E3S Web of Conferences **161**, 01097 (2020) https://doi.org/10.1051/e3sconf/202016101097
*ICEPP-2020*

# Research of structure formation of the dairy products containing functional ingredients

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**Abstract.** The objective of the research work is studying the process of structure formation of the cheese products containing functional ingredients. On the basis of conducted research it was found that the developed model mediums made it possible to recommend Carrageenan-C100 in the proportion of 1.5% of the weight of the cream for stabilizing and structure formation of the new product with the use of fermented cream. Combined use of an emulsifying salt and a thickener allows manufacturing a product having a stabile plastic consistency on the basis of a mixture of two basic ingredients (a solid and a liquid ones).

## 1 Introduction

Dairy products are the most important component of human diet. They satisfy 20% of human needs for protein and 30% of human needs for fat. The works in the field of dairy products manufacturing technology aimed at the development of technological processes of manufacturing products having predefined properties as well as at the complex use of raw materials have the highest priority. When designing a composition of a dairy product with predefined nutritional and biological values its texture should be taken into account as one of important quality indicators [1].

Texture is characterized in the first place as an organoleptic indicator. But under the present-day conditions the quality control of dairy products and particularly the control of their texture with the use of the techniques of physico-chemical mechanics has become widespread. The choice of a technique for quality evaluation of a dairy product depends on its texture.

Processed cheese may be defined as a product having plasticity and gel structure. The traditional technology of processed cheese manufacturing requires including into the formula such dairy products as various natural cheeses and special cheese masses, full fat and fat-free quarks, dried whey, butter milk, milk protein concentrates, cream, butter etc. The mixture of such ingredients usually undergoes fine dispersion and blending with emulsifying salts and also with non-dairy ingredients. The structure formation of such multicomponent mixture is a complex process and depends on a range of factors: the degree of ripeness of cheeses, the degree of dry products solubility, the type and proportion of emulsifying salt, melting temperature etc.

The technology of manufacturing of processed cheese for specialised nutrition differs in the fact that the basic (dairy) raw material is represented by two ingredients:

- cheese and/or cheese mass with shorter ripening duration and distinct ability for phase change under the influence of emulsifying salts which types and proportions are selected in an experimental way;
- fermented cream containing prebiotic and probiotic microflora which allows to define it as a symbiotic biocomponent [2].

We studied the influence of the thickener used to combine the said basic ingredients into a uniform structure and also binds free water and prevents synaeresis during storage. According to the technical regulations of the Eurasian Customs Union (TP TC 033/2013) the combination of an emulsifying salt and a thickener is a compulsory technological requirement.

Having studied the findings of the experimental research done by A.M. Shalygina, N.I. Dunchenko, I.A. Evdokimov, O.V. Lepilkina, A.B. Maremshaova in the field of substantiation of the foodstuff structurization process and the degree of influence of stabilization system we used in the present work the NMR relaxation technique [3, 4, 5, 6].

## 2 Materials and methods

Main study was conducted in the laboratories of Omsk State Agrarian University, now Kemerovo State University, certified production testing laboratory "Manros-M" the branch of OJCS "WBD", The Centre of New Chemichal Technologies, Federal Research Center Boreskov Institute of Catalysis (Omsk branch).

We conducted the research based on the following model systems:

- 30% fat cream and the thickener of plant origin Carrageenan-C100;
- the control system – cream without Carrageenan-C100;
- test 1 – addition of 0.5% of Carrageenan-C100;

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https://doi.org/10.1051/e3sconf/202016101097

- test 2 – addition of 1% of Carrageenan-C100;
- test 3 – addition of 1.5% of Carrageenan-C100;
- test 4 – addition of 2% of Carrageenan-C100.

The tested products were examined 60 minutes after the introduction of carrageenan.

The nuclear magnetic resonance technique (NMR), which is the main technique for the identification of organic compounds, is used also for foodstuffs analyzing. Particularly NMR relaxation technique was used for the determination of relative quantity of both bound and free water in dairy products [4, 5]. Despite the complexity of the analyzed systems and limited physico-mathematical rigor of the techniques used, the correlation between the values obtained through the NMR technique which supposedly represent relative quantity of both bound and free water and various properties of foodstuffs.

In the majority of published works in the considered field of study, the relaxation rate of transversal magnetization of protons of water is measured using a standard technique which utilizes Carr-Purcell-Meiboom-Gill pulse sequence introduced in 1958. In relaxation analysis of dairy products the obtained time dependency of the decrease in transversal magnetization is reasonably defined by exponent Ae-t/T2 (1) or in some cases by a sum of exponential functions:

$$A_1 e^{-t/T21} + A_2 e^{-t/T22}, \quad (1)$$

where $T_{21}$ and $T_{22}$ are the times of transversal or spin-spin ($T_2$) relaxation that correspond two types of protons in a molecule of water which are involved in relatively fast or slow in three-dimensional rotations in comparison with resonance Larmor frequency. The protons which are characterized by a slower spin-spin relaxation and a greater value of $T_2$ are found in faster moving free molecules of water. Another molecules of water in foodstuffs move slower for example as a result of interaction with hydrophylic macromolecules of proteins and polysaccharides hence the corresponding protons in them are characterized by a higher spin-spin relaxation rate or a lesser value of time $T_2$. Besides the sum of exponential functions (formula 1) theoretically may reasonably approximate the obtained curve only upon the condition that the diffusional transfer between the protons of bound and free water is slower compared to the relaxation rate.

It can be assumed that the values of preexponential factors $A_1$, $A_2$ in the formula 1 given above are in proportion to the quantities of bound and free water in the system and can be used to determine the correlation of these values with various properties of foodstuffs [6].

## 3 Results and discussion

The objective of the developed method was in adaptation of the above said technique to the determination of the correlation of the quantities of bound and free water in the samples of model mediums (cream - carrageenan) using the equipment and software available in Research Institute of Problems of Hydrocarbons Processing (RIPHP, Omsk).

For the processing of experimental data we used *Math CAD-14 Professional* software.

The measurements were made using NMR spectrometer *Avance-400* (produced by firm Bruker) at Larmor frequency of protons of water ~ 400 MHz with the use of cmpg impulse programme for the measurement of spin-spin ($T_2$) relaxation by Carr-Purcell-Meiboom-Gill technique. The obtained relaxation curves were approximated by the sum of one (2) or two (3) exponential functions with the help of *Origin* software.

Modelling of dropdown curves using the following functions

$$I(t) = A \cdot \exp\left(-\frac{t}{T_2}\right) \quad (2)$$

or

$$I(t) = A_1 \cdot \exp\left(-\frac{t}{T_{21}}\right) + A_2 \cdot \exp\left(-\frac{t}{T_{22}}\right), \quad (3)$$

was carried out with varying of the parameters A (or $A_1$ and $A_2$) and $T_2$ (or $T_{21}$ and $T_{22}$) using Origin 6.0 software (Microcal Software, Inc.) Convergence of the modelled curves with the experimental data was achieved by numerical minimization of $R^2$ criterion using the Levenberg-Marquardt algorithm. Convergence quality was evaluated using the correlation coefficient $r^2$.

The results of the modelling are represented in tables 1 and 2 as well as in figure 1-4. In the case of test 1 a better convergence is achieved using a two-exponential function (3). At that $r^2 = 1$ (table 2, fig. 1b). For tests 2-4 (see table 1) sufficient convergence was observed when one-exponential function (2) was used. This may happen due to very small contribution of the term containing $T_{22}$ value into the sum (3). The tending to zero of the second exponent is achieved in the case of very low values of $T_{22}$ (< 1 ms).

**Table 1.** The results of the modelling of the dropdown curves using a function (2).

| № | File path | A×10$^{-10}$ | $T_2$, s | $r^2$ |
|---|---|---|---|---|
| 1 | T2 090215 0/2/pdata/1 | 4.6±0.2 | 0.088±0.003 | 0.9952 |
| 2 | T2 090215 05/1/pdata/1 | 19.7±0.3 | 0.0341±0.0003 | 0.9998 |
| 3 | T2 090215 1/1/pdata/1 | 129.0±6.0 | 0.0265±0.0008 | 0.9989 |
| 4 | T2 090215 15/1/pdata/1 | 23.5±0.8 | 0.0321±0.0008 | 0.9990 |

**Table 2.** The results of the modelling of one of the dropdown curves using a function (3).

| File path | $A_1$×10$^{-10}$ | $A_2$×10$^{-10}$ | $T_{21}$, s | $T_{22}$, s | $r^2$ |
|---|---|---|---|---|---|
| T2 090215 0/2/pdata/1 | 3.32±0.03 | 3.25±0.08 | 0.1082±0 .0006 | 0.0260± .0008 | 1 |

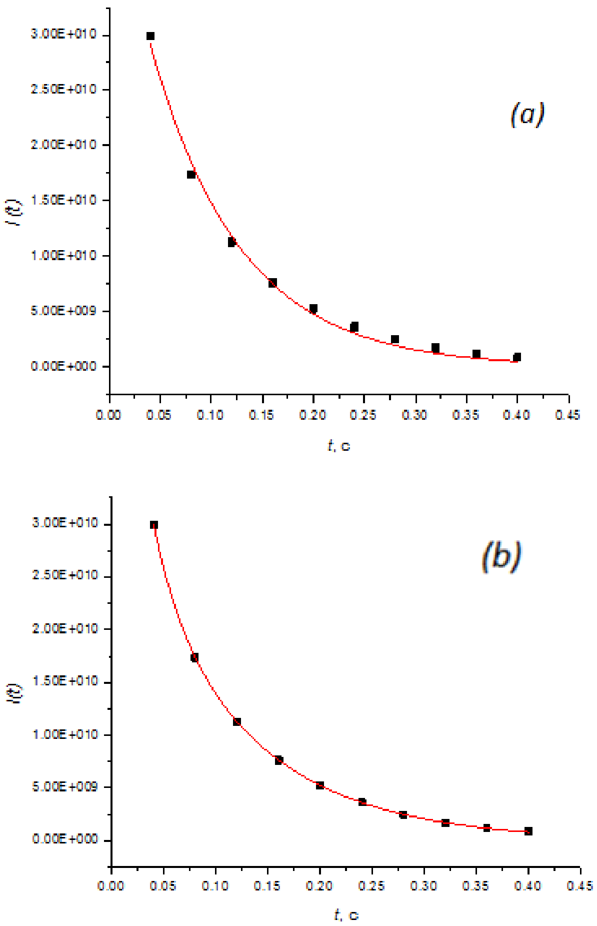


**Fig. 1.** T2 090215 0/2/pdata/1.

(a) Modelling using a function (2), the curve parameters are given in table 1. (b) Modelling using a function (3), the curve parameters are given in table 2.

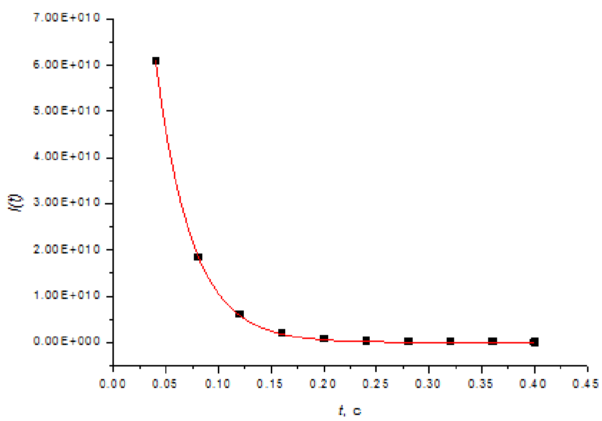


**Fig. 2.** T2 090215 05/1/pdata/1.

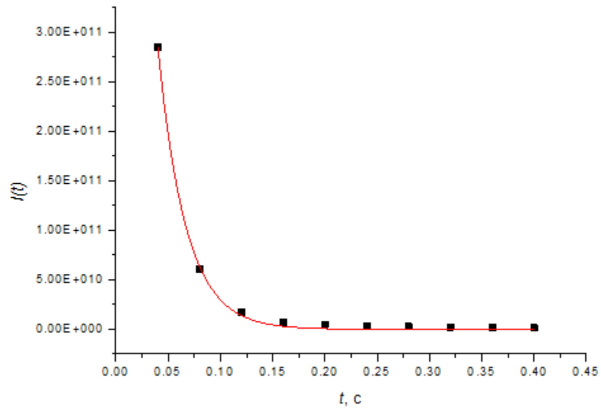


**Fig. 3.** T2 090215 1/1/pdata/1.

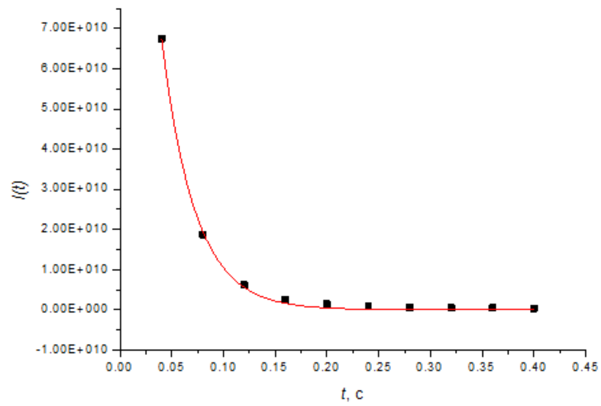


**Fig. 4.** T2 090215 15/1/pdata/1.

As is shown in figures 1-4 and in table 1 the exponential function (2) describes well the analyzed relaxation curves for all four samples and the obtained time values of spin-spin relaxation correspond the literature data [7, 8, 9]. Only in the case of a less viscous sample 1 we managed to show that a two-exponential function (3) approximates the obtained relaxation curve better than ordinary function (2) (figure 2, tables 1,2). Though even in this case the obtained relative values of preexponential factors $A_1$, $A_2$ are too close compared to similar values which are experimentally determined for milk and mozzarella cheese [7, 8, 9].

## 4 Conclusion

Therefore we obtained reliable values of spin-spin relaxation times T2 of the model mediums which made it possible to recommend Carrageenan-C100 in the proportion of 1.5% of the weight of the cream for stabilizing and structure formation of the new product with the use of fermented cream. Combined use of an emulsifying salt and a thickener allows manufacturing a product having a stabile plastic consistency on the basis of a mixture of two basic ingredients (a solid and a liquid ones).

On the basis of the conducted research technologies were developed and also corresponding regulatory and technical documents were approved in due order; the novelty of technologies and formulas of the described above processed cheese products is represented in

Russian Federation patents № 2380914, № 2466545, № 2450527, № 2431409, № 2458516, № 2465775, № 2477611 [10, 11, 12, 13, 14, 15].

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