



Using Nonconventional Processing to Develop Anisotropic and Biodegradable Composites of Starch-Based Thermoplastics Reinforced with Bone-Like Ceramics

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The development of polymer-matrix composites with sufficient mechanical properties may allow for an entirely new range of small-load-bearing biomedical applications for these systems. By combining polymers with bioactive ceramics, researchers hope to overcome the mismatch of mechanical properties that currently exists between bioceramics and natural load-bearing tissues.¹ The problem is that polymers by themselves are very ductile but not rigid enough, whereas ceramics are too stiff and brittle. The ideal material must evidence the best possible stiffness/ductility compromise, matching the modulus of bone but retaining some of the ductility of the composite matrix. A method of developing such a material should be based on trying to copy the structure (including anisotropy) and mechanical properties of

bone, while at the same time ensuring that the material, once implanted, will exhibit a bioactive behavior.

Composites of polyethylene reinforced with hydroxyl-apatite (HA) (initially developed by W. Bonfield et al.^{2,3}) have recently become commercially available (HAPEX, Smith & Nephew ENT, Memphis, TN) and are already being used in the production of middle-ear implants and for orbital floor reconstruction.³ However, these systems do not yet exhibit properties that allow their use in load-bearing applications. Furthermore, the processing methods that have been assessed with the aim of increasing the materials' mechanical performance—techniques such as hydrostatic extrusion—are not suitable for the production of materials with the thick cross sections and complex shapes typical of load-bearing implants.^{4,5}

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Condition	Injection Temperature (°C)	Mold Temperature (°C)	Injection Pressure (MPa)	Holding Pressure (MPa)	Holding Pressure Time (sec)	SCORIM (sec)	Pack Mode (Uni/Bi) (Async/Sync)	Maximum Pressure (MPa)
Conventional	185 ^a	60	70	50	20	—	—	150
S2	170 ^b	60	20	13	40	40	Bi/Asyn	210

^aTemperature profile of 140°, 155°, 175°, and 185°C.
^bTemperature profile of 140°, 155°, 165°, and 170°C.

Table I. Processing conditions of SCORIM equipment. Injection and holding pressures represent pressures in the hydraulic circuit with pistons oscillating out of phase.

An important breakthrough for temporary tissue-replacement uses would be the development of biodegradable matrix composites, reinforced with bone-like ceramics, that exhibit stiffness performance as near as possible to that of bone. In order to achieve this objective, several biodegradable polymers have been reinforced with bioactive ceramics, but as yet there has not been a reinforced system that exhibits adequate mechanical performance, bone-bonding properties, and controlled degradation behavior.^{6,7} Among candidate materials, starch-based polymeric blends have demonstrated a combination of degradation and mechanical properties that make them quite suitable for these types of applications.^{8,9}

This article reports on the development of starch/HA thermoplastic composites that can be injection molded into complex shapes and that show promising mechanical properties. Special attention was given to the compounding of the materials via corotating twin-screw extrusion (TSE). In addition, nonconventional composite-processing routes, including *shear-controlled orientation in injection molding* (SCORIM), were used to attain the required mechanical performance.^{10,11}

MATERIALS AND METHODOLOGY

In this study, a cornstarch/poly(ethylene-vinyl alcohol) thermoplastic blend (SEVA-C; produced by Novamont of Novara, Italy, under the trade name Mater-Bi 1128RR) was reinforced with hydroxylapatite. The HA (from Plasma Biotal, Tideswell, UK) was sintered at 1200°C for 12 hours. After sintering and crashing in a ball mill, the HA particles had an average diameter in the range of 3–9 μm (6.5-μm median).

The experimental plan included the preparation of compounds with 10-, 20-, and 30-wt% HA. Two different compounding methods were investigated: (1) simple mixing in a rotating drum (RD), and (2) corotating twin-screw extrusion followed by mechanical pelletizing. TSE was done in a Leistritz corotating twin-screw extruder with a barrel-temperature profile between 90° and 170°C.

The compounds were used to produce circular-cross-section tensile samples with two different diameters, 1.5 and 5 mm. The 1.5-mm samples were molded on a conventional injection machine (Klöckner-Ferromatik Desma

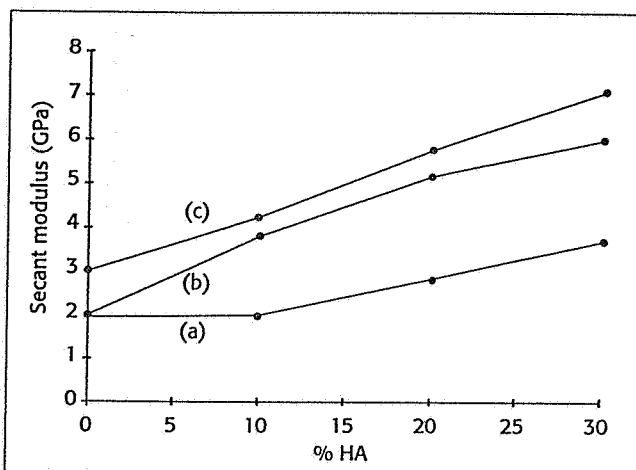


Figure 1. Modulus versus % HA for the following processing methodologies: (a) RD/conventional, (b) TSE/conventional, and (c) TSE/SCORIM.

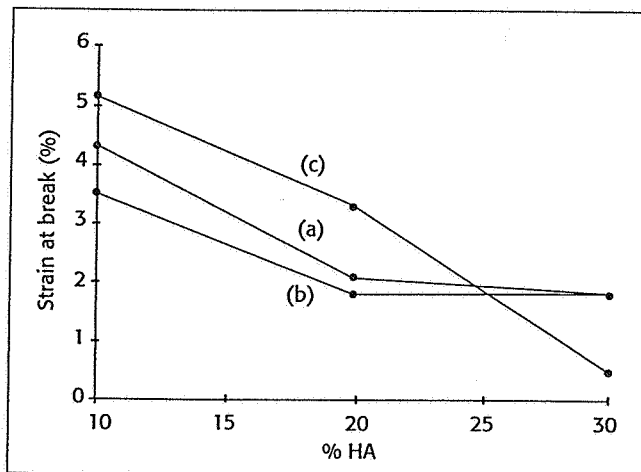


Figure 2. Strain at break versus % HA for the following processing methodologies: (a) RD/conventional, (b) TSE/conventional, and (c) TSE/SCORIM.

FM20). The 5-mm samples were injection molded on a Demag D-150 NCH-K machine fitted with a SCORIM head. This equipment was employed to produce both conventional and SCORIM samples, using a one-impression mold fitted with a pressure transducer. The processing conditions used for the injection molding of all the materials are presented in Table I.

The SCORIM technology is based on the action of two



oscillating pistons that induce a high shear field in the melt during the holding or solidification stage.^{10,11} What results is a highly oriented microstructure with enhanced mechanical properties—in some cases, both the stiffness and ductility of a particular polymeric system can be increased.

Several processing trials corresponding to a range of SCORIM conditions were initially assessed, as has been previously reported.⁸ These conditions differ mainly in the amount of maximum pressure applied during the compaction stage of the shearing cycle and during the packing mode (uniaxial or biaxial). In all cases, the pistons oscillated out of phase. After mechanical evaluation, the SCORIM conditions S2 (see Table I) were selected for further study, since they resulted in samples with the best combination of stiffness and ductility.⁸

The molded samples were tensile tested in order to determine the secant modulus at 1% strain ($E_{1\%}$) and the strain at break (ϵ_b). These tests were performed on an Instron 4505 universal mechanical testing machine fitted with a resistive extensometer (10-mm gauge length) under controlled conditions of 23°C and 55% RH. The crosshead speed was 5 mm/min (8.3×10^{-5} m/sec) until 1% strain was reached; the speed was then increased to 50 mm/min (8.3×10^{-4} m/sec) until fracture. The molded samples were stored under controlled temperature and moisture conditions until testing. Complementary materials-characterization procedures included scanning electron microscopy (SEM) of the fracture surfaces as well as energy-dispersive spectroscopy (EDS).

Materials degradation was assessed following several prefixed aging periods in a simulated physiological solution (HBSS [Hank's balanced salt solution], Gibco 041-04025M, from Life Technologies, Paisley, UK) at 37°C. After being removed from the solution, samples were dried in an oven for 48 hours at 70°C in order to determine the weight loss of each.

RESULTS AND DISCUSSION

The main results of the tensile tests are summarized in Figures 1 and 2. The effect of the SCORIM processing on the performance of the materials can be clearly seen, because it was possible to match the minimum value of the modulus of bone only for samples containing 30% HA. (The materials were tensile tested instead of undergoing the typical flexure tests that generate much higher modulus.⁴) The ductility of the composites also increased when SCORIM processing was used (see Figure 2). However, increments of HA quantity above 20% led to a deterioration of the composites' ductility, and lower ductility values were attained compared with conventionally molded samples. These results must be related to the much less oriented structure obtained for highly reinforced composites because of their much higher viscosity.

As mentioned previously, the SCORIM results are based on 5-mm samples and those for conventional injection

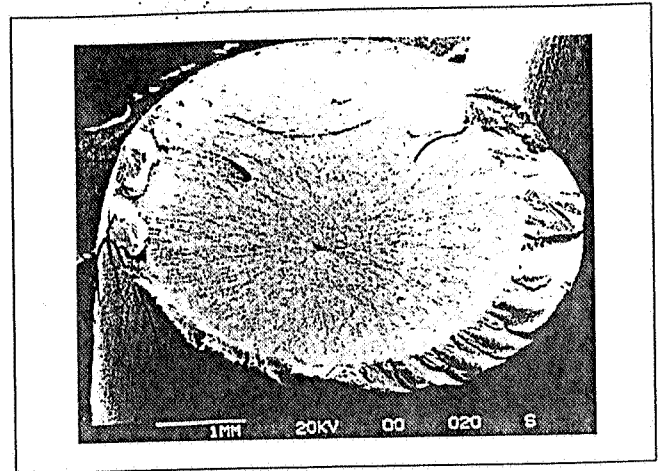


Figure 3. SEM micrograph of a tensile fracture surface of a conventionally molded 5-mm SEVA-C sample.

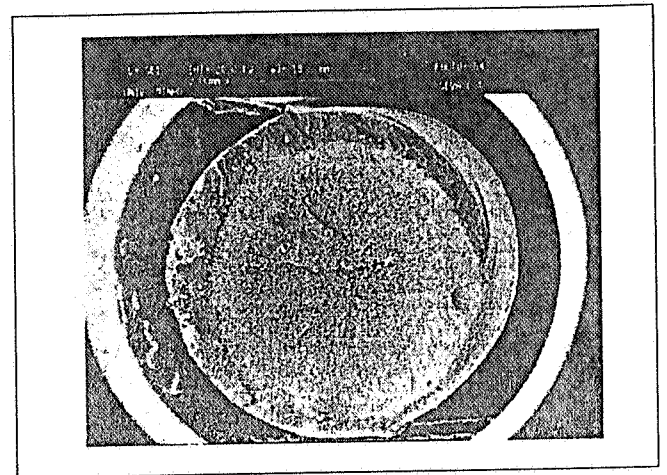


Figure 4. SEM micrograph of a tensile fracture surface of a SCORIM-S2-molded 5-mm SEVA-C sample.

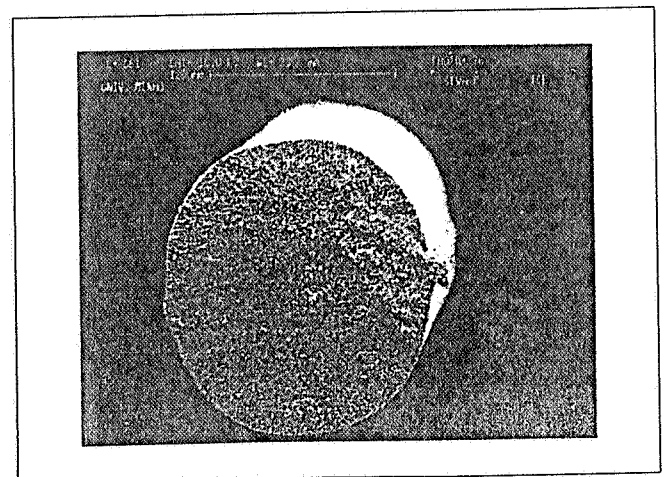


Figure 5. SEM micrograph of a tensile fracture surface of a conventionally molded 1.5-mm SEVA-C/30%-HA composite.

molding on 1.5-mm samples. When SCORIM was used—both for the matrix and for HA-reinforced composites—the thicker SCORIM-processed samples were always stiffer than the conventionally molded ones. These results strongly

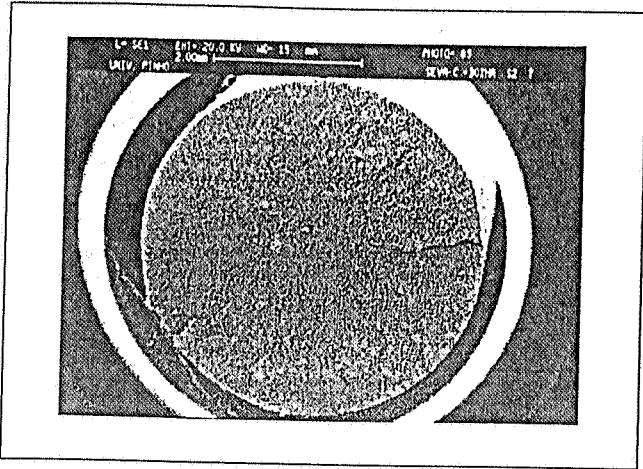


Figure 6. SEM micrograph of a tensile fracture surface of a SCORIM-S2-molded 5-mm SEVA-C/30%-HA composite.

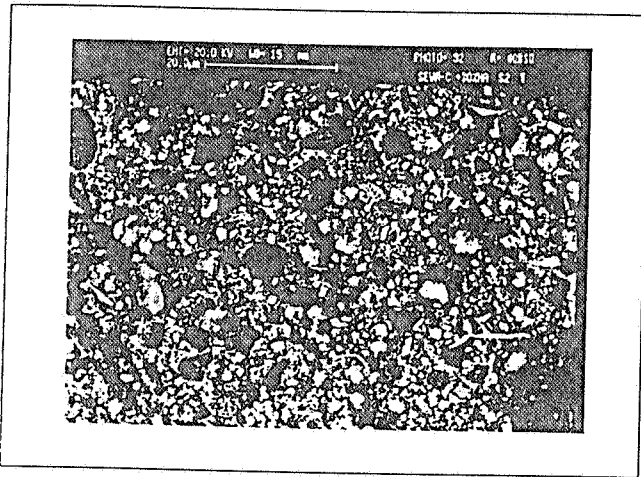


Figure 7. Superimposed secondary and back-scattered electron images showing the HA distribution in a SEVA-C/30%-HA composite.

reinforce the notion that the mechanical performance of these polymers is highly sensitive to molecular orientation imposed through processing.

Figures 3 and 4 show SEM micrographs of fracture surfaces for conventionally molded and SCORIM S2 samples, respectively. The conventional sample exhibits the more brittle pattern and a clear fracture nucleation point typical of conventionally molded SEVA grades, whereas the SCORIM shearing of the melt leads to a much more compact structure that eliminates these internal defects. The same type of result was obtained for HA-reinforced SEVA. Figures 5 and 6 show the respective tensile fracture surfaces, with the much more compact structure obtained with the SCORIM molding clearly evident. In fact, the stiffness of the materials was enhanced by the addition of bioactive bone-like ceramics. For SCORIM S2 processing conditions, one result of the more compact and oriented structure produced was that increasing the HA amounts (up to 30% by weight) tended to improve the modulus of the composites.

As could be anticipated, the ductility of both polymers

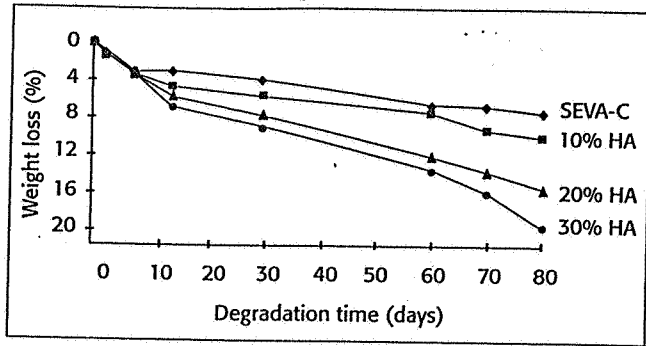


Figure 8. Dry weight loss versus degradation time in HBSS at 37°C for SEVA-C and several HA-reinforced composites.

decreased severely with the addition of HA. Nevertheless, the respective ductility figures are much higher than typical values for bulk-sintered HA, and are on the order of magnitude of values obtained with other reinforced polymeric systems. However, for the SCORIM-processed composites it has been possible to achieve a modulus matching that of cortical bone (7 to 21 GPa), with a simultaneous enhancement of sample ductility for HA levels up to 20%. This good mechanical performance can be attributed to the SCORIM processing and to the homogeneous HA dispersion in the matrix induced by the TSE compounding (see Figure 7). Such performance has the potential to open up an entirely new range of applications for this type of material, whose brittle behavior was previously a major constraint. Furthermore, the reported processing methodology can be used to fashion materials with an anisotropic behavior also similar to that of bone.

The degradation behavior of the several materials is plotted in Figure 8 as dry weight loss versus degradation time. The weight loss depends strongly on the HA additions, and higher amounts of HA reinforcement tend to increase the degradation rate in HBSS. This result indicates that both the matrix and the reinforcement are degrading simultaneously, which may mean that these materials will be fully absorbable when implanted.

CONCLUSION

The encouraging results obtained show that by using shear-controlled orientation in injection molding during the processing of SEVA/HA composites it is possible:

- To attain a remarkable mechanical performance of the composites that may allow their use in small-load-bearing applications (the goal of matching the minimum stiffness of cortical bone was accomplished for 30%-HA composites).
- To develop materials with a stiffness matching that of human cortical bone using much smaller amounts of HA reinforcement than has been previously reported.^{2-4,6}
- To process both thick and thin implants with controlled microstructure.
- To obtain materials simultaneously exhibiting both higher modulus and higher ductility for HA amounts up to 20%.



• To develop composites in which both the matrix and the reinforcement are degraded in simulated physiological solutions.

It can be said that, for the purpose of processing SEVA/HA composites, the use of SCORIM is a unique way of inducing anisotropy to thick sections and of producing stiff, but not brittle, materials that have potential in small-load-bearing applications.

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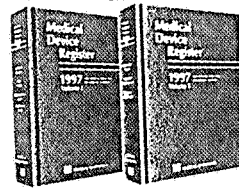
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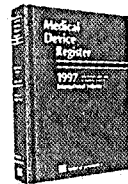
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