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THERMAL TRANSITIONS BY DIRECTLY EXPANDED EXTRUDED MAIZE GRITS

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Abstract

The maize grits is a biopolymer with partially amorphous structure, which is characterized both by glass transition temperature and by melting temperature. The purpose of this paper is presenting the importance of knowledge this temperatures and determination their values for the maize grits, when it is used to make snacks through direct expanding snack process (the granulation between 500 and 800 μm and humidity of 13%).

Keywords: *thermal transition, glass transition temperature, melts transition temperature, maize grits.*

Introduction

The direct expanding extrusion is a continuous process in which both extrusion and expansion take place in single equipment. To materialize this process it is necessary that the raw material's humidity is low in comparison with other extrusion processes and the equipment must achieve the high temperature necessary for physical and structural transformations that lead to obtaining the desired final extruded product.

Biopolymers or their components may have an amorphous or crystalline structure. However, most biopolymers exist in an amorphous or partially amorphous state.

By heating of a crystalline polymer at the constant rate, the temperature increase also with a constant rate that depends of his specific heat. When the melting temperature, Tg, is reached, the temperature is being stop to increase, remaining constant until the entire quantity of polymer has melted. If the polymer is heated further, the temperature startes to increase again, but with another rate. So on melting of a crystalline polymer two matters happen: it absorbs a certain amounth of heat, named the latent heat of melting, and a specific heat's change take place. This kind of transitions is named first order transition (figure 1a).

By heating of an amorphous polymer at the constant rate, the temperature increase also with a constant rate that depends of his specific heat, similar with heating of a crystalline polymer. But now, when a certain temperature is reached, increasing of temperature doesn't stop, this continues to increase but with a different rate. This is the glass transition temperature, Tg (figure 1b). At this temperature occurs only a change of specific heat of polymer, without having the latent heat of melting. This kind of transitions is named second order transition (Othmer, 1993; Slade, 1995).

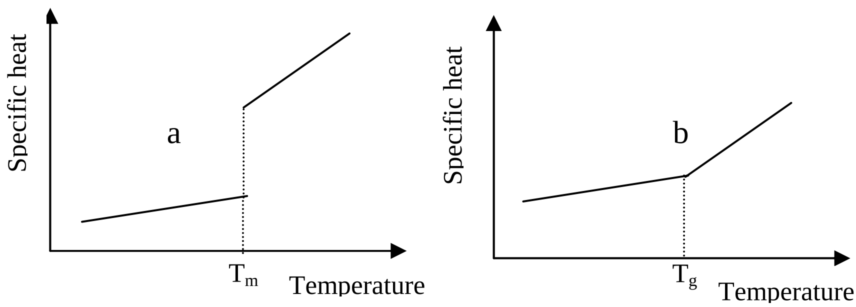

Fig. 1. The variation of specific heat with temperature for:
a) crystalline structure material; b) amorphous structure material

Hence it appears that biopolymers with partially crystalline structure have as characteristic temperatures both the glass transition temperature and the melting temperature.

If the temperature of material is smaller than Tg, this is considered "glassy". In this domain the material has an amorphous structure and it fractures easy with low effort. If the temperature of material is between Tg and Tm, it is in the high elastic state or "rubbery" state. It is easiest deformable but it doesn't flow. If the material's temperature is higher than Tm, it is considered "melt" and it's flowing like a liquid.

In figure 2 is showed the working diagram that describes the extrusion process with direct expansion of a partially crystalline polymer (Strahm, 1988). On this diagram it can see the transitions that the raw material undergo on heating and cooking, thank to his passing through Tg and Tm temperatures. On this diagram it could also see that Tg and Tm are influenced by the moisture content of material (Liu, 1999).

The raw material used most frequently on this type of extrusion is the maize grits. It is a partially amorphous polymer, having in its structure approximately 90% starch granules made from amylose with linear structure and amylopectin with branched structure. Amylopectin is that which gives the partially crystalline structure of maize grits.

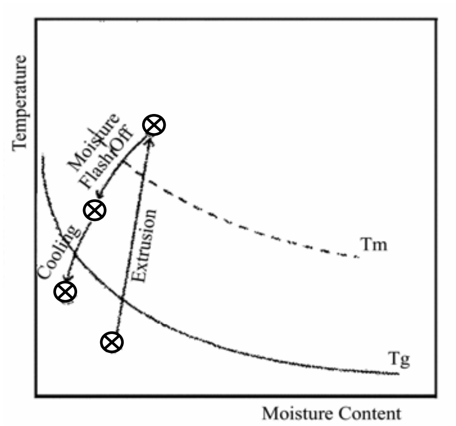

Fig. 2. The extrusion with direct expanding working diagram

If is analyses the running of an extruder for extrusion with direct expansion and takes into consideration the diagram from figure 2, could be concluded that maize grits passes by rapid heating and moistening from glassy state at the feed, into an high elastic state and then into a melting state in front of the die. As the material exits the die it take place the expansion by moisture flash off and rapid cooling of extrudate that passes through high elastic state at the glassy state. In fact when the material's temperature decreases below Tg, the extrusion stops and the material's structure stabilizes.

The temperatures Tg and Tm are necessary always for thermo-mechanical calculations or in simulation of polymers extrusion.

Experimental

The most used method in determination of the glass transition temperature Tg and melting temperature Tm is the Differential Scanning Calorimetry (DSC). This is a precise and fast method to view what happens to polymers when they're heated and to determine the transition temperatures of polymers. The experiments was made using a special calorimeter built by Perkin-Elmer and used at Plastics Processing Machines and Technology Institute from Essen University, Germany. The simplified scheme of the device is presented in figure 3.

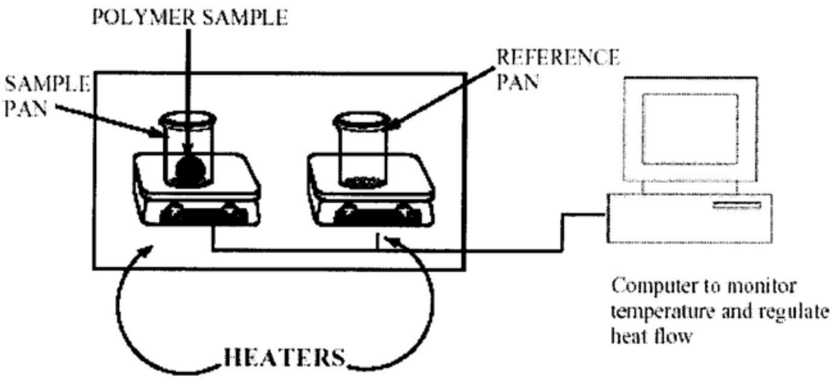

Fig. 3. Differential scanning calorimeter (www.missouri.edu/~crrwww/katti/)

A certain amount of polymer, generally between 10 and 20 mg, are put in a pan, after which this is introduced into the testing cell on the heater. On the other heater is put an identical pan but this is empty. The heating rate is selected generally between 10 and 20°C/min. It is also preselected the initial and final temperatures to which the sample must be heat. The experimental and the reference sample are heated separate but in parallel according to a linear increasing temperature program. The two heaters preserve the two samples at the same temperature. The computer makes absolutely sure that the two separate pans, with their two separate heaters, heat at the same preselected rate as each other.

The power absorbed by the two heaters for ensuring this heating rate is monitored and the difference between the two powers are diagramed against the temperature.

If this temperature increases and the experimental sample passes trough a transition, the necessary heat flow to preserve the same temperature to two samples will be more or less depending by the fact that the transition is endothermic or exothermic.

The device assures the measuring of heat flow as ratio between heat supplied to sample, **q**, and time, **t**, and the measuring of heating rate as ratio between the increasing of temperature, **ΔT**, and time, **t**. Dividing the two measures it results the specific heat:

$$c_p(T) = \frac{q}{\Delta T}\left[\frac{J}{g \cdot \text{degree}}\right]$$

The raw material used on this experiment was maize grits with 0.595 - 1.19 mm granulation. The moisture of sample was 13 %. The amount of sample was 26.740 mg. The heating rate was 20°C /min. The heating domain was 0-170°C.

Results and Discussions

After processing the experimental data resulted the specific heat variation curve against temperature showed in figure 4.

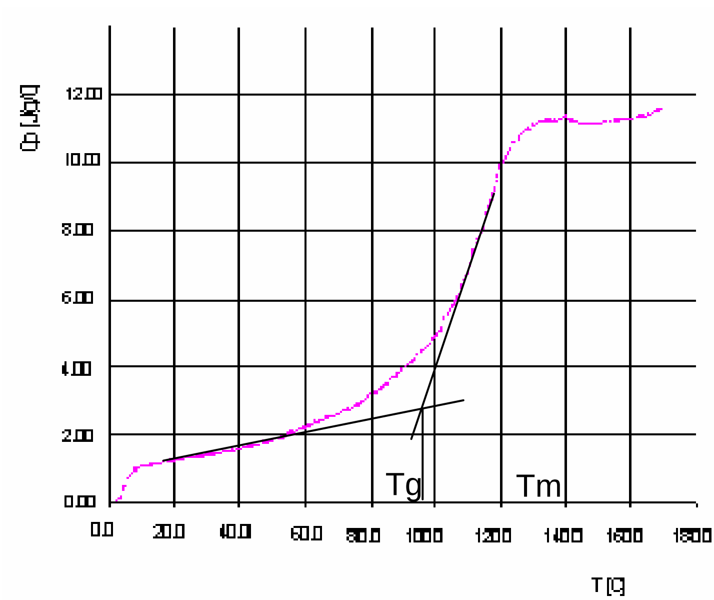

Fig. 4. The specific heat variation against temperature for maize grits with 13% moisture content

The shape of this diagram confirms that for polymers with partial amorphous structure, both the second order transition (glass transition) and the first order transition (melting) don't happen at a any certain temperature but on temperature range. Testing standards established that the glass transition temperature Tg is considered to be at the intersection between tangents at this curve in a glass transition domain, and the melting temperature Tm is considered to be that who the absorbed specific heat is maximum.

As shown in figure 4, in so doing were achieved for tested maize grits with 13% moisture content, a glass transition temperature Tg = 96°C and a melting temperature Tm = 139.8°C.

Conclusions

Therefore, at temperature condition below 96°C the maize grits can be described as glassy or essentially nondeformable, at temperature between 96°C and 139.8°C this is described as rubbery or easily deformable and at temperature above 139.8°C this is fluid enough to flow.

Acknowledgements

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Reference

Liu, Z., Yi, X. (1999). Effect of Bound Water on thermal Behaviours of Native Starch, Amylose und Amylopectin, *Starch/Starke*, 51(11-12), 406-410

Othmer, K. (1993). *Encyclopedia of Chemical Technology*. Ed. 4th, Vol. 12, A Wiley Intersci. Publ., John Wiley & Sons

Slade, L., Levine, H. (1995). Glass transitions and water – food structure interactions. *Adv. Food Nutr. Res.*, 38, 103-269

Strahm, B. (1998). Fundamentals of Polymer Scince as an Applied Extrusion Tool. *Cereal Foods World*, 43(8), 621-625

www.missouri.edu/~crrwww/katti/, *Thermal Behaviours of Polymers. Transition by DSC*