Reinforcement and Structure Development in Injection Molding of Bone-Analogue Composites

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Composites of high density polyethylene (HDPE) with hydroxyapatite (HA—the main inorganic constituent of human bone) were produced by extrusion compounding and subsequent injection molding. Shear controlled orientation in injection molding (SCORIM) was used deliberately to induce a strong anisotropic character in the composite materials. Bi-composite moldings featuring a sandwich like morphology were also produced by mono-sandwich injection molding. These composites combine a HDPE/HA outer layer and HDPE/carbon fiber reinforced core. For all the cases, the mechanical performance of the produced composites was assessed and the structure developed investigated and related to the processing conditions.

INTRODUCTION

The permanent replacement of hard tissues in load bearing applications demands mechanically strong biocompatible materials. The attainment of the envisaged mechanical performance depends on technological ability to mimic the bone's anisotropic character. This can be achieved with polymer based composites, as they combine adequate stiffness and strength with a viscoelastic character. Bonfield *et al.* (1) introduced the bone-analogue concept, when composites comprising a polymer ductile matrix (polyethylene—PE) and a ceramic stiff phase (hydroxyapatite—HA) were proposed. The idea is based on a semicrystalline material that can develop a considerable anisotropic character by means of adequate orientation techniques. This semicrystalline material is also reinforced with a bone-like ceramic that simultaneously ensures the mechanical reinforcement and the bioactive character of the implant (2). The use of hydrostatic extrusion to process PE/HA composites has been shown to be a successful route for the production of composites with bone-like mechanical performance (3, 4).

An alternative approach to the mechanical performance enhancement of HDPE/HA composites was followed by Reis *et al.* (5) with the use of shear controlled orientation in injection molding (SCORIM). In SCORIM processing, the molten material is forced between two piston chambers after the filling of the mold, while the solidification progresses from the mold wall to the core, causing a controlled macroscopic shear field at the moving melt/solid interface. The solidification of the aligned polymer molecules, as imposed by the shear field, results in the mechanical property enhancement desired for the intended biomedical field of application. In spite of the ability of SCORIM in controlling, to a certain extent, the structure development of the HDPE matrix and inducing, as a result of that, a clear anisotropic mechanical behavior into the molded part, the performance of the HDPE/HA composites is still below the envisaged goal. This lack of performance is mostly attributable to the HA particles, that are efficient from a bioactive point of view, but inefficient as a mechanical reinforcement of the polymer matrix. The poor ability of HA powders in extending the stiffness of the composites results from their particulate nature (low aspect ratio). Additionally, their poor chemical/physical interaction with the HDPE phase, which limits the load transfer in the composite and restricts the final mechanical behavior limits the stiffness extension.

The selective reinforcement of the implant core with very stiff fillers like carbon or aramid fibers and limiting the use of bioactive filler particles to the surface,

is believed to be a potential route to meet the levels of stiffness desired for the application. The HDPE/HA surface layer is aimed to ensure specific surface properties, while the HDPE/stiff fiber core is intended to guarantee the mechanical performance of the so-called bi-composite within the desired range of stiffness. This strategy is expected to enable the development of HDPE based load bearing implants with complex geometry, controlled chemical properties and high mechanical performance.

This work focuses on the SCORIM processing of HDPE and HDPE/HA composites and tries to establish the respective structure/properties relationships. Special emphasis is given to the structure development of the HDPE matrix. Furthermore, an alternative reinforcement strategy, based on the selective reinforcement with carbon fibers (C fibers) is proposed. For this case, the correlation between morphology and mechanical performance is briefly described.

MATERIALS AND METHODS

Materials

The study materials were three high density polyethylene (HDPE) grades, namely two high molecular weight HDPE grades with references HD8621 and GM 9255F produced respectively by DSM research (The Netherlands) and Elenac GmbH (Germany). The third grade is a HDPE, with the reference A6016, produced by Vestolen GmbH (Germany). Two commercially available synthetic HA grades were used: (i) a sintered HA (HAs) and (ii) a non-sintered HA (HAns), both supplied by Plasma Biotal Ltd (United Kingdom). Short fiber reinforced HDPE composites were produced using a C fiber type HTA, with 6 mm of length and a length/diameter (aspect) ratio of 860, from Tenax Fibers, GmbH & Co. (Germany).

Extrusion Compounding

Composites of HDPE with 25 and 50% wt. HA were compounded in a Leistritz AG-LSM 36/25D twin screw extruder (TSE) using a temperature profile between 160 and 190°C. The composite formulation for 50% wt. HA included 0.5% wt. (relative to the HA fraction) of a zirconate coupling agent (NZ12, Kenrich Petrochemicals, Inc., USA). In a previous study (6), the use of titanate and zirconate additives was found to improve considerably the filler dispersion in HDPE/HA composites.

Short fiber reinforced composites of HDPE, using 25% wt. C fibers, were also compounded in the TSE equipment, using a temperature profile between 160 and 210°C. Separate polymer and fiber feeding ports were used in order to minimize the breakage of the C fibers. The extrudate was chopped manually in 60 mm long segments for subsequent injection molding.

Injection Molding

Both conventional injection molding (CM) and SCORIM were used to produce axysimmetric tensile test bars with 5 mm cross section diameter and 25 mm of gauge length. The injection molding equipment used was a Demag D-150 NCIII-K machine fitted with a SCORIM I head.

Two specimen geometries were produced by mono-sandwich injection molding: i) tensile test bars with a rectangular cross of 4×10 mm^2 and ii) impact test bars with a rectangular cross section of 6×13 mm^2. Both specimens were produced in a two-component injection molding K-85 Ferromatik-Milacron machine.

Tensile Testing

The tensile tests were performed on an Instron 4505 universal testing machine fitted with a clip-on resistive extensometer. The tensile test bars were tested in order to determine the tangent modulus (E_t), the secant modulus at 0.8% strain ($E_{0.8\%}$), the ultimate tensile strength (UTS) and the strain at break point (ε_b). These tests were performed in a controlled environment (23ºC and 55% RH). The cross-head speed was 5 mm/min. (8.3×10^{-5} m/s) until 1.5% strain and then increased to 50 mm/min. (8.3×10^{-4} m/s) until fracture.

Impact Testing

Impact tests were conducted in an instrumented falling weight impact machine, Rosand Type 5. The tests were performed at a test speed of 3 m/s, using a support with 32 mm span and a 25 kg anvil. For each test the force at peak (F_p), the peak energy (U_p) and the failure energy (U_f) were determined.

Microhardness

Microhardness experiments were carried out at room temperature on selected specimens, along the diameter of the cross sections, on a Leica VMHT30A.

Polarized Light Microscopy (PLM)

Thin slices, with an average thickness of 15 μm, were obtained from the middle of the gauge length region of the bars and observed by optical polarized light microscopy (PLM) using an Olympus BH-A microscope.

Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) was performed for analysis of tensile failure surfaces on a Leica Cambridge LS360 SEM. All the surfaces were mounted on a copper stub and coated by ion sputtering with an Au/Pd alloy prior to examination.

Differential Scanning Calorimetry (DSC)

Calorimetric studies were performed on a differential scanning calorimeter (DSC) Perkin Elmer DSC 7. Each sample was cut from the middle point of the gauge length of the tensile test bars. The samples were placed in aluminum pans and heated at a rate of 10.0°C per minute from 30 to 180°C.

X-ray Diffraction

Ni filtered Cu K_α radiation was used to obtain X-ray diffraction spectra from the molded specimens. Sections were taken from the middle region of the gauge length and scanned over a Bragg range of $7 < 2\theta < 50^o$.

RESULTS AND DISCUSSION

Structure Development in HDPE/HA Composites

Figure 1 presents the WAXD spectra for conventional and SCORIM moldings together with the respective X-ray diffraction patterns obtained from the mold wall at a distance of 1.5 mm. The higher crystallinity of the SCORIM processed samples is evident as seen by the increase in intensity of the (110) and (200) reflections. Furthermore, the X-ray diffraction pattern acquired for SCORIM shows clear signs of c-axis orientation parallel to the main direction of flow (MDF). This is a sign of the development of a strong anisotropic character. This increase in crystallinity has also been observed by DSC measurements. The heating scans of SCORIM processed HDPE specimens revealed the existence of an additional melting peak endotherm at higher temperatures (not observed for conventional molding) that is an indication of a shear induced crystalline morphology referred to as shish-kebab. This strong anisotropic character results in improvements in stiffness up to 400% as compared to conventional injection molding. Values above 7 GPa and 150 MPa can be obtained respectively for E_t and UTS following a suitable optimization of the SCORIM process.

Scanning electron microscopy of the typical tensile fracture surfaces of SCORIM processed HDPE/HA composites revealed the existence of a distinct laminated morphology (6). This laminated morphology developed during shear application and features three well-defined zones: a skin layer, a core region and a layered zone in between. *Figure 2* presents the polarized light microscopy (PLM) photograph of the longitudinal section of a SCORIM processed HDPE, where this morphology is evident. Combined microhardness and calorimetric measurements along the cross section diameter revealed that a M-pattern profile is associated with this type of morphology. *Figure 3* presents the microhardness variation along the cross section diameter for SCORIM processed HDPE together with the

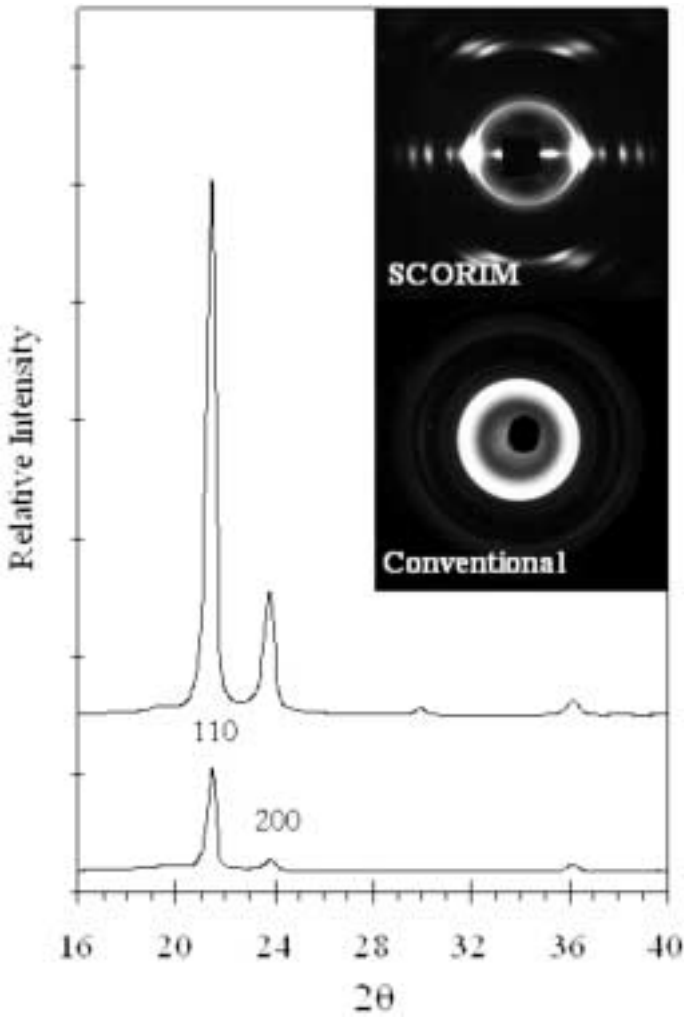

Fig. 1. Wide angle X-ray diffraction (WAXD) spectra and the respective X-ray diffraction patterns gained for samples produced by conventional injection molding (CM) and SCORIM.

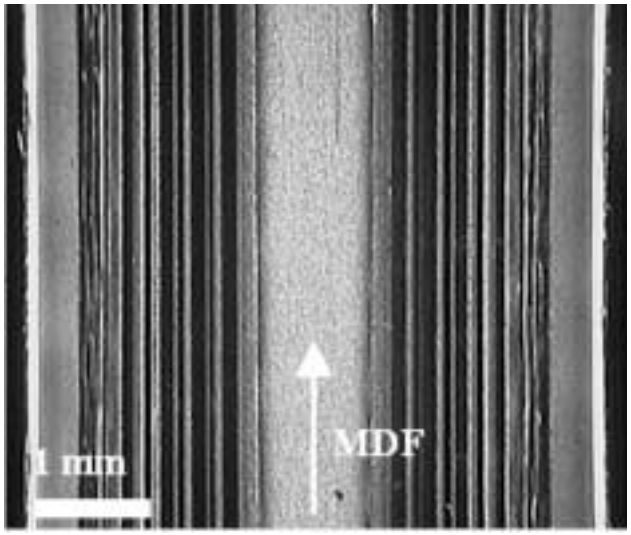

Fig. 2. Polarized light microscopy (PLM) photograph of the longitudinal section of a SCORIM processed HDPE. The arrow indicates the main direction of flow (MDF).

respective crystalline values as determined by DSC measurements. It is possible, from the observation of *Fig. 4*, to define three regions: a low crystallinity skin (in the vicinity of the frozen layer), a highly crystalline transition layer (associated with a clear laminated morphology) and a less crystalline core (central zone of the cross section). The layered morphology observed in SCORIM molded specimens feature a crystalline anisotropic structure that sustains the mechanical performance improvement observed. The delineation of the layered morphology upon tensile testing (*Fig. 2*) arises from the structure discontinuity of the SCORIM processed specimens. These specimens alternate highly orientated layers, crystallized under the influence of shear, with thin spherulitic layers in between the former, crystallized during the interruptions of the shear flow between consecutive piston strokes.

Figure 4 presents the microhardness profile combined with the X-ray diffraction patterns for both conventional molding and SCORIM processed HDPE/HA composites. The HDPE/HA composites also exhibit M-pattern microhardness profile, which suggests that a similar crystallinity profile variation as for unreinforced materials, occurs for the composite material. For all the patterns exhibited in this figure, the longitudinal direction of the tensile test bar (i.e. main direction of flow) is parallel to the S-N direction in the figures. At the skin region (0.5 mm from the mold wall), the X-ray patterns are very similar for conventional and SCORIM moldings. However, at the core region (2.5 mm) it is possible to observe some considerable arcing at the equatorial of the diffraction rings for the SCORIM moldings associated with the (110) and (200) reflections. This arcing reveals molecular orientation parallel to MDF as a consequence of the shear induced crystallization process.

Selective Reinforcement of HDPE/HA Composites

The degree of mechanical reinforcement of HDPE accomplished with HA powders is limited. This limitation arises from both the reduced aspect ratio of the

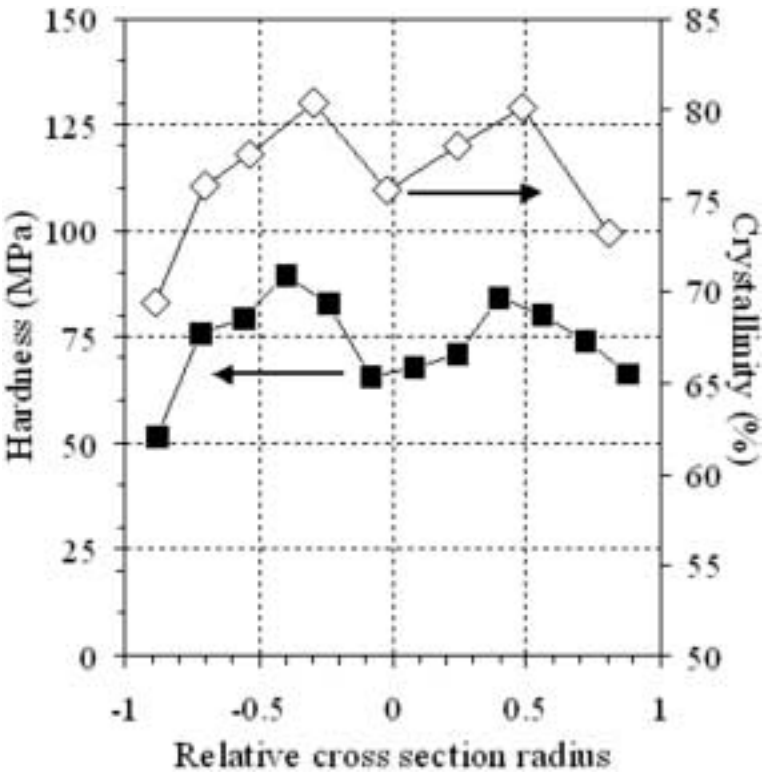

Fig. 3. Microhardness and crystallinity variation along the cross section diameter for SCORIM processed HDPE.

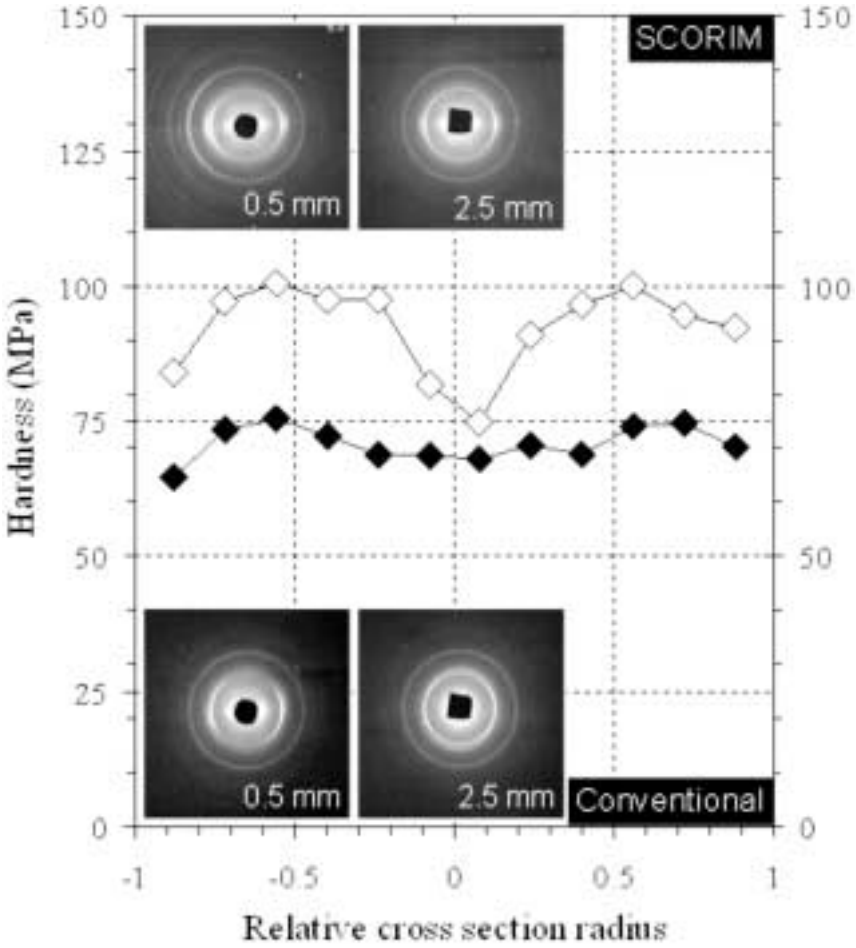

Fig. 4. Microhardness and X-ray diffraction patterns gained along the cross section diameter for conventional molded and SCORIM processed HDPE + 25% wt. HAs composites.

particles and the limited interfacial interaction between HA and the polyolefin matrix (6). The selective replacement of the HA particles in the bulk of molded parts, where its use is not needed or advantageous, by a very stiff filler, such as carbon fibers (C fibers), is a possible approach for the development of high mechanical performance, biocompatible composites. In a previous work (7), a compounding, injection molding machine that combines a co-rotating twin-screw extruder with an injection molding unit has been used to process HDPE/C fibers composites. Values of E_t up to 10 GPa were obtained for a fiber weight amount of about 20% wt. However, the range of stiffness obtained with such reinforcement strategy is still limited by a pronounced variation of the C fibers orientation along the part thickness.

The final aim is to develop sandwich moldings comprising a HDPE/HA composite outer layer and a HDPE/C fibers composite core. The HDPE/HA surface layer ensures specific surface properties while the HDPE/C fiber core guarantees the mechanical performance of the part within a desired range of stiffness. Sandwich moldings exhibit 5.6 GPa of E_t and 35.5 MPa of UTS. In terms of impact performance, sandwich moldings (rectangular cross section of 9×13 mm^2) exhibit a similar impact behavior to the HDPE/C fiber composite moldings. Nevertheless, the values of energy absorbed during the crack initiation (U_p) and propagation stages (U_f) for the bi-composite materials were still below those obtained for single HDPE/C fibers composites. *Figure 5* presents a typical PLM photograph of the bi-composite morphology together with the evolution of the respective average outer layer thickness along the flow length. An increase of the HDPE/HA composite layer thickness occurs, as would be expected, from the advancement of the progressively cooler melt front during the filling stage. *Figure 6* presents the SEM photograph of a typical tensile failure surface of a bi-composite molding. The HDPE/C fibers composite core evidences two distinct zones: a shell region, where the C fibers are mainly parallel to the MDF; and a central region where the C fibers are predominantly perpendicular to MDF. The shell region of the HDPE/C fiber core is located in the vicinity of the HDPE/HA outer layer and is the main reason for the stiffness exhibited by these moldings.

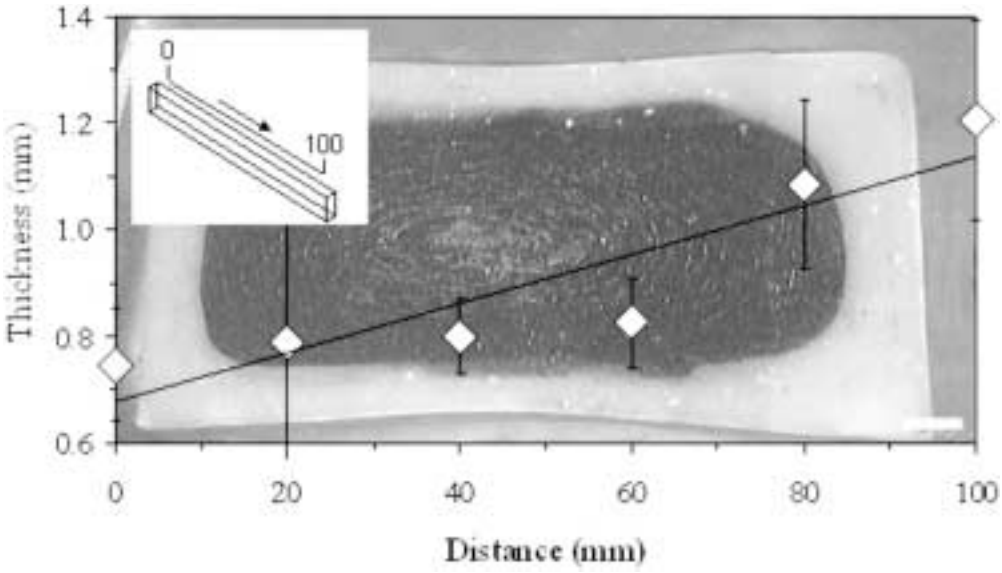

Fig. 5. Variation of the outer layer thickness along the flow path for HDPE/HA/C fiber composites (0 mm corresponds to the gate point).

CONCLUSIONS

Table 1 summarizes the mechanical properties of the composites produced. The high mechanical performance of the SCORIM processed composites is the result of the strong anisotropic matrix and, to a lesser extent, the higher degree of filler dispersion. The high anisotropy is associated with laminated morphology exhibiting the strong molecular orientation.

The particulate nature of the HA powder (low aspect ratio) acts as a severe constraint to the enhancement of stiffness. The use of alternative reinforcement, like C fibers, proved to be a valid approach to the further extension of the stiffness range. Composites featuring a sandwich-like morphology were successfully produced by injection molding. These moldings comprise a HA filled HDPE surface layer and C fiber reinforced core. So far, the mechanical performance of these bi-composite moldings is strongly limited by the high thickness and the uneven distribution of the outside HDPE/HA layer. Further improvements in the mechanical performance of these moldings are expected through the adequate control of the respective morphological development.

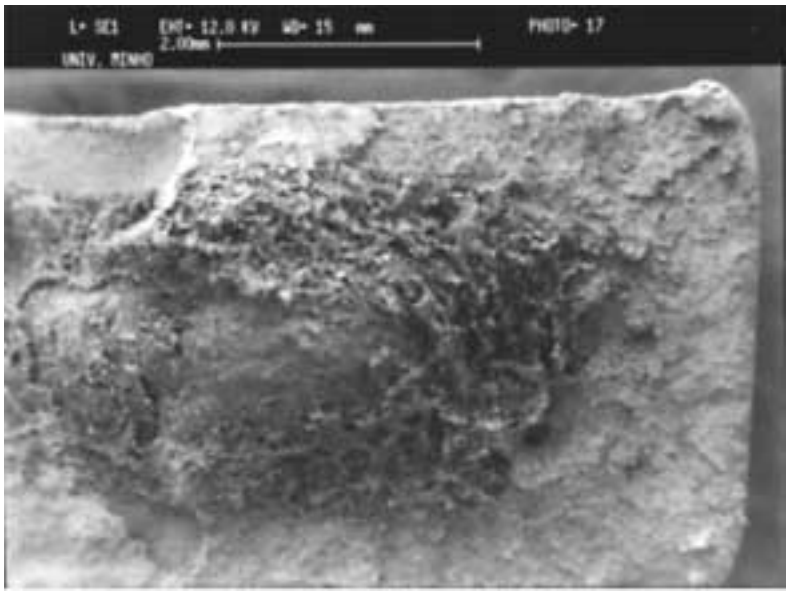

Fig. 6. Scanning electron microscope (SEM) photographs of the failure surface of a bi-composite molding after tensile testing featuring a HDPE/HA outer layer and a HDPE/C fibers core.

Table 1. Reference Mechanical Properties for HDPE/HA, HDPE/HA/HDPE/C Fibers Sandwich Composites.

		SCORIM		
	Filler wt. (%)	E_t (GPa)	UTS (MPa)	ε_f (%)
HDPE	0	3.0−7.1	55−155	12−21
HDPE/HA	25−50	5.9−7.5	74−91	19−31
		Sandwich molding		
HDPE/HA HDPE/C fibers	50 25	5.6	35	3

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