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Dielectric properties of chitosan and two ionic derivatives: Effect of counter anions

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38 1. Introduction

39 Due to the growing demand for energy and the reduction of fossil fuels, scientists have
40 been exploring alternative and more sustainable sources of energy. In this context,
41 supercapacitors are currently attracting growing interest due to their high-power density
42 and ability to charge quickly without causing any damage such as explosion or thermal
43 runaway. Today, electrodes and electrolytes used in supercapacitors contain non-
44 renewable and hazardous materials such as metal oxides and synthetic polymers, which
45 are often harmful to the environment. The use of polysaccharides could potentially be an
46 alternative to these materials. Polysaccharides such as cellulose are among the most
47 ancient electrically insulating materials used in cables (Le Bras et al., 2015). Alternative
48 biomass materials have attracted significant attention as innovative solutions in the field
49 of novel high-performance film dielectric capacitor (Salama & Hesemann, 2020a; Yin et
50 al., 2020).

51 Chitin is one of the most abundant natural polymers. It can be found in the exoskeleton
52 of crustaceans, mollusks, insects, and other invertebrates as well as in the cells of fungi
53 and moulds. Chitin is insoluble in all conventional solvents. However, partially
54 deacetylated chitin, *i.e.* chitosan (Ch), is well soluble in weakly acidic media, e.g. in acetic
55 acid (Salama et al., 2017). Under these conditions, the amino groups of chitosan undergo
56 protonation, thus forming a polyelectrolyte with cationic charges on the chitosan
57 backbone (Salama & El-Sakhawy, 2014). Chitosan, β -(1,4)-linked D-glucosamine,
58 attracted huge interest due to its non-toxicity and biodegradability. It also shows
59 interesting anti-bacterial activity (Salama et al., 2020; Salama & Hesemann, 2020b),
60 making it interesting for applications in the biomedical field. The amino group can be
61 modified chemically in a variety of ways (Salama & Hesemann, 2018a), in view of the
62 formation of biosourced polyelectrolytes (Salama, 2021). Chitosan therefore attracted
63 considerable attention as a promising functional polysaccharide with tunable properties
64 for several applications such as adsorption (Hassan et al., 2019; Monier et al., 2010),
65 wound healing (Salama, 2018) and drug release (Costa-Pinto et al., 2009). Chitosan and
66 its derivatives have been applied in various applications ranging from biomedical and
67 pharmaceutical materials to environmental remediation. For electrochemical applications,
68 chitosan has successfully been exploited to develop electrolytes and electrodes. These

69 materials have also attracted high interest due to their low cost, biodegradability, and
70 environmental safety (Roy et al., 2021). When protonated, chitosan's physico-chemical
71 properties are strongly modified, and cationic chitosan is capable of binding anionic
72 compounds via ion exchange. In this context, the functionalization of chitosan with
73 guanidine/guanidinium groups can bring significant benefits compared to the presence of
74 the classical amine/ammonium chitosan. Promising trials were carried out for preparing
75 guanidylated chitosan derivatives for enhancing the antimicrobial properties and
76 catalysis (Maleki et al., 2018; Sahariah et al., 2015). We already reported guanylation of
77 chitosan following a simple strategy starting from parent chitosan and cyanamide, using
78 scandium triflate as catalyst. The basicity of the guanidine group is several orders of
79 magnitude higher compared to the one of the ammonium groups (pK_a guanidine = 13.6 vs.
80 pK_a ammonia = 9.24). The basicity of guanidines further increases by substitution with
81 alkyl groups (Eckert-Maksić et al., 2008). Guanidines therefore exist in aqueous solution
82 nearly exclusively in their protonated, *i.e.*, the guanidinium form.

83 Dielectric spectroscopy is a technique that allows observing rotational molecular motions
84 by probing the dipolar fluctuations. It is a valuable technique for the investigation of
85 polymeric materials and in particular of polysaccharides (Einfeldt et al., 2001; Mohamed
86 et al., 2020). Polyelectrolytes have attracted tremendous attention in the last decade for
87 their ion-conducting properties (Bocharova & Sokolov, 2020; Ngai et al., 2016). High
88 attention was paid to these materials for their potential in technologies such as energy
89 storage (in batteries)(Cheng et al., 2018; Hallinan & Balsara, 2013), energy conversion
90 (e.g., fuel cells) (Lu et al., 2008; Wang et al., 2011), electrochromic devices (Leones et
91 al., 2017; Thakur et al., 2012), etc. In polyelectrolytes and poly(ionic liquid)s, the physico-
92 chemical properties depend both on the cation and anion in the conductive material which
93 can be altered or modified by ion exchange or by modulating the nature of substituents on
94 the cation. In this way, the presence of specific groups on the cation or on the anion is
95 able to impart highly specific properties to these systems (Anderson et al., 2005; Fei et
96 al., 2004).

97 The current work investigates the influence of the functionalization of chitosan
98 derivatives on their dielectric properties. More specifically, we studied the impact of the
99 nature of the counter anion of guanylated chitosan on their dielectric properties at variable

100 temperature, in order to clarify the dynamic behavior of guanidinium groups and the
101 counter anions. First, the guanylated chitosan derivatives, GChAc and GChCl were
102 synthesized and characterized. The effect of the guanidinium groups and the counter anion
103 as a function in electrical conductivity was studied.

104

105 **2. Experimental part**

106 **2.1. Synthesis of GChAc and GChCl**

107 The syntheses of chitosan derivatives (GChAc) and (GChCl) was accomplished by
108 dissolving 2 g medium molecular weight chitosan (degree of deacetylation, 75–85%,
109 Sigma-Aldrich) in 100 mL either 2 % acetic acid, or 2 % hydrochloric acid, respectively.
110 Then 0.84 g cyanamide and 0.3 g scandium(III) triflate were added for each solution with
111 continuous stirring at 100 °C for 48 h. The resulting mixtures were poured in acetone and
112 the precipitated products were washed several times with acetone. N-guanidinium chitosan
113 acetate (GChAc) and N-guanidinium chitosan chloride (GChCl) freeze-dried and obtained
114 light brown solids.

115

116 **2.3. Characterization methods**

117 ¹³C Cross-Polarization Magic Angle Spinning (CP-MAS) experiments were carried out on
118 a Varian VNMRS 400 MHz solid spectrometer by means of a two-channel probe with 7.5
119 mm ZrO₂ rotors. The attenuated total reflectance Fourier transform infrared (ATR FTIR)
120 spectra of the chitosan, GChAc and GChCl were measured through a Thermo Nicolet FT-
121 IR Avatar 320 with a diamond crystal. Spectra were documented from 500 to 4000 cm⁻¹.
122 TGA experiments were measured with a NETZSCH STA 409 PC device at a heating rate
123 of 5 °C/min.

124

125 **2.3.4. Dielectric measurements**

126 The dielectric measurements were performed on discs of Ch, GChAc and GChCl of 2 mm
127 thickness and 10 mm in diameter using broadband dielectric spectroscopy (BDS)
128 employing an Alpha-A machine from novocontrol covering wide ranges of frequency (10⁻¹
129 Hz - 10⁷ Hz) and temperature (223 K to 423 K), connecting to a Quatro temperature
130 controller system.

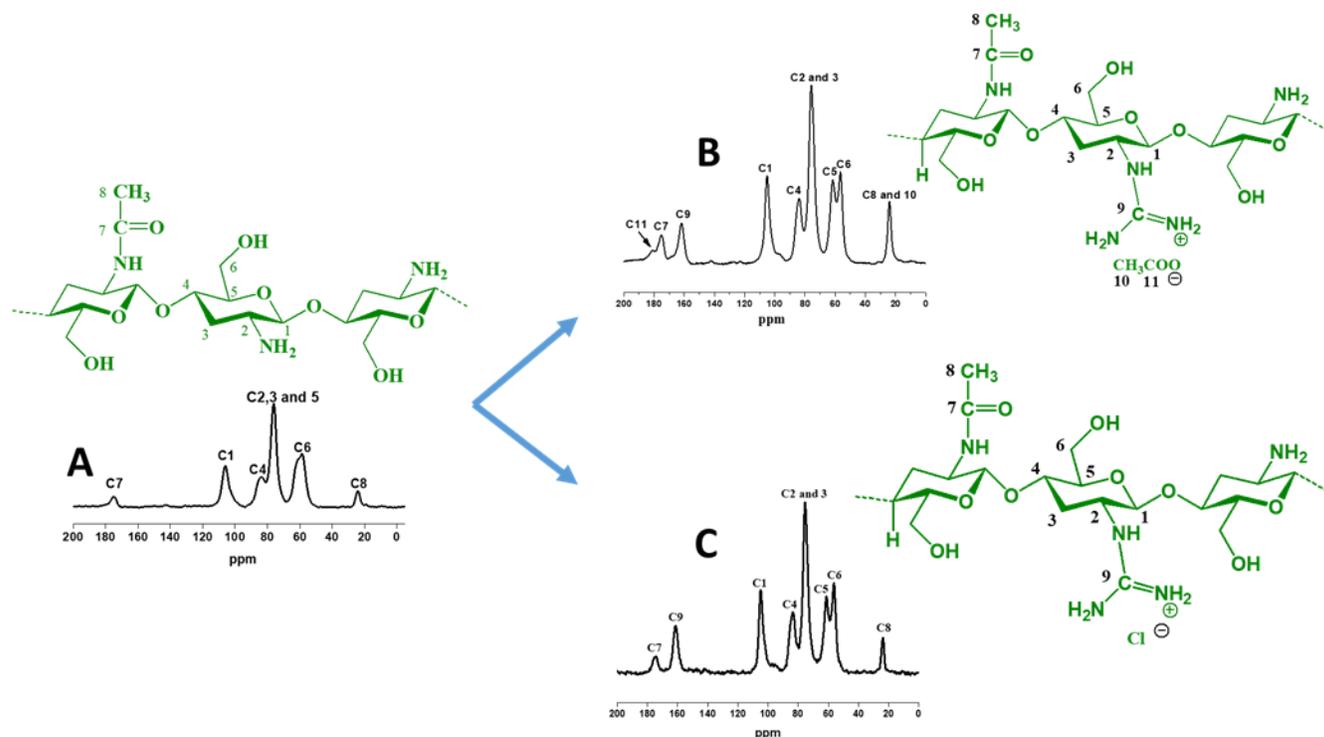
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132 **3. Results and Discussion**

133 **3.1. Characterization of chitosan derivatives**

134 Scandium (III) triflate has been applied as Lewis acid catalyst during the preparation of
135 guanidinium group through the reaction between primary amines and cyanamide
136 (Tsubokura et al., 2014). In the current study, two chitosan derivatives containing
137 guanidinium groups have been produced from aqueous medium at 100 °C. The synthesis
138 of guanidinium functions was proved using various techniques. Elemental analysis for Ch,
139 GChAc and GChCl were calculated. The results show nitrogen content increasing from
140 7.7 % for neat Ch to reach 11.1 % and 12.3 % for GChAc and GChCl, respectively,
141 indicating significant guanylation chitosan.

142 The suggested chemical structure and ¹³C CP-MAS solid state NMR of the two cationic
143 chitosan derivatives are displayed in figure 1. The chitosan backbone structure principally
144 gives rise to the signals in the range between 55–110 ppm, due to the carbon centers of the
145 anhydroglucose units in this material labeled from 1 to 8 (Figure 1). The cationic chitosan
146 derivatives show additional signals due to the presence of the newly formed guanidinium
147 groups. GChAc shows new signal at 160 ppm (C9) which mentions to the created
148 guanidinium groups. Additionally, the observed signal at 180 ppm may refer to the
149 presence of acetate counter ions, as the guanylation process was carried out in acetic acid
150 solution. Similarly, GChCl shows a new signal at 160 ppm (C9) which refers to the newly
151 formed guanidinium groups.



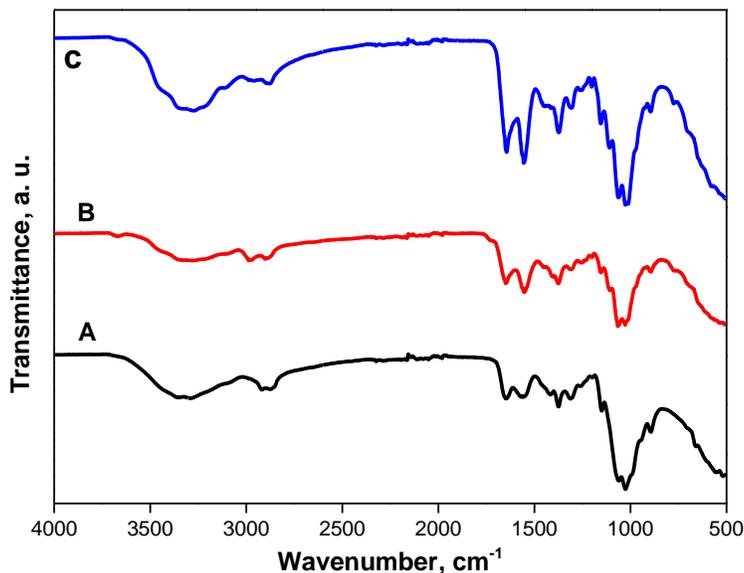
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153

154 **Figure 1:** Chemical structures and solid state ^{13}C CP-MAS NMR spectra of Ch (A),
 155 GChAc (B) and GChCl (C).

156

157 The presence of the various functional groups of chitosan and the two cationic derivatives
 158 was proved via by FT-IR spectroscopy (Figure 2). The spectrum of chitosan (A) shows the
 159 characteristic bands of chitosan backbone as previously described (Salama & Hesemann,
 160 2018b). The higher intensity of the adsorption band at 1629 cm^{-1} detected in the spectrum
 161 of the guanidinium derivatives B and C can be attributed to the generation of guanidinium
 162 moieties.



163

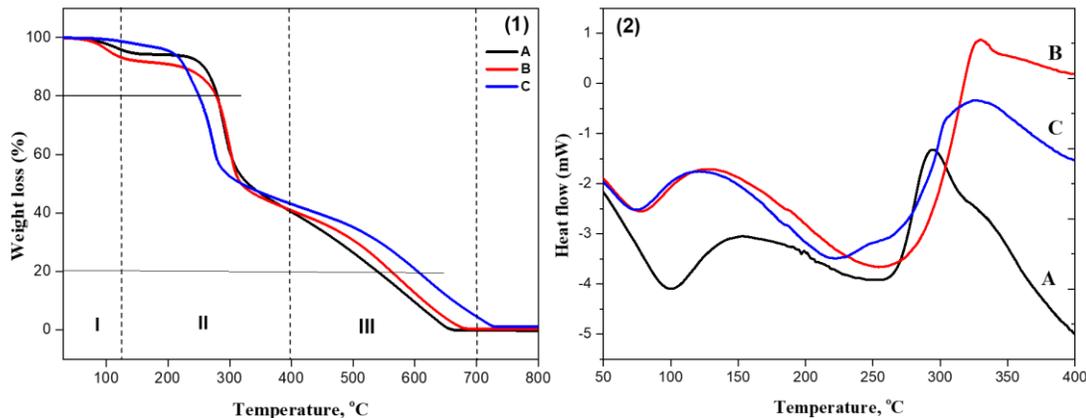
164 **Figure 2:** FT-IR spectra of Ch (A), GChAc (B) and GChCl (C).

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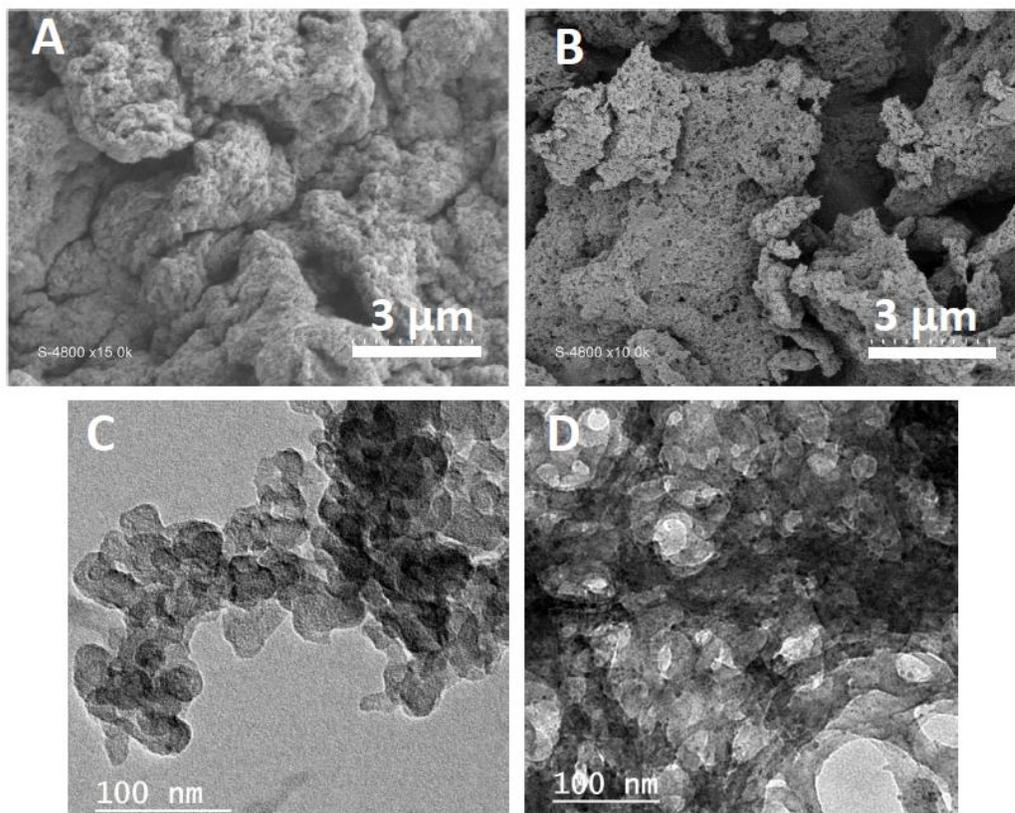
167 The thermogravimetric analysis (TGA) thermograms for neat chitosan and the two cationic
 168 derivatives are displayed in Figure 3 (1). The weight loss of chitosan and the two
 169 derivatives divided to three regions, considered as I, II and III. At the first region (region
 170 I), the weight loss ranging from 1.3%–6.9% can be attributed to the loss of physically
 171 adsorbed water. N-guanidinium chitosan acetate contains high amount of water, compared
 172 to N-guanidinium chitosan chloride, which reflect the hydrophilicity of acetate anion. In
 173 the second region, N-guanidinium chitosan chloride starts to decompose at lower
 174 temperatures compared to N-guanidinium chitosan acetate and neat chitosan. The
 175 degradation pattern recorded 20% weight loss at 279 °C for chitosan and N-guanidinium
 176 chitosan acetate and at 250 °C for N-guanidinium chitosan chloride. The high thermal
 177 stability of ch and GChAc may result from the intramolecular and intermolecular hydrogen
 178 bonds that are affected by the chloride introduction. The third weight loss, region III,
 179 documented a high stability for the two cationic derivatives comparing to neat chitosan.
 180 The complete degradation was reached at 730, 680, 660 °C for N-guanidinium chitosan
 181 chloride, N-guanidinium chitosan acetate and chitosan, respectively.

182 The differential scanning calorimetry (DSC) thermograms of Ch, GChAc and GChCl are
183 presented in figure 3(2). It can be seen that all the thermograms display two prominent
184 peaks. The endothermic peaks observed between 70 and 90 °C can be associated to the loss
185 of water (Chowdhury et al., 2022). The exothermic peaks at 295 °C for neat chitosan, 331
186 °C for GChAc and 317 °C for GChCl can be related to a thermal decomposition of amine
187 units in chitosan and guanidinium groups in the chitosan derivatives. In agreement with
188 TGA results, these results prove that the new guanylated chitosan derivatives exhibit
189 slightly higher thermal stability.
190
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192
193 **Figure 3:** Thermogravimetric analyses (1) and DSC curves (2) of Ch (A), GChAc (B) and
194 GChCl (C).

195
196 Finally, the morphologies and textures of the two cationic chitosan derivatives were
197 examined via scanning electron microscopy (SEM) and transmission electron microscopy
198 (TEM). Both materials show a relatively similar morphology as displayed by the two SEM
199 images in Figure 4 A and B and present a rough surface with a certain porosity on the
200 nanometric scale. Transmission electron microscopy (TEM) images (figure 4 C/D) also
201 indicate relatively similar textures of agglomerated particles of a diameter of ~ 50 nm.



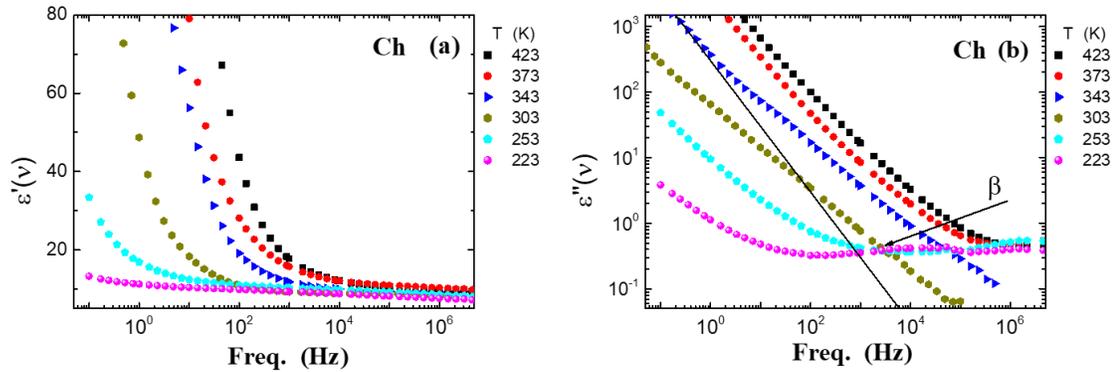
202
 203 **Figure 4:** SEM and TEM images of GChAc (A and C) and GChCl (B and D), respectively.

204

205 3.2. Electrical properties

206 The electrical properties of the materials were investigated via broadband dielectric
 207 spectroscopy (BDS). In particular, we studied the three complex functions dielectric, ϵ^* ,
 208 conductivity σ^* , and modulus functions, M^* . Although they are equivalent, they are often
 209 utilized to emphasize different features of the underlying mechanisms of charge carriers'
 210 transport and molecular relaxations. In the case of charge bearing systems at sufficiently
 211 low frequencies, cooperative ion hopping dominantly affects the dielectric spectra in the
 212 complex permittivity $\epsilon^*(\omega) = \epsilon'(\omega) - i\epsilon''(\omega)$; or in the complex conductivity; $\sigma^*(\omega) = \sigma'(\omega)$
 213 $+ i\sigma''(\omega)$. Therefore, the dielectric storage (ϵ'), dielectric loss (ϵ''), electric loss modulus
 214 (M'') as well as *ac* conductivity (σ_{ac}) and *dc* conductivity (σ_{dc}) for the systems under
 215 considerations are investigated over wide frequency and temperature ranges.

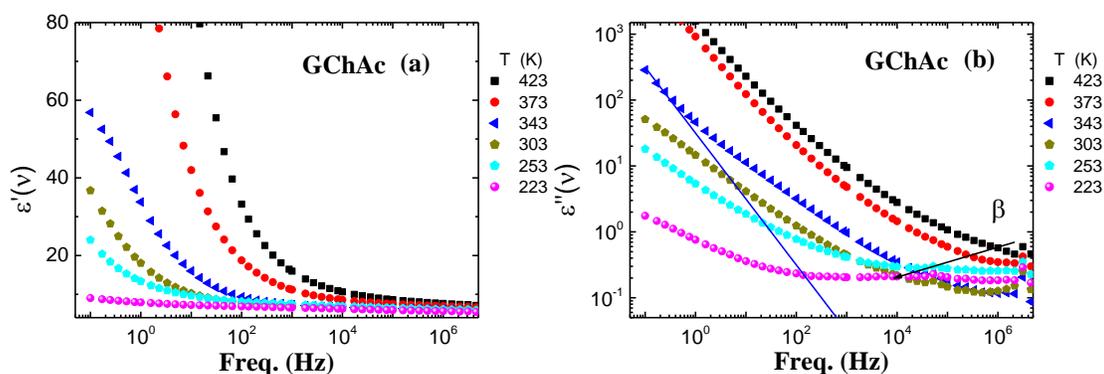
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217
 218 **Figure 5.** Dielectric storage (a) and dielectric loss (b) of chitosan (Ch) measured at
 219 variable temperatures
 220

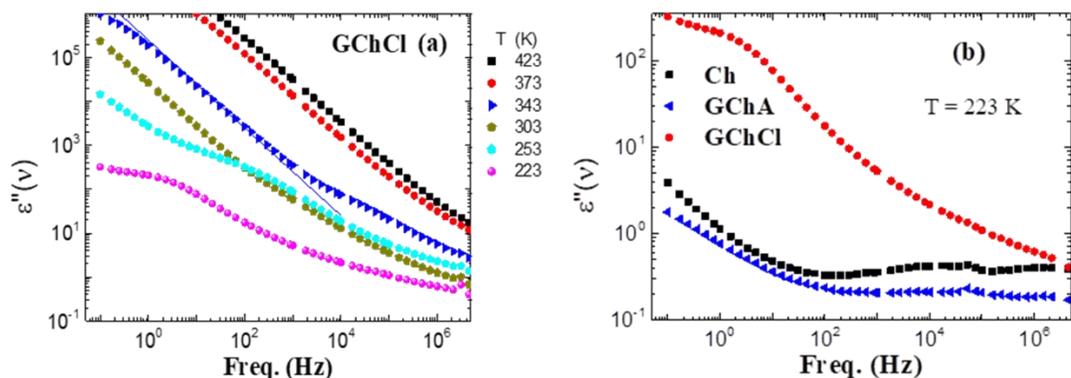
221 Figure 5 a and b display ϵ' and loss ϵ'' spectra of the Ch at different temperatures.
 222 From Figure 5a, it can be seen that ϵ' is approximately frequency independent at low
 223 temperature ($T = 223$ K), while it shows frequency dependence at higher temperatures (T
 224 > 223 K). At high frequencies, it slightly depends on the frequency, which is translated to
 225 a relaxation peak in the loss ϵ'' spectra, *cf.* Fig 5b. This is due to the lag of molecules behind
 226 the alternation of the electric field at higher frequency. At low frequencies, the ϵ' greatly
 227 increases. This is related to the well-known phenomenon that is the electrode polarization
 228 (Kremer & Schönhal, 2003).

229 In the dielectric loss ϵ'' and at low temperature ($T \leq 303$ K), a relaxation β -process
 230 is observed. The process originates from some local motion in the Ch chain, which is
 231 slowed down upon cooling. In polysaccharides, two secondary relaxation processes of
 232 different molecular origin were reported (Cervený et al., 2008; Kaminski et al., 2008;
 233 Salama et al., 2021). One secondary relaxation process is of cooperative molecular nature
 234 as large parts of molecule take part in the motion. This is generally referred to as Johari-
 235 Goldstein (JG-) relaxations, which aroused from the motions of all parts of the polymer
 236 segments. This process is not analyzed here since it is masked by the conductivity
 237 contribution. The conductivity contribution is given by a line of $\epsilon''(\omega) \approx \frac{\sigma'}{\epsilon_0 \omega}$ which is
 238 included in Fig 5b (Mohamed et al., 2020). The other secondary relaxation (β -relaxation)
 239 originates from the local motions within the chains of polysaccharides.



240
 241 **Figure 6.** Dielectric storage (a) and dielectric loss (b) of GChAc measured at different
 242 temperatures.

243 In the case of N-guanidinium chitosan acetate GChAc, the dielectric storage and
 244 loss are depicted in figure 6a and b, respectively. Here, the ϵ' is smaller compared to the
 245 case of Ch (figure 5a). The β -process is again observed at $T \leq 253$ K. However, the process
 246 is smaller in its height, see below.



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 248
 249 **Figure 7.** (a) Dielectric loss of GChCl measured at temperature as indicated. (b)
 250 dielectric loss of Ch, GChAc, and GChCl compared at the $T = 223$ K.

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262 For N-guanidinium chitosan chloride (GChCl), the ϵ'' is illustrated in figure 7a. It
263 is completely altered. The β -process is depleted. The ϵ'' spectra mimics that of conductive
264 materials. This means that the presence of chloride counter anions attached to N-
265 guanidinium chitosan backbone covers the fluctuations along the N-guanidinium chitosan
266 segments. A comparison between the dielectric loss of all systems at $T = 223\text{K}$ is displayed
267 in figure 7b. It can clearly be seen that the strength of the β -process is somewhat smaller
268 in the case of GChAc compared to the case of Ch, while it is completely depleted in the
269 case of GChCl, *i.e.*, the ion motion dominates the spectra and masks any process due to the
270 molecular relaxation.

271 In the modulus presentation, which reads

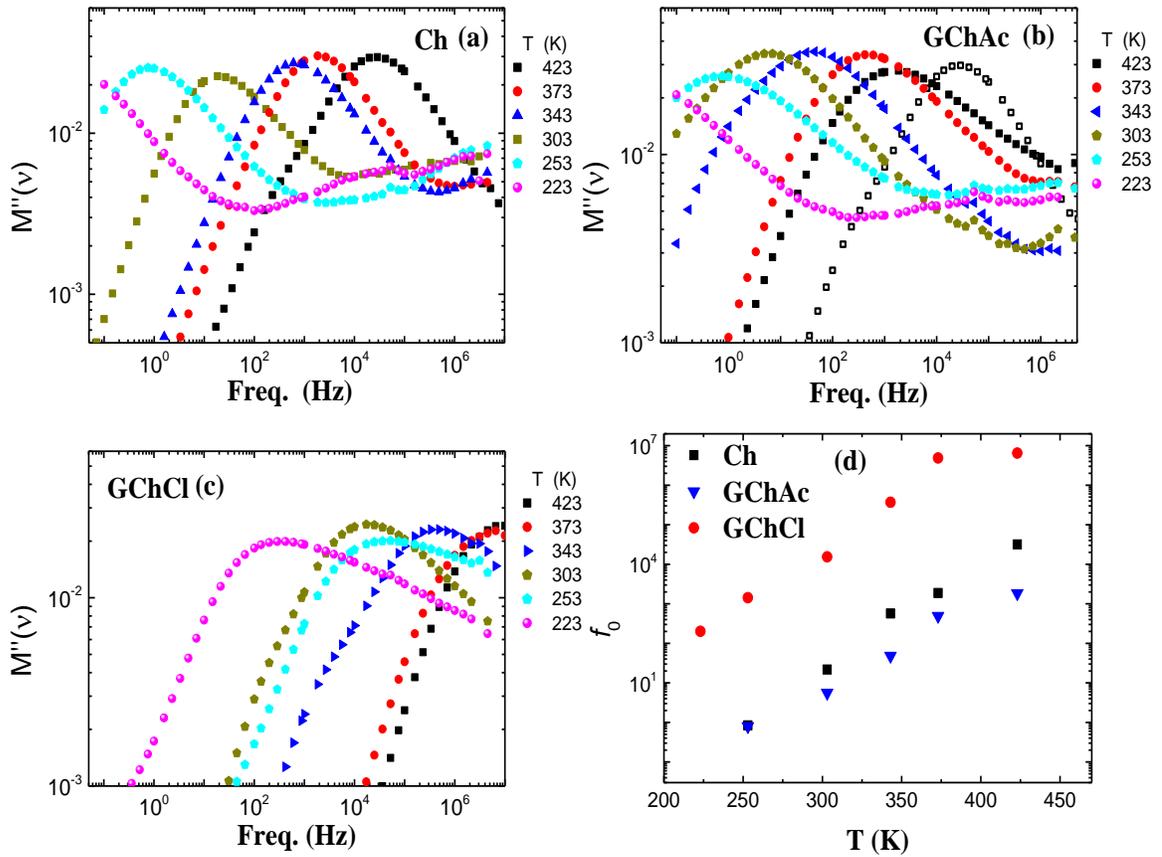
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$$M^* = M' + i M'' = 1/\epsilon^* = i\omega\epsilon_0/\sigma^* \quad (1)$$

273

274 with ϵ_0 is the permittivity of free space, two maxima are observed in the cases of Ch and
275 GChAc (figure 8a and b) at $T < 303\text{ K}$. The maxima seen in the case of GChAc is broader
276 compared to the case of Ch. For clarity, one modulus spectrum at $T = 423\text{K}$ for Ch is also
277 included in figure 8b. In the case of GChCl only one maximum can be recognized (figure
278 8c). This peak maximum denotes the conductivity relaxation σ -process (Kremer &
279 Schönhals, 2003; Vicioso et al., 2004). This process was widely investigated and revealed
280 to be associated with the hopping motion of ions in the disordered structure and correlated
281 to the dc conductivity (see below)(González-Campos et al., 2009; Meißner et al., 2000).
282 For all cases and by picking up the frequency position of this maximum f_0 , this process is
283 faster in the case of GChCl compared to the other cases reported here (see Figure 8d), *i.e.*,
284 this process is controlled by the presence of more mobile ions in the case of GChCl.

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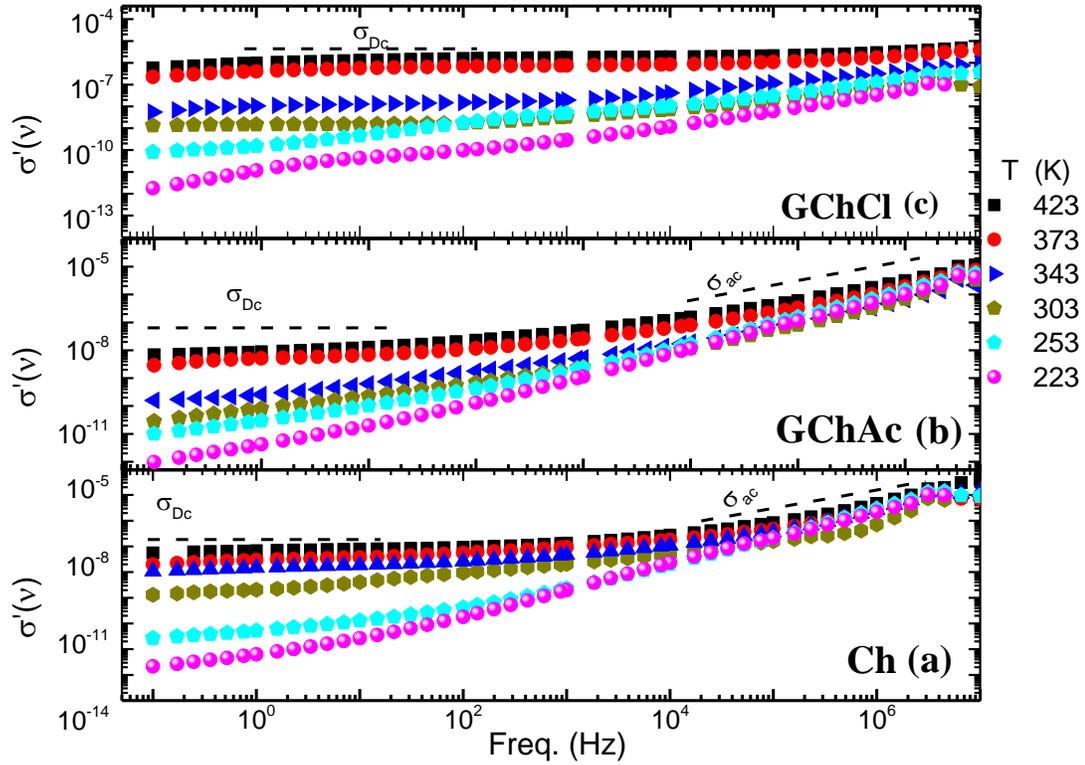
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287 **Figure 8.** Dielectric modulus $M''(\nu)$ of chitosan Ch (a), GChAc (b) and GChCl (c) at
 288 different temperatures. (d) peak maximum positions of the σ process.

289

290 The investigation of *ac* conductivity (σ_{ac}) is an essential for exploring the electrical
 291 conduction of a system upon employing an electrical field (Tan et al., 2016). The
 292 conductivity depends both on the density and the mobility of free charge carriers, *i.e.*, it
 293 increases with mobility and density of free charge carriers (Griffin et al., 2014; Jlassi et al.,
 294 2017; Sangoro et al., 2009).

295



296

297 **Figure 9.** The real part of conductivity $\sigma'(\nu)$ of chitosan Ch (a), GChAc (b) and GChCl
 298 (c) measured at temperature as indicated.

299

300 For all cases, the real part of the conductivity $\sigma'(\nu)$ as a function of frequency is displayed
 301 in figure 9. Two different power-law regimes are recognized following the power-law of
 302 Jonscher (Jonscher, 1981),

303

$$\sigma_{ac}(\omega) = \sigma_{Dc} + A\omega^s \quad (2)$$

304 with σ_{Dc} and A are the Dc conductivity, and the pre-exponential factor, respectively. The
 305 latter depends on temperature and material. Jonscher's exponent s correlates the degree
 306 of interaction between mobile ions with the lattices (Jonscher, 1981). In regime σ_{Dc} , there
 307 is no change with frequency (frequency independent), which dominates the low
 308 frequency regime. Our results indicate that in the case of GChCl, the σ_{Dc} is 4 orders of
 309 magnitude higher compared to Ch and GChAc. The $\sigma_{Dc}(T)$ for Ch, GChAc and GChCl

310 derivatives were determined and added to Figure 10 which shows the temperature
 311 dependance of the Dc conductivity, σ_{Dc} . The $\sigma_{Dc}(T)$ follows Arrhenius law, which reads,
 312

$$\sigma_{Dc} = \sigma_{\infty} \exp\left(\frac{-E_a}{k_B T}\right) \quad (3)$$

313

314 where σ_{∞} and k_B are the conductivity at infinite temperatures and Boltzmann constant,
 315 respectively. The E_a is the activation energy. The fitting parameters are summarized in
 316 table 1.

317

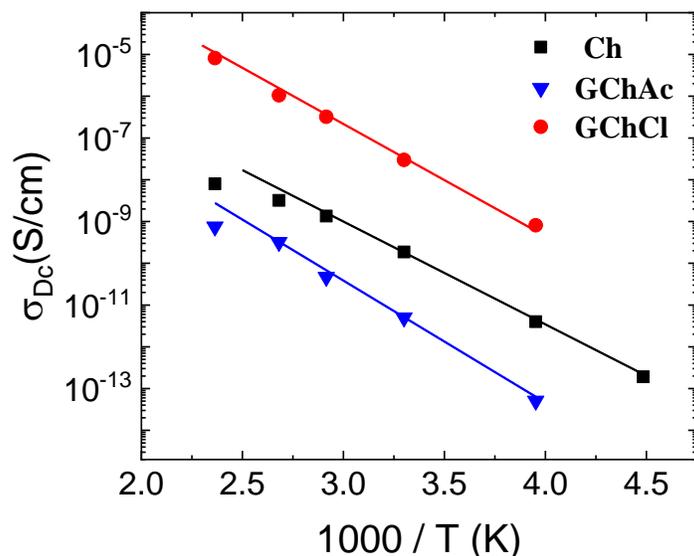
318 **Table 1.** Parameters used to fit using Eq.3

System	E_a [kJ/mol]	σ_{∞} [S/cm]
Ch	47	2.4×10^{-2}
GChAc	56	2.2×10^{-2}
GChCl	52	0.25×10^{-2}

319

320 As already mentioned, the Dc conductivity is proportional to the density of the charge
 321 carriers and their mobility. According to the Stokes–Einstein equation, the mobility is
 322 inversely related to the viscosity. Since the ratio of σ_{Dc} of GChCl to that of Ch at the same
 323 temperature increases, and if the viscosity is similar in the two cases, we can conclude that
 324 that the number density of the charge carrier increases significantly. On the other side, the
 325 ratio of σ_{dc} of GChAc to that of Ch decreases. Assuming again that the viscosity is similar,
 326 this would indicate an increase in the dynamic's radius (Rössler, 1990) or a decrease of the
 327 mobility of the charge carriers in the GChAc material. This phenomenon can certainly be
 328 attributed to strong hydrogen bonding between the guanidinium acetate backbone and the
 329 acetate counter ions, resulting in its significantly lower mobility. The interaction strength
 330 of the counterions with the Ch main chain may therefore give interesting insights in the
 331 dynamics of the counter-anions. The interactions of chloride anions with the guanylated
 332 chitosan backbone are weaker compared to those of acetate. Therefore, chloride resides
 333 shorter time on the main chain than acetate. For the same reason, the concentration of 'free'
 334 chloride should be higher than that of acetate, resulting in a higher conductivity.

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341 **Figure 10.** Dc conductivity σ_{Dc} (v) vs. temperature of chitosan Ch, GChAc and GChCl.

342

343 4. Conclusion

344

345 New chitosan-based guanidinium derivative, i.e., GChAc and GChCl, were prepared and
346 thoroughly characterized. In particular, we focused here on the investigation of the
347 dielectric properties of chitosan and its derivatives via dielectric measurements. In chitosan
348 and GChAc, two relaxation processes were identified, whereas no relaxation processes
349 could be identified in GChCl. Compared to chitosan, the electrical conductivity of GChCl
350 is four orders of magnitude higher due to both higher ion mobility and higher number of
351 ions conducting species. On the opposite, the conductivity of GChAc is lower compared to
352 neat chitosan. We attribute this result to the increase in the dynamic's radius or the decrease
353 of the mobility of the charge carriers. In conclusion, we report new biodegradable and
354 sustainable polymer electrolyte with controllable conductivity, and we believe that these
355 systems give interesting insight in ion conduction phenomena in these systems that have
356 high potential for the construction of “green” technological applications.

357

358 **Declaration of competing interest:**

359 The author declares no competing financial interest

360

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