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HYDROXYAPATITE REINFORCED POLYPROPYLENE BIO COMPOSITES

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There has recently been much interest in developing new materials for use in replacing and repairing natural bone. Bone is a composite material with a high modulus filler, hydroxyapatite, in a collagen matrix. Powder hydroxyapatite (HA) reinforced polymer composite has been developed since early 1980s as an analogue material for bone replacement. Hydroxyapatite reinforced polymer composites offer a robust system to engineer synthetic bone substitutes with tailored mechanical, biological, and surgical functions. The basic design rationale has been to reinforce a tough, compatible polymer matrix with a HA filler. In this investigation, composites of polypropylene and hydroxyapatite were prepared. The effects of hydroxyapatite ratio on the mechanical, thermal and morphological properties of the polymer composites is presented. Biological and synthetic hydroxyapatite, in three different concentrations (10, 20 and 30 wt %), was added to PP to produce composites. The mechanical properties, including the elastic modulus, yields strengths, tensile strengths, strain at tensile strength, Izod impact resistance, hardness, density and the thermal properties, such as the Vicat softening point, heat deflection temperature and melt-flow index, of the composites were investigated. The tensile test results showed that HA ratio were effective for the elastic modulus, tensile strength, and the strain at tensile strength. A considerable increase in the elastic modulus was found with a 30% HA concentration. The maximum hardness was obtained with 30% biological hydroxyapatite. The increased HA content caused the HDT and Vicat values to increased, whereas the melt-flow index and Izod impact strength showed a decreased as the HA content increased. The structure of the composites were investigated by scanning electron microscopy and compared to mechanical and thermal properties as a function of HA content.

Keywords: Polypropylene, Hydroxyapatite, Biocomposites, Mechanical properties.

Introduction

From quite some time, researchers have been looking for materials that can act as bone substitutes. Such materials must not produce inflammatory reactions or carcinogenic effects and must resist sterilization conditions. Among them, composites of polyolefins with hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$, have emerged as promising alternatives [1]. There has recently been much interest in developing new materials for use in replacing and repairing natural bone. Bone is a composite material with a high modulus filler, hydroxyapatite, in a collagen matrix. Bonfield et al. have previously developed HAPEX^{TM}, a composite of bioactive synthetic hydroxyapatite in a polyethylene matrix, and this has been shown to be readily incorporated into natural bone [2]. Polyolefins cannot interact by themselves effectively with living tissues. Hence, hydroxyapatite (HA), a material highly compatible with those of bones and bioactive, has

been incorporated into polyethylene and polypropylene to obtain bone implants or substitutes [3-5]. In fact, hydroxyapatite is one of the major components of human bones. The use of a polyethylene matrix does not preclude the use of other polymers as matrix materials, indeed the use of other materials may enhance the properties of the final composite. For this reason polypropylene has been investigated as a matrix material. Like polyethylene, polypropylene is biologically inert, but unlike polyethylene, polypropylene generally exhibits better performance in fatigue and suffers less reduction in mechanical properties at elevated temperatures [1]. Generally speaking, polymers have poorer mechanical properties than bone. But the possibility to be mechanically strengthened and to be biodegradable makes polymers very promising as candidates for bone replacement. The improvement of the mechanical properties of polymer can be achieved by either the modification of the structure of the polymer, or the strengthening of the polymer with fiber and/or filler.

A large number of studies have investigated modifications to the biocomposite structure and composition, aimed at improving the mechanical properties, often through modified or novel processing methods [6]. Various research groups in the past also successfully introduced an interfacial phase between the reinforcement and the matrix for respective polymer matrix composite. In general, such an introduction promotes the adhesion between the reinforcement and the matrix and hence improves mechanical properties of composites [7-11]. Hydroxyapatite-reinforced polymers offer the ability to tailor the composite's elastic modulus, presumably to meet performance criteria for a particular application or implant, by varying the HA-reinforcement content. The addition of up to 50 vol.% HA powder reinforcement has resulted in a six- to eight-fold increase in elastic modulus compared to un-reinforced polymer for HDPE [12–15], UHMWPE [16] and PAEK [17–19].

In this investigation, composites of polypropylene (PP) and hydroxyapatite were prepared. The effects of hydroxyapatite ratio on the mechanical, thermal and morphological properties of the polymer composites is presented.

Experimental Procedures

Seven different polymer composites were prepared. Compositions of Polypropylene/Hydroxyapatite (PP/HA) polymer composites that were formed are given in Table 1. PP (Moplen EP 3307) supplied by LyondellBasell. Its density is 0.900 g/cm^3, MFI value is 15 g/10 min (230 ^{o}C, 2,16 Kg) and its head deflection temperature (0.45 MPa, unannealed) is 95.0 ^{o}C.

Table 1. Composition of the PP/HA polymer composites formulations

Groups	Polypropylene (PP) Content (wt %)	Biological Hydroxyapatite Content (BHA) (wt %)	Synthetic Hydroxyapatite Content (SHA)(wt %)
1	100	-	-
2	90	10	-
3	80	20	-
4	70	30	-
5	90	-	10
6	80	-	20
7	70	-	30

In this study, bovine femur bones (obtained from Carrefour Company, Istanbul, Turkey), were used as the raw material to produce HA powders. Femur bone samples were firstly cleaned to remove visible tissues and substances on the surface of bones and then head parts of the bones were cut off and marrow in shafts of all bones removed via boiling within water in a pressure cooker for 4 h to avoid soot formation during the calcination process [20]. After the boiling process, the retained shafts were deproteinized with sodium hydroxide (NaOH) for 1 h, washed with distilled water and then calcinated at 850^{o}C with a heating rates of 5^{o}C/min for 4 h to ensure that the organics are completely removed to eliminate any microbial contaminations [21]. The resulting white solid samples were firstly ground and then crushed in a mortar to produce hydroxyapatite powders between −63 μm to +45 μm. Then, they were ball milled in a zirconia coated container by zirconia balls and ethanol in Restch PM 100 ball milling device at 150 rpm for 8 h until fine powder was obtained as shown in Fig. 1. After the ball milling process, the powders were dried at 105^{o}C for 24 h and exposed to X-ray diffraction to confirm the presence of HA into obtained powders as shown in Fig 2. Synthetic hydroxyapatite (acros 371260010) supplied by Acros Organics.

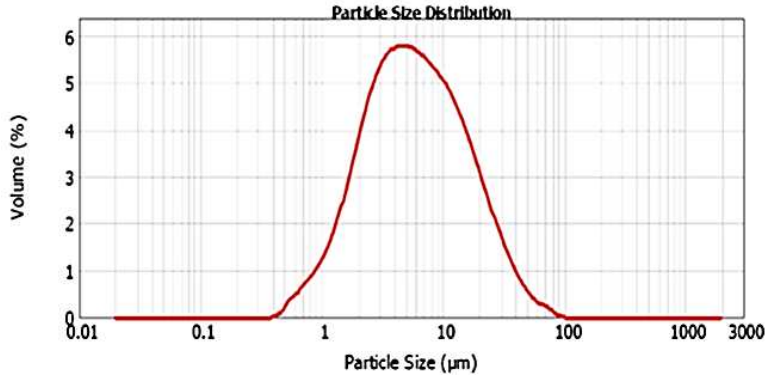

Figure 1. Particle size distribution of BHA after ball milling process

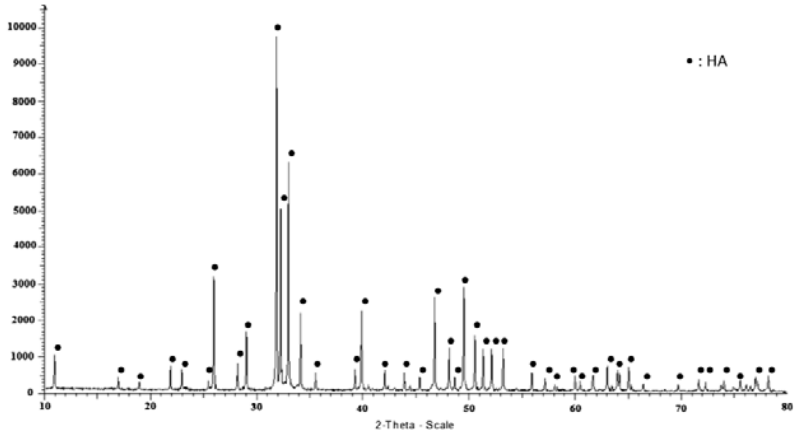

Figure 2. XRD analysis of BHA

Sample Preparation: Polypropylene, synthetic and biological hydroxyapatite were dried overnight at 105 ^{o}C for 24 h in a vacuum oven prior to melt blending. Mechanical premixing of solid compositions was done using a LB-5601 liquid-solids blender (The Patterson-Kelley Co., Inc.USA) brand batch blender for 15 min. Samples with various proportions of PP/HA polymer composites were produced between 190-220 ^{o}C at 15 bar pressure, and a rotation rate of 25-30 rpm, with a Microsan extruder (Microsan

Instrument Inc. Turkey). Polymer composites were also dried in vacuum oven at 105 ^{o}C for 24 hours after extrusion. Subsequently, test samples were manufactured by injection molding. Injection temperature was 190-220 ^{o}C, pressure was 90-110 bar and screw speed was 25 rpm.

Mechanical Characterization: The tensile modulus, tensile strength and strain at tensile strength of the compressed plates were measured by using a tensile testing machine (Zwick Z010, Germany) according to ASTM D638 at room temperature and crosshead speed of 50 mm/min. For every composition, seven samples were tested, and the averages of the seven measurements were reported. The hardness test was done according to the ASTM D2240 method with Zwick hardness tester. To investigate fracture behavior, Izod impact test (notched) was done at room temperature according to the ASTM D256 method with Zwick B5113 impact tester (Zwick, Germany). Flow behavior testing of all the mixtures was done according to ISO 1133 standard with Zwick 4100 MFI equipment. Heat deflection temperature (HDT) and Vicat softening point tests were done according to ISO 75 and ISO 307 standard with determined by CEAST 6521 (Ceast SpA, Italy) HDT-Vicat test equipment. Determination of density was done according to ISO 2781 test standard.

Microscopy: The fractured surfaces of the PP/MA polymer composites were coated to thickness of 20 Å of a gold (Au) to prevent electrical charging by Polaron SC7640 (high resolution sputter coater) (United Kingdom). The surfaces of the prepared samples were observed by the FEI Sirion XL30 FEG (Nederland) scanning electron microscopy (SEM) at an acceleration voltage of 20 kV.

Results and Discussion

The mechanical properties of PP/HA polymer composites is shown in the Fig 3. The elasticity modulus of the PP/MA polymer composites is shown in the Figure 3-A. Since biological hydroxyapatite has much higher stiffness values than the PP matrix, the elasticity modulus of the PP/BHA polymer composites increased as the BHA concentration increases from 0 to 30 wt %. On the other hand, the elasticity modulus of the PP/SHA polymer composites did not appear significant change as the SHA concentration increases. The yield strength of the PP/HA polymer composites is shown in the Figure 3-B. Yield strength values decreased with the addition of biological hydroxyapatite and synthetic hydroxyapatite in PP. For example, the yield strength of virgin PP and PP/BHA (70/30) polymer composites were 16,82 MPa and 14,48 MPa respectively. On the other hand, with the addition of HA in PP has been a little change in tensile strength values. For example, the tensile strength of virgin PP and PP/SHA (70/30) polymer composites were 12,60 MPa and 13,96 MPa respectively. The elongation at break of the PP/HA polymer composites is shown in the Figure 3-D. With the addition of biological hydroxyapatite and synthetic hydroxyapatite in PP has been a significant change in elongation at break values. For example, the elongation at break of virgin PP and PP/SHA (70/30) polymer composites were 28,34 % and 1.58 % respectively. Hardness of the PP/BHA polymer composites increased an increase weight percentage of biological hydroxyapatite from 0 to 30 wt %. Harness of the PP/SHA polymer composites did not appear significant change as the SHA concentration increases. With the addition of HA in PP has been a change in Izod impact strength (notched) values. For example, the Izod impact strength of virgin PP and PP/BHA (70/30) polymer composites were 39,85 kJ/m^2 and 6,05 kJ/m^2 respectively. The density of the PP/HA polymer composites increased an increase weight percentage of HA from 0 to 30 wt %. For example, the density of virgin PP and PP/BHA (70/30) polymer composites were 0,8859 g/cm^3 and 1,1081 g/cm^3 respectively.

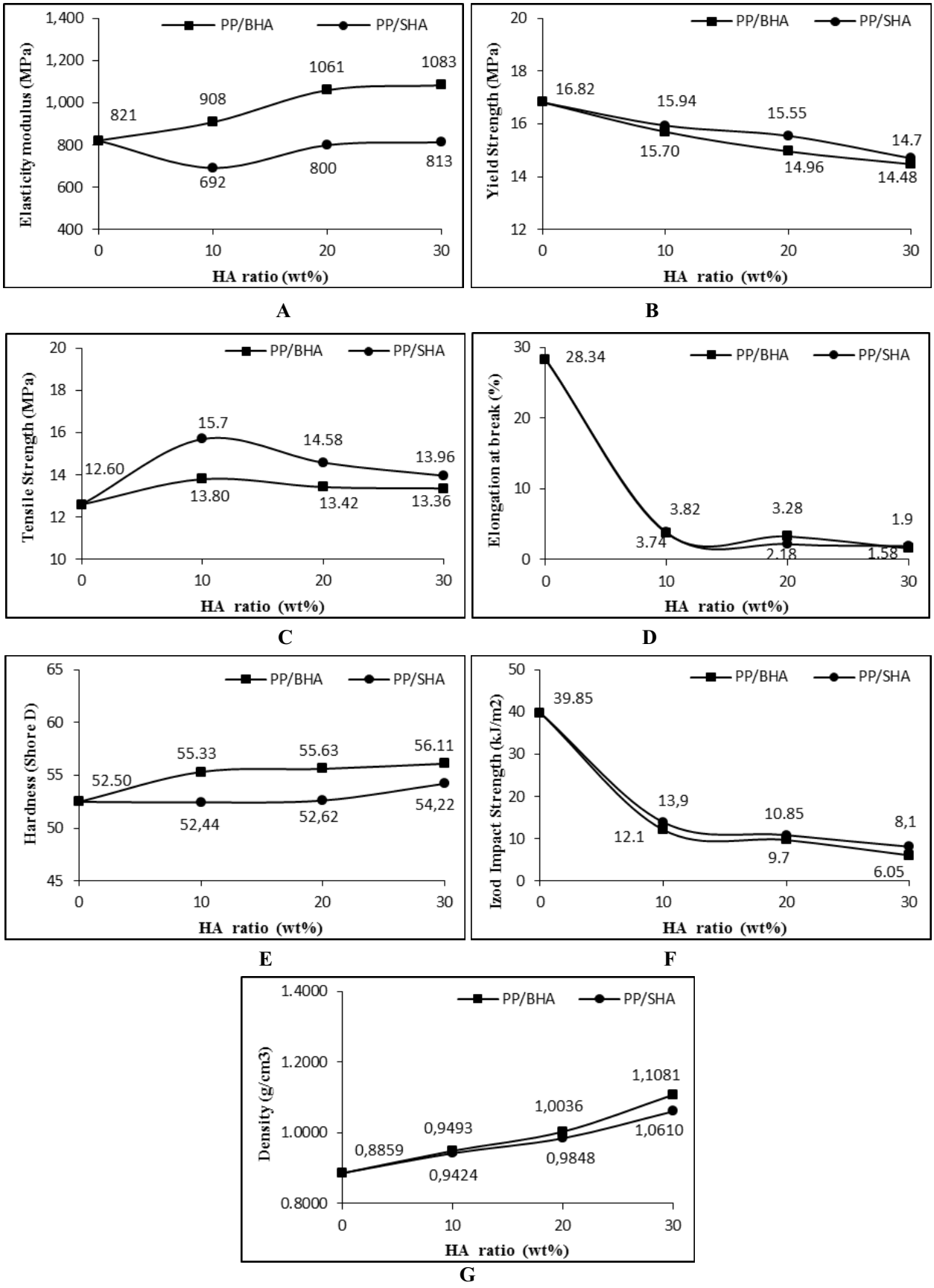

Figure 3. Mechanical properties of PP/HA polymer composites

The thermal properties of PP/HA polymer composites is shown in the Fig 4. MFI values of the PP/HA polymer composites did not appear significant change as the HA concentration increases (Fig. 4-A). The HDT of the PP/BHA polymer composites increased an increase weight percentage of HA from 0 to 30 wt %. For example, the HDT of virgin PP and PP/BHA (70/30) polymer composites were 54,65 ^{o}C and 62,4 ^{o}C respectively. HDT values of the PP/SHA polymer composites did not appear significant change as the HA concentration increases (Fig. 4-B). The Vicat softening temperature of the PP/BHA polymer composites increased an increase weight percentage of BHA from 0 to 30 wt %. For example, the Vicat softening temperature of virgin PP and PP/BHA (70/30) polymer composites were 137 ^{o}C and 142,6 ^{o}C respectively. On the other hand, Vicat softening temperature of the PP/SHA polymer composites decreased (Fig. 4-C).

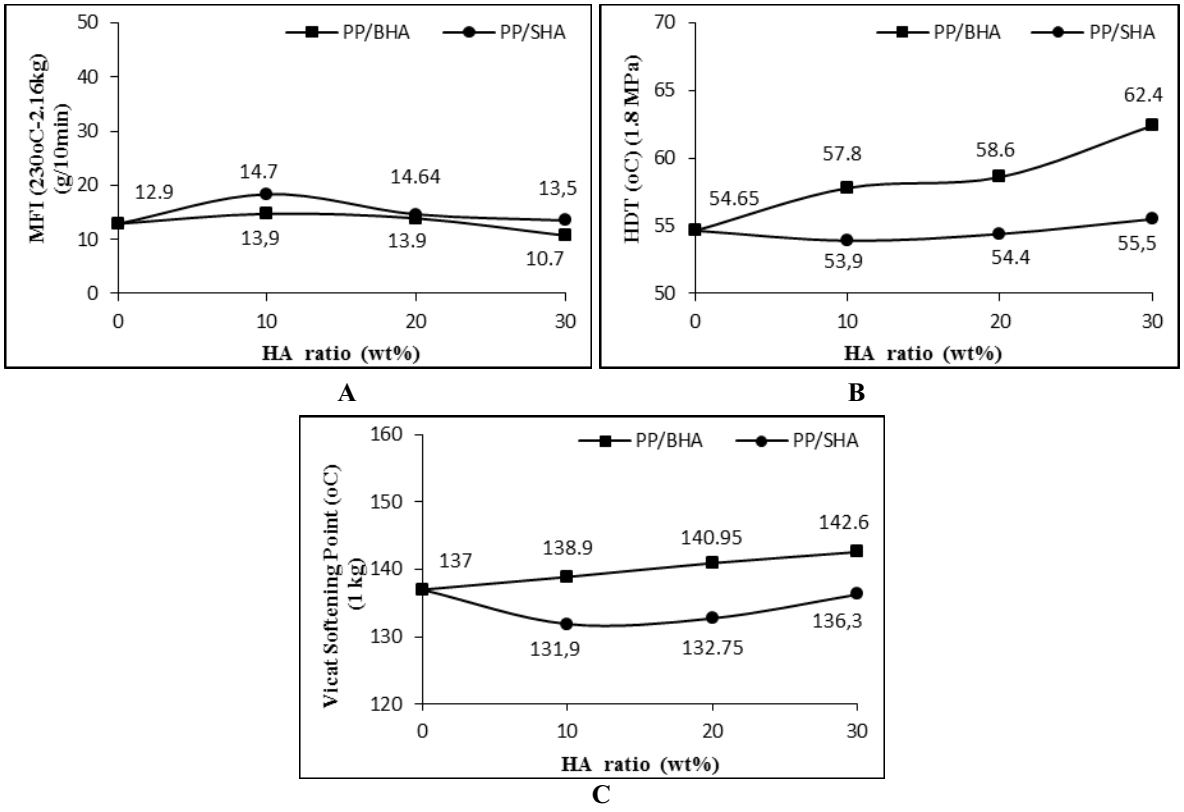

Figure 4. Thermal properties of PP/HA polymer composites

Figure 5 exhibits SEM micrographs of fracture surfaces of PP/HA composite. It can be seen that HA particles were held by the PP matrix, possibly through certain degree of mechanical bonding between the two phases. With addition of hydroxyapatite to the PP, the adhesion and distribution of the present phases were considerably enhanced as well.

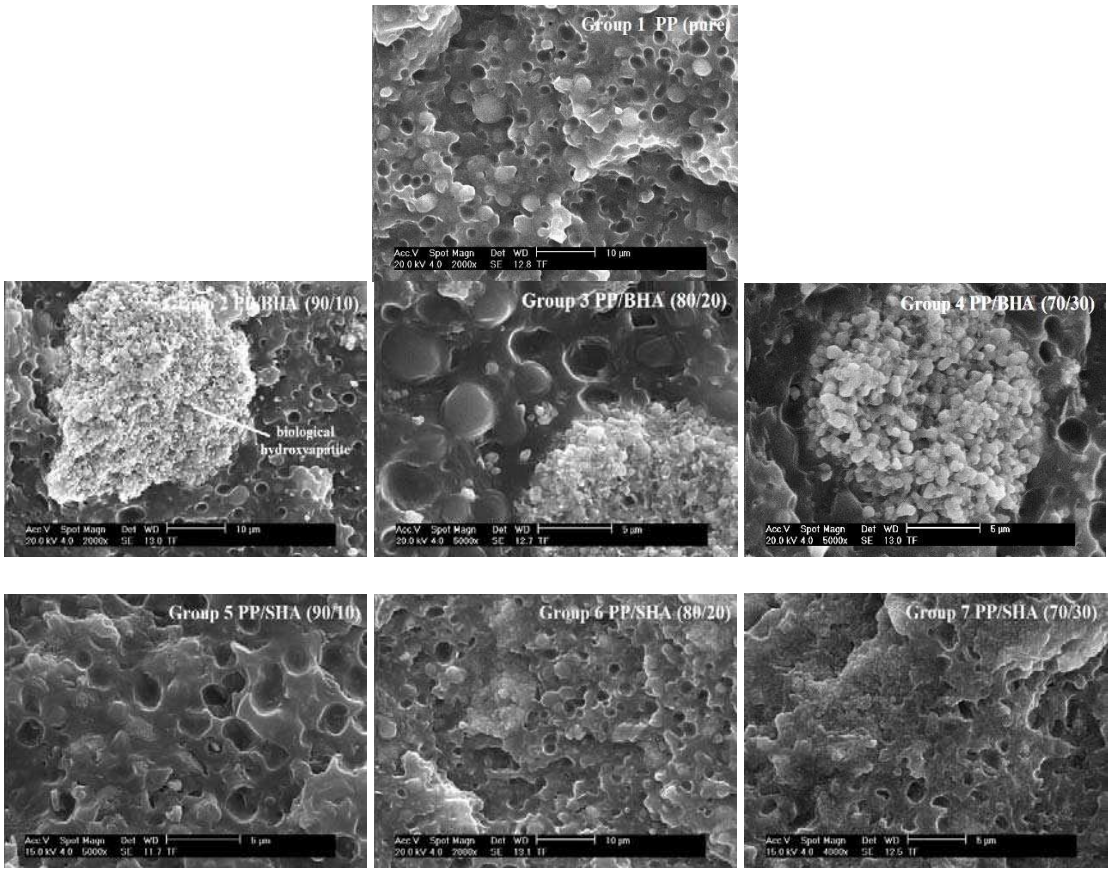

Figure 5. Scanning electron micrographs of PP/HA polymer composites

Conclusions

The effects of hydroxyapatite on the mechanical properties, such as the tensile strengths, elastic modulus, hardness, and Izod impact strength, and the thermal properties, such as HDT, Vicat and MFI, of PP/HA composites were investigated. The following results were obtained:

1. Elastic modulus increased gradually as the biological hydroxyapatite content increased. On the other hand, the elasticity modulus of the PP/SHA polymer composites did not appear significant change as the synthetic hydroxyapatite concentration increases.
2. Yield strength, % elongation and Izod impact strength decreased gradually as the biological hydroxyapatite and synthetic hydroxyapatite content increased. On the other hand, with the addition of HA in PP has been a little change in tensile strength values. Density increased as the biological hydroxyapatite and synthetic hydroxyapatite content increases.
3. Hardness of the PP/BHA polymer composites increased an increase weight percentage of biological hydroxyapatite.
4. MFI values of the PP/HA polymer composites did not appear significant change as the HA concentration increases.
5. The HDT of the PP/BHA polymer composites increased an increase weight percentage of biological hydroxyapatite. On the other hand, HDT values of the PP/SHA polymer composites did not appear significant change as the synthetic hydroxyapatite concentration increases.
6. The Vicat softening temperature of the PP/BHA polymer composites increased an increase weight percentage of biological hydroxyapatite. Vicat softening temperature of the PP/SHA polymer composites decreased

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