

Isophase Transitions of Cellulose – A Short Review

By Michael Ioelovich*

Cellulose has a complicated supramolecular structure consisting of nanofibrils, which are built of ordered crystallites and low ordered noncrystalline domains. In this critical review, isophase temperature transitions in noncrystalline domains of cellulose were described and discussed. It has been shown that due to structural heterogeneity the noncrystalline domains have three isophase temperature transitions, where the α_1 and α_2 transitions are caused by the occurrence of segmental mobility in dense mesomorphous and medium packed amorphous clusters, respectively; whereas the β transition is related to the mobility of small segments in loose packed amorphous clusters, which probably are located on the outer surface of nanofibrils. Under the action of water and other plasticizers all three isophase transitions are shifted to lower temperatures.

Keywords: Cellulose, Noncrystalline domains, Relaxation transitions, Mechanism.

Introduction

As is known, the properties of polymer materials are changed gradually in a certain temperature range until achieving the critical temperature or temperatures, at which an abrupt alteration of various characteristics is observed. This phenomenon can signify the so called isophase transition connected with structural reorganization within the same, e.g. amorphous, phase (Boyer, 1967; Shen et al., 1970). Typical examples of isophase transitions are glass or α relaxation transitions caused by a development of segmental mobility, and secondary or β and γ relaxation transitions, which are connected with change of mobility of some units or groups in an amorphous phase. The isophase transitions appear as inflection points on temperature dependences of volume, deformation, modulus and other mechanical characteristics; jumps of thermal expansion coefficient and heat capacity; extremum of dynamic properties; but these transitions do not change the thermodynamic characteristics of polymers.

Linear amorphous polymers with a simple structure typically have one glass temperature (T_g). For example, natural rubber transits from glass into viscoelastic state at 200 K. However, polymers with complicated structure can have multiple isophase transitions. One such polymer, polyethylene, has three glass transitions: 153 K for completely amorphous domains, 240 K for mesomorphous domains on, and at 200 K for intermediate amorphous domains (Bartenev et al., 1981; Fakirov et al., 2000).

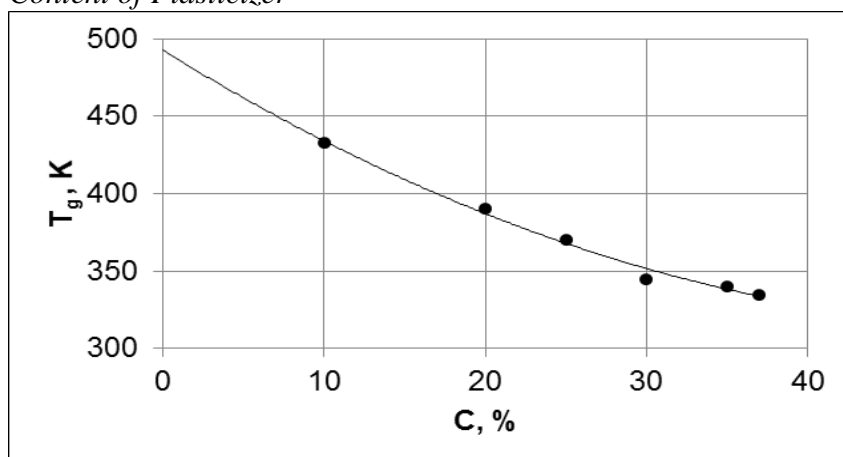
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Cellulose is the most abundant natural polysaccharide, which can be used as a renewable source for the production of diverse biomaterials, biochemicals and biofuels (Klemm et al., 2005). Since the processing and use of cellulose can be carried out over a wide temperature range, it is important to study the isophase transitions of this polymer. Cellulose is a semicrystalline polysaccharide composed of glucopyranose units (GPU) linked by β -1,4-glycosidic bonds. The linear macromolecules of cellulose form strong crystallites and weak non-crystalline (amorphous) domains by means of hydrogen bonds (Ioelovich, 2014). The relaxation state of strong cellulose crystallites does not change up to the melting point, which is above temperature of thermal decomposition (Ioelovich, 2016). On the contrary, the weak non-crystalline domains show isophase transitions of various types in a wide temperature range below temperature of thermal decomposition (Kaimin et al., 1979). Cellulose can be of various modifications and crystallinities, including natural, mercerized, regenerated, microcrystalline, nanocrystalline, amorphized, etc. Therefore, such a complex polymer as cellulose has multiple isophase transitions connected with abrupt changes in the relaxation state of non-crystalline domains, which are discussed in this article.

Isophase Transitions of Cellulose

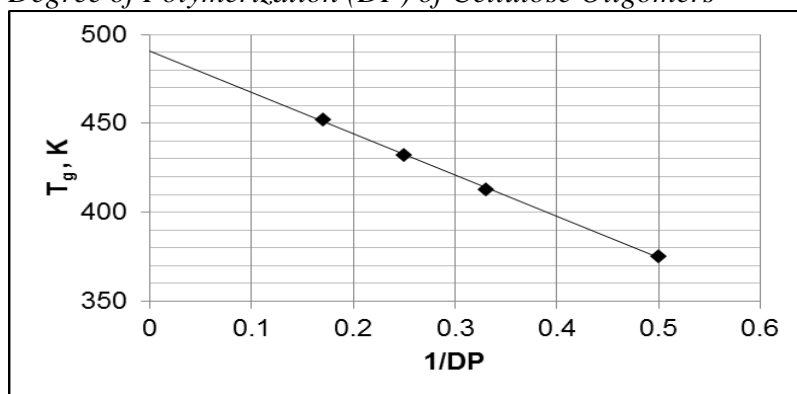
Currently it is supposed that primary α_1 glass transition of cellulose is located at high-temperatures, above 473 K (T_{g1}) (Back et al., 1969; Kaimin et al., 1979). However, a direct measurement of the exact value of T_{g1} is difficult due to the beginning of thermal decomposition of cellulose. To evaluate T_{g1} , indirect methods were used. One such method was the determination of glass temperatures (T_g) for plasticized cellulose samples at temperatures below temperature of thermal decomposition; the obtained glass temperatures were extrapolated to the value corresponding to zero content of plasticizer (Ioelovich et al., 1979; Ioelovich, 2016; Kargin et al., 1960), as it is shown in Figure 1.

Figure 1. Illustration of Dependence of Glass Transition Temperature on Content of Plasticizer



Another indirect method was the determination of glass temperatures (T_g) of oligosaccharides with various degree of polymerization (DP) (Alftha et al., 1973) with the subsequent extrapolation of linear dependence $T_g = (DP)^{-1}$ to zero value of DP^{-1} (Figure 2).

Figure 2. Illustration of Dependence of Glass Transition Temperature (T_g) on Degree of Polymerization (DP) of Cellulose Oligomers



The third method is a calculation based on the ratio: $T_g/T_m = 0.66$ (Boyer, 1967; Van Krevelen, 1972); where the melting point, $T_m \approx 720-770$ K, was indirectly estimated from an experiment of flash fusion of cellulose crystallites by a laser beam (Nordin et al., 1973). As a result of indirect evaluations, the following primary glass temperature of cellulose was obtained: $T_{g1} \approx 490-500$ K (Table 1). The apparent activation energy of this transition was above 200 kJ/mole (Manabe et al., 1986), which is typical for glass transition.

Table 1. Isophase Relaxation Transitions of Cellulose

*T _t , K	Interpretation	Methods	References
490-500	Primary α_1 glass transition	Indirect methods	Alftha et al., 1973; Ioelovich et al., 1979; Kargin et al., 1960.
390-410	Secondary α_2 glass transition	Dynamic methods, dilatometry, thermomechanics, calorimetry	Back et al., 1969; Fainberg et al., 1967; Kaimin et al., 1973; Klason et al., 1976; Manabe et al., 1986.
280-300	β transition of small segments	Dilatometry, thermomechanics, dynamic dielectric method, DSC, EPR	Aziz et al., 1973; Kaimin et al., 1973; Klason et al., 1976; Mochalov et al., 1982; Plotnikov et al., 1977; Ramiah et al., 1965; Roig et al., 2011.
180-200	γ transition of hydroxymethyl groups	Dynamic dielectric methods	Borisova et al., 1979; Michailov et al., 1967; Roig et al., 2011; Zelenev et al., 1972.

*T_t is the temperature of isophase transition.

Below T_{g1} , at the temperatures 390-410 K, the α_2 -relaxation transition was discovered by various experimental methods (Table 1): sharp decrease of dynamic modulus (Back et al., 1969), peak of mechanical absorption (Manabe et al., 1986), sharp increase of deformation (Kaimin et al., 1973), jumps of heat capacity (Fainberg et al., 1967) and thermal expansion coefficient (Kaimin et al., 1973; Klason et al., 1976) (see for example Figures 3 and 4). The apparent activation energy of the α_2 -transition was above 100 kJ/mole, which is higher than for the β transition. Therefore, most researchers attribute this transition to a secondary glass transition (Fainberg et al., 1967; Kaimin et al., 1973; Kaimin et al., 1979; Klason et al., 1976).

The third relaxation transition was detected at the temperatures 280-300 K by methods of thermomechanics (Kaimin et al., 1973), calorimetry (Mochalov et al., 1982), electron paramagnetic resonance (Plotnikov et al., 1977), dynamic dielectric method (Roig et al., 201), linear and volume dilatometry (Aziz et al., 1973; Kaimin et al., 1973; Klason et al., 1976; Ramiah et al., 1965) (see for example Figures 3, and 4). However, changes of various properties at a transition temperature were relatively small. The energy of activation of this transition was about 80 kJ/mole (Borisova et al., 1979), which is typical for β transition.

Figure 3. Linear Dilatometry of Dry Film of Regenerated Cellulose

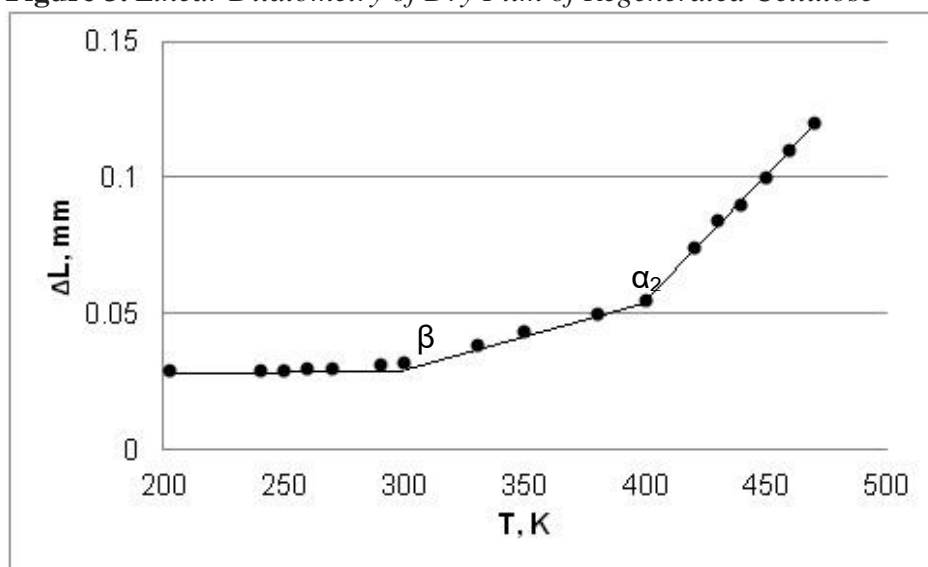
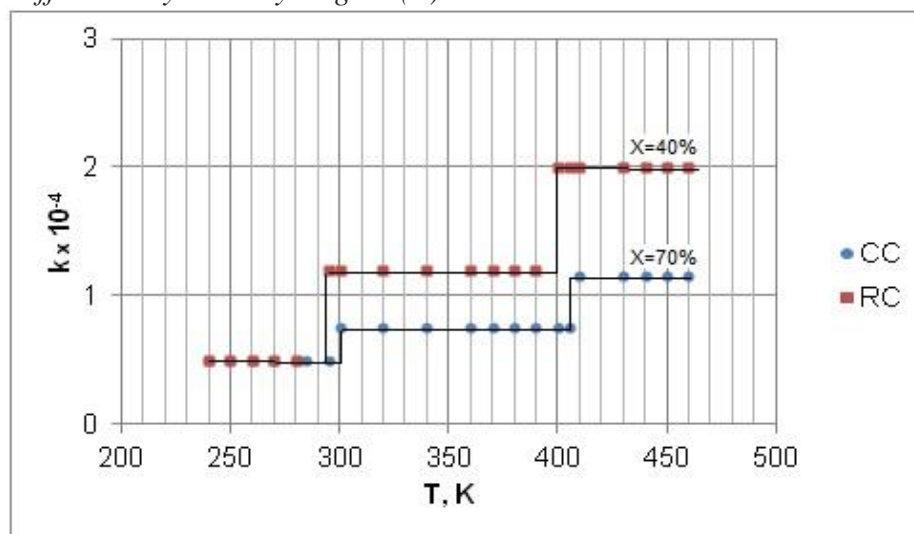


Figure 4. Temperature Dependence of Volume Expansion Coefficient for Dry Samples of Cotton Cellulose (CC) and Regenerated Cellulose (RC) with Different Crystallinity Degree (X)



The fourth relaxation transition was found at 180-200 K using a dynamic method of dielectric absorption at low temperatures (Borisova et al., 1979; Michailov et al., 1967; Roig et al., 2011; Zelenev et al., 1972). It has been proven that it is a γ transition with an activation energy of 40-50 kJ/mole, which is caused by the mobility of hydroxymethyl groups in non-crystalline domains.

With decreasing in the crystallinity degree, the intensity of α , β and γ transitions increases; thus all these transitions are related to non-crystalline domains of cellulose.

In contrast to elastomers, cellulose materials even above glass transition temperatures show a high modulus (1-3 GPa), low deformation (a few percents), as well as small changes of some other properties at transition temperatures. Therefore, to discover isophase temperature transitions in this polymer, a special high-precise research method should be used.

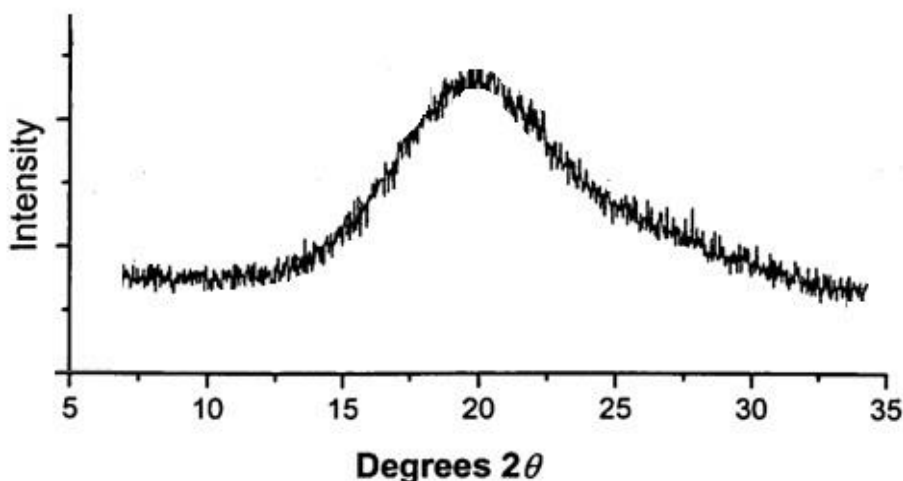
Structural Organization of Noncrystalline Domains

To explain multiple isophase transitions of cellulose the structural organization of non-crystalline domains (NCD) of this polymer should be studied in detail. However, these investigations are hampered by the presence of highly ordered crystalline domains, and by the lack of reliable methods for the study of noncrystalline components. For instance, various NMR methods gave a little information about the structure of NCD (Wickholm et al., 2001).

To study the structure of NCD by a method of X-ray diffraction, samples of amorphous cellulose are required. These samples can be prepared, for example, by ball-milling of dry cellulose or saponification of cellulose acetate in non-water alkali solutions (Paes et al., 2010; Togawa et al., 2007). The

typical X-ray scattering of amorphous cellulose samples has a wide peak with its maximum at $2\theta \approx 20^\circ$ (Figure 5).

Figure 5. X-ray Scattering of Amorphized Cellulose



Using the modified Scherer's equation for amorphous polymers,

$$D_{ms} = K\lambda / (B \cos \theta_0) \quad (1)$$

an average size of ordered mesomorphous clusters of NCD was calculated $D_{ms} = 1.9$ nm (Ioelovich et al., 2002); whereas the average Bragg's distance between planes in such mesomorphous cluster was $d_{ms} = 0.45$ nm:

$$d_{ms} = \lambda / (2 \sin \theta_0) \quad (2)$$

where $\lambda = 0.15418$ nm; B is corrected integral width of amorphous scattering in radians; K equals 1.8 and is the shape factor; θ_0 is the diffraction angle corresponding to maximum of amorphous scattering.

Further, the function of radial distribution of electron density, F , was also calculated for precision of the cluster structure:

where $i(s)$ is the corrected reduced intensity; $s = (4\pi/\lambda) \sin \theta$.

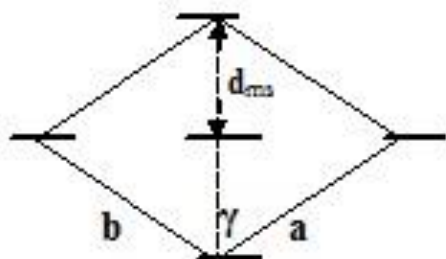
$$F = 2r/\pi \int si(s) \sin(rs) ds \quad (3)$$

The F -function has five maximums of electron density at distances r of 0.1; 0.45; 0.9; 1.4 and 1.9 nm (Ioelovich et al., 2002). The first maximum of F -distribution at 0.1 nm is intramolecular and relates to superposition of lengths between atoms in GPU. Other maximums of electron density are intermolecular and relate to average distance $d_{ms} = 0.45$ nm between layers in the mesomorphous cluster, while the third and fourth maximums – to the same distance d_{ms} increased two and three times. The radius of electron density at 1.9 nm is correlated with an average size of the cluster D_{ms} . As is follows from calculations, the cluster consists of about five GPUs. These clusters serve as

centers of growth of crystallites at the recrystallization process of amorphized cellulose (Ioelovich et al., 1982; Ioelovich, 2016a; Paes et al., 2010).

As a result of investigations, a model of mesomorphous cluster was proposed (Ioelovich et al., 2002; Ioelovich, 2014). This cluster has a unit cell with parameters a and b of about 0.9 nm, $c = 1.034$ nm and γ -angle about 120° (Figure 6).

Figure 6. Projection of Mesomorphous Unit Cell of the Clusters



Since only one distance between the layers in the cluster is nearly constant: $d_{ms} = 0.45$ nm, one maximum at $2\theta \approx 20^\circ$ appears on the X-ray diffractogram of amorphous cellulose. The calculated specific gravity of the mesomorphous cluster is 1.48-1.50 g/cm³, and the average specific gravity of NCD or the amorphous cellulose is 1.45 g/cm³ (Table 2).

Information about hydrogen bonds in NCD can be obtained using the method of FTIR spectroscopy in combination with deuteration. It was found that after deuteration of cellulose, stretching vibrations of OD-groups in NCD appeared in the range 2300-2680 cm⁻¹ with its maximum at 2500 cm⁻¹. The energy of H-bonds can be calculated from OD-frequency by the equation (Zhbakov et al., 1983):

$$E_H = E_o + K \sqrt{\Delta\nu} \quad (4)$$

where $E_o \approx 8$ kJ/mole is the minimum base energy; $K = 0.81$.

As a result it was discovered that the energy of H-bonds in NCD varies from 8 to 25 kJ/mole (Table 2).

Table 2. Structural Characteristics of Non-crystalline Domains of Cellulose*

Cluster	WP	d , g/cm ³	V , cm ³ /mole	E_H , kJ/mole	Transitions
DMC	0.6	1.48-1.50	108-110	23-25	α_1 glass transition
MAC	0.3	1.41-1.43	113-115	16-18	α_2 glass transition
LAC	0.1	1.29-1.31	124-126	8-10	β transition
Bulk NCD	1	1.45	112	20	α_1 , α_2 and β

*WP is estimated weight part of a cluster; d is specific gravity; V is molar volume

Thus, the detailed studies showed that NCDs of cellulose have heterogeneous structural organization, which consists of dense mesomorphous clusters (DMC), medium packed amorphous clusters (MAC) and loose packed

amorphous clusters (LAC). The consequence of structural heterogeneity of the NCD of cellulose is the presence of three isophase transitions, where the α_1 and α_2 transitions are caused by the occurrence of segmental mobility in dense mesomorphous and medium packed amorphous clusters, respectively; whereas the β transition is related to the mobility of GPUs or small segments in loose packed amorphous clusters, which probably are located on the outer surface of nanofibrils (Ioelovich, 2014).

Effect of Plasticizers on Isophase Transitions of Cellulose

Plasticization of cellulose causes a decrease of the temperatures of α_1 , α_2 and β transitions (Kaimin et al., 1979). The most widespread and active plasticizer of cellulose is water. Therefore, it is advisable to test the effect of this plasticizer on the relaxation transitions in NCD of cellulose. Unfortunately, water is an easily volatile substance, so its plasticizing effect can be studied only at moderate and low temperatures. As a result, a lowering of the β transition temperature under the effect of water was found (Kaimin et al., 1973; Kaimin et al., 1979; Montes et al., 1997; Stratton, 1973). The activation energy of the β relaxation involves an entropy contribution that varies with the water content (Stratton, 1973). However, the effect of water on temperatures of α_1 and α_2 transitions can be detected only at a high content of the plasticizer close to saturation point (Ioelovich et al., 1979).

Main investigations were devoted to the influence of water on the glass transition temperature of cellulose. It has been shown that at high relative humidity from 80 to 100% the temperature of glass transition (T_g) for moist cellulose is located below room temperature (Ioelovich, 2014; Ioelovich, 2016; Szczesniak et al., 2008). To determine the theoretical T_g of the cellulose-water system in the wide range of water content, several calculation methods were proposed. For this purpose, Salmen et al., 1977 used Kaelbe's equation (Kaelbe, 1971):

$$T_g = [T_{g2} X_2 + (h_1/h_2) T_{g1} X_1] / [X_2 + (h_1/h_1) X_1] \quad (5)$$

where T_{g1} and T_{g2} are glass transition temperatures of water and amorphous polymer; X_1 and X_2 are mole fraction of water and polymer; while h_1 and h_2 are constants of water and polymer, respectively.

Paes with co-authors (Paes et al., 2010) succeeded to obtain the T_g of amorphous cellulose (AC) with a certain moisture content, and calculate the dependence of T_g on moisture content by Couchman's equation (Couchman et al., 1978):

$$T_g = (W_1 \Delta C_1 T_{g1} + W_2 \Delta C_2 T_{g2}) / (W_1 \Delta C_1 + W_2 \Delta C_2) \quad (6)$$

where T_{g1} and T_{g2} are glass transition temperatures of water and amorphous cellulose (AC); W_1 and W_2 are weight fractions of water and AC; ΔC_1 and ΔC_2 are change in heat capacity of water at T_{g1} and AC at T_{g2} , respectively.

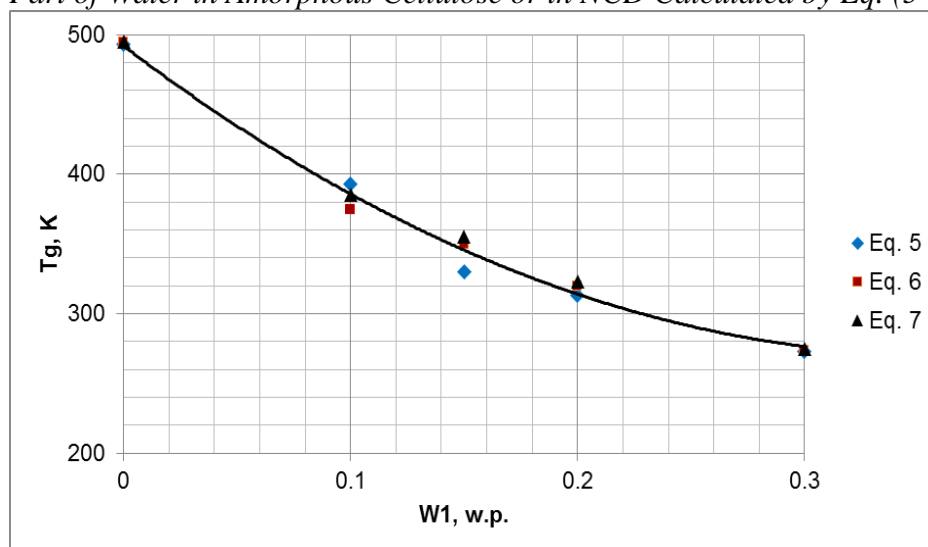
In our investigations, we used the Fox equation (Fox, 1956):

$$T_g^{-1} = W_1 T_{g1}^{-1} + W_2 T_{g2}^{-1} \quad (7)$$

where T_{g1} and T_{g2} are glass transitions temperatures of water and amorphous cellulose (AC); W_1 and W_2 are weight fractions of water and AC, respectively.

The results showed that calculations by means of all three equations (5-7) gave the equal values of theoretical glass transition temperature for wet amorphous cellulose, assuming that the glass transition temperature of dry polymer is 493 K and for the water is 136 K (Figure 7).

Figure 7. Theoretical Dependence of Glass Transition Temperature on Weight Part of Water in Amorphous Cellulose or in NCD Calculated by Eq. (5-7)



A serious problem arises regarding the extrapolation of the experimental values of T_g for the wet samples to the value corresponding to dry cellulose. In Figure 8, we tried to reproduce the experimental values of T_g obtained for wet cellulose samples in some papers (Batzer et al., 1981; Salmen et al., 1977; Szczesniak et al., 2008; Ogiwara et al., 1970). As can be seen from Figure 8, all the experimental T_g are obtained in the temperature range -50 to 80°C (223 - 353 K), i.e. far off 220 - 230°C (493 - 503 K), attributed to the temperature of primary α_1 glass transition of dry cellulose.

To compare the results of various wet cellulose samples obtained in the papers (Batzer et al., 1981; Salmen et al., 1977; Szczesniak et al., 2008; Ogiwara et al., 1970) the moisture content (W_{NCD}) in non-crystalline domains (NCD) of cellulose was calculated (Ioelovich 2016 c); then $T_{g,c}$ (K) of dry cellulose was calculated from the equation:

$$T_{g,c}^{-1} = [T_{g,s} (1 - W_{\text{NCD}})]^{-1} - [T_{g,w} (1 - W_{\text{NCD}}) / (W_{\text{NCD}})]^{-1} \quad (8)$$

where $T_{g,s}$ is experimental glass transition temperature of wet sample; $T_{g,w} = 136$ K is the glass transitions temperature of water; W_{NCD} is the weight fraction of water in NCD.

The calculations showed that the real $T_{g,c}$ of dry cellulose is about 408 K, i.e. it is the temperature of secondary α_2 glass transition of dry cellulose (Table 3).

Figure 8. Experimental Values of T_g of Wet Cellulose Samples with Different Crystallinity Indexes (CrI)

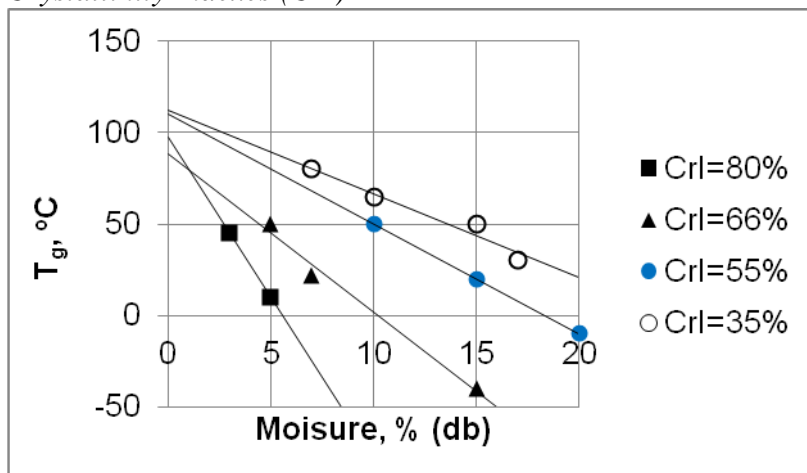


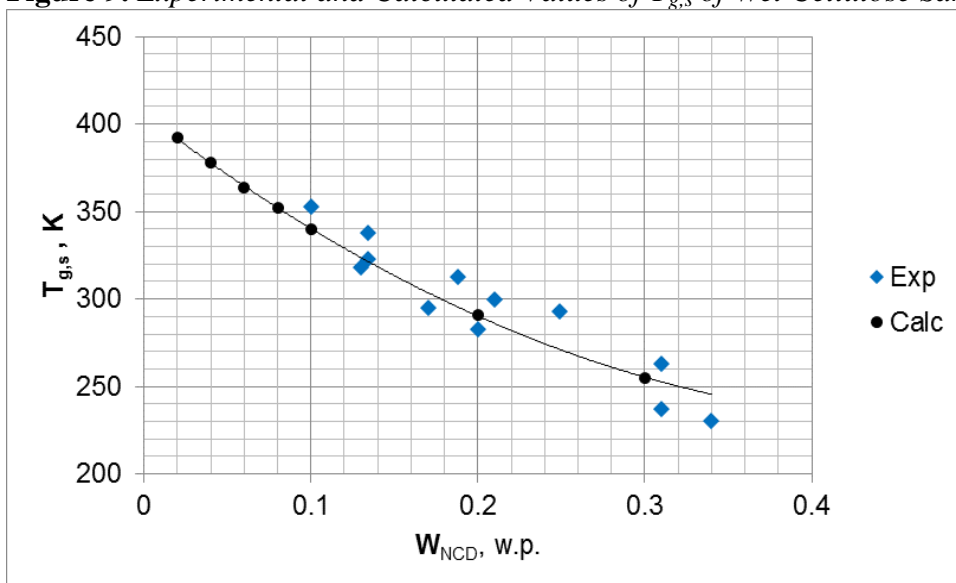
Table 3. Calculated Glass Transition Temperature ($T_{g,c}$) of Dry Cellulose

W_{NCD} , w.p.	Exp. $T_{g,s}$, K	Calc. $T_{g,c}$, K
0.1	345	416
0.2	300	420
0.3	255	408
0.35	235	386
		Average: 408

Note: Exp. $T_{g,s}$ is experimentally obtained glass temperatures of wet samples (Batzer et al., 1981; Salmen et al., 1977; Szczesniak et al., 2008; Ogiwara et al., 1970); Calc. $T_{g,c}$ is calculated glass temperature of dry cellulose.

Using this result, we performed also the reverse calculation $T_{g,s} = f(W_{NCD})$, shown in Figure 9.

Figure 9. Experimental and Calculated Values of $T_{g,s}$ of Wet Cellulose Samples

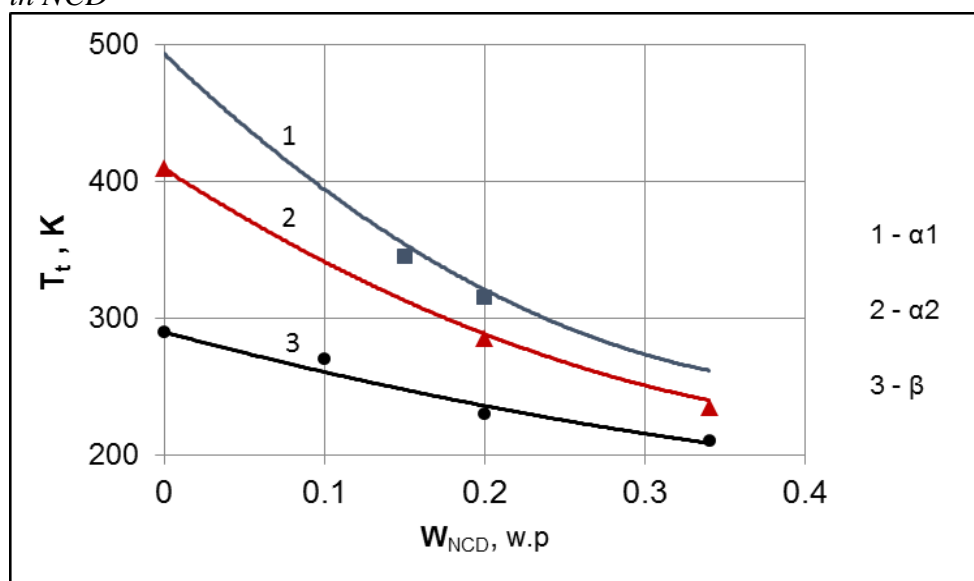


As it follows from Figure 9, in fact the experimental data presented in the papers (Batzer et al., 1981; Salmen et al., 1977; Szczesniak et al., 2008; Ogiwara et al., 1970) describes the dependence of α_2 glass transition temperature on the water content, i.e. $T_{g,\alpha_2} = f(W)$, instead of $T_{g,\alpha_1} = f(W)$.

Additional difficulties are connected with crystallization of the amorphous cellulose under the action of water, or water and temperature (Ioelovich et al., 1982; Ioelovich, 2016 b; Paes et al., 2010), which distorts the dependence of glass temperature on the water content (W_1). Furthermore, even for the non-crystallizable semicrystalline cellulose the dependence $T_g = f(W_1)$ cannot be obtained at temperatures more than 313-323 K due to water evaporation from the wet cellulose at elevated temperatures.

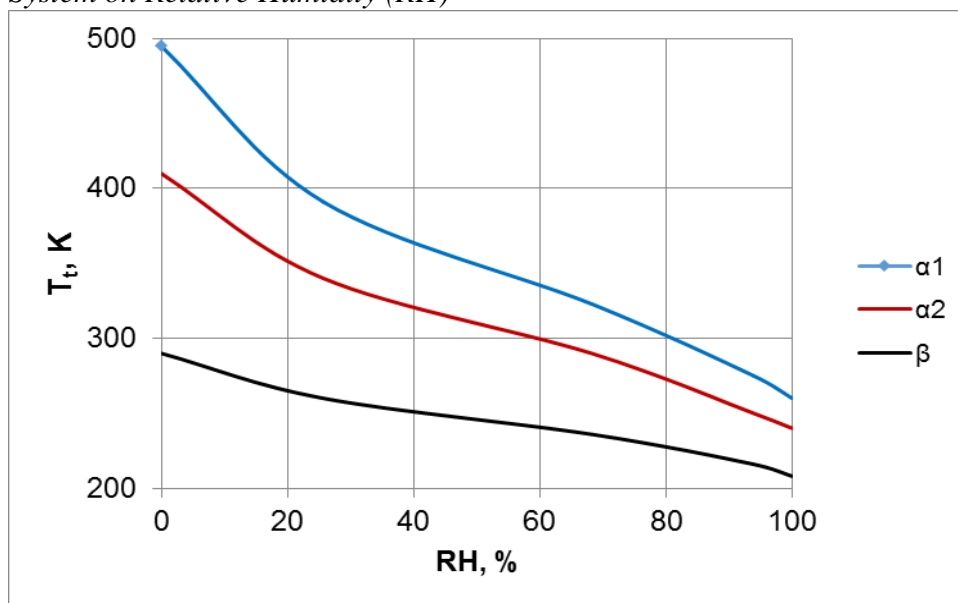
Some techniques allow the experiments to be conducted in sealed ampoules filled with aqueous solutions of high boiling liquid (e.g. low-molecular PEG), thus the evaporation of water from the sample can be avoided (Ioelovich et al., 1979). This technique allows the study of both the α_1 and α_2 glass transitions, and also the β transition, in the cellulose-water system (Ioelovich et al., 1979; Kaimin et al., 1979). These studies have revealed that with increase in the water content in NCD, temperatures of all three transitions decrease (Figure 10).

Figure 10. Dependences of Transition Temperatures on Weight Part of Water in NCD



Another problem is that for cellulose samples with various crystallinities, different dependences of the transition temperature on the water content are observed. To get the same results for various cellulose materials it is advisable to use the relative humidity (RH) instead of water content in cellulose (Figure 11).

Figure 11. Dependences of Transition Temperatures (T_t) in Cellulose-Water System on Relative Humidity (RH)



Like water, other polar liquids such as TEPAO, monoethanolamin, ethylenediamine, ethylene glycol, glycerol, and some other polar substances are also plasticizers of cellulose and cause a reduction in temperatures of α_1 , α_2 and β transitions (Ioelovich et al., 1979; Kaimin et al., 1979). On the contrary, the temperature of the γ transition increases with the moistening of cellulose (Roig et al., 2011).

Conclusions

It has been shown that due to structural heterogeneity the NCD cellulose has three isophase temperature transitions, where the α_1 transition, 490-500 K, and α_2 transition, 490-410 K, are caused by the occurrence of segmental mobility in dense mesomorphous and medium packed amorphous clusters, respectively; whereas the β transition, 280-300 K, is related to the mobility of small segments in loose packed amorphous clusters, which probably are located on the outer surface of nanofibrils. Under the action of water and other plasticizers, the α_1 , α_2 and β isophase transitions are shifted to lower temperatures. On the contrary, the temperature of the γ transition increases with the moistening of cellulose samples.

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