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New application of poly(butylene succinate) (PBS) based ionomer as biopolymer: a role of ion group for hydroxyapatite (HAp) crystal formation

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Abstract Sodium sulfonate ionic group bearing PBS ionomer (PBSi) and hydroxyapatite (HAp) composites were prepared by soaking in the simulated body fluid (SBF) solution, which is the biomimetic method, as well as the effects of the ionic group on the HAp crystal formation and growth were investigated. The introduced sodium sulfonate ionic groups operated as the functional groups with negative charge densities, which can bind plentiful Ca^{2+} ions efficiently, consequently serving as active sites allowing HAp crystals to grow on the surfaces of the PBSi matrix. By SEM analysis, it was observed that HAp became growing as the shape with the porous holes. These holes are thought to be very suitable for the ingrowths of the surrounding tissue and the assistance to the bone formation. Based on this finding, it can be clearly concluded that the ionic groups in the PBSi may be decisive factors in growing HAp, and it is anticipated that this novel materials can contribute to excellent biopolymer.

Introduction

A new type of thermoplastic resin, an ionomer, is a polymer that is partially ionized by the metallic ion [1]. As originally proposed by Eisenberg [2, 3], the interaction between ionic groups leads to the formation of multiplets containing a small number of ion pairs and ionic clusters, which constitute a second phase and contain many multiplets. These ionic structures have been shown to act as strong electrostatic crosslinks and enhance the mechanical properties of the polymer [2, 4].

Recently, we synthesized for the first time a series of poly(butylene succinate) (PBS), a typical biodegradable aliphatic polyester-based ionomer (PBSi), by the addition of sulfonated dimethyl fumarate (SDMF) with sodium sulfonate ionic group and extensively examined the relationship of the ionic group between nonisothermal crystallization behavior. The PBSi exhibited the enhanced nonisothermal crystallization rates than that of pure PBS, but the concentration of ionic substituents was not directly proportional to the increase in the crystallization rate [5]. Our subsequent study of the blend of it with poly(3-hydroxybutyrate-*co*-3-hydroxyhexanoate) (PHB-HHx), new PHA family, verified that PBSi induce to the superior miscibility with PHB-HHx as a result of sodium metal ion–carbonyl interaction between the ionic group and the carbonyl group [6]. As a result, we confirmed that the ionic group within the PBSi could help it apply as industrial fields.

Nowadays, investigation for hydroxyapatite (HAp), $(Ca_{10}(PO_4)_6(OH)_2)$ has been greatly focused in biomaterial research area, since its chemical and crystallographic properties are similar to the inorganic component found in nature bone. In addition, this inorganic material has favorable advantages such as excellent biocompatibility, bioactivity, and osteoconductivity [7–9]. However, some drawbacks, like mechanical brittleness, low flexibility, and difficult process ability, are often encountered with its application as artificial bone materials. In order to improve the shortcoming of HAp and obtain intelligent biomaterials, fabrication of the composites of HAp with some

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organic polymers has been widely examined via biomimetic methods [10–14].

In these HAp/polymer composites, the key point in brilliant composites fabrication is how the functional group can be efficiently introduced into the polymer matrix, since this functional group can operate as a nucleus to the formation of hydroxyapatite, consequently not only leading to the increase the interfacial adhesion but also restricting the phase separation between the polymer matrix and HAp. Xiao et al. [15, 16] radiated with UV light to introduce –OOH groups onto the surface of the PLA and fabricated HAp/PLA composites by this modified PLA. Wang et al. [17, 18] have examined the silanation of HAp and acrylic acid grafting on polyethylene for improving bonding between HAp and polyethylene in HAp/HDPE composites. However, theses studies have traditionally focused mainly monotonous alteration on the polymer surface. No systematic research has been published concerning the regulation of functional group, especially the ionic group, directly within the molecular chain.

Based on this consideration, for the purpose of putting PBSi into biopolymer practice, we report the fabrication of novel PBS ionomer/hydroxyapatite composites. The ionic groups in the PBSi molecules can act as effective functional group of HAp crystal formation, generating that not only enhance the interfacial adhesion between HAp and PBSi but also control its formation and growth. Furthermore, it is anticipated that this novel polyester-based ionomer has the infinitive potential as a superior biopolymer as well as industrial application.

Materials and methods

PBS ionomer synthesis

Pure PBS and PBS ionomers with 1.0, 3.0, and 5.0 mol% SDMF were synthesized in our previous study [5, 6]. The resulting PBS ionomers are denoted as follows: e.g., PBS1i represents PBS ionomer containing 1.0 mol% SDMF. The reaction route and structure of the PBS ionomer are shown in Fig. 1.

PBS ionomer/hydroxyapatite composites fabrication

PBSi/HAp composites were fabricated using a biomimetic methodology that involved immersing the polymers in simulated body fluid (SBF). The SBF solutions were prepared depending on references [19, 20]; NaCl, KCl, $MgCl_2$, $NaHCO_3$, K_2HPO_4, Na_2SO_4, and $CaCl_2$ were poured, in this order, into a 1000-mL volumetric flask that contained the nominated amount of 0.4 mol Tris $[(CH_2OH)_3CNH_2]$ solution, 90% of the corresponding tabulated amount of 0.36 M HCl solution, and 800 mL of distilled water. The remainder of the HCl solution and 200 mL of distilled water were added dropwise to obtain a pH of 7.4 while stirring gently. The final SBF product was a transparent solution. Films of PBS and its ionomers measuring 3 cm × 3 cm × 0.25 mm were immersed in the SBF solution and maintained at body temperature 36.5 °C in an incubator for immersion times of 10, 20, 40, 80, 160, or 320 h. Then, the saturated films were removed and washed with distilled water. Each sample was dried and kept at 40 °C in an oven while awaiting further analyses.

Measurement

The structure of PBS and its ionomers were determined using wide-angle X-ray diffraction (WAXD) with a Rigaku Denki D-Max2000 X-ray diffractometer operated at 40 kV, 100 mA. The X-ray source consisted of an 18-kW rotating anode X-ray generator equipped with a rotating anode Cu target. The X-ray diffraction patterns of the powdered samples were recorded at room temperature over the range $2\theta = 5$–$40°$ at a scan speed of 5°/min. WAXD was also used to examine the HAp crystals grown on both PBS and

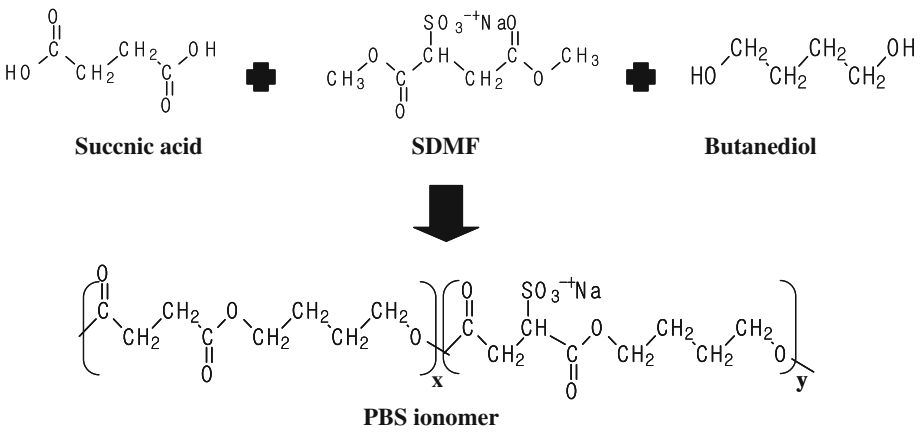

Fig. 1 The structure of PBS ionomer

its ionomers, but using film samples and a scan range of $2\theta = 10$–$60°$.

Thermogravimetric analysis (TGA) was used to determine on the dried samples to evaluate HAp content. The measurement was performed between 20 and 1000 °C at heating rate of 20 °C min^{-1} using a PYRIS TGA (Perkin–Elmer, Norwalk, CT, USA).

Fourier transform infrared (FT-IR) spectra were collected at room temperature on an IFS 88-IR spectrometer (Bruker AXS GmbH, Karlsruhe, Germany). The scanned wavenumber range was 4000–500 cm^{-1}. All spectra were recorded at a resolution of 4 cm^{-1} and 16 scans were co-added for each sample.

Scanning electron microscopy (SEM) of the PBS ionomer/HAp composite films was undertaken after drying the samples at room temperature under nitrogen. The samples were then Au–Pd coated by ion sputtering and examined by using field emission (FE) SEM (S-3000N, Hitachi).

Results and discussion

The crystal structure of PBS and its ionomers were investigated by WAXD patterns (data not shown). The pattern for pure PBS shows distinct peaks at 19.3, 21.7, 22.4, and 28.7°, which can be assigned to (020), (021), (110), and (111), respectively [21]. Regardless of ionic group content, no new peaks occur and there are no significant changes in the *d*-spacing, reflecting that the PBS ionomers have the same monoclinic crystal structure as pure PBS. This result may be attributed that the ionic unit in the PBS ionomer is excluded from the crystal regions of the butylene succinate sequence [4].

Figure 2a shows the magnified WAXD diffraction of PBS5i films immersed in SBF solutions for various times. In addition, the WAXD pattern of HAp, which was synthesized in our laboratory, is displayed on the right, where several unique peaks, reflective of HAp crystal, can be arranged. Especially, the most dominant HAp peak appears at 32°, which corresponds to the (211) plane of the hexagonal HAp crystal [22]. At initial SBF immersion time, no new peak is observed for the PBS5i. After immersing in SBF for 80 h, the new peak at 32°, the remarkable peak of HAp, can be detected. Besides, this peak gradually intensifies as the immersion time of the PBSi in SBF solution becomes longer. This result indicates that more HAp is formatted on the surface of PBS ionomer films in proportion to the immersion time. This result is consistent with the data of SEM (as shown in Fig. 3); at immersion time of 80 h, the formation of inorganic HAp particles was observed on the surface of PBSi films. As the immersion time increases, not only HAp particles grew with the larger

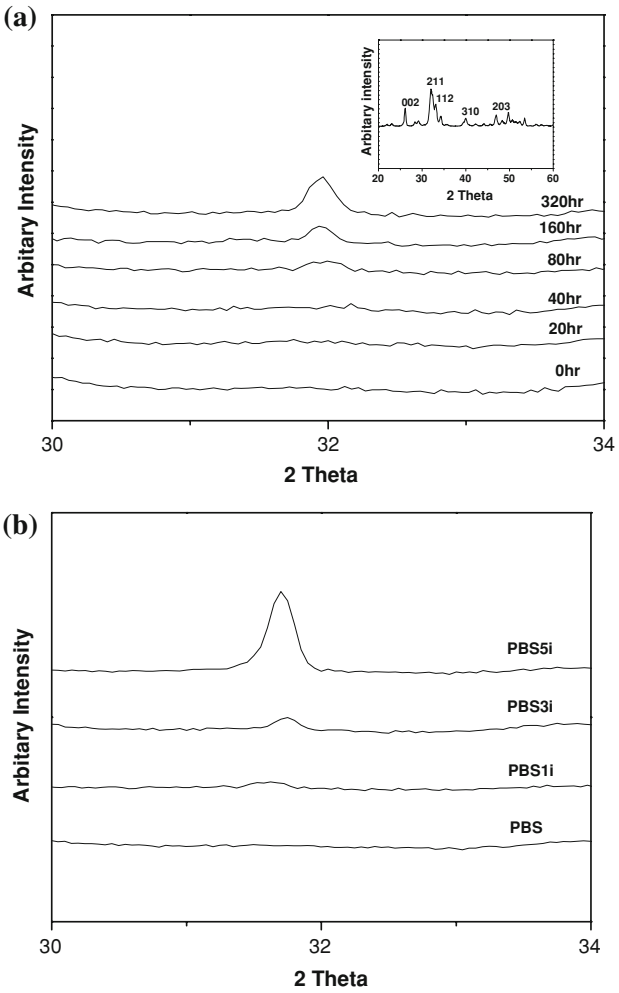

Fig. 2 **a** Wide-angle X-ray diffraction of PBS5i films immersed in SBF solutions for different intervals (*above right*: the X-ray diffraction of hydroxyapatite). **b** Wide-angle X-ray diffraction images of PBS and PBS ionomers immersed in SBF solutions for 320 h

size with sizes but also these particles were regularly dispersed. This result can be interpreted subsequently.

When the PBS ionomer was immersed in the SBF, it may release the positive Na^+ ions of $SO^{3-}Na^+$ ionic group into the surrounding fluid via exchange with H_3O^+ ions in the SBF fluid. As a result of this ion exchange, the PBS ionomer created $SO^{3-}H^+$ groups on its surface. In fact, as the immersion time increases, PBS ionomer liberated a large amount of Na^+ ion into the SBF, consequently generating a PH increase in the SBF fluid. These $SO^{3-}H^+$ groups immediately interacted with the calcium ions in the SBF fluid to form a calcium sulfonate. The calcium sulfonate thereafter incorporated the phosphate ions in the fluid to deposit the HAp on the surface of PBS ionomer. Here, the appearance of the calcium phosphate may be attributed to an electrostatic interaction between the positively charged calcium sulfonate and the negatively charged phosphate ions

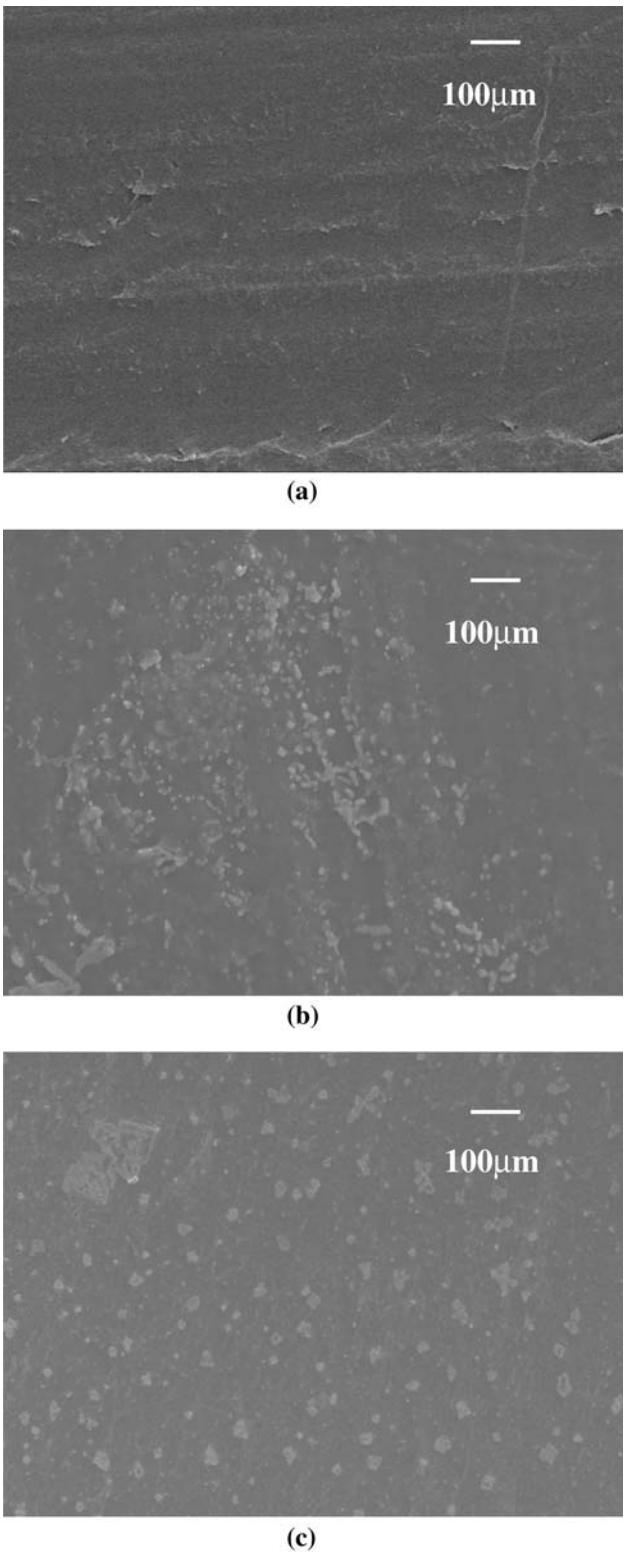

Fig. 3 SEM micrographs of PBS5i: **a** before SBF immersion, **b** after SBF immersion (80 h), and **c** after SBF immersion (320 h)

in the SBF. As the immersion time increases, HAp was shown to grow toward the outside of the PBS ionomer surface by continuously absorbing the calcium and phosphate

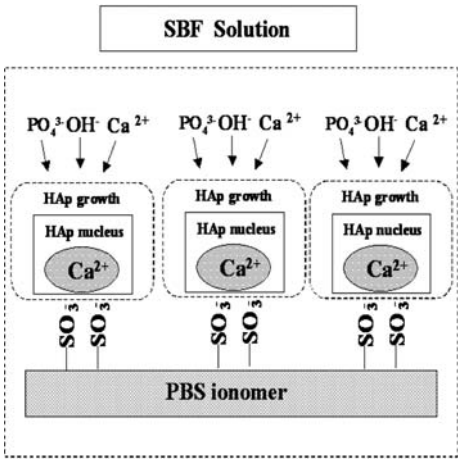

Fig. 4 Schematic illustration of the formation and growth of a HAp crystal on a PBS ionomer

ions in the SBF. As a result, it can be clearly summarized that the sodium sulfonate ionic group can play a main role in the formation of HAp crystalline on the surface of PBS ionomer. Furthermore, this observation is consistent with the work of Hiroaki et al., who investigated mechanism of biomineralization of HAp on a sodium silicate glass [23]. This mechanism is illustrated in Fig. 4.

Figure 2b displays the magnified WAXD images of PBS and its ionomers immersed in SBF solution for 320 h. As the ionic group concentration increases, the intensity of the characteristic HAp peak at about 32° also increases, proving that HAp crystal formation and growth is proportional to the ionic group concentration. This observation demonstrates that the added sodium sulfonate ionic groups operate as the functional groups with negative charge densities which can bind relatively plentiful Ca^{2+} ions in SBF solution, generating that not only contributes to enhance the interface bonding strength between HAp and PBS but also serve as active sites allowing HAp crystals to grow on the surfaces of the polymer matrix.

We also checked TGA curves of pure PBS and its ionomer immersed in SBF solution for 320 h, where pure PBS exhibits about 0.3% residual weight. With the increase of added ionic group mol%, the residual weight of PBS ionomer shows the higher value. The maximum extent may be observed for the PBS5i, where its value is about 2.5%. This result confirms that a large amount of inorganic HAp may remain with the increase of the sodium sulfonate ion groups, since there is little possibility that organic polymer molecules can be survived at very higher temperature (data not shown). Based on this finding, we can conclude that the sodium sulfonate ionic groups may take active part in the production of HAp crystalline, leading to the more deposition of HAp on the surface of PBS ionomer.

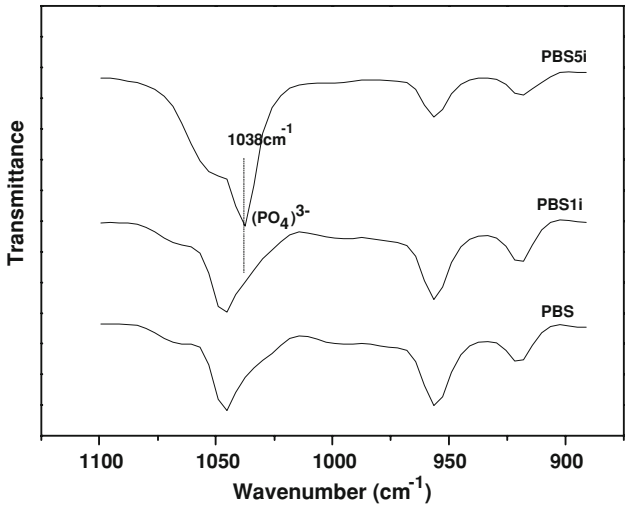

Fig. 5 FT-IR spectra of PBS and its ionomers after immersion in SBF solutions for 320 h

Figure 5 shows the FT-IR spectra of PBS and its ionomers following immersion in SBF solutions for 320 h. In PBS5i, the characteristic band of PO_4^{3-}, corresponding asymmetrical stretching [24, 25], can be apparently detected at 1038 cm^{-1} in comparison with pure PBS. This characteristic band as well as TGA curves may be powerful evidence that the sodium sulfonate ionic groups promote the creation and growth of HAp crystals and then much amount of HAp is formed on the surface of the PBS ionomers.

Figure 6 displays the SEM micrographs of PBSi films after SBF immersion (320 h). As for the PBS1i, the HAp crystal was successfully integrated into the matrix with no visible agglomerate formation at low particle amount. As the ionic group content grows richer, more and more HAp crystal deposits on the surface of PBSi. The reason for this phenomenon may be explained that large amount of sodium sulfonate ionic group interact favorably with the calcium ion and phosphate ion in the SBF solution, producing that the formation of HAp crystal may become easier. Additionally, in the SEM image of PBS5i, there are not only bulks of crystal deposits but also holes in the bulk of deposition. These holes are maybe very suitable for the ingrowths of the surrounding tissue and assist the bone formation. In summary, it can be clearly concluded that the ionic group in the PBSi may be decisive factors in growing HAp, and it is anticipated that this novel material can contribute to excellent biopolymer.

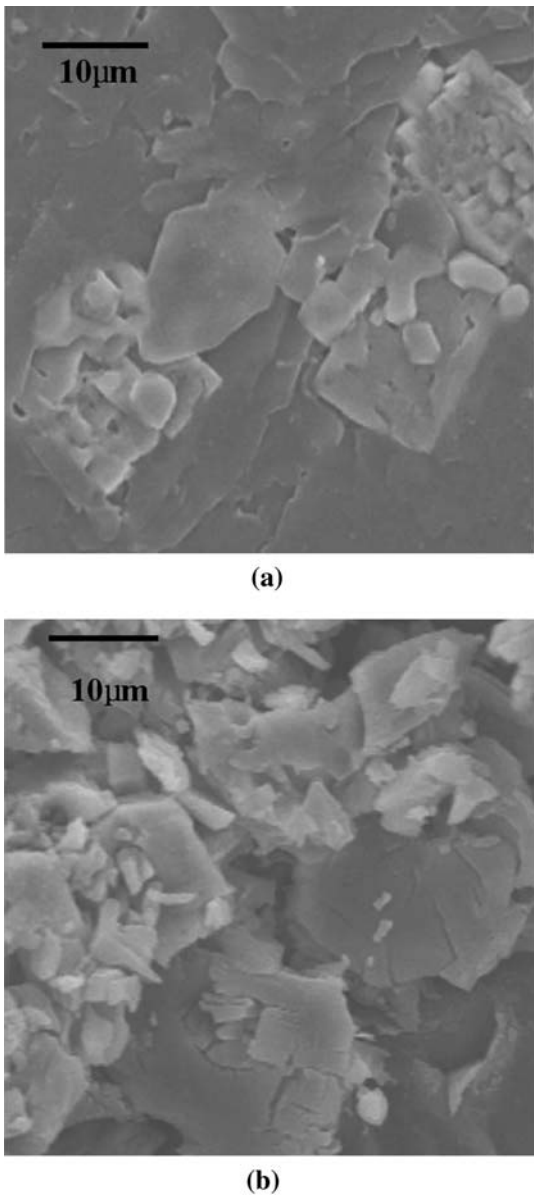

Fig. 6 SEM images of PBS ionomers after SBF immersion for 320 h: **a** PBS1i and **b** PBS5i

Conclusion

PBS-based ionomers (PBSi), incorporating the solfonated dimethyl fumarate (SDMF) with the sodium sulfonate ionic group, and hydoxyapatite (HAp) composites were fabricated by soaking in the SBF solution and we investigated the influence of ionic groups on the HAp crystal formation and growth. By WAXD, TGA and FT-IR analyses, relative to pure PBS, the biomimetic growth of HAp on the surface of PBS ionomer was remarkably increased and this ratio was predominated in proportion to the ionic group mol%. This demonstrated that the sulfonate groups, with the negative charge densities, interact favorably with the calcium ions and phosphate ions in the SBF solution, generating that the formation of HAp crystal may become more straightforward. The bulks of crystal deposits and holes, which were observed at PBS ionomer, may be anticipated

to be very satisfactory for the ingrowths of the surrounding tissue and the bone formation.

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