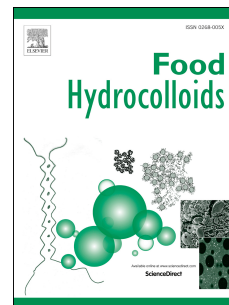


Journal Pre-proof

Enhanced structural properties of calcium cross-linked pectin gel beads incorporated with starch derivatives: Preparation, characterization, and *in vitro* prebiotic activity

Wenqing Zhu, Ruoxi Bai, Shulei Liang, Yuqin Yuan, Bin Zhang, Marie-Laure Fauconnier, Aurore Richel, Zhenjia Zheng



PII: S0268-005X(25)01146-4

DOI: <https://doi.org/10.1016/j.foodhyd.2025.112186>

Reference: FOOHYD 112186

To appear in: *Food Hydrocolloids*

Received Date: 6 August 2025

Revised Date: 28 October 2025

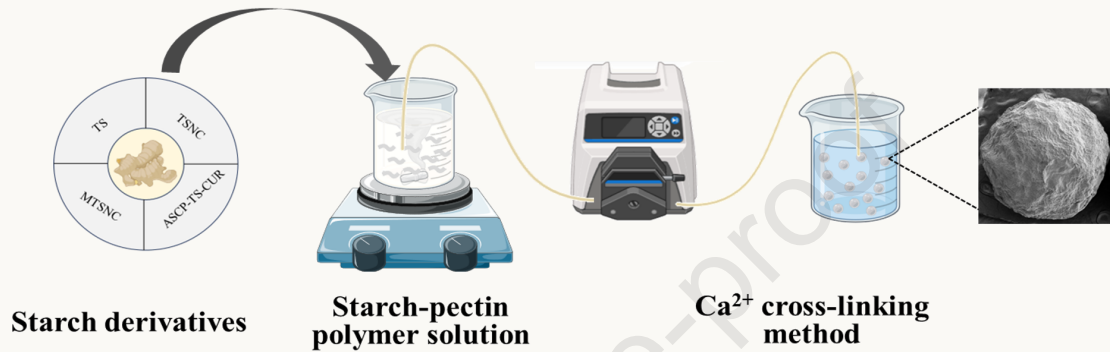
Accepted Date: 29 October 2025

Please cite this article as: Zhu, W., Bai, R., Liang, S., Yuan, Y., Zhang, B., Fauconnier, M.-L., Richel, A., Zheng, Z., Enhanced structural properties of calcium cross-linked pectin gel beads incorporated with starch derivatives: Preparation, characterization, and *in vitro* prebiotic activity, *Food Hydrocolloids*, <https://doi.org/10.1016/j.foodhyd.2025.112186>.

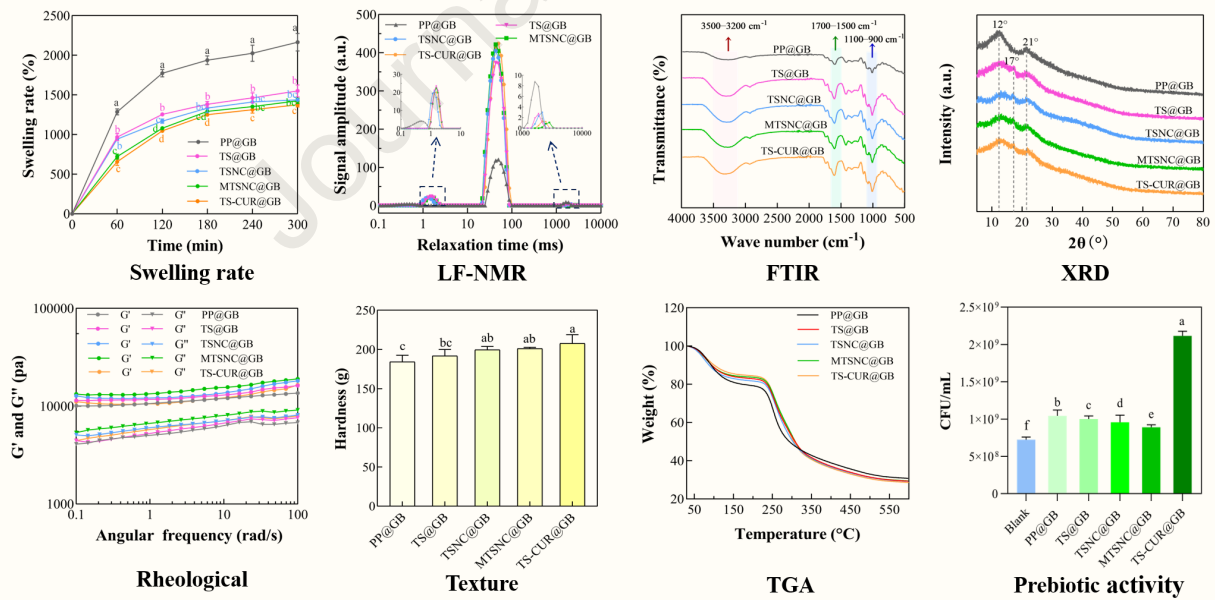
This is a PDF of an article that has undergone enhancements after acceptance, such as the addition of a cover page and metadata, and formatting for readability. This version will undergo additional copyediting, typesetting and review before it is published in its final form. As such, this version is no longer the Accepted Manuscript, but it is not yet the definitive Version of Record; we are providing this early version to give early visibility of the article. Please note that Elsevier's sharing policy for the Published Journal Article applies to this version, see: <https://www.elsevier.com/about/policies-and-standards/sharing#4-published-journal-article>. Please also note that, during the production process, errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

© 2025 Published by Elsevier Ltd.

Preparation method



Structural and functional characteristics



1 **Enhanced structural properties of calcium cross-linked**
2 **pectin gel beads incorporated with starch derivatives:**
3 **Preparation, characterization, and *in vitro* prebiotic activity**

4
5 Wenqing Zhu^{a,b}, Ruoxi Bai^a, Shulei Liang^a, Yuqin Yuan^a, Bin Zhang^a, Marie-Laure
6 Fauconnier^b, Aurore Richel^c, Zhenjia Zheng^{a,*}

7
8 ^a Key Laboratory of Food Nutrition and Health in Universities of Shandong, College of
9 Food Science and Engineering, Shandong Agricultural University, 61 Daizong Street,
10 Tai'an 271018, Shandong, China

11 ^b Laboratory of Chemistry of Natural Molecules, Gembloux Agro-Bio Tech, University
12 of Liège, Passage des déportés 2, B-5030 Gembloux, Belgium

13 ^c Laboratory of Biomass and Green Technologies, Gembloux Agro-Bio Tech,
14 University of Liège, Passage des déportés 2, B-5030 Gembloux, Belgium

15
16 * Corresponding author: Zhenjia Zheng (Email: zhengzhenjia@sdau.edu.cn)

17 **Abstract:** In this study, gel beads composed of pectin and four different starch-based
18 derivatives were prepared through calcium ion crosslinking, and their physicochemical
19 characteristics and functional properties were systematically evaluated. The results
20 indicated that the incorporation of starch derivatives increased the internal crosslinking
21 degree and strengthened intermolecular interactions, leading to a more compact and
22 densely arranged porous structure within the composite gel beads. Compared to pure
23 pectin gel beads, the water holding capacity of the composite gel beads improved by
24 6.06%–15.44% while the swelling rate decreased by 26.16%–37.02%, and the hardness,
25 springiness, chewiness, and gumminess increased by 4.16%–12.75%, 3.40%–4.96%,
26 1.71%–8.63%, and 8.09%–16.51%, respectively. Additionally, the incorporation of
27 starch derivatives reduced the crystallinity of the composite gel beads and enhanced
28 their thermal stability. Moreover, all five gel beads exhibited notable prebiotic activity,
29 significantly promoting the growth of *Lactiplantibacillus plantarum* Lp3a. Notably, the
30 gel beads incorporating starch-curcumin complexes (TS-CUR@GB) achieved the
31 highest colony count of 2.15×10^9 CFU/mL, which was 2.92-fold higher than the blank
32 group. These results demonstrate the potential of starch-based derivatives to improve
33 the structural integrity and functional performance of pectin-based gel systems, offering
34 promising applications in food science and bioactive delivery systems.

35 **Keywords:** Pectin, starch derivatives, gel beads, structural analysis, physicochemical
36 properties, *in vitro* prebiotic activity

37 **1. Introduction**

38 Hydrogels are three-dimensional networks of hydrophilic polymers, such as
39 sodium alginate, pectin, that can absorb and retain large amounts of water or other
40 substances. Their excellent biocompatibility and environmental friendliness have
41 sparked widespread interest in the fields of food science and biomedicine (Yang et al.,
42 2024). Among various hydrogel configurations, hydrogel beads have gained
43 widespread application due to their small size and spherical morphology, which
44 facilitates easy incorporation into food matrices. Moreover, the three-dimensional gel
45 network provides a protective barrier that stabilizes sensitive bioactive compounds and
46 protects them from adverse external conditions, thereby enabling their extensive use in
47 the encapsulation, protection, and controlled release of functional ingredients (Li et al.,
48 2024). A common method for producing gel beads is ionic gelation, in which divalent
49 cations (e.g., Ca^{2+}) cross-link charged hydrocolloids to form a stable three-dimensional
50 polymeric network (Almeida et al., 2021). Low-methoxy pectin is especially suitable
51 for this process due to its non-toxicity, biocompatibility, and ability to rapidly form a
52 stable “egg-box” gel structure upon calcium cross-linking (Lenie et al., 2024).
53 Nevertheless, pure pectin gel beads often exhibit certain structural limitations, such as
54 high porosity, a loosely structured network, and excessive swelling behavior, which can
55 lead to poor encapsulation efficiency and premature release of bioactive components
56 (Silveira et al., 2023).

57 To address these structural limitations, researchers have explored the integration
58 of various filler materials, including sodium alginate (Zhang et al., 2025), starch
59 (Silveira et al., 2023), chitosan (Reichembach et al., 2024), and proteins (Sun et al.,
60 2024) to reinforce the hydrogel network and enhance functional performance. Among
61 them, starch, one of the most abundant and important natural polysaccharides, is
62 considered a promising sustainable biomaterial due to its complete biodegradability,
63 low cost, and renewability (Wang et al., 2025). It has been widely used in the food
64 industry as a thickening agent, stabilizer, gelling agent, and water-retaining agent to
65 improve textural properties, viscoelasticity, and overall stability of food products (Ren,
66 Jiang, et al., 2020). Furthermore, native starch has been successfully incorporated into

67 the ionic gelation process as a filler matrix to enhance the swelling behavior and
68 structural characteristics of hydrogel beads (Lopes et al., 2023). For instance, Chan et
69 al. (2011) reported that corn starch not only enhances the structural characteristics of
70 alginate-based gel beads but also significantly improves the viability of *Lactobacillus*
71 *casei* during storage. Rohman et al. (2021) demonstrated that cassava starch acts as an
72 effective filler, improving the morphological features and encapsulation efficiency of
73 alginate hydrogels. Furthermore, corn starch fillers can reduce the swelling
74 phenomenon of the gel network and further enhance its mechanical properties (Chen et
75 al., 2024). However, the current research primarily focuses on the application of natural
76 starch as a structural regulator, while the regulating potential of starch derivatives with
77 progressively enhanced structures and functions on the properties of pectin-based gel
78 beads has not been explored.

79 We hypothesized that each structurally progressive starch system would enhance
80 the mechanical strength, swelling resistance, and thermal stability of gel beads through
81 differentially modulating the cross-linking density and network architecture, especially
82 those pre-loaded with bioactive components (such as curcumin), which can not only
83 improve the structural defects but also endow gel beads with biological function
84 benefits. To prove our hypothesis, this study aims to develop a series of pectin-based
85 gel beads that contain four starch-based derivatives (natural starch, starch nanoparticles,
86 modified starch nanoparticles, and starch-curcumin complexes), simulating the gradual
87 evolution of starch structure from natural form to nanoscale, modified state, and
88 functionalized complexes. Subsequently, a systematic evaluation was conducted on the
89 microstructure, mechanical properties, swelling behavior, and probiotic activity of these
90 gel beads, aiming to clarify the regulatory effect of the structural and functional
91 evolution of starch fillers on the overall performance of pure pectin gel beads, while
92 providing valuable insights for the design and development of novel hydrogel systems
93 with enhanced structure and functionality.

94 **2. Materials and methods**

95 *2.1. Materials and chemicals*

96 Pectin (food grade, apple-derived, APA210) was supplied by Yantai DSM Andeli

97 Pectin Co., Ltd. The galacturonic acid (GalA) content of this pectin is 85.6%, the degree
98 of esterification (DE) is 27.9%, and the weight-average molecular weight (Mw) is
99 161352 ± 6460 Da. Calcium chloride (food grade) was purchased from Shenzhen
100 Xingmu Bioengineering Co., Ltd. Turmeric starch (starch content 80.85%, moisture
101 content 13.15%, fat content 0.10%, protein content 0.15%, ash content 0.80%, amylose
102 content 55.06%) was extracted from turmeric rhizomes using the method described in
103 our previous study (Zhu et al., 2025), in which its structural characteristics were
104 comprehensively analyzed. All other reagents were of analytical grade.

105 *2.2. Synthesis of starch-based derivatives*

106 The synthesis of starch-based derivatives was carried out as described in our
107 previous study (Zhu et al., 2025).

108 Starch nanoparticles were synthesized using the antisolvent precipitation method.
109 Briefly, turmeric starch (TS) was gelatinized and added to an antisolvent (anhydrous
110 ethanol) under continuous stirring. The mixture was then regenerated at 4°C for 24 h,
111 followed by centrifugation at 4000 rpm for 10 min. The resulting precipitate was
112 collected, washed, and then subjected to freeze-drying, yielding a powdered sample
113 named TSNC.

114 Modified starch nanoparticles, named MTSNC, were prepared by incorporating
115 dioscin during the synthesis process. Specifically, anhydrous ethanol containing dioscin
116 was added to the turmeric starch gelatinization solution. Subsequently, the remaining
117 steps were carried out in the same manner as for TSNC.

118 The dioscin-modified turmeric starch-curcumin complex, named ASCP-TS-CUR,
119 was synthesized using the antisolvent co-precipitation (ASCP) method. The detailed
120 procedure has been reported in the referenced publication.

121 *2.3. Preparation of pectin-based gel beads filled with different starch derivatives*

122 The preparation of pectin-based gel beads incorporating various starch-based
123 derivatives was conducted following the procedures described by Jiang et al. (2024)
124 and Dahal et al. (2024), with slight modifications. In brief, 1.0 g of each starch-based
125 derivative (TS, TSNC, MTSNC, and ASCP-TS-CUR) was dispersed into a 5% (w/v)
126 pectin solution and stirred continuously for 30 min to ensure thorough mixing. The

127 resulting mixture was then inhaled into a peristaltic pump and extruded dropwise into
128 a 4% (w/v) CaCl_2 crosslinking solution under gentle stirring for 30 min to facilitate
129 curing. The formed gel beads were subsequently collected, rinsed three times with
130 deionized water to remove excess Ca^{2+} , and freeze-dried (-80°C , 10 Pa) for 12 hours to
131 obtain the final dried products. The pectin gel beads containing TS, TSNC, MTSNC,
132 and ASCP-TS-CUR were designated as TS@GB, TSNC@GB, MTSNC@GB, and TS-
133 CUR@GB, respectively. For comparison, pure pectin gel beads without any starch-
134 based materials were prepared using the same procedure and designated as PP@GB.

135 2.4. Appearance observation

136 The morphological characteristics and overall appearance of both fresh and freeze-
137 dried gel beads were observed and captured using a smartphone (OnePlus Ace 2,
138 PHK110).

139 2.5. Fourier transform infrared (FTIR) spectroscopy analysis

140 The chemical structure and functional groups of the dried gel beads were analyzed
141 using a Nicolet iS10 Fourier Transform Infrared (FTIR) spectrometer (Thermo Fisher
142 Scientific, USA), following the method described by Reichembach et al. (2024). The
143 spectra were recorded over a wavelength range of 4000 to 400 cm^{-1} with a resolution
144 of 4 cm^{-1} and 64 scans.

145 2.6. X-ray diffraction (XRD) analysis

146 The crystallographic properties of the dried gel bead samples were determined
147 using an EMPYREAN X-ray diffractometer (Malvern Panaco Instruments LTD., UK)
148 equipped with a Cu-K α radiation source. The diffractometer was operated at an
149 acceleration voltage of 40 kV and a current of 40 mA. The diffraction patterns were
150 recorded across a 2θ range of 5° to 80° with a scanning rate of $10^\circ/\text{min}$, following the
151 procedure described by Lee et al. (2020).

152 2.7. Thermogravimetric analysis (TGA)

153 The thermogravimetric behavior of the dried gel bead samples was analyzed using
154 a D-09123 thermogravimetric analyzer (Mettler Toledo Instruments Ltd., Zurich,
155 Switzerland), following the method described by Bu et al. (2023). Each sample was
156 heated from 30°C to 600°C at a heating rate of $10^\circ\text{C}/\text{min}$. All measurements were

157 conducted in a nitrogen atmosphere, with a continuous flow rate of 30 mL/min.

158 2.8. Scanning electron microscope (SEM) analysis

159 The surface and cross-sectional morphologies of the dried gel beads were
160 examined using a SUPRA 55 scanning electron microscope (Carl Zeiss Group,
161 Germany), following the procedure described by Cai et al. (2022). Briefly,
162 approximately 10 mg of dried gel bead samples were mounted onto the observation
163 table and sputter-coated with a thin layer of gold. The microstructural features were
164 then observed under an accelerating voltage of 10 kV.

165 2.9. Water holding capacity (WHC)

166 The WHC of the gel beads was determined according to the method described by
167 Feltre et al. (2020). Briefly, freshly prepared gel beads were weighed to record their
168 initial mass. The beads were then placed into centrifuge tubes and centrifuged at
169 4000 rpm for 20 min. Following centrifugation, the residual gel beads were reweighed.
170 The WHC was calculated using Eq. (1):

$$171 \quad WHC (\%) = \frac{\text{Mass of gel beads after centrifugation}}{\text{Mass of gel beads before centrifugation}} \times 100 \quad (1)$$

172 2.10. Swelling rate (SR) analysis

173 The swelling behavior of the dried gel beads over 6 hours was evaluated following
174 the method of Cai et al. (2022), with slight modifications. Briefly, approximately 50 mg
175 of freeze-dried gel beads were immersed in 20 mL of deionized water at room
176 temperature. At predetermined time intervals (60, 120, 180, 240, 300, and 360 min), the
177 swollen beads were retrieved, gently blotted with filter paper to remove excess surface
178 water, and immediately weighed. The SR was calculated using Eq. (2):

$$179 \quad SR (\%) = \frac{\text{Weight of swollen gel beads} - \text{Weight of dried gel beads}}{\text{Weight of dried gel beads}} \times 100 \quad (2)$$

180 2.11. Low-field nuclear magnetic resonance (LF-NMR) analysis

181 The water distribution within the gel beads was analyzed using a low-field nuclear
182 magnetic resonance (LF-NMR) spectrometer (Niumag Analytical Instrument
183 Corporation, China), following the method described by Jiang et al. (2024). Before
184 measurement, approximately 1 g of freshly prepared gel beads was placed into an NMR
185 tube and inserted into the sample chamber of the LF-NMR instrument. The transverse

186 relaxation time (T_2) was measured using the Carr-Purcell-Meiboom-Gill (CPMG) pulse
 187 sequence with a superposition number (NS) of 4, an echo time (TE) of 0.25 ms, and an
 188 echo number (NECH) of 18000. The obtained T_2 relaxation curves were analyzed
 189 through multi-exponential fitting to quantify the relative proportions of different water
 190 populations within the gel matrix.

191 2.12. Rheological analysis

192 According to the method described by Zhang et al. (2025), the rheological
 193 behavior of the fresh gel beads was evaluated at 25°C using an MCR102 Modular
 194 Intelligent Rheometer (Anton Paar Instruments Co. Ltd., Austria) equipped with a
 195 parallel plate geometry (diameter of 40 mm, gap height of 1 mm). Specifically, an
 196 appropriate amount of fresh gel beads was loaded onto the lower plate, and a layer of
 197 silicone oil was coated around the samples to prevent slippage and water evaporation.
 198 Dynamic oscillatory frequency sweeps were performed over a frequency range of 0.1
 199 to 100 rad/s under a constant strain of 0.5%, and the storage modulus (G') and loss
 200 modulus (G'') were recorded as functions of angular frequency to assess the viscoelastic
 201 properties of the samples. The G' and G'' curves obtained from frequency sweep data
 202 were modeled from 0.1 to 100 rad/s using a power law as defined in Eq. (3) and Eq. (4).

$$203 \quad G' = k' \times \omega^{n'} \quad (3)$$

$$204 \quad G'' = k'' \times \omega^{n''} \quad (4)$$

205 where ω is the frequency (rad/s), G' is the storage modulus at the given frequency, G''
 206 is the loss modulus at the given frequency, k' is the elastic stiffness coefficient ($\text{Pa}\cdot\text{s}^n$),
 207 k'' is the viscosity stiffness coefficient ($\text{Pa}\cdot\text{s}^n$), n' is the elastic frequency index
 208 (dimensionless), n'' is the viscosity frequency index (dimensionless). Additionally, k''/k'
 209 represents the overall loss tangent.

210 The steady-state scanning shear rate was 0.1 to 100 s^{-1} , and the viscosity was
 211 recorded as a function of the shear rate. The viscosity curve was fitted and analyzed
 212 using the Ostwald-de Wael power-law model defined in Eq. (5).

$$213 \quad \eta_a = K \times \dot{\gamma}^{n-1} \quad (5)$$

214 where η_a is the apparent viscosity ($\text{Pa}\cdot\text{s}$), K is the consistency coefficient ($\text{Pa}\cdot\text{s}^n$), $\dot{\gamma}$ is
 215 the shear rate (s^{-1}), and n is the flow behavior index (dimensionless).

216 2.13. Texture profile analysis (TPA)

217 The textural properties of the fresh gel beads were evaluated using a TA.XTC-20
218 texture analyzer (Shanghai Baosheng Industrial Development Co., Ltd., China), fitted
219 with a TA/0.5 gel probe. The analysis was carried out following the method of Wan et
220 al. (2021), with some modifications. The pre-test, testing, and post-test speeds were all
221 set at 1.0 mm/s, and the compression strain was adjusted to achieve 50% deformation
222 of the gel beads. A trigger force of 5.0 g was applied, with a holding time of 5 s between
223 compressions.

224 2.14. In vitro prebiotic activity evaluation

225 The effect of five different dried gel bead formulations on the proliferation of
226 *Lactiplantibacillus plantarum* Lp3a was evaluated following the method of Lee et al.
227 (2023), with slight modifications. Briefly, *Lactiplantibacillus plantarum* Lp3a powder
228 was activated in MRS broth at 37°C for 48 h before use. Subsequently, 200 µL of the
229 activated bacterial culture was inoculated into 10 mL of carbon-free MRS broth
230 supplemented with 1% (w/v) of each gel bead sample. Carbon-free MRS broth without
231 any added samples served as the control group. After incubation at 37°C for 48 h, the
232 bacterial suspension was serially diluted from 10⁻¹ to 10⁻⁸ and spread onto MRS agar
233 plates. Following an additional 48-h incubation at 37°C, the number of colony-forming
234 units (CFU) was counted and expressed as CFU/mL using Eq. (6):

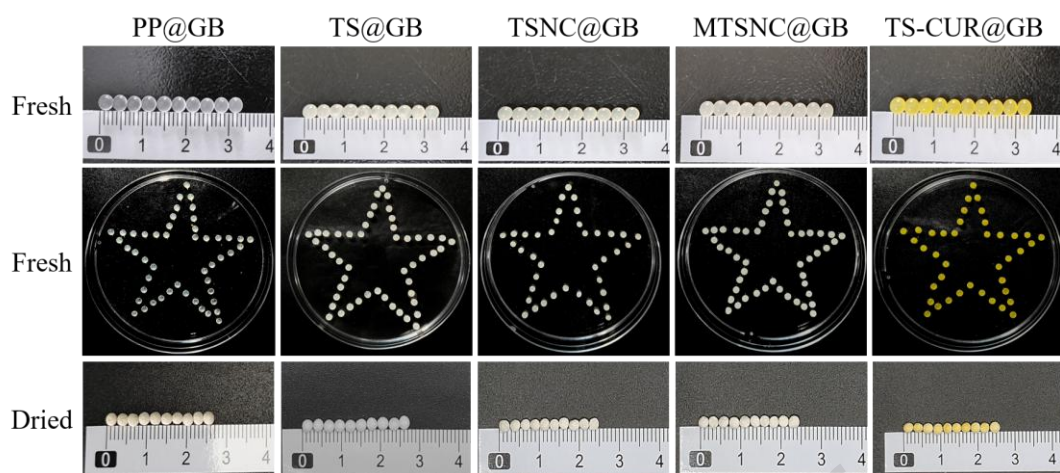
$$235 \quad CFU/mL = \frac{\text{Number of colonies} \times \text{Dilution factor}}{\text{Volume of inoculum (mL)}} \quad (6)$$

236 2.15. Statistical analysis

237 Experimental data were expressed as the mean ± standard deviation. Statistical
238 analysis was performed using one-way analysis of variance (ANOVA) with SPSS 25
239 software, with $P < 0.05$ indicating a significant difference. All experimental groups were
240 performed in triplicate.

241 3. Results and analysis

242 3.1. Visual appearance

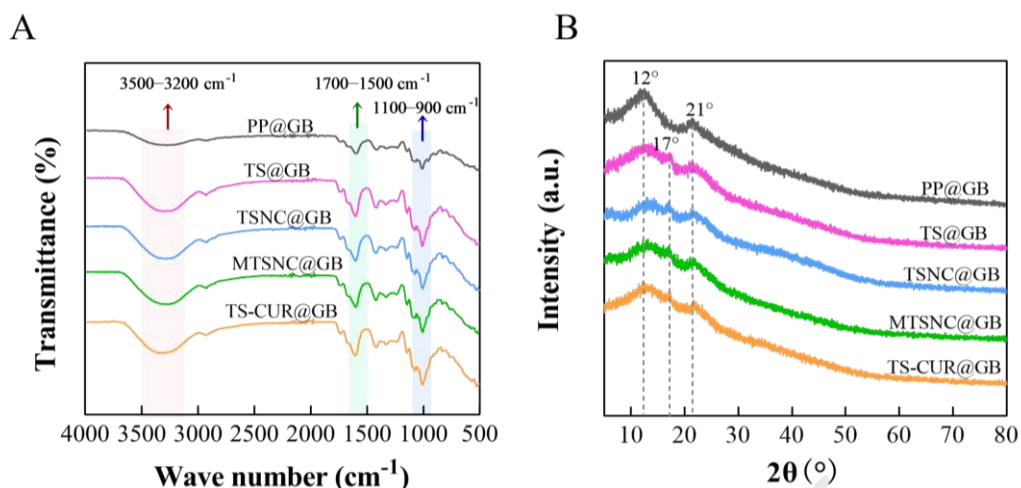


243

244 **Fig. 1.** Visual appearance of PP@GB, TS@GB, TSNC@GB, MTSNC@GB, and TS-
 245 CUR@GB gel beads.

246 The visual appearance of the fresh and dried PP@GB, TS@GB, TSNC@GB,
 247 MTSNC@GB, and TS-CUR@GB gel beads was illustrated in **Fig. 1**. All five types of
 248 fresh gel beads displayed a regular spherical shape, uniform size distribution, and
 249 smooth surface, with diameters ranging from approximately 3.3 to 3.4 mm. PP@GB
 250 appeared transparent, whereas the gel beads containing starch-based formulations
 251 (TS@GB, TSNC@GB, and MTSNC@GB) exhibited a milky-white appearance.
 252 Notably, the gel bead incorporating the starch-curcumin complex (TS-CUR@GB)
 253 displayed a distinct yellow coloration due to the intrinsic hue of curcumin. Previous
 254 studies have suggested that the average particle size suitable for direct swallowing by
 255 adults ranges from 2 to 4 mm (Jiang et al., 2024). Therefore, the gel beads developed in
 256 this study possess suitable dimensions for use as easily ingestible carriers in food or
 257 pharmaceutical applications. Additionally, a reduction in bead diameter was observed
 258 after freeze-drying compared to the fresh state. This shrinkage is likely due to water
 259 loss during the freeze-drying process, resulting in structural contraction and a decrease
 260 in overall volume (Lee et al., 2023).

261 *3.2. FTIR analysis*



262

263 **Fig. 2.** FTIR spectra (A) and XRD patterns (B) of PP@GB, TS@GB, TSNC@GB,
 264 MTSNC@GB, and TS-CUR@GB gel beads.

265 The chemical bonds and functional groups present in PP@GB, TS@GB,
 266 TSNC@GB, MTSNC@GB, and TS-CUR@GB were analyzed using FTIR to
 267 investigate potential molecular interactions among the constituent components, as
 268 shown in **Fig. 2A**. PP@GB exhibited a broad absorption peak in the range of
 269 $3500\text{--}3200\text{ cm}^{-1}$, which corresponds to the stretching vibration of the O–H group,
 270 indicating the presence of hydrogen-bonded hydroxyl functionalities. A peak between
 271 $2900\text{--}2800\text{ cm}^{-1}$ was attributed to the stretching vibrations of the –CH group. The wide
 272 peak in the region of $1700\text{--}1500\text{ cm}^{-1}$ was associated with the asymmetric and
 273 symmetric stretching vibrations of the COO– groups (Yang et al., 2024; Vaziri et al.,
 274 2018). Additionally, the absorption peaks observed between $1100\text{--}900\text{ cm}^{-1}$
 275 corresponded to the C–O and C–C stretching vibrations associated with glycosidic
 276 linkages and pyran ring structures. These characteristic FTIR absorption features are
 277 consistent with those previously reported for pectin-based gel beads by Sarkar et al.
 278 (2024) and Günter et al. (2022).

279 The FTIR spectra of TS@GB, TSNC@GB, MTSNC@GB, and TS-CUR@GB
 280 were similar to that of PP@GB, with no new absorption peaks observed upon the
 281 incorporation of different starch matrices, indicating that no new chemical bonds were
 282 formed during the formation of the composite gel systems. However, an increase in the
 283 intensity of the O–H stretching vibration band in the $3500\text{--}3200\text{ cm}^{-1}$ region was
 284 observed in the starch-containing gel beads, indicating enhanced hydrogen bonding

285 interactions between pectin and starch molecules, which is due to the increased
286 availability of hydroxyl groups in starch derivatives, forming additional hydrogen
287 bonds with the pectin main chain. This extended hydrogen bond network promotes the
288 formation of a more cohesive and rigid three-dimensional structure (Li et al., 2024). A
289 similar enhancement in hydrogen bonding within polysaccharide-starch composite gels
290 has been reported by Ren, Jiang, et al. (2024). Moreover, the increased intensity of the
291 absorption band in the $1700\text{--}1500\text{ cm}^{-1}$ range further supports the presence of stronger
292 intermolecular hydrogen bonding between starch and pectin (Lenie et al., 2024). The
293 intensification of the spectral features in the $1100\text{--}900\text{ cm}^{-1}$ range was assigned to
294 C–O–C glycosidic bond vibrations in glucose units, which was interpreted as evidence
295 of enhanced hydrogen bonding between hydroxyl groups and different glucose units
296 within the matrix (Han et al., 2023). These FTIR spectral changes provide direct
297 molecular-level evidence for the strengthening of hydrogen bonds in the composite gel.
298 Crucially, these enhancements are consistent with the improvement of macroscopic
299 properties: the enhanced hydrogen bond network directly corresponds to the denser
300 microstructure observed by SEM images (**Fig. 4**), the decrease in swelling rate
301 determined by swelling experiment (**Fig. 5B**), and the increase in mechanical strength
302 measured by texture analysis (**Fig. 7**). These multi-scale results collectively
303 demonstrated that enhanced hydrogen bonds play a crucial role in improving the
304 structural integrity and functional performance of composite gel beads.

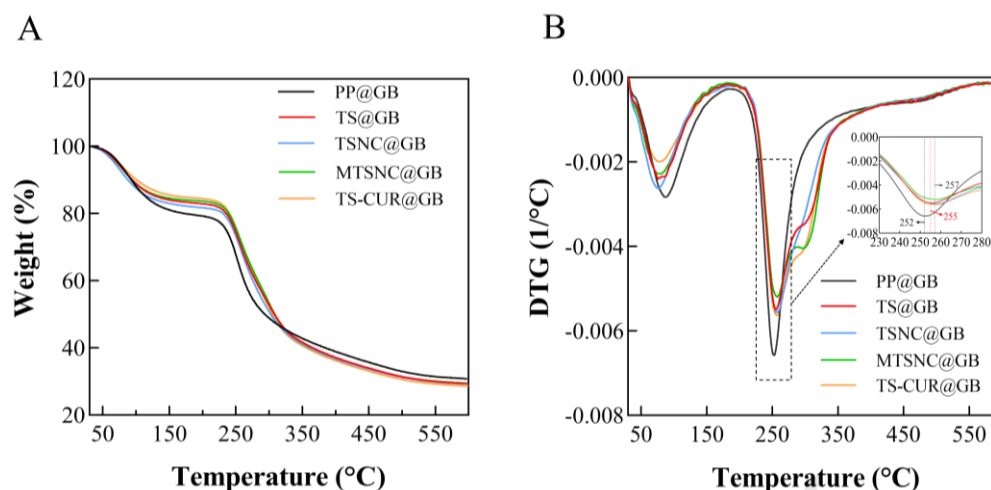
305 3.3. XRD analysis

306 The crystal properties of PP@GB, TS@GB, TSNC@GB, MTSNC@GB, and TS-
307 CUR@GB gel beads were characterized using XRD, as shown in **Fig. 2B**. PP@GB
308 exhibited two broad diffraction peaks at approximately $2\theta = 12^\circ$ and 21° , which are
309 characteristic of semi-crystalline materials (Liu et al., 2024). Upon incorporating
310 various starch-derived materials, the intensity of these diffraction peaks was reduced in
311 TS@GB, TSNC@GB, MTSNC@GB, and TS-CUR@GB, indicating the partial loss of
312 crystal order and the transition to amorphous structure in the composite system. This
313 phenomenon is commonly observed in polymer composite systems, where water
314 absorption during blend preparation, along with inter- and intramolecular hydrogen

315 bonds between polymers, leads to the loss of crystal structure (Lopes et al., 2023). The
316 decrease in crystallinity is particularly significant as it often correlates with enhanced
317 functional properties, such as improved encapsulation efficiency and faster dissolution
318 rate of the water-insoluble bioactive due to the free volume in amorphous regions and
319 an increase in the lattice free energy. Consequently, low-crystallinity formulations are
320 expected to exhibit higher bioavailability compared to higher-crystallinity formulations
321 (Ubeyitogullari et al., 2019).

322 Additionally, a new, weak diffraction peak appeared at $2\theta = 17^\circ$ in the composite
323 gel beads, which may correspond to the characteristic crystalline reflection of the
324 incorporated starch-based materials. As previously reported, turmeric starch and its
325 derivatives exhibited distinct diffraction peaks at $2\theta = 17^\circ$ (Zhu et al., 2025). Therefore,
326 the emergence of this peak in the composite systems confirmed the successful
327 incorporation of starch-derived materials into the pectin matrix. However, the low
328 intensity of this peak in our composites, compared to the sharp peak of native starch,
329 indicated that the starch crystals underwent partial destruction during the composite
330 formation process. This finding is consistent with those of Ren, Jiang, et al. (2020), who
331 demonstrated that gelatinization and complexation can lead to a transformation from a
332 crystalline to an amorphous structure in starch-polysaccharide complexes, as evidenced
333 by a decrease in the intensity of the characteristic peak. Therefore, the XRD results
334 demonstrated the successful formation of an amorphous-crystalline composite system
335 where the starch components are integrated into the pectin network, leading to a
336 material with an improved crystalline architecture that is anticipated to be more
337 amenable to bioactive compound encapsulation.

338 3.4. TGA analysis

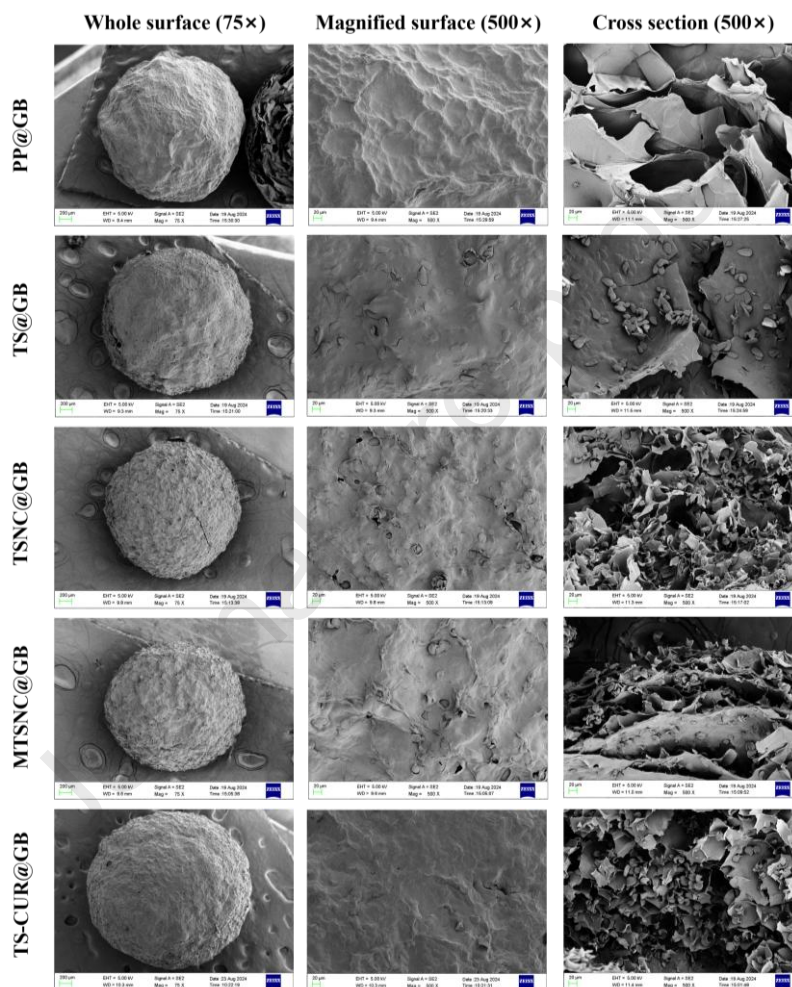


339
 340 **Fig. 3.** TGA curves (A) and DTG curves (B) of PP@GB, TS@GB, TSNC@GB,
 341 MTSNC@GB, and TS-CUR@GB gel beads.

342 The thermal stability of PP@GB, TS@GB, TSNC@GB, MTSNC@GB, and TS-
 343 CUR@GB gel beads was assessed using TGA, as shown in **Fig. 3**. The TGA curves of
 344 all samples exhibited three distinct stages of thermal degradation (**Fig. 3A**). The first
 345 stage occurred between 30°C and 120°C, primarily due to the evaporation of bound
 346 water within the gel matrix as the temperature increased (Xiao et al., 2022). The second
 347 stage centered around 250°C, during which all gel beads showed significant mass loss.
 348 This weight loss might be due to the dehydration of sugar rings, decomposition of pectin
 349 and starch structures, and volatilization of other organic components (Singh et al., 2017).
 350 Notably, PP@GB exhibited a maximum weight loss of approximately 34% during this
 351 stage, whereas the composite gel beads showed lower losses of around 29%.
 352 Furthermore, the peak degradation temperature for PP@GB was approximately 252°C,
 353 while the composite formulations exhibited a shift to higher degradation temperatures
 354 (**Fig. 3B**), indicating that the incorporation of starch-based materials enhanced the
 355 thermal resistance of the gel network, thereby improving overall thermal stability. This
 356 enhancement can be attributed to stronger intermolecular interactions among pectin,
 357 starch molecules, and Ca^{2+} , which increase cross-linking density and structural integrity
 358 within the composite network, thus resisting chain scission during heating and reducing
 359 thermal degradation (Raza et al., 2024). The third stage of degradation, occurring
 360 between 300°C and 600°C, reflects the complete breakdown of residual organic matter
 361 and the eventual formation of inorganic ash residues (Ubeyitogullari et al., 2016).

362 Combined with FTIR analysis, it is likely that starch-based derivatives promoted the
 363 formation of a more stable three-dimensional gel network by enhancing intermolecular
 364 interactions, ultimately improving thermal stability. These results can provide important
 365 references for designing hydrogel systems with excellent thermal stability and
 366 mechanical properties.

367 3.5. SEM analysis



368

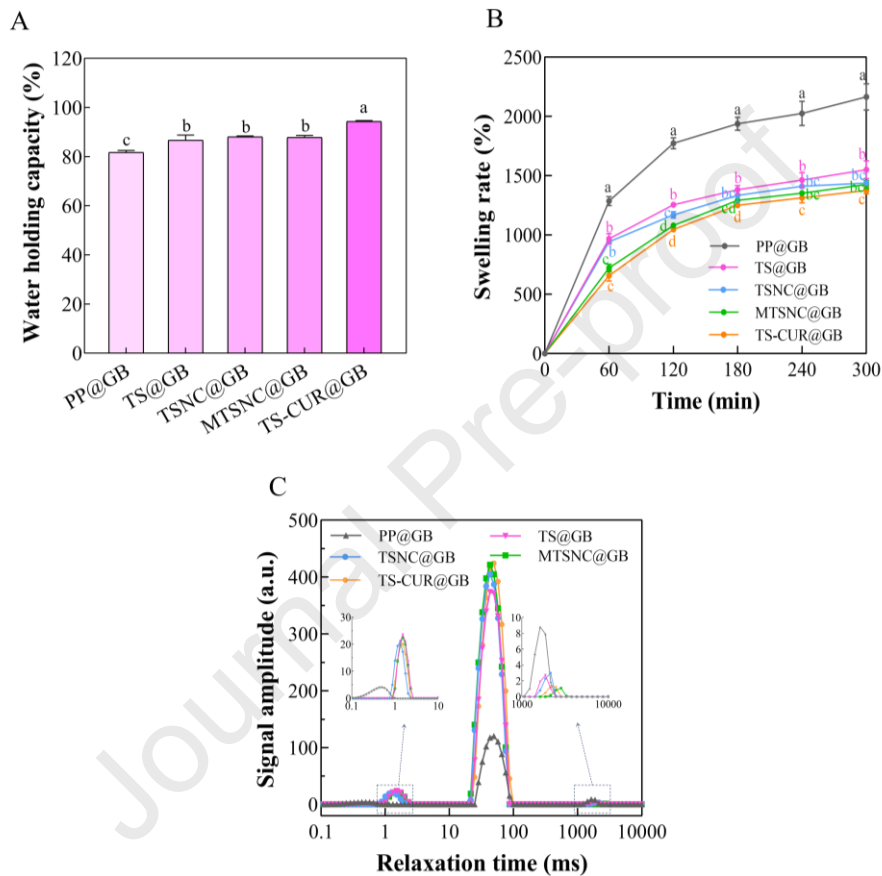
369 **Fig. 4.** SEM images of PP@GB, TS@GB, TSNC@GB, MTSNC@GB, and TS-
 370 CUR@GB gel beads.

371 The surface morphology and internal cross-sectional structure of dried PP@GB,
 372 TS@GB, TSNC@GB, MTSNC@GB, and TS-CUR@GB gel beads were observed
 373 using SEM, as shown in **Fig. 4**. At a lower magnification of 75 \times , all five gel beads
 374 exhibited a generally spherical morphology, confirming the successful formation of
 375 structurally intact beads through Ca²⁺-mediated cross-linking of the pectin-starch
 376 matrix. However, their surfaces appeared rough, rugged, and partially shrunken, which

377 may be attributed to structural collapse caused by moisture loss during freeze-drying
378 (Bušić et al., 2018). At a higher magnification of 500×, a distinct “vein”-like network
379 structure was observed on the surface of PP@GB, which is characteristic of ionically
380 cross-linked hydrogels formed between Ca^{2+} and carboxylate groups in polysaccharide
381 chains (Qi et al., 2020). Subsequently, the incorporation of various starch-derived
382 materials into the pectin matrix led to significant structural changes in the gel beads. As
383 reported in our previous study, turmeric starch exhibited a flat oval shape, while starch
384 nanoparticles and complexes displayed a helical morphology (Zhu et al., 2025). Upon
385 integration into the pectin-based gel matrix, these starch components altered the bead
386 surface, resulting in a progressive reduction in surface wrinkles and protrusions.
387 Moreover, distinct morphological features corresponding to the respective starch
388 matrices were observed on the surfaces of the composite gel beads, indicating
389 successful embedding and uniform dispersion of starch-derived materials within the
390 pectin network.

391 Additionally, the internal cross-sectional structure of the gel beads was also
392 observed. All five formulations exhibited a laminar structure with irregular cavities,
393 which may be attributed to structural shrinkage and deformation during the freeze-
394 drying process (Li et al., 2021). Notably, PP@GB displayed relatively larger pores and
395 cavities, whereas the starch-containing composite gel beads exhibited a more uniform
396 honeycomb-like porous structure with smaller and densely packed pores. This tightly
397 interconnected microstructure suggests enhanced cross-linking among starch, pectin,
398 and Ca^{2+} , highlighting the role of starch-based fillers as structural modifiers that
399 promote the formation of a robust and compact gel network (Raza et al., 2024; Cortés-
400 Camargo et al., 2023). Dumitriu et al. (2011) previously demonstrated that increased
401 cross-linking density correlates with reduced pore size, resulting in a denser and more
402 mechanically stable hydrogel structure. Similarly, Lozano-Vazquez et al. (2015)
403 reported that the incorporation of modified tapioca starch into sodium alginate-based
404 gel beads acted as a reinforcing filler, enhancing structural integrity and promoting the
405 formation of a well-defined porous network. The presence of a well-developed porous
406 structure is also relevant to the hydration behavior of the gel systems. Porosity and

407 internal cavities have been associated with improved water penetration and retention
 408 capacity within the matrix, thereby contributing to enhanced water-holding properties
 409 (Paswan et al., 2024). These observations are consistent with the WHC and LF-NMR
 410 results, which collectively indicate that the composite gel bead formulations exhibit
 411 superior water retention capabilities compared to the pure pectin-based system.
 412 *3.6. Water holding capacity (WHC)*



413
 414 **Fig. 5.** Water holding capacity (A), swelling behavior (B), and water distribution
 415 profiles (C) of PP@GB, TS@GB, TSNC@GB, MTSNC@GB, and TS-CUR@GB gel
 416 beads. Different lowercase letters indicate significant differences ($P < 0.05$).

417 Water holding capacity (WHC) is a key functional property of hydrogel systems,
 418 reflecting the ability of the three-dimensional polymeric network to retain water. The
 419 WHC values of the five gel bead formulations were presented in **Fig. 5A**. As shown,
 420 the WHC of PP@GB was approximately 80%, while the WHC of TS@GB, TSNC@GB,
 421 and TS-CUR@GB increased to around 85% ($P < 0.05$). This improvement may be
 422 attributed to the enhanced ionic interactions between calcium ions and the carboxyl
 423 groups of pectin or hydroxyl groups of starch, which facilitate the formation of a more

424 compact hydrogel network capable of effectively entrapping water molecules (Bu et al.,
425 2022). Both the swelling rate (**Fig. 5B**) and texture analysis (**Fig. 7**) results can support
426 this trend. The reduced swelling rate, enhanced hardness and springiness of the
427 composite gel beads jointly indicate a denser, more cross-linked, and less porous
428 network structure, which effectively inhibits water diffusion and improves water-
429 holding capacity. In addition, similar findings have also been reported by Ren, Jiang, et
430 al. (2020) in polysaccharide-starch complex systems, who demonstrated that the
431 interaction between polysaccharides and starch granules can lead to greater repulsion
432 and retain more water molecules in the gel matrix, further supporting our conclusion.
433 Notably, the WHC of TS-CUR@GB reached 90.84% ($P<0.05$), representing an
434 increase of approximately 13.6% compared to PP@GB, suggesting that the
435 incorporation of the starch-curcumin complex further enhanced the water-holding
436 capacity of the gel beads. This enhancement may be attributed to the phenolic hydroxyl
437 groups of curcumin forming strong hydrogen bonds with both starch and pectin
438 molecules, leading to a more densely cross-linked and ordered microstructure that
439 entangles more water within the gel matrix (Wang et al., 2018). This high WHC is
440 crucial for the application of these beads as delivery carriers, as the retained water
441 molecules help to stabilize the interactions among the system components and maintain
442 the structural integrity of the bead throughout the delivery process, thereby protecting
443 the encapsulated bioactive compound (Li et al., 2024).

444 3.7. Swelling rate

445 The swelling behaviors of PP@GB, TS@GB, TSNC@GB, MTSNC@GB, and
446 TS-CUR@GB in deionized water were measured and presented in **Fig. 5B**. All five gel
447 beads exhibited similar swelling profiles, with a rapid increase in swelling rate during
448 the initial 60 min, followed by a gradual deceleration as equilibrium was approached.
449 This initial rapid uptake can be attributed to the immediate hydration of hydrophilic
450 functional groups present in both pectin and starch molecules, as well as the presence
451 of porous structures formed during the freeze-drying process, which facilitate efficient
452 water penetration and retention (Yang et al., 2024). A comparable swelling profile has
453 been observed in alginate-based gel beads by Li et al. (2021), who reported that the

454 swelling rates of all samples gradually increased within 6 h, reaching the highest
455 swelling rate after 6 h.

456 Among all formulations, PP@GB exhibited the highest swelling rate, which may
457 be attributed to its relatively loose gel structure and larger pores, as observed in the
458 SEM analysis (**Fig. 4**), facilitating enhanced water penetration and retention (Hu et al.,
459 2021). In contrast, the incorporation of various starch-based matrices resulted in a
460 significant decrease in the swelling rates of TS@GB, TSNC@GB, MTSNC@GB, and
461 TS-CUR@GB compared to PP@GB ($P<0.05$). This reduction is likely due to enhanced
462 cross-linking interactions among starch, pectin, and calcium ions, which promote
463 stronger intermolecular bonding and the formation of a more compact and ordered gel
464 network, thereby limiting water diffusion and reducing the overall swelling capacity
465 (Hu et al., 2021). A similar trend was reported by Chen et al. (2024), who found that
466 incorporating starch and protocatechuic acid into the shell layer of alginate-based gel
467 beads significantly reduced their swelling behavior. Notably, the mean swelling rate of
468 TS-CUR@GB was slightly lower than that of the other composite groups, although the
469 differences were not all statistically significant. This trend indicates that the presence
470 of curcumin may partially weaken the repulsive force between carboxyl groups, thereby
471 reducing the expansion of hydrogel beads and resulting in a lower swelling
472 phenomenon (Chen et al., 2024; Wang et al., 2021). This reduced swelling behavior is
473 consistent with the SEM observation, gel beads with a lower swelling rate exhibited
474 denser and more uniform pore morphology (**Fig. 4**), thus restricting the penetration of
475 water molecules. Meanwhile, the increasing trend in mechanical hardness (**Fig. 7A**)
476 also provided supportive observations for a more robust network structure and a higher
477 degree of cross-linking, although this difference did not reach statistical significance.
478 These findings are consistent with previous results that gel beads with lower swelling
479 rates typically exhibit denser microstructures, which can enhance mechanical stability
480 and shape retention (Su et al., 2023). In summary, our findings demonstrated that the
481 integration of starch and bioactive compounds can effectively modulate the
482 microstructure and swelling properties of pectin gel beads, offering promising potential
483 for controlled release applications in both food and biomedical fields.

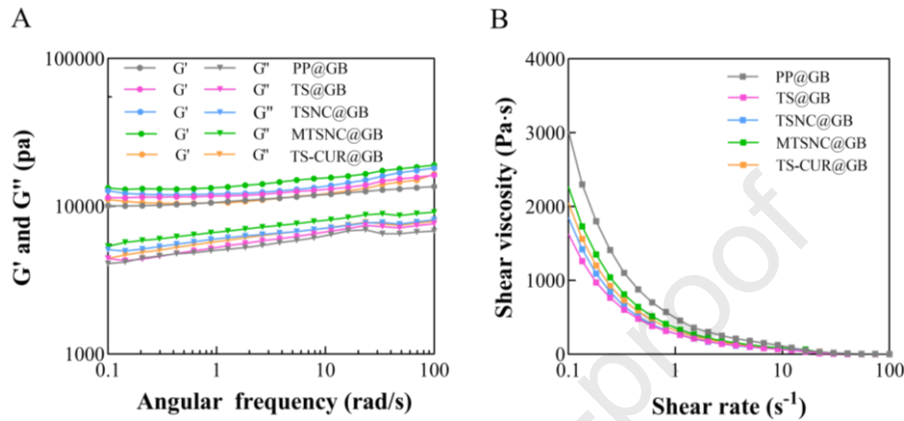
484 3.8. Low-field nuclear magnetic resonance (LF-NMR) analysis

485 Water distribution within hydrogel matrices plays a critical role in determining
486 their structural properties, stability, and functional performance. To investigate the
487 water distribution within the gel networks, LF-NMR was employed, with the transverse
488 relaxation time (T_2) serving as a highly sensitive indicator of water molecule dynamics
489 and a key parameter reflecting the physical state of water (Ren, Rong, et al., 2020). The
490 water migration behavior of PP@GB, TS@GB, TSNC@GB, MTSNC@GB, and TS-
491 CUR@GB was analyzed using T_2 relaxation measurements obtained by LF-NMR, as
492 shown in **Fig. 5C**. The NMR relaxation curves of all samples exhibited three distinct
493 peaks within the relaxation time range of 0.1–10000 ms, corresponding to three
494 different states of water. Specifically, T_{21} (1–10 ms) corresponds to bound water tightly
495 associated with the polymer matrix, T_{22} (10–100 ms) represents immobilized or fixed
496 water trapped within the gel network, and T_{23} (>100 ms) reflects free water with high
497 mobility (Wang et al., 2024). Moreover, the peak area under each relaxation component
498 reflects the relative proportion of the corresponding water state.

499 Among all samples, the T_{22} peak was the most prominent, indicating that
500 immobilized water constituted the dominant fraction within the gel matrix, followed by
501 bound water, while free water accounted for the smallest proportion. Notably, PP@GB
502 exhibited the lowest proportion of immobilized water and a relatively higher content of
503 free water, which is consistent with its relatively porous and loosely structured network,
504 resulting in greater water mobility and reduced water retention capacity. In contrast, the
505 starch-containing gel beads showed a shift toward more tightly bound water, indicating
506 stronger interactions between water molecules and the polymer network due to
507 enhanced cross-linking and hydrogen bonding within the gel network, which restricted
508 water mobility and reduced the amount of diffusible free water (Jiang et al., 2022). This
509 observation was further supported by the reduced T_{23} peak area observed in the
510 composite gel beads, indicating a lower content of free water. Moreover, these findings
511 are consistent with the WHC analysis results shown in **Fig. 5A**, further demonstrating
512 that the composite gel system maintains a high water-holding capacity due to the
513 restricted movement of water molecules within the gel matrix. The consistency between

514 T₂ relaxation behavior and WHC measurements highlights the role of starch in
 515 modifying the hydrogel's architecture, thereby improving its capacity to entrap and
 516 stabilize water. These findings are supported by previous reports on polysaccharide-
 517 starch composite systems (Jiang et al., 2024; Ye et al., 2018).

518 3.9. Rheological properties analysis



519
 520 **Fig. 6.** Dynamic modulus variation curves (A) and shear viscosity variation curves (B)
 521 of PP@GB, TS@GB, TSNC@GB, MTSNC@GB, and TS-CUR@GB gel beads.

522 Dynamic rheological properties provide critical insights into the viscoelastic
 523 behavior of materials under mechanical stress, offering valuable guidance for process
 524 optimization and quality control in food and pharmaceutical applications (Qiu et al.,
 525 2024). In dynamic oscillatory testing, the storage modulus (G') reflects the elastic
 526 behavior of a material, whereas the loss modulus (G'') represents its viscous
 527 characteristics. The variation of G' and G'' with angular frequency for PP@GB,
 528 TS@GB, TSNC@GB, MTSNC@GB, and TS-CUR@GB was presented in **Fig. 6A**.
 529 Across the entire angular frequency range, G' remained consistently higher than G'' for
 530 all samples, indicating that the gel beads exhibited predominantly elastic behavior and
 531 displayed typical characteristics of gels (Xiao et al., 2022). Among all samples, PP@GB
 532 exhibited the lowest G' and G'' values, suggesting a relatively weak gel network. This
 533 can be attributed to the pure pectin system, which relies solely on calcium ion-mediated
 534 cross-linking of pectin molecules, resulting in a less dense and structurally weaker
 535 network (Almeida et al., 2021). However, the incorporation of various starch-based
 536 fillers significantly enhanced both G' and G'' to varying extents, reflecting improved
 537 structural rigidity and viscoelastic performance. This improvement can be attributed to

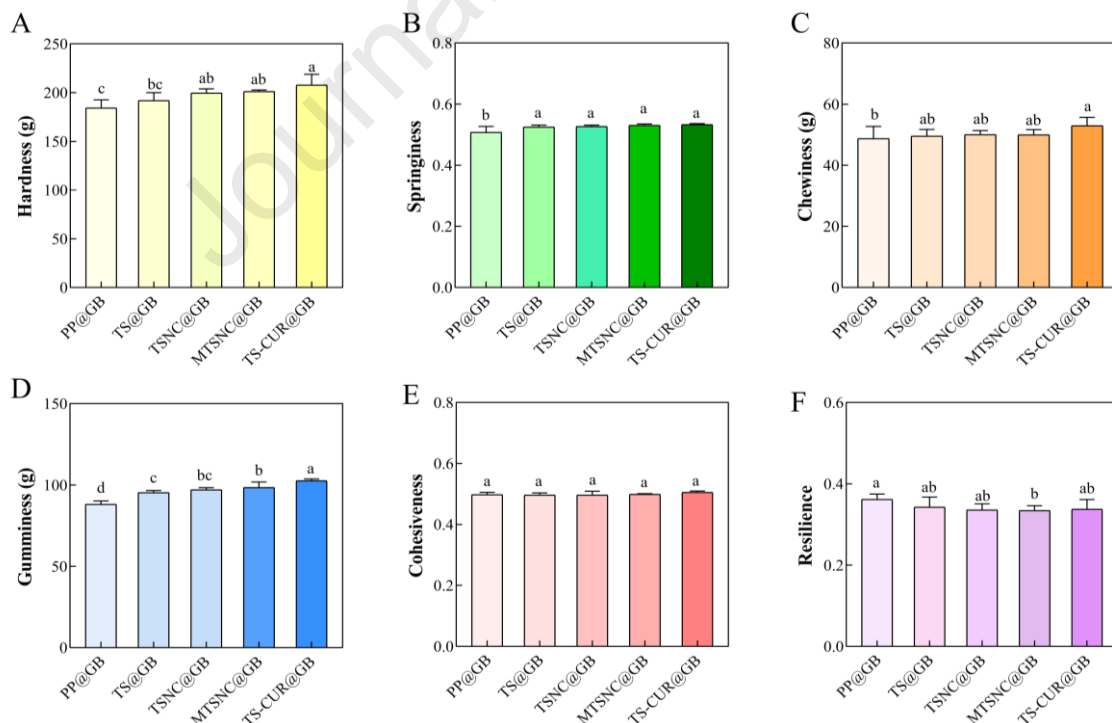
538 stronger cross-linking among starch, pectin, and calcium ions, which contribute to a
539 more compact and ordered gel matrix. A similar trend was observed by Li et al. (2024),
540 who demonstrated that the addition of sodium alginate to a pectin-based gel increased
541 the network density and consequently enhanced both G' and G'' . Notably, the G' and G''
542 values of TS@GB, TSNC@GB, and MTSNC@GB increased progressively compared
543 to PP@GB, as presented in **Table S1** in the supplementary materials. This sequential
544 enhancement may be attributed to that as starch filler evolved from its natural form, to
545 the nanoparticle state, and then to the modified nanoparticle form, the binding sites and
546 intermolecular among starch fillers, pectin molecules, and calcium ions increased
547 successively, promoting the formation of calcium ion-mediated ionic crosslinking and
548 leading to a more ordered and densely cross-linked gel structure (Wang et al., 2018).
549 Interestingly, TS-CUR@GB exhibited lower G' and G'' values than MTSNC@GB,
550 suggesting that the incorporation of curcumin reduced the dynamic modulus. We
551 speculated that the reason might be that the incorporation of curcumin interfered with
552 the original cross-linking process of starch, pectin matrix, and calcium ions, reducing
553 the fluidity of polymer chain segments, thereby resulting in a decline in the overall
554 viscoelastic response ability of the material under minor deformation, manifested as a
555 decrease in modulus. This inference is consistent with the conclusion reported by Xiao
556 et al. (2023) that curcumin may affect the binding of starch to other matrix components
557 through molecular competitive interactions, hinder the cross-linking and entanglement
558 of starch molecular chains, reduce the number of effective junction regions within the
559 gel network, and ultimately diminish the viscoelastic strength of the system. The power-
560 law model fitting parameters for the frequency dependence of G' and G'' further
561 corroborated these observations (**Table S2**). The flow behavior indices (n' and n'') and
562 the ratio k''/k' for all samples were substantially less than 1, collectively confirming
563 typical “solid-like” gel behavior (Zhang et al., 2021). Within this framework, PP@GB
564 exhibited the lowest stiffness coefficients ($k' = 10.80 \text{ kPa}\cdot\text{s}^n$, $k'' = 5.08 \text{ kPa}\cdot\text{s}^n$),
565 consistent with a sparse Ca^{2+} -pectin network. The incorporation of starch fillers led to
566 a stepwise increase in both k' and k'' ($P < 0.05$), indicating enhanced cross-linking
567 density and the formation of a more rigid gel structure.

568 Shear viscosity is defined as the resistance of a fluid to flow under applied shear
569 stress. The steady-state shear viscosity profiles of PP@GB, TS@GB, TSNC@GB,
570 MTSNC@GB, and TS-CUR@GB are shown in **Fig. 6B**. All samples exhibited a
571 progressive decrease in viscosity with increasing shear rate, demonstrating shear-
572 thinning behavior characteristic of pseudoplastic fluids (Ren, Jiang, et al., 2020). This
573 behavior can be attributed to the disruption of the internal gel network under shear
574 forces, resulting in the transition of molecules from a structured network to a more
575 fluid-like state, thereby reducing the apparent viscosity (Li et al., 2024). Similar
576 rheological behavior has been reported in other starch-based and hydrogel systems
577 (Chen et al., 2014). Among all samples, PP@GB exhibited the highest shear viscosity,
578 indicating that greater shear stress is required to disrupt the pectin gel matrix. This may
579 be due to the high intrinsic viscosity of pectin, which results in extensive chain
580 entanglements that confer strong resistance to deformation (Jiang et al., 2015). In
581 contrast, the shear viscosities of all starchy gel beads (TS@GB, TSNC@GB,
582 MTSNC@GB, and TS-CUR@GB) were lower than that of PP@GB (**Table S3**),
583 indicating that the starch fillers, as the “diluent phase” incorporated into the pectin
584 network, had a dominant weakening effect on the overall viscosity, manifested as a
585 decrease in viscosity. It was further observed that the viscosities of TS@GB,
586 TSNC@GB, and MTSNC@GB showed a gradually increasing trend. This may be due
587 to as the starch filler evolved from its natural form to nanoparticles and then to modified
588 nanoparticles, the interaction among starch, pectin, and calcium ions gradually
589 strengthened, and the structural integrity of the gel network gradually improved,
590 thereby enhancing the shear resistance. Notably, TS-CUR@GB exhibited lower shear
591 viscosity than MTSNC@GB, indicating that the incorporation of curcumin further
592 weakened the shear resistance of the gel network. Such interactions may reduce
593 physical entanglement nodes among starch molecular chains, leading to a less organized
594 structure and reduced resistance to shear stress (Wang et al., 2018). The parameters
595 obtained through power-law model fitting further revealed the mechanism of the above
596 changes (**Table S4**). The correlation coefficients (R^2) of all samples were greater than
597 0.99, indicating that the power law equation can be used to fit the steady-state shear

598 curve. The flow behavior index (n) reflects a fluid's deviation from Newtonian behavior,
 599 where $n=1$ indicates a Newtonian fluid and $n<1$ characterizes a pseudoplastic (shear-
 600 thinning) fluid. The obtained n values of all formulations were less than 1, further
 601 verifying the shear-thinning characteristics of these systems (Lin et al., 2021). The
 602 variation of the consistency coefficient K value reflects the strength of the network
 603 structure. The K value of PP@GB was the highest (474.60 Pa·s ^{n}), confirming the
 604 stronger chain entanglement and flow resistance in the pure pectin network. However,
 605 after the addition of starch derivatives, the K values of the composite gel beads
 606 decreased significantly to varying degrees ($P<0.05$), demonstrating that the
 607 introduction of starch fillers weakened the network continuity.

608 In conclusion, rheological analysis revealed that the composite gel beads possess
 609 both excellent mechanical strength (high dynamic modulus) and superior processing
 610 fluidity (low shear viscosity), which provides an ideal material basis for the controllable
 611 processing and targeted delivery of functional gel products.

612 3.10. Textural properties



613

614 **Fig. 7.** Texture properties of PP@GB, TS@GB, TSNC@GB, MTSNC@GB, and TS-
 615 CUR@GB gel beads. Different lowercase letters indicate significant differences
 616 ($P<0.05$).

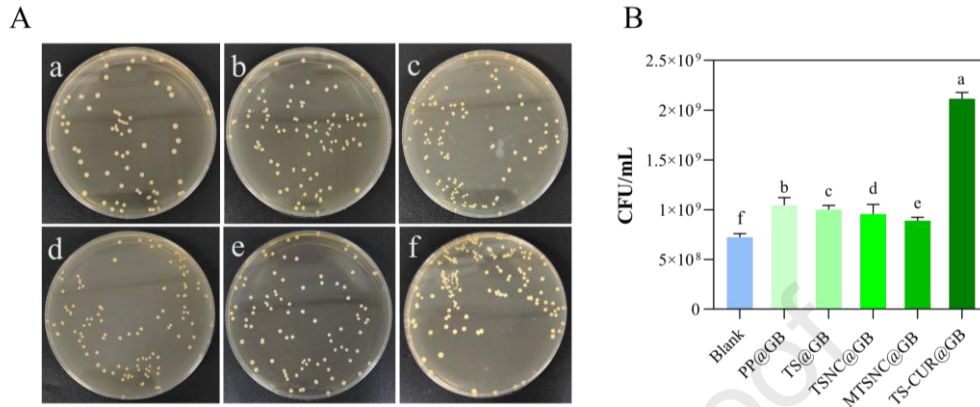
617 Texture analysis offers valuable insight into the mechanical and structural
618 characteristics of gel systems. The texture properties, including hardness, springiness,
619 chewiness, gumminess, cohesiveness, and resilience, of PP@GB, TS@GB,
620 TSNC@GB, MTSNC@GB, and TS-CUR@GB were evaluated and shown in **Fig. 7**.
621 Compared to PP@GB, the hardness of TS@GB, TSNC@GB, MTSNC@GB, and TS-
622 CUR@GB increased by 4.16%, 8.40% ($P<0.05$), 9.23% ($P<0.05$), and 12.75%
623 ($P<0.05$), respectively. This enhancement can be attributed to the formation of
624 hydrogen bonds between the hydroxyl groups of starch and pectin molecules, which
625 strengthen the gel network and enhance the mechanical integrity of the beads (Bu et al.,
626 2023). Notably, TS-CUR@GB exhibited the highest hardness, which may be attributed
627 to the incorporation of curcumin that establishes strong hydrogen bonding interactions
628 with both starch and pectin molecules, thereby reinforcing the structural integrity and
629 stability of the gel matrix (Wang et al., 2018).

630 Similar trends were observed for springiness, chewiness, and gumminess.
631 Compared to PP@GB, the enhanced interactions between starch and pectin in the
632 composite gel beads contribute to a denser gel network, which increases water-holding
633 capacity and helps maintain the softness and extensibility of the gel beads, thereby
634 enhancing their springiness (Wang et al., 2018). The simultaneous increase in hardness
635 and springiness indicates an enhanced gel network structure. This network possesses
636 higher mechanical strength and greater elasticity, requiring more energy for
637 deformation, which is consistent with the increased chewiness and gumminess. In
638 contrast, the resilience of TS@GB, TSNC@GB, MTSNC@GB, and TS-CUR@GB
639 exhibited a decreasing trend compared to PP@GB. This reduction may be due to the
640 interference of starch-based fillers with the alignment and cross-linking of pectin chains,
641 potentially hindering the molecular rearrangements required for structural recovery
642 after deformation. Consequently, the ability of the gel beads to recover their original
643 shape upon removal of mechanical stress was diminished (Wang et al., 2021).

644 Overall, the texture properties are consistent with the microstructure morphology
645 (**Fig. 4**) and swelling properties (**Fig. 5B**), jointly indicating that the addition of starch
646 derivatives and curcumin enhances the mechanical strength and water retention of

647 pectin gels, which provides a comprehensive material basis for designing functional
648 gels with customized performance, suitable for food and pharmaceutical applications.

649 3.11. *In vitro* probiotic activity evaluation



650
651 **Fig. 8.** Colonization of *Lactiplantibacillus plantarum* Lp3a at a concentration of 10^{-6}
652 after different sample treatments (A): Blank (a), PP@GB (b), TS@GB (c), TSNC@GB
653 (d), MTSNC@GB (e), and TS-CUR@GB (f). Effect of different samples on the
654 proliferation of *Lactiplantibacillus plantarum* Lp3a (B). Different lowercase letters
655 indicate significant differences ($P < 0.05$).

656 *Lactiplantibacillus plantarum* is a common and representative probiotic strain that
657 has been demonstrated to stimulate the growth of intestinal microbiota, inhibit the
658 proliferation of harmful microorganisms, and reduce the incidence of gastrointestinal
659 diseases, thereby conferring multiple health benefits (Razavi et al., 2021). Previous
660 studies have shown that pectin can be fermented by colonic microbiota and exerts
661 prebiotic effects, promoting the growth of beneficial bacteria (Zhang et al., 2025).
662 Therefore, in this study, *Lactiplantibacillus plantarum* Lp3a was selected as the
663 representative model strain to systematically evaluate the prebiotic potential of the five
664 gel bead formulations.

665 As shown in **Fig. 8B**, in the carbon-source-free medium, the colony count in the
666 control group was 7.23×10^8 CFU/mL, while the colony counts of PP@GB, TS@GB,
667 TSNC@GB, MTSNC@GB, and TS-CUR@GB groups significantly increased to 1.05
668 $\times 10^9$, 1.00×10^9 , 9.57×10^8 , 8.90×10^8 , and 2.12×10^9 CFU/mL ($P < 0.05$), respectively.
669 These results indicated that all five gel beads exhibited prebiotic activity by positively
670 influencing the growth of *Lactiplantibacillus plantarum* Lp3a. Notably, the colony

671 counts in the PP@GB, TS@GB, TSNC@GB, and MTSNC@GB groups followed a
672 gradually decreasing trend. This may be attributed to the relatively low crosslinking
673 degree in the pure pectin gel beads (PP@GB), which allows for easier water absorption,
674 swelling, and even structural disintegration, thereby facilitating the decomposition and
675 utilization of the gel matrix by microorganisms and resulting in higher colony counts.
676 In contrast, the cross-linking density increases progressively in TS@GB, TSNC@GB,
677 and MTSNC@GB, leading to more compact structures, restricting water penetration
678 and swelling capacity, thereby reducing the accessibility of microbial to the prebiotic
679 components and consequently weakening the stimulatory effect on the growth of
680 *Lactiplantibacillus plantarum* Lp3a.

681 Interestingly, the TS-CUR@GB group exhibited a significantly higher colony
682 count, reaching 2.92 times that of the control group ($P<0.05$). Previous studies have
683 indicated that curcuminoids possess prebiotic activity and can promote the proliferation
684 of beneficial gut bacteria while modulating the composition of the intestinal microbiota
685 (Bhola et al., 2024). Therefore, the significant increase in probiotic counts in the TS-
686 CUR@GB group may be attributed to two potential mechanisms. On the one hand,
687 curcumin itself may directly regulate gut microbiota and stimulate the growth of
688 *Lactiplantibacillus plantarum* Lp3a. On the other hand, the strong interaction between
689 curcumin and pectin molecules may generate a synergistic effect, potentially enhance
690 the bioavailability or metabolic accessibility of the prebiotic substrate, and further
691 promote microbial growth (Li et al., 2022). In summary, integrating curcumin into a
692 pectin-based delivery system not only helps preserve its original bioactive properties
693 but also enhances its proliferation-promoting effect on representative probiotic strains.
694 More importantly, this dual functionality highlights the potential of the prebiotic
695 activity of such composite systems, providing an effective material basis and strategic
696 direction for the development of new formulations with enhanced prebiotic functions.

697 **4. Conclusions**

698 In this study, pectin/starch composite gel beads were successfully prepared using
699 a simple ionic gelation method, and their structural characteristics, physicochemical
700 properties, and functional performance were systematically investigated. The results

701 indicated that all five gel beads exhibited well-defined spherical morphologies with
702 diameters ranging from 3.3 to 3.4 mm. Microstructural analysis revealed that the
703 internal structure of the gel beads was composed of irregular cavities and a layered
704 morphology, and the incorporation of starch derivatives enhanced structural
705 compactness, resulting in a denser and uniformly distributed porous architecture. FTIR
706 and XRD analysis confirmed increased intermolecular interactions and reduced
707 crystallinity upon starch integration. TGA results indicated enhanced thermal stability
708 in the starch-containing gel systems. WHC and LF-NMR analysis demonstrated that
709 the addition of starch matrix significantly improved moisture retention by 6.06%–
710 15.44%, while reducing the swelling rate by 26.16%–37.02%. Texture profile and
711 rheological testing further revealed significant improvements in hardness (4.16%–
712 12.75%), springiness (3.40%–4.96%), chewiness (1.71%–8.63%), and gumminess
713 (8.09%–16.51%), along with enhanced viscoelastic behavior. Furthermore, all five gel
714 bead formulations exhibited favorable prebiotic activity, significantly promoting the
715 growth of *Lactiplantibacillus plantarum* Lp3a. Notably, the TS-CUR@GB formulation,
716 which incorporated curcumin, demonstrated a synergistic enhancement in probiotic
717 proliferation. Overall, starch-based derivatives with gradient-enhanced structure and
718 function exhibited a gradually enhancing regulatory effect on the structural properties
719 of pectin gel beads, especially those enriched with the bioactive component curcumin,
720 demonstrating a dual enhancement in both structural characteristics and functional
721 performance. These findings provide a comprehensive understanding of the mechanism
722 by which starch-based fillers modulate pectin gelation and offer valuable insights into
723 the design and development of novel functional gel bead formulations with enhanced
724 performance.

725 However, this study has certain limitations that should be acknowledged. Although
726 the current findings initially confirmed that these gel beads have a growth-promoting
727 effect on a specific model strain, experiments on a single strain are not sufficient to
728 fully reflect their actual role in the complex intestinal flora. In subsequent studies, more
729 strains should be introduced to systematically evaluate the effects of gel beads on the
730 proliferation of multiple probiotics, thereby comprehensively assessing their prebiotic

731 efficacy. In addition, this gel bead system can be further applied in real food
732 environments (such as yogurt or beverage systems) to evaluate its impact on the
733 physicochemical properties and sensory attributes of products, thereby providing a
734 theoretical basis and technical foundation for practical food applications.

735 **Acknowledgement**

736 This work was supported by the Key Technology Research and Development
737 Program of Shandong Province, China (2024TZZXD007).

738 **References**

- 739 Almeida, S. F., Silva, G. K. C., Toledo, M. N. A., & Sato, A. C. K. (2021). Modulating
740 porosity and mechanical properties of pectin hydrogels by starch addition. *Journal*
741 *of Food Science and Technology*, *58*, 302–310. [https://doi.org/10.1007/s13197-](https://doi.org/10.1007/s13197-020-04543-x)
742 [020-04543-x](https://doi.org/10.1007/s13197-020-04543-x)
- 743 Bu, K. X., Huang, D. J., Li, D. P., & Zhu, C. H. (2022). Encapsulation and sustained
744 release of curcumin by hawthorn pectin and Tenebrio Molitor protein composite
745 hydrogel. *International Journal of Biological Macromolecules*, *222*, 251–261.
746 <https://doi.org/10.1016/j.ijbiomac.2022.09.145>
- 747 Bu, Q. Y., Chen, Y., Ding, Y., Zhang, K. X., Li, Y. C., You, X. Y., & Zhao, G. P. (2023).
748 Preparation and characterization of tea polyphenol composite microspheres
749 encapsulated using sodium alginate and crosslinked starch. *LWT-Food Science and*
750 *Technology*, *184*, 114888. <https://doi.org/10.1016/j.lwt.2023.114888>
- 751 Bušić, A., Belščak-Cvitanović, A., Cebin, A. V., Karlović, S., Kovač, V., Igor Špoljarić,
752 Mršić, G., & Komes, D. (2018). Structuring new alginate network aimed for
753 delivery of dandelion (*Taraxacum officinale* L.) polyphenols using ionic gelation
754 and new filler materials. *Food Research International*, *111*, 244–255.
755 <https://doi.org/10.1016/j.foodres.2018.05.034>
- 756 Bhola, J., & Bhadekar, R. (2024). Prebiotic effect of daily dietary polyphenols and
757 oligosaccharides on *lactobacillus* species. *Bioactive Carbohydrates and Dietary*
758 *Fibre*, *31*, 100407. <https://doi.org/10.1016/j.bcdf.2024.100407>
- 759 Cai, R., Pan, S. Y., Li, R. X., Xu, X. Y., Pan, S. Y., & Liu, F. X. (2022). Curcumin
760 loading and colon release of pectin gel beads: Effect of different de-esterification

- 761 method. *Food Chemistry*, 389, 133130.
762 <https://doi.org/10.1016/j.foodchem.2022.133130>
- 763 Chan, E. S., Wong, S. L., Lee, P. P., Lee, J. S., Ti, T. B., Zhang, Z. B., Poncelet, D.,
764 Ravindra, P., Phan, S. H., & Yim, Z. H. (2011). Effects of starch filler on the
765 physical properties of lyophilized calcium-alginate beads and the viability of
766 encapsulated cells. *Carbohydrate Polymers*, 83, 225–232.
767 <https://doi.org/10.1016/j.carbpol.2010.07.044>
- 768 Chen, N., Feng, Z. J., Gao, H. X., He, Q., & Zeng, W. C. (2024). Core-shell structured
769 alginate-based hydrogel beads modified by starch and protocatechuic acid:
770 Preparation, characterization, phenolic slow release and stable antioxidant
771 potential. *Food Chemistry*, 459, 140389.
772 <https://doi.org/10.1016/j.foodchem.2024.140389>
- 773 Chen, L., Tong, Q. Y., Ren, F., & Zhu, G. L. (2014). Pasting and rheological properties
774 of rice starch as affected by pullulan. *International Journal of Biological*
775 *Macromolecules*, 66, 325–331. <https://doi.org/10.1016/j.ijbiomac.2014.02.052>
- 776 Cortés-Camargo, S., Román-Guerrero, A., Alvarez-Ramirez, J., Alpizar-Reyes, E.,
777 Velázquez-Gutiérrez, S. K., & Pérez-Alonso, C. (2023). Microstructural influence
778 on physical properties and release profiles of sesame oil encapsulated into sodium
779 alginate-tamarind mucilage hydrogel beads. *Carbohydrate Polymer Technologies*
780 *and Applications*, 5, 100302. <https://doi.org/10.1016/j.carpta.2023.100302>
- 781 Dahal, P., & Janaswamy, S. (2024). Hydrocolloid-based nutraceutical delivery systems:
782 Potential of κ -carrageenan hydrogel beads for sustained release of curcumin. *Food*
783 *Research International*, 183, 114223.
784 <https://doi.org/10.1016/j.foodres.2024.114223>
- 785 Dumitriu, R. P., Mitchell, G. R., & Vasile, C. (2011). Rheological and thermal behaviour
786 of poly (*N*-isopropylacrylamide)/alginate smart polymeric networks. *Polymer*
787 *International*, 60, 1398–1407. <https://doi.org/10.1002/pi.3093>
- 788 Feltrea, G., Almeida, F. S., Sato, A. C. K., Dacanalb, G. C., & Hubinger, M. D. (2020).
789 Alginate and corn starch mixed gels: Effect of gelatinization and amylose content
790 on the properties and *in vitro* digestibility. *Food Research International*, 132,

- 791 109069. <https://doi.org/10.1016/j.foodres.2020.109069>
- 792 Günter, E. A., Martynov, V. V., Ananchenko, B. A., Martinson, E. A., Litvinets, S. G.
793 (2022). The gel strength and swelling in the gastrointestinal environment of
794 pectin/ κ -carrageenan gel particles based on pectins with different degrees of
795 methylesterification. *Materials Today Communications*, 33, 104986.
796 <https://doi.org/10.1016/j.mtcomm.2022.104986>
- 797 Han, X. Y., Ma, P., Shen, M. Y., Wen, H. L., & Xie, J. H. (2023). Modified porous
798 starches loading curcumin and improving the free radical scavenging ability and
799 release properties of curcumin. *Food Research International*, 168, 112770.
800 <https://doi.org/10.1016/j.foodres.2023.112770>
- 801 Hu, M., Du, X. Q., Liu, G. N., Huang, Y. Y., Qi, B. K., Li, Y. (2021). Sodium
802 alginate/soybean protein-epigallocatechin-3-gallate conjugate hydrogel beads:
803 evaluation of structural, physical, and functional properties. *Food & Function*,
804 12(24), 12347–12361. <https://doi.org/10.1039/d1fo03099j>
- 805 Jiang, B., Li, W., Hu, X., Wu, J., & Shen, Q. (2015). Rheology of mung bean starch
806 treated by high hydrostatic pressure. *International Journal of Food Properties*, 18,
807 81–92. <https://doi.org/10.1080/10942912.2013.819363>
- 808 Jiang, X. Y., Li, L., Yan, J. N., Zhang, L. C., Wang, C., Lai, B., & Wu, H. T. (2024).
809 Characterization of hydrogel beads constructed from gelatinized lotus rhizome
810 starch and sodium alginate by calcium cross-linking. *Food Hydrocolloids*, 154,
811 110102. <https://doi.org/10.1016/j.foodhyd.2024.110102>
- 812 Jiang, X., Gu, Y., Zhang, L., Sun, J., Yan, J., & Wang, C. (2023). Physicochemical
813 properties of granular and gelatinized lotus rhizome starch with varied proximate
814 compositions and structural characteristics. *Foods*, 12(23), 4330.
815 <https://doi.org/10.3390/foods12234330>
- 816 Lee, T., & Chang, Y. H. (2020). Structural, physicochemical, and in-vitro release
817 properties of hydrogel beads produced by oligochitosan and de-esterified pectin
818 from yuzu (*Citrus junos*) peel as a quercetin delivery system for colon target. *Food*
819 *Hydrocolloids*, 108, 106086. <https://doi.org/10.1016/j.foodhyd.2020.106086>
- 820 Lee, Y. E., Kang, Y. R., & Chang, Y. H. (2023). Effect of pectic oligosaccharide on

- 821 probiotic survival and physicochemical properties of hydrogel beads for synbiotic
822 encapsulation of *Lactobacillus bulgaricus*. *Food Bioscience*, *51*, 102260.
823 <https://doi.org/10.1016/j.fbio.2022.102260>
- 824 Lenie, M. D. R., Ahmadzadeh, S., Bockstaele, F. V., & Ubeyitogullari, A. (2024).
825 Development of a pH-responsive system based on starch and alginate-pectin
826 hydrogels using coaxial 3D food printing. *Food Hydrocolloids*, *153*, 109989.
827 <https://doi.org/10.1016/j.foodhyd.2024.109989>
- 828 Li, H., Gao, Z. X., Xu, J. J., Sun, W., Wu, J. R., Zhu, L., Gao, M. J., & Zhan, X. B.
829 (2022). Encapsulation of polyphenols in pH-responsive micelles self-assembled
830 from octenyl-succinylated curdlan oligosaccharide and its effect on the gut
831 microbiota. *Colloids and Surfaces B: Biointerfaces*, *219*, 112857.
832 <https://doi.org/10.1016/j.colsurfb.2022.112857>
- 833 Li, Q., Duan, M. R., Hou, D., Chen, X. Q., Shi, J. L., & Zhou, W. (2021). Fabrication
834 and characterization of Ca (II)-alginate-based beads combined with different
835 polysaccharides as vehicles for delivery, release and storage of tea polyphenols.
836 *Food Hydrocolloids*, *112*, 106274. <https://doi.org/10.1016/j.foodhyd.2020.106274>
- 837 Li, Y. H., Zhang, C., Li, S. Y., Zhu, Z. Z., Wang, X. H., & Cravotto, G. (2024).
838 Improving complexation of puerarin with kudzu starch by various ultrasonic
839 pretreatment: Interaction mechanism analysis. *Ultrasonics Sonochemistry*, *111*,
840 107095. <https://doi.org/10.1016/j.ultsonch.2024.107095>
- 841 Li, Z. X., Geng, Y. X., Bu, K. X., Chen, Z. T., Xu, K., & Zhu, C. H. (2024). Construction
842 of a pectin/sodium alginate composite hydrogel delivery system for improving the
843 bioaccessibility of phycocyanin. *International Journal of Biological*
844 *Macromolecules*, *269*, 131969. <https://doi.org/10.1016/j.ijbiomac.2024.131969>
- 845 Liu, R., Ci, X. M., Liu, L. L., Wang, X. T., Rifky, M., Liu, R., Sui, W. J., Wu, T., &
846 Zhang, M. (2024). Chitosan entrapping of sodium alginate/*Lycium barbarum*
847 polysaccharide gels for the encapsulation, protection and delivery of
848 *Lactiplantibacillus plantarum* with enhanced viability. *International Journal of*
849 *Biological Macromolecules*, *260*, 129615.
850 <https://doi.org/10.1016/j.ijbiomac.2024.129615>

- 851 Lopes, M. M., Oliveira-Paiva, C. A., & Farinas, C. S. (2023). Modification of
852 pectin/starch-based beads with additives to improve *Bacillus subtilis*
853 encapsulation for agricultural applications. *International Journal of Biological*
854 *Macromolecules*, 246, 125646. <https://doi.org/10.1016/j.ijbiomac.2023.125646>
- 855 Lozano-Vazquez, G., Lobato-Calleros, C., Escalona-Buendia, H., Chavez, G., Alvarez-
856 Ramirez, J., & Vernon-Carter, E. J. (2015). Effect of the weight ratio of alginate-
857 modified tapioca starch on the physicochemical properties and release kinetics of
858 chlorogenic acid containing beads. *Food Hydrocolloids*, 48, 301–311.
859 <https://doi.org/10.1016/j.foodhyd.2015.02.032>
- 860 Lin, S. Y., Liu, X. E., Cao, Y., Liu, S. C., Deng, D. W., Zhang, J. S., & Huang, G. H.
861 (2021). Effects of xanthan and konjac gums on pasting, rheology, microstructure,
862 crystallinity and *in vitro* digestibility of mung bean resistant starch. *Food*
863 *Chemistry*, 339, 128001. <https://doi.org/10.1016/j.foodchem.2020.128001>
- 864 Paswan, M., Chandel, A. K. S., Malek, N. I., & Dholakiya, B. Z. (2024). Preparation of
865 sodium alginate/Cur-PLA hydrogel beads for curcumin encapsulation.
866 *International Journal of Biological Macromolecules*, 254, 128005.
867 <https://doi.org/10.1016/j.ijbiomac.2023.128005>
- 868 Qi, X. X., Simsek, S., & Chen, B. C. (2020). Alginate-based double-network hydrogel
869 improves the viability of encapsulated probiotics during simulated sequential
870 gastrointestinal digestion: Effect of biopolymer type and concentrations.
871 *International Journal of Biological Macromolecules*, 165, 1675–1685.
872 <https://doi.org/10.1016/j.ijbiomac.2020.10.028>
- 873 Qiu, Z. C., Li, L. Y., Zhu, W. Q., Qiao, X. G., Zheng, Z. J., & Sun-Waterhouse, D. X.
874 (2024). Pectins rich in RG-I and galactose extracted from garlic pomace:
875 Physicochemical, structural, emulsifying and antioxidant properties. *Food*
876 *Hydrocolloids*, 149, 109559. <https://doi.org/10.1016/j.foodhyd.2023.109559>
- 877 Raza, H., Zhou, Q., Cheng, K. W., He, J. Y., & Wang, M. F. (2024). Synergistic impact
878 of ultrasound-high pressure homogenization on the formation, structural properties,
879 and slow digestion of the starch-phenolic acid complex. *Food Chemistry*, 445,
880 138785. <https://doi.org/10.1016/j.foodchem.2024.138785>

- 881 Razavi, S., Janfaza, S., Tasnim, N., Gibson, D. L., & Hoorfar, M. (2021).
882 Microencapsulating polymers for probiotics delivery systems: Preparation,
883 characterization, and applications. *Food Hydrocolloids*, *120*, 106882.
884 <https://doi.org/10.1016/j.foodhyd.2021.106882>
- 885 Reichembach, L. H., Petkowicz, C. L. O., Guerrero, P., & Caba, K. (2024). Pectin and
886 pectin/chitosan hydrogel beads as coffee essential oils carrier systems. *Food*
887 *Hydrocolloids*, *151*, 109814. <https://doi.org/10.1016/j.foodhyd.2024.109814>
- 888 Ren, Y. M., Jiang, L., Wang, W. J., Xiao, Y. H., Liu, S. C., Luo, Y., Shen, M. Y., & Xie,
889 J. H. (2020). Effects of Mesona chinensis Benth polysaccharide on
890 physicochemical and rheological properties of sweet potato starch and its
891 interactions. *Food Hydrocolloids*, *99*, 105371.
892 <https://doi.org/10.1016/j.foodhyd.2019.105371>
- 893 Ren, Y. M., Rong, L. Y., Shen, M. Y., Liu, W. M., Xiao, W. H., Luo, Y., & Xie, J. H.
894 (2020). Interaction between rice starch and Mesona chinensis Benth
895 polysaccharide gels: Pasting and gelling properties. *Carbohydrate Polymers*, *240*,
896 116316. <https://doi.org/10.1016/j.carbpol.2020.116316>
- 897 Rohman, S., Kaewtatip, K., Kantachote, D., & Tantirungkij, M. (2021). Encapsulation
898 of *Rhodopseudomonas palustris* KTSSR54 using beads from alginate/starch
899 blends. *Journal of Applied Polymer Science*, *138*, 50084.
900 <https://doi.org/10.1002/app.50084>
- 901 Sarkar, S., Manna, S., Das, E., Jana, P., Mukherjee, S., Sahu, R., Dua, T. K., Paul, P.,
902 Kaity, S., & Nandi, G. (2024). Fabrication and optimization of extended-release
903 beads of diclofenac sodium based on Ca²⁺ cross-linked Taro (*Colocasia esculenta*)
904 stolon polysaccharide and pectin by quality-by-design approach. *International*
905 *Journal of Biological Macromolecules*, *271*, 132606.
906 <https://doi.org/10.1016/j.ijbiomac.2024.132606>
- 907 Silveira, M. P., Almeida, F. L. C., Andreola, K., Alvim, I. D., & Prata, A. S. (2023).
908 Influence of composition on the internal diffusion mechanism of pectin-starch gel
909 beads. *Journal of Applied Polymer Science*, *140*(9), E53570.
910 <https://doi.org/10.1002/app.53570>

- 911 Singh, P., Medronho, B., Alves, L., Silva, G.J., Miguel, M.G., Lindman, B. (2017).
912 Development of carboxymethyl cellulose-chitosan hybrid micro- and
913 macroparticles for encapsulation of probiotic bacteria. *Carbohydrate Polymers*,
914 *175*, 87–95. <https://doi.org/10.1016/j.carbpol.2017.06.119>
- 915 Su, C. Y, Xia, T., Li, D., Wang, L. J, & Wang, Y. (2023). Hybrid biodegradable materials
916 from starch and hydrocolloid: fabrication, properties and applications of starch-
917 hydrocolloid film, gel and bead. *Critical Reviews in Food Science and Nutrition*,
918 *64*(33), 12841–12859. <https://doi.org/10.1080/10408398.2023.2257786>
- 919 Sun, W. X., Bu, K. X., Meng, H. M., & Zhu, C. H. (2024). Hawthorn pectin/soybean
920 isolate protein hydrogel bead as a promising ferrous ion-embedded delivery
921 system. *Colloids and Surfaces B: Biointerfaces*, *237*, 113867.
922 <https://doi.org/10.1016/j.colsurfb.2024.113867>
- 923 Ubeyitogullari, A., & Ciftci, O. N. (2016). Formation of nanoporous aerogels from
924 wheat starch. *Carbohydrate Polymers*, *147*, 125–132.
925 <https://doi.org/10.1016/j.carbpol.2016.03.086>
- 926 Ubeyitogullari, A., & Ciftci, O. N. (2019). A novel and green nanoparticle formation
927 approach to forming low-crystallinity curcumin nanoparticles to improve
928 curcumin's bioaccessibility. *Scientific Reports*, *9*, 19112.
929 <https://doi.org/10.1038/s41598-019-55619-4>
- 930 Vaziri, A. S., Alemzadeh, I., Vossoughi, M., & Khorasani, A. C. (2018). Co-
931 microencapsulation of *Lactobacillus plantarum* and DHA fatty acid in alginate-
932 pectin-gelatin biocomposites. *Carbohydrate Polymers*, *199*, 266–275.
933 <https://doi.org/10.1016/j.carbpol.2018.07.002>
- 934 Wang, H., Yang, L., Yang, Y. N., Zhang, D. S., & Hao, G. L. (2025). Multifunctional
935 natural starch-based hydrogels: Critical characteristics, formation mechanisms,
936 various applications, future perspectives. *Carbohydrate Polymers*, *357*, 123458.
937 <https://doi.org/10.1016/j.carbpol.2025.123458>
- 938 Wan, L., Yang, Z. X., Cai, R., Pan, S. Y., Liu, F. X., & Pan, S. Y. (2021). Calcium-
939 induced-gel properties for low methoxyl pectin in the presence of different sugar
940 alcohols. *Food Hydrocolloids*, *112*, 106252.

- 941 <https://doi.org/10.1016/j.foodhyd.2020.106252>
- 942 Wang, S. J., Wu, Z. N., Jia, L. Y., Wang, X. H., He, T., Wang, L., Yao, G. J., & Xie, F.
943 Y. (2024). Soybean protein isolate-sodium alginate double network emulsion gels:
944 Mechanism of formation and improved freeze-thaw stability. *International*
945 *Journal of Biological Macromolecules*, 274, 133296.
946 <https://doi.org/10.1016/j.ijbiomac.2024.133296>
- 947 Wang, W. J., Shen, M. Y., Liu, S. C., Jiang, L., Song, Q. Q., & Xie, J. H. (2018). Gel
948 properties and interactions of *Mesona blumes* polysaccharide-soy protein isolates
949 mixed gel: The effect of salt addition. *Carbohydrate Polymers*, 192, 193–201.
950 <https://doi.org/10.1016/j.carbpol.2018.03.064>
- 951 Wang, X. W., Feng, Y. W., & Feng, T. T. (2021). Modulation effect of glycerol on
952 plasticization and water distribution of vacuum-dried calcium alginate gel beads
953 encapsulating peppermint oil/ β -cyclodextrin complex. *Food Bioscience*, 41,
954 100968. <https://doi.org/10.1016/j.fbio.2021.100968>
- 955 Xiao, W. H., Shen, M. Y., Li, J. W., Li, Y. L., Qi, X., Rong, L. Y., Liu, W. M., & Xie, J.
956 H. (2023). Preparation and characterization of curcumin-loaded debranched
957 starch/*Mesona chinensis* polysaccharide microcapsules: Loading levels and in
958 vitro release. *Food Hydrocolloids*, 141, 108697.
959 <https://doi.org/10.1016/j.foodhyd.2023.108697>
- 960 Xiao, W. H., Shen, M. Y., Ren, Y. M., Wen, H. L., Li, J. W., Rong, L. Y., Liu, W. M., &
961 Xie, J. H. (2022). Controlling the pasting, rheological, gel, and structural
962 properties of corn starch by incorporation of debranched waxy corn starch. *Food*
963 *Hydrocolloids*, 123, 107136. <https://doi.org/10.1016/j.foodhyd.2021.107136>
- 964 Yang, J. Y., Song, J. L., Miao, S., Gao, Y. X., & Mao, L. K. (2024). Alginate-based gel
965 beads with bigel structures: Preparation, characterization and bioactive
966 encapsulation. *Food Hydrocolloids*, 146, 109294.
967 <https://doi.org/10.1016/j.foodhyd.2023.109294>
- 968 Ye, J. P., Yang, R., Liu, C. M., Luo, S. J., Chen, J., Hu, X. T., & Wu, J. Y. (2018).
969 Improvement in freeze-thaw stability of rice starch gel by inulin and its mechanism.
970 *Food Chemistry*, 268, 324–333. <https://doi.org/10.1016/j.foodchem.2018.06.086>

- 971 Zhu, W. Q., Bai, X. Y., Du, W. B., Li, L. Y., Fauconnier, M. L., Richel, A., Dong, H. J.,
972 & Zheng, Z. J. (2025). Comparison of the properties of turmeric starch-dioscin-
973 curcumin nanocarriers prepared by antisolvent co-precipitation and antisolvent
974 precipitation. *Carbohydrate Polymers*, 353, 123263.
975 <https://doi.org/10.1016/j.carbpol.2025.123263>
- 976 Zhang, F., Zheng, X. J., Ma, Y., Nan, W. Q., Wu, W. J., Chu, Z. R., Sun, X., Huang, J.
977 H., Muratkhan, M., Yue, F. F., Wang, X., & Lv, X. (2025). Sodium alginate/low
978 methoxyl pectin composite hydrogel beads prepared via gas-shearing technology
979 for enhancing the colon-targeted delivery of probiotics and modulating gut
980 microbiota. *International Journal of Biological Macromolecules*, 300, 140375.
981 <https://doi.org/10.1016/j.ijbiomac.2025.140375>
- 982 Zhang, Y., Zhao, T., Ma, & X. R. (2025). Innovative modified pectins enriched with
983 galactose: Preparation, characterization, and gel-based properties of curcumin-
984 delivered hydrogel beads. *Food Hydrocolloids*, 2025, 160, 110757.
985 <https://doi.org/10.1016/j.foodhyd.2024.110757>
- 986 Zhang, Y., Zhao, X. T., Bao, X. Y., Xiao, J., & Liu, H. S. (2021). Effects of pectin and
987 heat-moisture treatment on structural characteristics and physicochemical
988 properties of corn starch. *Food Hydrocolloids*, 117, 106664.
989 <https://doi.org/10.1016/j.foodhyd.2021.106664>

990 **Figure captions**

991 **Fig. 1.** Visual appearance of PP@GB, TS@GB, TSNC@GB, MTSNC@GB, and TS-
992 CUR@GB gel beads.

993 **Fig. 2.** FTIR spectra (A) and XRD patterns (B) of PP@GB, TS@GB, TSNC@GB,
994 MTSNC@GB, and TS-CUR@GB gel beads.

995 **Fig. 3.** TGA curves (A) and DTG curves (B) of PP@GB, TS@GB, TSNC@GB,
996 MTSNC@GB, and TS-CUR@GB gel beads.

997 **Fig. 4.** SEM images of PP@GB, TS@GB, TSNC@GB, MTSNC@GB, and TS-
998 CUR@GB gel beads.

999 **Fig. 5.** Water holding capacity (A), swelling behavior (B), and water distribution
1000 profiles (C) of PP@GB, TS@GB, TSNC@GB, MTSNC@GB, and TS-CUR@GB gel
1001 beads. Different lowercase letters indicate significant differences ($P<0.05$).

1002 **Fig. 6.** Dynamic modulus variation curves (A) and shear viscosity variation curves (B)
1003 of PP@GB, TS@GB, TSNC@GB, MTSNC@GB, and TS-CUR@GB gel beads.

1004 **Fig. 7.** Texture properties of PP@GB, TS@GB, TSNC@GB, MTSNC@GB, and TS-
1005 CUR@GB gel beads. Different lowercase letters indicate significant differences
1006 ($P<0.05$).

1007 **Fig. 8.** Colonization of *Lactiplantibacillus plantarum* Lp3a at a concentration of 10^{-6}
1008 after different sample treatments (A): Blank (a), PP@GB (b), TS@GB (c), TSNC@GB
1009 (d), MTSNC@GB (e), and TS-CUR@GB (f). Effect of different samples on the
1010 proliferation of *Lactiplantibacillus plantarum* Lp3a (B). Different lowercase letters
1011 indicate significant differences ($P<0.05$).

- Pectin-starch composite gel beads were successfully fabricated by ion cross-linking
- Starch derivatives enhanced the structural integrity and texture properties of gel beads
- Starch derivatives improved the swelling behavior and thermal stability of gel beads
- Curcumin and pectin synergistically enhance the prebiotic activity of TS-CUR@GB
- Curcumin-enriched starch fillers exhibited superior modification effects

Journal Pre-proof

Declaration of interest statement

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.

Journal Pre-proof