

Crystallisation in water-in-cocoa butter emulsions: Role of the interface on fat crystallisation and polymorphic transitions

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Introduction and motivation of the work

Water-in-cocoa butter emulsions have been suggested as novel ingredient for fat content reduction in confectioneries¹. In these emulsions kinetic stability is provided by emulsifier molecules and cocoa butter (CB) fat crystals formed in the bulk and at the interface. Fat crystals adsorbed at the droplets interface grow together to form a solid crystalline *shell*. This latter phenomenon implies a process of interfacial crystallisation. While triglycerides crystallisation in O/W emulsions has shown to be affected by the type of emulsifiers present in the system², the crystallisation phenomena occurring in W/O emulsions remain mostly unknown. The aim of this work was to study the crystallisation behaviour of water-in-cocoa butter emulsions. The aspects considered were the kinetics of crystallisation and the polymorphic evolution bulk and emulsified CB.

Hypothesis

It was hypothesised that water droplets promote CB crystallisation *via* an *interfacial heterogeneous nucleation* mechanism. Emulsified CB is expected to crystallise faster than the bulk fat phase. With respect to CB polymorphic evolution, it was hypothesised that the liquid acyl chains of polyglycerol polyricinoleate (PGPR) molecules interact with CB high melting point triglycerides at the water droplets interface enhancing polymorphic evolution.

Materials

Emulsions lipid phase was prepared by blending molten CB with PGPR; both ingredients were a kind gift from Cargill. The aqueous phase was double distilled water. Two emulsions were prepared containing a dispersed phase mass fraction of 20% and 40% (wt%), respectively; PGPR concentration was 5% (wt%) of the dispersed phase for both emulsions.

Methods

Emulsification and crystallisation study methodology

Water-in-cocoa butter emulsions were produced as described in literature³. Emulsions droplet size was determined using pulsed NMR (Bruker, Minispec). To erase the crystal memory, systems were melted to 50°C for 20 minutes and re-crystallised at different temperatures (5, 10, 15, 20°C). Bulk CB and CB containing a PGPR concentration as for the 20% emulsion were used as reference materials.

Kinetics of crystallisation

Solid fat content (SFC) evolution of CB systems was determined using pulsed NMR *via* the “indirect method” and data fitted to the Avrami model to determine the crystallisation kinetic parameters.

Polymorphic evolution analysis

Polymorphic evolution in CB systems was studied *via* DSC. Molten samples were crystallised (at 10°C/min) for different lengths of time (5, 10, 15, 20, 30, 45, 60, 120, 180 minutes) at each temperature and re-melted at 5°C/min. On analysis, endotherms were first converted to “excess of heat capacity” curves and then deconvoluted. This analysis consists in dividing the original curve in a number of Gaussian curves (Eq. 1), each of which corresponds to one CB polymorph (Fig. 1). The analysis was carried out using the “Solver” tool (Excel, Microsoft Office, version 2010).

$$y = a \exp\left(-\frac{(x-b)^2}{2c^2}\right)$$

Eq. 1: Equation representing a curve with Gaussian form, where, a , b , and c are three constants representing *height*, *position*, and *width* of the polymorph curve, respectively.

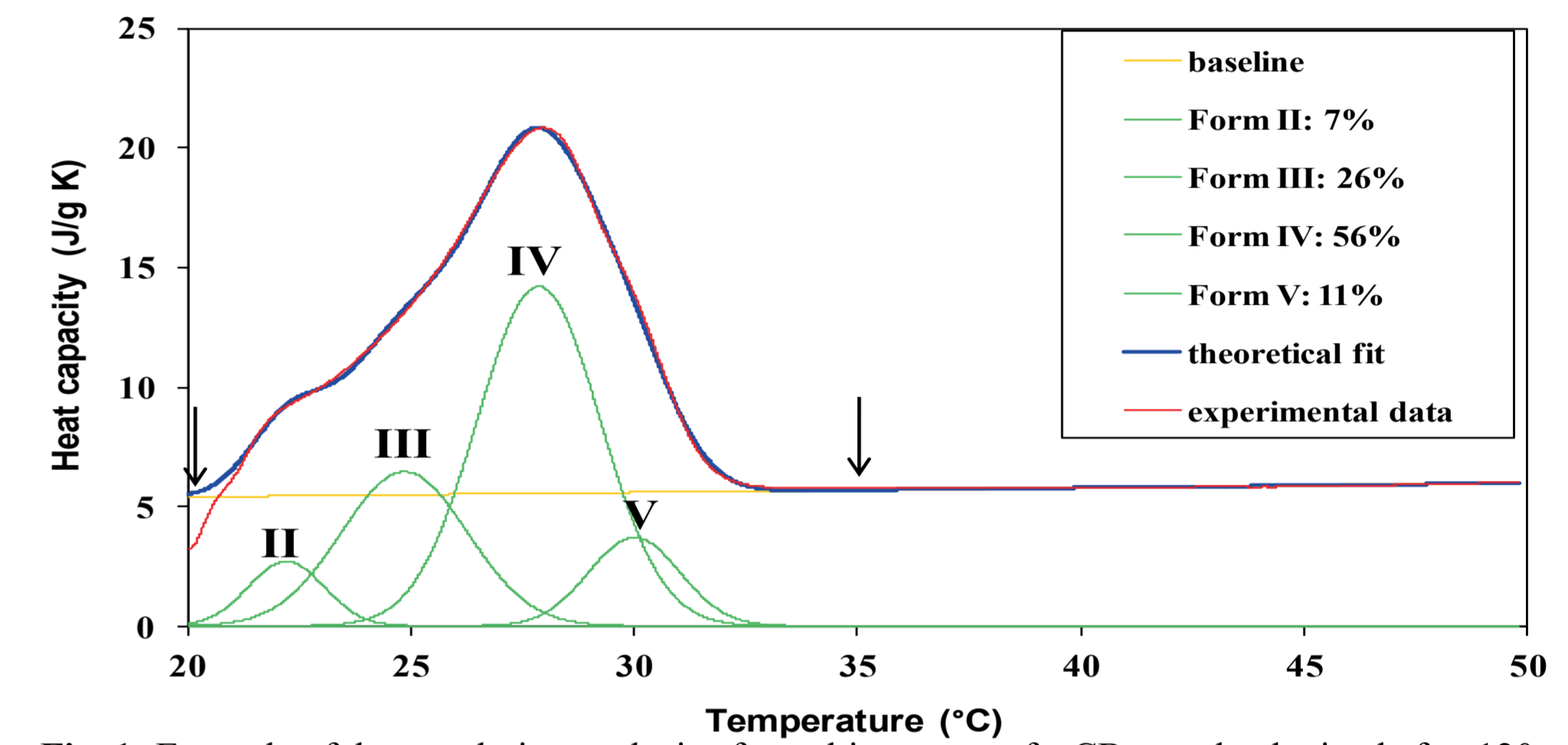


Fig. 1: Example of deconvolution analysis of a melting curve of a CB sample obtained after 120 minutes isothermal holding at 20°C. The red, blue, and yellow line represents the experimental, theoretical, and baseline curve. Each green line represents CB polymorphs referred by the Roman numeral. The “relative mass fraction” of each polymorph is referred in the legend. Arrows indicate the extremes of integration for total enthalpy calculation.

Results

Emulsions stability

To evaluate the effect of the heating step (to erase crystal memory) on emulsion stability, droplet size was determined prior and after the crystallisation experiment. Data in Table 1 show that emulsions remained stable.

Tab. 1: Droplet size data for emulsions before and after re-crystallisation

Emulsion system	After production			After re-crystallisation		
	$d_{3,2}$ (μm)	σ (σ)	Free water (%)	$d_{3,2}$ (μm)	σ (σ)	Free water (%)
20%	2.0 ± 0.1	0.6	0.0	2.8 ± 0.3	0.4	3.4
40%	2.8 ± 0.2	0.4	2.6	3.7 ± 0.4	0.4	3.1

Solidification curves and crystallisation kinetics

Crystallisation curves of CB systems at 20°C (Fig. 2). The curve measured for bulk CB displays the longest induction time. All systems plateau to the same final SFC content. Values of the Avrami kinetic constant (k) and exponent (n) measured at the different crystallisation temperatures are shown in Fig. 3a and 3b, respectively.

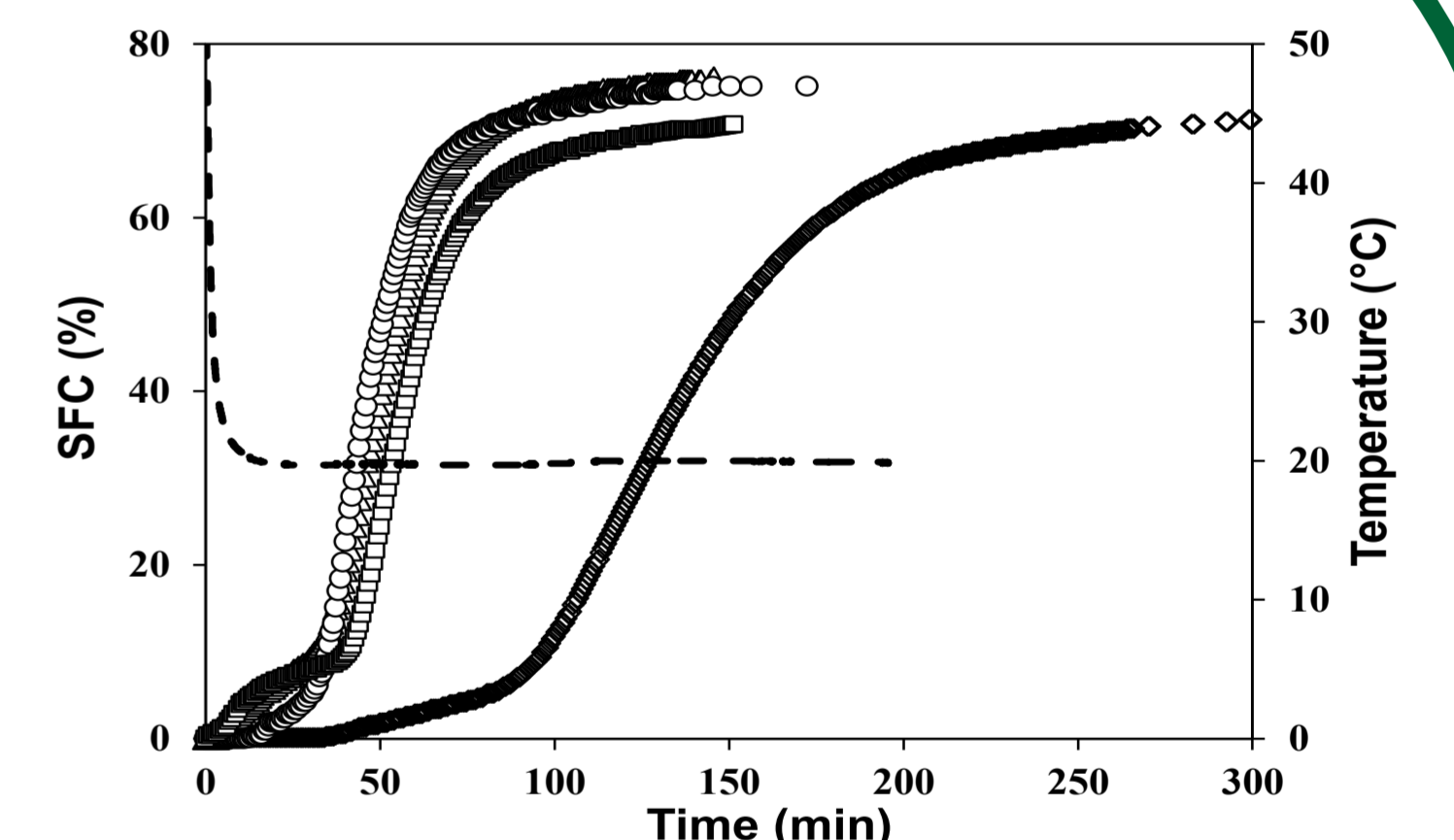


Fig. 2: Crystallisation curve at 20°C. Triangle, circle, and square represents 40% water, 20% water and CB-PGPR system, respectively. Diamond represents bulk CB. Dashed line represents the measured cooling profile.

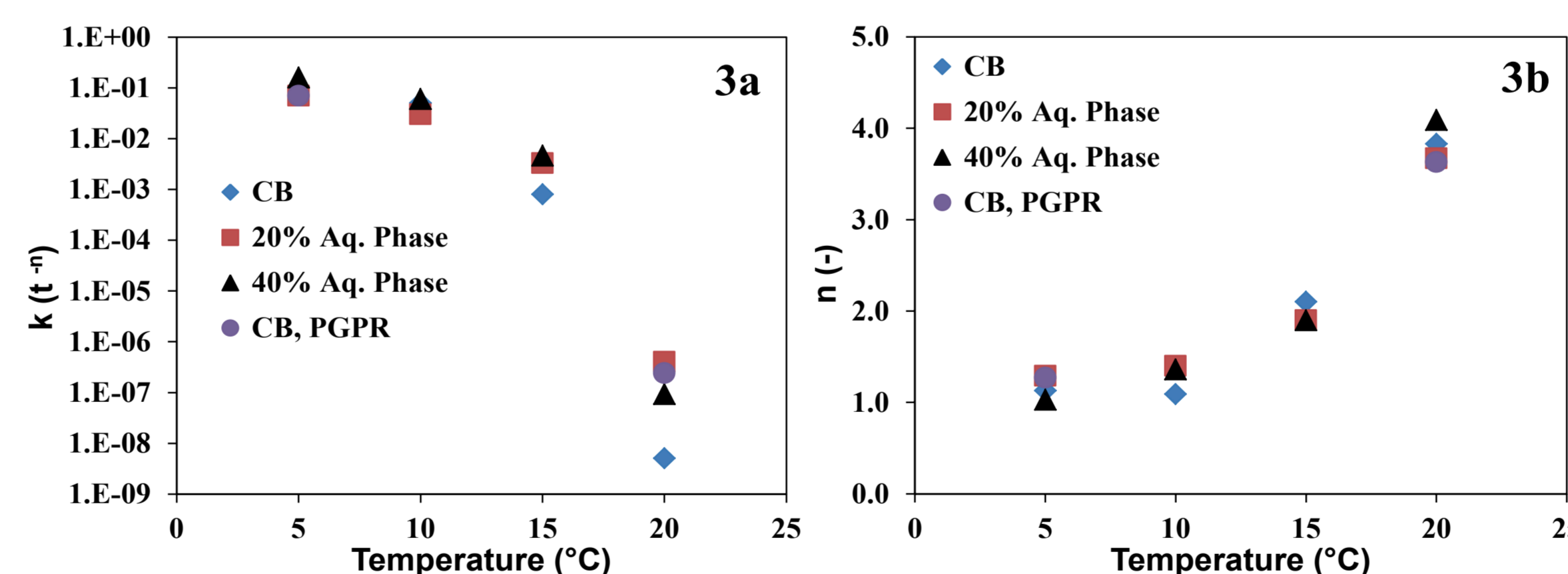


Fig. 3: (a) Avrami constant; (b) Avrami exponent at all crystallisation temperatures. Triangle, circle, and square represents 40% water, 20% water and CB-PGPR system, respectively. Diamond represents bulk CB.

Polymorphic evolution at 5°C

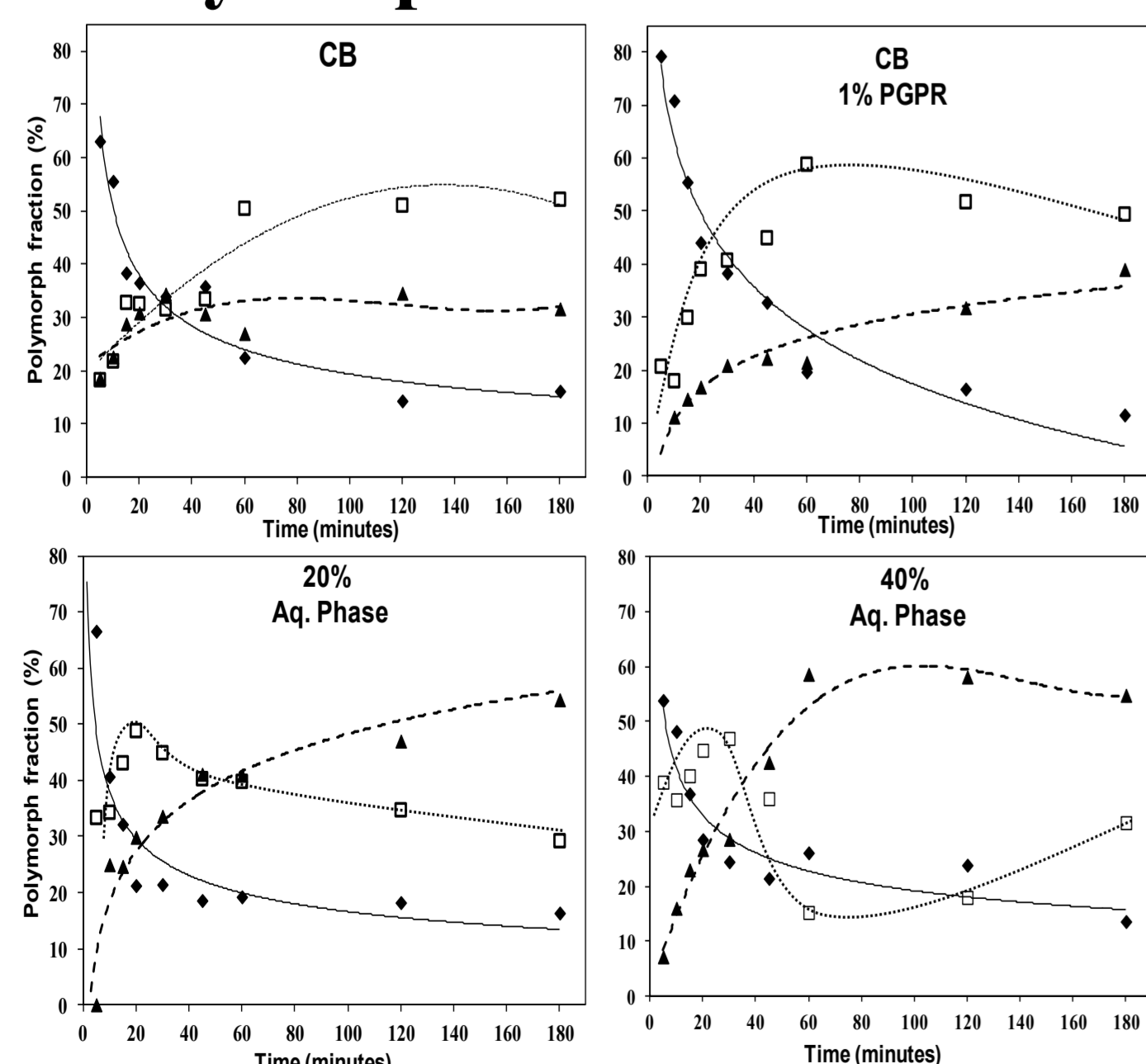


Fig. 4: Polymorphic evolution of CB systems crystallised at 5°C. Diamond: Form II; square: Form III; triangle: Form IV

Average endotherms at 5°C

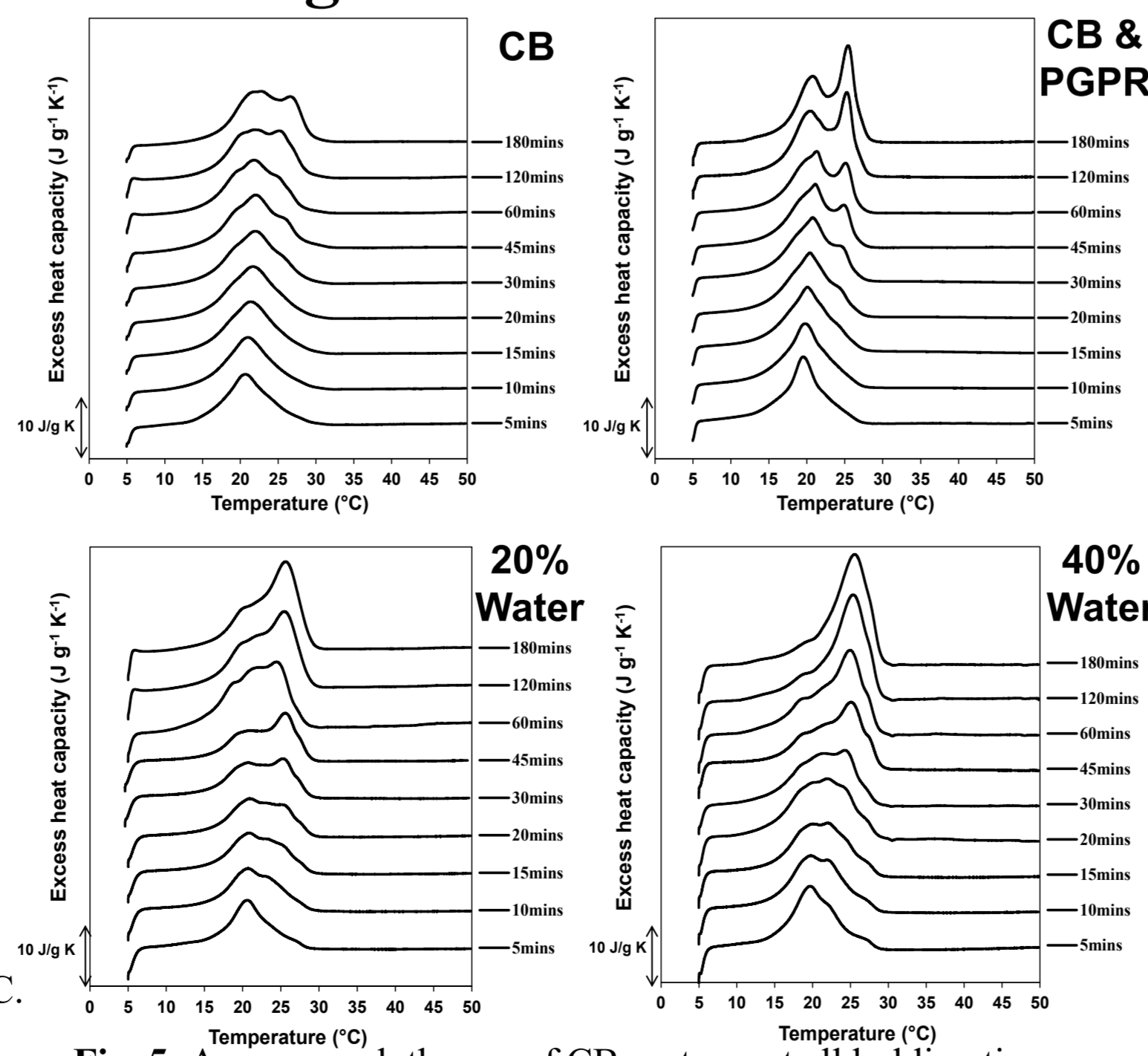


Fig. 5: Average endotherms of CB systems at all holding times.

Polymorphic evolution at 20°C

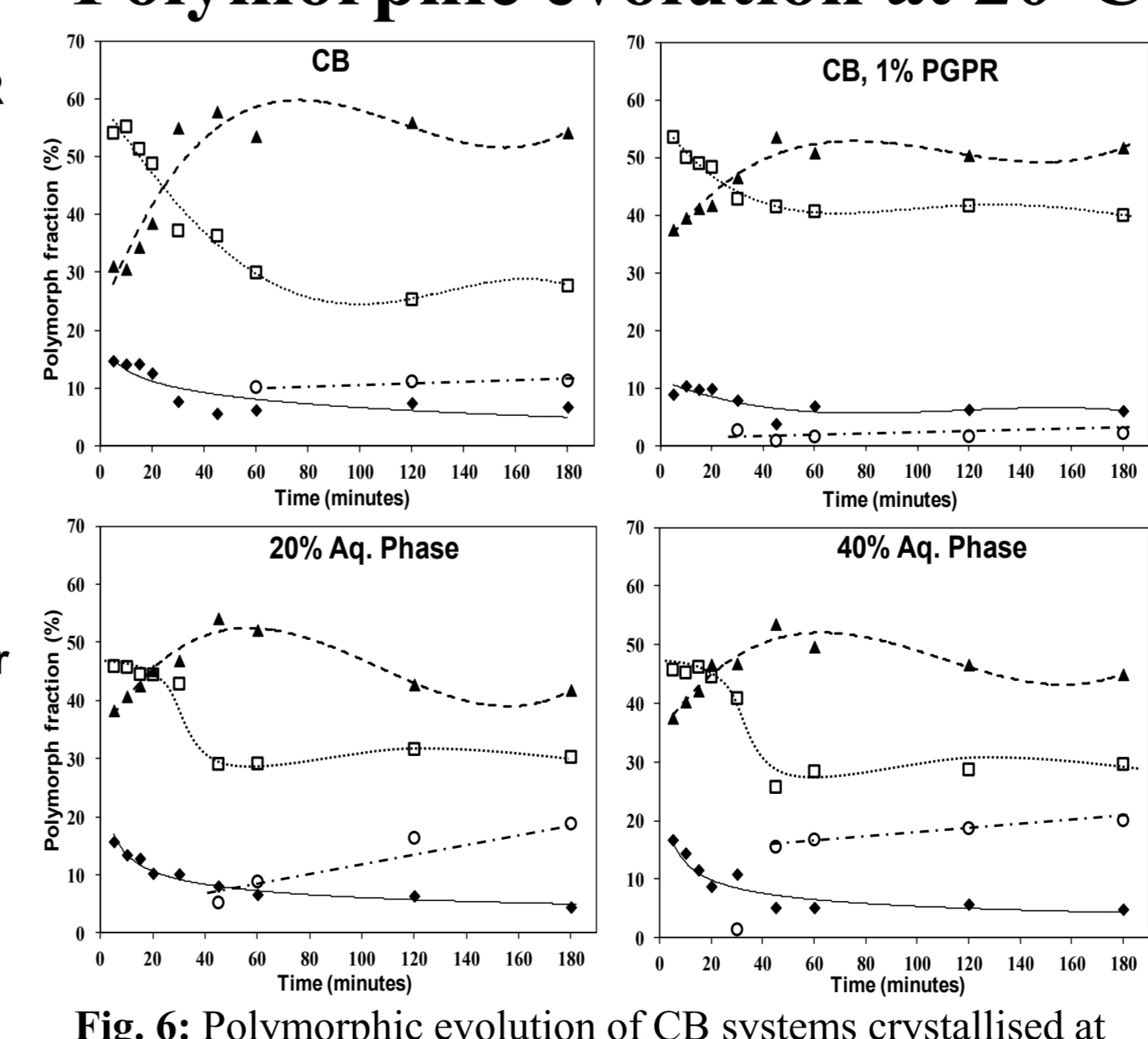


Fig. 6: Polymorphic evolution of CB systems crystallised at 20°C. Diamond: Form II; square: Form III; triangle: Form IV; circle: Form V.

Conclusions

- Emulsions remained stable on multiple heating cycles
- Values of k suggest that crystallise faster at $T \geq 15^\circ\text{C}$
- Values of n suggest that among CB systems the mechanisms of crystallisation are the same. The n increase at $T \geq 15^\circ\text{C}$ suggest a change in crystal growth dimensions
- Polymorphic evolution is faster in emulsions

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