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Mechanical and Thermal Characterisation of Poly (Ethylene) and Thermoplastic Starch Filled with Keratin Horn Powder from Bovine Claws

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Abstract

In this work, composites with two different thermoplastic matrices, a polyethylene and a thermoplastic starch, have been prepared by the introduction of waste from cattle slaughtering, in particular keratin horn powder from bovine claws. The amount of filler used for the purpose was varied from 10 to 30 parts in weight, considering as 100 the amount of polymer. Thermal characterisation indicated that the properties of keratin horn are compatible with the extrusion process adopted. The obtained composites showed some degree of interfacial adhesion between matrix and filler, as confirmed by electron microscopy observation. An enhanced rigidity, with a three-fold increase of stiffness for the introduction of the highest amount of filler in both matrices, was measured. However, brittle behaviour was particularly observed on thermoplastic starch composites.

Introduction

Keratin horn has a long tradition of use, usually trying to preserve as much as possible its structure, such as it has been the case for other skeletal materials e.g., bone, antler and ivory. In particular, during history horn was effectively bent, carved and pierced, representing a material with considerable flexibility and value. Horns are composed by α-keratin, with its characteristic helical structure [1]. In this structure, glycine and alanine, the smallest amino acids, are found in high concentrations. The keratin molecules are held together by H-bonding and disulfide cross-linked bonds, due to the presence of cysteine, therefore being considerably rigid and insoluble [2]. These characteristics can be considered to be preserved even at a microscopic level, as demonstrated from previous studies on the use of keratin waste as the reinforcement for poly(lactic) acid matrices [3-4].

Horn is largely present in cattle, sometimes in locations and extensions that make it difficult to use it as received, such as it is the case for claws, which can be considered as a waste product to dispose of after bovine slaughtering. In this case, waste material has been obtained from bovine claws, in particular from the wall, which is formed by tough tubular horn, normally smooth and shiny, with faint ridges running parallel to the coronary band [5]. It is nonetheless important to consider that the mechanical properties of bovine horn can considerably vary, depending on the origin of the cattle [6-7] and also as the possible consequence of the development of diseases [8]. It can be suggested therefore that selected cattle as the one destined to slaughtering for consumption purposes, would possibly offer a horn with reduced variability of mechanical characteristics.

Here, the horn material used to reinforce two different thermoplastic matrices, an oil-derived one (polypropylene) and a biopolymer (thermoplastic starch), had been ground to powder after slaughtering and separated from a batch of it, which is normally to be disposed of by incineration. The objective of this work is therefore to evaluate an alternative use of this waste to reduce its environmental burden, possibly conferring an added value upon it by its enclosure into polymer matrices.

Experimental

To produce the materials employed in the present investigation, two kinds of thermoplastic matrices have been selected, a synthetic matrix, the high density Polyethylene (HDPE) Purell 33 AC resin (by Lyondel Basell) and, as a biodegradable counterpart, Mater-Bi NF01U (by Novamont) thermoplastic starch (TPS) resin. As filler, bovine keratin claws reduced in fine (micrometric) powder has been used, which has been obtained at a local slaughterhouse.

As a preliminary stage, matrices in the shape of granules and claws powder have been hand-mixed until a homogeneous dry blend has been obtained, using different filler amounts. In particular, the nominal mixture compositions are the following:

- Matrix (HDPE or Mater-Bi)/claws-based filler (CBF): 100:10;
- Matrix (HDPE or Mater-Bi)/claws-based filler (CBF): 100:20;
- Matrix (HDPE or Mater-Bi)/claws-based filler (CBF): 100:30;

The dry blend has been subjected to a mixing and subsequent extrusion stage inside a twin co-rotating screw micro-extruder, DSM Model Xplore MC 15. Both in the case of the HDPE based composite and in the Mater-Bi (MB) based one, the mixing time amounted to 2 minutes at a mixing rate of 100 rpm.

As regards the temperature profile, the extruders are equipped with three heating zones, whose temperature can be separately fixed, as from the scheme in Figure 1 (T1, T2, T3, indicate the three different temperatures). In the case of the HDPE based composites, the three temperatures are 110°C, 130°C and 150°C, respectively, whereas in the case of the Mater-Bi based ones their values are 130°C, 140°C and 150°C, respectively.

The production of samples, namely those subjected to mechanical characterisation, has been carried out by means of a micro injection moulding machine: DSM, model Xplore IM 12. With this purpose, for both kinds of composites, injection temperature was set to 150°C, injection pressure to 9 bar and holding time to 12 seconds. Mould temperature has been set up at 45 °C in the case of the HDPE based system injection and 40°C in the Mater-Bi based counterpart. Samples dimensions and geometry comply with the prescriptions of ISO 527 standard (sample typology 1BA).

Mechanical testing activity has been carried out according to the standard ISO 527. An electronic dynamometer LLOYD INSTRUMENTS 30 K model has been used to perform the mentioned tensile test, with a load cell of 30 KN. Tests have been carried out at a room temperature and at elongation rate of 1 mm/min.

Results and Discussion

The results obtained from thermal characterization of bovine keratin horn powder are reported in Figure 1 (thermogravimetry) and in Figure 2 (differential scanning calorimetry). Apart from the initial peak, corresponding to the loss of humidity in the samples, the following peak, which starts at around 226°C, as suggested by DSC, and then peaks at 321°C, as indicated by TGA, is the result of the α-helix denaturation of the material [9]. Denaturation would result in the disruption and possible destruction of both the secondary and tertiary structures of the proteins by reducing the proteins to their bare primary structure, hence an unfolded sequence of amino-acids. The loss of structural water, which is known to be an integral part of the folded structure of the proteins, is the main contribution to the weight reduction of up to around 75% at 500°C, as from Figure 3 [10].

These data are interesting, in that they suggest that the application of thermoplastic matrices, such as those used in the present study, hence requiring maximum processing temperatures in the order of 150°C, would not result in significant degradation of bovine keratin horn properties.

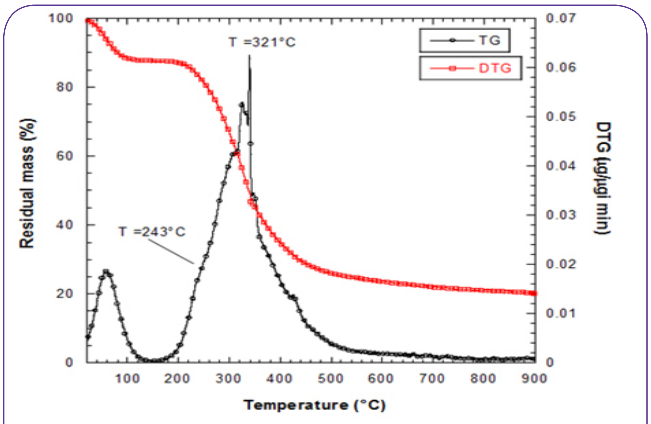

Figure 1: Thermogravimetric data on keratin horn powder

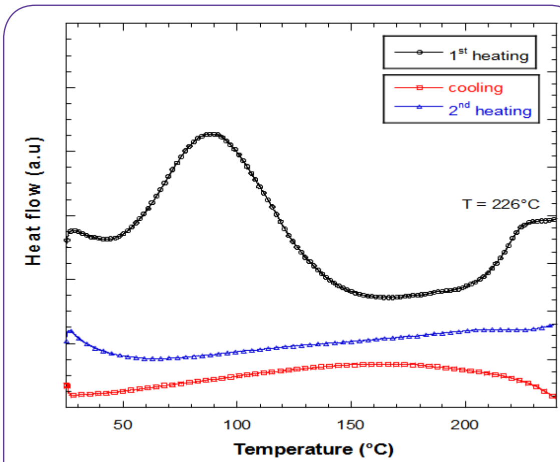

Figure 2: DSC data for keratin horn powder

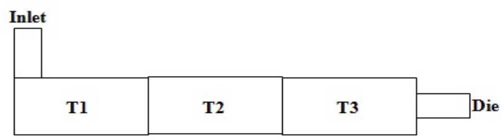

Figure 3: Extruder heating zones

In Figure 4 and in Table 1 results related to the HDPE based composites mechanical testing have been summarized. As shown, the addition of bovine claws based powder to the HDPE based matrix leads to a dramatic decrease in the ultimate strain, with higher evidence with increasing amounts of filler. As a consequence of this increased rigidity of the composite, the region of the stress-strain curve beyond the proportionality limit has progressively less evidence the higher the amount of bovine claws powder in the composite, until becoming hardly noticeable for 30 wt.% powder composites. Also the tensile strength experiences some decrease for the HDPE based composites

Table 1: Results related to the tensile tests developed on the HDPE based composites.

Material	Strength (MPa)	Strain (at yield) (%)	Young's Modulus (MPa)
Neat HDPE	20.9 ± 3.0	39.0 ± 3.9	249.3 ± 25.1
HDPE + 10 wt.% CBF	16.7 ± 1.6	16.7 ± 1.8	367.4 ± 12.4
HDPE + 20 wt.% CBF	17.4 ± 1.0	11.2 ± 0.6	487.3 ± 47.6
HDPE + 30 wt.% CBF	14.4 ± 0.1	4.7 ± 0.2	727.1 ± 37.7

in comparison to the neat matrix, with more evidence for the 30 wt.% powder composite, which highlights the non optimal compatibility between the filler and the matrix, leading to the composites embrittlement.

Quite to the contrary, the addition of the mentioned fillers determines a significant increase in the Young's modulus. At this purpose, the composite containing the 10% in weight of the filler experience an increase in the mentioned properties of the 50% in comparison to the neat matrix. An increase of the 95% is obtained in Young's modulus relative to the composite filled with 20% in weight of claws based micropowder. Finally, the addition of 30% in weight of keratin horn based micropowder leads to an increase of the aforementioned properties by 191% in comparison to the neat matrix.

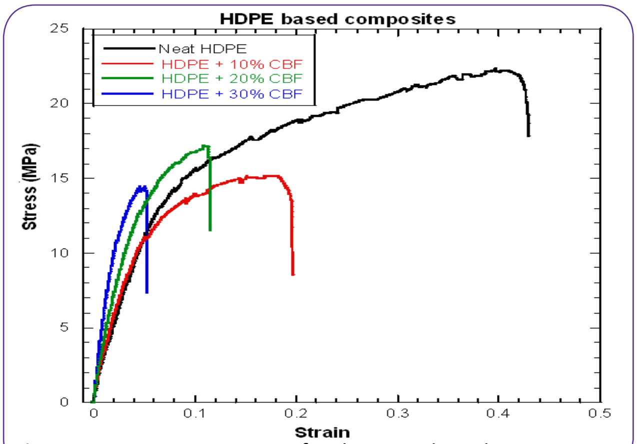

Figure 4: Stress-Strain curves for the HDPE based composites

In Figure 5, as well as in Table 2, results related to the tensile testing of the Mater-Bi based composites have been summarized. Also in this case, the addition of claws based powder to the matrix leads to a dramatic decrease in the strain at break, proportional to the amount of fillers included into the matrix. Moreover, composites with Mater-Bi matrix present a stress-strain curve with basically very limited evidence of a plastic region, so that yield strength and ultimate strength appear to virtually coincide for any amount of claws based powder introduced in the matrix.

As seen in the case of the synthetic matrix based composites, the addition of the mentioned fillers determines a significant increase in the Young's modulus, which grows proportionally to the amount of filler introduced in the matrix, until reaching an approximate three-fold increase with the highest amount of filler, 30 wt.%. It is worth noting that, in general, increase of rigidity is highly desirable especially in the case of Mater-Bi, to extend field of applications for this material: a number of fillers have been tried for the scope, in particular selected among the biodegradable ones, such as for example wood flour [11]. A general observation on mechanical test results would also concern the fact that the scattering of properties did not exceed a few percent, which is significantly good for the introduction of an organic material, such as keratin horn, as filler.

SEM micrographs, reported in Figure 6, indicate that both for the lowest and at the highest tenor of filler introduced, effective embedding of the powder in the matrix is obtained. Moreover, some degree of adhesion at the interface between matrix and filler is observable for the very limited amount of detached powder granules revealed, even when 30 wt.% of filler is introduced.

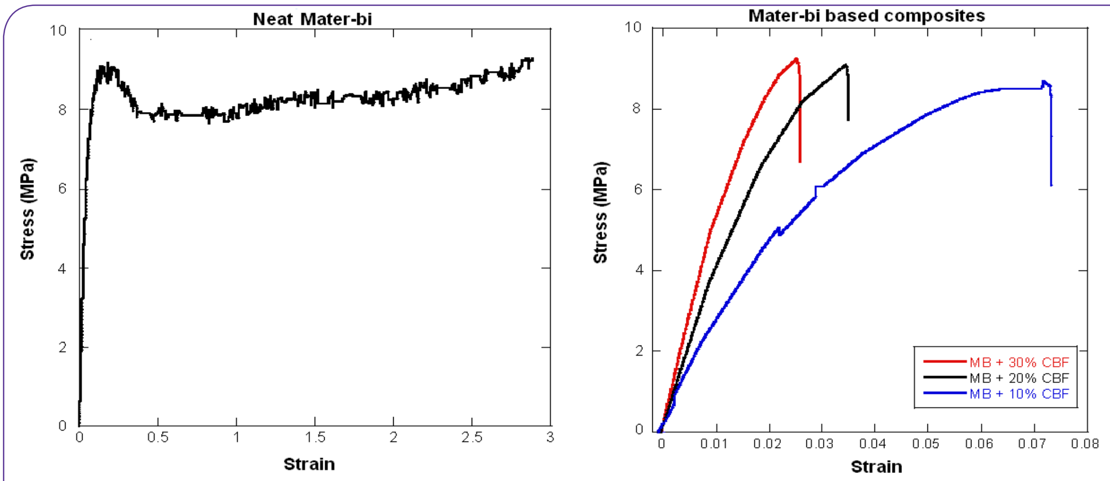

Figure 5: Stress-Strain curves for neat Mater-Bi and Mater-Bi based composites

Table 2: Results related to the tensile tests performed on the Mater-Bi (MB) based composites

Material	Strength (MPa)	Yield Strain (%)	Young's Modulus (MPa)
Neat MB	9.1 ± 0.2	18.5 ± 2.8	159.3 ± 10.4
MB + 10 wt.% CBF	8.8 ± 0.4	6.8 ± 1.3	246.7 ± 10.5
MB + 20 wt.% CBF	9.2 ± 0.3	3.6 ± 0.2	394.5 ± 18.2
MB + 30 wt.% CBF	9.2 ± 0.2	2.6 ± 0.1	469.1 ± 41.3

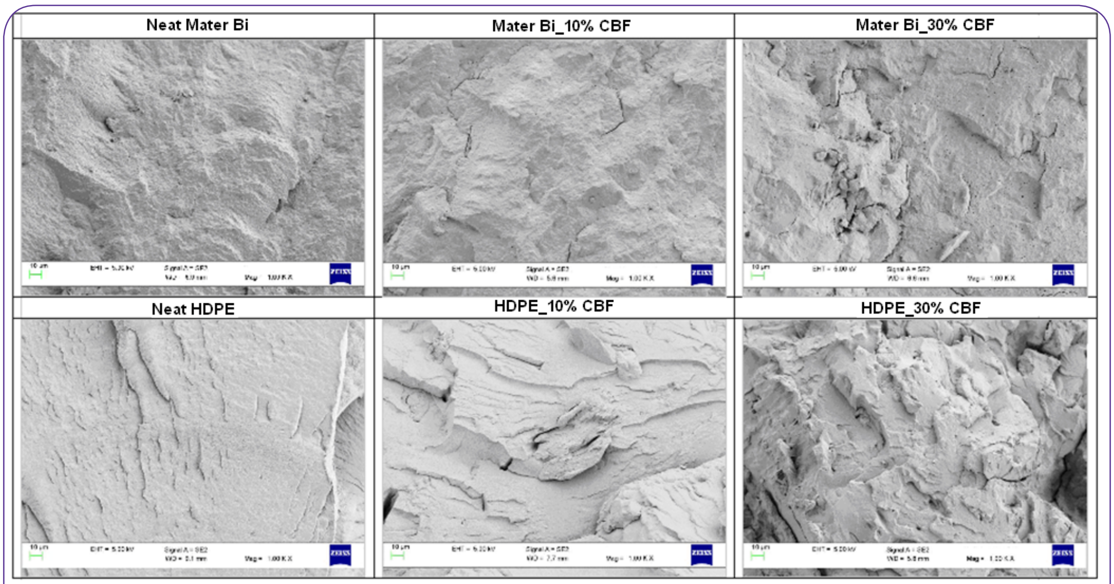

Figure 6: Morphology of fracture surfaces of different composites

Conclusions

The tentative introduction of some amount of keratin horn, obtained in the form of ground powder from bovine claws after slaughtering, in two types of thermoplastic matrices, namely high density polyethylene and thermoplastic starch (Mater-Bi), indicated in both cases the possibility to produce a composite with sufficient properties. The thermal properties of filler materials allowed their processing in the composite at temperatures required for extrusion of the above polymers. The fabrication of the composite allowed a considerable increase of the rigidity of the material with respect to the pure matrix, although this resulted also, particularly in the case of thermoplastic starch matrix composites, in significant brittleness. Further improvement of this process would consist in a thorough control over the granulometry of the filler powder and in its improved mixing process to obtain a more homogeneous material, aspects that have not been considered in the present study.

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