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Synthesis and Characterization of Stretchable Ionic Cable

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ABSTRACT

A transparent and flexible polymer with unique electric and sound signal transmission capability under highly stretchable conditions has been synthesized. In this paper the milestone achieved in the polymerization of intrinsic ionic Ω–conjugated polymer, hereinafter known as Ionic Cables (ICs), through free radical cross-linking co-polymerization process/technique and structural modifications encountered so far in our experiments are discussed. EIS and stress-strain assessments had showed that ionic conductivity and flexibility are dependent on the amount of accelerator Tetramethylethylenediamine (TEMED) and curing time (CT). By varying the amount of accelerator, in our case TEMED, and CT the ICs with ionic conductivity of 0.021 S/cm to 0.111S/cmand 350% elongation to 448% elongation conditions was synthesized with highly water absorption capability up to 78% of its total volume. The synthesized ICs with ultra-stretchability, transparency and conductivity can be used in versatile applications, including stretchable ionic cables, tissue engineering, ionic mass transport systems and bio sensors.

Keywords: Ionic cable, ionic conductivity, elongation, consolidation, ionic crystal, transparent cables

1. INTRODUCTION

In most of the cases metallic wires and metallic connectors in electronics are utilized for transfer of electric current and signals. The losses in electronic signal and current followed by circuit heating, rigid in nature and expensive for production are some of the major drawbacks of metal wires and connections [1-3]. Hence, to overcome such issues, the material scientists and engineers are not only engaged in improving conventional electronic components, but also in the race of producing novel materials. The recent openings in the discipline of materials have introduced a new class of polymeric materials with higher conductivity. The estimation of development and characterization of Polymeric Ionic Cables (PICs) has recently attracted scientific community with an effort towards commercialization. The preliminary experimental work had shown that PICs could transmit electrical and sound signals over long distances with enough speed with no variation in current even when stretched eight times of its original length. It is anticipated that ions in PICs are more effective to channel the electrical and audio signals as compared to electrons in metallic electric wires. It is speculated that due to outstanding signal transmitting features, PICs can be used in artificial intelligence, bio sensing functions and electronic conductors with higher stretchability and transparency [4].

The high-water absorbent three-dimensional hydrogel pass through our everyday life in a variety of forms like in the commercial products like shampoo, hair gel, silica gel and other cosmetics, optical lenses,

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microchips, flexible smart screens etc. This man-made hydrogel is used from general applications to advance cases like sophisticated electronic skin [5, 6], active adaptive lenses [7], stretchable electronics and batteries [8, 9].

Long-chain, stretchy polymer can be cross-linked by polymerization techniques with the formation of covalent bonds. A three dimensional network using various monomers, initiators and terminators with the addition of substitutes, the three-dimensional network can absorb the solvent and swells, thus formed material is known as polymer gel, but if water is used as solvent than it would be construed as hydrogel [10]. Various types of polymerization methods are used to make polymers synthetically from which free radical cross-linking co-polymerization of acrylamide is one of the ways for making polymers where molecular weight is built up with slow rate of reaction. It is therefore easy to control variables in the reaction mechanism of polymerization. The functional groups have vital role in holding reactions. Hydrogels are usually prepared by free radical co-polymerization of acrylamide (AAm) based monomers with the chemical cross-linker such as N,N' Methylenebisacrylamide [1-13].

The polyacrylamide is a type of hydrogel in which acrylamide is used as a base monomer using thermo initiators, dopants and cross linkers to make a conductive hydrogel with higher flexibility, electrical conductivity and transparency [14, 15]. The dopants have stable charged sites due to the presence of positive counter ions, where the mobilized ions emerge during doping. In this process free ions move and make hydrogels electrical and sound signal conductors.

The synthesized transparent hydrogel can play a vital role to replace conventional electronic system with flexible and bio compactable electronics. The current and voltage characteristics of conductive hydrogel make an amazing match with high conductive metals like copper and silver.

The current research work presents the formation and characterization of transparent hydrogel which comprises both abilities to stretch and conduct electrical and sound signals with acceptable intensities. The mechanical behavior is also managed to fulfill the engineering factors of safety. The contemporary research will help us to use a capable ionic conductor instead of metallic wires and plug-in-displays in special cases where higher transparency, ionic conductivity and stretchability is required.

2. EXPERIMENTAL SECTION

2.1 Materials and Method

All chemicals, including acrylamide, lithium chloride (ionic dopants), N,N'-Methylenebisacrylamide (cross linker), ammonium per sulfate (Thermo initiator) and TEMED (accelerator) were obtained from LABCHEM products, BDH Chemicals and Sigma_Aldrich Merck respectively.

Highly water absorbent, conductive, transparent and flexible polyacrylamide base ionic cables (ICs) were synthesized using free radical co-polymerization and cross-linking method. Total of 186gm solution was prepared using 14% of acrylamide (monomer), 5% of lithium chloride (doping agent), 0.043% of N, N'-Methylenebisacrylamide (cross linking agent), 0.07% of ammonium per sulfate (thermo initiator) and TEMED (Thermo initiator) relative to amount of solvent. There were two quantities of TEMED including 0.1% and 0.2% used separately to see the effect of TEMED quantity on the characteristics of hydrogel, another factor investigated was CT from 01 to 04 hour(s) applied in muffle furnace. In this practice the TEMED and CT were assorted, samples were labeled as 0.1/X and 0.2/X, where 0.1 and 0.2 are the amounts of TEMED and X is CT, after taking distilled water the amount of each chemical is added simultaneously and agitated for 5 minutes at 50^{o}C constant curing temperature.

Swelling and de-swelling characteristics under the impact of moisture and temperature was investigated. The shrinkage was measured through weight reduction method where solution was transferred in Petri dish, after drying; it reduced considerable amount of volume in weight reduction as shown in Fig.1.

Volumetric change was calculated using change in initial and final weight of hydrogel after and before

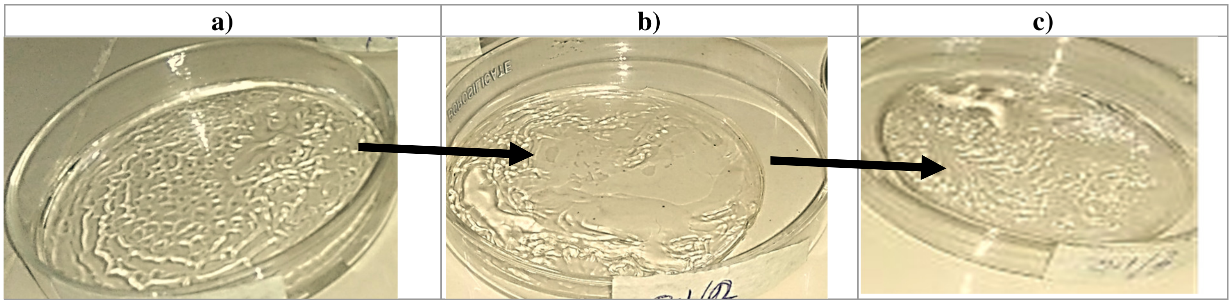


Fig. 1: Volumetric Changes of Hydrogel after (a) One Hour (b) Two Hours and (c) Three Hours Curing

hydrogel curing, using following equation:

$$\% \text{ Weight Reduction} = \frac{\text{Difference in weight (gm)}}{\text{Initial Weight (gm)}} \times 100$$

In assessment of the increasing importance, the structure confirmation of polyacrylamide (PAAm) based hydrogels have received considerable attention in the last two decades. In this respect, the vibrational spectroscopy is a potentially useful tool for structural analysis [12]. The IR spectra of synthesized LiCl doped polyacrylamide gel incorporated in Potassium Bromide pellet was recorded by Fourier Transform Infrared Spectroscopy (FTIR) of Perkin Elmer (Model: Spectrum 2) in the range of 4000-400 cm^{-1}.

The morphology of polyacrylamide hydrogel was investigated using scanning electron microscope (Model: JOEL JSM-6380L) at magnification of X15,000 and X2,000 and 20kV. The samples for SEM were prepared by freeze drying followed by sputter-coating with gold to achieve satisfactory results. For mechanical properties, Universal Tensile Machine (Model: ZwickRoell Z005) was used by following ASTM standard D-638 (type V). Electrochemical impedance spectroscopy were carried out using potentiostat (Model: VersaSTAT-500), data was analyzed using Z-view software and bulk resistance was pointed out from those plots at maximum frequencies in real axis.

3. RESULTS AND DISCUSSION

3.1 Volumetric Changes in Hydrogel

It has been observed that the proportion of TEMED and CT has substantial influence on volumetric changes in ICs. Porosity increment makes ICs more water absorbent and flexible deprived of polymer dissolution in water and keeping ions more activated. Fig.2 (X is used as variable for CT) shows the volumetric changes of ICs. it is apparent that giving extra CT the samples were dried and permeability minimized during elimination of water, and weight was reduced simultaneously. After increasing the amount of accelerator, the weight reduction rate is recorded much higher than the low amount of TEMED (accelerator). It was due to the higher activation reaction mechanism in polymerization.

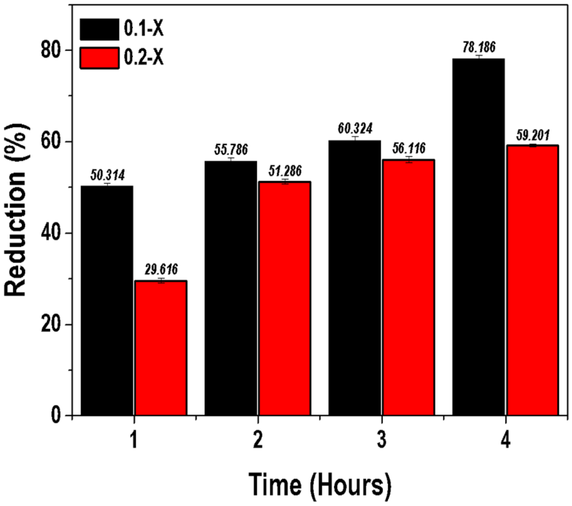


Fig. 2: Reduction of Hydrogel Samples 0.1-1 to 0.1-4 and 0.2-1 To 0.2-4

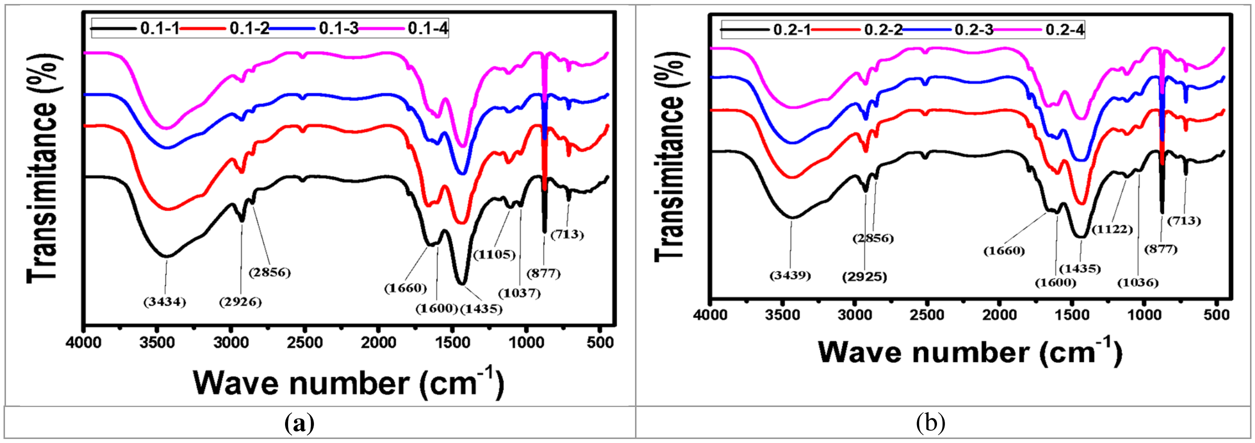
3.2 Fourier Transform Infrared Spectroscopy of ICs

The absorption band at 3433 cm^{-1} shown in Fig.3 is attributed to the valence vibration corresponding to the N-H groups from the cross linking bridges, while the asymmetric valence vibration from 2926 cm^{-1} is assigned to the CH_2 groups included in the macromolecular chains and cross linking bridges. The absorption band at 2856 cm^{-1} is attributed to the –N–CH^{2}– bonds from the cross linking bridge, as shown in IR spectra of PAAm in Fig.3. The peak is seen at 1650 cm^{-1} was a direct result of the amide-I band of the amide group (>C = O stretching vibration frequency). The amide-I band was relocated from 1661cm^{-1} in the cross-connected polyacrylamide to 1650cm^{-1} [16]. Since ClO^{-4} is also absorbed at 1100 cm^{-1}, the presence of a strong absorption band at this wavenumber in both PAAm shows that these polymers are doped with this anion. Moreover, the sharp peak around 1650 cm–1 corresponding to C=O in the polyacrylamide appears clearly in the copolymer. The conductive properties of polymers are strongly dependent on conjugation length. Defects interrupt conjugation including sp3 carbons, carbonyl groups and crosslinks [17, 18]. Peak of IR spectra at 1095 cm^{-1} is due to the addition of LiCl [19].

Peak at 860cm^{-1} to 877cm^{-1} was stretching of C-Cl of alkyl halide group. A weak peak at 713cm^{-1} shows the bending of the C-S group which is during ammonium per sulfate used in polymerization.

3.3 Morphological Studies of ICs

Structures observed after freeze-drying of the ICs are shown in Fig.4 and Fig.5. the white and bright areas of SEM images are matrices of acrylamide, the intermolecular cross linking is shown through interconnected darker areas, dark areas in SEM images are water possessed porous structure of ICs.



(a) (b)

Fig. 3: FTIR Spectra of Sample a) 0.1/X And Sample b) 0.2/X

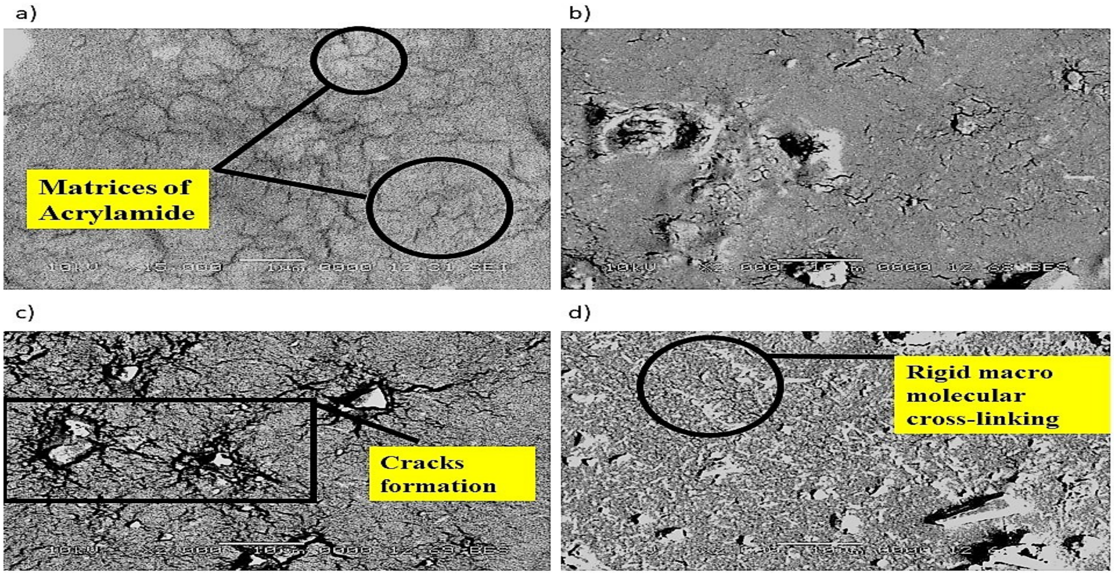


Fig. 4: Scanning Electron Microscopy of Freeze-Dried ICs 0.1/X a) 0.1/1 b) 0.1/2 c) 0.1/3 d) 0.1/4

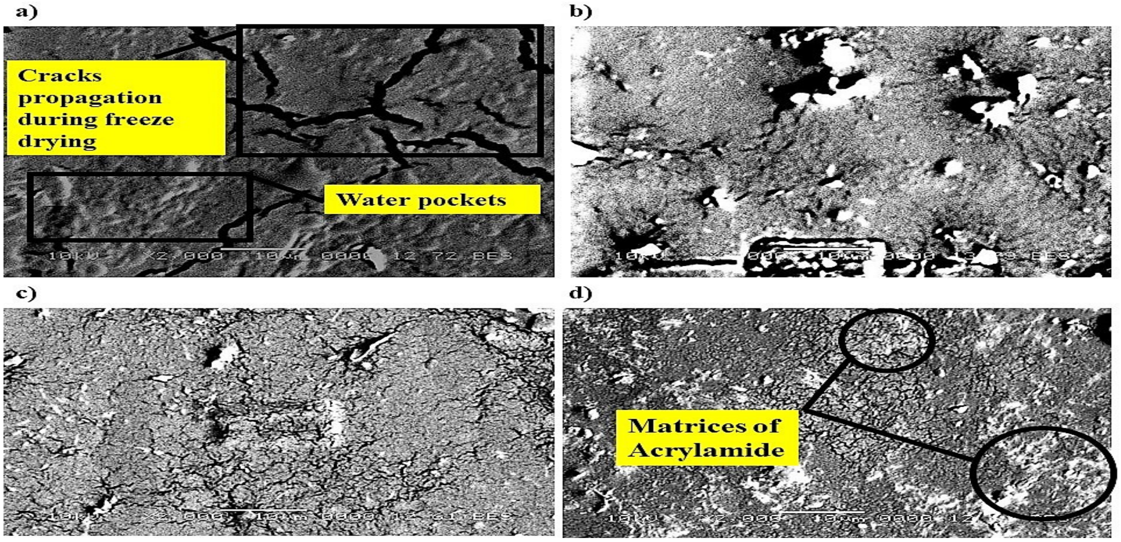


Fig. 5: Scanning Electron Microscopy of Freeze-Dried Hydrogel 0.2/X a) 0.2/1 b) 0.2/2 c) 0.2/3 d) 0.2/4

Fig.4 shows the SEM images of sample 0.1/X which displays the higher concentration of acrylamide matrices than vacant spaces due to the amount of TEMED which accelerate and increases the rate of temperature. The interconnected porous structure is clearly shown in Fig.5. The capillary channels in this observation enable water molecules to inter in hydrogel and make them able to conduct more electricity in the presence of LiCl ions.

3.4 Tensile Behavior of ICs

The large mechanical deformation do not affect the conductivity of ICs, while comparing the tensile strength both the compositions cured at four hours has higher ultimate tensile strength and low ionic conductivity; it is due to the low porosity and removal of condensate water from material, it is also a challenge for materials scientists to maintain both the mechanical properties and electrical properties simultaneously [20], these properties are inversely proportional to each other in ionic conductive hydrogels. It has been observed from the results that increasing the CT in both compositions the UTS and Toughness (area under stress-strain curve) increased. The tensile strength noted was higher in 0.1-4 and 0.2-4 where maximum water elimination occurred at 50°C temperature for four hours as shown in Fig.6.

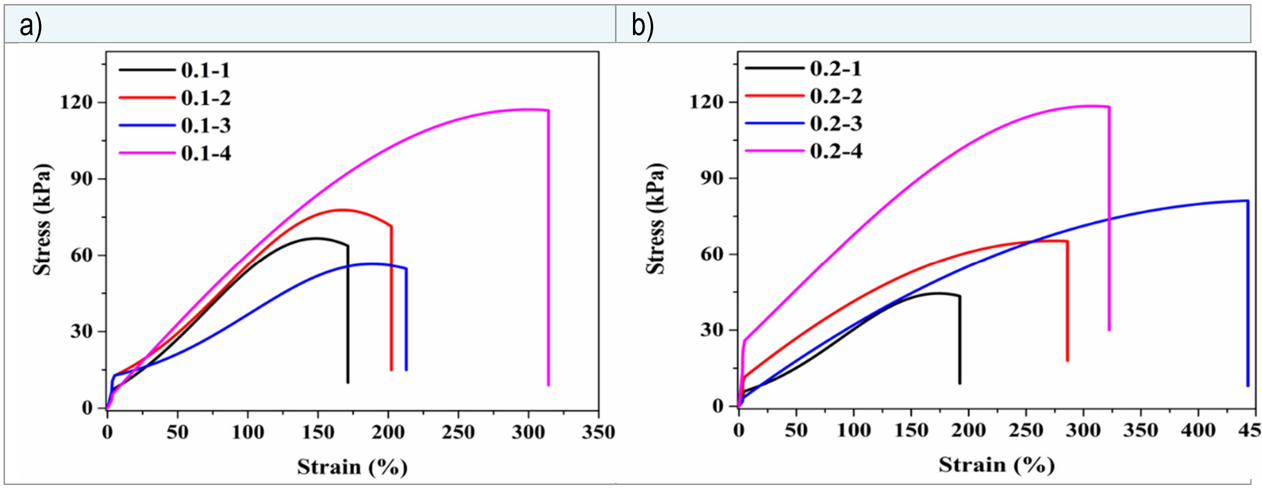


Fig. 6: Stress-Strain Diagram of Polyacrylamide Hydrogel of a) Sample 0.1/X and b) Sample 0.2/X

Using 0.1% of TEMED results 125% to 325% strain and 45kPa to 120kPa maximum strength shown in Fig.6(a) and by increasing TEMED from 0.1% to 0.2% it increases strain from 200% to 450% and tensile strength from 30kPa to 120kPa as shown in Fig.6(b). The %age elongation has been noted higher in 0.2/X than 0.1/X while equivalent ultimate tensile strength has been recorded. It is also suggested in literature that high friction coefficient in hydrogels comprises more elongation, and in our case this happened when the moisture is removed from hydrogel [21]. It is therefore suggested that the ionic conductivity (See Section 4) and tensile strength could be controlled under diverse environmental conditions.

4. CONDUCTIVITY MEASUREMENT IN ICs

Ionic conductivity is subjected to enhance by increasing the amount of water, the amount of accelerator (TEMED) and decreased when decreasing the CT. The bulk resistance was calculated from the Nyquist plots as shown in Fig.7 and the ionic conductivity was calculated using the equation.1. [22]

$$\sigma = \frac{t}{(R_b)A} \qquad (1)$$

where R_b is bulk resistance, t is thickness of the electrolyte and A is electrode contact area.

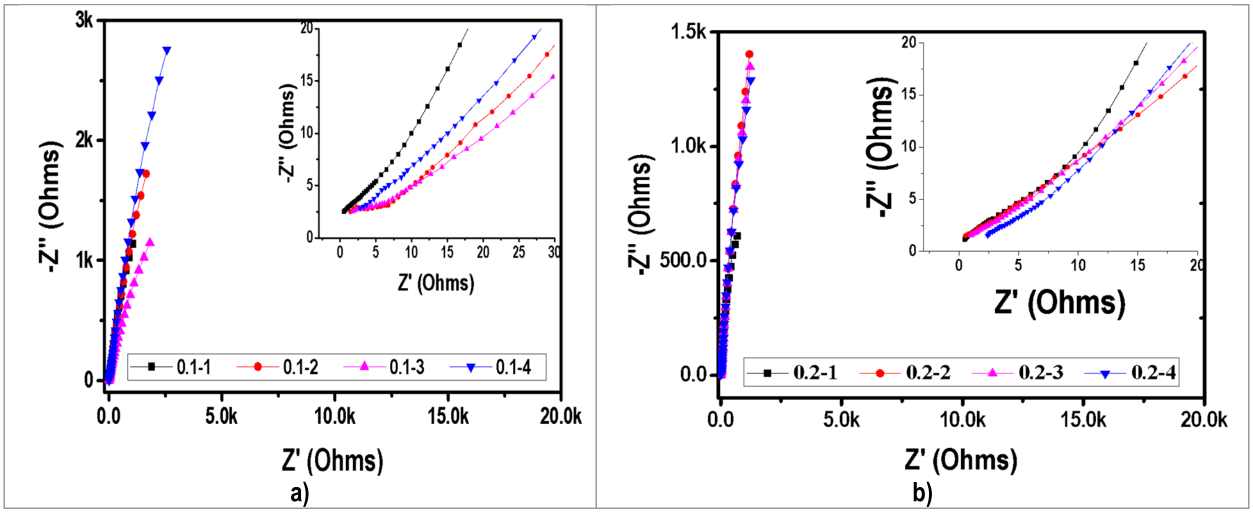


Fig. 7: Nyquist and Bode Plots of ICs of a) Sample 0.1/X and b) Sample 0.2/X

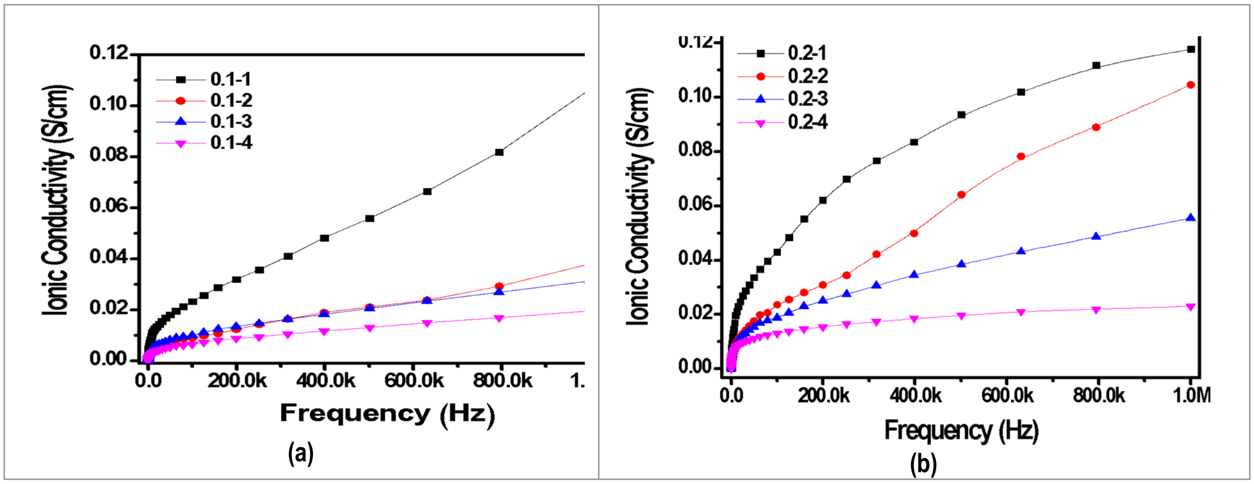


Fig. 8: Ionic Conductivity of ICs of a) Sample 0.1/X and b) Sample 0.2/X

From the Nyquist plots the measured ionic conductivity as shown in Fig.8 is further figured out in Table 1 and Table 2 for clear understanding and comparison. It has been noted in given tables that increasing the CT in both the samples, the ionic conductivity decreases due to the low transport medium and water content, 0.1-1 and 0.2-1 have been observed more ionic conductive than other samples It is observed that moderate level of moisture in polymer structure improves membrane flexibility without much decrease in mechanical strength and ionic conductivity, with increasing the amount of TEMED from 0.1 to 0.2 the conductivity increases, with the comparison of literature the conductivity is achieved in order to 10^{-8} in previous reports[23, 24], which is much lower conductivity as compared to our current work rather than in current research.

Table 1: Ionic conductivity of sample 0.1/X

S.No.	Sample No.	Ionic Conductivity (S/cm)
1.	0.1-1	0.106420
2.	0.1-2	0.037974
3.	0.1-3	0.031414
4.	0.1-4	0.019596

Table 2: Ionic conductivity of sample 0.2/X

S.No.	Sample No.	Ionic Conductivity (S/cm)
1	0.2 – 1	0.117702
2	0.2 – 2	0.104624
3	0.2 – 3	0.055500
4	0.2 – 4	0.022938

Ionic conductivity measured in this experiment was about 0.02 S/cm to 0.11 S/cm which is higher than be noted in previous reports[24, 25].

It can also be noted here that the ionic conductivity is much higher in 0.1-1 and 0.1-2 than other samples which witness the higher ionic transportation in hyderogel containing higher water content in porous structure of three-dimensional network.

5 CONCLUSION

Following conclusions were drawn from present work:

- The UTM results showed that the strength of ionic cables (ICs) is increasing with increasing the amount of TEMED and curing time (CT).
- EIS results showed that ionic conductivity of ICs is decreasing with the increasing the amount of TEMED.
- The effect of CT on ionic conductivity showed that with increasing CT ionic conductivity also increased.
- It was noted that ionic conductivity is reciprocal to the UTS and percent elongation features of ICs
- Present study showed that ICs with maximum ionic conductivity 0.11 S/cm were obtained when 0.2% of TEMED was added at CT of 1 hour and strength 120kPa and percent elongation 450% was obtained when 0.2% of TEMED was added. The ionic conductor can perform better in the moist environment under higher ionic mobilization requirement, while under the requirement of higher mechanical strength, the hydrogel must be free or negligible amount of water causes to weaken the bonding among polymer chain.

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