# Storage of Commercial Margarine at Different Temperatures

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**The effect of storage temperature on the consistency of commercial margarine was analyzed by viscometry, differential scanning calorimetry (DSC), microscopy at low temperature and X-ray diffraction. The results obtained show that samples harden at 13°C and soften at 4°C. The greater strength of samples was apparently associated with crystals of higher melting points. Recrystallization takes place during storage leading to more stable solid solutions with higher melting points.**

KEY WORDS: Fat crystals, margarine, storage, triglycerides.

Characteristics which determine margarine quality such as consistency, spreadability, etc., are strongly influenced by processing, formulation and other variables. A number of studies have shown the tendency of triglycerides to crystallize as different crystalline forms which depend on the chemical composition of the fat-phase and on the cooling conditions prevailing during crystallization. It is also known that processing conditions affect the type of interaction among crystals and between the liquid and aqueous phases. These interactions, in turn, determine the final structure of the product (1-11).

The objective of this work was to study the effect of storage temperature on the consistency of a commercial margarine.

## MATERIALS AND METHODS

*Samples.* Samples were commercial margarine containing 82% fat phase formed from 57% hydrogenated sunflowerseed oil, 23% hydrogenated cottonseed oil and 20% sunflowerseed oil.

*Storage assay.* Samples were collected immediately after manufacture and placed in a box of expanded polystyrene for transport to the storage site. Two hours later, samples randomly taken were placed in two rooms, at 4 and 13°C, respectively. This time was considered as zero time. By then, the temperature of samples was 11°C. During storage, samples were randomly taken from both rooms at different times and were analyzed by means of viscometry, differential scanning calorimetry, microscopy at low temperature and X-ray diffraction.

*Rheological studies.* These studies were carried out in a Haake Rotavisco RV viscometer (Haake Mess Technik Co., Karlsruhe, Germany) equipped with a system of cone and plate, 0.3° conicity and 20 mm-diameter (PKI, 03). All runs were performed in duplicate at 15°C. To minimize structural alterations of the product by handling prior to the run, viscometer loading was systematized. Samples were subjected to a shear rate ( $\partial$ ) of 320 $s^{-1}$.

*Differential scanning calorimetry (DSC).* A differential scanning calorimeter (model 910 Du Pont Co., Wilmington, DE) was used for these experiments. Indium (In) was used as standard to measure the temperature and cell constant.

Fifteen to twenty mg of sample were placed in hermetically sealed aluminum pans and run at 10°C/min against air as a reference. *Calculations:* Melting of a piece of pure substance may be determined in a differential scanning calorimeter as the heat absorption peak which is thought to have a normal distribution. Complex mixtures, such as the fat phase of margarine, show patterns of complex melting. Taking into account that the sum of normal samples is another normal sample whose mean is equal to the average of individual means and its variance represents the sum of individual variances, it may be assumed that if a mixture of triglycerides exhibits this behavior (component distributions show the same mean), an overall endotherm will be obtained by differential calorimetry, this endotherm being the sum of all individual distributions of each component. In contrast, if such a mixture presents two or more distributions with different means, the addition of individual meltings will result in two or more differential distributions.

When triglycerides exhibit more than one crystalline form, they will be found as independent distributions.

In order to determine the number of different species in a given thermogram, each transition was analyzed as a single Gaussian curve, taking also into account whether the square error markedly decreased after the addition of one or more distributions. However, if the introduction of another distribution did not produce a further improvement, this procedure was then concluded. The procedure used was:

$$H = ae^{(-(T - b)^{2/\sigma})} + ce^{(-T - d)^{2/\sigma})} + \ldots \quad [1]$$

where a, c, etc. are the maximum peak heights; b,d,etc. the peak temperatures, and $\sigma$ the standard deviation.

An IBM personal computer with a simplex method program was used for these calculations. The application of the curve resolving technique was confirmed using artificial mixtures of triglycerides which have overlapping DSC melting peaks.

A similar procedure was used to study the iron binding to conalbumin (12).

*Microscopy at low temperature.* Size distributions of drops forming the aqueous phase were determined. For this purpose, different samples were analyzed; the drops were observed in a Leitz microscope (Ernst Leitz Co., Wetzlar, Germany) fitted with an automatic microphotographic apparatus, Leitz-Vario-Orthomat (Ernst Leitz Co., Wetzlar, Germany). Both transmitted and polarized light were used for some determinations. In each case, at least 500 drops were measured. Data obtained were analyzed statistically on an IBM personal computer using SYSTAT and LOTUS 1-2-3 programs.

*X-ray diffraction.* X-ray diffraction spectra were obtained by means of a Philips 1730 instrument (Philips, Argentina, South America) fitted with a system for temperature control. The sample holder placed within the refraction chamber was maintained at a constant temperature with a 3:1 solution of ethyleneglycol coming from a Lauda UK 30 cryostat (Messgerate-Werk Lauda, Lauda-Konigshofen, Germany). Radiations $K_{a1a2}$ from copper with 40 K V, 20 mA and a scanning velocity of 1°/min were used.

## RESULTS AND DISCUSSION

Two fractions, corresponding to a lot of commercial margarine containing hydrogenated sunflowerseed and cottonseed oils and liquid sunflowerseed oil, were stored 2 hr after production, at 4 and 13°C, respectively. At different storage times, samples were randomly taken, and their strength was determined by viscometry. Figure 1 shows a characteristic run, analyzed by equation 2 developed in our laboratory (13):

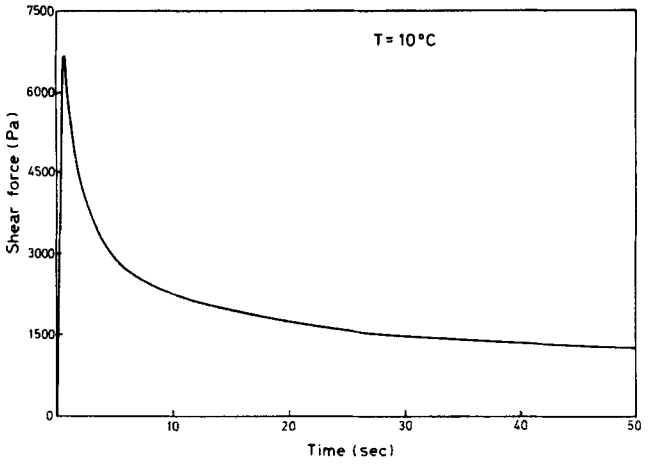


**FIG. 1. Shear force at 320 $s^{-1}$ as a function of time.**

$$\tau_0 = \tau_\infty + ae^{k_1 t} + be^{k_2 t} \quad [2]$$

where $\tau_\infty$ corresponds to the effort necessary for the sample to flow after the thixotropic effect had disappeared, the value of which corresponds to that of the constituent equation (14); $K_1$ and $K_2$ represent different constant destruction rates of proposed structure ($K_1 = 0.9\ s^{-1}$, $K_2 = 0.1\ s^{-1}$), a and b are the contributions of each structure to the cutting effort at zero time and t is the time.

Taking into account the physical interpretation of equation 2 given by us, sample strength resulted from two structures: the first one representing the fracture of primary structures among triglyceride crystals (2nd term of equation 2), and the other represents the interaction among drops of the aqueous phase and triglyceride crystals (3rd term of equation 2) (13).

Figures 2 and 3 show the values reached by each variable ($\tau_0$, $\tau_\infty$ a and b) during the storage time. It can be observed that the strength of samples stored at 4°C (Fig. 2) rapidly diminished from the beginning, reaching a minimum after 28 hr, and progressively increasing thereafter for at least 24 days. The contribution of parameter b to this behavior was fundamental, since it changes in a similar way. With regard to parameters a and $\tau_\infty$ they did not show any changeover during this period of time.

It must be noted that, at 13°C, strength (Fig. 3) changed in a different way. When storage started, it exhibited a marked increase, reaching its maximal value after 22 hr. After a 2-day storage, strength began to decrease significantly. Parameter b showed the greatest effect on sample strength, either at 4°C or at 13°C; a showed almost no change and $\tau_\infty$ increased slightly. Interestingly, samples stored at 4°C never reached the same strength as those kept at 13°C.

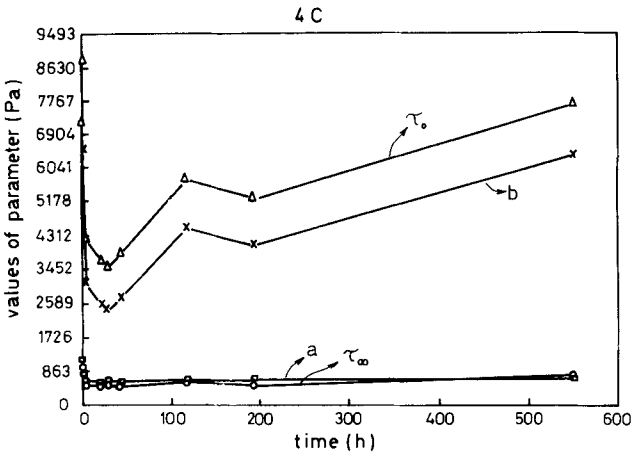


**FIG. 2. Variables (a, b, $\tau_\infty$) and the shear force ($\tau_0$) at 320 $s^{-1}$ as a function of storage time at 4°C. Determinations were performed at 15°C.**

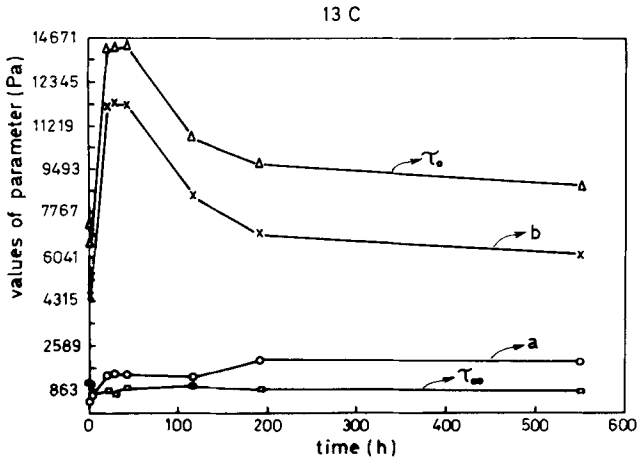


**FIG. 3. Variables (a, b, $\tau_\infty$) and the shear force ($\tau_0$) at 320 $s^{-1}$ as a function of storage time at 4°C. Determinations were performed at 15°C.**

All samples were from the same lot, nevertheless all of them showed different solid contents during the storage time, because some of them were maintained at 4°C while the others were kept at 13°C (higher and lower solid content, respectively). Instead, all rheological determinations were performed at 15°C; consequently no differences in solid content were found among the samples analyzed. The consistency of margarine is closely related to several factors, such as solid content of the fat phase, particle size and morphological state of crystals (15,16). In order to determine their influence, the size distribution of drops forming the margarine aqueous phase was analyzed at both temperatures and during the storage time; moreover, characteristics of crystals in the fat phase were analyzed by means of X-ray diffraction and differential scanning calorimetry.

No significant differences in size distribution (diameter, area and volume) of water drops (Table 1) were detected. This indicated stability of the mixture throughout the storage time. A consistent feature of all samples analyzed was

that very similar X-ray diagrams which indicated the predominance of crystals type $\beta'$ (Fig. 4) were obtained both at 4 and 13°C.

Calorimetric analyses, carried out during storage, demonstrated relevant differences among the samples (Fig. 5). Each thermogram obtained was analyzed using a mathematical method described in Materials and Methods. These data are shown in Figures 6 and 7. In Figure 6, at 4°C, it is noted that a marked increase of species with low melting point, especially those with a melting point of 17°C, could be observed at the beginning of storage (first 24 hr). Then, these species started to decrease, sometimes reaching proportions lower than 10%. Concomitantly, a significant increase was shown by species with a higher melting point (those with a 26°C melting point reached 30% and the others with a 33°C melting point reached more than 50%). At 13°C, a steady decrease was detected in species with low melting point just from the beginning of storage time, reaching proportions lower than 10% after a 24 hr storage. This decrease was parallel to an increase of species with greater melting point. Species of 26°C and 33°C melting point reached a maximum after 24 hr, which then diminished slightly.

TABLE 1

**Size Distribution: Diameter, Area and Volume of Water Drops as a Function of Storage Time at 13°C and 4°C**

| Storage time (days) | Mean diameter $\mu$ | $\sigma$ | Mean area ($\mu^2$) | $\sigma$ | Mean volume ($\mu^2$) | $\sigma$ |
|---|---|---|---|---|---|---|
| Storage temperature 4°C | | | | | | |
| 0.1 | 1.2 | 0.4 | 5.6 | 5.4 | 1.5 | 3.3 |
| 0.2 | 1.2 | 0.6 | 6.0 | 8.3 | 2.1 | 5.7 |
| 0.9 | 1.3 | 0.7 | 6.5 | 9.8 | 2.5 | 6.9 |
| 2.2 | 1.4 | 0.6 | 7.3 | 7.7 | 2.4 | 5.0 |
| 7.0 | 1.3 | 0.6 | 6.7 | 7.9 | 2.2 | 6.2 |
| 21.0 | 1.4 | 0.6 | 7.1 | 8.2 | 2.4 | 5.8 |
| Storage temperature 13°C | | | | | | |
| 0 | 1.5 | 0.7 | 9.3 | 10.7 | 3.6 | 8.0 |
| 0.7 | 1.4 | 0.5 | 6.8 | 6.2 | 2.1 | 3.7 |
| 0.8 | 1.3 | 0.5 | 6.1 | 7.0 | 1.9 | 4.8 |
| 2.0 | 1.3 | 0.5 | 6.3 | 6.2 | 1.9 | 3.5 |
| 7.0 | 1.5 | 0.6 | 8.6 | 7.6 | 2.9 | 4.7 |
| 21.0 | 1.2 | 0.6 | 5.7 | 7.2 | 1.8 | 4.5 |

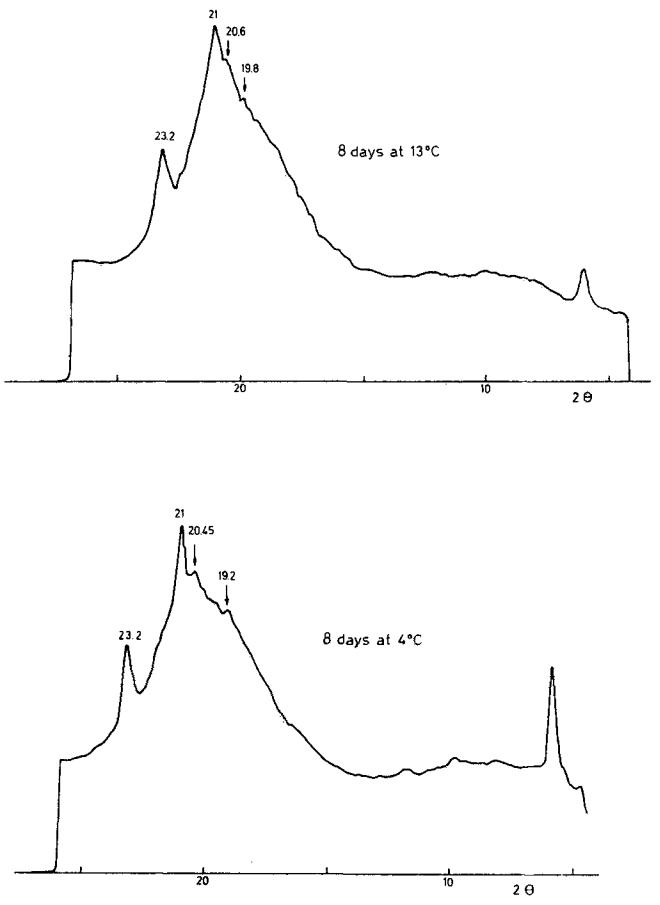


**FIG. 4. X-ray diffraction spectra of a commercial margarine stored 8 days at 4°C and 13°C.**

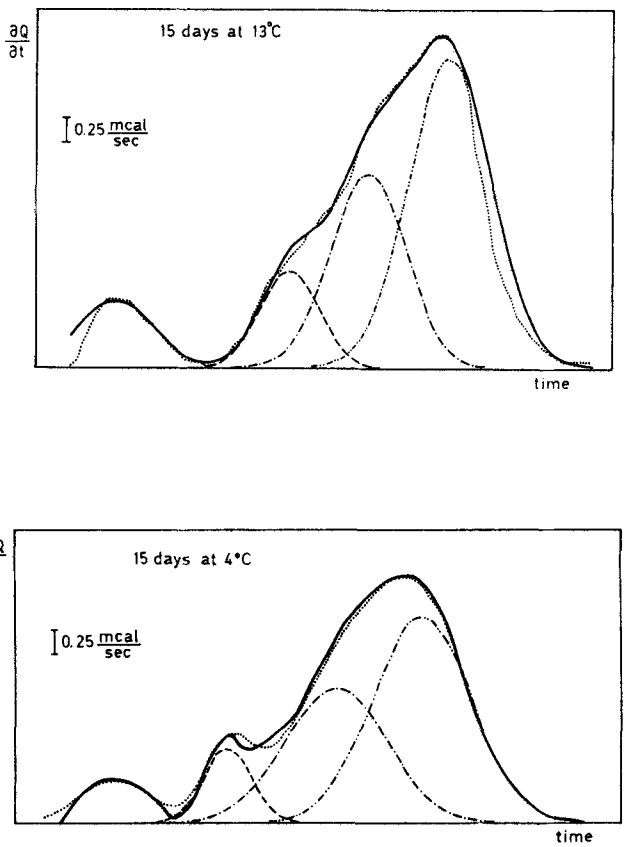


**FIG. 5. DSC thermograms fitted by computer of a commercial margarine stored 15 days at 4°C and 13°C.**

It must be taken into account that calorimetric runs were performed starting from −10°C. Under these conditions, it is likely that a portion of the liquid fraction which has a 7°C melting point crystallized in samples stored at 13°C during the DSC run. However, it is not necessary to evaluate it since after three hours of storage, the above mentioned fraction represents less than 10%.

It is to be noted that when the results obtained by viscometry and differential scanning calorimetry were analyzed a good correlation was found between them. The

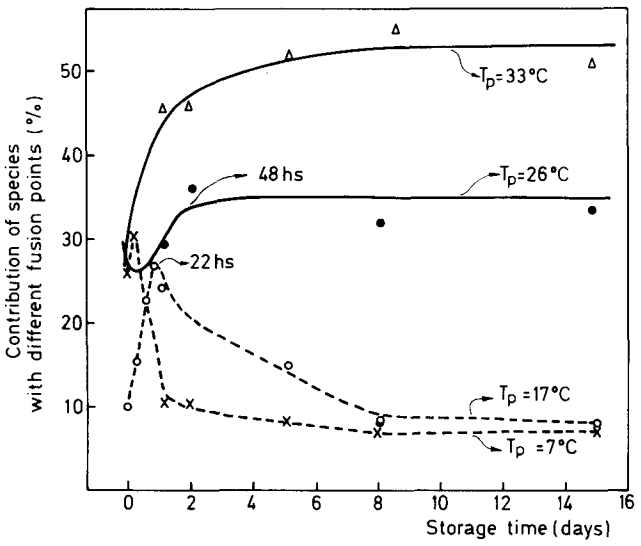


**FIG. 6. Distribution of species of different melting points as a function of storage time at 4°C.**

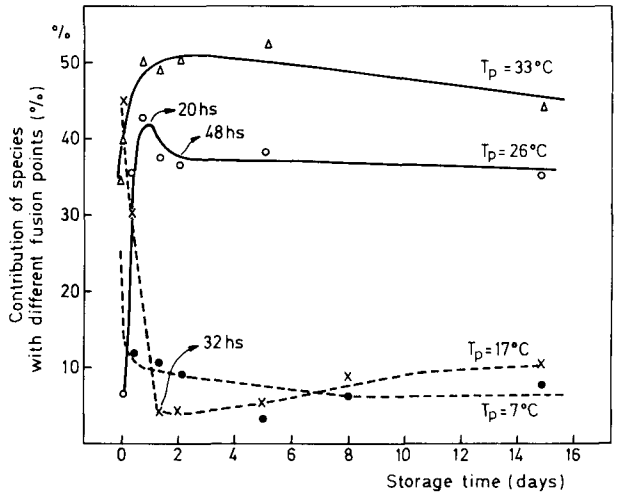


**FIG. 7. Distribution of species of different melting points as a function of storage time at 13°C.**

greater strength of samples was apparently associated with crystals of higher melting point. As the presence of the same crystal type (type $\beta'$) during storage was confirmed, the different endotherms forming the thermograms could be related to the formation of solid solutions with different melting points. Consequently, recrystallizations might take place during storage, leading to more stable solid solutions with higher melting points.

Taking into account the physical interpretation of the factors which contribute to the strength of margarine mentioned above (13), it can be observed that during storage at low temperature (4°C), the interactions between the fat phase crystals and the water drops of the dispersed phase (variation of parameter b) had significantly increased. At 13°C, this phenomenon was only detected at the beginning of storage. Later, those interactions decrease and those corresponding to triacylglycerol crystals increased (variation of parameter a). It is likely that this behavior could be affected not only by the type of crystals segregated from the solution but also by the crystal size, because a decrease of crystal-water interactions could be due to an increase of the crystal size. Unfortunately, it was impossible to determine that size without altering the sample structure.

It seems valid to conclude that samples harden during storage at 13°C and soften during storage at 4°C.

These measurements were also carried out using commercial margarine formed from hydrogenated soybean and cottonseed oil and liquid soybean oil. The results were found to be similar to those reported here.

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