

Carboxymethyl Cellulose Grafted Acrylic Acid Hydrogel Membrane as Humidity Sensor

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Abstract: Humidity sensors are widely used to characterize electrical components as the working will be greatly affected by the presence of humidity. A study is conducted here with carboxymethyl cellulose grafted with acrylic acid based hydrogel membranes and its function as an absorbing layer in a resistive-based humidity sensor. The hydrogel membrane is prepared by coating the electrodes with 2 wt% CMC solution (in 3:1 water: ethanol mixture). CMC -g- AA membrane is cross-linked with citric acid. The measurement results show that the CMC -g- AA hydrogel can function as humidity sensor at high humidity range. The sensor was tested by measuring the resistance of the CMC hydrogel membrane at various relative humidity. Sensitivity and reliability of humidity sensors depend on the design of electrical components and the characteristics of material used as absorbing layer.

Keywords: Humidity sensor, hydrogel, membranes etc

1. Introduction

Controlling and monitoring humidity is important in industrial & domestic applications. In semiconductor industry, humidity or moisture levels needs to be properly controlled & monitored during processing. Humidity control is required for medical, chemical agriculture and in many areas. There are many ways to measure humidity depending on units used. Typical sensors are designed to measure relative humidity, while some are for the determination of absolute humidity. The operational principle of a humidity sensor is based on the assumption that the change of a physical parameter of a sensor is a one-to-one function with the humidity and the temperature. The physical parameters, used for the transduction, include, for examples, capacitance, resistance, and magnetoelasticity. Various types of materials like ceramic, polymer, electrolyte and hybrid can be used for sensing [1-3]. Compared to other organic substance, cellulose is the most abundance substance on earth. Carboxymethyl cellulose is a derivative of cellulose. A recent study of CMC shows that, comparing with cellulose, standardized cotton fabric, CMC samples have the mass growth about eight times higher [4]. Besides the high swelling ratio, the increases of CMC sample weighs due to water absorption are also relatively constant as a function of time and water temperature. As humidity-sensitive polyelectrolytes, CMC is an alternative sensing material [5]. But, similar to other polyelectrolytes, CMC is not so stable in high humidity environment because CMC is water-soluble. However, previous research shows that sensor durability can be enhanced simply by using cross-linked electrolytes [6-8]. Hydrogels are cross linked hydrophilic polymers. Compared with other absorbing materials, hydrogels can absorb water with higher swelling ratios, above 1000. Hydrogels with very-high swelling ratios are made from synthetic polymers which have relatively long life-time in normal environment. So, alternative materials are required if the ecological impact of a corresponding industrial-scale production is considered. Cellulose and sodium carboxymethyl cellulose can be seen as alternatives to synthetic polymers. Similar to other types of biopolymers, CMC are both biodegradable and biocompatible [9-10]. They are therefore ideal for future "green" engineering and

design. In this research work, a hydrogel made from carboxymethyl cellulose is used as the sensing material, and resistance is chosen as the physical parameter for the transduction mechanism.

2. Experimental

Materials: Carboxy methyl cellulose sodium salt (CMC), Sodium hydroxide, copper sulphate(CuSO_4) and deionised Water were supplied by Nice Chemicals. Citric acid, Acrylic acid(AA), Hydrochloric acid, were supplied by Merck Life Science Private Limited.

A series of hydrogels with different Acrylic Acid contents were prepared by the following procedure. CMC was added to distilled water stirred to form a transparent sticky solution at 75°C . Acrylic acid solution of different percentage was prepared in water containing citric acid was blended and stirred for 4 hours at 80°C . A film of hydrogel with appropriate thickness was obtained by drying the resulting hydrogel solution. Hydrogels with and without crosslinker were also prepared. The yield of each hydrogel was determined.

Swelling rate: The tea bag method was used to measure the equilibrium swelling of the hydrogel in water. The optimum hydrogel was selected on the basis of swelling test. The tea bag was prepared by using filter paper. An accurately weighed sample was placed into a tea bag and the bag was immersed in an excess amount of water at room temperature. The bag was removed from the solution, the excess water was removed superficially with tissue paper and the bag was weighted. This process was repeated for several times until the swelling equilibrium was reached, that is until the bag attained a constant weight. The swelling profiles and the absorption capacity of the hydrogel in units of amount of water absorbed per gram of hydrogel, can be calculated.

Thickness of cast film: The thickness measurements of all the 10 samples were carried out by using thickness gauge made by Mitutoyo In which the samples were clamped between the anvil. The measured values were read directly on the dial gauge.

Density of hydrogel: The density of all the 10 samples was measured and an average is reported.

UV absorption spectroscopy: Ultraviolet-visible spectroscopy refers to absorption spectroscopy or reflectance spectroscopy in the ultraviolet-visible spectral region. The UV-visible spectrum of the best sample was recorded by placing it in the copper sulphate solution, prepared by dissolving 0.39g copper sulphate (CuSO₄.5H₂O) in distilled water. The spectrum was recorded in regular intervals of time. The UV spectrum of the sample was not only recorded by varying time but also recorded by varying pH. The UV-visible spectrophotometer was made by M/s.Regol having measurement range 190 nm to 1100nm. Its test standard was IS 12235 part-12. The applications are spectrum measurement, kinetic measurement, photometric measurement and quantization measurement.

Optical microscopy: Optical microscopic image of the best sample was taken by using optical microscope of model BX 51 made by Olympus having resolution 10,20,50,100 Pixels. The main application was to study the morphology of the sample.

Insulation Resistance: The insulation resistance test of the best sample was conducted by using sigma million mega ohm meter made by ELMECH having open circuit voltage and accuracy 0 to 5 KV and ±2% respectively. The test was done on the basis, that, good insulation has high resistance; poor insulation has low resistance. The test was done by applying 500 voltage of current continuously through the sample then the resistance was noted at multiplier 1 on the scale of insulation resistance tester.

3. Results and Discussion

Swelling Characteristics: Water absorption capacity of the hydrogels shown in figure 1. Materials have excellent swelling properties and very high water absorption capacities. The second sample which contains 4% acrylic acid was identified as the best sample because it has high water absorption capacity. The graph shows the absorption capacities of different compositions of samples at different time intervals.

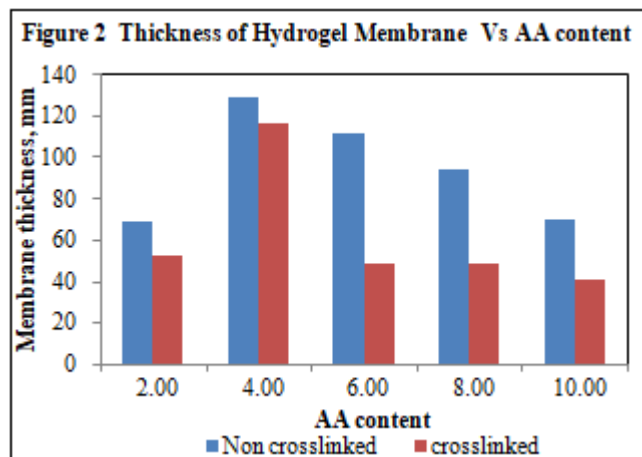
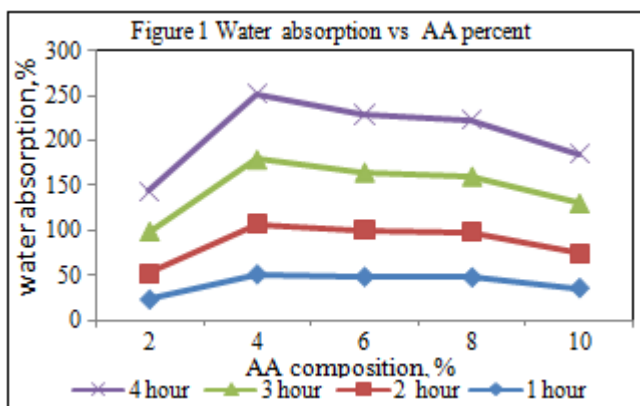


Figure 2 shows the thickness variations of the membrane with Acrylic acid content and also the effect of crosslinking the hydrogel. It is clearly visible that thickness of crosslinked films is comparatively lower than uncrosslinked as the swelling behavior is restricted by crosslinks.

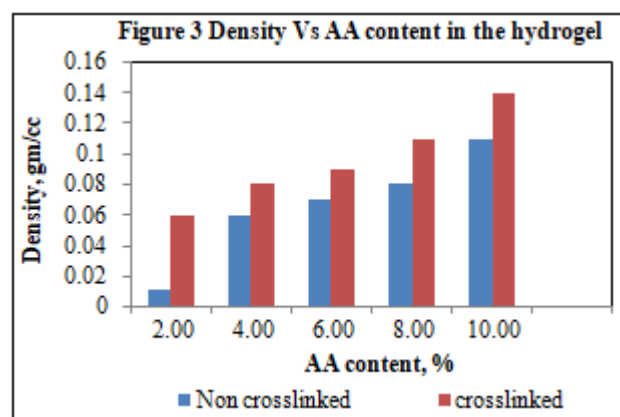


Figure 3 shows the density of the hydrogel with variation in AA content. The graph clearly giving evidence that density is increasing with AA content and also for crosslinked Hydrogels. The crosslinks are providing network structure to the hydrogel and increasing density of the system.

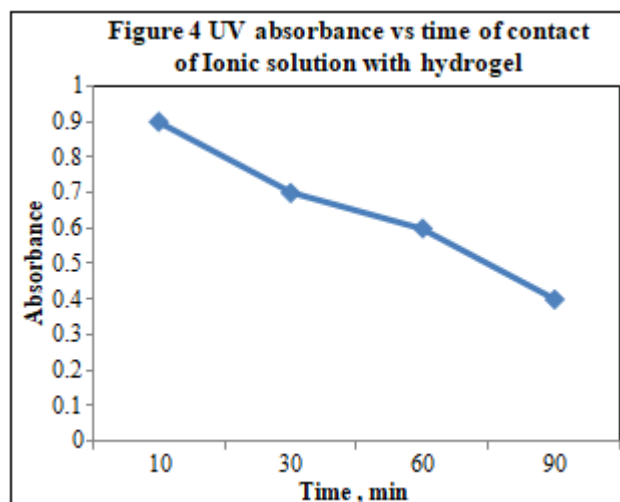


Figure 4 shows the UV absorbance values for the Hydrogels. When the crosslinked hydrogel are in contact with ionic solutions it can absorb the ions thus the absorbance

decreases. Hydrogels are widely used for the ion absorbance and ion removal from the solutions and act as purifiers for waste water.

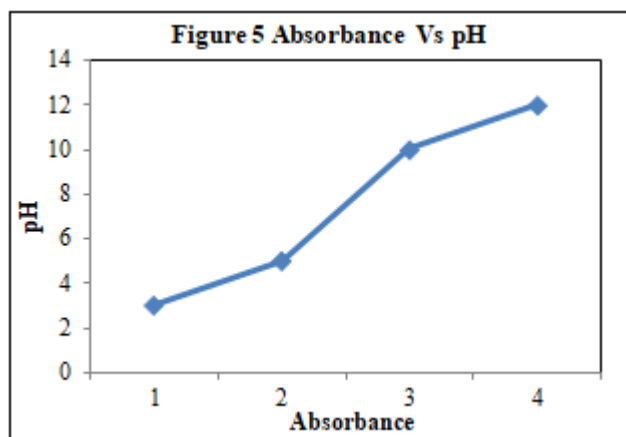
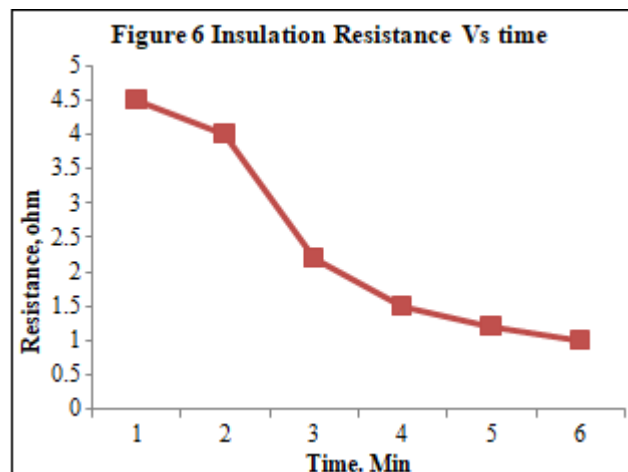


Figure 5 shows the UV spectrum of CMC/AA hydrogel in acidic (dil.HCl) and alkaline(dil.NaOH) systems. The absorption spectra of hydrogel increases with increase in pH. The maximum value of absorption is found to be in pH 12. The variations of absorbance with pH of the solution is given in figure, absorbance of solutions is more in alkaline pH.



The figure 5 shows the decreasing of resistance with increasing time. The resistance of the sensor is measured by varying humidity conditions. The results show that the resistance varies from $4.5M\Omega$ to $1M\Omega$, When the humidity is varied between the time 0 to 10 minutes. The response is higher when the time of humidity conditions increases. That is resistance, decreases with increasing water absorption or humidity condition. The dry film has high resistance but the humid film has low resistance. That means there is no electricity passes when the hydrogel film is in dry condition. But the electricity passes when the hydrogel film is in humid condition. As the humidity increases resistance decreases, and current flows through the hydrogel.

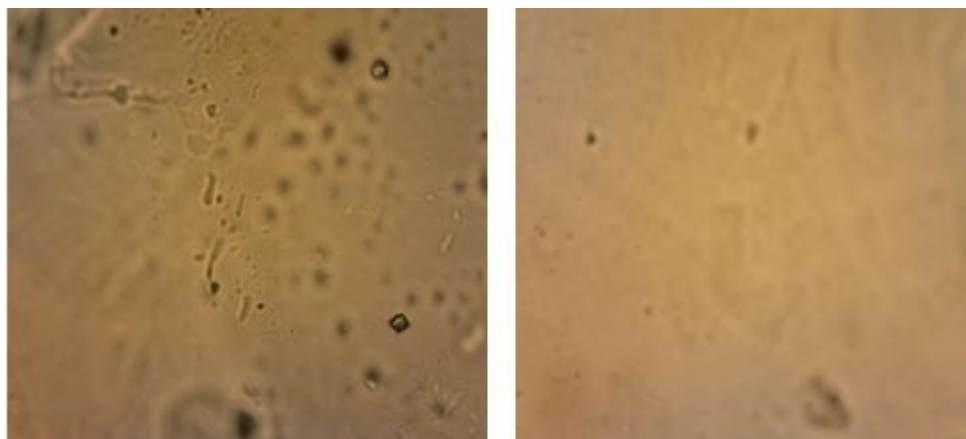


Figure 7: Optical microscopy images

4. Conclusions

Carboxy methyl cellulose/Acrylic acid hydrogels have been successfully prepared. Swelling behaviour of hydrogel films shows that the film containing 4% acrylic acid has the maximum swelling ability. As the time increases the absorption capacity also increases. Thickness and density of samples were determined. UV absorbance for the solution containing hydrogel was analyzed with Cu^{2+} ions. Effect of pH also studied. Resistance studied with the hydrogel and found sensitive. The results show that the CMC/AA hydrogel film can function as the humidity sensing material and act as sensors.

References

- [1] Zhi Chen and Chi Lu, "Humidity sensors: a review of materials and mechanisms," *Sensor Letters*, Vol. 3, 274-295, 2005.
- [2] Chia-Yen Lee and Gwo-Bin Lee, "Humidity sensors: a review," *Sensor Letters*, Vol. 3, 114, 2005.
- [3] H. Farahani, R. Wagiran, and M. N. Hamidon, "Humidity sensors principle, mechanism, and fabrication technologies: A comprehensive review," *Sensors*, 14(5), 7881-7939, 2014.
- [4] K. Boruvkova and J. Wiener, "Water absorption in carboxymethyl cellulose," *AUTEX Research Journal*, Vol. 11, No. 4, 110113, 2011.
- [5] C. W. Lee, J. G. Kim, and M. S. Gong, "Humidity-sensitive properties of self-assembled polyelectrolyte

- system,” *Macromolecular Research*, Vol. 13, No. 3, 265-272, 2005.
- [6] Qiaohui Zhang, J. R. Smith, L. V. Saraf, and Feng Hua, “Transparent humidity sensor using cross-linked polyelectrolyte membrane,” *IEEE Sensor Journal*, Vol. 9, No. 7, 2009.
- [7] C. W. Lee, Y. Kim, S. W. Joo, and M. S. Gong, “Resistive humidity sensor using polyelectrolytes based on new-type mutually cross-linkable copolymers,” *Sensors and Actuators B*, 88, 2129, 2003.
- [8] A. Sannino, A. Maffezzoli, and L. Nicalais, “Introduction of molecular spacers between the crosslinks of a cellulose-based superabsorbent hydrogel: effects on the equilibrium sorption properties,” *J. Appl. Polym. Sci.* 90:168-174, 2003.
- [9] G. Marci, G. Mele, L. Palmisano, P. Pulito, and A. Sannino, “Environmentally sustainable production of cellulose-based superabsorbent hydrogels,” *Green Chem.*, 8:43944, 2006.
- [10] C. Chang, B. Duan, J. Cai and L. Zhang, “Superabsorbent Hydrogels based on cellulose for smart swelling and controllable delivery,” *Eur. Polymer. J.*, 46, 92100, 2010.