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Title:

Relaxation temperature and storage stability of the functionalized cell wall material residue from lemon peel Authors:

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11/20/24, 10:18 AM

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Food Hydrocolloids values your contribution and I look forward to receiving your revised manuscript.

Kind regards,

Carmen Petkowicz
Editor
Food Hydrocolloids

Editor and Reviewer comments:

Reviewer 1: This manuscript is a fairly straightforward report of measuring thermal transformations. Conversely, original data obtained are not made available to readers. For example, data for glass transitions measured by DSC are discussed, but it is hard to understand what sort of curves may have been analysed. Considering the material analysed, there are publications on glass transitions occurring in cellulose and cell wall materials. In general, these materials are large macromolecules and they may exist in crystalline or partially crystalline states. The data reported do not agree well with possible crystallinity and it would be extremely important to include an x-ray diffraction measurement before this paper can be published. One should also note that possible crystallinity would also suggest hydration water occurrence in crystalline regions. Such hydration water could be responsible for the mechanical relaxation properties. As reader, and based on reported evidence, I would not be convinced that the authors found any glass transitions in the materials studied.

Reviewer 2: This is an interesting piece of work in an area of relevance. This research paper focuses on relaxation

temperature and storage stability of the functionalized cell wall material (CWM) residue from lemon peel. Specifically, the study described in this paper aims to include different methods to measure glass transition temperature (Tg) and relaxation temperature of lemon peel CWM residue and relate them to the stability of the material's rheological property as influenced by storage. Overall, the manuscript is clearly presented and written. However, some parts of the manuscript need to be modified and/or clarified. I recommend therefore a revision of the article, considering the following remarks and/or questions.

1- The second and third parts of the introduction (see lines 67-88) are not fully documented regarding available literature on the subject. Indeed, the authors have "partially" described in both parts the concept of Tg, the methods and limitations of the Tg analysis for food materials without addressing fully the gaps and what is already known in the literature about the mechanisms behind the CWM residue's functionality loss upon storage of over time in various environmental conditions. Is there any available data about: (i) the behavior upon storage of non-functionalized and functionalized CWM in relation to their chemical composition; (ii) the reversibility or not of the functionality loss upon storage while using higher energy of re-dispersing of the cellulose-rich fiber upon reconstitution in aqueous media? Would the chemical composition or the level of functionalization (or defibrillation) affect how does the CWM residue will behave upon storage? All this need to be clearly addressed while revising the parts corresponding to lines 67-88 and ensure a good alignment with the objective of the study.

2- It would have been interesting to:

* Justify the reason why the storage stability of the CWM's residue has been monitored for 14 weeks? Do the authors assume that this time of storage is sufficient to understand fully the mechanisms behind the functionality loss?

* Monitor the behavior of the non-functionalized CWM's residue additionally to the functionalized AR in order to better understand the role of functionalization, and check if the loss upon storage is an intrinsic characteristic of CWM or not?

* Build a modelling approach to fit and better describe the data shown in Figure 5.

* Evaluate the reversibility or not of the functionality loss upon storage while using higher energy of re-dispersing of the cellulose-rich fiber upon reconstitution in aqueous media.

Could you please explain why this approach was not carried out, and discuss in depth how might some aspects of this could impact the main findings and key learnings?

3- In order to make easier further reading, revision should be also performed in some parts of the manuscript where some sentences are "very" long and complicated to understand.

Reviewer 3: This manuscript is very well prepared and presents valuable contribution to development of more sustainable food crops management by improvement of functionality evaluation of fruit cell walls. In this case cell wall material from citrus peel was used after pectin extraction. Thus, the manuscript deals with product that is considered as waste. This research shows that DSC is not the best approach to evaluate stability during storage of this material, instead TMC-DMTA is proposed. This main result is sufficiently proven.

Manuscript needs just minor revision before publication. There is important lack of determination of composition of AIR and AR. These two samples are not characterized with exception of pectin extraction protocol. Although nitric acid removes pectin, but some pectin still remains. Authors in few places suggest role of pectin or cellulose crystallinity in mechanical/plasticizing properties, therefore at least monosaccharide composition is needed to support interpretation of results.

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III. Revised Manuscript 1

1 **Relaxation temperature and storage stability of the functionalized cell wall material**

2 **residue from lemon peel**

3

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24 Journal : Food Hydrocolloids

25

26 Declarations of interest : none

27 **ABSTRACT**

28

29 Lemon peel cell wall material (CWM) residue obtained after acid pectin extraction can be
30 functionalized into a texturizing ingredient using mechanical treatments such as high-pressure
31 homogenization. The application of CWM as a texturizing ingredient is most likely through a dry
32 powder and thus the stability of its functionality (rheological property) during storage becomes an
33 obvious question. However, studies on the glass transition properties of this CWM residue and
34 its relation to storage stability are largely lacking. This study aims to first evaluate the potential of
35 two methods, i.e. DSC analysis and combined TMCT-DMTA (thermal mechanical compression
36 test – dynamic mechanical thermal analysis) to measure the Tg and relaxation temperature of
37 lemon peel CWM and subsequently relate the results to the stability of the material's rheological
38 property. The results showed that DSC-based Tg measurements may not be the most appropriate
39 indicator for storage stability of the lemon peel CWM residue, despite being the most commonly
40 used method to explain state transition in materials. On the other hand, the structural relaxation
41 phenomena elucidated by the change in mechanical properties measured by TMCT-DMTA
42 correlated with the results of storage stability of the material. To ensure the stability of the CWM
43 residue, storage should be carried out at conditions (temperature and moisture content) before
44 the onset of $\tan \delta$ curve change. In conclusion, relaxation phenomena observed through the
45 measurement of mechanical properties, in particular the $\tan \delta$ curve from DMTA, provides a
46 suitable starting point for inferring the stability of the functionalized CWM residue.

47

48 **Keywords :** *cell wall material, glass transition, structural relaxation, storage stability*

49

50

51

52

53 **1. Introduction**

54

55 Lemon peel, by-products from the citrus processing industry, is produced in relatively high
56 amounts which puts a significant burden on the environment. An efficient by-product management
57 strategy is needed to minimize its environmental impact and to increase the overall valorization.
58 To date, the extraction of citrus pectin, an ingredient widely used as thickening agent in food
59 production, is the most widely implemented valorization route of lemon peels. However, the
60 industrial pectin extraction process leaves another significant amount of fiber-rich material.
61 Previous studies have shown that suspensions prepared from the residue left after acid pectin
62 extraction (AR) have excellent rheological properties (high storage modulus), especially after
63 mechanical treatment such as high pressure homogenization (HPH) (Putri et al., 2022; Willemse
64 et al., 2017). **The functionalization with HPH caused changes on the microstructure of the AR**
65 **particles, including fragmentation (size reduction) and aggregation. The aggregation formed a**
66 **network which entraps water, creating a gel-like structure in suspension.** This means that the
67 functionalized pectin-depleted residue has a high potential as a texturizing ingredient, therefore a
68 study of this ingredient's stability during storage becomes necessary.

69

70 The concept of glass transition temperature (Tg) has been used widely to predict the stability of
71 foods and food ingredients (Sabiani et al., 2007). When a material is in its glassy state (at a
72 temperature below the Tg), it is regarded as stable due to its limited molecular mobility. Contrary,
73 when a material is put into a condition (temperature-moisture combination) above its Tg, the rate
74 of physical, chemical and biological changes largely increases and the material becomes unstable
75 (Champion et al., 2000). The glass transition phenomena can be perceived from changes in the
76 thermal and mechanical properties of the material as it is heated/cooled. The most common
77 method to determine the Tg of a material is by measuring the change in the heat capacity using
78 differential scanning calorimetry (DSC). However, the changes in the thermal properties of some

79 food materials, such as the cell wall material (CWM), can be very small during the transition,
80 making it difficult to detect (Boonyai et al., 2006; Roos, 1998). Therefore, in this study, the Tg of
81 the functionalized lemon peel residue after pectin extraction was measured by both the change
82 in thermal and mechanical properties.

83

84 To date, only few studies are available on CWM stability during storage and moreover studies on
85 pectin-depleted CWM, to the best of our knowledge, are not existing. The available studies on
86 fiber-rich materials (Fernandez-Lopez et al., 2009; Sharma et al., 2017) mostly demonstrate the
87 degradation of fiber quality during storage without correlating it to the concept of molecular
88 mobility and glass transition, possibly due to the limitation of the Tg analysis. The quality
89 degradation could be attributed to the collapse of the material due to moisture absorption
90 (Fernandez-Lopez et al., 2009). Collapse happens when a material loses its structure and
91 volumetric shrinkage occurs causing loss of porosity (Levi & Karel, 1995). Collapse of amorphous
92 food materials, occurs because of a solid flow resulting from a decreasing viscosity whereby the
93 matrix is no longer capable to support and carry its own mass (Fan & Roos, 2017). This solid flow
94 arises from an increased molecular mobility. However, the characterization of the molecular
95 mobility and its relation to the storage stability of CWM has not been extensively studied.
96 Therefore, this study attempts to fill this gap by describing the molecular mobility of CWM based
97 on the changing mechanical properties and how these changes relate to the functionality
98 (specifically rheological property) of the material.

99

100 This study aims to include the different methods to measure Tg and relaxation temperature of
101 lemon peel CWM residue and relate them to the stability of the material's rheological property as
102 influenced by storage. An understanding of how the material behaves during storage may
103 encourage its application in industry and support the effort to valorize the residue of lemon peel
104 after pectin extraction.

105

106 **2. Materials and Methods**

107

108 **2.1. Materials**

109 Dry and milled lemon peel (LP) powder was provided by Cargill R&D Centre Europe (Vilvoorde,
110 Belgium). All the chemicals used for moisture content equilibration were of analytical grade.

111

112 **2.2. Dried Functionalized Acid Residue Preparation**

113

114 The dry LP was treated to obtain the Alcohol Insoluble Residue (AIR) and subsequently pectin
115 was extracted from the AIR using nitric acid at pH 1.6, 80°C for 1 hour. The unextractable fraction
116 were collected as Acid Residue (AR). The AR was then resuspended at 2% solid concentration,
117 the pH was adjusted to 4.5 and then high pressure homogenized at 20 MPa (Panda 2k NS 1001L,
118 GEA Niro Soavi, Parma Italy). All these procedures have been described in detail in our previous
119 studies (Putri et al., 2022; Willemse et al., 2017). **For the detailed composition of AIR and AR**
120 **from lemon peel, readers are directed to the previous publication (Willemse et al., 2017)**. After
121 HPH, the functionalized AR was air-dried after water-alcohol exchange. For this, the
122 functionalized AR was mixed with technical ethanol 99% at a 1:4 (v/v) ratio for 10 minutes and
123 then allowed to stand for 60 minutes. This mixture was vacuum filtered (Machery-Nagel MN 615).
124 A second round of alcohol-water exchange were carried out with the technical ethanol 99% at the
125 ratio of 1:1 from initial volume of material. This mixture was allowed to stand for 30 minutes, and
126 vacuum filtered. The solids after filtration were air-dried overnight to obtain the dried functionalized
127 AR. The moisture content after drying was 11.1 ± 1.1 % w.b. The dried functionalized AR was
128 kept in vacuum bags in a freezer at -40°C until further use.

129

130 **2.3. Moisture content equilibration and sorption isotherm**

131

132 In order to achieve various moisture content, the AIR and functionalized AR powder were stored
133 at 4°C for at least 3 weeks in containers with P₂O₅ (a.w. 0.00) or saturated salt solutions : LiBr
134 (a.w. 0.07), LiCl (a.w. 0.12), CH₃COOK (a.w. 0.24), MgCL₂ (a.w. 0.34), K₂CO₃ (a.w. 0.43),
135 Mg(NO₃)₂ (a.w. 0.59), NaBr (a.w. 0.64), KI (a.w. 0.73) and KCl (a.w. 0.87) (Greenspan, 1976).
136 The moisture content of the material was measured at the end of the equilibration period by
137 gravimetric analysis. The moisture sorption isotherm was obtained and fitted to the GAB equation
138 (see below) by non-linear regression.

139

$$W = \frac{CKW_m a_w}{(1-Ka_w)(1-Ka_w+CKa_w)} \quad (\text{eq.1})$$

140 W is the equilibrium moisture content of the material on dry basis and a_w is the water activity. W_m,
141 C and K are the fitted constants. W_m represents the amount of water adsorbed in the monolayer.
142 The W_m value indicates the availability of active water sorption sites on the material. C represents
143 the strength of water binding with a larger C value indicating a stronger binding of water in the
144 monolayer. K is a correction factor, when K approach one, there is no distinction between the
145 water molecules beyond the monolayer and pure water (Quirijns et al., 2005).

146

147 2.4. *Molecular mobility analysis with different methods*

148

149 2.4.1. *Differential Scanning Calorimetry*

150

151 A Differential Scanning Calorimeter Q-2000 (TA instruments, USA) was used to scan the thermal
152 behavior of AIR and functionalized AR powder with different moisture contents. Approximately 20
153 mg of the powder was weighted into hermetically sealed T_{zero} aluminium pans. An empty pan was
154 used as a reference and two cycles of heating-cooling were carried out, first from -60°C to 90°C
155 and second from -60°C to 120°C, both at a rate of 10°C/min. Glass transition temperature, further

156 referred to as Tg, was defined as the mid-point of the transition range observed in the heat flow
157 curve of the second heating cycle (Kymugasho et al., 2021; Pelgrom et al., 2013). [An example](#)
158 of such heat flow curve and the analysis of the transition is presented in the Supplementary
159 Materials (Figure S-1). The analysis was carried out in triplicate.

160

161 *2.4.2. Thermal Mechanical Compression Test - Dynamic Mechanical Thermal Analysis*

162

163 Combined TMCT-DMTA analyses were carried out according to the methods described in
164 Aravindakshan et al. (2022) using an Anton Paar MCR302 rheometer (Graz, Austria) equipped
165 with a CTD450 oven. Approximately 2 g of the sample (AIR or functionalised AR powder) was
166 loaded into the measuring system (cylindrical cup Ø 22 mm ; cylindrical bob Ø 20 mm) and the
167 oscillation-compression force was applied at normal force 30 N, shear strain 0.05% and frequency
168 1 Hz. The temperature scan spanned -60°C to 120°C at the rate of 2°C/min.

169

170 From the TMCT-DMTA data, two different values of relaxation temperature were obtained. First,
171 the relaxation temperature from TMCT analysis (Tr-TMCT), determined based on the change of
172 the sample compressibility due to the normal force by measuring the displacement of the probe
173 during the heating scan (with correction of the measuring system's thermal expansion from a scan
174 on microcrystalline cellulose). Secondly, the relaxation phenomena from the DMTA were based
175 on the change of the ratio between loss and storage modulus (or loss factor, $\tan \delta$) obtained using
176 oscillatory shear measurements.

177

178 *2.4.3. Gordon-Taylor equation fitting*

179

180 The Tg values obtained from DSC and relaxation temperature from TMCT analysis (Tr-TMCT)
181 were fitted into the Gordon-Taylor (G-T) equation below using non-linear regression analysis.

182
$$T = \frac{T_s \times X_s + X_w \times T_w \times k}{X_s + X_w \times k} \quad (\text{eq. 2})$$

183 where s denotes the solid fraction (CWM) of the sample, w denotes the water fraction, T is the
184 temperature of transition or relaxation, T_w is the glass transition temperature of water = -135°C, X
185 is the mass fraction and k is the constant that corresponds to the plasticizing effect of water on
186 the material.

187

188 **2.5. Storage Study Setup**

189

190 A storage study was set up for the dried functionalized AR based on the results of the DSC and
191 TMCT-DMTA analysis. Various storage conditions were identified to encompass various states
192 of the functionalized AR, from stable to unstable. A combination of three moisture contents (11%,
193 14% and 16% w.b.) and three storage temperature (10, 25, and 40°C) was used. An additional
194 temperature condition (-10°C) was used to store the material at 16%w.b. moisture content to
195 ensure that storage at an anticipated stable condition was well covered. To adjust the moisture
196 content prior to the storage study, the functionalized AR were equilibrated in airtight containers
197 above saturated salt solutions (MgCl_2 , MgNO_3 and KI) for 5 weeks. After moisture equilibration,
198 the functionalized AR were packed into inert glass jars with minimum headspace to prevent
199 moisture exchange and stored for 2, 5 and 14 weeks. **At the end of each storage period, the dried**
200 **functionalized AR samples were regenerated (in duplicate) into 2% w/w solid suspensions. The**
201 **regeneration was done by letting the material stand in water for 1 hour and followed by mixing**
202 **using L5M-A mixer with an emulsion screen workhead (Silverson, East Longmeadow, MA, USA)**
203 **at 4300 RPM for 10 minutes.** The rheological properties of these suspensions were measured as
204 an indicator of the material's functionality.

205

206 The results of the storage study were fitted by non-linear regression using a first order fractional
207 conversion model :

208
$$G'(t) = G'_f + (G'_i - G'_f)e^{-kt} \quad (\text{eq. 3})$$

209 where G'_f is an estimated final extend of functionality loss, G'_i is the average initial value of G'
210 observed, t is the storage time (week) and k is the reaction rate constant.

211

212 2.6. *Rheological property analysis*

213

214 The rheology of the CWM suspension was analyzed using the method according to (Willemsen
215 et al., 2018). An Anton Paar MCR302 rheometer (Graz, Austria) equipped with a custom-built cup
216 and concentric cylinder with conical bottom was used. The gap between the cylinder and the cup
217 was 2 mm. Strain sweep (at ω 1 Hz and strain 0.01% - 100%) was done to determine the linear
218 viscoelastic region and a frequency sweep (at ω 100 to 0.1 Hz and strain 0.1%) was carried out
219 at 25°C. Rheology analysis was carried out in duplicate, each with newly loaded samples.

220

221 2.7. *Statistical analysis*

222

223 Significant statistical difference ($\alpha = 0.05$) between model-fitting parameter were determined by
224 confidence interval calculation. GAB and G-T curve fitting was carried out in JMP Pro 17 statistical
225 software (SAS Institute Inc, Cary, NC, USA) and fractional conversion model fitting for the storage
226 study results was done in SAS statistical software (SAS Institute Inc, Cary, NC, USA).

227

228 3. **Results and Discussions**

229

230 3.1. *Isotherm Sorption of the materials*

231

232 The relation between water activity and moisture content (moisture sorption isotherm) is an
233 important characteristic in the study of the stability of low-moisture food product (Koç et al., 2010;
234 Lee & Robertson, 2022; Sant'Anna et al., 2014). The moisture sorption isotherm (at 4°C) for both
235 materials in the present study, AIR and functionalized AR from lemon peel, is shown in Figure 1.
236 Both materials showed a type II behavior according to the Brunauer-Emmet-Teller classification,
237 which is frequently found in food products (Andrade P. et al., 2011). The experimental data was
238 fitted to the GAB equation and the estimated value for the parameters are shown in Table 1. Both
239 AIR and functionalized AR showed similar C and K values but significantly different monolayer
240 values (W_m). AIR had a significantly higher W_m which indicating that it has more active (or better
241 accessible) water sorption sites. This is also shown in the moisture sorption isotherm graph, in
242 which AIR had higher moisture content at a given a_w value compared to the functionalized AR.
243 This difference is expected since AIR contained more hygroscopic components, such as low
244 molecular weight compounds and pectin, that were partially extracted for the functionalized AR.
245 It has been largely acknowledged that the composition of the materials affected the moisture
246 sorption capacity (Sormoli & Langrish, 2015; Timmermann et al., 2001). The sorption isotherm
247 data at 4°C were used to prepare samples at specific moisture contents in view of the Tg/Tr
248 measurements and the storage experiment.

249

250 3.2. *Glass transition and structural relaxation of the cell wall material from lemon peel*

251

252 3.2.1. *Differential Scanning Calorimetry (DSC)*

253

254 DSC is one of the commonly used methods to measure Tg. It measures the transition in the
255 thermal properties of the material by measuring the change of specific heat (Le Meste et al.,
256 2002). However, DSC was not sensitive enough to measure the Tg of the functionalized lemon
257 peel AR. On the other hand, transition in the DSC thermogram, albeit weak and broad, was

258 observed for lemon peel AIR, except for samples with very low moisture content (<9% w.b.). AIR
259 contains larger amounts of components that may contribute to the thermal glass transition, for
260 example sugars, oligosaccharides, or acids. These components were extracted from the AIR
261 during the AR preparation and consequently, the functionalized AR from lemon peel contains
262 mainly cellulose and multiple other biopolymers such as pectin and hemicellulose (Putri et al.,
263 2022). The change in the heat capacity occurring over the glass transition of biopolymers is
264 relatively small and therefore difficult to be captured by DSC (Roos, 1998; Sablani et al., 2010).
265 Consequently, the DSC results could not provide precise specific transitions for food containing
266 predominantly component with large molecular weight, such as the functionalized AR. Therefore,
267 to describe the glass transition phenomena of CWM residues with DSC, the data from the AIR
268 samples at higher moisture content (\geq 9% w.b.) are used in this study.

269

270 The mid-point of the transition shown in the thermogram of the second heating cycle of AIR
271 samples was identified as its Tg-value. The Tg of the AIR sample in function of dry matter content
272 is presented in Figure. 2. Despite the insensitivity of the DSC method for Tg measurement of
273 CWM, few studies reported Tg values for papaya (Nieto-Calvache et al., 2019) and carrot CWM
274 (Georget et al., 1999), with similar and slightly higher Tg compared to lemon peel AIR,
275 respectively. As the moisture content of the lemon peel AIR increased, the Tg decreased, which
276 is a common behavior in many biological materials. It is a well-established fact that water acts as
277 a plasticizer and causes a depreciation of Tg in low moisture food (Le Meste et al., 2002; Roos,
278 1998). Previous studies also showed this moisture plasticizing effect in fiber-rich material obtained
279 from apple pomace and carrot (Georget et al., 1999; Zlatanović et al., 2019). The value of Tg in
280 function of dry matter content of the lemon peel CWM were fitted to G-T equation and the
281 parameters obtained, T_s and k, are presented in Table 2. The moisture plasticizing effect (as
282 indicated by the k value of G-T equation) measured by DSC was 4.81, which is similar to other

283 fruit- and vegetable-based food materials and food products (Fongin et al., 2017; Stępień et al.,
284 2020).

285

286 3.2.2. *Thermal Mechanical Compression Test – Dynamic Mechanical Thermal Analysis (TMCT-*
287 *DMTA)*

288

289 Contrary to the DSC method, the TMCT-DMTA managed to clearly show structural relaxation
290 phenomena in both lemon peel AIR and functionalized AR. This supported the well-established
291 fact that the mechanical property analysis is more sensitive in measuring the transition or
292 relaxation phenomena in food products (Roos, 1998). TMCT-DMTA analysis reveals structural
293 relaxation phenomena based on the change in the material's mechanical properties, more
294 specifically the compressibility and the moduli obtained from oscillatory shear analysis. As the
295 result of the TMCT-DMTA is highly dependent on the measurement frequency (Le Meste et al.,
296 2002), please note that all the structural relaxation temperatures described here are based on
297 measurement at a frequency 1 Hz.

298

299 Tr-TMCT in function of dry matter content for both AIR and functionalized AR is shown in Figure
300 3. Representative Δ gap curves used for the calculation of Tr-TMCT are presented in the
301 Supplementary Materials (Figure S-2). AIR and functionalized AR have similar values of Tr-TMCT
302 and show similar changes due to the moisture plasticizing effect. The values of Tr-TMCT slightly
303 decreased as the sample's moisture content increased. However, the moisture plasticizing effect
304 on the TMCT results (and DMTA) in this study was very limited, especially if compared to the
305 plasticizing effect on the thermal transition. The mechanism of the moisture plasticizing effect on
306 the structural relaxation of glassy biopolymers, especially amorphous carbohydrates (using
307 maltodextrin as an example), has been proposed (Kilburn et al., 2004). First, the absorbed water
308 would fill small voids in the glassy matrix of the material, changing the matrix free volume. Second,

309 the water would interfere with intermolecular hydrogen bonds, increasing the degree of freedom
310 of the carbohydrate molecules and eventually caused coalescence of the voids. This proposed
311 mechanism seems to suggest that the plasticizing effect is limited by the diffusion of water into
312 the small voids in the matrix. The complex and rigid structure of CWMs may have hindered the
313 plasticizing mechanism on its structural relaxation behavior and thus limiting the effect of
314 moisture.

315

316 When the Tr-TMCT values were fitted to the G-T equation, the values of anhydrous relaxation
317 temperature (Ts) and k obtained were exceptionally low compared to the parameters obtained for
318 the DSC based Tg curve (Table 2). This indicates that the material behavior reflected by the Tr-
319 TMCT value change with moisture content is vastly different from the Tg values obtained by DSC.
320 This may suggest that the two methods captured different mechanism of relaxation. This
321 hypothesis will be substantiated further with the storage study results discussed in section 3.3.
322 below. Based on the Tr-TMCT behavior and the fitted parameters value, the G-T equation may
323 not be appropriate to describe the relaxation phenomena obtained by TMCT.

324

325 The result from the DMTA analysis, specifically the $\tan \delta$ curve in function of temperature, is
326 presented (Figure 4) to describe the structural relaxation phenomena of the lemon peel CWM
327 residue. The storage (G') and loss modulus (G'') curves in function of temperature are presented
328 in the Supplementary Materials (Figure S-3). Comparable behavior of the moduli and loss factor
329 as a function of temperature was observed for pea and soybean cotyledon (Ballesteros & Walters,
330 2011, 2019). They showed that over the range of -120°C to 120°C, the G' measured declined in
331 the beginning (at low temperature) and started to increase from a certain temperature onwards.
332 The G'' was constant in the beginning and started to increase towards a plateau, and $\tan \delta$
333 increased towards a plateau or a peak. The value of relaxation temperature (Tr-DMTA) generally
334 could be determined by the peak of loss factor ($\tan \delta$) (Liu et al., 2006). However, the peak of the

335 tan δ in this study was difficult to be precisely determined, especially for samples with very low
336 moisture content. Therefore, the structural relaxation phenomena will be discussed based on the
337 behavior of the tan δ curve. **As a reference, the tan δ curve of microcrystalline cellulose in function**
338 **of temperature is presented in the Supplementary Materials (Figure S-4).**

339

340 The tan δ curve of lemon peel CWM, can be approximately divided into three regions : (i) a lower
341 temperature range with the onset of tan δ change (preceded by a constant value, especially for
342 the low moisture systems) (ii) a medium temperature range with a steep increase of tan δ , and
343 (iii) a final region where tan δ reached its highest value and became constant or started to decline.
344 At low temperature region (between -60°C to 20°C, with different range for samples with different
345 moisture content), the tan δ was mostly constant. As the CWM residue was heated, tan δ started
346 to increase (onset region) at a temperature between -30°C and 20°C. The increase of tan δ upon
347 heating suggests that the material started to lose its stiffness and a more plastic deformation could
348 occur. The loss of stiffness continued at the second region with a steep increase of tan δ and it
349 reached a maximum point at temperature between 40°C - 50°C.

350

351 The plasticizing effect of moisture could be observed in the DMTA results based on the changes
352 of tan δ curve behavior. First, the absolute values of tan δ increased with the increase in the
353 moisture content of the samples. The increase of tan δ after the onset region also became more
354 drastic as the moisture content in the sample increased and it occurred at lower temperatures for
355 samples with higher moisture contents. Lastly, the maximum value of tan δ was reached at lower
356 temperatures as the moisture content of the samples increased. The tan δ curve for AIR (Figure
357 4A) and functionalized AR (Figure 4B) showed very similar behavior. However, the plasticizing
358 effect of moisture was more pronounced in the tan δ curve of AIR, as also observed in the Tr-
359 TMCT results.

360

361 In order to compare all methods of the transition/relaxation analysis, Tg and Tr-TMCT points were
362 overlayed on the tan δ curve (Figure 4). DSC-based Tg values (based on AIR results) seem to be
363 located approximately at the onset of the tan δ change. On the other hand, Tr-TMCT values are
364 located at around the middle (inflection point) of the rapidly increasing section of tan δ curve
365 (Figure 4), coinciding with the lowest value of G' and on the point where G" starts to increase
366 (Figure S-3). Therefore, these points on the DMTA curves seems to indicate the onset of the
367 change in compressibility of the material.

368

369 The value of Tr-TMCT of lemon peel CWM (AIR) at each moisture content was higher than the
370 measurable Tg value from DSC, except for sample with the lowest moisture content (9% w.b.).
371 This observation agrees with many studies that showed higher mechanical relaxation
372 temperatures compared to thermal glass transition (Boonyai et al., 2006; Fan & Roos, 2017;
373 Georget et al., 1998; Rahman et al., 2007). However, the temperature of transition for anhydrous
374 material (T_s) obtained from the G-T equation fitted parameter were much lower for Tr-TMCT result
375 (~40°C) compared to DSC (117°C). **The huge difference in the anhydrous transition/relaxation**
376 **temperature and the moisture plasticizing effect may indicate completely different**
377 **transition/relaxation phenomena observed between the thermal and mechanical method of**
378 **analysis. This raises the question of which temperature (structural relaxation or glass transition)**
379 **is better suited to predict the storage stability of CWM.**

380

381 The increasing tan δ behavior suggests higher translational molecular mobility in the CWM
382 residue which is suspected to have a detrimental effect on the stability of the functionalized AR
383 during storage. Higher molecular mobility increased the solid flow of molecules in the matrix of
384 CWM which may induce collapse (Fan & Roos, 2017). **Thus, a storage study was subsequently**
385 **performed on the functionalized AR from lemon peel in order to corroborate whether the change**
386 **in the behavior of tan δ curve could be useful in predicting CWM residue's stability during storage.**

387 The behavior of the $\tan \delta$ curve depicted in Figure 4 was used to determine different storage
388 conditions that will cover different regions, from stable to unstable. Three temperature conditions
389 were chosen, 10, 25 and 40 °C to represent the temperature before onset of $\tan \delta$ change, after
390 onset when the $\tan \delta$ curve began to increase rapidly (but still below Tr-TMCT) and when the $\tan \delta$
391 curve almost reached its maximum value (above Tr-TMCT), respectively. Three moisture
392 content values (11%, 14% and 16%) were selected, each corresponding to a different $\tan \delta$ curve
393 profile to include the effect of water plasticization on the storage stability. An additional storage
394 temperature of (-10)°C was added to the samples with highest moisture content to ensure that
395 also in this case, a stable storage point (well before the onset of $\tan \delta$ change) was covered.

396

397 3.3. *Storage stability and its relation to the molecular mobility*

398

399 The storage stability study was focused on the change of the functionality of lemon peel CWM
400 residue. Therefore, the rheological property, specifically G' , was measured to indicate the stability
401 (or deterioration) of the texturizing potential of the functionalized AR. The values of G' throughout
402 14 weeks of storage are presented in Figure 5. Samples stored at conditions before the onset of
403 $\tan \delta$ change (at -10°C and 10°C) showed a stable G' up to 14 weeks of storage. When the
404 storage temperature was higher than the onset of $\tan \delta$ change (at 25°C and 40°C), a significant
405 decline in the G' -values was observed during storage. **To quantify the rate of the G' decline or the**
406 **rate of functionality loss during storage, the fractional conversion model was fitted to the results.**
407 The rate constant (k) values are presented in Table 3 below. The rate of the decline significantly
408 increased as the storage temperature increased. Samples stored at 25°C show a lower k -value
409 compared to samples stored at 40°C. However, after 14 weeks of storage, the G' value of samples
410 stored at 25°C declined significantly, reaching a similar value to the samples stored at 40°C. On
411 the other hand, samples stored at 40°C already experienced a severe decline after 5 weeks of
412 storage.

413

414 The samples stored at 25°C showed a decline in G' value despite stored under the Tr-TMCT
415 values, indicating that Tr-TMCT did not correspond to the stability of CWM functionality during
416 storage. In conclusion, the relaxation phenomena described in the tan δ curve correlate well to
417 the storage stability of the lemon peel CWM. When the storage condition (temperature and
418 moisture content) is located in the more progressed region of the tan δ curve which may indicate
419 higher molecular mobility, the faster the decline on the G'. As long as the storage conditions were
420 kept below the onset of the tan δ curve change, degradation of the functionality of the CWM
421 residue were limited.

422

423 The declining G' during storage that happened when samples were stored at conditions where
424 the tan δ curve was increasing could be attributed to the structure collapse of the cell wall matrix.
425 Such physical change could occur due to increasing molecular mobility when the material is
426 transformed into a more viscous state (Fan & Roos, 2017). When tan δ increased, stiffness of the
427 molecules decreased which also suggests the reduction of the material viscosity to a level that is
428 no longer sufficient to support the structure of the solid material. The increased viscous flow
429 caused subsequent densification (Fan & Roos, 2017; To & Flink, 1978). In this case, the structural
430 units (for example the repetitive element of the biopolymers in the CWM) can move independently
431 from each other (Champion et al., 2000). Thus, interactions between cellulose microfibrils became
432 possible which hindered the formation of an open CWM network that entraps water during the
433 reconstitution of the material into suspension. Collapse of CWM, which could be prompted by
434 many factors and treatments such as mechanical breaking (Van Audenhove et al., 2022) and
435 chemical treatment, e.g. with alkaline solution, could lead to the reduction of CWM suspension's
436 functionality. This transformation in the mechanical properties of solid materials may lead to
437 substantial alterations of its performance in processing, storage stability, and sensory properties
438 (Fan & Roos, 2017).

439

440 Previous study (Fernandez-Lopez et al., 2009) showed that degradation of the fiber-rich material
441 functional properties, such as water binding capacity, became more severe as the moisture
442 content increased during storage. Contrary, in this study, the rate of functionality loss (k -value)
443 was not significantly different between samples stored at different moisture content (Table 3). At
444 the same storage temperature, the moisture content of the samples (within the moisture content
445 range studied) did not significantly affect the G' of the functionalized AR during storage. The
446 plasticization effect of moisture was not pronounced in the storage study, contrary to common
447 low-moisture food product behavior (Fan & Roos, 2017; Le Meste et al., 2002). As discussed
448 previously, the limited moisture plasticizing effect, that was also observed in the results of TMCT-
449 DMTA of CWM samples, was suspected to be caused by the composition of functionalized AR.
450 Functionalized AR is composed mainly of cellulose and cellulose in its native form is a rigid
451 polymer with some crystalline region in its structure, which may prevent the water migration into
452 the particles and thus limit the moisture plasticizing effect. A NMR experiment which studied the
453 effect of hydration on polymer mobility in onion CWM showed that water readily penetrated the
454 pectin network and increased its mobility, whereas cellulose mobility was unaffected by hydration
455 (Hediger et al., 1999).

456

457 Furthermore, although the moisture plasticizing effect on the T_g of lemon peel CWM was clearly
458 observed from the DSC results, this effect could not be seen in the storage study results. Larger
459 differences between the storage temperature and T_g should normally cause faster deterioration
460 of materials (Kyomugasho et al., 2021; Roos, 1995; Zlatanović et al., 2019), however this
461 phenomena also could not be observed in the results of the storage study. The substantial
462 transition in the TMCT and DMTA result was not visible in the DSC thermogram for both AIR nor
463 functionalized AR. However, this transition that is measurable by TMCT-DMTA and unmeasurable
464 by the DSC seems to be the major driving force in the mechanical property changes of the

465 material. Therefore, thermal glass transition obtained from DSC should not be considered an
466 appropriate property to predict the stability of CWM residue, especially when being used as
467 texturizing ingredient where the mechanical properties of the material is of ultimate importance.

468

469 **4. Conclusion**

470

471 The glass transition temperature of CWM has not been frequently reported due to the limitations
472 of available methods of analysis. DSC has been widely used to predict the changes of materials
473 during storage and its stability. **However, DSC lacks sufficient sensitivity to measure the glass**
474 **transition temperature of biopolymers such as CWMs.** On the other hand, the change in
475 mechanical properties measured by combined TMCT-DMTA analysis could reveal the structural
476 relaxation phenomena of CWM based on the change of the compressibility and stiffness (loss
477 factor / $\tan \delta$). **Thus, the results from the TMCT-DMTA in this study could fill the gap as stability**
478 **indicator that cannot be accomplished by DSC analysis of CWM.** The relaxation phenomena
479 observed by the mechanical property measurement, especially the $\tan \delta$ curve from DMTA, is a
480 more appropriate prediction to infer the stability of CWM, especially when used as texturizing
481 ingredient where the rheological properties of the material is essential. In order to maintain
482 stability of CWM residue, the storage condition (temperature and moisture) should be maintained
483 below the onset region where $\tan \delta$ curve started to increase. Conditions above the onset region
484 of $\tan \delta$ curve may indicate increased molecular mobility and lead to the degradation of the CWM
485 rheological properties due to collapse. The ability of the TMCT-DMTA analysis to illustrate the
486 relaxation phenomena could provide an opportunity for further study, for example on how
487 processing could affect the behavior of the mechanical properties in order to design a shelf-stable
488 functionalized CWM.

489

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496

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623

624 Table 1. GAB parameters of moisture sorption isotherm

Materials	W _m	C	K
AIR	8.76 ± 0.52 ^a	13.92 ± 3.53 ^a	0.81 ± 0.02 ^a
Functionalized AR	8.04 ± 0.43 ^b	12.26 ± 2.46 ^a	0.79 ± 0.02 ^a

625

626 Table 2. Gordon-Taylor parameters from lemon peel CWM measured using different methods

Materials	k	T _s (°C)
DSC		
AIR	4.81 ± 0.83 ^a	117.2 ± 17.5 ^a
TMCT		
AIR	0.67 ± 0.10 ^b	43.16 ± 2.55 ^b
Functionalized AR	0.59 ± 0.15 ^b	37.36 ± 3.24 ^c

627

628 Table 3. Reaction rate constant (± approx. standard error) of the functionality loss during
 629 storage (14 weeks) for functionalized AR at different condition

Moisture content (%w.b)	Storage condition		rate constant (k)
	Temperature (°C)		
11	10		0.010 ± 0.006 ^a
11	25		0.087 ± 0.013 ^b
11	40		0.493 ± 0.064 ^c
14	10		0.015 ± 0.004 ^a
14	25		0.091 ± 0.009 ^b
14	40		0.497 ± 0.073 ^c
16	-10		0.006 ± 0.002 ^a
16	10		0.016 ± 0.004 ^a
16	25		0.093 ± 0.003 ^b
16	40		0.441 ± 0.033 ^c

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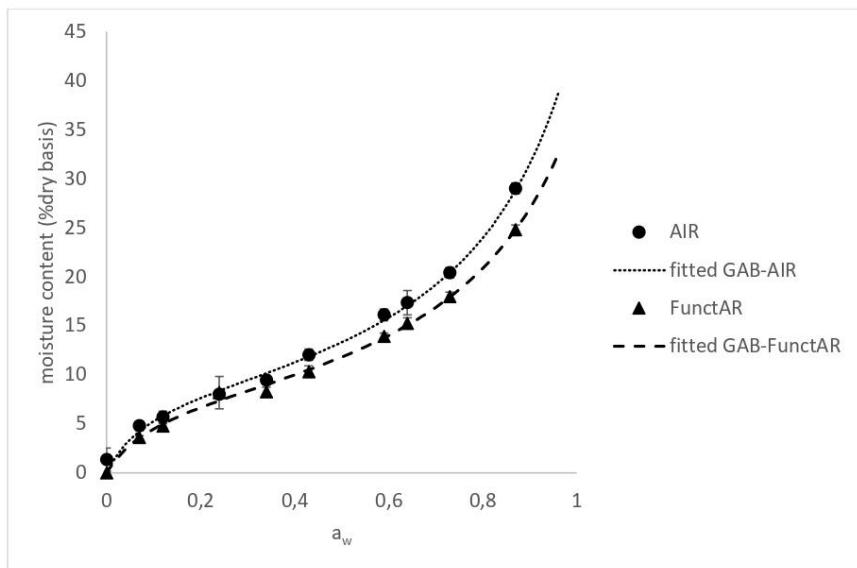
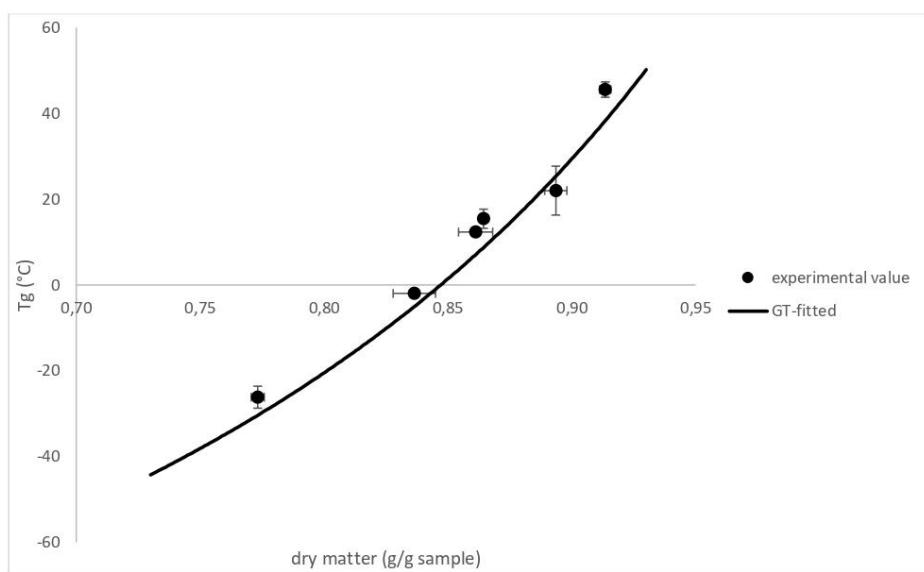


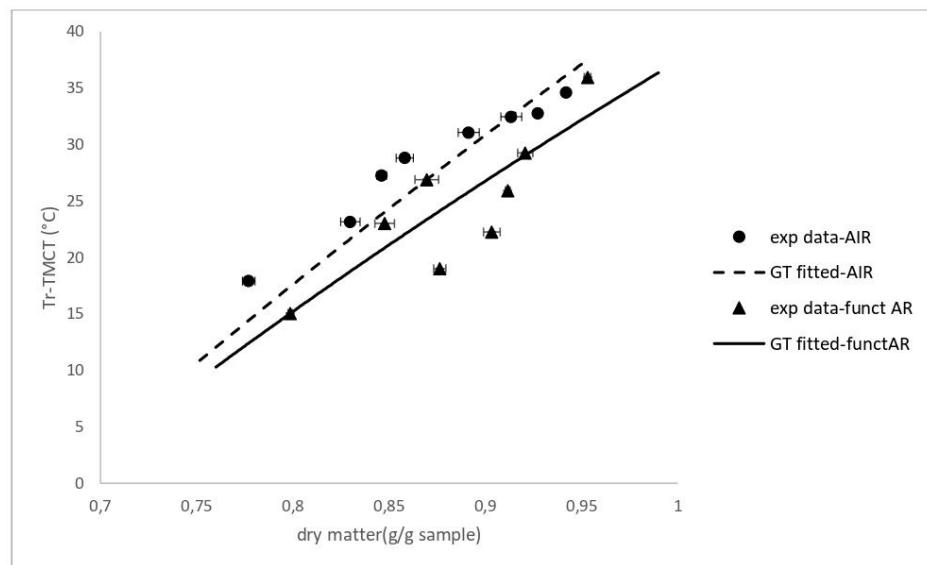
Figure 1. Moisture Sorption isotherm at 4°C for AIR and functionalized AR from lemon peel

634



635

Figure 2. T_g of lemon peel AIR as measured by DSC



636

637
638

Figure 3. Temperature of relaxation for AIR and functionalized AR from lemon peel as measured by TMCT

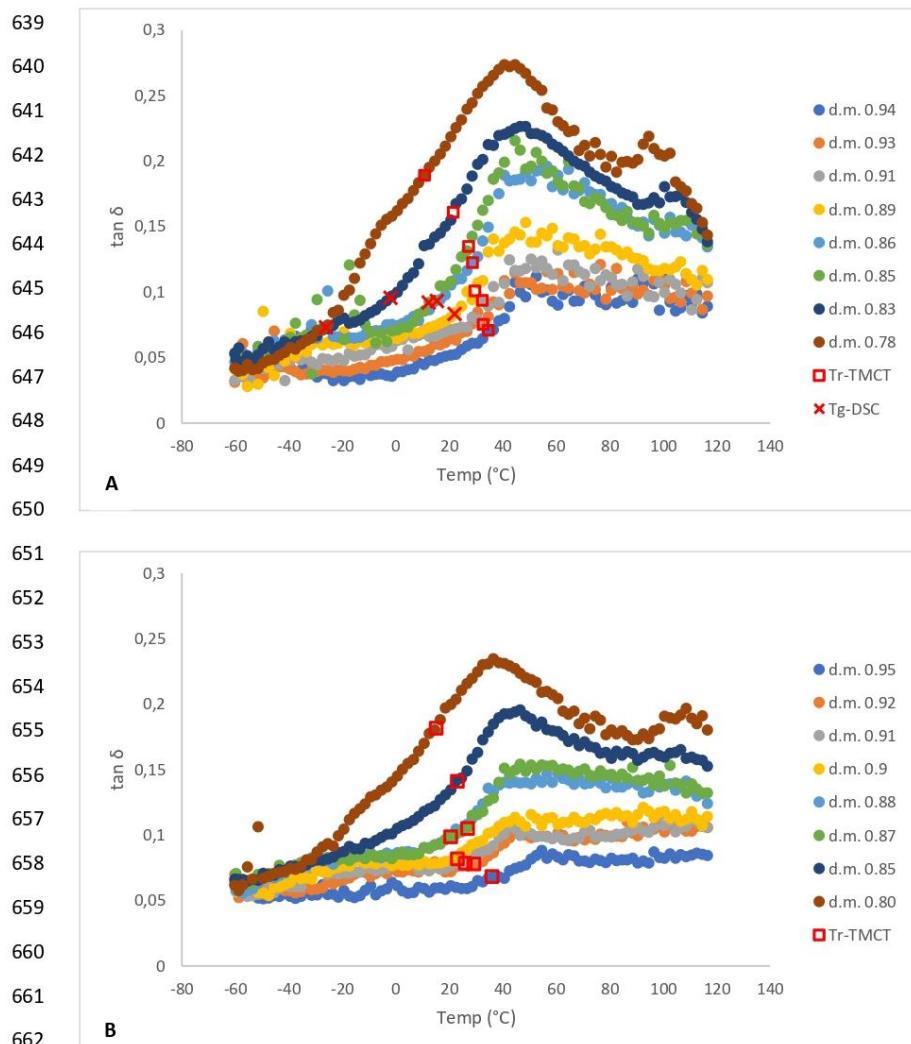
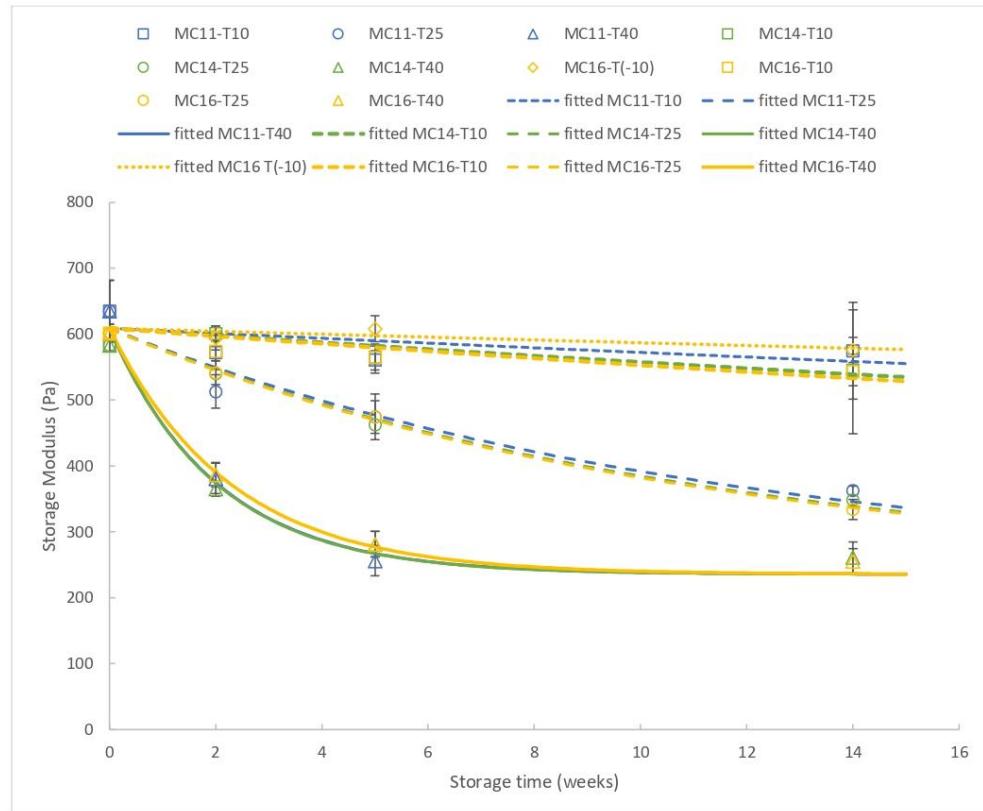


Figure 4. Tan δ curve from DMTA analysis together with Tr-TMCT and Tg for (A) AIR and (B) Functionalized AR

668



669

670
671

Figure 5. Storage modulus (G') of CWM residue suspensions (2% d.m) at $\omega = 1$ Hz from functionalized AR with different moisture content and storage temperature

672

IV. Confirmation Revision 1

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Relaxation temperature and storage stability of the functionalized cell wall material residue from lemon peel

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Carmen Petkowicz
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Editor and Reviewer comments:

Reviewer 2: The responses provided by the authors to all questions and comments are convincing. In addition, all requested revisions have been made. Therefore, the manuscript is now suitable for publication in Food Hydrocolloids.

Reviewer 3: Dear Authors,

In the first round of review I asked for providing at least monosaccharides composition of AIR and AR. In the response, authors referred me to previously published paper (line 119-120):

Willemsen, K. L. D. D., Panozzo, A., Moelants, K., Debon, S. J. J., Desmet, C., Cardinaels, R., Moldenaers, P., Wallecan, J., & Hendrickx, M. E. G. (2017). Physico-chemical and viscoelastic properties of high pressure homogenized lemon peel fiber fraction suspensions obtained after sequential pectin extraction. *Food Hydrocolloids*, 72, 358-371. <https://doi.org/10.1016/j.foodhyd.2017.06.020>

The above paper was published 6 years ago. In M&M of the current paper authors write that "Dry and milled lemon peel (LP) powder was provided by Cargill R&D Centre Europe (Vilvoorde, Belgium)." Does it mean that this study was performed on the same batch of lemon peel as 6 years ago by Willemse et al (2017)? If yes, please state it clearly in current manuscript.

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VI. Revised Manuscript 2

1 **Relaxation temperature and storage stability of the functionalized cell wall material**

2 **residue from lemon peel**

3

4 Novita I Putri*, Jelle Van Audenhove, Clare Kyomugasho, Ann Van Loey, Marc Hendrickx**

5

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24 Journal : Food Hydrocolloids

25

26 Declarations of interest : none

27 **ABSTRACT**

28

29 Lemon peel cell wall material (CWM) residue obtained after acid pectin extraction can be
30 functionalized into a texturizing ingredient using mechanical treatments such as high-pressure
31 homogenization. The application of CWM as a texturizing ingredient is most likely through a dry
32 powder and thus the stability of its functionality (rheological property) during storage becomes an
33 obvious question. However, studies on the glass transition properties of this CWM residue and
34 its relation to storage stability are largely lacking. This study aims to first evaluate the potential of
35 two methods, i.e. DSC analysis and combined TMCT-DMTA (thermal mechanical compression
36 test – dynamic mechanical thermal analysis) to measure the Tg and relaxation temperature of
37 lemon peel CWM and subsequently relate the results to the stability of the material's rheological
38 property. The results showed that DSC-based Tg measurements may not be the most appropriate
39 indicator for storage stability of the lemon peel CWM residue, despite being the most commonly
40 used method to explain state transition in materials. On the other hand, the structural relaxation
41 phenomena elucidated by the change in mechanical properties measured by TMCT-DMTA
42 correlated with the results of storage stability of the material. To ensure the stability of the CWM
43 residue, storage should be carried out at conditions (temperature and moisture content) before
44 the onset of $\tan \delta$ curve change. In conclusion, relaxation phenomena observed through the
45 measurement of mechanical properties, in particular the $\tan \delta$ curve from DMTA, provides a
46 suitable starting point for inferring the stability of the functionalized CWM residue.

47

48 **Keywords** : *cell wall material, glass transition, structural relaxation, storage stability*

49

50

51

52

53 **1. Introduction**

54

55 Lemon peel, by-products from the citrus processing industry, is produced in relatively high
56 amounts which puts a significant burden on the environment. An efficient by-product management
57 strategy is needed to minimize its environmental impact and to increase the overall valorization.
58 To date, the extraction of citrus pectin, an ingredient widely used as thickening agent in food
59 production, is the most widely implemented valorization route of lemon peels. However, the
60 industrial pectin extraction process leaves another significant amount of fiber-rich material.
61 Previous studies have shown that suspensions prepared from the residue left after acid pectin
62 extraction (AR) have excellent rheological properties (high storage modulus), especially after
63 mechanical treatment such as high pressure homogenization (HPH) (Putri et al., 2022; Willemsen
64 et al., 2017). The functionalization with HPH caused changes on the microstructure of the AR
65 particles, including fragmentation (size reduction) and aggregation. The aggregation formed a
66 network which entraps water, creating a gel-like structure in suspension. This means that the
67 functionalized pectin-depleted residue has a high potential as a texturizing ingredient, therefore a
68 study of this ingredient's stability during storage becomes necessary.

69

70 The concept of glass transition temperature (Tg) has been used widely to predict the stability of
71 foods and food ingredients (Sablani et al., 2007). When a material is in its glassy state (at a
72 temperature below the Tg), it is regarded as stable due to its limited molecular mobility. Contrary,
73 when a material is put into a condition (temperature-moisture combination) above its Tg, the rate
74 of physical, chemical and biological changes largely increases and the material becomes unstable
75 (Champion et al., 2000). The glass transition phenomena can be perceived from changes in the
76 thermal and mechanical properties of the material as it is heated/cooled. The most common
77 method to determine the Tg of a material is by measuring the change in the heat capacity using
78 differential scanning calorimetry (DSC). However, the changes in the thermal properties of some

79 food materials, such as the cell wall material (CWM), can be very small during the transition,
80 making it difficult to detect (Boonyai et al., 2006; Roos, 1998). Therefore, in this study, the Tg of
81 the functionalized lemon peel residue after pectin extraction was measured by both the change
82 in thermal and mechanical properties.

83

84 To date, only few studies are available on CWM stability during storage and moreover studies on
85 pectin-depleted CWM, to the best of our knowledge, are not existing. The available studies on
86 fiber-rich materials (Fernandez-Lopez et al., 2009; Sharma et al., 2017) mostly demonstrate the
87 degradation of fiber quality during storage without correlating it to the concept of molecular
88 mobility and glass transition, possibly due to the limitation of the Tg analysis. The quality
89 degradation could be attributed to the collapse of the material due to moisture absorption
90 (Fernandez-Lopez et al., 2009). Collapse happens when a material loses its structure and
91 volumetric shrinkage occurs causing loss of porosity (Levi & Karel, 1995). Collapse of amorphous
92 food materials, occurs because of a solid flow resulting from a decreasing viscosity whereby the
93 matrix is no longer capable to support and carry its own mass (Fan & Roos, 2017). This solid flow
94 arises from an increased molecular mobility. However, the characterization of the molecular
95 mobility and its relation to the storage stability of CWM has not been extensively studied.
96 Therefore, this study attempts to fill this gap by describing the molecular mobility of CWM based
97 on the changing mechanical properties and how these changes relate to the functionality
98 (specifically rheological property) of the material.

99

100 This study aims to include the different methods to measure Tg and relaxation temperature of
101 lemon peel CWM residue and relate them to the stability of the material's rheological property as
102 influenced by storage. An understanding of how the material behaves during storage may
103 encourage its application in industry and support the effort to valorize the residue of lemon peel
104 after pectin extraction.

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102 influenced by storage. An understanding of how the material behaves during storage may
103 encourage its application in industry and support the effort to valorize the residue of lemon peel
104 after pectin extraction.

105

106 **2. Materials and Methods**

107

108 *2.1. Materials*

109 Dry and milled lemon peel (LP) powder was provided by Cargill R&D Centre Europe (Vilvoorde,
110 Belgium). All the chemicals used for moisture content equilibration were of analytical grade.

111

112 *2.2. Dried Functionalized Acid Residue Preparation*

113

114 The dry LP was treated to obtain the Alcohol Insoluble Residue (AIR) and subsequently pectin
115 was extracted from the AIR using nitric acid at pH 1.6, 80°C for 1 hour. The unextractable fraction
116 were collected as Acid Residue (AR). The AR was then resuspended at 2% solid concentration,
117 the pH was adjusted to 4.5 and then high pressure homogenized at 20 MPa (Panda 2k NS 1001L,
118 GEA Niro Soavi, Parma Italy). All these procedures have been described in detail in our previous
119 studies (Putri et al., 2022; Willemsen et al., 2017). ~~For the detailed composition of AIR and AR
120 from lemon peel, readers are directed to the previous publication (Willemsen et al., 2017).~~ After
121 HPH, the functionalized AR was air-dried after water-alcohol exchange. For this, the
122 functionalized AR was mixed with technical ethanol 99% at a 1:4 (v/v) ratio for 10 minutes and
123 then allowed to stand for 60 minutes. This mixture was vacuum filtered (Machery-Nagel MN 615).
124 A second round of alcohol-water exchange were carried out with the technical ethanol 99% at the
125 ratio of 1:1 from initial volume of material. This mixture was allowed to stand for 30 minutes, and
126 vacuum filtered. The solids after filtration were air-dried overnight to obtain the dried functionalized
127 AR. The moisture content after drying was 11.1 ± 1.1 % w.b. The dried functionalized AR was
128 kept in vacuum bags in a freezer at -40°C until further use.

129

130 *2.3. Composition analysis of the samples*

131
132 The composition of both AIR and functionalized AR was determined by neutral sugar analysis
133 (using HPAEC-PAD), galacturonic acid content analysis (using spectroscopy) and protein content
134 analysis (using combustion method). The analyses were carried out in triplicates using the method
135 explained in our previous study (Putri et al., 2022).

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136
137 2.3.2.4. Moisture content equilibration and sorption isotherm

138

139 In order to achieve various moisture content, the AIR and functionalized AR powder were stored
140 at 4°C for at least 3 weeks in containers with P₂O₅ (a.w. 0.00) or saturated salt solutions : LiBr
141 (a.w. 0.07), LiCl (a.w. 0.12), CH₃COOK (a.w. 0.24), MgCl₂ (a.w. 0.34), K₂CO₃ (a.w. 0.43),
142 Mg(NO₃)₂ (a.w. 0.59), NaBr (a.w. 0.64), KI (a.w. 0.73) and KCl (a.w. 0.87) (Greenspan, 1976).
143 The moisture content of the material was measured at the end of the equilibration period by
144 gravimetric analysis. The moisture sorption isotherm was obtained and fitted to the GAB equation
145 (see below) by non-linear regression.

146
$$W = \frac{CKW_m a_w}{(1-Ka_w)(1-Ka_w+CKa_w)} \quad (\text{eq.1})$$

147 W is the equilibrium moisture content of the material on dry basis and a_w is the water activity. W_m,
148 C and K are the fitted constants. W_m represents the amount of water adsorbed in the monolayer.
149 The W_m value indicates the availability of active water sorption sites on the material. C represents
150 the strength of water binding with a larger C value indicating a stronger binding of water in the
151 monolayer. K is a correction factor, when K approach one, there is no distinction between the
152 water molecules beyond the monolayer and pure water (Quirijns et al., 2005).

153

154

155 2.4.2.5. Molecular mobility analysis with different methods

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156

157 2.4.1-2.5.1. Differential Scanning Calorimetry

158

159 A Differential Scanning Calorimeter Q-2000 (TA instruments, USA) was used to scan the thermal
160 behavior of AIR and functionalized AR powder with different moisture contents. Approximately 20
161 mg of the powder was weighted into hermetically sealed T_{zero} aluminium pans. An empty pan was
162 used as a reference and two cycles of heating-cooling were carried out, first from -60°C to 90°C
163 and second from -60°C to 120°C, both at a rate of 10°C/min. Glass transition temperature, further
164 referred to as T_g , was defined as the mid-point of the transition range observed in the heat flow
165 curve of the second heating cycle (Kymugasho et al., 2021; Pelgrom et al., 2013). An example
166 of such heat flow curve and the analysis of the transition is presented in the Supplementary
167 Materials (Figure S-1). The analysis was carried out in triplicate.

168

169 2.4.2-2.5.2. Thermal Mechanical Compression Test - Dynamic Mechanical Thermal Analysis

170

171 Combined TMCT-DMTA analyses were carried out according to the methods described in
172 Aravindakshan et al. (2022) using an Anton Paar MCR302 rheometer (Graz, Austria) equipped
173 with a CTD450 oven. Approximately 2 g of the sample (AIR or functionalised AR powder) was
174 loaded into the measuring system (cylindrical cup Ø 22 mm ; cylindrical bob Ø 20 mm) and the
175 oscillation-compression force was applied at normal force 30 N, shear strain 0.05% and frequency
176 1 Hz. The temperature scan spanned -60°C to 120°C at the rate of 2°C/min.

177

178 From the TMCT-DMTA data, two different values of relaxation temperature were obtained. First,
179 the relaxation temperature from TMCT analysis (Tr-TMCT), determined based on the change of
180 the sample compressibility due to the normal force by measuring the displacement of the probe
181 during the heating scan (with correction of the measuring system's thermal expansion from a scan

182 on microcrystalline cellulose). Secondly, the relaxation phenomena from the DMTA were based
183 on the change of the ratio between loss and storage modulus (or loss factor, $\tan \delta$) obtained using
184 oscillatory shear measurements.

185

186 2.4.3-2.5.3. Gordon-Taylor equation fitting

187

188 The T_g values obtained from DSC and relaxation temperature from TMCT analysis (Tr-TMCT)
189 were fitted into the Gordon-Taylor (G-T) equation below using non-linear regression analysis.

190
$$T = \frac{T_s \times X_s + X_w \times T_w \times k}{X_s + X_w \times k} \quad (\text{eq. 2})$$

191 where s denotes the solid fraction (CWM) of the sample, w denotes the water fraction, T is the
192 temperature of transition or relaxation, T_w is the glass transition temperature of water = -135°C , X
193 is the mass fraction and k is the constant that corresponds to the plasticizing effect of water on
194 the material.

195

196 2.5.2.6. Storage Study Setup

197

198 A storage study was set up for the dried functionalized AR based on the results of the DSC and
199 TMCT-DMTA analysis. Various storage conditions were identified to encompass various states
200 of the functionalized AR, from stable to unstable. A combination of three moisture contents (11%,
201 14% and 16% w.b.) and three storage temperature (10, 25, and 40°C) was used. An additional
202 temperature condition (-10°C) was used to store the material at 16% w.b. moisture content to
203 ensure that storage at an anticipated stable condition was well covered. To adjust the moisture
204 content prior to the storage study, the functionalized AR were equilibrated in airtight containers
205 above saturated salt solutions (MgCl_2 , MgNO_3 and KI) for 5 weeks. After moisture equilibration,
206 the functionalized AR were packed into inert glass jars with minimum headspace to prevent

207 moisture exchange and stored for 2, 5 and 14 weeks. At the end of each storage period, the dried
208 functionalized AR samples were regenerated (in duplicate) into 2% w/w solid suspensions. The
209 regeneration was done by letting the material stand in water for 1 hour and followed by mixing
210 using L5M-A mixer with an emulsion screen workhead (Silverson, East Longmeadow, MA, USA)
211 at 4300 RPM for 10 minutes. The rheological properties of these suspensions were measured as
212 an indicator of the material's functionality.

213

214 The results of the storage study were fitted by non-linear regression using a first order fractional
215 conversion model :

$$G'(t) = G'_f + (G'_i - G'_f)e^{-kt} \quad (\text{eq. 3})$$

216 where G' is an estimated final extend of functionality loss, G'_i is the average initial value of G'
217 observed, t is the storage time (week) and k is the reaction rate constant.

218

219 2.6.2.7. Rheological property analysis

220

221 The rheology of the CWM suspension was analyzed using the method according to (Willemsen
222 et al., 2018). An Anton Paar MCR302 rheometer (Graz, Austria) equipped with a custom-built cup
223 and concentric cylinder with conical bottom was used. The gap between the cylinder and the cup
224 was 2 mm. Strain sweep (at ω 1 Hz and strain 0.01% - 100%) was done to determine the linear
225 viscoelastic region and a frequency sweep (at ω 100 to 0.1 Hz and strain 0.1%) was carried out
226 at 25°C. Rheology analysis was carried out in duplicate, each with newly loaded samples.

227

228 2.7.2.8. Statistical analysis

229

230 Significant statistical difference ($\alpha = 0.05$) between model-fitting parameter were determined by
231 confidence interval calculation. GAB and G-T curve fitting was carried out in JMP Pro 17 statistical

233 software (SAS Institute Inc, Cary, NC, USA) and fractional conversion model fitting for the storage
234 study results was done in SAS statistical software (SAS Institute Inc, Cary, NC, USA).

235

236 **3. Results and Discussions**

237

238 *3.1. Composition of AIR and functionalized AR*

239
240 The monosaccharides that comprise the CWM samples (both AIR and functionalized AR) and
241 their protein content are presented in Table 1. Both AIR and functionalized AR are mainly
242 composed of cell wall polysaccharides, i.e. cellulose, hemicellulose and pectin. A small portion of
243 protein (5 – 7% d.b.) was detected in both AIR and functionalized AIR. The main difference
244 between AIR and functionalized AR are the galacturonic acid content, which can be an indicator
245 of pectin content. Since functionalized AR underwent pectin extraction process in order to
246 increase the CWM functionality as texturizing ingredient (Putri et al., 2022), approx. 50% of the
247 pectin were removed. Consequently, the proportion of cellulose and hemicellulose, as indicated
248 by the glucose, xylose and galactose content, in the functionalized AR sample increased.

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249
250 *3.1.3.2. Isotherm Sorption of the materials*

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251
252 The relation between water activity and moisture content (moisture sorption isotherm) is an
253 important characteristic in the study of the stability of low-moisture food product (Koç et al., 2010;
254 Lee & Robertson, 2022; Sant'Anna et al., 2014). The moisture sorption isotherm (at 4°C) for both
255 materials in the present study, AIR and functionalized AR from lemon peel, is shown in Figure 1.
256 Both materials showed a type II behavior according to the Brunauer-Emmet-Teller classification,
257 which is frequently found in food products (Andrade P. et al., 2011). The experimental data was
258 fitted to the GAB equation and the estimated value for the parameters are shown in Table 4

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259 2. Both AIR and functionalized AR showed similar C and K values but significantly different
260 monolayer values (W_m). AIR had a significantly higher W_m which indicating that it has more active
261 (or better accessible) water sorption sites. This is also shown in the moisture sorption isotherm
262 graph, in which AIR had higher moisture content at a given a_w value compared to the
263 functionalized AR. This difference is expected since AIR contained more hygroscopic
264 components, such as low molecular weight compounds and pectin, that were partially extracted
265 for the functionalized AR. It has been largely acknowledged that the composition of the materials
266 affected the moisture sorption capacity (Sormoli & Langrish, 2015; Timmermann et al., 2001). The
267 sorption isotherm data at 4°C were used to prepare samples at specific moisture contents in view
268 of the Tg/Tr measurements and the storage experiment.

269

270 3.2.3.3. Glass transition and structural relaxation of the cell wall material from lemon peel

271

272 3.2.4.3.3.1. Differential Scanning Calorimetry (DSC)

273

274 DSC is one of the commonly used methods to measure Tg. It measures the transition in the
275 thermal properties of the material by measuring the change of specific heat (Le Meste et al.,
276 2002). However, DSC was not sensitive enough to measure the Tg of the functionalized lemon
277 peel AR. On the other hand, transition in the DSC thermogram, albeit weak and broad, was
278 observed for lemon peel AIR, except for samples with very low moisture content (<9% w.b). AIR
279 contains larger amounts of components that may contribute to the thermal glass transition, for
280 example sugars, oligosaccharides, or acids. These components were extracted from the AIR
281 during the AR preparation and consequently, the functionalized AR from lemon peel contains
282 mainly cellulose and multiple other biopolymers such as pectin and hemicellulose (Table 1) (Putri
283 et al., 2022). The change in the heat capacity occurring over the glass transition of biopolymers
284 is relatively small and therefore difficult to be captured by DSC (Roos, 1998; Sablani et al., 2010).

285 Consequently, the DSC results could not provide precise specific transitions for food containing
286 predominantly component with large molecular weight, such as the functionalized AR. Therefore,
287 to describe the glass transition phenomena of CWM residues with DSC, the data from the AIR
288 samples at higher moisture content ($\geq 9\%$ w.b.) are used in this study.

289

290 The mid-point of the transition shown in the thermogram of the second heating cycle of AIR
291 samples was identified as its Tg-value. The Tg of the AIR sample in function of dry matter content
292 is presented in Figure. 2. Despite the insensitivity of the DSC method for Tg measurement of
293 CWM, few studies reported Tg values for papaya (Nieto-Calvache et al., 2019) and carrot CWM
294 (Georget et al., 1999), with similar and slightly higher Tg compared to lemon peel AIR,
295 respectively. As the moisture content of the lemon peel AIR increased, the Tg decreased, which
296 is a common behavior in many biological materials. It is a well-established fact that water acts as
297 a plasticizer and causes a depreciation of Tg in low moisture food (Le Meste et al., 2002; Roos,
298 1998). Previous studies also showed this moisture plasticizing effect in fiber-rich material obtained
299 from apple pomace and carrot (Georget et al., 1999; Zlatanović et al., 2019). The value of Tg in
300 function of dry matter content of the lemon peel CWM were fitted to G-T equation and the
301 parameters obtained, T_s and k , are presented in [Table 2](#)[Table 3](#). The moisture plasticizing effect
302 (as indicated by the k value of G-T equation) measured by DSC was 4.81, which is similar to other
303 fruit- and vegetable-based food materials and food products (Fongin et al., 2017; Stępień et al.,
304 2020).

305

306 [3.2.2-3.3.2.](#) *Thermal Mechanical Compression Test – Dynamic Mechanical Thermal Analysis*
307 *(TMCT-DMTA)*

308

309 Contrary to the DSC method, the TMCT-DMTA managed to clearly show structural relaxation
310 phenomena in both lemon peel AIR and functionalized AR. This supported the well-established

311 fact that the mechanical property analysis is more sensitive in measuring the transition or
312 relaxation phenomena in food products (Roos, 1998). TMCT-DMTA analysis reveals structural
313 relaxation phenomena based on the change in the material's mechanical properties, more
314 specifically the compressibility and the moduli obtained from oscillatory shear analysis. As the
315 result of the TMCT-DMTA is highly dependent on the measurement frequency (Le Meste et al.,
316 2002), please note that all the structural relaxation temperatures described here are based on
317 measurement at a frequency 1 Hz.

318

319 Tr-TMCT in function of dry matter content for both AIR and functionalized AR is shown in Figure
320 3. Representative Δ gap curves used for the calculation of Tr-TMCT are presented in the
321 Supplementary Materials (Figure S-2). AIR and functionalized AR have similar values of Tr-TMCT
322 and show similar changes due to the moisture plasticizing effect. The values of Tr-TMCT slightly
323 decreased as the sample's moisture content increased. However, the moisture plasticizing effect
324 on the TMCT results (and DMTA) in this study was very limited, especially if compared to the
325 plasticizing effect on the thermal transition. The mechanism of the moisture plasticizing effect on
326 the structural relaxation of glassy biopolymers, especially amorphous carbohydrates (using
327 maltodextrin as an example), has been proposed (Kilburn et al., 2004). First, the absorbed water
328 would fill small voids in the glassy matrix of the material, changing the matrix free volume. Second,
329 the water would interfere with intermolecular hydrogen bonds, increasing the degree of freedom
330 of the carbohydrate molecules and eventually caused coalescence of the voids. This proposed
331 mechanism seems to suggest that the plasticizing effect is limited by the diffusion of water into
332 the small voids in the matrix. The complex and rigid structure of CWMs may have hindered the
333 plasticizing mechanism on its structural relaxation behavior and thus limiting the effect of
334 moisture.

335

336 When the Tr-TMCT values were fitted to the G-T equation, the values of anhydrous relaxation
337 temperature (T_g) and k obtained were exceptionally low compared to the parameters obtained for
338 the DSC based T_g curve (Table 2Table 3). This indicates that the material behavior reflected by
339 the Tr-TMCT value change with moisture content is vastly different from the T_g values obtained
340 by DSC. This may suggest that the two methods captured different mechanism of relaxation. This
341 hypothesis will be substantiated further with the storage study results discussed in section 3.3.
342 below. Based on the Tr-TMCT behavior and the fitted parameters value, the G-T equation may
343 not be appropriate to describe the relaxation phenomena obtained by TMCT.
344
345 The result from the DMTA analysis, specifically the $\tan \delta$ curve in function of temperature, is
346 presented (Figure 4) to describe the structural relaxation phenomena of the lemon peel CWM
347 residue. The storage (G') and loss modulus (G'') curves in function of temperature are presented
348 in the Supplementary Materials (Figure S-3). Comparable behavior of the moduli and loss factor
349 as a function of temperature was observed for pea and soybean cotyledon (Ballesteros & Walters,
350 2011, 2019). They showed that over the range of -120°C to 120°C, the G' measured declined in
351 the beginning (at low temperature) and started to increase from a certain temperature onwards.
352 The G'' was constant in the beginning and started to increase towards a plateau, and $\tan \delta$
353 increased towards a plateau or a peak. The value of relaxation temperature (Tr-DMTA) generally
354 could be determined by the peak of loss factor ($\tan \delta$) (Liu et al., 2006). However, the peak of the
355 $\tan \delta$ in this study was difficult to be precisely determined, especially for samples with very low
356 moisture content. Therefore, the structural relaxation phenomena will be discussed based on the
357 behavior of the $\tan \delta$ curve. As a reference, the $\tan \delta$ curve of microcrystalline cellulose in function
358 of temperature is presented in the Supplementary Materials (Figure S-4).
359
360 The $\tan \delta$ curve of lemon peel CWM, can be approximately divided into three regions : (i) a lower
361 temperature range with the onset of $\tan \delta$ change (preceded by a constant value, especially for

362 the low moisture systems) (ii) a medium temperature range with a steep increase of $\tan \delta$, and
363 (iii) a final region where $\tan \delta$ reached its highest value and became constant or started to decline.
364 At low temperature region (between -60°C to 20°C, with different range for samples with different
365 moisture content), the $\tan \delta$ was mostly constant. As the CWM residue was heated, $\tan \delta$ started
366 to increase (onset region) at a temperature between -30°C and 20°C. The increase of $\tan \delta$ upon
367 heating suggests that the material started to lose its stiffness and a more plastic deformation could
368 occur. The loss of stiffness continued at the second region with a steep increase of $\tan \delta$ and it
369 reached a maximum point at temperature between 40°C - 50°C.

370

371 The plasticizing effect of moisture could be observed in the DMTA results based on the changes
372 of $\tan \delta$ curve behavior. First, the absolute values of $\tan \delta$ increased with the increase in the
373 moisture content of the samples. The increase of $\tan \delta$ after the onset region also became more
374 drastic as the moisture content in the sample increased and it occurred at lower temperatures for
375 samples with higher moisture contents. Lastly, the maximum value of $\tan \delta$ was reached at lower
376 temperatures as the moisture content of the samples increased. The $\tan \delta$ curve for AIR (Figure
377 4A) and functionalized AR (Figure 4B) showed very similar behavior. However, the plasticizing
378 effect of moisture was more pronounced in the $\tan \delta$ curve of AIR, as also observed in the Tr-
379 TMCT results.

380

381 In order to compare all methods of the transition/relaxation analysis, Tg and Tr-TMCT points were
382 overlayed on the $\tan \delta$ curve (Figure 4). DSC-based Tg values (based on AIR results) seem to be
383 located approximately at the onset of the $\tan \delta$ change. On the other hand, Tr-TMCT values are
384 located at around the middle (inflection point) of the rapidly increasing section of $\tan \delta$ curve
385 (Figure 4), coinciding with the lowest value of G' and on the point where G'' starts to increase
386 (Figure S-3). Therefore, these points on the DMTA curves seems to indicate the onset of the
387 change in compressibility of the material.

388

389 The value of Tr-TMCT of lemon peel CWM (AIR) at each moisture content was higher than the
390 measurable Tg value from DSC, except for sample with the lowest moisture content (9% w.b.).
391 This observation agrees with many studies that showed higher mechanical relaxation
392 temperatures compared to thermal glass transition (Boonyai et al., 2006; Fan & Roos, 2017;
393 Georget et al., 1998; Rahman et al., 2007). However, the temperature of transition for anhydrous
394 material (T_g) obtained from the G-T equation fitted parameter were much lower for Tr-TMCT result
395 (~40°C) compared to DSC (117°C). The huge difference in the anhydrous transition/relaxation
396 temperature and the moisture plasticizing effect may indicate completely different
397 transition/relaxation phenomena observed between the thermal and mechanical method of
398 analysis. This raises the question of which temperature (structural relaxation or glass transition)
399 is better suited to predict the storage stability of CWM.

400

401 The increasing $\tan \delta$ behavior suggests higher translational molecular mobility in the CWM
402 residue which is suspected to have a detrimental effect on the stability of the functionalized AR
403 during storage. Higher molecular mobility increased the solid flow of molecules in the matrix of
404 CWM which may induce collapse (Fan & Roos, 2017). Thus, a storage study was subsequently
405 performed on the functionalized AR from lemon peel in order to corroborate whether the change
406 in the behavior of $\tan \delta$ curve could be useful in predicting CWM residue's stability during storage.
407 The behavior of the $\tan \delta$ curve depicted in Figure 4 was used to determine different storage
408 conditions that will cover different regions, from stable to unstable. Three temperature conditions
409 were chosen, 10, 25 and 40 °C to represent the temperature before onset of $\tan \delta$ change, after
410 onset when the $\tan \delta$ curve began to increase rapidly (but still below Tr-TMCT) and when the $\tan \delta$
411 curve almost reached its maximum value (above Tr-TMCT), respectively. Three moisture
412 content values (11%, 14% and 16%) were selected, each corresponding to a different $\tan \delta$ curve
413 profile to include the effect of water plasticization on the storage stability. An additional storage

414 temperature of (-10)°C was added to the samples with highest moisture content to ensure that
415 also in this case, a stable storage point (well before the onset of $\tan \delta$ change) was covered.

416

417 3.3.3.4. *Storage stability and its relation to the molecular mobility*

418

419 The storage stability study was focused on the change of the functionality of lemon peel CWM
420 residue. Therefore, the rheological property, specifically G' , was measured to indicate the stability
421 (or deterioration) of the texturizing potential of the functionalized AR. The values of G' throughout
422 14 weeks of storage are presented in Figure 5. Samples stored at conditions before the onset of
423 $\tan \delta$ change (at -10°C and 10°C) showed a stable G' up to 14 weeks of storage. When the
424 storage temperature was higher than the onset of $\tan \delta$ change (at 25°C and 40°C), a significant
425 decline in the G' -values was observed during storage. To quantify the rate of the G' decline or the
426 rate of functionality loss during storage, the fractional conversion model was fitted to the results.

427 The rate constant (k) values are presented in [Table 3](#)[Table 4](#) below. The rate of the decline
428 significantly increased as the storage temperature increased. Samples stored at 25°C show a
429 lower k -value compared to samples stored at 40°C. However, after 14 weeks of storage, the G'
430 value of samples stored at 25°C declined significantly, reaching a similar value to the samples
431 stored at 40°C. On the other hand, samples stored at 40°C already experienced a severe decline
432 after 5 weeks of storage.

433

434 The samples stored at 25°C showed a decline in G' value despite stored under the Tr-TMCT
435 values, indicating that Tr-TMCT did not correspond to the stability of CWM functionality during
436 storage. In conclusion, the relaxation phenomena described in the $\tan \delta$ curve correlate well to
437 the storage stability of the lemon peel CWM. When the storage condition (temperature and
438 moisture content) is located in the more progressed region of the $\tan \delta$ curve which may indicate
439 higher molecular mobility, the faster the decline on the G' . As long as the storage conditions were

440 kept below the onset of the $\tan \delta$ curve change, degradation of the functionality of the CWM
441 residue were limited.

442

443 The declining G' during storage that happened when samples were stored at conditions where
444 the $\tan \delta$ curve was increasing could be attributed to the structure collapse of the cell wall matrix.
445 Such physical change could occur due to increasing molecular mobility when the material is
446 transformed into a more viscous state (Fan & Roos, 2017). When $\tan \delta$ increased, stiffness of the
447 molecules decreased which also suggests the reduction of the material viscosity to a level that is
448 no longer sufficient to support the structure of the solid material. The increased viscous flow
449 caused subsequent densification (Fan & Roos, 2017; To & Flink, 1978). In this case, the structural
450 units (for example the repetitive element of the biopolymers in the CWM) can move independently
451 from each other (Champion et al., 2000). Thus, interactions between cellulose microfibrils became
452 possible which hindered the formation of an open CWM network that entraps water during the
453 reconstitution of the material into suspension. Collapse of CWM, which could be prompted by
454 many factors and treatments such as mechanical breaking (Van Audenhove et al., 2022) and
455 chemical treatment, e.g. with alkaline solution, could lead to the reduction of CWM suspension's
456 functionality. This transformation in the mechanical properties of solid materials may lead to
457 substantial alterations of its performance in processing, storage stability, and sensory properties
458 (Fan & Roos, 2017).

459

460 Previous study (Fernandez-Lopez et al., 2009) showed that degradation of the fiber-rich material
461 functional properties, such as water binding capacity, became more severe as the moisture
462 content increased during storage. Contrary, in this study, the rate of functionality loss (k -value)
463 was not significantly different between samples stored at different moisture content (Table 3Table
464 4). At the same storage temperature, the moisture content of the samples (within the moisture
465 content range studied) did not significantly affect the G' of the functionalized AR during storage.

466 The plasticization effect of moisture was not pronounced in the storage study, contrary to common
467 low-moisture food product behavior (Fan & Roos, 2017; Le Meste et al., 2002). As discussed
468 previously, the limited moisture plasticizing effect, that was also observed in the results of TMCT-
469 DMTA of CWM samples, was suspected to be caused by the composition of functionalized AR.
470 Functionalized AR is composed mainly of cellulose and cellulose in its native form is a rigid
471 polymer with some crystalline region in its structure, which may prevent the water migration into
472 the particles and thus limit the moisture plasticizing effect. A NMR experiment which studied the
473 effect of hydration on polymer mobility in onion CWM showed that water readily penetrated the
474 pectin network and increased its mobility, whereas cellulose mobility was unaffected by hydration
475 (Hediger et al., 1999).

476

477 Furthermore, although the moisture plasticizing effect on the Tg of lemon peel CWM was clearly
478 observed from the DSC results, this effect could not be seen in the storage study results. Larger
479 differences between the storage temperature and Tg should normally cause faster deterioration
480 of materials (Kyomugasho et al., 2021; Roos, 1995; Zlatanović et al., 2019), however this
481 phenomena also could not be observed in the results of the storage study. The substantial
482 transition in the TMCT and DMTA result was not visible in the DSC thermogram for both AIR nor
483 functionalized AR. However, this transition that is measurable by TMCT-DMTA and unmeasurable
484 by the DSC seems to be the major driving force in the mechanical property changes of the
485 material. Therefore, thermal glass transition obtained from DSC should not be considered an
486 appropriate property to predict the stability of CWM residue, especially when being used as
487 texturizing ingredient where the mechanical properties of the material is of ultimate importance.

488

489 **4. Conclusion**

490

491 The glass transition temperature of CWM has not been frequently reported due to the limitations
492 of available methods of analysis. DSC has been widely used to predict the changes of materials
493 during storage and its stability. However, DSC lacks sufficient sensitivity to measure the glass
494 transition temperature of biopolymers such as CWMs. On the other hand, the change in
495 mechanical properties measured by combined TMCT-DMTA analysis could reveal the structural
496 relaxation phenomena of CWM based on the change of the compressibility and stiffness (loss
497 factor / $\tan \delta$). Thus, the results from the TMCT-DMTA in this study could fill the gap as stability
498 indicator that cannot be accomplished by DSC analysis of CWM. The relaxation phenomena
499 observed by the mechanical property measurement, especially the $\tan \delta$ curve from DMTA, is a
500 more appropriate prediction to infer the stability of CWM, especially when used as texturizing
501 ingredient where the rheological properties of the material is essential. In order to maintain
502 stability of CWM residue, the storage condition (temperature and moisture) should be maintained
503 below the onset region where $\tan \delta$ curve started to increase. Conditions above the onset region
504 of $\tan \delta$ curve may indicate increased molecular mobility and lead to the degradation of the CWM
505 rheological properties due to collapse. The ability of the TMCT-DMTA analysis to illustrate the
506 relaxation phenomena could provide an opportunity for further study, for example on how
507 processing could affect the behavior of the mechanical properties in order to design a shelf-stable
508 functionalized CWM.

509

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516

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645 **Table 1.** Compositions of AIR and functionalized AR (g/100 g dry matter). Values presented are mean \pm standard deviation (n=6)

A

647

648 Table 42. GAB parameters of moisture sorption isotherm

Materials	W_m	C	K
AIR	8.76 ± 0.52^a	13.92 ± 3.53^a	0.81 ± 0.02^a
Functionalized AR	8.04 ± 0.43^b	12.26 ± 2.46^a	0.79 ± 0.02^a

649

650 Table 32. Gordon-Taylor parameters from lemon peel CWM measured using different methods

Materials	k	T_s (°C)
DSC		
AIR	4.81 ± 0.83^a	117.2 ± 17.5^a
TMCT		
AIR	0.67 ± 0.10^b	43.16 ± 2.55^b
Functionalized AR	0.59 ± 0.15^b	37.36 ± 3.24^c

651

652 Table 43. Reaction rate constant (\pm approx. standard error) of the functionality loss during

653 storage (14 weeks) for functionalized AR at different condition

Storage condition		rate constant (k)
Moisture content (%w.b)	Temperature (°C)	
11	10	0.010 ± 0.006^a
11	25	0.087 ± 0.013^b
11	40	0.493 ± 0.064^c
14	10	0.015 ± 0.004^a
14	25	0.091 ± 0.009^b
14	40	0.497 ± 0.073^c
16	-10	0.006 ± 0.002^a
16	10	0.016 ± 0.004^a
16	25	0.093 ± 0.003^b
16	40	0.441 ± 0.033^c

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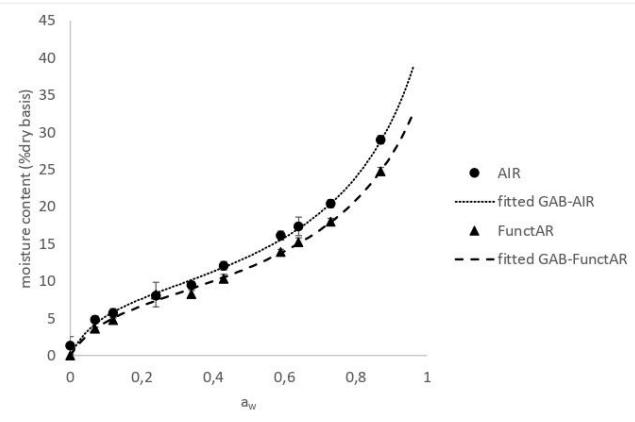
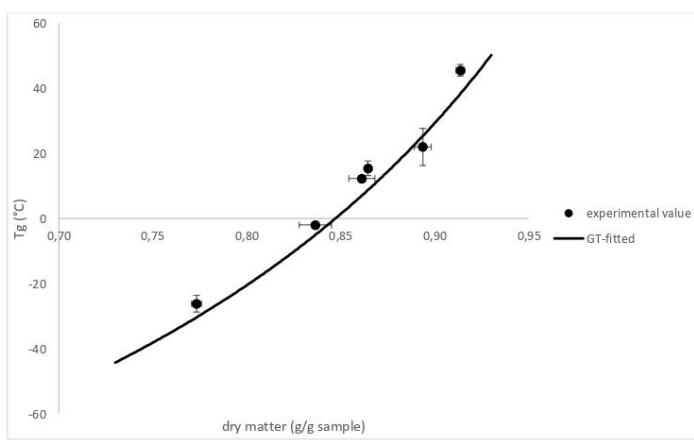


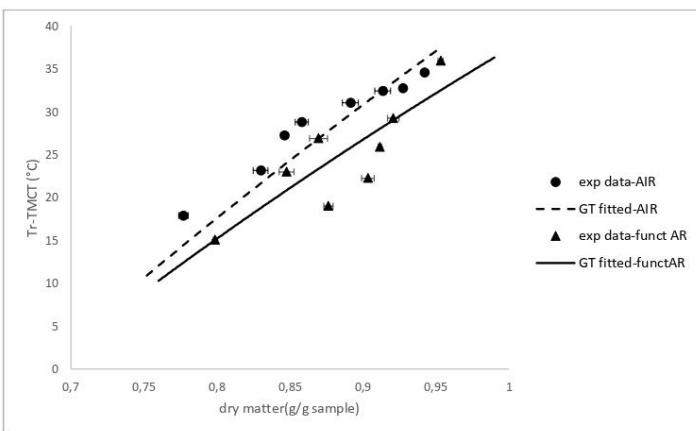
Figure 1. Moisture Sorption isotherm at 4°C for AIR and functionalized AR from lemon peel

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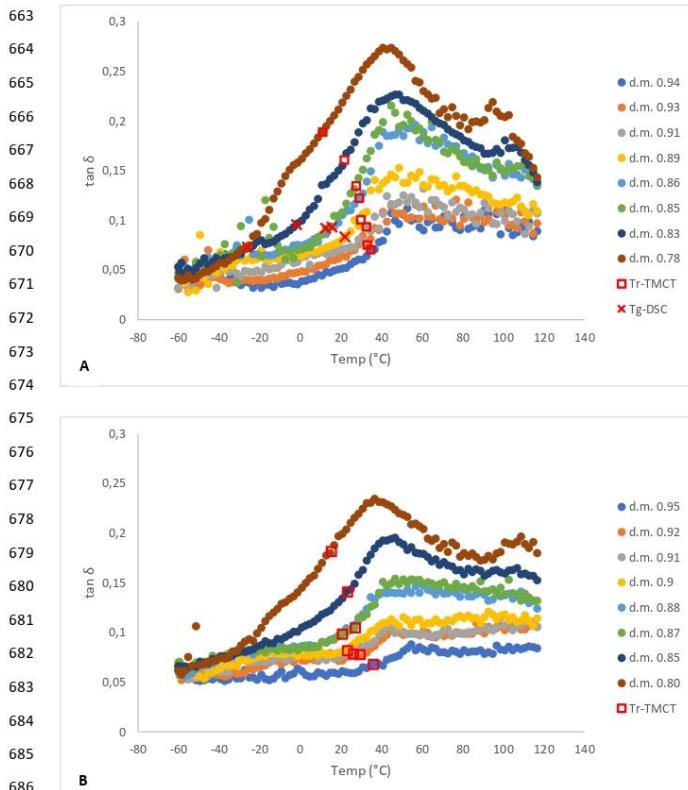
Figure 2. Tg of lemon peel AIR as measured by DSC



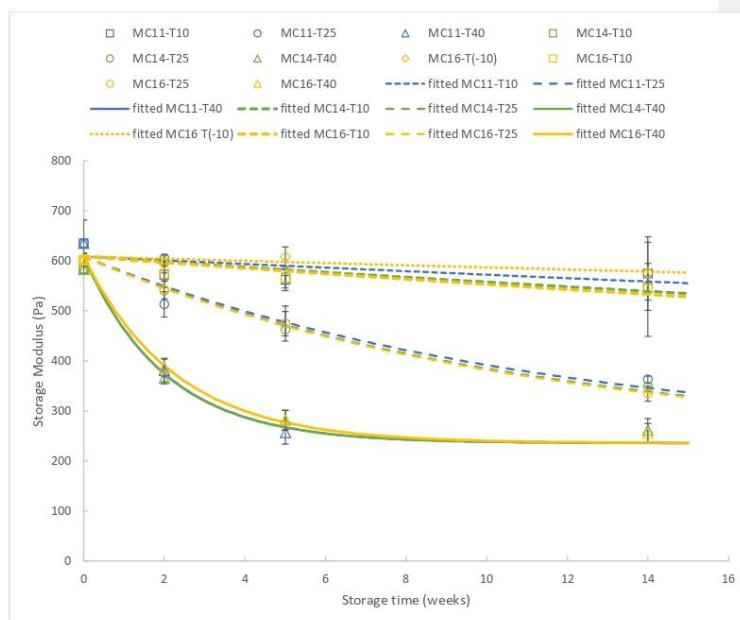
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Figure 3. Temperature of relaxation for AIR and functionalized AR from lemon peel as measured by TMCT

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694 Figure 5. Storage modulus (G') of CWM residue suspensions (2% d.m) at $\omega = 1$ Hz from functionalized AR
695 with different moisture content and storage temperature

696

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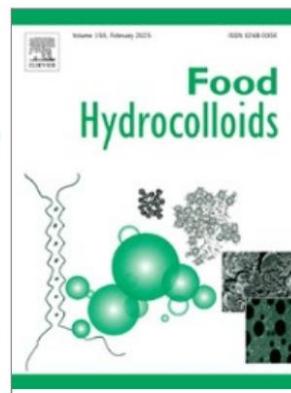
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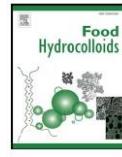
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Relaxation temperature and storage stability of the functionalized cell wall material residue from lemon peel

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ABSTRACT

Lemon peel cell wall material (CWM) residue obtained after acid pectin extraction can be functionalized into a texturizing ingredient using mechanical treatments such as high-pressure homogenization. The application of CWM as a texturizing ingredient is most likely through a dry powder and thus the stability of its functionality (rheological property) during storage becomes an obvious question. However, studies on the glass transition properties of this CWM residue and its relation to storage stability are largely lacking. This study aims to first evaluate the potential of two methods, i.e. DSC analysis and combined TMCT-DMTA (thermal mechanical compression test–dynamic mechanical thermal analysis) to measure the Tg and relaxation temperature of lemon peel CWM and subsequently relate the results to the stability of the material's rheological property. The results showed that DSC-based Tg measurements may not be the most appropriate indicator for storage stability of the lemon peel CWM residue, despite being the most commonly used method to explain state transition in materials. On the other hand, the structural relaxation phenomena elucidated by the change in mechanical properties measured by TMCT-DMTA correlated with the results of storage stability of the material. To ensure the stability of the CWM residue, storage should be carried out at conditions (temperature and moisture content) before the onset of tan δ curve change. In conclusion, relaxation phenomena observed through the measurement of mechanical properties, in particular the tan δ curve from DMTA, provides a suitable starting point for inferring the stability of the functionalized CWM residue.

1. Introduction

Lemon peel, by-products from the citrus processing industry, is produced in relatively high amounts which puts a significant burden on the environment. An efficient by-product management strategy is needed to minimize its environmental impact and to increase the overall valorization. To date, the extraction of citrus pectin, an ingredient widely used as thickening agent in food production, is the most widely implemented valorization route of lemon peels. However, the industrial pectin extraction process leaves another significant amount of fiber-rich material. Previous studies have shown that suspensions prepared from the residue left after acid pectin extraction (AR) have excellent rheological properties (high storage modulus), especially after mechanical treatment such as high pressure homogenization (HPH) (Putri et al., 2022; Willemse et al., 2017). The functionalization with HPH caused changes on the microstructure of the AR particles, including

fragmentation (size reduction) and aggregation. The aggregation formed a network which entraps water, creating a gel-like structure in suspension. This means that the functionalized pectin-depleted residue has a high potential as a texturizing ingredient, therefore a study of this ingredient's stability during storage becomes necessary.

The concept of glass transition temperature (Tg) has been used widely to predict the stability of foods and food ingredients (Sablani et al., 2007). When a material is in its glassy state (at a temperature below the Tg), it is regarded as stable due to its limited molecular mobility. Contrary, when a material is put into a condition (temperature-moisture combination) above its Tg, the rate of physical, chemical and biological changes largely increases and the material becomes unstable (Champion et al., 2000). The glass transition phenomena can be perceived from changes in the thermal and mechanical properties of the material as it is heated/cooled. The most common method to determine the Tg of a material is by measuring the change in the heat capacity

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using differential scanning calorimetry (DSC). However, the changes in the thermal properties of some food materials, such as the cell wall material (CWM), can be very small during the transition, making it difficult to detect (Boonyai et al., 2006; Roos, 1998). Therefore, in this study, the T_g of the functionalized lemon peel residue after pectin extraction was measured by both the change in thermal and mechanical properties.

To date, only few studies are available on CWM stability during storage and moreover studies on pectin-depleted CWM, to the best of our knowledge, are not existing. The available studies on fiber-rich materials (Fernandez-Lopez et al., 2009; Sharma et al., 2017) mostly demonstrate the degradation of fiber quality during storage without correlating it to the concept of molecular mobility and glass transition, possibly due to the limitation of the T_g analysis. The quality degradation could be attributed to the collapse of the material due to moisture absorption (Fernandez-Lopez et al., 2009). Collapse happens when a material loses its structure and volumetric shrinkage occurs causing loss of porosity (Levi & Karel, 1995). Collapse of amorphous food materials, occurs because of a solid flow resulting from a decreasing viscosity whereby the matrix is no longer capable to support and carry its own mass (Fan & Roos, 2017). This solid flow arises from an increased molecular mobility. However, the characterization of the molecular mobility and its relation to the storage stability of CWM has not been extensively studied. Therefore, this study attempts to fill this gap by describing the molecular mobility of CWM based on the changing mechanical properties and how these changes relate to the functionality (specifically rheological property) of the material.

This study aims to include the different methods to measure T_g and relaxation temperature of lemon peel CWM residue and relate them to the stability of the material's rheological property as influenced by storage. An understanding of how the material behaves during storage may encourage its application in industry and support the effort to valorize the residue of lemon peel after pectin extraction.

2. Materials and methods

2.1. Materials

Dry and milled lemon peel (LP) powder was provided by Cargill R&D Centre Europe (Vilvoorde, Belgium). All the chemicals used for moisture content equilibration were of analytical grade.

2.2. Dried functionalized Acid Residue preparation

The dry LP was treated to obtain the Alcohol Insoluble Residues (AIR) and subsequently pectin was extracted from the AIR using nitric acid at pH 1.6, 80 °C for 1 h. The unextractable fraction was collected as Acid Residue (AR). The AR was then resuspended at 2% solid concentration, the pH was adjusted to 4.5 and then high pressure homogenized at 20 MPa (Panda 2k NS 1001L, GEA Niro Soavi, Parma Italy). All these procedures have been described in detail in our previous studies (Putri et al., 2022; Willemse et al., 2017). After HPH, the functionalized AR was air-dried after water-alcohol exchange. For this, the functionalized AR was mixed with technical ethanol 99% at a 1:4 (v/v) ratio for 10 min and then allowed to stand for 60 min. This mixture was vacuum filtered (Machery-Nagel MN 615). A second round of alcohol-water exchange was carried out with the technical ethanol 99% at the ratio of 1:1 from initial volume of material. This mixture was allowed to stand for 30 min, and vacuum filtered. The solids after filtration were air-dried overnight to obtain the dried functionalized AR. The moisture content after drying was 11.1 ± 1.1 % w.b. The dried functionalized AR was kept in vacuum bags in a freezer at -40 °C until further use.

2.3. Composition analysis of the samples

The composition of both AIR and functionalized AR was determined

by neutral sugar analysis (using HPAEC-PAD), galacturonic acid content analysis (using spectroscopy) and protein content analysis (using combustion method). The analyses were carried out in triplicates using the method explained in our previous study (Putri et al., 2022).

2.4. Moisture content equilibration and sorption isotherm

In order to achieve various moisture content, the AIR and functionalized AR powder were stored at 4 °C for at least 3 weeks in containers with P_2O_5 (a.w. 0.00) or saturated salt solutions: LiBr (a.w. 0.07), LiCl (a.w. 0.12), CH_3COOK (a.w. 0.24), $MgCl_2$ (a.w. 0.34), K_2CO_3 (a.w. 0.43), $Mg(NO_3)_2$ (a.w. 0.59), NaBr (a.w. 0.64), KI (a.w. 0.73) and KCl (a.w. 0.87) (Greenspan, 1976). The moisture content of the material was measured at the end of the equilibration period by gravimetric analysis. The moisture sorption isotherm was obtained and fitted to the GAB equation (see below) by non-linear regression.

$$W = \frac{CKW_m a_w}{(1 - Ka_w)(1 - Ka_w + CKa_w)} \quad (eq.1)$$

W is the equilibrium moisture content of the material on dry basis and a_w is the water activity. W_m , C and K are the fitted constants. W_m represents the amount of water adsorbed in the monolayer. The W_m value indicates the availability of active water sorption sites on the material. C represents the strength of water binding with a larger C value indicating a stronger binding of water in the monolayer. K is a correction factor, when K approach one, there is no distinction between the water molecules beyond the monolayer and pure water (Quinjins et al., 2005).

2.5. Molecular mobility analysis with different methods

2.5.1. Differential scanning calorimetry

A Differential Scanning Calorimeter Q-2000 (TA instruments, USA) was used to scan the thermal behavior of AIR and functionalized AR powder with different moisture contents. Approximately 20 mg of the powder was weighted into hermetically sealed T_{zero} aluminum pans. An empty pan was used as a reference and two cycles of heating-cooling were carried out, first from -60 °C to 90 °C and second from -60 °C to 120 °C, both at a rate of 10 °C/min. Glass transition temperature, further referred to as T_g , was defined as the mid-point of the transition range observed in the heat flow curve of the second heating cycle (Kyonugasho et al., 2021; Pelgrom et al., 2013). An example of such heat flow curve and the analysis of the transition is presented in the Supplementary Materials (Figure S-1). The analysis was carried out in triplicate.

2.5.2. Thermal mechanical compression test - dynamic mechanical thermal analysis

Combined TMCT-DMTA analyses were carried out according to the methods described in Aravindakshan et al. (2022) using an Anton Paar MCR302 rheometer (Graz, Austria) equipped with a CTD450 oven. Approximately 2 g of the sample (AIR or functionalized AR powder) was loaded into the measuring system (cylindrical cup Ø 22 mm; cylindrical bob Ø 20 mm) and the oscillation-compression force was applied at normal force 30 N, shear strain 0.05% and frequency 1 Hz. The temperature scan spanned -60 °C-120 °C at the rate of 2 °C/min.

From the TMCT-DMTA data, two different values of relaxation temperature were obtained. First, the relaxation temperature from TMCT analysis (Tr-TMCT), determined based on the change of the sample compressibility due to the normal force by measuring the displacement of the probe during the heating scan (with correction of the measuring system's thermal expansion from a scan on microcrystalline cellulose). Secondly, the relaxation phenomena from the DMTA were based on the change of the ratio between loss and storage modulus (or loss factor, $\tan \delta$) obtained using oscillatory shear measurements.

2.5.3. Gordon-Taylor equation fitting

The T_g values obtained from DSC and relaxation temperature from TMCT analysis (Tr-TMCT) were fitted into the Gordon-Taylor (G-T) equation below using non-linear regression analysis.

$$T = \frac{T_s \times X_s + X_w \times T_w \times k}{X_s + X_w \times k} \quad (\text{eq. 2})$$

where s denotes the solid fraction (CWM) of the sample, w denotes the water fraction, T is the temperature of transition or relaxation, T_w is the glass transition temperature of water = -135 °C, X is the mass fraction and k is the constant that corresponds to the plasticizing effect of water on the material.

2.6. Storage study setup

A storage study was set up for the dried functionalized AR based on the results of the DSC and TMCT-DMTA analysis. Various storage conditions were identified to encompass various states of the functionalized AR, from stable to unstable. A combination of three moisture contents (11%, 14% and 16% w.b.) and three storage temperature (10, 25, and 40 °C) was used. An additional temperature condition (-10 °C) was used to store the material at 16%w.b. moisture content to ensure that storage at an anticipated stable condition was well covered. To adjust the moisture content prior to the storage study, the functionalized AR were equilibrated in airtight containers above saturated salt solutions (MgCl_2 , MgNO_3 and KI) for 5 weeks. After moisture equilibration, the functionalized AR were packed into inert glass jars with minimum headspace to prevent moisture exchange and stored for 2, 5 and 14 weeks. At the end of each storage period, the dried functionalized AR samples were regenerated (in duplicate) into 2% w/w solid suspensions. The regeneration was done by letting the material stand in water for 1 h and followed by mixing using LSM-A mixer with an emulsion screen work-head (Silverson, East Longmeadow, MA, USA) at 4300 RPM for 10 min. The rheological properties of these suspensions were measured as an indicator of the material's functionality.

The results of the storage study were fitted by non-linear regression using a first order fractional conversion model:

$$G(t) = G_f + (G_i - G_f)e^{-kt} \quad (\text{eq. 3})$$

where G_f is an estimated final extend of functionality loss, G_i is the average initial value of G' observed, t is the storage time (week) and k is the reaction rate constant.

2.7. Rheological property analysis

The rheology of the CWM suspension was analyzed using the method according to (Willemse et al., 2018). An Anton Paar MCR302 rheometer (Graz, Austria) equipped with a custom-built cup and concentric cylinder with conical bottom was used. The gap between the cylinder and the cup was 2 mm. Strain sweep (at ω 1 Hz and strain 0.01%–100%) was done to determine the linear viscoelastic region and a frequency sweep (at ω 100 to 0.1 Hz and strain 0.1%) was carried out at 25 °C. Rheology analysis was carried out in duplicate, each with newly loaded samples.

2.8. Statistical analysis

Significant statistical difference ($\alpha = 0.05$) between model-fitting parameter were determined by confidence interval calculation. GAB and G-T curve fitting was carried out in JMP Pro 17 statistical software (SAS Institute Inc, Cary, NC, USA) and fractional conversion model fitting for the storage study results was done in SAS statistical software (SAS Institute Inc, Cary, NC, USA).

3. Results and discussions

3.1. Composition of AIR and functionalized AR

The monosaccharides that comprise the CWM samples (both AIR and functionalized AR) and their protein content are presented in Table 1. Both AIR and functionalized AR are mainly composed of cell wall polysaccharides, i.e. cellulose, hemicellulose and pectin. A small portion of protein (5–7% d.b.) was detected in both AIR and functionalized AIR. The main difference between AIR and functionalized AR is the galacturonic acid content, which can be an indicator of pectin content. Since functionalized AR underwent pectin extraction process in order to increase the CWM functionality as texturizing ingredient (Putri et al., 2022), approx. 50% d.b. of the pectin was removed. Consequently, the proportion of cellulose and hemicellulose, as indicated by the glucose, xylose and galactose content, in the functionalized AR sample increased.

3.2. Isotherm sorption of the materials

The relation between water activity and moisture content (moisture sorption isotherm) is an important characteristic in the study of the stability of low-moisture food product (Koç et al., 2010; Lee & Robertson, 2022; Sant'Anna et al., 2014). The moisture sorption isotherm (at 4 °C) for both materials in the present study, AIR and functionalized AR from lemon peel, is shown in Fig. 1. Both materials showed a type II behavior according to the Brunauer-Emmett-Teller classification, which is frequently found in food products (Andrade P. et al., 2011). The experimental data was fitted to the GAB equation and the estimated value for the parameters are shown in Table 2. Both AIR and functionalized AR showed similar C and K values but significantly different monolayer values (W_m). AIR had a significantly higher W_m which indicating that it has more active (or better accessible) water sorption sites. This is also shown in the moisture sorption isotherm graph, in which AIR had higher moisture content at a given a_w value compared to the functionalized AR. This difference is expected since AIR contained more hygroscopic components, such as low molecular weight compounds and pectin, that were partially extracted for the functionalized AR. It has been largely acknowledged that the composition of the materials affected the moisture sorption capacity (Sormoli & Langrish, 2015; Timmermann et al., 2001). The sorption isotherm data at 4 °C were used to prepare samples at specific moisture contents in view of the T_g /Tr measurements and the storage experiment.

3.3. Glass transition and structural relaxation of the cell wall material from lemon peel

3.3.1. Differential scanning calorimetry (DSC)

DSC is one of the commonly used methods to measure T_g . It measures the transition in the thermal properties of the material by measuring the change of specific heat (Le Meste et al., 2002). However, DSC was not sensitive enough to measure the T_g of the functionalized lemon peel AR. On the other hand, transition in the DSC thermogram, albeit weak and broad, was observed for lemon peel AIR, except for samples with very low moisture content (<9% w.b.). AIR contains larger amounts of components that may contribute to the thermal glass transition, for example sugars, oligosaccharides, or acids. These components were extracted from the AIR during the AR preparation and consequently, the functionalized AR from lemon peel contains mainly cellulose and multiple other biopolymers such as pectin and hemicellulose (Table 1). The change in the heat capacity occurring over the glass transition of biopolymers is relatively small and therefore difficult to be captured by DSC (Roos, 1998; Sablani et al., 2010). Consequently, the DSC results could not provide precise specific transitions for food containing predominantly component with large molecular weight, such as the functionalized AR. Therefore, to describe the glass transition phenomena of CWM residues with DSC, the data from the AIR samples at higher moisture

Table 1Compositions of AIR and functionalized AR (g/100 g dry matter). Values presented are mean \pm standard deviation (n = 6).

Sample	Fucose	Rhamnose	Arabinose	Galactose	Non-cellulosic Glucose	Cellulosic Glucose	Xylose	Mannose	Galacturonic acid	Protein
AIR	0.21 \pm 0.06 ^a	1.45 \pm 0.39 ^a	14.48 \pm 1.82 ^a	6.83 \pm 2.16 ^a	6.87 \pm 0.92 ^a	19.29 \pm 4.31 ^a	4.13 \pm 1.59 ^a	2.67 \pm 0.58 ^a	35.80 \pm 0.44 ^a	5.73 \pm 0.49 ^a
Functionalized AR	1.03 \pm 0.62 ^b	0.80 \pm 0.34 ^b	2.91 \pm 0.50 ^b	11.32 \pm 4.10 ^b	6.12 \pm 2.29 ^a	58.48 \pm 2.21 ^b	12.03 \pm 3.59 ^b	5.94 \pm 1.90 ^b	16.50 \pm 0.51 ^b	7.36 \pm 0.11 ^b

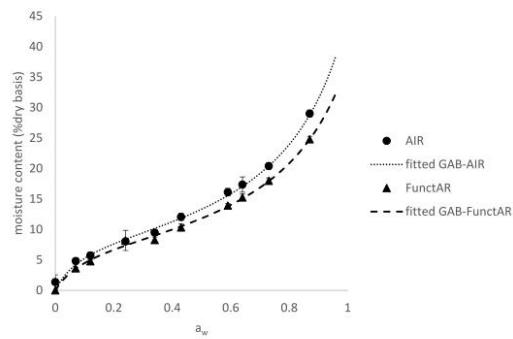


Fig. 1. Moisture Sorption isotherm at 4 °C for AIR and functionalized AR from lemon peel.

Table 2

GAB parameters of moisture sorption isotherm.

Materials	W _m	C	K
AIR	8.76 \pm 0.52 ^a	13.92 \pm 3.53 ^a	0.81 \pm 0.02 ^a
Functionalized AR	8.04 \pm 0.43 ^b	12.26 \pm 2.46 ^a	0.79 \pm 0.02 ^a

content ($\geq 9\%$ w.b.) are used in this study.

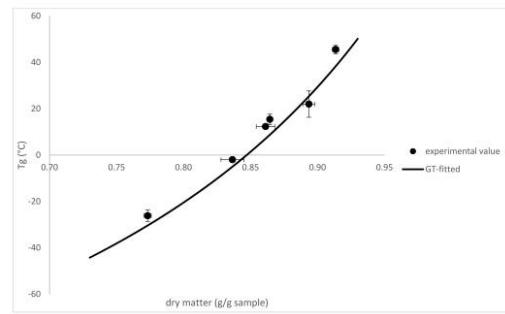
The mid-point of the transition shown in the thermogram of the second heating cycle of AIR samples was identified as its T_g-value. The T_g of the AIR sample in function of dry matter content is presented in Fig. 2. Despite the insensitivity of the DSC method for T_g measurement of CWM, few studies reported T_g values for papaya (Nieto-Calvache et al., 2019) and carrot CWM (Georget et al., 1999), with similar and slightly higher T_g compared to lemon peel AIR, respectively. As the moisture content of the lemon peel AIR increased, the T_g decreased, which is a common behavior in many biological materials. It is a well-established fact that water acts as a plasticizer and causes a

depreciation of T_g in low moisture food (Le Meste et al., 2002; Roos, 1998). Previous studies also showed this moisture plasticizing effect in fiber-rich material obtained from apple pomace and carrot (Georget et al., 1999; Zlatanović et al., 2019). The value of T_g in function of dry matter content of the lemon peel CWM were fitted to G-T equation and the parameters obtained, T_g and k, are presented in Table 3. The moisture plasticizing effect (as indicated by the k value of G-T equation) measured by DSC was 4.81, which is similar to other fruit- and vegetable-based food materials and food products (Fongin et al., 2017; Stepien et al., 2020).

3.3.2. Thermal mechanical compression test – dynamic mechanical thermal analysis (TMCT-DMTA)

Contrary to the DSC method, the TMCT-DMTA managed to clearly show structural relaxation phenomena in both lemon peel AIR and functionalized AR. This supported the well-established fact that the mechanical property analysis is more sensitive in measuring the transition or relaxation phenomena in food products (Roos, 1998). TMCT-DMTA analysis reveals structural relaxation phenomena based on the change in the material's mechanical properties, more specifically the compressibility and the moduli obtained from oscillatory shear analysis. As the result of the TMCT-DMTA is highly dependent on the measurement frequency (Le Meste et al., 2002), please note that all the structural relaxation temperatures described here are based on measurement at frequency 1 Hz.

Tr-TMCT in function of dry matter content for both AIR and functionalized AR is shown in Fig. 3. Representative Δ gap curves used for the calculation of Tr-TMCT are presented in the Supplementary Materials (Figure S-2). AIR and functionalized AR have similar values of Tr-TMCT and show similar changes due to the moisture plasticizing effect. The values of Tr-TMCT slightly decreased as the sample's moisture content increased. However, the moisture plasticizing effect on the TMCT results (and DMTA) in this study was very limited, especially if compared to the plasticizing effect on the thermal transition. The mechanism of the moisture plasticizing effect on the structural relaxation of glassy biopolymers, especially amorphous carbohydrates (using maltodextrin as an example), has been proposed (Kilburn et al., 2004). First, the absorbed water would fill small voids in the glassy matrix of the material, changing the matrix free volume. Second, the water would interfere with intermolecular hydrogen bonds, increasing the degree of freedom of the carbohydrate molecules and eventually caused coalescence of the voids. This proposed mechanism seems to suggest that the plasticizing effect is limited by the diffusion of water into the small voids in the matrix. The complex and rigid structure of CWMs may have hindered the plasticizing mechanism on its structural relaxation behavior and thus limiting the effect of moisture.

Fig. 2. T_g of lemon peel AIR as measured by DSC.**Table 3**

Gordon-Taylor parameters from lemon peel CWM measured using different methods.

Materials	k	T _g (°C)
DSC		
AIR	4.81 \pm 0.83 ^a	117.2 \pm 17.5 ^a
TMCT		
AIR	0.67 \pm 0.10 ^b	43.16 \pm 2.55 ^b
Functionalized AR	0.59 \pm 0.15 ^c	37.36 \pm 3.24 ^c

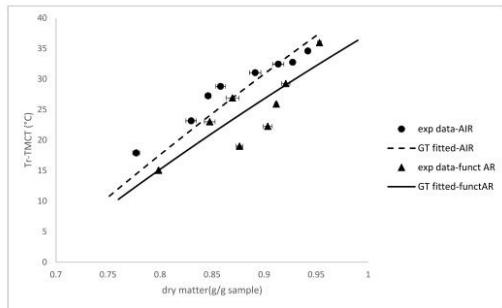


Fig. 3. Temperature of relaxation for AIR and functionalized AR from lemon peel as measured by TMCT.

When the Tr-TMCT values were fitted to the G-T equation, the values of anhydrous relaxation temperature (T_g) and k obtained were exceptionally low compared to the parameters obtained for the DSC based T_g curve (Table 3). This indicates that the material behavior reflected by the Tr-TMCT value change with moisture content is vastly different from the T_g values obtained by DSC. This may suggest that the two methods captured different mechanism of relaxation. This hypothesis will be substantiated further with the storage study results discussed in section 3.3. below. Based on the Tr-TMCT behavior and the fitted parameters value, the G-T equation may not be appropriate to describe the relaxation phenomena obtained by TMCT.

The result from the DMTA analysis, specifically the $\tan \delta$ curve in function of temperature, is presented (Fig. 4) to describe the structural relaxation phenomena of the lemon peel CWM residue. The storage (G')

and loss modulus (G'') curves in function of temperature are presented in the Supplementary Materials (Figure S-3). Comparable behavior of the moduli and loss factor as a function of temperature was observed for pea and soybean cotyledon (Ballesteros & Walters, 2011, 2019). They showed that over the range of -120 °C– 120 °C, the G' measured declined in the beginning (at low temperature) and started to increase from a certain temperature onwards. The G'' was constant in the beginning and started to increase towards a plateau, and $\tan \delta$ increased towards a plateau or a peak. The value of relaxation temperature (Tr-DMTA) generally could be determined by the peak of loss factor ($\tan \delta$) (Liu et al., 2006). However, the peak of the $\tan \delta$ in this study was difficult to be precisely determined, especially for samples with very low moisture content. Therefore, the structural relaxation phenomena will be discussed based on the behavior of the $\tan \delta$ curve. As a reference, the $\tan \delta$ curve of microcrystalline cellulose in function of temperature is presented in the Supplementary Materials (Figure S-4).

The $\tan \delta$ curve of lemon peel CWM, can be approximately divided into three regions: (i) a lower temperature range with the onset of $\tan \delta$ change (preceded by a constant value, especially for the low moisture systems) (ii) a medium temperature range with a steep increase of $\tan \delta$, and (iii) a final region where $\tan \delta$ reached its highest value and became constant or started to decline. At low temperature region (between -60 °C and 20 °C, with different range for samples with different moisture content), the $\tan \delta$ was mostly constant. As the CWM residue was heated, $\tan \delta$ started to increase (onset region) at a temperature between -30 °C and 20 °C. The increase of $\tan \delta$ upon heating suggests that the material started to lose its stiffness and a more plastic deformation could occur. The loss of stiffness continued at the second region with a steep increase of $\tan \delta$ and it reached a maximum point at temperature between 40 °C and 50 °C.

The plasticizing effect of moisture could be observed in the DMTA results based on the changes of $\tan \delta$ curve behavior. First, the absolute values of $\tan \delta$ increased with the increase in the moisture content of the samples. The increase of $\tan \delta$ after the onset region also became more drastic as the moisture content in the sample increased and it occurred at lower temperatures for samples with higher moisture contents. Lastly, the maximum value of $\tan \delta$ was reached at lower temperatures as the moisture content of the samples increased. The $\tan \delta$ curve for AIR (Fig. 4A) and functionalized AR (Fig. 4B) showed very similar behavior. However, the plasticizing effect of moisture was more pronounced in the $\tan \delta$ curve of AIR, as also observed in the Tr-TMCT results.

In order to compare all methods of the transition/relaxation analysis, T_g and Tr-TMCT points were overlayed on the $\tan \delta$ curve (Fig. 4). DSC-based T_g values (based on AIR results) seem to be located approximately at the onset of the $\tan \delta$ change. On the other hand, Tr-TMCT values are located at around the middle (inflection point) of the rapidly increasing section of $\tan \delta$ curve (Fig. 4), coinciding with the lowest value of G' and on the point where G'' starts to increase (Figure S-3). Therefore, these points on the DMTA curves seems to indicate the onset of the change in compressibility of the material.

Tr-TMCT value of lemon peel CWM (AIR) at each moisture content was higher than the measurable T_g value from DSC, except for sample with the lowest moisture content (9% w.b.). This observation agrees with many studies that showed higher mechanical relaxation temperatures compared to thermal glass transition (Boonyai et al., 2006; Fan & Roos, 2017; Georget et al., 1998; Rahman et al., 2007). However, the temperature of transition for anhydrous material (T_g) obtained from the G-T equation fitted parameter was much lower for Tr-TMCT result (~ 40 °C) compared to DSC (117 °C). The huge difference in the anhydrous transition/relaxation temperature and the moisture plasticizing effect may indicate completely different transition/relaxation phenomena observed between the thermal and mechanical method of analysis. This raises the question of which temperature (structural relaxation or glass transition) is better suited to predict the storage stability of CWM.

The increasing $\tan \delta$ behavior suggests higher translational molecular mobility in the CWM residue which is suspected to have a

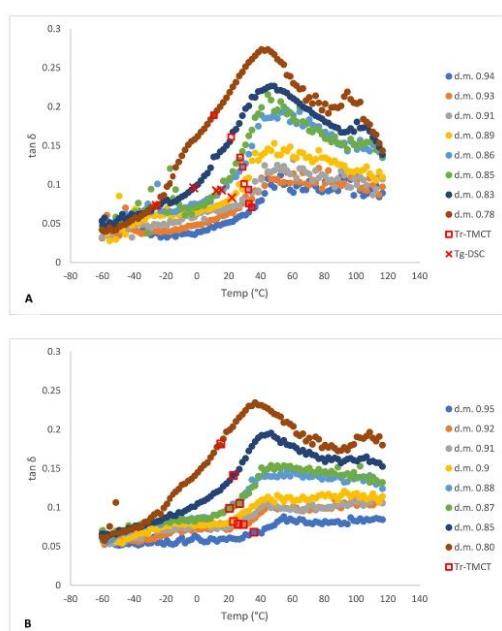


Fig. 4. $\tan \delta$ curve from DMTA analysis together with Tr-TMCT and T_g for (A) AIR and (B) Functionalized AR.

detrimental effect on the stability of the functionalized AR during storage. Higher molecular mobility increased the solid flow of molecules in the matrix of CWM which may induce collapse (Fan & Roos, 2017). Thus, a storage study was subsequently performed on the functionalized AR from lemon peel in order to corroborate whether the change in the behavior of $\tan \delta$ curve could be useful in predicting CWM residue's stability during storage. The behavior of the $\tan \delta$ curve depicted in Fig. 4 was used to determine different storage conditions that will cover different regions, from stable to unstable. Three temperature conditions were chosen, 10, 25 and 40 °C to represent the temperature before onset of $\tan \delta$ change, after onset when the $\tan \delta$ curve began to increase rapidly (but still below Tr-TMCT) and when the $\tan \delta$ curve almost reached its maximum value (above Tr-TMCT), respectively. Three moisture content values (11%, 14% and 16%) were selected, each corresponding to a different $\tan \delta$ curve profile to include the effect of water plasticization on the storage stability. An additional storage temperature of (-10)°C was added to the samples with highest moisture content to ensure that also in this case, a stable storage point (well before the onset of $\tan \delta$ change) was covered.

3.4. Storage stability and its relation to the molecular mobility

The storage stability study was focused on the change of the functionality of lemon peel CWM residue. Therefore, the rheological property, specifically G' , was measured to indicate the stability (or deterioration) of the texturizing potential of the functionalized AR. The values of G' throughout 14 weeks of storage are presented in Fig. 5. Samples stored at conditions before the onset of $\tan \delta$ change (at -10 °C and 10 °C) showed a stable G' up to 14 weeks of storage. When the storage temperature was higher than the onset of $\tan \delta$ change (at 25 °C and 40 °C), a significant decline in the G' -values was observed during storage. To quantify the rate of the G' decline or the rate of functionality loss during storage, the fractional conversion model was fitted to the results. The rate constant (k) values are presented in Table 4 below. The rate of the decline significantly increased as the storage temperature increased. Samples stored at 25 °C show a lower k -value compared to samples stored at 40 °C. However, after 14 weeks of storage, the G' value of samples stored at 25 °C declined significantly, reaching a similar value to the samples stored at 40 °C. On the other hand, samples stored at 40 °C already experienced a severe decline after 5 weeks of storage.

The samples stored at 25 °C showed a decline in G' value despite

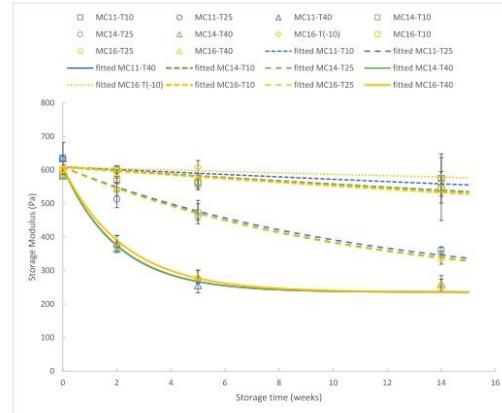


Fig. 5. Storage modulus (G') of CWM residue suspensions (2% d.m.) at ω 1 Hz from functionalized AR with different moisture content and storage temperature.

Table 4
Reaction rate constant (\pm approx. standard error) of the functionality loss during storage (14 weeks) for functionalized AR at different condition.

Storage condition		
Moisture content (%w.b)		
Temperature (°C)		rate constant (k)
11	10	0.010 ± 0.006^a
11	25	0.087 ± 0.013^b
11	40	0.493 ± 0.064^c
14	10	0.015 ± 0.004^a
14	25	0.091 ± 0.009^b
14	40	0.497 ± 0.073^c
16	-10	0.006 ± 0.002^a
16	10	0.016 ± 0.004^a
16	25	0.093 ± 0.003^b
16	40	0.441 ± 0.033^c

stored under the Tr-TMCT values, indicating that Tr-TMCT did not correspond to the stability of CWM functionality during storage. In conclusion, the relaxation phenomena described in the $\tan \delta$ curve correlate well to the storage stability of the lemon peel CWM. When the storage condition (temperature and moisture content) is located in the more progressed region of the $\tan \delta$ curve, which may indicate higher molecular mobility, the faster the decline on the G' . As long as the storage condition was kept below the onset of the $\tan \delta$ curve change, degradation of the functionality of the CWM residue was limited.

The declining G' during storage that happened when samples were stored at conditions where the $\tan \delta$ curve was increasing could be attributed to the structure collapse of the cell wall matrix. Such physical change could occur due to increasing molecular mobility when the material is transformed into a more viscous state (Fan & Roos, 2017). When $\tan \delta$ increased, stiffness of the molecules decreased which also suggests the reduction of the material viscosity to a level that is no longer sufficient to support the structure of the solid material. The increased viscous flow caused subsequent densification (Fan & Roos, 2017; To & Flink, 1978). In this case, the structural units (for example the repetitive element of the biopolymers in the CWM) can move independently from each other (Champion et al., 2000). Thus, interactions between cellulose microfibrils became possible which hindered the formation of an open CWM network that entraps water during the reconstitution of the material into suspension. Collapse of CWM, which could be prompted by many factors and treatments such as mechanical breaking (Van Audenhove et al., 2022) and chemical treatment, e.g. with alkaline solution, could lead to the reduction of CWM suspension's functionality. This transformation in the mechanical properties of solid materials may lead to substantial alterations of its performance in processing, storage stability, and sensory properties (Fan & Roos, 2017).

Previous study (Fernandez-Lopez et al., 2009) showed that degradation of the fiber-rich material functional properties, such as water binding capacity, became more severe as the moisture content increased during storage. Contrary, in this study, the rate of functionality loss (k -value) was not significantly different between samples stored at different moisture content (Table 4). At the same storage temperature, the moisture content of the samples (within the moisture content range studied) did not significantly affect the G' of the functionalized AR during storage. The plasticization effect of moisture was not pronounced in the storage study, contrary to common low-moisture food product behavior (Fan & Roos, 2017; Le Meste et al., 2002). As discussed previously, the limited moisture plasticizing effect, that was also observed in the results of TMCT-DMTA of CWM samples, was suspected to be caused by the composition of functionalized AR. Functionalized AR is composed mainly of cellulose and cellulose in its native form is a rigid polymer with some crystalline region in its structure, which may prevent the water migration into the particles and thus limit the moisture plasticizing effect. A NMR experiment which studied the effect of hydration on polymer mobility in onion CWM showed that water readily penetrated the pectin network and increased its mobility, whereas cellulose

detrimental effect on the stability of the functionalized AR during storage. Higher molecular mobility increased the solid flow of molecules in the matrix of CWM which may induce collapse (Fan & Roos, 2017). Thus, a storage study was subsequently performed on the functionalized AR from lemon peel in order to corroborate whether the change in the behavior of $\tan \delta$ curve could be useful in predicting CWM residue's stability during storage. The behavior of the $\tan \delta$ curve depicted in Fig. 4 was used to determine different storage conditions that will cover different regions, from stable to unstable. Three temperature conditions were chosen, 10, 25 and 40 °C to represent the temperature before onset of $\tan \delta$ change, after onset when the $\tan \delta$ curve began to increase rapidly (but still below Tr-TMCT) and when the $\tan \delta$ curve almost reached its maximum value (above Tr-TMCT), respectively. Three moisture content values (11%, 14% and 16%) were selected, each corresponding to a different $\tan \delta$ curve profile to include the effect of water plasticization on the storage stability. An additional storage temperature of (-10)°C was added to the samples with highest moisture content to ensure that also in this case, a stable storage point (well before the onset of $\tan \delta$ change) was covered.

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The samples stored at 25 °C showed a decline in G' value despite

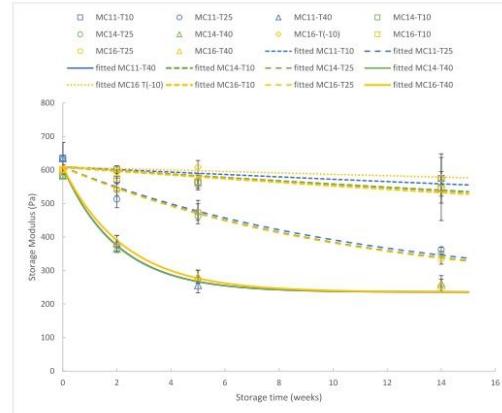


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Storage condition		
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Temperature (°C)		rate constant (k)
11	10	0.010 ± 0.006^a
11	25	0.087 ± 0.013^b
11	40	0.493 ± 0.064^c
14	10	0.015 ± 0.004^a
14	25	0.091 ± 0.009^b
14	40	0.497 ± 0.073^c
16	-10	0.006 ± 0.002^a
16	10	0.016 ± 0.004^a
16	25	0.093 ± 0.003^b
16	40	0.441 ± 0.033^c

stored under the Tr-TMCT values, indicating that Tr-TMCT did not correspond to the stability of CWM functionality during storage. In conclusion, the relaxation phenomena described in the $\tan \delta$ curve correlate well to the storage stability of the lemon peel CWM. When the storage condition (temperature and moisture content) is located in the more progressed region of the $\tan \delta$ curve, which may indicate higher molecular mobility, the faster the decline on the G' . As long as the storage condition was kept below the onset of the $\tan \delta$ curve change, degradation of the functionality of the CWM residue was limited.

The declining G' during storage that happened when samples were stored at conditions where the $\tan \delta$ curve was increasing could be attributed to the structure collapse of the cell wall matrix. Such physical change could occur due to increasing molecular mobility when the material is transformed into a more viscous state (Fan & Roos, 2017). When $\tan \delta$ increased, stiffness of the molecules decreased which also suggests the reduction of the material viscosity to a level that is no longer sufficient to support the structure of the solid material. The increased viscous flow caused subsequent densification (Fan & Roos, 2017; To & Flink, 1978). In this case, the structural units (for example the repetitive element of the biopolymers in the CWM) can move independently from each other (Champion et al., 2000). Thus, interactions between cellulose microfibrils became possible which hindered the formation of an open CWM network that entraps water during the reconstitution of the material into suspension. Collapse of CWM, which could be prompted by many factors and treatments such as mechanical breaking (Van Audenhove et al., 2022) and chemical treatment, e.g. with alkaline solution, could lead to the reduction of CWM suspension's functionality. This transformation in the mechanical properties of solid materials may lead to substantial alterations of its performance in processing, storage stability, and sensory properties (Fan & Roos, 2017).

Previous study (Fernandez-Lopez et al., 2009) showed that degradation of the fiber-rich material functional properties, such as water binding capacity, became more severe as the moisture content increased during storage. Contrary, in this study, the rate of functionality loss (k -value) was not significantly different between samples stored at different moisture content (Table 4). At the same storage temperature, the moisture content of the samples (within the moisture content range studied) did not significantly affect the G' of the functionalized AR during storage. The plasticization effect of moisture was not pronounced in the storage study, contrary to common low-moisture food product behavior (Fan & Roos, 2017; Le Meste et al., 2002). As discussed previously, the limited moisture plasticizing effect, that was also observed in the results of TMCT-DMTA of CWM samples, was suspected to be caused by the composition of functionalized AR. Functionalized AR is composed mainly of cellulose and cellulose in its native form is a rigid polymer with some crystalline region in its structure, which may prevent the water migration into the particles and thus limit the moisture plasticizing effect. A NMR experiment which studied the effect of hydration on polymer mobility in onion CWM showed that water readily penetrated the pectin network and increased its mobility, whereas cellulose

mobility was unaffected by hydration (Hediger et al., 1999).

Furthermore, although the moisture plasticizing effect on the T_g of lemon peel CWM was clearly observed from the DSC results, this effect could not be seen in the storage study results. Larger differences between the storage temperature and T_g should normally cause faster deterioration of materials (Kyonugasho et al., 2021; Roos, 1995; Zlatanović et al., 2019), however this phenomena also could not be observed in the results of the storage study. The substantial transition in the TMCT and DMTA result was not visible in the DSC thermogram for both AIR nor functionalized AR. However, this transition that is measurable by TMCT-DMTA and unmeasurable by the DSC seems to be the major driving force in the mechanical property changes of the material. Therefore, thermal glass transition obtained from DSC should not be considered an appropriate property to predict the stability of CWM residue, especially when being used as texturizing ingredient where the mechanical properties of the material is of ultimate importance.

4. Conclusion

The glass transition temperature of CWM has not been frequently reported due to the limitations of available methods of analysis. DSC has been widely used to predict the changes of materials during storage and its stability. However, DSC lacks sufficient sensitivity to measure the glass transition temperature of biopolymers such as CWMs. On the other hand, the change in mechanical properties measured by combined TMCT-DMTA analysis could reveal the structural relaxation phenomena of CWM based on the change of the compressibility and stiffness (loss factor/tan δ). Thus, the results from the TMCT-DMTA in this study could fill the gap as stability indicator that cannot be accomplished by DSC analysis of CWM. The relaxation phenomena observed by the mechanical property measurement, especially the tan δ curve from DMTA, is a more appropriate prediction to infer the stability of CWM, especially when used as texturizing ingredient where the rheological properties of the material is essential. In order to maintain stability of CWM residue, the storage condition (temperature and moisture) should be maintained below the onset region where tan δ curve started to increase. Conditions above the onset region of tan δ curve may indicate increased molecular mobility and lead to the degradation of the CWM rheological properties due to collapse. The ability of the TMCT-DMTA analysis to illustrate the relaxation phenomena could provide an opportunity for further study, for example on how processing could affect the behavior of the mechanical properties in order to design a shelf-stable functionalized CWM.

CRediT authorship contribution statement

Novita I. Putri: Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Jelle Van Audenhove:** Writing – review & editing, Methodology. **Clare Kyomugasho:** Methodology, Investigation. **Ann Van Loey:** Supervision, Resources, Methodology. **Marc Hendrickx:** Writing – review & editing, Supervision, Resources, Methodology, Funding acquisition, Conceptualization.

Declaration of competing interest

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.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.foodhyd.2023.109711>.

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