STUDIES ON ß-RECRYSTALLIZATION IN LOW ERUCIC ACID RAPESEED OIL BLENDS

Klas Anjou, Research Laboratory, AB Karlshamns Oljefabriker,
S-292 00 Karlshamn, Sweden

Introduction

Most fats can exist in different polymorphic forms with different properties i.e. melting point. These forms are called α, ß' and ß and the fatty acid chains are packed in hexagonal, orthorombic and triclinic crystals respectively. There are several ways to study the polymorphy of fats, but the most direct way is by X-ray-techniques. From the melted fat the α-form is first crystallized, but it is usually very quickly transformed to the ß'-form, which in turn may more slowly transform to the stable ß-form.

From a practical standpoint these different forms may give a fat product right or wrong properties. In producing margarine the ß'-form is quickly formed and it is then with good recipes stable during the keeping time for the margarine. The crystals are very small giving the margarine a smooth texture. With certain oils in the recipe, however, ß-crystals may form during storage. This ß-recrystallisation gives a margarine with a sandy taste, caused by the large ß-crystals. Fats that can give this effect are i.e. lard, hydrogenated sunflower oil and hydrogenated low erucic acid rapeseed oil. This last oil is called LOBRA in Sweden from Low Brassica oil. Hydrogenated oils can be characterized by their slip melting point and iodine values.

The study here will report some data on the interaction of hydrogenated LOBRA and other components in a margarine fat blend on the ß-recrystallization behaviour.

Method

The most appropriate way to study polymorphic behaviour of margarine, would be to produce margarines of different composition and look for changes during storage. A simplified method have been used in this study. The different oil blends have been quickly chilled in a very small stirrer-cooler without other margarine ingredients. The capacity of this was 85 g/min and it was chilled by a cooling medium of -4°C. The end temperature of the chilled oil blends was 8-9°C. This simple method gave the possibility to easily simulate the cooling of margarine on a larger number of small samples.

The chilled fats were then stored at different temperatures usually 20 and 23°C. At regular intervals (between once a day and once a week) the samples were examined by X-ray-diffraction, looking for the changes from the originally formed ß' to the recrystallized ß-form. The X-ray spectroscopy was performed on a Philips diffractometer with 1°/min scanning between 18 and 26° (5,9-3,4 Å). The measurements were done at room temperature.

For the quantitative estimation of the amounts of the ß'-form and the ß-form, an oil sample was allowed to completely recrystallize to the ß-form by keeping it at room temperature for a long time. This sample was then mixed with a freshly prepared sample in ß'-form in several proportions giving reference samples with a ß-content between 0% and 100%. Examples of X-ray spectra from these reference samples are given in fig 1. By comparing spectra of stored sample with reference spectra a coarse estimation of the content of ß-form in the samples was possible.

Materials

In the trials two hydrogenated LOBRA oils were used. One was hydrogenated to a slip melting point of 34°C (iodine value 73) and the other to 40°C (iodine value 64). These are called LOBRA 34 and LOBRA 40 respectively. These were used in the margarine oil blends together with hydrogenated soya oil (slip melting point 33 and 41°C), coconut oil, palm oil and soy oil. The recipes were so constructed, that their solid fat contents (NMR) at 20°C were as similar as possible, 17-20% in most cases (table 1). This was made by adjusting the amount of hydrogenated soya oils, which are regarded as "neutral" in influencing the ß-recrystallizing speed.

Trials

Four series of tests were done (recipes in table 1). In the first (serie A) the level of LOBRA 34 and LOBRA 40 were varied and the level of coconut oil was constant 20%. In serie B the level of coconut oil was varied (0-30%) with constant 15% LOBRA 40. In serie C the amount of palm oil was varied (0-15%) with coconut oil constant at 20% and LOBRA 40 constant at 15%. In the last serie (D) the proportion of different solid fats was constant and the liquid soya oil content varied (15-50%). This means that the solid fat content (NMR) varied between the recipes too.

Results and discussion

The results from storage at 20°C are shown in fig 1-4. The estimated amount of the ß-form of the solid fat is plotted against the storage time in these figures. The data fitted very well with linear regression curves, which are also shown in the figures. Correlation coefficients of more than 0.95 and usually more than 0.98 were obtained. Intercepts of the lines are at or near origo. The ß-recrystallization rate could thus be rather accurately estimated and it also starts immediately after the cyrstallization in the stirrer-cooler. The time for a 100% ß-recrystallization may be taken as the measure of the rate.

Increasing the amount of hydrogenated LOBRA increases the ß-recrystallization rate (serie A, fig 1). A LOBRA hydrogenated to a higher melting point also increases the ß-recrystallization rate. This is twice a large with 15% and three times with 25% LOBRA 34 than without LOBRA. 15% LOBRA 40 gives a ß-recrystallizing rate almost as large as 25% LOBRA 34 does. A recipe with both 15% LOBRA 34 and 15% LOBRA 40 has a rate 6 times higher than with only hydrogenated soya oil. These results confirm older data both on pure hydrogenated LOBRA oils and margarine blends. However, this is the first time more accurate calculations of the different rate have been done.

The effect of different levels of coconut oil were studied in serie B (fig 2). All recipes contained 15% LOBRA 40 and a varying coconut oil content of 0-30%. The coconut oil have a dramatic effect on the ß-recrystallization rate. Already with 10% coconut oil the rate was increased 7 times and with 30% coconut oil 20 times.

The effect of palm oil on ß-recrystallization was studied in serie C (fig 3). All recipies contained 15% LOBRA 40 and a varying palm oil content of 0-15%. The results show here that palm oil in rather small amounts retard the ß-recrystallization rate very much. The rate is retarded 4 times with 5% palm oil and as much as 16 times with 15%. A palm oil level of 10-15% fully compensate the effect of 20% coconut oil.

In the last serie (D) the effect of diluting a recipe with soya oil was studied. Old data have shown that just diluting a hydrogenated LOBRA with 50% oil will increase the ß-recrystallization rate. In this case a margarine blend containing 20% coconut oil and 15% LOBRA 40 was used. The proportions of these and other solid fats (Soya 41, Soya 33) were constant in all recipes, but the soya oil content varied between 15 and 50%. The results were first a little unexpected with no variation in ß-recrystallization rate but the 50% oil sample giving lower rate. The explanation may be that not only the LOBRA 40 but also the coconut oil was diluted. Thus it was found that minor variations in solid fat content of different recipes compared in this study, do not influence the ß-recrystallization rate. It may be different with blends containing only one hydrogenated product.

There are sometimes some varations of the results from the same recipe. These are not depending on parameters of the chilling system. Further investigations may explain these variations. Within a serie the results are always consistent.

The results at 23°C storage shows exactly the same pattern but the ß-recrystallization rate is about twice as large varying somewhat between recipes. Other trials at lower temperatures show also much lowered rates.

Comparisions between this method and the same recipes used in real margarines, show that the same effect is obtained in margarines but the ß-recrystallization rates are 2-5 times lower. From a practical standpoint usually a 20-30% content of ß-form in a margarin will give it unacceptable sandiness.

There is a hypothesis that hydrogenated oils with most of their fatty acids of C18 type will be vulnerable to ß-recrystallization. This is true for hydrogenated LOBRA (about 90% C18 fatty acids). Palm oil may put palmitic acid in the crystals stopping the recrystallization. On the contrary lauric acid from coconut oil cannot cocrystallize with C18 fatty acids and perhaps in some way purifying them giving the increased rates.

Conclusions

With a new metod for measuring ß-recrystallization rats it has been shown that this rate is linear with storage time. Higher amounts and higher melting points of hydrogenated low erucic acid rapeseed oils give higher rates. These are further increased by increasing levels of coconut oil and lowered by small amounts of palm oil. The rates are also very much dependent of the storage temperature. The new method should be valuable for quickly testing new margarine oil blends for their stability.

Table 1: Recipes and solid fat content (NMR) of the different oil blends

Oil	Recipe, % of oil																	
	A1	A2	A3	A4*	A5	B1	B2	B3*	B4	C1*	C2	C3	C4	D1	D2	D3*	D4	D5
LOBRA 34		15	25		15													
LOBRA 40				15	15	15	15	15	15	15	15	15	15	18	17	15	13	10
Coconut	20	20	20	20	20		10	20	30	20	20	20	20	24	23	20	17	14
Palm											5	10	15					
Soya	29	28	27	29	28	42	35	29	23	29	29	29	29	15	20	29	39	50
Soya 33	25	10		25	10	32	26	25	24	25	20	13	6	30	28	25	21	16
Soya 41	26	27	28	11	12	11	14	11	8	11	11	13	15	13	12	11	10	8
Solid fat content, % at																		
10°C	38.4	39.0	39.3	39.0	38.6	36.6	38.6	38.3	43.3	38.3	38.6	39.4	39.0	51.1	46.9	37.8	31.5	22.9
20°C	18.1	18.7	18.9	18.4	18.8	21.1	20.9	17.5	15.0	17.5	17.4	17.8	17.8	23.5	21.0	17.6	14.8	10.8
30°C	5.6	6.7	6.7	5.7	6.5	7.3	7.3	5.8	4.5	5.8	5.7	5.7	5.8	8.1	7.0	5.8	4.8	2.8
35°C	2.2	2.7	2.6	2.1	2.2	2.8	2.6	2.1	0.9	2.1	2.0	1.7	2.3	2.9	2.8	1.6	1.4	0.9

* Reference oil of the same composition.

Fig 1: Calibration X-ray spectra with different ß-content

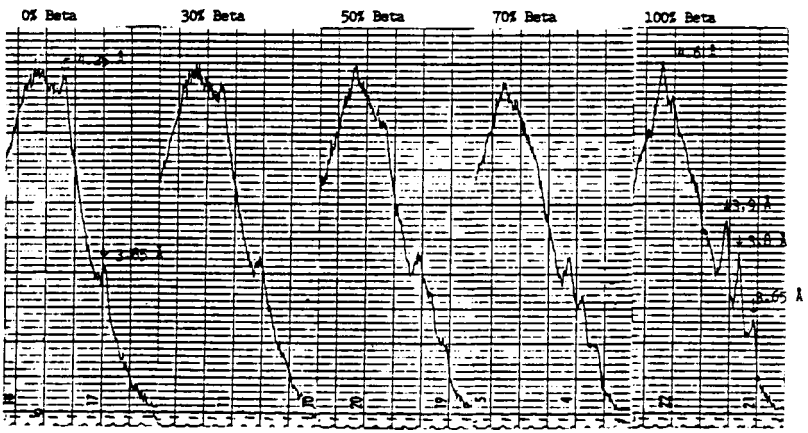

Fig 2: Serie A, 20% coconut oil

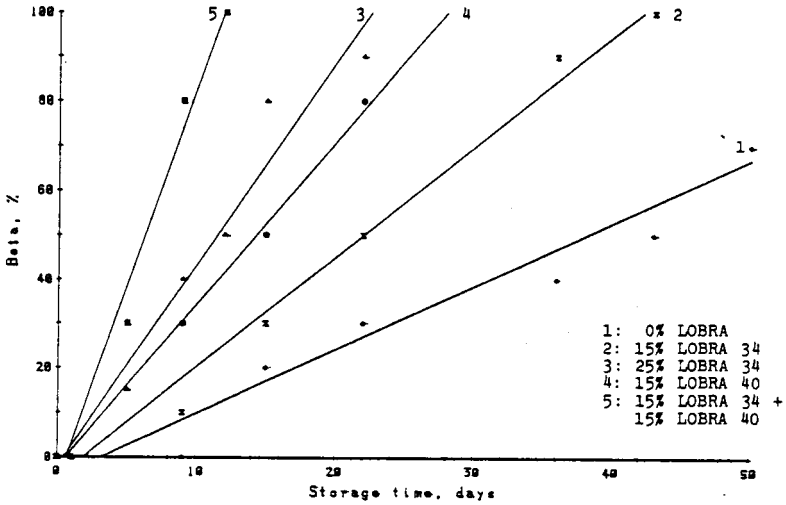

Fig 3: Serie B, 15% LOBRA 40, 20°C

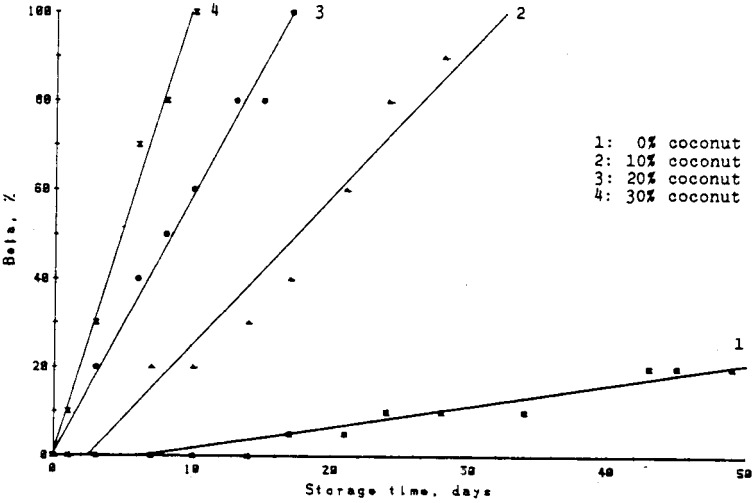

Fig 4: Serie C, 20% coconut oil 15% LOBRA 40, 20°C

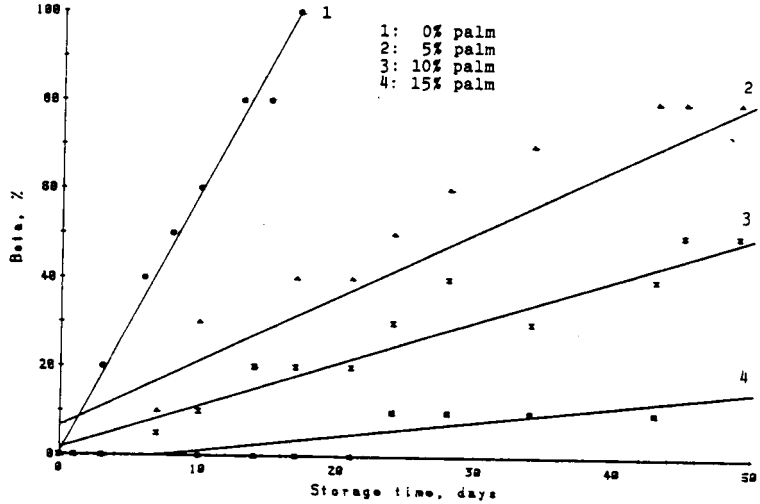

Fig 5: Serie D, constant proportions of solid fats, 20°C