



Research paper

On the origin of sorption hysteresis in cellulosic materials

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ARTICLE INFO

Keywords:

Cellulose

Chemical modification

Glass transition temperature

Dialcohol cellulose

Kraft pulp

Moisture sorption

Sorption hysteresis

Temperature

ABSTRACT

Moisture sorption and moisture sorption hysteresis of carbohydrates are phenomena which affect the utilisation of products made thereof. Although extensively studied, there is still no consensus regarding the mechanisms behind sorption hysteresis. Attempts have been made to link the behaviour to molecular properties, in particular to softening properties, and the moisture sorption hysteresis has therefore here been investigated by modifying cellulosic fibres to affect their softening properties. The results show that the moisture sorption hysteresis diminishes with decreasing softening temperature, and was even completely absent at the higher degrees of modification. The moisture sorption characteristics also changed from a type II sorption to a more type III sorption behaviour, a feature more prominent the higher the degree of modification and the higher the temperature. For the highest degree of modification studied the sorption characteristics changed from sorbing less water the higher the temperature to sorbing more water with increasing temperature.

1. Introduction

The phenomenon of sorption hysteresis of gases, i.e. that the amount of gas sorbed at a given relative activity of the gas differs during adsorption and desorption, or, in other words, that the mass sorbed is not a strict function of the specific activity of the gas, has been observed in many different systems (Al-Muhtaseb, McMin, & Magee, 2002; Gregg and Sing, 1982; Kamiya, Bourbon, Mizoguchi, & Naito, 1992; Lowell, Shield, Thomas, & Thommes, 2004). The most commonly addressed hysteresis phenomenon is perhaps that involving moisture sorption in wood and other cellulose-based materials. When these hygroscopic materials are utilized in, for example, wood constructions, wall panels and floors, or in paper-based products, moisture sorption and sorption hysteresis result in a volume change in the material, commonly referred to as hygroexpansion. As the ambient environment is constantly subjected to changes in relative humidity (RH) and temperature, the properties of a carbohydrate material may never be fully specified unless its RH and temperature history is known. The sensitivity to moisture sorption and the difficulty in specifying important material properties also hampers the use of cellulosic materials as replacements for petroleum-based polymeric materials in modern products. Thus, a fundamental understanding of the basic mechanisms behind this phenomenon is of particular interest. Even though moisture sorption in wood, paper and other biomaterials has been studied for more than a century, there is still a lack of consensus regarding the

origin of the hysteresis phenomenon. For cellulosic materials, it has been suggested that the effect is tied to the adsorption to hydroxyl groups and to changes in the availability of such sites during the different phases of the RH cycle (Urquhart, 1929). Others have related the phenomenon to effects of capillary condensation occurring at high RH (Chen and Wangaard, 1968), a theory that in a modified form is still used to explain results of moisture sorption and hysteresis studies in cellulosic materials (Shi and Avramidis, 2017). However, NMR-experiments indicate that capillary condensation may not occur in wood up to an RH of at least 99.5% (Thygesen, Englund, & Hoffmeyer, 2010) suggesting that capillary condensation is a less likely explanation of hysteresis. Sorption hysteresis has in many cases also been tied to specific features of the wood cell wall, linking the phenomena to cell wall elasticity and the cell wall polymer arrangement (Chirkova, Andersons, & Andersons, 2009; Hill, Keating, Jalaludin, & Mahrtdt, 2012), an explanation which was proposed already in the 1940s by Barkas (Barkas, 1949) who suggested that the hysteresis is due to plastic deformation. Moisture hysteresis can however also be observed in isolated wood polymers in the form of film materials (Kulasinski, Salmén, Derome, & Carmeliet, 2016). In synthetic polymers, the occurrence of sorption hysteresis has been linked to changes in the free volume in conditions of a glassy state of the polymer (Fleming and Koros, 1986; Vrentas and Vrentas, 1996). According to this hypothesis, the hysteresis phenomenon is linked to the swelling and glass transition of the polymer system and, based on these ideas, it has been suggested

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that the sorption hysteresis of wood is related to the softening properties of the constituent wood polymers (Engelund, 2011; Engelund, Thygesen, Svensson, & Hill, 2013). It has also been noted that the difference between the moisture content reached by desorption to a given relative humidity from the wet state and that reached by adsorption to the same relative humidity from the dry state decreases with increasing temperature (Djolani, 1972; Hill, Norton, & Newman, 2010). It has also been shown that at temperatures higher than 75 °C, the hysteresis phenomenon no longer exists for wood (Weichert, 1963). Such a temperature would be high enough for the hemicelluloses and lignin, and possibly also the less ordered parts of the cellulose in the wood cell wall to be softened (Back and Salmén, 1982; Olsson and Salmén, 2004). Thermodynamic analysis (Willems, 2014) also supports the idea of hysteresis being related to relaxation phenomena of the amorphous wood material. However, at present, no experimental data linking changes in softening properties to changes in moisture hysteresis are available.

In order to further elucidate the relationship between the occurrence of moisture sorption hysteresis and the softening properties, it is of interest to study cellulosic materials with a distinct glass transition behaviour; dry native cellulose typically decomposes before reaching its glass transition (Salmén and Back, 1977). Recently, Larsson and Wågberg (2016) and Linvill, Larsson, & Östlund (2017) observed a distinct temperature-induced softening in materials made from cellulose fibres where the cellulose had been partly derivatised to dialcohol cellulose. Such a modification of the glucose chain results in a more thermoplastic material. In this work chemically modified cellulose materials, with moisture induced softening, i.e. a glass transition, in the temperature interval of 20–65 °C have been utilized to facilitate sorption studies in the same temperature range. The intention was to examine if any relation between sorption hysteresis and the softening phenomena could be determined.

2. Materials and methods

2.1. Materials

The same cellulose material that was used in a previous study (Larsson and Wågberg, 2016) was used in this study, i.e. sheets made from chemically modified kraft pulp (SCA Östrand mill, Timrå, Sweden). The chemical modification consisted of a sequential periodate oxidation to dialdehyde cellulose, followed, after washing, by a borohydride reduction to dialcohol cellulose. The degree of modification was determined by the stoichiometric reaction with hydroxylamine after the periodate oxidation step, i.e. to determine the degree of oxidation, and was calculated to be approximately 13, 24 or 40% corresponding to oxidation times of 6, 12 and 24 h respectively; the crystallinity indices of the reference and these three samples were, as earlier reported, determined by X-ray diffraction to be 82.3, 80.8, 77.5 and 73.5, respectively (Larsson and Wågberg, 2016). The materials were chosen in order to display a broad variation in glass transition temperature.

2.2. Methods

2.2.1. Dynamic mechanical thermal analysis with humidity control

Dynamic mechanical thermal analysis, DMTA, was performed in the tensile mode on a TA Instruments Q800 equipped with a TA humidifying unit. The test pieces had an approximate width of 3 mm, a thickness of 100–180 µm and the distance between the clamps was 10–12 mm. The oscillation frequency and amplitude were 1 Hz and 5 µm, respectively, and humidity scans were performed at a rate of 0.4% RH per minute in the humidity range of 20–90% RH. Prior to each run, the sample was equilibrated for 120 min at 20% RH at the chosen temperature of 30, 45 or 60 °C (+/– 0.3 °C). The temperature interval chosen was based on earlier studies on similar materials (Larsson,

Berglund, & Wågberg, 2014a) and on the possibility of having a constant and stable measurement temperature (the instrument was not equipped with any cooling accessory) and of avoiding the risk of moisture condensation at the highest temperature. The storage and loss moduli, E' and E'' respectively were evaluated. Data are presented as the relative changes in moduli as a function of RH with respect to the moduli at 20% RH, E'_{0} and E''_{0} for each temperature. The softening RH, corresponding to the glass transition temperature, was determined from the peak of the relative loss modulus from RH-scans.

2.2.2. Moisture sorption

Moisture sorption measurements were performed on a TA Instruments Q5000 SA. Approximately 10 mg material was used for each measurement. Adsorption–desorption curves were obtained at selected temperatures of 25, 45 and 65 °C, in the humidity range of 0–90% RH. At 25 °C, some of the samples were measured up to 95% RH; the selection of the highest humidity to be studied was based on the need to avoid condensation in the instrument due to temperature fluctuations in the air surrounding the apparatus. The temperature was maintained stable by circulating water connected to a water bath with a temperature precision better than +/– 0.05 °C. Humidity was regulated by mixing dry and saturated air at the specified temperature in accurate proportions for the desired RH +/– 0.1%. A somewhat larger temperature interval than that possible to use in the DMTA measurements were exploited in order to ensure that differences in hysteresis would be clearly visible. Scans were performed by first equilibrating the sample at 0% RH for three days, after which the RH was increased in steps of 10% RH up to 90% RH and then decreased in steps of 10% RH down to 0% RH. The RH was kept constant until the weight change was less than 0.001% over a 20-min period or the time exceeded 3000 min. Moisture content is given as the moisture ratio based on the mass of the sample conditioned at 0% RH.

3. Results and discussion

Studies of cellulose materials partly derivatised to dialcohol cellulose have shown that the modification results in a material with increased thermo- and hygroplasticity (Larsson, Berglund, & Wågberg, 2014b; Larsson & Wågberg, 2016). Furthermore, an increase in the moisture content of this material lowers its glass transition temperature (Linvill et al., 2017). This phenomenon is also clearly evident in the present DMTA measurements. Fig. 1 shows the relative storage and loss moduli, E'/E'_{0} and E''/E''_{0} respectively, as functions of RH at different temperatures. As can clearly be seen, the materials are greatly influenced by both temperature and moisture, the more so the higher the degree of modification. For all degrees of modification studied, the softening RH decreases with increasing temperature, as is evident both from the onset of the reduction in storage modulus and from the peak in the loss modulus. With increasing degree of modification, the softening RH at a given temperature was also lowered. The decrease in the softening RH with increasing modification was also more significant at higher temperatures, as is clearly seen in Fig. 2 where the estimated softening RH (based on the loss modulus peak) is plotted in a temperature–RH graph. The RH dependence of the softening is of the same, or even lower, magnitude as that reported for isolated wood hemicelluloses (Olsson and Salmén, 2004).

Fig. 3 shows the sorption isotherms determined for all degrees of modification at temperatures of 25 and 65 °C (data provided as Supporting information). For the original cellulose material, the typical sigmoidal type II sorption curve is evident (Brunauer, Deming, Deming, & Teller, 1940; Engelund et al., 2013). With increasing temperature and increasing degree of substitution, the sigmoidal shape diminished and, at 40% modification and a measurement temperature of 65 °C, changed into a typical type III sorption isotherm (Brunauer et al., 1940). Furthermore, by comparing the data for materials of different degrees of modification, it is clear that the amount of moisture

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