

Crystallisation of Low- Trans Shortenings

¹Michael H. Gordon , ¹Wongsiri Jirasubkunakorn, ¹Alan E. Bell, ²Loek Favre and ³Kevin W. Smith

¹University of Reading, ²IOI- Loders Croklaan, and ³Unilever Research Colworth

Background

Shortenings are important for the properties of bakery products (Hodge 1986):

- Shortening power and lubrication
- Batter aeration
- Emulsifying properties
- Provide an impervious layer
- Good keeping properties and flavour

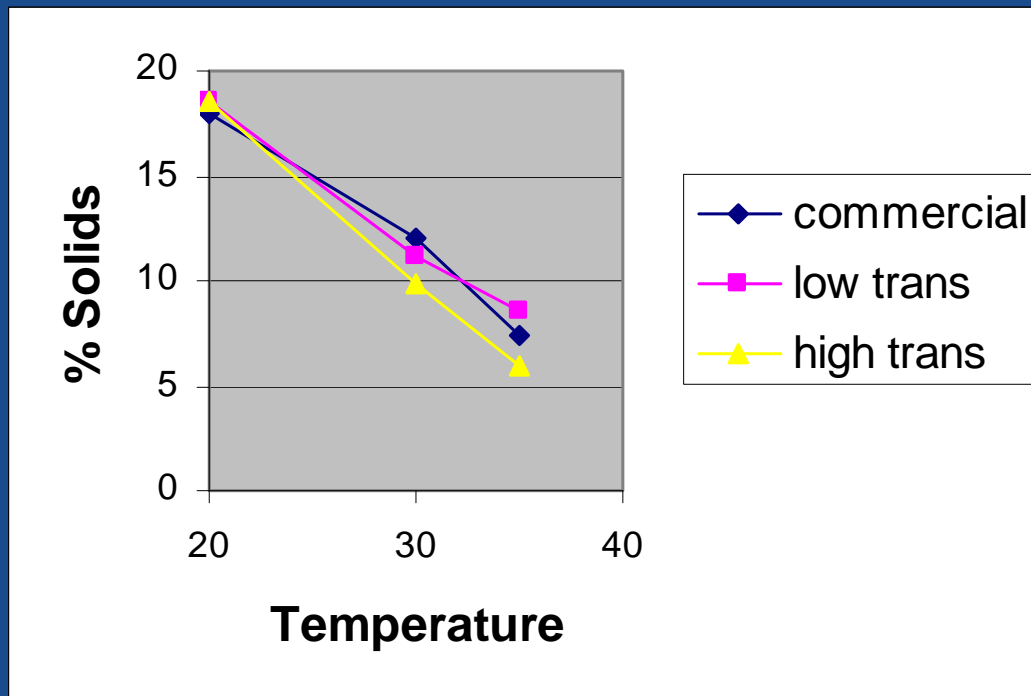
- Traditional shortenings - lard or hydrogenated fats

Aims (Part 1)

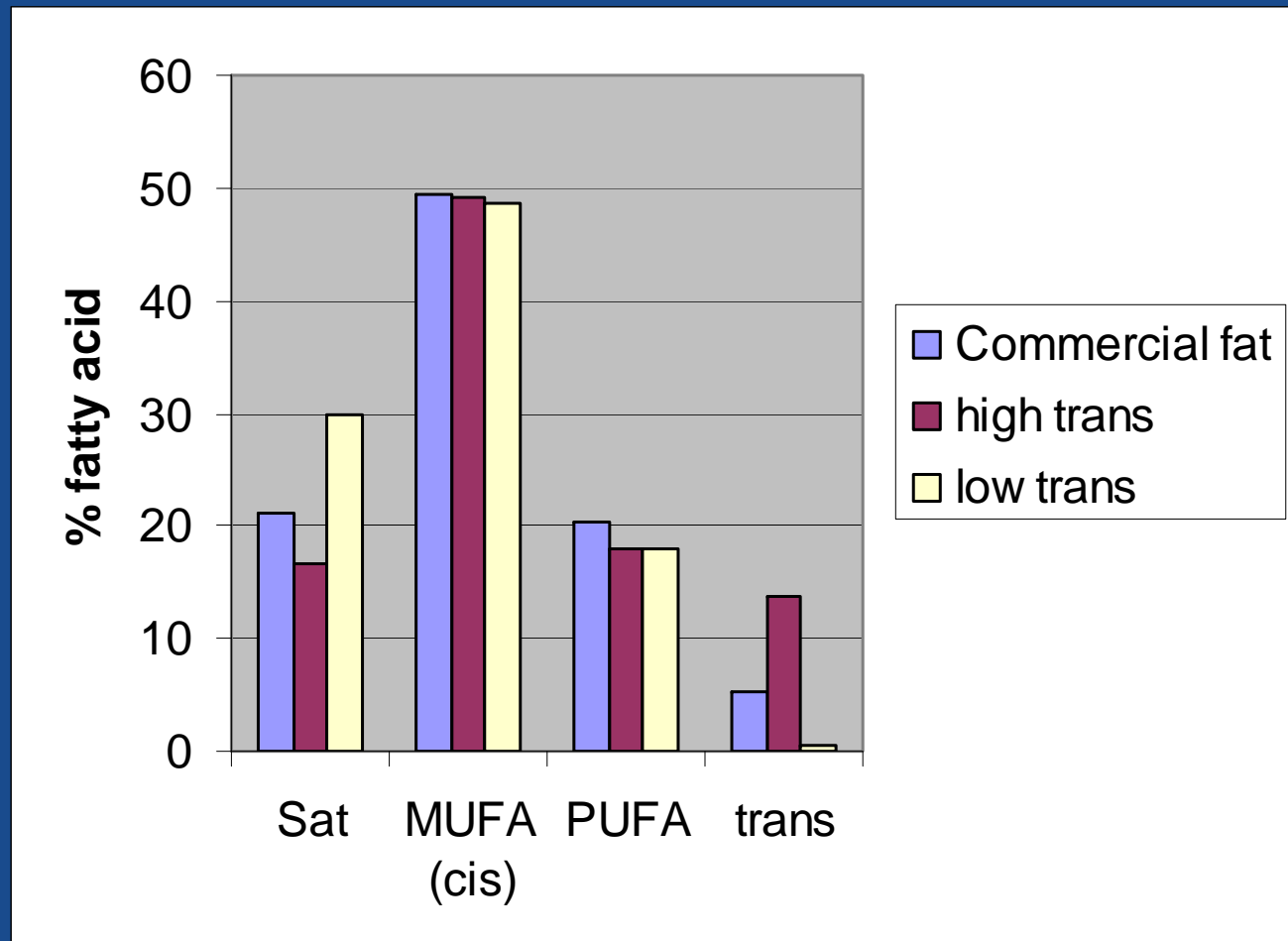
- To study the crystallisation behaviour of fat blends containing rapeseed oil, palm stearin (POs) and palm olein (POf)
- to consider their potential for replacing high *trans* fats as shortenings.

Solid fat content values

- high *trans* shortening (66% Rp, 30% Rp38, 4% BO65)
- low *trans* shortening (56% Rp, 22% PO_f, 22% PO_s)
- Commercial bakery shortening



Fatty acid content of shortenings



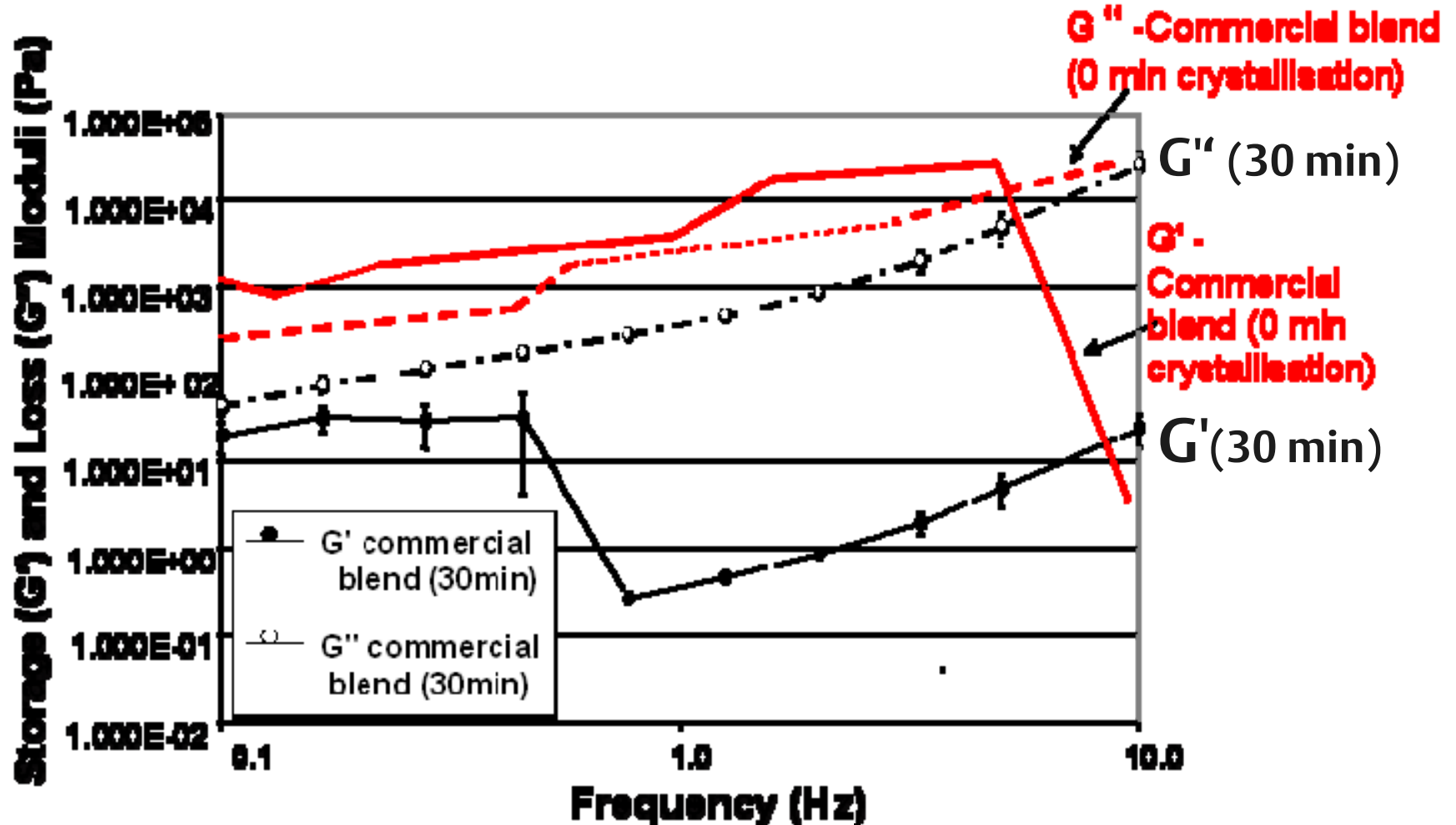
Methods

- Crystallisation - fat blends (250g) melted at 87°C; cooled to 31°C with stirring. Samples removed periodically for rheology or DSC.
- Rheology - a controlled stress rheometer (RTI Ltd), a frequency sweep procedure (6 replicates)
- DSC melting profiles:- Perkin Elmer DSC 7 with heating rate of 5°C/min from 15 to 60°C.

Rheology theory

- Storage (elastic) modulus G' – ratio of stress: strain (in phase)
- Loss (viscous) modulus (G'') - ratio of stress: strain (out of phase)
- If G' and G'' are close together, there is some structure in the fat
- Loss of structure may occur when the frequency is changed.

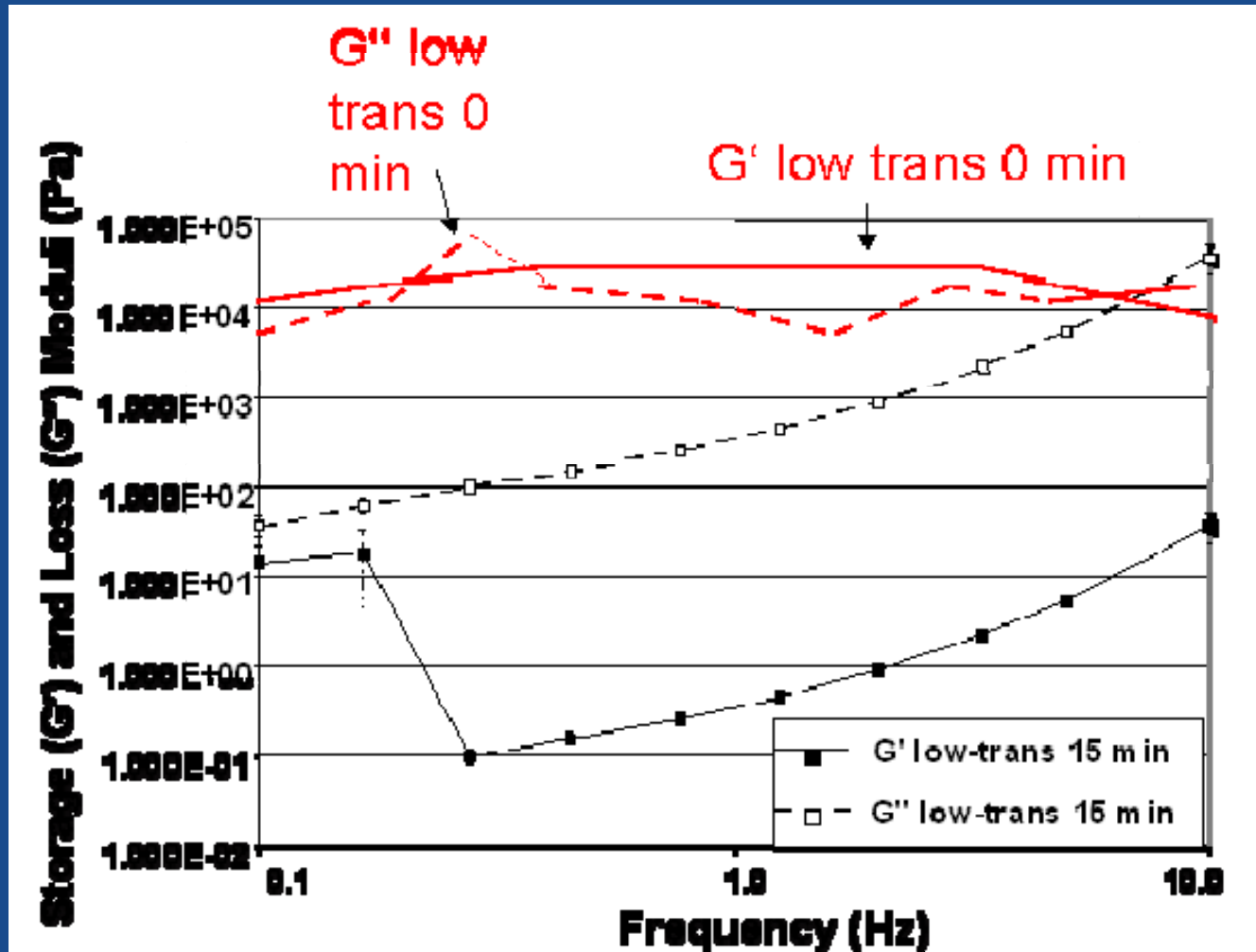
Frequency sweep curve showing changes in storage modulus (G') and loss modulus (G'') due to crystallisation of commercial shortening



Interpretation of changes in commercial shortening

- At 0 mins, Weak viscoelastic gel ($G' > G''$) – few large crystals; little structure.
- After 30 mins of stirring at 31°C, G' and G'' fall. System reverts to apparent weak viscoelastic liquid behaviour ($G'' > G'$) – more liquid slip planes develop between larger number of small solid fat crystals

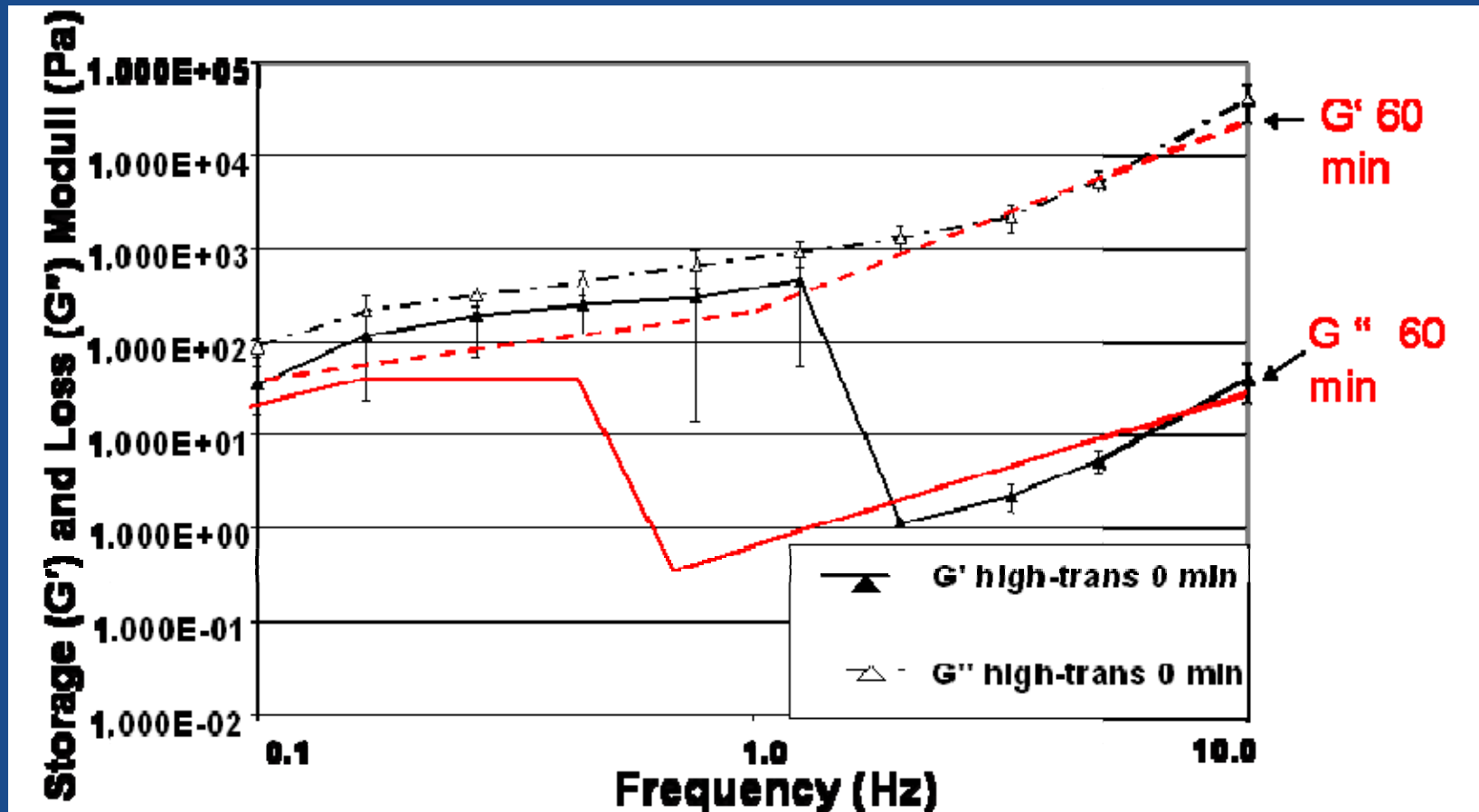
Frequency sweep curve showing changes
in storage modulus (G') and loss modulus (G'')
due to crystallisation of palm based low *trans*
shortening (56% Rp, 22% PO_f, 22% PO_s)



Interpretation of changes in low *trans* shortening (56% Rp, 22% POf, 22% POs)

- At 0 mins at 31°C , very weak viscoelastic properties with more liquid like behaviour (almost no change with frequency; storage modulus G' similar to loss modulus G'') – few large crystals
- After 15 mins of stirring at 31°C, G' and G'' fall. System reverts to very weak viscoelastic gel ($G'' > G'$) with fall in G' at low frequency – increased number of crystals with increased crosslinking between crystals

Frequency sweep curve showing changes in storage modulus (G') and loss modulus (G'') due to crystallisation of high *trans* shortening (66% Rp, 30% Rp38, 4% BO65)

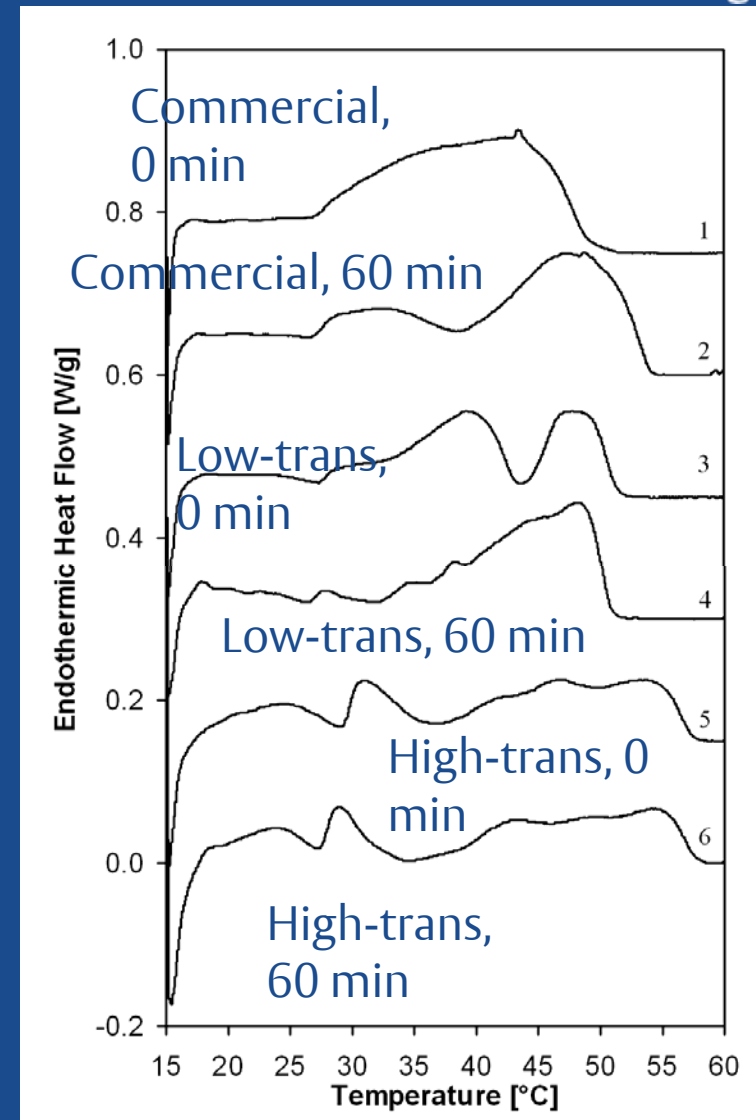


Interpretation of changes in high *trans* shortening

- Considerable crystallisation occurred before 0 mins at 31° C, so very small changes between 0 and 60 mins of stirring at 31° C
- very weak viscoelastic gel (loss modulus $G'' >$ storage modulus G') – large number of crystals with crosslinking between crystals

DSc melting curves

DSC melting curves of commercial fat and low *trans* fats solidified at -20°C after 0 and 60 min of stirring at 31°C, measured at 15 to 60°C with melting rate of 5°C/min.



Interpretation of melting behaviour of solidified shortenings

- Commercial fat: - Stirring at 31° C for 60 min causes some fractionation so it shows 2 melting peaks in 30 – 55 °C region with increase in final melting point compared with 1 peak if sample is not stirred.
- Low trans fat:- Crystallisation into 2 fractions occurs without stirring at 31° C. Lower melting fraction reduced by stirring but final melting point does not increase after stirring. Possible polymorphic change.
- High trans fat – little effect of stirring. Most crystallisation occurred before 0 mins at 31° C.

Aims (ii)

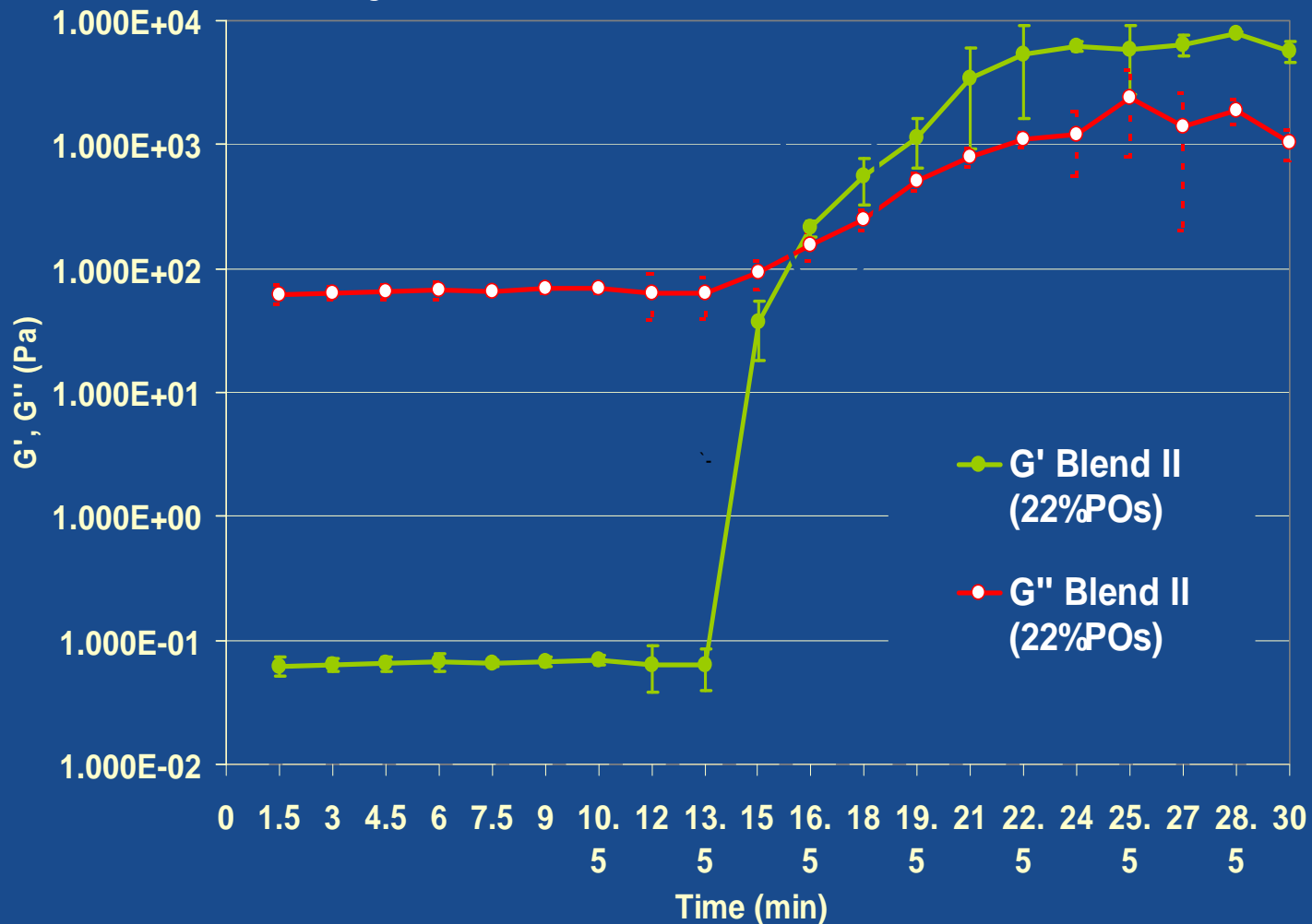
- To determine the effect of variation in palm stearin (POs) : palm olein (POf) ratio on the crystallisation behaviour of low *trans* shortenings – a comparison of:
- (I) 56% Rp, 27% POs, 17% POf
- (II) 56% Rp, 22% POs, 22% POf
- (III) 56% Rp, 17% POs, 27% POf

Methods

- Stirred fat at 80°C (50rpm, 120min) to destroy existing crystal nuclei
- RTI rheometer → frequency sweep (30 mm diameter flat plate, 2.00 mm gap) at 0.005 mNm, 1 Hz for a certain time while cooling fat (cooling water 20 °C)
- Storage (G') & loss moduli (G'') obtained as a function of time. (6 replicates)

Changes in rheology of 22% Palm stearin blend

Onset of crystallisation at 13.5 min



Times for rheological changes

Time (mins to):

Onset $G' > G''$

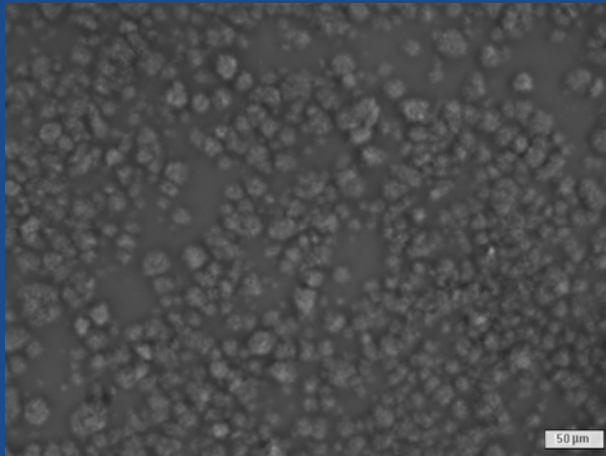
- 27% POs, 17% PO_f 12 15 -18
- 22% POs, 22% PO_f 13.5 16.5
- 17% POs, 27% PO_f 15 16.5
- Reduce POs -nucleation rate reduced, but time to develop solid characteristics not changed.

Fat Crystal Morphology

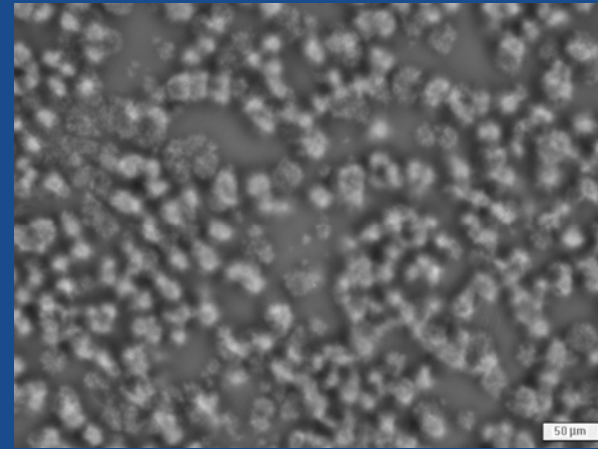
- Stirred fat at 80°C (50 rpm, 120 min)
- Sample transferred to rheometer and cooled
- 35 °C → Light microscopy (LM) (phase contrast)
- Crystals removed at onset of crystallisation
washed with isobutanol (24hr)
- - Confocal Laser Scanning Microscopy (CLSM)
(inverted microscope) x40 obj
- - Environmental Scanning Electron Microscopy
(ESEM)

LM (phase contrast)

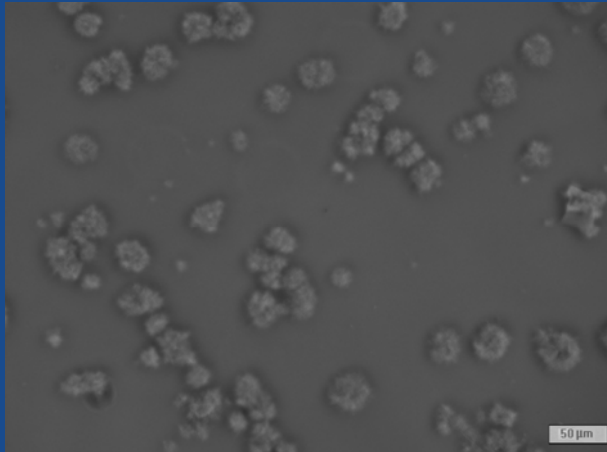
Liquid sample taken from rheological plate at 35°C, and solidified on slide (x10 objectives)



Blend I (27% POs)



Blend II (22% POs)



Blend III (17% POs)

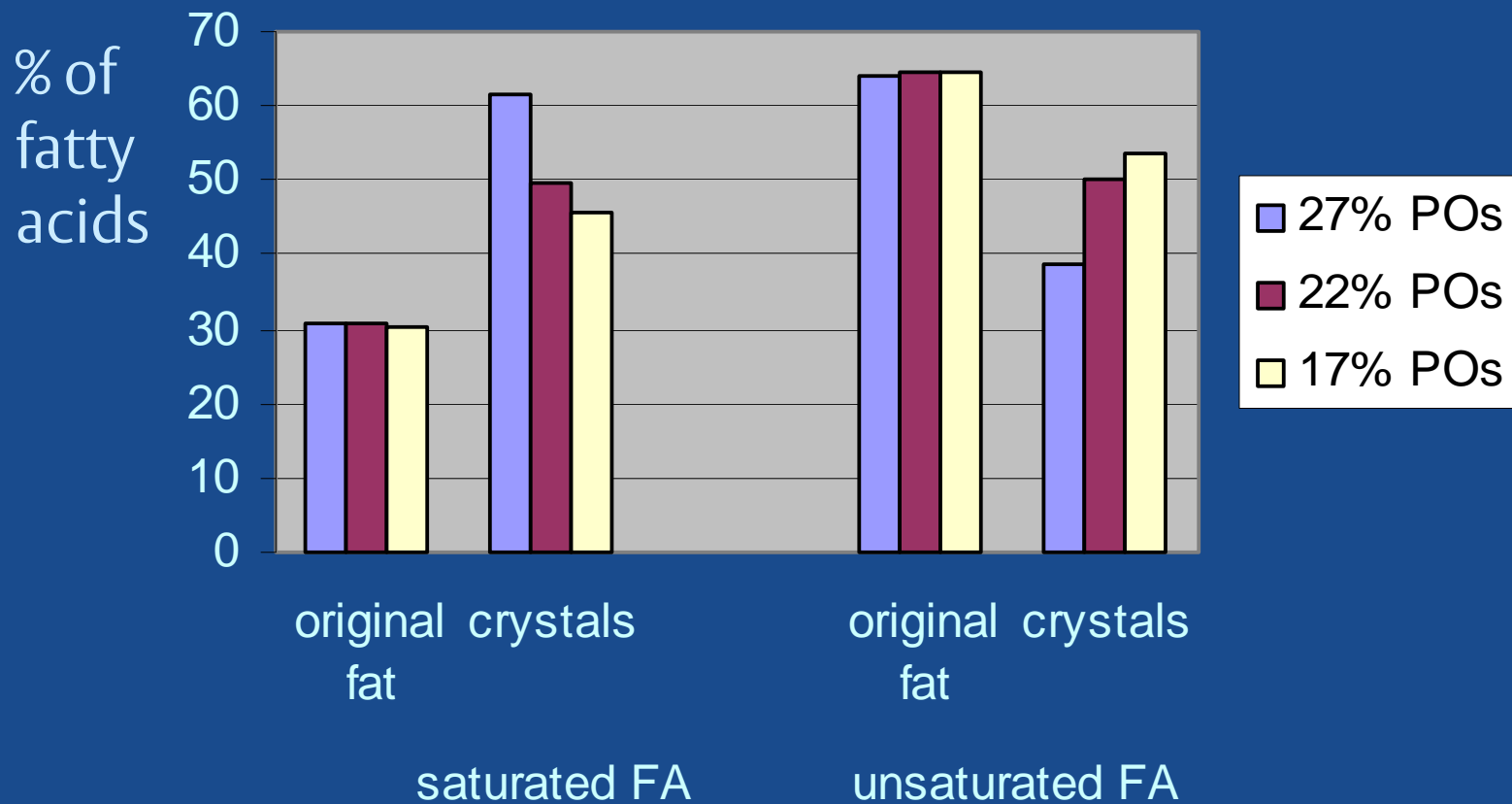
POs content



Nucleation



Saturated and unsaturated fatty acids in original blend and in fat crystals at early stage of crystallisation



Conclusion (I)

- High trans shortening crystallises significantly during cooling to 31°C (weak viscoelastic semi-solid).
- Low trans shortening – very weak viscoelastic properties with more liquid like behaviour (few large crystals) changes to very weak viscoelastic gel (increased crosslinking between crystals) on crystallisation
- Commercial shortening- weak viscoelastic gel changes to apparent weak viscoelastic liquid behaviour (more liquid slip planes develop between larger number of small solid fat crystals) on crystallisation

Conclusion (II)

Higher POs content in the blend causes:

- Earlier onset of crystallisation
- No change in time to reach solid state rheology ($G' > G''$)
- Increased rate of nucleation
- Clusters of spherulites form in all the fats
- Increase in saturated FA and reduction in unsaturated FA is greater in the crystals at onset of crystallisation

Acknowledgement

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