

Fabrication of Coir Pith Lignin-Based Fibers Using Electrospinning Method

Nguyen Thi Nhu Y¹, Nguyen Thi Ven², Luong Huynh Vu Thanh^{2,*}

¹Department of Chemistry, Faculty of General Sciences, Can Tho University of Technology, Vietnam

²Department of Chemical Engineering, College of Engineering Technology, Can Tho University, Vietnam

Abstract—The electrospinnability of lignin derived from coir pith in Mekong Delta, Vietnam was investigated by electrospinning method which has attracted great attention in recent years. Lignin was blended with polyethylene oxide (PEO) in order to enhance the electrospinning performance. The addition of PEO was contributed reducing electrical conductivity and improving viscoelastic properties, assisting in lignin fiber formation. The electrospun parameters containing various Lignin/PEO ratios, feeding rates, working distances were studied. The electrospun lignin fibers were characterized using scanning electron microscopy (SEM) to evaluate their morphology. Experimental results showed that lignin-based fibers were successfully fabricated and fiber performance was highly depending on Lignin/PEO content rate, flow rate and needle-disk distance. The optimal fibers were obtained at experimental conditions: Lignin/PEO content rate of 85/15, flow rate of 0.2 mL/h and performing distance of 11 cm.

Keywords— Lignin, coir pith, PEO, fiber, electrospinning.

I. INTRODUCTION

Lignin is a natural aromatic polymer accounting 12-39% terrestrial plant cell with amorphous heteropolymer. By experimental methods, lignin is identified as three major monomers: coniphenyl alcohol, sinapyl alcohol and p-caryaric acid. Briefly, lignin contains several function groups: hydroxyl, phenolic and ester groups. The covalent bond between lignin and carbohydrate consists of four main types of bonds: benzyl ester, benzyl ether, phenyl glycosides and hemiacetal [1-3]. Monomers are linked by C-C and C-O bonds. However, lignin is still a challenge for scientists because the understanding of its chemical structure is still not clarified [4, 5].

Lignin polymer is abundant, biodegradable, natural biomaterial which received plenty of attention of researchers in biomedical field due to its unique mechanical, chemical, biological properties, low cost and environmental concerns. Many researches on the application potential of lignin have been explored in the fields of: chemicals [6-8], biofuels [9,10], pharmaceuticals [11], composite materials [12], environment [13], nonporous materials, nanoparticles, nano carriers [14-16], carbon fiber [17], color-sensitive solar cell [18]. In addition, lignin has been shown its antimicrobial and antifungal activities, antioxidant, UV absorption, and fire resistance [1, 19].

Electrospinning is a simple, low cost and flexible method for fabrication of micrometer to nanometers materials and it is also well-suited for production of biopolymer fibers for a wide variety of applications: energy harvest and storage, environmental protection, biomedical engineering, nanosensors and military protection clothing [20-23]. Besides electrospun nanofibers of lignin are identified to have great potential application in producing carbon fiber, catalysis, chemical industry, they may also be useful in a wide range of biomedical applications especially in tissue scaffolds and drug delivery techniques. Obviously, natural polymer nanofibers may be particularly well suited for biomedical fields because

they are biocompatible, biodegradable and non-toxic. Moreover, lignin possesses outstanding properties as anti-oxidation, anti-viral effect, good mechanical properties and it is also easy to be functionalized.

Lignin-PEO is one of the most effective precursor solutions for electrospinning method [15, 24-30]. PEO is electrospunable polymer enhancing electrospun performance [70]. Used solvents such as dimethylformamide (DMF), dimethyl sulfoxide (DMSO) Tetrahydrofuran (THF) and acetone are disclosed previously [15, 28, 31]. However, these solvents are toxic leading to limit lignin applications in biomedical field.

In order to create truly green lignin fibers, the used solvent should be considered. Sodium lignin dissolved in dilute alkaline solution (NaOH 0.6 M) is one of the most environmentally friendly solutions for lignin fiber production compared to others.

II. MATERIALS AND METHODS

A. Materials

Alkali lignin particles with size range of some tens to hundreds micrometer and average molecular weight of 27.6 kDa were extracted and purified from coir pith in Mekong Delta, Vietnam according to a previously reported method [32]. PEO of 2000 kDa molecular weight was obtained from Dow Chemical, USA. NaOH was purchased from Merck and DI water was used.

B. Preparation of Lignin/PEO Solution

Briefly, mixed polymer (Lignin/PEO) accounted 10% (w/w) total polymer concentration in alkali solution. Lignin solution was created with Lignin/NaOH ratio is 1/0.3 (w/w) so that lignin can dissolve completely in solution. Lignin/PEO ratios were investigated at 100/0, 95/5, 90/10, 85/15, 80/20 and 70/30 (w/w). The solutions are stirred at room temperature until completely dissolved before filtration. Viscosity of solutions was measured using a Brookfield DV-II + Pro viscometer at room temperature before producing fibers by

electrospinning method. Scheme 1 showed lignin fibers producing process.

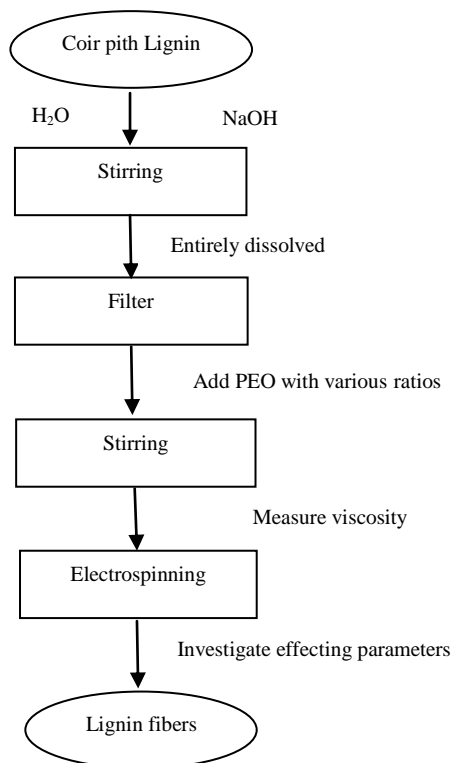
C. Electrospinning of PEO/Lignin Nanofibers

Three major components of electrospinning apparatus include a high voltage power supply using direct current (DC) and generated the voltage up to 12 kV, a syringe of 1 mL with 24 gauge metallic needle which used to control the flow rate, and a collector using a sheet of aluminum foil.

Lignin-PEO solutions were contained into a syringe for electrospinning at applied voltage of 12 kV. Flow rates of solutions and tip-to-collector distances were respectively carried out at 0.05 to 0.5 mL/h and 7 to 15 cm while the rest variables were held constant. Electrospun nanofibers were deposited on glass with a volume of 1x1 cm³ at room temperature.

D. Characterization of Electrospun Lignin/PEO Nanofibers

Surface morphology of Lignin/PEO was determined by using a scanning electron microscope (SEM) Hitachi-TM1000 Tabletop in uncoating goal condition.



Scheme 1. The preparation of Lignin/ PEO fibers from coir pith lignin particles.

III. RESULTS AND DISCUSSION

A. Effect of Lignin/PEO Ratio on Viscosity of Polymer Solution

Figure 1 showed that PEO played a critical role of improving the viscosity of lignin solution and viscosity values highly depended on the Lignin/PEO ratio. The intrinsic viscosity of neat lignin is 4 cP, the values of viscosity increased with the reducing lignin and increasing PEO contents in the order of 95/5, 90/10, 85/15, 80/20. The

viscosity value sharply increased to 1100 cP at Lignin/PEO ratio of 70/30. This phenomenon might be attributed to higher PEO content that made the solution become saturated, and the polymers were no longer free to move [30]. Moreover, site linkage were done by combination of lignin and PEO because both of them possessed lower viscosities individually [24, 26, 28, 30].

B. Effect of Lignin/PEO Ratio on Electrospinability

SEM analysis was conducted to identify the morphology of electrospun fibers with different Lignin/PEO ratios while other variables were kept unchanged as shown in Figure 2. Neat lignin (Lignin/PEO ratio of 100/0) with internal viscosity of 4 cP was unable to create electrospun nanofibers. The reasons could be that (i) the viscosity of the solution is lower than the minimum viscosity value of the method, (ii) the nature of the lignin structure is not capable of producing fibers [15, 26, 33]. At Lignin/PEO ratio of 95/5 with the viscosity of 38 cP unable to form fiber and almost entire beads were obtained (Figure 2a). Some likely causes for this were that (i) the viscosity value was lower than the minimum viscosity to form the yarn, (ii) the PEO content was insufficient to promote the effect of PEO [15, 27], (iii) the high lignin content in the solution resulted in the high inherent negative charges of solution. These negative charges neutralized amount of the positive charges applied by the high voltage power supplied and caused a strong reduction of system's net charge density [28, 30]. In this case, it is necessary to investigate to reduce lignin content and increase PEO content or the voltage power supplied.

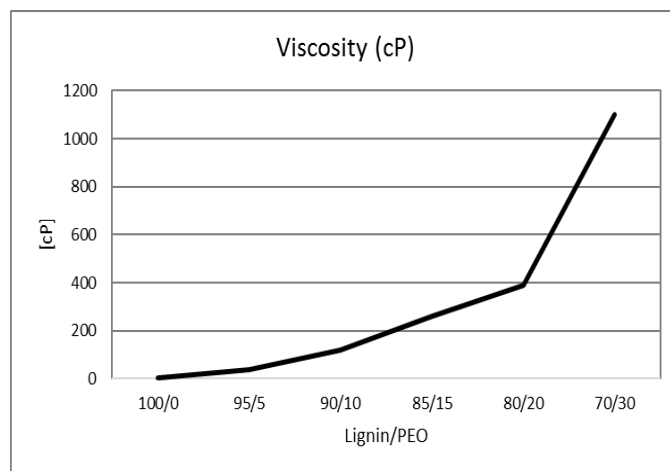


Fig. 1. Viscosity of polymer solution at different Lignin/PEO ratios.

At Lignin/PEO ratio of 90/10, the resulting fibers were a mixture of mat fibers on the collector and floating fibers between the collector and the needle, collected fibers were long with high incidences of beads (Figure 2b). This trend suggested that (i) the polymer solution with relatively high lignin content increases negative charges of the resulting fibers. When floating fibers are formed and drawn toward the positively charged needle, they must be negatively charged and have a net charge density large enough that the electrical attraction between the needle and floating fibers overcome the

gravitational forces on the fibers, (ii) PEO promoted the role but the Lignin/PEO mix ratio is not optimal [15, 26]. The minimum viscosity value of the polymer solution enabled to create fibers in this process was about 120 cps. The viscosity of the polymer solution was one of the main determinants that obviously enhance the performance and quality of nanofibers [21, 30, 34].

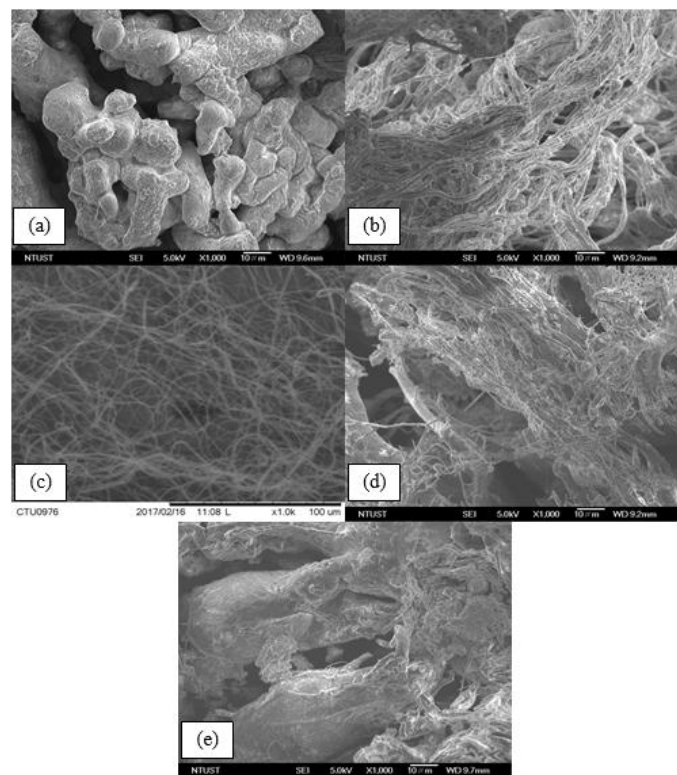


Fig. 2. SEM images of electrospun Lignin fibers with different Lignin/PEO ratios:
(a) 95/5; (b) 90/10; (c) 85/15; (d) 80/20; (e) 70/30

At Lignin/PEO ratio of 85/15, mat fibers obtained were almost on the receiver plate and were difficult to observe floating fiber between the collector and the needle. Figure 2c showed continuous and homogeneous fibers with non-bead, smooth and small diameter. This tendency enhanced the formation electrospun nanofibers (i) the PEO neutralized most of the negative charge of lignin, (ii) the viscosity value of the solution was suitable for the processing. In other words, the PEO illustrated excellent role in viscosity control, electrochemical balance, straightening direction at Lignin/PEO ratio of 85/15.

At Lignin/PEO ratios of 80/10 and 70/30, the fibers were obtained in the collector and no floating fibers were observed with the naked eye. With 70% lignin content, droplets of intermittent polymer solution were formed on the needle for a period of time before falling onto the collector and easily visible by naked eye. Figure 2 (d-e) indicated fibers with large diameter, discontinuous fracture and multiple fibers were adhered together. The amount of negative charges in the polymer solution sharply decreased when the PEO content increased. Moreover, the viscosity value of the polymer solution is not suitable for electrospun fiber processing. In this

case, it is possible to further investigate the optimal condition at higher source voltage. According to SEM analysis above, Lignin/PEO ratio of 85/15 was chosen for further experiments.

C. Effect of Flow Rate on Feasibility of Producing Fibers

SEM images of electrospun Lignin/PEO nanofibers with different flow rates were shown in Figure 3. Flow rates were examined from 0.05 mL/h to 0.5 mL/h whereas other parameters were kept constant. At a flow rate of 0.05 mL/h (Figure 3a), entire granular was formed (Figure 3a) due to (i) the discontinuous polymer stream, (ii) low negative charge density of polymer solution was neutralized by positive charges of the positive electrode of needle, which caused the polymer becoming less conductive [21, 30]. Continuous and uniform fibers were obtained at flow rate of 0.2 mL/h (Figure 3b). Combination of these parameters for the system was appropriate and flow rate plays a crucial role in forming and maintaining the Taylor cone stably.

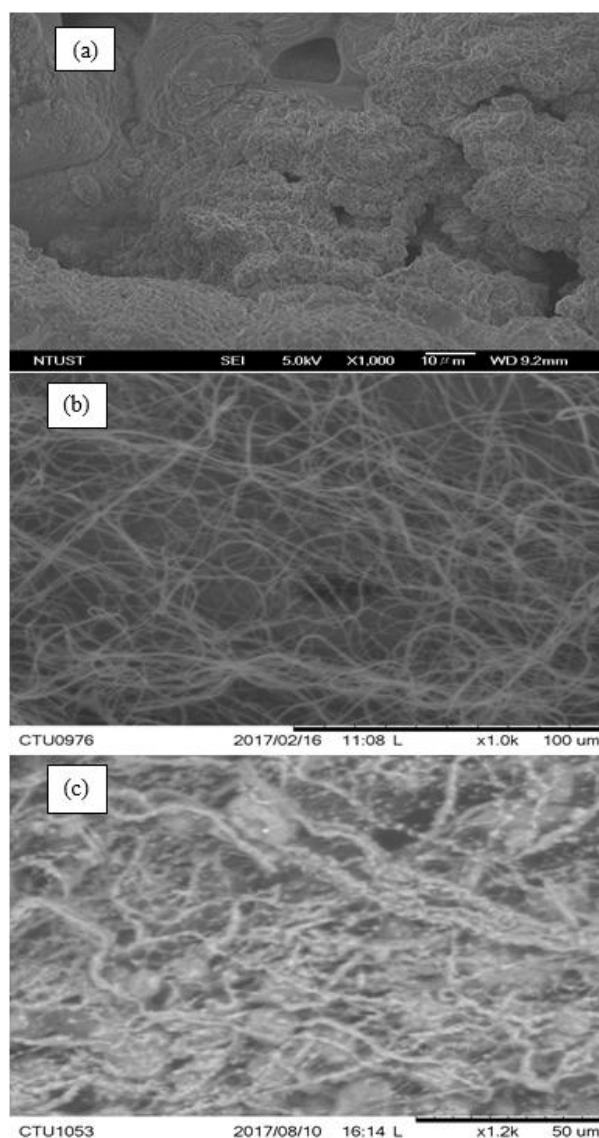


Fig. 3. SEM images of electrospun lignin fibers with different flow rate of the polymer solution.
(a): 0.05 mL/h; (b): 0.2 mL/h; (c): 0.5 mL/h

Figure 3c showed that at a flow rate of 0.5 mL/h, lignin fibers with larger diameter, appearance of beads on the fibers and multiple fibers were stuck together because (i) the diameter of electrospun fibers increase if flow rate increases while the Taylor cone is getting stable (ii) high viscosity of polymer led to initiate droplets onto the collector disk [22, 35]. In this system, the optimal flow rate of 0.2 mL/h was applied for next experiments.

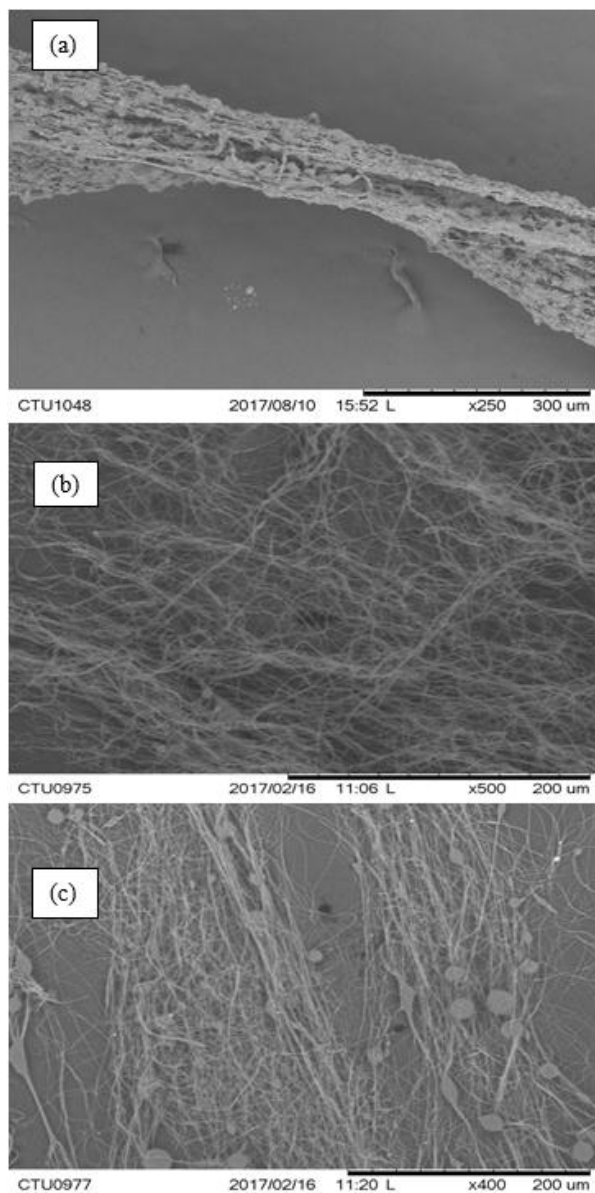


Fig. 4. SEM images of electrospun lignin fibers with different tip-to-collector distances.
(a): 7 cm; (b): 11 cm; (c): 15 cm

D. Effect of Tip-to-Collector Distance on Fiber Morphology

Figure 4a showed all obtained fibers were floating fibers and they tended to bundle together at distance of 7 cm (Figure 6). Visible floating fibers were attracted towards the electric needle and seemed to push each other. When the applied voltage stopped, all the floating fibers fell down on the collector disk. Continuous and homogeneous fibers were

collected at distance of 11 cm (Figure 4b), at distance of 15 cm the fibers were broken down and much larger in diameter. The reason could be that the dependence of the system's electric field strength and the distance between the two electrodes. The optimized distance of 0.2 mL/h was identified.

Figure 5 at magnification levels shows single fibers are continuous with smooth surface, ca. 400 nm in diameter. The results reflect the good compatibility between lignin and PEO as well as the suitability of electrospinning parameters.

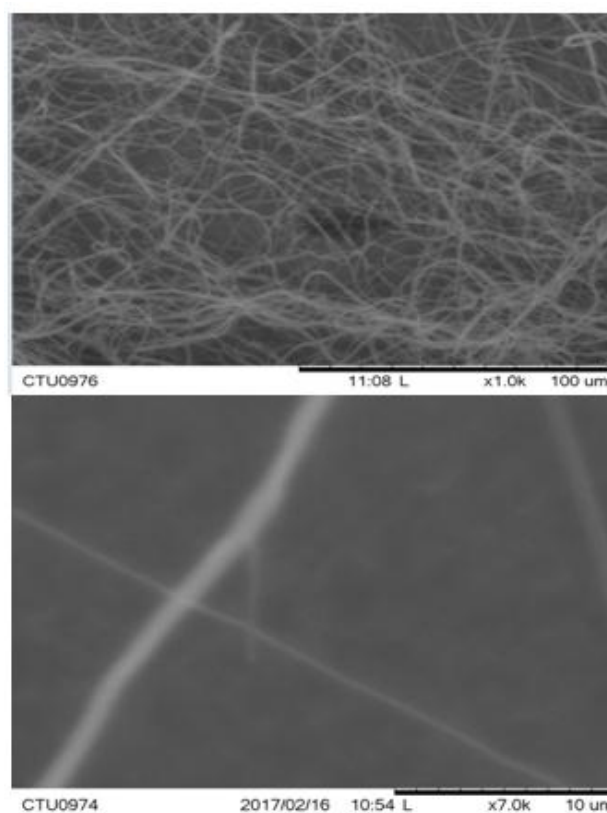


Fig. 5. SEM images of electrospun lignin fibers with different magnification levels.

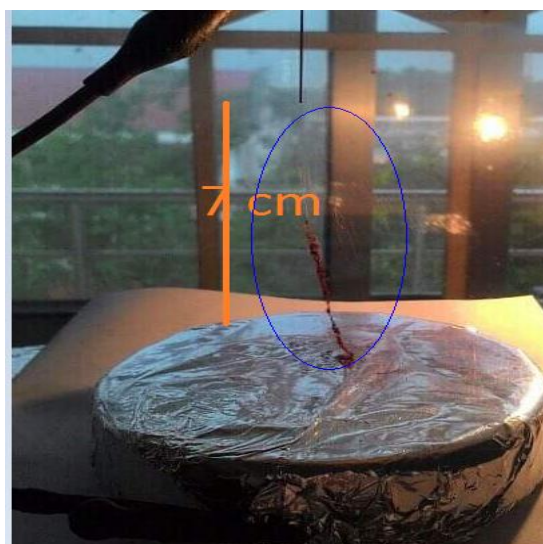


Fig. 6. Floating fibers.

IV. CONCLUSION

Lignin fibers were successfully fabricated by electrospinning process with Lignin-PEO precursor solution. PEO played a crucial role in facilitating electrospun lignin fibers due to its effects on the solution's viscosity, the electrospinning behavior and morphology of fiber. The single fibers were about 400 nm in diameter, continuous, smooth surface as that are synthesized at optimal conditions: Lignin/PEO ratio of 85/15, viscosity of 263 cP, flow rate of 0.2 mL/h and performing distance of 11 cm. Lignin fiber would be a potential material in drug delivery applications.

REFERENCES

- [1] W. O. S. Doherty, M. Payam, and M. F. Christopher, "Value-adding to cellulose ethanol: Lignin polymers," *Industrial Crops and Products*, vol. 33, issue 2, pp. 259-276, 2011.
- [2] S. Laurichesse and A. Luc, "Chemical modification of lignins: Towards biobased polymers," *Progress in Polymer Science*, vol. 39, issue 7, pp. 1266-1290, 2014.
- [3] E. Ten, and W. Vermerris, "Recent developments in polymers derived from industrial lignin," *Journal of Applied Polymer Science*, vol. 132, issue 24, 2015.
- [4] U. S. Sarma, and A. Das Rabindranath, "Extraction of Lignosulphonates from Coir Pith- An Agrowaste, Central Coir Research Institute (Coir Board), Kalavoor, Alleppey, Kerala, 1952.
- [5] D. M. Watkins, A. T. Hosur, and J. Shaik, "Extraction and characterization of lignin from different biomass resources," *Journal of Materials Research and Technology*, vol. 4, issue 1, pp. 26-32, 2015.
- [6] D. Stewart, "Lignin as a base material for materials applications: Chemistry, application and economics," *Industrial Crops and Products*, vol. 27, issue 2, pp. 202-207, 2008.
- [7] A. Tejado, C. Pena, J. Labidi, J. M. Echeverria, and I. Mondragon, "Physico-chemical characterization of lignins from different sources for use in phenol-formaldehyde resin synthesis," *Bioresource Technology*, vol. 98, issue 8, pp. 1655-1663, 2007.
- [8] M. N. M. Ibrahim, N. Zakaria, C. S. Sipaut, O. Sulaiman, and R. Hashim, "Chemical and thermal properties of lignins from oil palm biomass as a substitute for phenol in a phenol formaldehyde resin production," *Carbohydrate Polymers*, vol. 86, issue 1, pp. 112-119, 2011.
- [9] B. A. Simmons, D. Loqué, and J. Ralph, "Advances in modifying lignin for enhanced biofuel production," *Current Opinion in Plant Biology*, vol. 13, issue 3, pp. 312-319, 2010.
- [10] D. Kai, K. Zhang, L. Jiang, H. Z. Wong, Z. Li, Z. Zhang, and X. J. Loh, "Sustainable and antioxidant lignin-polyester copolymers and nanofibers for potential healthcare applications," *ACS Sustainable Chemistry and Engineering*, vol. 5, issue 7, pp. 6016-6025, 2017.
- [11] M. P. Vinardell, V. Ugartondo, and M. Mitjans, "Potential applications of antioxidant lignins from different sources," *Industrial Crops and Products*, vol. 27, issue 2, pp. 220-223, 2008.
- [12] K. Akato, C. D. Tran, J. Chen, and A. K. Naskar, "Poly (ethylene oxide)-assisted macromolecular self-Assembly of lignin in ABS matrix for sustainable composite applications," *ACS Sustainable Chemistry and Engineering*, vol. 3, issue 12, pp. 3070-3076, 2015.
- [13] T. Dizhbite, G. Zakis, A. Kizima, E. Lazareva, G. Rossinskaya, V. Jurkane, and U. Viesturs, "Lignin—a useful bioresource for the production of sorption-active materials," *Bioresource Technology*, vol. 67, issue 3, pp. 221-228, 1999.
- [14] H. Vázquez-Torres, G. Canché-Escamilla, and C. A. Cruz-Ramos, "Coconut husk lignin. I. Extraction and characterization," *Journal of Applied Polymer Science*, vol. 45, issue 4, pp. 633-644, 1992.
- [15] D. A. Baker and G. R. Timothy, "Review Recent advances in low-cost carbon fiber manufacture from lignin," *Journal of Applied Polymer Science*, vol. 130, issue 2, pp. 713-728, 2013.
- [16] C. W. Dence, The determination of lignin, *Methods in Lignin Chemistry*, Springer Berlin Heidelberg, pp. 33-61, 1992.
- [17] M. Norgren and H. Edlund, "Lignin: recent advances and emerging applications," *Current Opinion in Colloid and Interface Science*, vol. 19, issue 5, pp. 409-416, 2014.
- [18] X. Ma, H. Elbohy, S. Sigdel, C. Lai, Q. Qiao, and H. Fong, "Electrospun carbon nano-felt derived from alkali lignin for cost-effective counter electrodes of dye-sensitized solar cells," *RSC Advances*, vol. 6, issue 14, pp. 11481-11487, 2016.
- [19] M. P. Vinardell, and M. Mitjans, "Lignins and their derivatives with beneficial effects on human health," *International Journal of Molecular Sciences*, vol. 18, issue 6, 1219, 2017.
- [20] A. Mataram, A. F. Ismail, M. S. Abdullah, B. C. Ng, and T. Matsuura, "A review of assembled polyacrylonitrile-based carbon nanofiber prepared electrospinning process," *International Journal of Nanoscience*, vol. 10, issue 3, pp. 455-469, 2011.
- [21] J. D. Schiffman, and C. L. Schauer, "A review: Electrospinning of biopolymer nanofibers and their applications," *Polymer Reviews*, vol. 48, issue 2, pp. 317-352, 2008.
- [22] M. Hasanzadeh, V. Mottaghtalab, R. Ansari, B. H. Moghadam, and A. K. Ghagi, "Issues in production of carbon nanotubes and related nanocomposites: A comprehensive review," *Cellulose Chemistry and Technology*, vol. 49, issue 3-4, pp. 237-257, 2015.
- [23] M. A. Salami, F. Kaveian, M. Rafienia, S. Saber-Samandari, A. Khandan, and M. Naeimi, "Electrospun polycaprolactone/lignin-based nanocomposite as a novel tissue scaffold for biomedical applications," *Journal of Medical Signals and Sensors*, vol. 7, issue 4, 228-238, 2017.
- [24] S. Hu, S. Zhang, N. Pan, and Y. L. Hsieh, "High energy density supercapacitors from lignin derived submicron activated carbon fibers in aqueous electrolytes," *Journal of Power Sources*, vol. 270, pp. 106-112, 2014.
- [25] J. F. Kadla, S. Kubo, R. D. Gilbert, and R. A. Venditti, "Lignin-based carbon fibers," *Chemical Modification, Properties, and Usage of Lignin*, pp. 121-138, 2002.
- [26] J. F. Kadla, and S. Kubo, "Lignin-based polymer blends: analysis of intermolecular interactions in lignin-synthetic polymer blends," *Composites Part A: Applied Science and Manufacturing*, vol. 35, issue 3, pp. 395-400, 2004.
- [27] S. Kubo and J. F. Kadla, "Lignin-based carbon fibers: Effect of synthetic polymer blending on fiber properties," *Journal of Polymers and the Environment*, vol. 13, issue 2, pp. 97-105, 2005.
- [28] A. E. Imel, K. N. Amit, and D. D. Mark "Understanding the Impact of Poly (ethylene oxide) on the Assembly of Lignin in Solution toward Improved Carbon Fiber Production," *ACS Applied Materials and Interfaces*, vol. 8, issue 5, pp. 3200-3207, 2016.
- [29] C. D. Saquing, C. Tang, B. Monian, C. A. Bonino, J. L. Manasco, E. Alsberg, and S. A. Khan, "Alginate-polyethylene oxide blend nanofibers and the role of the carrier polymer in electrospinning," *Industrial and Engineering Chemistry Research*, vol. 52, issue 26, pp. 8692-8704, 2013.
- [30] M. Schreiber, S. Vivekanandhan, A. K. Mohanty, and M. Misra, "A study on the electrospinning behaviour and nanofiber morphology of anionically charged lignin," *Adv. Mater. Lett.*, vol. 3, issue 6, pp. 476-480, 2012.
- [31] R. Ding, H. Wu, M. Thunga, N. Bowler, and M. R. Kessler, "Processing and characterization of low-cost electrospun carbon fibers from organosolv lignin/polyacrylonitrile blends," *Carbon*, vol. 100, pp. 126-136, 2016.
- [32] Luong Huynh Vu Thanh, Nguyen Thi Nhu Y, Truong Huu Thong, Nguyen Thi Ven Nguyen Huu Thanh. Lignin derived from coir pith: Extraction process and characterization," *Vietnam Journal of Chemistry*, 55(5E3,4), pp. 531-536, 2017.
- [33] A. Awal, and M. Sain, "Characterization of soda hardwood lignin and the formation of lignin fibers by melt spinning," *Journal of Applied Polymer Science*, vol. 129, issue 5, pp. 2765-2771, 2013.
- [34] S. Beisl, A. Miltner, and A. Friedl, "Lignin from micro-to nanosize: Production methods," *International Journal of Molecular Sciences*, vol. 18, issue 6, 1244, 2017.
- [35] Doan Van Hong Thien, Ha Thanh Toan, Tran Thi Bich Quyen, Dang Huynh giao, "Preparation of Chitosan/PEO nanofibers by an electrospinning method," *Vietnam Journal of Chemistry*, 55(5E3,4), pp. 562-567, 2017.