

Application of the optical and positron spectroscopy to the study of structural transformations in milk fat and its simple purified fractions

V. Y. Kudryavtsev, S. M. Yablochkov
Taras Shevchenko Kyiv University, Physics Dept.
252127, Kyiv, Ukraine

S. P. Likhtorovich, M. M. Nishchenko
Institute of Metal Physics, National Acad. Sci of Ukraine,
252680, Kyiv, Ukraine

T. A. Rashevskaya, I. S. Gulyi
Ukraine State University of Food Technologies,
252033, Kyiv, Ukraine

The structural transformations in milk fat (MF) from amorphous to crystalline state as well as in simple purified fractions (SPF) were investigated by using optical and positron spectroscopy. The crystallization of amorphous MF leads to appearance of the prominent peak in the luminescence spectra of MF. The transmission and excitation of the luminescence spectra were also investigated at different temperatures. The results of optical study of MF and SPF are supplemented by the results of the positron spectroscopy of MF and SPF.

Introduction

Long chain compounds, such as MF, contain a various fractions, which can be occurred in different crystal forms, a phenomenon is known as polymorphism. It is widely acknowledged that the habit (size and shape) of crystals in a fat is related to the polymorphic state of the fat [1].

The most widely used method for studying of lipid polymorphism is X-ray diffraction. There are other well-known methods for studying of polymorphism such as low temperature infrared spectroscopy, differential scanning calorimetry, microscopy. In this work the photoluminescence and positron spectroscopy were employed in order to obtain an additional information on the influence of the structural transformations in milk fats and their simple purified fractions on their physical properties .

Experimental details

Amorphous phase of MF was obtained by the quenching of the melted MF from 340 K into the liquid nitrogen. Structural relaxation of amorphous phase to more equilibrium crystalline phase was obtained due to aging of this amorphous samples at different (273 and 293 K) temperatures during 90 days. Besides MF, two SPF were also investigated. SPF were extracted from MF by using fractional crystallization from its solution in acetone by separation at 286 and 273 K on the so-called "high-melting-point" (HM) and "low-melting-point" (LM) fractions, respectively.

Results and discussion

The luminescence spectrum of as-quenched amorphous MF is characterized by an intense peak with a maximum at 3.1 eV and several weak features on its low-energy shoulder

located at 2.6 and 2.8 eV. The aging of amorphous MF at 273 K as well as room temperatures during 90 days has led to an appearance of an additional prominent luminescence peak with a maximum at 2.38 eV. The relative intensity of this additional peak as well as weak features on the low-energy shoulder of main peak (in respect with main peak) is higher at the larger temperature of aging. It can be supposed that such a transformation of the luminescence spectrum of MF due to aging reflects the structural relaxation of amorphous structure towards the crystalline phase or crystallization of MF. Indeed, the structural study of MF by using microphotography as well as results of electron-positron annihilation confirms this supposition. An observed changes in the luminescence spectra are reversible, i. e. heat treatment of the aged MF to the liquid state (up to 340 K) nearly completely restores the primary luminescence spectrum measured in solid state (at 293 K). The intensity of the luminescence in the liquid state (measured at 340 K) is significantly lower than in the solid state. This decrease in intensity can be caused by several mechanisms, for example, temperature quenching. Even without an additional peak in the luminescence spectrum of aged MF which is located at 2.38 eV, main peak exhibits rather complicated structure and contains at least 3 components. It can be supposed that these peaks occur from the different SPF of MF. LM and HM SPF have a complicated luminescence spectra with maximums at 2.6 and 3.0 eV, respectively.

The transmission spectra of MF were investigated at room and elevated temperatures. All this spectra are characterized by absorption peaks at 3.9, 4.4 and 4.6 eV on the background. Transition from the solid state to the liquid one (with the increasing of the temperature up to 340 K) has led to the remarkable decrease in value of background, while the intensity and location of the 4.4 and 4.6 eV absorption peaks have not changed. The excitation spectrum of the luminescence for the MF exhibits intense peak at 3.9 and two weak peculiarities at 4.4 and 4.6 eV. The location of the components in the excitation spectrum exactly corresponds to the locations of the peculiarities in absorption spectra.

According to the results of the positron spectroscopy study the radius of nanopores depends on structural state of triglycerides of MF and its SPF and for all the investigated samples varies from 2.3 to 3.9 Å. The correlation dependence between an average radius of pores, R_p , and the probability of the positronium annihilation, S , was established that the larger R_p , the smaller S . The maximum value of radius for various structural states is changed in a very narrow range and varied from 3.6 to 3.9 Å. These values are rather close to the distances between chains in fat acids for different modifications of triglycerides (α , β and β'), that are 4.14, 3.78 and 3.68 Å, respectively [2]. Long term aging of HM SPF at room temperature during 90 days leads to a decrease in R_p from 3.6 to 2.2 Å. This decrease in average pore radius may reflect the structural ordering (crystallization) due to aging.

References

- [1] A. E. Baily, "Melting and Solidification of Fats and Fatty Acids, Interscience," New York, pp. 117 - 178, (1950).
- [2] W. W. Walker, W. G. Merrit, and G.D. Cole, "Phase dependence of positron annihilation in tristearin, Physics Letters," 40, 157, (1972).