Songklanakarin J. Sci. Technol.
35 (1), 57-61, Jan. - Feb. 2013

SJST SONGKLANAKARIN JOURNAL OF SCIENCE AND TECHNOLOGY
http://www.sjst.psu.ac.th

Original Article

Mechanical and thermal properties of biodegradable hydroxyapatite/ poly(sorbitol sebacate malate) composites

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Received 16 December 2011; Accepted 29 October 2012

Abstract

In this project, novel hydroxyapatite (HAp)/poly(sorbitol sebacate malate) (PSSM) composites for potential application in soft tissue engineering were developed. The composites consist of the biodegradable polyester prepared from sorbitol, sebacic acid, malic acid and various amount of HAp (5, 10, and 15 wt%). Effects of different weight percents of HAp on the properties of the composites were studied. Fourier transform infrared spectroscopy was performed to analyze chemical interactions between HAp/PSSM. Tensile tests and differential scanning calorimetry were conducted to evaluate the mechanical and thermal properties of HAp/PSSM composites. Tensile testing on HAp/PSSM composites showed that their mechanical properties improved with increasing concentration of HAp. The Young's modulus and tensile strength of the composites ranged from 16.20±1.73 to 23.96±2.56 MPa and 626.96±81.04 to 1,026.46±105.12 MPa, respectively. The glass transition temperature of all samples was slightly higher than room temperature.

Keywords: biodegradable, composites, hydroxyapatite, mechanical properties, tissue engineering

1. Introduction

Synthetic biodegradable polymers as biomaterials have been one of the research focuses in the last decade. Biodegradable polymers offer advantages over ceramic- and metallic-based biomaterials as they can be manipulated to exhibit a wide range of mechanical, degradational, and physiochemical properties (Pasupuleti *et al.*, 2011). In particular, biodegradable aliphatic polyesters have recently received attention for their potential use in biomedical applications due to their degradability and biocompatibility (Gunatillake *et al.*, 2003). Aliphatic polyesters can be synthesized from monomers endogenous to human metabolism and on the other hand, they degrade via hydrolysis in aqueous medium into non-toxic carboxylic acid and hydroxyl group short chain oligomers or monomers (Gunatillake *et al.*, 2003).

Hydroxyapatite (HAp) ($Ca_{10}(PO_4)_6(OH)_2$), which is a form of calcium phosphate has been widely investigated for both dental and orthopedic applications due to their outstanding biocompatibility and osteoconduction (Nejati *et al.*, 2008, Jayabalan *et al.*, 2010, Sadat-Shojai *et al.,* 2010). However, the brittleness of calcium phosphate and formation of microcracks induced during harsh processing conditions limited the application of hydroxyapatite to non-load bearing parts of the skeleton (Burdick *et al.*, 2011, Chung *et al.*, 2011). In order to overcome these limitations, many research groups have combined biodegradable polyesters with HAp to form composites (Rizzi *et al.*, 2001; Sharifi *et al.*, 2011). Until now, HAp has been incorporated with synthetic polymers such as poly(L-lactide) and poly(lactic-co-glycolide) (Zhang *et al.*, 1999; Russias *et al.*, 2006), poly(e-caprolactone) (PCL) (Choi *et al.*, 2004), polyhydroxyalkanoates (Misra *et al.*, 2006), poly

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(1,8-octanediol citrate) (Chung *et al.*, 2011, Qiu *et al.*, 2006), and poly((1,2-propanediol-sebacate)-citrate) (Lei *et al.*, 2009). Findings have shown that under certain conditions, incorporation of HAp particles can improve the mechanical properties of the polyesters.

Bruggeman *et al.* (2008) has recently described the synthesis and characterization of a biodegradable polyester elastomers without the present of catalysts or solvent, referred to as poly(sorbitol sebacate) (PSS), for soft tissue engineering applications. The mechanical properties and degradation rates of these elastomers can be altered by varying the type of polyols and the synthesis conditions. Furthermore, the synthesis method for PSS is very simple and does not require expensive raw materials. However, PSS exhibited low tensile strength and modulus, which limit their applications where higher load-bearing is required (Bruggeman *et al.*, 2008). In order to improve the mechanical properties of PSS, multifunctional monomer such as citric acid or tartaric acid has been incorporated to act as secondary crosslink agent. The resulting polyesters, poly(sorbitol citrate sebacate) (PSCS) and poly(sorbitol tartarate sebacate) (PSTS) showed significant improvements in the mechanical properties (Pasupuleti *et al.*, 2011).

Herein, we report the synthesis and characterization of hydroxyapatite/poly(sorbitol sebacate malate) (HAp/PSSM) composites. The monomers, including sorbitol (Bruggeman *et al.*, 2008) and sebacic acid (Wang *et al.*, 2002), are endogenous to human metabolism and polyester based on malic acid (Wan *et al.*, 2007) and were found to be biocompatible. The preparation of the composites was carried out by catalyst-free polycondensation, which can avoid the toxicity induced by catalyst or initiator during polymerization reaction that would reduce the biocompatibility of the composites. We hypothesized that the mechanical properties of PSS can also be improved after adding a multifunctional monomer, malic acid into the polymer. Moreover, the incorporation of hydroxyapatite is expected to further increase the mechanical properties of the composites. The tensile and thermal properties of the composites were evaluated.

2. Research Methodology

2.1 Synthesis and characterization of HAp/PSSM composites

Sorbitol (S), sebacic acid (SA), and hydroxyapatite (HAp) were purchased from Sigma Aldrich (Malaysia). Malic acid (MA) was purchased from R & M Chemicals (Malaysia) and tetrahydrofuran (analytical grade) was purchased from Merck (Malaysia). All chemicals were used as received. The synthesis of HAp/PSSM composites was adapted from a technique that has previously been described (Qiu *et al.*, 2006; Lei *et al.*, 2009). Briefly, equimolar amounts of the polyol and diacids (S:SA:MA = 1:1:1) were mixed with various amount of HA (5, 10, 15 wt%) in a reaction flask. The mixture was melted under stirring at 150-155°C under a constant flow of nitrogen gas. Following melting, the reaction was continued for 1 hr to create the PSSM prepolymer with HAp. The prepolymer was cast into PTFE mold with ~1 mm thickness and kept in an oven at 110°C for 2 days for post-curing to obtain HAp/PSSM composites. The composites with 0, 5, 10 and 15 wt% of HAp were named as C0, C5, C10, and C15, respectively.

2.2 Characterization of HAp/PSSM composites

Fourier transform infrared (FTIR) spectroscopy was carried out on a Perkin Elmer Spectrum One spectrometer (UTM, Malaysia) to analyze the chemical bonds of prepolymers and the composites. The samples were scanned in spectrometer over the range of 4,000-600 cm^{-1}. The glass transition temperatures (Tg) of cured composites were characterized using a differential scanning calorimeter (Mettler-Toledo DSC822^e/400, SIRIM, Malaysia) operating in nitrogen atmosphere. The samples were heated from -50°C to 200°C at 10 °C/min, cooled from 200°C to -50°C at 10°C/min and subsequently heated for second cycle up to 200°C at 10°C/min.

The sol contents (low molecular weight of polyesters that can be dissolved in tetrahydrofuran) and the swelling degrees of the composites were simultaneously tested from the following methods (Liu *et al.*, 2009a; 2009b). Small square samples (1 cm x 1 cm with 1 mm in thickness) were weighted (W_1) and soaked in tetrahydrofuran (20 mL). Samples were taken out 24 hrs, the solvents on its surface were absorbed using filter papers and the weights W_2 were recorded. Then the sample was dried completely to the final weight of W_3 in an oven. Sol content was calculated as $S=(W_1-W_3)/W_1 x100$, and swelling degree was reported as $Q=(W_2-W_3)/W_3 x100$. Average values were taken from three samples for each composite.

Tensile test was conducted at room temperature on Lloyd tensile LRX testing machine (UTM, Malaysia) equipped with 2.5 kN load cell. Briefly, the dumbbell-shaped samples according to ASTM standard D638 (26x4x1.5 mm, length x width x thickness) were prepared and pulled at a rate of 50 mm/min. For all composites, five specimens were tested and the values were averaged.

3. Results and Discussion

3.1 Characterization of chemical structure

The aliphatic polyester, PSSM and HAp/PSSM composites were successfully prepared via polycondensation without the presence of catalyst and the reaction scheme for PSSM was shown in Figure 1. The prepolymers and composites of HAp/PSSM were characterized by FTIR. Figure 2 shows the FTIR spectra for HAp, prepolymer C0, prepolymer C5, prepolymer C10, and prepolymer C15, while the spectra for C0, C5, C10 and C15 were shown in Figure 3. The peaks corresponding to the HAp structure include the broad peaks at 1,091 cm^{-1} and 1,039 cm^{-1} were assigned to vibration of

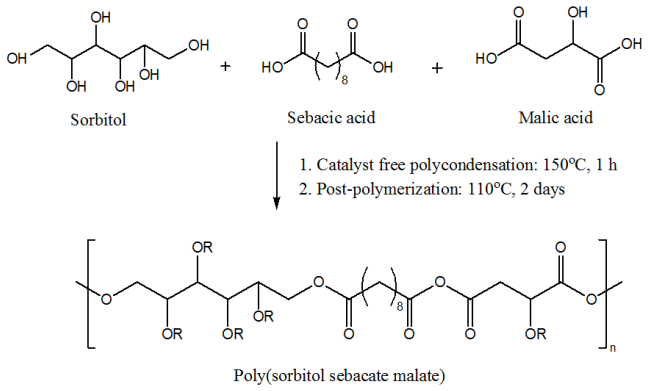

Figure 1. Synthesis of poly(sorbitol sebacate malate) polymer.

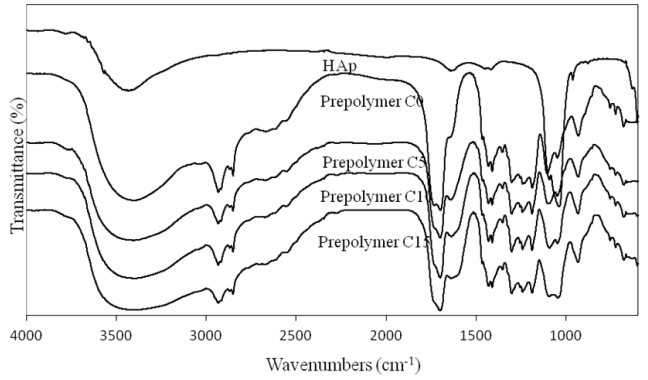

Figure 2. FTIR spectra for HAp, prepolymer C0, prepolymer C5, prepolymer C10, and prepolymer C15.

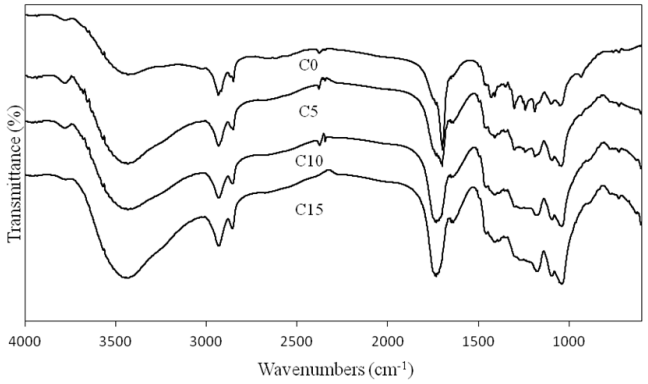

Figure 3. FTIR spectra for C0, C5, C10, and C15.

phosphate group, the peaks at 1,629 and 3,435 cm^{-1} were corresponded to the hydroxyl group in the adsorbed water, while the double peak at 1,414 and 1,448 cm^{-1} was attributed to the carbonated impurities in the structure of HAp (Rehman *et al.*, 1997, Sadat-Shojai *et al.*, 2010). The intense peak within 1,695-1,740 cm^{-1} in the spectrums of prepolymers and composites were assigned to carbonyl (C=O) groups, which proves the presence of ester bonds and carboxylic groups. The carbonyl peak in the composite spectra are sharper compare to the prepolymer spectra, this demonstrated that most of the diacids monomers have reacted to form polyester. Also, there is a small shift to the right (1,730 cm^{-1}) in the carbonyl peak of C5, C10, and C15 compared to sample C0. These changes may be attributed to the formation of hydrogen bonding between C=O groups of PSSM and the surface hydroxyl (–OH) group of HAp. The peaks at 2,931 and 2,850 cm^{-1} were assigned to the methyl groups. The broad peak at 3,450 cm^{-1} in the spectrums of prepolymers should be assigned to hydroxyl groups on the unreacted monomers, terminal hydroxyl groups in the PSSM matrix and the hydroxyl groups on the surface of HAp. On the other hand, the stretches observed in the composite spectra at 3,450 cm^{-1} should be attributed to hydrogen bonded hydroxyl groups and unreacted hydroxyl groups remained in the polyester molecular chains (originating from monomers with multifunctional groups).

3.2 Glass transition of HAp/PSSM

The thermal data for the composites were listed in Table 1. The glass transition temperature (Tg) for HAp/PSSM composites ranged from 39.83 to 42.61°C. The values indicate that the composites are stiff at room temperature. Glass transition temperature usually reflects the ability of polymer chains to move freely which are normally affected by chemical crosslinking, hydrogen bonding, and physical interaction between polymer matrix and HAp particles. Herein, increasing HAp loading cause the Tg of the composites to become higher. The presence of HAp particle in the PSSM hindered the formation of random crosslink network in the matrix, which will lower the Tg; In contrast, the presence of malic acid as secondary crosslink agent and HAp particles will also hindered the mobility of the polymer chains, which could increase the Tg (Lei *et al.*, 2009). In this situation, the effect of the low mobility of the polymer chains predominates and

Table 1. Mechanical and thermal properties of HAp/PSSM composites.

Sample	Tensile strength at yield (MPa)	Tensile Modulus (MPa)	Elongation at break (%)	Tg (°C)
C0	16.20 ± 1.73	626.96 ± 81.04	49.04 ± 4.30	39.83
C5	19.74 ± 1.71	710.56 ± 100.34	36.06 ± 6.70	40.71
C10	22.13 ± 4.73	875.42 ± 157.58	27.04 ± 3.50	41.47
C15	23.96 ± 2.56	1026.46 ± 105.12	10.10 ± 2.10	42.61

thus, the glass transition temperature increased.

3.3 Sol contents and swelling degrees of HAp/PSSM composites

The results from swelling tests showed that the composites were composed of the sols (can be dissolved in tetrahydrofuran) and the gels (cannot be dissolved in tetrahydrofuran). A small part of sols which can be dissolved in some solvents often appeared in polyester matrix, and these sols usually act as plasticizers and contribute to the formation of hydrogen bonding (Liu *et al.*, 2009a). Generally, high sol content indirectly means lower polymerization degree and crosslink density. Listed in Table 2, the sol contents and swelling degrees ranged from 10.05 to 14.25% and 81.99 to 127%, respectively. The swelling degrees decreased with an increase of the HAp weight percent, mainly because of the volume effect of the increased HAp particles and more physical adsorptions. The sol content of composites C5 and C10 was slightly higher than C0 (pure PSSM polymer). This may be due to many sols enclosed by the HAp particles. This hindered the curing of low molecular weight polymer chain cured into the polyester network. This is in agreement with previous finding reported by Liu *et al.* (2009a).

3.4 Mechanical properties

Figure 4 and Table 1.show the tensile stress-strain curves and test results for HA composites containing 0, 5, 10, and 15 wt%, respectively. Previously, PSS elastomer reported by Bruggeman *et al*. (2008) exhibited Young's modulus, tensile strength, and ultimate elongation of 0.37 MPa, 0.57 MPa, and 192%, respectively. When malic acid was added as a secondary crosslink agent to form PSSM, the mechanical properties of the polymer increase significantly. PSSM polymers achieved a Young's modulus of 626.96 MPa, a tensile strength of 16.20 MPa, and an elongation at break of 49.04%. Malic acid reacted with free hydroxyl group in sorbitol to form polyester chains and random crosslinking within the polymer network which result in a higher degree of crosslinking and thus, a stiffer thermoset was obtained.

Table 2. Sol content (S) and swelling degree (Q) of the composites with different weight percents of Hap.

HAp (wt%)	Q (%)	S (%)
0	127.72	12.29
5	123.07	14.25
10	100.04	13.24
15	81.99	10.05

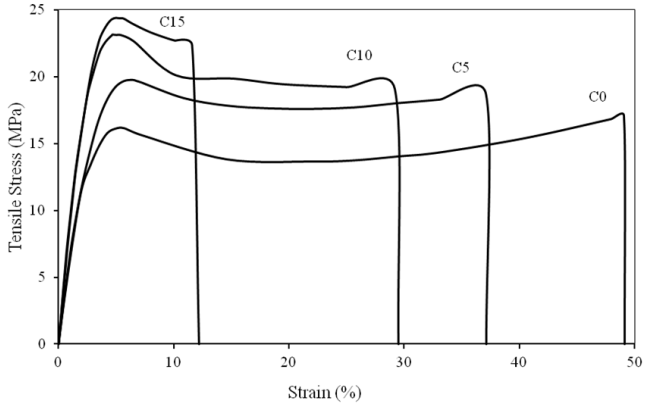

Figure 4. Typical tensile stress versus strain curves for composites (C0, C5, C10, and C15).

The tensile strength and modulus of the composites increased gradually with an increase of the HAp loading, ranged from 16.20 to 23.96 MPa and 626.96 to 1,026.46 MPa, respectively. Meanwhile, the presence of HAp reduced the flexibility of the composites as the elongation at break decreased from 49.04 to 10.10% when the HAp content increased from 0 to 15 wt%. From the result, it was obvious that the mechanical properties of the polymer after incorporation of malic and HAp particles has increase and can cover many biomedical applications. The high stiffness allows that HAp/PSSM could be used in bone tissue engineering, such as repairs/replacements for cartilage (0.7-15.3 MPa), ligament (65-541 MPa), tendon (143-2,310 MPa), and cancellous bone (50-500 MPa) (Burdick *et al.*, 2011). It is also possible to tune the mechanical properties of the composites by varying the reaction time and temperature, monomer feed ratio, particle size of HAp and choice of diol and/or diacids.

4. Conclusion

The HAp/PSSM composites were successfully developed in this project. All these raw materials, such as, sorbitol, sebacic acid, malic acid and hydroxyapatite are biocompatible to the human body. The preparation of the composites is relatively simple as it does not involve the use of harsh solvents and catalysts. The incorporation of HAp particle improved the mechanical properties of PSSM polymers.

Acknowledgement

This work is supported by Universiti Teknologi Malaysia (UTM) and funded by Ministry of Science, Technology and Innovation for E-Science grant (Vote No: 79400). All financial supports are highly grateful.

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