Materials Letters 230 (2018) 12–15

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/mlblue

Mineralization of plasma treated polymer surfaces from super-saturated simulated body fluids

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ARTICLE INFO

Article history:
Received 1 February 2018
Received in revised form 11 July 2018
Accepted 17 July 2018
Available online 18 July 2018

Keywords:
Calcium phosphates
Coatings
Plasma treatment
Nucleation
Precipitation

ABSTRACT

This study aims to obtain mechanistic understanding of the formation and development of biomedical CaP coating on a model polymer surface of plasma treated polycaprolactone (PCL). Oxygen plasma treatment changed the surface morphology at nanometre scale and introduced negatively charged groups to PCL surface. Nucleation of CaP on the treated PCL surface occurred via two modes of growth, Volmer–Weber and Stranski–Krastanov. EDX and FTIR analysis suggested that the coating progressed from compositions with low Ca/P ratios and solubility to the phases of higher ratios and stability. The results also indicated that CaP clusters formed through Volmer–Weber mode were rich in the CaP phases of the higher Ca/P ratios. This study thus provided mechanistic insights into the coating process of CaP from solution onto functionalized surfaces which could be useful in designing coatings to suit different requirements.

1. Introduction

Calcium phosphates (CaP) coating has been extensively investigated as a means to improve integration of an implant with host bone and in periodontal and bone tissue engineering [1]. This biomimetic approach is based on the research in hydroxyapatite (HA) in bones and the transformation of other CaP phases into HA [2–4]. Simulated body fluids (SBFs) are among the most often used solutions to form CaP coatings on metals, ceramics and polymers. Polymers such as chitosan [5], polyimide [6],polyethylene oxide-polybutylene terephthalate copolymers [7], PCL and PCL-based composite have been coated with CaP via SBF immersion method [8,9]. Hydrophobic synthetic polymers were often plasma treated to improve hydrophilicity before deposition of CaP from solutions [9,10]. Heterogeneous nucleation and growth of CaP has been well documented on surfaces following immersion in SBF [23,24]. CaP coating on Ti surfaces were shown forming initially as an amorphous calcium titanate in which P was then incorporated to form an amorphous calcium phosphate of low Ca/P ratio which was finally converted to bonelike crystalline apatite of higher ratios. Surface nano-topography also exhibited strong influence on the mineralization r [11].

Since different calcium phosphate phases have different bioactivity and resorption kinetics, understanding their formation and growth during the coating process would be particularly useful for optimizing the coatings for different applications. Reports in literature have referred to three major models of epitaxial growth of thin films[12], Volmer–Weber (VW, islanding mode), Frank-van der Merwe (FM, layer-by-layer mode) and Stranski–Krastanov (SK, mixed islanding and layer-by-layer mode) to describe the morphologies of SBF-induced CaP formation on substrates [13–15]. These modes are strongly associated with substrate's wettability with FM mode on highly hydrophilic, VW on hydrophobic and SK on the intermediate [16,17]. The current study investigated the CaP coating formation on PCL surface with and without plasma treatment and the coating's compositions and phases in association with these growth modes.

2. Materials and methods

Polycaprolactone (Purasorb, Mw ~ 120 kDa) films with a thickness of 110–130 μm were prepared and treated in O_2 plasma (flow rate of 7.9 mL/min) for 1,3,7 and 15 mins to improve the surface hydrophilicity which is important for immersion in SBF and CaP formation. Negatively charged group densities on PCL surfaces

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https://doi.org/10.1016/j.matlet.2018.07.078

were determined using toluidine blue assay as described elsewhere [18].

Static contact angle were measured using a FTA200 with MilliQ water.

A formulation of 10X SBF containing high ion concentrations was used to study the coating process [14,15]. The PCL films were immersed in this solution at 37 °C for 30 min, 60 min to form the coatings and rinsed in milliQ water. Some 60 mins coated samples were treated with NaOH 0.5 M for 30 min as some researchers use this method to remove amorphous phase in the coatings [19–21].

Samples were carbon coated and used for imaging and EDS analysis with scanning electron microscopy.

Samples were also analysed using ATR-FTIR spectroscopy (Nicolet iS50). At least three samples per group and 3 areas per sample were analysed and *student's t test* was used for statistics.

3. Results and discussion

We first investigated the effects of plasma treatment on PCL films which showed increased nanometre roughness when treated for extended periods (7 and 15 mins, Fig. 1A and D). 15 mins treatment significantly increased the surface roughness from c.a 350 nm to c.a. 580 nm (Fig. 1A–D). Phase images (Fig. 1C) showed slight decrease indicating a softer surface after plasma treatment. Negatively charged group density increased with extended plasma treatment and significantly more hydrophilic PCL surface was achieved after 3 min (E,F). Surface hydrophilicity and negative surface charges were found important for coating formation as the untreated PCL showed poor CaP coating (data not shown). Negatively charged surface groups were suggested to attract positive Ca^{2+} resulting in charge build-up that in turns precipitates negative ions and eventually forming amorphous calcium phosphate species [22].

3.1. CaP coating morphological analysis

The coatings exhibited wo key components including spherical clusters and planar layers (Fig. 2A–C). The clusters were attributed to the deposited CaP formed through Volmer–Weber (islanding) growth mode and the planar through Stranski–Krastanov mode (islanding + planar layer) [23,24]. Clusters also formed more directly on PCL surface than on CaP planar layer (Fig. 2D) and also seem smaller (Fig. 2E).

The coatings had thickness of c.a. 0.8–1.2 µm with some slight increase from 30 to 60 mins and slight decrease following NaOH treatment (no statistical significance, Fig. 2F–I). This result was also supported by the signal attenuation of PCL-carbonyl groups (peak at 1720 cm^{-1}) (Fig. 2K). The 7 min plasma treatment groups showed similar changes only with the dominant presence of planar plate layer at earlier time point (30 mins) which was attributed to the more negatively charged group density.

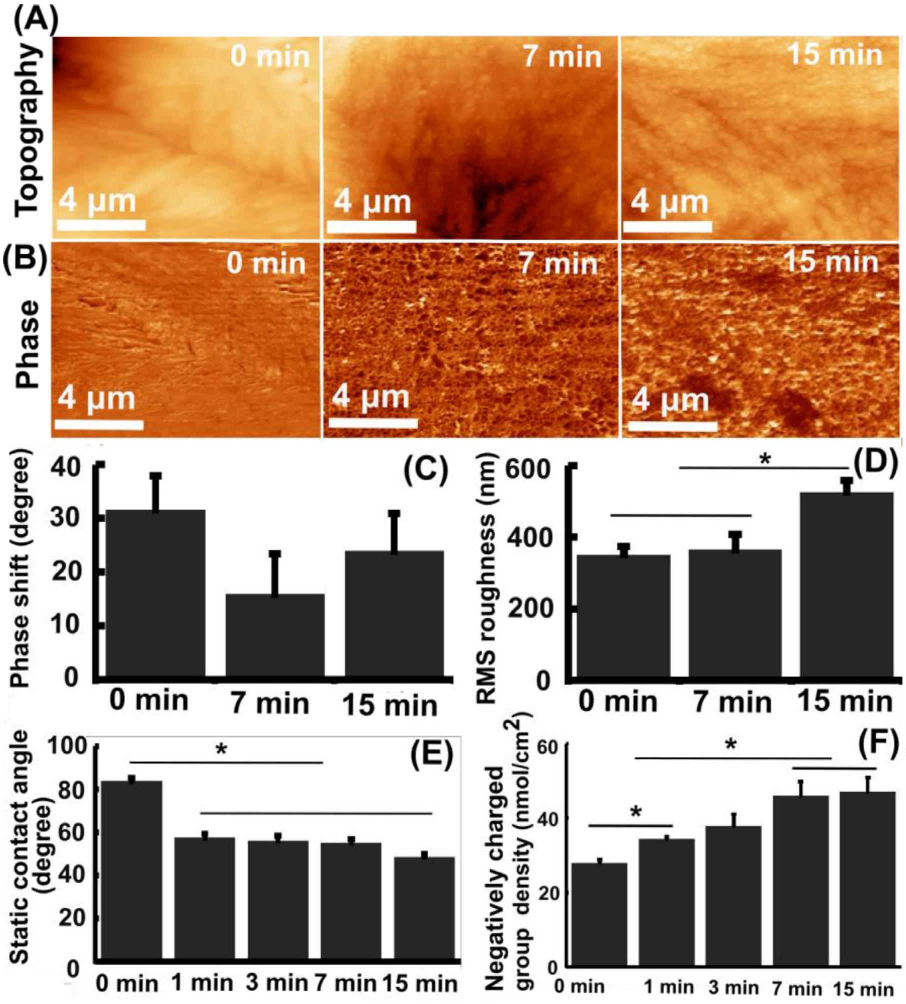

Fig. 1. Effects of plasma treatment on PCL surfaces using AFM (AD), contact angle measurement (E) and surface functional groups. $p^* < 0.05$.

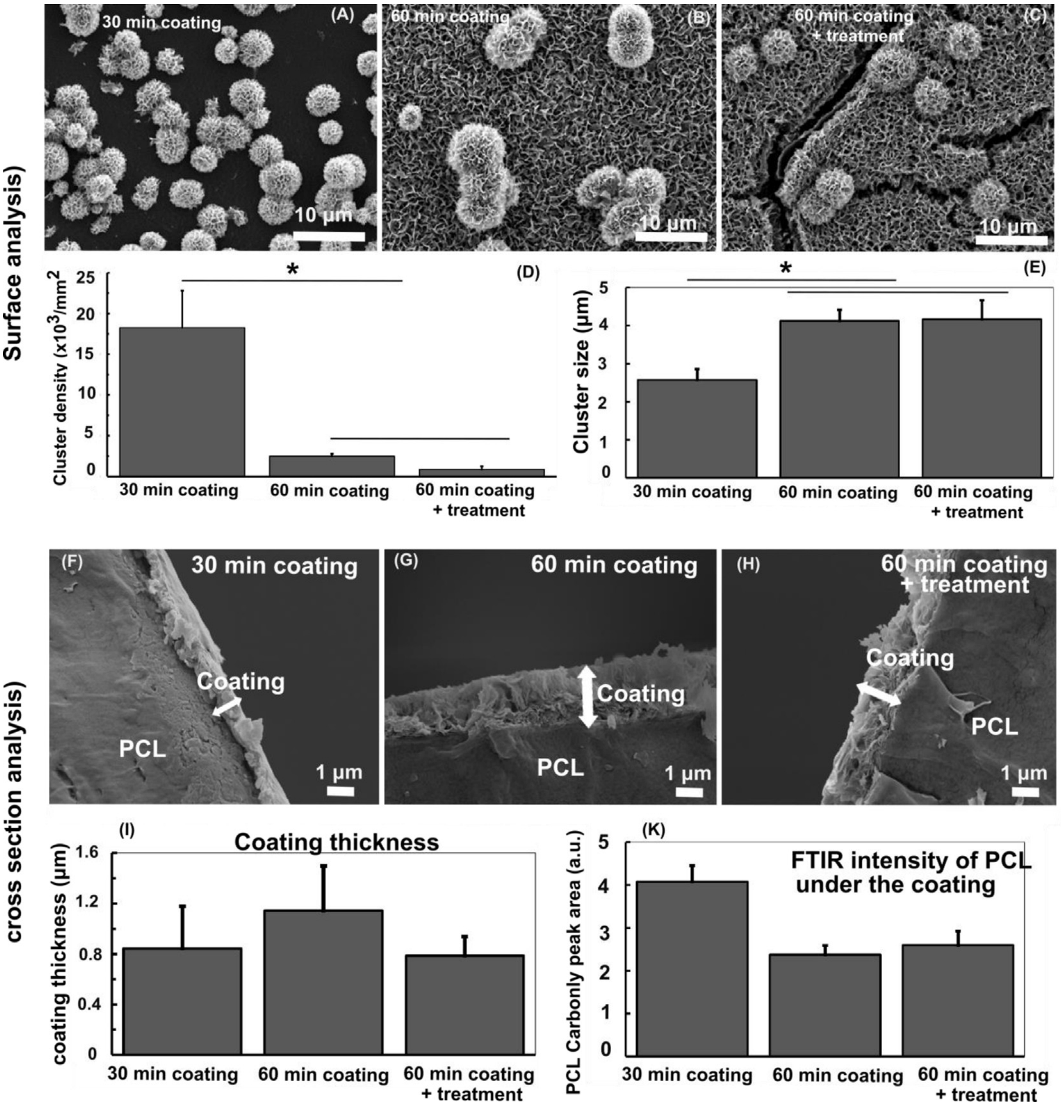

Fig. 2. Morphological (A-E) and thickness analysis (F-K) of the coatings formed on plasma treated PCL for coatings after 30 mins and 60 mins and post treatment. $^{*}p < 0.05$.

3.2. Compositional analysis

Elemental maps showed co-localization of Ca, P and O with the clusters (Fig. 3A). Coupled with the fact that Ca/P ratios were higher when analysed on the clusters only compared to whole field of view (i.e., both clusters and planar layer) (Fig. 3B and C), the results suggested that the clusters composed of high Ca/P ratio phases such as tricalcium phosphate (TCP, Ca/P = 1.5), octacalcium phosphate (OCP, Ca/P = 1.33).

3.3. Phase analysis

Two key phases of interest were v_3 PO_4^{3-}phosphate domain (c. a.1020 cm^{-1} wave number) and dicalcium phosphate dihydrate (DCPD at c.a. 1064 cm^{-1} wave number) associated with main CaP and high solubility phases respectively. The 1020 cm^{-1} peak areas increased from 30 min to 60 min coating as expected and was attributed to the increase in total amount of CaP coating deposited (Fig. 3F). A further but slight increase was detected after post treatment which was likely due to the differential effects of NaOH treatment on Ca and P in the coating related to the high electronegativity of O and/ or the transformation of phases such as DCPD and β-TCP to HA [25].

The DCPD phase increased sharply from 30 min to 60 min of coating indicating the higher formation rate of DCPD, and significantly decreased with post treatment likely due to DCPD degradation by NaOH (Fig. 3G). We attributed the changes in υ_3 PO_4^{3-} and DCPD to the precipitation and deposition of multiple CaP phases on PCL surface and the differential effects of NaOH on them due to their different solubility (e.g., log(Ksp) of DCP is ~6.5–6.9 and of HA is ~58 [26]).

There are only few studies on CaP which reported formation of high Ca/P ratio materials (such as HA) and association with the VW growth mode[13,27] yet there is lack of direct comparison between VW and SK on CaP coating in the literature. In terms of bioactivity, higher Ca/P ratio materials such as hydroxyapatite (HA) are argued to offer mechanical stability and are biomimetic to the mineral phase of bones [28,29]. Yet more resorbable, lower Ca/P materials such as tricalcium phosphate (TCP) are argued to be efficient intermediate species facilitating the in situ maturation and formation of HA-like materials [30]. In fact, strategies have emerged to combine high and low Ca/P ratio materials (for example biphasic CaP materials consisted of HA and β-TCP). Our work here presents correlations of the growth modes with the CaP phases as important insight for researchers when designing their coatings according to specific needs.

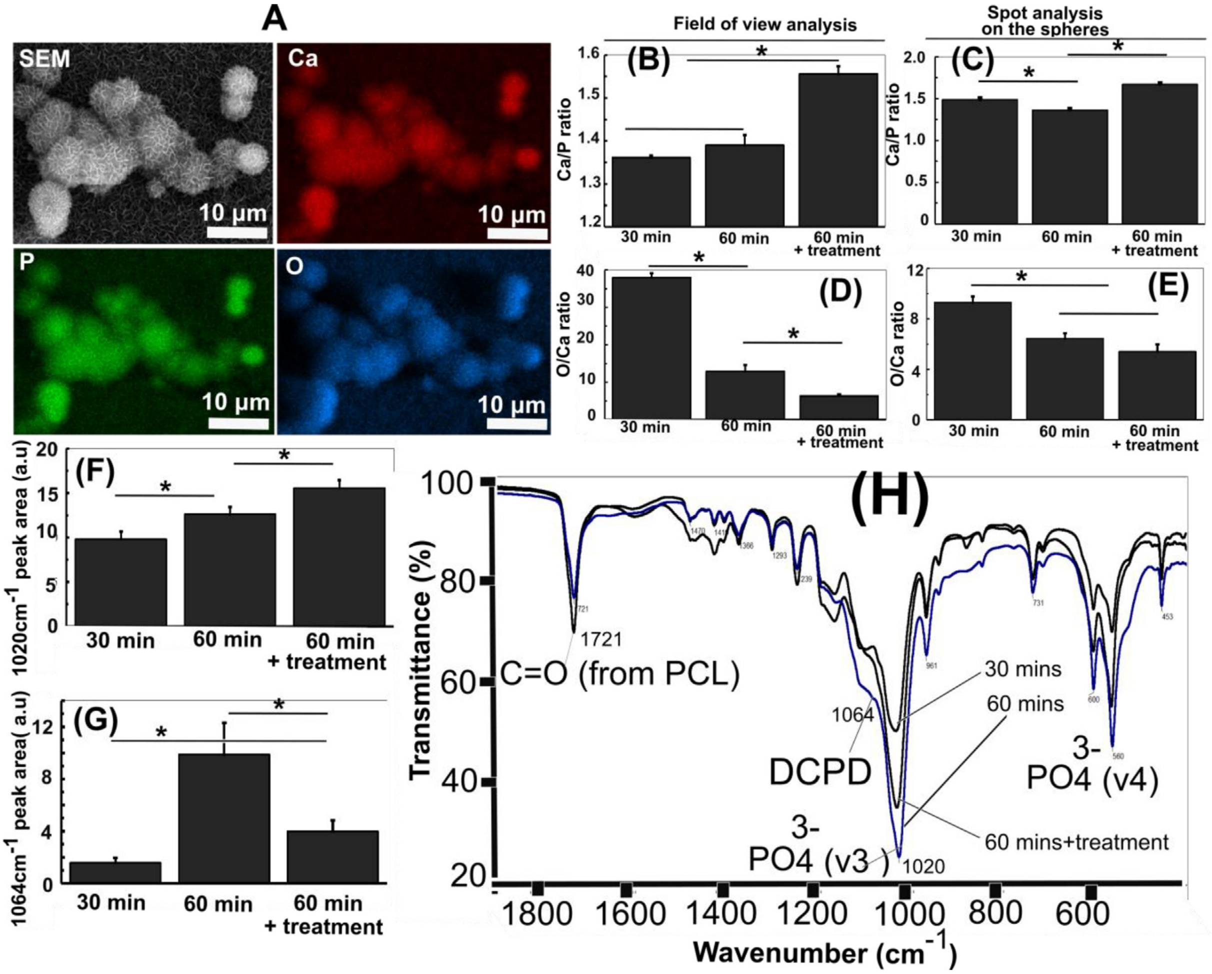

Fig. 3. Composition analysis of coatings using EDX (A-E) and FTIR (F-H).

4. Conclusion

This study aimed to obtain mechanistic understanding of the mineralization process of polymer surface through precipitation from supersaturated solutions like 10X SBF. We showed the presence of both Volmer–Weber (islanding) and Stranski–Krastanov (mixed islanding and layer formation) growth modes and the former created phases of higher Ca/P ratios. The changes in different CaP phases demonstrated the evolution from phases of lower Ca/P ratio to higher Ca/P and stability. This study therefore provides important insight into the process of solution-based CaP coating which could be useful for developing coating suitable for specific needs.

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