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Condensed Tannin-glucose-based NIPU Bio-Foams of Improved Fire Retardancy

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1 **Abstract:**

2 Glucose-based self-blowing non-isocyanate polyurethanes foams were prepared in our
3 previous work. They showed excellent properties comparable to commercial foams by
4 just using a simple preparation procedure. These foams, nevertheless, present a critical
5 drawback that is their flammability. In the research presented here a natural phenolic
6 compound, condensed tannin, was tested as a flame-retardant to improve the fire
7 resistance of glucose-based NIPU foams. A number of tannin-substituted glucose-based
8 NIPU foams (mimosa tannin replacing glucose at 0%, 25% and 50%, respectively) were
9 prepared and characterized by scanning electron microscopy (SEM), Fourier transform
10 infrared spectroscopy (FT-IR), Thermogravimetric analysis (TG), ignition experiment
11 and limiting oxygen index (LOI). Other physical and mechanical properties, such as
12 foaming processes, density, compression strength, etc. were also investigated. The
13 results indicated that the tannin-modified glucose-based NIPU foams (T/G (1/3)-Fs and
14 (T/G (1/1)-Fs)) exhibit smaller mean cell size, improved compression strength and
15 higher density than (T/G (0/4)-Fs). The FT-IR analysis showed that urethane linkages
16 were formed, the chemical structure of glucose-based NIPU foam being nonetheless
17 preserved even if the glucose was partially replaced by the condensed tannin.
18 Thermogravimetric analysis showed that the presence of condensed tannin decreased
19 the thermal stability of the tannin-glucose NIPU foam composites slightly. In addition,
20 ignition experiments were also carried out in which the glucose-based NIPU foams with
21 a condensed tannin showed longer burning time than neat (T/G (0/4)-Fs). Finally,

22 limiting oxygen index (LOI) values from 17.5% to 25.5%, show a higher value with the
23 increasing condensed tannin substitution.

24 **Key words:**

25 condensed tannin, biomass foam, fire resistance, glucose-based NIPU, compressive
26 strength

27

28 **1 Introduction**

29 Polyurethane foams (PUs), being light-weight, and presenting excellent insulating
30 property, as well as superior mechanical properties, have been extensively utilized in
31 buildings as thermal and acoustic insulation materials [1-3]. However, PUs exhibit
32 substantial drawbacks, including toxic and expensive raw materials, flammability and
33 dripping after combustion, even though they are widely utilized [4].

34 Demands for safer, non-toxic and inexpensive materials have driven researchers to
35 explore new technologies and starting materials. Lignin [5-7], tannin [8-10], sugar [11,
36 12], forestry and agriculture waste [6, 13, 14] and other natural hydroxy-carrying
37 compounds, are typical biomass resources that as partial or complete replacement of
38 petroleum-based polyhydric alcohols have been tried to prepare PUs. It is the most
39 commonly utilized strategy and this kind of foams is known, incorrectly, as “bio-foams”.
40 Besides, another one is that non-isocyanate strategies for PU foams have been reported
41 in the literature [15, 16]. For example, such a latter approach used easily available, cost-
42 effective materials and methods, such as the aminolysis of five-membered cyclic
43 carbonates, to replace isocyanate when making PUs [4, 17-22]. Unfortunately, some
44 shortcomings were still discovered, including harsh reaction conditions and
45 environment (high temperature, catalyst) [23], high toxic reagent (epichlorohydrin) [22]
46 and high pressure [18, 20].

47 We had initially sought a more environment friendly preparation strategy recently.
48 Fortunately, a bio-mass resource-based (mimosa tannin, a condensed tannin), low

49 temperature (around 90 °C) and atmospheric pressure synthesis route was found [24,
50 25]. Meanwhile, the glucose-based NIPUs so prepared have been used for wood
51 coatings and wood bonding as well as to prepare foams [11, 12, 26]. The open cell
52 foams obtained by high-temperature induced foaming has excellent properties, and its
53 cellular structure is recovered after the pressure on it is released, even if the cell walls
54 were flattened by compression.

55 Nevertheless, in common with traditional PUs, the all glucose-based NIPU foams,
56 regardless if obtained at high temperature or room temperature, are flammable [12, 26].
57 This limits their applications as fire resistance materials. Therefore, to improve their
58 fire resistance still remained the key aim of the research work presented here. The
59 literature reports that numerous types of flame retarding additive can improve the fire
60 resistance of materials effectively, for instance, halogenated compounds [27],
61 phosphorus-containing compounds [28, 29] and nano-additives [30-34]. They either
62 trigger a flame retarding barrier, or play a role as a layer blocking flammable gases, or
63 both [35]. However, they will release toxic halogen- or phosphorus-containing gases
64 which can threaten the environment during burning and the foam properties will
65 deteriorate because of the high content of additives.

66 Nowadays, some researchers have turned their attention to bio-based flame retardants,
67 such as tannin [36, 37], caseins [38], phytic acid [39] and banana pseudo-stem sap liquid
68 [40]. Tannins became the first candidate bio resourced material, which can be obtain
69 from the bark, seeds and other parts of plentiful species of trees [41-43]. Moreover, they

70 have many special properties such as antibacterial and antioxidant [44, 45], precipitate
71 proteins [46], reductants and stabilizers [47]. It was reported that tannins can act as a
72 natural fire resistance to aid tree survival [48]. This is mainly attributed to their similar
73 reactivity to phenol, phenoxy radicals could quench the oxygen free radicals when the
74 polymer is decomposed during heating [35]. In addition, tannins have high char
75 production efficiency when burning (55% char for condensed tannin and 28% char for
76 tannic acid) [37, 49, 50], resulting in a protective layer, which is made of char and can
77 block heat, oxygen, and flammable gases [51]. At the same time, due to their effect, the
78 tannins can increase the foam mechanical properties while acting as a fire retardant [35].
79 Thus, the work presented here is focused on condensed tannin as a natural fire retardant
80 to improve the flame resistance of glucose-based non-isocyanate polyurethane foams.
81 The resins and foams prepared were obtained at ambient pressure, at different ratios of
82 glucose and tannin. The morphology and performance of glucose/tannin foams were
83 investigated by SEM, FT-IR and TG and other techniques. The fire resistance of all
84 foams was determined by means of direct ignition and limiting the oxygen index (LOI)
85 measurement.

86 **2. Materials and methods**

87 2.1 Materials

88 Mimosa tannin extract is a commercial product, namely mimosa tannin extracted from
89 the bark of *Acacia mearnsii* (*De Wild*), supplied by Silva Chimica (St. Michele
90 Mondovi, Italy). Glutaraldehyde (C₅H₈O₂, 50% water solution) was obtained from

91 Acros Organics, France; Glucose (99.99%, anhydrous), Hexamethylenediamine
92 (HDMA, 98%), Dimethyl carbonate (DMC, 99%, anhydrous),
93 Hexamethylenetetramine (99%, ACS reagent), Citric acid (99.5%, ACS reagent), were
94 supplied by Sigma-Aldrich (Saint Louis, France). All these chemical reagents did not
95 need any further purification before use. Deionized water (DI) was produced in the
96 laboratory.

97 2.2. Preparation process

98 2.2.1 Preparation of the glucose or glucose-tannin-based Non-Isocyanate Polyurethanes 99 (NIPUs)

100 The neat glucose or glucose-tannin-based NIPUs were prepared according to a
101 procedure already reported [52]. Three kinds of NIPUs mixtures for foaming preparing
102 were prepared in this work. Glucose or glucose/tannin mixture and deionized water
103 were placed into three-necked flask with condensing reflux, magnetic stirring and
104 thermometer. And then, dimethyl carbonate (DMC) was added into the mixture and
105 stirred thoroughly, mixed evenly, and heated to 65 °C and remained for 1 h.
106 Subsequently, 70% solution (in water) of hexamethylenediamine was added into the
107 mixture under mechanical stirring, while the mixture was heated to 90 °C and remained
108 for 2 h. Finally, the glucose or glucose-tannin-based NIPUs were obtained and cooled
109 down to room temperature, standby application. The proportions of materials used are
110 shown in Table 1.

111 Table 1 The formulation of glucose or glucose-tannin-based NIPUs

Samples	Tannin (g)	Glucose (g)	DMC (g)	HDMA (g)	Water (g)
T/G (0/4)- NIPUs	0	40	27	77.6	33.34
T/G (1/3)- NIPUs	10	30	27	77.6	33.34
T/G (1/1)- NIPUs	20	20	27	77.6	33.34

112 2.2.2 Foam preparation

113 All foam samples were prepared according to our previous work already reported [12].
114 10 g of G-NIPUs or T/G-NIPUs and 1 g hexamethylenetetramine were added into a 100
115 mL plastic beaker and then stirred at for 1 min. 8 g of the complex acid blowing agent
116 (citric acid: glutaraldehyde = 3:1) was added and then the mixtures were stirred at room
117 temperature for 10-15 s. The as-obtained flexible foams were placed at in ambient
118 environment until the foam structure trend to stable. According to the species of T/G
119 (0/4)-NIPUs, T/G (1/3)-NIPUs and T/G (1/1)-NIPUs as utilized in the experiments, the
120 obtained flexible foams were recorded as T/G (0/4)-Fs, T/G (0/4)-Fs and T/G (0/4)-Fs,
121 respectively. Subsequently, all flexible foam samples were put into the oven overnight
122 at 70-80 °C and were taken out from the plastic beakers. The final cured foam samples
123 were placed at ambient temperature (25°C and 12% relative humidity) for 2 days prior
124 to characterization.

125 2.3. Measurements

126 2.3.1 Behavior of foaming process

127 The behavior of the foaming process was investigated in terms of previous reported
128 [53]. The rising time (the time from pouring the complex acid blowing agent into the
129 NIPUs until full expansion of the resulting foam) and tack free time (the time from
130 pouring the complex acid blowing agent into the NIPUs until the skin of the foam was
131 no longer sticky) were two critical parameters of foaming process. A thermometer was
132 fixed and deposited into inner of T/G-NIPUs to measure the foaming temperature
133 changes in the foaming process. The rising time, tack free time and foaming
134 temperature were accurate recorded and monitored, respectively. Each foaming process
135 replicate was tested five times and average value was taken.

136 2.3.2 Fourier transform infrared (FT-IR) spectroscopy

137 The functional groups of all foam samples were analyzed with a PerkinElmer Frontier
138 ATR-FT-MIR provided by an ATR Miracle diamond crystal. The sample powders were
139 laid on the diamond eye (1.8 mm) of the ATR equipment and the contact for the sample
140 was ensured by tightly screwing the clamp device. Each sample was scanned registering
141 the spectrum with 32 scans with a resolution of 4 cm^{-1} in the wave number range
142 between 600 and 4000 cm^{-1} .

143 2.3.3 Scanning electron microscopy (SEM) observation

144 To investigate the cell microstructure and morphology of glucose or tannin-glucose-
145 based NIPUs foams, the scanning electron microscopy (Gemini SEM 300, Germany)
146 was used with an acceleration voltage of 10 kV. The cell morphologies were statistically

147 analyzed depend on the SEM images by Nano Measurer 1.2 [54]. The cell size
148 distributions of all foams were calculated. The abovementioned parameters were
149 calculated by averaging several tens of individual cells for each sample.

150 2.3.4 Apparent density

151 The apparent densities were obtained as the ratio of weight to cubic specimen volume,
152 according to ASTM D1622-08. The size of the samples was 30 mm × 30 mm × 30 mm.
153 The average of five samples was determined.

154 2.3.5 TG analysis

155 The thermal stability of the foams was measured by using a TGA5500 analyzer (TA
156 instruments, USA). Sample powder amounting to 5-8 mg was transferred to a platinum
157 pan, with the temperature ranging from 25°C to 790°C at a heating rate of 10 °C·min⁻¹
158 in a nitrogen atmosphere.

159 2.3.6 Compression strength

160 The compression strength of the foams in the direction parallel to that of the foam rise
161 were determined under ambient conditions by using a universal testing machine
162 (Instron 3300, Elancourt, France). The size of the samples was 25 mm × 25 mm × 25
163 mm, and the crosshead rate was fixed at 2.0 mm·min⁻¹ for each sample. At least three
164 samples were tested to determine the average value.

165 2.3.7 Direct ignition test

166 The direct ignition test was carried out according to a method already described in the
167 literature [12]. Foam samples were made to specification size, 30 mm × 30 mm × 30

168 mm, and then were exposed facially to a stainless-steel frame preheated on a Bunsen
169 burner (around 1000°C). Making sure the samples were located in the outer flame area
170 of the Bunsen burner. The burning time was calculated starting by the samples were
171 placed on the burner, till the flame of sample was considered as extinguished.
172 Subsequently, the sample chars were weighted and noted as quality of residue. All tests
173 were carried out in a closed environment to minimize the influence of other factors.
174 Each foam type was tested three times.

175 2.3.8 Limiting oxygen index (LOI)

176 The limiting oxygen index (LOI) was measured according to a method reported in the
177 literature [53] using an HC-2 oxygen index meter (Jiangning Analysis Instrument
178 Company, China). All samples were prepared to specification size of 80 mm ×10 mm
179 × 10 mm. The LOI values used were the averages for the five samples.

180 **3 Results and discussion**

181 3.1 Preparation of Tannin-glucose-based NIPUs foams (T/G (0/4)-Fs, T/G (1/3)-Fs and 182 T/G (1/1)-Fs)

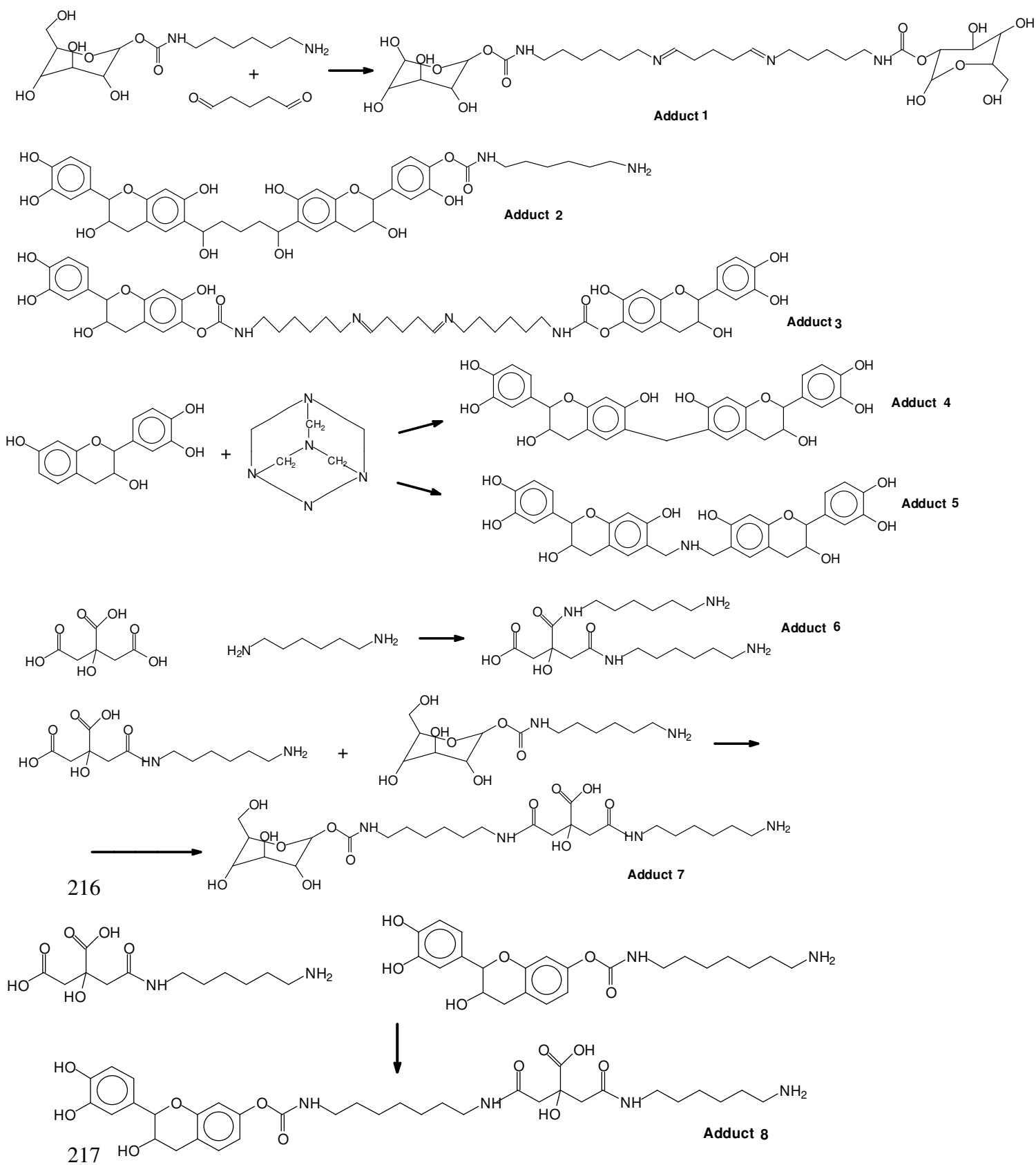
183 The tannin-glucose-based NIPUs foams (T/G (0/4)-Fs, T/G (1/3)-Fs and T/G (1/1)-Fs)
184 were prepared with ease at ambient temperature. The main foreseeable adducts formed
185 by multiple reactions eventually leading to structural networks in the foam are shown
186 in Scheme 1. The foaming process can be divided into two main processes: the first one
187 is the foaming process. The energy in this stage was produced from the rather violent
188 reaction with citric acid and -NH₂ groups (obtaining the adducts 6, 7 and 8), which

189 provides the self-blowing energy at room temperature [12]. The second one is the
190 network crosslinking. Hexamethylenetetramine and glutaraldehyde act as crosslinkers
191 to ensure that the liquid foam formed does not collapse and be maintained (obtaining
192 the adducts 1, 2, 3, 4 and 5). And then, these adducts can further crosslink to form large
193 molecules, which can intertwine with each other. Ultimately, this effect causes the sharp
194 increase of the viscosity of the mixture and then its gelling, resulting in a three-
195 dimensional network (cf. Scheme 2). In fact, these two processes occur almost
196 simultaneously. The reason for this analysis is to better understand the whole foaming
197 process.

198 3.2 Apparent density

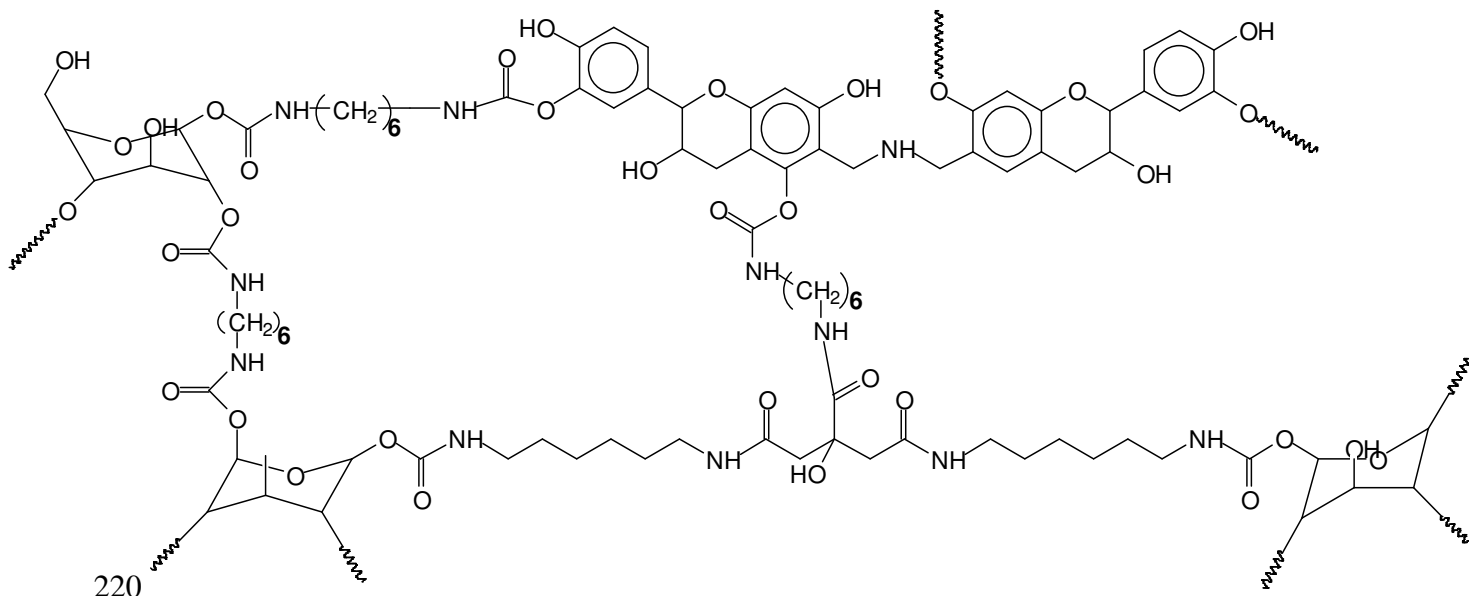
199 The prepared liquid flexible foams so prepared need to be hardened by heating, which
200 was necessary to obtain and measure stable physical properties. Consequently, tannin-
201 glucose-based foams (T/G (0/4)-Fs, T/G (1/3)-Fs and T/G (1/1)-Fs) with stable
202 properties were prepared and shown in Figure 1. Some subtle differences between these
203 three foam types can be seen, such as apparent color, foam cell status and cells size.
204 The foam structures will be discussed in the following section, by comparing the
205 scanning electron microscopy (SEM) observation. All foams, once the tannin was
206 introduced, showed a black/red surface color. The reason of this is the reddening of
207 mimosa tannin under acid conditions. Moreover, the apparent densities of the foams (cf.
208 Table 2) increased as a function of the increase in the proportion of tannin. Thus, 50%
209 tannin substitution yielded foams (T/G (1/1)-Fs) with the higher density, approximately

210 0.25 g·cm⁻³, while the T/G (0/4)-Fs without tannin presented the lower density, around
211 0.15 g·cm⁻³. This increase in foam density is ascribed to the more rapid gelling with
212 tannin and glutaraldehyde resulting in a higher cross-linking level much earlier in the
213 foaming process. Moreover, hexamethylenetetramine can provide further cross-linking
214 with tannin when the soft foams are heat-hardened. Thus, it appears that the extent of
215 cross-linking progressively increases with the addition of tannin.

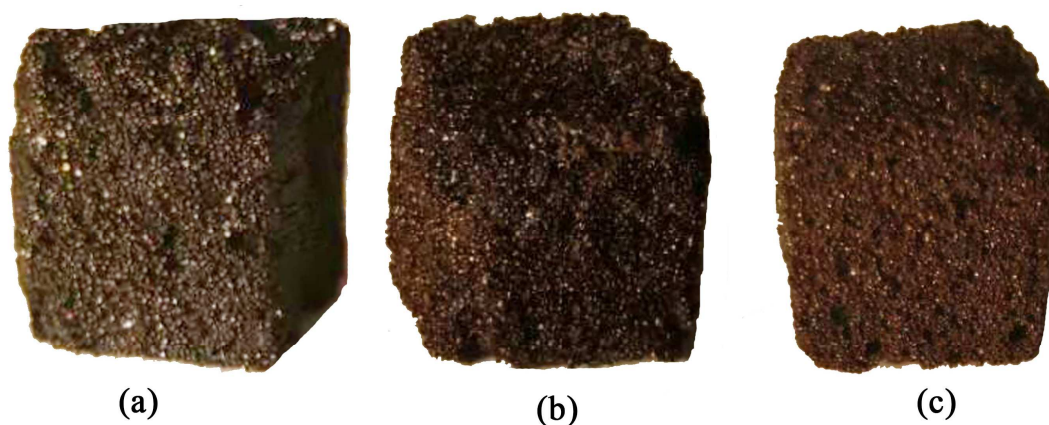


218 Scheme 1 The main foreseeable adducts formed by multiple reactions eventually

219 leading to structural networks in the foam.



220
 221 Scheme 2 A schematic example of some of the mixed linkages present in a possible
 222 network structure of tannin/glucose foam



223
 224 Figure 1 Digital images of three kinds of target foam samples. (a) T/G (0/4)-Fs; (b) T/G
 225 (1/3)-Fs; (c) T/G (1/1)-Fs.

226 Table 2 Apparent density mean cell size and specific compressive strength of T/G (0/4)-
 227 Fs, T/G (1/3)-Fs and T/G (1/1)-Fs

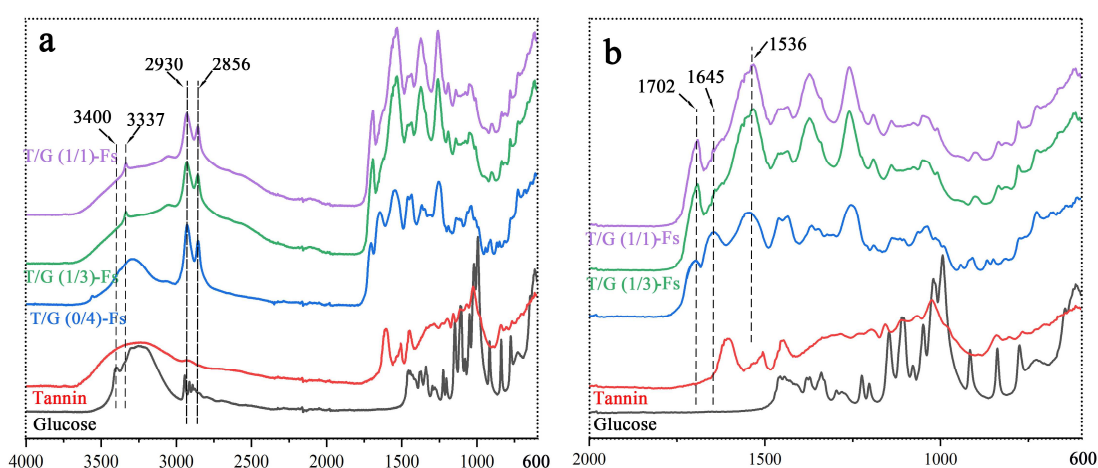
Samples	Apparent density (g cm ⁻³)	Mean cell size (μm)	Specific compressive strength (kPa/kg m ⁻³)
---------	---	---------------------	--

T/G (0/4)- Fs	0.15 ± 0.02	252.18 ± 41.55	1.22 ± 0.19
T/G (1/3)- Fs	0.19 ± 0.02	246.23 ± 49.19	1.27 ± 0.23
T/G (1/1)- Fs	0.25 ± 0.03	243.08 ± 50.40	1.51 ± 0.20

228 3.3 Fourier transform infrared (FT-IR) spectroscopy

229 Fourier Transform Infrared (FT-IR) spectra of all foams are shown in Figure 2, to
 230 investigate the functional groups changes occurring in these foam preparations. The
 231 results indicate that T/G (0/4)-Fs, T/G (1/3)-Fs and T/G (1/1)-Fs presents similar
 232 chemical structures, however, and quite distinct from neat tannin (red curve) and
 233 glucose (black curve). The main absorption peaks on the spectra were identified by
 234 arrows and imaginary segmented lines. In view of Figure 2, an intense broad absorption
 235 band between 3500 and 3100 cm^{-1} is characteristic of the -OH groups [16, 55]. This
 236 broad peak is clearly apparent in the FT-IR spectra of neat tannin and glucose as well.
 237 The 3337 cm^{-1} -N-H stretching peak is attributed to secondary amides, and concerns
 238 two kinds of reaction products obtained (one of them being urethane groups) [24].
 239 Furthermore, there are two clear absorption peaks at 2930 cm^{-1} and 2856 cm^{-1} ,
 240 especially in the NIPU foams, which are attributed to the C-H stretching vibration of -
 241 CH_2 and $-\text{CH}_3$ [16, 52]. As shown in Figure 2 (b), there is some strong evidence for
 242 the formation of carbamate bonds. Of these the 1702 cm^{-1} band was attributed to the

243 C=O from urethane groups and the 1645 cm^{-1} band to the C=O from ester groups [16,
244 52]. Moreover, the 1536 cm^{-1} band is also characteristic of the urethane group
245 confirming the formation of carbamate structures [16]. In the FT-IR spectrum of neat
246 tannin and glucose, nevertheless, these kinds of absorption peaks have not been detected.
247 Such evidence shows that glucose-based NIPU foams are obtained by the non-
248 isocyanate approach taken under atmospheric pressure and low temperature. Therefore,
249 even if glucose was only partially replaced by condensed tannin, the chemical structure
250 of glucose-based NIPUs foams does not appear to be affected.



251
252 Figure 2 FT-IR spectra of neat tannin, glucose, glucose based NIPUs foam and
253 tannin/glucose based NIPUs foam. (a) the wavenumber from $600\text{-}4000\text{ cm}^{-1}$; (b) the
254 wavenumber from $600\text{-}2000\text{ cm}^{-1}$.

255 3.4 SEM analysis

256 SEM was used to investigate the foams morphology at different replacement levels of
257 condensed tannin. The SEM images of the T/G (0/4)-Fs, T/G (1/3)-Fs and T/G (1/1)-Fs
258 are shown in Figure 3. From this it appears that all foams present a regular cells
259 morphology. A considerable number of open pores are observed in Figure 3 (a), (d) and

260 (g), attributed to water evaporation in the precursor resins during foaming and drying.

261 Furthermore, some ruptures or debris also can be observed in all foams, these being

262 ascribed to the cutting process in preparing the samples [54]. Comparing Figure 3(b)

263 and Figure 3(e), (h), thicker cell walls were obtained with increasing the presence of

264 condensed tannin. This phenomenon belongs to the thickening function of tannin-

265 derived products on glucose-based NIPU foam. Furthermore, in Figure 3(f), (i), some

266 fibrous polymers can also be clearly seen, interspersed in the cell wall or attached to

267 their surfaces. These fibrous polymers as filler interspersed in glucose-based NIPU

268 foam, resulted not only in an expansion effect that thickened the cell wall, but in the

269 progressive increases of compression strength. As well as the number of fibrous

270 polymers and cell walls thickness progressively increases by tannin addition the

271 compression strength also progressively increases. Just because of this reason, the

272 condensed modified foams obtained a smaller mean cell size (cf. Table 2).

273 According to literatures [55], condensed tannins have higher temperature (above 500°C)

274 carbonization efficiency under an atmospheric environment. Therefore, in view of

275 Figure 3(f), (i), the tannin-derived fibrous polymers inserted into, or covering the cell

276 walls can be transformed into char or a char covering layer after high temperature

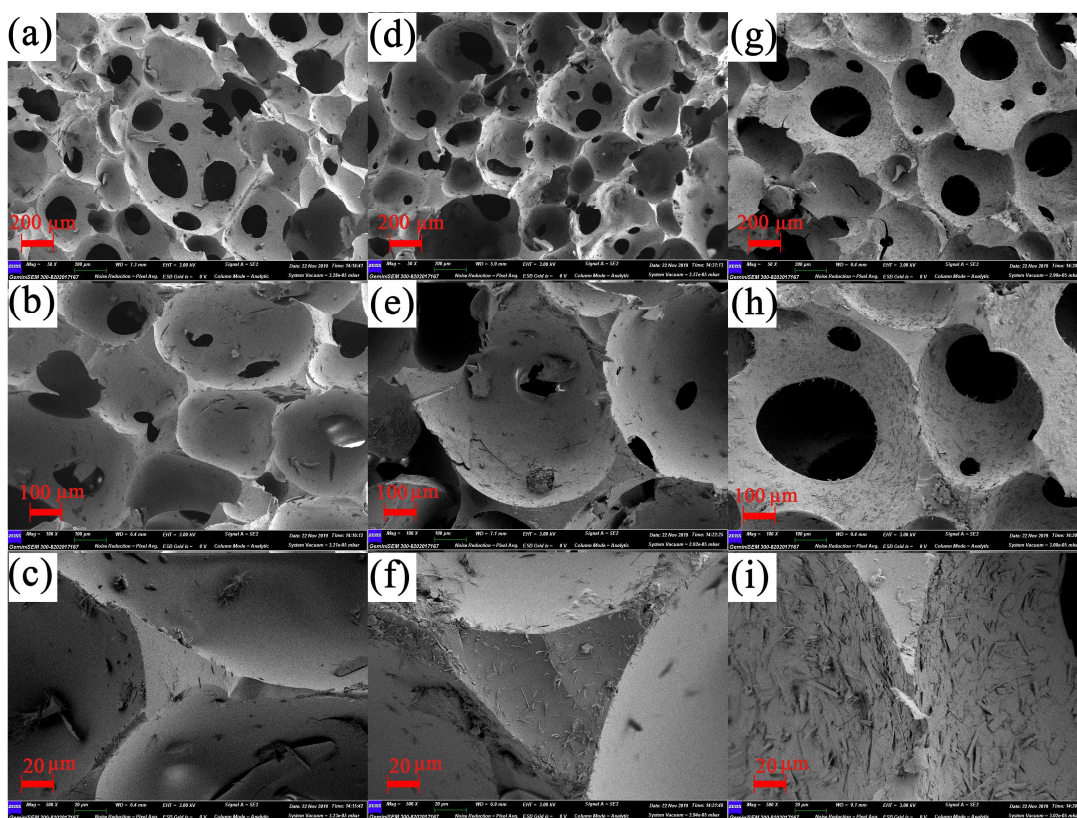
277 decomposition. This is mainly attributed to their similar reactivity to phenol, phenoxy

278 radicals being able to quench the oxygen free radicals when the polymer is decomposed

279 during heating [35]. Therefore, the char so formed can either retard or even prevent

280 effectively the combustion process of the foams. Conversely, without any tannin

281 addition a smooth fracture surface and inner surface of T/G (0/4)-Fs can be seen in
282 Figure 3(c). Precisely due to this surface smoothness of T/G (0/4)-Fs, glucose-derived
283 products alone do not have high carbonization efficiency so that they can only provide
284 a limited protection during ignition and LOI testing. Hence, the interspersed and
285 attached tannin-derived polymers in T/G (1/3)-Fs and T/G (1/1)-Fs cell wall can form
286 a protecting char layer when these foams are exposed to high temperatures condition.
287 These can well explain why in ignition experiments only a much smaller flame can be
288 seen and a higher LOI was obtained for T/G (1/3)-Fs and T/G (1/1)-Fs foams, compared
289 to T/G (0/4)-Fs.



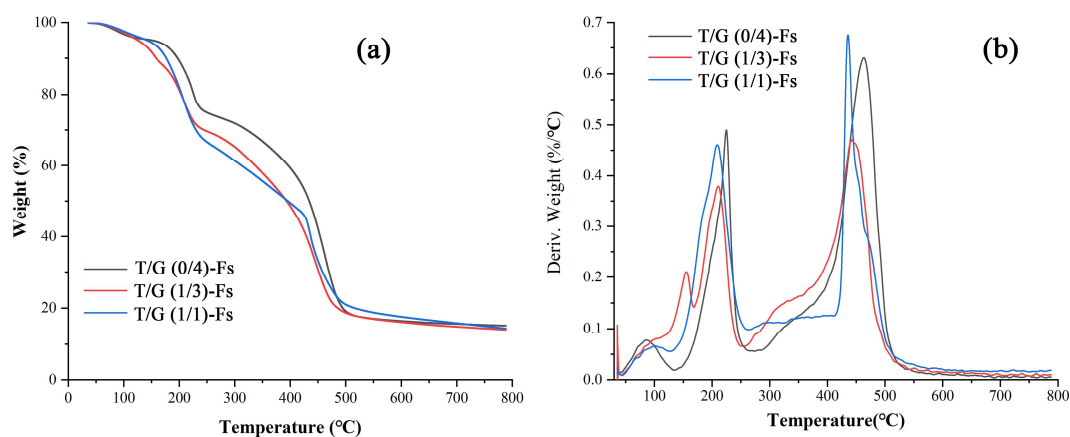
290

291 Figure 3 SEM images of the T/G (0/4)-Fs (a-c), T/G (1/3)-Fs (d-f) and T/G (1/1)-Fs

292 (g-i)

293 3.5 Thermogravimetric analysis (TGA)

294 Thermogravimetric analysis (TGA) has been routinely used to evaluate the thermal
295 stability of various foams [54-57]. Thus, the TGA (a) and DTG (b) curves of T/G (0/4)-
296 Fs, T/G (1/3)-Fs and T/G (1/1)-Fs under N₂ atmosphere are shown in Figure 4. The
297 corresponding specific degradation temperatures and char yields at 790°C are listed in
298 Table 3. The T_{max} value reported in Table 3 is the maximum temperature shown by DTG
299 curves peaks at different pyrolysis stages. It can be observed that all foam samples
300 present a similar pyrolysis behavior, with two-stage decomposition which are typical of
301 the pyrolysis of polyurethane foams [58]. The first mass loss stage occurs within the
302 temperature range of 150°C-300°C, which belongs to the decomposition reaction of the
303 bond cleavage of urethane [56]. The second mass loss stage occurs between 380°C and
304 600°C, this been attributed to the breaking of C-C bonds and the further decomposition
305 of pyrolysis residual products from the first stage [55, 56]. It is still worth noting that
306 the DTG curve views a small peak at low temperature between 50°C and 100°C, which
307 may be ascribed to decompose of excess acid and hexamethylenetetramine, as well as
308 volatilize of absorbed water.



310 Figure 4 TGA (a) and DTG (b) curves of T/G (0/4)-Fs, T/G (1/3)-Fs and T/G (1/1)-Fs
311 (under N₂ atmosphere)

312 In Figure 4, some significant differences can be observed when increasing the
313 condensed tannin content, resulting in a slight decrease of the pyrolysis temperature of
314 the foams. Nevertheless, the percentage value of the final residual mass at 790 °C
315 indicates that all foam samples have a similar percentage mass loss, their residual mass
316 being around 14-15% under a N₂ atmosphere. Between T/G (0/4)-Fs, T/G (1/3)-Fs and
317 T/G (1/1)-Fs, a noticeable change can be seen, which is a shift of the decomposition
318 temperature to lower temperatures, from 225°C (first stage) 462°C (second stage)
319 decrease to 210°C (first stage) and 441°C (second stage) and 208 °C (first stage) 435°C
320 (second stage), respectively (cf. Table 3). This is likely to be the initial thermal
321 depolymerization of mimosa tannin extract at lower temperature, this occurring around
322 146°C and the partial breakage of the intermolecular bonds of condensed tannin at
323 around 450°C [55]. This phenomenon was similar with others described in the literature
324 [54, 55]. Therefore, condensed tannin addition reduced thermal stability of NIPU foams
325 under a N₂ atmosphere.

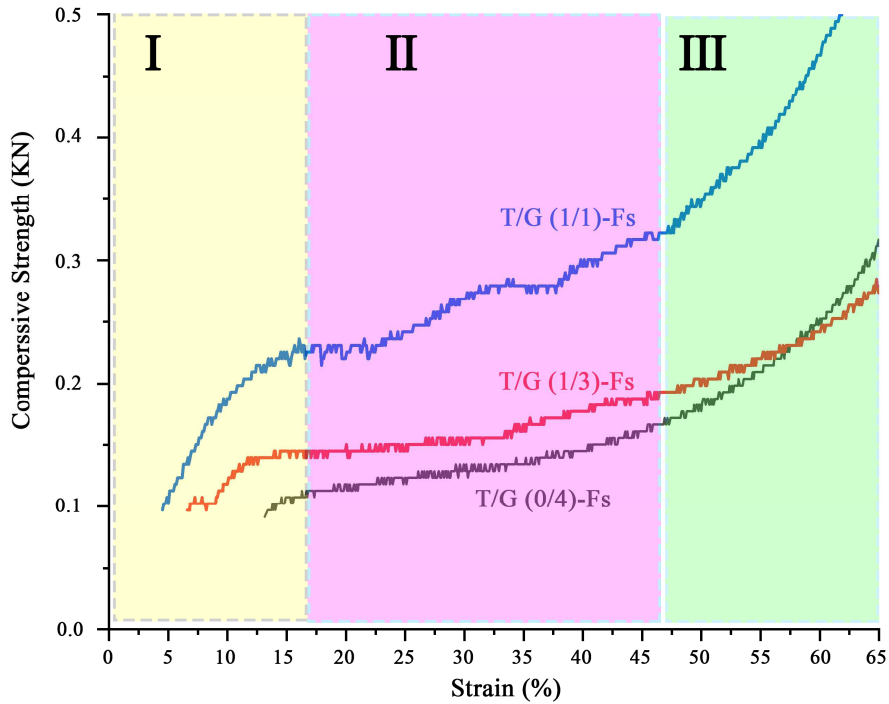
326 Table 3 DTG data of T/G (0/4)-Fs, T/G (1/3)-Fs and T/G (1/1)-Fs (under N₂ atmosphere)

Samples	T _{max} (°C)		Residual mass at 790°C (%)
	Step I	Step II	
T/G (0/4)-Fs	225	462	15.1
T/G (1/3)-Fs	210	441	14.4

327 3.6 Compressive mechanical properties

328 Compression experiments were conducted to determine the effect of different tannin
329 substitution on the compressive mechanical properties of glucose-based NIPU foams.
330 The compressive stress-strain curves of T/G (0/4)-Fs, T/G (1/3)-Fs and T/G (1/1)-Fs
331 samples are shown in Figure 5. The three-section curve is composed of three stages,
332 namely the elastic behavior of the foam's cell wall bending(I), cell collapse(II) and
333 densification(III) [59]. As shown in Figure 5, T/G (1/1)-Fs shows the highest
334 compression strength and then T/G (1/3)-Fs and T/G (0/4)-Fs samples. The reason one
335 for this is that the T/G (1/1)-Fs sample shows greater density than T/G (1/3)-Fs and T/G
336 (0/4)-Fs samples, as the foams density is directly proportional to compression strength.
337 This result echo those of many other studies, i.e. higher density leads in general to
338 higher strength [8, 53]. In addition, the second reason is attributed to thicker cell walls
339 of tannin modified foams (T/G (1/3)-Fs and T/G (1/1)-Fs), resulting to obtain a better
340 compression loading distribution over the cell walls and thus an improved compression
341 resistance [54]. Thicker cell walls originate from the tannin-derived products, which
342 are interspersed within the foam cell walls and which tend to thicken the cell walls by
343 their expanding action. This conclusion is supported by the results in Figure 3.
344 Interestingly, there may still be another possible explanation for the higher compression
345 properties. The inserted tannin-derived products may have served as a framework to
346 improve the compression resistance as well.

347 According to the relevant literatures [54] and the tests described here, lower density
348 foam samples have thinner cell walls, thereby they can only provide a rather limited
349 contribution to compression resistance [60]. Thus, to investigate whether any upgrading
350 in mechanical properties is only attributed to the increasing density of materials, the
351 specific compressive strength of all foams was measured depending on the literature
352 [53]. The specific compressive strength of all foam samples is shown in Table 2, which
353 indicated that the specific strength exhibits the increasing trend with the increasing of
354 condensed tannin addition. For T/G (0/4)-Fs, T/G (1/3)-Fs and T/G (1/1)-Fs samples,
355 the corresponding of specific compressive strength is 1.22 kPa/kg m⁻³, 1.27 kPa/kg m⁻³
356 ³ and 1.51 kPa/kg m⁻³, respectively. The results showed the improvement of mechanical
357 properties of tannin modified-foams that this progress of strength is not exclusively
358 attributed to the density alone, but related to the contribution of the cell wall [53]. This
359 conclusion also justifies the above-mentioned analysis. Therefore, taking into account
360 Table 3 and Figure 5, the results further indicate that the compression strength of these
361 foams is improved by adding increasing proportions of condensed tannin.



362

363 Figure 5 Compressive stress-strain curves of T/G (0/4)-Fs, T/G (1/3)-Fs and T/G

364 (1/1)-Fs

365 3.7 Ignition experiment of T/G (0/4)-Fs, T/G (1/3)-Fs and T/G (1/1)-Fs samples

366 Although there are some limitations in the fire resistance evaluation of the ignition

367 experiments reported here, they can indicate to a certain extent the combustion

368 resistance of the material. Therefore, we designed this test to investigate the

369 flammability of T/G (0/4)-Fs, T/G (1/3)-Fs and T/G (1/1)-Fs ignition combustion

370 experiments were conducted on the foam samples directly. The digital photos of

371 ignition experiments and the results are shown in Figure 6 and Table 4, respectively.

372 The burning time increased with the increase of tannin addition, from 175s for T/G

373 (0/4)-Fs to 245s for T/G (1/3)-Fs, and then 372s for T/G (1/1)-Fs. The burning time of

374 T/G (1/1)-Fs was more than twice longer of T/G (0/4)-Fs. This conclusion being also

375 related to the density of the foams [12]. Furthermore, the residual weight of the foam

376 samples after burning was also evaluated. The same trend as the burning time was
 377 observed, with the T/G (1/1)-Fs foam sample presenting the higher residual weight at
 378 15.52 %. This is attributed to the higher char rate of condensed tannin when heating.
 379 Therefore, condensed tannin modified foams obtained longer burning time and higher
 380 residual mass.

381 Table 4 The results of the ignition experiments

Samples	Burning time (s)	Residue (g)	Residual (%)
T/G (0/4)-Fs	175 ± 11	0.13 ± 0.02	9.87 ± 0.13
T/G (1/3)-Fs	245 ± 10	0.15 ± 0.02	12.54 ± 0.09
T/G (1/1)-Fs	372 ± 18	0.34 ± 0.03	15.52 ± 0.15

382 As shown in Figure 6, T/G (0/4)-Fs and T/G (1/3)-Fs shows a high flammability and a
 383 very intense flame was observed in just a very short time (30s), when the foams are
 384 either devoid of tannin or have a lower tannin content. Simultaneous, in this case a large
 385 number of black fumes (dotted blue frame) was released while the foam was burning.
 386 T/G (0/4)-Fs (Figure 6 (b)) and T/G (1/3)-Fs (Figure 6 (a)) samples do not show major
 387 differences in combustion flame. This is similar to traditional isocyanate-based
 388 polyurethane foams, indicating that these two foams are a highly flammable. However,
 389 the final burning product of T/G (1/3)-Fs samples can be maintained approximately in
 390 its original shape, compared to the completely irregular residue shape of T/G (0/4)-Fs.
 391 In addition, the combustion behavior of T/G (1/1)-Fs, shows a delicate small flame of
 392 which can be seen at the beginning of the burning experiment, are shown in Figure 6(c).

393 The intense flame and black fumes of T/G (0/4)-Fs and T/G (1/3)-Fs cannot be seen,
394 from the beginning to the end of the experiment. Furthermore, the final product after
395 burning keeps the original shape as well. These combustion phenomena show that while
396 T/G (0/4)-Fs or T/G (1/3)-Fs and T/G (1/1)-Fs are all combustible, nevertheless, the
397 ignitability is markedly lower when condensed tannin addition reached a certain
398 proportion. All this suggests that condensed tannin have a certain inhibitory effect on
399 the combustion behavior of T/G-Fs foam.



400

401 Figure 6 The digital photos of ignition experiments: (a) T/G (1/3)-Fs; (b) T/G (0/4)-

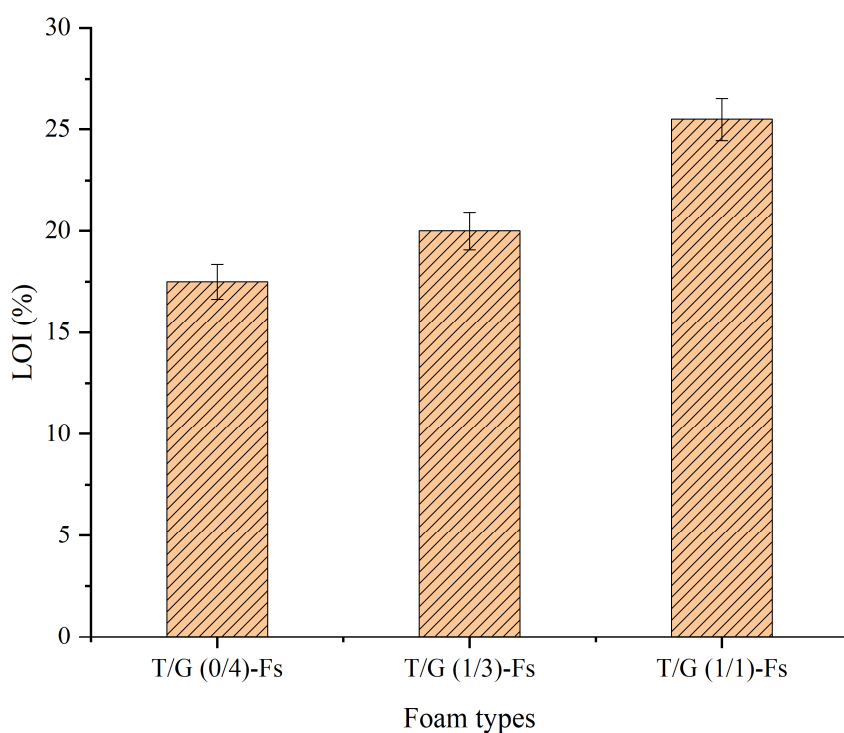
402 Fs; (c) T/G (1/1)-Fs

403 3.8 Limiting oxygen index (LOI)

404 The limiting oxygen index (LOI) reflects the minimum oxygen concentration while the

405 polymer is burning in the mixed oxygen and nitrogen atmosphere to evaluate effectively
406 the flame retardancy in polymers [54]. A material can be defined as flame-retardant
407 when its LOI value is greater than 27%. Conversely, it can be defined as inflammable
408 when its LOI value is less than 22% [61]. The LOI values of each foam samples were
409 then evaluated and the results obtained are shown in Figure 7. The LOI values of neat
410 glucose-based NIPU foam (T/G (0/4)-Fs) are around 17.5 %, indicating that this kind
411 of foam belong to the class of inflammable materials, needing additional flame
412 retardants to improve its fire resistance if we want to expand its application field [12].
413 As expected, the condensed tannin-glucose NIPU foams, T/G (1/3)-Fs and T/G (1/1)-
414 Fs, presented improved LOI values of 20.0 % and 25.5 %, respectively. The cause of
415 this improved results is probably attributed to the presence of the condensed tannin,
416 which have a considerable proportion of aromatic rings. Therefore, the condensed
417 tannin-glucose NIPU foams are more easily carbonized when the carbon atoms reach a
418 high proportion level [35, 54, 62, 63]. In addition, from the structure of all foams, due
419 to the enlarged cells (lower density) and a greater number of perforations of G-Fs (as
420 shown in Figure 3(a), (d) and (g)), the oxygen can enter to the inner parts of the foam,
421 thereby increasing the oxygen concentration and thus rendering the foam more
422 inflammable [54]. Combined with the SEM images, the tannin-derived fibrous
423 polymers either interspersed in the cell walls of T/G (1/3)-Fs and T/G (1/1)-Fs or
424 covering them may well be the one of critical factors of the improved fire resistance of
425 these foams. Exactly as explained above, these tannin-derived fibrous polymers can

426 then be easily converted into a char layer to improve the fire resistance of tannin-
427 glucose-based NIPU foams. The ignition experiment results of all foam samples does
428 also support such a conclusion. Therefore, the addition of condensed tannin can
429 improve the LOI values of T/G (0/4)-Fs.



430

431 Figure 7 LOI of T/G (0/4)-Fs, T/G (1/3)-Fs and T/G (1/1)-Fs

432 **4 Conclusions**

433 Condensed tannin as a natural flame retardant to modify the fire resistance of glucose-
434 based NIPU foam was investigated. It is concluded that the presence of mimosa tannin
435 substituting different proportions of glucose in the NIPU foam can improve the
436 ignitability of glucose-based NIPU foams. FT-IR results indicated that urethane
437 linkages were formed in all foam formulations. The three kind of foams exhibited
438 similar regular cell morphology, i.e. plenty of open pores can be seen clearly, but the
439 T/G (1/3)-Fs and T/G (1/1)-Fs foams had smaller mean cell sizes than the T/G (0/4)-Fs.

440 The compressive mechanical properties were all enhanced on account of the different
441 amount replacement of glucose by condensed tannin. The thermal stability of T/G (1/3)-
442 Fs and T/G (1/1)-Fs with added condensed tannin decreased then T/G (0/4)-Fs.
443 However, the ignition experiment shows that with an increasing proportion of
444 condensed tannin, the burning time lengthened, from 175s for T/G (0/4)-Fs to 372s for
445 T/G (1/1)-Fs, respectively. The LOI values were determined to investigate the fire
446 resistance of glucose-based NIPU foams, indicating that T/G (1/1)-Fs obtained the
447 highest LOI value (25.5%, still belonging to the combustible grade, but not to the
448 inflammable range) due to its highest condensed tannin content. Conversely, the LOI
449 values of neat glucose-based NIPU foams (T/G (0/4)-Fs) are around 17.5 %, belonging
450 to inflammable grade. It can be seen from this, that condensed tannin can improve the
451 fire resistance of T/G (0/4)-Fs, and yield better mechanical properties. This low-cost
452 and highly effective biobased self-blowing glucose-/tannin-based foam presents a
453 definite potential for practical application.

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