

Role of water content in food and product texture*

J. Blahovec

Department of Physics, Czech University of Life Sciences, 16521 Praha 6 – Suchbátka, Czech Republic

Received July 3, 2007; accepted August 3, 2007

Abstract. Water is very important component forming practically all important properties of the agricultural products, the foods and the biological objects. Among the properties, the important role is played by mechanical properties including the visco-elastic ones. These properties are influenced mainly by temperature and the strain rate but water plays the role of the main plasticizer in the controlling mechanisms. The relative simple models were developed for deformation of the soft homogeneous substances and character of the theories is discussed in this paper. Moreover, the role of water in the real agricultural products is structurally and concentration dependent. This role can be well described by sorption properties expressed by the sorption isotherms.

Key words: water, texture, plasticizer, sorption, water activity, turgor

INTRODUCTION

Mechanical properties of simple substances is given by the balance between bonding force among the substance structure units (atoms and molecules) on one side and the structure units proper energy on the other. This balance forms the basis of the state classification of the substances into solids, the materials with difficult shaping, and fluids, the materials with easy flowability. In cases where the mean energy of the structure units overcomes the bond energy among the structure units, the fluid's molecules become relatively free and the liquid is changed to gas. The development of the internal energy in water is displayed graphically in Fig. 1. This figure shows that the main part of the internal energy in the gas state consists in the state heats of melting and evaporation. Total internal energy at temperature just above the boiling point represents approximately 60 kJ mol^{-1} . The bond energies between atoms and

molecules vary in wide ranges from hundreds of kJ mol^{-1} for covalent bonds over $10\text{-}40 \text{ kJ mol}^{-1}$ for hydrogen bonds and group electrostatic bonds to wide spectrum of really soft bonds in units of kJ mol^{-1} (Vodrák, 1982). Figure 1 shows that the bond forces between molecules of water are relatively soft and they are given in tens of kJ mol^{-1} and they are mainly of the hydrogen origin.

The properties of pure water are changed after going into solutions, by interaction with other substances and/or structures and by influence of physical effects *eg* pressure. These changes and the further role of water in forming food and agroproduct texture are discussed in this paper.

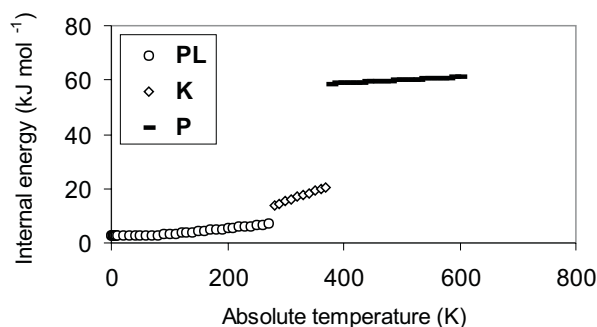


Fig. 1. Internal energy of water plotted against absolute temperature. The first part describe the solid state (PL - ice) followed by step increase of the internal energy connected with the melting heat. Further part between 273 and 373 K describes internal energy in liquid water (K) followed by the evaporation step given by state heat of evaporation and further development in the gas state (P).

Corresponding author's e-mail: blahovec@tf.czu.cz

*The paper was supported by the Research Intention MSM Czech Republic No. 6046070905.

NONCRYSTALLIC STATE OF MATTER

Solid and liquid states are the main states participated in agroproducts. The physical states of product solids are generally: the amorphous (liquid-like, rubber-like, solid) state and the crystalline state. Whereas in crystalline solids the solid state is changed in the melting point into the liquid state, in amorphous solids the change from solid to liquid state is more complicated (Jones, 2002) and new change termed as glass transition (T_g) is observed. Typical temperature plot of deformation of the amorphous polymeric material is given in Fig. 2. The arbitrary temperature scale in Fig. 2 is strain rate dependent: when strain rate increases the temperature scale with the characteristic points is shifted to higher temperatures and vice versa. The flowing is temperature sensitive mainly in glassy and viscous states.

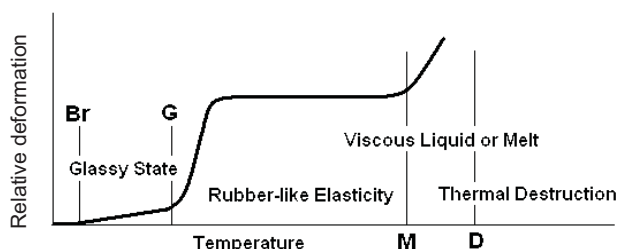


Fig. 2. Relative deformation of the amorphous polymeric material at the same stress plotted versus temperature (thermo-mechanical curve). The temperature scale depends on deformation rate: at higher deformation rates the temperature scale is shifted to higher temperatures (Jones, 2002). At lowest temperatures the material is brittle; at brittle transition (Br) is changed into the brittle state changing at glass transition (G) into rubbery state characterised by relatively high but temperature sensitive deformation. M denotes melting of the polymer with transition to the viscous and/or viscoelastic state with temperature sensitive flow. In some cases the temperature corresponding to thermal destruction (D) can be observed.

Under the above mentioned notes, the states of matter are distinguished by the energy ratio between the thermal movement and the intermolecular interaction, and by the mutual arrangement of individual macromolecules relative to one another. In the solid state, the intermolecular interaction energy exceeds the energy of thermal motion while in the liquid state, these values are comparable and macromolecules are movable. In the absence of external forces a solid body has a defined shape whereas any liquid has only a definite volume but not the shape. The liquid state is more disordered than the solid state. An external force causes molecular movement that corresponds to flow, the irreversible deformation of the liquid. Due to its extremely high viscosity, a glassy system behaves like a solid, and has both a definite shape and a definite volume, so that the amorphous glassy system can be classified as the solid-like substances with their structure typical for liquids.

Glassy state requires partial fixation of the chain segments. The higher the rigidity of the chains the lower the number of the chain segments which has to be fixed during change to glassy state. Mechanical stress helps to re-activate motion of some fixed segments and makes possible longer deformation of the glassy material. The stress necessary for this effect reaches the material strength when the temperature decreases from the glass transition to the temperatures of brittleness.

The crystalline state is very rigid. The rate of crystallization increases at melting temperature (T_m). Since the probability of crystallization increases with time, crystallization can be avoided by rapid cooling of the liquid to temperatures well below the melting point, transferred liquid into overcooled liquid state (see also Fig. 1). Further cooling changes the liquid to glassy state *ie* to solid-like system at around T_g . In the vicinity of the T_g , the system's viscosity greatly increases with a decreasing temperature. The formation of the glass is accompanied by a gradual change in temperature dependencies of the mechanical properties, specific volume and heat capacity. Normally, the specific heat capacity of a glass is close to that of the crystal *ie* remarkably below that of the liquid. The absolute values of the changes in thermodynamic variables are quite comparable to those observed during crystallisation and/or melting. Accordingly, T_g in polymers can be measured by various techniques termed complexly as thermal analysis (Haines, 2002). The glass transition is a kinetically controlled structure formation process. The T_m , which is well defined by an abrupt change in the temperature dependence of thermodynamic variables, the glass transition usually covers quite a wide region (up to 10-30°C around T_g) on the temperature-scale. The size of this region depends on the rate of cooling/heating and loading.

The T_g and the T_m are influenced by the chain stiffness, the intermolecular interactions, and the molecular weight. Some role is played also by the presence of other macromolecules, water and other plasticizers. Figure 2 schematically shows a thermo-mechanical curve typical for both low moisture biopolymers. The thermo-mechanical curve characterizes a change in deformability of a material during heating at a constant rate (Jones, 2002). It presents the relative deformation-temperature (D-T) dependence at a constant value of periodically applied stress and constant loading-unloading times. The thermo-mechanical curve shows that during heating the deformability of a glassy material is greatly increased in the vicinity of T_g and T_m . These two jumps in deformability correspond to the transitions from the solid glassy state to the rubber-like elastic state at T_g and then transition to the viscous liquid state at T_m . Above T_g , the deformability increases, becoming nearly constant and reversible in the so called rubbery plateau. Relatively small changes in deformability are observed at temperatures between T_g and T_m , and also below T_g . The changes in

this temperature range are reversible. Above T_m the deformation is partly irreversible. Figure 2 presents three sub-states of the amorphous solid state distinguishable on a temperature-scale. These sub-states are: brittle, non-brittle glassy, and a rubber-like. Many biopolymers and agroproducts can exist in each of these sub-states of matter. It should be noted the term rubbery-like, which is widely used in food science, is quite arbitrary. Contrary to rubbers, biopolymers cannot usually be reversibly deformed over several hundred percent.

The dynamics of polymer chains is different above, below and in vicinity of T_g . The glass transition can be determined as the temperature range at which segment motion of macromolecules becomes thermally activated. The physical cross-links are labile above T_g and frozen below T_g . The cross-linking density decreases the distance between the cross-links. Movement of more flexible chains leads to a denser packaging of macromolecules in the glassy state.

Figure 3 represents the typical thermo-mechanical properties of materials with rigid (a) and flexible (b) macromolecular chains. The biopolymers are rigid due to large side groups, high degree of conformation and presence of groups forming hydrogen bonds *ie* strong inter- and intra-molecular attractive forces. An increase of intermolecular attractive forces *ie* of the cohesive energy density, reduces chain flexibility and increases of the T_g . Usually biopolymers form rigid dry materials with higher T_g values so that they are more similar to plastics than rubbers.

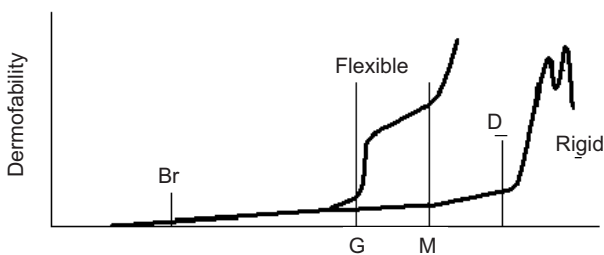


Fig. 3. Hypothetical thermo-mechanical curves for flexible and rigid macromolecules. There are used similar symbols as in Fig. 2.

WATER ROLE IN BIOPOLYMERS

Water is the main solvent and plasticizer in biological and food systems (Jones, 2002). Figure 4 schematically illustrates the effect of a plasticizer over a wide range of concentration on the thermo-mechanical properties of a rigid chain polymer. It shows the transition from the function of plasticizer to that of a solvent (Fig. 4, the curve on the left) corresponding to the transition from a plasticized, low moisture, glassy solid to a concentrated liquid solution of the macromolecular compound. Addition of a plasticizer to a rigid

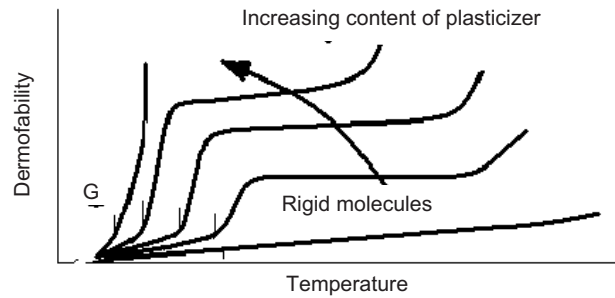


Fig. 4. Change of thermo-mechanical curve after addition of plasticizer. The addition of plasticizer leads to increase of the sample deformation, shortening of the rubbery part and to the shifting of the characteristic points (G and M) to lower temperatures. There are used similar symbols as in Fig. 2.

chain material (Fig. 4) can transform the system to a highly viscous liquid or a rubber-like solid. The absence of rubber-like elasticity is typical for highly rigid macromolecules. A plasticizer decreases and brings closer both T_g and T_m , and reduces the viscosity and the elastic modulus of the system. Plasticization is due to several factors. The first is an affinity of the plasticizer, water, to the macromolecular compound, and its interactions with charged and polar groups. The second factor is an increase in the distance between macromolecules and a decrease in intermolecular interaction due to dilution with water. The plasticizing role of water is supported by its properties: low molecular weight, low density, high dielectric constant, high ability of forming H-bonds and low T_g . The plasticizing effect is most efficient at relatively small amount of adsorbed water, which is not available as a solvent. High mobility of water molecules usually results in water losses either by evaporation or by extraction.

AGGREGATED BIOLOGICAL STRUCTURES

The biological structures are usually aggregated so that the substances of different states participate one with another. This is typical also for the other structures based on structure units of complicated properties. Generally, we can wait that all the basic matter states could participate at the aggregate architecture. The aggregate architecture could be crudely described in the three state diagrams (Fig. 5) describing all the possible participations of the basic state components in the material. We can now speculate about the state property of the aggregate and we have to take into account the main properties laying in basis of the state classification of the aggregate: its compressibility and shape change ability.

Analysis of the properties of many cellular (Gibson and Ashby, 1988) and particular materials shows that participation of the basic state components in volume of the aggregated material is not so important for the resultant state character of the aggregate. The concentration of the gaseous

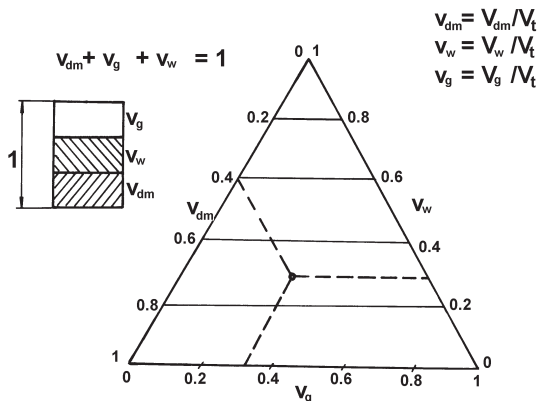


Fig. 5. Three state diagram used for crude evaluation of the state participation in the aggregated material. The relative volumes of the basic states in the aggregate are: v_{dm} relative volume of solids (so called dry matter), v_w relative volume of liquid (water), and v_g relative volume of gas (air). These three co-ordinates in three state diagram express full state composition of the material for which the sum of all co-ordinates has to be 1.

components is usually meaningless for the gaseous character of the aggregate. The aggregates with high gas concentration are usually unstable in the gravitational field and they form the real gas-like aggregates only in the special cases in which the gaseous state is stabilized by motion of the gaseous component to overcome gravitational sedimentation due to different densities of different state components. This is very frequent in dusts, fogs, boils, droplets etc. These two state aggregates are located close to the side parts of the three state diagram in Fig. 5. They can then be classified really as fluids during the permanent stabilization process.

The solid-like and liquid-like aggregates are more stable than the aggregates previously described. Most of them are built on the solid and/or liquid basis like solutions, colloids, gels, suspensions, emulsions, etc. The most frequent are the multi-state aggregates with relatively big structural units being in contact by their external surfaces. When the contact forces between the structural units are low eg of the frictional character, then the structural units are relatively free and movable one to another, and we speak about particles forming the particular materials. The particular materials easily change their shape in the flowing processes, classifying them as fluids even in cases in which the important part of the material volume is formed by solids. The sands are the good example of this kind of material; in sands about half of their volume is occupied by stony particles and the other volume, the inter-particle spaces, is occupied either by water or by air. It is well known that the sands are fluid-like materials despite their high content of solids.

In other aggregates, the contact forces among the structural units are high ie they are formed by chemical bonds of the soft character at least, and the connections among the structural units cover big amount of their surface. We speak then about cellular structures that behave rather as a solid material even in cases where big amount of the cellular volume is represented by fluids. The examples of some agricultural aggregates are given in Fig. 6. Soil is a material that can be classified in many cases as a particular one: really, sands and light non-compressed soils are easy deformable. Another aggregates, in which the bonding forces among particles are high eg clay are classified as the cellular structures. It is clear that the final decision about the state character of soils depends mainly on the level of the cohesion forces rather than on dry matter content. Figure 6 shows that the water and air contents in wood are very variable but the state character of the wood is not changed by this change and the wood is classified as a solid.

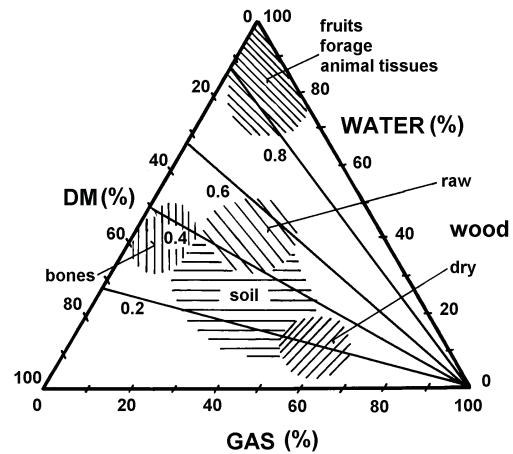


Fig. 6. Three state diagram for some selected types of agricultural products and soils.

The relative independence of the aggregate's mechanical state on the relative participation of substances of different states is clearly demonstrated by fruit or vegetable tissues. The moisture content in many of those aggregates is higher than 90% (Fig. 6) but these aggregates behave as solids! These rather surprising results are based on tough cellular walls connected one to another by many bonds of medium strength and filled by quasi-liquid sap of high turgor pressure (Fig. 7). The solid properties of the cellular aggregates are determined by the complex properties of the cellular walls.

STATE EQUILIBRIUM AND SORPTION PHENOMENA

Moisture content in every material is not independent value; during storing of the material in box with some definite air humidity, the moisture content changes depending on difference between water activity in the material and

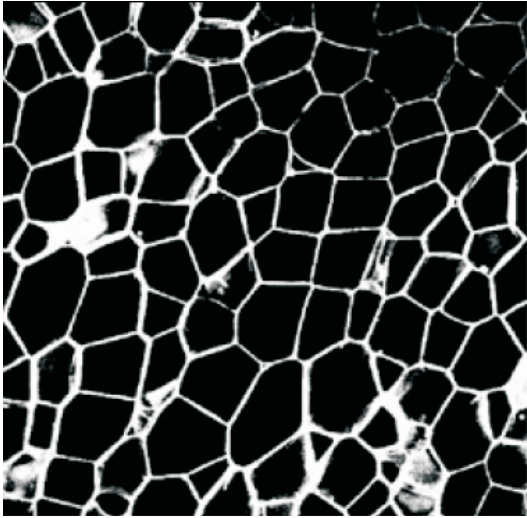


Fig. 7. Typical cellular structure of the potato parenchyma (Zdunek and Umeda, 2005). Cell walls are nearly planar with limited intercellular spaces. The thin but tough cell walls are connected by many bonds of medium strength and form then rigid superstructure supported by turgor, the internal cell pressure produced by difference in water activity inside and outside the cells.

humidity of the surrounding air. These changes are drying or adsorption depending on the material water activity and the air humidity difference (Fig. 8). This process finishes in the equilibrium – the state in which the air humidity has the same value as the water activity of the material. It means that there exists some equilibrium moisture content for given temperature and water activity. The plots of the equilibrium moisture contents (usually of dry basis) versus water activities *eg* different air humidity at the same temperature are termed sorption isotherms. In many cases the details of sorption isotherms depend on the procedure used in determination of its values (drying or adsorption) forming so called sorption hysteresis. Water activity is very important

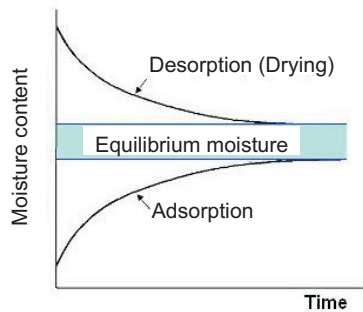


Fig. 8. Equilibrium moisture content reached either by drying or by adsorption. The processes are based on spontaneous tendency to reach thermodynamic equilibrium (in temperature, concentration of the components etc.) with the same water activity in the systems being in contact. The materials left at the same temperature in the air with some humidity tends to the state with water activity of the same value as the surrounding air.

parameter because its value predetermines the rate of many biochemical and biological processes in the materials including the rate of microbial growth (Karel, 1975). Water activity lower than 0.65 is usually requested for preservation of many materials.

The examples of sorption isotherms are given in Fig. 9. This figure shows that water activity at the same moisture content increases with increasing temperature. This means among others that increasing temperature in some limits causes increase of the biochemical and biological rates. The sorption isotherms measured at different temperatures form the basis for calculation of so called isosteric (at the same moisture content) heat of adsorption (IHA) q_{st} :

$$q_{st} = R \left(\frac{d(\ln a_w)}{d(1/T)} \right)_w,$$

where: R is universal gas constant, a_w water activity and T absolute temperature (Adamson, 1976). The subscript w denotes that derivative is calculated at constant moisture content. The IHAs calculated for some agricultural products are given in Fig. 10. This figure shows that at high moisture contents (above ~ 30% w.b.) the IHAs are very low and decreases with increasing moisture content. With decreasing moisture content, the product IHA increases steeper and steeper, having maximum at moisture contents 5-10%. At moisture contents lower than ~5% this trend is suspended at IHAs about 20-30 kJ mol⁻¹. This result follows from the fact that the sorption phenomena are formed by the least bound water of the product, and it means that decrease of the moisture content is followed by observation of the more bound water. The process is connected with increasing IHA-values with decreasing moisture content up to the moisture content at which the whole left water is bound to the internal surface by approximately the same bond intensity: all product water participates in the monomolecular layer on the product's surface. The IHA at monomolecular

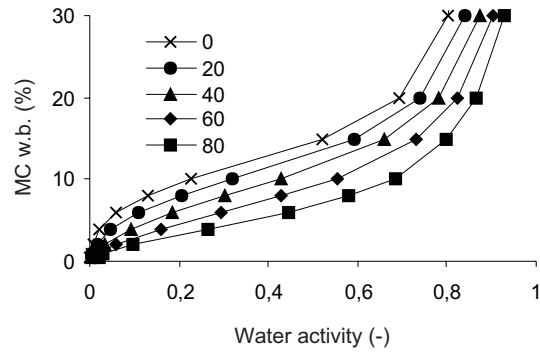


Fig. 9. Sorption isotherms of potato tissue at different temperatures (denoted by numbers in °C in the figure – adapted under Heiss, 1968).

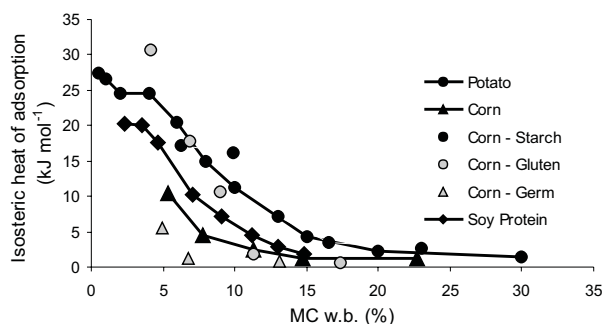


Fig. 10. Isosteric heat of adsorption plotted against moisture content w.b. for potatoes (data from Fig. 9). Similar data obtained for corn and its parts (adapted data of Chung and Pfof, 1967a, b, c) and soybean concentrate (adapted data of Hansen, 1976, 1978) are also given for comparison.

layer ($20\text{--}30\text{ kJ mol}^{-1}$) is of the same magnitude as the internal energy in liquid water (Fig. 1) and $1/3\text{--}1/2$ of the energy of the water vapour at 100°C eg removing of the bound water at 100°C follows by $30\text{--}50\%$ increase of energy in comparison to state heat of evaporation of the free water.

TEXTURE AND MOISTURE CONTENT

The role of water in real materials of biological origin is more complicated than in the simple polymeric material. Water serves as a plasticizer also in this case and deformability of those materials increases with increasing moisture content significantly. The yield strain increases in hundreds % eg apples (Ta-Te-Lin and Pitt, 1986) This trend is typical for materials with moisture content higher than 10% w.b. (Fig. 10) at the beginning of the corresponding sorption isotherm. The materials with moisture content below 10% w.b. can be classified as brittle and increasing water content reduces the probability of the brittle fracture. In wet conditions, the moisture content in cells increases causing the increase of the turgor pressure and then also modulus of elasticity.

The role of water in the texture properties can be divided then into three regions with different moisture content:

1. Cellular structures with high water content and high water activity. Water penetrates cell walls and causes increase of internal pressure on the cellular walls as a source of the product toughness. This process is influenced by the cellular solutions and the solutes concentration in the solutions depending on the cell wall permeability. There exist important differences among different products as it is demonstrated on potato and apple tissues in Figs 11 and 12: the role of this type of processes is limited to lower mannitol concentrations (lower than 0.35 for potato and 0.55 for McIntosh apple). Sources of the differences should be found not only in the cellular walls but also in the concentrations and properties of the cellular solutions. The toughness of the structure decreases with increasing mannitol concentration

but the yield stress increases at the same conditions. The region 1 in plants is well limited by point of wilting at water potential -1.5 MPa (Richter, 1976) that corresponds to mannitol concentration less about 0.6 M (Ta-Te-Lin and Pitt, 1986), (Figs 11, 12).

2. Cellular structures of medium water content and medium water activity in conditions where the turgor pressure does not play previous important role (Fig. 12) but the yield stress still increases with decreasing water activity and increasing mannitol concentration. In Figs 11 and 12 this region is limited by mannitol concentrations higher than 0.6 M . Water plays its role of the polymer plasticizer. The higher mannitol concentration, the lower water potential, the lower moisture content and then the yield point and strength points are higher. The changes of deformation curves due to changes in moisture content in this area are displayed schematically in Fig. 13.

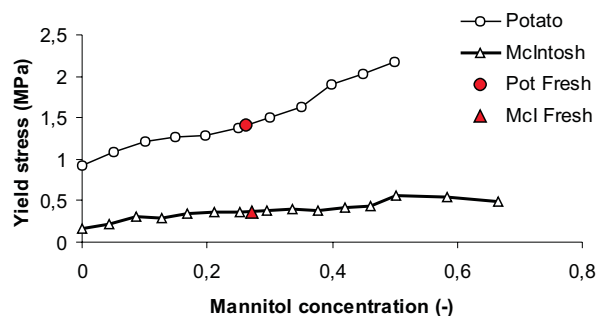


Fig. 11. Yield stress in soft plant tissue (adapted under Ta-Te-Lin and Pitt, 1986) plotted versus mannitol concentration in solution. The compression tests of the cylindrical samples (diameter 1.35 mm , length 1.35 cm) previously soaked $30\text{--}36\text{ h}$ in mannitol solutions of different molar concentrations were performed at strain rate 0.1 s^{-1} . The data are plotted for potato and apple (McIntosh) tissue. The dark point corresponds to the fresh tissue without soaking (pot – potato, Mcl – MacIntosh apple).

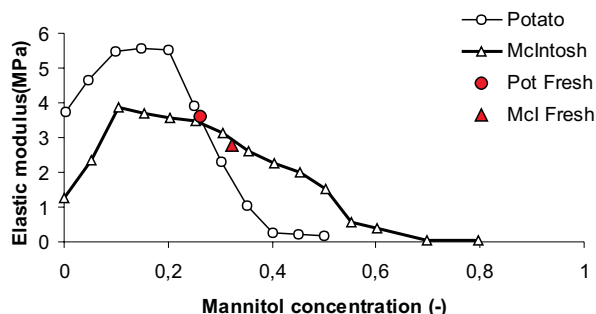


Fig. 12. Modulus of elasticity of soft plant tissue (adapted under Ta-Te-Lin and Pitt, 1986) plotted versus mannitol concentration in solution). Further details are given at Fig. 11.

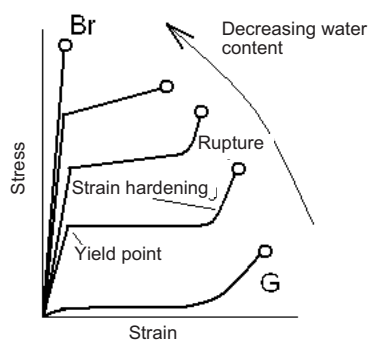


Fig. 13. Material deformation curves at constant deformation rate in Region II changing their shape due to decreasing water content from the Glassy(G) to Brittle (Br) state.

3. Brittle state of the cellular structure at moisture content lower than 10%. In this state the cracks formation is so frequent that this process becomes to be the important source of strength decrease with decreasing moisture content. The brittle state in cellular structures does not differ substantially from the same state of the other polymeric materials. The role played at higher moisture content by the cellular structure is nearly lost in this state: the cell wall biopolymers behaves similarly as biopolymers in their homogeneous arrangements.

CONCLUSIONS

1. Water content in agricultural products plays similar role as in the other polymeric and soft materials. Water plays its role of plasticizer (region 2) connecting the brittle state with rubbery and viscous states in wide range of moisture contents from ~ 10% w.b. up to high moisture contents corresponding to water potential about -1.5 MPa.

2. In comparison to the simple polymeric materials, the high values of moisture content are typical by cellular turgor pressure and the texture consequences like relatively high values of modulus of elasticity and its increasing value with increasing moisture content.

REFERENCES

- Adamson A., 1976.** Physical Chemistry of Surfaces. Wiley, New York.
- Chung D.S. and Pfost H.B., 1967a.** Adsorption and desorption of water vapor by cereal grains and their products. Part I. Heat and free energy changes of adsorption and desorption. Transactions of the ASAE, 10, 549-551.
- Chung D.S. and Pfost H.B., 1967b.** Adsorption and desorption of water vapor by cereal grains and their products. Part II. Hypothesis for explaining the hysteresis effect. Transactions of the ASAE, 10, 552-555.
- Chung D.S. and Pfost H.B., 1967c.** Adsorption and desorption of water vapor by cereal grains and their products. Part III. A hypothesis for explaining the hysteresis effect. Transactions of the ASAE, 10, 556-557.
- Gibson L.J. and Ashby M.F., 1988.** Cellular Solids. Structure and Properties. Pergamon Press, Oxford.
- Haines P.J., 2002.** Principles of Thermal Analysis and Calorimetry. Royal Society of Chemistry Press, Cambridge.
- Hansen J.R., 1976.** Hydration of soybean protein. J. Agric. Food Chem., 24, 1136-1141.
- Hansen J.R., 1978.** Hydration of soybean protein. 2. Effect of isolation method and various other parameters on hydration. J. Agric. Food Chem., 26, 301-304.
- Heiss R., 1968.** Haltbarkeit und Sorptionsverhalten wasserarmer Lebensmittel. Springer Verlag, Berlin.
- Jones R.A.L., 2002.** Soft Condensed Matter. Oxford University Press, New York.
- Karel M., 1975.** Water activity and food preservation. In: Principles of Food Science (Ed. O.R. Fennema). Part II. Physical Principles of Food Preservation (Eds M. Karel, O.R. Fennema, and D.B. Lund). M. Dekker Inc., New York.
- Richter H., 1976.** The water status in the plant experimental evidence. In: Water and Plant Life. Problems and Modern Approaches (Eds O.L. Lange, L. Kappen, and E.-D. Schultze). Springer-Verlag, Berlin.
- Ta-Te-Lin and Pitt R.E., 1986.** Rheology of apple and potato tissue as affected by cell turgor pressure. J. Text. Stud., 17, 291-313.
- Vodrá ka Z., 1982.** Physical Chemistry for Biological Sciences (in Czech). Academia, Praha.
- Zdunek A. and Umeda M., 2005.** Influence of cell size and cell wall volume fraction on failure properties of potato and carrot tissue. J. Text. Studies, 36, 25-43.