Observation of Phase Behavior of Fat Crystals during Rapid Cooling

Elucidation of mechanism behind the formation of molecular compound

Achievements

- *In situ* observation of phase behavior and polymorphic changes of fat crystals during rapid cooling in margarine manufacturing process
- Determination of cooling rate and post-cooling heating temperature required for the formation of **molecular compound (MC)***
- The formation of MC will be controlled by adjusting the manufacturing conditions

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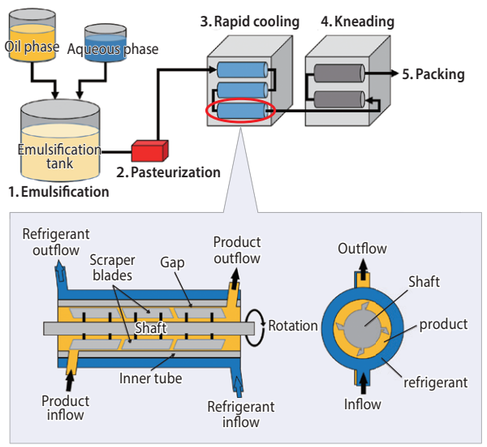
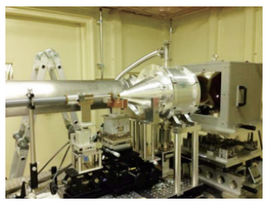
***MC**: Molecular compound crystal formed by binding different molecules at a certain ratio. Its properties are different from those of their component molecules. POP and OPO, the main components of palm oil and pork lard, respectively, form MC at a ratio of 1:1.

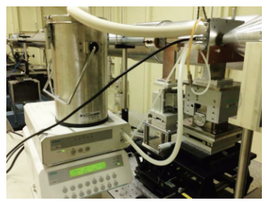
Manufacturing process of margarine

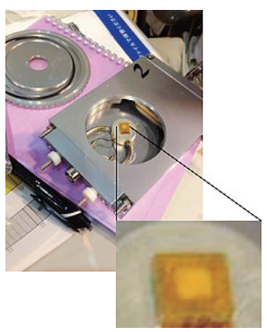


Margarine is manufactured by emulsifying the oil and aqueous phases, pasteurizing, rapidly cooling, kneading, and packing. In the process of rapid cooling and kneading, the product is cooled by a scraped-surface heat exchanger. The cooling rate is estimated to be at least 100 °C/min.

Time-resolved X-ray diffraction measurement at SPring-8







Time-resolved X-ray diffraction measurement was carried out using a small-angle scattering device at BL19B2. The sample was cooled slowly (5 °C/min) and rapidly (40 °C/min) from 100 to −50 °C using liquid nitrogen. Next, it was heated at a rate of 10 °C/min from −50 to 100 °C.

Role of SPring-8

Background

Recently, it has been reported that the consumption of foods with high contents of saturated and trans fatty acids increases the risk of diseases such as myocardial infarction and diabetes. However, oil and fat products such as margarine are required to have some degree of firmness for consistency and plasticity. If the contents of the saturated and trans fatty acids are decreased, the properties of oil and fat products will greatly change.

We focused on the MC as a means of solving the above problem. The MC crystals are rich in oleic acids, giving them a healthy image, and have moderate hardness because they are solid at room temperature. Thus, we expect to use them as alternatives to saturated and trans fatty acids. However, their crystal phase behavior during rapid cooling at a rate of ≥ 100 °C/min in the manufacturing process has not yet been clarified.

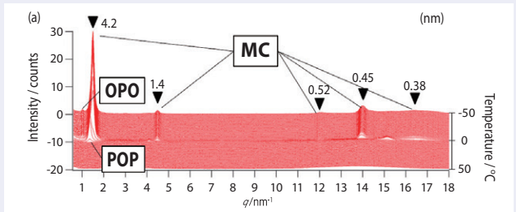
Results

In a preliminary experiment, we prepared a sample of MC crystals by mixing 1,3-dioleoyl-2-palmitoyl glycerol (OPO) and 1,3-dipalmitoyl-2-oleoyl-sn- glycerol (POP) at a ratio of 1:1 and measured a thermogram by differential scanning calorimetry (DSC) while changing the cooling rate. The thermogram clearly shows that the formation of MC greatly depended on the cooling rate and drastically changed at 40 °C/min and above.

Next, time-resolved X-ray diffraction measurement was carried out using high-brilliance synchrotron radiation at SPring-8, which enables the continuous observation of the behavior of fat crystals as they quickly change over a few seconds, as follows. The sample was cooled slowly (5 °C/min) and rapidly (40 °C/min). Next, it was heated (10 °C/min). The analysis of the phase behavior and polymorphic changes of the sample revealed the cooling rate required to form MC and the optimum temperature for its efficient formation. Therefore, the MC formation can be controlled by adjusting the cooling rate and product temperature.

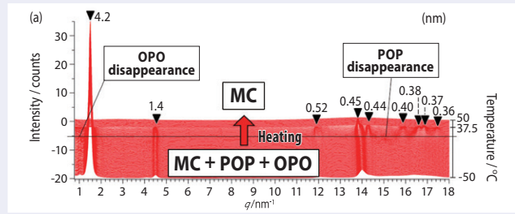
X-ray diffraction measurement under different cooling and heating conditions

A sample was prepared by mixing POP and OPO, the main component of palm oil and lard, respectively, at a ratio of 1:1. Time-resolved X-ray diffraction measurement was carried out during slow and rapid cooling and also during heating in the temperature range from −50 to −100 °C. We analyzed the phase behavior and polymorphic changes of MC crystals during cooling and heating. The results suggest the possibility of controlling MC formation by adjusting the cooling rate.



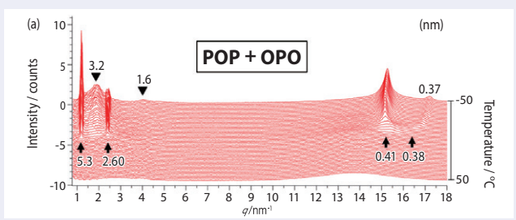
(1) Cooling rate, 5 °C/min

Strong diffraction peaks of MC crystals were observed, confirming that the MC was formed during slow cooling. Moreover, weak diffraction peaks of POP and OPO crystals were also observed, indicating that some of the POP and OPO were independently formed.



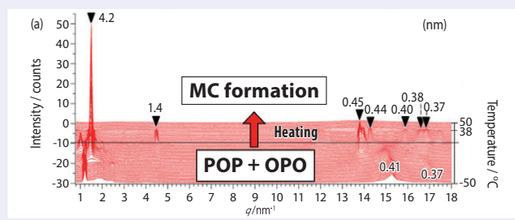
(3) Heating at 10 °C/min after slow cooling at 5 °C/min

The weak diffraction peaks of POP and OPO crystals disappeared upon heating. This indicates that the POP and OPO transformed into MC.



(2) Cooling rate, 40 °C/min

No diffraction peaks of MC crystals were observed, indicating that no MC was formed during rapid cooling.



(4) Heating at 10 °C/min after rapid cooling at 40 °C/min

As the diffraction peaks of POP and OPO crystals weakened, diffraction peaks of MC crystals started to appear and increased in the intensity while heating. This suggests that the POP and OPO that had formed independently transformed into MC upon heating.