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# A novel poly(xylitol-co-dodecanedioate)/hydroxyapatite composite with shape-memory behaviour



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## ABSTRACT

A novel shape-memory polymer, poly(xylitol-co-dodecanedioate) (PXDD) was developed and the effect of hydroxyapatite (HA) in PXDD/HA composites on the chemical interactions, shape-memory and crystallization behaviours was studied. FTIR confirmed the formation of PXDD and also showed that the chemical structure did not change with the addition of HA. DSC and XRD revealed that the degree of crystallinity ( $X_c$ ) of PXDD/HA composites improved in parallel to increasing HA content. The permanent shape is recovered with a precision of almost 100% as soon as the recovery temperature ( $T_{rec}=48\text{ }^\circ\text{C}$ ) is reached. The findings of the study showed that PXDD/HA composites have great potential as shape-memory implant in minimal invasive surgeries.

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## 1. Introduction

Shape-memory polymers (SMPs) are a class of smart polymeric materials that can be deformed and subsequently fixed into a temporary shape, which would remain stable unless an appropriate external stimulus triggers the recovery to its permanent shape [1,2]. Although various forms of external stimuli may be utilized as a recovery trigger, the most typical one is direct heating. Despite the shape-memory trait which is vital for minimal invasive surgeries, SMP must also show a good combination of biocompatibility, tunable stiffness and defined shape deformation properties for its suitability in bone replacement applications [3]. Meanwhile, hydroxyapatite (HA) has been widely used as bone fillers and implant materials for many years due to their close resemblance with the mineral phase of natural bone [4,5]. The ability of HA to promote osteoconduction has enabled it to be used as bone defect filler, tissue engineering scaffolds, bone graft substitutes and also as bioactive coating on polymeric implants.

In the present study, a novel sugar alcohol-based SMP/HA composite aimed for bone replacement application was explored. Poly(xylitol-co-dodecanedioate)/hydroxyapatite (PXDD/HA) composites

were synthesized by reacting xylitol with 1,12-dodecanedioic acid in the presence of HA. The non-toxic xylitol offers good biocompatibility while the multifunctional monomer (1,12-dodecanedioic acid) is expected to provide more crosslinking sites to form network which will be advantageous in shape memory behaviour. The chemical interactions, shape memory and crystallization behaviours of PXDD/HA composites with various HA contents were studied.

## 2. Materials and methodology

*Synthesis of poly(xylitol-co-dodecanedioate)/hydroxyapatite (PXDD/HA) composites:* All chemicals were obtained from Sigma-Aldrich (Milwaukee, WI). Xylitol and 1,12-dodecanedioic acid were melted simultaneously in equimolar amounts at 165 °C in a 500 mL reaction flask purged with nitrogen. Hydroxyapatite (HA) powder (10, 15, and 20 wt%) was added to the molten mixture. Then, the temperature of water bath was slowly lowered to 155 °C followed by vigorous stirring at 250–300 rpm for 5 h to obtain prepolymer/HA composites. The product was then casted on a preheated Teflon mould and was afterwards cured for 48 h at 140 °C. The designation of 90/10 is denoted to the matrix consisting 90 wt% of poly(xylitol-co-dodecanedioate) (PXDD) and 10 wt% of HA, similarly here in after for PXDD/HA composites with 15 and 20 wt% of HA.

*Characterizations and testing:* Fourier transform infra-red (FTIR) spectra of PXDD/HA composites were obtained with a Spectrum

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One IR Spectrometer (Perkin-Elmer). Heating and cooling behaviours were determined under nitrogen atmosphere with heating and cooling rates  $10\text{ }^{\circ}\text{C min}^{-1}$  using a differential scanning calorimeter (DSC) 820 (Mettler Toledo). X-ray diffraction (XRD) analysis was conducted using a Rigaku Diffractometer using Cu  $K\alpha$  radiation ( $\lambda=1.54\text{ \AA}$ ) with accelerating voltage of 40 kV and current of 30 mA, from  $2\theta=5\text{--}60^{\circ}$  with step size of  $0.02^{\circ}$  at  $20\text{ }^{\circ}\text{C}$ . The crystallinity percentage ( $X_c$ ) was calculated from X-ray diffraction (XRD) method according to Guo et al. [6]. Shape-memory properties were quantified by determination of recovery angles from bending test [7–9].

### 3. Results and discussion

FTIR spectra of cured PXDD/HA composites and neat HA are shown in Fig. 1. FTIR spectra of the cured PXDD/HA composites show the presence of ester bond with the appearance of C=O (ester) stretching band at  $\sim 1750\text{ cm}^{-1}$  corresponding to ester linkages. A bond stretch was also observed at  $\sim 3450\text{ cm}^{-1}$  owing to the presence of hydrogen bonded hydroxyl groups. It can be observed that the PXDD/HA spectra do not change with increasing HA content. This indicates that HA has no influence on the functional groups of PXDD. Similar FTIR spectra of polyesters were reported in the literature [10–12].

The DSC heating and cooling curves of PXDD/HA composites are shown in Fig. 2. The presence of HA did not alter the melting point ( $T_m$ ) at  $\sim 55\text{ }^{\circ}\text{C}$ , which suggests that there is no chemical interaction between PXDD matrix and HA particles [13]. However, a slight increase of crystallization temperature ( $T_c$ ) with increasing HA content was observed with values of  $42\text{ }^{\circ}\text{C}$  for 10 wt% HA,  $44\text{ }^{\circ}\text{C}$  for 15 wt% HA, and  $45\text{ }^{\circ}\text{C}$  for 20 wt% HA (Table 1). This implies that HA particles may provide nucleation sites for PXDD chain segments to be able to crystallize at a higher temperature when PXDD/HA composites were cooled down from amorphous state [13]. Melting enthalpies ( $H_m$ ) of PXDD/HA composites were found increasing with HA content, which indicates the increasing crystallinity [14].

Fig. 3 displays the XRD curves of neat HA and PXDD/HA composites. The PXDD/HA curves show peaks with small ripples and a relatively sharp peak centred at  $2\theta=22^{\circ}$ , which reveals its semicrystalline nature [15]. This peak corresponds to (100) refraction signal. The crystallinity ( $X_c$ ) of PXDD/HA composites was seen to increase with increasing HA content with values of  $X_c$  increased to 21.9%, 22.6%, and 24.1% for 10, 15 and 20 wt% HA, respectively.

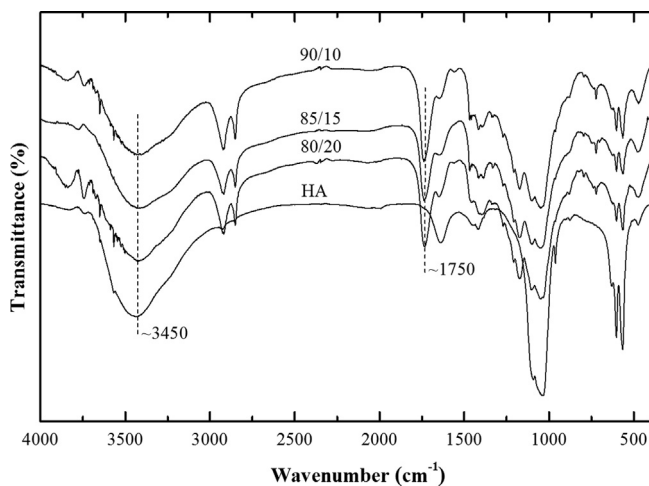


Fig. 1. FTIR spectra of neat HA and PXDD/HA composites.

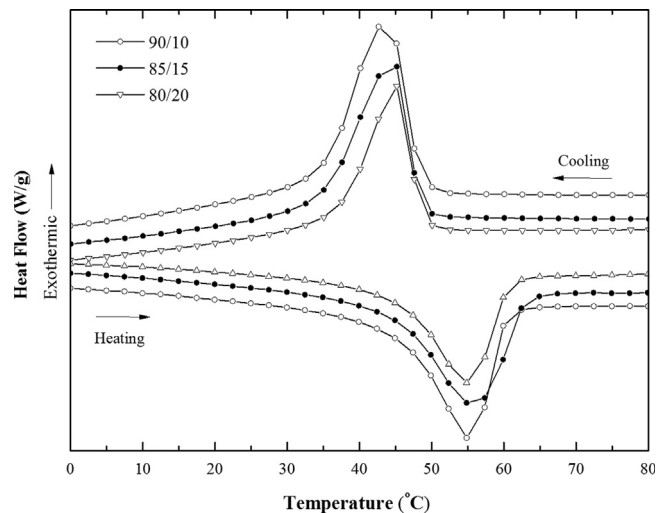


Fig. 2. DSC heating and cooling curves of PXDD/HA composites.

Table 1  
Characterization of PXDD/HA composites.

PXDD/HA	$R_f$ (%)	$R_r$ (%)	$T_c$ ( $^{\circ}\text{C}$ )	$T_m$ ( $^{\circ}\text{C}$ )	$H_m$ (J/g)	$X_c$ (%)
90/10	$\sim 97$	$\sim 100$	42	55	37.7	21.9
85/15	$\sim 99$	$\sim 100$	44	55	38.5	22.6
80/20	$\sim 100$	$\sim 100$	45	55	39.8	24.1

The designation of 90/10 is denoted to the matrix consisting 90 wt% of poly(xylitol-co-dodecanedioate) (PXDD) and 10 wt% of HA, similarly here in after for PXDD/HA composites with 15 and 20 wt% of HA.

Shape fixity ( $R_f$ ), shape recovery ( $R_r$ ), crystallization temperature ( $T_c$ ), melting temperature ( $T_m$ ), melting enthalpy ( $H_m$ ), crystallinity calculated from the XRD method ( $X_c$ ).

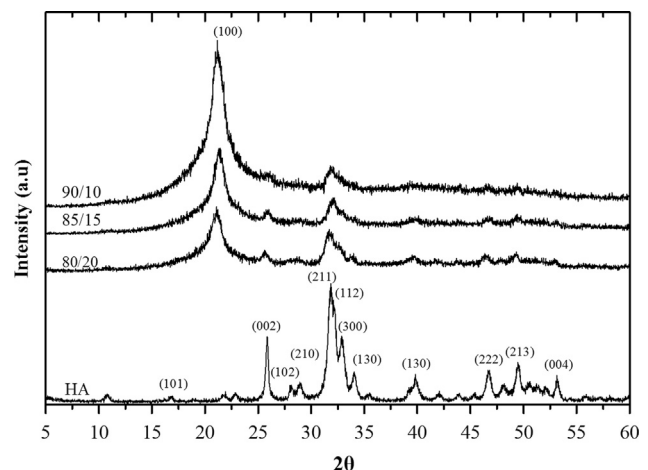


Fig. 3. XRD of neat HA and PXDD/HA composites.

The observation is in accordance with the findings of increasing  $T_c$  values from the DSC measurement (Fig. 2), which indicates the role of HA as a nucleating agent. The increasing  $X_c$  plays a positive role in improving the dimension stability of the desired temporary shape [6,16]. Besides, the position of diffraction peaks (attributed to HA and PXDD matrix) was found slightly shifted as compared among PXDD/HA composites, which suggests the formation of hydrogen bonding between PXDD matrix and HA [17].

It is worth to note that a shape-memory behaviour is detected during the temperature study of PXDD/HA composites. Table 1

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