

## Preparation and Characterization of PolyLactide-Hydroxyapatite Biocomposites

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**Abstract.** In the present study, the preparation and characterization of polylactide-Hydroxyapatite(HA) composite films for biomedical applications have been studied. The effects of number of parameters such as polymer type, HA loading, surface modification and its concentration on the mechanical and microstructural properties of the composites were investigated. Poly-L-Lactide and 96/4 Poly(L-Lactide co D-Lactide) copolymer-HA composites containing 10-40 wt % HA particles have been prepared by solvent casting technique. The HA powder was synthesized by precipitation technique. Interfacial interactions between HA and polylactide polymer were modified to improve filler compatibility and mechanical properties of the composites by surface treatment of the HA with two different silane coupling agents; 3-aminopropyltriethoxysilane (AMPTES) and 3-mercaptopropyltrimethoxysilane (MPTMS) at three different concentrations(0.5-2 wt%).

Silane treatment indicated improvements in the mechanical properties of the composites compared to the untreated HA loaded polylactide composites. Tensile test results showed that the maximum improvement in the mechanical properties of the composites was obtained for PLA composites containing 1 wt% aminofunctional silane treated HA and 0.5-wt % mercaptopropyltrimethoxy silane treated HA for PDLA composites. Scanning electron microscopy studies also revealed better dispersion of silane treated HA particles in the polymer matrix.

### Introduction

Bioabsorbable devices for load bearing applications, based on bioabsorbable polymer or composites can overcome some problems associated with metallic implants or devices applied in orthopaedics (1). These devices made of biodegradable polymers such as poly (L-lactide), poly (L-lactide co DL Lactide) copolymers are already in clinical use for the last twenty years [1-2]. Mechanical properties of these polymers gradually reduce as they degrade, allowing loads to be transferred to the bone, therefore reducing stress shield effect. Although they have many advantages over metallic implants, the major drawn back of such resorbable polymers is that they have weak mechanical properties especially for the load bearing applications [3]. Recently hydroxyapatite (HA) reinforced polylactide based composites have attracted great attention due to the favourable characteristics of HA which is expected to confer a bone bonding behaviour and to improve mechanical properties of these composites [4-5].

Many researchers have examined the preparation and characterization of hydroxyapatite/PLA composites in the last two decades [4-6]. In spite of the promising results obtained so far, nobody has studied the improvement of the interfacial interaction and adhesion between polylactide polymer and HA filler. The interaction and adhesion between filler and polymer matrix have a significant effect on the properties of the particulate filled reinforced materials, being essential to transfer the load between two phases and thus improve the mechanical properties. To improve the mechanical properties, it is necessary to render the surface of the filler and the polymer compatible, which can be achieved using several types of surface coupling agents. In the literature, there are many studies dealing with the characterization of interfaces and their influence on the mechanical

properties of particulate filled composites. The studies on the effects of silane coupling agents indicate that surface treatment of the fillers with silane coupling agents provide the improvement in the interfacial and mechanical properties of filled polymer composites considerably [7-9].

The objective of this study was, therefore, to prepare and characterize Poly(lactide-HA) biocomposites for biomedical applications. The effects of a number of parameters such as polymer types, HA loading, surface modification of HA and their concentrations on the mechanical and microstructural properties of the poly(lactide) based -HA composites have been studied.

### Materials and Methods

**Materials:** Poly (L-Lactide ) (PLA) and 96/4 L-Lactide/D-Lactide copolymer (PDLA) were purchased from PURAC Biochem with the inherent viscosities 1.75 and 5.68 dl/g, respectively. These polymers were used without further purification. Hydroxyapatite powders (HA) were synthesized by the precipitation technique using starting materials of  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  and  $(\text{NH}_4)_2\text{HPO}_4 \cdot \text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  in our laboratory . The average particle size of hydroxyapatite was found as 0.28  $\mu\text{m}$  using particle size analyser. Chloroform was used as a solvent for the preparation of polymer solutions. Two different silane-coupling agents were used for the surface modification of Hydroxyapatite particles. These agents were (3-aminopropyl) triethoxysilane (AMPTES) (Fluka) and (3 Mercaptopropyl trimethoxysilane) (MPTMS) (Merck).

**Surface Modification of Hydroxyapatite:** Silane coupling agents were applied from an aqueous ethanol solution to ensure a uniform coverage of the HA surface,. HA powder was added to a solution of silane coupling agent (0.5, 1, and 2 wt %) in aqueous ethanol solution (90 v %). HA to solution ratio was taken as 1:2 on weight/volume basis. Hydrolysis reaction was carried out by stirring silane ethanol solution. The slurry was stirred for 1 h by magnetic stirrer and then kept for 2 hrs at room temperature for treatment of the HA with hydrolysed solution to improve the stability of the coating. The resulting slurry was dried at 100-120  $^{\circ}\text{C}$  subsequently to form silanol structure. The powder was then stored in a desiccator until use.

**Preparation of Poly(lactide-HA) Composites:** The poly (L-Lactide) (PLA) and poly (L-Lactide-co-D-Lactide) (PDLA) composites containing 10 to 40 wt % untreated and treated hydroxyapatite were prepared using solvent casting technique. In this technique, chloroform was used as a solvent to prepare polymer solution. PLA/ solvent ratio and PDLA / solvent ratio were in the range of 5-10 % (w/v) and 3-7 % (w/v), respectively. HA powders were dispersed in chloroform in ultrasonic bath for 1 hr and then, PLA or PDLA were added to the solution. The HA / solvent / PLA or PDLA mixture was stirred for 12 hrs on the magnetic stirrer until HA was totally dispersed in the solution. The resulting mixture was then poured on glass surface using a film applicator. It was dried overnight at room temperature, then finally dried under vacuum oven at 40  $^{\circ}\text{C}$  for 3 h. The dried films were gently removed from the glass surface and stored in a desiccator.

**Characterization:** Tensile tests on Poly(lactide-HA) composites containing 10, 20, 30, and 40 wt % untreated and treated hydroxyapatite were performed with Testometric Universal Testing Machine with a 5 kgf load cell, a crosshead speed at 10 mm/min and a gauge length of 50 mm. Tensile tests were carried out at room temperature. Tensile test specimens were prepared as strips 10 mm in width according to ASTM D-882. At least three specimens were tested for each composite film and the mean values were reported on the basis of the three specimens.

Scanning electron microscopy (SEM) was used to examine the morphology of poly(lactide-HA) composites. Surface microscopy of the composites loaded with untreated and treated HA and fracture surfaces of tensile tested composites were observed with a Philips XL-30S FEG scanning electron microscope (SEM). Samples were coated with gold.

## Results and Discussion

Tensile tests of Poly(L-Lactide) and Poly (D-Lactide-L-Lactide) copolymer composites filled with the untreated and treated hydroxyapatite (10, 20, 30, and 40 wt %) were conducted to determine the effects of surface modifiers (AMPTES and MPTMS) and their concentrations, polymer types and HA loading on mechanical properties. The effects of untreated HA content and polymer type on Young Modulus (Elastic Modulus) of PLA-HA composites were studied. Young's Modulus clearly had a positive correlation with the mixing ratio of composites. Thus, Young's Modulus of the composites depends on the loading of HA. In this study, Young's Modulus of the composites increased as HA content increases except at the 40 wt % HA loading. Young Modulus of PLA and its composites are found to be significantly higher than that of PDLA. This is again due to the fact that PLA is a semi crystalline polymer and its mechanical strength should be higher compared to the amorphous PDLA polymer as expected. Figure 1(a) shows the effect of surface treatment concentration of the silane coupling agent on Young's Modulus of the both PLA and PDLA composites containing 20 wt % HA. Young's modulus of the composites was measured for three different types of silane concentrations, which were 0.5, 1, and 2 wt %. As seen in the figure, silane treatment leads to increase in Young Modulus due to the improvement of adhesion between polymer and filler and dispersion of filler in the polymer matrix. Although 1 wt % AMPTES coupling agent concentration shows maximum on Young Modulus of the PLA composites, 0.5 wt % MPTMS coupling agent concentration shows a maximum for the PDLA composites. For both composites, Young Modulus decreases with increasing silane concentration after the maximum point. This decrease could be due to the plasticizing effect of surface modifier. The maximum Young's Modulus values indicate the maximum strength of interaction between polylactide and hydroxyapatite. Therefore, 1 wt % AMPTES concentration was chosen for PLA composites, on the other hand, 0.5-wt % MPTMS coupling agent concentration for PDLA composites.

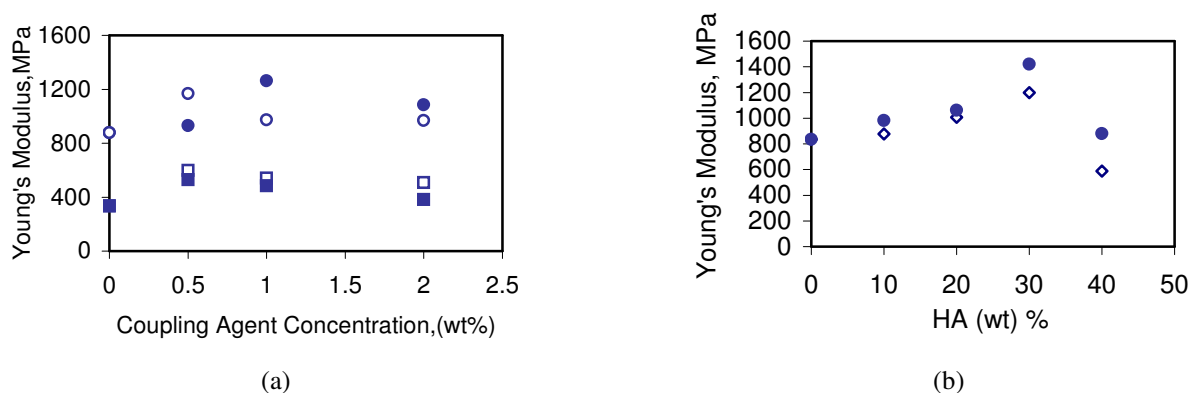


Figure 1. (a) Effect of Silane Coupling Agents Concentration on the Young's Modulus of PLA and PDLA Composites Containing 20 wt % HA. (■,●; Treated with AMPTES, □,○; Treated with MPTMS ) (b) Effect of Coupling Agent treatment on Young Modulus of PLA Composites with Respect to HA Content. (● Treated HA with AMPTES, ◇ Untreated HA)

Figure 1(b) show the Young's modulus of the PLA composites containing untreated and treated HA with 1 wt % AMPTES. The modulus of composites increased with increasing untreated and treated HA content up to 30-wt % and then decreased. This may be due to an increase in the agglomerate size with an increase in HA loading which could cause poor adhesion between polymer and HA. The adhesion between polymer-filler plays an important role on the improvement of mechanical properties. As seen in the figure, Young's Modulus of the PLA composites loaded with treated HA was greater than that loaded with untreated ones. This result indicated that a better dispersion HA into the polymer matrix and possibly enhancement of interfacial chemical bonding between hydroxyapatite and poly-L-Lactide or poly D,L-Lactide matrix were achieved by the treatment of HA with silane coupling agents. According to other mechanical test results; two important points

can be discussed. Yield stress of the composite decreases with an increase in HA content for both polymer types. Both coupling agent used at optimum concentration yielded a higher yield stresses compared to untreated ones. The percent elongation becomes much smaller in the composites with higher HA contents as expected due to the reduction in polymer matrix, which causes elongation in composites. Figure 2 (a) and (b) shows the SEM micrographs of PLA composites loaded with 20 wt % untreated and treated HA with 1 wt % AMPTES. A more homogeneous distribution of treated HA particles in the polymer matrix compared to the untreated HA particles, which had a maximum of 10  $\mu\text{m}$  agglomerate size in the polymer matrix can be seen from SEM images. However, some agglomeration and void formation was observed in composites containing larger volume fractions of HA. Although a more homogeneous distribution of HA was observed with silane treatment at microscopic level, the level of agglomeration increased with an increase in HA loading.

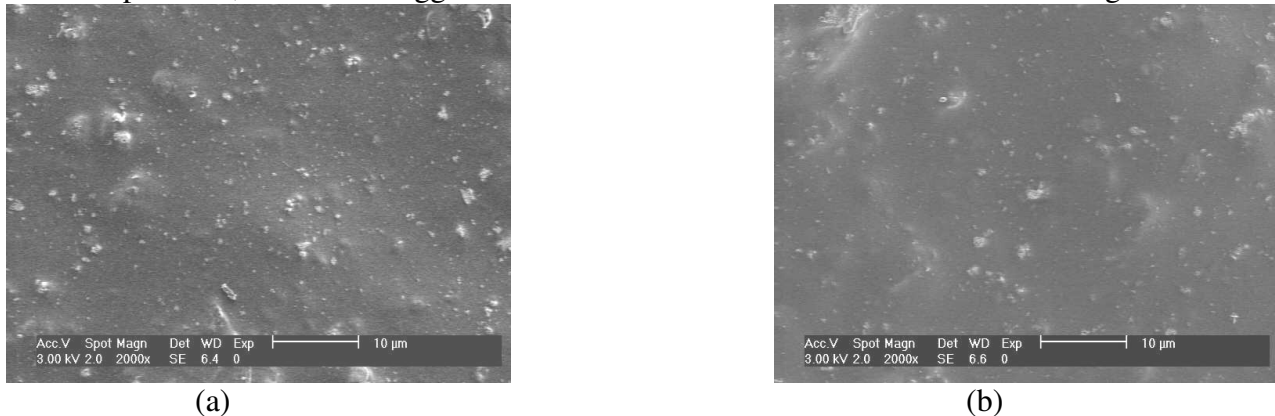


Figure 2. SEM micrographs of 20 wt % PLA Composites Consist of (a) Untreated and (b) Treated HA with 1 wt % AMPTES.

### Conclusion

The effect of HA loading and surface treatment of HA with silane coupling agents on the mechanical and structural properties of polylactide-HA composites was investigated. It was found that silane treatment improved the dispersion of HA in the polymer matrix as well as the mechanical properties of the composites. According to the tensile test results, the maximum improvement in the mechanical properties of the composites was obtained for PLA composites containing 1 wt % AMPTES treated HA and 0.5 wt % MPTMS treated HA for PDLA composites.

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