

# **CHAPTER III**

## **A COMPARATIVE OBSERVATION ON PHYSICAL PROPERTIES OF BOVINE BONE BASED HA/PLA COMPOSITES FROM MELT-MIXING AND SOLUTION-MIXING TECHNIQUES**

### **3.1 Abstract**

Bovine bone based hydroxyapatite (u-HA) powder was produced by grinding heated bovine bone. SEM micrograph showed that the obtained powder, after calcination at 1100°C, composed of agglomerated HA particles. u-HA/PLA composites at various contents of HA were prepared by either melt-mixing or solution-mixing techniques. The u-HA/PLA composites prepared by melt-mixing exhibited the more homogeneous distribution of u-HA in PLA matrix as compared with the composites prepared by solution-mixing technique. In comparison, tensile modulus, tensile strength and impact strength of the melt-mixed composites were higher than those of the solution-mixed composites. Moreover, decomposition temperatures of the melt-mixed composites were higher than those of the solution-mixed composites. Nonetheless, average molecular weights of PLA in the solution-mixed composites, as confirmed by GPC, were significantly higher than those in the melt-mixed composites.

### 3.2 Introduction

Hydroxyapatite (HA:  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ ) has been investigated as a biomaterial and used in various medical applications because of its excellent biocompatibility, osteoconductivity and bone-bonding ability (Kothapalli, Shaw, and Wei, 2005; Shikinami *et al.*, 2001; Ruksudjarit *et al.*, 2008). HA can be obtained not only from chemical synthesis but also from natural sources, *e.g.* coral, bovine bone. In recent years, natural HA is attracting much attention from points of natural and less expensive material. HA can be used either in a single component form, or as a filler for polymer composites (Ruksudjarit *et al.*, 2008; Coutand, Cyr, Deydier, Guilet, and Clastres, 2008; Fathi, Hanifi, and Mortazavi, 2008; Ooi *et al.*, 2007; Deng *et al.*, 2001). Many kinds of bioresorbable polymers have been developed and used in medical applications. Among those polymers, poly(lactic acid) (PLA) is a good candidate due to its biodegradability and yielding nontoxic byproducts after hydrolysis reaction (Kothapalli *et al.*, 2005; Shikinami *et al.*, 2001; Russias *et al.*, 2006; Tsuji *et al.*, 2004). Hence, a composite between HA and PLA is a good alternative for using as a biomaterial since it combines strength and stiffness of HA with flexibility and resorbability of PLA and, then, solves the drawbacks of both materials. Additionally, HA/PLA composite is easy to process into required shapes and is expected to be a promising composite as an implant in non-load bearing parts (Deng *et al.*, 2001; Russias *et al.*, 2006; Zhang *et al.*, 2005).

However, one of the major problems for manufacturing of the HA/PLA composite is the agglomeration of the HA powder in the PLA matrix. In general, fine HA particles tend to combine together, through electrostatic or van der Waals forces to form agglomerated particles. This agglomeration of HA tends to decrease

mechanical properties of the composite. So, the selected technique for preparing the HA/PLA composites must have the ability to break down agglomerated HA and disperse them into the PLA matrix (Mathieu, Bourban, and Manson, 2006). By an effective mixing process, homogeneous distribution of HA powder in PLA matrix and enhancement of mechanical properties of the composite are obtained. Nowadays, many techniques have been used to prepare HA/PLA composite, such as solution mixing (Lin *et al.*, 2007), forging (Shikinami *et al.*, 2001) and hot pressing method (Jamshidi, Hyon, and Ikada, 1988).

Melt-mixing and solution-mixing are frequently used techniques for preparing HA/PLA composites. Upon preparing the composite, melt-mixing technique generates higher shear force and higher temperature than solution-mixing technique. The high shear force and the high mixing temperature would promote the distribution of HA in PLA matrix. Nevertheless, melt-mixing technique would cause adverse effect to the PLA matrix since PLA is a thermally sensitive polymer leading to the deterioration of its molecular weight (Ignjatovic *et al.*, 2004). In contrast, solution-mixing technique causes lower shear force and lower temperature than melt-mixing technique. The low shear force and the low mixing temperature would protect PLA from thermal degradation. Conversely, the low shear force and the low mixing temperature might affect the distribution of HA in PLA matrix.

In this present study, bovine bone based HA was prepared and, then, incorporated into PLA by either solution-mixing or melt-mixing techniques. Effects of preparation technique and filler content on morphological, mechanical and thermal properties of HA/PLA composites were determined. Furthermore, degradation of PLA chains in the composites prepared by those two techniques was also investigated.

### **3.3 Experimental**

#### **3.3.1 Materials**

PLA (4042D) was purchased from NatureWorks LLC Co, Ltd. Bovine bones were supplied by Limeiseng Co., Nakhon Ratchasima. Chloroform (AR grade) was purchased from Labscan Co, Ltd.

#### **3.3.2 Preparation of u-HA powder**

Bovine bones were burned in open air and were ground into powder using a ball milling machine. Then, the powder was calcined at 1100°C for 3 h and the obtained powder was called u-HA.

#### **3.3.3 Characterization of u-HA powder**

The calcined bovine bone powder was analyzed by X-ray diffractometer (XRD) (OXFORD/D5005) with a Cu-K $\alpha$  as a radiation source. A step size of 0.02° and a scan speed of 0.4°/min were used while the voltage was held at 35 kV.

Functional groups of u-HA powders were identified by a Fourier transform infrared spectrometer (FTIR) (BIO-RAD/FTS175C, KBr pellet technique). The spectrum was recorded in the 4000-400 cm<sup>-1</sup> region with 2 cm<sup>-1</sup> resolution.

In addition, a scanning electron microscope (SEM) (JOEL/JSM-6400) operating at 15 kV was used to reveal microstructure of the HA powder.

#### **3.3.4 Preparation of u-HA/PLA composites**

u-HA/PLA composites were prepared through either solution-mixing or melt mixing techniques. The weight ratios of HA/PLA are shown in Table 3.1.

For solution-mixing technique, 20 g of PLA was dissolved in 100 ml of chloroform at room temperature for 3 h. Then, u-HA was added to PLA solution

and the mixture was ball milled for 4 h. The mixture was poured onto clean Petri dishes and dried at room temperature for 48 h and at 70°C in a vacuum-oven for 24 h. Then, each composite resin was ground into small pieces (about 0.3 cm in length).

For melt-mixing technique, HA/PLA composites were prepared using an internal mixer (HAAKE/RHEOMIX). PLA and u-HA were mixed at 170°C with a rotor speed of 70 rpm for 10 min. Each HA/PLA composite was left at room temperature for 24 h and ground into small pieces (about 0.3 cm in length).

Various molding dies according to ASTM D638-03 and D256 standards were used to prepare composite specimens for mechanical testing. The HA/PLA composite was heated in the dies from room temperature to 180°C and maintained at that temperature for 15 min. Subsequently, it was hot-pressed at 180°C by a compression molding machine (GOTECH/GT-7014-A30) for 10 min under a pressure of 2000 psi and cooled to room temperature.

**Table 3.1** Composition of HA/PLA composites

<b>Designation</b>	<b>Filler content (wt%)</b>	<b>Preparation technique</b>
PLA-S	-	solution-mixing
PLA-M	-	melt-mixing
1S	10	solution-mixing
2S	20	solution-mixing
3S	30	solution-mixing
4S	40	solution-mixing
1M	10	melt-mixing
2M	20	melt-mixing
3M	30	melt-mixing
4M	40	melt-mixing

### **3.3.5 Determination of morphological properties of u-HA/PLA composites**

A scanning electron microscope (SEM) (JEOL/JSM-6400) operating at 15 kV was used to visualize fractures surfaces of the HA/PLA composites. All samples were coated with a thin layer of gold before examining.

### **3.3.6 Determination of thermal properties of u-HA/PLA composites**

Thermal decomposition temperature and weight loss of u-HA/PLA composite were determined by a thermogravimetric analyzer (TGA) (TA INSTRUMENT/SDT2960). The sample was heated from room temperature to 600°C under a nitrogen atmosphere at a heating rate of 10°C/min.

### 3.3.7 Determination of PLA molecular weight

Molecular weights of the as-received PLA and the PLA in the HA/PLA composites were evaluated using a gel permeable chromatography (GPC). The GPC instrument was equipped with universal styrene-divinylbenzene copolymer columns (PLgel Mixed-C, 300×7.5 mm, 5 $\mu$ m), differential refractometer detector (AGILENT/RI-G1362A), online degasser (AGILENT/G1322A), autosampler (AGILENT/G1329A), thermostatted column compartment (AGILENT/G1316A) and quaternary pump (AGILENT/G1311A). Chloroform was used as an eluent. The eluent flow rate was kept constant at 0.5 ml/min. Temperature of the column and the detector was maintained at 40°C and 35°C respectively. Polystyrene standards (Shodek standard) with a molecular weights of  $3.90\times 10^6$ ,  $6.29\times 10^5$ ,  $6.59\times 10^4$ ,  $9.68\times 10^3$  and  $1.30\times 10^3$  g/mol were used to generate a calibration curve. Compression-molded specimens of PLA and HA/PLA composites were dissolved and diluted using chloroform (2 mg/ml), and filtered before injection.

### 3.3.8 Determination of mechanical properties of u-HA/PLA composites

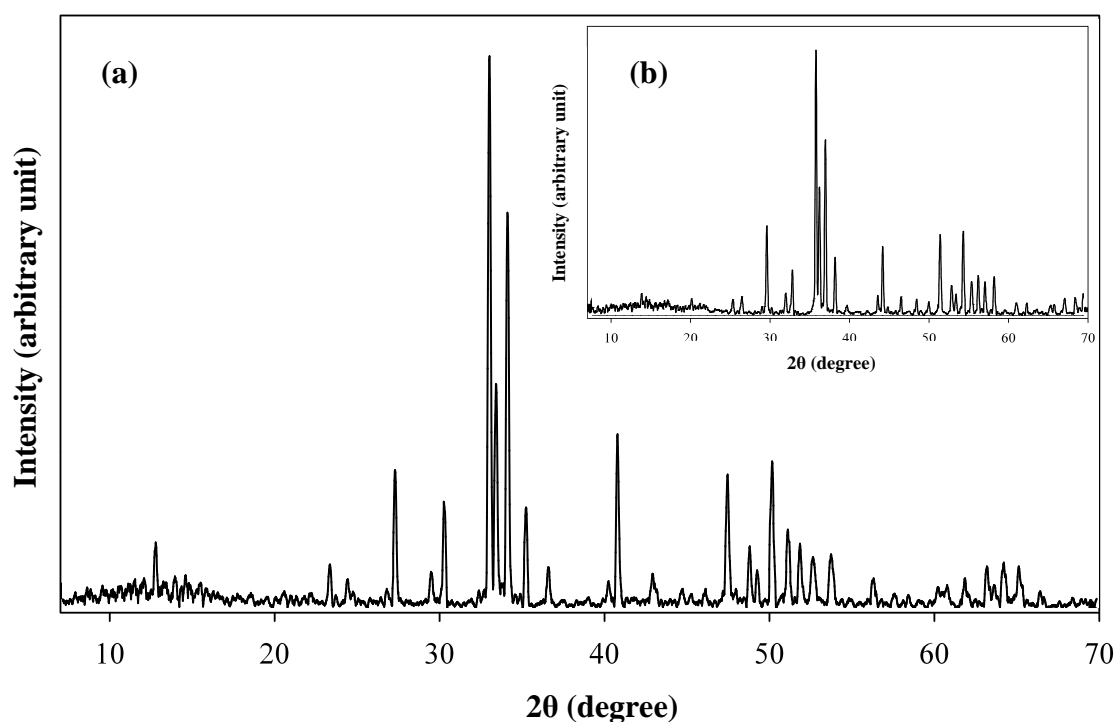
Tensile properties of HA/PLA composites were investigated according to ASTM D638-03 using a universal testing machine (INSTRON/5569).

Izod impact strength of unnotched HA/PLA specimens were determined using an impact testing machine (ATLAS/BPI) according to ASTM D256.

### 3.4 Results and discussion

#### 3.4.1 Characterization of u-HA powder

XRD patterns of calcined bovine bone powder and pure HA are shown in Figure 3.1. All the peaks of the calcined bone powder matched with those of pure HA confirming that the bovine bone powder mainly composed of HA. In addition, the XRD pattern also indicated that the calcined bovine bone powder was in crystalline form. So, the bovine bone powder was called u-HA in this present study.

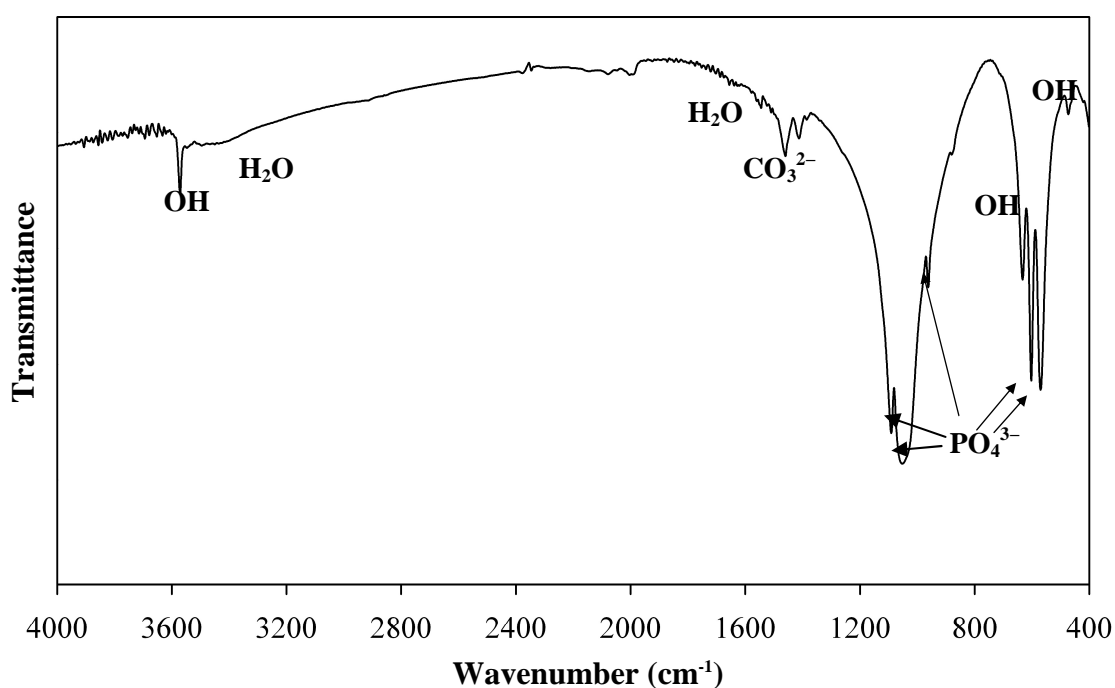


**Figure 3.1** XRD pattern of (a) calcined bovine bone powder and (b) pure HA.

FTIR spectrum of u-HA is shown in Figure 3.2. The peaks at 1085, 1036, 963, 600 and 575  $\text{cm}^{-1}$  were assigned to different vibration modes of  $\text{PO}_4^{3-}$  group in HA powder. The stretching and the bending vibration of structural OH



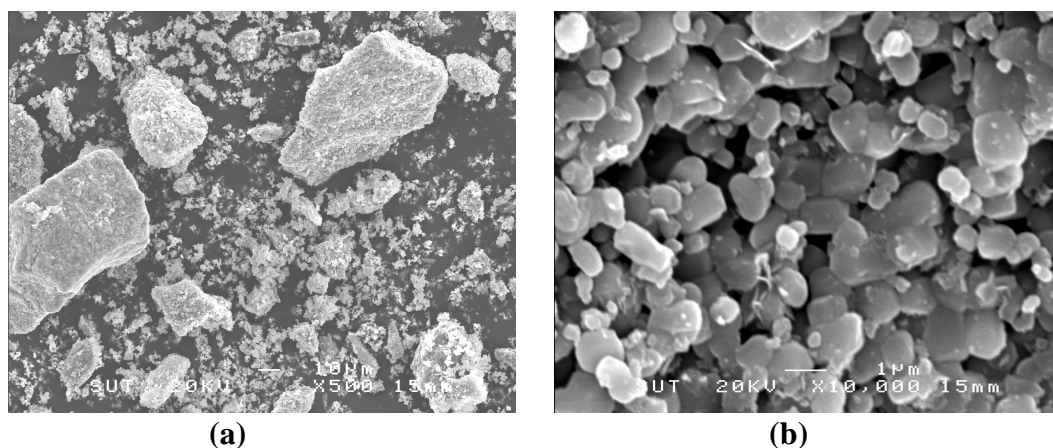
groups in the apatite lattice were observed at  $3571\text{ cm}^{-1}$  and  $632\text{ cm}^{-1}$ , respectively. Additionally, vibrational peaks corresponding to  $\text{CO}_3^{2-}$  groups were also observed at 1457, 1411 and  $878\text{ cm}^{-1}$  (Fathi *et al.*, 2008; Ooi *et al.*, 2007). Therefore, these vibration peaks indicated that the calcined bovine bone powder was carbonated HA. The appearance of carbonate functional groups on surface of the obtained powder could be explained as follows: (1) During heating process, adsorbed carbon from atmosphere substituted the  $\text{PO}_4^{3-}$  groups of the HA or (2) The incompletely pyrolyzed carbon dissolved into the hydroxyapatite crystal (Shinzato *et al.*, 2001; Furuzono *et al.*, 2001; Wen *et al.*, 2008).



**Figure 3.2** FTIR spectrum of bovine bone based HA after calcined at 1100°C.

SEM micrographs of u-HA are shown in Figure 3.3 (a-b). The micrograph in Fig. 3.3 (a) shows the agglomeration of u-HA powder. The micrograph

at higher magnification (Fig. 3.3 (b)) revealed that the agglomerated u-HA composed of particles with irregular shape.

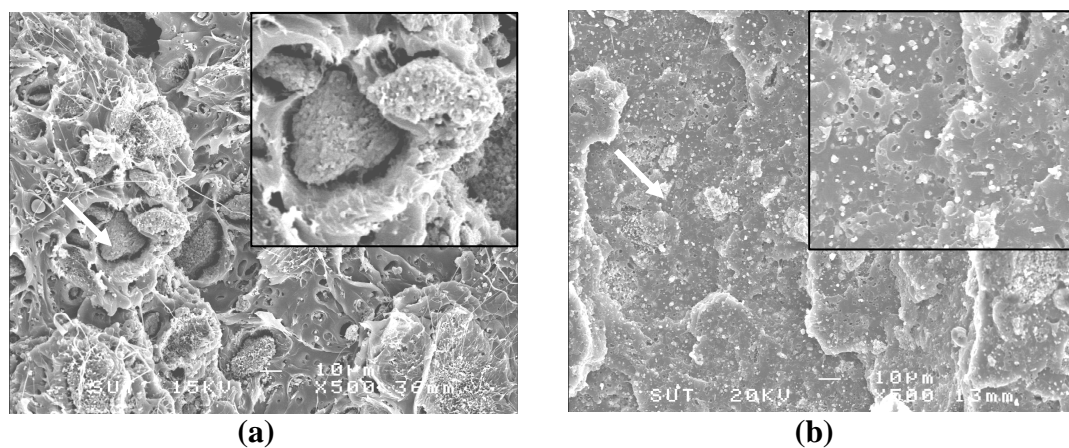


**Figure 3.3** SEM micrographs of HA powders: (a) u-HA at low magnification (X500), (b) u-HA at high magnification (X 10<sup>4</sup>).

### 3.4.2 Morphological properties of u-HA/PLA composites

Figure 3.4 shows SEM micrographs of tensile fracture surfaces of the u-HA/PLA composites containing 20wt% of u-HA prepared by solution-mixing and melt-mixing techniques. In Figure 3.4 (a), agglomeration of u-HA in the composite prepared by solution-mixing technique was clearly observed. Also, a gap was noticeable at the interface between u-HA and PLA matrix. This indicated that there was no adhesion between u-HA surface and PLA matrix. On the other hand, u-HA in the composite prepared by melt-mixing technique exhibited more homogenous distribution and less agglomeration in the PLA matrix, as shown in Figure 3.4 (b). However, some u-HA agglomeration and the gap between two phases was also observed.

From the morphological micrographs, it was clearly shown that the melt-mixing technique led to a homogeneous distribution of u-HA particles in the PLA matrix whereas solution-mixing technique gave more agglomerated HA particles, isolating PLA rich zones and less intimate blending of the two components. According to the less homogeneous distribution of u-HA in the solution-mixed composites, the filamentous structure of PLA, after tensile testing, was observed (Figure 3.4 (a)), indicating the higher ductility of the composites as mentioned in the mechanical properties section (elongation at break).



**Figure 3.4** SEM micrographs of fracture surfaces of u-HA/PLA composites at 20wt% of u-HA: (a) solution-mixed composite and (b) melt-mixed composite.

### 3.4.3 Thermal properties of u-HA/PLA composites

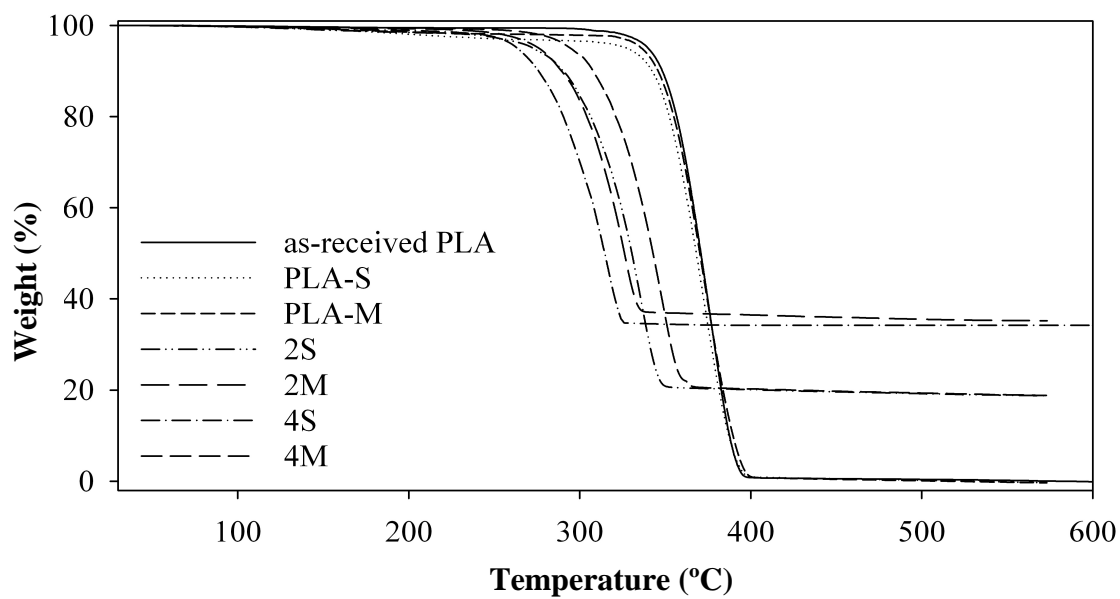
Figure 3.5 (a-b) shows TGA and DTG thermograms of as-received PLA, processed PLA and u-HA/PLA composite prepared by either solution-mixing technique or melt-mixing technique. In addition, the onset of degradation temperature and the peak of degradation temperature of each sample are summarized in Table 3.2. According to the onset and the peak of degradation temperatures, as-received PLA had higher thermal stability than the processed PLA. These results implied that the chain scissions of PLA occurred during preparation.

In comparison at an equal content of u-HA, the melt-mixed composites had higher thermal stability than the solution-mixed composites. In the composites prepared by melt-mixing technique, the volatile products were probably blocked by the good distribution of u-HA in PLA matrix (Figure 3.4 (b)). In contrast, the composites prepared by solution-mixing technique exhibited more agglomeration of u-HA ((Figure 3.4 (a)), therefore, the composites would lose their volatilization blocking ability.

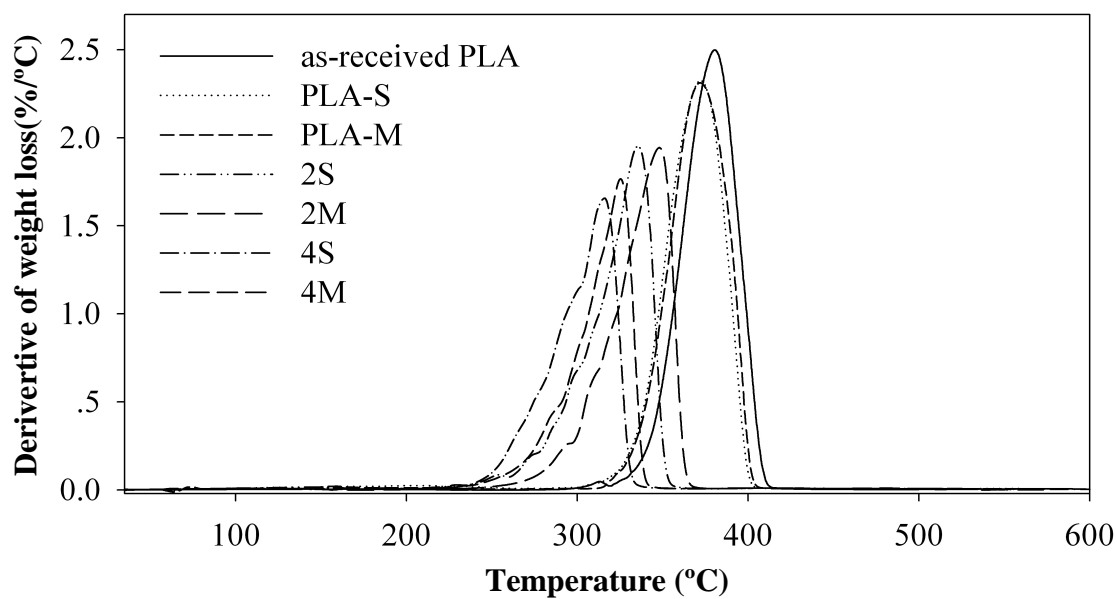
Moreover, the thermal stability of the composites prepared by both techniques decreased with increasing u-HA content. This may be because of the poor distribution of u-HA in PLA. At higher content of u-HA, u-HA tended to agglomerate in PLA matrix much more than it did at lower content of u-HA since there was polarity difference between HA surfaces and PLA matrix.

**Table 3.2** The onset and the peak of degradation temperature of as-received PLA and the composites at various processing conditions.

Designation	Preparation technique	Degradation temperature (°C)	
		Onset	Peak
as-received PLA	-	297	380
PLA-S	solution-mixing	293	372
PLA-M	melt-mixing	293	372
2S	solution-mixing	272	335
2M	melt-mixing	285	348
4S	solution-mixing	254	316
4M	melt-mixing	265	325



(a)



(b)

**Figure 3.5** (a) TGA and (b) DTGA thermograms of as-received PLA, PLA and u-HA/PLA composite prepared by solution-mixing technique (PLA-S, 2S, 4S), PLA and u-HA/PLA composites prepared by melt-mixing technique (PLA-M, 2M, 4M).

Several researchers have studied thermal properties of polymer composites. They found in their system that the thermal decomposition temperature of the polymer composites increased as compared with that of the neat polymer. According to their works, an increase in thermal stability of a polymer composite could be explained in two aspects: either decomposition products are blocked by a high thermally stable filler (Fukushima, Tabuani, and Camino, 2009) or the filler in the composite acts as a barrier preventing heat transfer (Ignjatovic *et al.*, 2004). This was in contrast to the present results. All processed samples exhibited lower thermal stability than as-received PLA. This was probably due to the limit in the distribution and dispersion of u-HA in PLA matrix.

#### **3.4.4 Average molecular weight of PLA in u-HA/PLA composites**

It was known that PLA chains can be easily broken at a particular temperature range resulting in lower molecular weight PLA, oligomers, monomers and gas-products (Ignjatovic *et al.*, 2004). Therefore, during the preparation of HA/PLA composite, the PLA chains could possibly be degraded by the high processing temperature. Molecular weight of PLA in as-received PLA and in HA/PLA composites prepared by different preparation technique were further investigated by GPC techniques. Table 3.3 illustrates molecular weights and molecular weight distribution of PLA in as-received PLA, processed PLA and u-HA/PLA composites which were affected by preparation techniques and u-HA content.

Based on the GPC results,  $\overline{M}_n$  and  $\overline{M}_w$  of PLA after solution-mixing (PLA-S) and PLA after melt-mixing (PLA-M) were lower than those of as-received PLA. Also, its MWD was increased. The decrease in molecular weight and the

increase in MWD of the processed PLA after passing through both mixing techniques revealed the occurrence of PLA chain scission. As compared between two techniques,  $\overline{M}_w$  and  $\overline{M}_n$  of PLA-S were higher than those of PLA-M while MWD of PLA-S was narrower than that of PLA-M. It was due to the thermal oxidative degradation of PLA chain during melt-mixing process. These results were similar to the research work investigated by Signori, Coltelli, and Bronco (2009). They have found that the increase in MWD of PLA after thermal degradation. This was a course of a random rearrangement of PLA chains upon chain scission and chain recombination. Additionally, Perego, Cella, and Bastioli (1996) reported a decrease in PLA molecular weight during high temperature processing. They have found that after injection molding of PLA at 195°C, molecular weight of PLA was decreased by 14-40%.

In comparison, the PLA chains in melt-mixed composites had lower  $\overline{M}_w$  and  $\overline{M}_n$  than those in solution-mixed composites. Additionally, MWD of PLA in the composites prepared by melt-mixing technique were higher than those of the composites prepared by solution-mixing technique. At an equal content of u-HA, the more distribution of u-HA in the melt-mixed composites (Figure 3.4 (b)) increased the chance of OH groups on u-HA surface to interact with PLA chains and, further, the breaking of bonds in the PLA chains would occur. The interaction between OH on u-HA surface and PLA chains led to the more decrease in the molecular weight of PLA. This result was similar to the research work done by Ignjatovic *et al.* (2004). They have investigated the effect of the hot pressing on the structure and characteristics of HA/PLLA composite and found that the OH groups at the end of PLA chain can destroy the PLA basic chain under the influence of thermal energy.



In addition, the molecular weight of PLA of the composites prepared by both techniques decreased with increasing u-HA content while their MWD increased. These results indicated that PLA chain scission upon composite preparation increased with increasing of u-HA content. As increasing u-HA content in the composites, the PLA matrix was more exposed to OH-containing surface of u-HA by which PLA molecules underwent more chain scission.

However, there are various factors affecting the decrease in molecular weight of PLA during melt-mixing preparation which have been reported by other research works (Wang, Joseph, and Bonfield, 1998; Mathieu *et al.*, 2006). The mechanisms leading to breakdown of PLA chains are proposed as follows; firstly, hydrolysis of ester bond on PLA backbone. An increase in hydrolysis degradation of PLA chains is potentially due to the presence of water absorbed on filler surface, therefore, the filler should also be thoroughly dried to eliminate water traces. Secondly, zipper-like depolymerization will be occurred when trace amount of catalyst still present in the system. Thirdly, oxidative random chain scission will be occurred if melt-mixing processing were done under air atmosphere. The last two mechanisms are intermolecular transesterification to monomer or oligomers and intramolecular transesterification to form monomers or oligomers. According to the results in this section, it should be noted that oxidative random chain scission of PLA was the reasonable mechanisms for the lowering in  $\overline{M}_n$  and  $\overline{M}_w$  and the increasing in MWD of PLA chains in the u-HA/PLA composites. Also, this mechanism was accelerated in the presence of OH-containing surface of HA.

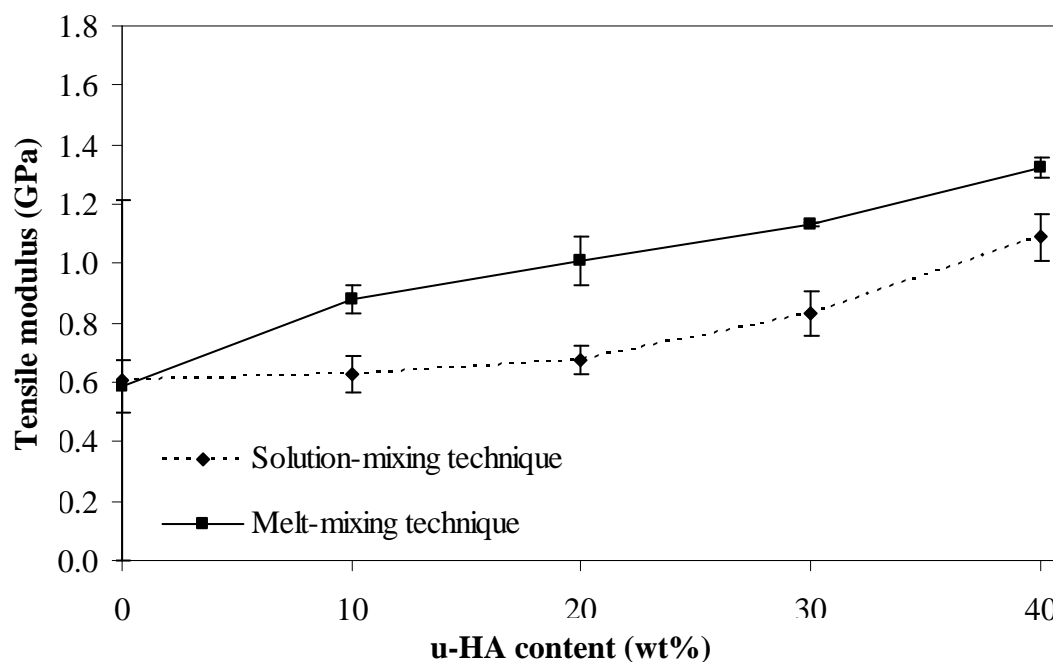
**Table 3.3** Molecular weight of PLA in as-received PLA and the composites at various processing conditions.

Designation	Preparation technique	Average molecular weight		MWD
		$\bar{M}_w$	$\bar{M}_n$	
as-received PLA	-	$2.83 \times 10^5$	$1.31 \times 10^5$	2.16
PLA-S	solution-mixing	$2.54 \times 10^5$	$1.02 \times 10^5$	2.49
PLA-M	melt-mixing	$1.94 \times 10^5$	$0.76 \times 10^5$	2.55
1S	solution-mixing	$2.34 \times 10^5$	$0.97 \times 10^5$	2.41
2S	solution-mixing	$2.21 \times 10^5$	$0.87 \times 10^5$	2.54
3S	solution-mixing	$2.11 \times 10^5$	$0.75 \times 10^5$	2.81
4S	solution-mixing	$2.02 \times 10^5$	$0.69 \times 10^5$	2.93
1M	melt-mixing	$0.67 \times 10^5$	$0.11 \times 10^5$	6.09
2M	melt-mixing	$0.61 \times 10^5$	$0.10 \times 10^5$	6.10
3M	melt-mixing	$0.56 \times 10^5$	$0.09 \times 10^5$	6.22
4M	melt-mixing	$0.53 \times 10^5$	$0.08 \times 10^5$	6.63

### 3.4.5 Mechanical properties of u-HA/PLA composites

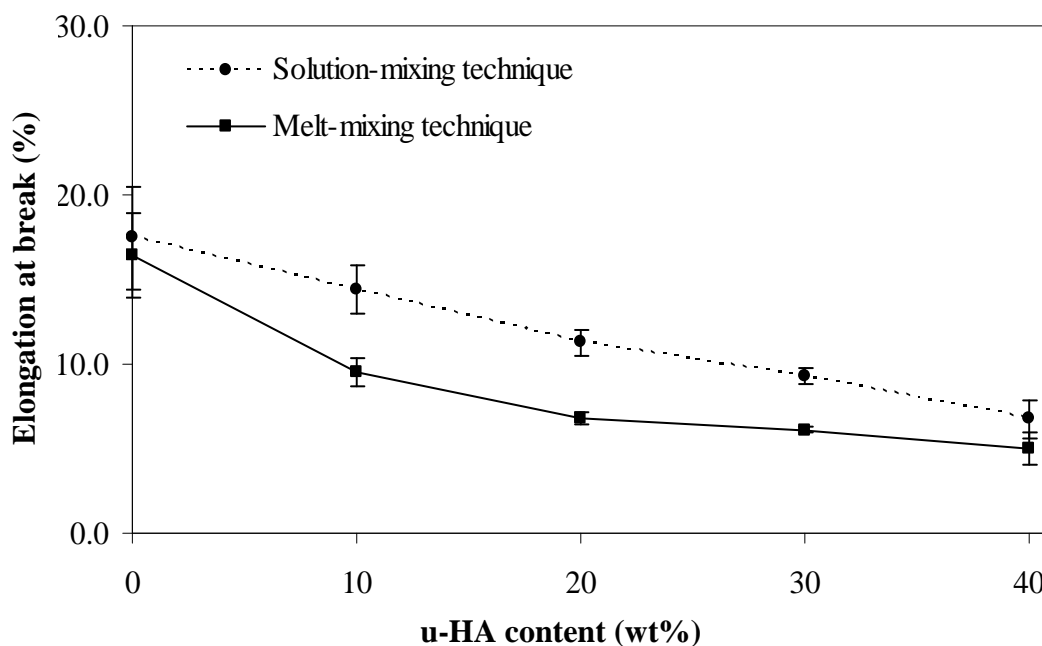
Tensile modulus, elongation at break, tensile strength and impact strength of u-HA/PLA composites are illustrated in Figure 3.6-3.9, respectively. Tensile moduli of u-HA/PLA composites were higher than those of the as-received PLA as observed in Figure 3.6. In comparison, at the same filler content, the composites prepared by melt-mixing technique has higher tensile moduli than the composites prepared by solution-mixing technique. The higher stiffness of the melt-mixed composites was because of the good distribution and dispersion of u-HA in PLA matrix (Figure 3.4 (b)). In addition, the tensile moduli of the composites

prepared by both techniques increased with increasing u-HA content since the rigid u-HA filler has more chance to restrict the molecular motion and the deformation of the PLA chains.



**Figure 3.6** Tensile modulus of HA/PLA composites at various u-HA contents.

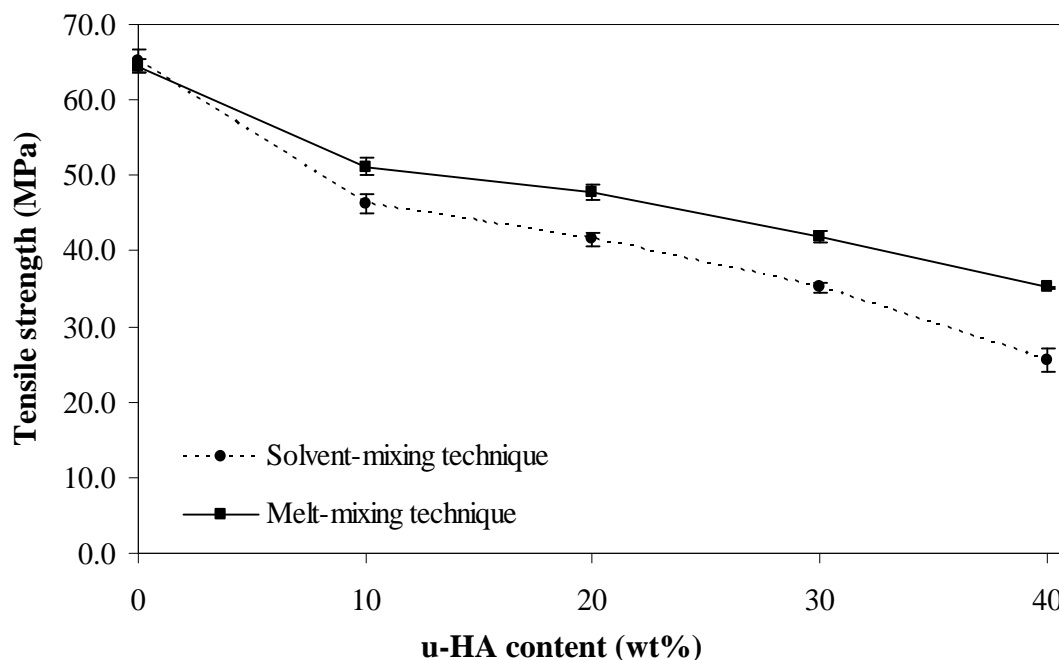
Elongation at break of all HA/PLA composites was lower than that of the as-received PLA, as shown in Figure 3.7. The incorporated HA decreased the mobility of PLA chains and led to the decreasing in ductility of the composites. In comparison, the solution-mixed composite had slightly higher elongation at break than the melt-mixed composite of the corresponding HA content. According to the SEM micrographs, the less homogeneous distribution of u-HA in the solution-mixed composites created the filamentous structure of PLA indicating the higher ductility of the composites.



**Figure 3.7** Elongation at break of HA/PLA composites at various u-HA contents.

As shown in Figure 3.8, the lowering in tensile strength of the composites than those of PLA-S and PLA-M was observed. This was because u-HA as foreign inclusion disrupted the interaction between PLA molecules. Moreover, tensile strength of the composites prepared by both techniques was decreased with increasing u-HA content. This indicated the weak interaction between the two phases.

In addition, the tensile strength of the composites prepared by melt-mixing technique was higher than that of the composites prepared by solution-mixing technique. The u-HA agglomeration and the poor adhesion between agglomerated u-HA and PLA matrix illustrated in Figure 3.4 (a) could be the main reason that was responsible for the obvious reduction in the tensile strength of the solution-mixed composites. On the other hand, the more homogeneous distribution and the less agglomeration of u-HA in PLA matrix of melt-mixed composites create smaller size of voids by which tensile strength was increased.

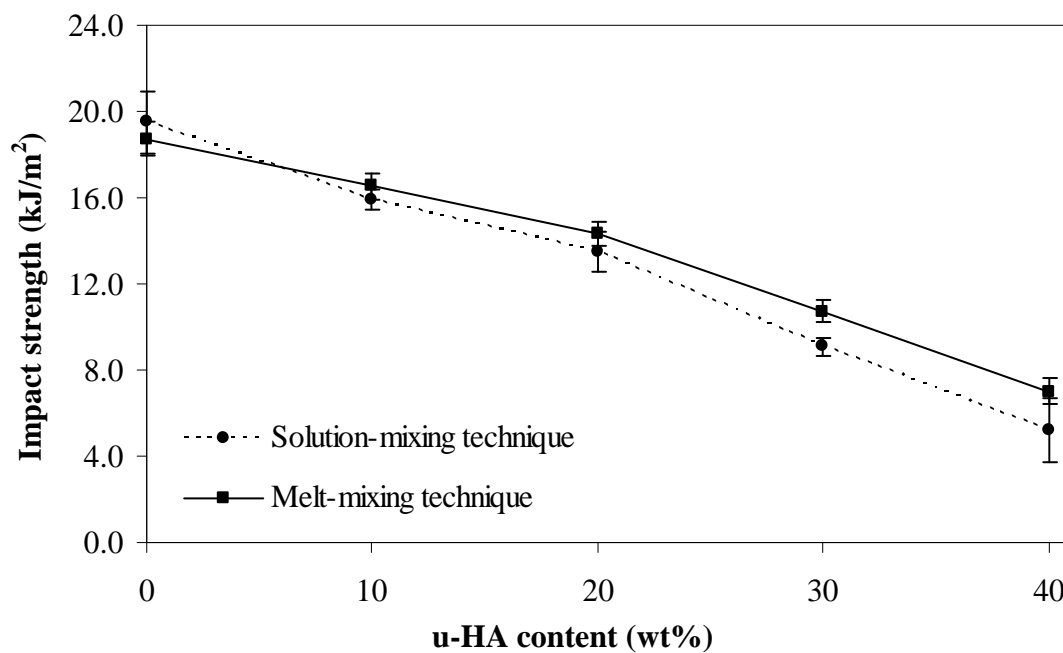


**Figure 3.8** Tensile strength of HA/PLA composites at various u-HA contents.

Based on tensile modulus and tensile strength results, it should be noted that the difference between two techniques was much more emphasized with increasing u-HA content. This could be explained as follows ; at low content of u-HA, the u-HA could easily distribute into PLA matrix by both preparation techniques. On the other hand, at high content of u-HA, the melt mixing technique with high shear force and high temperature could distribute u-HA into PLA matrix better than the solution-mixing technique. This led to the more effective enhancement of tensile modulus and tensile strength of the u-HA/PLA composites.

In addition, impact strength of all u-HA/PLA composites was lower than that of the as-received PLA as shown in Figure 3.9. This was because u-HA disturbed matrix continuity and limited the ability of polymer chains to absorb impact energy. The large agglomerates and a large gap around agglomerated u-HA are the

site of stress concentration, which can act as a microcrack initiator. However, the composites prepared by melt-mixing technique showed less reduction in impact strength than the composites prepared by solution-mixing technique. This result was because the melt-mixed process dispersed u-HA into PLA matrix better than the solution-mixed process. Therefore, the melt-mixed composites with smaller size of agglomerated u-HA could dissipate impact energy better than the solution-mixed composites.



**Figure 3.9** Impact strength of HA/PLA composites at various u-HA contents.

In comparison, the results showed that the composites prepared by melt-mixing technique had higher tensile modulus, tensile strength and impact strength (Figure 3.6, 3.8 and 3.9, respectively) than those of the composite prepared by solution-mixing technique. This was because of better distribution, better dispersion and smaller size of u-HA in PLA matrix as the results of high temperature

and high shear force during the melt-mixing process. The high rotor speeds generated the force and thus pressure exerted on the PLA melt and leading to a more homogeneous composite. Also, a high mixing temperature led to an improved dispersion of the u-HA in the PLA matrix, due to a lower viscosity of the melted PLA (Ignjatovic *et al.*, 1999). The degradation of PLA chains at high mixing temperature were observed. Nonetheless, the degradation of PLA chains was in an acceptable level as seen from the mechanical properties of the melt-mixed composites.

Moreover, the major drawback found in the composite prepared by solution-mixing technique is the use of an organic solvent. Mathieu *et al.* (2006) reported the presence of residual chloroform in PLA composites, determined by nuclear magnetic resonance ( $^1\text{H}$  NMR). It was well known that organic solvents are potentially toxic for living organisms. Therefore, the remaining chloroform in the composites, that expected to be used in biomedical applications, may cause adverse effects to biocompatibility of the materials.

According to the results, it should be noted that the homogeneously distributed HA in PLA matrix had more influence on the mechanical properties of the composites than the degradation of PLA chains upon preparation. In order to obtain u-HA/PLA composites with good mechanical properties and avoid the use of an organic solvent, melt-mixing technique was selected.

### 3.5 Conclusions

In this study, HA powder was prepared from natural source, *i.e.* bovine bone, and used as a filler for preparing PLA composites. Processing technique and u-HA content were the factors that influenced mechanical properties of u-HA/PLA composites. To form HA/PLA composites, u-HA was incorporated into PLA matrix by either melt-mixing or solution mixing techniques. With increasing u-HA content, tensile strength and impact strength of the composites were decreased while the tensile moduli of the composites were increased. In comparison between two preparation techniques, the melt-mixed composites have higher tensile strength, tensile modulus and impact strength than those prepared by solution-mixing technique. However, the PLA chains in the composites prepared by melt-mixing technique degraded much more than those in the composites prepared by solution-mixing technique as confirmed by GPC results.

### 3.6 References

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