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Ultrasonic effect for the acceleration of polymorphic crystallization on fats

Satoru UENO*[1], Morio TAKEUCHI[2], Jun-ichi SAKATA[1], Yoshinobu NOZUE[2], Yoshiyuki AMEMIYA[2], Kiyotaka SATO[1]
[1]Hiroshima Univ., Higashi-Hiroshima, 739-8528, Japan
[2]The Univ. of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

Introduction

A considerable interest has been shown recently in the use of high power ultrasound for encouraging nucleation and for modifying crystal growth [1]. It has been demonstrated that a high power ultrasound (sonication) can increase significantly the rate of nucleation in a crystallisation medium (sono-crystallisation) [2]. Quite recently, sono-crystallisation has been examined in confectionery fats, indicating the possibility that tempering is achieved by sono-crystallisation [3]. However, the events accompanying sono-crystallisation processes in fats still remain mysterious with the need to understand them in order to achieve the control.

This paper presents experimental studies on the effects of high power ultrasound on the crystallisation behaviour of the typical triacylglycerols, tripalmitin (PPP) and trilaurin (LLL), examined *in-situ* by time-resolved SAXS and WAXS techniques. An attempt is made to suggest a mechanism by which a sonication leads to the formation of a particular polymorph in these materials.

Experimental Section

Tripalmitin (PPP) and trilaurin (LLL) were used as the samples and were purchased from Sigma Chem.Co (St. Louis, MO). Both of them had a purity of more than 99% and were used without further purification.

Experiments were carried out using *in-situ* synchrotron radiation time resolved small angle X-ray scattering and wide angle X-ray scattering (SAXS/WAXS) simultaneous measurement combined with a sono-crystallisation system assembled from commercial components; a computer-controlled ultrasound generator (model DG-100-20; Telsonic Co., Bronschhoften, Switzerland) at 20 kHz and 100W. The duration of sonication was 2 s. The sample of 5 ml was put in a handmade special glass cell jacketed by circulating water and connected to two thermostats: one for melting (hot) and the other for crystallisation (cool). The window of the cell was made of Capton film of 25 μm thickness. A sample thickness exposed to a synchrotron X-radiation was 3 mm. In both cases, without and with sonication, the sample was first melted and heated up to 80 ℃ for (PPP) and 60°C for (LLL), then the sample was cooled down with jacketed water to a desired level. Experiments presented in this work were performed at BL-15A. Camera length of the SAXS was 1.1 m. For the WAXS, this length was 0.27 m for both samples. The system was operating at a wavelength of 0.15 nm.

Results and Discussion

Without ultrasound application, both polymorhic forms β' and β crystallised in the melt of each substance.

With ultrasound treatment of the melt the following effects were observed: (i) a marked decrease of induction times for crystallisation of both (PPP) and (LLL), (ii) an increased nucleation rate, and (iii) a crystallisation of only β forms for both (PPP) and (LLL) under conditions of initial crystallisation temperature of 50 ℃ and 30 ℃, respectively, and applied ultrasound of 2 s. The last finding demonstrates that ultrasound irradiation can be used as an efficient tool for controlling polymorphic crystallisation of fats. In addition to this, a crystallisation of (LLL) under lower initial crystallisation temperature of 25 °C and with the same ultra-sonication time of 2 s, revealed the presence of both β' and β polymorphs. This suggests that crystallisation of only β form depends on the initial temperature of crystallisation as well as on the duration of ultrasound treatment of the melt.

When a sonication is applied to the melt, three major simultaneous processes are taking place: (1) the local changes of compression, (2) absorption of energy from the applied sounds waves, and (3) cavitation. The effect (1) is manifested by a corresponding increase in local pressure. This will result in a local increase of melting points. As a consequence, the corresponding supercoolings with respect to the selected initial crystallisation temperature will increase, too. The higher supercoolings will lead to: (a) a higher probability for nucleation, (shorter induction time), and (b) an increase of nucleation rate. As for explanation of the nucleation of only form, we need to consider the additional effect (2), which is a consequence of interaction of ultrasound wave with a melt. The effect (2) causes the increase of temperature of samples. This results in a larger number of melting of β' clusters than that of β cluster.

As for the effect (3), cavitation, it is a future study for involving it to explain the results in this work.

References

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* sueno@hiroshima-u.ac.jp