

Nghiên cứu tính chất trương nước của vật liệu siêu hấp thụ trên cơ sở poly(vinyl alcohol)/lignin/chitosan

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TÓM TẮT

Màng hydrogel trên cơ sở poly(vinyl alcohol), lignin và chitosan (PLCG) được tổng hợp với chất tạo liên kết ngang glyoxal. Hỗn hợp PLCG được chuẩn bị bằng phương pháp đổ khuôn, sau đó hydrogel hình thành bằng phản ứng đóng rắn ở nhiệt độ 80 °C trên khuôn petri trong một khoảng thời gian nhất định. Mẫu hydrogel sau đó được phân tích và khảo sát tính chất bằng kính hiển vi điện tử quét (SEM), quang phổ hồng ngoại Fourier (FTIR), nhiễu xạ tia X, và thí nghiệm trương nở. Kết quả đo độ trương nở cho thấy màng PLCG hydrogel có khả năng trương nước vượt trội lên đến 797% sau 24 giờ thử nghiệm ngâm trong nước cất ở 25 °C và đạt độ trương nước tối đa đến 826% khi so với khối lượng khô của mẫu. Quan sát ảnh SEM cho thấy, bề mặt hydrogel có nhiều cấu trúc xốp làm tăng khả năng hấp thụ. Với những đặc tính nổi bật, màng PLCG hydrogel được coi là vật liệu tổng hợp thân thiện môi trường, không độc hại, có tính trương nước tốt.

Từ khóa: *Màng hydrogel, hấp thụ nước, chitosan, lignin, poly(vinyl alcohol).*

**Tác giả liên hệ chính.*

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Study on swelling properties of the super-absorbent hydrogel film based on poly(vinyl alcohol)/lignin/chitosan

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ABSTRACT

The composite hydrogel film based on poly(vinyl alcohol), lignin, and chitosan (PLCG) was synthesized with glyoxal crosslinker. PLCG mixture was prepared by hydrothermal method, then the film was formed by casting method on a petri dish and crosslinked at 80 °C within some periods. Well-prepared samples were analyzed with Scanning Electron Microscopy (SEM), Fourier Transform Infrared Spectroscopy (FTIR), X-Ray Diffraction (XRD), and swelling behavior. The obtained results of the water swelling measurements show that the PLCG hydrogel film had outstanding water swelling ability up to 797% after 24 hours of immersion test in neutral distilled water at 25 °C and obtained maximum swelling ratio to 826% compared to the dried sample. The surface has many porous structures that increase the adsorption capacity as revealed by SEM images. With outstanding properties, PLCG hydrogel film is considered as environmentally friendly and non-toxic material with good water-swelling materials.

Keywords: *Hydrogel film, chitosan, lignin, poly(vinyl alcohol), water swelling.*

1. INTRODUCTION

Nowadays, hydrogels attract the interests of most scientists due to their biomedical application with remarkable characteristics. Hydrogel biomaterial therapy containing active ingredients that promote regeneration is a new trend for effective prevention and treatment of wounds. They can create an environment with appropriate conditions to support the regeneration cells and promote skin regeneration, such as absorbing purulent drainage from the wound to reduce infection, functioning as a barrier against microbial invasion and easily removed without causing pain.¹ They could be applied as wound dressing, wound healing agent, scaffolds, contact lenses and drug-releasing.

In the present studies, PVA, chitosan and lignin are typical substances for hydrogel

synthesis with excellent properties such as water swelling capacity, high hydrophilicity, and biocompatibility of PVA^{2,3} along with superior properties such as antioxidant character, antibacterial, good biocompatibility of chitosan and lignin.³⁻⁶

Some studies have shown that hydrogel from PVA-chitosan has a broad potential in biomedical applications. Liang Quan Peng et al. have synthesized hydrogels with a ratio of PVA/Chitosan by freeze-thaw cycles method. The film has good mechanical properties, and it also shows stable physical and chemical properties with porosity and over 90% water content, no cytotoxicity and was able to promote cell proliferation. The research achieved the best cartilage healing.⁷ Hitesh Chopra et al. have prepared chitosan/polyvinyl alcohol

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(PVA)-based honey hydrogel films which were developed by a solvent-casting method for potential wound healing application. Membrane with excellent swelling, absorbency, and mechanical properties are ideal for therapeutic and wound healing applications.⁸

Despite the outstanding biocompatibility and antibacterial properties of PVA-chitosan composite hydrogel, its applicability as a wound dressing is constrained by its lack of mechanical strength. Lignin is being considered as a solution to add to PVA-Chitosan composite to improve the product's mechanical properties. In addition, lignin also possesses some additional properties, such as antioxidant, adsorbent UV receptor, and nanoscale antibacterial agent,^{9,10} which improves the wound protection effect.

This research focuses on studying the properties of PLCG hydrogel films based on polyvinyl alcohol, chitosan, and lignin with glyoxal crosslinker, utilizing numerous analytical methods including Scanning Electron Microscopy (SEM), Fourier Transform Infrared Spectroscopy (FTIR) and conducting swelling test to measure water absorbing ability.

2. MATERIALS AND METHODS

2.1. Materials

PVA - $(\text{CH}_2\text{CH-OH})_n$ has Mw ~ 205000g/mol was purchased from Sigma Aldrich, Germany. Chitosan has Mw ~ 5000 g/mol was purchased from China. Lignin has Mw ~ 2330 ÷ 21500 g/mol from Nacalai Tesque. Deionized water is used for all the formulations that were prepared in the lab.

2.2. Methods

2.2.1. Preparation of PVA/lignin/chitosan mixture (PLC mixture)

PVA solution: 1 g of PVA is dissolved in 40 mL of distilled water, the solution was stirred continuously for 2 hours at room temperature. After the PVA was dissolved, the solution was heated to 80°C and remained stable for about 15 min.

PVA/lignin mixture: Weigh 0,2 g of lignin and add lignin into PVA solution. After the lignin was used up, continue stirring the solution for 2 hours at 80 °C to homogenize the mixture.

Chitosan solution: Use 0,5 g Chitosan to dissolve with 25 mL of 2% acetic acid solution, let the mixture soak in the acetic acid 2% at room temperature for 24 hours, then use stirring device to stir the solution at 60 °C for 1 hour.

Mix the PVA/lignin mixture and chitosan solution, using a stirring device to speed up the homogenization process, stirring at 40 °C for 2 hours, then increase the solution temperature to 60 °C and keep stirring to obtain a PLC homogenized mixture. After that, the PLC mixture will be crosslinked by glyoxal.

2.2.2. Crosslinking PLCG hydrogel film

Slowly add 1,4 g glyoxal (drop by drop) to the PLC mixture, stirring for 30 minutes at 60 °C. Pour the mixture into the mold to heat at 80 °C to form the crosslinking between the chemicals with the timelines: 30, 60 and 90 minutes. The samples were labelled as PLCG_30, PLCG_60, PLCG_90, shown in Table 1.

Table 1. Notation of the samples

Sample	Glyoxal/PVA ratio	Crosslinked reaction time (minutes)
PLCG_30	1,4 / 1	30
PLCG_60	1,4 / 1	60
PLCG_90	1,4 / 1	90

2.2.3. Swelling behavior of PVA/lignin/chitosan/glyoxal (PLCG) hydrogels

Prepare a 10 mm x 10 mm PVA/lignin/chitosan hydrogel film. Then, the residual glyoxal and lignin components in the sample were removed by immersing the film in distilled water until the film reached constant weight. Finally, the film was again dried to constant weight W_e . W_e is used in the calculation of gel fraction and swelling ratio.⁸

• Swelling ratio (SR%): Measuring the ability to absorb solution (usually water) by immersing. The formula is shown below:

$$SR\% = \frac{W_s - W_e}{W_e} \times 100 \quad (1)$$

After soaking the analytical sample for a specific period, remove the sample from the water and weigh the analyzed sample to get W_s .

When the sample reaches the equilibrium point (cannot absorb more water), the ESR% saturation point is obtained. The calculation formula for ESR% is similar to SR%.

• Gel fraction (GF%): Measuring the efficiency of the crosslinking reaction by immersing, usually the better the gel ratio results, the lower the water swelling results. The formula is shown below:

$$GF\% = \frac{W_{d2}}{W_{d1}} \times 100 \quad (2)$$

For the gel fraction measurement, the sample will be soaked for 48 hours, then the weight of the sample will be weighed and noted as W_{d2} . W_{d1} is the mass of the sample that was dried before testing.

2.2.4. FTIR

FTIR spectra of PLCG hydrogel samples was measured in transmittance mode at room temperature by Frontier FT-IR/NIR instrument model at Center of Scientific Equipment & Biological, Chemical and Physical Analysis - Institute of Applied Materials Science, Ho Chi Minh City, Vietnam. The number of scans is 20 and the resolution is 4 cm^{-1} . The scan range is $4000 - 450 \text{ cm}^{-1}$, the scan speed is $0,2 \text{ mm/s}$.

2.2.5. SEM

Sample surface structure was observed with Hitachi S-4800 High Resolution SEM system

at SHTPLAB, Research Laboratories of Saigon HI-TECH Park, HCM City, Vietnam. Hydrogel film samples after drying at 60°C for 2 h under normal conditions were kept in a desiccator for 12 h, then taken for SEM, FTIR and other analytical methods.

3. RESULTS AND DISCUSSION

3.1. FTIR spectra

In the FTIR spectrum of chitosan (Figure 1a), it could be seen that the absorption peak at 3607 cm^{-1} was specific for -OH group.¹¹ The peak at 3075 cm^{-1} was characterized for $-\text{NH}_2$ vibration. The peak 281 cm^{-1} reflected for the $-\text{CH}_2$ group of stretching oscillations caused by the pyranose ring.¹² The absorption peak 1679 cm^{-1} referred for the prolonged C=O group (amides). The 1005 cm^{-1} peak was associated with the C-H bond.¹³

The peaks of PVA at $3282, 2922, 1716, 1374, 1085$, and 833 cm^{-1} (Fig. 1d) were associated with O-H, $-\text{CH}_2$, C=O, C-H, C-O and C-C groups vibration.¹⁴ In the PVA/lignin/glyoxal (Fig. 1c), because of the interaction between PVA and lignin, a redshift appeared from 3282 cm^{-1} to 3311 cm^{-1} for hydroxyl group.¹⁵

In the Figure 1b, the peak at 3458 cm^{-1} was for the O-H group, which was contributed from PVA, chitosan and lignin components of the PLCG hydrogel.¹⁶⁻¹⁷ The appearance 1060 cm^{-1} peak, as previously reported,⁷ was associated with vibration of C-O-C-O-C linkage, demonstrating that there was a cross-linking between chitosan and glyoxal.¹⁶ The hydrogel became a network because of the reaction between glyoxal and -OH groups in chitosan,¹² PVA,¹⁴ and lignin.¹⁸

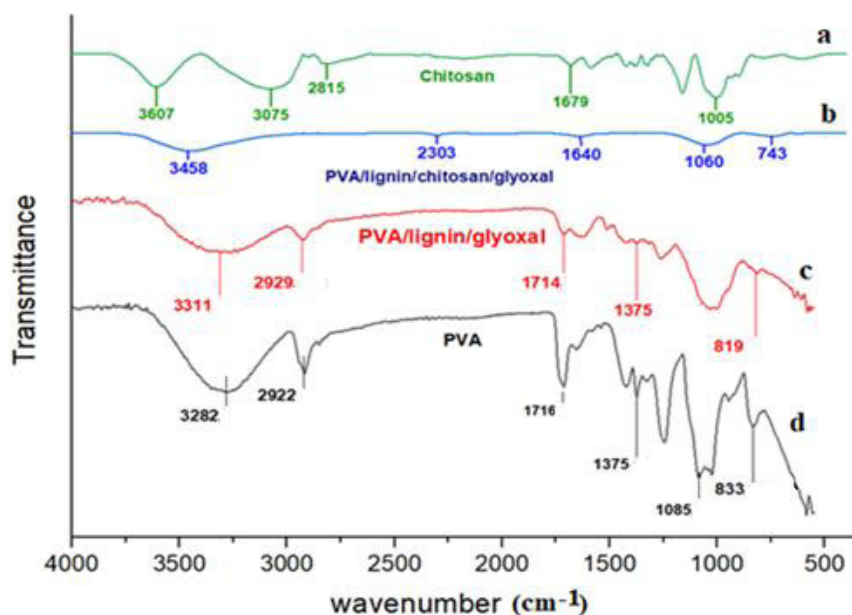


Figure 1. FTIR of Chitosan (a), PLCG_30 sample (b), PLG (c) and PVA (d).

3.2. SEM Image

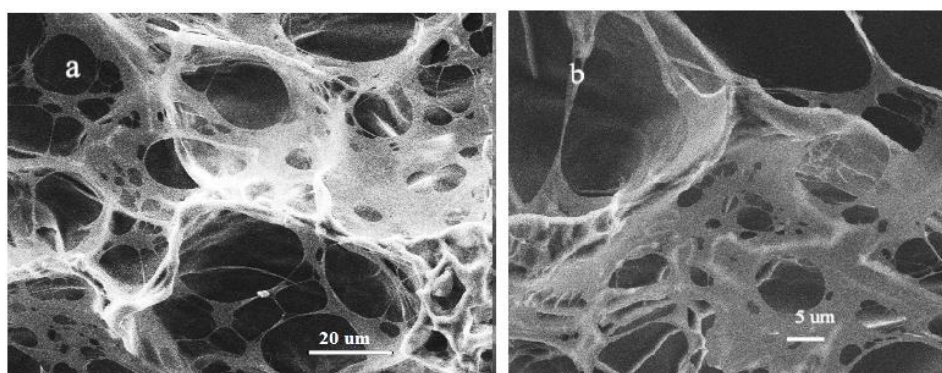


Figure 2. SEM images (a, b) of PLCG_30 hydrogel sample.

From the SEM image (Figure 6), the surface of the sample had many pores, and the density of holes is dense. In order to create porous screen materials, it was necessary to have additional curing agents, specifically glyoxal here.

The cross-linking between polymers in 3-dimensional space help them connect to each other to form a continuous network and appeared porous holes distributed from the inside to the outside of the material. This was consistent with the good water swelling properties of the sample.

3.3. XRD

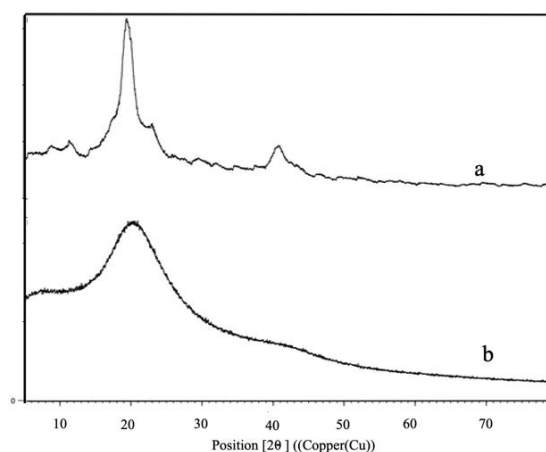


Figure 3. XRD of PVA (a) and PLCG_30 (b).

It could be seen on the XRD pattern of the PVA sample (Figure 3a) that there were two characteristic diffraction peaks located in the 2θ region at $19 - 20^\circ$ and $40 - 41^\circ$, which were typical for the semi-crystalline nature of the PVA film.¹⁹ This semi-crystalline structure of PVA was caused by intramolecular and intermolecular hydrogen bonds. The XRD image of PLCG_30 (Figure 3b) still showed the characteristic crystal peaks of PVA, but somewhat weaker with blunted and less sharp peaks. This indicated that the polar groups in lignin and chitosan linked with the hydroxyl groups of PVA and combined with glyoxal, resulting in an increased amorphous structure of the polymer complex compared to PVA sample.

3.4 Swelling behavior investigation

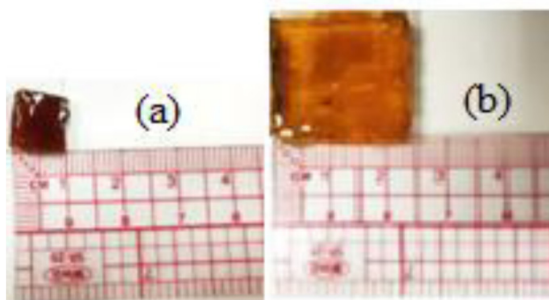


Figure 4. The size of the film before and after swelling test.

After the hydrogel test, the hydrogel films tended to absorb water and expanded the film structure, as seen in Figure 4 (a, b). The film got more translucent and changed color from dark brown to light brown. Additionally, the films' entire dimensions had increased.

Based on Figures 5 and 6, the hydrogel films had excellent water absorption speed and capacity. During the first six hours, the PLCG films absorbed a lot of water, about 80% of the water absorption compared to the equilibrium point. The sample PLCG_30 obtained about 797% after 24 hours of soaking in neutral distilled water at 25°C and up to maximum value about 826%, a rise of about 8-9 times the initial weight, which possessed the highest water absorbing ability. It could be seen that the equilibrium points of water swelling generally

decreased with increasing crosslinking time, which was 677% for PLCG_60 and 530% for PLCG_90.

The hydrogel films absorbed less water as the crosslinking time increased, which could be explained that the -OH group of PVA structure, one of the water-absorbing components of the film, reacted with the crosslinking agent during the crosslinking agent - glyoxal. The crosslinking reaction strengthened the film structure and made it more difficult to expand when absorbing water, which reduced water absorption.

According to Figure 7, the gel ratio gradually increased from sample PLCG_30 to PLCG_90, and overall, all samples produced gel fraction more than 80%, a good result which was drawn from the excellent crosslinking reaction forming hydrogel network in investigated samples, PLCG_30, PLCG_60, and PLCG_90. The gel fraction referred to the number of cross-links connecting the polymers in the hydrogel.²⁰

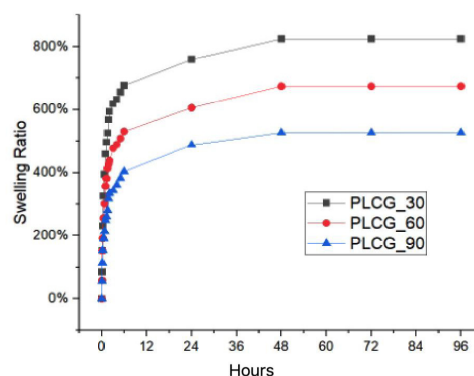


Figure 5. Swelling Ratio test of the hydrogel PLCG films.

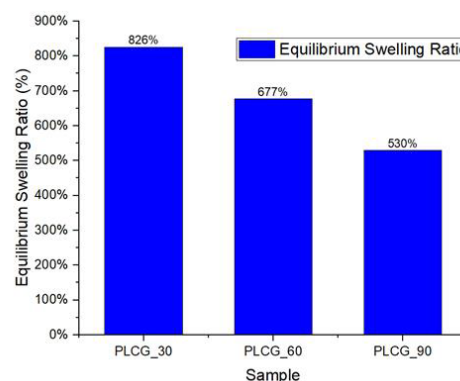


Figure 6. Equilibrium swelling ratio (ESR%) of 3 hydrogel samples.

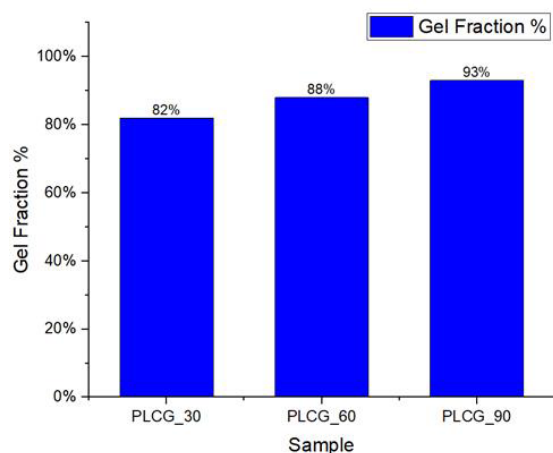


Figure 7. Gel fraction (GF%) of hydrogel samples

4. CONCLUSION

PLCG hydrogel films were prepared, and their characteristics were investigated using techniques including FTIR, SEM, XRD and swelling measurement. The swelling results showed that the hydrogel film sample had a very good swelling capacity and PLCG_30 hydrogel sample obtained maximum value to 826% in distilled water (pH = 7) at room temperature. In addition, the gel ratios of hydrogel samples gave good results about 80%, showing very good effectiveness of crosslinking reactions in creating matrix in hydrogel. The FTIR and SEM results could explain the good water swelling ability of the composite hydrogel films through the existence of the -OH groups of the composite and the surface pore structures of the hydrogel films. The measurements' results indicated that PLCG hydrogel films with remarkable water swelling had the potential for a wide range of actual application.

REFERENCES

1. P. N. Le, C. K. Huynh & N. Q. Tran. Advances in thermosensitive polymer-grafted platforms for biomedical applications, *Materials Science and Engineering: C*, **2018**, 92, 1016-1030.
2. S. Kubo & J. F. Kadla. The Formation of strong intermolecular interactions in immiscible blends of poly(vinyl alcohol) (PVA) and lignin, *Biomacromolecules*, **2003**, 4, 561-567.
3. G. Crini & P. M. Badot. Application of chitosan, a natural amino polysaccharide, for dye removal from aqueous solutions by adsorption processes using batch studies: A review of recent literature, *Progress in Polymer Science*, **2008**, 33(4), 399-447.
4. M. N. V. Ravi Kumar. A review of chitin and chitosan applications, *Reactive & Functional Polymers*, **2000**, 46, 1-27.
5. M. Rinaudo. Chitin and chitosan: Properties and applications, *Progress in Polymer Science*, **2006**, 31(7), 603-632.
6. J. Chedly, S. Soares, A. Montembault, Y. V. Boxberg, M. V. Ravaille, C. Mouffle, M. N. Benassy, J. Taxi, L. David & F. Nothias. Physical chitosan microhydrogels as scaffolds for spinal cord injury restoration and axon regeneration, *Biomaterials*, **2017**, 138, 91-107.
7. L. Peng, Y. Zhou, W. Lu, W. Zhu, Y. Li, K. Chen, G. Zhang, J. Xu, Z. Deng & D. Wang. Characterization of a novel polyvinyl alcohol/chitosan porous hydrogel combined with bone marrow mesenchymal stem cells and its application in articular cartilage repair, *BMC Musculoskelet Disord*, **2019**, 20(1), 257-265.
8. H. Chopra, S. Bibi, S. Kumar, M. S. Khan, P. Kumar & I. Singh. Preparation and evaluation of Chitosan/PVA based Hydrogel films loaded with honey for wound healing application, *Gels*, **2022**, 8(2), 111-120.
9. D. Kai, M. J. Tan, P. L. Chee, Y. K. Chua, Y. L. Yap & X. J. Loh. Towards lignin-based functional materials in a sustainable world, *Green Chemistry*, **2016**, 18(5), 1175-1200.
10. V. K. Thakur, M. K. Thakur, P. Raghavan & M. R. Kessler. Progress in green polymer composites from lignin for multifunctional applications: A review, *ACS Sustainable Chemistry & Engineering*, **2014**, 2(5), 1072-1092.
11. B. Krishnaveni & R. Ragunathan. Extraction and characterization of chitin and chitosan from *F. solani* CBNR BKRR, synthesis of their Bionanocomposites and study of their productive application, *Journal of Pharmaceutical Sciences and Research*, **2015**, 7(4), 197-205.

12. Q. Yang, F. Dou, B. Liang & Q. Shen. Studies of cross-linking reaction on chitosan fiber with glyoxal, *Carbohydrate Polymers*, **2005**, *59*, 205–210.
13. J. A. Sirviö, M. Visanko & H. Liimatainen. Synthesis of imidazolium-crosslinked chitosan aerogel and its prospect as a dye removing adsorbent, *The Royal Society of Chemistry*, **2016**, *6*, 56544–56548.
14. Y. Zhang, P. C. Zhu & D. Edgren. Crosslinking reaction of Poly(Vinyl Alcohol) with Glyoxal, *Journal of Polymer Research*, **2009**, *17*, 725–730.
15. P. Posoknistakul, C. Tangkrakul, P. Chaosuanphae, S. Deepentharn, W. Techasawong, N. Phonphirunrot, S. Bairak, C. Sakdaronnarong & N. Laosiripojana. Fabrication and characterization of lignin particles and their ultraviolet protection ability in PVA composite film, *American Chemical Society Omega*, **2020**, *5*(33), 20976–20982.
16. Y. Zhang, M. Jiang, Y. Zhang, Q. Cao, X. Wang, Y. Han, G. Sun, Y. Lia & J. Zhou. Novel lignin–chitosan–PVA composite hydrogel for wound dressing, *Materials Science & Engineering C*, **2019**, *104*, 110002.
17. K. W. Choo, Y. C. Ching, C. H. Chuah, J. Sabariah, & N. S. Liou. Preparation and characterization of polyvinyl alcohol-chitosan composite films reinforced with cellulose nanofiber, *Materials*, **2016**, *9*, 644.
18. S. Chaleawlerthumpon & C. Liedel. More sustainable energy storage: lignin based electrodes with glyoxal crosslinking, *Journal of Materials Chemistry A*, **2017**, *5*, 24344–24352.
19. S. B. Aziz, O. Gh. Abdullah, S. A. Hussein & H. M. Ahmed. Effect of PVA blending on structural and Ion transport properties of CS:AgNt-based Polymer electrolyte membrane, *Polymers*, **2017**, *9*, 622.
20. M. T. S. Alcântara, A. J. C. Brant, D. R. Giannini, J. O. C. P. Pessoa, A. B. Andrade, H. G. Riella & A. B. Lugão. Influence of dissolution processing of PVA blends on the characteristics of their Hydrogels synthesized by radiation-Part I: Gel fraction, swelling, and mechanical properties, *Radiation Physics and Chemistry*, **2012**, *81*(9), 1465–1470.