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DIFFERENTIAL SCANNING CALORIMETRY RESEARCH OF BIODEGRADABLE FILMS FOR CONFECTIONERY AND BAKERY PRODUCTS

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Abstract. Biodegradable films for bakery and confectionery products using differential scanning calorimetry are studied in this work. Expediency for the use of biodegradable films for marmalade, gingerbread, bakery products, and fondant confectionery according to organoleptic characteristics is established. The influence of the type of starch on film structure is studied with DSC analysis. DSC analysis was used to determine functionality of using glycerol as plasticizer, as this can reduce the temperature of melting point and glass transition of original compounds.

Keywords: biodegradable films, edible film, differential scanning calorimetry, confectionary, bakery products.

1. Introduction

In confectionary industry problems of preserving freshness and reducing caloric content are still topical. Depending on the group of confectionery (sugar or flour) there are different ways to extend their shelf life [1]. Caloric content can be reduced by adding dietary fiber into products along with energy content (flour, starch, *etc*.) reduction [2], fat content reduction by adding modified starch [3], replacing of fat or sugar glaze by other ways of surface protecting [4]. A method of protecting surface with film coating is the most economical one because it does not require a lot of raw material. In addition, the use of film coatings allows to use biologically active substances that can not withstand thermal treatment.

Research of biodegradable films is one of the most common areas of plastic packaging industry. A wide range of raw materials is used for their production that influences qualitative and quantitative characteristics of the finished film depending on the type and proportion of raw material. Raw material is subjected to thermal effects during manufacturing, so it is reasonable to discover both thermal characteristics of certain raw materials and their compositions. One of the methods of doing that is differential scanning calorimetry (DSC).

DSC is a physical and chemical research method of phase transitions in which the energy difference, which is given to the substance under research and the sample (for reference) to achieve the same temperature is recorded as a function of temperature, which varies by a program.

The amount of energy absorbed by the sample or released from the sample during continuous increase or decrease of temperature or under constant temperature is measured according to the DSC method. This method is the most effective way to study melting, crystallization, thermal degradation temperature, and determining the glass transition zone, which is also determined by scanning thermal microscopy [5]. DSC analysis allows to determine the crystallinity degree of polymer and crystallization kinetics. DSC analysis also allows to determine quantitative information about the content of various additives in the composition. The study of thermographs (heat patterns) allows to assess behavior of the material in the whole temperature range from glass transition temperature to the zone of destruction, as well as changes that occur between these two extreme points [6].

Expediency for the use of DSC analysis for the study of polymeric packaging materials is supported by the works of A. Ershov *et al.* [7], in which they examined six samples of biodegradable polymer films with the addition of d2w; E. Ulrich *et al.* [8] carried out comparative analysis of samples based on corn starch, amylose starch and carageenan. The authors A. Golovanov *et al.* [9] conducted an analysis of monolayer and multilayer films for food packaging.

The aim of this article is to study the influence of biodegradable films, namely edible coating, on the organoleptic properties of gingerbread products, fondant sweets, marmalade, and bakery products with edible film and to determine changes occurring in the film with DSC (differential scanning calorimetry) analysis.

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2. Experimental

Samples were made according to classic recipes in the laboratory. The film was applied on gummy gingerbreads, fondant sweets (without invertase), marmalade (on gelatin), and wheat bakery.

Complex organoleptic index was determined by the method [10] according to the formula:

$$K_o = M_1 \frac{P_1}{P_1^b} + M_2 \frac{P_2}{P_2^b} + M_3 \frac{P_3}{P_3^b} + M_4 \frac{P_4}{P_4^b} + M_5 \frac{P_5}{P_5^b} \quad (1)$$

where P_1, P_2, P_3, P_4, P_5 – indicators characterizing the organoleptic properties of the samples (taste, color, smell, texture, appearance, form); P_1^b, P_2^b, P_3^b, P_4^b, P_5^b – the value of basic indicators of the organoleptic properties of samples ($P_1^b = P_2^b = P_3^b = P_4^b = P_5^b = 5$); M_1, M_2, M_3, M_4, M_5 – weight coefficients of corresponding organoleptic indicators ($M_1 + M_2 + M_3 + M_4 + M_5 = 1.0$).

The samples were made of chemically modified food starch from high amylose corn, modified food starch, gelatin, glycerin, and water. Film-forming solution was applied on finished products and kept for 25–35 min to form a film on the surface.

The samples were examined in a nitrogen atmosphere on Universal V4.7A TA Instruments Q2000 (DSC), the mass of the sample was 10–20 mg, and TGA Q50 V20.10, sample weight was 2.5–7 mg; heating rate of samples – 20 K/min at temperatures ranging from 293 to 523 K.

The glass transition temperature (Tg) and the glass transition interval (ΔT), the heat jump (ΔCp), melting temperature (Tm) and the enthalpy of melting (ΔH) were determined. The samples were heated twice. The glass transition temperature (Tg) was determined as the middle of the glass transition interval ($\Delta T = T_0 - T_e$, where T_0 – temperature in the beginning of glass transition; T_e – temperature at the end of glass transition).

3. Results and Discussion

One of the factors determining the consumer choice is organoleptic characteristics of confectionery with particular film, which is calculated by complex indicator of quality. The investigated products were evaluated in accordance with Ukrainian regulations. Organoleptic indicators were determined by complex organoleptic index of quality and calculated according to Eq. (1).

The highest complex organoleptic index of quality 1.0 is for products with films; 0.9 is for products without film, since a film has a positive effect on the look of the products leveling uneven surfaces and giving glitter, as shown in Fig. 1.

Besides, the use of the film will allow not to use single-piece packaging of fondant candies and bakery products, the syrup for gingerbreads and sugar for the surface marmalade products. That's why the use of film for these products is undeniable.

To improve processing properties of the film it is necessary to examine the changes taking place with the constituents of the film during its thermal treatment. With this aim DSC analysis was used.

Fig. 2 shows thermograms of film examples during the first heating. Several endothermic peaks are observed on all thermograms. Wide endopeak in the range of 323–423 K with maximum peaks at the temperatures of 358–373 K corresponds to evaporation while the presence of a narrow peak on 3 and 5 samples at the temperature of 368–373 K can correspond to melting of crystalline region of gelatin. In films with greater content of glycerol (Table 1, samples 3, 5) we can observe a significant shift of narrow peak of gelatin melting (Fig. 2) into a region of lower temperatures and peaks overlapping.

In the samples with lower content of glycerin (Table 1) there is a higher separation of these endopeaks (Fig. 2, samples 1-4).

When comparing the melting temperature (Fig. 2) it appears that increase of gelatin proportion in the composition of the film increases the melting point, due to higher interaction of components through hydrogen bonding and polarity of gelatin chemical structure.

The increase of glycerol fraction reduces the melting temperature, which corresponds to authors' studies [11], who noted that a plasticizer with low volatility, high boiling temperature and low freezing temperature has a bigger free volume than a polymer free volume. Thus, the appending of plasticizer increases the free volume in the system, which leads to lower melting temperature.

Reduction of intermolecular interaction is particularly becoming apparent if polymer has strong intermolecular bonds, such as hydrogen. Moreover, plasticizer screens polar groups of gelatin, which prevents the formation of polymer-polymer bonds. The more of plasticizer is added, the more intensely melting point is reduced.

In the second heat-up (Fig. 3), melting phase transition is not observed, which indicates amorphization of composites after heating.

According to the obtained results the glass transition temperature is lower while reducing the beginning of glass transition temperature (see Table 2). Besides, the increase of gelatin in the gelatin and starch ratio in the film and gelatin in the ratio with dry matters leads to raise of the glass transition temperature (see Table 2). Over the same ratio of starch and gelatin in the composition of the film, even in a different value of their content, samples have similar glass transition temperature (Table 2, samples 4-6). The obtained results can be explained by the structure of gelatin, which due to the polarity of its structure connects other components of the film, which also helps to strengthen the system as a whole.

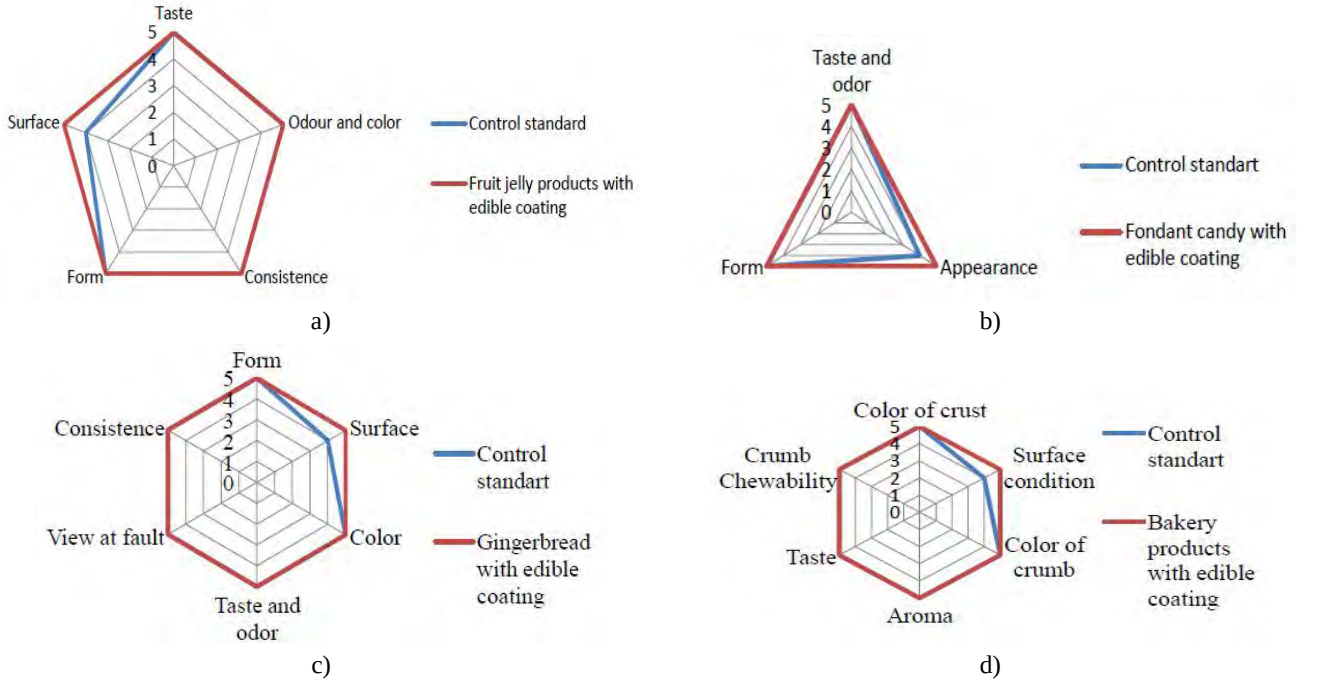

Fig. 1. Profilographs of examined marmalade (a); fondant sweets (b); gingerbread cakes (c) and bakery products (d)

Table 1

Film content

Samples	Film content, g/100 g film solution		
	Starch from high amylose corn starch	Gelatin	Glycerin
1	3	1.5	1
2	1	2	1
3	4	2	2
	Starch from modified food starch		
4	3	3	1.5
5	3	3	3
6	1	1	0.5

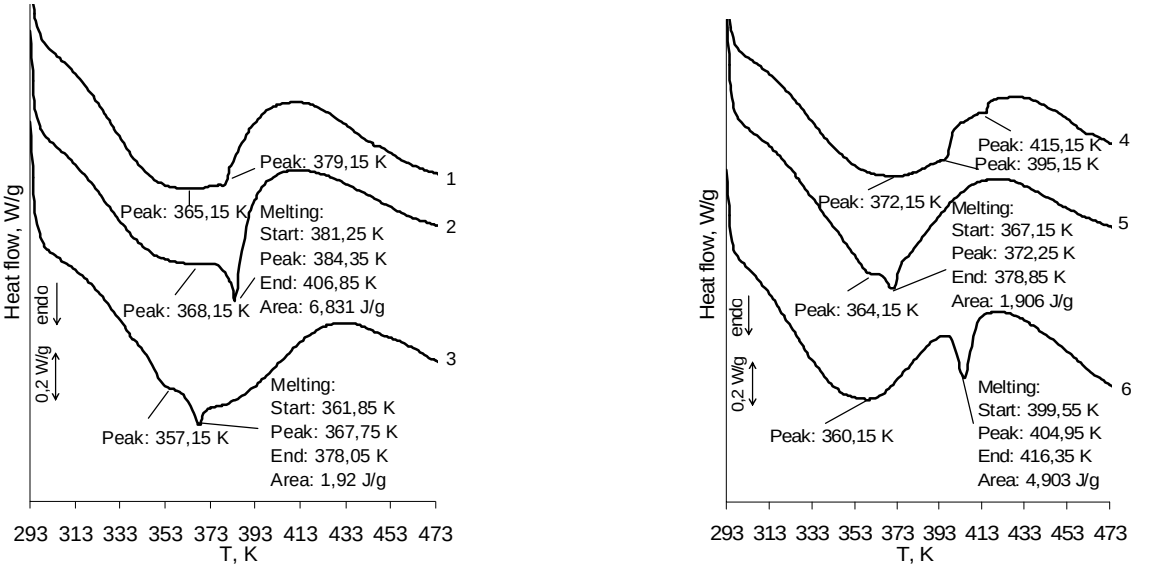

Fig. 2. Thermographs of sample films from starch, gelatin, glycerin of the first heat-up

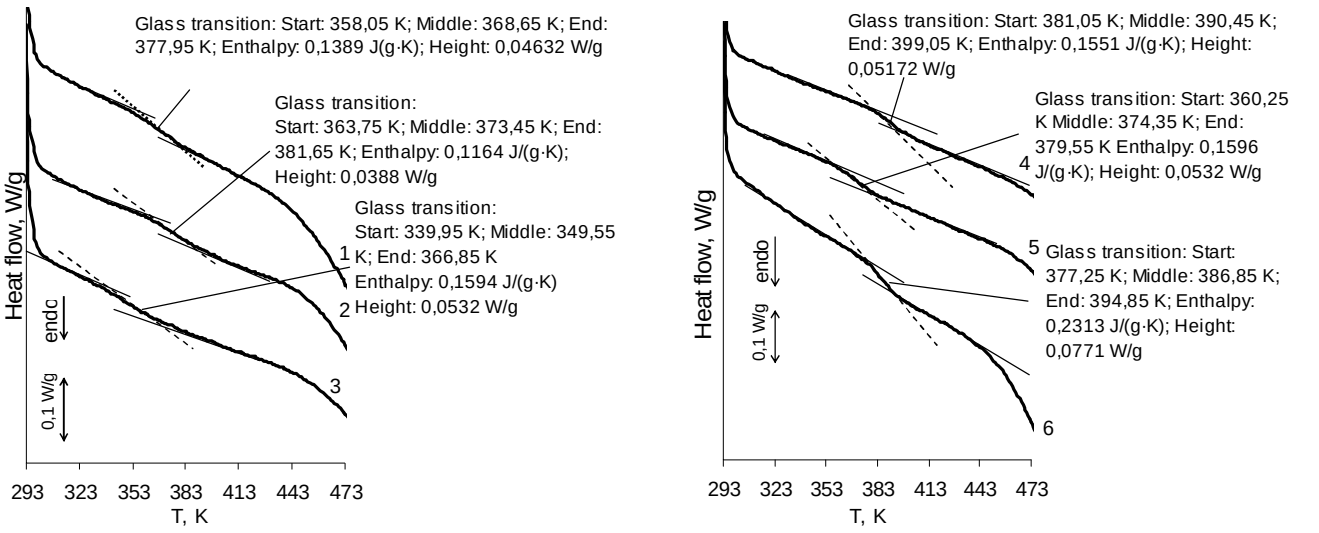

Fig. 3. Thermographs of film samples from starch, gelatin, glycerin of the second heat-up

Table 2

Change in the glass transition temperature, depending on the ratio of raw ingredients

Film samples	Dry substance content in the film, %	Temperature at the beginning of glass transition, K	Interval of glass transition temperatures, K	Ratio of film constituents			
				starch and gelatin	gelatin and starch	starch and dry substances	gelatin and dry substances
1	5.5	368.65	292.65	2:1 (2.0)	1:2 (0.5)	3:5.5 (0.54)	1.5:5.5 (0.27)
2	4.0	373.45	291.35	1:2 (0.5)	2:1 (2.0)	1:4 (0.25)	1:2 (0.5)
3	8.0	349.55	300.05	2:1 (2.0)	1:2 (0.5)	1:2 (0.5)	1:4 (0.25)
4	7.5	390.45	291.15	1:1 (1.0)	1:1 (1.0)	3:7.5 (0.4)	3:7.5 (0.4)
5	9.0	374.35	292.45	1:1 (1.0)	1:1 (1.0)	1:3 (0.33)	1:3 (0.33)
6	7.5	386.85	290.75	1:1 (1.0)	1:1 (1.0)	1:2.5 (0.4)	1:2.5 (0.4)

In works [12-17] it was found that heating of gelatin to the temperature that is much higher than the glass transition temperature (glass transition temperature is 343–363 K, heat-up is 433–453 K) causes destruction of the gelatin crystalline area and it behaves like a molecular-dispersed molten plastic. However, endothermic peak remained when heated to a temperature slightly above the melting temperature (378–388 K).

The occurrence of glass transition temperature in melting area can also be explained, according to the works [18, 19], by conformational reorganization of links, taking place during stress relaxation. The authors of this works consider that the endothermic peak in the glass transition area reflects physical aging of polymer. However, relaxations of residual stresses (enthalpy relaxation) occur. To determine *Tg* accurately it is necessary to relieve the internal stresses in the material by heating to the temperature that is at least 25 K higher than the glass transition temperature.

The data in the Table 2 show that higher concentration of solids in the film solution leads to higher interval of glass transition temperature (sample 3) and, accordingly, the lowest concentration of solids in the film solution leads to shortest interval of glass transition temperature (sample 6).

Two types of modified starch are used in mixtures with gelatin and glycerin. Among the films of starch from high amylose corn (samples 1-3), sample 3 with the ratio of components 2:1:1 must be noted, which stands out by its thermophysical characteristics. The smallest glass transition temperature during the highest jump in heat capacity (ΔC_p) and increase of the interval of glass transition range may indicate lower density of hydrogen bonds and its higher heterogeneity. Reduced temperature and enthalpy of melting indicate a higher degree of amorphous system.

Modified food starch films (samples 4-6) are characterized by higher glass transition and melting temperatures, which may be caused by formation of a more densely linked system than the previous ones. Such starch contains more amylopectin in its composition, which has a more branched structure because of the presence of 1,6-glycoside bonds as compared with amylose, whereas high amylose starch 4 has mainly 1,4-glycosidic bonds, creating a linear structure (Fig. 4).

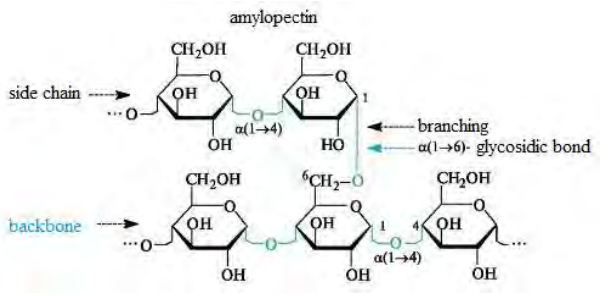

Fig. 4. The spatial structure of starch components

Fig. 4 shows that each molecule of glucose, which is a part of amylopectin chain, is closer to each other, which enhances formation of hydrogen bonds, fastening the system, and thereby increasing the phase transition temperature.

4. Conclusions

Using biodegradable films, namely edible coatings, to prolong the shelf life of confectionery positively affects the organoleptic properties of gingerbread, marmalade, fondant sweets, and bakery products and improves the surface look of these products.

The glycerol as plasticizer allows to lower the melting point and glass transition temperature of starter compounds of biodegradable film. Increase of gelatin in the compound of gelatin and starch and gelatin fraction in solids increases the glass transition temperature of the film. A more linked and therefore stronger structure is formed in the samples from modified food starch. The smallest chemical interaction is observed in samples from chemically modified food high amylose corn starch and, as a result, in samples from modified starch lower glass transition temperature (349.4–373.3 K) *versus* (374.2–390.3 K) is observed.

As a result, DSC analysis confirmed the functionality of using glycerol as plasticizer of a film. Besides, the relation established by DSC allows to select components for film with desired properties.

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ДИФЕРЕНЦІЙНО-СКАНУЮЧА КАЛОРИМЕТРІЯ ДЛЯ ДОСЛІДЖЕННЯ БІОДЕГРАДАБЕЛЬНОЇ ПЛІВКИ КОНДИТЕРСЬКИХ ТА ХЛІБОБУЛОЧНИХ ВИРОБІВ

Анотація. *В роботі досліджено біодеградабельні плівки для хлібобулочних і кондитерських виробів за допомогою диференційно-скануючої калориметрії. Визначено ступінь кристалічності полімеру та кінетику кристалізації. Досліджено вплив пластифікатора у складі плівки (гліцерину) на температури плавлення та склування вихідних сполук біодеградабельної плівки.*

Ключові слова: *біодеградабельні плівки, диференційно-скануюча калориметрія, кондитерські вироби, хлібобулочні вироби.*