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Synthesis and Characterisation of a Polysulfone-Polyvinyl Alcohol Hydrogelic Material

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Hydrogels are flexible materials that have found a niche in membrane science owing to their ability to absorb water without dissolving. The synthesis of polyvinyl alcohol-polysulfone hydrogel in the presence of *N*-hydroxy succinimide is presented herein. This hydrogel is characterised using FTIR spectroscopy, UV-visible spectroscopy, SEM and electrochemical techniques. The FTIR spectroscopic analysis shows that the hydrogel retains bonds that are related to both polysulfone and polyvinyl alcohol moieties. The new hydrogel displays a highly branched morphology with reduced pore size in comparison with polysulfone. The hydrogel also has a lower charge transfer resistance (R_{ct}: 12.065 kΩ) in comparison with the polysulfone (R_{ct}: 23.260 kΩ), which implies that the hydrogel is more conductive than the original polysulphone.

Keywords: hydrogel, polysulfone, polyvinyl alcohol, cross linker, *N*-hydroxyl succinimide

1. INTRODUCTION

Hydrogels are water-absorbing organic materials that can undergo size and mass change but are not decomposed by the water absorbed. Due to this property they are used in the development of sensors, drug delivery protocols and energy storage systems (such as capacitors). [1-4]. Examples of hydrogels that have been frequently reported are those based on polyvinyl alcohol, methacrylates and methacrylamides [4,5]. Generally hydrogels are synthesised by ultraviolet and gamma ray radiation polymerisation techniques or by crosslinking reaction [6-10].

Crosslinking reactions involving the formation of covalent bonds lead to the formation of permanent hydrogels. The examples of permanent hydrogels include poly(methyl methacrylate) (pMMA) and poly-(2-hydroxylethyl methacrylate) (pHEMA). If the hydrogels are formed due to the physical interactions, viz. molecular entanglement, ionic interaction and hydrogen bonding, among the polymeric chains, then the hydrogels are regarded as physical hydrogels. The most investigated hydrogels are pHEMA, PVA, poly (*N*-vinyl-2-pyrrolidine) (PNVP), polyethylene glycol (PEG). Polysulfones also exhibit the characteristics that are displayed by the most widely used hydrogel, pHEMA, that is the chemical (stable acidic and basic media) and thermal stability (up to 170 ^oC). These characteristics are being mostly utilised in membrane science. Reports have been made by Nechifor *et al.* [11] on the use of a nanostructured polysulfone-carbon nanotube composite for hemodialysis, which is removal of heavy metals such as lead from blood. Atomic adsorption method allowed for the monitoring and quantifying of the adsorption of the metals, it was observed that the heavy metal take up was influenced by the carbon nanotube concentration. Polysulfone based membranes have been investigated by Homayoonfal *et al.* to act as an ultrafiltration and nanofiltration membranes for the removal of sulphate ions [12]. The grafted polysulfone was modified by polyethylene glycol and acrylic acid, this nanofiltration membrane was very efficient in the removal of the sulphate ions with reports of up to 96 % of Na_2SO_4 being removed from water at low operating pressure. Sangermano *et al.* (2011) [13] have reported the formation of diacrylate polysulfone/silver nanoparticles composite in the presence of ultraviolet light. The composite formed has the potential to be used in wound dressing because silver acts as antiseptic and the polysulfone offers a large surface area because of its porosity.

The most recent areas that polysulfones and their derivative have been used are in the development of sensors: gas sensor, immunosensor, biosensor and humidity sensor [14]. Telipan *et al.* have investigated the use of polysulfone as a gas sensor [15], specifically for the detection of NOx. The suitability of the synthesized polysulfone as a sensor was probed using voltage against time studies and from the results it was concluded that the sensor is a suitable electrochemical device for the detection of NO_x. Use of polysulfone in the field of electrochemical sensors and catalyst is mostly limited to polyaniline/polysulfone composites [16, 17]. The latter is due to that the polysulfone has a much lower degree of conjugation in comparison with the polyaniline (PANi), this means that even its conductivity is very low since conductivity is influenced by the degree of conjugation. The polysulfone acts as a mechanical support in these electrocatalysts as reported by Xiao-Juan and co-workers.

The current study will involve the synthesis of hydrogel based on polysulfone (PSF) and polyvinyl alcohol (PVA) in the presence of *N*-hydroxysuccinimide (NHS). Spectroscopic characterisation is done in order to deduce the mechanism of formation of the hydrogel. The electrochemistry of the synthesised hydrogel (PVA-NHS-PSF) is investigated using electrochemical impedance spectroscopy and cyclic voltammetry.

2. EXPERIMENTAL

2.1. Materials and Techniques

Polysulfone (PSF), polyvinyl alcohol (PVA), *N*-hydroxysuccinimide (NHS), hydrochloric acid, lithium perchlorate was supplied by sigma Aldrich. Fourier Transform infrared (FTIR) spectroscopy was used as a predominant tool to monitor the formation of the hydrogel from the different polymeric units by looking at the presence and absence of some functional groups. FTIR-ATR spectroscopy was done by was loading the sample unto the sample holder without prior sample preparation. The spectra were recorded within the 400-4000 cm^{-1} wavenumber region. UV-Vis absorption spectrum of the materials was recorded at room temperature on a GBC UV/Vis 920 spectrophotometer (GBC Scientific Instruments, Australia) between 200 and 500 nm using a 1 cm path length quartz cuvette. Morphology of the hydrogels and the starting materials was studied using a Hitachi model X-650 scanning electron microanalyser. Screen printed electrodes were used as a substrate for the SEM analysis.

2.2. Electrochemical measurements

Cyclic voltammetry (CV) experiments were carried out with a BAS100 electrochemical analyzer from BioAnalytical Systems (BAS) Technicol, Stockport, UK. Electrochemical impedance spectroscopy (EIS) measurements were recorded with VoltaLab PGZ 402 potentiostat from Radiometer Analytical (Lyon, France).

The working electrode was a platinum disk encapsulated in an epoxy resin (electrode geometric area: 0.071 cm^2). A platinum wire and an Ag|AgCl electrode were used as auxiliary and references electrodes, respectively. The Pt disk electrode surface was cleaned by polishing on aqueous slurries of 1 mm, 0.3 mm and 0.05 mm alumina powder consecutively, with subsequent rinsing with deionised water (obtained by passing distilled water through a Milli-Q water purification apparatus (Millipore)) after each polishing.

Polysulfone modified Pt electrode was prepared by placing 2 μl polysulfone on the surface of the clean Pt disk electrode. After 12 h the modified electrode was placed in an electrochemical cell containing 0.10 M $LiClO_4$ and CV was performed at a scan rate of 50 mV s^{-1}. The same method was used for the electrosynthesis of polyvinyl alcohol-polysulfone hydrogel on a Pt disk electrode from 2 μl mixture of PVA, NHS and PSF. The EIS spectra of bare and modified Pt working electrode systems were recorded with a VoltaLab PGZ 402 potentiostat at a frequency range of 1 kHz to 100 mHz, amplitude of 10 mV and a potential of 250 mV.

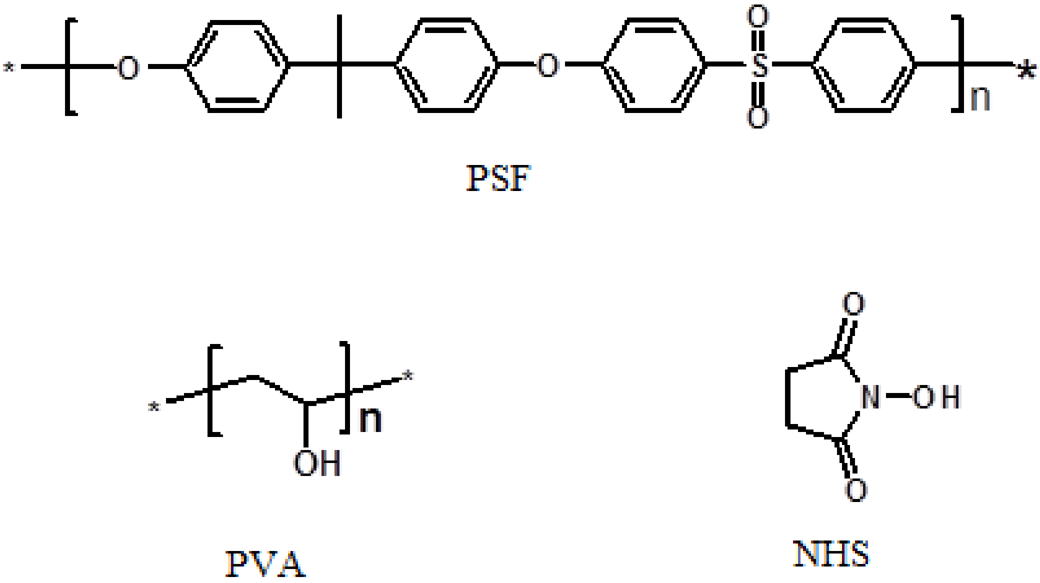
2.3. Synthesis of the hydrogel

To a vigorously stirred solution of 0.005 g of PVA, 0.0013 g of *N*-hydroxysuccinimide in 2 M HCl, 200 μl solution of polysulfone was added. Stirring of the mixture was continued at 60 ^{o}C for 3 h. A sticky compound was formed.

3. RESULTS AND DISCUSSION

The synthesis of the hydrogel was done using the starting material that is shown in Figure 1, at 60 ^{o}C, because at temperatures that are closer to 100 ^{o}C and more polyvinyl alcohol can undergo changes in its characteristics because of esterification and epoxide formation[18].

The FTIR spectroscopy showed that the hydrogel formed using PSF, PVA and NHS showed most of the characteristic vibrations due to the starting materials, Figure 2. The stretching vibration due to the hydrogen bond of the hydroxyl moiety of the polyvinyl alcohol is observed at 3290 cm^{-1}[19]. The vibration due to hydrogen bonding is observed in the hydrogel at a lower wavenumber, 3260 cm^{-1}, this suggests that there is hydrogen bonding between the PVA and the PSF polymer chain.

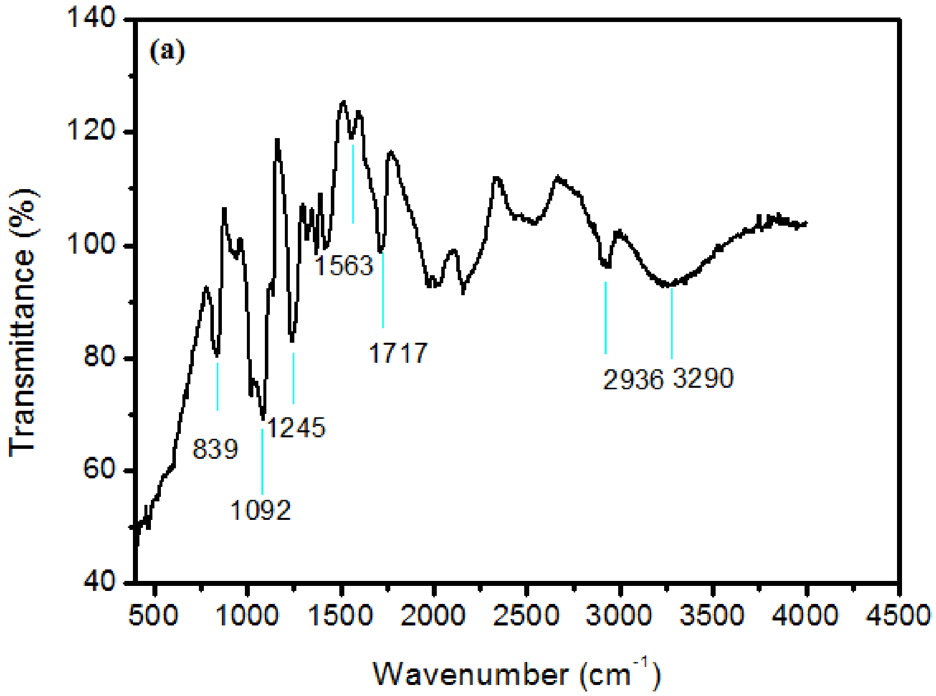


PSF

PVA

NHS

Figure 1. Schematic representation of the starting materials used in the preparation of the hydrogel.



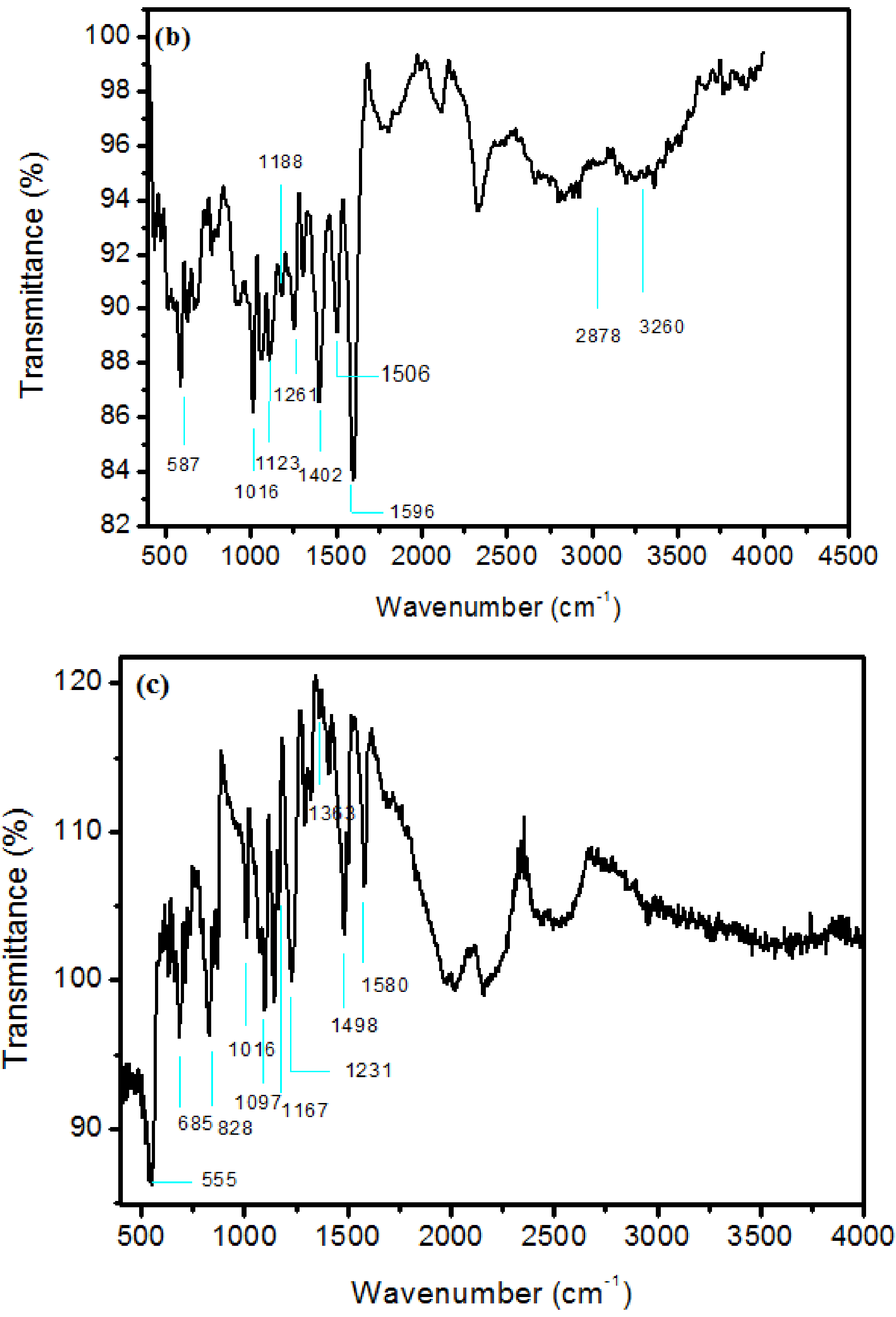


Figure 2. The FTIR-ATR of (a) PVA (b) Hydrogel (c) PSF.

It is not expected that the vibration is due to PVA since NHS has a hydroxyl moiety that can readily react with the PVA. In the past it has been shown that PVA in acidic media readily reacts with other compounds that have a hydroxyl moiety resulting in a loss of water [20-22]. If that is taken into consideration it is expected that the PVA will link with NHS at the -N-OH backbone. The CH stretching vibrations are observed at 2938 cm^{-1} and 2878 cm^{-1} for the PVA and hydrogel respectively.

The latter implies that the PVA characteristics are retained in the compound that is formed. This is further proved by the occurrence of the C-O stretching vibration at 1261 cm^{-1} for the hydrogel. The aromatic ring stretching vibrations are observed at 1598 cm^{-1} and 1506 cm^{-1} for the hydrogel which is comparative with the vibration that are seen for the PSF. The vibrations due to the sulfone moiety are also observed at 1328 cm^{-1} and 1167 cm^{-1} for the asymmetric and symmetric stretching vibrations respectively. Overall it can be seen that the compound displays characteristics of the two polymeric starting materials which implies a blending of the two materials to form the new compound.

Figure 3 shows the UV-visible spectrum of NHS, PSF and the hydrogel. As expected for the all the compounds electronic transitions are observed within the UV-visible region. Electronic transitions were expected even in the starting materials because of the existence of π bonds for all the compounds. The maximum absorption wavelength for the NHS is at 218 nm, 242 nm for the polysulfone and 252 nm for the hydrogel. Transitions observed for the hydrogel are as a result of the promotion of an electron from the π-bonding to the π-antibonding orbital of the sp^2 hybridised carbon atoms [22].

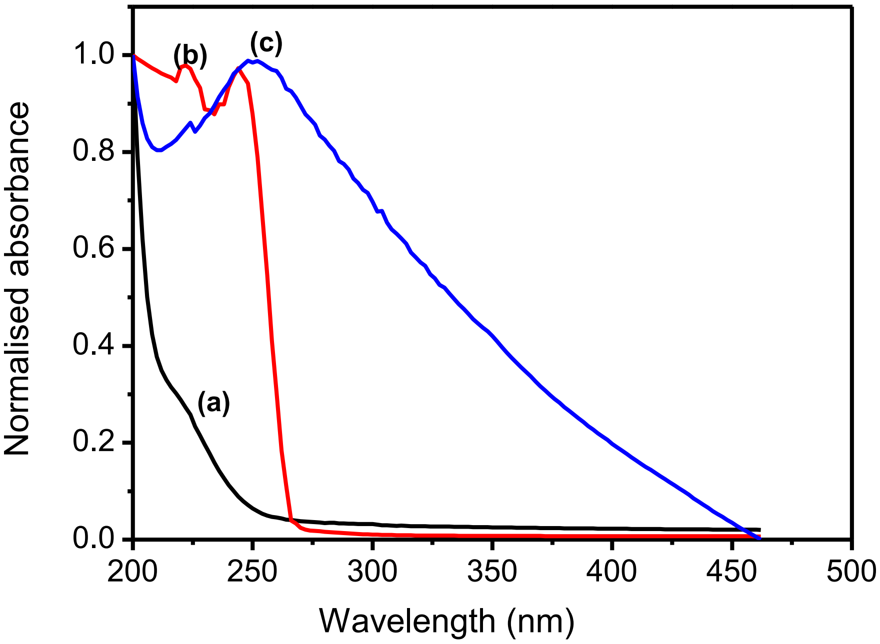


Figure 3. UV-visible of (a) NHS, (b) PSF in DMA (c) Hydrogel.

The SEM image of the hydrogel shows an intertwined branched network with very small pores, as shown in Figure 4a. This is significantly different from the clearly identifiable beaded structure of PSF on its own, Figure 4b. In contrast, A SEM image depicting polysulfone with a layer of polyvinyl alcohol (with *N*-hydroxy succinimide) on top showed that the polyvinyl alcohol formed a sheet on top of the polysulfone beads, with the PSF beads still visible underneath, Figure 4c. Therefore, the PSF and PVA have clearly formed a new composite that is distinctly different from the starting materials in terms of its morphology. The novel hydrogel composite is stable at room temperature with a well-defined porosity and homogeneous dispersion.

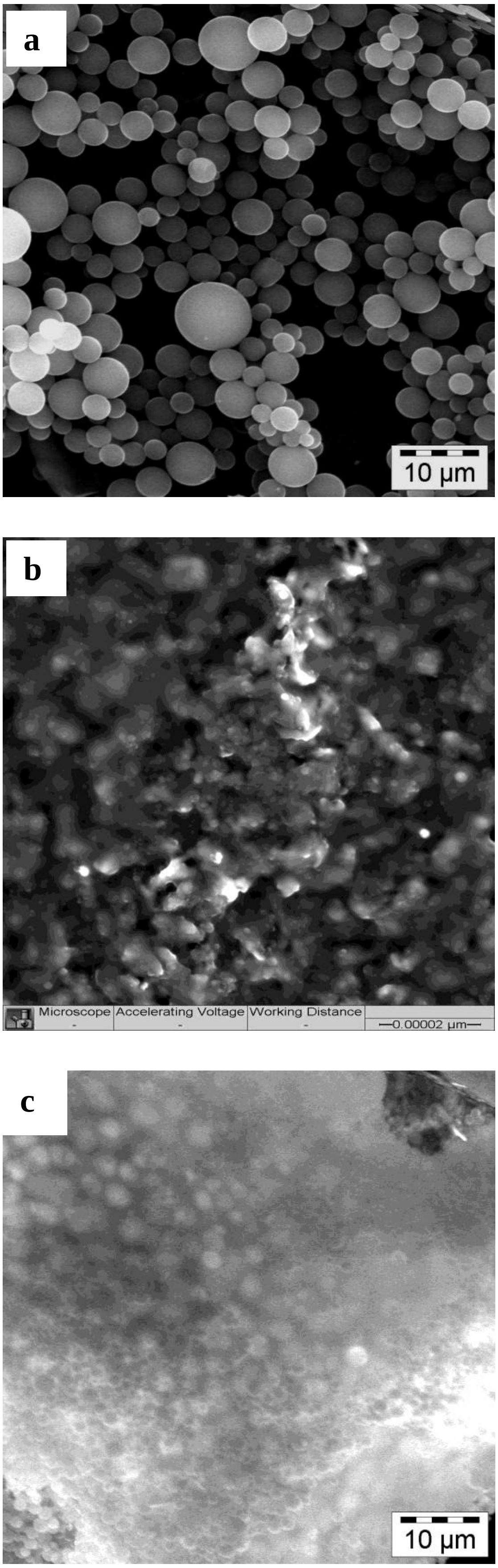


Figure 4. SEM images obtained at X 2000 magnification for: (a) polysulfone; (b) hydrogel; and (c) polysulfone with a top layer of polyvinyl alcohol and *N*-hydroxy succinimide.

When the cyclic voltammetry of the compounds were ran using the potential window of -600 mV to 800 mV, it was observed that the peaks observed are the same as those that are seen when using a platinum bare electrode, Figure 5. The differences observed are a slight shift in the position of the peaks in response to modification of the Pt electrode. When the cyclic voltammograms of the polysulfone modified electrode, PVA-NHS-PSF modified electrode are compared, Figure 5, it is observed that the electrochemical reaction occurs at more negative potentials. This is denoted by the shift in the cathodic peak potential from 312 mV (for the PSF) to 246 mV (for the PVA-NHS-PSF hydrogel).

An irreversible cathodic peak is observed at 246 mV (vs Ag|AgCl) for the hydrogel, Figure 6. Irreversibility within an electrochemical system can occur due to very slow electron transfer reactions and also other side chemical reactions [23]. The cathodic peak potentials, E_{pc}, as well as the corresponding peak currents, I_{pc}, vary with scan rate, Figure 5. This latter depicts a surface confined electroactive material [24].

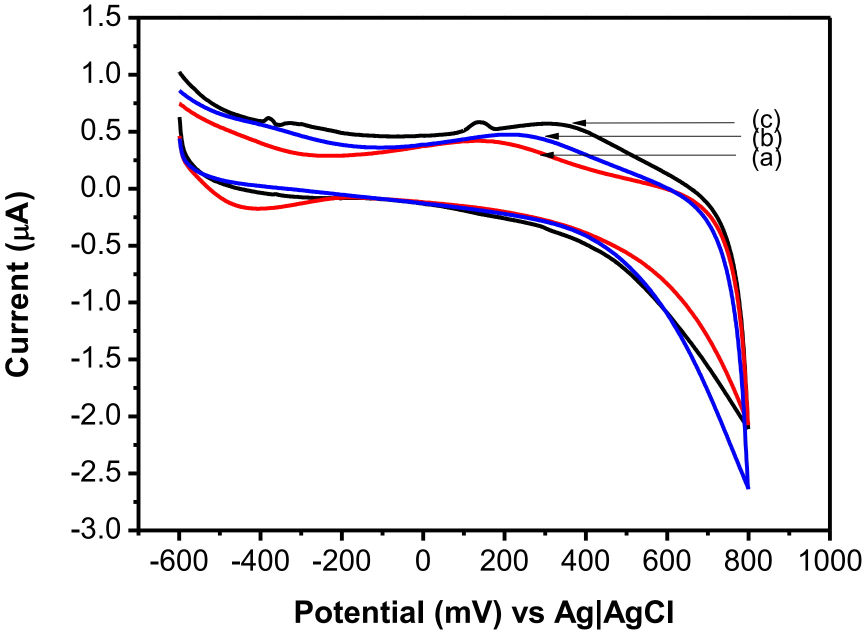


Figure 5. Cyclic voltammograms of (a) bare Pt electrode, (b) Pt|PVA-NHS-PSF, and (c) Pt|PSF, in 0.10 M $LiClO_4$ at a scan rate of 50 mV s^{-1}.

The Nyquist plots that are depicted in Figure 7 are considered an effective way of determining the electron transfer resistance of materials [25,26]. The diagrams are shown with the equivalent circuit that was fitted effectively so as to determine the charge transfer resistance (R_{ct}). The data that was produced showed that polysulfone (R_{ct}: 23.260 kΩ) has a higher charge transfer resistance in comparison to the hydrogel (R_{ct}: 12.065 kΩ). This implies that the hydrogel is more highly conductive than the polysulfone.

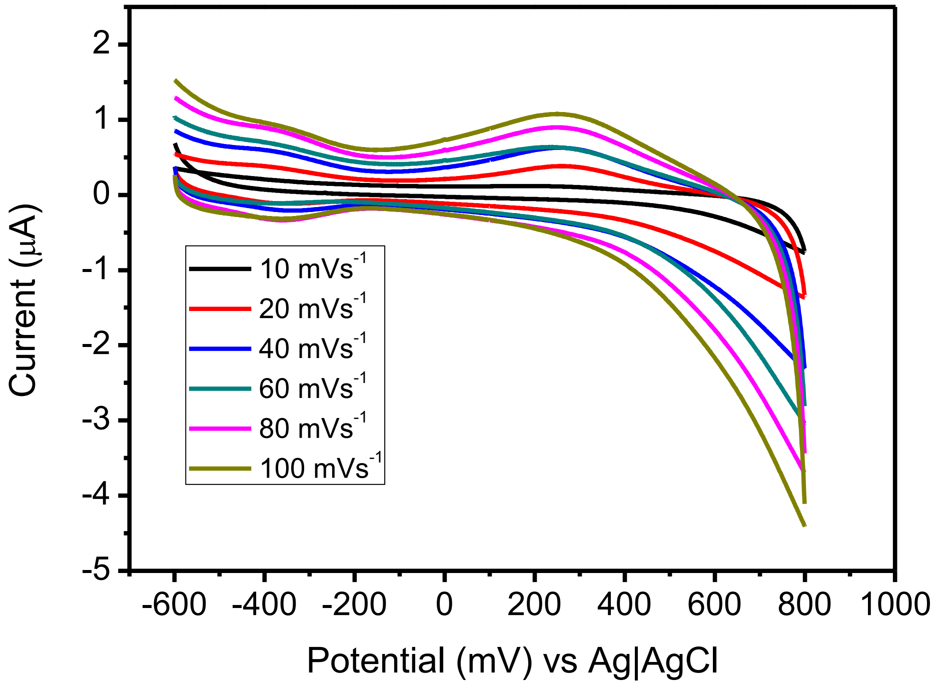


Figure 6. Cyclic voltammograms of Pt|PVA-NHS-PSF in 0.10 M $LiClO_4$ at different scan rates.

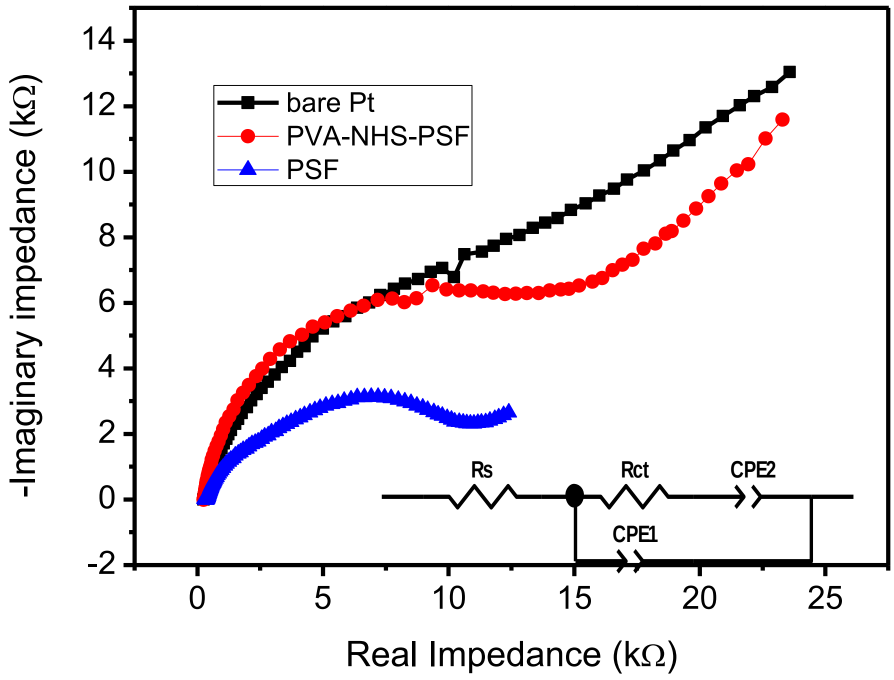


Figure 7. Nyquist plot of (-■-) Bare Pt electrode, (-●-) Pt|PVA-NHS-PSF and (-▲-) Pt|PSF with a Randles equivalent circuit; in 0.10 M $LiClO_4$.

4. CONCLUSION

The synthesis of a new hydrogel based on a polysulfone and polyvinyl alcohol has been synthesised successfully utilising the cross linking methodology. The hydrogel UV-vis and FTIR spectra data confirmed that it exhibited characteristics that are significantly different from the starting material. The hydrogel formed a highly interlinked network that has small pores in comparison with the pure polysulfone which has much larger pores. The small pores make the hydrogel to be attractive with regard to possible application in ultrafiltration technologies, particularly for the filtration of samples containing very small molecules.

References

1. S. Sampath, N.A. Choudhury, A.K. Shukla, *J. Chem. Sci.*, 121 (2009) 727.
2. K. McAllister, P. Sazani, M. Adams, M.J Cho, M. Rubinstein, R.J Samulski, *J. Am. Chem. Soc.*, 124 (2002) 15198.
3. E.F. Reis, F.S. Campos, A.P. Lage, R.C. Leite, *Materials Research*, 9 (2006) 185.
4. F.A. Dorkoosh, J. Brussee, J.C. Verhoef, G. Borchard, M. Rafiee-Tehrani, H.E. Junginger, *Polymer*, 41 (2000) 8213.
5. E.H. Schacht, *Journal of Physics: Conference Series* 3, (2004) 22-28.
6. H. Bodugöz, N. Pekel, O. Güven, *Radiat. Phys. Chem.*, 55 (1999) 667.
7. X. Zhu, P. Lu, W. Chen, J. Dong, *Polymer*, 51 (2010) 3054.
8. M. M. Lakouraj, M. Tajbakhsh, M. Mokhtary, *Iranian Polym. J.*, 14 (2005) 1022.
9. J. L Valentin, D. Lopez, R. Hernandez, C. Mijangos, K. Saalwachter, *Macromolecules*, 42 (2009) 263.
10. E.A. Bursali, S. Coskun, M. Kizil, M. Yurdakoc, *Carbohyd. Polym.*, 83 (2011) 1377.
11. G. Nechifor, S.I Voicu, A.C. Nechifor, S. Garea, *Desalination*, 241 (2009) 342.
12. M. Homayoonfal, A. Akbari, *Iran J. Environ. Health Sci. Eng.*, 7 (5) (2010) 407.
13. M. Sngermano, I. Roppolo V.H.A Camara, C. Dizman, S. Ates, L. Torun, Y. Yagci, *Macromol. Mater. Eng.*, 296 (2011) 820.
14. M. Ciobanu, L. Marin, V. Cozan, M. Bruma, *Rev. Adv. Mater. Sci.*, 22 (2009) 89.
15. G. Telipan, M. Ignat, V. Cozan, *J. Optoelectr. Adv. Mater.*, 8 (2006) 582.
16. Ş.I. Voicu, F. Aldea, M. RĂDUȚ, G. Nechifor, *U.P.B. Sci. Bull.: Series B*, 70 (2008) 39.
17. X-J. Feng,Y-L. Shi, Z-A. Hu, *Int. J. Electrochem. Sci.*, 5 (2010) 489.
18. A.I. Vogel, *A Text Book of Practical Organic Chemistry*, 3rd Ed., 1974: Longman Group Limited, London.
19. J. Coates, *Interpretation of Infrared Spectra: A Practical Approach. In Encyclopedia of Analytical Chemistry*, 2000, Wiley, New York.
20. K. Kumeta, I. Nagashima, S. Matsui, K. Mizoguchi, *J. Appl. Polym. Sci***.,** 90 (2003) 2420.
21. Y. Zhang, P.C. Zhu, D. Edgren, *J. Polym. Res.*, 17 (2010) 725.
22. O. M'barki, A. Hanafia, D. Bouyer, C. Faur, R. Sescousse, U. Delabre, C. Blot, P. Guenoun, A. Deratani, D. Quemener, C. Pochat-Bohatier, *J. Membrane Sci*., 458 (2014) 225.
23. T.L. Gilchrist, R.C. Storr, *Organic Reactions and Orbital Symmetry*, 2nd Ed., 1979: Cambridge University Press, Cambridge.
24. P.M.S. Monk, *Fundamentals of Electroanalytical Chemistry*, 2001: Wiley, New York.
25. A. J. Bard, L.R. Faulkner, *Electrochemical Methods: Fundamentals and Applications*, 1980: Wiley, New York.

26. A. Lasia, *Electrochemical Impedance Spectroscopy and its Applications*, 2014: Springer, New York.