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1 **Tannin-Furanic Foams Modified by Soybean Protein Isolate (SPI)**
2 **and Industrial Lignin Substituting Formaldehyde Addition**

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15 **Abstract:**

16 Soybean protein isolate (SPI) was tested in this study as a crosslinker and
17 formaldehyde substitute for preparing high biomass content sustainable rigid
18 tannin-furanic-SPI (TFS) and lignin-tannin-furanic-SPI (LTFS) versatile foams.
19 Additionally, flame retardancy was improved by lignin used as a natural fire-retardant.
20 Fourier-transform infrared spectroscopy (FT-IR), coupled with matrix-assisted laser
21 desorption/ionization time-of-flight mass spectrometry (MALDI-ToF-MS), revealed a
22 covalent cross-linking reaction between tannin and SPI. TFS and LTFS foams showed
23 by scanning electron microscopy (SEM) a closed cell structure without any pores. The
24 incorporation of SPI resulted in enhanced mechanical properties and reduced
25 pulverization ratios, improved thermal stability and increased thermal conductivity
26 (approximately 0.042–0.044 W/m·K) compared with control foam. Furthermore, the
27 TFS foams exhibited outstanding flame retardancy and suppressed smoke generation
28 while undergoing combustion. These results were supported by a higher limiting
29 oxygen index (LOI) value, a lower heat-release rate, and a higher char residue,
30 obtained by LOI and cone calorimetry. The addition of lignin further enhanced the
31 thermal properties and flame retardancy of TFS foams although it decreased their
32 mechanical performance. The TFS and LTFS foams were environmentally friendly, as
33 shown by the low formaldehyde emission measurements. This novel sustainable TFS
34 foam appears to have a good potential for industrial application.

35 **Key words:**

36 Mimosa tannin, SPI, Sustainable rigid foam, Limiting oxygen index (LOI), Flame
37 retardancy

38 **1 Introduction**

39 Sought-after characteristics, such as flame retardancy, better thermal stability, lightweight, and
40 thermal insulation, are found in phenolic foam (PF). Yet PF has high friability and inferior
41 mechanical properties and is a fossil fuel-based resource, which limits somewhat its large-scale
42 commercial applications (Chen et al., 2020a; Wu et al., 2020). Therefore, foams with improved
43 mechanical properties using natural renewable feedstocks have attracted much attention.
44 Condensed tannin—a vegetal polyphenolic material which is widespread—has been applied in
45 several field (Chen et al., 2020a; Meikleham and Pizzi, 1994; Pizzi, 2019).

46 Phenolic tannin-furanic-formaldehyde foams were first reported by Meikleham and Pizzi in 1994
47 and have since received significant attention (Meikleham and Pizzi, 1994; Pizzi, 2019). The
48 interest of these foams is not only because they are based on a renewable resource but also
49 because of their self-blowing preparation under ambient/moderate temperature, and their
50 comparable performance with commercial PF foams (Meikleham and Pizzi, 1994; Pizzi, 2019;
51 Tondi and Pizzi, 2009; Tondi et al., 2008a; Tondi et al., 2009c; Zhou et al., 2019).

52 The preparation approaches for these foams are based on a heat-generated expansion initiated by
53 a blowing agent evaporation coupled with an acid-catalysis self-condensation of furfuryl alcohol,
54 without (Basso et al., 2011) or with a cross-linker ensuring the foam structure does not collapse
55 (Celzard et al., 2010; Tondi et al., 2009b; Tondi and Pizzi, 2009; Tondi et al., 2008a; Tondi et al.,
56 2009c; Zhou et al., 2019). Various foams have been obtained for different application fields, such
57 as rigid, semi-rigid, and flexible foams via formulation and/or processing adjustment (Basso et
58 al., 2014a; Basso et al., 2014b; Basso et al., 2011; Celzard et al., 2011; Celzard et al., 2010;
59 Lacoste et al., 2013; Li et al., 2012c; Meikleham and Pizzi, 1994; Pizzi, 2019; Tondi et al., 2009a;
60 Tondi et al., 2009b; Tondi and Pizzi, 2009; Tondi et al., 2008a; Tondi et al., 2009c; Zhou et al.,
61 2019). Yet, because of their brittleness they powder easily on frictioning them and present lower
62 mechanical compression properties, these foams have limited commercial application. Their
63 susceptibility to powdering under friction has been solved well (Rangel et al., 2016). However,
64 to reduce the foam brittleness and to enhance other properties (flame retardancy, thermal stability,
65 and thermal insulation) so as to achieve their industrialization, some improved formulations have
66 been developed by introducing organic/inorganic additives, such as polymeric diphenylmethane

67 diisocyanate (p-MDI) (Li et al., 2012a), hyperbranched poly(amino-ester) (Li et al., 2012b),
68 multi-walled carbon nanotubes (Li et al., 2013), disordered carbon matrix and graphite fillers
69 (Jana et al., 2015), cellulose nanofibers (CNF) (Zhou et al., 2019), wood cellulosic fiber(Wu et
70 al., 2020), hydroxy-methylated lignin (Pizzi, 2019) and boric and/or phosphoric acid (Celzard et
71 al., 2011). Formaldehyde-free modifications have been introduced early on to take into account
72 human health and the environment. Thus, formulations with no aldehydes at all (Basso et al.,
73 2013; Basso et al., 2011), or with non-toxic and non-volatile aldehydes such as glyoxal and
74 glutaraldehyde (Lacoste et al., 2013), or fossil-based resources such as PEG-400 and polymeric
75 diphenylmethane diisocyanate (p-MDI) (Li et al., 2012a), and biorefinery byproduct such as
76 polyfuranic humins (Chen et al., 2020a) have been reported as the part of feedstocks that can
77 replace formaldehyde to produce tannin-furanic foams. Mechanical or/and chemical expansion
78 methods have also been utilized to prepare tannin-based rigid foams with lower density, thermal
79 insulation, and robust cell structure (Santiago-Medina et al., 2018a; Santiago-Medina et al.,
80 2018b; Szczurek et al., 2014).

81 Plant or animal proteins have also attracted attention for their successful utilization for bio-foams
82 preparation. Albumin was initially used to design and manufacture flexible biofoams (Basso and
83 Pizzi, 2017; Basso et al., 2015; Li et al., 2012c; Li et al., 2012d) with a series of different natural
84 albumin and albumin/tannin cellular foams following (Basso and Pizzi, 2017; Basso et al., 2015;
85 Lacoste et al., 2015). Biomass foams based on wheat gluten have also been reported (Chiou et al.,
86 2020). However, soy flour and soy protein isolate (SPI) are plant-sourced, renewable, sustainable,
87 and easily obtained from soybean-oil production processing, which is why it has been a
88 commonly applied bioresource for the food industry (Guo et al., 2018; Ma et al., 2020), film
89 preparation (Cao et al., 2007; Gu et al., 2019; Wang et al., 2017), in biomedicine (Zhao et al.,
90 2018), and for wood adhesive applications (Liu et al., 2017; Zhao et al., 2018). SPI was once the
91 main raw material or reinforcement filler for different kinds of foam design (Frihart and Lorenz,
92 2019; Frihart et al., 2019; Liu et al., 2017; Liu et al., 2015; Wang et al., 2019; Xi et al., 2020;
93 Xiao et al., 2013; Zhao et al., 2019). This encouraged us to design and investigate SPI for
94 tannin-furanic foam preparation because of the reputed reaction crosslinking reaction between
95 tannin and SPI (Ghahri et al., 2018a; Ghahri and Pizzi, 2018; Ghahri et al., 2018b; Liu et al.,

96 2017) as only a small amount of SPI addition can achieve unexpected effectiveness.
97 Thus, here are presented novel mimosa tannin-furanic-SPI (TFS) and lignin-tannin-furanic-SPI
98 (LTFS) versatile foams. Lignin was selected as the natural flame-retardant to improve the flame
99 retardancy of the-resultant TFS foams. The reaction between tannin and SPI was examined. The
100 combined properties of the control, TFS, and LTFS foams, including apparent density,
101 morphology, pulverization ratios, and mechanical properties, were systematically evaluated.
102 Furthermore, the thermal stability, thermal conductivity, and especially fire retardancy of the
103 foams were investigated. The formaldehyde emission of the foams obtained was determined to
104 further demonstrate its environment-friendly characteristics.

105 **2 Materials and methods**

106 2.1 Materials

107 Commercial mimosa tannin extract (*Acacia mearnsii*, *De Wild*, its main components as shown in
108 Table S1) was provided by Silva Chimica (St. Michele Mondovi, Italy). Soy protein isolate (SPI)
109 was purchased from Ruikang Biotechnology Co., LTD (Dezhou, China). Lignin was obtained
110 from Anhui BASF Biotechnology Co. LTD (Anhui, China). Furfuryl alcohol (FA, 98%),
111 Formaldehyde (F, 37%), p-toluene-4-sulfonic acid (p-TSA, 65%) and Diethyl ether (DE, 98%)
112 were purchased from Sigma-Aldrich (Saint Louis, France). All materials and chemicals used the
113 experiments were employed directly without further treatment.

114 2.2 Preparation of tannin-based foams

115 This research reported tannin-based foams were prepared according to the formulation showed in
116 Table 1. The control foam was obtained according to reference (Zhou et al., 2019) and the
117 principle originally presented in reference (Meikleham and Pizzi, 1994). In brief, tannin extract
118 was mixed with furfuryl alcohol thoroughly. A certain amount of deionized water (as shown in
119 Table 1) was added into the mixture and stirred intensely for 10 s. A mixture solution containing
120 formaldehyde and p-TSA was added to the tannin and furfuryl alcohol mixture and stirred for 5 s.
121 The blowing agent diethyl ether was added into the mixture and then stirred for 20 s till to obtain
122 a homogenous slurry. The product was placed in an oven for foaming and aging for at 24 h. The
123 resulting black foam was obtained and labeled as the control.

124 The TFS and LTFS foams were prepared following the control sample processes, as outlined in

125 Table 1. The SPI or lignin/SPI mixture was used to substitute for formaldehyde completely. The
126 SPI addition amount in TFS and LTFS foams depended on the formaldehyde solid content of the
127 control. In parallel, the results of pre-experiments showed that 1–4 g SPI and 0.5–2 g lignin were
128 appropriate. The resultant foams without lignin were labelled as TFS and the foams with lignin
129 were labelled as LTFS. All resulting foams were stored under ambient conditions for at least two
130 days before sample preparation and testing.

131 *[Table 1 near here]*

132 2.3 Foam characterization

133 The apparent densities of the foams prepared were checked according to the ASTM D1622-03
134 standard (Li et al., 2019). The foam dimensions were 30 × 30 × 30 mm. Five repeated trials were
135 conducted to calculate the mean values and standard deviations.

136 The foam morphology was observed by scanning electron microscopy (SEM, Hitachi TM-3000,
137 Milexia, Paris, France) under the acceleration voltage of 15 kV. To increase the electric
138 conductivity of samples, a thin gold coating process was conducted before measuring.

139 Fourier-transform infrared spectroscopy (FT-IR, PerkinElmer Frontier ATR-FTMIR) was
140 utilized to investigate the functional groups during the foam preparation. Each sample were
141 recorded with 32 scans between the wave range of 600 and 4000 cm⁻¹, with a scan resolution of 4
142 cm⁻¹.

143 Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-ToF-MS,
144 AXIMA Performance, Shimadzu, Manchester, UK) was adopted to detect products-derived from
145 the reaction between tannin and SPI. The measurements were carried out making 1000 profiles
146 per sample with two shots accumulated per profile. The spectrum precision was of ±1 Da
147 (Jahanshahi et al., 2016).

148 The viscosity of foaming resin precursor was tested with a Brookfield DV-II+ Viscometer, chose
149 spindle No. 4 at 12 rpm under ambient environmental conditions.

150 The pulverization ratios were evaluated following the reference (Li et al., 2021). The samples
151 were cut to the uniform size of 50 × 50 × 50 mm. The repeat experiments were performed five
152 times.

153 The compression strengths were carried out by using the universal testing machine (Instron 3300,

154 Elancourt France) with a foam dimension of $30 \times 30 \times 30$ mm (Chen et al., 2020b). Each
155 experiment's average value was from the three repeated measurements.

156 Thermal conductivity experiments were performed under ambient conditions by using a YBF-2
157 apparatus (Dahua Ltd., Hangzhou) with the foam slice radius 50 mm and thickness 10 mm,
158 according to the method reported by references (Li et al., 2019; Zhou et al., 2019). Three
159 repeated experiments were conducted, and we report the average and standard deviations.

160 Thermogravimetry analysis (TGA) was carried out using a TGA5500 analyzer (TA Instruments,
161 USA). The measurements of foams were made between 25°C and 790°C with a heating rate of
162 10°C/min under nitrogen atmosphere.

163 Limiting oxygen index (LOI) measurements of samples were conducted based on the China
164 National Standards GB/T 2406.2-2009 utilizing XWR-2046 oxygen index apparatus (Yilu
165 Instrument Co., LTD, Changzhou, China) (Li et al., 2019). The size of samples was $80 \times 10 \times 10$
166 mm for testing. The average value and standard deviations were obtained from five experiments
167 trials.

168 A cone calorimeter (CC, FTT, UK) was used to estimate the combustion behavior of the control,
169 TFS and LTFS samples according to ISO 5660 standards (Kong et al., 2018). The size of the
170 samples was $100 \times 100 \times 50$ mm. The testing was carried out under a heat flux of 35 kW/m².

171 The formaldehyde emission was tested according to China National Standards GB/T 17657-2013.
172 The samples were pre-balanced at 65% humidity and 20°C at least 7 days before testing. Three
173 repeated trials were conducted.

174 **3 Results and discussions**

175 **3.1 The preparation of tannin-furanic-SPI foams**

176 The fabrication of versatile tannin-furanic-SPI foams with high biomass content (~88%) derived
177 from natural lignocellulosic biomass-derived products (furfuryl alcohol and tannin) and a
178 sustainable soybean derivative (SPI) is schematically illustrated in Figure 1. This formulation
179 avoided the toxic formaldehyde utilization, improving the fabrication safety and environmentally
180 friendly nature of the foams with enhanced properties.

181 There are a number of simultaneous reactions occurring, as described by MALDI-ToF-MS
182 analysis in this work, and they contribute to the expansion of the foams and to their stability of

183 crosslinking. The furfuryl alcohol self-condensation exotherm accelerated the evaporation of the
184 blowing agent, resulting in a volume expansion of the resultant foam. Furfuryl alcohol not only
185 links to the tannin, but also reacts with the amino groups of the amino side-chains of SPI, namely
186 of arginine. The MALDI-ToF-MS analysis confirmed the formation of such covalent bonds. In
187 addition, esterification of the carboxylic acids side-chain of SPI, aspartic and glutamic acid, also
188 probably occurs with the tannin flavonoid units alcoholic C3 hydroxyl groups and possibly also
189 with its phenolic hydroxyl groups. Ionic bonds between the same groups, that are also known to
190 occur at ambient temperature between soy protein and tannin (Ghahri et al., 2018a; Ghahri and
191 Pizzi, 2018; Ghahri et al., 2018b) reduce drastically under the action of a higher temperature.
192 Thus, the three-dimensional structure of the foams was obtained and maintained also by the
193 additional cross-linking engendered by the interaction between tannin and SPI.
194 The contributing function of the crosslinker in this reaction processing was confirmed. The
195 experimental results showed that the volume expansion reached a maximum and then shrank
196 with the collapse of the cellular structure. As shown in Figure S1, the homogeneous, dark, and
197 rigid control, TFS, and LTFS foams were obtained.

198 *[Figure 1 near here]*

199 **3.2 The suggested reaction mechanism between tannin and SPI**

200 **3.2.1 MALDI-ToF-MS analysis**

201 The MALDI-ToF-MS spectra reported in the literature indicate that under the conditions used not
202 only there are the reactions of furfuryl alcohol self-polymerization (Tondi et al., 2008b), furfuryl
203 alcohol with the tannin (Abdullah and Pizzi, 2012; Pizzi et al., 2008), and furfuryl alcohol with
204 the amino groups of the side chains of the protein (Liang et al., 2017), but that there are also
205 reactions that occur between the tannin and SPI without any intervention of other compounds. It
206 is for this reason that a MALDI-ToF-MS analysis of the reaction of tannin with SPI alone under
207 the same conditions used for the foam was carried out, the corresponding spectra being
208 summarized in Figure 2 (a) – (c).

209 These MALDI-ToF-MS spectra showed that tannin and aminoacids such as arginine presenting
210 amino groups on their side chain do react by substituting some of the hydroxyl groups of the
211 tannin linking it to the protein, as shown in Table 2 (a). This amination reaction of tannin is

212 known and used, for instance, with ammonia (Braghiroli et al., 2013; Santiago-Medina et al.,
213 2017; Thébault et al., 2017). Also, esterification reactions of the alcoholic and possibly even of
214 the phenolic -OH groups of the tannin with the carboxylic acid function of the side chain of other
215 amino acids, such as aspartic acid or glutamic acid do occur as shown in Table 2 (b) and (c).
216 Thus, mono flavonoids reacted with a single aminoacid, such as fisetinidin-leucine, with the
217 flavonoid in both its normal and its open form as at 410 Da, and at 390 Da do occur, their
218 corresponding structures being summarized in Table S2.

219 Although several such compounds are found in the spectra, they do not contribute to the tannin
220 and protein cross-linking because once the amino acid is not free but linked within the skeletal
221 peptide chain of the protein the amino group is changed to an amide, and the -NH- amide group
222 is less likely to react with the tannin (both for its lower reactivity and for the steric hindrance
223 engendered). Thus, the amination of the tannin can occur only through amino acids with amino
224 or imino groups on the side chains of the protein. In soy these are arginine, lysine and proline.
225 The existence of this reaction is then proved by the reaction of tannin monomers and dimers with
226 peptides containing one of these three aminoacids, such as the structure represented by the series
227 of peaks at 857 Da, 873.1 Da, 889.2 Da, 1128.1 Da, 1144.1 Da, 1162 Da, 1177.4 Da, 1193.5 Da,
228 1260.5 Da, 1450 Da, and 1466 Da which are presented in Table S2. The latter one of these, for
229 example, is a catechin-fisetinidin flavonoid dimer linked on one site to a peptide fragment of four
230 amino acids, arginine-leucin-aspartic acid-tryptophan, through the side chain -NH₂ of arginine,
231 but also linked and linked to a second peptide chain fragment formed by tryptophan-aspartic acid
232 in which the free -NH₂ not converted to skeletal amide of one of the two amino acids has reacted
233 with the flavonoid dimer too, thus a structure as of the type in Table 2 (d).

234 To illustrate, as an example, the possibility that the reaction of the protein with the flavonoid
235 units of the tannin can occur either through the amino group of a protein side chain or by
236 esterification with the acid group of a side chain of the protein, the peak at 1260 Da can be
237 brought as an example (Table 2 (e) and (f)).

238 It must be considered that in the case of the structure assigned to the 1260 Da peak (Table 2 (f)),
239 esterification is most likely to occur first at the alcoholic -OH on the flavonoids C3 before
240 occurring on the more acid phenolic -OH groups. The assigned compounds to the

241 MALDI-ToF-MS peaks in Table S2 confirm that reactions contributing to cross-linking directly
242 between tannin and soy protein do occur. It confirms also that their interaction is not only based
243 on the classical protein tanning reaction like in leather making thought to be based exclusively
244 on secondary forces interactions between the two materials (Ghahri et al., 2018a; Ghahri and
245 Pizzi, 2018; Ghahri et al., 2018b). Moreover, depending from the condition of reaction also
246 coupling by ionic bonds between -NH_3^+ of the protein and the phenolic -O^- of the tannin as
247 shown already for both condensed and hydrolysable tannins (Ghahri et al., 2018a; Ghahri and
248 Pizzi, 2018; Ghahri et al., 2018b).

249 *[Table 2 near here]*

250 **3.3.2 Fourier transform infrared (FT-IR) spectroscopy**

251 The FT-IR spectra of pristine SPI, raw tannin, and the reaction product of tannin and SPI are
252 shown in Figure 2. In region I of Figure 2 (d), a broad absorption band approximately 3400 cm^{-1}
253 is related to the characteristic peak of free and bound -NH- or/and -OH groups (Liu et al., 2017;
254 Wang et al., 2017). The hydrogen bonds could be formed between -NH- or/and -OH groups and
255 the carbonyl groups of protein-peptide linkages (Wang et al., 2017). Furthermore, an adsorption
256 peak at 2925 cm^{-1} (region II) can be seen, which is ascribed to symmetric and asymmetric
257 stretching vibrations in $\text{-CH}_2/\text{-CH}_3$ groups (Chen et al., 2020b). In addition, the SPI characteristic
258 peaks, such as 1635 cm^{-1} , 1515 cm^{-1} , and 1235 cm^{-1} (Figure 2(e)), which are attributed to C=O
259 stretching (amide I), -NH- deformation (amide II), and -CN- stretching and -NH- vibration
260 (amide III), respectively (Wang et al., 2017). The peaks 1391 cm^{-1} (-COO-), 1235 cm^{-1} (amide
261 III), and 1044 cm^{-1} (-C-O-) of SPI disappeared after reacting with tannin, which is assigned to the
262 reaction between SPI and tannin. Furthermore, in Figure 2 (e), there are indications that reactions
263 occur through the primary amines in SPI by forming secondary amines, this being indicated by
264 the two characteristic peaks at 1333 cm^{-1} and 1292 cm^{-1} . The esterification of the tannin
265 hydroxyls by the protein side-chain acids is demonstrated by the 1735 cm^{-1} shoulder. These
266 bands appear to support the MALDI-ToF-MS results that both the reaction of the protein with the
267 flavonoid units of the tannin can occur either through the amino group of a protein side chain or
268 by esterification with the acid group of a side chain of the protein.

269 *[Figure 2 near here]*

270 **3.3 Physical and mechanical properties**

271 The physical and mechanical properties of TFS and LTFS foams were determined and are
272 summarized in Table 3 and Figure 3. The control sample showed a lower density, 83.5 kg/m³,
273 which is similar to literature-reported values of conventional tannin-furanic-formaldehyde foams
274 (Celzard et al., 2010; Tondi et al., 2009b). The tannin-furanic-formaldehyde foam exhibited high
275 brittleness, and the pulverization ratios was 13.68%, because of their lower cross-linking
276 densities and/or their incomplete solidification behaviors. Generally, low density
277 tannin-furanic-formaldehyde foams shows a large mass-loss when gently touched or frictioned it
278 (Li et al., 2021) unless some special arrangements are made (Rangel et al., 2016). The densities
279 of TFS foams were higher than the control, around 94.4 - 112.5 kg/m³. This result is related to
280 the increased viscosity of the foaming precursor mixture (Table 3). The strong gelation ability of
281 SPI along with the reaction of tannin and SPI can rapidly increase the viscosity of the foaming
282 precursor, even with a small addition of it. Therefore, higher viscosity seems to be a
283 disadvantage for raw materials homogeneous mixing, as well as for bubble formation and
284 volume expansion, resulting in a higher density than the control. This is also found for phenolic
285 foams manufacturing (Jing et al., 2014; Yang et al., 2014; Yang et al., 2013). Additionally, the
286 pulverization ratios (Table 3) of TFS foams had a lower value, only reaching 2.64% to 4.83%.
287 This result is probably because of the higher densities of TFS foams, resulting in a lower
288 brittleness than the control sample. Besides, the covalent cross-linking of tannin with SPI
289 contributes to decrease brittleness. With the introduction of lignin, the foam densities decreased
290 slightly (93.8 - 99.6 kg/m³) compared to TFS foams. One reason for this phenomenon is the
291 larger cells of the lignin-modified TFS foams, which can be observed from their morphology.
292 The larger cells obtained were probably due to the cell nucleation being affected by lignin
293 addition during the foam preparation (Dolomanova et al., 2011; Xue et al., 2014). Besides, a
294 small amount of lignin reduced the viscosity of the foaming precursor (Table 3) due to the high
295 dispersion and wettability, resulting in lower densities for LTFS than for TFS foams. Therefore,
296 the pulverization ratios increased, as summarized in Table 3.

297 Figure 3 (a) shows the morphological characteristics of the control, TFS, and LTFS foams. As
298 expected, a closed cell structure with many “pores”, regular cellular structure, and a smooth

299 cellular surface were obtained, as previously reported (Pizzi, 2019; Wu et al., 2020; Zhou et al.,
300 2019). Nevertheless, the TFS and LTFS cellular structures exhibited larger, inhomogeneous, and
301 rough surface performance compared to the control sample. The major reason for this
302 phenomenon is that the homogenous cellular structure was squeezed in the direction
303 perpendicular to the foam growth because of the slightly shrinkage of foam blocks after the foam
304 reached maximal expansion showing a marked anisotropy. Therefore, some elliptical foam cells
305 can be seen in Figure 3 (a). The cell walls were squeezed and then some wrinkles formed on the
306 surface. For lignin-modified LTFS foams, relatively larger cells were observed than for the
307 control and the TFS samples. This was because the cell nucleation process was influenced by
308 lignin addition (Xue et al., 2014). Therefore, fewer foam nuclei would entrap more blowing gas,
309 leading to a larger cell structure and lower density (Li et al., 2017). As shown in Figure 3 (a) and
310 (b), some clear particles are noticeable on the surface of LTFS foams, but are not visible on the
311 surface of control and TFS foams. The numbers of particles increased with gradually increasing
312 lignin additions. This indicates that lignin can form a protective layer on the surface of the foams
313 as it can be converted to a carbon char layer when in a fire. These particles are one of the factors
314 providing better fire resistance for LTFS than TFS foams.

315 Figure 3 (c) and (d) show the compressive stress-strain curves and values of control, TFS, and
316 LTFS foams when undergoing a compressive load. The multi-stage deformation observed is
317 consistent with several studies on polymer foams (Chen et al., 2020b; Chen et al., 2020c; Gao et
318 al., 2021; Wu et al., 2020). When comparing TFS and control foams, the compression strength of
319 TFS foams was higher than the control. This can be attributed to the increased density of TFS
320 foams. Moreover, as shown in Table 2, the specific compressive strength increases with the SPI
321 amount. This result indicates that the improved compression strength of TFS foams is not only
322 influenced by the density but also related to the stronger foam cell wall structure resulting from
323 the greater crosslinking between tannin and SPI. Also, the physical enwind between tannin and
324 long chains SPI can promote the improvement of cell wall intensity. The LTFS foams exhibit a
325 lower compression strength than TFS, but similar to that of the control foam. Its less densities are
326 the one of mainly factors for this result. Moreover, the compressive strength possesses the same
327 trend in foam densities, which suggests that the foam density is not the only factor for the

328 compression strength. The existence of lignin can influence the crosslinking of tannin and SPI
329 which is likely to decrease the strength of the cell wall. In addition, the larger cell structures for
330 LTFS than TFS foams reduced the supporting capacity within the unit pressure range, which
331 were attribute to the reduced cell struts (Li et al., 2021).

332 *[Table 3 near here]*

333 *[Figure 3 near here]*

334 **3.4 Evaluation of thermal conductivity and thermal stability**

335 The thermal conductivity of the control, TFS, and LTFS foams were evaluated by the hot plate
336 method and the results are shown in Figure 4 (a). The control sample displayed the lowest
337 thermal conductivity, only 0.0391 W/m·K, lower than from other studies of
338 tannin-furanic-formaldehyde foams (Wu et al., 2020; Zhou et al., 2019). The TFS foams had a
339 higher thermal conductivity value, from 0.0431 W/m·K for TFS1 to 0.0442 W/m·K for TFS4
340 than the control sample, and increasing trend with the increase of SPI. This result probably is
341 attributed to changes in foams density, in general, the higher density will have a higher thermal
342 conductivity (Pizzi, 2019; Szczurek et al., 2014; Tondi and Pizzi, 2009). In parallel, the
343 non-homogenous cell structures (as shown in SEM results) from TFS foams improved their
344 thermal conductivity. Cell morphology can influence the thermal conductivity of polymer foams
345 which as reported by previous study (Li et al., 2021). Lignin-modified LTFS samples had a
346 lowered thermal conductivity value, from 0.04198 W/m·K for L0.5TFS3 to 0.0425 W/m·K for
347 L1.5TFS3, lower than TFS foams but higher than the control. One of the most obvious changes
348 in the lignin-modified TFS foams was the lower foam density. Therefore, this change can directly
349 lead to the decreased thermal conductivity of LTFS foams. Moreover, by comparing TFS and
350 control samples, the uneven morphology and structure of the cells of the former is the reason that
351 it can achieve a higher thermal conductivity than the latter even at similar foam density. For TFS
352 and LTFS foams in this study, the thermal conductivity was higher than the control, still
353 presenting a better performance compared to other insulating materials, thus indicating their
354 outstanding thermal insulation properties.

355 The thermal stability of the control, TFS, and LTFS foams was studied by thermogravimetric
356 analysis under air conditions. The TG and DTG curves were obtained and are shown in Figure 4

357 (b) and (c), respectively, and the corresponding data are listed in Table 4. For the control sample,
358 the first weight-loss stage appeared at a temperature range of 25 – 150°C, which is ascribed to
359 the evaporation of the residual blowing agent as well as of absorbed water (Chen et al., 2020b; Li
360 et al., 2019; Wu et al., 2020). The second prominent weight loss (38.14%, as shown in Table 4)
361 stage occurred between 150 – 500°C because of the degradation of the polymer chain forming
362 small molecules (Wu et al., 2020). For instance, the basic structure of soy protein cleaves and
363 decomposes from 250 – 350°C (Liu et al., 2011). The aromatic skeleton of lignin and tannin has
364 better thermal stability, however, thermolysis will occur when the temperature is above 450°C
365 (Chen et al., 2020b; Li et al., 2019; Xue et al., 2014; Zhang et al., 2017). The last one abrupt
366 weight loss (51.33%, as shown in Table 4) occurred when the temperature was above 500°C
367 from pyrolysis of the residual compounds, such as carbon-based char from the second stage
368 (Chen et al., 2020b). These carbon-based compounds formed and covered on the surface of the
369 polymer, thus isolating it from the air and improving the thermal stability of materials. The
370 complete pyrolysis of the control foam, with ~96% weight loss, occurred when the temperature
371 increased to 790°C, resulting in thermally-stable char residues (4.59%, as shown in Table 4).

372 For the TFS foams, the thermal degradation temperature peaks of the second and third stages
373 were higher than the control, as shown in Table 4. This is related to the stable and compact
374 crosslinked structure between tannin and SPI (Ghahri et al., 2018a; Ghahri and Pizzi, 2018;
375 Ghahri et al., 2018b). The final thermally-stable char residues reached 37.16% at 4 g SPI
376 addition, but only 5.15% at 1 g SPI addition, which was still higher than the control. Hence, such
377 high final residues of TFS foams indicated that the SPI substitution for formaldehyde increased
378 char formation and improved thermal stability. As for the lignin addition, from the DTG curves,
379 it can be seen that the initial and second thermal degradation temperature peaks presented a
380 similar trend with the TFS foams. The degradation temperature peak in the third stage appears to
381 have shifted from ~640°C to ~770°C, as shown in Table 4. Therefore, this phenomenon can show
382 that the high carbon content lignin improved the formation of thermally-stable char
383 (carbonization) (Kong et al., 2018). Moreover, its final mass residue has increased by introducing
384 of lignin, approximately 38–43%. Hence, the thermal stability of TFS foams can further be
385 improved by lignin.

386 *[Figure 4 near here]*

387 *[Table 4 near here]*

388 **3.5 Evaluation of flame-retardant properties**

389 The flame resistance of the control, TFS, and LTFS samples was evaluated by measuring the
390 limiting oxygen index (LOI) and the results are shown in Figure 5a. As expected, the LOI of a
391 typical tannin-furanic-formaldehyde foam, i.e., the control sample in this work, is 29.37%,
392 indicating it is a flame-retardant material (Zhou et al., 2019). The SPI-substituted TFS samples
393 had higher LOI values, from 38.17% to 40.37%, when the SPI replacement addition was from 1
394 g to 4 g, 29.96–37.45% higher than the control sample. This effect can be ascribed to the
395 closed-cell morphology structure of TFS and LTFS foams. SEM images (Figure 3) show that
396 closed-cell structures with many “pores” are in the control sample. The air can then circulate in
397 the foam interior through these opened pores, thereby providing a more suitable environment for
398 combustion (Li et al., 2019). Conversely, the TFS and LTFS foams relatively closed-cell
399 structures block the air exchange between the inside and outside of the foam cells, acting as a
400 flame retardant.

401 Lignin-modified TFS samples (LTFS) have a higher LOI value than TFS foams (Figure 5). The
402 LOI value of L0.5TFS3 is 40.5% which increased to 41.33% with 1.5 g lignin addition
403 (L1.5TFS3). These results indicated that lignin contributed to the flame-retardant performance of
404 LTFS foams. Its high carbon-containing polyphenol structure contributes to higher char carbon
405 productivity at higher temperatures (Chen et al., 2020b; Wu et al., 2020; Yang et al., 2012).
406 Hence, the char covering layer further obstructs contact of the combustion interface with the air,
407 thereby protecting the materials (Yang et al., 2012). However, the LOI value is lower with 2 g
408 lignin (40.83%). This decreased in the LOI value for L2TFS3 is attributed to the inflammability
409 of lignin when applied in larger amounts.

410 Cone calorimetry was used to simulate and evaluate the combustion behavior of the control,
411 TFS3, and L1.5TFS3 samples in a real fire scenario under a constant heat flux of 35 kW/m² from
412 a conical heater. The legible peaks of the heat-release rate (PHRR) flaming combustion for the
413 control and TFS3 foams are shown in Figure 5(b). This peak is attributed to the oxidation
414 reaction of volatile pyrolysis substances in the high-temperature environment (Kong et al., 2018).

415 For TFS, the maximum peak value was significantly lower than the control. In parallel, as shown
416 in Figure 5(c), the TFS foam had a lower THR value than the control. These results indicate that
417 the TFS foams have better flame-retardancy than the control. A valley characterizes the HRR
418 curves which means the char layer protected the materials as combustion continued. The HRR
419 curves increased, thereafter maintaining a stable level longer than 2000 s. No strong flame was
420 observed when the foams were put on the butane torch. These foams are then self-extinguishing
421 after the flame is removed from the sample surface, as shown in Figure S2 and Video S1.

422 For the L1.5TFS3 sample, the initial peak disappeared and the curve merged in the exothermic
423 phase. Compared to the TFS foam, a lower THR value (Table 5) was obtained which indicated
424 that as the lignin was introduced, the flame-retardant properties of LTFS improved. This was
425 because of the high char production performance of lignin in the high-temperature environment.
426 It covers the surface of materials and forms a barrier of further contact between air and the
427 combustion interface, enhancing the flame-retardancy of TFS foams.

428 The values of this peak reached 19.49 to 42.16 kW/m² (Table 5), lower than most other foams,
429 such as PU foams (Cao et al., 2019; Rao et al., 2018) or wood-based materials (Kong et al.,
430 2018). These results indicated that these foams have lower HRR, better than others that have
431 been developed. Apart from the HRR, the release of smoke (especially CO) also influences the
432 quality of the safety of the material when in a fire (Kong et al., 2018). The control sample
433 exhibited the highest TSP value (Table 5), and after the modification of foam preparation, the
434 novel biomass TFS and LTFS had a lower TSP value. This further indicated that the fire
435 retardancy of TFS and LTFS was better than that of the control sample. The residue trend of all
436 samples can be seen in the TGA results. For Figure 5(d), the control sample almost lost its
437 original shape, turning to a fragile condition after burning. The TFS3 and L1.5TFS3 preserved
438 their original shapes better, with the latter performing best. This feature is particularly important
439 for materials in a fire.

440 *[Figure 5 near here]*

441 *[Table 5 near here]*

442 **3.6 Formaldehyde emission**

443 To examine if the foams are environment-friendly, formaldehyde emission tests were conducted

444 and the results are listed in Table 6. As expected, the control sample released the most
445 formaldehyde, two times that of TFS3 and L1.5TFS3. This indicates that the final
446 tannin-furanic-formaldehyde foam released free formaldehyde despite this also being released
447 during the foam curing process. Yet, the formaldehyde emission of the control sample was still
448 lower than the relevant standard requirement. The TFS and LTFS foams do not utilize
449 formaldehyde, avoiding the release of free-formaldehyde. Thus, the application of soybean
450 protein resources was expanded in this study as a substitute for a toxic substance. In short, these
451 novel biomass foams have many improved properties suggesting a wide of industrial production
452 and application prospects.

453 *[Table 6 near here]*

454

455 **4 Conclusions**

456 High biomass, environment-friendly, and flame retardant TFS foams were developed in this
457 study. Mechanical properties, thermal performance, and flame retardancy were measured by
458 substituting SPI for formaldehyde.

459 The main results obtained were:

460 (1) A strong crosslinking reaction between tannin and SPI, yielding closed cells foam structures,
461 thus enhancing mechanical properties, reducing pulverization ratios, and improving thermal
462 conductivity (approximately 0.042–0.044 W/m·K) of the modified tannin foams as well as
463 yielding a better thermal stability.

464 (2) The increased LOI value, a lower heat-release rate, and increased char residue were
465 obtained. The TFS foams exhibited strong flame retardancy and suppressed smoke generation
466 while undergoing combustion.

467 (3) Lignin addition decreased the crosslinking of tannin and SPI, increased foam cell size,
468 thereby altering the mechanical properties of TFS foams. The addition of lignin further improved
469 the thermal stability of TFS foams, along with a lower heat-release rate and lower smoke
470 production. This indicates that LTFS enhanced flame retardancy more than that of TFS.

471 (4) The low formaldehyde emission confirms the good environmental performance of these
472 novel biomass foams. Such novel sustainable TFS foams have thus a good potential for industrial

473 application.

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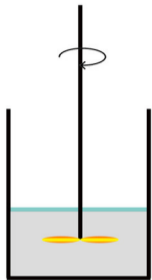
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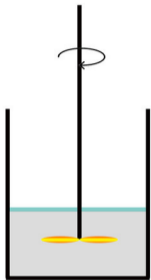
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Mixing



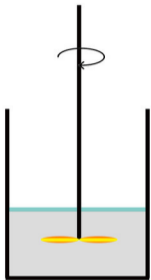
Tannin
Furfuryl Alcohol
Deionized Water

Mixing



Adding SPI

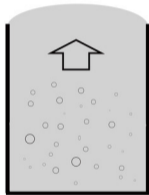
Mixing

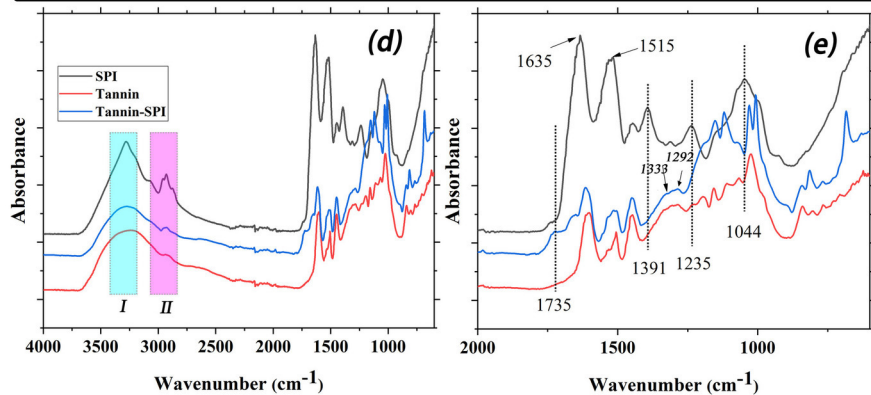
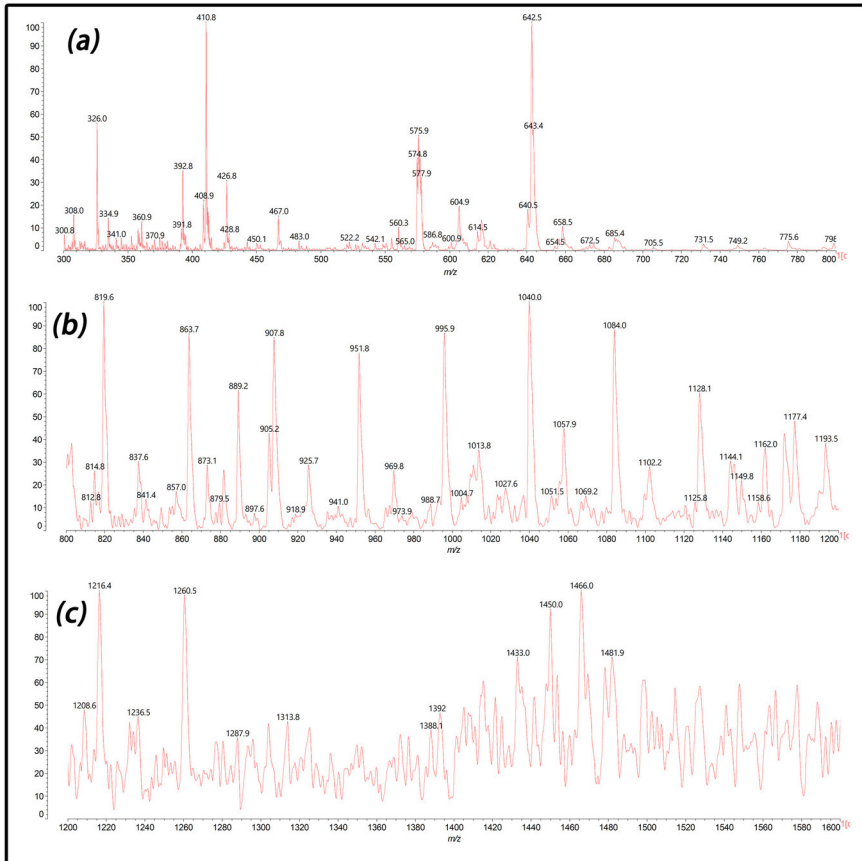


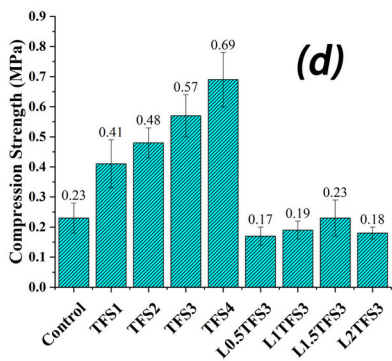
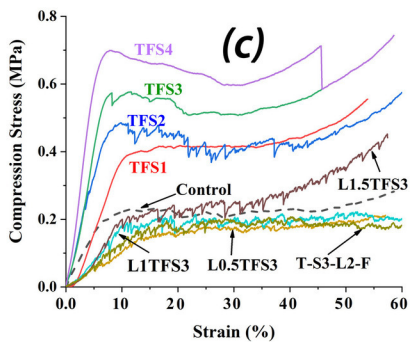
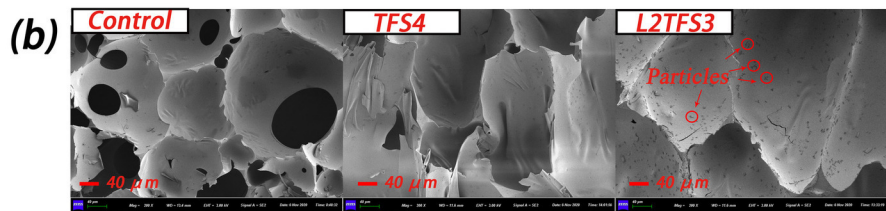
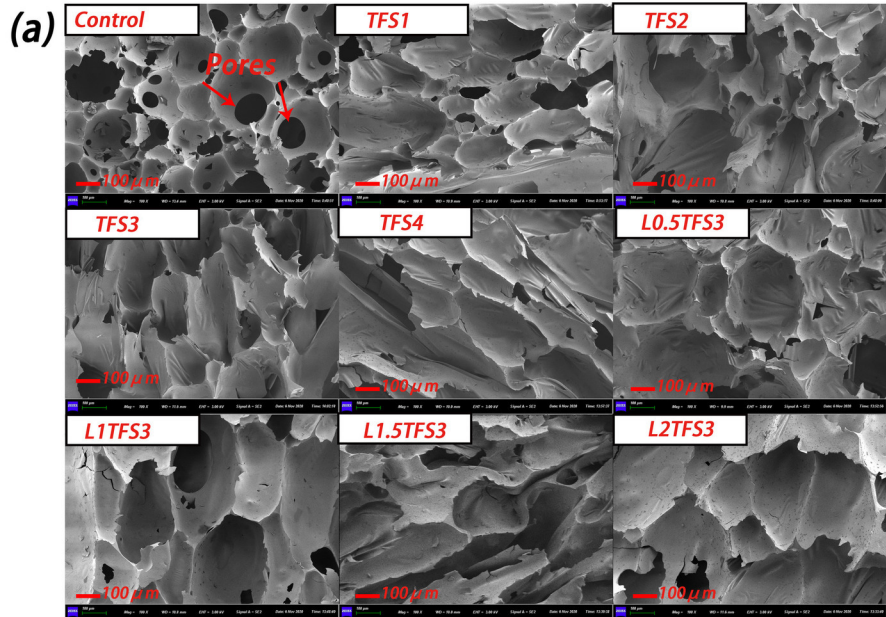
Adding p-TSA
Blowing agent

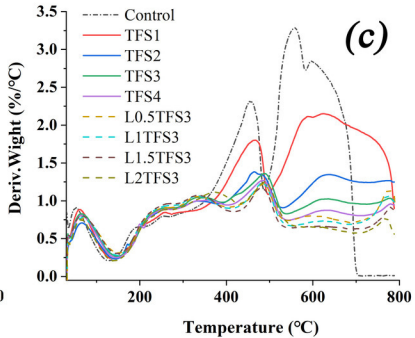
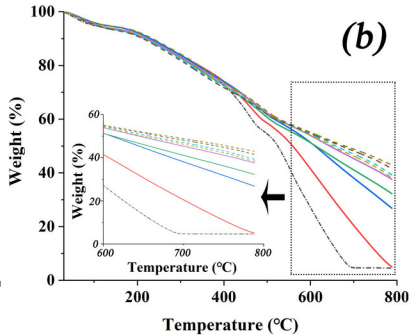
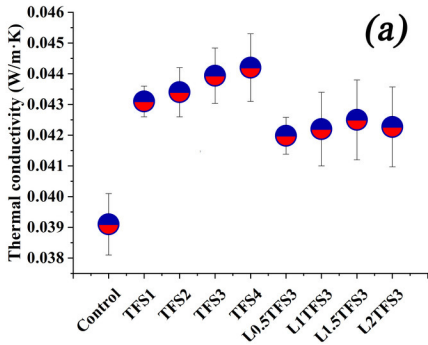
Foaming

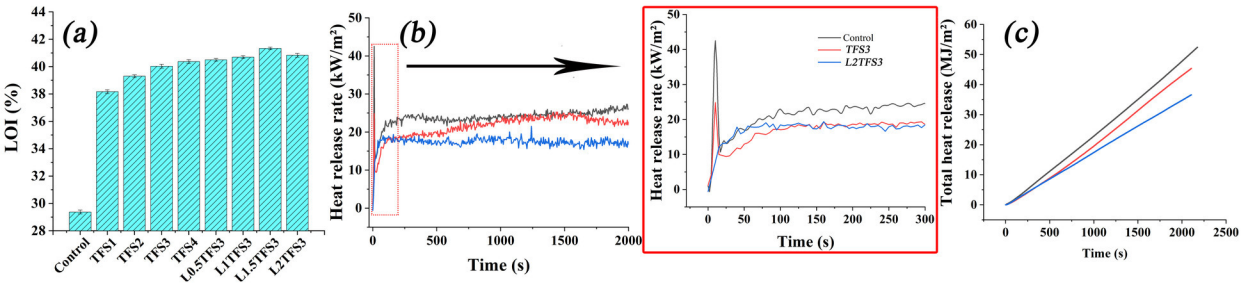
Curing











(d) Control



TFS3



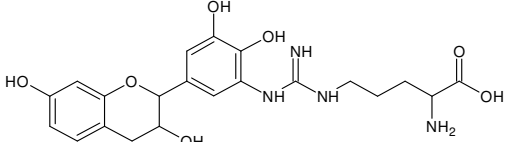
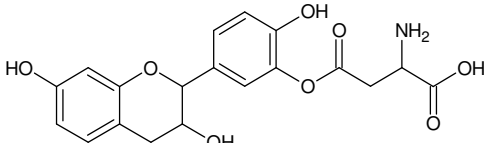
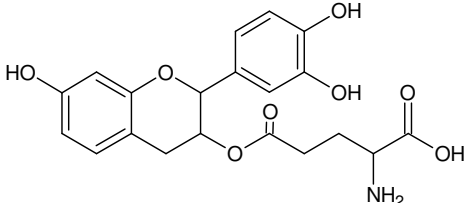
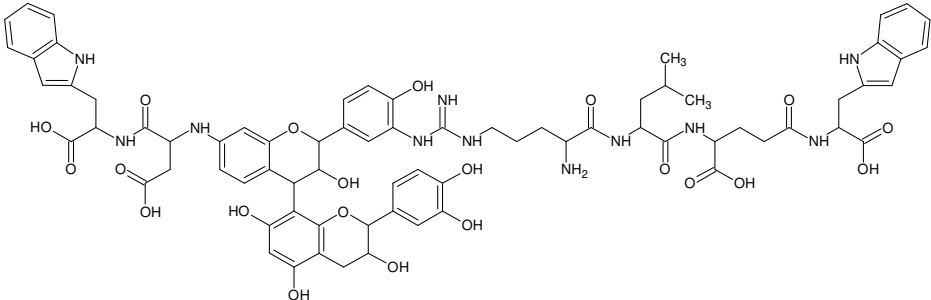
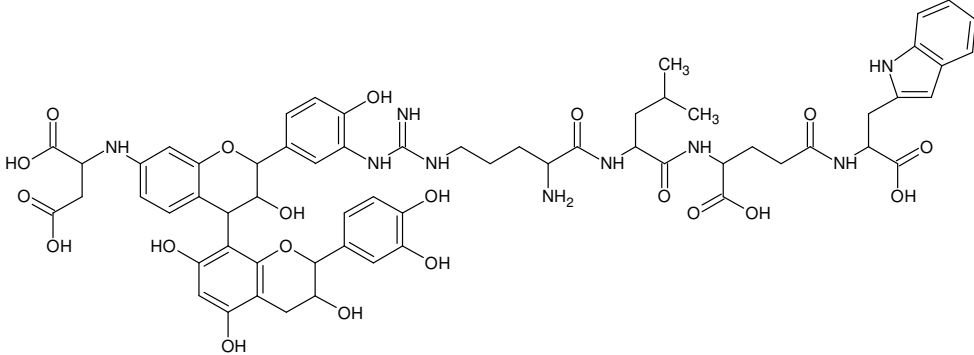
L2TFS3



Table 1 Formulation of series of tannin-SPI-based and tannin-SPI-lignin-based foams

Samples	Tannin (g)	FA (g)	F (g)	SPI (g)	Lignin (g)	Water (g)	p-TSA (g)	DE (g)
Control	30	10.4	7.4			10	12	2.2
TFS1				1				
TFS2				2				
TFS3				3				
TFS4				4				
L0.5TFS3	30	10.4		3	0.5	4	12	2.2
L1TFS3				3	1			
L1.5TFS3				3	1.5			
L2TFS3				3	2			

Table 2 (a) Robinetinidin *or* Catechin-Arginine with Na⁺; (b) Fisetinidin-Aspartic acid without Na⁺; (c) Fisetinidin-Glutamic acid with Na⁺; (d) Tryptophan-Aspartic acid-Robinetinidin *or* Catechin-Fisetinidin-Arginine-Leucin-Aspartic acid-Tryptophan without Na⁺; (e) and (f) Aspartic acid-Robinetinidin *or* Catechin-Fisetinidin-Arginine-Leucin-Aspartic acid-Tryptophan without Na⁺.

Types	Oligomers
(a)	
(b)	
(c)	
(d)	
(e)	

(f)

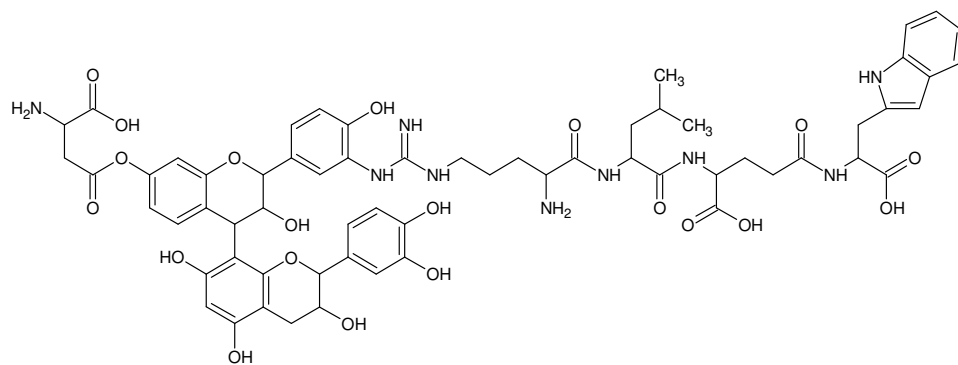


Table 3 The viscosity of foaming resins, density, pulverization ratios and specific compressive strength of control, TFS, and LTFS foams ^a.

Foams	Viscosity (mPa•s)	Density (kg/m ³)	Pulverization ratios (%)	Specific compressive strength (kPa/kg•m ⁻³)
Control	2200(35)	83.5(2.5)	13.68(1.03)	2.75
TFS1	17500(145)	94.4(3.1)	4.83(0.72)	4.34
TFS2	27650(221)	98.3(2.6)	4.22(0.49)	4.88
TFS3	35500(187)	108.6(4.8)	3.68(0.21)	5.24
TFS4	48500(180)	112.5(5.5)	2.64(0.38)	6.13
L0.5TFS3	26250(195)	96.5(1.8)	10.01(2.15)	1.76
L1TFS3	32900(207)	98.6(2.1)	8.55(1.12)	1.93
L1.5TFS3	36750(214)	99.6(3.4)	8.24(1.74)	2.31
L2TFS3	40850(224)	93.8(2.2)	11.48(2.21)	1.91

^aThe values in the parentheses are standard deviations

Table 4 TGA data of the control, TFS and LTFS foams.

Foams	T-max ^a (°C)			Weight loss (%)			Residual mass at 790°C (%)
	Step I	Step II	Step III	Step I	Step II	Step III	
Control	52.28	455.64	558.82	5.94	38.14	51.33	4.59
TFS1	61.24	466.59	624.81	5.80	35.17	53.88	5.15
TFS2	63.73	468.72	634.44	5.19	35.70	32.25	26.84
TFS3	65.45	486.21	639.01	6.35	36.21	25.13	32.28
TFS4	64.78	487.81	639.71	6.10	34.79	21.5	37.61
L0.5TFS3	65.73	484.88	774.73	6.18	34.49	20.80	38.52
L1TFS3	66.39	485.53	773.40	5.96	36.03	18.76	39.25
L1.5TFS3	67.38	482.96	772.53	6.57	36.79	15.10	41.54
L2TFS3	65.59	481.35	779.78	5.24	37.27	14.48	43.01

^a Temperature corresponding to the maximum weight loss rate.

Table 5 Detailed cone calorimetry data of the control, TFS, and LTFS samples ^a

Foams	PHRR ^b (kW/m ²)	THR ^b (MJ/m ²)	TSP ^b (m ²)	Residue ^b (wt %)	Ref.
Control	42.16(2.62)	42.65(2.16)	0.13(0.02)	26.73(1.55)	
TFS3	25.38(2.05)	38.65(1.08)	0.11(0.01)	32.41(2.34)	★ ^c
L1.5TFS3	19.49(1.68)	31.57(1.98)	0.05(0.01)	41.34(3.66)	
Wood	167.86(4.06)	68.69(2.29)	2.18(0.28)	-	(Kon
Wood/PFA	233.21(34.94)	83.36(2.65)	5.37(0.35)	-	g et
Wood/PFA/ADP	156.61(4.94)	45.10(0.16)	0.22(0.04)	-	al., 2018)
PUF-0	232.7(21)	10.7(2)	5.93(0.6)	-	(Cao
PUF-EG	207.9(23)	10.1(1.7)	5.36(0.3)	-	et al.,
PUF-200	103(13)	5.9(1.0)	2.08(0.2)	-	2019)
Pure FPUF	310(11)	22.5(0.5)	4.51(0.06)	4.3(0.7)	(Rao et al., 2018)

^a The values in the parentheses are standard deviations;

^b PHRR, THR, TSP and residue represented the time to ignition, peak heat release rate, total heat release, total smoke production and residue after tests, respectively;

^c ★ represents this work.

Table 6 Formaldehyde emission of the control, TFS3, and L1.5TFS3 foams ^a

Samples	Formaldehyde emission (mg/m ³)
Control	0.08 (0.02)
TFS3	0.03(0.01)
L1.5TFS3	0.03(0.01)
GB/T 17657-2013	≤0.124

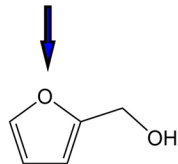
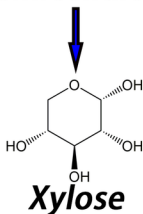
^aThe values in the parentheses are standard deviations



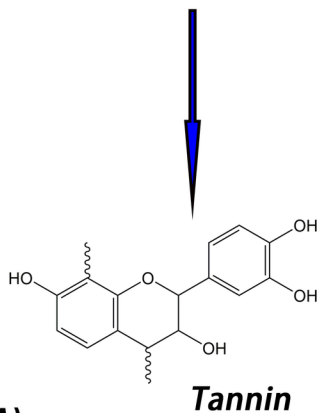
Lignocellulosic Biomass



Hemicellulose



Extractive



Soy Protein Isolate (SPI)

Water+Diethyl ether (DE)

p-toluene-4-sulfonic acid (pTSA)

