

Structural, thermal, and mechanical properties of gelatin-based films integrated with tara gum

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# Polymer

## Structural, Thermal, and Mechanical properties of gelatin-based films integrated with tara gum

--Manuscript Draft--

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<b>Abstract:</b>	<p>Film gels of improved quality composed by a mixture of fish gelatin, Tara gum and glycerol are prepared and characterized. The morphological differences within gels produced by different amount of glycerol, which acts as plasticizer, and by pre-treating by ball milling the Tara gum, can be highlighted by SEM and AFM analyses. Gels containing milled Tara showed higher densities and a different morphology. The structural differences due to different compositions reflect diverse thermal and mechanical behaviour of the gels. The glycerol content results to deeply influence the gels performances and it should be used in an amount not higher than 20 wt%. Also, Tara gum, especially if previously milled, can be employed for increase the thermal stability and reinforce the material again mechanical stress and deformation. Ten film gels composed by where prepared and characterized in terms of morphology, thermal stability, and mechanical performances. The effects on such aspects of fish gelatine / Tara ratio, of the glycerol content, and of the type of Tara were assessed. In particular, by tuning opportunely the amount of the glycerol, which acts as plasticizer, and by pre-treating by ball milling the Tara gum, it is possible to improve the thermal and the mechanical properties of the gels.</p>



Dear Editor

Please find enclosed the revised version of the manuscript "Structural, Thermal, and Mechanical properties of gelatin-based films integrated with tara gum", ID POLYMER-20-1852. First of all, all the Authors would like to thank you and the Reviewers for the work done in suggesting and commenting improvements of our manuscript. All the Authors agreed to revise the text according to the indication received, which will be addressed point by point as follows.

Reviewer #1:

Title: Structural, thermal, and mechanical properties of gelatin-based films integrated with tara gum

Overall comments:

This work deals with preparation and property analysis of gelatin based film modified with glycerol as plasticizer and Tara gum at various levels. This work is generally not novel. The influence of glycerol as plasticizer as well as incorporation of polysaccharide-based gum on properties of protein-based films including gelatin films have been extensively studied and reported. This work does not provide new knowledge but simply give further information in this field which are generally predictable. Therefore, the results reported in this paper are not scientifically interested. The significance of incorporation of Tara gum in the film was not clearly shown. Moreover, the scientific discussion and interpretation provided were rather poor and not intensive. Therefore, the scientific or application significances are not obtained from this paper. Another weak point of this manuscript is that the English grammar and style are rather poor. Thus, I would like to recommend rejecting this paper to be publishing in Polymer due mainly to lack of novelty as well as insufficient discussion and poor English.

We appreciate the efforts of the Reviewer in reviewing the manuscript and we agree that it needed a deep revision. Regarding some specific aspects pointed out in the Reviewer's report, it is true that the effect of the plasticizer (glycerol) on the morphology, on the structure, and on the thermal and mechanical behaviours of gelatin-based films is not particularly new. Nevertheless, it is also known that when natural gums (as Tara) are employed as reinforcement agents, the resulting films are not particularly thermally stable and with a reduced elasticity. In this context, the possibility to improve thermal and mechanical properties of these films by milling the commercial Tara represents a novelty which deserve some attention.

For this reason, we performed several tests in order to assess the structural and morphological differences in films with different composition and in particular containing milled or non-milled Tara gum. In describing our results, we also highlighted the important effect of the plasticizer,



although it was expectable. In addition, interesting combined effects of plasticizer and milled (or not milled) Tara gum are discussed. In the revised version of the manuscript, all these aspects have been better highlighted and presented, with the hope that the current version of the manuscript can be now re-considered by the Reviewer.

Reviewer #2: This paper mainly investigated the physical and structural properties of Ta/FG based films. And it showed that the FG-Ta based films had good thermal and mechanical properties. It sounds interesting and provide some useful information of the production of bio-film. But it is lack of deeply discussions. It could be accepted before major revision.

Thanks to the Reviewer for the efforts in suggesting corrections for the manuscript improvement. The Authors agree with the Reviewer in revise the manuscript in major form.

Some suggestions are following:

Abstract Line 17-32 The abstract writing should be revised carefully and totally, it makes confused for its ambiguous sentences. What's the "Films gel", it looks like solution, not gel.

Thanks for the suggestion, the abstract has been totally re-written and the term film gel has been replaced with film all over the manuscript.

"Films with different morphology can be obtained by mixing fish gelatin, Tara gum and glycerol in different ratio and by subjecting the Tara gum to a ball milling treatment before its use. The amount of the plasticizer glycerol, as well as the type of Tara gum employed (as received or milled) resulted, from SEM and AFM analyses, to strong influencing the morphology of the films and their density. Also, the morphological differences determine different thermal and mechanical behaviours. In particular, the employment of milled Tara gum allows to improve the thermal stability, as well as the mechanical properties of the polymers. A similar outcome can be obtained by increasing the glycerol content, which can be used up to 20 wt%. Glycerol amounts exceeding that percentage, are detrimental for the quality of the films and reduce their thermal and mechanical performances."

Line 46, "its melting point above 30 °C", different gelatin had different melting points, and melting points of mammalian gelatin are higher than those of warm and cold fish gelatin. It is not preciseness, corrected.

Thanks, that part has been arranged as follows:

Thermal properties of gelatin have been characterized in different papers. For example, Rahman et al. [11] presented a complete study about the glass transition and melting points of commercial mammalian gelatin, tuna gelatin, bovine gelatin and porcine gelatin. Glass transitions temperatures varied from 23 to 75 °C, whereas melting points were measured between 115 and 190 °C. These wide range of values, combined to their biocompatibility, make



them suitable in many different biomedical applications, such as drug delivery or tissue engineering [12,13].

Line 85, what's the basic component of Ta and gelatin? What's the bloom of gelatin?

Detailed information on the employed gelatin have been added.

For methods of DSC, SEM, authors should add proper references, and also some references should be updated. eg "Physical properties and release kinetics of electron beam irradiated fish gelatin films with antioxidants of bamboo leaves"; "Preparation and characterization of irradiated kafirin-quercetin film for packaging cod (*Gadus morhua*) during cold storage at 4 °C"; Effects of fish gelatin and tea polyphenol coating on the spoilage and degradation of myofibril in fish fillet during cold storage"

Thanks, the suggested references have been added with others referred to the DSC and SEM methods.

Line 152 "Ten film gels" what's do you mean?

Thanks, it has been replaced by "films".

Line 196 added proper references

Thanks, the discussion about the FT-IR analyses has been improved and new references have been added (please see the revised manuscript file).

Line 202-203, 206, "Error! Bookmark not defined." what do you mean?

Thanks, it has been corrected.

For results of FTIR, X-ray, and SEM, authors should add some relevant and useful discussions. Eg, what's the relationship between FG/Ta and FTIR or X-ray results; what's the deeply relationship between physical results and structural results.

Thanks, the manuscript has been improved in this meaning by adding key sentences to the text, especially between the different subsections of the *Results and discussion* paragraph.

Please see the revised manuscript enclosed.

Line 444-445 please rephrased

Thanks, the sentence has been corrected as follows.

"The raw data required to reproduce these findings cannot be shared at this time due to technical limitations."

References: updated some new papers.

A total of nine new references have been added to the manuscript.

## Structural, Thermal, and Mechanical properties of gelatin-based films integrated with tara gum

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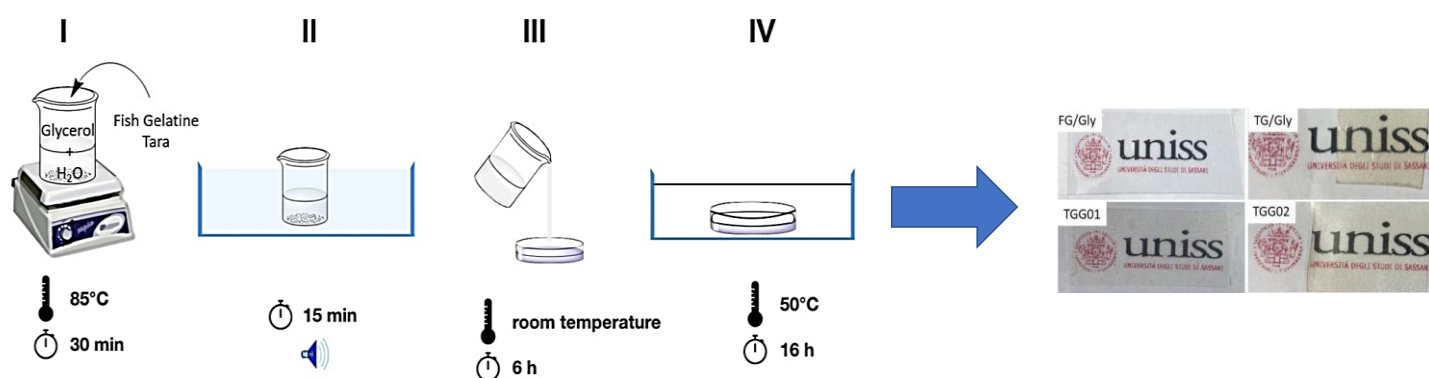
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### Easy fabrication process of Fish gelatin/tara films with high thermal stability



1     **Structural, Thermal, and Mechanical properties of gelatin-based films**  
2                                    **integrated with tara gum**

3  
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14

## Abstract

Films with different morphology can be obtained by mixing fish gelatin, Tara gum and glycerol in different ratio and by subjecting the Tara gum to a ball milling treatment before its use. The amount of the plasticizer glycerol, as well as the type of Tara gum employed (as received or milled) resulted, from SEM and AFM analyses, to strongly influencing the morphology of the films and their density. Also, the morphological differences determine different thermal and mechanical behaviours. In particular, the employment of milled Tara gum allows to improve the thermal stability, as well as the mechanical properties of the polymers. A similar outcome can be obtained by increasing the glycerol content, which can be used up to 20 wt%. Glycerol amounts exceeding that percentage, are detrimental for the quality of the films and reduce their thermal and mechanical performances.

**Keywords:** Tara gum; gelatin fish; biofilms

### 1. Introduction

During the last years, fervent research activities have been conducted on the engineering of composite gels. The possibility to tune gel properties combining specific components has gained increasing importance in many application fields, including food, drug delivery, tissue engineering and wound dressing [1,2,3].

Among the several components usually employed for composite gels engineering, gelatin, a mix of denaturated proteins derived by collagen [4,5,6], have attracted particular interest for biomedical and food packaging sectors, due its remarkable properties. As a matter of fact, gelatin is biocompatible, biodegradable, shows high capacity of cell adhesion and migration [7], shows antimicrobial properties [8], and it has been successfully exploited for tissue engineering [9,10]. Thermal properties of gelatin have been characterized in different papers. For example, Rahman *et al.* [11] presented a complete study about the glass transition and melting points of commercial mammalian gelatin, tuna gelatin, bovine gelatin and porcine gelatin. Glass transitions temperatures varied from 23 to 75 °C, whereas melting points were measured between 115 and 190 °C. These wide range of values, combined to their biocompatibility, make them suitable in many different biomedical applications, such as drug delivery or tissue engineering [12,13]. Of particular interest, especially for the packaging and biomedical sectors, are the Fish Gelatin (FG) based films. FG is cheap, biodegradable and easy to process for making films. In addition, its mechanical and optical properties can be modulated by adding polyols which act as plasticizers. The main role of

49 such additives consists in the denaturation of the FG's proteins by reducing the interactions  
50 between protein chains and modifying the secondary, tertiary and quaternary structures [14].  
51 Within the polyols commonly employed for such purpose, glycerol stands out as the ideal  
52 candidate. It showed good ability to interact with FG, eco-compatibility, and it is available in  
53 large amount as by-product of waste vegetable oils treatment [15], e.g. from biodiesel  
54 production [16]. On the other hand, the use of fish gelatin in composite films is still limited  
55 by several factors such as low stability, poor mechanical strength and low elasticity [17].  
56 Many studies have been then conducted with the aim to solve these weaknesses by  
57 exploring the doping with different additives including synthetic and biological polymers [18].  
58 Although different studies have been performed on the use of FG in composites in  
59 combination with various additives, the interaction between gelatin and different natural  
60 gums in modifying the thermal and mechanical properties of gelatin has been only recently  
61 explored [19]. Natural gums have shown to allow structural engineering of thin films while  
62 guaranteeing the biodegradability and edibility of the material [20]. Specific combinations  
63 between natural gelatin, glycerol and natural gums have found important application  
64 especially in food packaging [18].

65 Regarding the most employed natural gums (Tara, guar, and locust bean), Tara gum (Ta)  
66 shows intermediate water solubility with respect to guar (cold soluble) and locust bean gum  
67 (cold insoluble), making it ideal e.g. as food hydrocolloid [20]. Tara gum is obtained by  
68 grinding the endosperm of the seeds of *Caesalpinia spinosa* (Fam. Leguminosae) and it is  
69 composed by polysaccharide chains of high molecular weight based on the galactomannan  
70 unit (See **Scheme S1** of the Electronic Supplementary Information file, **ESI**). It has been  
71 approved as food additive due to its non-toxicity and thus it has gained value as film additive  
72 [21]. When employed in gel composites, tara gum acts as thickening agent and stabilizer.

73 In this context, herein, the fabrication and characterization of novel films based on fish  
74 gelatin (FG), Tara gum (Ta), and glycerol (Gly), is reported. Ten films containing different  
75 ratio of FG/Ta, different glycerol content and different types of Ta, are described and  
76 characterized. For each film the structural, thermal, and mechanical properties are  
77 discussed by means of, respectively, IR, X-ray, and SEM, Thermogravimetry (TG) and  
78 differential scanning Calorimetry (DSC), and tensile properties analyses.

79

## 80 **2. Materials**

81 Tara gum (Aglumix 01, particle size 149  $\mu\text{m}$ ) and Fish Gelatin (LapiFish, particle size 2380  
82  $\mu\text{m}$ ) were purchased, respectively, from Silvateam Food Ingredients S.r.l. and Lapi gelatin

83 S.p.a.. Fish gelatin with the following characteristics was employed: Bloom 280, mesh size  
84 8-70, protein amount between 85% and 90%, water content 10-12%, and salts content 1-  
85 2% [22].

86 Glycerol (90%) was purchased from Analyticals Carlo Erba, while acetone (>99%) and  
87 ethanol (>99.5%) from VWR. All chemicals were used as received without any further  
88 purification.

89

### 90 **3. Experimental equipment and methods**

91 Fourier transform infrared (FTIR) analysis was performed using a Bruker infrared Vertex 70  
92 interferometer. The spectra were recorded on the films in transmission mode, in the 400-  
93 4000  $\text{cm}^{-1}$  range by averaging 64 scans with 4  $\text{cm}^{-1}$  of resolution.

94 Principal Component Analysis (PCA) as well as Partial Least Squares Discriminant Analysis  
95 (PLS-DA) were conducted using of the tool Metaboanalyst 4 [23]. The spectral data were  
96 centered and auto-scaled before the PCA and PLS-DA analysis.

97 The XRD patterns were collected using a Rigaku SmartLab X-ray powder diffractometer  
98 aligned according to a Bragg–Brentano geometry with Cu  $K\alpha$  radiation ( $\lambda = 1.54178 \text{ \AA}$ ) and  
99 equipped with a graphite monochromator in the diffracted beam. Since the polymers showed  
100 broad haloes typical of amorphous condition, it was deliberately assumed to restrict the  
101 reciprocal space investigation in the angular range from  $5^\circ$  to  $80^\circ$  in  $2\theta$ , which allows to  
102 determine the main shape features of specimen. Powders have been deposited in an  
103 amorphous glass sample holder for measurements.

104 Ball milling of the Ta powders (15 g) was carried out in a SPEX Mixer/Mill 8000 at a rotation  
105 speed of 875 rpm during 1 h, using two zirconia balls of 2 g each one. Taking in consideration  
106 the very low amount of powders which are usually trapped (1 mg) at each impact, and the  
107 stochastic nature of the ball milling process, over 200k collisions, occurring under the  
108 mechanochemical conditions above reported, should be enough for refining homogenously  
109 all the batch powders [24]. Then, two different Tara gum powders were obtained: as received  
110 (or non-milled) and milled.

111 The morphologies of the powders and films were observed by different techniques. First,  
112 SEM images were taken using a FEI Quanta 200 scanning electron microscope. The  
113 samples were placed on a double-sided carbon tape and examined at an acceleration  
114 voltage of 20 kV under high vacuum. Also, Atomic Force Microscopy (AFM) images were  
115 taken at RT using a confocal AFM-RAMAN model Alpha300R – Alpha300A from WITec,  
116 using an AFM tip of 42 N/m.

117 The thermogravimetric analysis data were recorded on a TA Instrument Q50 TGA analyzer.  
118 TGA tests were performed under O<sub>2</sub> (synthetic air) atmosphere using the next procedure:  
119 first, samples were heated from RT to 100 °C at 10 °C/min, and then kept during 10 min to  
120 eliminate the moisture content. Then, samples were heated up to 800 °C at 10 °C/min.

121 DSC analyses were performed using a DSC Q200 TA Instruments equipment. Samples  
122 were tested using a four-cycle procedure [25]. In the first cycle, after 5 min of stabilization at  
123 RT, samples were heated up to 150 °C at 10 °C/min and then stabilized during 5 min before  
124 cooling down in the second cycle to 30 °C at 20 °C/min. In the third cycle, samples were  
125 heated up to 150 °C at 10 °C/min and after 5 min of stabilization at 150 °C, the fourth cycle  
126 was performed: samples were cooled down to 30 °C at 20 °C/min. All the tests were  
127 performed under N<sub>2</sub> atmosphere (flow rate 50 ml/min). Mass of the samples was fixed at  
128 approximately 20 mg in each test. Glass transition temperature ( $T_g$ ) was determined in the  
129 third cycle.

130 To determine the tensile properties of the films, strips of 5 mm in width and 35 mm in length  
131 were cut from each film. Tensile tests were carried out on a SHIMADZU EZ Test Compact  
132 Table-Top Universal Tester at 20 °C. Mechanical clamps were used and an extension rate  
133 of 5 mm/min was applied using a gauge length of 9.44 mm. At least 4 strips were tested for  
134 each film in order to calculate the average value for each parameter determined.

135

#### 136 4. Preparation of films

137 The preparation of gelatin-based films is here detailed and schematized in **Figure S1** of the  
138 **ESI**. Tara powder was added to a solution of glycerol and distilled water and the mixture  
139 was stirred at 85°C during 30 minutes until a homogeneity was reached (I). Then, Fish  
140 gelatin was added at 85 °C and stirred until dissolution (II). The mixture was subjected to  
141 ultrasound for 15 minutes to remove air bubbles (III). Film-forming solutions were poured  
142 into Steriplan® petri dished (80 mm x 15 mm) and dried at room temperature for 6 h and  
143 then located at 50 °C in humidity-controlled oven for 16 hours (IV). The corresponding film  
144 was thoroughly washed with ethanol and acetone to afford the desired gel.

145

#### 146 5. Results and discussion

##### 147 5.1 Density and visual aspect of the films

148 Ten films composed by Fish gelatin (FG), Tara powder (Ta) and glycerol (Gly) were  
149 prepared with different Ta/FG ratio (1/2, 1/1, and 2/1) and Gly amount (20, 40, and 60 wt%).  
150 Additionally, two reference films (FG/Gly and Ta/Gly) were also prepared to compare their

151 properties with the FG/Ta/Gly films. Finally, two types of Ta were considered: as received  
152 by the purchaser, and milled. Nomenclature, density and composition of the films fabricated  
153 are reported in **Table 1**.

154

155

156 **Table 1**. Nomenclature, density and composition of the films fabricated.

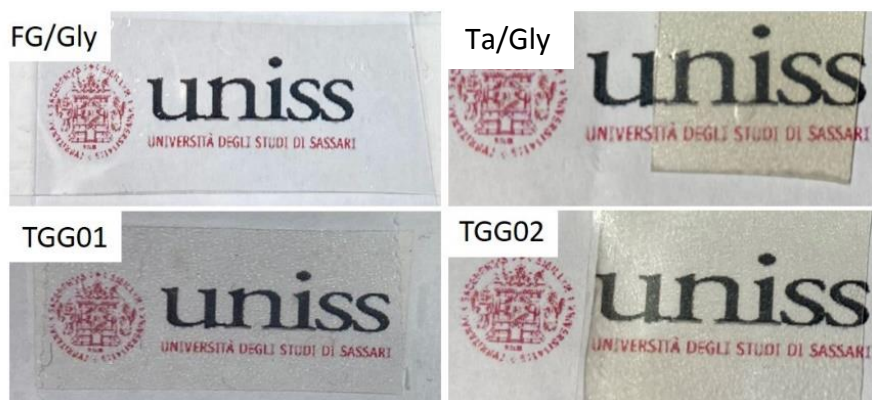
Film	FG (eq. wt.)	Ta (eq. wt.)	Ball Milling	Gly (wt%)	Density (g/cm <sup>3</sup> )
TGG01	1	1	No	20	7.9
TGG02	1	1	Yes	20	8.6
TGG03	1	1	No	40	6.8
TGG04	1	1	Yes	40	8.2
TGG05	1	1	No	60	6.5
TGG06	1	1	Yes	60	7.2
TGG07	2	1	No	20	7.8
TGG08	2	1	Yes	20	8.7
TGG09	1	2	No	20	9.1
TGG10	1	2	Yes	20	9.8
FG/Gly	1	0	No	20	4.7
Ta/Gly	0	1	No	20	10.0

157

158 **Table 1** shows that densities obtained vary from 6.5 g/cm<sup>3</sup> for TGG05 film to 9.8 g/cm<sup>3</sup> for  
159 TGG10 film. Also, it can be noticed that the density of the as-casted films increases for  
160 systems containing milled Tara powder compared to those produced using the non-milled  
161 one (TGG02 vs TGG01). A relevant influence glycerol content on the density values was  
162 observed, which decrease at higher wt% of glycerol (TGG06 vs TGG02). As expected, pure  
163 FG film shows the lower density value (4.7 g/cm<sup>3</sup>), while pure Tara film presents the higher  
164 density value (10.0 g/cm<sup>3</sup>).

165 From a qualitative visual analysis, film specimens were transparent despite Ta/Gly  
166 presented a slightly yellow to brown appearance with respect to FG/Gly film. On the other  
167 hand, in TGG01 to TGG10 films opaqueness is reduced. This means that opacity could be  
168 related to the Tara adding effect and its dispersion during film preparation, causing the  
169 reduction of the film transparency with respect to starting Fish gelatin film. This characteristic  
170 could limit the use of films composed by only Tara in food packaging applications. In **Figure**  
171 **1** the photographs of the films FG/Gly, Ta/Gly, TGG01 and TGG02 are shown.

172



**Figure 1.** Photographs of the FG/Gly, Ta/Gly, TGG01 and TGG02 films.

## 5.2 FT-IR analysis

A first quality check on the effect of the preparation procedure on the chemical composition of the constituents of films TGG01-TGG10 was performed by FTIR analysis. Results are displayed in **Figure S2** of the **ESI**. The absorption bands for gelatin-based composite films in the IR spectra are situated in the amide band region. The band situated around 3299, 1635, 1550, 1238  $\text{cm}^{-1}$  correspond to amide-A (NH-stretching coupled with hydrogen bonding) and water molecules, amide I (C=O stretching/hydrogen bonding coupled with COO), amide II (bending vibration of N-H groups and stretching vibrations of C-N groups), and amide III (vibrations in the plane of C-N and N-H groups of bound amid). The bands in the FTIR spectrum of Tara powder appear in two major regions, 3700-2500  $\text{cm}^{-1}$  and 1700-700  $\text{cm}^{-1}$ . The broad band at 3700-3000  $\text{cm}^{-1}$  is a result of O-H stretching vibration which is associated with free, inter and intra-molecular bonded hydroxyl groups. The shoulder-shaped band at about 2920  $\text{cm}^{-1}$  is the stretching vibration of  $-\text{CH}_2$ . The bands at 1020  $\text{cm}^{-1}$  is characteristic of the O-C stretching vibration of the anhydro glucose ring. These bands indicate that Tara powder has the general properties of a polysaccharide [26,**Error! Bookmark not defined.**].

If from one side the FT-IR data confirm the expected composition of the films, ruling out any thermal decomposition which can occur during the synthesis from the other side, [27,**Error! Bookmark not defined.**] by a visual analysis of the plots reported in **Figure S2**, few information can be obtained on the differences between films with different composition [28,29].

In order to analyse better the available FT-IR data and to extrapolate as more information as possible, a multivariate analysis of the spectral data was conducted. The normalized frequencies relative to films TGG01-TGG10 were considered for building a spectral fingerprint of each film. The aim of such statistical analysis was to distinguish between films

207 containing milled and not-milled Tara. At first, non-supervised Principal Component Analysis  
208 (PCA) was conducted, as shown in **Figure S3** of the **ESI**.

209 As expected, PCA analysis of the FT-IR intensities doesn't allow to reach a perfect  
210 discrimination. In fact, unbiased PCA method works properly when within-group variation,  
211 [30] in this case related with FG/Ta ratio and glycerol content, is sufficiently less than  
212 between-group variation (milled and not-milled Tara). Nevertheless, a supervised approach  
213 as the Partial Least Squares Discriminant Analysis (PLS-DA) can be used for classify the  
214 two considered groups and discuss properly differences between films, as it is presented in  
215 **Figure S4** of the **ESI**, in which 2D Component 1 vs Component 2 Plot of FT-IR intensities  
216 of films TGG01-TGG10, containing milled (M) and not-milled (NM) Ta are shown.

217 From the information of **Figure S4** it is possible to appreciate the discrimination between  
218 films contained milled and not-milled Ta obtained through multivariate PLS-DA analysis. The  
219 analysis, even qualitative, of the distances between the labels in the Scores Plot is of  
220 particular interest. Comparing films containing milled (M) and not-milled (NM) Tara, it is  
221 possible to notice incremental differences following the trend TGG03-TGG04, TGG05-  
222 TGG06, TGG07-TGG08, and TGG09-TGG10, indicating an increasing effect of the Ta grain  
223 size which depend on the amount of glycerol and on the FG/Ta ratio. More glycerol is  
224 present, more the milled Tara is distinguishable from the not-milled one (TGG02, TGG04,  
225 TGG06 vs TGG03, TGG05, and TGG07). As matter of fact, films containing an FG/Ta ratio  
226 of 1/2 or 2/1 seems to be more sensitive to the type of Tara (TGG08, TGG10 vs TGG09,  
227 and TGG10). **FT-IR qualitative analysis highlighted important chemical differences within  
228 films with different glycerol content and Tara typology. If the effect of the plasticizer (glycerol)  
229 it is known and expected, the possibility to affect the composition of a film by changing the  
230 granulometry of the Tara deserves more attention.**

231

### 232 **5.3 X-ray diffraction analysis**

233 **With the aim to better assess the structural differences between films TGG01-TGG10, X-  
234 ray diffraction analysis was conducted.** Figure **S5** of the **ESI** displays the XRD patterns of  
235 all the films prepared. Ta presents a broad peak at  $\sim 19^\circ$  indicating amorphous and  
236 crystalline regions existed because a large amount of -OH groups interacted via  
237 intermolecular hydrogen bonds. This peak partially disappeared in the composite film,  
238 indicating that a part of Tara molecules was in ordered arrangement, which was interrupted  
239 in the grafting process; therefore, the obtained composite is amorphous. After grafting, the

240 peak strength decreased, which indicated that intermolecular hydrogen bonds were  
241 damaged.

242 The diffractogram pattern acquired on the FG/Gly film was typical of a partially crystalline  
243 gelatin with a sharp peak located at  $2\theta = 7.1^\circ$  ( $d_{101} = 12.29 \text{ \AA}$ ) and a broad peak located at  
244  $2\theta = 20^\circ$  ( $d_{101} = 4.09 \text{ \AA}$ ), as shown in **Figure S5**. These characteristic peaks are usually  
245 assigned to the triple-helical crystalline structure in gelatin. In particular, the first diffraction  
246 peak at  $7^\circ$  (sharp and intense) is directly related to the diameter of the triple helix. It was  
247 also found that the addition of polyols such as glycerol most often decreases the intensity  
248 of the first peak ( $2\theta = 7^\circ$ ). Furthermore, it has been observed that the addition of tara gum  
249 shifted the diffraction angle from  $7.1^\circ$  to  $9.12^\circ$  (for TGG05/06 and TGG09/10 films) then  
250 decreasing the diameter of the inter reticular triple helix. On the other hand, this intensity of  
251 peaks decreases and, in some cases, completely disappeared (TGG01/02, TGG03/04 and  
252 TGG07/08 films). The disappearance of X-ray diffraction peaks corresponding to the  
253 composites films confirms the interaction between two biopolymers. This phenomenon  
254 illustrates the reduction hydrogen bonds between hydroxyls group of gelatin and those of  
255 anhydroglucose of Tara gum, which limited the movement of molecules and thus prevented  
256 crystallization.

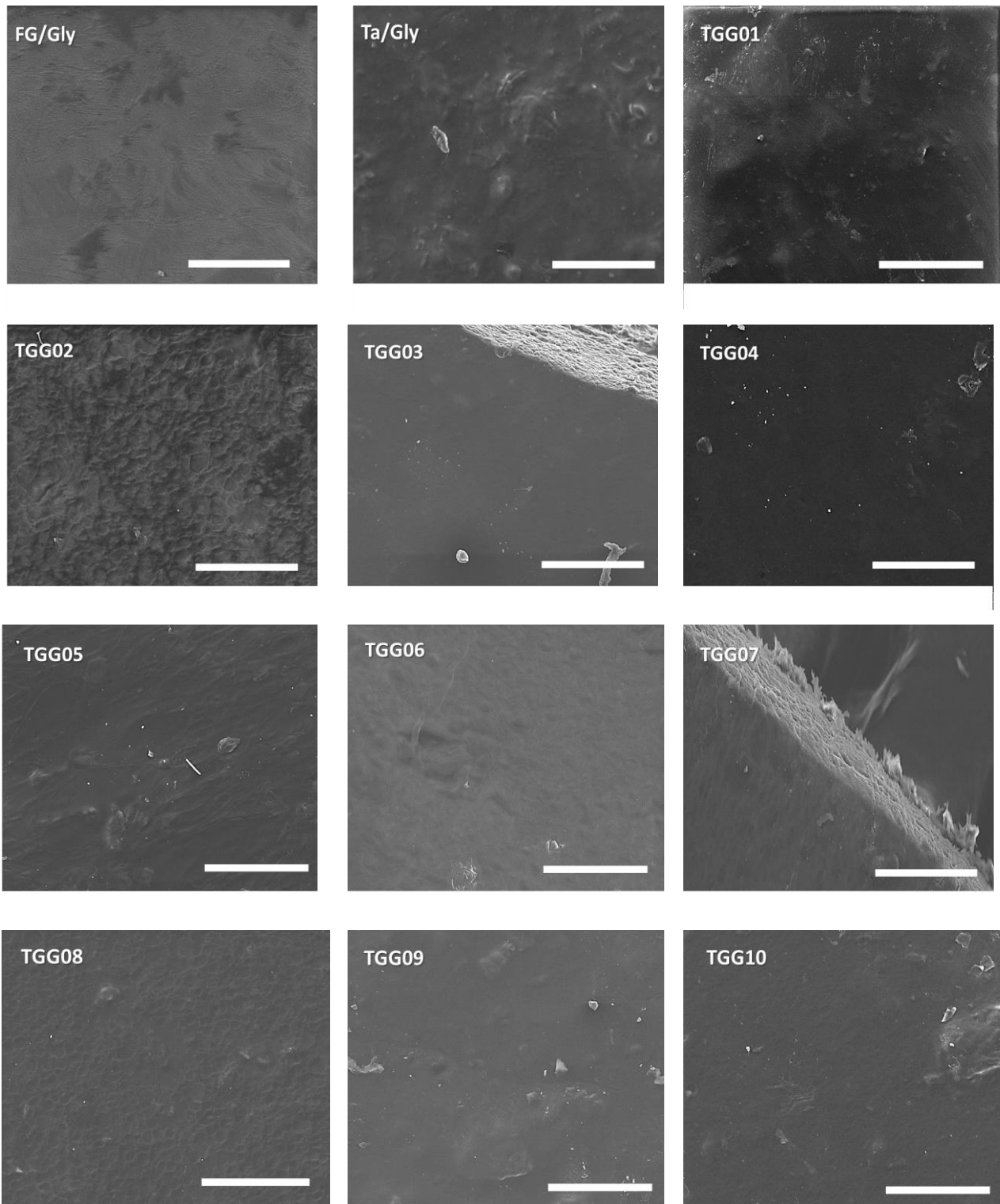
257 The addition of glycerol seems to decrease the intensities of the gelatin peak making the  
258 film more amorphous as compared to control gelatin film. This is probably due to the high  
259 stability of these films when glycerol was added. Finally, a clear effect of BM was observed  
260 only on TGG06 system which presented a significant decrease on the peak intensity at  $2\theta$   
261  $=19.9^\circ$  with respect to TGG05. This effect could be related with the synergic effect of glycerol  
262 addition and Tara gum added with refined particle size, and it confirms the influence of Tara  
263 granulometry qualitatively observed by FT-IR.

264

#### 265 **5.4 Morphological analysis**

266 An exhaustive morphology analysis of the films TGG01-TGG10 was conducted by different  
267 approaches. Firstly, Scanning Electron Microscopy (SEM) images of the films were collected  
268 as shown in **Figure 2**.

269



**Figure 2.** SEM images of the films prepared (bar scale 100  $\mu\text{m}$ ).

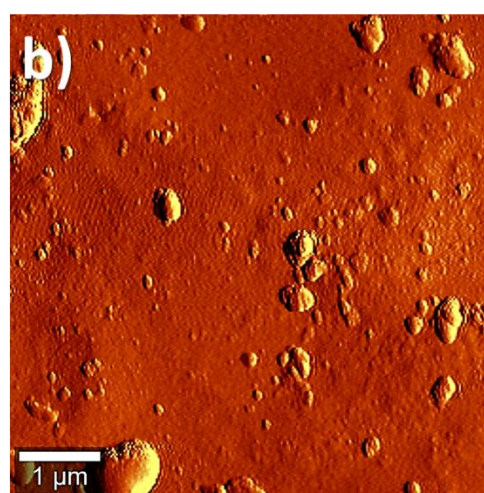
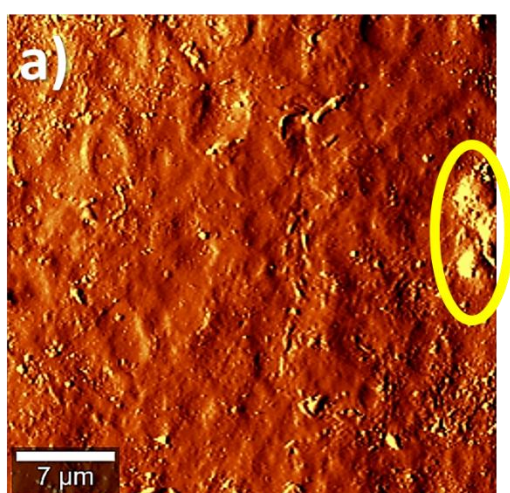
270

271 Micrographs in **Figure 2** show that surfaces of TGG films were homogeneous although  
 272 pores were observed on the top of each system, except in the case of FG/Gly film. In  
 273 addition, bigger and fewer pores were found in the TGG01, TGG03, TGG05, TGG07 and  
 274 TGG09 films, all of them fabricated using the un-milled Ta powder. On the other hand, more

275 and smaller uniform pores were observed on the surface of the TGG02, TG004, TGG06,  
276 TG008 and TGG10 films, in which ball milled Tara powders were introduced. Then, it is clear  
277 that this difference could be ascribable to the reduced Tara particles sizes obtained upon  
278 ball milling.

279 **Figure 4** presents the AFM surface images of TGG09 and TGG10 films, in which the  
280 distribution of Tara powder (non-milled in the case of TGG09 film and milled in the case of  
281 TGG10) is observed. AFM surface images do not show great differences in the Tara powder  
282 distribution, showing that, in general, Tara powder is well dispersed in the film surface. Only  
283 a few agglomerated Tara particles are observed in the surface of the films, as it can be seen  
284 in the yellow circles spotted of **Figures 4a** and **4c**.

285 The effect of the milling ball can be analyzed from two different points of view. First, it seems  
286 that the size of the agglomerated particles is slightly higher when non milled Tara is  
287 employed, as it can be seen in the agglomeration of Tara particles in **Figures 4a** (TGG09,  
288 non-milled Tara) and **4c** (TGG10, milled Tara). Secondly, the size distribution of Tara  
289 particles can be observed in the AFM surfaces images presented in **Figures 4b** (TGG09)  
290 and **4d** (TGG10). In this case, there is not a very clear difference between the particles size  
291 of non-milled (**Figure 4b**) and milled Tara (**Figure 4d**), but it can be detected that milling the  
292 Tara powder could reduce the particle size compared to non-milled Tara. In this sense,  
293 **Figure 4d** show Tara particles with sizes below 1  $\mu\text{m}$  of diameter, and on the other hand,  
294 **Figure 4b** presents, in the bottom-left zone, Tara particles with higher sizes (around 1  $\mu\text{m}$ ).  
295



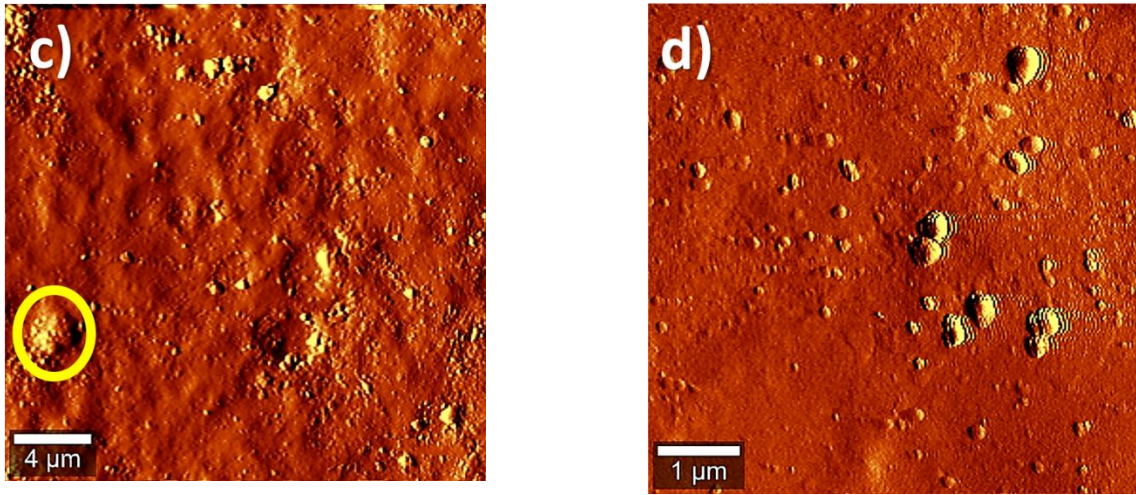


Figure 4. AFM surface images of TGG09 (a and b) and TGG10 (c and d) films.

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297

### 5.5 Thermal stability of films

298

299

300

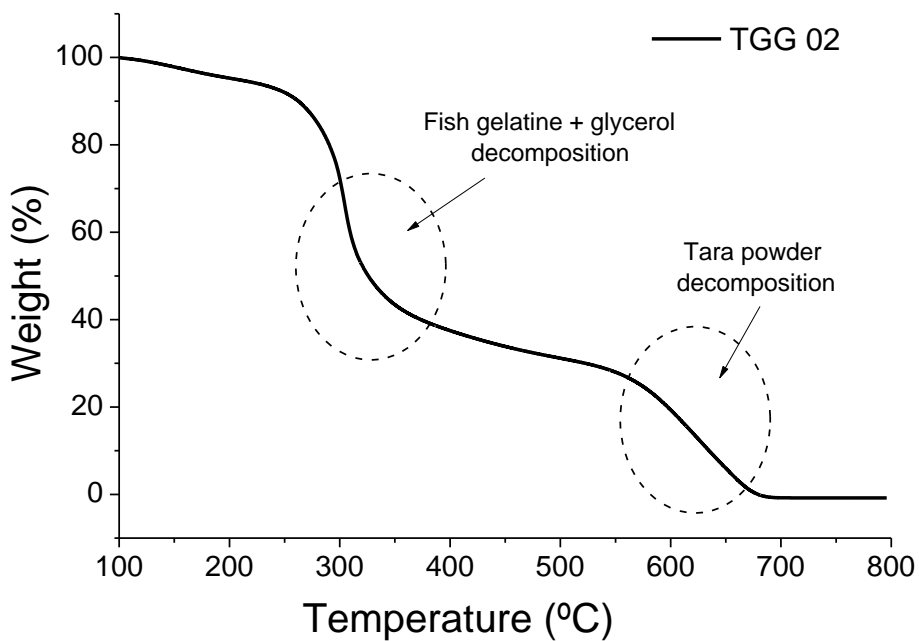
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Preliminary structural and morphological analyses on films TGG01-TGG10 revealed a not negligible effect of Tara granulometry. Films with different structures should manifest different thermal and mechanical behavior. Regarding the thermal stability, it was assessed by TGA analysis. Information about the degradation and mode of decomposition under the effect of heat were also acquired. In Figure 4, the TGA thermogram of film TGG02 is presented as an example.



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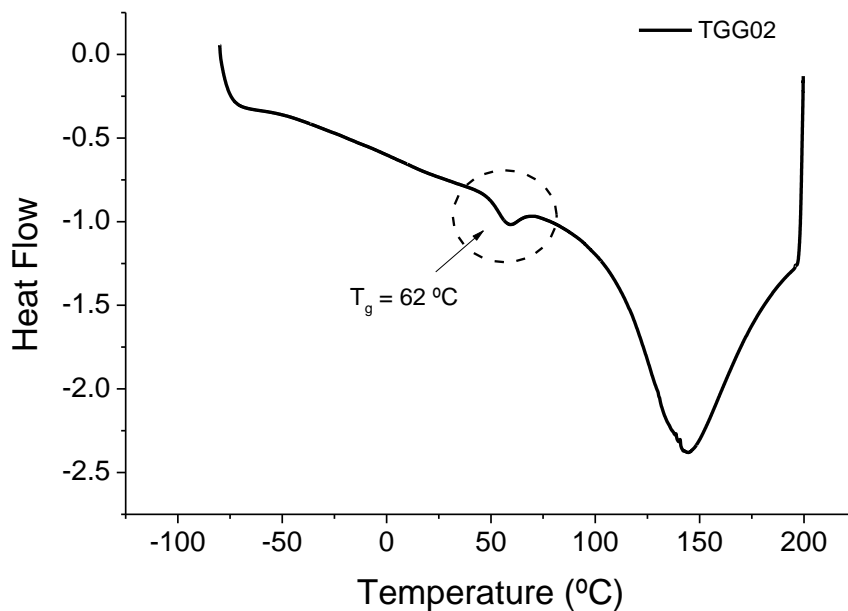
307

Figure 4. TGA profile of film TGG02.

308 From the thermogram presented in **Figure 4**, two weight losses are clearly detected.  
 309 Decomposition of fish gelatin-glycerol polymeric structure is detected around 300 °C,  
 310 whereas Tara powder degradation begins at 550 °C. The complete set of thermograms  
 311 obtained from all the films fabricated are presented in **Figure S6** of the **ESI**.

312 Additionally, Differential Scanning Calorimetry (DSC) analysis were performed on TGG01-  
 313 TGG10 films. The DSC measurements were employed for the determination of the glass  
 314 transition temperature ( $T_g$ ), measured during the third cycle of the measurement procedure.  
 315 An example of the glass transition region is presented in **Figure 5**, in which the DSC curve  
 316 of the TGG02 film is showed, in which the  $T_g$  is appears around 62 °C. The DSC curves  
 317 obtained from all the films, in which the  $T_g$  region is observed, is shown in **Figure S7** of the  
 318 **ESI**.

319



320

321 **Figure 5.** DSC curve (third cycle) obtained for TGG02 film.

322

323 All the thermal data derived from TGA and DSC tests corresponding to all the films  
 324 fabricated are reported in **Table 2**.

325

326 **Table 2.** Thermal properties of all the films prepared.  $T_g$  is the glass transition temperature, humidity  
 327 loss percentage was measured directly as the quantity of mass loss at 100 °C,  $T_{5\%}$  and  $T_{10\%}$  are the  
 328 temperatures at which 5 % and 10 % of mass is lost, and Onset temperature is defined as the  
 329 temperature at which the decomposition of the material begins.

Film	$T_g$ (°C)	Humidity loss (%)	$T_{5\%}$ (°C)	$T_{10\%}$ (°C)	Onset (°C)
------	------------	-------------------	----------------	-----------------	------------

<b>TGG 01</b>	63	9.8	213	245	274
<b>TGG 02</b>	62	6.9	224	268	294
<b>TGG 03</b>	52	10.7	190	218	266
<b>TGG 04</b>	54	10.1	193	237	287
<b>TGG 05</b>	50	10.5	175	207	259
<b>TGG 06</b>	51	7.3	244	261	275
<b>TGG 07</b>	69	9.7	207	244	274
<b>TGG 08</b>	61	8.1	215	251	277
<b>TGG 09</b>	63	6.1	217	263	287
<b>TGG 10</b>	58	5.3	228	268	293
<b>FG/Gly</b>	48	4.1	121	191	264
<b>Ta/Gly</b>	52	11.7	258	269	319

330

331 As it can be seen in data in **Table 2**, pure FG films (FG/Gly) present the lower  $T_{5\%}$ ,  $T_{10\%}$   
332 and onset temperature values, with temperatures of 121 °C, 191 °C and 264 °C,  
333 respectively. Comparing these data with the thermal behavior of pure Tara films (Ta/Gly),  
334 values are considerably increased ( $T_{5\%}$ ,  $T_{10\%}$  and onset values are 258 °C, 269 °C and 319  
335 °C), indicating that the Tara powder has a better thermal stability than Fish gelatin. In both  
336 cases, the quantity of glycerol employed is 20 wt%.

337 Values of  $T_{5\%}$ ,  $T_{10\%}$  and onset temperature in Tara-gelatin films (TGG01 to TGG10) lie  
338 between the limit values showed by the FG/Gly and Ta/Gly. In this sense, it is demonstrated  
339 the good thermal behavior of composite films respect to pure FG film. This improvement on  
340 the thermal behavior depends strongly on the quantity of glycerol, but we can even remark  
341 that films with high glycerol content (TGG 05 and TGG 06, with 60 wt% of glycerol) present  
342 a good thermal stability (onset temperatures are 259 °C and 275 °C).

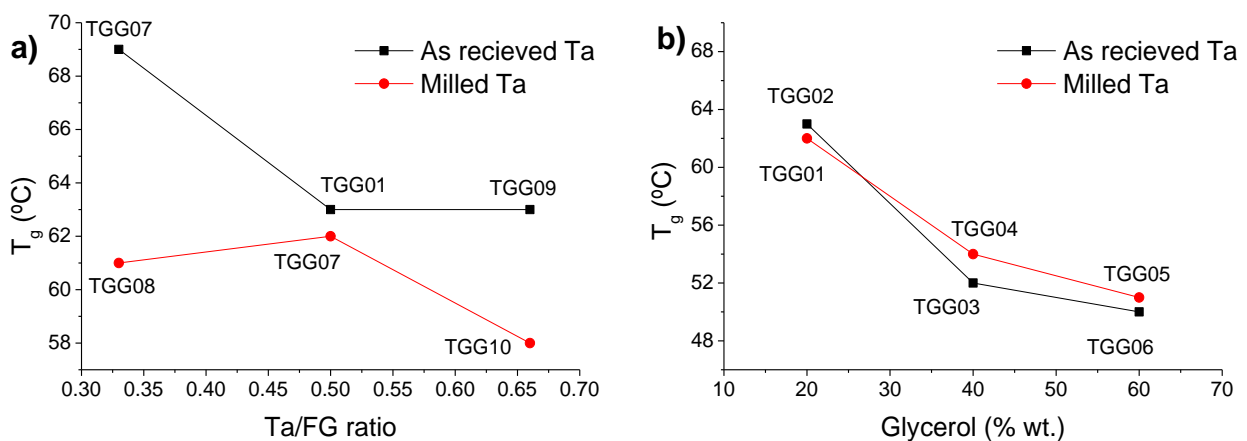
343 As expected, the quantity of glycerol has a predominant effect in the thermal stability of the  
344 films. In this sense, increasing the glycerol content lowers the  $T_{5\%}$  and  $T_{10\%}$  temperatures,  
345 then affecting negatively to the thermal stability and to the processing or working  
346 temperatures. On the other hand, using milled Tara seems to affect positively in the thermal  
347 stability of the films. For example, comparing the TGA data of TGG 01 (non-milled Tara) and  
348 TGG 02 (milled Tara), it can be seen that  $T_{5\%}$ ,  $T_{10\%}$  and onset temperatures are increased  
349 up to 20 °C, indicating that the use of milled Tara also increases the thermal stability of the  
350 films, obtaining films stable up to 300 °C, making them easy processable [31]. Finally, the  
351 humidity content values for TGG films vary between the limit values marked for pure Fish  
352 gelatin film (4.1 %) and pure Tara film (11.7 %). In this case, the use of milled Tara reduces

353 the humidity content respect to films with non-milled Tara (compare, for example, humidity  
354 content values of TGG 01 and TGG 02 films). This is also a very positive effect in terms of  
355 stability and handleability of the films. It is important to remark that similar humidity loss and  
356 thermal decomposition profiles were reported by Pulieri *et al.* in the case of Chitosan/gelatin  
357 blends [32].

358 Concerning the analysis of the glass transition temperature, it emerges that TGG films show  
359 higher  $T_g$  values with respect to FG/Gly, although this difference is not very important (in  
360 Ta/Gly film was not possible to measure the  $T_g$  temperature precisely). The discussion of  
361 the results can be carried out taking into account three different separated effects: (i) The  
362 influence of the Ta/FG ratio on the  $T_g$ , (ii) The effect of glycerol weight percentage, and (iii),  
363 the type of Ta employed (milled or not milled).

364 **Figure 6** shows the  $T_g$  variation in all the films as a function of the Ta/FG ratio (**Figure 5a**)  
365 and also as a function of glycerol weight percentage (**Figure 5b**).

366



**Figure 6.**  $T_g$  values of films fabricated. a) Films with different Ta/FG ratio; b) Films with different glycerol weight percentage.

367

368 **Figure 6a** shows the influence of the Ta/FG ratio in the glass transition temperature. Having  
369 a look at films fabricated using non milled Tara, a reduction of  $T_g$  is observed when the  
370 Ta/FG ratio increases. On the other hand, the effect of the glycerol weight percentage is  
371 clearly observed (**Figure 6b**). As expected, the addition of glycerol decreases the  $T_g$ ,  
372 confirming the role of glycerol as plasticizer. Finally, the third effect is related to the Tara  
373 powder employed (non-milled or milled). The analysis of the data in **Figure 6** shows that  
374 using milled Tara increases the glass transition temperature, but only when TGG07 vs

375 TGG08 and TGG09 vs TGG10 films are compared (see **Figure 6a**). In these particular  
376 cases,  $T_g$  is increased around 7 °C.

377

## 378 **5.6 Tensile properties**

379 To analyse the mechanical behaviour of films TGG01-TGG10, tensile properties were  
380 measured. Three different parameters were determined from the stress ( $\sigma$ )-strain ( $\varepsilon$ ) curves:  
381 Young modulus  $E$ , stress ( $\sigma_{break}$ , (MPa)) and deformation at break ( $\varepsilon_{break}$ , (%)). **Figure S8**  
382 of the **ESI** shows the stress-strain curves obtained for all the films fabricated, while **Table 3**  
383 presents the corresponding mechanical data.

384

385

386

387

388 **Table 3. Mechanical data of the films TGG01-TGG10.**

Film	$E$ (MPa)	$\Delta^1$ (MPa)	$\sigma_{break}$ (MPa)	$\Delta^1$ (MPa)	$\varepsilon_{break}$ (%)	$\Delta^1$ (%)
<b>TGG 01</b>	97	13.3	24	2.5	75	7.3
<b>TGG 02</b>	195	18.8	23	1.5	58	6.4
<b>TGG 03</b>	11	2.7	9	2.9	100	11.1
<b>TGG 04</b>	27	5.4	15	3.1	73	9.2
<b>TGG 05</b>	5	1.2	4	0.3	107	8.6
<b>TGG 06</b>	12	4.4	7	2.5	96	14.1
<b>TGG 07</b>	194	19.8	27	3.1	62	13.2
<b>TGG 08</b>	94	21.1	13	2.1	78	4.1
<b>TGG 09</b>	234	17.8	35	5.2	74	17.2
<b>TGG 10</b>	200	21.2	23	1.5	63	12.3
<b>FG/Gly</b>	243	5.9	36	3.8	95	6.1
<b>Ta/Gly</b>	550	31.7	40	13.2	23	7.0

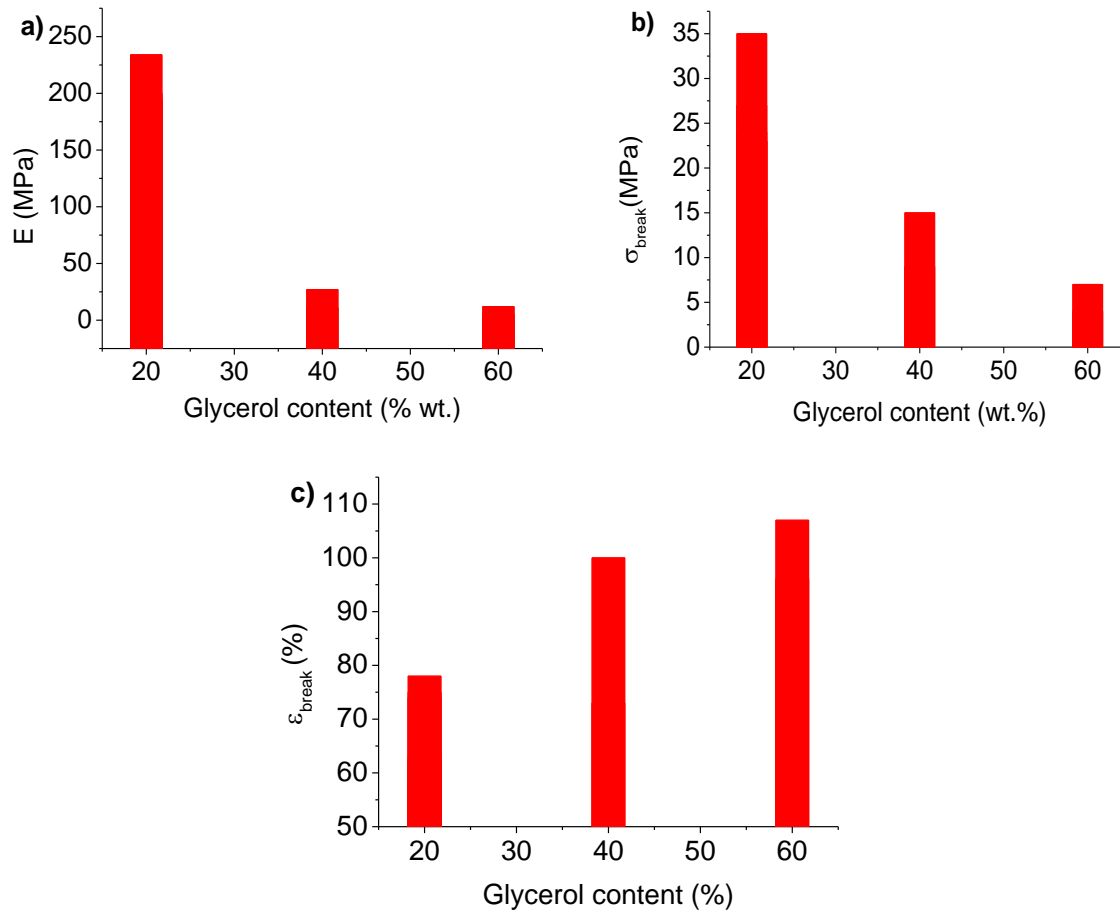
389 <sup>1</sup> $\Delta$  indicate the standard deviation of each value.

390

391 Mechanical data presented in **Table 3** indicate that Young's moduli values show a wide  
392 variability, from 5 MPa (TGG 05) to 234 MPa (TGG 09), as well as the stress at break,  
393 included between 4 MPa (TGG05) and 35 MPa (TGG09). Consequently, the deformation at  
394 break range between 23% and 107%.

395 This variability in the mechanical data can be related to the glycerol content and its  
396 plasticization effect, which plays a key role in the mechanical performance of the materials.

397 In order to better highlight this effect, the dependence of the mechanical parameters with  
398 the glycerol content is reported in **Figure 7**.



399

400

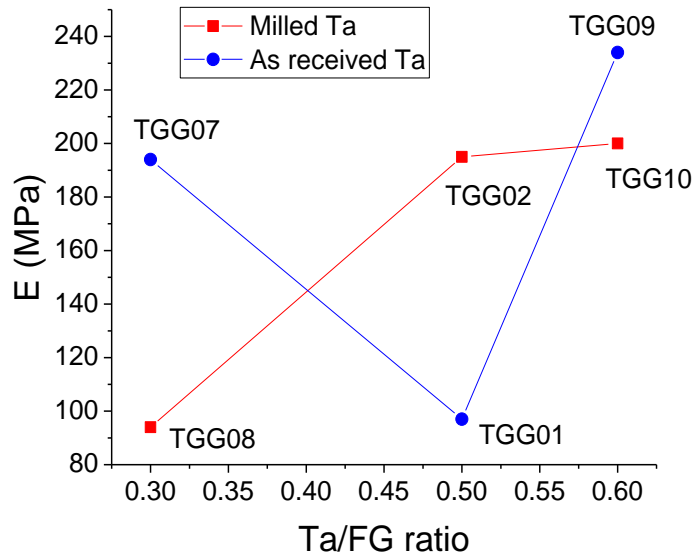
401 **Figure 7.** Dependence of the mechanical data of the films with glycerol content. a) Young's moduli,  
402 b) Stress at break, and c) Deformation at break.

403

404 It can be observed that the Young's moduli, as well as the stress at break decrease when  
405 glycerol is added, while the deformation at break increases with the content of glycerol. This  
406 behaviour confirms the plasticization effect expected through the addition of glycerol in the  
407 initial formulation of the materials.

408 Having a look at the values individually, TGG09 and TGG10 films present the higher values  
409 of Young's moduli (234 and 200 MPa). This is directly related to the Tara powder content,  
410 which is higher in these films (2 wt. eq).

411 In addition to the two main effects discussed above, a not-negligible influence of the Tara  
412 grain size on the mechanical properties can be observed. In **Figure 8**, the variation of  $E$  as  
413 function of Ta/FG ratio and type of Tara (milled and not milled) is reported.



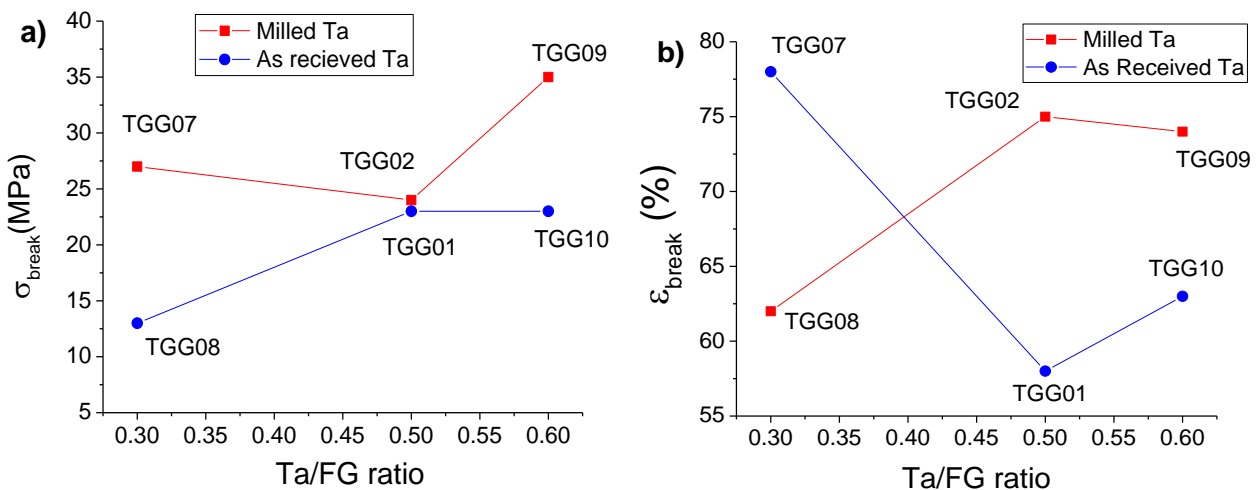
414

415 **Figure 8.** Variation of Young modulus E with the Ta/FG ratio and effect of the ball-milling of Tara  
 416 gum powder.

417

418 From the plots showed in **Figure 8** it is possible to notice a different mechanical behaviour  
 419 of films containing milled Ta which influences differently the trends of the two series TGG07-  
 420 TGG01-TGG09 and TGG08-TGG02-TGG10 (**Figure 8**, circled and squared points). Films  
 421 prepared with not milled Tara show a difference in Young's moduli value of about 100 MPa  
 422 for Ta/FG 1/2 ratio (TGG07 vs TGG08) and for Ta/FG ratio of 1/1 (TGG02 vs TGG01), but  
 423 with opposite trends. In the presence of an excess of Tara, the Young's moduli values are  
 424 quite similar, with not milled films showing a **value slightly higher**. Finally, to better compare  
 425 the curves relative to films containing non-milled and milled Tara, the variation of stress at  
 426 break and deformation at break of films containing the two different Tara powders is **reported**  
 427 in **Figure 9**.

428



429

430 **Figure 9.** Mechanical data as function of Ta/FG of films containing non-milled or milled Tara gum  
431 powder. a) Stress at break; b) Deformation at break.

432

433 Data in **Figure 9** indicates that stress at brake is affected by the presence of milled Tara  
434 only in films containing with Ta/FG ratio 2/1 or 1/2, while the mechanical values for Ta/FG  
435 ratio of 1/1 are almost coincident (**Figure 9a**). On the contrary, the deformation at brake  
436 shows a different behaviour depending of the Tara employed. When non-milled Tara is used,  
437 deformation at break grows with the increasing of Tara content, whereas on the other hand  
438 when milled Tara is employed the trend is the opposite (**Figure 9b**).

439

## 440 **6. Conclusions**

441 Morphological, thermal and mechanical properties of films composed by fish gelatin, Tara  
442 gum and glycerol can be tuned by oportune engeneering processes. **In particular**, by  
443 changing the amount of the **plasticizer glycerol**, it is possible to optimize the composition in  
444 terms of thermal behaviour and mechanical properties. Also, the structural effect obtained  
445 by the addition of Tara gum **resulted relevant**. By employing **milled Tara instead to the**  
446 **commercial one**, it is possible to **enhance the thermal stability and improve the mechanical**  
447 **performances of the films**. The origin of such effects can be found in a change of the  
448 **morfology of films prepared with different ingredients, and observed by IR spectroscopy and**  
449 **through SEM and AFM analyses**. Influencing the performances of the films by reducing the  
450 **grain size of the natural gum (Tara in our case) represents a novelty and can lead the way**  
451 **toward further optimization of similar polymers**.

452

## 453 **Acknowledgments**

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457

## 458 **Data Availability**

459 **The raw data required to reproduce these findings cannot be shared at this time due to**  
460 **technical limitations**.

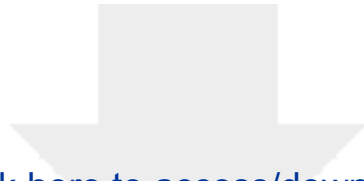
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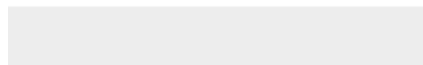
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**Highlights:**

- Novel films based on fish gelatin and tara gum were obtained.
- Films were fabricated following a simple casting process.
- Density of films varied between 6.5 and 9.8 g/cm<sup>3</sup>, using glycerol as plasticizer.
- High degradation temperatures (up to 300 °C) were observed.
- Milling Tara gum improved both thermal stability and mechanical strength.

**Declaration of interests**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: