Dynamic Mechanical Analysis on Regenerated Cellulose

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Dynamical mechanical analysis was applied to two samples of cellulose (Cell 1 and Cell 2), obtained using the N-methylmorpholine-N-oxide blown technology in order to shed light on the secondary relaxations of cellulose. By tracking the storage modulus (E'), the loss modulus (E'') and loss factor (tan δ) vs. temperature it becomes possible to ascertain the dynamic molecular phenomena. A multiplex experiment (0.1, 0.5, 1, 5 and 10 Hz) was performed to calculate the apparent activation energy for the sub-glass transitions. Water and peculiarities of the fabrication process influence the dynamic mechanical behaviour of cellulose. To evidence the plasticizer/antiplasticizer role of water molecules four consecutive heating-isothermal-cooling cycles were accomplished.

Keywords: cellulose, dynamic mechanical analysis, sub-glass transition relaxations

Cellulose represents a regnant natural polymer all over the world, known as the prevailing structural part of the plant cell walls [1,2]. It consists of glucose rings linked by β-(1-4) glycosidic bonds and has two hydroxyl groups and one hydroxymethylene group per glucose ring (fig. 1).

![Chemical structure of cellulose](image)

The structural peculiarities of cellulose assign various characteristics to cellulose-based materials (stiffness, biodegradability) that make them well-suited for high-added value applications (pulp for paper manufacturing, excipient materials in pharmaceutical industry, reinforcing compound in blends and composites) [3-9]. The high content of hydroxyl groups in cellulose is responsible for its remarkable sensitivity to moisture and they create multitudinous hydrogen bonds between contiguous macromolecular chains or between these ones and water molecules [10-17]. As a consequence, the natural polymer is not meltable or soluble in usual solvents and this fact generated a burdensome task in the incipient ages of cellulose processing. The technology developed based on the N-methylmorpholine-N-oxide (NMMO) solvent system represents a milestone in cellulose industry [18,19]. It led to the regenerated cellulose via an environmentally friendly method. On account of the strong inter-chain network of hydrogen bonds, the molecular mobility is notably diminished in cellulose. There are plenty of studies on molecular mobility of cellulose and a great variety of methods have been used to investigate the secondary relaxations of cellulose, dynamic mechanical analysis (DMA) included [20-27]. It is generally accredited that this method is very sensitive to molecular motions for assessing transitions and transformations in polymers. Mechanical spectroscopy results collected on cellulose evidenced two secondary relaxations, β and γ. Both the magnitude and the temperature of the secondary relaxations depend on the presence of moisture or the origin of cellulose [3,10,14,16,22,23,27]. Actually, cellulose is an excellent example on the manner whereby each item from the so-called chain of knowledge (structure formation - processing - product design) alters the final material [28]. Taking these backgrounds into consideration, we report on this paper how the molecular dynamics of cellulose can be finely tuned just by adjusting an ingredient in the procedure of cellulose film manufacture.

Experimental part

Two cellulose samples, generically named Cell 1 and Cell 2, were kindly supplied by Fraunhofer Institute for Applied Polymer Research, Potsdam-Golm, Germany. The cellulose films were manufactured using the NMMO blown technology, as described elsewhere [18]. In the case of the sample Cell 2 a wider nozzle was used.

DMA experiments were conducted using a PerkinElmer Diamond apparatus that applies a sinusoidal stress to the sample and measures the resulting strain. The used force amplitude was well within the linear viscoelastic range for both investigated samples. The main variables monitored in a DMA experiment include the storage modulus (E'), the loss modulus (E'') and the loss factor (tan δ) [29,30,31]. The storage modulus (E') refers to the ability of a material to store energy and is related to the stiffness of the material. The loss modulus (E'') represents the heat dissipated by the sample as a result of molecular motions. The loss factor (tan δ=E''/E') is a dimensionless property and reveals whether a material absorbs or loses energy. The samples were scanned with a heating rate of 2°C/min between -150°C and 250°C, in a multiplex experiment (0.1, 0.5, 1, 5, 10 Hz), under a nitrogen atmosphere. The drops in E' curves and the peaks in E'' and tan δ plots report on the physical transitions in the polymer films. Usually, the transitions are taken at the maximum rate of turndown of the storage modulus E'. Moreover, the loss modulus E'' and the tan δ indicate definite peaks for all transitions. The loss modulus E'' peak appears always at lower temperature than the tan δ peak [29]. The apparent activation energies of the transitions were determined from the Arrhenius equation:

\[ f = A \exp\left(-\frac{E_a}{R \cdot T}\right) \]  

using the plot of the log frequency vs. reciprocal temperature of transition:

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\[ \ln f = \ln A - \frac{E_a}{R} \cdot \frac{1}{T} \]  

(2)

where \( f \) is the frequency (Hz), \( A \) is the pre-exponential factor, \( R \) is the gas constant (8.314 \text{ J/mol·K}), \( T \) is the absolute peak temperature (K), and \( E_a \) is the activation energy (\text{J/mol}). Former reports stated that the Arrhenius equation is appropriate to be used for non-cooperative processes (sub-glass transitions relaxations) [32]. In the case of \( \alpha \)-transition it is recommended to apply the relation within a narrow range of frequencies (two to three orders of magnitude). Anyway, we chose frequencies between 0.1 and 10 Hz, albeit our principal focus was directed to the sub-glass transitions relaxations.

Additionally, the films were subjected to four consecutive scans, i.e. heating (-140°C; 10°C/min) - isothermal step (120°C; 60 min) - cooling (120°C to -140°C, 4°C/min), and the changes in the sample were followed by tracking \( E' \), \( E'' \) and \( \tan \delta \) changes.

The size of films was 10 . 10 . 0.03 mm for the tension attachment.

**Results and discussions**

Figure 2 and figure 3 presents the storage modulus \( E' \), the loss modulus \( E'' \) and the loss factor \( \tan \delta \) vs. temperature for the Cell 1 and Cell 2 samples, at five frequencies, between 0.1 and 10 Hz. For the sake of clarity, in order to avoid too many overlapping data, the figures include only the results for three frequencies: 0.1, 1 and 10 Hz.

At very low temperatures (under –100°C) both samples exhibited high storage modulus values (level with or over 10^9 \text{ Pa}), which is typical for glassy polymers. On the glassy plateau the \( E' \) value of Cell 2 is higher than the \( E' \) value of Cell 1. Some relevant dynamic mechanical characteristics for the samples Cell 1 and Cell 2 are summarized in table 1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( E' \times 10^9/\text{Pa} ) (1 Hz)</th>
<th>( T/\text{C} ) (1 Hz)</th>
<th>( E'' )</th>
<th>( \tan \delta )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cell 1</td>
<td>-95°C</td>
<td>50°C</td>
<td>10</td>
<td>-61</td>
</tr>
<tr>
<td>Cell 2</td>
<td>15</td>
<td>4.7</td>
<td>-62</td>
<td></td>
</tr>
</tbody>
</table>

At very low temperatures, due to the traces of water, 

\[ \delta = \frac{1}{\frac{R}{A} - \frac{E_a}{R} \cdot \frac{1}{T}} \]

(3)

This equation is typical for glassy polymers. On the glassy plateau the \( E' \) value of Cell 2 is higher than the \( E' \) value of Cell 1. Some relevant dynamic mechanical characteristics for the samples Cell 1 and Cell 2 are summarized in table 1.

A large and quite important drop in \( E' \) is noticed for both samples above –100°C, that span a temperature range of at least 100°C. The analogical marks on the \( E' \) and \( \tan \delta \) curves are very broad peaks centred at the temperatures indicated in table 1. The storage modulus values for the second plateau features as well a glassy domain, being over 10^9 \text{ Pa}.

The literature describes a large disparity of the results concerning the positions of the sub-glass transitions in cellulose. The examination of the sub-glass transitions should be made in a broader context because the investigated cellulosics are invariably manifold [8,16,20]. The operations performed during cellulose production result in different orientation and crystallinity in the film. Mostly, two relaxation processes were noticed for cellulose in the low temperature range (-170°C to 0°C). The \( \gamma \) relaxation is attributed to local side movements (\(-\text{CH}_2\text{OH}, \text{-OH}\)) and is indicated by a broad \( \tan \delta \) peak centred around –120°C. The \( \beta \) relaxation (usually above –75°C) is associated with the localized movements of the chain segments, which depend on the flexibility of the glycosidic linkage [10,23]. The process is induced by the rotation of glucose unit around the glycosidic linkage. The most conspicuous property of these sub-glass transitions is their huge dependence on moisture content [10,12,13,15]. Wet samples of cellulose show only one relaxation process that spans between –123°C and –50°C. This situation is changed after special thermal treatment (heating under cryogenic vacuum), i.e. the joined broad peaks are gradually differentiated into two separate, independent peaks [10].

Going back to our samples, Cell 1 and Cell 2, there is only one broad peak in the sub-glass transition region that stretches between –100°C and –50°C, and nothing happens under –100°C. Intuitively, we may attribute this to the overlapping of \( \beta \) and \( \gamma \) transitions, due to the traces of water. When the transitions are very broad and the maximum values of the temperature peaks corresponding to the samples are quite close (table 1), caution should be exercised in wording of a categorical conclusion as regards the samples Cell 1 and Cell 2. The phenomena that happen close to 50°C are due to the removal of water. Further comments on this event will be done in the later discussion of the results. The reported cellulose glass transition is around 220°C to 230°C [33]. However, it is well known that for cellulose the thermal decomposition starts in the glass transition temperature range. Therefore, glass transition process is predominantly responsible for \( E' \) decrease above 170°C, but incipient thermal degradation should be
considered. For an amorphous linear polymer in the glass transition range the storage modulus drops a factor of about 1000 in a narrow temperature range (20–30°C). In our case the descent factor less than 10 hints the presence of crystalline domains in both cellulose samples. In the range of glass transition $E'$ has a more important decrease in the case of Cell 1 sample, due to an enhanced chain flexibility.

Considering the effect of frequency on the dynamic molecular behaviour, a feature common to both systems is the shift of the transitions to higher temperatures and the increase of the storage modulus for a specific temperature, as the frequency increases. When the applied stress is faster, the macromolecules have less time to react and a higher temperature is claimed to stimulate molecular movements.

The apparent activation energies calculated from the Arrhenius plot, taking the transition temperatures from $E''$, are 88.85 kJ/mol for Cell 1 and 100 kJ/mol for Cell 2, with a linear relative coefficient of 0.999 and 0.996, respectively. These values are a bit high for sub-glass transitions and are consistent with a reduction in the molecular mobility. It was already reported that water acts as an anti-plasticizer for the low temperature relaxation [15,22]. A typical plasticizer increases the polymer free volume, allowing more chain motion. Consequently, the intermolecular cohesion of the polymer chains is lessened entailing the reduction of the storage modulus. This situation is opposite to the effect caused by water in some systems that involve hydrogen bonds with water, i.e. the storage modulus below the glass transition temperature increases with rising water content. Water induces a synergy on the cumulating effect of water-polymer-polymer hydrogen bonds, generating an increased stiffness. This mechanism prevails at low water content (under 6%), while after a certain content the plasticizing effect takes over [15]. Our results are consistent with the presence of moisture in the samples, water functioning as an anti-plasticizer. The amount of moisture is higher in Cell 2 than in Cell 1, given the values of the storage modulus ($E'_\text{Cell}_2 > E'_\text{Cell}_1$) and the lower flexibility of Cell 2 in the glass transition range, induced by additional hydrogen bonds.

Repeated DMA experiments on thermally treated cellulose samples did not yield comprehensive and comparable data, so that to be able to gain further evidence for the above rationale, the thermal treatment was made in the DMA oven. We conducted four series of DMA experiments that included heating (-140°C) - isothermal step (120°C) - cooling (120°C -140°C). It is important to mention that all the parameters ($E'$, $E''$, and $\tan\delta$) maintain a constant value during the isothermal step. Figure 4 and figure 5 picture the variation of storage modulus $E'$ and loss factor $\tan\delta$ vs. temperature for the heating stages.

Both samples have the maximum of the loss factor peak at a noticeable higher temperature for the first heating step than the one of the next three heating stages. In addition, the storage modulus $E'$ rises in the second heating step as compared with the first one, more pronounced for Cell 1 sample. This increase in stiffness after the first heating designates that during the first step water that acts as plasticizer is eliminated from the film. Afterwards, Cell 2 sample registers a decreasing trend of $E'$ in the glassy range as the number of heating cycle increases. The $\tan\delta$ peak decreases in intensity, accompanied by the increasing of the low temperature edge. This pattern is a diagnostic of the removal of water involved in the hydrogen bonds, as stated above. According to [15], when these water molecules are expelled, they leave instead holes, this inducing the decrease in density and modulus. In the glassy state the cellulose chains are not able to rearrange themselves and the configuration of cellulose is frozen. As opposed to Cell 1, the DMA experiment records the same behaviour during heating steps 2-4 for the sample Cell 2. The $E'$ and $\tan\delta$ curves in figure 5 are practically superimposed in these last heating stages. One may contend that the water molecules that participate in hydrogen bonds are so strongly linked in Cell 2 that their removal is not possible under the thermal conditions created in the DMA oven. This result is consistent with the higher rigidity of the Cell 2 hydrogen-bonding network, inferred in the previous discussion.

Conclusions

Two cellulose films (Cell 1 and Cell 2) prepared through the N-methylmorpholine-N-oxide blown technique were evaluated as regards their dynamic mechanical behaviour. The presence of only one very broad peak in the $\tan\delta$ vs. $T$ curve, localized under the glass transition, and the quite high activation energy associated with it suggests that the $\gamma$-relaxation (attributed to the local side movements of the $\text{–CH}_2\text{OH}$ and $\text{–OH}$ groups) and $\beta$-relaxation (assigned to the localized movements of the chain segments) are merged due to the presence of water. As it was expected for cellulose that has a high propensity to moisture, water functions mostly as an anti-plasticizer. The effect is more significant in Cell 2 that is characterized by a higher stiffness ($E'$) than the sample Cell 1. DMA experiments performed in consecutive heating cycles sustain that water is very tightly linked in the Cell 2 sample. For both samples only
the onset of the glass transition process was distinguished, due to overlapping with thermal degradation phenomena. 

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