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Ionic conductivity enhancement for PVA/ 20wt.% $CuSO_4$ gel polymer electrolyte by using glycerin

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Gel polymer electrolyte based on PVA+20wt.%$CuSO_4$ was plasticized with (1,2 and 3) mL glycerin and prepared by casting method. Ionic conductivity for gel electrolytes enhancement occurs primarily as a result of increased carrier concentration and secondarily as a result of increased carrier mobility. Using X-ray diffraction (XRD) characterization, they observed that the glycerin-free electrolyte matrix has a regular arrangement with the crystalline phase. After adding glycerin, the observed orderly organization and crystalline phase fully transformed to amorphous. Fourier transform infrared spectroscopy (FTIR) result shows that the stretching vibration region of the O–H at 3261 cm^{-1} The hydrogen bonds formed by the hydroxyl groups of both PVA and glycerol structures explanation for the hydrophilic behavior of glycerol and the increased area. The new intense and strong peak that emerged at 2359.62 cm^{-1} is related to the aromatic Cu-O stretching of the salt $CuSO_4$, The interaction of the PVA with the electrolyte elements increases its intensity with increasing glycerol.

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Keywords: Glycerin, Gel polymer electrolyte, Copper sulfate salt, Plasticizer

1. Introduction

Gel polymer electrolytes (GPEs) are organic liquid electrolyte incorporated in the polymer matrix, usually formed by incorporating conducive ionic salts having mobile cations Li^+, Na^+, Mg^{2+} etc in the polar polymer matrix like PEO, PPO, PVA, PEG etc [1,2]. Because of their potential use as solid electrolytes in solid electrochemical devices such as batteries and fuel cells, FGPEs are typically prepared by solution casting or electro-deposition [3]. GPEs (gel polymer electrolytes) have a number of benefits over a liquid electrolyte that is leak-free good compatibility with the electrode, Ionic conductivity is high, as is chemical and thermal conductivity. stabilities, low volatility and safety, design flexibility, light weight, and possibility of high energy and power density [2, 4].

PVA is the most widely used synthetic water-soluble polymer used as a green material with the a wide range of dopant-dependent properties PVA has good resistance and physical properties [5]. Most of the polymers have high degree of crystallinity and high glass transition temperature (T_g) which makes them poor ionic conductors[6]. To obtain higher conductivity at lower temperature, the degree of crystallinity and T_g of the GPEs must be decreased[5]. Crosslinking is one of the techniques used to increase the conductivity of GPEs , blending and plasticizer[7]. Plasticized polymer electrolytes (PEs) are made by combining a polymer host with low molecular weight compounds [7,8]. Plasticizers or mixed plasticizers are added to polymer electrolytes to soften rigid polymers and lower the glass transition temperature, T_g, of a polymer by increasing the segmental motion of the polymer backbone, which aids ion transport along the polymer chain[6]. Furthermore, adding plasticizer can help increase ionic conductivity by increasing the number of free ions and improve amorphousness [9]. The plasticizer, such as glycerin, stimulates ion dissociation, which helps the electrolytes operate well, especially in future applications. [8,10]. More salts can be dissociated by the glycerin, and hydrogen bonds between polymer chains can be disrupted. As a result, the amorphous phase of the prepared samples improves, acting as a pathway for ion conduction [10]. In addition, there will be more free ions available for conduction [10,11]. Glycerin has also been recognized and proven to be an

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good plasticizer for polymer electrolytes. Its aqueous dispersions are easily gelatinized, resulting in highly amorphous microstructured films[10,12]. Indeed, amorphous microstructure is desired in ionic transport mechanisms to achieve high electrical (e.g., conductivity and capacitance) performance [12]. This paper investigates the structure and ionic conductivity values of gel polymer electrolytes based on PVA that contain 20 wt% $CuSO_4$ as an ionic salt and (1,2 and 3) mL glycerin..

2. Experimental

2.1. Materials

Polyvinyl alcohol (PVA; Mw = 14,000) with a hydrolysis degree of (98-99%) glycerin (Gly; $HOCH_2CH(OH)CH_2OH$; M_w= 1.26 g/cm³) with purity ≥99.5% were purchased from SD Fine Chemicals (India) and copper sulfate ($CuSO_4$) were purchased from Aldrich chemicals (USA), was used for the study. All experiments were conducted with deionized water (DI).

2.2. Materials and methods

The PVA polymer electrolyte (PE) The solution cast technique was used to create the films. For this, 0.8g of PVA were dissolved in 15 mL DI water. For 1 hour at 20 ^{o}C, the mixture was continuously stirred with a magnetic stirrer until the PVA had completely dissolved in DI water. Finally, different plasticizer concentrations (1, 2, 3, 3) mL glycerol were added, followed by 1 hour of continuous stirring to obtain a homogeneous solution. The solution was then poured into a clean, dry petri dish and allowed to evaporate for 72 hours at room temperature until films were formed.

To prepare the $CuSO_4$ salt based PVA polymer electrolyte (PE), 0.8 g PVA was dissolved in 15 ml DI water to make the stock solution. The PVA was completely dissolved by stirring the solution , the 20 wt.% $CuSO_4$ was then added to PVA solutions and stirred continuously for 1hour at 20 ^{o}C until homogeneous solution mixtures were achieved, Finally, different plasticizer concentrations (1, 2, 3) mL glycerol were added, followed by 1 h of continuous stirring in order to obtain homogeneous solution. These mixtures were then poured into glass petri dishes and dried for 72 hours to obtain a thick film, which was then peeled off and stored in desiccators to dry further.

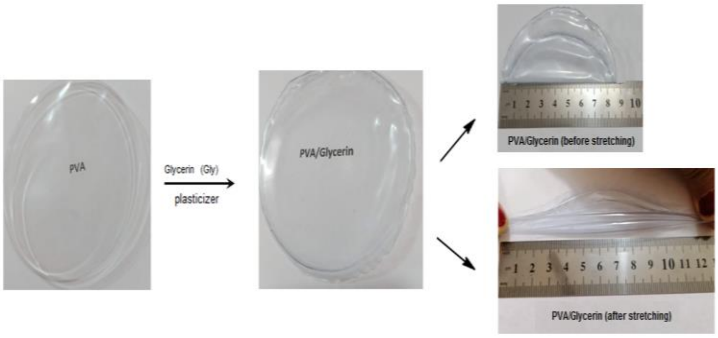

Fig.1. Digital photographs of a ductility experiment on PVA/3mL glycerin.

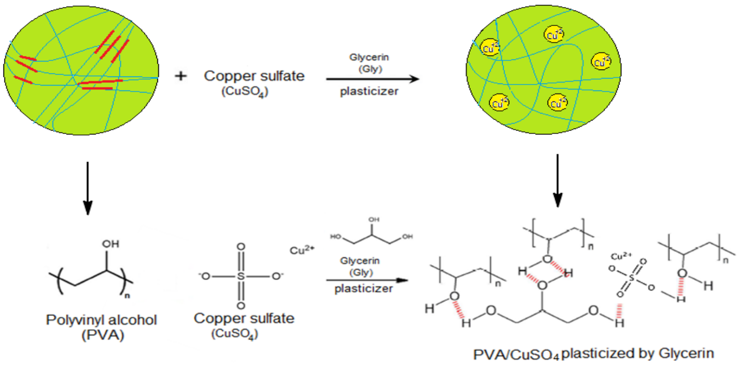

Fig. 2. Schematic diagram PVA+$CuSO_4$ plasticized by glycerin gel polymer electrolyte.

2.3. Techniques of characterization

The X-Ray Diffraction (XRD) analysis was carried out by using LabX (XRD:6000 SHIMADZU) samples were scanned at 2 ranging from $(10–60)^{o}$ with X-rays wavelength 1.5406 generated by a CuK source to study the nature of the film. Fourier transform infrared spectroscopy was used for the measurement (FTIR). Wave number range Tensor 27 BRUKER spectrometers (475-4000) cm^{-1}. The resistivity's were measurement by using (GWINSTEK LCR-6100) and were done over a frequency range of (1–100) kHz at room temperature (27 ^{o}C).

3. Result and discussions

Fig. 3 shows the X-ray diffraction (XRD) patterns of all the polymer films. The pattern of XRD the high broad peak at 2θ=19.44° is seen in pure PVA. indicate the semi-crystalline nature of PVA is highlighted. and this peak become weak for PVA+20wt.% $CuSO_4$[12].

The observed sharp peaks of PVA+20 wt.%$CuSO_4$ at 27.48°, 31.84°, 45.56° and 56.6° which are assigned to the (111), (200), (220), and (311) orientation planes, are well matched with the standard data from JCPDS card numbers, respectively [JCPDS card no. 00-002-0107] for copper sulfate[13].

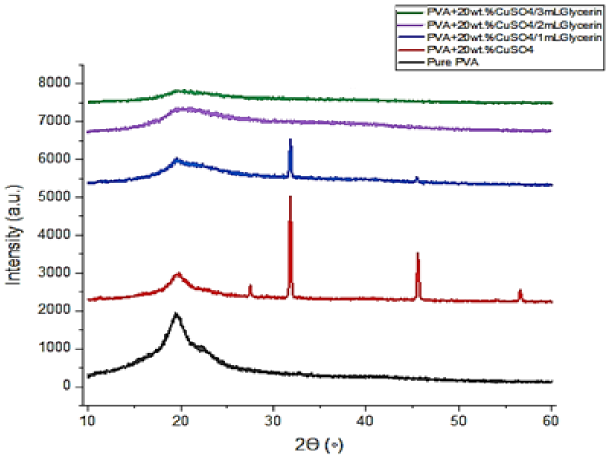

Fig. 3. Represents XRD patterns of pure PVA, PVA+20wt.%$CuSO_4$ salt and PVA+20wt.%$CuSO_4$ gel electrolyte films plasticized by (1,2,3) mL glycerin respectively.

In addition to these crystalline peaks, there is also a broad hump between 15° and 25°, which is attributed to the formation of phase of amorphous gel electrolyte[14]. These findings show that the pure PVA polymer is semi-crystalline and has an orthorhombic crystal structure

[12]. The $CuSO_4$ salt's sharp peaks vanished due its the complexed system has no salt, indicating that the salt has completely dissociated in the polymer matrix[14]. All of the crystalline for$CuSO_4$ with increasing glycerin concentrations from (1 to 3)mL, the peaks broaden and their relative intensities decrease, This can be explained by the host polymer becoming more amorphous [14]. The interactions between PVA-$CuSO_4$ and glycerin decrease the intermolecular interaction among the polymer chains when glycerin is added to the PVA host, as a result, the crystalline phase is reduced and the amorphous region is increased. Furthermore, the peaks have shifted slightly, when 1mL glycerin was added, the peak at 2θ=31.84° and 2θ=56.6° vanished, and the peak intensity at 31.84° and 45.56° decreased and vanished with increasing glycerin concentration, indicating the formation of a new complex system. [15].

Furthermore, the intensities of all crystalline peaks are also observed in Fig. 2. for the PVA+20 wt.%$CuSO_4$ are higher than those for the polymer electrolyte PVA+20wt.%$CuSO_4$ gel electrolyte films plasticized by 1 mL glycerin, indicating that the PVA+20 wt% $CuSO_4$ electrolyte of polymer has a higher degree of crystallinity and the highest amorphous nature for the PVA+20wt.%$CuSO_4$ gel electrolyte films plasticized by 1 mL glycerin.

When all of the spectra are compared, it is clear that when the optimum concentration of glycerin increase from (1-3) mL, all crystalline peak intensities of $CuSO_4$ decrease and vanish suggesting that the PVA matrix's amorphicity has increased. This could be due to salt and plasticizer dissolution disrupting the polymer's semicrystalline structure [14,15].

With increasing PVA concentrations, all of the crystalline peaks are broadened and their relative intensities decrease the XRD peaks (Fig. 1) to determine the degree of crystallinity of the polymer films by[16].

$$Xc = \frac{A_c}{A_c + A_a} \times 100 \tag{1}$$

The total area under the crystalline peaks is A_c, and the total area under the amorphous peak is A_a. As shown in table 1. Pure PVA has a calculated degree of crystallinity of 45.22%, which decreases gradually to 32.56 % with adding 20wt.% $CuSO_4$ salt then when adding different concentration of glycerin(1,2 and3) mL the degree of crystallinity at 3 mL glycerin, it reaches a minimum of 21.13 %.

Table 1. The calculated crystallinity degree of Pure PVA, PVA+20wt.%$CuSO_4$ salt and PVA+20wt.%$CuSO_4$ gel electrolyte films plasticized by (1,2,3) mL glycerin respectively.

	$CuSO_4$concentration wt.%	Glycerin concentration in mL	degree of crystallinity %
PVA	0	0	25.22
	20	0	22.56
	20	1	20.22
	20	2	19.12
	20	3	16.13

This means that the PVA+20wt% $CuSO_4$/ 3mL glycerin the amorphicity of the gel polymer electrolyte film is quite high. The polymeric chain is more flexible in the amorphous phase, resulting in an enhancement of segmental motion in the polymer and thus increased ionic conductivity[16,17]. As a result, the electrolyte gel polymer film containing PVA+20wt% $CuSO_4$/ 3mL glycerin shows a high ionic conductivity as shown in Fig.7.

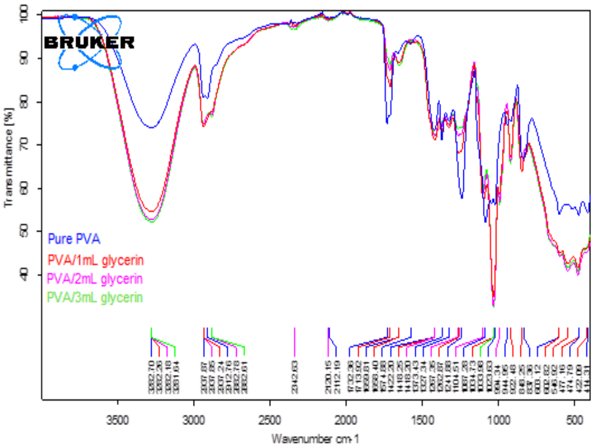

Fig. 4. Pure PVA FTIR spectra, PVA plasticized with (1,2 and 3) mL glycerin.

Pure PVA FTIR spectra, PVA plasticized with (1,2 and 3) mL glycerin gel films of electrolyte are given in Fig. 4

It is clear from Fig.4 that for pure PVA, a broad band at 3282.7 cm^{-1} is observed, which is attributed to hydroxyl group O–H stretching vibrations. C–H asymmetric and C–H symmetric stretching vibrations are represented by bands at 2937.87 cm^{-1} and 2912.76 cm^{-1}, respectively [6,10]. C=O stretching vibrations are assigned to the observed band at 1732.36 cm^{-1}, while C=C group stretching vibrations are assigned to the band at 1574.88 cm^{-1}. Bands at 1422 cm^{-1} and 1373 cm^{-1} correspond to CH_2 vibrations bending and wagging. The observed band at 1023.63 cm1 corresponds to C–H deformation and a sharp band at 1087.28 cm^{-1} corresponds to C–O stretching of the acetyl group present in PVA back bone [14]. The FTIR spectra of PVA plasticized with (1,2 and 3) mL glycerin gel electrolyte shows bands at (3282.7, 2937.7 and 1023.93) cm$^{−1}$ become stronger and deeper when adding glycerin characteristic of bonded O–H hydrogen stretching, C–H hydrogen stretching, carbonyl, carboxyl, and carboxyl salt double bond stretching, and O–H hydrogen bending, respectively [16].

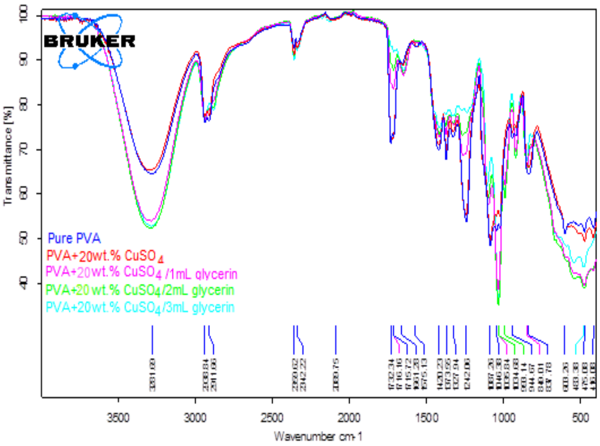

Fig. 5. Pure PVA FTIR spectra, PVA+20wt.% $CuSO_4$ plasticized with (1,2 and 3) mL glycerin.

FTIR for PVA+20wt.%$CuSO_4$/glycerol are shown in Fig.5. Changes in peak intensities and shifting are crucial for confirming the formation of a complex between the $CuSO_4$ salt and the polymer [16]. The stretching and bending vibrations of O–H in PVA have decreased significantly when adding 20 wt.% $CuSO_4$. These results are shown in bands at (3261, 1732.4, 1327 and 993) cm^{-1}, which are attributed to hydrogen stretching of bonded O–H, carbonyl, carboxyl, and carboxyl salt double bond stretching, and carboxyl salt double bond stretching, respectively. The intensity of stretching and bending vibrations of O–H peaks in polymer gel electrolytes increase[14]. The hydroxyl band region broadens in all of the gel electrolytes, but it is most noticeable in PVA+20wt. percent CuSO4/3mL glycerin, which has the highest ionic conductivity at room temperature. For glycerol, the area corresponding to the O–H stretching vibration region at 3261 cm^{-1} is larger [11]. The increased area is due to hydrogen bonds formed by the hydroxyl groups of both PVA and glycerol structures, demonstrating the hydrophilic behavior of glycerol. The fresh, intense, and powerful peak appeared at 2359.62 cm^{-1} is related to aromatic Cu-O stretching of $CuSO_4$ of the salt, and its intensity increases with increasing glycerol due to PVA interaction with the electrolyte elements (see Fig. 5) [10]. A peak at 2937.87 cm^{-1} is associated with asymmetric stretching of C–H [6], and its intensity is shifted to 2938.49 cm^{-1} and decreased in the case of plasticized PVA.

The decrease intensities of C=O at 1732.08 cm^{-1} stretching with adding glycerin (in comparison to PVA and PVA+20 wt.%$CuSO_4$) and shifting in the spectra of gel electrolytes are visible because of the electrolyte's components interacting, which verify the complex formation. band at 1023.63 cm^{-1} in the case of plasticized PVA, the C– H deformation intensity is shifted to 1046.38 cm^{-1} and increased. [10,11].

Glycerin as a More salts can be dissociated with plasticizer. into cations and anions, resulting in more ions to interact with the PVA [9,14]. The absorption band at 1638 cm^{-1} in PVA [14] is related to C=O stretching of the acetate group, whereas in plasticized PVA. it shifted to smaller wavenumbers. The band at 1412 cm^{-1} in PVA is related to CH_2 wagging C–H bending, and the band at 1318 cm^{-1} in PVA is related to C–H deformation [15-17]. The electrolyte's interaction with each other reduced and shifted the intensity of the two peaks in the plasticized PVA.

Glycerol causes changes in the band region between (800 and 1400) cm^{-1}, which provides information about the alcoholic (C– O) stretching bands as well as the asymmetric and symmetric (C–O– C) stretching vibration's band. The stretching vibration of C–O in C–O–H bonds causes the 1034.68 cm^{-1} band[18-20].

Moreover, the bands at (944.67 and 837.78) cm^{-1} correspond to the C–O stretching vibration in the C–O–C bond, confirming the film's stronger C–O stretching vibration [21-23].

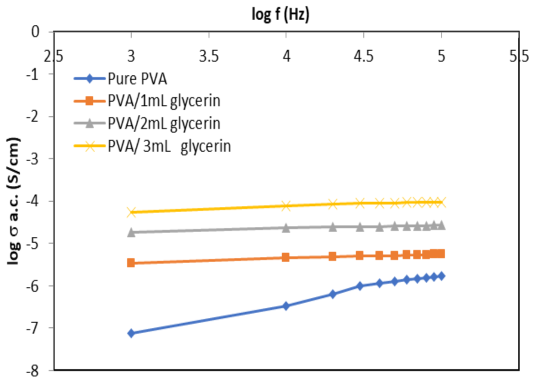

Fig. 6. Variation of log $\sigma_{a.c.}$ with logf for pure PVA, PVA plasticized with (1,2 and 3) mL glycerin.

The ionic conductivity was calculated using the formula below using the measured bulk resistance, area, and thickness of the polymer film [17]:

$$\sigma = \frac{t}{RA} \tag{2}$$

where t is the polymer electrolyte thickness (cm) as measured by the micrometre screw gauge, A is the blocking electrode contact area (cm^2), and R is the resistance (Ω).

Fig. 6 and Fig. 7 shows the ionic conductivity of PVA gel polymer electrolytes as a function of frequency. The Due to electrode–electrolyte interfacial phenomena, spectra have two regions, a low-frequency dispersive region .

More charge accumulates at the electrode–electrolyte interfaces as the frequency lowers, leading in a reduction in the amount of mobile ions and, finally, a decrease in conductivity in the lower frequency range. Because charge carriers have a high mobility in the high-frequency region, conductivity increase as frequency increase [23-25].

Figure 6 shows the effect of glycerin on the ionic conductivities of pure PVA electrolytes at the frequency range studied. As a result of the addition of the plasticizer (glycerin), the ion concentration in pure PVA is increased. In the amorphous phase, the polymeric chain is more flexible, enhancement of segmental motion in the polymer and thus increased ionic conductivity [25,26].

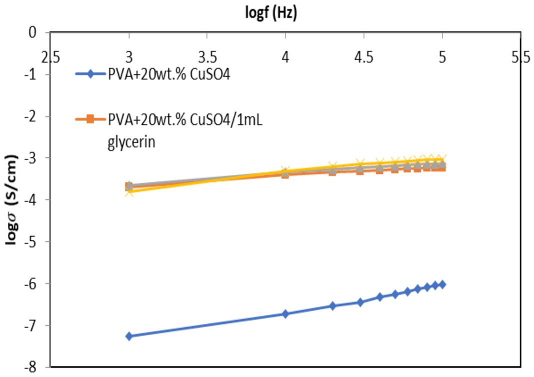

Fig. 7. Variation of log $\sigma_{a.c.}$ with logf for PVA+20wt.%CuSO$_4$, PVA+20wt.%CuSO$_4$ plasticized with (1,2 and 3) mL glycerin.

Clearly observed from Fig. 7 that the addition of 20 wt.% CuSO$_4$ had significantly increased the ionic conductivity. the ionic conductivity slight increased from (1.385805655×10^{-8} to 7.43966242×10^{-8}) S/cm at same frequency(1kHz). When a salt with a higher lattice energy or a large inter-coulombic interaction is added to the as an ionic dopant in a polymer host a little increase in ionic conductivity is observed [27,28].

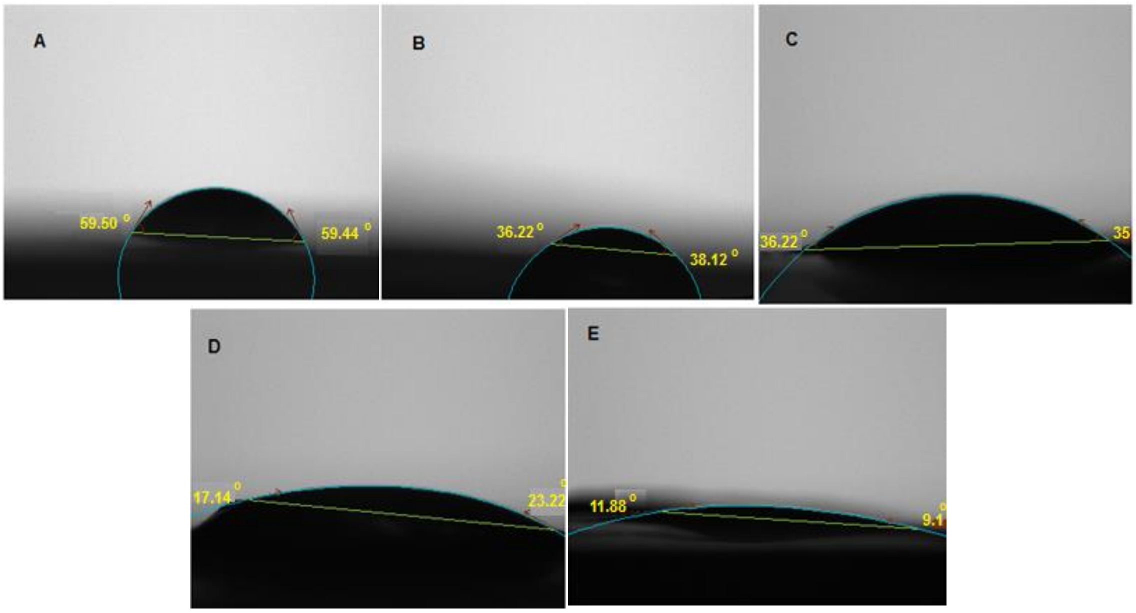

Fig. 8. Contact angle of pure PVA, PVA+20wt.%CuSO$_4$ and PVA+20wt.%CuSO$_4$ plasticized with (1,2 and 3) mL glycerin.

But we can see when adding 3mL glycerin as plasticizer the ionic conductivity increasers with several order and reached to 1.570478918×10^{-4} S/cm at (1kHz), because the plasticizer's energy is high Contact ion pair formation is prevented, but solvent-separated ion pairs are formed. pair formation, which leads to quasi-free ions, results in significant ionic conduction [20,29].

The wettability of pure PVA, PVA+20wt.%$CuSO_4$ and PVA+20wt.%$CuSO_4$ plasticized with (1,2 and 3) mL glycerin was investigated by micro-droplet test. As shown in Fig.8 and Table 2. that the contact angle has slightly increased from 59.525° for pure PVA to 38.22° for PVA+20wt.%$CuSO_4$, The hydrophilic behavior was enhancement for PVA+20wt.%$CuSO_4$ after plasticized by (1,2 and 3) mL glycerin, Therefore, PVA+20wt.% $CuSO_4$/3 mL glycerin shows contact angle of 10.49° shows a highest contact angle , this behavior is due to improve increased hydroxyl groups on the surface of PVA+20wt% $CuSO_4$ and a large number of hydroxyl groups from the polymer chain [30].

Table 2. Contact angle of pure PVA, PVA+20wt.%$CuSO_4$ plasticized with (1, 2 and 3) mL glycerin.

sample	Left contact angle (o)	Right contact angle (o)	Contact angle (average) (o)
PVA	59.50	59.55	59.525
PVA+20wt.%$CuSO_4$	38.32	38.12	38.22
PVA+20wt.%$CuSO_4$/1mL glycerin	36.22	35	35.61
PVA+20wt.%$CuSO_4$/2mL glycerin	17.14	23.22	20.18
PVA+20wt.%$CuSO_4$/3mL glycerin	11.88	9.1	10.49

4. Conclusions

Effect of inclusion of glycerin as a plasticizer on ionic conductivity and structural properties of PVA+20wt.% $CuSO_4$ electrolytes of polymer were discussed derived from our work The addition of a considerable amount of plasticizer has significantly improved the amorphous character of the material. as evidenced by this work. Glycerol promotes salt dissociation and provides an additional coordinating site for ions to conduct, As a result, gel polymer electrolytes' ionic conductivity improves. The ion transport properties of PVA+$CuSO_4$ prepared with glycerin are investigated. It is found From XRD analyzer that adding 3mL glycerin amorphusity performs better and Ion transport characteristics are improved. The addition of plasticizer increases the Polymer-salt compounds have both static and dynamical disorder, which is linked to increased conductivity.

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