

Study of Electrical and Mechanical properties of PVA/PVP blends with CuSO₄.5H₂O .

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Abstract

In this research, a series of polymer blends consisting of polyvinyl pyrrolidone PVP, and polyvinyl alcohol PVA were prepared using the solution casting method. Different concentrations of copper sulfate (CuSO₄.5H₂O) were added to these blends (PPCuS). X-ray diffraction (XRD) analysis was conducted to examine the crystalline structure of PPCuS. Results of the XRD study confirmed the presence of crystallinity in the PPCuS complex. Additionally, FTIR was performed to verify the formation of a complex between the blend polymer and CuSO₄.5H₂O. Furthermore, direct current (DC) conductance measurements on the films were made, revealing that the conductivity of the blends increased with higher concentrations of CuSO₄.5H₂O. The conductivity values ranged from 1.79×10^{-1} S/cm at 0.5 wt% CuSO₄.5H₂O to 3.35×10^{-1} S/cm at 1.5 wt% CuSO₄.5H₂O concentrations. Experiment results showed that 0.5% of powdered additive is the best percentage for polymer elongation, which is 4.9%. The hardness of the mixture starts at the lowest value, which is 3.63 MPa at the percentage of 1%, and then the hardness value increases when the fillers are increased, especially at the percentage of 1.5%, to reach the highest value, which is 16.2 MPa. The addition of CuSO₄.5H₂O improves the morphology and strengthens the composite polymeric blend. Additionally, the polymers blend PVP, PVA with additives CuSO₄.5H₂O is a suitable material in many applications, especially optoelectronic, electrical and optical devices.

Keyword: DC conductive measurement, mechanical properties, SEM, XRD, CuSO₄.5H₂O.

1. Introduction

Because polymer blends have so many useful features, they are becoming increasingly well-known in a wide range of sectors and fields. The enhanced mechanical, electrical, thermal, optical, and structural properties of polymer blends have demonstrated their remarkable performance in these applications. Polyvinyl alcohol is a favored polymer in

many industries due to its semi-crystalline qualities and beneficial physical attributes [1]. Conversely, polyvinyl pyrrolidone's high solubility makes it a good casting solution for creating polymeric mixes. Because of this, scientists from all over the world have expressed a great deal of interest in PVA/PVP blends in an effort to maximize these advantageous characteristics [2]. Numerous studies have been carried out on polymer blends with varying PVA and PVP ratios in order to examine the changes in electrical, optical, and physical properties. Finding the blend composition that would work best for a given application was the goal [3]. Polymer blends offer a significant advantage in customizing the properties of the final product to meet specific needs, which is not possible with a single polymer. The miscibility of the polymer blend plays a crucial role in determining the properties of the resulting film. Various interactions, including, dipole-dipole forces, charge transfer complexes and hydrogen bonding, play a significant role in determining the miscibility of polymers in homopolymer mixtures [4–9]. PVA, a semi crystalline polymer, has attracted considerable interest because of its intriguing physical properties. PVP is a notable conjugated polymer that exhibits remarkable dielectric strength (1,000 kV/mm), notable electrical and optical properties and impressive charge storage capacity. Hydrogen bond formation and the existence of hydroxyl (OH) groups affect these characteristics. PVP also stands out for its favorable environmental stability, ease of processing, moderate electrical conductivity, and intriguing charge transport mechanisms. Both two polymers are water-soluble[10]. offering the added advantage of avoiding the use of potentially harmful organic solvents. PVP is commonly employed as a hydrophilization agent in applications such as water purification and dialysis membranes [11,12]. Additionally, it is utilized for the physical stabilization of suspensions [13]. Blending these two polymers (PVA and PVP) together is anticipated to result in interactions between the carbonyl group of polyvinyl pyrrolidone with the hydroxyl group of polyvinyl alcohol through interchange hydrogen bonding. However, to the best of our knowledge, there is currently no existing literature available on the subject of PVP/PVA blend membranes and their impact on the separation performance of facilitated transport membranes. PVA, a commonly utilized water-soluble synthetic polymer, is widely recognized as an environmentally friendly material due to its versatile dopant-dependent properties. It possesses excellent resistance and physical characteristics [14]. However, many polymers exhibit high crystallinity and glass transition temperature (T_g), which hinders their efficiency as ionic conductors [15]. Thus, in order to achieve enhanced conductivity at lower temperatures, it becomes essential to reduce the degree of crystallinity and T_g of the GPEs (Gel Polymer Electrolytes) [14]. Veena and Blaise [16] used SEM, FTIR and XRD to study the thermal properties, microstructural properties and spectroscopic characteristics of potassium permanganate ($KMnO_4$) filled polyvinyl pyrrolidone (PVP) with polyvinyl alcohol (PVA) blend films. The filled samples' FTIR spectra revealed a significant molecular structural alteration involving the hydroxyl (OH) group's conversion into ketones at higher FL. The PVA-PVP blend became more

amorphous when KMnO_4 was added, according to the XRD data. Only at the lowest filler levels of 0.01% mass can micrographs demonstrate evidence for the production of nanoparticles in the host polymeric material. The study by Huang [17]. creation of PVP/PVA/borax hydrogels using a freeze-thaw method in varying compositional ratios. Comparisons of PVP and borax's effects on hydrogels were made both chemically and physically. PVA/borax hydrogel properties: PVP, Borax, and PVC. Since PVA/PVP/borax hydrogel has less intermolecular hydrogen bonding than PVA/borax hydrogel, PVA/PVP/borax hydrogel with 4% PVP and a PVA/borax ratio of 1% has the best mechanical properties. TiO_2 NPs were synthesized using the sol-gel method, and subsequently employed as nanofillers in an alternating blend of polymers consisting of CMC, PVA, and PVP to fabricate polymer nanocomposite (PNC) films. XRD, FTIR, and UV/VIS-NIR techniques were used to extensively study the structures, morphologies, and optical properties of the generated pure mix polymers and the polymer nanocomposite (PNC) films with TiO_2 NPs levels of 0.5, 1.5, and 3 wt%. These methods showed that the interactions between the polymer chains and the nanofiller were really good. The results of the electrical and dielectric measurements indicated an increase in the values of σ_{ac} , M' , M'' , ϵ' , and ϵ . Furthermore, the DC conductivity improved from $2.30 \times 10^{-12} \text{ S cm}^{-1}$ to $2.88 \times 10^{-11} \text{ S cm}^{-1}$ for a 3% TiO_2 NP blend (for a pure PVA/PVP/CMC blend) [18]. Hydrogels can be conveniently adjusted for a variety of agricultural applications with the help of the PVA/PVP combination. It was suggested that these hydrogels be made synthetically, employing a range of preparatory strategies, including physical cross-linking through freeze-thaw cycles, chemical cross-linking, and radiation. The desired hydrogel qualities determine which approach is best. These characteristics were then assessed chemically and physically, and their effect on biological activity was looked at [19]. The best percentage of the manufactured polyvinyl alcohol (PVA)-polyvinyl pyrrolidone (PVP) blend films was found to be (40/60) wt.% according to the recorded maximum value absorption, the minimum value energy gap ($E_g = 4.66 \text{ eV}$), and the maximum value of electric conductivity ($\sigma_{dc} = 3.08 \times 10^{-9} \Omega^{-1} \text{ cm}^{-1}$) [20]. ZnO , PVA and PVP (PPZnO) composite nanofibers were prepared by electrospinning zinc oxide nanoparticles dissolved in a homogeneously mixed polyvinyl pyrrolidone with polyvinyl alcohol blend solution in the electrospinning system. In order to analyze the structure and composition of the nanostructured fibrous membrane, XRD, SEM, FTIR, Raman, and XPS experiments were used. The creation of a ZnO /PVA/PVP polymer nanocomposite was validated by XRD analysis. The fibers were the subject of antibacterial activity research, and the findings were positive, suggesting that the generated nanofibrous material could be beneficial for antimicrobial face masks [21]. In this study, polymer samples of PPCuS were prepared, incorporating varying concentrations of copper sulfate. The objective was to examine the impact of the dopant on the properties of PVP/PVA. To analyze the doped polymer samples, characterization techniques such as

ultraviolet (UV)-visible spectroscopy, Fourier transform infrared spectroscopy, X-ray diffraction, Mechanical properties and DC conductivity measurements were employed.

2. Experimental:

To create the PVA/PVP films, a solution cast method was employed. Poly vinyl alcohol (PVA) with a molecular weight of 40000, sourced from Central Drug House (P), Polyvinylpyrrolidone (PVP) with a molecular weight of 14000 was used. Initially, the necessary weights of each polymer powder were dissolved in distilled water at 90°C to create separate bulk solutions. The solutions were continuously stirred for 3 hours to ensure thorough mixing. Following that, the bulk solutions of PVA and PVP were combined at various ratios (0.5, 1, and 1.5) wt%, of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, with continuous stirring, until achieving clear and transparent solutions.

3. Characterization:

Spectrometric analysis of polyvinyl alcohol (PVA) and polyvinyl pyrrolidone (PVP) polymer blends added with various concentrations of copper sulphate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) (PPCuS) was obtained using the Instrument FTIR-4200 from JASCO, Japanese-made. In this spectrometric analysis, the wave number range utilized is $(4\text{cm}^{-1} - 40\text{cm}^{-1}) \times 10^2$. Samples for laboratory measurement were prepared using potassium bromide (KBr) powder with polymer, in a 3:1 ratio of polymer and potassium bromide (KBr). To study the morphological characteristics of the samples, a scanning electron microscope (SEM), model Quattro S, manufactured in the United States of America was used. The magnification power was $(10 \times - 20 \times) \times 10^3$, the applied voltage was 10KV, and the working pressure of was 6×10^{-2} mbar. X-ray diffraction (XRD) is a widely used analysis method to evaluate the crystallinity and structure of solid samples for polymer blend with $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$.

4. Results and discussion:

4.1 X-ray diffraction analysis:

Fig. 1(a,b,c) displays the XRD patterns of the PVA/PVP with copper sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) (PPCuS). The X-ray pattern in Fig. 1 for PPCuS at different ratios of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (0.5, 1, 1.5) indicates that the films exhibit crystalline properties, with peaks observed at 22.30, 22.20, and 20.20. Notably, the peaks gradually decrease in intensity in the PPCuS films, as shown in the figure. When the concentration of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ is reduced, there is an observed increase in the degree of crystallinity of the PVP/PVA polymers. This increase in crystallinity is attributed to the addition of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$.

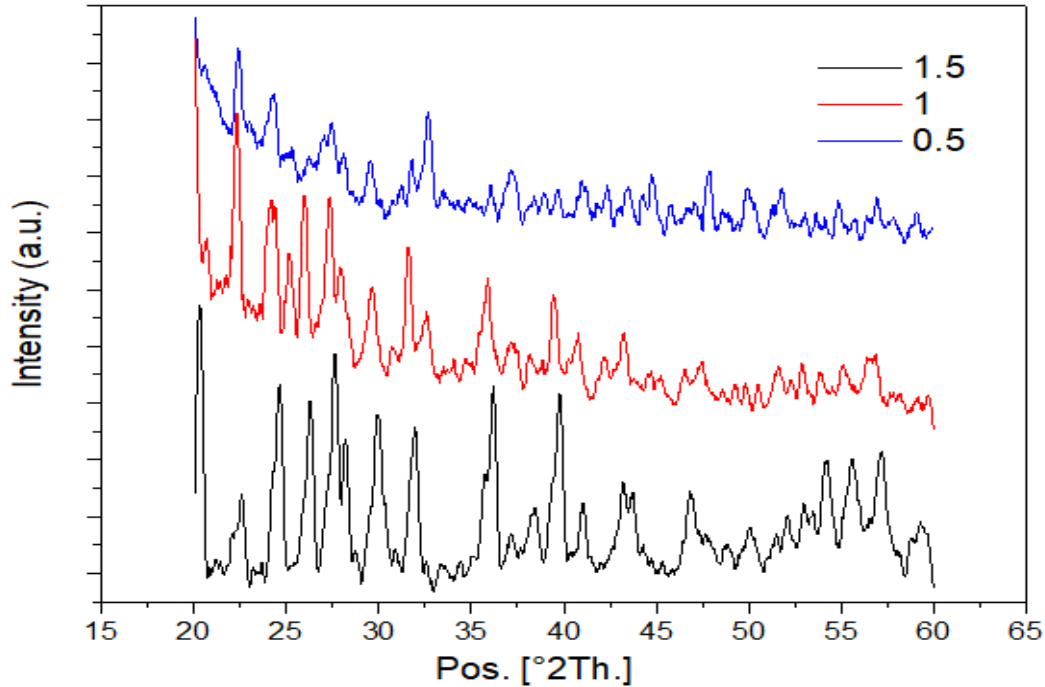
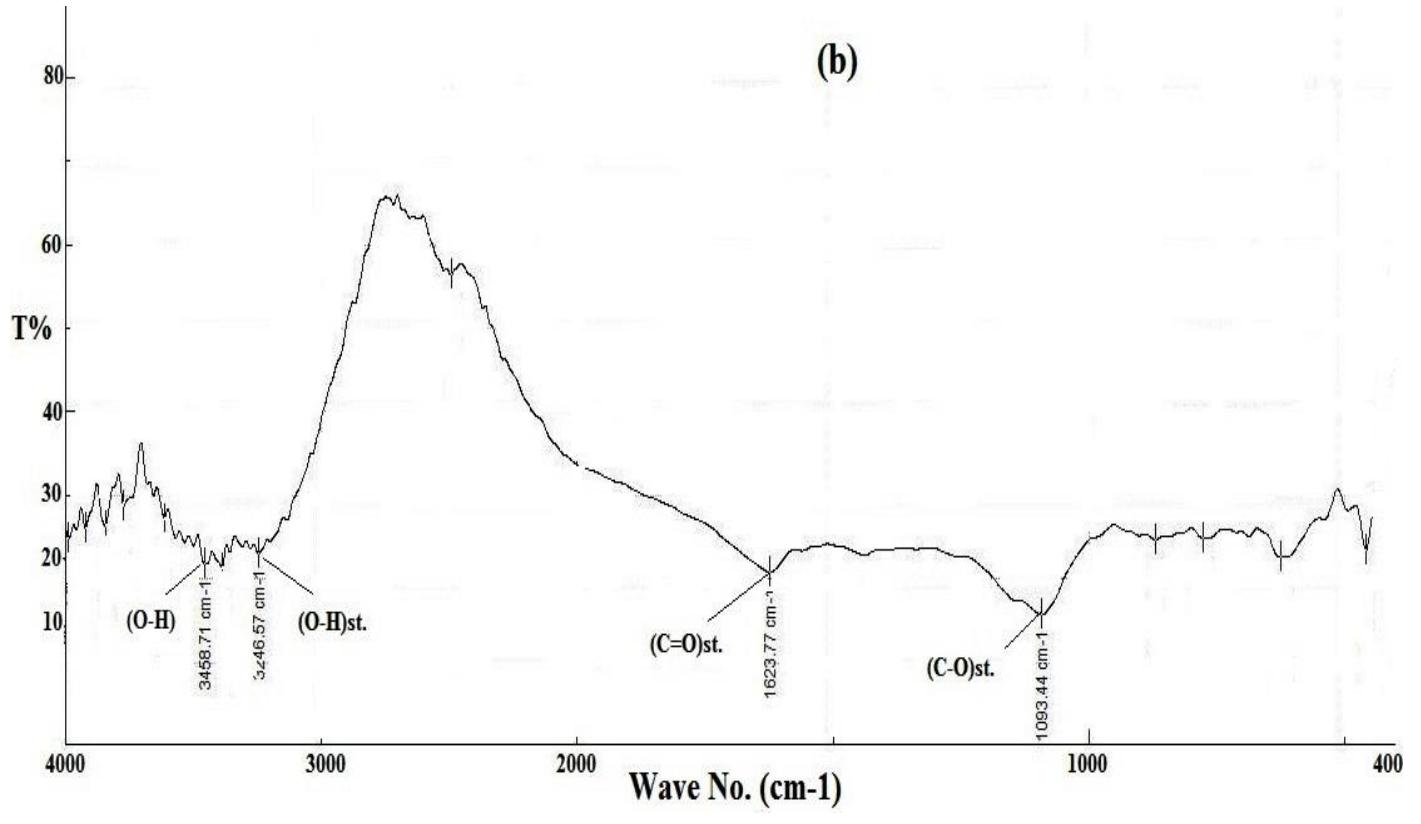
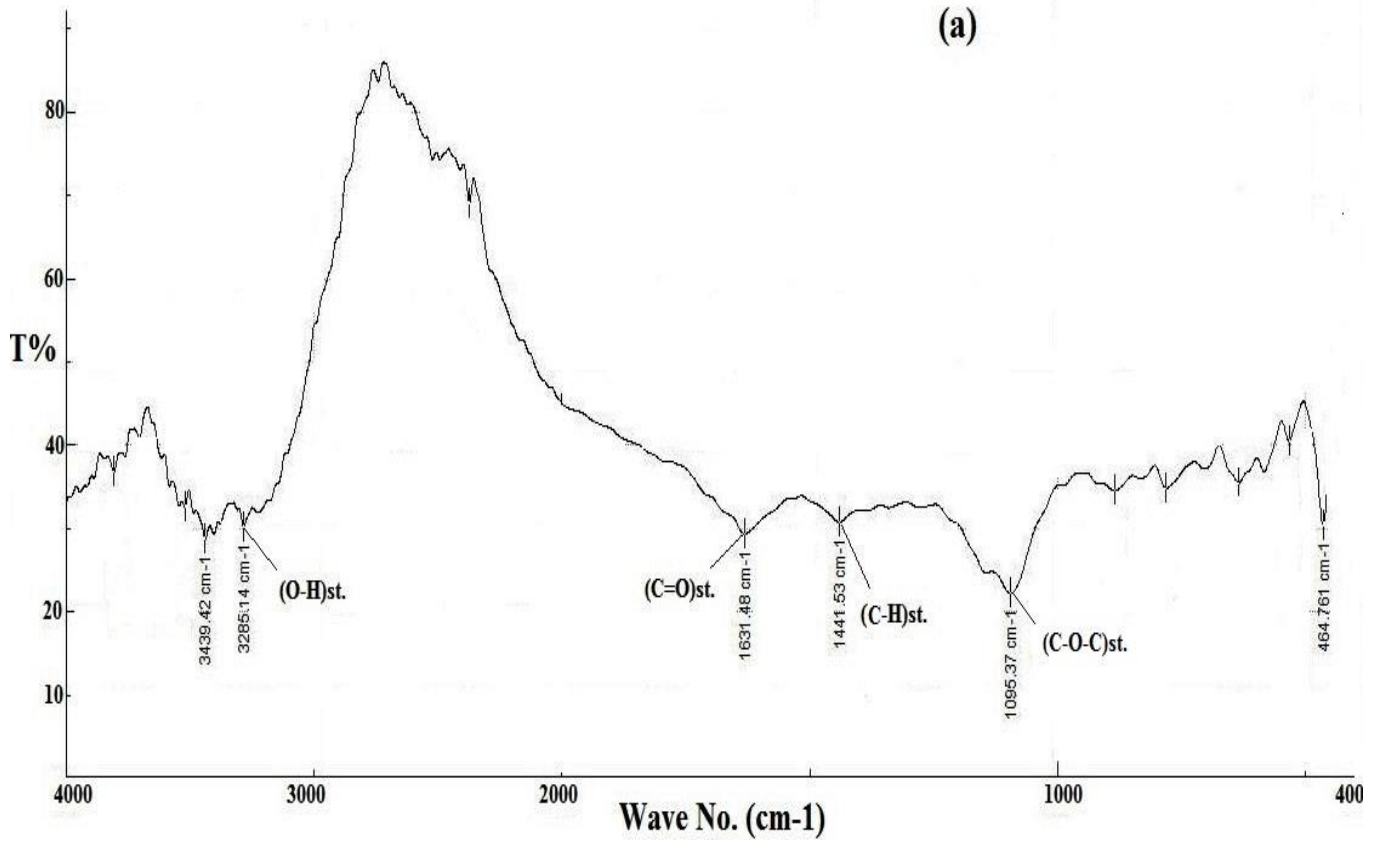


Figure 1: XRD of PPCuS with added weight ratios: (a) 0.5% ,(b) 1% and (c) 1.5%.

4.2 Fourier transforms infrared Spectroscopy (FTIR):

To study interactions in polymer blends, FTIR spectroscopy was employed, focusing on the atomic or ionic interactions in systems of electrolyte. Figure (2) exhibits the FTIR spectra of the PVP - PAP polymer blend at various concentrations, recorded at room temperature. Moreover, Fig. 2 show cases the FTIR spectra of the PPCuS blend, also at different concentrations. Fig.2 (a,b,c) displays the FTIR spectra of the PAP/PVP blend with varying concentrations of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, recorded at laboratory temperature. The observed bands at 3285, 3246, and 3116 cm^{-1} in Fig.2 (a,b,c) corresponding to PPCuS (0.5,1,1.5) wt% were identified as O–H stretching vibrations. Furthermore, the bands at 1095, 1093, and 1092 cm^{-1} in PPCuS (0.5,1,1.5) wt% were attributed to the presence of carbonyl groups (C=O). Additionally, in PPCuS (0.5,1,1.5) wt%, the observed bands at 885, 869, and 715 cm^{-1} were attributed to CH_2 bending vibrations. The observed bands at 3251 cm^{-1} in Fig.2 (a,b,c) corresponding to PPCuS (0.5,1,1.5)wt% were identified as (O–H)st. Notably, when $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ was introduced to the PVA: PVP blend, these aforementioned bands associated with PVA and PVP exhibited shifts[22].



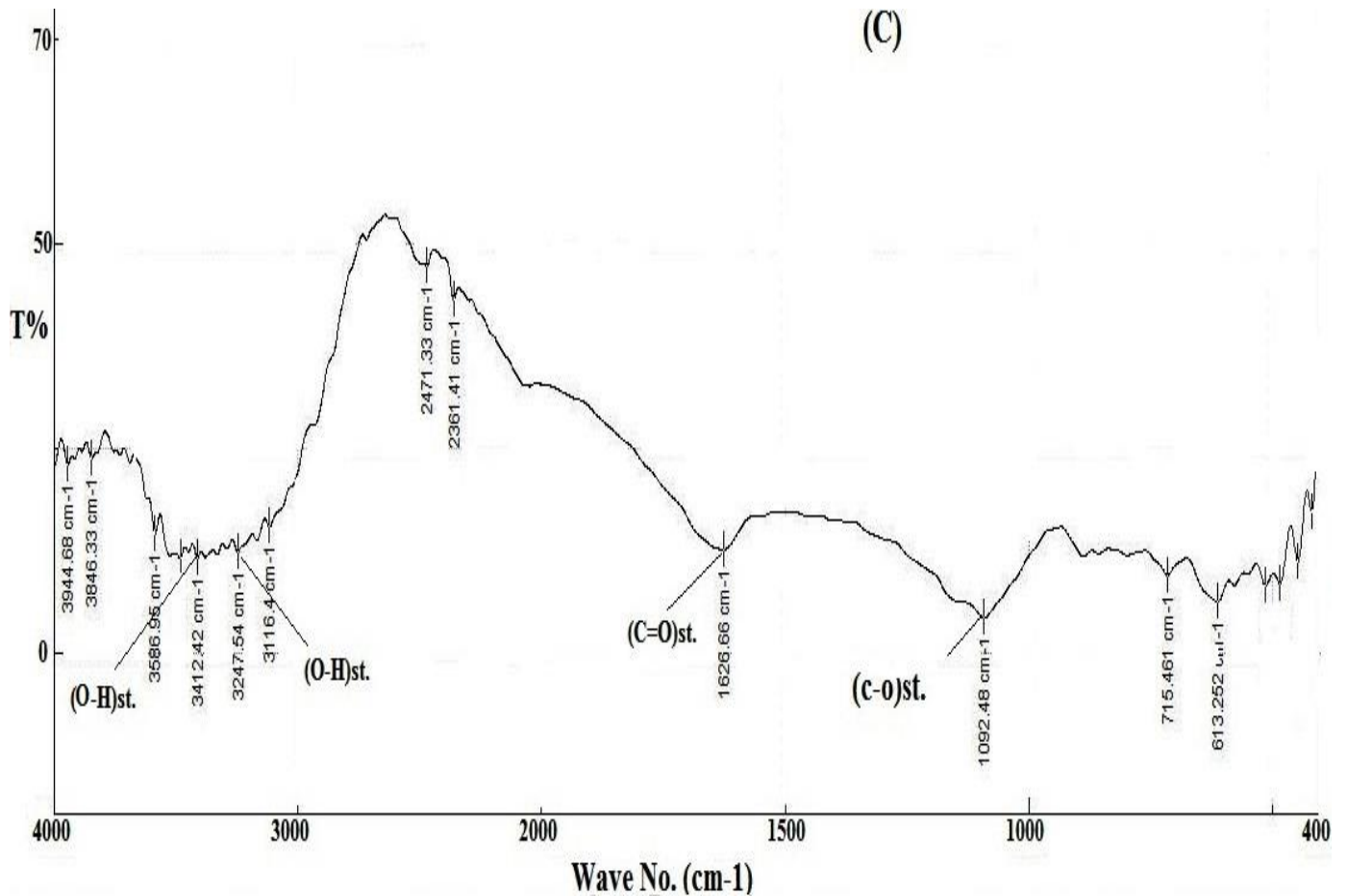


Figure 2: FTIR spectroscopy of PPCuS with added weight ratios: (a) 0.5% ,(b) 1% and (c) 1.5%.

4.3 Scanning Electron Microscope (SEM):

Fig. 3 (a-c) depicts the scanning electron microscope SEM images of the polyvinyl alcohol (PVA) and polyvinyl pyrrolidone (PVP) with copper sulphate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) (PPCuS) films. We utilized SEM to examine the surface morphology of the films and observe the impact of loading the PVA/PVP polymer blend with $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. As shown in Figure 3(a-c), the SEM images of the loaded polymer blends revealed a slightly rougher surface and the development of white patches. Notably, the presence of these patches was more pronounced in the doped blend with $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$.

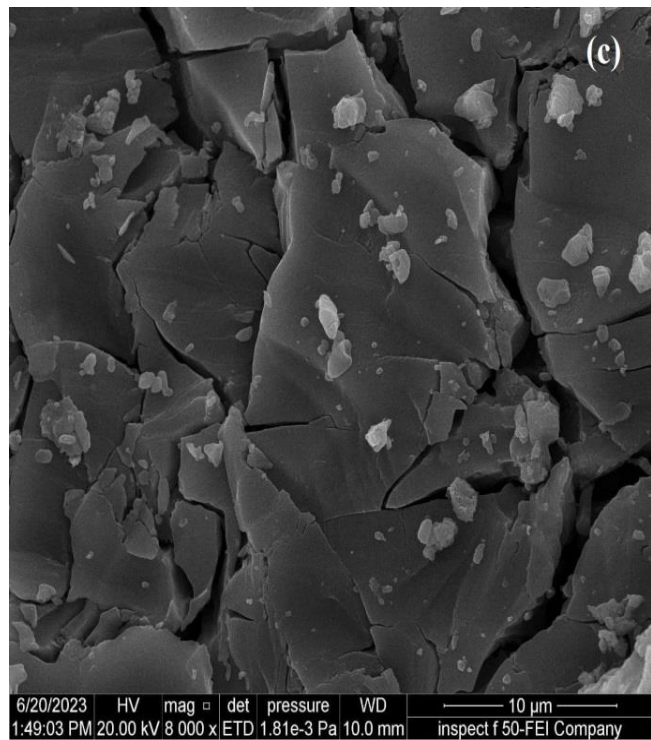
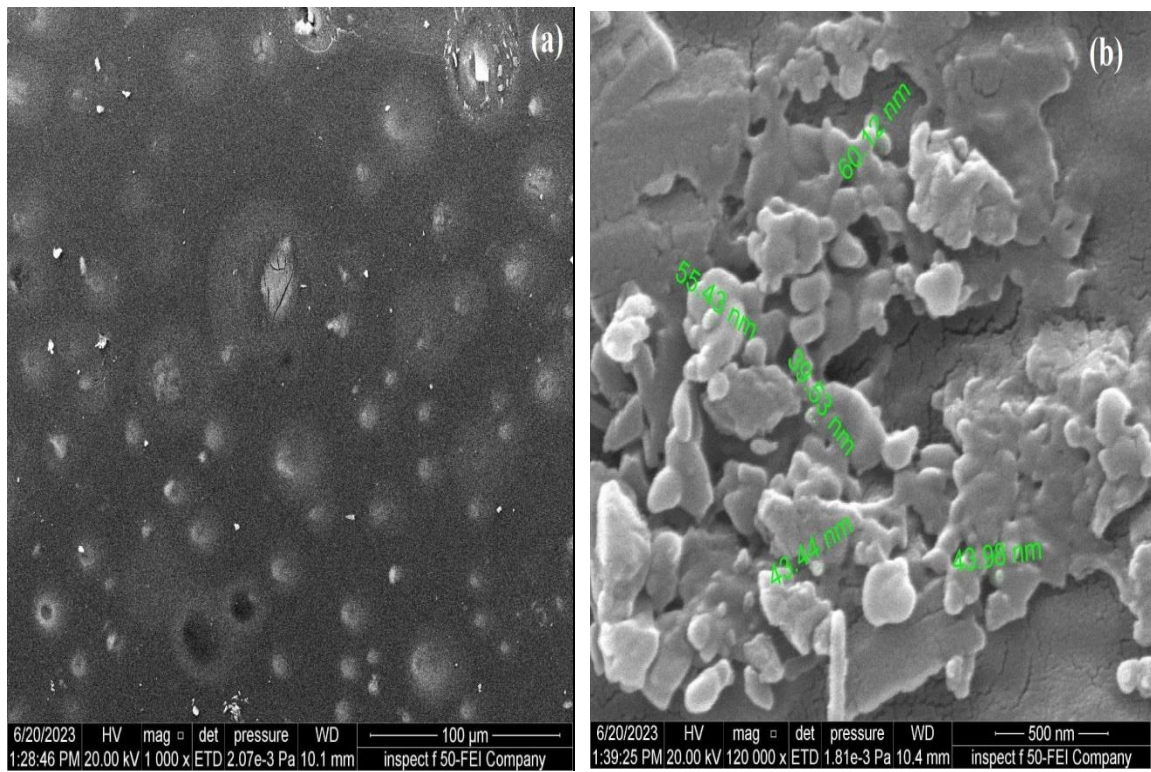


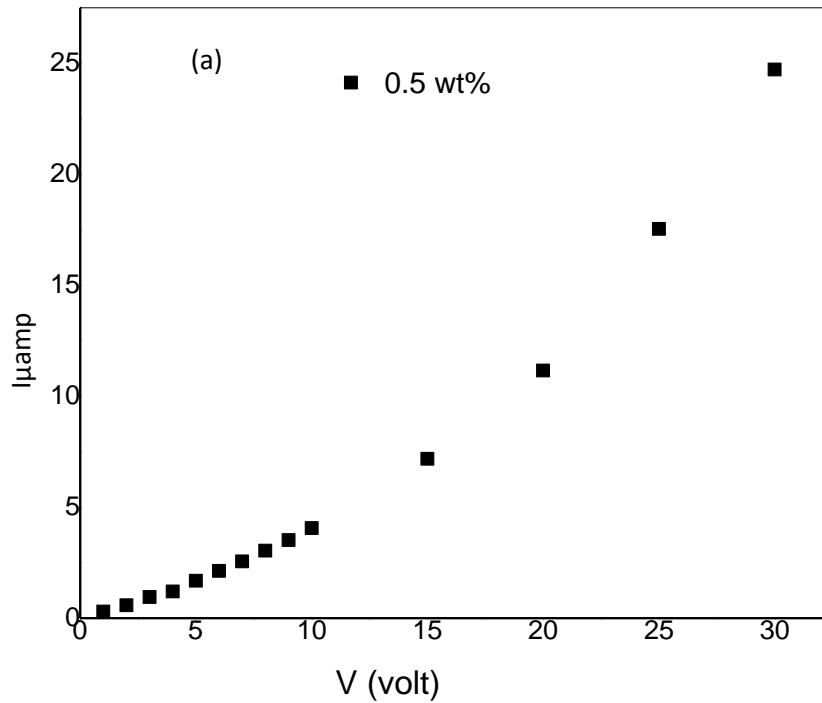
Figure 3: SEM image of PPCuS : (a) 0.5% ,(b) 1% and (c) 1.5%.

4.4 Electrical conductivity:

Fig. 4(a-c) illustrates the current-voltage characteristic of PVA/PVP blends with varying concentrations (0.5, 1, 1.5 wt%) of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ at room temperature. The electric conductivity was determined for each concentration. The results indicate that the electrical conductivity increases as the concentration of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ increases, which aligns with the findings of [23] that higher concentrations of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ exhibit higher conductivity. Notably, the conductivity reaches its maximum value at 1.5 wt% $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. The experimental results showed that as the concentration of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ increased, the electrical conductivity also increased. DC conductivity measurements were conducted at normal room temperature. The formula used to calculate the electrical conductivity (σ) is [24]:

$$\sigma = \frac{d \times I}{V \times A} \text{ ----- (1)}$$

where d represents the thickness of the sample, A the cross-sectional area of the sample, I the electric current, and V represents the applied voltage. The conductivity values ranged from 1.79×10^{-1} S/cm at 0.5 wt% $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ to 3.35×10^{-1} S/cm at 1.5 wt% $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ concentrations.



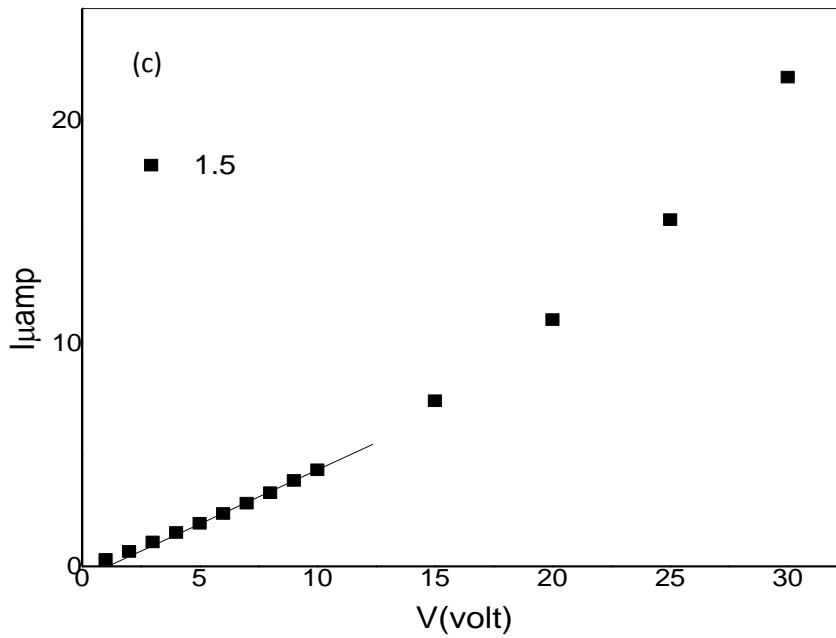
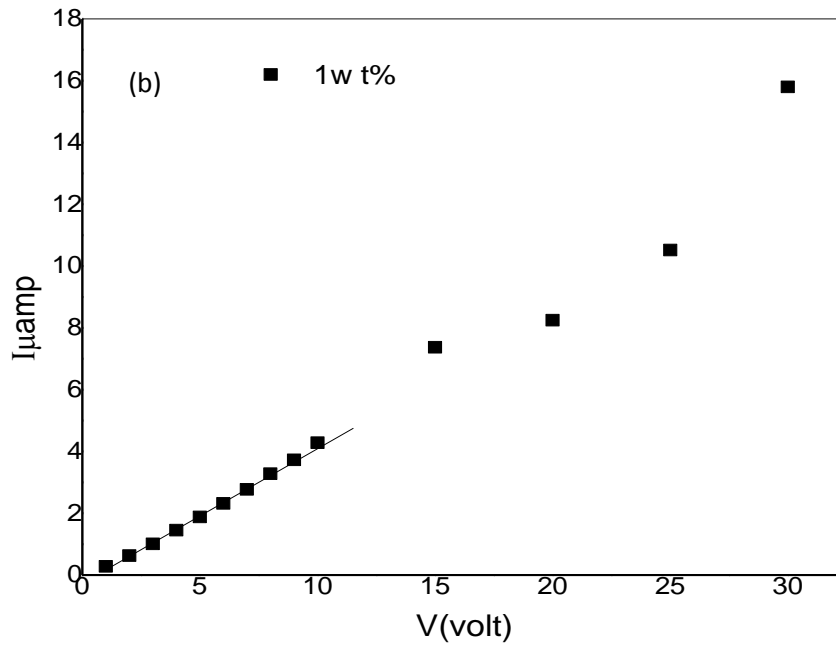


Figure 4: Current-voltage characteristic of PPCuS : (a) 0.5% ,(b) 1% and (c) 1.5%.

4.5 Mechanical properties:

The impact of incorporating filler into the PVA/PVP blend on the elongation percentage was significantly reduced as the $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ concentration increased. The elongation behavior of polymers with filler content is depicted in Fig. 5. The elongation notably decreased, particularly at a concentration of 1.5 wt% $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, with the maximum stress observed at 0.5 wt%. As the filler particles fill up the spaces between the chains of polymer, That is, the movement of these chains is restricted. As a result, the elongation decreased with increasing polymer filler content [25].

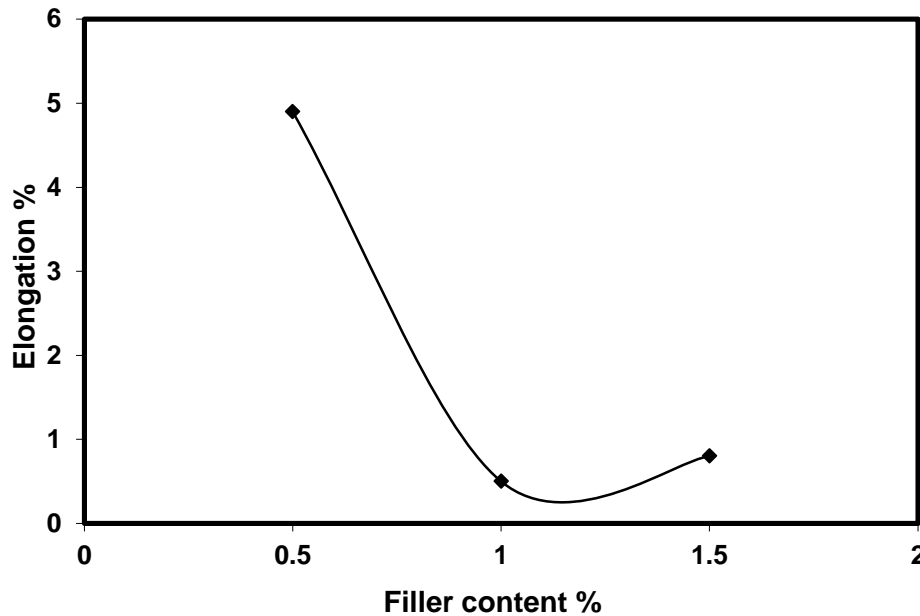


Figure 5: Elongation of PPCuS different percentage of additives.

When the filler content in an additive is 0.5 wt%, the tensile force, also referred to as the stress force, initially demonstrates a slight effect. However, at 1 wt% filler content, the tensile strength decreases to 3.6 MPa. On the other hand, the addition of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ leads to an increase in tensile force. Specifically, when the percentage of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ is increased from 1.5 wt% to 16.3 Mpa, the tensile strength increases. At a filler content percentage of 1.5 wt%, the addition of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ enhances the hardness property. This improvement is observed through the even distribution of additive powder among the polymeric chains. The relationship between the percentage of filler content and the stress force, also known as tensile force, is illustrated in Fig. 6 [26].

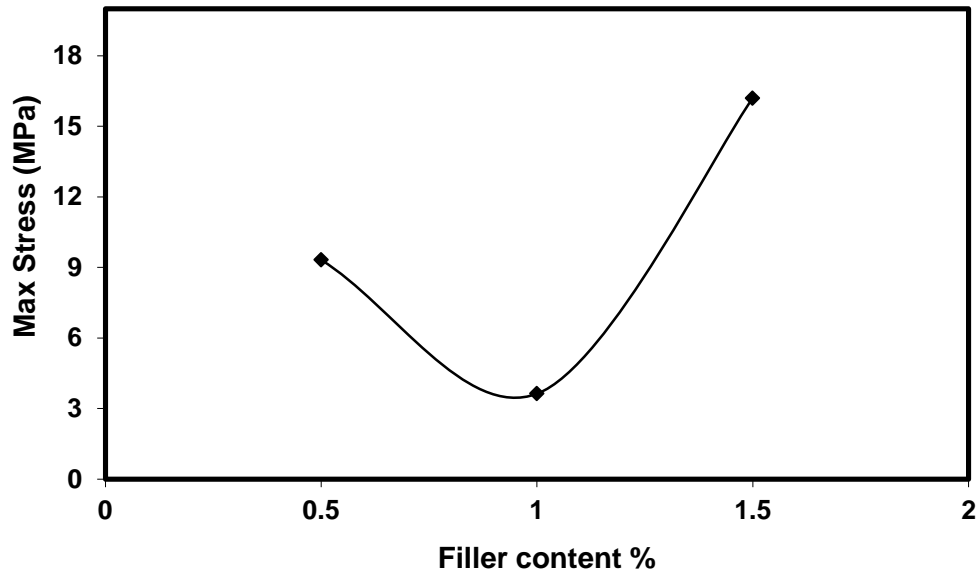


Figure 6 : Max Stress of PPCuS different percentage of additives.

Conclusions:

Using the casting technique, a PVA/PVP blend in a 1:1 ratio was prepared and doped with various weight percentages (0.5, 1, 1.5) wt% of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. The objective of this study is to investigate the impact of copper sulfate pentahydrate on the electrical and mechanical properties of the resulting of the PVA-PVP with copper sulphate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) (PPCuS). The crystal nature of the PVA/PVP polymer blend with $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ was examined using X-ray diffraction (XRD) characterization. SEM images were also utilized to observe the impact of the blend on the morphology of the copolymer. The results indicated that the blend exhibited a higher level of compactness compared to the unreinforced copolymer. Experimental findings demonstrated that a 0.5% inclusion of powdered additive yielded the optimum polymer elongation, with a value of (4.9%). The hardness of the mixture initially begins at its lowest value, measuring 3.63 MPa when the fillers are present at a 1% percentage. Subsequently, as the fillers are increased, particularly at a 3% percentage, the hardness value steadily increases. It reaches its peak value of 16.2 MPa at this concentration. The conductivity values ranged from 1.79×10^{-1} S/cm at 0.5 wt% $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ to 3.35×10^{-1} S/cm at 1.5 wt% $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ concentrations. The addition of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ improves the morphology and strengthens the composite polymeric blend. Additionally, the polymers blend PVP, PVA with additives $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ is a suitable material in many applications, especially optoelectronic, electrical and optical devices.

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