Thermal and Viscoelastic Properties of Cellulosic Gels with Different Ionic Liquids and Coagulation Agents

Ruth Ariño, Malin Brodin, Antal Boldizar, and Gunnar Westman

Thermal and viscoelastic properties of three-component gels consisting of microcrystalline cellulose, ionic liquid, and coagulation agent were studied. The amount and type of components was varied to obtain different gel properties. The absorption of coagulation agent (13 to 35 % wt of water or ethanol) was found to depend on the types of ionic liquid and cellulose. Surface hydrophobization of cellulose prior to preparation of the gel remarkably resulted in the gels containing the most coagulation agent (35%wt). Rheological studies indicated a linear viscoelastic behavior in storage modulus but not in loss modulus, which is a behavior that, according to our knowledge, has not been seen before for gels. Increasing the cellulose concentration from 1:20 to 1:10 increased the stiffness of the gels. The highest critical stress value (1050 Pa) was obtained for a gel containing 1-butyl-3-methylimidazolium chloride and water. Finally, it was confirmed by dynamic-mechanical experiments that the gels had a cross-linked structure.

Keywords: Microcrystalline cellulose; Ionic liquid; Coagulation agent; Gel; Rheology; Thermogravimetric analysis; Differential scanning calorimetry; Storage modulus; Loss modulus

INTRODUCTION

Cellulose is the most abundant natural polymer on earth and it is used in a large number of applications (Schurz 1999), for instance in the paper, textile, construction, polymer, and food industries. Assuming that oil resources are depleting, and with the decrease in newsprint production, there is an interest in finding new applications for cellulose and for using it as a substitute for oil-based materials. Pulp fibers have low processability and compatibility with polymers in formation of reinforced composites, but this can to some extent be overcome by chemical modification and/or the use of additives.

In addition to bulk production of chemically modified cellulose, usually by functionalization of cellulose under heterogeneous conditions, there is also the possibility to manipulate cellulose by dissolution and regeneration processes. Solutions of cellulose can be obtained only with specialized solvent systems (Edgar et al. 1995; Fischer et al. 2003; Heinze et al. 2000; Rosenau et al. 2001). Recently it has been shown that cellulose can be dissolved in imidazolium-based salts, which are a class of ionic liquids (IL’s). Depending on the structure of the imidazolium cation and the anion, solutions with a cellulose content as high as 25% have been reported (Swatloski et al. 2002). The IL’s have a low vapor pressure and high thermal stability; thus they are considered to give negligible exposure to workers and environment and may therefore be a replacement for

volatile organic compounds (VOC) in industrial chemistry (Meindersma et al. 2007). Unlike other salts, ionic liquids are liquid (and can thus be used as solvents) at relatively low temperatures (Meindersma et al. 2007). As an example, the melting temperature of 1-butyl-3-methylimidazolium chloride is ca. 70 °C, and the melting temperature of 1-ethyl-3-methylimidazolium acetate is ca. -20 °C.

In the dissolution process of cellulose the large amount of intra- and inter-molecular hydrogen bonds of the semi-crystalline cellulose are broken (Michels and Kosan 2005). Upon regeneration from the solution, hydrogen bonds are reformed, and the aggregation leads to material formation with an order and crystallinity highly dependent upon the regeneration method/process used. The dissolution process has been studied with nuclear magnetic resonance spectroscopy (NMR) and rheology (Fukaya et al. 2008; Kosan et al. 2008; Moulthrop et al. 2005; Remsing et al. 2008; Remsing et al. 2006; Swatloski et al. 2002; Zhang et al. 2010). Both anions and cations of imidazolium-based ionic liquids form hydrogen bonds to cellulose hydroxyl groups and hence interrupt the hydrogen bond system of cellulose, causing disintegration of its crystalline parts. The structure of the imidazolium cation also affects the rheological behavior of the mixture (Kosan et al. 2008). Through screening of a large number of ionic liquids, by means of computational modeling, it was found that the anion had the major effect on the solubility of cellulose but that with some anions the solubility should be highly affected also by the cation (Kahlen et al. 2010). Recently, Lindman et al. (2010) proposed a theory on the mechanism of cellulose dissolution, stressing importance of the solvents ability to disrupt also hydrophobic interactions in cellulose.

Dissolved cellulose can be shaped and regenerated from the solution by the addition of an anti-solvent. Turner et al. (2005) made cellulose-polyamine composites from the ionic liquid 1-butyl-3-methyl imidazolium chloride (BMIMCl) both as films and as beads to be applied in biocatalyst immobilization. Recently, 1-ethyl-3-methyl imidazolium acetate (EMIMAc) and 1-allyl-3-methylimidazolium chloride (AMIMCl) were used to produce regenerated cellulose fibers (Hermanutz et al. 2008) and nanocomposites (Zhang et al. 2007), respectively. Cellulose fibers have also been electrospun from ionic liquid solutions (Härdelin et al. 2012; Viswanathan et al. 2006). At present, there are no commercial products based on cellulose-IL solutions, but there are laboratory-scale fiber spinning equipment used for such solutions (Kosan et al. 2008; Viswanathan et al. 2006). These are claimed to be safer and more feasible alternatives to the traditional viscose process (Hermanutz et al. 2008). Cellulose processing in ionic liquids is also considered to be more advantageous than the traditional N-methylmorpholine-N-oxide (NMMO) method, due to the thermal stability of the solvent (Hermanutz et al. 2008). The cellulose-ionic liquid solutions are hygroscopic, and an unlimited excess of water or other anti-solvent will precipitate cellulose. Upon anti-solvent absorption the interaction between the anion and cellulose is reduced and inter- and intra-molecular hydrogen bonds in cellulose are formed. The new aggregates may be more or less ordered than the virgin cellulose. During the regeneration process the solution may go through a gel state.

Gels are soft, solid, or solid-like materials consisting of at least two components, where one is a liquid in a considerable amount (Almdal et al. 1993). Their solid behavior is due to the three-dimensional cross-linked structure within the liquid. The cross-links may result not only from chemical bonds but also from physical interactions, crystallites, or some other kind of junction (Ferry 1980). The properties of gels are affected by several parameters such as concentration, solvent, and time for gel formation. For example, fast
gel formation by pouring the solution into a large amount of anti-solvent such as water will lead to the precipitation of cellulose fibers and dissolution of the solvent in the anti-solvent.

Slow gel-formation, used by Kadokawa et al. (2008) and in the present work, may instead lead to the formation of three-component gels consisting of cellulose, solvent, and coagulation agent (water or other anti-solvent). The cited authors prepared flexible gels by dissolving microcrystalline cellulose (MCC) in the ionic liquid BMIMCl, followed by water absorption. They found that the introduction of water into the solution induced the formation of flexible cellulotic gels that could be shaped and reshaped. It was shown that non-crystalline aggregates were formed in the gels when water was added (Kadokawa et al. 2008).

Gels of this kind are of interest since they are potentially shapeable into different products at elevated temperatures. In order to evaluate the cellulotic gels from a processing point of view, some material properties need to be better understood. In the present study, the thermal and viscoelastic properties of three-component gels consisting of cellulose, ionic liquid, and coagulation agent (i.e. water or ethanol) were determined, and the relations between the gel components and the performance of the material were evaluated. To study the effect on the gels of cellulose surface hydrophobization, gels containing lauric acid esterified MCC (LACE) were also prepared. In general, gels exhibit a viscoelastic behavior that can be characterized by dynamic experiments (Mitchell 1980). In this case, the viscoelastic properties of the gels were evaluated using a stress-controlled parallel-plate rheometer. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were the methods used in order to assess the thermal stability of the gels, structural changes, and content of coagulation agent.

EXPERIMENTAL

Materials
All chemicals were purchased from Sigma Aldrich. The MCC, Avicel PH-101, was dried in an oven at 105 °C overnight before use. EMIMAc (two batches with identical specifications were used) and BMIMCl were dried at 55 °C under reduced pressure for 3 h, and N, N-dimethylformamide (DMF) and pyridine were dried over molecular sieves with pore size of 4 Å overnight prior to being used. Lauroyl chloride was used as purchased.

Lauric Acid Cellulose Ester (LACE) Synthesis
The LACE was synthesized according to the description given by Freire et al. (2006) (Fig. 1). MCC (3.02 g, 18.6 mmol) was added to a flask of lauroyl chloride (4.30 mL, 18.6 mmol), pyridine (1.48 mL, 18.3 mmol), and DMF (140 mL). The heterogeneous mixture was stirred at 115 °C under nitrogen for 6 h. The mixture was filtered, and the solid was rinsed with DMF, acetone, ethanol, water, and again with ethanol. After drying at 50 °C under reduced pressure, 3.86 g of LACE was obtained as a white powder. In Fourier Transform Infrared Spectroscopy (FT-IR), peaks were found at 3350 cm⁻¹ (O-H), 2925 cm⁻¹ (C-H), 2854 cm⁻¹ (C-H), and 1745 cm⁻¹ (C=O). The degree of substitution (DS) calculated from elemental analysis using the method reported by Vaca-Garcia et al. was 0.38 (Vaca-Garcia et al. 2001). An observed weight percentage gain (WPG) of 128% corresponds to a DS of 0.34.
A typical experimental procedure for preparation of the gel with ionic liquid was as follows. MCC or LACE (0.5 g) was dissolved in the ionic liquid (5 or 10 g) at 70 °C overnight in a closed round-bottomed flask to obtain solutions with cellulose: IL ratios of 1:10 and 1:20, respectively. Four grams of the solution was poured into a Petri dish (diameter 50 mm) and kept in an oven at 105 °C for 10 min to minimize any heterogeneity in the solution and to remove residual air bubbles. The dish containing the solution was placed under an overturned glass bowl together with a dish with coagulation agent in order to obtain slow absorption of coagulation agent to the solution (Fig. 2). The gelling period was set to 4 days and, in order to prevent any side-effect from light exposure, the system was placed in the dark. Excess ionic liquid was rinsed off with coagulation agent and the gels were bench-dried for 2 days.

**Fig. 2.** The installation used for the coagulation of cellulose-ionic liquid solutions

**Measurements and Methods**

The FT-IR spectrum was recorded on potassium bromide tablets with a Perkin Elmer Spectrum One instrument. The elemental analysis measurement was provided by Mikroanalytisches Laboratorium Kolbe (Germany). DSC measurements were performed with a Perkin Elmer DSC7 equipped with an intracooler. Each sample was heated from 10 to 300 °C at a heating rate of 10 °C/min in an inert atmosphere. TGA measurements were performed using a Perkin Elmer TGA 7 instrument with a heating rate of 5 °C/min from 20 to 150 °C followed by 10 °C/min from 150 °C to 400 °C.

The viscoelastic behavior of the gels was characterized by dynamic-mechanical experiments using a stress-controlled parallel-plate rheometer (Rheometrics SR200) with 25 mm diameter geometry. A sinusoidal shear stress with an amplitude $\tau_0$ and an angular frequency $\omega$ was applied, and the correspondent shear strain with an amplitude $\gamma_0$ was measured as well as the phase angle $\delta$. The shear storage modulus $G'(\omega)$ and the shear loss modulus $G''(\omega)$ were determined, according to the following definitions (Ferry 1980):

\[
G'(\omega) = \frac{\tau_0}{\gamma_0} \cos \delta \tag{1}
\]

\[
G''(\omega) = \frac{\tau_0}{\gamma_0} \sin \delta \tag{2}
\]

The damping characteristics of the material are expressed in the form of the loss factor; i.e.,

\[
\tan \delta = \frac{G''}{G'} \tag{3}
\]

The samples were disks with a diameter of 25 mm and a thickness of 2 mm obtained by cutting with a circular tool (25 mm diameter). The thickness of the gels depended on the amount of solution poured into the Petri dish during gel preparation, but they were all approximately 2 mm thick. The dynamic-mechanical properties were evaluated at temperatures between 25 and 180 °C (heating rate 5 °C/min) and at circular frequencies between 0.01 and 10 Hz.

RESULTS AND DISCUSSION

Gel Preparation and Ocular Examination

The gels were prepared by coagulation with either water or ethanol. Two different imidazolium-based ionic liquids were used; BMIMCl, and the less toxic EMIMAc with lower zero shear viscosity due to the shorter aliphatic side-chain on the cation and the usage of acetate as anion (Kosan et al. 2008). Different amounts of MCC and also LACE with a DS of 0.38 were added to the solutions.

The different gels prepared are summarized in Table 1, and a picture of them is shown in Fig. 3. Through visual examination, it could be observed that the clear cellulose-EMIMAc solution became slightly cloudy upon coagulation, whereas the cellulose-BMIMCl solution kept its clearness when coagulated.

The difference in transparency might suggest a difference in structure between BMIMCl and EMIMAc gels, which may be expected since the molecular weight of cellulose in BMIMCl solutions was different (lower) than in EMIMAc solutions (Gazit and Katz 2012).

It was observed that a weaker gel was obtained when the MCC concentration in the solution was lower or when LACE substituted cellulose where used. This was expected since a lower concentration would give rise to less interaction points between the cellulose polymers in the gel.
Fig. 3. Gels made of cellulose (MCC or LACE), ionic liquid (EMIMAc or BMIMCl), and coagulation agent (water or ethanol). The color of the gels resembles that of the ionic liquid. The EMIMAc used in 1:10Ee, 1:20Ew, and 1:20EwLACE was slightly brown whereas the EMIMAc used in 1:10Ew and 1:20Ee was uncolored. All the BMIMCl used was slightly brown.

Table 1. Composition of the Gels

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Cellulose</th>
<th>Ionic liquid</th>
<th>Coagulation agent</th>
<th>Cellulose-IL ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:20Ee</td>
<td>MCC</td>
<td>EMIMAc</td>
<td>Ethanol</td>
<td>1:20</td>
</tr>
<tr>
<td>1:10Ee</td>
<td>MCC</td>
<td>EMIMAc</td>
<td>Ethanol</td>
<td>1:10</td>
</tr>
<tr>
<td>1:20Ew</td>
<td>MCC</td>
<td>EMIMAc</td>
<td>Water</td>
<td>1:20</td>
</tr>
<tr>
<td>1:10Ew</td>
<td>MCC</td>
<td>EMIMAc</td>
<td>Water</td>
<td>1:10</td>
</tr>
<tr>
<td>1:20Be</td>
<td>MCC</td>
<td>BMIMCl</td>
<td>Ethanol</td>
<td>1:20</td>
</tr>
<tr>
<td>1:10Be</td>
<td>MCC</td>
<td>BMIMCl</td>
<td>Ethanol</td>
<td>1:10</td>
</tr>
<tr>
<td>1:20Bw</td>
<td>MCC</td>
<td>BMIMCl</td>
<td>Water</td>
<td>1:20</td>
</tr>
<tr>
<td>1:10Bw</td>
<td>MCC</td>
<td>BMIMCl</td>
<td>Water</td>
<td>1:10</td>
</tr>
<tr>
<td>1:20EwLACE</td>
<td>LACE</td>
<td>EMIMAc</td>
<td>Water</td>
<td>1:20</td>
</tr>
</tbody>
</table>

a In the sample codes, the numbers refer to the cellulose-IL ratio, the capital letter refers to the ionic liquid (E for EMIMAc and B for BMIMCl), and the small letter refers to the coagulation agent (e for ethanol and w for water). b Refers to the ratio of cellulose (MCC or LACE) to ionic liquid by weight in the cellulose-ionic liquid solution.

Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry (DSC) showed a change in heat capacity denoted as thermal transition within the measuring range (Fig. 4). Table 2 shows the observed thermal transition intervals of the gels. All the gels made with MCC had a thermal transition between 160 °C and 180 °C. The gel with lauroyl acylated cellulose (sample 1:20EwLACE) exhibited a thermal transition temperature between 110 °C and 130 °C, ca. 50 °C lower than that of the other gels (Fig. 4). As discussed earlier, it is possible that the hydrophobic groups of LACE interfere with the interactions making up the gel network, leading to a less stable gel. It was concluded that the thermal transition depended mainly on the type of cellulose and was related to the stability of the network.
Fig. 4. DSC curves of 1:20Ew, 1:20Bw, and 1:20EwLACE

Table 2. Weight Loss at 150 °C, Transition Temperatures, Average Values of G’ Plateau, and the Critical Stresses for all the Gels

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Weight loss at 150 °C [%]</th>
<th>Transition T [°C]</th>
<th>G’ [kPa]</th>
<th>Critical stress [Pa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:20Ee</td>
<td>26</td>
<td>160-180</td>
<td>82.7 (4.62)</td>
<td>325 (35)</td>
</tr>
<tr>
<td>1:10Ee</td>
<td>22</td>
<td>175-180</td>
<td>446 (44.5)</td>
<td>700 (20)</td>
</tr>
<tr>
<td>1:20Ew</td>
<td>27</td>
<td>170-180</td>
<td>116 (16.3)</td>
<td>400 (15)</td>
</tr>
<tr>
<td>1:10Ew</td>
<td>27</td>
<td>170-185</td>
<td>313 (54.3)</td>
<td>212 (89)</td>
</tr>
<tr>
<td>1:20Be</td>
<td>17</td>
<td>165-185</td>
<td>259 (78.1)</td>
<td>383 (29)</td>
</tr>
<tr>
<td>1:10Be</td>
<td>17</td>
<td>160-180</td>
<td>519 (85.8)</td>
<td>567 (58)</td>
</tr>
<tr>
<td>1:20Bw</td>
<td>13</td>
<td>170-180</td>
<td>127 (4.16)</td>
<td>1050 (71)</td>
</tr>
<tr>
<td>1:10Bw</td>
<td>14</td>
<td>170-185</td>
<td>406 (50.4)</td>
<td>500 (173)</td>
</tr>
<tr>
<td>1:20EwLACE</td>
<td>35</td>
<td>110-130</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>


\(^a\) The values are average values for five samples of each gel. \(^b\) The values are average plateau values for three samples of each gel tested at 70 °C and 1 Hz. Shown in parentheses are the standard deviations. \(^c\) The values are the average for three samples of each gel tested at 70 °C and 1 Hz. Shown in parentheses are the standard deviations.

Thermogravimetric Analysis (TGA)

In the TGA curves (Fig. 5) a weight loss was observed between 20 °C and 150 °C, which could be attributed to the loss of the anti-solvent. It can also be concluded that more water evaporated from the LACE gel (sample 1:20EwLACE) than from the corresponding MCC gel (sample 1:20Ew), as shown in Table 2. It might seem unexpected that the gel containing cellulose with hydrophobic side-chains absorbed more water than the comparable gel. This can be clarified, by considering the water-solubility of substituted cellulose. Kondo reported in 1997 that O-methylated cellulose with low DS was swollen or even dissolved by water (Kondo 1997), although it was more hydrophobic than cellulose itself. The explanation to this is that the O-methyl groups interfere with the
intramolecular hydrogen bond system and as a consequence make the cellulose more accessible for water. These TGA results, together with the DSC results which showed that the LACE gel (sample 1:20EwLACE) had a lower transition temperature than the MCC gel (sample 1:20Ew), imply that using LACE with a DS of 0.38 results in increased water absorption and a weakening of the network in the gel. It was also seen in the TGA curves that from the gels containing EMIMAc more coagulation agent evaporated than from the gels containing BMIMCl. The well-defined weight loss onset at about 250 °C for gels made from EMIMAc and at about 300 °C for gels made from BMIMCl can be attributed to the decomposition of cellulose and ionic liquid, as shown in Fig. 5 (Kadokawa et al. 2008). These are considerably lower decomposition temperatures than that of MCC, suggesting that the stable crystallites of the MCC were partly or fully dissolved during gel preparation or that ionic liquid hydrolyzed the cellulose. As mentioned earlier, Kadokawa et al. (2008) found some aggregation in gels made with microcrystalline cellulose, BMIMCl, and water that was not present in the cellulose-ionic liquid solution.

**Fig. 5.** TGA curves of MCC, EMIMAc, BMIMCl, 1:20Ew, and 1:20Bw

**Viscoelastic Behavior**

All gels except the weak one with LACE (1:20EwLACE) were subjected to a dynamic stress sweep at room temperature (25 °C) and a frequency of 1 Hz. The stress amplitude region studied was from 0.4 Pa to 1500 Pa. Typical results are shown in Fig. 6, where a clear plateau in $G'$ can be observed up to a certain stress, defined as the critical stress, at which $G'$ started to decrease. This critical stress can in a sense be regarded as a measure of the mechanical strength of the cross-linked structure. In the studied region, the behavior of $G''$ could not be considered linear viscoelastic. This behavior of $G''$ has, as far as we know, never been reported before. All the gels exhibited a similar type of behavior in terms of $G'$ and $G''$. Even though differences in $G'$, $G''$, and critical stress were seen between different gels, a stress amplitude of 50 Pa was considered reasonable for the rheological assessment within the linear region of $G'$. 

The influence of temperature on the viscoelastic properties was evaluated at a frequency of 1 Hz and a stress of 50 Pa between 25 and 180 °C. The temperature sweep indicated that the thermal stability of $G'$, which was considered to be the region where the value of the modulus was independent of temperature within the studied range, depended only on the ionic liquid. Gels containing BMIMCl were more thermally stable than those containing EMIMAc. This indicated that the interactions in the BMIMCl gels are stronger than in the EMIMAc gels, which correlates with the results from the TGA. Changing the coagulation agent or the cellulose concentration did not affect the thermal stability of the gels. A temperature of 70 °C was found to be reasonable for the further rheological assessments, since good contact between the sample and the sample holder was observed at this temperature and linearity in $G'$ could still be assumed.

A stress sweep analysis was performed between 0.4 and 1500 Pa at 70 °C and 1 Hz. All the gels exhibited the same behavior as in earlier experiments at 25 °C. The non-linearity in $G''$ was again observed, even though the contact with the sample was improved due to the higher temperature. Differences between gels were, however, observed, and the influence of cellulose content, ionic liquid, and coagulation agent in the resulting gel structure was analyzed. Table 2 shows the average plateau value of $G'$ and the average critical stress observed. If the cellulose content is increased, the number of interaction points giving rise to the gel structure increases and as a consequence a stiffer and stronger gel is expected. The stiffness $G'$ agreed with this expectation, but not the critical stress in the case of the gels containing water, where the critical stress decreased when the MCC concentration was increased from 1:20 to 1:10. This could be interpreted in terms of an increased “brittleness”. When comparing ionic liquids, all the gels made with BMIMCl had a higher $G'$ value than those containing EMIMAc, but not all of them exhibited higher critical stress values. There was thus a dependence on the combination of ionic liquid and coagulation agent. The strongest gel structure in terms of the critical stress was obtained when 5% MCC was combined with BMIMCl and water. The
frequency dependence of $G'$ and $G''$ of all the gels except for the one with LACE (1:20EwLACE) was also studied.

Frequency sweeps were performed between 0.01 Hz and 10 Hz at 70 °C and 50 Pa. An example of a frequency sweep curve is shown in Fig. 7, and the plateau values of $G'$ and $G''$ for each type of gel are given in Table 3. For all the gels, the storage modulus was higher than the loss modulus and both were independent of frequency higher than approximately 0.02 Hz. Since a $G'$ higher than $G''$ and independency of frequency are known characteristics for cross-linked gels (Heldman and Lund 2007), it may be concluded that the gels are cross-linked, e.g. by cellulose aggregation. Since the $G''$ irregularities in this case were observed only at very low frequencies where the precision of the rheometer can be considered low, these do not alter the conclusion.

Fig. 7. Double logarithmic plot of the storage modulus ($G'$) and the loss modulus ($G''$) vs. frequency for sample 1:20Ee at 70 °C and a stress amplitude of 50 Pa

Table 3. Average Values of $G'$ and $G''$ Plateaus over the Frequency Range of 0.01 Hz and 10 Hz

<table>
<thead>
<tr>
<th>Sample code</th>
<th>$G'$ [kPa]$^a$</th>
<th>$G''$ [kPa]$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:20Ee</td>
<td>177 (55.1)</td>
<td>40.2 (19.7)</td>
</tr>
<tr>
<td>1:10Ee</td>
<td>325 (256)</td>
<td>54.7 (66.6)</td>
</tr>
<tr>
<td>1:20Ew</td>
<td>64.0 (29.4)</td>
<td>7.40 (7.47)</td>
</tr>
<tr>
<td>1:10Ew</td>
<td>394 (191)</td>
<td>177 (116)</td>
</tr>
<tr>
<td>1:20Be</td>
<td>181 (23.1)</td>
<td>26.6 (10.6)</td>
</tr>
<tr>
<td>1:10Be</td>
<td>429 (247)</td>
<td>138 (104)</td>
</tr>
<tr>
<td>1:20Bw</td>
<td>71.9 (30.1)</td>
<td>7.51 (2.36)</td>
</tr>
<tr>
<td>1:10Bw</td>
<td>202 (51.7)</td>
<td>40.8 (21.0)</td>
</tr>
</tbody>
</table>

$^a$ The values are average plateau values for three samples of each gel tested at 70 °C and 50 Pa. Shown in parentheses are the standard deviations.
CONCLUSIONS

1. From the DSC measurements performed, it was concluded that the thermal transition range was mostly affected by the type of cellulose and that the lowest thermal transition temperature was obtained for the gel containing LACE (1:20EwLACE).

2. TGA analysis showed that the type of cellulose and ionic liquid affected the content of coagulation agent in the final gel with the gel containing LACE (1:20EwLACE) being the one containing most coagulation agent.

3. The rheological measurements showed that the thermal stability of the gels containing BMIMCl was greater and independent of the cellulose concentration and the coagulation agent used. Interestingly, all the gels exhibited linear viscoelastic behavior in $G'$ but not in $G''$. The behavior of $G''$ needs further studies due to its complexity. In general, gels having a higher concentration of MCC yielded higher plateau values for the storage modulus $G'$. BMIMCl forms gels with higher $G'$ but it was observed that the combination of ionic liquid and coagulation agent affected the critical stress value, BMIMCl and water being the combination that gave stronger gels (at an MCC concentration of 1:20).

4. Finally, from the frequency measurements, it was observed that $G'$ was higher than $G''$, indicating a cross-linked structure in the gel, and both were independent of the frequency within the studied region.

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