Effects of PEG-polysaccharide coating on electrospun PLA nanofiber

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Abstract. This paper reports the preparation of electrospun polylactic (PLA) nanofiber coated with carrageenan (CRG) and polyethylene glycol (PEG). CRG was utilized to increase the hydrophilicity while PEG was used to create strong bonding between the two polymers. The nanocomposites films (PLA/CRG-PEG) were successfully prepared. The presence of CRG improves the hydrophilicity of the nanofiber mat (22.45º) while the addition of PEG increased the mechanical strength. This new approach would enable the applications of electrospun PLA for more hydrophilic environment, especially for medical devices or materials

1. Introduction

Nowadays, electrospinning has become one of the most versatile, cost-effective, and ease of handling technique to engineer advance materials to be used in biomedical applications. Apart of being, flexible in the spinning of a wide variety of polymeric fibres, it is also able to produce continuous fibres. The products gain from this method was consistent in term of its fibre diameter [1]. In tissue engineering and wound dressing, electrospun nanomembranes act as tissue scaffolds which improve cells growth and proliferation. In case of damaged tissues, the nanomembranes scaffolds with seeded cells can be fixed to patient's body to repair the damage [2].

Poly(lactic acid) (PLA) is known as one of the most widely used synthetic polymers due to its non-toxicity which is naturally present in human body. PLA is thermoplastic, high strength and high modulus polymer [3]. Due to these characteristics, PLA has become one of the most famous material in electrospinning. However, there are some major limitation of PLA such as hydrophobic nature and poor ductility which hinder its practical used as substitute materials in tissue regeneration [4].

In order to overcome this problem, CRG has been attached to the surface of the PLA to increase its hydrophilicity. CRGs are polysaccharides derived from red seaweeds that are well known in the food industry. They are highly soluble in water and very popular gelling agents [5]. Research on CRG hydrogels in biomedical and pharmaceuticals are still on-going. Even though CRG have been extensively explored particularly in food packaging applications [6-8], recent studies have shown that CRG exhibit potentials to be formulated as dressings for drug delivery to wounds [9] and possible enhanced bioactivity for bone tissue engineering [10].

Another material that plays a crucial role in this study is polyethylene glycol (PEG). PEG has been extensively studied for biomedical application such as drug delivery and tissue engineering [11]. PEG has the ability to attach a variety of reactive functional group to the terminal sides of PEG polymers.
Hence, we hypothesized that PEG can promote good binding between PLA and CRG. PLA was electrospun and coated with CRG and CRG/PEG in order to increase the hydrophilicity.

2.1 Experimental

2.1 Preparation of electrospun PLA/CRG-PEG

The electrospun PLA was fabricated by using electrospinning method at a feed rate of 1ml/hour and applied voltage of 12.5 V. 2g of PLA was used for each batch. The CRG (0.1, 0.3, 0.5g) and PEG (wt% of 1, 2, 4, 6) were dissolved together and the solution was poured on the surface of the electrospun PLA. They were heated to the glass transition temperature ($T_g$) of PLA for 3 days.

2.2 Mechanical testing

The tensile test was performed on the electrospun nanofibre samples using a computer controlled Instron machine with crosshead speed of 1mm/min at a standard laboratory atmosphere of 23°C. Thicknesses of the specimens were measured and the experiment was conducted in triplicate.

2.3 Water contact angle

Wetting degree of the electrospun nanofibre was determined by water contact angle using sessile drop method. The contact angles were calculated from images captured by the camera of contact angle measuring system, VCA Optima, AST Products, Inc.

3. Results and discussion

3.1 Tensile strength

Tensile strength of the neat electrospun PLA nanofibre and its modification were shown in Table 1. Presence of 0.1g of CRG on the PLA surface revealed a lower tensile strength compared to that of neat electrospun PLA. This mainly caused by the poor coverage of the CRG on the PLA cavities that lead to poor load transfer. Meanwhile 0.3g of CRG seemed to increase the tensile strength while higher amount of CRG (0.5g) decrease the nanocomposites’ tensile strength. The reduction of mechanical strength may due to the detachment of the CRG from the nanofiber surfaces. Thus 0.3g of CRG was utilized for the next stage.

| Samples        | Ultimate tensile strength (MPa) |
|----------------|---------------------------------|
| PLA            | 3.35 ±0.05                      |
| PLA/0.1g CRG   | 3.24 ±0.07                      |
| PLA/0.3g CRG   | 3.50 ±0.02                      |
| PLA/0.5g CRG   | 3.18 ±0.05                      |

Tensile strength of PLA/0.3g CRG with the addition of different composition of PEG are shown in Table 2. It can be observed that the tensile strength increased with increasing percentage of PEG. This shows that addition of PEG promote the binding between PLA and CRG. Though higher amount of
PEG was not prepared, we predict that the tensile strength to be reduced at a certain PEG concentration.

**Table 2.** Mechanical properties of PLA/0.3g CRG with the addition of PEG

| Samples                | Ultimate tensile strength (MPa) |
|------------------------|---------------------------------|
| PLA/0.3g CRG/1% PEG    | 4.85 ±0.05                      |
| PLA/0.3g CRG/2% PEG    | 5.76 ±0.10                      |
| PLA/0.3g CRG/4% PEG    | 5.88 ±0.20                      |
| PLA/0.3g CRG/6% PEG    | 6.71 ±0.32                      |

### 3.2 Water contact angle

The water contact angle of the specimens can be seen in Figure 1. Figure 1a shows that the contact angle for neat electrospun PLA nanofiber was at 120.88 ± 5.22° and the contact angle for PLA/0.3CRG/6PEG was at 22.45 ± 3.25°. Contact angle is determined by the physiochemical nature of the material tested. When polar substances are being used, it is plausible to have a partial rearrangement of the functional groups towards the surface during casting. In this case, diols and carbonyls of PLA should create a three dimensional network with the cellulose -OH, and the non-polar part of the structure may be reoriented to the presence of CRG and PEG, the polarity of the PLA increased due to the presence of more -OH group, thus resulting in lower value of contact angle. Nanofiber patch with lower contact angle would provide preferable environment when in contact with body fluid.

![Figure 1](image-url)

*Figure 1. Water contact angle of a) neat electrospun PLA nanofiber and b) PLA/0.3CRG/6PEG*

### 4. Conclusion

In conclusion, the incorporation of CRG has successfully improved the tensile strength and the hydrophilicity of the electrospun PLA nanofiber. The presence of PEG has increase the bonding between the PLA and CRG. The modified electrospun PLA nanofiber has the advantages being mechanically reliable for biomedical applications. In addition, cost-effective approach utilizing natural resources based on renewable synthetic polymer and polysaccharide might open up new frontiers in biomedical materials.
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References
[1] Lasprilla-Botero J, Álvarez-Láinez, M, & Lagaron, J. M. 2018. The influence of electrospinning parameters and solvent selection on the morphology and diameter of polyimide nanofibers. Materials Today Communications 14, p 1-9.

[2] Liang W, Hou J, Fang X, Bai F, Zhu T, & Lang, M. 2018. Synthesis of cellulose diacetate based copolymer electrospun nanofibers for tissues scaffold Applied Surface Science 443, p 374-381.

[3] Lesage F., Roman S, Pranpanus S, Ospitalieri S, Zia S, Jimenez J, & Deprest J. 2018. Modulation of the early host response to electrospun polylactic acid matrices by mesenchymal stem cells from the amniotic fluid European Journal of Pediatric Surgery 28, p 285-292.

[4] Abdal-Hay A, Hussein K H, Casettari L, Khalil K A, & Hamdy A S. 2016. Fabrication of novel high performance ductile poly (lactic acid) nanofiber scaffold coated with poly (vinyl alcohol) for tissue engineering applications Materials Science and Engineering:C 60, p 143-150.

[5] He H, Ye J, Zhang X, Huang Y, Li X, & Xiao M. 2017. κ-Carrageenan/locust bean gum as hard capsule gelling agents Carbohydrate Polymers 175, p 417-424.

[6] Sedayu B B, Cran M J, & Bigger S W. 2018. Characterization of semi-refined carrageenan-based film for primary food packaging purposes Journal of Polymers and the Environment p 1-8.

[7] Farhan A, & Hani N M. 2017. Characterization of edible packaging films based on semi-refined kappa-carrageenan plasticized with glycerol and sorbitol Food Hydrocolloids 64, p 48-58.

[8] Thakur R, Pristijono P, Golding J B, Stathopoulos C E, Scarlett C J, Bowyer M, & Vuong Q. V. 2017. Amylose-lipid complex as a measure of variations in physical, mechanical and barrier attributes of rice starch-ι-carrageenan biodegradable edible film Food Packaging and Shelf Life 14, p 108-115.

[9] Zepon K M, Marques M S, da Silva Paula M M, Morisso F D P, & Kanis, L A. 2018. Facile, green and scalable method to produce carrageenan-based hydrogel containing in situ synthesized AgNPs for application as wound dressing International Journal of Biological Macromolecules 113, p 51-58.

[10] Kavoli S, Mirzaie M, Feizi F, Rakhshan V, Arash V, & Bijani A. 2017. Local injection of carrageenan accelerates orthodontic tooth movement: A preliminary experimental animal study. International Orthodontics 15, 588-599.

[11] Grossen P, Witzigmann D, Sieber S, & Huwyler J. 2017. PEG-PCL-based nanomedicines: A biodegradable drug delivery system and its application Journal of Controlled Release 260, p 46-60.

[12] Khalid A, Abdel-Karim A, Atieh M A, Javed S, & McKay G. 2018. PEG-CNTs nanocomposite PSU membranes for wastewater treatment by membrane bioreactor Separation and Purification Technology, 190, pp 165-176.