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CHARACTERISATION OF GARLIC FREEZE DRYING WITH THE USE OF DIFFERENTIAL SCANNING CALORIMETRY

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ABSTRACT

Differential Scanning Calorimetry Method (DSC) was used for determining the parameters of garlic freeze drying process. Garlic with moisture content ranging from 17 to 87% in temperatures from -28 to 5°C (245-278 K) was investigated. The transitions, including change of water into ice (crystallization) and condensed inter-crystalline solution into amorphous solid, were considered. The melting point of ice crystallites T_m and glass transition temperature T_g' were read out from the registered thermographs. Critical moisture of garlic, determining the onset of forced drying stage, was estimated.

It was stated that both glass transition temperature as well as the melting point can be quite accurately described with the set of second-order equations, depending on garlic moisture.

Key words: Freeze drying, garlic, glass transition temperature, melting point

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INTRODUCTION

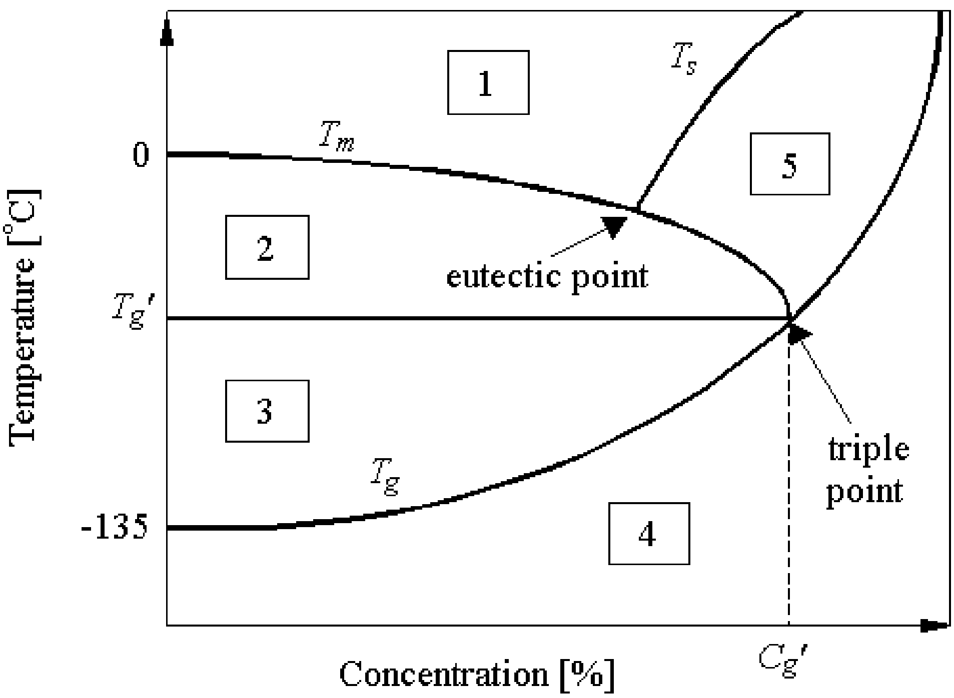
Foodstuff preservation by drying methods should aim at possibly good conservation of its mechanical properties and chemical composition so as after the rehydration of dried product it will maintain its taste value. Freeze drying belongs to the most advanced methods of drying [1]. The material processed using the method is at first frozen under the atmospheric pressure and then subjected to vacuum sublimation and forced drying up to the required final moisture content.

Water contained in plants (cell sap and bound water) behaves quite different from chemically pure water, described by phase diagram. Among the phase states of the water contained in plant material, there are glassy and amorphous structures in equilibrium with solid phase.

Ice crystallites arising while freezing the plant material, cause an increase in concentration and viscosity of the liquid phase. After reduction of the material temperature to the value of T_g' (glass transitions temperature), the growth of ice crystallites is interrupted and the remaining inter-crystalline solution, having maximum concentration of solute, reveals the properties of amorphous material. The process of further temperature reduction results in over-cooling of the concentrated liquid and a rapid increase of its viscosity. Among the ice crystallites, the structure similar to glass arises.

Figure 1 shows the phase diagram of water. The melting curve T_m determines the state of equilibrium of liquid and solid. The glass transition curve T_g is the boundary between the mobile and stable physical state of the system. The point of intersection of both curves corresponds to the triple point with the highest concentration of solute C_g'.

Figure 1. Phase diagram of water while freezing plant material (by Roos): 1 – water solution, 2 – ice + concentrated water solution, 3 – ice + the solution with the highest concentration, 4 – amorphous solid (glaze), 5 – over-saturated solution with viscous-elastic consistency



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As the result of freezing, the separation of the solution into two-phase mixture – ice crystallites and concentrated water solution – occurs. Sublimation of ice crystallites causes that the unfrozen matrix loses the structure, securing its stiffness. The temperature at which the structure is completely destroyed is strictly connected with the temperature of T_g'. Below the point, the viscosity of the unfrozen matrix ranges from 10^3 to 10^8 [Pa·s], which ensures stability of the structure of dried material [2, 3, 4].

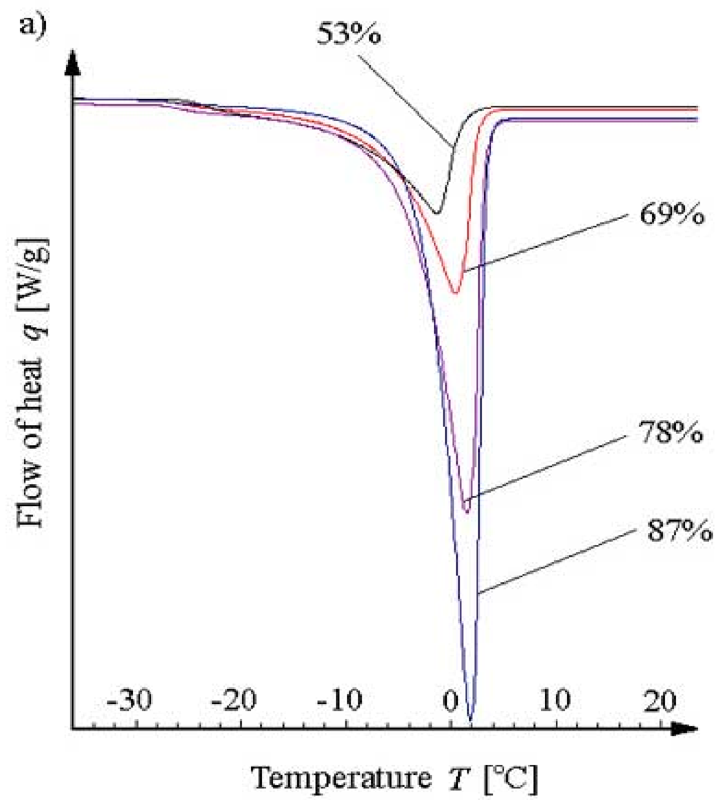
The biggest loss of nutritive components and worsening of sensorial properties of the dried material occur at the forced drying stage [5]. At the stage, the water should be maintained at the vitrification state, which stops the chemical reactions and reduces shrinkage of the tissue. The temperature of the material should increase with the increase of vitrification temperature.

The aim of the work was to establish the relationship of vitrification temperature T_g' and melting point T_m versus material moisture and to estimate the critical moisture value, determining the onset of the forced drying stage.

MATERIALS AND METHODS

The material used in the study was common garlic (*allium sativum*) – the annual plant, easy to reach on the market. The measurements were carried out using differential scanning calorimetry method, with Mettler Toledo DSC 821 set. Aluminium calorimetric crucibles, filled with garlic were placed in the head of calorimeter next to the empty standard container. The samples were frozen down to the temperature of -25°C (248 K) and then heated up to 5°C (278 K). The process rate (both freezing and heating) was 5 K/min. The course of the melting process was registered on the plot heat flux versus temperature. The obtained curves were applied for evaluation of vitrification temperature and the melting point.

Figure 2. Exemplary DSC thermographs for garlic: a) endothermic peaks, featuring the melting point, b) curves characterising glass transition



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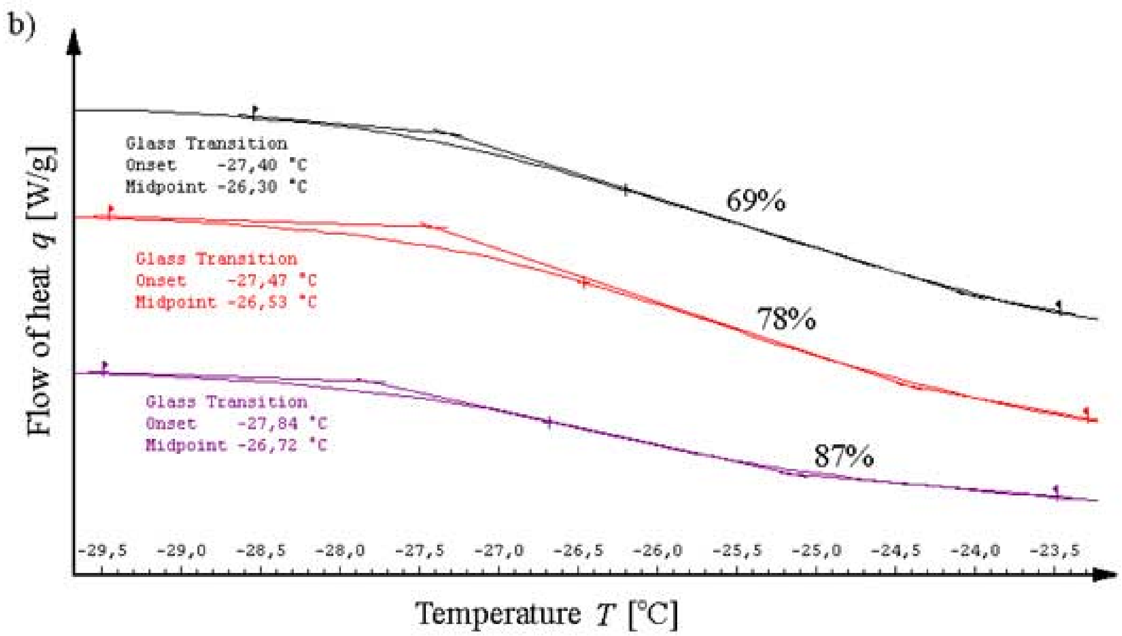
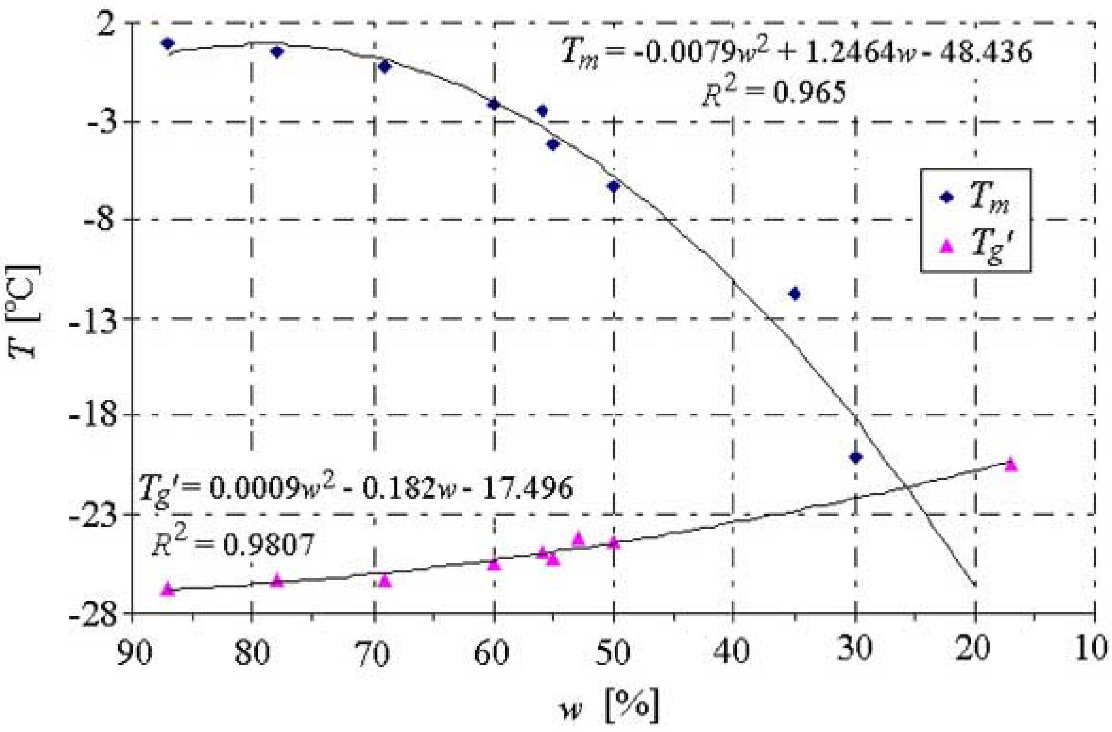


[Figure 2](#) shows some exemplary DSC thermographs obtained during the tests. The melting point was read out as the maximum endothermic peak (Figure 2a), whereas the change in the base line of the thermograph established glass transition temperature (T_g – midpoint, Figure 2b).

RESULTS

Phase transitions in freeze dried garlic are shown in [Figure 3](#), where the course of glass transition temperature and the melting point versus material moisture are presented.

Figure 3. The effect of moisture on water phase transitions in garlic



With the drop in material moisture, reduction of melting point temperature T_m takes place. Temperature dependence on garlic moisture is approximated with $T_m = -0.0079w^2 + 1.2464w - 48.436$ function, with regression coefficient $R^2 = 0.965$.

Glass transition temperature T_g' also depends on the moisture of the tested materials. The curve T_g' versus material moisture has a rising character and can be quite adequately described with the equation $T_g' = 0.0009w^2 + 0.182w - 17.496$ with regression coefficient $R^2 = 0.9807$.

Material moisture at the point of intersection of the curves is called critical moisture W_{kr} [6]. The water, contained in the material with the moisture content less than W_{kr}, makes up together with the solute a completely amorphous solution, which means that the solution is entirely deprived of water in crystalline form. The value of critical moisture for garlic, estimated on the basis of the studies, approaches the value of $W_k \approx 26\%$.

CONCLUSIONS

1. The value of glass transition temperature T_g' of condensed inter-crystalline solution for garlic ranges from -20 to -26°C (253-247 K).
2. Glass transition temperature is only slightly dependent on the moisture of the tested material, which imposes that for preserving the structure stability and reduction of destructive effect of ice crystallites, the temperature of the processed material should be kept below -26°C (247 K), at the preliminary stage of the forced drying process.
3. The melting point of garlic ice crystallites decreases with the drop in its moisture content.
4. The determined value of garlic critical moisture amounts to approx. 26% mass. The value characterises the onset of the forced drying stage.

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