ELECTRICAL RESISTIVITY AND CHARACTERIZATION OF INDIUM DOPED ZINC OXIDE COATED KENAF FIBER

N.A. Sani[1], M.E.A. Manaf[1], Q. Ahsan[1], E. Osman[1] and V.A. Doan[2]

[1]Faculty of Manufacturing Engineering,
Universiti Teknikal Malaysia Melaka, Hang Tuah Jaya,
76100 Durian Tunggal, Melaka, Malaysia.

[2]Faculty of Materials Science, Phenikaa University,
Yen Nghia Ward, Ha Dong District,
Hanoi, Vietnam.

Corresponding Author's Email: [1]edee@utem.edu.my

Article History: Received 31 October 2019; Revised 22 December 2019; Accepted 18 March 2020

ABSTRACT: Research on conductive coating on natural or plant fibers has gained attention due to arising drive for green technology in electronic and electrical industry. This study aims to investigate the effects of alkaline treatment (2%, 4%, 6% and 8%) and indium doping concentration (In/Zn: 5%, 7%, 9% and 11%) on the surface resistivity and characteristics of indium doped zinc oxide (IZO) coated kenaf fiber. The process starts with chemical treatment of kenaf fiber by sodium hydroxide (NaOH). Then, the treated fibers are immersed in indium doped zinc oxide sol gel and annealed in a furnace. The final samples are characterized using FTIR and SEM-EDX, while the surface resistivity is measured by using Monroe portable resistivity meter. The results show that the alkaline treatment promotes good interfacial bonding between kenaf and IZO coating as demonstrated by smooth coating and low surface resistivity with the best result was obtained using 8% of NaOH concentration. This finding can be attributed mainly to the elimination of impurities, wax, lignin and hemicellulose, of which could act as interface barrier. The doping of indium on ZnO contributes to a significant decrease of surface resistivity of IZO coated kenaf. The resistivity is decreased to the lowest at 9% of indium doping but increases at further addition which is probably due to doping solubility limit.

KEYWORDS: *Indium-Doped Zinc Oxide; Kenaf Fiber; Sol Gel Coating*

1.0 INTRODUCTION

Zinc oxide (ZnO) is commonly used as transparent conducting oxide thin film for solar cell and other applications. Apart of having great optical properties, ZnO also has promising electrical properties which make it a potential candidate for conductive coating on natural fiber. In addition, ZnO has low processing temperature that makes it suitable as substrate for materials with low degradation temperature such as natural fiber [1].

Various studies have been carried out to produce a conductive material made of zinc oxide film on natural fibers [2-4]. However, zinc oxide usually has higher electrical resistivity and unstable without doping material. Hence, additional doping with metal elements of Group III such as gallium (Ga), aluminium (Al) and indium (In) is necessary to increase the film conductivity and functionality of the coated materials [5]. There are also several methods to impregnate the conductive zinc oxide on natural fiber and among those methods, solution dip method is the most economic yet productive either for small or large scale production [6].

Common issue with the natural fiber is the incompatibility with non-polar substrate. It is known to have high moisture content and hydrophilic with strong polarity of hydroxyl groups. In other words, it has tendency to form cohesive bonding with water molecules which causes interfacial barrier to hydrophobic substrate that leads to poor adhesion [7]. Due to that, various additional surface modification have been applied to improve the interfacial adhesion such as silane treatment, alkaline treatment and acetylation [8-9]. Alkaline treatment is one of the methods of surface modification that reduces the hydrophilicity of natural fiber by promoting ionization of hydroxyl group to alkoxide [10]. It also has been used widely on natural fiber to eliminate impurities, amorphous lignin and hemicellulose content that mostly contribute to incompatibility between natural fiber and coating material. Alkaline treatment is claimed to increase the fiber surface area, thus contributes to larger contact area and more reaction sites between fiber and coating material.

Although various studies have been carried out on conductive film, limited studies have been performed on transparent coating oxide (TCO) coated on kenaf fiber at low temperature. Previous study on this subject only focused on parameters such as annealing temperature and annealing time [11]. However, there has been no reported study discussing on the effects of indium doping and kenaf fiber surface treatment on indium zinc oxide coating properties. Thus, this paper attempts to analyze the properties of indium doped zinc oxide coated on kenaf fiber in order to create conductive kenaf fiber as potential filler. In particular, this study focuses on the effects of alkaline treatment and indium doping concentration as the varying parameters.

2.0 METHODOLOGY

2.1 Materials

Untreated kenaf non-woven mats were supplied from a local supplier, Innovative Pultrusion Sdn Bhd. The chemicals including sodium hydroxide (NaOH) pallet, zinc acetate dihydrate, indium chloride and ethanol were purchased from Polyscientific Sdn Bhd.

2.2 Alkaline Treatment of Kenaf

Kenaf non-woven mat was cut into smaller pieces of about 10 x 10 cm and then soaked in sodium hydroxide solution of different concentrations (2%, 4%, 6% and 8%) for 3 hours. Then, the fibers were removed and washed with water for several times until neutral and followed by rinsing with distilled water. Lastly, the fibers were dried at temperature of 70 °C for 24 h and ready to be coated.

2.3 Fabrication of IZO Coated Kenaf

Initially, coating solution of indium zinc oxide (IZO) was prepared by dissolving 0.1 M zinc acetate dihydrate in absolute ethanol. Then the solution was stirred at room temperature for 1 hour. Subsequently, indium chloride was added into the solution and stirred for another 2 hours at 75 °C. In order to study the doping percentage effect on surface resistivity, the concentration of indium chloride was varied at In/Zn 5%, 7%, 9% and 11% of zinc acetate dihydrate amount. While the solution was being stirred, deionized water was added into the solution until clear solution was obtained. Then, the solution was left for 24 hours for aging. As for the coating process, kenaf fibers were immersed in the prepared IZO solution in sonication bath for 10 minutes. Lastly, the fibers were dried in an oven at 70 °C for 1 hour before annealed at 150 °C for another 4 hours.

2.4 Characterization of IZO Coated Kenaf

The surface resistivity (Ω/sq) was measured by using Monroe portable resistivity meter. The voltage was set to 100 V and reading of each sample was recorded after 60 seconds once the probe placed onto the kenaf mat. The morphology of IZO coated kenaf fiber with and without treatment were observed by using scanning electron microscopy (SEM). Energy Dispersive X-Ray (EDX) analysis was performed to identify the elemental composition of the coated kenaf fibers. Fourier transform infrared (FTIR) spectroscopy (Jasco FTIR-6100) was applied to the IZO coated kenaf. The samples were analysed for the wave number range of 400-4000 cm^{-1}. The samples of untreated kenaf, NaOH treated kenaf, IZO coated untreated kenaf and IZO coated treated kenaf were analyzed to verify the IZO coating on both treated and untreated kenaf.

3.0 RESULTS AND DISCUSSION

3.1 Scanning Electron Microscope-Energy Dispersive X-Ray Spectroscopy (SEM-EDX)

The main purpose of surface treatment of kenaf is to enhance the interaction between coating material and kenaf surface. Thus, morphological characteristics were studied by using SEM and the results are shown in Figure 1. SEM images of neat kenaf and treated kenaf as shown in Figure 1(a) and (b) reveal the changes on the kenaf surface before and after alkaline treatment as the result of lignin and hemicellulose removal. The treatment does not only remove impurities from the surface but also makes it rougher. The rough surface of treated kenaf provides more reaction sites between fiber and coating material [12]. In Figure 1(c), IZO coating on the untreated kenaf appears rough and irregular which believed due to poor interfacial bonding between the inorganic and organic surface. As highlighted in a previous study [13], the content of wax and lignin in natural fiber hinders the interaction between the surfaces. Meanwhile, the resulted IZO coating on treated kenaf in Figure 1(d) shows a smoother appearance with some areas showing visible 2D nanosheet shape of zinc oxide structure [14] which proves the existence of ZnO coating. The results indicate that alkaline treatment of the kenaf fiber is effective in preparing the fiber surface as substrate for better IZO coating property.

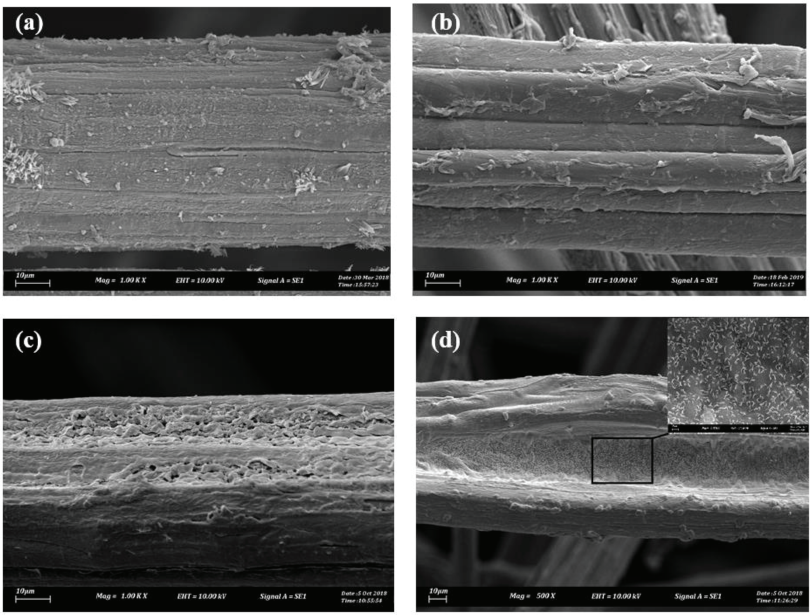


Figure 1: SEM images of (a) neat kenaf, (b) NaOH treated kenaf, (c) IZO coated untreated kenaf and (d) IZO coated NaOH treated kenaf

Figure 2 shows the EDX analysis for IZO coated kenaf fiber at its surface and cross-sectional areas. Each element is color-coded as to identify the presence of different elements. The main elements supposedly presence in this study such as C, O, Zn and In are represented by red, green, blue and grey color, respectively. All the mentioned elements are presented in the figures indicating that kenaf surface is successfully covered by the coating materials and proves the presence of conductive element of zinc and indium on the kenaf substrate. However, the surface area (Figure 2(a)) obviously shows much higher concentration of coating elements as compared to the cross section (Figure 2(b)), as the surface is directly in contact with the IZO solution. The use of sonication during the dip coating helps in distributing the element all over the surface and at the same time into the cross section of kenaf. Hence, the coating element loading on kenaf is optimized.

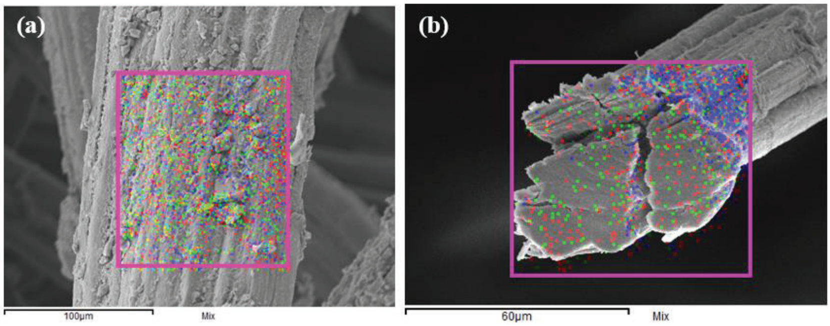
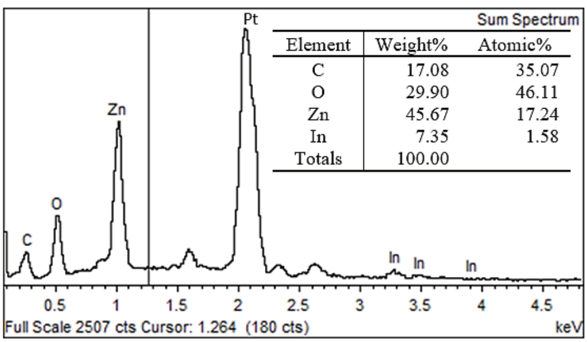


Figure 2: SEM-EDX analysis of IZO coated kenaf fiber on (a) surface and (b) cross section of fiber



Element	Weight%	Atomic%
C	17.08	35.07
O	29.90	46.11
Zn	45.67	17.24
In	7.35	1.58
Totals	100.00	

Figure 3: EDX spectrum of IZO coated kenaf fiber with percentage of each element for 5 at% of indium doping

The EDX spectrum of the IZO coated kenaf fiber is shown in Figure 3, with the inserted table showing the weight and atomic percentages of the elements. Apart from a prominent Pt peak, which is due to platinum thin coating applied prior to EDX measurement, the presence of other elements such as Zn, C, O and Pt are clearly observed. The C and O are attributed to the organic elements composing the kenaf fiber, while the Zn and In are the elements constituting the IZO coating material. The indium element appears relatively small in the EDX spectrum due to its minimal amount of about at 9%. The relatively small atomic percentage of Zn and In as compared to C and O elements, reflects the thin structure of the coating in comparison to the kenaf fiber.

3.2 Fourier Transform Infrared (FTIR) Spectroscopy

The FTIR spectra of untreated kenaf, NaOH treated kenaf, IZO coated untreated kenaf and IZO coated treated kenaf are presented in Figure

4. For the FTIR analysis, the alkaline treatment used was 6% NaOH, while indium chloride concentration was 5%. Generally, all the samples clearly illustrate the same peaks at 3400-3500 cm^{-1} and 2800-3000 cm^{-1}, which represent the presence of -OH groups and C-H stretching vibration of methyl group in cellulose, respectively [15]. Meanwhile, there are presence of peaks at 1029 cm^{-1}, 1237 cm^{-1} and 1712 cm^{-1} denotes the C–O stretching of the aryl group in the lignin and C=O stretching of aldehydic group in lignin and acetyl group in hemicellulose [16]. As for the IZO coated kenaf, the FTIR patterns confirm the presence of Zn-O at peak 410-415 cm^{-1} for both untreated and treated kenaf [17].

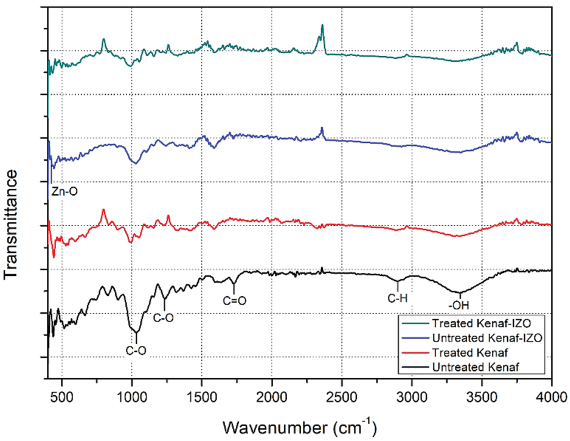


Figure 4: FTIR spectroscopy patterns of untreated kenaf, treated kenaf, untreated kenaf-IZO and treated kenaf-IZO samples

There are significant changes in FT-IR absorption bands patterns recorded, which confirm the occurrence of chemical interaction upon alkaline treatment and indium chloride doping. The reduction of intensity of –OH and C-H stretching vibration at 3400-3500 cm^{-1} and 2800-3000 cm^{-1}, respectively, is mainly due to dissolution of hydrogen bonding in cellulose after alkaline treatment. The decrease of intensity at 1029 cm^{-1}, 1237 cm^{-1} and 1712 cm^{-1} proves the significant removal of hemicellulose and lignin content in kenaf fiber. As shown in Figure 5, the IZO coating on the treated kenaf shows a broader peak compared to that on untreated kenaf indicating the presence of more zinc oxide on the kenaf surfaces. The peak becomes more apparent for treated kenaf indicating increased surfaces activation due to alkaline treatment that allows more significant zinc oxide to be located on kenaf surfaces.

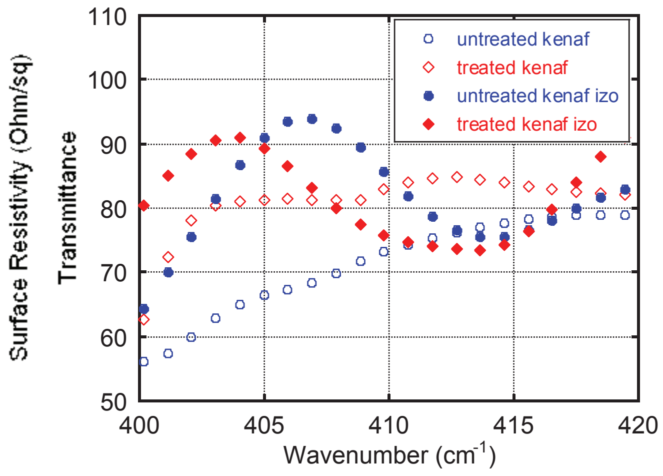


Figure 5: A close-up FTIR spectra showing the peak associated to Zn-O at 410-415 cm^{-1}

3.3 Surface Resistivity of Kenaf Fiber

The surface resistivity of IZO coated kenaf fiber was analyzed by placing Monroe portable resistivity meter probe onto the kenaf fiber mat. The uncoated kenaf shows a higher surface resistivity than IZO coated kenaf at 5.6×10^{11} Ω/sq and 1.2×10^{10} Ω/sq, respectively. Surface resistivity significantly decreases upon IZO coating onto kenaf fiber, which emphasizes the effect of IZO coating as the conductive element to the kenaf. It shows the improvement of conductivity in IZO coated kenaf compared to uncoated kenaf fiber.

Figure 6(a) and (b) illustrate the result of surface resistivity of IZO coated kenaf at different NaOH and indium doping concentration, respectively. It is shown that alkaline treatment is effective in reducing surface resistivity from 1.2×10^{10} Ω/sq to 4.6×10^{9} Ω/sq, as much as 64.2% decrease after 2% NaOH treatment. The resistivity continues to decrease as the NaOH is further increased. At 8% NaOH, the result gives the lowest surface resistivity of 1.7×10^{9} Ω/sq with 83.3% of decrease in resistivity. The results indicate that alkaline treatment gives a significant influence on quality of coating itself as demonstrated by the resistivity values as shown in Figure 6(a). The main purpose of alkaline treatment is to eliminate or reduce of wax, lignin and hemicellulose on kenaf fiber by alkaline promotes larger contact area and reactions sites between fiber and coating material. The reduction of polarity of -OH hydroxyl group in cellulose will increase the interaction between kenaf fiber and the non-polar hydrophobic ZnO coating. This outcome is in agreement with the result obtained in the morphological study, which confirms the uniformity of coating on the treated surface of kenaf compared to untreated kenaf.

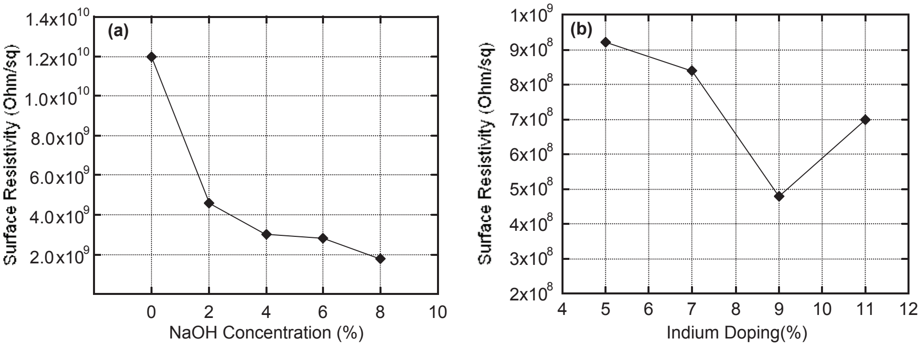


Figure 6: Effects of (a) NaOH concentration and (b) Indium doping on surface resistivity of IZO coated kenaf

Meanwhile, the result of surface resistivity obtained with different percentage of doping is demonstrated in Figure 6(b). It reveals a decrease of resistivity with increased In-doping. Similar behavior has been reported previously [18] which proves the lower resistivity of In-doped ZnO as compared to intrinsic ZnO thin film. This phenomenon suggests the effectiveness of indium doping in creating additional single free electron as donor resulting from In^{3+} ion substitution at Zn^{2+} site [19]. Thus, as the doping concentration increases, concentration of free electrons is increased. These free electrons function as charge carrier which contributes to the decreased resistivity (increase conductivity). From the graph, the lowest resistivity of 5.1×10^8 Ω/sq is obtained at 9% of indium doping. It can be said that around this figure, the amount of electron substitution between In^{3+} and Zn^{2+} is at the optimum since above this doping percentage, the resistivity begins to rise again. As it reaches the solubility limit of In doping into ZnO lattice, further additional doping will not give the intentional effect. These excess In doping will cause segregation of the insoluble In atoms along grain boundaries and hinder the charge mobility thus increases the resistivity [20].

4.0 CONCLUSION

In this study, indium doped zinc oxide coated kenaf fiber has been successfully fabricated using simple and economical sol gel dip coating method. The alkaline treatment on kenaf fiber gives positive effect on the interaction between coating material and substrate, which leads to the reduced surface resistivity. As the alkaline concentration increases, more impurities, amorphous lignin and hemicellulose content, hence, greater bonding between IZO coating and kenaf fiber is obtained. This finding is in agreement with the FTIR results, which indicate the disappearance of peaks associated with lignin and hemicellulose functional group. Moreover, the effect of alkaline treatment on coating property is supported by the SEM micrograph, which suggesting its significant influence on surface resistivity. On the other hand, increase in the concentration of indium doping effectively reduces the surface resistivity of IZO coated kenaf. However, the effect reaches its optimum value around 9% In, due to the solubility limit of indium in ZnO lattice.

ACKNOWLEDGMENTS

The authors would like to thank Universiti Teknikal Malaysia Melaka (UTeM) for supporting this research under PJP Grant Scheme: PJP/2019/FKP(1A)/S01652. Advanced Manufacturing Centre and Faculty of Manufacturing Engineering, UTeM are acknowledged for providing the equipment and technical supports.

REFERENCES

[1] S.E. Yamny and M.A. Rafea, "Preparation and characterization of ZnO: In transparent conductor by low cost dip coating technique", *Journal of Modern Physics*, vol. 3, no. 9, pp. 1060–1069, 2012.

[2] P. Lekpittaya, N. Yanumet, B.P. Grady and E.A. O'Rear, "Resistivity of conductive polymer-coated fabric", *Journal of Applied Polymer Science*, vol. 92, no. 4, pp. 2629–2636, 2004.

[3] S. Vihodceva and S. Kukle, "Cotton textile surface investigation before and after deposition of the ZnO coating by sol-gel method", *Journal of Nano- and Electronic Physics*, vol. 5, no. 1, pp. 1–5, 2013.

[4] E. Osman, T. Moriga, K. Murai and A.R.M. Warikh, "Study of morphology and electrical properties of indium zinc oxide-modified kenaf fiber", *Industrial Crops and Products*, vol. 100, pp. 171–175, 2017.

[5] R. Bel-Hadj-Tahar and A.B. Mohamed, "Sol-gel processed indium-doped zinc oxide thin films and their electrical and optical properties", *New Journal of Glass and Ceramics*, vol. 4, no. 4, pp. 55–65, 2014.

[6] R. Baranyai, Á. Detrich, E. Volentiru and Z. Hórvölgyi, "Peparation and characterization of ZnO and TiO_2 sol-gel thin films deposited by dip coating", *Hungarian Journal of Industrial Chemistry*, vol. 37, no. 2, pp. 131–137, 2009.

[7] E.B.C. Santos, C.G. Moreno, J.J.P. Barros, D.A.D. Moura, F.D.C. Fim, A. Ries, R.M.R. Wellen and L.B.D Silva, "Effect of alkaline and hot water treatments on the structure and morphology of piassava fibers", *Materials Research*, vol. 21, no. 2, pp. 1–11, 2018.

[8] Y. Liu, X. Lv, J. Bao, J. Xie, X. Tang, J. Che, Y. Ma and J. Tong, "Characterization of silane treated and untreated natural cellulosic fibre from corn stalk waste as potential reinforcement in polymer composites", *Carbohydrate Polymers*, vol. 218, pp. 179–187, 2019.

[9] M.N. Akhtar, A.B. Sulong, M.F. Radzi, N.F. Ismail, M.R. Raza, N. Muhamad and M.A. Khan, "Influence of alkaline treatment and fiber loading on the physical and mechanical properties of kenaf/polypropylene composites for variety of applications", *Progress in Natural Science: Materials International*, vol. 26, no. 6, pp. 657–664, 2016.

[10] D. Ariawan, Z.A.M. Ishak, M.S. Salim, R. M. Taib and M.Z. Ahmad Thirmizir, "Wettability and interfacial characterization of alkaline treated kenaf fiber-unsaturated polyester composites fabricated by resin transfer molding", *Polymer Composites*, vol. 38, no. 3, pp. 507–515, 2017.

[11] O. Edynoor, A.R.M. Warikh, T. Moriga, K. Murai, E. Mohammad and M.R. Salleh, "Effect of annealing time on resistivity of kenaf fiber modified indium zinc oxide prepared via dip coating process", *Journal of Advanced Manufacturing Technology*, vol. 11, no. 1, pp. 139–150, 2017.

[12] H.M. Akil, M.F. Omar, A.A.M. Mazuki, S. Safiee, Z.A.M. Ishak and A.A. Bakar, "Kenaf fiber reinforced composites: A review", *Materials and Design*, vol. 32, no. 8–9, pp. 4107–4121, 2011.

[13] Y.A.E. Shekeil, S.M. Sapuan, A. Khalina, E.S. Zainudin and O.M. Al-Shuja'a, "Effect of alkali treatment on mechanical and thermal properties of kenaf fiber-reinforced thermoplastic polyurethane composite", *Journal of Thermal Analysis and Calorimetry*, vol. 109, no. 3, pp. 1435–1443, 2012.

[14] D. Ju, H. Xu, J. Zhang, J. Guo and B. Cao, "Direct hydrothermal growth of ZnO nanosheets on electrode for ethanol sensing", *Sensors and Actuators, B: Chemical*, vol. 201, pp. 444–451, 2014.

[15] H. Sosiati, A. Nahyudin, D. A. Wijayanti and K. Triyana, "Effect of alkali treatment and MAPP addition on tensile strength of sisal/polypropylene composites", *Journal of Advanced Manufacturing Technology*, vol. 12, no. 2, pp. 65–78, 2018.

[16] N.A. Ibrahim, K. A. Hadithon and K. Abdan, "Effect of fiber treatment on mechanical properties of kenaf fiber-ecoflex composites", *Journal of Reinforced Plastics and Composites*, vol. 29, no. 14, pp. 2192–2198, 2010.

[17] S. Ebrahimiasl, A. Zakaria, A. Kassim and S.N. Basri, "Novel conductive polypyrrole/zinc oxide/chitosan bionanocomposite: synthesis, characterization, antioxidant, and antibacterial activities", *International Journal of Nanomedicine*, vol. 10, no. 1, pp. 217–227, 2014.

[18] S. Edinger, N. Bansal, M. Bauch, R.A. Wibowo, G. Ujvari, R. Hamid, G. Trimmel and T. Dimopoulos, "Highly transparent and conductive indium-doped zinc oxide films deposited at low substrate temperature by spray pyrolysis from water-based solutions", *Journal of Materials Science*, vol. 52, no. 14, pp. 8591–8602, 2017.

[19] N.A. Dahoudi, A. Alkahlout, S. Heusing, P.H. Engel, R. Karos and P. Oliveira, "Indium doped zinc oxide nanopowders for transparent conducting coatings on glass substrates", *Journal of Sol-Gel Science and Technology*, vol. 67, no. 3, pp. 556–564, 2013.

[20] S.S. Shinde, P.S. Shinde, C.H. Bhosale and K.Y. Rajpure, "Optoelectronic properties of sprayed transparent and conducting indium doped zinc oxide thin films", *Journal of Physics D: Applied Physics*, vol. 41, no. 10, pp. 1-6, 2008.