Preparation of Hydroxyapatite-Polyethylene Biocomposites Using HA-nanoparticles by Mechanically-Coating Method

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ABSTRACT

New preparation routes have been investigated for enhancing mechanical properties of a biocomposite prepared with high-density polyethylene (HDPE) reinforced with hydroxyapatite (HA). HA nanoparticles, having mean particle size of 200 nm, were employed as fine particles to coat each coarse particle of HDPE with an elliptical-rotor-type mixer and with a high-speed rotational impact blending machine. The effects of the particle size of HDPE and the mixing conditions were studied on mechanical properties of the composite material, such as the rotor speed, the total treatment time, the number of preparation steps and the total volume fraction of HA. In comparison, it was found that the embedment besides uniform coating and dispersion of HA nanoparticles onto the surface of HDPE core particle was easily achieved by rotational impact blending due to high impact energy to yield the relatively high properties. Nevertheless, due to the slight embedment of fine particles by gentle shear and compressive stress, HA nanoparticles could not disperse uniformly due to aggregates generated by the molten HDPE of core particles esceping through the thick and loose coating layer during material formation which results in weak bonding among coated particles to yield lower mechanical properties.

Key words: Nanoparticles, Rotational impact blending, Elliptical-rotor-type mixer, Biocomposites, Coated particle

INTRODUCTION

High-density polyethylene (HDPE), reinforced with hydroxyapatite (HA), is one of the biocomposite materials which has been developed since early 1980s as an analogue for bone replacement. Bonfield et al., (1981) employed HA particles of 10–40 % by volume dispersed in HDPE matrix by means of a twin-screw extruder as a macroscopic mixing method. It was demonstrated that an optimum combination of mechanical and biological performance was achieved with the composite containing HA of 40% by volume (Bonfield, 1988). Such a composite has a modulus value approaching to that of cortical bone, superior toughness and considerably high bioactivity. The close modulus matching of the composite is promising to solve the problem of implants produced with conventional materials which have much higher modulus values than the bone. Implants made of the HA/HDPE composites encouraged bone apposition rather than fibrous encapsulation, which was encountered with other implant materials (Tanner et al.,1994). Recent progress in hydrostatic extrusion of HA/HDPE has indicated that composites with higher modulus (Young's as well as flexural modulus) and strength within the bounds of cortical bone can be manufactured for major load-bearing skeletal implants (Wang et al., 1997). Various aspects of HA/HDPE composites have been investigated since their invention. One particular topic of great interest is the mechanical properties of

HA/HDPE composites. Tensile modulus and strength of HA/HDPE composites increased significantly with HA volume fraction, while the fracture strain decreased (Wang et al., 1998). Necking was noted only for composites with less than 20% of HA during a tensile test. At higher HA volume, composites exhibited considerable ductility. As the HA filler content increased, the recorded stress-strain curves got steeper and the elongation at yield lower. For composites with 45% of HA, the elongation at yield was equal to that at breaking point as the fracture occurred without any yield. At this HA volume fraction, the material fractured with reduced tensile strength. HA/HDPE composites exhibited a sensitivity of modulus and strength to the strain rate as well. Some results obtained from HA/HDPE composites had already been reported (Wang et al., 1994; Suwanprateeb et al., 1997; Suwanprateeb et al., 1998).

Besides the composition, the uniformity of the distribution of HA particles in HDPE matrix should also influence the mechanical properties of the composite materials. In general, it is almost impossible to achieve the uniform mixing of fine particles of a few micrometers in diameter, in other words, the microscopic mixing by conventional powder mixing such as ball milling, commercial mixing and extrusion. One of the approaches to enhance particle mixing is the preparation of an ordered mixture using coated particles. The fine particles are fixed on the large one that acts as a core particle. Thus, the highly- uniform dispersion of fine particles as well as the large ones is attained in a particle scale. Undoubtedly, the final microstructure of the formed composite sample should correspond to the characteristics of particle mixture (Pfeffer et al., 2001).

This paper concentrates on the feasibility study of improving mechanical properties of HA/HDPE composites by utilizing coated particles due to microscopic mixing. HA is used as fine particles to coat each coarse particle of HDPE with a high-speed elliptical-rotor-type mixer and a high-speed rotational impact blending machine for comparison. As the mixing conditions, the rotor speed, the total treatment time, the number of preparation steps and the total volume fraction of HA are changed for different particle sizes of HDPE. The formed sheet of composite material is investigated on the relationship between the apparent structure and the tensile strength and Young's modulus.

MATERIALS AND METHODS

Apparatus

Elliptical-rotor-type mixer

For the preparation of particle mixture, θ-composer (Tokuju Manufacture) was used, as shown in Figure 1. The process consists of a slowly-rotating elliptical vessel (around 30 rpm) and a faster (500–3000 rpm) elliptical rotor. As the rotor inversely rotates inside the vessel, the powder mixture consisting of large and small particles is subjected to shear and compressive stresses, as it is forced to be brought into the small clearance between the vessel and the rotor. As the rotor continues to move and the clearance changes, there occurs bulk mixing of the large and small particles.

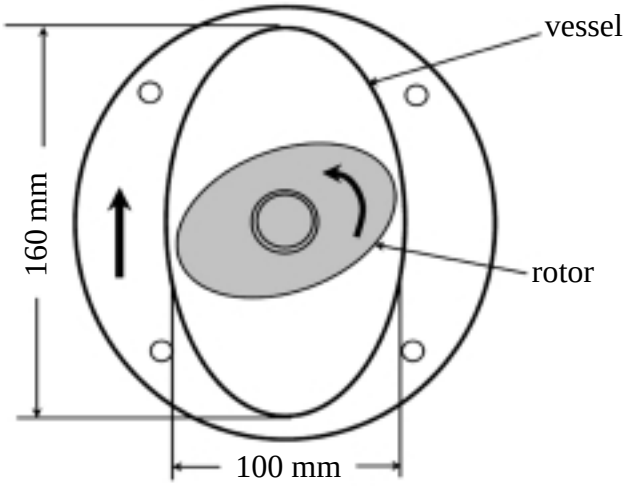


Figure 1. Schematic diagram of high-speed elliptical-rotor-type powder mixer.

Rotational impact blending machine (Hybridizer, HYB)

For the preparation of surface composite particles, Hybridizer (Type NHS-1; Nara Machinery) was applied, as schematically shown in Figure 2. The coating chamber is surrounded with a jacket in which coolant is circulated. This processing can be summarized as follow: particles inside the casing of Hybridizer are mixed and circulated in an air stream generated by a high-speed rotating rotor, and are hit repeatedly among other particles, the wall of a stator and the blades of the rotor. As a result of these mechanical actions, small particles become fixed on the surface of large ones. Hybridizer can be operated by changing the rotational speed for a certain period of treatment time (Kangwantrakool and Shinohara, 2001).

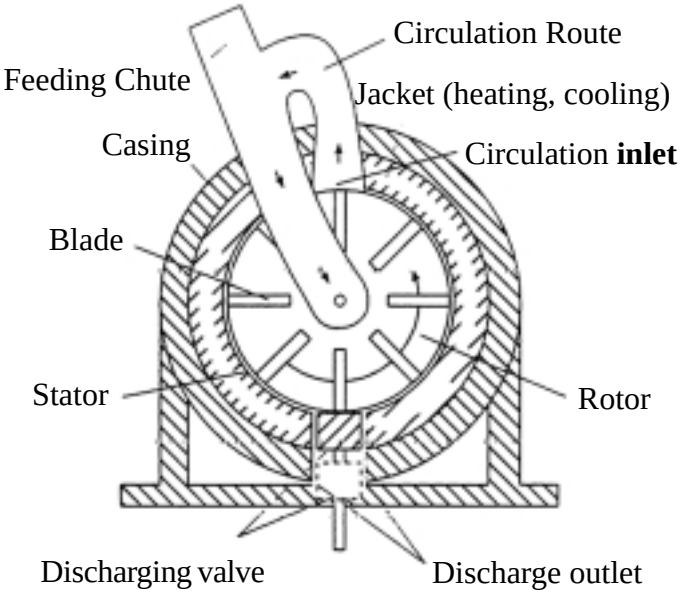


Figure 2. Experimental apparatus of Hybridizer for fabricating surface composite particles.

Raw materials

HDPE particles (HE-3040, Sumitomo Seika Co., Ltd.), having a density of 0.975 g/cm^3 and mean particle size of 7.2 and 12 (m, were used as a core material and HA powder (HAP-100, Taihei Chemical Industrial Co., Ltd.) having a density of 2.888 g/cm^3 and a mean particle size of 200 nm, was employed as fine coating particles for both elliptical-rotor-type mixer and high-speed rotational impact blending machine.

Powder preparations

Mixing ratio

When the surface of a coarse particle is coated with a monolayer of fine particles, the number of fine particles, N, depends on their geometrical arrangement. The maximum number, N_m, corresponds to the case of hexagonal close packing of equal-sized spheres on a plane and is given by Jones and Pilpel (1965).

$$N_m = \frac{2\pi}{3^{-}}\left(\frac{\mathrm{D}}{\mathrm{d}} + 1\right) \tag{1}$$

where D is the diameter of coarse particle, and d_i is the diameter of fine particle.
Then the mixing ratio of small coating component, Mr, is given as

$$M_{\mathrm{ri}} = \frac{N_{mi}.d_i^3}{\sum_{i=1}^{n} N_{mi}.d_i^3 + D^3} \tag{2}$$

In the present experiment, the composition of HA/HDPE composite was chosen as 10, 20, 30 and 40% by volumetric percentage of HA particles.

Surface coating

The particle preparations with HYB and (-composer were carried out by several steps to form multi-layer coated particles suggested by Koishi et al., (1989). The steps and mixing conditions of each method are shown in Tables 1 and 2.

Table 1. Mixing condition of Hybridizer for HA/HDPE composites.

Mixing condition	Rotational speed, Treatment time					Core particle
	14,000 rpm, 5 min	16,000 rpm, 10 min			Total (vol%HA)	HDPE (μm)
	Number step of preparation					
Sample	1st step (vol%HA)	2nd (vol%HA)	3rd (vol%HA)	4th (vol%HA)		
HYB1-1	3	7	-	-	10	12
HYB1-2	3	7	10	-	20	
HYB1-3	3	17	10	-	30	
HYB1-4	3	17	10	10	40	

Sample Preparation

Composite sheets of 2 mm in thickness were prepared by a compression moulding technique. Thus, after the powder had been dried in an oven at 80°C for 24 h, the coated powders were poured into a flash mold. The molding temperature was around 200°C.

Mechanical properties and microstructures

The specimens were tested on a universal tensile testing machine (Instron 4502) at a crosshead speed of 0.5 mm min-1. For microstructure analysis, the dispersion and distribution of HA particles in the HDPE matrix were investigated for composites of all HA volume fractions after mixing and compression molding. The specimen preparation procedure included sectioning, mounting, grinding, polishing and ultrasonic bath cleaning. Specimens were polished progressively using suspensions of alumina down to 0.1 mm in particle size. The polished surfaces were coated with gold and examined by means of scanning electron microscopy (SEM), (JSM-5410, JEOL Ltd., Tokyo, Japan).

Table 2. Mixing conditions of Theta-composer for HA/HDPE composites.

Sample	Total HA (vol%)	HA/step (vol%)	Step (no.)	Time/step (min)	Total time (min)	HDPE (μm)	Rotor speed (rpm)
Z1-1	10	10	1	10	10	7.2	1050
Z1-2	20		2		20		
Z1-3	30		3		30		
Z1-4	40		4		40		
Z2-1	10	10	1	10	10	12	1050
Z2-2	20		2		20		
Z2-3	30		3		30		
Z2-4	40		4		40		
Z3-1	40	20	2	10	20	7.2	1050
Z3-2		10	4		40		
Z3-3		5	8		80		
Z4-1	40	10	4	5	20	7.2	1050
Z4-2				10	40		
Z4-3				15	60		
Z5-1	40	10	4	10	40	7.2	900
Z5-2							1050
Z5-3							1200

RESULTS AND DISCUSSION

Coated particles

Figure 3 shows the coated particles prepared with HYB and θ-composer devices. It can be seen that both preparation techniques produced totally different morphology of the coated particles. Tight or dense coating and embedment of HA fine particles onto the surface of HDPE core particle was easily achieved by high-speed rotational impact blending with HYB. The coated layer was observed to be plate-like. In contrast, θ-composer yielded loose coating, and individual HA particles could be observed to stick to one another as a coated shell.

Effect of total volume percentage of HA on mechanical properties

At the same percentage of HA, composites prepared by HYB technique yielded higher tensile strength and Young's modulus than those prepared by θ-composer one, as shown in Figures 4 and 5. In the case of HYB, both of strength and modulus increased with HA content, while they somewhat decreased in the case of θ-composer. This is due to the gentle shear and compressive stress with θ-composer giving rise to the loose coating to generate the aggregates for ineffective HDPE bonding layer. This caused weak grain boundary among individual HA and HDPE particles during processing of thermal forming which may not be sufficient to transfer the stress from the HDPE matrix to the HA filler under static loading conditions. This accounts for the reduction in the yield strength of the composite with increasing HA volume percentage. In contrast, high uniform dispersion and tight coating layer of HA in the molten layer of HDPE with HYB caused strong grain boundary among individual HA and HDPE particles to yield higher mechanical properties.

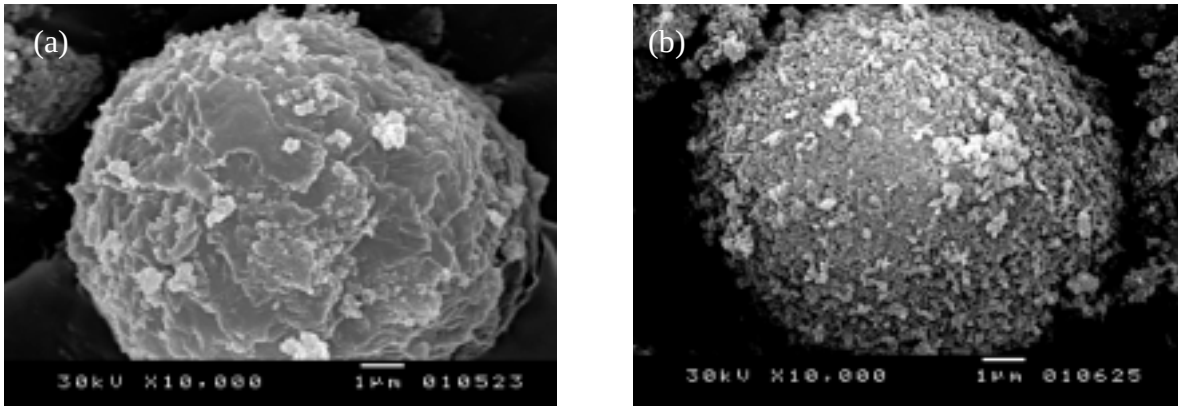


Figure 3. Coated particles prepared by means of (a) Hybridizer and (b) θ-Composer with 40 vol%HA.

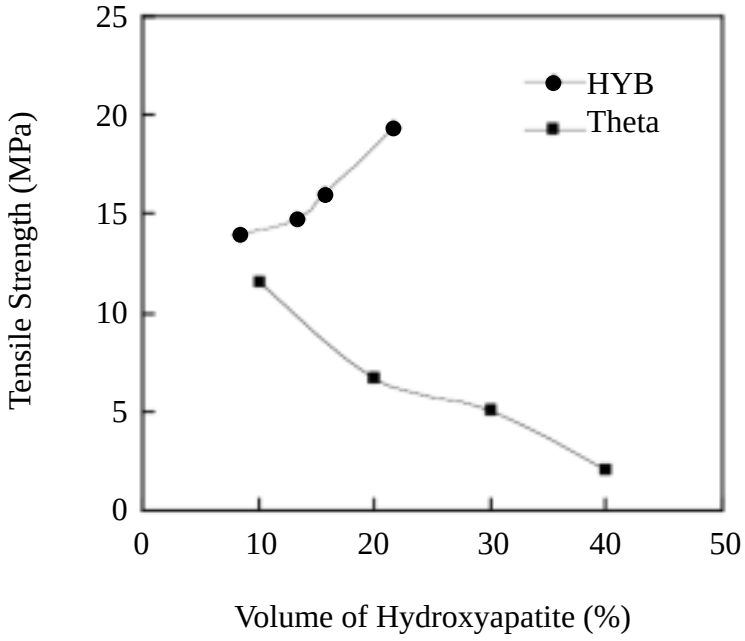


Figure 4. Tensile strength as a function of HA volume for HA/HDPE composites prepared by means of HYB and Theta-composer.

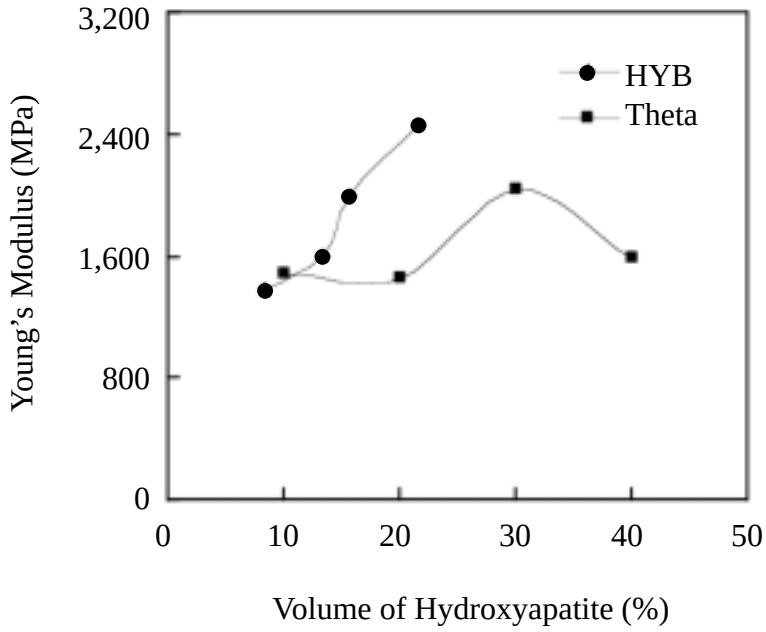


Figure 5. Young's modulus as a function of HA volume for HA/HDPE composites prepared by means of HYB and Theta-composer.

Effect of HDPE particle size on mechanical properties

It was observed that different median sizes of HDPE core particle of 7.2 and 12 (m prepared by means of θ-composer influenced the mechanical properties. HDPE with smaller particle size yielded higher mechanical properties due to larger specific surface area or more contact points among HDPE and HA particles (Wang et al., 1994), as shown in Figure 6. However, the tensile strength of the composite still decreased with increasing volume percentage of HA, which is caused by the loose coating layer or the slight molten HDPE bonding with HA particles with the θ-composer, as mentioned in the Section 3.1. Also, Young's modulus of the composite initially increased with the HA content and started to

decrease at around 30% volume fraction of HA. Further addition of HA will cause the reduction in composite modulus due to decrease in the amount of molten HDPE to spread all over the surfaces of HA particles, as shown in Figure 7.

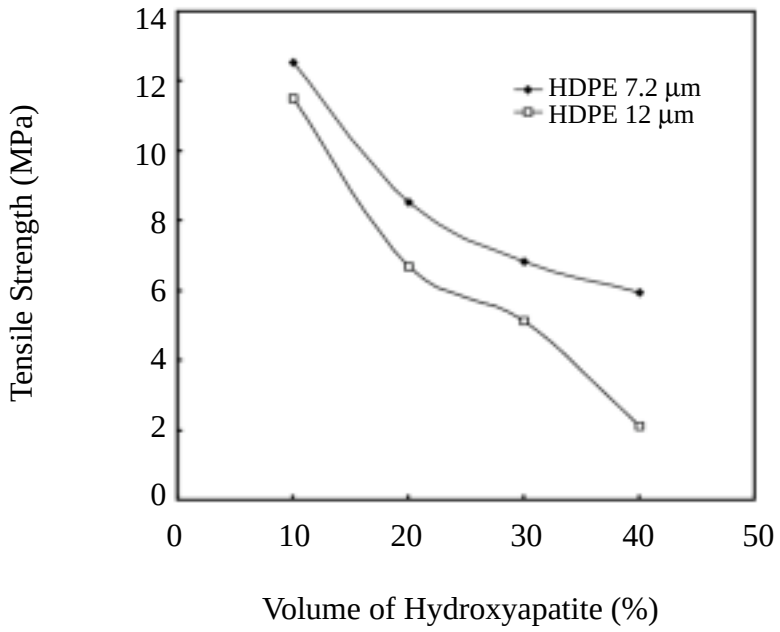


Figure 6. Tensile strength as a function of HA volume for HA/HDPE composites prepared by means of Theta-composer with difference in size of HDPE core particles.

Effect of number of preparation steps on mechanical properties

In order to investigate the effect of the number of preparation steps on mechanical properties, the HA/HDPE composites were prepared by several coating steps (2, 4 and 8 steps) with θ-composer, as listed in Table 2. It can be seen in Figure 8 that the highest tensile strength was obtained by 4 steps of preparation. This is because HDPE core particles could spread out of the relatively thin and loose HA coating layer of individual coated particles to form the network of bonding layer among HA/HDPE-coated particles and yield high strength, as illustrated in Figure 9(b). The moderate strength was obtained by 2 steps due to HA aggregation which came from the excess amount of HA for each layer to be embedded into the surface of HDPE core particle at each time of the coating step, as shown in Figures 9(a) and 10. However, the preparation by 8 steps generates too dense coating layer of HA, that is, the coating layer is hard enough to prevent the molten HDPE from spreading out sufficiently or flowing out through the dense HA layer from inside to outside during compression moulding. Thus, the reduction in HDPE bonding layer between individual coating particles of HA causes lower strength, as illustrated in Figure 9(c). As compared with (c), (b) it should have some cracks inside the coating layer for the molten HDPE to flow out. Young's modulus of the composites prepared by 2 and 8 steps gave higher modulus than that by 4 steps, as shown in Figure 11, this is because these composites had lower amount of HDPE bonding layer between individual coating particles of HA and the fragments of coated particles in the mixture were obtained, as shown in Figure 10.

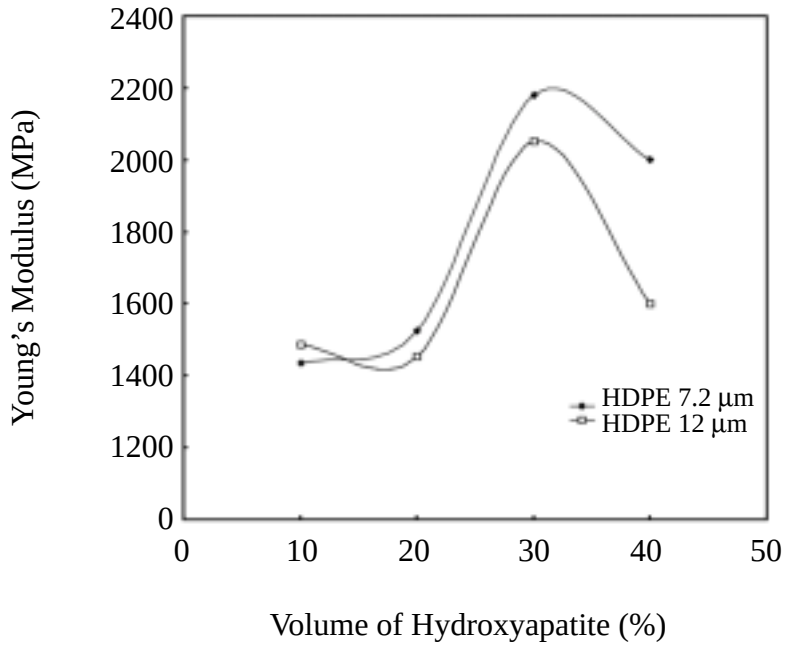


Figure 7. Young's modulus as a function of HA volume for HA/HDPE composites prepared by means of Theta-composer with difference in size of HDPE core particles.

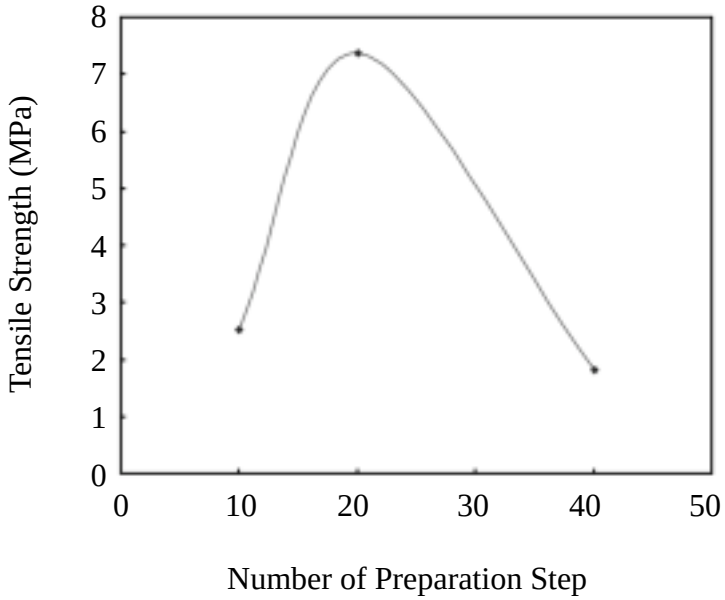


Figure 8. Tensile strength as a function of number step of preparation for HA/HDPE composites prepared by means of Theta-composer with difference in size of HDPE core particles.

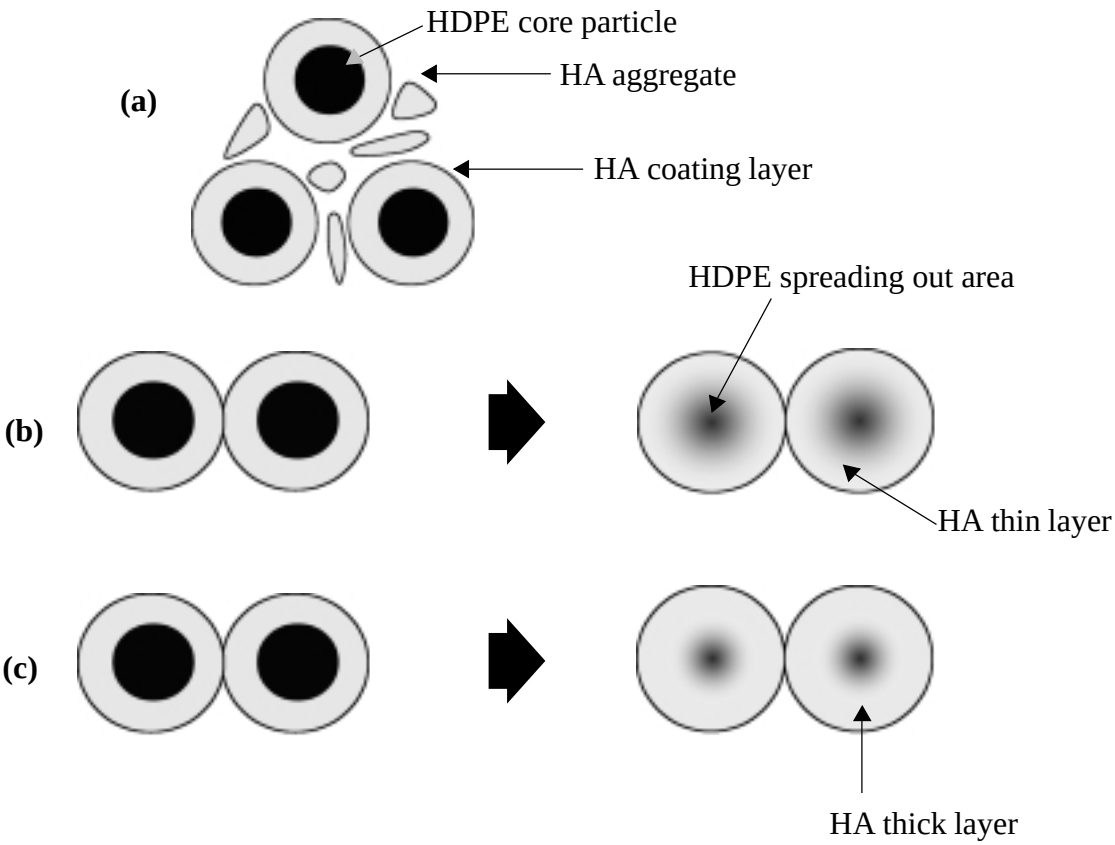
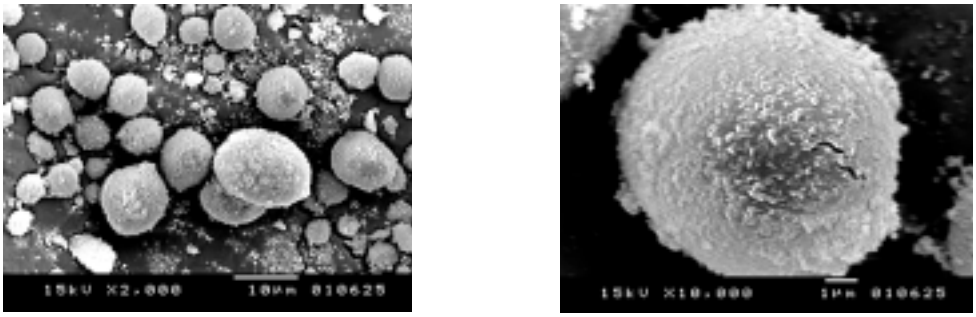


Figure 9. Illustrate melt flow behavior of HDPE core particles during thermal forming processing of HA/HDPE composites (a) with HA aggregates, (b) HA thin coating layer and (c) HA thick coating.

Effect of total treatment time on mechanical properties

HA/HDPE composites were prepared with different total treatment times of 20, 40 and 60 min, as mentioned in Table 2. Figure 12 represents the highest tensile strength of composites with the treatment time of 40 min, and the moderate strength was obtained with 20 min and the lowest one with 60 min. The explanation of these results is the same as that of the effect of step number for preparation, as mentioned in Section 3.4, and that of Young's modulus as well, as shown in Figure 10.



2 steps for 20 min

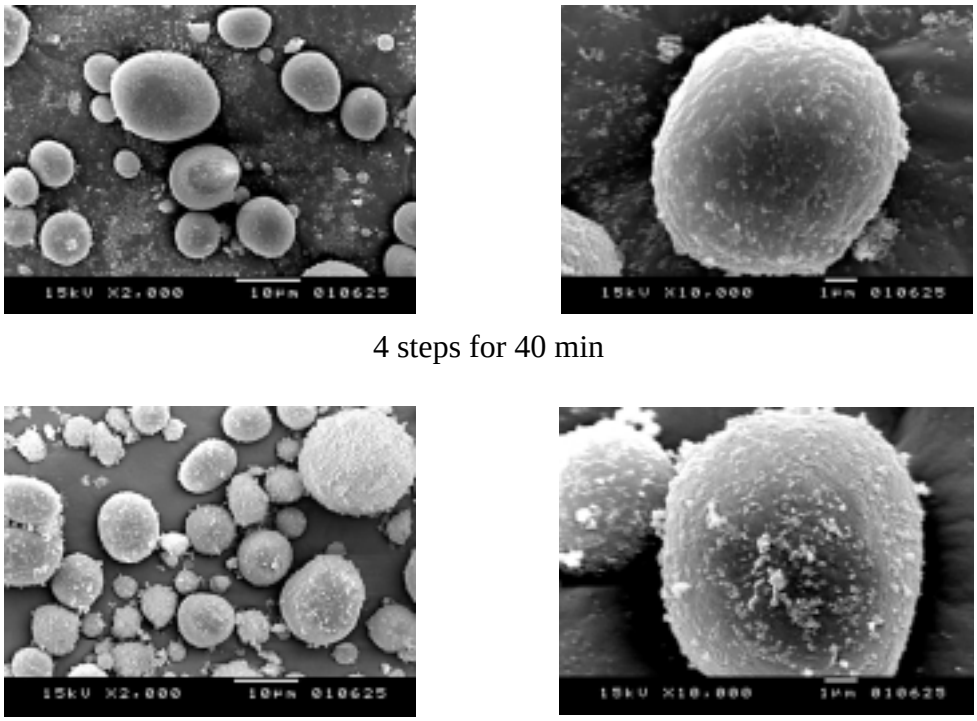


Figure 10. HA/HDPE composite particles prepared by means of Theta-composer with different number of steps.

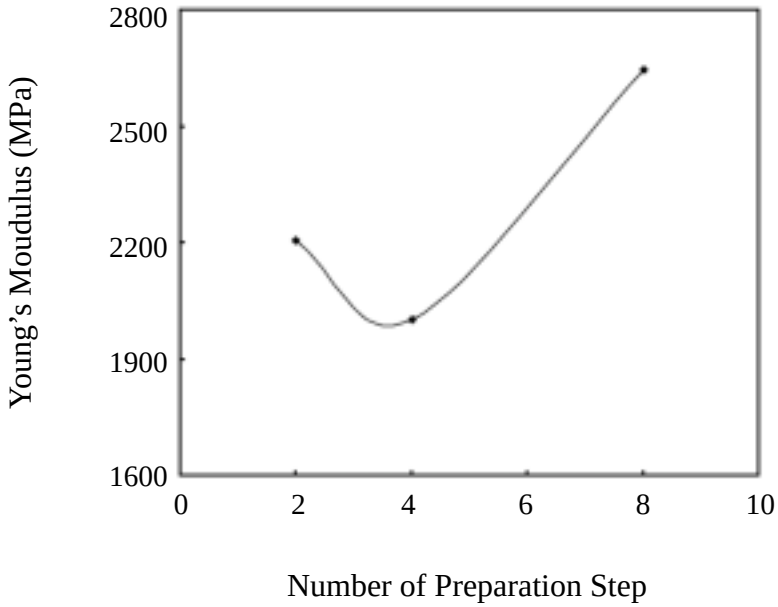


Figure 11. Young's modulus as a function of number step of preparation for HA/HDPE composites prepared by means of Theta-composer with difference in size of HDPE core particles.

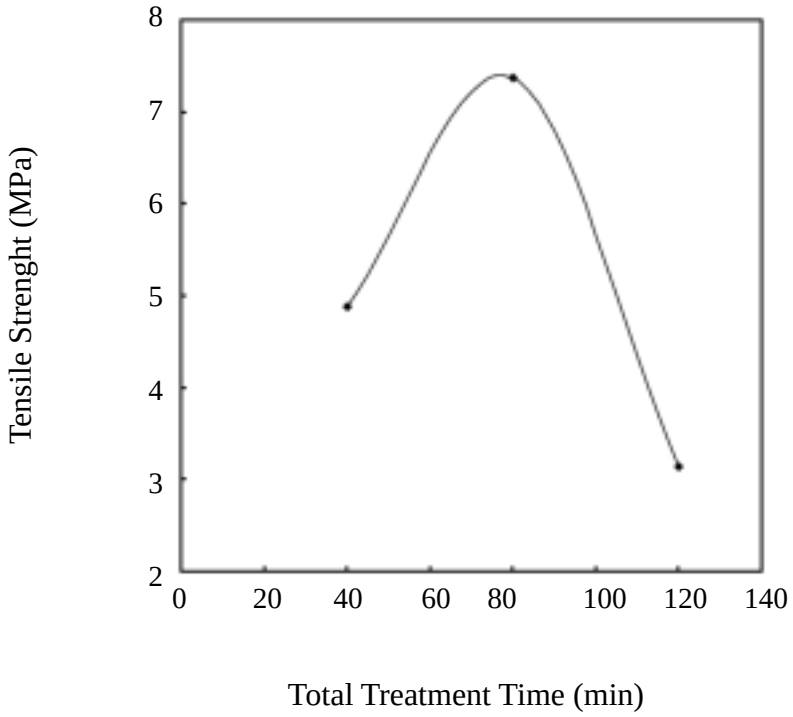


Figure 12. Tensile strength as a function of total treatment time for HA/HDPE composites preparation by means of Theta-composer with difference in size of HDPE core particles.

CONCLUSION

The coating and embedment of HA fine particles onto the surface of HDPE core particle was easily achieved by high-speed rotational impact blending (Hybridizer) due to high impact energy. And the uniform dispersion of HA in the formed composite material yielded relatively high mechanical properties. Furthermore, the mixing conditions of Hybridizer exhibit the approximate conditions to enhance the mechanical properties of HA/HDPE composites, which include the total treatment time and the number of preparation steps besides the total volume fraction of HA. But, the multi-coating steps or layers were required owing to high percentage of powder loss during operation, and there are optimum numbers of coating layers due to densification of multi-layers under high impact to prevent the spreading out of the molten HDPE during the compression molding.

On the other hand, uniform and loose coating of core particles was performed without particle loss during operation by elliptical-rotor-type mixing (θ-composer). However, owing to the slight embedment of fine particles due to gentle shear and compressive stress, the weak bonding among HA and HDPE coated particles yielded the lower mechanical properties. The excess increase in hydroxyapatite volume fraction leads to a decrease in tensile strength and increase in Young's modulus due to less embedment and dispersion. The smaller HDPE core particles increased both tensile strength and Young's modulus of the composites due to larger specific surface.

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initiate the preparation of bioceramic-coated particles with Hybridizer and found suitable operational conditions. And thanks to Dr.Jintamai Suwanprateeb, MTEC contributed the mechanical properties testing.

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