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3 **Production and Tensile Characterization of**  
4 **Thermoplastic Starch Films filled with Iron**  
5 **Scrap Powder Waste and Molded on Different**  
6 **Support Materials**

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10 **ABSTRACT**

This work concerns the application of waste filler, consisting of scrap iron powder as received from machining in a small-scale workshop, in a self-produced thermoplastic starch (TPS) based on corn starch acidified with acetic acid and plasticized with glycerol. The films obtained had a target thickness of 250 microns. The maximum amount of waste introduced was 0.8% and the material was produced on different supports, consisting either of a glass plate or of a silicone mould.

Tensile testing was performed and the best performance was obtained by the one prepared on glass support, although in general terms it was very far from similar industrial material, not exceeding a 10% maximum strain and being very sensitive to the disposition and geometry of the waste introduced. The value of the work is in the use of waste, which is rarely re-used, and in the possible production of conductive and magnetic biopolymer films

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12 *Keywords: Iron scrap waste; starch **bio-composites**; DIY bioplastics; tensile characterization*

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14 **1. INTRODUCTION**

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16 Scrap iron is an abundant waste on blacksmith operations, which have found some  
17 application to treat some other waste streams containing hazardous materials, for example  
18 in the case of the reduction of hexavalent chromium to trivalent one [1]. Large steel works  
19 have from a few decades policies leading more recently to “zero waste strategies” [2]. On  
20 the other side, the use of scrap iron powder as filler in materials encounters some difficulties  
21 in normal working of small blacksmith workshops located e.g., in family enterprises, technical  
22 school, etc., where scrap iron powder have to be disposed in special waste collection, which  
23 may involve some costs. In particular, reuse as filler may encounter some difficulties for the  
24 dimensional scattering of the powder obtained, which can go from around 20 microns to over  
25 500 microns, and also the presence of some impurity, such as dust.

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27 A possibility would be to exploit the electrical conductivity and magnetic properties of this  
28 waste material to offer them to other materials, which typically have limited conductivity,  
29 such as biopolymers. The production of the so-called DIY bioplastics, based mainly on  
30 starch-glycerol mixtures and therefore identifiable as “thermoplastic starches” (TPS) may  
31 offer an opportunity in this sense, since TPS are adapted to the introduction of fillers in  
32 powder form, such as clay, even with limited control of their dimensions [3]. In a number of  
33 cases, these were able to effectively include waste, mostly from the food-production sector  
34 [4-5]. The considerable cost of conductive polymer structures, obtained normally e.g.,  
35 through appropriate doping [6], or else by the introduction of carbon **nanofibers** [7], does  
36 suggest that the use of waste filler could be an option. In the case of starch-based

37 bioplastics, which have a, though limited conductivity, yet normally no magnetic properties,  
38 this appears particularly reasonable [8].

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40 In this work, some experiments have been performed by introducing unfiltered iron scrap  
41 powder in the production of a thermoplastic starch, based on corn starch, glycerol and acetic  
42 acid using three slightly different procedures. The materials have been subjected to tensile  
43 tests to compare the three procedures, and to suggest which can be the most suitable and  
44 which improvements can be possibly applied in future studies leading to the development of  
45 a material film for possible application where electrical conductivity is desirable. In particular,  
46 an opportunity envisaged for the prospective material would be its application in the chassis  
47 of cell phones as a conductive yet biodegradable, hence sustainable, material [9]. Other  
48 possibilities would be for example in the production of small magnets as gadgets, etc.  
49 However, so far magnetization of bioplastics has only been proposed with complexes based  
50 on iron, which do not fit the purpose of low cost application, for which a market would be  
51 available though [10]. To conclude, it appears that this material obtained from waste could  
52 be a solution for these low profile uses, although it would need for a start a first  
53 characterization to set-up a proper and effective fabrication method.

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## 55 **2. MATERIAL AND METHODS**

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### 57 **2.1 Production of the material**

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59 To a self-produced thermoplastic starch (TPS) mixture, which included 84% water, 7.7%  
60 corn starch, 7.7% glycerol and 0.6% acetic acid, an amount of untreated iron scrap waste  
61 was added of either 0.4 or 0.8%, putting the TPS as equal to 100.

62 The ingredients were placed in a container and mixed with care in order to amalgamate  
63 the starch component and prevent the formation of lumps. When the compound appears well  
64 amalgamated, cook it mixing constantly on a low fire, taking care that **jellification**  
65 temperature is reached and not exceeded. This occurs when the compound starts becoming  
66 dense and similar to a gel. After this, the TPS can be uniformly poured on a flat support and  
67 flattened using a roller to a 250 microns film in order to include in the thickness even the  
68 largest iron scrap particles. The thickness was accurate up to a  $\pm 20$  microns.

69 It needs to be worked for 30 seconds, and then dried for a time of 1-3 days at ambient  
70 temperature.

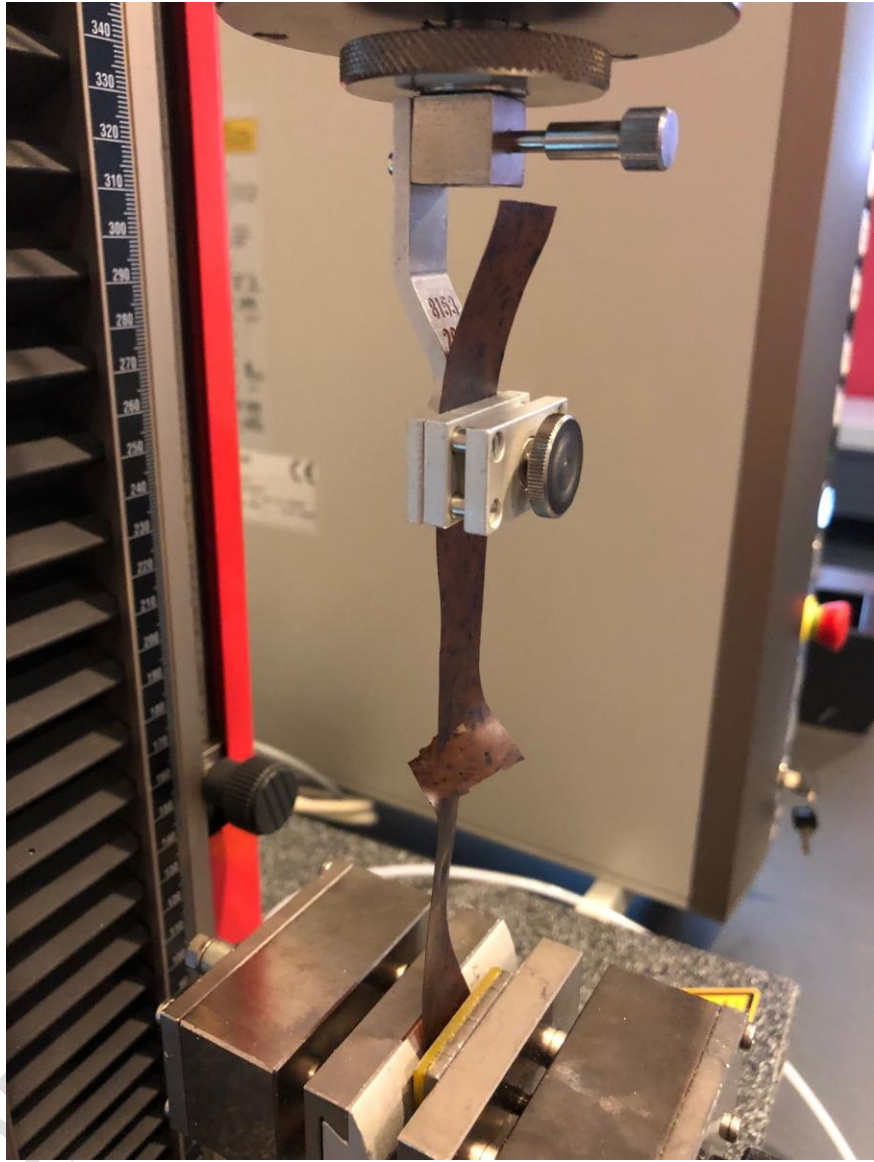
71 Two different supports were selected for production, one of which was a glass plate of 5  
72 mm thickness and the other a silicon mould of 2 mm thickness. On the glass plate a TPS  
73 loaded with 0.8% iron scrap waste was produced, hereinafter referred to as "glass", whereas  
74 on the silicon mould a TPS loaded with either 0.4% (MAT1) or 0.8% iron scrap waste  
75 (MAT2) was produced.

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### 77 **2.2 Tensile tests**

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79 Tensile tests have been carried out on the three materials produced, preparing a minimum  
80 number of five samples for each of them, cut using scissors from a material plate, with 250  
81 mm length and 25 mm width. Elongation was measured over 150 mm length using an  
82 extensometer. As the result, one of the ends was kept loose, as depicted in Figure 1. This  
83 was done to avoid fracture at the end of the samples, to ensure that the tests were valid,  
84 after some attempts that proved this problem was present. A Zwick Roell Z005 universal  
85 screw-driven tensile machine was used with a maximum load of 2.5 kN, fitted with a 5 N load  
86 cell and with pneumatic grips. Tests were carried out according to the ISO527 standard. In  
87 particular, a pre-load of 0.05 N was applied and the velocity applied for the measurement of  
88 the tensile modulus was 1 mm/minute, while the general test speed was equal to 10  
89 mm/minute.



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**FIG. 1** Image of the set-up for tensile testing

93 **3. RESULTS AND DISCUSSION**

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95 **3.1 Results-**. The three types of samples produced led to different results, in the sense that  
96 those, MAT 1 and MAT 2, obtained using a silicone support, did not come out mainly flat, yet  
97 with considerable lumps and with pronounced aggregation of the scrap iron particles, as it is  
98 shown in Figure 2. This led, when a larger amount of waste is introduced, hence in MAT 2,  
99 to some kind of detachment in a part of the composite plate obtained, which becomes partly  
100 non usable for testing. On the other side though, the detachment of the sample after  
101 production is easier with silicone than from the glass support, possibly due to the fact that  
102 some moisture from the film tends to spread out on the glass plate.

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104 As regards tensile testing, the image in Figure 3 clarifies how the samples typically break,  
105 the fracture passes through the film in a quite fragile mode, only being deviated by the  
106 possible presence of larger iron particles. Necking was also tentatively measured to correct  
107 the values of Young's modulus, though with some inaccuracy, due to the fact that the  
108 samples were not possibly gripped at both ends, but only at one of them. In terms of sample  
109 width, necking brought to its reduction in the order of around 10%.

110

111 Passing to tensile curves obtained from all films, it can be observed first qualitatively from  
112 Figure 4 that in all cases, the results yielded by the tests were not much dispersed, the main  
113 issue being given by some variation of the strain, which led to discarding some results from  
114 the following evaluation. Only those that are closer to the general trend were considered in  
115 the evaluation, in particular five per series of samples. This variation of strain was attributed  
116 to the presence of larger iron particles, which were able to impede necking of the sample,  
117 hence producing early fracture.

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119 The results obtained are summarized in Table 1. It can be noticed that the maximum  
120 stress remains about constant with the three types of samples and the presence of 0.4%  
121 (MAT1) or 0.8% of scrap iron waste does not produce any particular difference in the  
122 strength of the films. The samples produced on the silicone support with 0.4% of scrap iron  
123 waste have a higher elongation, confirming the previous assumption that early fracture may  
124 be due to the presence of iron particles along the crack propagation path during the pulling  
125 process of the sample. In contrast, those produced using the glass support appear  
126 considerably more rigid, as from Young's modulus values.

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128 **3.2 Discussion-**. To compare the results obtained, literature on TPS has to be considered:  
129 it can be easily considered that the tensile strength obtained is largely inferior to what has  
130 been obtained with industrial products, for example in [11] values of maximum tensile stress  
131 in the order of 47 to 59 MPa were measured, the latter being obtained by using sorbitol  
132 instead of glycerol as plasticizer. Another important remark is that it would be possible to  
133 increase the amount of filler used, since as such starch-based plastics are able to contain  
134 effectively very large quantities of waste filler, of course depending on its geometry [12]. This  
135 is quite routinely done using nanofillers [13], however with **micro-fillers** other considerations  
136 need to be done, which are developed here below.

137

138 This has to be considered as a preliminary work. For this reason, some considerations  
139 can be done to continue along the way towards producing a material suitable for application.  
140 The first important question is related to filtering the particles, in a way that only those that  
141 are considerably smaller than the film thickness are retained in the material. Other aspects  
142 would concern the need to analyze which other materials are present in the scrap iron  
143 powder that is specifically used for production. This is scarcely investigated on the small  
144 scale, although studies are present, which concern cast iron waste from machining on the  
145 large scale, which can be of reference [14]. A possible suggestion in this sense can be

146 applying magnetic selection, to exclude non-metallic materials from the filler. Another  
147 indication, which can be given, is that the scrap iron, used as-received, could include rusty  
148 materials: these can be made more suitable for use by removing rust for example by a  
149 process of pickling, which is normally used e.g., to prepare pigments from iron waste [15].  
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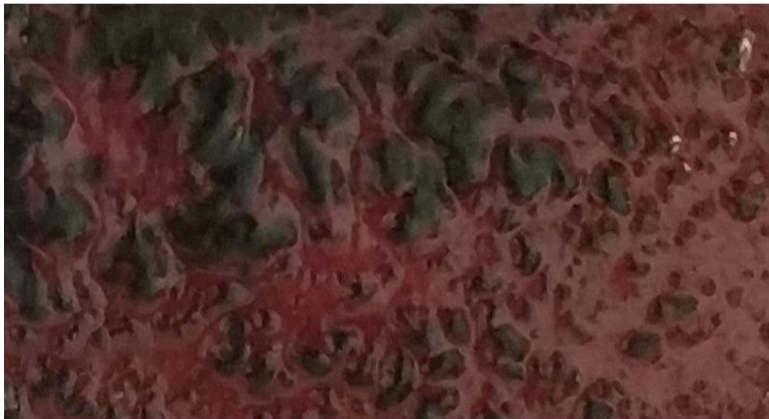
151 All the above considerations need to be integrated in further studies that will need to  
152 involve further characterization, such as thermal, especially in view of the scarce resistance  
153 of bioplastics to temperature and microstructural analysis, to investigate the interface  
154 between filler particles and the host material. In addition, of course the measurement of  
155 electrical conductivity and magnetic properties would need to be carried out.

UNDER PEER REVIEW



GLASS

100  $\mu\text{m}$



MAT 1

100  $\mu\text{m}$



MAT 2

100  $\mu\text{m}$

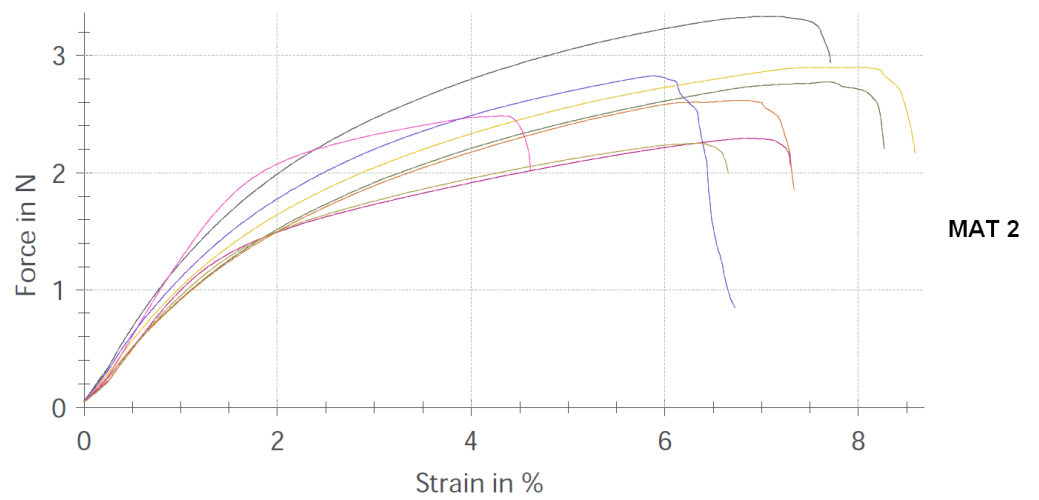
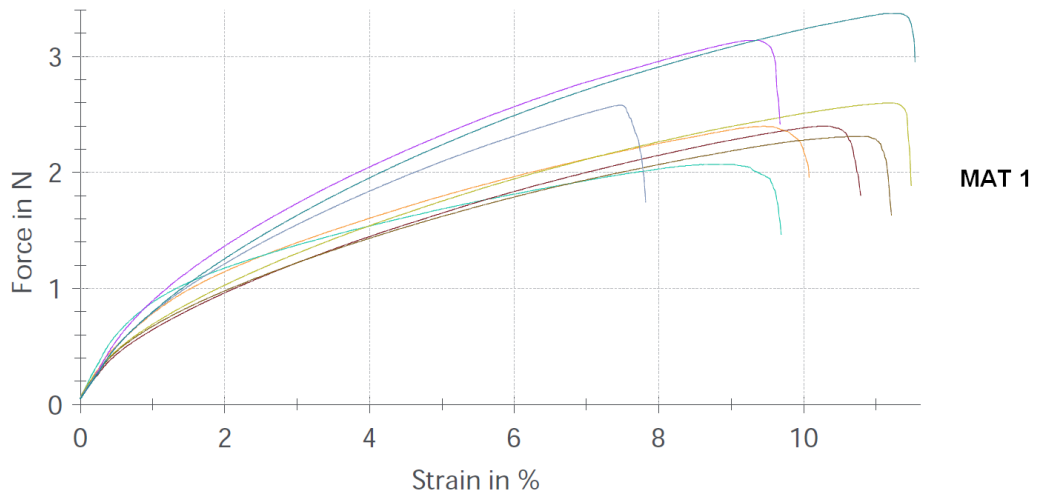
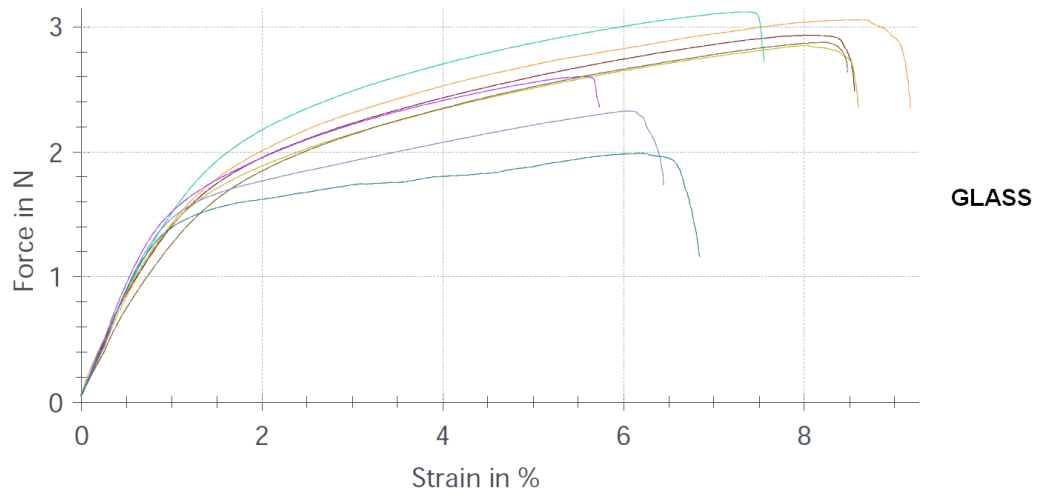
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**FIG. 2** Images of the three types of **produced samples**



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**FIG. 3** Image of a tensile sample during breakage



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**FIG. 4** Tensile tests curves for the materials produced with the three supports



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**TABLE 1 Tensile tests results**

Samples	Max. stress (MPa)	Max. strain (%)	Young's modulus (MPa)
GLASS	0.544 ± 0.078	7.2 ± 1.2	32.2 ± 2.6
MAT1	0.522 ± 0.087	9.8 ± 1.3	18.9 ± 2.5
MAT2	0.537 ± 0.071	7.1 ± 1.2	18 ± 3.2

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#### **4. CONCLUSIONS**

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The study concentrated on the possibility to produce biopolymers including scrap iron waste powder as received. Three types of possible production were attempted using either a glass plate with 0.8% waste filler or silicon flat mould with either 0.4 or 0.8% waste filler. The production with glass support proved more reliable, although all of the methods supplied a sufficient number of tensile samples with close properties to validate the tests. Concerns can be raised about the dimensions of the filler particles which need to be filtered and/or ground for better properties and about the possible presence of rust, which further reduces the mechanical performance especially in terms of elongation. However, the tests are considered successful as preliminary experiments in order to lead to further refinement of the production process and subsequent characterization.

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#### **COMPETING INTERESTS**

Authors have declared that no competing interests exist.

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