The pressure–volume–temperature relationship of cellulose

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Abstract Pressure–volume–temperature (PVT) measurements of α-cellulose with different water contents, were performed at temperatures from 25 to 180 °C and pressures from 19.6 to 196 MPa. PVT measurements allowed observation of the combined effects of pressure and temperature on the specific volume during cellulose thermo-compression. All isobars showed a decrease in cellulose specific volume with temperature. This densification is associated with a transition process of the cellulose, occurring at a temperature defined by the inflection point T_t of the isobar curve. T_t decreases from 110 to 40 °C with pressure and is lower as moisture content increases. For isobars obtained at high pressures and high moisture contents, after attaining a minimum, an increase in volume is observed with temperature that may be related to free water evaporation. PVT α-cellulose experimental data was compared with predicted values from a regression analysis of the Tait equations of state, usually applied to synthetic polymers. Good correlations were observed at low temperatures and low pressures. The densification observed from the PVT experimental data, at a temperature that decreases with pressure, could result from a sintering phenomenon, but more research is needed to actually understand the cohesion mechanism under these conditions.

Keywords Cellulose · Pressure–volume–temperature relation · Biodegradable plastic · Tait equation

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Introduction

Modern society has replaced many ordinary objects with petrochemical plastic materials, which at the end of their useful life become litter (Scott 2000), and Derraik (2002) for example has shown that plastic pollution has very harmful effects on the ocean ecosystems. This initial enthusiasm for plastic materials is explained by their interesting properties such as long shelf life, low density plus high mechanical resistance. But nowadays, faced with the environmental problems linked to the use of more and more plastic, there is a growing need for biodegradable materials obtained from renewable sources.

Production of these biodegradable materials is more complex than for petrochemical plastics, mainly

because of the diversity of the structures and compositions of new renewable materials, on the one hand, and the possible competition between food and industrial applications, on the other. Three main ways are used to produce these biodegradable polymers: chemical synthesis from renewable or fossil monomers (PLA, PCL…), bacterial fermentation (PHA's…) or the use of natural polymers (Avérous 2004). The first two routes lead to traditional thermoplastic polymers that can be processed using classical technologies (e.g. injection, molding, extrusion) while the last produce agro-materials (Rouilly and Rigal 2002) for which new thermo-mechanical processes are required.

Cellulose is the most abundant biological molecule on Earth. It is an organic, semi-crystalline polymer of $\beta - 1$, 4-linked D-glucose units, and the macromolecule does not have a melting point because degradation occurs before. Two ways for making cellulose-based materials have been investigated: a wet way using the ability of fibers to organize themselves upon drying (paper industry, paper slurry molding) or a dry way using compression. In the pharmaceutical domain, cellulose compaction properties have come under intense study for producing tablets (Jain 1999). Other relevant work reported covers studies on the physics of the compression (Patel et al. 2006), on the influence of cellulose structure on the compaction (Picker-Freyer 2007; Picker 2003) or on the effect of pressure on cellulose crystallinity (Kumar and Kothari 1999). However, since most drugs are temperature sensitive, the experimental protocol for the formation of tablets does not use this parameter.

Compression of pure cellulose at high temperatures and pressures is, however, a new innovative way of producing biodegradable materials. Production of bulk cellulose plastic has been investigated recently using a specific high shear and high-pressure device (Zhang et al. 2011), a multi-step non-solvent approach (Nilsson et al. 2010), or direct compression on cotton linters (Navard 2012). Our group has studied the influence of the compressing operating conditions on α-cellulose compressed materials (Pintiaux et al. 2013), and the effect of temperature on the compression of various celluloses (Vaca-Medina et al. Accepted).

To understand the behavior of cellulose under high-pressure compression, a complete PVT profile is needed. The addition of a temperature component limits the utilization of pharmaceutical models or protocols. Most synthetic polymers have been tested to establish their PVT diagrams, and data for polymers is measured either during cooling (most usually) or during heating. A pure state equation is used to describe polymers in the liquid state (Dee and Walsh 1988), and an isothermal compressibility function, the Tait equation, is generally employed. This equation has been used for synthetic and natural polymers, especially by Otaigbe and Jane (1997) who computed the model for soy protein. However, no thermal study exists for cellulose under high pressure, and thus no model has been tested for this kind of material.

The present study first covers the experimental protocol used, then the influence of operating parameters (such as pressure and moisture content) on the PVT behavior of α-cellulose, and finally the capacity to model the diagrams obtained. In parallel, the effect of humidity during the isobar heating has been studied for use in future work on PVT simulation.

Experimental

α-cellulose (96 % purity) was purchased from Sigma-Aldrich (St Louis, USA). Samples with different moisture contents were generated by allowing the α-cellulose to equilibrate with different relative humidities for at least 2 weeks, using a Fisher scientific (Illkirch, France) climatic chamber.

Dilatometer

The experimental system used was a piston-type dilatometer. The principle of the PVT100 high-pressure dilatometer (Thermo, Karlsruhe) is shown in Fig. 1. The sample of mass m is placed in a cylindrical cell and a piston exerts a pressure on it. Since the cell diameter (d) is known, the specific volume change (ΔV) (Eq. 1) is obtained by measuring the change in length (Δl).

$$\Delta V = \frac{\Delta l \pi (\frac{d}{2})^2}{m} \tag{1}$$

The diameter of the cell was 7.77 mm, and the weight of the sample was about 0.7–1 g. The lower piston was fixed, but could be removed to extract the sample. The upper one was moved to exert pressure on the sample.
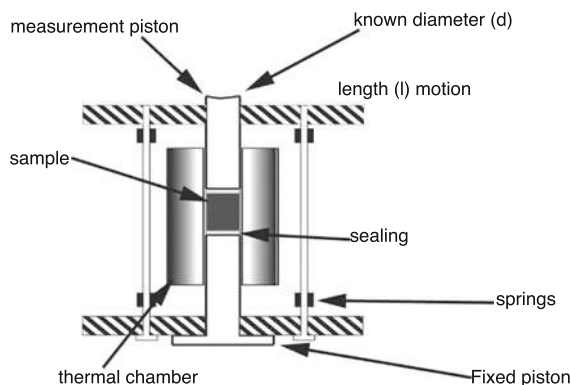
Fig. 1 The pressure dilatometer

In order to avoid leaks, the sample was placed between two polytetrafluoroethylene seals (PTFE), supporting high temperatures and pressures. And the first step was to calibrate the system under compression with the two seals only, to determine the seal thickness to be subtracted from each measurement. Measuring the displacement of the upper piston thus provided the length of the sample, and thanks to two springs, the pressure was applied from both ends. The sample was heated by an electric heater band and cooled with a system of cold-water cooled air. This temperature was measured by a thermocouple located near the edge of the sample.

Contrary to the normal protocol for synthetic polymers, dilatometric measurements were performed under isobaric heating mode to avoid cellulose degradation. Each measurement was made by raising the temperature from 25 to 180 °C at a rate of 5 °C min^{-1} under constant pressures ranging from 19.6 to 196 MPa.

Precompression

For the PVT100 system a precompression system—the pressure applied for 1 min on the sample before the measurement—had to be fixed. Its effect was then examined to obtain better reproducibility and industrial potential. Figure 2 shows the variation in PVT diagrams with changing precompression, and the good reproducibility with the two 60 MPa isobar curves. When precompression was lower than the applied pressure, there was a specific volume drop at the beginning of the diagram. This densification was not a thermal effect under compression and so was clearly

of no interest, and detrimental for the present study. Conversely, when the precompression was higher than the pressure subsequently applied, the measurement began with an expansion of the sample. Also from Fig. 2 it can be seen that the ratio $\frac{V_{initial}}{V_{min}}$ had a greater effect (stronger densification) when the precompression was equal to the applied pressure. In the light of these two points, it appeared that the best way to obtain reproducible PVT diagrams was to use the same pressure for the precompression and applied pressure ($P_0 = P$).

Temperature range

A large temperature range has been tested and it appeared that above 180 °C, α-cellulose was degraded. This phenomenon was visible on the sample after measurement (burning), and can be seen in Fig. 3, with an unusual increase in the specific volume for temperatures starting around 200 °C.

Concerning the initial temperature, 50 °C was not cold enough, and the volume change between 25 and 180 °C seemed an interesting range. Moreover, due to our dilatometer's technical limits, samples could not be cooled below room temperature, so the initial temperature was fixed at 25 °C.

Dynamic vapor sorption analyses

Water sorption isotherms were obtained using a dynamic vapor sorption (DVS) Advantage System from Surface Measurement Systems (Alperton, UK). This apparatus uses an ultra sensitive balance capable of measuring changes in sample mass as low as 0.1 µg. Samples were equilibrated at a constant temperature and different relative humidities. The changes in relative humidity were induced using mixtures of dry and moisture-saturated nitrogen flowing over the samples. The sample mass used was around 10 mg, and the programmed relative humidities were from 0 to 95 %, divided into 5 % increments (20 steps). The temperature was set at 25 °C and a sample was considered to be in equilibrium when changes in its mass were lower than $5 \times 10^{-3} \%$ min^{-1}. At the beginning of each measurement, samples were dried for 300 min under a stream of dry nitrogen (0 %RH) at 103 °C, to obtain the dry weight.

Fig. 2 Four PVT diagrams
showing precompression
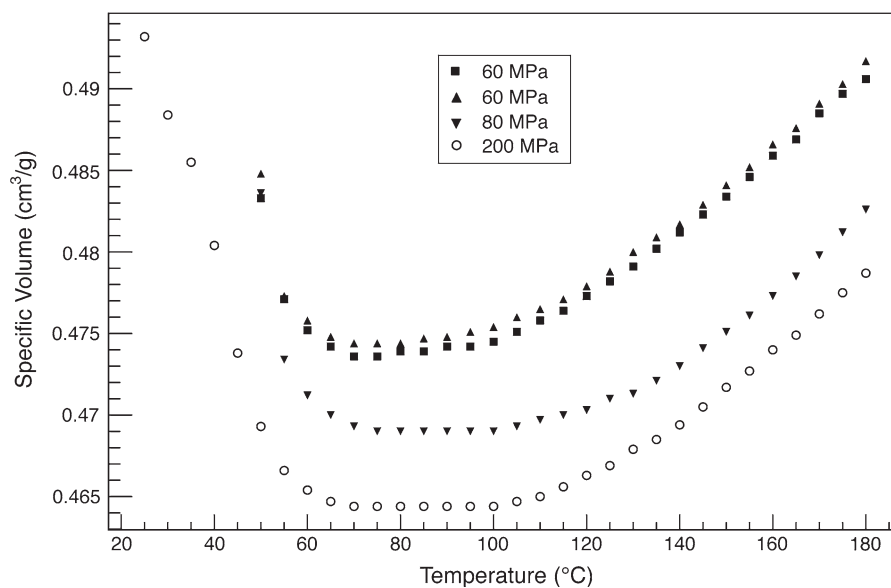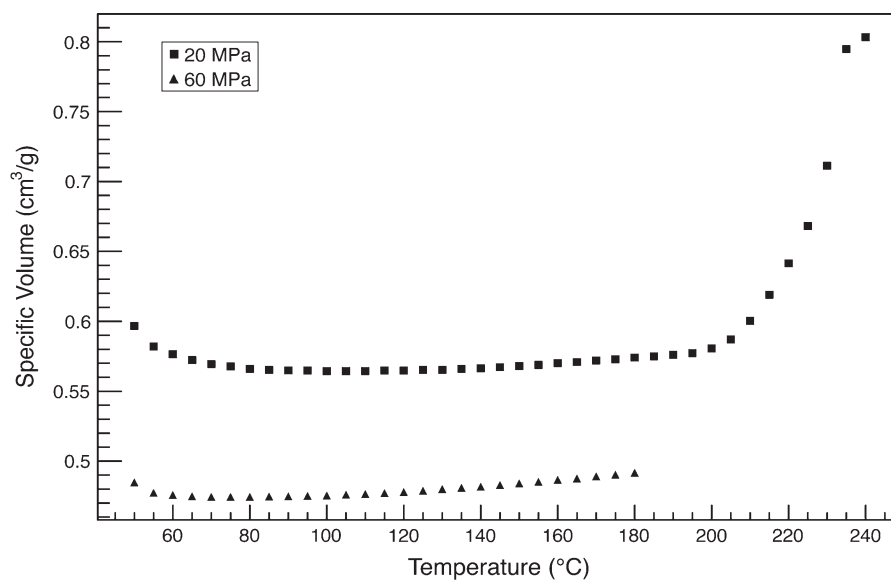(P_0) dependence,
measurement made using
196.1 MPa

Fig. 3 *blacktriangle* PVT
19.6 MPa [25–180] °C;
blacksquare PVT 19.6 MPa
[50–180] °C

Density determination

Specific gravity was measured with the Density Determination Kit from Sartorius AG (Goettingen, Germany). This device uses the Archimedes' principle for determining the density of a solid. A solid immersed in a liquid is buoyed up by a force equal to the weight of the liquid displaced by the volume of the solid:

$$\rho = \frac{W(a).[\rho_{fl} - 0.0012]}{0.99983[W(a) - W(fl)]} + \rho_a \qquad (2)$$

where ρ is the density of the solid, $W(a)$ the weight of the solid in air, $W(fl)$ the weight of the solid in liquid, ρ_a the density of air under standard conditions (0.0012g cm^{-2}) and ρ_{fl} the density of the liquid. In our measurements cyclohexane was used as immersion liquid at room temperature.

Theoretical considerations

The purpose of this article is to study the behavior of the specific volume of α-cellulose and to determine a mathematical expression to describe the PVT dependence. Many models have already been proposed to describe the dependence of melt volume on pressure and temperature of synthetic polymers. Real state equations give a very accurate description of liquid polymers (Dee and Walsh 1988).

There are few studies of natural model polymers, but Otaigbe and Jane (1997) for example, have studied the Pressure-Volume-Temperature relationship of Soy Protein Isolate/Starch Plastic and used the Tait equation to model the PVT diagrams.

Normally this equation is used for polymers (Simha et al. 1973) with a glass transition and a melting point. The model works very well for low and high temperatures, but for a range of intermediate temperature, transition states, modeling the PVT diagrams is impossible (Quach and Simha 1971). However, it should be very different for α-cellulose, a natural polymer without a melting point. The Tait equation (Eq. 3) is an empirical expression and thus composed of a set of parameters to be determined from the experimental data, and generally, some of these are derived from the PVT diagrams at atmospheric pressure. However, the PVT100 with a minimum 19.6 MPa applied, does not allow this range of pressures to be obtained, therefore we did not have direct access to these parameters. The constant C is a universal value for all hydrocarbon synthetic polymers (Rodgers 1993), independent of the temperature (Nanda and Simha 1964). V_t has been introduced to account for the volume decrease due to crystallization (Chang et al. 1996).

$$V(P,T) = V(0,T)\left(1 - Cln\left(1 + \frac{P}{B(T)}\right)\right) + V_t$$

$$V(0,T) = b_1 + b_2\bar{T}$$

$$B(T) = b_3 e^{-b_4\bar{T}}$$

$$\bar{T} = T - b_5 \tag{3}$$

Thus to model the PVT curves of α-cellulose the Tait equation must be modified (Eqs. 4 and 5) according to the occurrence of an inflection point using the set of parameters determined from all the PVT diagrams.

If $T < T_t$ we have:

$$V(T) = ((b_{1l} + b_{2l}(T - Tt))$$
$$\times \left(1 - C \times ln\left\{1 + \frac{P}{(b_{3l} \times e^{-b_{4l}(T-Tt)})}\right\}\right)$$
$$\times 1,000 \tag{4}$$

and if $T > T_t$ we have:

$$V(T) = (1 - ((b_{1h} + b_{2h}(T - Tt))$$
$$\times \left(1 - C \times ln\left\{1 + \frac{P}{(b_{3h} \times e^{-b_{4h}(T-Tt)})}\right\}\right)$$
$$\times 1,000) \tag{5}$$

Table 1 lists the parameters and the constants that are used in the Eqs. (4) and (5) and the concordances with the Tait equation (Eq. 3). The parameters underlined correspond to those normally derived from the experimental data, and the significance of temperature T_t will be covered in the next section. b_{1l} and b_{1h}, l and h corresponding respectively to low and high temperatures, are used for the continuity of the modeled diagrams at T_t temperature.

Table 1 Parameters of the Tait equation

$T < T_t$		$T > T_t$
	P	
	T	
	$C = 0.0894 \text{(constant)}$	
$\underline{b_{3l}}$		$\underline{b_{3h}}$
$\underline{b_{4l}}$		$\underline{b_{4h}}$
$\underline{b_{2l}}$		$\underline{b_{2h}}$
	$T_t(b_5)$	
b_{1l}		b_{1h}
$b_{1l} = \dfrac{(V(T_t))}{(1 - C \times ln(1 + \frac{P}{b_{3l}}))} \times 1000$		$b_{1h} = \dfrac{(V(T_t))}{(1 - C \times ln(1 + \frac{P}{b_{3h}}))} \times 1000$

To model the PVT diagrams, Xcode (developed by Apple) was used to edit the program, and ROOT (developed by the CERN) to make the simulations and the analyses.

Results and discussion

PVT diagrams

The PVT diagrams are shown on Fig. 4, and to avoid cluttering the data, only some graphs have been plotted. For each water content, nine pressures between 19.6 and 196 MPa were tested. It can be seen that the general specific volume behavior of α-cellulose was completely different to that of other biodegradable polymers (Sato et al. 2000).

Experimental results clearly showed the influence of both temperature and pressure on the densification of the sample. All isobar curves could be separated into several parts. The first corresponded to the increase in specific volume, i.e. α-cellulose thermal expansion. This was only present on the graph corresponding to the lowest pressure, the rise in pressure for the next isobar causing the replacement of this first step by the second. Here, a specific volume decrease was observed, the densification phase. In both phases there has to be a reorganization of matter. This second step was split into two distinct parts because of the presence of an inflection point defined as temperature T_t (Fig. 4).

Finally on the last part, the specific volume increased again, and this was the result of the expected thermal expansion following reorganization of the polymer, and the effect of the water vapor pressure. When the heated sorbed water vaporized, it exerted a counter pressure on the piston that was measured as an increase in the sample volume, as confirmed by subsequent analyses of dry samples (not included).

Water content effect

As already mentioned, water content is important for the PVT study of α-cellulose. Indeed the water adsorption isotherm (Fig. 5) illustrates its sensitivity to humidity. Therefore to study the effect of water content, α-cellulose was conditioned in different chambers at 25 °C, at three different relative humidities (45 %RH, 60 %RH and 75 %RH) before performing the PVT analyses. The corresponding water contents were calculated directly from the isotherm obtained by dynamic measurement on a sorption balance (DVS).

The PVT measurements have been made on α-cellulose samples with different moisture contents and are shown in Fig. 6.

The samples conditioned at 45 % (point A) and 60 % (B) relative humidity, Fig. 5, behaved identically when they were exposed to the same temperature. Conversely, α-cellulose conditioned at 75 % (C) relative humidity, showed an obviously different trend. On the normalized PVT diagrams, Fig. 6, this surprising behavior was noticeable for each of the three pressures.

On the water adsorption isotherm graph (Fig. 5), points A and B are not on the same parts of the curve as the point C. Initially, the water was in capillary form,

Fig. 4 Isobar curves of α-cellulose preconditioned at four different pressures (P) at 60 %RH. (*1*) α-cellulose thermal dilatation, (*2*) first densification phase, (*3*) second densification phase, (*4*) specific volume increase. For each PVT curve there is an inflection point corresponding to temperature T_t (*cross*)
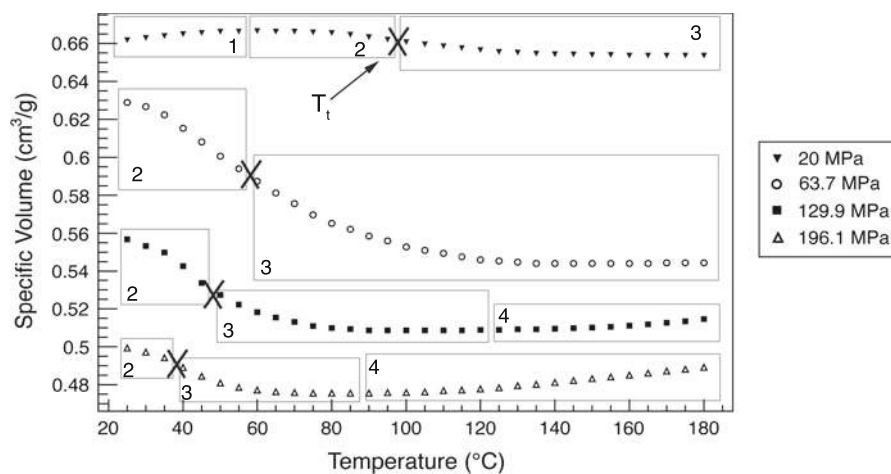
Fig. 5 Water sorption isotherm of α-cellulose obtained with DVS. Points *A*, *B* and *C* correspond to the different water contents used. *WC* water content, *PP* partial pressure of water
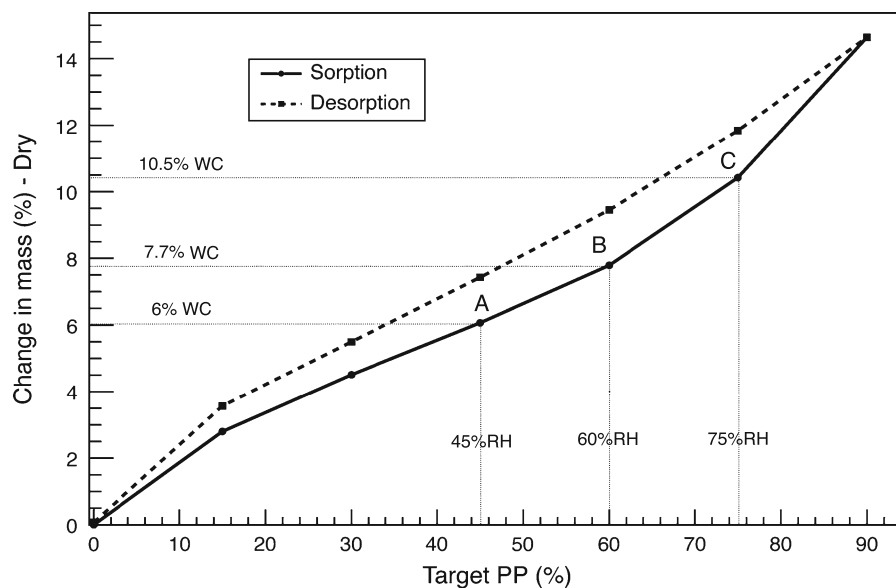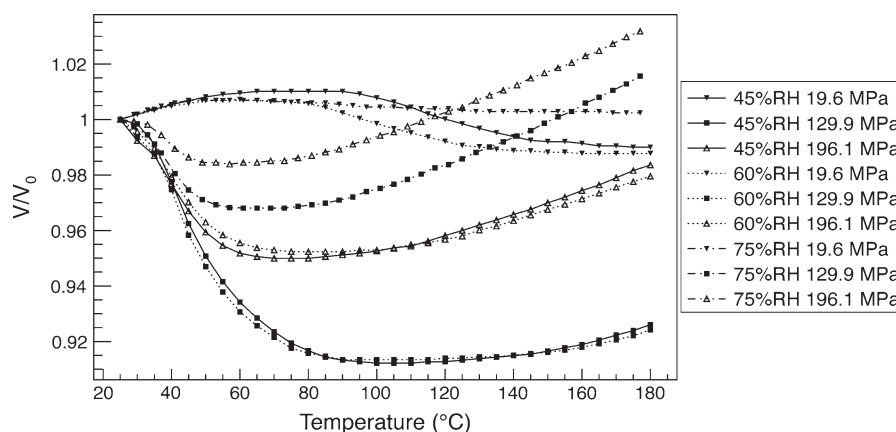

Fig. 6 Normalized PVT diagrams of α-cellulose conditioned at various moisture contents

meaning that it was in an intermediary state between liquid and solid. Therefore the samples' water molecules were very hard to remove (H-Bonding). At point C, part of the water was in the liquid state in the α-cellulose pores and therefore available to escape and to exert a counter pressure when vaporized. And therefore this explains the stronger increase in specific volume for the sample at 10.5 % of moisture content.

Thermal effects

The effects of temperature at different pressures are shown on Fig. 7. The density measured (Eq. 6) was obtained using the final specific volume measured with the dilatometer.

$$d_r = \frac{1}{V_f} \qquad (6)$$

Actual or 'real' density was measured a few days after the PVT experiment, from the cylindrical samples kept under hermetic conditions. Figure 8 shows that the difference between these two densities increases with the pressure. However, because of the scale, the very small increase in real density is not visible on the graph. The relative density (d_r) increased faster and more than the real density.

This difference between the two measurements is thought to come from an elastic relaxation of the sample and this elastic energy increases with pressure (Akande et al. 1997).
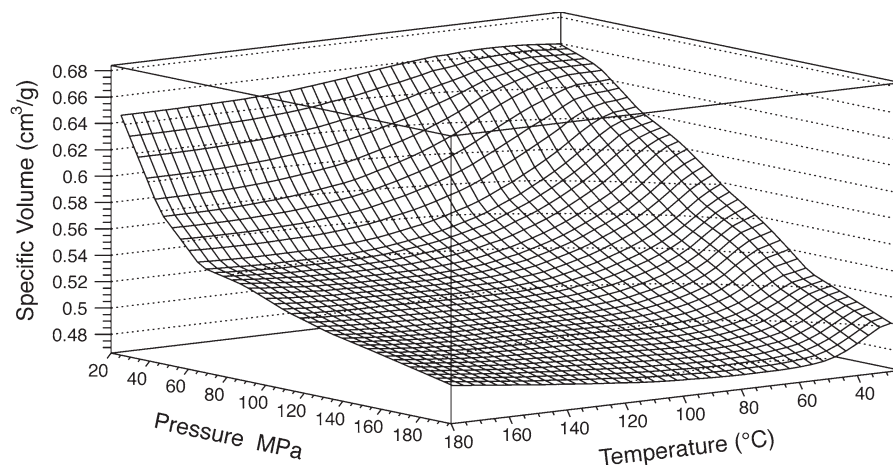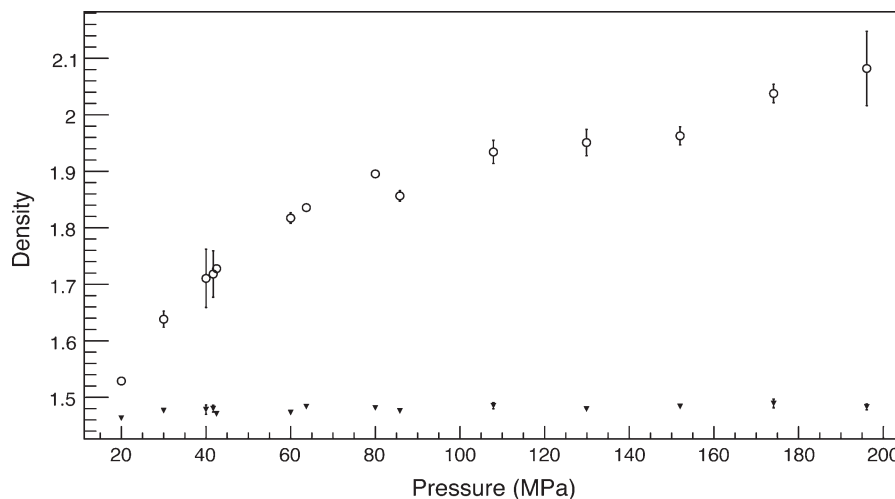
Fig. 7 3 Dimensional PVT diagram of α-cellulose

Fig. 8 Densities of α-cellulose conditioned at 60 % relative humidity; *circle* relative density; *inverted triangle* real density

This variation in the initial volume poses problems for modeling or studying PVT graphs. Because although, in itself, the specific volume's numerical value is not without interest, it is its variation compared to the initial volume that is important. Thus it was better to work with normalized $\left(\frac{V}{V_0}\right)$ isobar curves (Fig. 6).

Different samples did not show the same behavior when heated. The greatest variation in specific volume occurred for α-cellulose compressed at an intermediate pressure and conditioned at 45 or 60 % relative humidity.

Figure 7 could invite confusion concerning the pressure effect. As explained in a previous section, a precompression was applied before measurement. Therefore initially, samples were not in the same state of compaction, and this variation in volume according to pressure was not directly represented on classic PVT diagrams. Unfortunately with PVT 100, as already mentioned, precompression is always required. Nonetheless, the effect of temperature at different pressures had to be evaluated with caution. Normally, the greater the pressure on the sample, the weaker the densification due to temperature, and this was true for the graphs at higher pressure, but at 19.6 MPa the variation in volume was significantly low. This phenomenon could be explained by the ability of the solid's molecules to vibrate with the input of thermal energy, the high pressure forming a compact agglomerate of grains, thus limiting their motion.

PVT diagrams model

Assuming that a transition state of α-cellulose is unknown, the Tait equation distinguishes two parts of

Fig. 9 Transition temperature, T_t, plotted for three water contents of α-cellulose
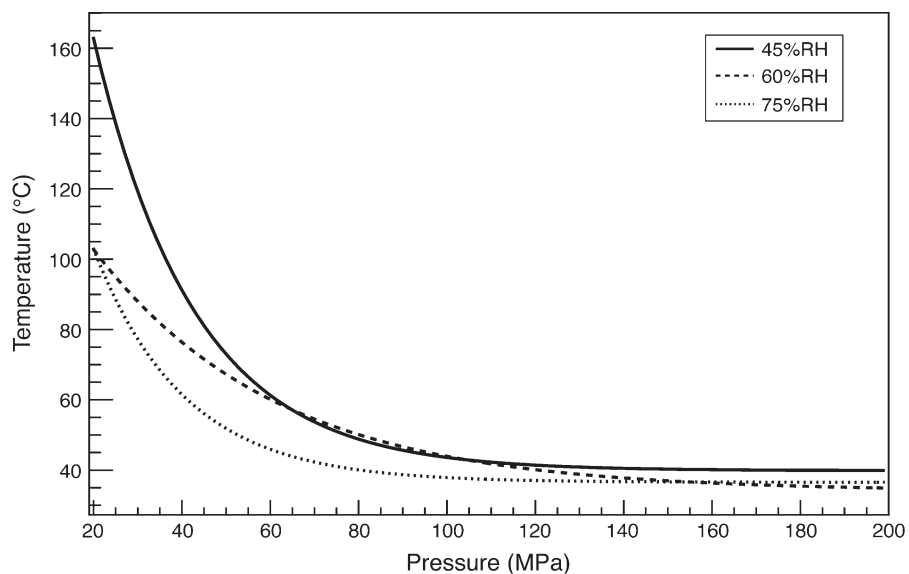
the graphs separated by an inflection point (Table 1; Eq. 4; Fig. 4). The T_t temperature was determined by taking the temperature corresponding to the minimum of the derivative for each diagram. T_t has then been determined and plotted for all PVT diagrams for each humidity level (Fig. 9).

T_t temperature decreased exponentially with the pressure and flattened off at approximately 130 MPa. This phenomenon confirmed the existence of a pressure limit, beyond which there was no more effect. Moisture content influenced the transition temperature at low pressure more than the overall

trend. Contrary to the general PVT behavior, for 45 %RH and 60 %RH (Fig. 6), T_t curves were different.

The results of the modeling for some PVT diagrams are shown on Fig. 10. The solid line represents the theory on which experimental points are superimposed. The Tait equation model was unsatisfactory at high pressures after T_t.

The aim of this modeling was to be able to predict the behavior of the specific volume of a chosen material as a function of the temperature and for a defined pressure. The faithful reproduction of the

Fig. 10 PVT modeling of α-cellulose conditioned at 60 % relative humidity
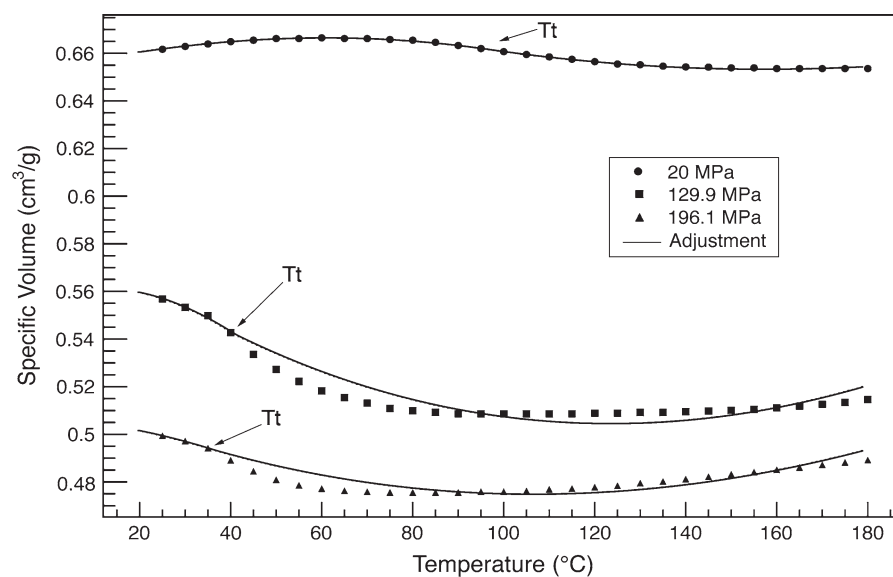
experimental data was one condition for the model's applicability. The other was the capacity for each set of parameters deduced to be correlated between themselves. The final results of these computations has been evaluated by plotting parameters varying with pressure and water content. From the standard deviations, it was seen that the parameters did not follow any obvious physical law that would allow the Tait equation to be used for α-cellulose.

Discussion

The important point concerns the T_t temperature. In the previous sections, the presence of an inflection point during the densification processes of α-cellulose has been demonstrated. The existence of a change in the structure of the matter was undeniable.

With differential scanning calorimetry (DSC) measurements, no rise in heat capacity has been found at the corresponding T_t temperature. Moreover, the inflection point corresponded to a decrease in volume, which is clearly opposed to the behavior of a polymer with a glass transition.

No crystallization temperature has ever been observed for cellulose, but Vaca-Medina et al. (Accepted) showed an increase in the crystallinity index of α-cellulose during compression at higher temperatures. Moreover, Pintiaux et al. (2013) have tested the mechanical properties of the thermo-compressed samples, and demonstrated an increase in these properties with temperature. Therefore during thermo-compression, crystallization must be associated with another phenomenon responsible for consolidating the powder.

The behavior of the sample with increasing temperature seemed similar to phenomena observed during sintering (Coble 1958), a process usually used for ceramics at very high temperatures (hundreds of degrees). The decrease in specific volume can be explained by the interpenetration of the particles and the elimination of the different pores. The pressure effect is considered as a parameter that will accelerate the process and reduce the sintering temperature. However, the decrease in the specific surface during the process is the most obvious way to identify the sintering phenomenon. This decrease in surface free energy of α-cellulose during the process has been measured from DVS (Vaca-Medina et al. Accepted)

data and calculated from water sorption isotherms using the BET model. This demonstrated that there was a specific surface decrease during the compression and thus the process responsible for the matter densification of α-cellulose could be sintering. α-cellulose particles may interpenetrate in their amorphous phase and the pressure would then induce the crystallization of some part of this phase. This phenomenon has never been studied on natural polymers and would obviously need more work to understand the mechanism and evaluate the applications of such a process. A change of the crystalline structure could also occur. Simon et al. (1988) have shown that cellulose has a few kind of unit cell with similar energy but with rather different dimensions and inner structure. So, under high mechanical conditions, the crystalline packing within the fiber could change. Additional work on the crystalline structure of the samples is actually pending in our group to understand more about the changes involved in cellulose inner structure upon compression.

Conclusion

The equipment used and the different choices for the experimental protocol have been described. These choices have enabled repeatable measurements to be made, and have been evaluated to best serve any future industrial compression molding process.

The thermal behavior of α-cellulose under pressure (19.6–196 MPa) has been measured with a dilatometer, and unconventional PVT behavior found, with the specific volume of α-cellulose decreasing with increasing temperature. Some samples with different water content have been studied, and it appeared that for α-cellulose conditioned at 75 % relative humidity, the PVT diagrams were significantly different. Densification was lower and the PVT curve showed a faster increase in volume, because of the vapor pressure. Moreover, after compression, an elastic relaxation of the sample has been shown.

During the decrease in the specific volume, the existence of an inflection point T_t temperature has been shown. The behavior with varying pressure and moisture content at this temperature has been studied. T_t decreased exponentially with the pressure and it became constant around 130 MPa. Furthermore the variation of the inflection point changed slower with increasing water content.

Finally, the Tait equation has been used to model the PVT diagrams. For low pressures good correlation with the experimental data has been obtained. However, considering the differences at high pressures after the T_t temperature on the curve, and the results obtained for the six parameters, the Tait equation cannot be validated for α-cellulose behavior modeling. Further work, will study the sintering process for the densification phenomena of α-cellulose.

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