International Journal of Surface Science and Engineering

ISSN online: 1749-7868 - ISSN print: 1749-785X
https://www.inderscience.com/ijsurfse

Nanofibre composite PCL/HA coating by spray method on metallic implant materials for medical applications: a study on the different spraying distances and pressures

Ahmad Kafrawi Nasution, Ferril Andrean, Rendy Gunawan, Rahmadini Syafri, Novia Gesrian Tuti, Syafiqah Saidin, Muhammad Hanif Ramlee

DOI: 10.1504/IJSURFSE.2023.10060123

Article History:

Received:	25 July 2022
Last revised:	24 September 2022
Accepted:	09 October 2022
Published online:	15 February 2024

Nanofibre composite PCL/HA coating by spray method on metallic implant materials for medical applications: a study on the different spraying distances and pressures

Ahmad Kafrawi Nasution*, Ferril Andrean and Rendy Gunawan

Department of Mechanical Engineering,
Faculty of Engineering,
Universitas Muhammadiyah Riau,
Pekanbaru, Riau 28294, Indonesia
Email: ahmadkafrawi@umri.ac.id
Email: 180102023@student.umri.ac.id
Email: 180102007@student.umri.ac.id
*Corresponding author

Rahmadini Syafri

Department of Chemistry,
Faculty of Mathematics, Natural Sciences and Health,
Universitas Muhammadiyah Riau,
Pekanbaru, Riau 28294, Indonesia
Email: rahmadini@umri.ac.id

Novia Gesrian Tuti

Department of Biology,
Faculty of Mathematics, Natural Sciences and Health,
Universitas Muhammadiyah Riau,
Pekanbaru, Riau 28294, Indonesia
Email: noviagesriantuti@umri.ac.id

Syafiqah Saidin

IJN-UTM Cardiovascular Engineering Centre,
Institute of Human Centered Engineering,
Universiti Teknologi Malaysia,
81310 UTM Johor Bahru, Johor, Malaysia
Email: syafiqahsaidin@biomedical.utm.my

Muhammad Hanif Ramlee

Bone Biomechanics Laboratory (BBL),
Bioinspired Devices and Tissue
Engineering (BIOINSPIRA) Research Group,
School of Biomedical Engineering and Health Sciences,
Faculty of Engineering,
Universiti Teknologi Malaysia,
81310 UTM Johor Bahru, Johor, Malaysia
Email: m.hanif@utm.my

Abstract: Surface modifications and implant coatings are implemented to control the contact between an implant material and a corrosive medium, which can delay the onset of damage and improve the implant performance, such as osseointegration acceleration. There are several limitations associated with surface modification, including low porosity, slow fibre production rate, high production cost, and complexity in the production process. Therefore, this study concentrated on modifying the surface of metal implant materials using a spray method to overcome those limitations and to obtain the porous nanofibre morphology with high coating adhesion property. A spray method was used to form a nanofibre polycaprolactone (PCL)/hydroxyapatite (HA) composite coating. The composite solution was sprayed onto the substrate surface with variations in air pressure of 350 and 450 kPa, with a distance between the nozzle and the substrate from 10, 15, 20, 25, 30, to 35 cm.

Keywords: spray coating; nanofibre; polycaprolactone; PCL; hydroxyapatite; bone integration.

Reference to this paper should be made as follows: Nasution, A.K., Andrean, F., Gunawan, R., Syafri, R., Tuti, N.G., Saidin, S. and Ramlee, M.H. (2024) 'Nanofibre composite PCL/HA coating by spray method on metallic implant materials for medical applications: a study on the different spraying distances and pressures', *Int. J. Surface Science and Engineering*, Vol. 18, No. 1, pp.55–70.

Biographical notes: Ahmad Kafrawi Nasution is a Senior Lecturer at the Department of Mechanical Engineering, Faculty of Engineering, Universitas Muhammadiyah Riau, Pekanbaru, Riau, Indonesia, and the Head of the Biomaterial Technology Laboratory (BTL). His major field is related to biomaterial degradation, welding metallurgy, failure analysis, and corrosion.

Ferril Andrean conducted a study on surface modification of implant materials for medical applications under the supervision of Ahmad Kafrawi Nasution for her Bachelor of Engineering at the Faculty of Engineering, Universitas Muhammadiyah Riau, Pekanbaru, Riau, Indonesia.

Rendy Gunawan conducted a study on surface modification of implant materials for medical applications under the supervision of Ahmad Kafrawi Nasution for her Bachelor of Engineering at the Faculty of Engineering, Universitas Muhammadiyah Riau, Pekanbaru, Riau, Indonesia.

Rahmadini Syafri received her MSc degree from Universiti Kebangsaan Malaysia, Malaysia in 2011. She is currently conducting her Doctoral study related to polymer materials and their applications.

Novia Gesrian Tuti received her Bachelor of Science degree from Andalas University, Indonesia in 1991 and subsequently received an MSi from Gadjah Mada University, Indonesia, in 2001. Her main fields of research she has been pursuing to date are histology and cell culture.

Syafiqah Saidin is a Senior Lecturer at the School of Biomedical Engineering and Health Sciences, Faculty of Engineering, Universiti Teknologi Malaysia Johor Bahru (UTM JB), Malaysia, and a research position as the Director at IJN-UTM Cardiovascular Engineering Centre, Institute of Human Centered Engineering, UTM JB. She is conducting her research under health and wellness research alliance.

Muhammad Hanif Ramlee is a Senior Lecturer at the School of Biomedical Engineering and Health Sciences, Faculty of Engineering, and Deputy Director of Medical Devices and Technology Centre (MEDiTEC) at Universiti Teknologi Malaysia (UTM). His expertise is in biomechanics, biomaterials, rehabilitation engineering, biomedical design, and medical devices.

This paper is a revised and expanded version of a paper entitled 'Fibrous composite PCL/HA coating on metallic implant materials for implant reconstruction applications' presented at 7th International Conference of Science, Technology, and Interdisciplinary Research (IC-STAR 2021), Bandar Lampung, Indonesia, 26–27 October 2021.

1 Introduction

Various fabrication technologies have been used to produce and form an ideal coating on bone implants (Rajzer, 2014). Modifying the implant and coating surfaces is mainly intended to improve implant performance and biological interaction between the implant and physiological bone surrounding, thus sustaining the implant's success rate (Mandracci et al., 2016; Zhang et al., 2014). In addition, surface modification and implant coating have roles in preventing implant corrosion and delaying the onset of damage (Agarwal et al., 2016; Smith and Lamprou, 2014). An ideal implant coating should adapt specific tissue engineering properties to integrate well with bone tissues where a fibre-based structure has been recognised to imitate most extracellular matrix (ECM) (Yue, 2014). Some important factors which influence bone cell behaviour and new tissue formation are the coating morphology, associated with porosity and pore size of the coating (Pooshidani et al., 2021). Small pore size can limit cellular infiltration (Catauro et al., 2014), while large porosity will affect cell penetration and attachment (Rajzer, 2014). The interconnected porous network is essential for cell survival, migration, and tissue regeneration (Pooshidani et al., 2021).

Fabrication technologies that are widely used to produce porous polymer coating on implants are sol-gel (Catauro et al., 2014), dip coating (Catauro et al., 2017), electrospinning (Kohse et al., 2018), electrophoretic deposition (Razavi et al., 2015), laser spallation (Karthika et al., 2015), sputter coating (Boyd et al., 2015), and spray coating (Schlaich et al., 2018) techniques. Recently, electrospinning nanofibres have been extensively investigated for the fabrication of composite nanofibres, which contain bioactive molecules to meet bone tissue requirements (Rajzer et al., 2014). However, the main limitation of the electrospinning method is low porosity (Pooshidani et al., 2021).

Electrospinning is also limited by the slow rate of fibre production and the need for a high voltage power source, which adds to the cost and complexity of the production process (Abdal-Hay et al., 2013b).

Abdal-Hay et al. (2013b) developed a new strategy for the manufacture of micro-nano scale fibre scaffolds in a simpler, effective, and low-cost process using an air-jet spinning. This fabrication technology is classified as a spraying method (Abdal-Hay et al., 2014, 2013b). Spraying methods can be applied to large-scale production by forming thin coating layers (Abdal-Hay et al., 2013b). Importantly, it allows the formation of coating polymers at room temperature without disrupting and denaturing the molecular bonds where most biomolecules, antimicrobials, and drugs are categorised as polymers (Catauro et al., 2015; Himma et al., 2017; Vital et al., 2017; Zoolfakar et al., 2017). Therefore, in this study, a spraying method is used to modify the surface of metallic implant for the production of nanofibre morphology where the composition of spray materials was set to polycaprolactone (PCL) and hydroxyapatite (HA), to improve the biological properties of the metallic implant for better osseointegration.

The use of PCL as a coating matrix for biomedical applications is widely approached due to its biocompatibility and biodegradability (Zirak Hassan Kiadeh et al., 2017). PCL is a group of polymers, also known as semi-crystalline aliphatic polyesters, that has been approved by The United States Food and Drug Administration (US-FDA), to be used in the human physiological environment (Nithya and Meenakshi Sundaram, 2015). However, PCL also has limitations in functionally enhancing cell attachment and proliferation (Ghosal et al., 2017). Incorporating bioactive components or compounds is necessary to improve the biological function of PCL. In bone implant application, inorganic bone components such as HA have a highly promising value to support cell attachment and proliferation while providing a better interface for bone integration (Bianco et al., 2009). HA itself is considered as an ideal bioactive material and has the ability to bind aggressively with the bone due to its calcium and phosphorus composition that mimicking the ECM of bone (Abdal-Hay et al., 2013a). The addition of HA into PCL sprayed coating is a convenient candidate for metal implant materials that will increase the biological interaction of the coating.

In this study, the PCL/HA sprayed coatings were formed at different spraying distances and pressures on stainless steel 316L (SS316L). The composition of the PCL/HA coatings was identified with attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR) and X-ray diffractometer (XRD). The coating's morphology was viewed under scanning electron microscopy (SEM) with the conduction of porosity measurement and coating adhesion analyses.

2 Materials and methods

2.1 Materials

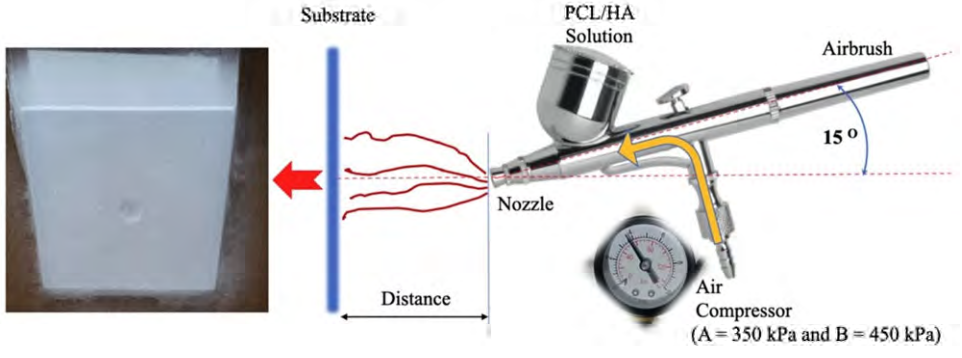
Metal plates of SS316L were cut into square dimensions of 10 mm × 10 mm × 3 mm and polished with abrasive papers #grit 1200. The SS316L plates were then air cleaned with a compressor and further ultrasonically cleaned in ethanol for 30 minutes. The metal plates were immersed in distilled water to remove surface dirt and finally dried for the coating process.

PCL pellets (M_w = 40,000) were purchased from Hunan Juren Chemical Hitechnology Co., Ltd., China to be used as the main material for the coating matrix. While HA (99% pure) from Haihang Industry Co., Ltd., China was used as an additive component to enhance the bioactivity and biological functions of the coating. Dichloromethane (DCM) was purchased from Junsei Chemical Co., Japan, with 99.5% purity and was used as the solvent for coating solution.

2.2 Fabrication of PCL/HA nanofibrous spray coating

Experimental setup of spray coating (Double Action Airbrush – H&L Airbrush Pen Kit EW-440B, China) was done as shown in Figure 1 by modifying existing methods (Ballarre et al., 2020; Abdal-Hay et al., 2017, 2014, 2013b) for the deposition of PCL/HA nanofibrous coating. The coating solution was made from 10 mL of DCM at a concentration of 99.5% and 1 gram of PCL, while the dissolved HA was 5% (wt.%) of the PCL weight. The first step is to dissolve the HA powder in 10 mL of DCM while stirring for 10 minutes. Then the PCL pellet was added to the solution while stirred rapidly for 30 minutes at 40oC. This composite solution was sprayed onto the cleaned SS316L substrate surfaces at two variations of spray pressure (A = 350 kPa and B = 450 kPa). The spray distance between the nozzle and the metal substrate was adjusted from 10, 15, 20, 25, 30, to 35 cm. The PCL/HA coating was made layer by layer with the parameters mentioned above, followed by the drying process at room temperature for 48 hours.

Figure 1 Schematic diagram of the spray coating fabrication process (see online version for colours)



2.3 Porosity test

The porosity percentage was calculated using a liquid displacement method (Pooshidani et al., 2021). In this method, ethanol was used as the displacement liquid due to its ability not to dissolve or swell the composite coating. Ethanol is a non-polar liquid that does not interfere with polymer fibres and will easily penetrate into the nanofibre coating and occupies all coating pores, giving the total volume of the pores (Pooshidani et al., 2021). The PCL/HA coated metal substrate was first weighted prior to the immersion in ethanol. The coated metals were then immersed in ethanol for 300 seconds. They were collected and subjected to weight measurement. The porosity percentage was calculated based on

equation (1) where m_a, m_p, ρ_a, and ρ_p are saturated mat mass, dry mat mass, liquid density (ethanol), and polymer density, respectively (Pooshidani et al., 2021).

$$P(\%) = \frac{\left(m_a - m_p\right)/\rho_a}{\left(m_a - m_p\right)/\rho_a + m_p/\rho_p} \times 100 \quad (1)$$

2.4 Surface characterisations

The size, distribution, and morphology of the nanofibre coating were observed by SEM (SEM-EDS, JEOL-6510 LA, Japan) at 10 kV accelerating voltage, and 10,000× magnifications. The SEM images were analysed using the J-NIH image software (Image J, National Institutes of Health, USA) to determine the fibre mean diameter and coating thickness based on the black and white intensity mapping.

The chemical composition and crystalline properties of the PCL/HA nanofibre coating were confirmed by wide angle XRD (Rigaku Dymax, Japan) with Cu-Kα radiation at 40 kV and 200 mA, with a step size of 0.02°. The XRD scanning was performed in the 2θ range between 10°–50° at a scan speed of 4°/min. The FTIR (Perkin Elmer, USA) was also used to identify the functional groups of the PCL/HA nanofibre coating. The scanning was made in the wavelength range of 750 to 4,500 cm^{-1}.

2.5 Coating adhesion test

The adhesion of the PCL/HA nanofibre coating on the metal substrate was evaluated through a peel test using a universal testing machine (Gotech GT-7001-LC30, Taiwan) at five times a repetition. The device was setup by retaining the tape at an angle of 90° due to very thin coating film. The adhesion test was conducted at a constant speed of 9 ± 0.5 mm/s and at an angle of 90 degrees according to ASTM D3330 (2018).

3 Results

3.1 Fabrication and characterisation of nanofibre coating

The nanofibre PCL/HA coatings at different spray pressures and distances were successfully deposited by the spray coating technique. The porosity measurement by the liquid transfer method is listed in Table 1. The porosity percentages were obtained in a range from 4.1 ± 0.3% to 9.4% ± 0.6%. Increasing the spray distances from 10 cm to 35 cm roughly reduced the porosity percentages. Similarly, to the increment of spray pressure where higher pressure of 450 kPa has reduced the porosity percentages compared to the 350 kPa.

The morphology and porosity of the nanofibre coatings were verified using SEM, as shown in Figures 2 and 3. The micro and nanofibrous structures represent highly porous cavities with an average diameter of 184.6 ± 40.7 nm to 1843.5 ± 507.6 nm, as listed in Table 1.

A specific trend was noticed in the variation of fibre diameter at different spray pressures and distances. The fibre diameter was known to be smaller when the pressure distances increased from 10 cm to 25 cm for both spray pressures. Increasing the distances to 35 cm has generated a bigger fibre diameter. The coating thickness for the

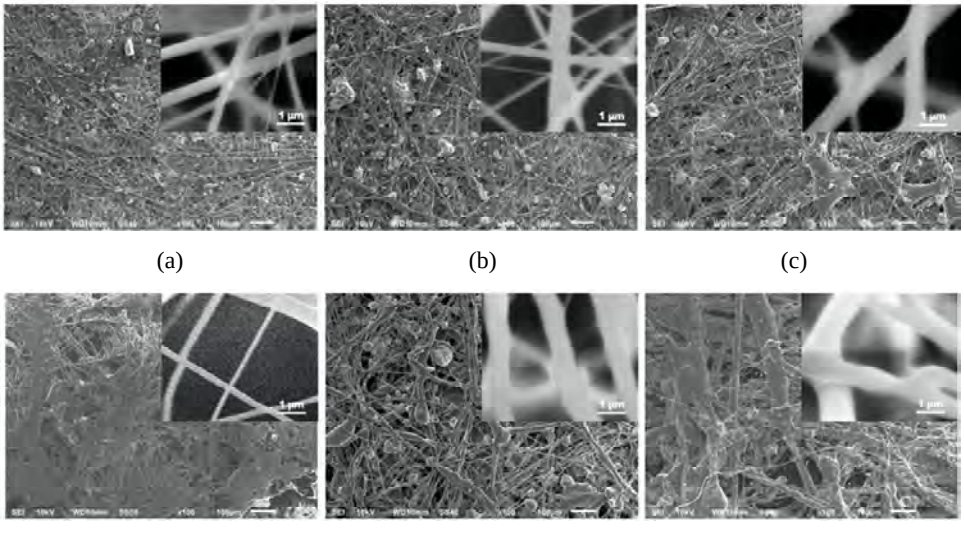
PCL/HA nanofibre coatings was also measured and was found to be between 266 ± 61 µm and 646 ± 104 µm. Greater distances and pressures have produced thinner coating.

Table 1 Porosity percentages, fibre diameter, and coating thickness of PCL/HA nanofibre coatings at different spraying pressures and distances

*Sample**	*Porosity (%)*	*Diameter (nm)*	*Thickness (µm)*
A10	9.2 ± 1.1	479.8 ± 95.1	646 ± 104
A15	7.6 ± 1.3	329.0 ± 27.0	612 ± 77
A20	9.4 ± 0.6	387.2 ± 29.4	444 ± 75
A25	6.3 ± 0.8	184.6 ± 40.7	266 ± 61
A30	4.1 ± 0.3	576.4 ± 21.4	407 ± 117
A35	5.1 ± 0.3	1,320.6 ± 97.4	489 ± 113
B10	8.4 ± 1.9	335.3 ± 60.9	511 ± 41
B15	4.6 ± 1.0	1,272.5 ± 208.8	474 ± 77
B20	6.4 ± 0.3	243.3 ± 70.2	436 ± 14
B25	4.9 ± 0.2	426.8 ± 64.1	407 ± 123
B30	5.2 ± 0.5	1,843.5 ± 507.6	389 ± 23
B35	5.4 ± 0.5	1,090.7 ± 158.8	378 ± 49

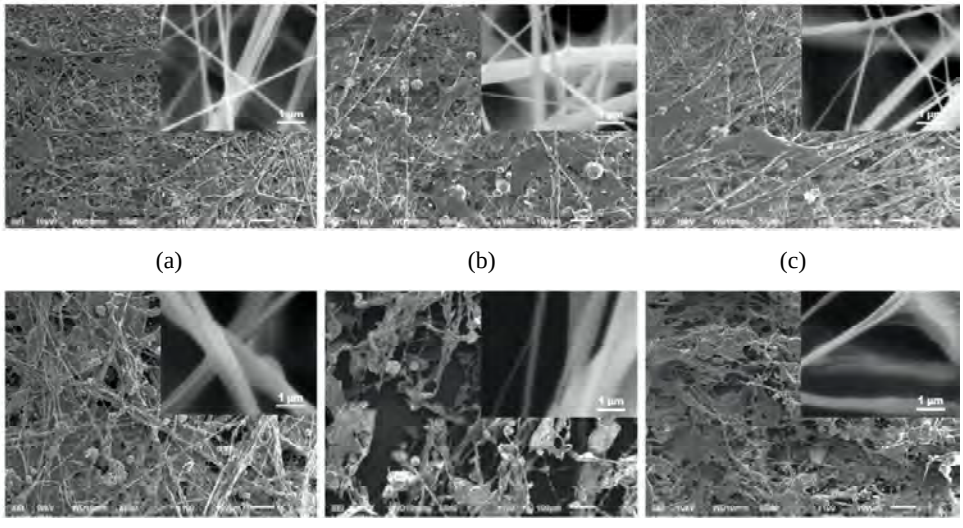
Notes: *Data are shown as mean with standard deviation (x ± SD). Letter 'A' indicates the pressure parameter of 350 kPa, and letter 'B' indicates the pressure parameter of 450 kPa. The distance parameters were 10, 15, 20, 25, 30, and 35 cm.

Figure 2 SEM images of nanofibre PCL/HA coatings at pressure and distance parameters of (a) A10, (b) A15, (c) A20, (d) A25, (e) A30, and (f) A35



Note: Letter 'A' indicates the pressure parameter of 350 kPa, and the distance parameters are 10, 15, 20, 25, 30, and 35 cm.

Figure 3 SEM images of nanofibre PCL/HA coatings at pressure and distance parameters of (a) B10, (b) B15, (c) B20, (d) B25, (e) B30, and (f) B35



(a) (b) (c)

(d) (e) (f)

Note: Letter 'B' indicates the pressure parameter of 450 kPa, and the distance parameters are 10, 15, 20, 25, 30, and 35 cm.

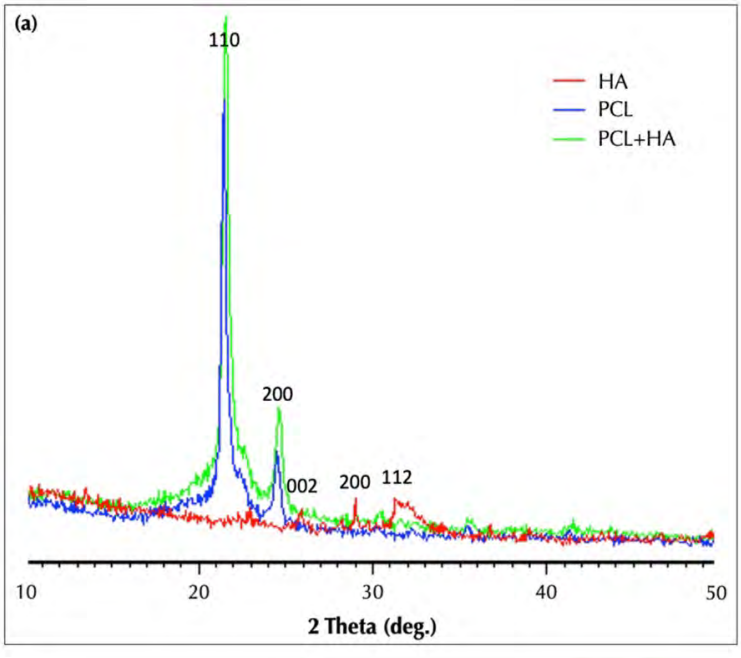
The XRD profiles of pure HA powders, pristine PCL nanofibres, and PCL/HA nanofibre coating are shown in Figure 4(a). High reflection peaks of the HA powders at $2\theta = 25.7°$, 31.7°, 32.8°, and 39.7° are seen in the XRD spectrum, which confirmed the presence of HA composition. When compared to the pristine PCL nanofibres, there are two peaks that were equal to PCL fingerprints at 21.5° and 24.5°. While for the PCL/HA nanofibre coatings, both peaks of PCL and HA were found at 21.5°, 24.5°, 28.5°, 30.5°, 35.5°, and 41.5°, which could be attributed to the characteristics of the diffraction angles. Those peaks clarified the composition of crystalline PCL and HA in the PCL/HA coating as sharp peaks were visualised on the XRD spectrum.

Figure 4(b) shows the FTIR spectra of the HA powders, PCL nanofibres, and PCL/HA nanofibre coating. The presence of HA in the HA powders and PCL/HA coating is shown through a wide FTIR band centred around 1,000–1,100 cm^{-1}, which was identified as –PO and –CO bands of non-stoichiometric apatite. In addition, the peaks at 1,420 and 1,460 cm^{-1} were associated with the –OH band, while the carbonyl group (C=O) extended at 1,724 cm^{-1}. The C–H stretching was also observed at 2,945 and 2,866 cm^{-1}.

3.2 Mechanical properties

The mechanical performances of the PCL/HA nanofibre coating fabrication are represented in Figure 5 on the smallest order of three fibre diameters. The results of the peel adhesion test was increased from 57.3 N ± 12.7 N to 161.0 N ± 65.2 N when the spray pressures and distances changed from 350 kPa; 15 cm to 450 kPa; 20 cm.

Figure 4 (a) X-RD profiles and (b) FTIR spectra of the composite PCL/HA coatings (see online version for colours)



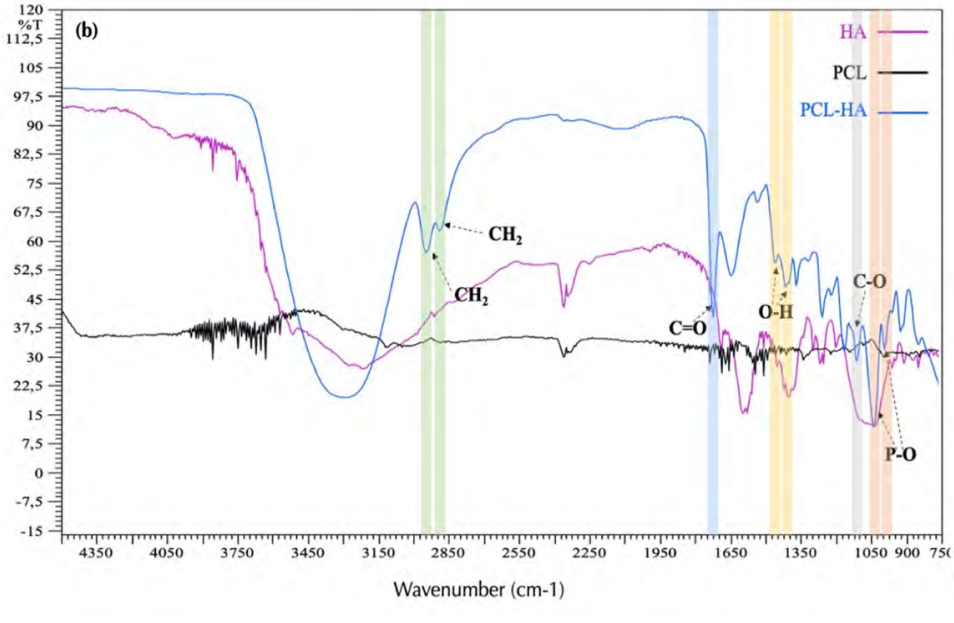


Figure 5 (a)–(c) Representative curves of adhesion tests on PCL/HA nanofibre coatings, and (d) force-displacement curve from peel tests on A15, A25 and B20 (see online version for colours)

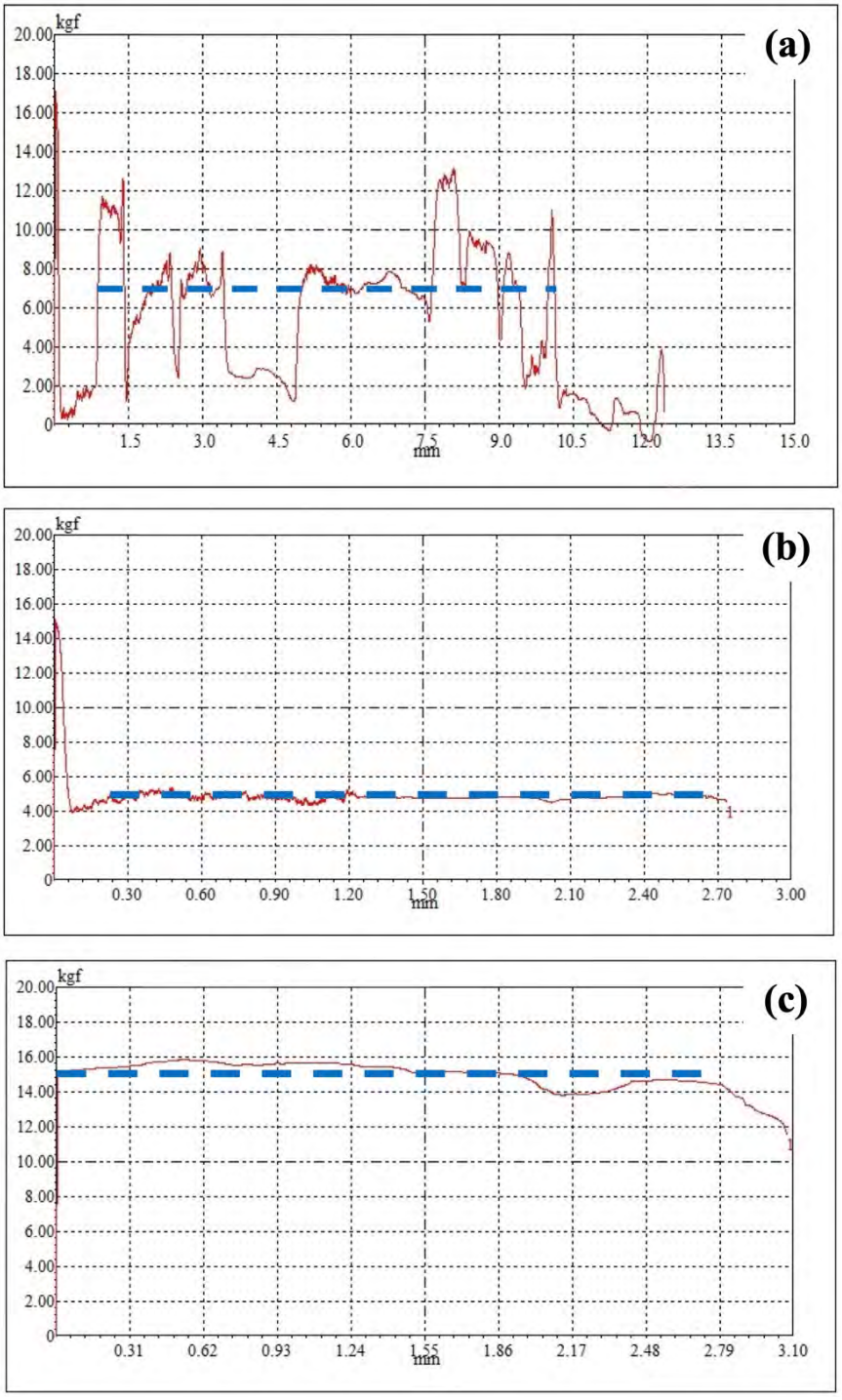
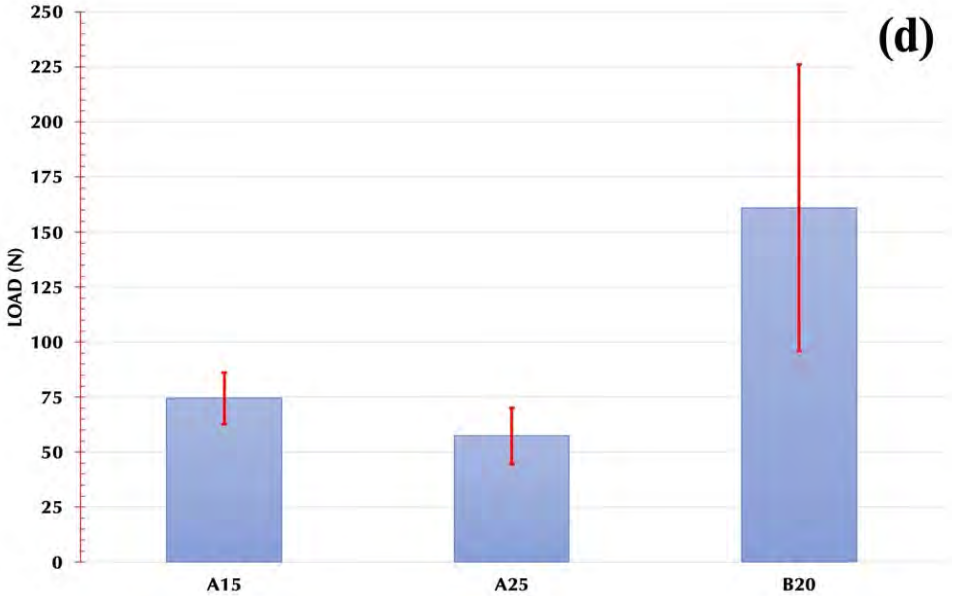


Figure 5 (a)–(c) Representative curves of adhesion tests on PCL/HA nanofibre coatings, and (d) force-displacement curve from peel tests on A15, A25 and B20 (continued) (see online version for colours)



4 Discussion

The coating technique with the spray method is usually used in coating medical devices because of the ease of processing and homogeneous coating (Horprasertkij et al., 2019). This study is the use of the spray method for the fabrication of nanofibre PCL/HA composite coating. The results showed that the PCL/HA composite coating with variations in fibre diameter (Table 1) revealed that most of the fibres were between 184.6 and 479.8 nm, with the highest frequency occurring in the 300 nm range for PCL/HA nanofibres. For a pressure variation of 350 kPa, it is recommended to use a distance of 15 to 25 cm, while for a pressure of 450 kPa, it is recommended to use a distance of 20 to 25 cm. The results obtained confirm the general view that the coating technique by the spray method makes it possible to get a nano-sized fibrous coating with a network of interconnected pores. Our results are similar to those reported by Abdal-Hay et al. (2017) wherein they observed the formation of PCL and PA-6 fibrous scaffolds. These findings are consistent with those previously reported by Abdal-Hay et al. (2014) who observed the formation of a pure PCL fibrous scaffold having a web-like structure.

Porosity is an important requirement in making network engineering constructions. Porosity is one of the factors affecting the biological performance of cell adhesion and proliferation (Hasan et al., 2014). The results obtained confirm the general view that the spray coating technique makes it possible to get nanofibre PCL/HA composite coating with a porous network. The results show that the PCL/HA composite coating with various percentages of porosity is in the range of 4.1% to 9.4%, with the highest frequency occurring at 5% for PCL/HA nanofibres. The resulting porosity percentages

were not significantly different because the composition of the PCL/HA composite solution did not differ. Pooshidani et al. (2021) revealed in their research that to get the desired percentage of porosity, it was done by giving different compositions to the electrospinning of the polyethylene oxide (PEO) sacrificial material. Care should be taken in making tissue engineering constructions where high porosity has the potential to improve biological function (Abdal-Hay et al., 2017), but on the other hand, higher porosity is responsible for lower tensile strength (Rajzer, 2014) and Young's modulus (Hasan et al., 2014).

Surface modification through coating can change the cytocompatibility and corrosion resistance properties of implant materials (Asri et al., 2017). It is not explained in detail how the thickness of the spray coating on the implant material only mentions that the effect of the thickness of the coating is correlated with the consumption of the material. Meanwhile, Luangkularb et al. (2014) stated that the efficiency of the spray coating process was identified based on material consumption and thickness.

The obtained XRD spectra showed associated crystal peaks for PCL of 21.5° and 24.5°, with crystal structures (110) and (200), respectively, and these were similar to those reported in previous studies for the crystalline behaviour of PCL scaffolds (Augustine et al., 2014; Kim et al., 2004). While the crystal peaks at 2θ = 25.7°, 31.7°, 32.8°, and 39.7° are shown in Figure 3(a), which confirms the presence of the HA structure (Kim et al., 2004). Thus, the crystalline phase did not show any specific change in the case of PCL/HA composite coatings using spray processing parameters. Meanwhile, Kim et al. (2004), in their study, said there were no other peaks or peak shifts in the composite, indicating that no chemical reaction occurred. Similar results in the study of Linh, NTB., et al., which retain the respective crystal structures shown during the electrospinning process of nHA loaded in PCL fibres (Ba Linh et al., 2013).

FTIR analysis showed corresponding bands of HA and PCL materials were observed in the spectrum, confirming that no chemical reaction took place between the components of the mixture. The C=O, C-O, and C=H bands are associated with PCL (Rezk et al., 2019; Entekhabi et al., 2016), while the P-O and O-H bands are associated with HA (Li et al., 2018; Hasan et al., 2014; Rezaei and Mohammadi, 2013). The same result was confirmed by Rajzer (2014) against the successful incorporation of n-HAp particles into nano and micro-fibrous scaffolds. No difference in the FTIR spectrum from the study conducted by Li et al. (2018) for the presence of HAp nanoparticles in PCL nanofibres.

Figure 5 shows a representative curve of the adhesion strength of the PCL/HA fibrous composite coating on the surface of the SS 316 substrate determined from the load-displacement curve. The value of the adhesive strength of the composite coating shown in Figure 5(a) seems to fluctuate when compared to Figures 5(b) and 5(c), which have more stable adhesion. The fluctuations in the adhesive power of the composite coating are thought to be from the evenness of the coating and the size of the pores formed so that it can reduce the adhesion of the porous composite coating. This is the same as the explanation of Wong et al. (2008) studied the effect of plastic deformation on peel strength on variations in PCL laminate thickness, which stated that increasing the laminate thickness would increase the measured peel strength.

5 Conclusions

This paper presented a study that resulted in the nanofibre PCL/HA composite coating was successfully formed using the spray method. The optimum parameters were recorded at the pressure of 450 kPa and the distance between the nozzle and the substrate of 20 cm. These parameters resulted in nanofibre diameter and porosity of 243.3 ± 70.2 nm and 6.4 ± 0.3%, respectively. The thickness of the PCL/HA nanofibre layer is strongly influenced by the volume of the composite solution. FTIR analysis found that no chemical reaction took place between the components of the mixture. The optimum peeling adhesion for the PCL/HA nanofibre coating was obtained at 161.0 N ± 65.2 N. This work suggests the ability of the spray method to form a porous nanofibre coating on metallic implant materials.

Acknowledgements

This research is fully supported financially through the Basic Research Scheme with contract number: 009/LL10/PG.AK/2022 from The Ministry of Education, Culture, Research, and Technology of The Republic of Indonesia.

References

Abdal-Hay, A., Barakat, N.A.M. and Lim, J.K. (2013a) 'Hydroxyapatite-doped poly(lactic acid) porous film coating for enhanced bioactivity and corrosion behavior of AZ31 Mg alloy for orthopedic applications', *Ceramics International*, Vol. 39, No. 1, pp.183–195, https://doi.org/10.1016/j.ceramint.2012.06.008.

Abdal-Hay, A., Sheikh, F.A. and Lim, J.K. (2013b) 'Air jet spinning of hydroxyapatite/poly(lactic acid) hybrid nanocomposite membrane mats for bone tissue engineering', *Colloids and Surfaces B: Biointerfaces*, Vol. 102, pp.635–643, https://doi.org/10.1016/j.colsurfb.2012.09.017.

Abdal-Hay, A., Memic, A., Hussein, K.H., Oh, Y.S., Fouad, M., Al-Jassir, F.F., Woo, H-M., Morsi, Y., Mo, X. and Ivanovski, S. (2017) 'Rapid fabrication of highly porous and biocompatible composite textile tubular scaffold for vascular tissue engineering', *European Polymer Journal*, Vol. 96, pp.27–43, https://doi.org/10.1016/j.eurpolymj.2017.08.054.

Abdal-Hay, A., Oh, Y.S., Yousef, A., Pant, H.R., Vanegas, P. and Lim, J.K. (2014) 'In vitro deposition of Ca-P nanoparticles on air jet spinning nylon 6 nanofibers scaffold for bone tissue engineering', *Applied Surface Science*, Vol. 307, pp.69–76, https://doi.org/10.1016/j.apsusc.2014.03.161.

Agarwal, S., Curtin, J., Duffy, B. and Jaiswal, S. (2016) 'Biodegradable magnesium alloys for orthopaedic applications: a review on corrosion, biocompatibility and surface modifications', *Materials Science and Engineering: C*, Vol. 68, pp.948–963, https://doi.org/10.1016/j.msec.2016.06.020.

Asri, R.I.M., Harun, W.S.W., Samykano, M., Lah, N.A.C., Ghani, S.A.C., Tarlochan, F. and Raza, M.R. (2017) 'Corrosion and surface modification on biocompatible metals: a review', *Materials Science and Engineering: C*, Vol. 77, pp.1261–1274, https://doi.org/10.1016/j.msec.2017.04.102.

ASTM D3330 (2018) *Standard Test Method for Peel Adhesion of Pressure-Sensitive Tape*, ASTM International, West Conshohocken, PA.

Augustine, R., Malik, H.N., Singhal, D.K., Mukherjee, A., Malakar, D., Kalarikkal, N. and Thomas, S. (2014) 'Electrospun polycaprolactone/ZnO nanocomposite membranes as biomaterials with antibacterial and cell adhesion properties', *Journal of Polymer Research*, Vol. 21, No. 3, p.347, https://doi.org/10.1007/s10965-013-0347-6.

Ba Linh, N.T., Min, Y.K. and Lee, B.T. (2013) 'Hybrid hydroxyapatite nanoparticles-loaded PCL/GE blend fibers for bone tissue engineering', *J. Biomater. Sci. Polym. Ed.*, Vol. 24, No. 5, pp.520–538, https://doi.org/10.1080/09205063.2012.697696.

Ballarre, J., Aydemir, T., Liverani, L., Roether, J.A., Goldmann, W.H. and Boccaccini, A.R. (2020) 'Versatile bioactive and antibacterial coating system based on silica, gentamicin, and chitosan: improving early stage performance of titanium implants', *Surface and Coatings Technology*, Vol. 381, p.125138, https://doi.org/10.1016/j.surfcoat.2019.125138.

Bianco, A., Di Federico, E., Moscatelli, I., Camaioni, A., Armentano, I., Campagnolo, L., Dottori, M., Kenny, J.M., Siracusa, G. and Gusmano, G. (2009) 'Electrospun poly(ε-caprolactone)/Ca-deficient hydroxyapatite nanohybrids: microstructure, mechanical properties and cell response by murine embryonic stem cells', *Materials Science and Engineering: C*, Vol. 29, No. 6, pp.2063–2071, https://doi.org/10.1016/j.msec.2009.04.004.

Boyd, A.R., Rutledge, L., Randolph, L.D. and Meenan, B.J. (2015) 'Strontium-substituted hydroxyapatite coatings deposited via a co-deposition sputter technique', *Materials Science and Engineering: C*, Vol. 46, pp.290–300, https://doi.org/10.1016/j.msec.2014.10.046.

Catauro, M., Bollino, F. and Papale, F. (2014) 'Biocompatibility improvement of titanium implants by coating with hybrid materials synthesized by sol-gel technique', *J. Biomed. Mater. Res. A*, Vol. 102, No. 12, pp.4473–4479, https://doi.org/10.1002/jbm.a.35116.

Catauro, M., Bollino, F., Papale, F. and Lamanna, G. (2015) 'TiO_2/PCL hybrid layers prepared via sol-gel dip coating for the surface modification of titanium implants: characterization and bioactivity evaluation', *Applied Mechanics and Materials*, Vol. 760, pp.353–358, https://doi.org/10.4028/www.scientific.net/AMM.760.353.

Catauro, M., Papale, F., Piccirillo, G. and Bollino, F. (2017) 'PEG-based organic-inorganic hybrid coatings prepared by the sol-gel dip-coating process for biomedical applications', *Polymer Engineering & Science*, Vol. 57, No. 6, pp.478–484, https://doi.org/https://doi.org/10.1002/pen.24488.

Entekhabi, E., Haghbin Nazarpak, M., Moztarzadeh, F. and Sadeghi, A. (2016) 'Design and manufacture of neural tissue engineering scaffolds using hyaluronic acid and polycaprolactone nanofibers with controlled porosity', *Materials Science and Engineering: C*, Vol. 69, pp.380–387, https://doi.org/10.1016/j.msec.2016.06.078.

Ghosal, K., Manakhov, A., Zajíčková, L. and Thomas, S. (2017) 'Structural and surface compatibility study of modified electrospun poly(ε-caprolactone) (PCL) composites for skin tissue engineering', *AAPS PharmSciTech*, Vol. 18, No. 1, pp.72–81, https://doi.org/10.1208/s12249-016-0500-8.

Hasan, A., Memic, A., Annabi, N., Hossain, M., Paul, A., Dokmeci, M.R., Dehghani, F. and Khademhosseini, A. (2014) 'Electrospun scaffolds for tissue engineering of vascular grafts', *Acta Biomaterialia*, Vol. 10, No. 1, pp.11–25, https://doi.org/10.1016/j.actbio.2013.08.022.

Himma, N.F., Wardani, A.K. and Wenten, I.G. (2017) 'Preparation of superhydrophobic polypropylene membrane using dip-coating method: the effects of solution and process parameters', *Polymer-Plastics Technology and Engineering*, Vol. 56, No. 2, pp.184–194, https://doi.org/10.1080/03602559.2016.1185666.

Horprasertkij, K., Dwivedi, A., Riansuwan, K., Kiratisin, P. and Nasongkla, N. (2019) 'Spray coating of dual antibiotic-loaded nanospheres on orthopedic implant for prolonged release and enhanced antibacterial activity', *Journal of Drug Delivery Science and Technology*, Vol. 53, p.101102, https://doi.org/10.1016/j.jddst.2019.05.051.

Karthika, A., Kavitha, L., Surendiran, M., Kannan, S. and Gopi, D. (2015) 'Fabrication of divalent ion substituted hydroxyapatite/gelatin nanocomposite coating on electron beam treated titanium: mechanical, anticorrosive, antibacterial and bioactive evaluations', *RSC Advances*, Vol. 5, No. 59, pp.47341–47352, https://doi.org/10.1039/C5RA05624A.

Kim, H-W., Knowles, J.C. and Kim, H-E. (2004) 'Hydroxyapatite/poly(ε-caprolactone) composite coatings on hydroxyapatite porous bone scaffold for drug delivery', *Biomaterials*, Vol. 25, No. 7, pp.1279–1287, https://doi.org/10.1016/j.biomaterials.2003.07.003.

Kohse, S., Arbeiter, D., Reske, T., Stiehm, M., Schmitz, K-P. and Grabow, N. (2018) 'Electrospinning for polymeric implants in cardiovascular applications: accelerated degradation of electrospun poly(L-lactide) scaffolds', *Current Directions in Biomedical Engineering*, Vol. 4, No. 1, pp.89–92, https://doi.org/10.1515/cdbme-2018-0023.

Li, H., Huang, C., Jin, X. and Ke, Q. (2018) 'An electrospun poly(ε-caprolactone) nanocomposite fibrous mat with a high content of hydroxyapatite to promote cell infiltration', *RSC Advances*, Vol. 8, No. 44, pp.25228–25235, https://doi.org/10.1039/C8RA02059K.

Luangkularb, S., Prombanpong, S. and Tangwarodomnukun, V. (2014) 'Material consumption and dry film thickness in spray coating process', *Procedia CIRP*, Vol. 17, pp.789–794.

Mandracci, P., Mussano, F., Rivolo, P. and Carossa, S. (2016) 'Surface treatments and functional coatings for biocompatibility improvement and bacterial adhesion reduction in dental implantology', *Coatings*, Vol. 6, No. 1, p.7, https://doi.org/https://doi.org/10.3390/coatings6010007.

Nithya, R. and Meenakshi Sundaram, N. (2015) 'Biodegradation and cytotoxicity of ciprofloxacin-loaded hydroxyapatite-polycaprolactone nanocomposite film for sustainable bone implants', *International Journal of Nanomedicine*, Vol. 10, Suppl. 1, pp.119–127, https://doi.org/10.2147/ijn.S79995.

Pooshidani, Y., Zoghi, N., Rajabi, M., Haghbin Nazarpak, M. and Hassannejad, Z. (2021) 'Fabrication and evaluation of porous and conductive nanofibrous scaffolds for nerve tissue engineering', *Journal of Materials Science: Materials in Medicine*, Vol. 32, No. 4, p.46, https://doi.org/10.1007/s10856-021-06519-5.

Rajzer, I. (2014) 'Fabrication of bioactive polycaprolactone/hydroxyapatite scaffolds with final bilayer nano-/micro-fibrous structures for tissue engineering application', *Journal of Materials Science*, Vol. 49, No. 16, pp.5799–5807, https://doi.org/10.1007/s10853-014-8311-3.

Rajzer, I., Menaszek, E., Kwiatkowski, R. and Chrzanowski, W. (2014) 'Bioactive nanocomposite PLDL/nano-hydroxyapatite electrospun membranes for bone tissue engineering', *Journal of Materials Science: Materials in Medicine*, Vol. 25, No. 5, pp.1239–1247, https://doi.org/10.1007/s10856-014-5149-9.

Razavi, M., Fathi, M., Savabi, O., Vashaee, D. and Tayebi, L. (2015) 'In vivo assessments of bioabsorbable AZ91 magnesium implants coated with nanostructured fluoridated hydroxyapatite by MAO/EPD technique for biomedical applications', *Materials Science and Engineering: C*, Vol. 48, pp.21–27, https://doi.org/10.1016/j.msec.2014.11.020.

Rezaei, A. and Mohammadi, M.R. (2013) 'In vitro study of hydroxyapatite/polycaprolactone (HA/PCL) nanocomposite synthesized by an in situ sol-gel process', *Materials Science and Engineering: C*, Vol. 33, No. 1, pp.390–396, https://doi.org/10.1016/j.msec.2012.09.004.

Rezk, A.I., Mousa, H.M., Lee, J., Park, C.H. and Kim, C.S. (2019) 'Composite PCL/HA/simvastatin electrospun nanofiber coating on biodegradable Mg alloy for orthopedic implant application', *Journal of Coatings Technology and Research*, Vol. 16, No. 2, pp.477–489, https://doi.org/10.1007/s11998-018-0126-8.

Schlaich, C., Li, M., Cheng, C., Donskyi, I.S., Yu, L., Song, G., Osorio, E., Wei, Q. and Haag, R. (2018) 'Mussel-inspired polymer-based universal spray coating for surface modification: fast fabrication of antibacterial and superhydrophobic surface coatings', *Advanced Materials Interfaces*, Vol. 5, No. 5, p.1701254, https://doi.org/10.1002/admi.201701254.

Smith, J.R. and Lamprou, D.A. (2014) 'Polymer coatings for biomedical applications: a review', *Transactions of the IMF*, Vol. 92, No. 1, pp.9–19, https://doi.org/10.1179/0020296713Z.000000000157.

Vital, A., Vayer, M., Tillocher, T., Dussart, R., Boufnichel, M. and Sinturel, C. (2017) 'Morphology control in thin films of PS:PLA homopolymer blends by dip-coating deposition', *Applied Surface Science*, Vol. 393, pp.127–133, https://doi.org/https://doi.org/10.1016/j.apsusc.2016.09.151.

Wong, S-C., Baji, A. and Gent, A.N. (2008) 'Effect of specimen thickness on fracture toughness and adhesive properties of hydroxyapatite-filled polycaprolactone', *Composites Part A: Applied Science and Manufacturing*, Vol. 39, No. 4, pp.579–587, https://doi.org/10.1016/j.compositesa.2007.09.004.

Yue, B. (2014) 'Biology of the extracellular matrix: an overview', *J. Glaucoma*, Vol. 23, No. 8, Suppl. 1, pp.S20–S23, https://doi.org/10.1097/ijg.0000000000000108.

Zhang, B.G.X., Myers, D.E., Wallace, G.G., Brandt, M. and Choong, P.F.M. (2014) 'Bioactive coatings for orthopaedic implants – recent trends in development of implant coatings', *International Journal of Molecular Sciences*, Vol. 15, No. 7, pp.11878–11921, https://www.mdpi.com/1422-0067/15/7/11878.

Zirak Hassan Kiadeh, S., Ghaee, A., Mashak, A. and Mohammadnejad, J. (2017) 'Preparation of chitosan-silica/PCL composite membrane as wound dressing with enhanced cell attachment', *Polymers for Advanced Technologies*, Vol. 28, No. 11, pp.1396–1408, https://doi.org/10.1002/pat.4016.

Zoolfakar, A.S., Bazar, N.M.M.A., Khairir, N.S., Husaini, Y., Talip, M.A.A., Mamat, M.H., Rani, R.A. and Rusop, M. (2017) 'Synthesis and enhanced photocatalytic property of CuO nanostructure via dip coating method', *2017 IEEE Regional Symposium on Micro and Nanoelectronics (RSM)*, 23–25 August, pp.30–33.