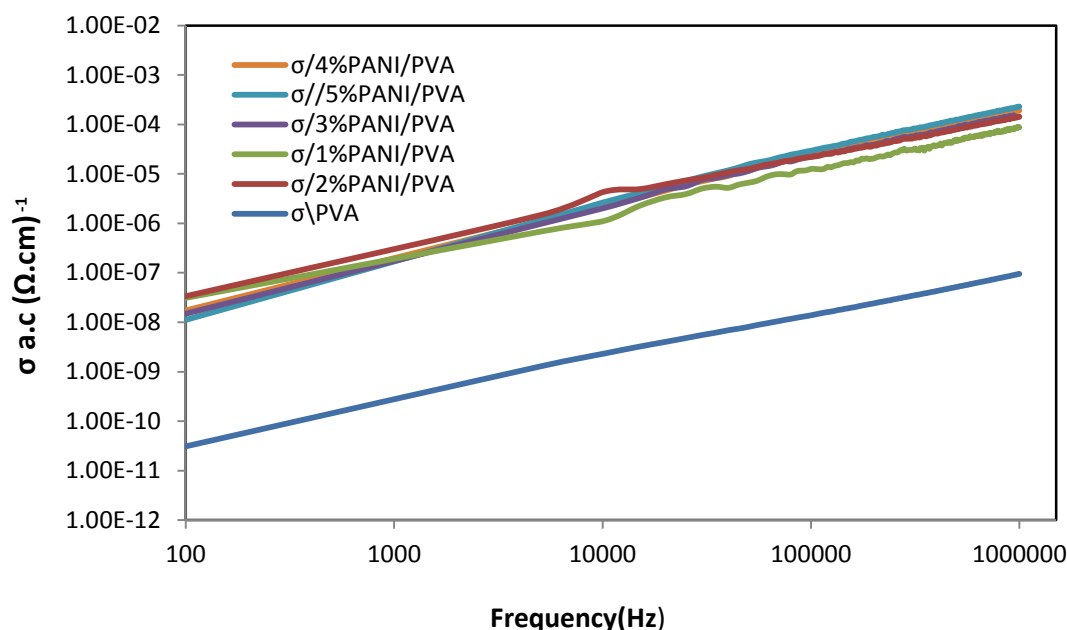

Figure 3: A.C conductivity as a function of frequency for PVA before and after PANI addition.

3.3.2. Dielectric Constant

Figure 4 shows the dielectric constant changes with frequencies for PVA and PANI/PVA at different weight ratios (1-5wt%). It was seen a dielectric constant increase during PANI ratio increase, which was attributed to polar group increase and then the polarization ability increase. The total polarization was the sum of electric, atomic and rotational polarization. It was seen dielectric constants decrease with a frequency which was due to rotational motion of polar molecules of dielectric material that was not speeding enough to reach the equilibrium state with the electric field at high frequencies that was in good agreement with [30-32].
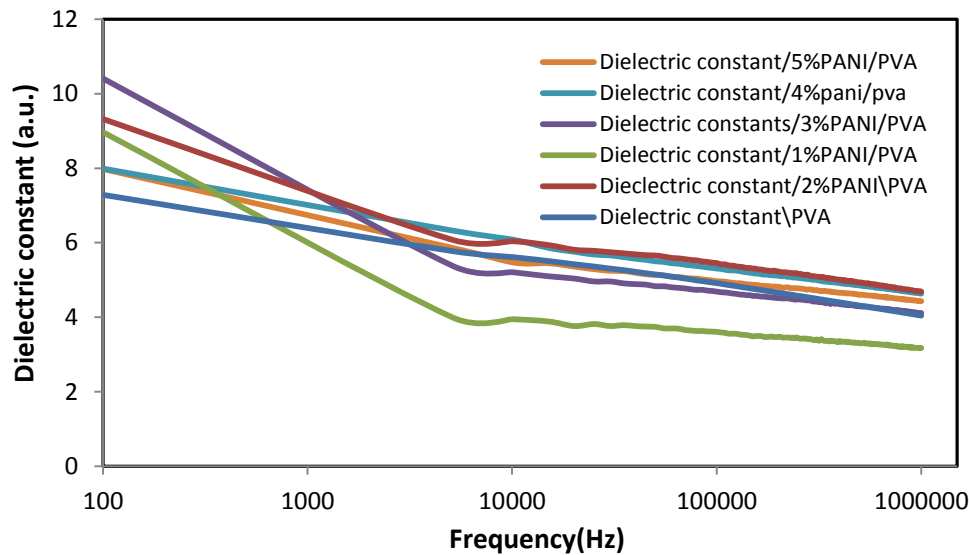
Figure 4: Dielectric constant as a function of frequencies for PVA before and after PANI addition.

3.3.3. Loss Factor

The loss factor (tanδ) means the dissipated power in the material according to total power in the electric circuit. The viscoelastic term means the material property, which possesses viscose and elastic properties at the same time. It can respond to electric and mechanical simulations and transferred it to heat within materials, that heat caused heat rise of the dielectric material and deterioration in the material involved. Figure 5 shows loss factor changes with frequency for PVA before and after PANI addition at different weight ratios (1-5 wt%). The results proved an unsystematic increase in Loss factor with PANI weight ratio increase up to 3Wt%PANI, and the loss was for PVA. Whereas there was a decrease in loss factor with frequency increase, that was due to space charge polarization decrease at high frequencies, that was in good agreement with [30, 31].
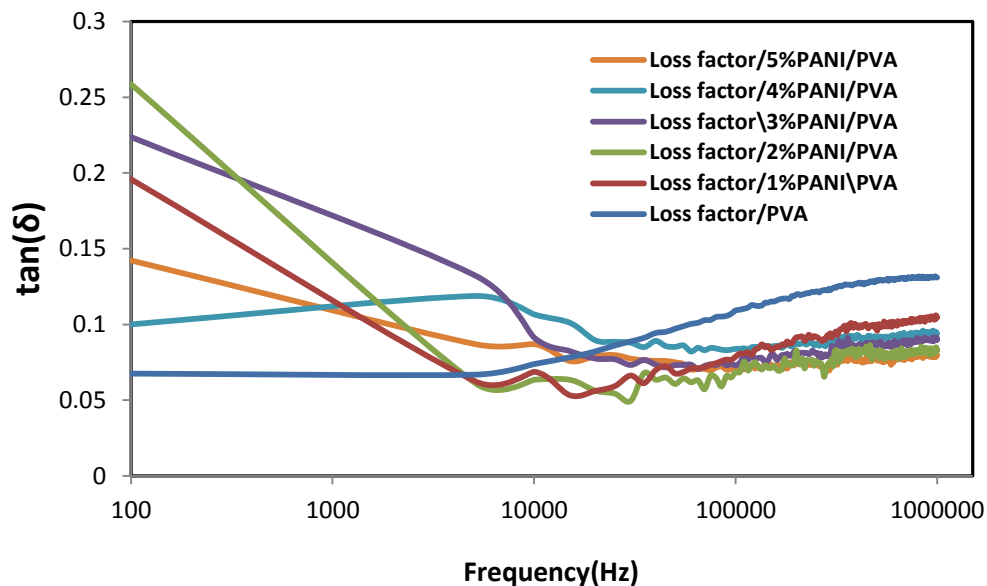

Figure 5: loss factor (tan δ) as a function of frequencies for PVA before and after PANI addition.

3.4. Ionic Conductivity

Figure 6 shows the correction of ionic conductivity with temperature with a range of (25-150˚C) for PVA and PANI at different weight ratios (1-5wt%). It was noticed that the ionic conductivity increase with temperature increase. So, that was due to the negative thermal coefficient of the involved samples. This fact is explained by the polymer chain, which acts as (trapping site) for charge carriers that were transferred by the hopping process. As the temperature increased the segments of polymers moved and trapped charges were released. The trapped charges releasing was a suited with molecular motion, and cased current increase with temperature increase [32, 33]. The results proved that 4 wt% PANI was of the highest conductivity.
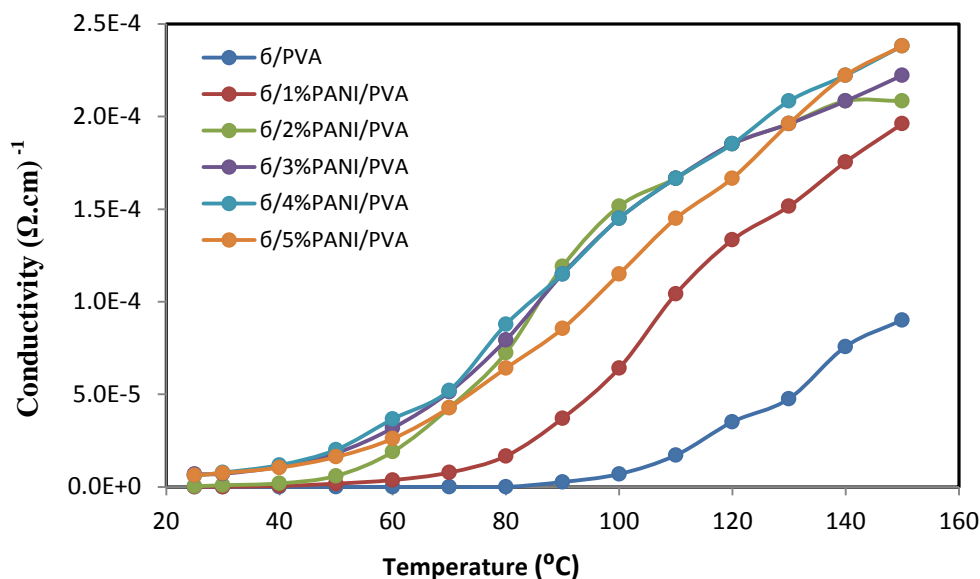

Figure 6: Ionic conductivity as a function of Temperature for PVA before and after PANI addition.

4. Conclusion

The results proved increased the a.c. conductivity with frequency and PANI weight ratio increase. The conductivity increased with PANI weight ratio was enhanced with SEM micrographs The results showed. The ionic conductivity increases with temperature increases. The best ionic conductivity was for 4 wt% PANI 10^{-4} $(cm.\Omega)^{-1}$, whereas the worst was for PVA10^{-12} $(cm.\Omega)^{-1}$. The conductivity improved to $10^{-4}(cm.\Omega)^{-1}$ suggested that the involved samples can be used as electrolyte materials.

Acknowledgement

Conflict of Interest

There are no conflicts of interest regarding the publication of this manuscript.

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