DEVELOPMENT OF CROSS-LINKED POLYVINYL ALCOHOL-TITANIUM DIOXIDE (PVA/TIO_2) FILM FOR ANTIBACTERIAL COATING ON STEEL

Nurul Fatiha Mohd Padzli, Najihatul Fatihah Ahmad, Zuhailawati Hussain*, Anasyida Abu Seman, Mohamad Danial Shafiq and Pung Swee Yong

School of Materials and Mineral Resources Engineering, Universiti Sains Malaysia 14300, Nibong Tebal, Penang, Malaysia.

*zuhaila@usm.my

Abstract. Development of cross-linked film coating on steel surface was made through the embedment of titanium dioxide (TiO_2) nanoparticles in poly-vinyl alcohol (PVA) matrix. The film was prepared by mixing TiO_2 powder (3 wt%) into PVA solution. Glutaraldehyde (GA) was then added as the crosslinking agent in order to improve physical properties of the film. The resulting coating film was obtained after dried on steel plate in room temperature for 48 hours. PVA/TiO_2 coatings were characterized using X-ray diffractometer (XRD), field emission scanning electron microscopy (FESEM) and contact angle goniometer. TiO_2 anatase-structured presence on PVA was confirmed using Brucker Advanced X-ray Solution D8 Diffractometer (XRD). ZEISS SUPRA 55VP FESEM-EDX analysis conducted showed homogenous and uniform dispersion of TiO_2 on the film after crosslinking. The cross-linked sample demonstrated higher contact angle at 71.74^o indicating the reduction of coating hydrophilicity. In brief, the improved water stability of GA cross-linked PVA film with uniformly distributed TiO_2 nanoparticles as the active material for anti-bacterial agent on the PVA matrix was successfully done. The cross-linked PVA/TiO_2 coating may potentially be used for steel surfaces on public facilities such door-knobs, train handlebars, stairs handrail and lift buttons to reduce the transmission infection and improving the communal hygiene.

Keywords: Anti-bacterial coating, steel coating, poly-vinyl alcohol, titanium dioxide, glutaraldehyde

Article Info

Received 29th March 2022
Accepted 23rd June 2022
Published 23rd December 2022

ISSN: 1823-7010, eISSN: 2600-7444

Introduction

Bacterial colonization on surfaces has become an engaging post-pandemic issue since direct or indirect contact towards the infectious surfaces may results in fatal diseases. Hence, the needs of having an immediate mechanism to inhibit the growth of dangerous pathogen on the surfaces especially of those that exposed in crowded and hectic areas are extensively up surged. One of the ways to provide an effective anti-bacterial activity is by introducing self-disinfecting coating film on the surfaces, fabricated with the incorporation of metal oxides nanoparticles. Metal oxides are semiconductors that photo-reactively capable to harvest bactericidal agent known as reactive oxygen species (ROS). ROS work through series of redox reactions in the presence of oxygen (O_2) and water (H_2O) molecules causing critical damage to the cellular structures hence leads to microbial death [1,2]. Additionally, films impregnated with nanoparticles have been reported to propose improved structural strength with higher wear resistance. Yang et al. [3] in their work recorded an increased value of tensile strength for PVA nanocomposite film containing cellulose nanocrystal and lignin nanoparticles. A well-dispersed SiO_2 nanoparticles on PVA film coating was found by Wu et al. [4] to exhibit an excellent mechanical property through wear resistance and water resistance tests due to structural compatibility of the materials. Another prior study performed by El-Shamy et al. [5] demonstrated the increased values of Young's modulus as well as strength at the break for PVA-based nanocomposite films which significantly influenced by the loading of silver (Ag) nanoparticles.

TiO_2 nanoparticles have emerged to become an established material to be impregnated in composite film coatings. With excellent photocatalytic activity, chemical stability and high surface-area-to-volume ratio [6], TiO_2 nanocomposites have been reported to provide remarkable antibacterial properties as well as enhanced mechanical strength for coating films. Xing et al. [7] revealed bacterial inactivation was improved by 89.3% and 95.2% for E.coli and S.aureus respectively in polyethylene (PE) film impregnated with TiO_2. The study also showed incorporation of TiO_2 nanoparticles increased the tensile strength and elongation at break of the PE-based film. Later, Zhang et al. [8] found that stainless steel surface coated with TiO_2-PTFE nanocomposite demonstrated minimal bacterial adhesion against Gram negative Escherichia coli WT F1693 and Gram-positive Staphylococcus aureus F1557 with improved corrosion resistance. Ni-P-TiO_2 nanocomposite coatings fabricated by Weiwei et al. [9] demonstrated a significant increase of micro-hardness compared to conventional composite coatings. Meanwhile, Ni-P-TiO_2 coatings on stainless steel prepared by Zhao et al. [10] afterwards showed anti-bacterial activity up to 75% compared to uncoated steel and Ni-P coating.

Polyvinyl alcohol (PVA) is one of the most utilized polymer base for nanoparticle coating with distinctive features such as excellent cohesiveness biocompatibility [11] biodegradability [12] and soluble in water [13]. Embedment of TiO_2 nanoparticles into PVA matrix has been evidenced to produce photocatalysts with improved strength, adsorption capabilities, and surface morphology. A study carried out by Maryam et al. [14] concluded an improved mechanical strength and barrier properties were developed in PVA/TiO_2 nanocomposite film prepared for food packaging application. Meanwhile, earlier work performed by Etefagh et al. [15] found a decreased number of surviving E. coli HB101 on the PVA-TiO_2 film surface after 24 hours of exposure. However, because of the extended hydrophilic nature, PVA-based films/composites possess high water uptake and water absorption that reduce the structural integrity of the PVA film/composite which become the major concern since water molecules are the essential reactant for bactericidal effect of ROS. To overcome the drawback, PVA crosslinking by multifunctional chemicals such as glutaraldehyde (GA) has been carried out. GA has acquired the most attention as an effective crosslinking agent for PVA given by its low cost, commercial availability, low toxicity and good reactivity in facile condition with less energy required [12]. Therefore, this present work focused on the development and characterization of GA cross-linked PVA embedded with TiO_2 nanoparticles film composite.

Materials and Methods

Poly(vinyl) alcohol (PVA) 93.5% purity purchased from Qingdao Easthony Inc. Titanium Dioxide Nanoparticles (TiO_2) anatase 99.5% purity purchased from SkySpring Nanomaterials Inc. Glutaraldehyde (GA) 50 wt% solution in water purchased from ACROS ORGANICS. Sodium silicate (Na_2SiO_3), 1.39 g.cm^{-3} density obtained from MERCK.

Preparation of cross-linked PVA/TiO_2 film coating

2 g of PVA was dissolved in 50 mL distilled water and heated at 90 ºC with continuous stirring until homogenous solution was formed. TiO_2 (3 wt% in proportion to PVA) was added into the solution with continuous stirring for 30 minutes then sonicated for another 30 minutes to enhance the particle dispersion. Na_2SiO_3 was next added as dispersing agent into the solution mixture with mass ratio 1:2 (TiO_2:Na_2SiO_3) and stirred with heat at 50 ºC for 1 hours. GA solution (50 wt% in water) with 10% concentrations by GA/PVA ratio was added in dropwise into the solution. The cross-linked solution was continued to heat at 40 ºC with stirring for 3 hours. Final solution was then casted on steel plate to dry in room temperature for 48 hours.

Characterization

Crystalline phase of TiO_2 nanoparticles, PVA powder and PVA/TiO_2 composites in with and without the presence of GA was confirmed using Brucker Advanced X-ray Solution D8 Diffractometer, Cu Kα, $\lambda = 0.154$ nm and Copper (Cu) as source of radiation operating at 40 kV and 30 mA at a rate of 2°/min. The diffractometer was operated in the interval of angles $0° \leq (2\theta) \geq 90°$ using Cu Kα radiation. X'Pert HighScore Plus software was used to analyze data obtained from XRD. The scanning angle, 2θ, and intensity (counts) were plotted in a graph using OriginPro 2022 software.

Surface morphology, elemental analysis and materials interaction of the samples were investigated by Field Emission Scanning Electron Microscopy with Energy Dispersive X-ray Microscopy (FESEM-EDX) Zeiss Supra 55VP. Thin layer of the films was fixed on sample holder using double-sided tape and gold coated before being inserted into sample chamber. The images were scanned under high voltage at 5.0 Kx magnification to observe the presence and dispersion of TiO_2 nanoparticles over the PVA matrix.

Water-film interaction was determined using Ossila Contact Angle Goniometer, with a 20 µm water droplet. Sessile drop assay was performed to measure the water contact angle on the samples by optical contact angle measurement. A water droplet was gently deposited onto the surface of the sample films and photographs of the film surface were taken after droplet deposition.

Results and Discussion

Crystallinity phase

The crystallinity of PVA and TiO_2 along with the composite membranes were examined by X-ray diffraction technique (XRD). The diffraction patterns were shown in Figure 1. Based on the figure, strong peak intensity at position $2\theta = 19.37^{o}$ of PVA powder that corresponds to the (101) crystal planes was observed. This intense peak revealed the high degree of monoclinic crystal system of the powder which given by the strong asymmetrical intermolecular and intramolecular hydrogen bonding on the hydroxyl sites of the polymer. This characteristic of PVA agreed with the earlier studies reported [16,17]. TiO_2 powder diffractogram exhibited several significant peaks with mild variation at position $2\theta = 25.63^{o}$, 38.17^{o}, 48.31^{o}, 54.28^{o}, 55.30^{o}, 62.9^{o}, and 75.34^{o} corresponded to the anatase form with tetragonal crystal system of the nanoparticles. These values matched precisely with the standard data (ICSD collection code: 92363).

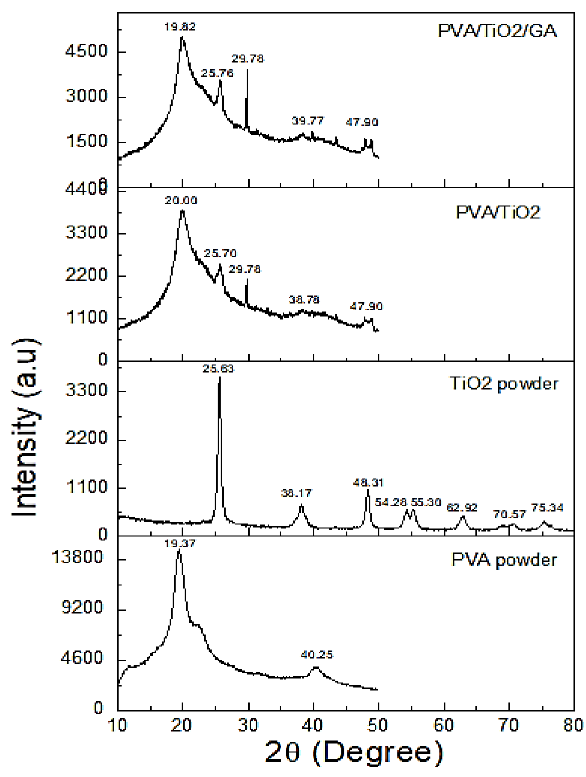

Figure 1: XRD patterns of PVA powder, TiO_2 powder, PVA/TiO_2 and PVA/TiO_2/ GA composites

The XRD patterns of PVA/TiO_2 composite films reflected the reduction the polymer lattice size compared to the pure PVA powder as the diffraction angle was shown to increase from 19.37° to 20.00° and 19.82° either with or without the presence of GA. The embedment of TiO_2 nanoparticles on PVA matrix was observed by the diffraction peaks appear at $2\theta = 38.78°$ and 47.90° for the PVA/TiO_2 film and $2\theta = 38.77°$ and 47.90° for the PVA/TiO_2/GA film. However, due to the low concentration of TiO_2 nanoparticles in the composites relatively, the peaks formed in the films were not readily obvious as those of TiO_2 powder.

Surface morphology and elemental composition

FESEM-EDX analysis was performed to understand the morphology of TiO_2 powder, pure PVA, PVA/TiO_2 and PVA/TiO_2/GA. Figure 2(a) showed the agglomerated-spherical and porous structure of TiO_2 while Figure 2(b) showed the clearly smooth surface of pure PVA film. Rougher surface morphologies were observed in PVA/TiO_2 film in Figure 2(c) and PVA/TiO_2/GA film in Figure 2(d) due to the appearance of TiO_2 cluster on the PVA matrices.

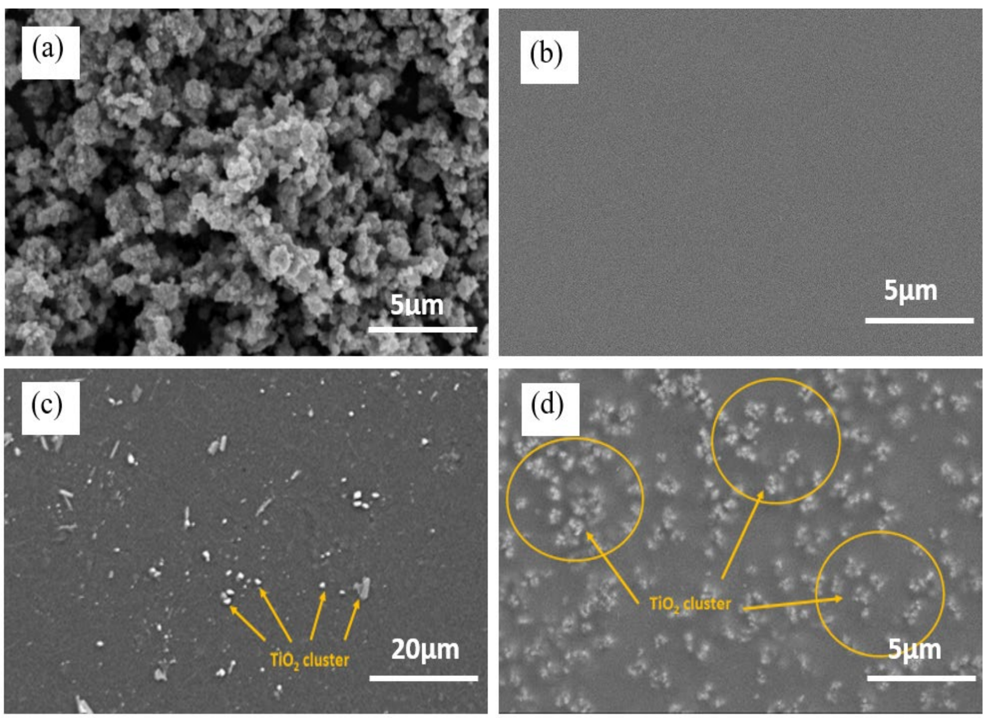

Figure 2: FESEM images of (a) TiO_2 powder, (b) pure PVA (c) PVA/TiO_2 and (d) PVA/TiO_2/ GA films

It was shown that the density per area of TiO_2 nanoparticles in PVA/TiO_2/GA film was higher compared to that of in PVA/TiO_2 film indicating the increase of nanoparticles-matrix compatibility by GA crosslinking reaction. This result agreed with the work carried out by El-Aassar et al. [18] which confirmed the increased viscosity of GA cross-linked PVA/PEG nanofibers blend, increased the polymers interaction by decreasing the surface tension of the blend thus, resulted to a homogenous fiber morphology. Similarly, homogenous distribution of silver nanoparticles in silica matrix, as composite coating was found by Ferraris et al. [19] after sample treatment with 2.5% of glutaraldehyde solution.

EDX analysis shown in Table 1 verified the improvement of TiO_2 particle dispersion on PVA matrix upon the addition of GA in Figure 2(d) illustrated by the significantly higher weight (%) of Titanium (Ti) presented in the PVA/TiO_2/GA film compared to PVA/TiO_2 film.

Table 1: EDX result on elemental composition of the sample

Sample	Element Weight %		
	Ti	O	C
PVA/TiO_2	2.84	37.83	59.33
PVA/TiO_2/GA	32.11	41.04	26.85

Contact angle measurement

Contact angle analysis was performed to study the hydrophilicity of PVA-based films by a drop of water on the films surfaces. Angle that formed at the intersection of water droplet and film surface showed the interaction between the polymer matrix and water. Contact angle that formed at less than 90° reveals the hydrophilic surface while contact angle that higher than 90° indicates hydrophobic surface. Figure 4 showed the contact angle formed as water was dropped on to pure PVA, PVA/TiO_2 and PVA/TiO_2/GA films. Pure PVA film exhibited lower contact angle at 33.88° indicating higher hydrophilicity due to the readily formation of hydrogen bonding between the polymer and water molecules given by the abundance of O-H groups in the polymer chain [4]. As the TiO_2 was added on the PVA matrix, the hydrophilicity of the film reduced which shown by the increase of contact angle from 33.88° to 60.39° for pure PVA and PVA/TiO_2 respectively. TiO_2 on the matrix occupied the O-H sites through bonding of Ti^{4+} with oxygen hence limiting the formation of polymer-water bonding. Crosslinking reaction by GA increased the stability of PVA/TiO_2 in water by increasing the contact angle to 71.74° similar to the studies reported by Vashisth et al. [20]. The hydrogen bonding of PVA with water was further decreased upon addition of GA as the O-H groups were consumed in the formation of acetal linkage producing tighter polymer chain that restricting the film wettability. Hence, this result presumed, as the contact angle increase upon the addition of TiO_2 and GA, the hydrophilicity of the films proceeded as:

PVA> PVA/TiO_2> PVA/TiO_2/GA.

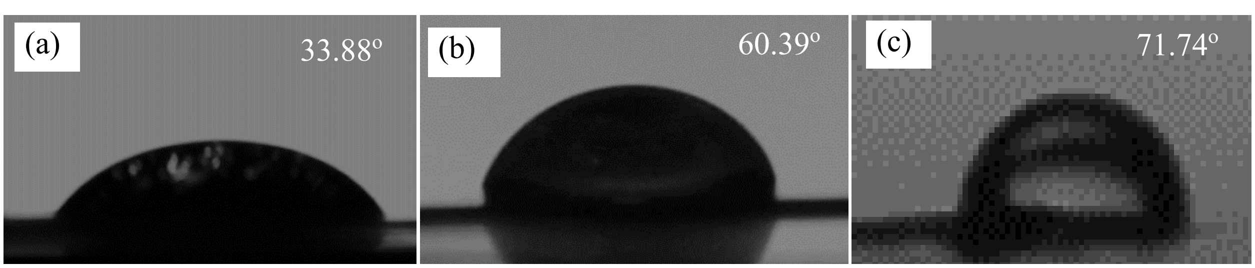

Figure 4: Water contact angle on film surface (a) pure PVA, (b) PVA/TiO_2 and (c) PVA/TiO_2/GA

Conclusions

In this work, PVA/TiO_2 coating films were produced in the presence of glutaraldehyde as crosslinking agent. The effect of crosslinking reaction was studied through the characterizations of pure TiO2 nanoparticles, pure PVA, PVA/TiO_2 and PVA/TiO_2/GA films. XRD analysis performed confirmed the present of anatase structure of TiO_2 nanoparticles on the PVA matrix and reduction of the polymer lattice size in the composite films. FESEM analysis conducted revealed the agglomerated-spherical structure of TiO_2 nanoparticles and smooth morphology of pure PVA film. The images obtained confirmed the embedment of TiO_2 nanoparticles on the PVA as rougher surfaces were observed PVA/TiO_2 and PVA/TiO_2/GA films. Crosslinking reaction resulted in improved TiO_2-PVA compatibility through homogenous dispersion with less particles aggregation on the matrix. Reduction ability of the polymer to interact with water through hydrogen bonding. was shown as PVA/TiO_2/GA film demonstrated higher contact angle of 71.74^o than PVA/TiO_2 and pure PVA films indicating lower hydrophilicity. Therefore, it is deduced that addition of GA as crosslinking agent for the coating film is necessary to improve the TiO_2 distribution and film stability in water. Nevertheless, it is crucial to determine the optimum amount of GA along with adequate period of reaction required to cross-link the PVA in order to achieve complete reaction and excellent coating performance.

Acknowledgments

The authors would like to express their thanks to Universiti Sains Malaysia (USM) for providing the laboratory facilities. Thanks also to Japan International Cooperation Agency (JICA) through the project Special Program for Research Against Covid-19 (SPRAC) for financial support.

Author Contributions

All authors contributed to the data analysis, drafting, and critical revision of the paper, and they all agree to accept responsibility for all aspects of the work.

Disclosure of Conflict of Interest

The authors have no disclosures to declare.

Compliance with Ethical Standards

The work is compliant with ethical standards.

References

[1] Fanny, C.O.S, Hang K.J. & Thuya T. M. (2018). Antibacterial activity by ZnO nanorods and ZnO nanodisks: A model used to illustrate "Nanotoxicity Threshold". *Journal of Industrial Engineering Chemistry*, 62, 333-340.

[2] Liu, B., Mu, L., Han, B., Zhang, J. & Shi, H. (2017). Fabrication of TiO_2 /Ag_2O heterostructure with enhanced photocatalytic and antibacterial activities under visible light irradiation. *Applied Surface Science*, 396, 1596-1603.

[3] Yang, W., Qi, G., Kenny, J.M, Puglia, D. & Ma, P. (2020). Effect of cellulose nanocrystals and lignin nanoparticles on mechanical, antioxidant and water vapour barrier properties of glutaraldehyde crosslinked PVA films. *Polymers*, 12(6).

[4] Wu, G., Yang, Y. & Lei, Y. (2020). Hydrophilic nano-SiO_2/PVA-based coating with durable antifogging properties. *Journal of Coatings Technology and Research*, 17(5), 145-1155.

[5] El-Shamy, A.G., Attia, W. & Abd El-Kader, K.M. (2014). The optical and mechanical properties of PVA-Ag nanocomposite films. *Journal of Alloys and Compounds*, 590, 309-312.

[6] Dicastillo, C.L., Correa M.G., Martínez, F.B., Streitt, C. & Galotto, M.J. (2020). Antimicrobial Effect of Titanium Dioxide Nanoparticles. In *Antimicrobial Resistance - A One Health Perspective*. Mares, M., Lim. S. H. E., Lai, K. & Christina R. (IntechOpen Limited, London), pp.95-112.

[7] Xing, Y., Li, X. & Zhang, L. (2012). Effect of TiO_2 nanoparticles on the antibacterial and physical properties of polyethylene-based film. *Progress in Organic Coatings*, 73, 219-224.

[8] Zhang, S., Liang, X., Gadd, G.M. & Zhao, Q. (2019) Advanced titanium dioxide-polytetrafluorethylene (TiO_2-PTFE) nanocomposite coatings on stainless steel surfaces with antibacterial and anti-corrosion properties. *Applied Surface Science*, 490, 231-241.

[9] Chen, W., Gao, W. & He, Y. (2010). A novel electroless plating of Ni-P-TiO_2 nano-composite coatings. *Surface & Coatings Technology*, 204(15), 2493-2498.

[10] Zhao, Q., Liu, C. & Su, X. (2013). Antibacterial characteristics of electroless plating Ni-P-TiO_2 coatings. *Applied Surface Science*, 274, 101-104.

[11] Moreau, D., Chauvet, C., Etienne, F., Rannou, F.P. & Corté, L. (2016). Hydrogel films and coatings by swelling-induced gelation. *Proceedings of the National Academy of Sciences of the United States of America,* 113(47), 13295-13300.

[12] Choi, D., Khan, M.H. & Jung, J. (2019). Crosslinking of PVA/alginate carriers by glutaraldehyde with improved mechanical strength and enhanced inhibition of deammonification sludge. *International Biodeterioration & Biodegradation*, 145, 104788.

[13] Jain, N., Singh, V.K. & Chauhan, S. (2017). A review on mechanical and water absorption

properties of polyvinyl alcohol based composites/films. *Journal of the Mechanical Behavior of Materials*, 26(5-6), 213-222.

[14] Zamanian, M., Sadrnia, H., Khojastehpour, M., Hosseini, F. & Thibault, J. (2020) Effect of Tio_2 nanoparticles on barrier and mechanical properties of PVA films. *Journal of Membrane Science & Research,* 7(2), 67-73.

[15] Etefagh, R., Rozati, S.M., Azhir, E., Shahtahmasebi, N. & Hosseini, A.S. (2017). Synthesis and antimicrobial properties of ZnO/PVA, CuO/PVA, and TiO_2/PVA nanocomposites. *Scientia Iranica,* 24(3), 1717-1723.

[16] Koteswararao, J., Satyanarayana, S.V., Madhu, G.M. & Venkatesham, V. (2019). Estimation of structural and mechanical properties of Cadmium Sulfide/PVA nanocomposite films. *Heliyon*, 5(6), e01851.

[17] Suganthi, S., Vignesh, S., Kalyana, Sundar, J. & Raj, V. (2020). Fabrication of PVA polymer films with improved antibacterial activity by fine-tuning via organic acids for food packaging applications. *Applied Water Science*, 10(4):1-11.

[18] El-aassar, M., Elnouby, M., Kamal, F., Badawy, N. & Amer, S. (2016). Chemical crosslinking of poly (vinyl alcohol)/ poly ethylene glycol with glutaraldehyde nanofibers. *Al-Azhar Bulletin of Science*, 27(2), 9-17.

[19] Ferraris, M., Perero, S. & Ferraris, S. (2016). Antibacterial silver nanocluster/silica composite coatings on stainless steel. *Applied Surface Science*, 396, 1546-1555.

[20] Vashisth, P. & Pruthi, V. (2016). Synthesis and characterization of crosslinked gellan/PVA nanofibers for tissue engineering application. *Materials Science and Engineering: C*, 67, 304-312.