# Physical and Textural Characteristics of Hydrogenated Low-Erucic Acid Rapeseed Oil and Low-Erucic Acid Rapeseed Oil Blends

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**ABSTRACT:** Low-erucic acid rapeseed oil (LERO) and hydrogenated low-erucic acid rapeseed oil (HLERO) were blended in binary systems. The blends were then studied for their physical properties such as solid fat content, melting curves by DSC, textural properties, and polymorphism. Phase behavior diagrams were constructed from the DSC and X-ray results, and isosolid diagrams were constructed from the NMR results. The mixture of HLERO and LERO displayed a monotectic behavior for all the storage time at 15°C. The aim of this work was to evaluate physical characteristics of binary blends of HLERO and nonhydrogenated LERO in order to use only LERO and hardened LERO in bakery shortenings. The mixture of 60% HLERO and 40% LERO is suitable to use as a plastic shortening. This blend is β tending upon storage at 15°C. It could be used in pie crust applications.

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**KEY WORDS:** Binary mixture phase, fat, polymorphism, rapeseed oil, shortening, texture.

The material makeup of shortening has changed from a natural fat to blends of oils with hard fats. Soybean oil, rapeseed oil, and palm oil and their products are among the fats that are commonly used.

The melting profile of a shortening plays an important role in its performance. This profile can be analyzed using DSC. In product development work involving oils and fats, the solid fat content (SFC) profile of the oils and fats or their blends is of considerable importance and is used as a guideline to judge whether a certain oil, fat, or blend is suitable for a particular application (1).

In margarine or shortening formulations, the solids content should be defined at a number of temperatures, typically from 15 to 40°C, covering the range of use.

Physicochemical properties of a shortening influence its performance in the final products. For a cake shortening, a rather flat SFC curve with a tail at the end is desirable. The tail end indicates that some solids are present at a high temperature (about 40°C), which is necessary to aid in the structural formation of the cake. One of the objectives in the manufacture of shortenings is the formulation of a product that retains its plasticity over a wide temperature range. The solids content of typical plastic shortenings ranges between 15 and 30%, and they exhibit a relatively flat SFC profile over a temperature range from 15°C to the melting point.

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The aim of this work was to evaluate the physical characteristics of binary blends of hydrogenated low-erucic acid rapeseed oil (HLERO) and nonhydrogenated low-erucic acid rapeseed oil (LERO) in order to develop bakery shortenings that use only these two fats.

## EXPERIMENTAL PROCEDURES

Samples of commercial LERO and HLERO (iodine value = 59) were obtained from Cargill N.V. (Izegem, Belgium). Iodine values were determined using the Wijs method (2).

*Sample preparation.* Various blends were prepared at composition intervals of 10 ± 0.1% by melting each type of oil or fat and mixing them in a glass vessel in the appropriate proportion. Total weight for each blend was 250 g. Fifty grams of each blend was put into a small plastic vessel. Two samples were used for textural analyses, two for NMR analyses, and one for DSC and X-ray analyses. The blends were kept in liquid form at a temperature of 50°C. Shortenings were produced by crystallizing the blends for 30 min in a freezer at −20°C in order to mimic at laboratory scale an industrial scraped-surface heat exchanger. They were then stored at 15°C in a room controlled at 15 ± 0.5°C for different times.

*Physical evaluation. (i) DSC.* The DSC analyses were carried out using a 2920 Modulated DSC (TA Instruments, Brussels, Belgium). Calibration was carried out using eicosane and dodecane. After being crystallized and tempered, blend samples were weighed into solid fat index (SFI) aluminum pans (TA Instruments). Samples were quickly frozen at −50°C in the DSC cell. A melting curve was then obtained by heating the sample from −50 to 90°C at 15°C/min (3). Each analysis was run in triplicate.

*(ii) X-ray diffraction analyses.* The polymorphic forms of the blends were established by X-ray diffraction using a PW1710 Philips diffractometer ($\lambda_{Cu}$ = 1.54178 Å, power 1200 W) with a temperature control system (Pt probe). Short spacing was determined according to the Bragg relation (4). Each analysis was run twice.

*(iii) SFC determination.* Samples were analyzed for their SFC after being crystallized and tempered by NMR using a pulsed NMR spectrometer (Minispec-mq20; Bruker, Karlsruhe, Germany). These results were compared with those obtained by other means (i.e., DSC, X-ray diffraction analyses, textural measurements).

The NMR tubes were filled by means of a sampling device consisting of a glass tube with a tight-fitting plunger. The SFC in the products were determined after conditioning the samples for 10 min at temperatures of 15, 20, 25, 30, 35, 40, 42, 45, 47, and 50°C. Each analysis was run at least twice.

*(iv) Texture measurements.* Texture measurements of the products were carried out after tempering at 15°C. Samples were then held at 20°C for 1 h before measuring penetration force in a controlled temperature room.

*Constant speed penetration.* A SMS TA.XT2i/5 texturometer (Stable Micro Systems, Surrey, United Kingdom) with a cone probe (P/45C; Stable Micro Systems) was used in the penetration tests. The probe penetrated the product at a constant speed of 0.5 mm/s for a distance of 5 mm. The maximum penetration force and the final penetration force were registered. At least four penetration tests were run on each sample; two samples of each blend were analyzed.

## RESULTS AND DISCUSSION

The melting behavior of the mixtures was studied by DSC after different times of storage at 15°C. Figure 1A shows the evolution of melting curves of HLERO upon storage, and Figure 1B shows melting curves of different compositions of studied blends after tempering 1 mon at 15°C. It can be seen from these data that the final melting temperature and the proportion of the high-melting peak of the blends increase upon storage and then stabilize at some value. These increases cor-

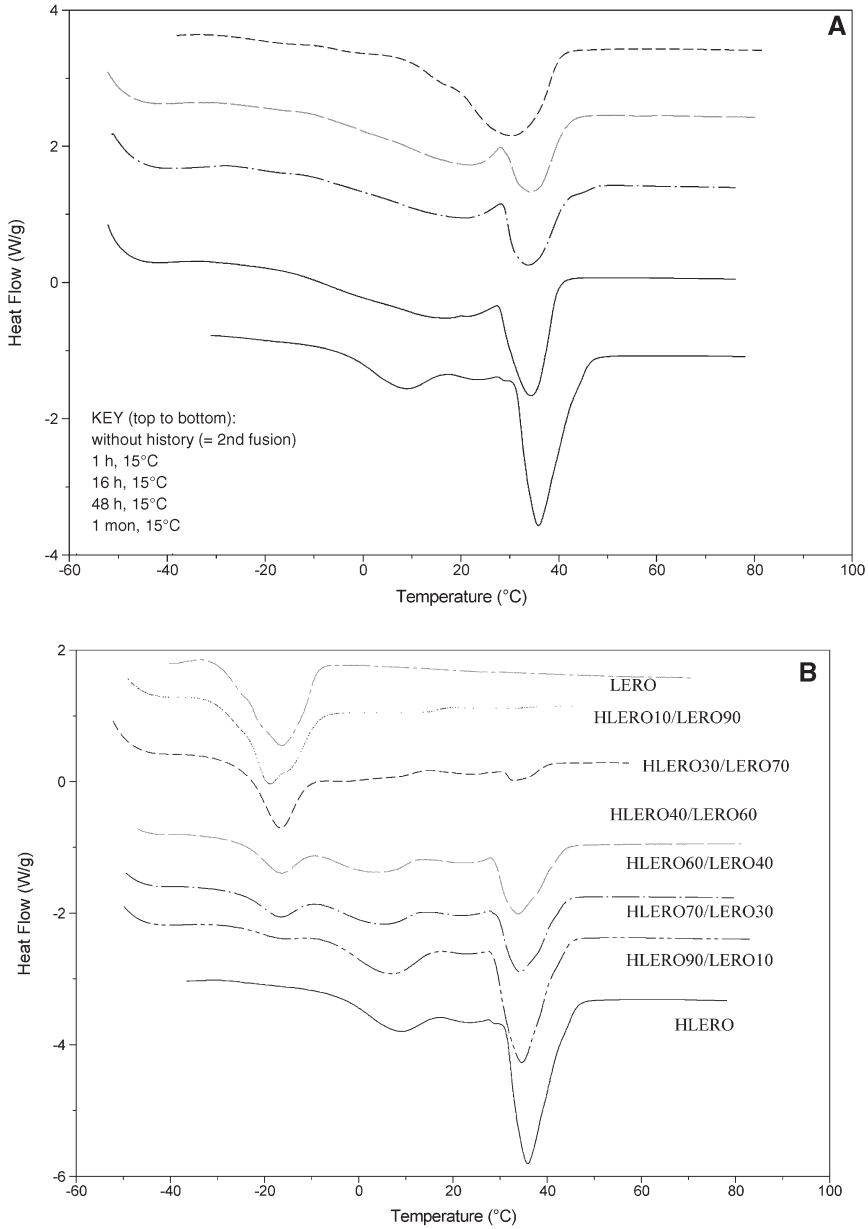


**FIG. 1.** (A) Evolution of melting curves of hydrogenated low-erucic acid rapeseed oil (HLERO) upon storage at 15°C. (B) Melting curves of different compositions of studied blend after tempering 1 mon at 15°C. LERO, low-erucic acid rapeseed oil.

respond to the polymorphic transition of β′ to β crystals (see discussion of X-ray results below). Furthermore, the high-melting peak became longer and thinner upon storage, indicating that the crystals reorganized themselves.

Phase diagrams were constructed from the DSC and X-ray results. The solidus and liquidus lines were fixed from DSC data. The liquidus line was recorded as the final melting temperature of the last peak. The solidus line was recorded as the beginning temperature of the first peak. Low-temperature peaks correspond to TG that are liquid at the temperature of storage. Nevertheless, they were not ignored in this study because one of the blend components (LERO) was totally liquid at storage temperature.

Figure 2 shows the phase diagram after tempering (A) for 1 h at 15°C and (B) for 16 h at 15°C. The binary mixture of HLERO and LERO displays a monotectic behavior for every storage time studied. This type of behavior is characteristic of eutectic systems that shift to monotectic systems when the difference in the melting points of the two components is 20°C or above (5). The melting points of the components involved in the studied blends are indeed different by more than 20°C.

Table 1 shows the evolution of polymorphism during storage of the blends at 15°C. All the studied blends are β tending upon storage. Furthermore, the higher the level of LERO, the more rapidly the fat crystals transform to the β polymorph. LERO and, to a certain extent, soybean oil are known to be β-tending fats when hydrogenated (6,7). The β′ form is preferred for margarine and for plastic shortenings, as the crystals tend to be small and uniform in size. The shortenings then provide good aeration for cakes and icing. For this reason, a β′-tending hard fat such as hydrogenated palm oil is usually incorporated into margarine and cake shortening formulations (8). Shortenings that have β-crystalline form aerate poorly but perform well in pie crust applications. The studied blends are β-crystalline in form after storage at 15°C and thus are probably able to perform in pie crust applications. The use of a β′-tending hard fat or 1,2-DG, as suggested by Hernqvist *et al.* (9,10), could be a solution to stabilize the blends in the β′ form and use one of the studied blends as a cake shortening.

Figure 3 shows SFC profiles of the various blends after 16 h of tempering at 15°C. One of the objectives in the manufacture of shortenings is the formulation of a product that retains its plasticity over a wide temperature range. Typical

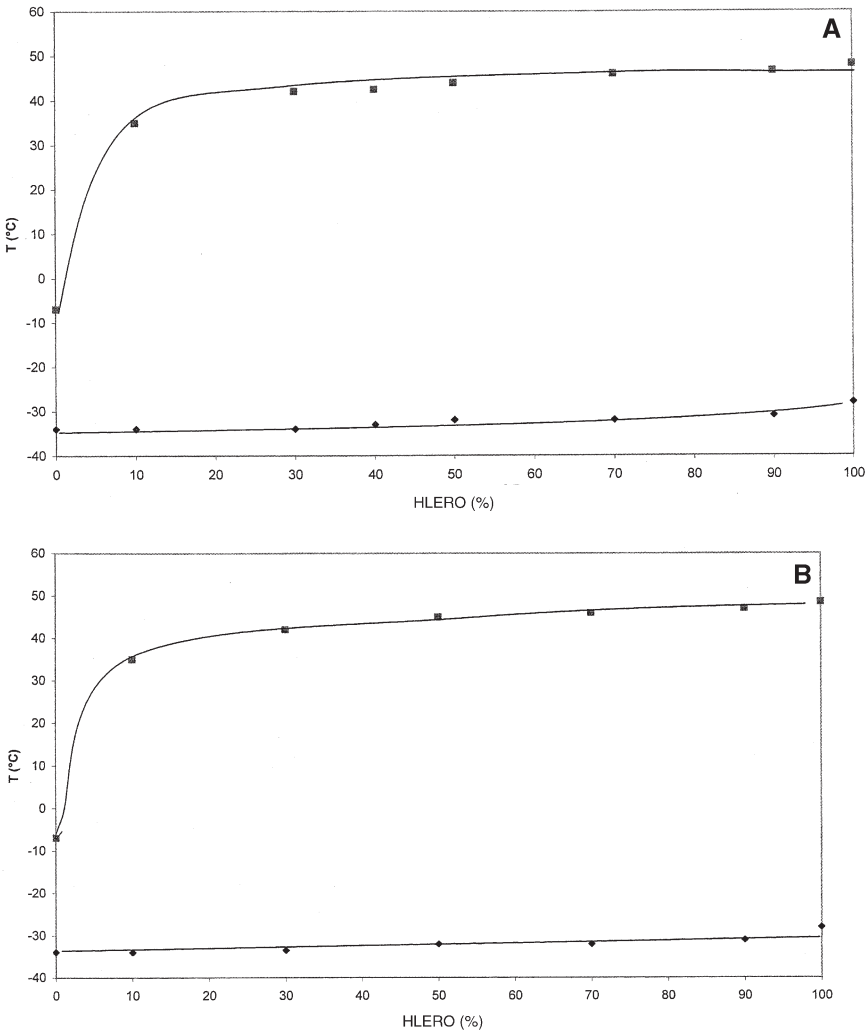


**FIG. 2.** Phase diagram of HLERO/LERO blends (A) after tempering 1 h at 15°C , (B) after tempering 16 h at 15°C. For abbreviations see Figure 1. ♦, Solidus line; ■, liquidus line.

**TABLE 1**
**Polymorphism Evolution During Storage of the Blends at 15°C**

| | Temperature DRX (°C) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| HLERO/LERO[a] | −35 | −20 | −10 | 0 | 10 | 15 | 20 | 25 | 28 |
| 0/100 | | | | | | | | | |
| No tempering | β′ + (β) | (β′) + psβ′ + β | liq | | | | | | |
| 30/70 | | | | | | | | | |
| No tempering | α + β | β′ + psβ′ | | psβ′ (+liq) | psβ′ + liq | | liq (+β) | | |
| 1 h, 15°C | | | | | | β′ + liq | | liq | |
| 16 h, 15°C | | | | | | β + liq | | β + liq | |
| 48 h, 15°C | | | | | | β + liq | | β + liq | |
| 1 mon, 15°C | | | | | | β + liq | | β + liq | |
| 50/50 | | | | | | | | | |
| No tempering | α + β′ | | β′ | | β′ (+liq) | | | | liq |
| 1 h, 15°C | | | | | | β′ | | | |
| 16 h, 15°C | | | | | | β | | β | β + liq |
| 48 h, 15°C | | | | | | β | | β | |
| 1 mon, 15°C | | | | | | β | | β | |
| 70/30 | | | | | | | | | |
| No tempering | α + β′ | α + β′ | | β′ | β′ | | | β′ | β′ + liq |
| 1 h, 15°C | | | | | | (α) + β′ | | β′ | |
| 16 h, 15°C | | | | | | β′ (+β) | | β′ + β | |
| 48 h, 15°C | | | | | | β (+β′) | | β (+β′) | |
| 1 mon, 15°C | | | | | | β ((+β′)) | | β ((+β′)) | |
| 90/10 | | | | | | | | | |
| No tempering | | | | | | | | | |
| 1 h, 15°C | | | | | | (α) + β′ | | β′ | |
| 16 h, 15°C | | | | | | β′ | | β′ (+β) | |
| 48 h, 15°C | | | | | | β′ (+psβ′) | | β′ + β | β′ + β (+liq) |
| 1 mon, 15°C | | | | | | β (+β′) | | β ((+β′)) | |
| 100/0 | | | | | | | | | |
| No tempering | α + β′ | | α + β′ | | β′ | | | β′ (+ β growing) | |
| 1 h, 15°C | | | | | | (α) + β′ | | β′ | |
| 16 h, 15°C | | | | | | β′ | | β′ | β′ (+ liq + β growing) |
| 48 h, 15°C | | | | | | β′ ((+β)) | | β′ (+β) | |
| 1 mon, 15°C | | | | | | β (+β′) | | β ((+β′)) | |

[a]HLERO/LERO, composition of hydrogenated low-erucic acid rapeseed oil/low-erucic acid rapeseed oil (%/%). DRX, X-ray; psβ′, pseudo β′; double parentheses [(( ))], very few.

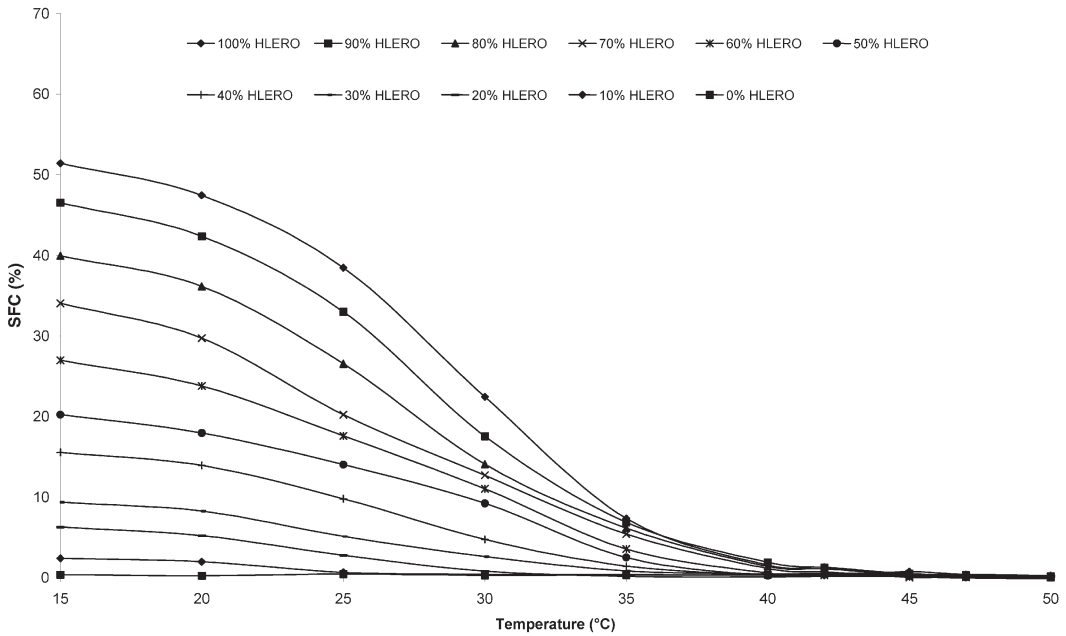


**FIG. 3.** Solid fat content (SFC) profiles of the various blends after 16 h of tempering at 15°C. For other abbreviations see Figure 1.

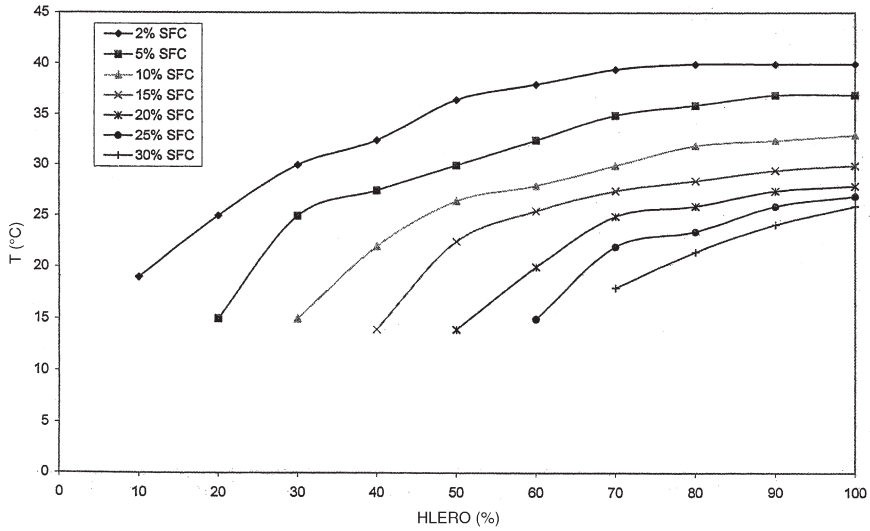


**FIG. 4.** Isosolid diagram for the HLERO/LERO mixture after 16 h at 15°C. For abbreviations see Figure 1.

plastic shortenings have a solids content of 15–30% and exhibit a relatively flat SFC profile from 15°C to the melting point. The studied mixture of 60% HLERO and 40% nonhydrogenated LERO displays a flat SFC profile (15–25%), like a plastic shortening, over the temperature range of 15–25°C, with a small tail after 40°C.

Isosolid diagrams were also constructed from NMR data as described by Timms (5). This procedure constitutes a useful way of qualitatively judging the compatibility of fats. Figure 4 is an isosolid diagram for the studied mixture after 16 h at 15°C. The mixture of HLERO and LERO displays a monotectic behavior, as already seen by phase behavior diagrams.

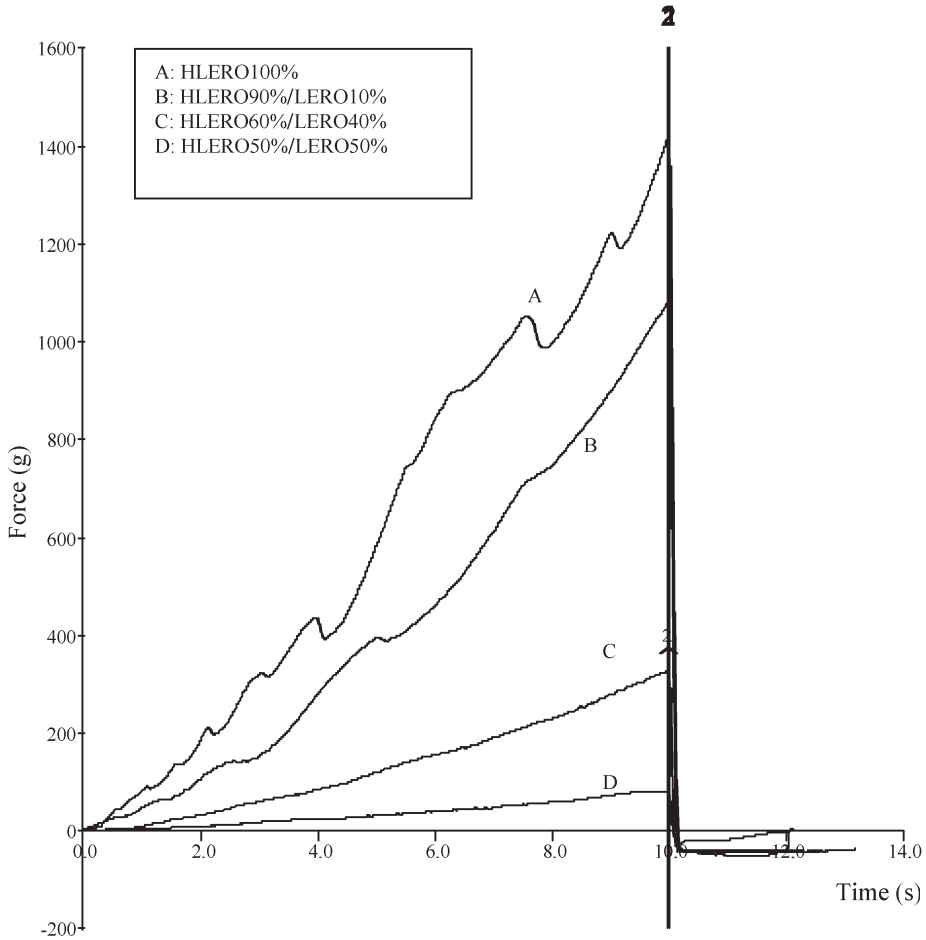


**FIG. 5.** Typical curves obtained by penetration test (for description see the Experimental Procedures section). Peak 1 (final force) and peak 2 (maximal force) are superimposed. For abbreviations see Figure 1.

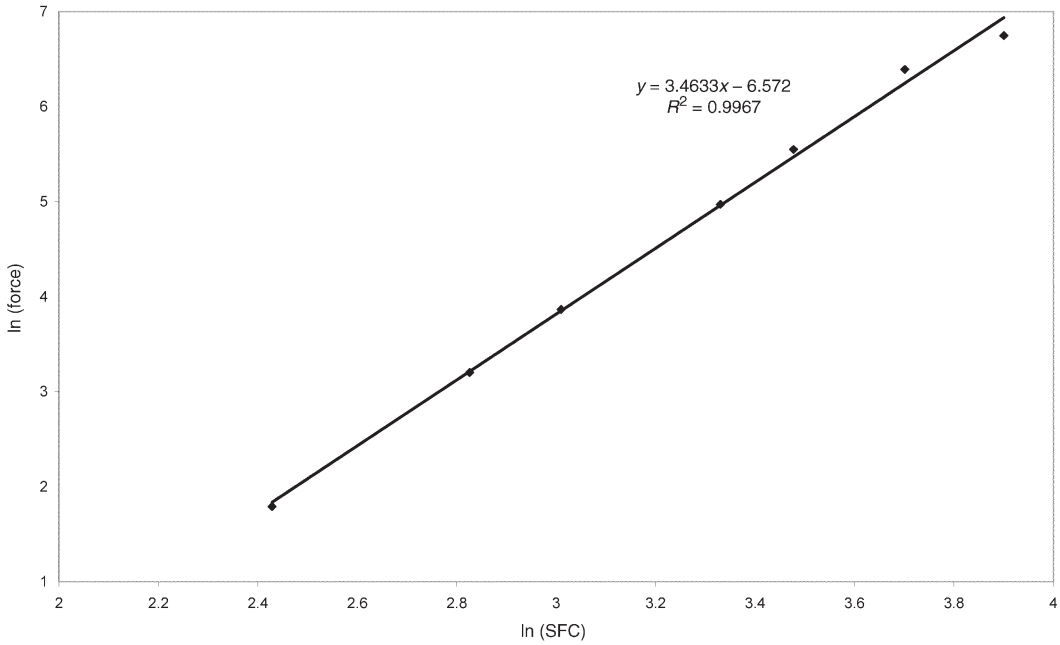


**FIG. 6.** Relationship between textural measurements (maximal penetration force) and SFC of products tempered at 15°C (measurements done at 20°C). For abbreviation see Figure 3.

*Textural analyses.* Some typical curves obtained by penetration are displayed in Figure 5. Curve A represents 100% HLERO; this sample is very brittle as shown by the irregularities of the curve. The mixture of 60% HLERO/40% LERO is not brittle at all; it is a very smooth product like a typical plastic shortening (curve C). Textural analyses done with a texturometer estimate brittleness of a product, whereas cone penetrometry, a convenient method of evaluating the texture of a fat product, does not.

Furthermore, a relationship was found between the textural measurements (maximal penetration force) and the SFC of the products tempered at 15°C (measurements done at 20°C). Indeed, a linear relationship exists between the logarithm of SFC and the logarithm of penetration force. As can be seen in Figure 6, the correlation coefficient of this relation was 0.997 ($P = 0.001$). This result can be related to those of Narine *et al.* (11), who obtained a linear relation between the logarithm of the storage modulus or shear elastic modulus $G'$ and the logarithm of the SFC, as well as a linear relation between $G'$ and the hardness index for the studied samples.

The mixture of 60% HLERO/40% LERO is suitable to use as a plastic shortening. This blend is β tending upon storage at 15°C and could be used in pie crust applications. The use of a β′-tending hard fat or DG, as recommended by deMan and de Man (8) and Hernqvist *et al.* (10), could be a way of stabilizing this blend in the β′-crystal form for use as a cake shortening.

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