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CHARACTERIZATION OF HYDROXYAPATITE/POLYPYRROLE/POLY (CAPROLACTONE) BASED SOLVENT CAST THIN FILMS

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ABSTRACT

This study addressed the fabrication of thin films composed of Polypyrrole (PPy), hydroxyapatite (HA) and poly (Ɛ-caprolactone) (PCL) via solvent casting method. The polymer and composite films were subsequently characterized in terms of morphology, wettability and water uptake properties using different techniques. The characterization of the thin films were determined using a Scanning Electron Microscope (SEM), Energy Dispersive X-ray (EDX), water contact angle and water uptake. The addition of HA and PPy reduced the hydrophobic properties of PCL in the thin films. An energy dispersive x-ray (EDX) analysis supported the existence of HA in composite thin films. Water uptake of PCL thin film was lower than HA/PCL and HA/PPy/PCL composite thin films.

Keywords: solvent casting method, PCL, PCL/HA, PCL/HA/PPy, tissue engineering (TE), SEM, water contact angle (WCA).

1. INTRODUCTION

Biopolymer can be either synthetic or natural. Natural biopolymers such as chitosan, gelatin and collagen are biodegradable and can increase the cells performance in biological system [1, 2]. Synthetic biopolymers have suitable properties and are reliable materials. The degradation rate and mechanical strength can be controlled [3]. Examples of synthetic polymers are poly-lactid acid (PLA), poly-lactide-co-glycolide (PLGA) and poly (Ɛ-caprolactone) (PCL).

PCL is biodegradable polyester with a melting point of 60 ^{o}C. The degradation of PCL is through its ester linkages and has a degradation rate slower than polylactic [4]. PCL is a hydrophobic and semi crystalline polymer [4]. For the past years, advance in the field of medical materials tend to use ceramic materials for skeletal repair and reconstruction. Hydroxyapatite (HA) is an example of bio-ceramics which is widely used in biomedical applications for orthopedics and dental implant [5]. HA is highly flexible which makes it suitable for non-loaded parts. Thus, the integration of HA with another material may improve its characteristic [6].

Conductive polymer is a part of the electro-active biomaterials that allow the direct transports of electrical, electrochemical and electromechanical stimulation to cells [7]. One of the important conductive polymer is Polypyrrole (PPy) which indicated good in vitro and in vivo biocompatibility and good chemical stability [8].

In this study, by using solvent casting solvent method, three types of films were fabricated. The focus of this study was to prepare three types of thin films namely, PCL, HA/PCL and HA/PPY/PCL films. The polymer and composite films were assessed using a scanning electronic microscope (SEM), an energy dispersive x-ray (EDX). The water contact angle and water uptake properties were measured and compared.

2. MATERIALS AND METHODS

2.1 Materials

Poly (Ɛ-caprolactone) (PCL) (MW: 70, 000-90, 000) and Polypyrrole (Ppy) were purchased from Sigma. By using the nanoemulsion technique hydroxyapatite nanoparticles were prepared in house [9]. 1, 4 dioxane was used as a solvent with the analytical grade.

2.2 Fabrication of thin films using solvent casting

In order to produce solvent cast thin films, three different solutions with PCL, HA/PCL and HA/PPy/PCL were prepared. The first sample was prepared by dissolving of 0.50 g PCL polymer in 10 ml of 1, 4 dioxane under magnetic stirrer. The second sample, HA/PCL was prepared by addition of 10% (w/w) HA into the PCL solution. The solution was homogenized by using a homogenizer IKA T25 (IKA Works) for dispersing HA nanoparticles in the polymer solution. In order to prepare the third sample, 10% (w/w) of PPy was added in the 10% HA containing 5% (w/v) PCL solution, magnetically stirred and homogenized. The solution was taken in glass petri dishes and kept in a fume hood for 48 hrs.

2.3 Characterization

Morphology: A section from each thin film was cut to small pieces. The samples were arranged in a metal plate and labelled. Then by using a Scanning Electron Microscope (SEM, TM3000) the morphology of prepared film surfaces were studied. The samples were visualized under SEM at different magnifications.

Energy Dispersive X-ray (EDX): The EDX analysis system were coupled with SEM machine. The samples were analysed by using energy dispersive X-ray spectroscopy to examine the presence of HA of the films.
Contact Angle. By VCA Optima contact angle measuring unit, the wettability of the samples was calculated. That

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machine dropped 1 µl of water on the samples of each thin film. Then, the angle of the water droplet on the sample was measured and recorded by using computer integrated software.

Measurement of water uptake: The initial weight of each sample PCL, HA/PCL, HA/PPy/PCL was calculated. Then, the samples were immersed in distilled water. The immersed samples were taken out and weighed after 2 min. The water uptake is calculated by using the following equation:

$$\text{Wateruptake (\%)} = (W_w - W_d) / W_d \times 100 \qquad \text{(i)}$$

3. RESULTS AND DISCUSSIONS

3.1 Morphology analysis

General appearance of PCL, HA/PCL and HA/PPy/PCL films are shown in Figure-1. The SEM image of PCL film in Figure-2(a) indicated a smooth surface. The regular organization of this film architecture is due to the evaporation mechanism, which in turn was affected by the solvent evaporation properties and polymer concentration. The Figure-2(b) shows the distribution of HA nanoparticle on the HA/PCL film. The overall morphology was similar to PCL film.

With the incorporation of HA nanoparticles and PPy, the composite film possessed irregular and tiny pores together with some closed pores (Figure2(c)). This happened during the solvent evaporation process of the composite mixture at room temperature. The composite film of HA/PPy/PCL had irregular and rough surface which could be a helpful property for cell adhesion and spreading.

Figure-1. General appearance of (a) PCL; (b) HA/PCL and (c) HA/PPy/PCL thin films.

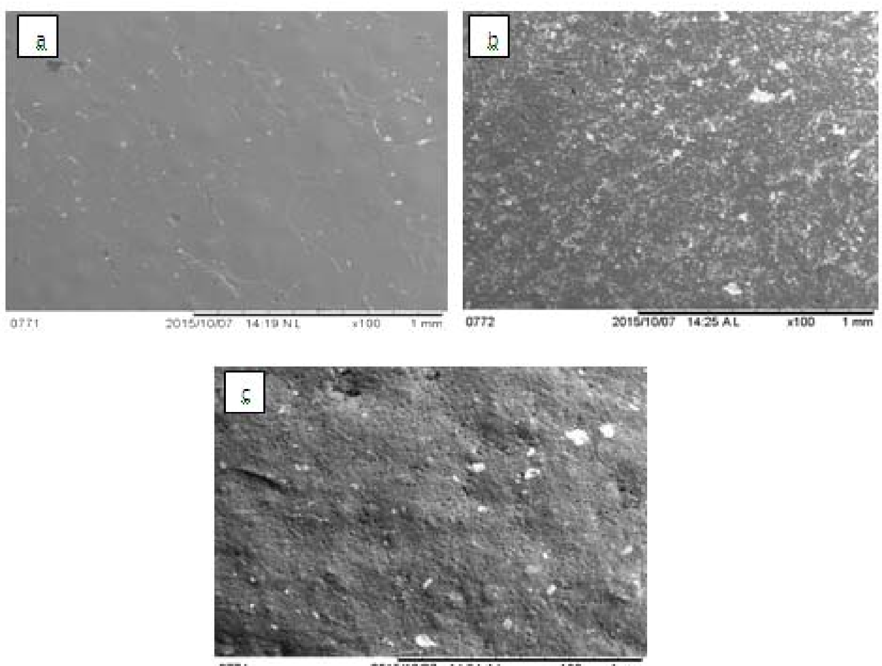

Figure-2. SEM micrographs of composite films of (a) PCL (b) HA/PCL (c) HA/PPy/PCL, respectively.

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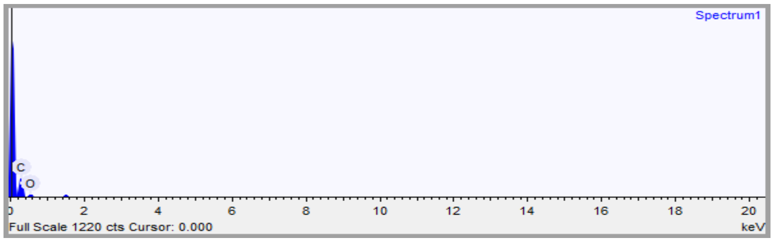
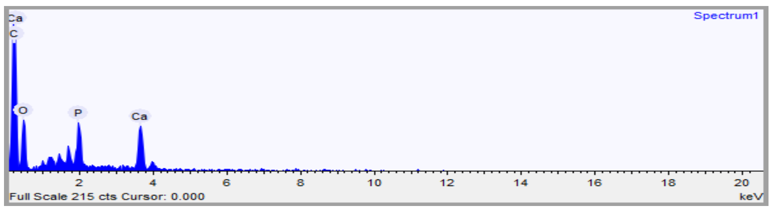
3.2 Energy Dispersive X-Ray (EDX) analysis

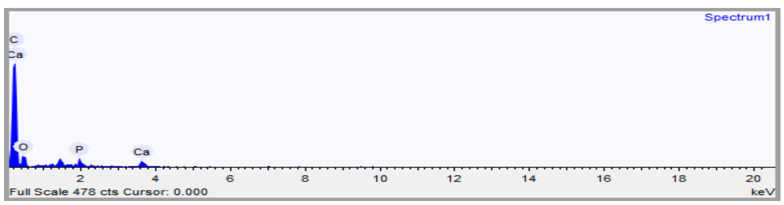
An EDX spectrum in Figure-3 shows the presence of elements in different types of films. The PCL film had only C and O (Figure-3a). The presence of Ca and P confirms the incorporation of HA in HA/ PCL and HA/PPy/PCL films (Figures 3(b) and 3(c)). However, the element N which is an element of PPy could not be detected using EDX.



(a)



(b)



(c)

Figure-3. EDX spectra of (a) PCL; (b) HA/PCL and (c) HA/PPy/PCL films.

3.3 Water Contact Angle (WCA)

The water contact angle measurement results are shown in Figure-4. The contact angle of the PCL films was higher. The contact angle decreased with the addition of HA and PPy. The PCL film had higher contact angle of 85° ± 4.6 than PCl/HA (72° ± 3.5) and PCl/HA/PPy (74° ± 5.4). Therefore, the addition of conductive PPy did not further decrease the wettability. The increasing hydrophilic properties in HA/PCL composite film made them potentially suitable to promote cell proliferation and attachment on its surface than PCL films [10].

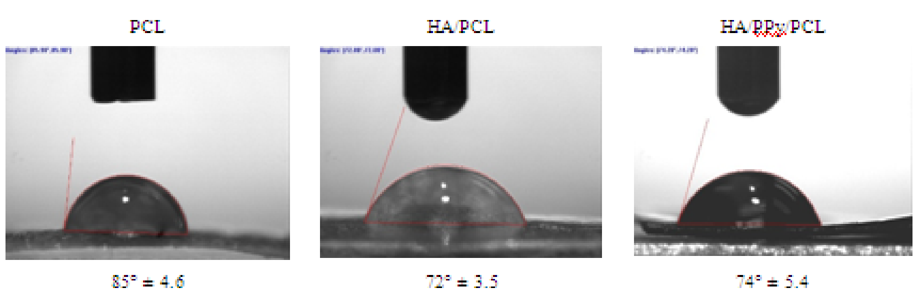


Figure-4. The contact angles of different thin films.

3.4 Water uptake measurement

Figure-5 shows the water uptake properties of PCL, HA/PCL and HA/PPy/PCL films after 2 min. It can be clearly seen that the pure PCL composite film had a lower water uptake than the others. The PCL composite films showed lower water uptake due to hydrophobic property which was also supported from water contact angle result. With the addition of HA, HA/PCL composite film showed higher water uptake property. The addition of PPy did not further increase the water uptake. It was

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reported that the structure and surface morphology also effect on water uptake [11, 12].

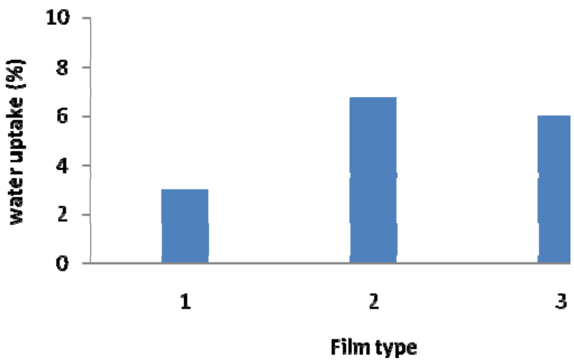

Figure-5. Water uptake of thin films (1) PCL; (2) HA/PCL; (3) HA/PPy/PCL.

5. CONCLUSIONS

Three types of composite films PCL, HA/PCL and HA/PPy/PCL were fabricated and characterized. Pure PCL had higher wettability than other samples. The addition of HA and PPy decreased the wettability of composite films and increased their water uptake properties. The SEM results indicated smooth and clear surface for PCL sample. The addition of HA and PPy turned the surface to rougher. HA/PPy/PCL composite film had micropores due to the interaction of solvent evaporation and PPy polymer. EDX analysis proved the presence of HA in composite films. The composite film of HA/PPy/PCL has potential to be used in biomedical application.

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