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POSITRON ANNIHILATION STUDY OF STRUCTURAL RELAXATION AND CRYSTALLIZATION OF GLASSIFIED MILK FAT

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Abstract. Kinetics of the milk-fat phase transformations and the features of its defect structure in amorphous, crystalline and liquid states were studied using the positron annihilation technique. The highest concentration of the free-volume type defects with the average radius of 0.36 nm was found for the amorphous state and the lowest concentration for the crystalline one. It is shown that glassified milk fat can be transformed to the liquid state (bypassing crystallization stage) upon rapid heating.

Keywords: milk fat, amorphous, crystallinity, defect structure

INTRODUCTION

Consistence of butter as a nutrition product is its major characteristics depending on a number of physical properties such as strength, plasticity, and elasticity [1]. Earlier the features of milk-fat crystallization from the melt were studied as well as their effects on the properties of butter [1]. Properties of the glassified milk fat and peculiarities of its structural relaxation have not been investigated yet. At low temperatures (near the glass-transition temperature), the viscous flow is characteristic of all amorphous (glassy) materials and is due to the absence of crystallographic planes which are usually the cause of crack formation, cleavage and brittle fracture of crystalline solids [8]. In this regard, an increase in the fracture strength of the butter's fat component could be achieved through the formation of an amorphous structure under rapid and deep cooling.

Amorphous materials obtained by rapid cooling from the liquid state below the glass-transition temperature exhibit disorderly and unstable structure which undergoes temporal relaxation towards the 'ideal' metastable state with lower free energy. As in the case of metal glasses and polymers, structural relaxation of the glassified milk fat is not the initial stage of crystallization and may be a cooperative molecular process involving the decrease of the excess free volume as a result of defect annealing, healing of voids and intermolecular cavities as well as the variation in the short-range molecular order.

Disturbances in ordered (crystalline) arrangement of molecules, which occur under melting or glassification, result in the increase of volume and decrease of the packing index. Free volume also undergoes an abrupt change upon crystal-to-liquid transition and the most disordered state (with the largest entropy) is thought to be the liquid one [8].

In the case of milk fat consisting (up to 98%) of triglycerides of different composition and structure with the melting points varying in the wide temperature range (from -40 to +40 °C), thermodynamics and kinetics of phase transformations can essentially differ from those characteristic of the aforementioned materials.

Experimental study of the milk fat is expedient to be performed by means of the positron annihilation technique (PAT). Positron spectroscopy is an effective tool for the studies of free volume variations in polymers and molecular substances. Annihilation of positronium (Ps) atom (the bound hydrogenlike state of an electron-positron pair) inside intermolecular cavities allows to determine the average radius and size distribution [7] as well as the shape asymmetry [4] of these subnanovoids. The method is highly sensitive to the local imperfections of the ideal crystalline structure and, in particular, to those occurring under the phase transitions of pure triglycerides [9,10]. It should be expected that transition from a disordered glassy state to the most stable crystalline state (with the lowest defect concentration) which is commonly accompanied by an abrupt variation of PAT parameters [5] could be also detected for milk fat.

The PAT studies of glassification, structural relaxation, and crystallization processes are important in forecasting the kinetics and possible means of the milk-fat transfer from an amorphous to crystalline and liquid states. Therefore, the present study was pertormed to elucidate the features of the structural relaxation in the glassified milk fat, an extent of structural disorder in the rapidly cooled solid state, as well as in the liquid one, compared with the most stable and perfect crystalline state.

MATERIALS AND METHODS

The angular correlation of annihilation radiation (ACAR) was measured using a standard long-slit spectrometer with sodium-22 of 1 mCi activity as a positron source. The ACAR spectra were fitted to a sum of two gaussians, the broad (BG) and narrow (NG) one, by means of the least-squares method:

$$N(\theta) = I_1(\mathrm{BG}) \exp(-\theta^2/2\sigma_1^2) + I_2(\mathrm{NG}) \exp(-\theta^2/2\sigma_2^2) \qquad (1)$$

where θ is an angular deviation of the two annihilation gamma-quanta from 180°; I_1(BG) and I_2(NG) are the maximum intensities of broad and narrow gaussians, respectively; σ_1^2 and σ_2^2 are their dispersions.

Positrons which contribute to the BG, annihilate mainly with core-electrons of oxygen ions (as the most electronegative element of triglyceride molecules). The NG results from the self-annihilation of Ps localized inside the free-volume defects. Localization radius, r_m, for the core-electron wave functions was determined from the expression [3]:

$$r_m = (3/2)^{0.5}\, \hbar / mc\sigma \qquad (2)$$

where m is an electron mass, $\hbar$ is the Planck constant; c is the light velocity. Relative areas of gaussian components are equal to the probabilities of positron annihilation with electrons localized at oxygen ions and Ps annihilation in the free-volume regions.

Equation (2) satisfies the uncertainty relation:

$$\Delta x\, \Delta p = \hbar / 2 \qquad (3)$$

from which it follows that the smaller is the excess free volume (defect size), the larger the widths (σ_i) of narrow and broad gaussians of ACAR spectra which provide information on the momentum distribution of electron-positron pairs.

The intensity of ACAR spectra near the maximum, I_m, (within the angular range about 5 mrad wide) was also measured as a function of time or temperature. This quantity is a sum of two gaussians` intensities at the maxima:

$$I_m = I_1(\mathrm{BG}) + I_2(\mathrm{NG}). \qquad (4)$$

The increase in the concentration of vacancies, voids, intermolecular cavities and other free-volume defects results in the increase of each gaussian intensity.

The average radius R of voids, intermolecular cavities and other free-volume defects where Ps self-annihilation occurs was calculated using the relation [4]:

$$R = 1.66/\sigma_{1/2} - 0.166 \quad (\mathrm{nm}) \qquad (5)$$

where $\sigma_{1/2}$ is the full width at half maximum (measured in mrad) of the narrow gaussian component. $\sigma_{1/2}$ and dispersion σ_i are related by the equation $\sigma_{1/2} = 2.35\sigma_i$. The values of $\sigma_{1/2}$ were corrected taking into account the angular resolution function (supposedly gaussian) with the full width at half maximum σ_{ang}=1.29 mrad. An effective radius of the oxygen anion, which depends on the nearest atomic environment and the presence of defects, was estimated using the formula $R_i = 1.35\ r_m$ [6].

The milk fat for PAT measurements was poured into a thin-walled cuvette (2 mm high and 15 mm in diameter), kept at 60 °C for 30 min and dipped into the liquid nitrogen. The sample was subsequently placed into the camera of the PAT spectrometer and the measurements of the ACAR shape variations were performed as a function of time (at 17 and 30 °C) and temperature (with individually cooled samples).

RESULTS AND DISCUSSION

Temporal dependence of the ACAR intensity at the maximum, $I_m(\theta = 0)$, for the rapidly quenched milk fat is shown in Fig. 1. For both curves measured at 17 (a) and 30 °C (b) two characteristic regions are visible: before (stage I) and after (stage II) the abrupt decrease in the intensity I_m. At the stage I, monotonous (with slight oscillation) decrease of the I_m occurs. At higher temperature (30 °C, (b)) decrease becomes more pronounced, transition to the stage II occurs earlier, and the drop ΔI_m between the first and second stages is smaller. After transition to the stage II, the intensity I_m also exhibits an oscillating behaviour. The ACAR spectrum for the milk fat and its decomposition into the gaussian components are shown in Fig. 2.

The results of calculation (Table 1) show that after rapid cooling of milk fat to the liquid

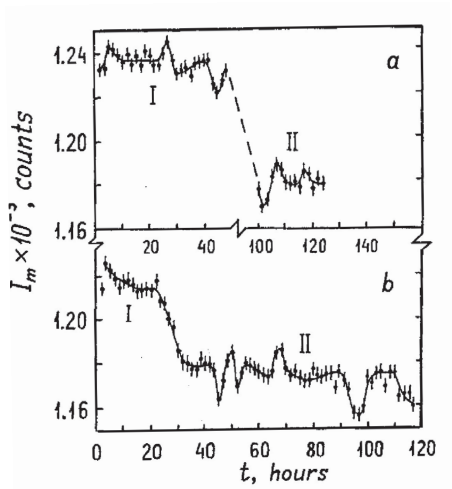

Fig. 1. Temporal dependence of the ACAR spectrum intensity (I_m) at the maximum for the milk fat at 17 °C (a) and 30 °C (b): I - stage I; II - stage II.

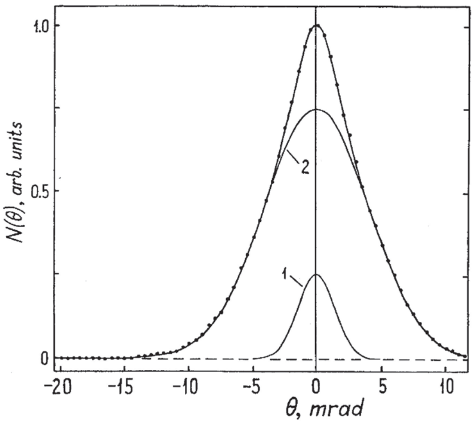

Fig. 2. Decomposition of the ACAR spectrum for the milk fat: 1, 2 - the narrow (NG) and broad (BG) gaussian components, respectively.

Table 1. Core-electron localization radius (r_m) at oxygen ions, the average radius (R) of positronium-trapping voids, and the relative areas (S) of the narrow (NG) and broad (BG) gaussians calculated from ACAR spectra for the milk fat

Parameter	Amorphous state (stage I)		Liquid-crystalline mixture (stage II)	
	NG	BG	NG	BG
S (%)	8.6 (±0.2)	91.4 (±0.2)	13.3 (±0.2)	86.7 (±0.2)
r_m (nm)	-	0.120 (±0.001)	-	0.113 (±0.001)
R (nm)	0.36 (±0.004)	-	0.27 (±0.004)	-

nitrogen temperature (stage I), both the average radius R of Ps-trapping voids and the average ionic radii are essentially (by 30 and 6%, respectively) larger than those characteristic of the milk fat at the stage II. This is the evidence that at the stage I, the milk fat was in the glassy state [2]. Oscillating behaviour of $I_m(t)$ for the rapidly cooled milk fat as well as its general decrease at the stage I are caused by the structural relaxation processes in amorphous phase including the reshuffle of the most weakly bound molecules towards configurations with lower Gibbs free energy. These processes are accompanied by the free-volume reduction and formation of liquid consisting of the low-melting components of the milk fat. Transition to the stage II at the $I_m(t)$ (Fig. 1) is due to the transition of the solid amorphous phase to the crystalline state consisting of high-melting glycerides of the milk fat.

To provide additional information on the states of milk fat at the stages I and II, temperature dependence of I_m was measured. The $I_m(T)$ curves shown in Fig. 3 were measured for the two states of milk fat: glassified and the mixture of crystalline and liquid phases (in the temperature dependent ratio). I_m is decreasing with growing temperature at the stage I (amorphous state) and increasing at the stage II (crystalline-liquid mixture). Dashed vertical lines denote transitions from the amorphous to crystalline state for the two milk fat samples kept at 17 and 30 °C. In the upper part of the plot there is the time elapsed from the milk fat's rapid cooling to its transition to the crystalline state. From Fig. 3 follows that the glassified solid milk fat can be easily transformed to the liquid state (bypassing the crystallisation stage) under rapid heating. Vice versa, the time needed to transform milk fat from amorphous to crystalline state is increasing with a decreasing temperature. This variation is accompanied by the increment of a distance ΔI_m between lines 1 and 2 (Fig. 3) reaching 7.3% at + 12 °C.

The PAT studies of the amorphous metallic glasses [5] show that during structural relaxation, the intensity of ACAR spectra at the maximum decreases, indicating the annealing of free-volume type defects. Simultaneously, the structure of the amorphous alloys relaxes towards a more stable (equilibrium) state. Taking account of the aforementioned results and general features of structural relaxation in the amorphous materials [8], stage I in the kinetic curves $I_m(t)$ (Fig. 1) is probably due to the structural relaxation of glassified milk fat. Transition to the stage II results from the crystallization of the most high-melting components of milk fat and subsequent formation of a crystalline-liquid mixture. As the mixture's temperature is raised, the relative fraction of the liquid phase grows due to the melting of the milk-fat components with higher melting points and, the intensity I_m increases linearly (Fig. 3). At 36 °C the $T_m(t)$ curve exhibits its maximum. It may account for the formation of defects at the interface between the liquid and the most high-melting crystalline fraction, followed by their subsequent disappearance as the temperature increases up to complete melting of the milk fat.

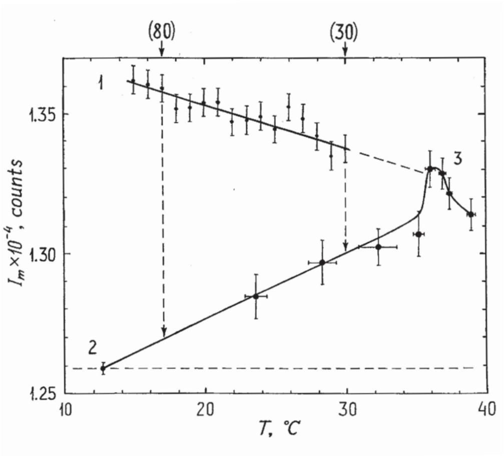

Fig. 3. Temperature dependence of the ACAR spectrum intensity (I_m) at the maximum measured for the milk fat in: 1 - the glassified state (least-squares linear fit); 2 - the mixture of crystalline and amorphous phases; 3 - the liquid state ('cusp'). Dashed vertical lines indicate the transfer of the glassified milk fat exposed at 17 and 30 °C to the crystalline state. In the brackets at the top there is time (in hours) elapsed from the milk fat's amorphization to its transition to the crystalline state.

CONCLUSIONS

1. The glassified milk fat is shown to contain the highest concentration of free-volume defects which decreases upon its transition to the liquid state, in contrast to inorganic and polymer materials.

2. Structural relaxation of the glassified milk fat is found to be a kinetic process, which is accompanied by the reduction of defect concentration and occurs faster with increasing temperature.

3. A decrease in the temperature of the glassified milk exposure leads to the increased persistence of its amorphous solid state and to a lower fraction of the liquid phase in the subsequently formed liquid-crystalline mixture.

4. It is shown that the glassified milk fat can be transformed to the liquid state (bypassing crystallization stage) under rapid heating.

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