

1 **Effect of shear work input on steady shear rheology and melt functionality**  
2 **of model Mozzarella cheeses**

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11 **Abstract**

12 Model Mozzarella cheeses with varied amounts of shear work input were prepared by  
13 working molten cheese mass at 70 °C in a twin screw cooker. Rheology and melt  
14 functionality were found to be strongly dependent on total shear work input. A non-linear  
15 increase in consistency coefficient (K from power law model) and apparent viscosity and  
16 decrease in flow behaviour index (n from power law model) were observed with increasing  
17 amounts of accumulated shear work, indicating work thickening behaviour. An exponential  
18 work thickening equation is proposed to describe this behaviour. Excessively worked cheese  
19 samples exhibited liquid exudation, poor melting and poor stretch. Nonfat cheese exhibited  
20 similar but smaller changes after excessive shear work input. We concluded that the dominant  
21 contributor to the changes in properties with increased shear work was shear induced  
22 structural changes to the protein matrix. A good correlation was found between the steady  
23 shear rheological properties and the melting properties of the cheeses.

24 Key words: Shear work, Work thickening, Rheology, Melt functionality, Mozzarella cheese

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## 26        **1. Introduction**

27    The Mozzarella cheese process includes a cooking and stretching step that gives a plastic  
28    appearance to the curd and promotes formation of a fibrous protein network (Lucey, Johnson  
29    & Horne, 2003). The stretching step not only brings about desirable textural changes but also  
30    helps in redistributing the fat-serum channels within the cheese matrix and this is important  
31    for attaining optimum melt characteristics during pizza baking (Rudan & Barbano, 1998).  
32    Traditionally Mozzarella cooking was accomplished by melting the curd in hot water (60-  
33    85°C) and then working the molten curd by stretching and kneading manually until the  
34    desired texture was achieved. Modern processes use mechanical workers/mixers that perform  
35    stretching and kneading action by rotation of single or twin screws in the presence of hot  
36    water (Noronha, O’Riordan & O’Sullivan, 2008). The mechanical process rapidly transforms  
37    curd particles into a heterogeneous but continuously flowable mass (Mulvaney, Rong,  
38    Barbano & Yun, 1997). However, the process may cause heterogeneous distribution of  
39    moisture at a microstructural level in fresh Mozzarella cheese (Kuo, Gunasekaran, Johnson &  
40    Chen, 2001) making it a non-equilibrium system as the cheese may subsequently undergo  
41    further changes during processing and storage such as salt and moisture migration  
42    (McMahon, Fife & Oberg, 1999). Blentech, Stephan and Brabender Farinograph are common  
43    small scale cheese cookers that have recently been used to study preparation of imitation  
44    cheeses (Noronha et al., 2008; El-Bakry, Duggan, O’Riordan & O’Sullivan, 2010a, b) and  
45    process cheese (Glenn, Daubert, Farkas & Stefanski, 2003; Kapoor, Lehtola & Metzger,  
46    2004). These recent studies mainly focused on the effect of processing variables on melt  
47    functionality and firmness of cheese. The Brabender Farinograph has been used for preparing  
48    imitation cheeses with or without chelating salts and the torque responses and functional  
49    characteristics of the cheeses have been reported (El-Bakry et al., 2010a, b; El-Bakry,  
50    Duggan, O’Riordan & O’ Sullivan, 2011a, b, c).

51    The rheology, stretch and melt functionality of cheeses at higher temperatures is determined  
52    by the strength and number of casein-casein interactions (Park, Rosenau & Peleg, 1984)  
53    mainly hydrophobic, calcium cross-linking, electrostatic interactions and hydrogen bonds.  
54    The overall effect of increasing temperature on these interactions is weakening of the cheese  
55    matrix. Lucey et al. (2003) reviewed the chemistry and physics of cheese stretching which is  
56    relevant both to the stretching stage during manufacture and to stretch functionality during  
57    application on a pizza. There is a critical level of energy storage and dissipation that enables  
58    melt and stretch of a casein network. This energy level is related to the relaxation times of

59 casein-casein interactions. If the interactions are too strong then internal stresses generated in  
60 the cheese during stretching are not easily released and the fibres are more likely to break  
61 rather than stretch or flow. If the interactions are too weak then the cheese will not stretch but  
62 will act as a viscous liquid. For cheese to stretch well the casein molecules must interact  
63 closely but the bonds must relax and reform very quickly.

64 Two studies were found considering the effect of working on rheology and functionality of  
65 Mozzarella cheese (Mulvaney et al., 1997; Yu & Gunasekaran, 2005). Both studies  
66 investigated the effect of thermomechanical treatments on rheological and functional  
67 properties and used temperature of working and specific mechanical energy as their system  
68 variables. Both studies concluded that it was possible to create the desired functionality by  
69 manipulating these two system variables. However, the very small range of shear work  
70 applied (2-6.5 kJ/kg) led to a narrow range of melt.

71 Mozzarella cheese has recently been shown to strain harden during tensile testing and to work  
72 thicken during a manual rolling process (Bast, Sharma, Easton, Dessev, Lad & Munro, 2015).  
73 Work thickening was defined as an increase in mechanical strength when a material is  
74 worked. The structure of three Mozzarella-type cheeses has also been shown to change  
75 during rheological testing in a rotational rheometer (Sharma et al., 2015). It was therefore  
76 interesting to explore whether work thickening occurred in a Mozzarella cheese mechanical  
77 cooker. Sharma et al. (2015) have recently developed a technique to successfully measure  
78 steady shear viscosity of Mozzarella cheese at relatively high shear rates ( $\sim 200 \text{ s}^{-1}$ ) at 70 °C.  
79 Our objectives were to study the effect of shear work on steady shear rheology and melt  
80 functionality of model Mozzarella cheeses. Shear work inputs were extended well beyond  
81 normal working times to exaggerate any work thickening effects. Nonfat cheese was included  
82 in the study to observe rheological and structural changes occurring in the protein matrix in  
83 the absence of fat.

## 84 **2. Materials and methods**

### 85 *2.1 Materials*

86 Renneted and acidified protein gel manufactured from skim milk was obtained at -20 °C from  
87 Fonterra Research and Development Centre (FRDC) pilot plant, Palmerston North, NZ. The  
88 proximate composition of the protein gel was typically about 50% moisture and 46% protein.  
89 The frozen blocks were thawed for 1 d at 11 °C and ground in a Rietz grinder (Rietz

90 Manufacturing, Santa Rosa, CA, USA) with 6 mm grind size. Cream was obtained from  
91 FRDC as a fresh lot on each trial day. Cheese salt was obtained from Dominion Salt, Mount  
92 Maunganui, New Zealand. Tri-sodium citrate (TSC) was obtained from Jungbunzlauer,  
93 Basel, Switzerland.

## 94 *2.2 Manufacture of model Mozzarella cheeses*

95 Model Mozzarella cheese was made at FRDC by mixing, cooking and working protein gel,  
96 cream, water and salt in a counter rotating twin-screw cooker (Blentech, model CC-0045,  
97 Blentech Corporation, Rohnert Park, CA, USA). The specified working volume of this  
98 cooker was 29.45 L and the batch size in our study was 25 kg cheese, based on previous  
99 experience at FRDC. Three types of model Mozzarella cheese were made - full fat, nonfat  
100 and full fat with 0.5 % TSC as a chelating agent. Using TSC is atypical for Mozzarella cheese  
101 but its addition created another model system that gave useful insights. The target  
102 composition of full fat cheese was 23% fat, 21 % protein, 53% moisture and 1.4 % salt. All  
103 results are for full fat cheese unless otherwise noted. Nonfat cheese used the same  
104 protein/moisture and protein/salt ratios as full fat cheese. 31 batches of model Mozzarella  
105 cheese were prepared using the conditions outlined in Table 1.

106 Previous experience at FRDC with the cooker plus preliminary experiments had shown that a  
107 preworking treatment was useful in order to create macroscopically homogenous and  
108 workable molten cheese with all the cream and water incorporated. The preworking involved  
109 mixing of curd, cream, salt and water in the cooker with direct steam injection till the  
110 temperature reached 70 °C, typically after 320 - 350 s. The expected mass of condensate  
111 added by steam injection was included in the target composition calculations.

112 Preworking was followed by working the molten cheese mass using different screw speeds  
113 for various times (Table 1). Temperature was maintained at 70 °C by indirectly injecting  
114 steam intermittently into the Blentech jacket by manually opening a needle valve. A load cell  
115 was fixed to the Blentech frame 0.2 m from the axis of one of the mixer shafts and set up to  
116 enable torque on the shaft to be continuously logged. Cheese samples from the experiments  
117 were placed in plastic containers or plastic bags and cooled rapidly in salt-ice-water slurry.  
118 Samples were then either frozen and stored at -20 °C or were tested after storage at 4 °C for  
119 up to 7 d.

## 120 *2.3 Shear work calculation*

121 Force measured by the load cell was converted to torque,  $M$ , using

$$122 \quad M(t) = [F(t) - F_0] \times L \quad (1)$$

123 where  $F(t)$  is the force at time  $t$ ,  $F_0$  is the baseline force value and  $L$  is the distance of the  
124 force sensor from the shaft axis, 0.2 m.  $F_0$  was measured at 70 °C and at each screw speed  
125 used in the trials both with water and with air in the Blentech to measure frictional force  
126 created by the bearings and mechanical seals when wet.  $F_0$  values in air were used in the  
127 calculations. The load cell calibration was checked periodically using standard weights. Shear  
128 work input (Steffe & Daubert, 2006) to the molten cheese mass was obtained by calculating  
129 area under the torque-time curve and applying the following equation.

$$130 \quad \text{Shear work, } W_s \text{ (J/kg)} = \frac{\omega}{m} \int_0^t M(t) dt \quad (2)$$

131 where  $\omega$  (rad.s<sup>-1</sup>) is the screw speed,  $m$  (kg) is the mass of cheese in the Blentech,  $M$  (Nm) is  
132 the torque calculated at time  $t$  (s) using Eq.1. Numerical integration of the torque-time curve  
133 with respect to time was conducted using the trapezoidal rule in Microsoft Excel. Shear work  
134 calculation included the shear work input during the preworking period. As it was a twin  
135 screw mixer with independent motor drives for each shaft and a load cell was fitted on only  
136 one shaft, shear work was multiplied by 2.

#### 137 *2.4 Meltability of Mozzarella cheese*

138 The modified Schreiber test (Muthukumarappan, Wang & Gunasekaran, 1999) was used with  
139 some variations. Shreds of approximate size 15x5x5 mm were prepared from a block of  
140 cheese using wire and a roller cutter. For each test, 5 g shredded cheese was formed into a  
141 ~40 mm diameter disc by placing shredded cheese into a hollow plastic cylinder aligned  
142 vertically in a petri dish and compressing using a piston with 5 kg mass on it for 15 s. The  
143 petri dish was covered, placed at 4 °C for 10 min for temperature equilibration, then placed  
144 for 5 min in a forced-air convection oven at 232 °C. After removing from the oven, molten  
145 cheese samples were cooled on a flat surface for ~30 min. The extent of spread, expressed as  
146 melt score, was measured using the method suggested by Park et al. (1984). Cheese spread  
147 on the petri dish was read on a target-type concentric-circle graph with melt score starting as  
148 0 at 40 mm diameter and increasing by 1 melt score unit for each radial distance increase of  
149 2.54 mm. To correct for non-uniformity of melt spread, i.e. non-circular shape, six readings

150 were obtained from six equally spaced radial vectors and averaged. For each cheese sample,  
151 the meltability test was conducted in quadruplicate.

## 152 *2.5 Steady shear rheology*

153 Steady shear rheological measurements on the cheese samples were conducted on an Anton  
154 Paar MCR 301 rheometer (Anton Paar, Graz, Austria) with a 20 mm diameter serrated plate  
155 geometry (PP20/P2) and a Peltier temperature hood (H-PTD 200). A cheese cylinder was  
156 drawn from a block of cheese stored at 4 °C using a cork borer. Cheese discs 20 mm diameter  
157 and ~2 mm thick were cut from this cylinder using a wire cutter. Cheese discs were wrapped  
158 in plastic and stored at 4 °C to prevent moisture loss. Discs were equilibrated to 21 °C, placed  
159 in the rheometer gap and the gap closed till normal force reached 5 N. The sample was heated  
160 to 70 °C and equilibrated for 120 s before rheological measurement started. A ring of soybean  
161 oil was put at the outer periphery of the sample to prevent moisture loss. The flow curve  
162 method described by Sharma et al. (2015) was used for measuring steady shear rheology at  
163 70 °C. Shear rates from 0.01 to 200 s<sup>-1</sup> were applied with measurement times as follows: 60 s  
164 at 0.01 s<sup>-1</sup>, 6.25 s at 0.1 s<sup>-1</sup>, 0.5 s at 1 s<sup>-1</sup>, 0.05 s at 10 s<sup>-1</sup>, 0.05 s at 100 s<sup>-1</sup>, 0.05 s at 200 s<sup>-1</sup>. A  
165 power law model was used to fit the flow curve and calculate the consistency coefficient, K,  
166 and flow behaviour index, n (Sharma et al., 2015). Steady shear rheological measurements on  
167 each sample were conducted in triplicate.

## 168 *2.6 Statistical analysis*

169 Descriptive statistics, non-linear regression and correlation analysis were conducted on the  
170 data using SPSS software (version 13). Test of significance for correlation coefficients was  
171 conducted using a two-tailed t- test at P<0.01.

# 172 **3 Results**

## 173 *3.1 Processing characteristics and physical properties of model Mozzarella cheese*

174 Table 1 shows the total mixing times and compositions of all samples and the corresponding  
175 values of shear work. Torque-time curves during mixing at three screw speeds are presented  
176 in Fig. 1. The end of the preworking period when the temperature reached 70 °C is indicated  
177 by a vertical straight line. Accumulated shear work during the preworking period varied  
178 between runs but was always in the range 1.2-2.0 kJ/kg. Post-preworking, the torque at 50  
179 rpm remained relatively constant for the whole working time, accumulating shear work in the  
180 range of 12 kJ/kg (run 12) to 14.5 kJ/kg (run 6). In contrast at 150 and 250 rpm the torque

181 progressively increased with time to a maximum, then decreased steeply and finally increased  
182 a second time after prolonged working. The rate of increase of torque with time was higher at  
183 250 rpm. The increase of torque with time indicates work thickening of the cheese mass  
184 while the steep decline coincided with rapid changes to the macroscopic cheese structure. The  
185 maximum values of torque for 150 and 250 rpm occurred at 3820 s and 2685 s (Fig. 1)  
186 corresponding to shear work inputs of 66 and 129 kJ/kg respectively. An earlier start of  
187 torque decline at 250 rpm indicates earlier onset of macroscopic structural breakdown.  
188 Throughout the working time, torque values were highest for 250 rpm followed by 150 rpm  
189 and then 50 rpm. At short times this may be attributed to higher inertial forces at higher  
190 speeds, but at longer times the higher work thickening at higher speeds also makes a  
191 contribution. Manski, van der Zalm, van der Goot and Boom (2008) reported similar changes  
192 in torque with time as a result of structure formation and breakdown during prolonged  
193 shearing of fat-containing Ca-caseinate dispersions.

194 Periodically the appearance and characteristic elongation of the cheese was used as an  
195 assessment of the pasta filata quality (Figs. 2 & 3). Insufficient shear work input results in a  
196 runny cheese often with the presence of buttery liquid indicating that the cream has not yet  
197 been well incorporated into the protein matrix (Fig. 2a). Retention of fat and moisture in the  
198 finished product is an important consideration in achieving desired functionality (Rizvi,  
199 Shukla & Srikiatden, 1999). The cheese had developed a typical pasta filata structure (Figs.  
200 2b & 3a) after 635 s at 150 rpm corresponding to shear work inputs of 6.6-8.8 kJ/kg (runs 15  
201 & 21). Prolonged shearing led to a damaged and short texture with an oatmeal like  
202 appearance and very limited stretch (Figs. 2d & 3b). The long fibrous strands typical of  
203 Mozzarella-type cheeses were absent. Emergence of this grossly overworked structure  
204 coincided with expulsion of small amounts of a watery fluid (whey like in appearance) from  
205 the cheese (Fig. 2d).

206 Nonfat cheese prepared by working at 150 rpm showed similar behaviour to full fat cheese  
207 with torque increasing then declining with time and with expulsion of watery fluid after  
208 overworking. Expelled serum after overworking for both full fat and nonfat cheese had a low  
209 total solids content of 4.5 - 6.0 % with salt as the main solid component and little fat (Table  
210 1).

211 Cheese prepared at 150 rpm with the addition of TSC showed uniform torque versus time  
212 with less fluctuation than the curves in Fig. 1. El-Bakry et al. (2010 a, b; 2011a, b, c) also



213 reported relatively stable torque readings after attaining a homogenous mass during mixing at  
214 constant temperature for cheeses with added chelating salts. The typical fibrous structure of  
215 Mozzarella cheese was absent and the cheese showed a grainy visual appearance instead.  
216 TSC would be expected to chelate some calcium resulting in reduced casein-casein  
217 interactions (Mizuno & Lucey, 2005). This may result in dispersion of caseins (Brickley,  
218 Govindaswamy-Lucey, Jaeggi, Johnson, McSweeney & Lucey, 2008). Cheese with TSC  
219 added was very sticky. It stuck to plastic bags, rubber gloves and stainless steel. This could  
220 be attributed to the tendency of para-casein to stick to hydrophobic materials such as nylon  
221 gloves (Paulson, McMahon & Oberg, 1998). Brickley et al. (2008) attributed this stickiness  
222 to a decrease of hardness upon addition of TSC as a result of weakening of the casein matrix  
223 because of sequestering of calcium and increase of pH resulting in increased electrostatic  
224 repulsion.

### 225 *3.2 Effect of accumulated shear work on steady shear rheology of model Mozzarella cheese*

226 Preliminary experiments included comparison of rheological parameters for fresh samples  
227 direct from the Blentech, samples stored at 4 °C for 3-7 d and samples frozen then thawed.  
228 No significant difference was observed between the sample treatments for either K or n.  
229 Samples stored at 4 °C for 3-7 d were therefore used for most runs though for runs 25, 28, 30  
230 and 31 frozen and thawed samples were used. Cervantes, Lund and Olson (1983) also  
231 reported no significant effect of a freeze-thaw cycle and frozen storage on textural and  
232 sensory properties of Mozzarella cheese. However, Dahlstrom (1978) reported changes in  
233 textural attributes of Mozzarella cheese immediately after thawing, but the cheese regained  
234 its original properties some weeks after thawing. We thawed frozen samples by storing at 4  
235 °C for 3-7 days. This holding period may allow the structure to approach equilibrium with  
236 uniform distribution of moisture, avoiding any possible effects from localised moisture  
237 pockets.

238 K and melt score showed better reproducibility between the two sets of runs at 150 rpm when  
239 plotted as a function of shear work input than when plotted as a function of shearing time  
240 (Fig. 4). Further plots were therefore done as a function of shear work. A further advantage of  
241 plotting versus shear work is that results at different screw speeds can be plotted together.  
242 Runs 19-24 took a longer time and higher shear work level to produce a given change in  
243 either consistency coefficient or melt score than runs 13-18. One reason for this difference  
244 was that the mean moisture content of runs 19-24 was higher (53.8%) than runs 13-18

245 (52.9%). This higher moisture content is probably because the ambient temperature was  
246 much colder in May than in January and the steam used for direct injection was therefore  
247 probably wetter. However, the protein gel and cream are both natural raw materials so some  
248 daily and seasonal variation is also expected.

249 Figs. 5 and 6 show the flow behaviour index and apparent viscosity obtained for all the full  
250 fat cheeses without TSC plotted together as a function of shear work. For determination of  
251 apparent viscosity (Fig. 6), a shear rate of  $0.01\text{s}^{-1}$  was chosen as low strain rates produced on  
252 the cheese by gravity are relevant during the modified Schreiber melt test and also during  
253 baking on a pizza (Zhu, Brown, Gillies, Watkinson & Bronlund, 2015). Data from all 33  
254 samples show definite trends with shear work and also fitted reasonably well on one  
255 correlation line.  $K$  ( $K = 137.82e^{0.02Ws}$  with  $R^2=0.85$ ) and apparent viscosity at  $0.01\text{ s}^{-1}$  (Fig. 6)  
256 both increased exponentially with shear work input whereas  $n$  (Fig. 5) declined with shear  
257 work input. All three variables changed relatively slowly up to a shear work input of about 45  
258 kJ/kg, but much more rapidly above that. The rapid decline in  $n$  at high shear work input (60-  
259 68 kJ/kg) corresponded well with the stage when peak torque was attained (66 kJ/kg, Fig.1)  
260 and when the macroscopic structural breakdown occurred (Fig. 2). Over the shear work range  
261 considered  $K$  increased from 97 to 2,928  $\text{Pa}\cdot\text{s}^n$ ,  $n$  decreased from 0.78 to 0.37 and apparent  
262 viscosity at  $0.01\text{ s}^{-1}$  increased from 277 to 54,700  $\text{Pa}\cdot\text{s}$ . The 30 fold increase in  $K$  and 198  
263 fold increase in apparent viscosity at  $0.01\text{ s}^{-1}$  indicate very significant work thickening over  
264 the shearing period. The decrease in  $n$  indicates that on working the cheese was progressively  
265 becoming more shear thinning.

266 Rheological parameters for nonfat cheese and cheese with added TSC are compared with  
267 those of full fat cheese in Fig. 7. Shear work input had a very small effect on the rheological  
268 parameters of cheese with added TSC, i.e. no significant work thickening. Nonfat cheese  
269 exhibited significant work thickening with a big increase in both  $K$  and apparent viscosity at  
270  $0.01\text{ s}^{-1}$  as shear work increased. Shear work input had the biggest effect for full fat cheese.

### 271 *3.3 Effect of accumulated shear work on melt functionality of model Mozzarella cheese*

272 Melt scores for all full fat samples without TSC demonstrated reasonable alignment plotted  
273 versus shear work (Fig. 8), suggesting the validity of shear work as a process control variable  
274 to achieve the desired product functionality. Melt scores did not change significantly with  
275 shear work below 10 kJ/kg, but decreased with shear work above 10 kJ/kg reaching very low  
276 values in the range 0.2-0.5 at shear work inputs  $>70\text{ kJ/kg}$ .

277 Melt score versus shear work curves for nonfat cheese and cheese with added TSC are  
278 compared with that for full fat cheese in Fig. 9. Melt score changed very little with shear  
279 work for cheese with added TSC. Nonfat cheese was much less shear work sensitive than full  
280 fat cheese reaching a lowest melt score of 3.7 after prolonged working compared to 0.2 for  
281 full fat cheese.

282 Fig. 10 shows the appearance of several cheese samples after melting and then cooling in the  
283 modified Schreiber melt test. Optimal working (Fig. 10a) resulted in good melting, a  
284 reasonable spread, browning around the periphery and the desired free oil release. The series  
285 of events during the melt test for cheese with optimal functionality would be expected to be  
286 similar to those described by Rudan and Barbano (1998) during pizza baking. First fat started  
287 melting within the shreds and then travelled to the heat exposed surfaces. The rate of fat  
288 migration to the surface is very important because fat prevents surface drying and skin  
289 formation (Rudan & Barbano, 1998). This enables shreds to melt and then fuse together to  
290 make one molten mass followed by spreading or flow of the molten cheese by biaxial  
291 expansion/stretching under gravity.

292 However, excessively worked (>70kJ/kg) samples did not exhibit this behaviour. Some of the  
293 shreds retained their individual identity throughout the heating regime, fusion was limited  
294 and flow across the petri dish was very small (Fig. 10b). One possible reason for this  
295 behaviour could be that toughening of the protein matrix by excessive working is limiting fat  
296 migration through the protein matrix to the shred surface resulting in surface drying and skin  
297 formation thus inhibiting shred fusion and cheese flow. To check this possibility a sample of  
298 excessively worked cheese was coated with a vegetable oil spray before placing in the oven.  
299 This increased the melt score slightly from 0.2 to 0.5 (Fig. 10c) but did not give flow  
300 anywhere near that of the samples with low shear work input. This suggested that changes to  
301 the protein matrix itself were having a major role in limiting the melting and flow of the  
302 excessively worked samples.

303 Nonfat cheese with low shear work input melted and flowed well (Fig. 10d). These melting  
304 results for nonfat cheese were surprising given the explanation above of the role of fat in  
305 preventing surface drying and skin formation and contrast with the pizza baking results of  
306 Rudan & Barbano (1998), who reported that low fat Mozzarella cheeses had limited melting.  
307 The melt of nonfat cheese was less impacted by excessive shear work (Fig. 10e) than that of  
308 full fat cheese. Again coating with vegetable oil spray had only a small positive effect on

309 melt score (Fig. 10f). This suggests that there is a significant contribution of the fat phase to  
310 the poor melting properties of excessively worked full fat cheese. Changes to the protein  
311 matrix alone cannot explain the results. Molten nonfat cheese was white in appearance while  
312 still hot but transformed into a transparent plastic like sheet upon cooling to room  
313 temperature (Fig. 10d). Pastorino, Dave, Oberg and McMahon (2002) reported increased  
314 opacity of nonfat Mozzarella cheese upon heating from 10 °C to 50 °C and attributed this to  
315 heat induced changes in protein interactions as manifested by structural changes in the  
316 cheese. Heating would favour hydrophobic interactions and would possibly allow re-  
317 association of  $\beta$ -casein and calcium within the protein matrix, causing enhanced protein-  
318 protein interactions (Pastorino et al., 2002). Translucency of nonfat Mozzarella cheese in the  
319 presence of salt has also been attributed to limited light scattering from pockets of free serum  
320 distributed in the protein matrix (Paulson et al., 1998). Translucency of cheese has been  
321 attributed to the formation of a fine stranded protein network that allows light to pass through  
322 (Brickley et al., 2008).

### 323 *3.4 Relationships between melt functionality and steady shear rheology*

324 Apparent viscosity at 0.01 s<sup>-1</sup> (Fig. 6) was able to distinctly differentiate the effect of shear  
325 work input for all the full fat cheese samples without added TSC. Therefore, an attempt was  
326 made to establish a relationship between melt functionality and apparent viscosity at 0.01 s<sup>-1</sup>.  
327 A significant (P<0.01) negative correlation fitted by an exponential relationship with good fit  
328 ( $R^2 = 0.91$ ) was found for apparent viscosity at 0.01s<sup>-1</sup> as a function of melt score (Fig. 11).  
329 Brickley et al. (2008) also reported an inverse relationship between meltability and hardness  
330 of cheese.

## 331 **4 Discussion**

332 The torque profiles (Fig. 1) were different to those observed for imitation cheese by El-  
333 Bakry, Beninati, Duggan, O’Riordan & O’Sullivan (2011). They typically observed a peak-  
334 trough-peak profile and linked the first peak to hydration of dry rennet casein and the second  
335 peak to emulsification. However, our protein gel had never been dried so was already  
336 hydrated. Also emulsification was not expected to be a major event in our mixing as we used  
337 dairy cream instead of vegetable fat. Different torque profiles might therefore be expected.

338 The results give two main sets of evidence for very significant work thickening during  
339 working of the model Mozzarella cheeses: increase of torque with time at the 150 rpm and

340 250 rpm screw speeds (Fig. 1), and 198 fold increase in apparent viscosity at  $0.01s^{-1}$  (Fig. 6)  
 341 with increasing shear work input from 6 kJ/kg to >70 kJ/kg. The detailed chemical basis for  
 342 the work thickening is not clear. Cheese rheological properties are largely governed by the  
 343 strength of casein-casein interactions (Lucey et al., 2003). Work thickening is a result of the  
 344 strengthening of these interactions upon shearing at 70 °C. The presence of shear is a critical  
 345 element - merely holding at 70 °C would cause little change as even at 50 rpm shearing for  
 346 4,000 s (shear work input of 14 kJ/kg) caused little change in rheology. The presence of  
 347 calcium is also critical as the model cheese with added TSC to chelate calcium showed  
 348 almost no work thickening even with shear work input of 81 kJ/kg (Fig. 7). The importance  
 349 of calcium cross-linking to the casein-casein interactions in cheese and the changes in cheese  
 350 properties on adding chelating salts have both been well covered in many publications  
 351 (Brickley et al., 2008; Lucey & Fox, 1993; Lucey et al., 2003; Mizuno & Lucey, 2005; El-  
 352 Bakry et al., 2010 a, b; 2011a, b, c). Some of the factors suggested by Bast et al. (2015) as  
 353 important for strain hardening of Mozzarella cheese are also likely to be important for work  
 354 thickening – movement of the casein fibres past one another and the “stickiness” of the  
 355 adjacent casein chains both increasing casein-casein interactions.

356 What type of reaction or mechanism results in an exponential increase in apparent viscosity  
 357 (Figs. 6, 7) with shear work? Particle growth by coalescence is one of the few process models  
 358 that exhibits this functional form and is based on the distortion and kneading of the fluid  
 359 eddies that bring the particles together (Levenspiel, 1996). There are parallels between the  
 360 Blentech mixing-shearing action and interaction of fluid eddies. Let us define the rate of  
 361 work thickening as  $d\eta/dt$ . Work thickening in our molten cheese system is caused by  
 362 increases in the number or strength of effective molecular interactions, specifically protein-  
 363 protein interactions. Fundamentally, viscosity is a measure of the strength of intermolecular  
 364 interactions providing a resistance to flow. It is therefore reasonable to propose that

$$365 \quad d\eta/dt \propto \eta \quad (3)$$

366 Rearranging and integrating between limits

$$367 \quad \eta = \eta_0 e^{at} \quad (4)$$

368 As we have found that shear work input ( $W_s$ ) as an independent variable is a stronger  
 369 predictor than time of the outcome with respect to rheology and melt functionality (Fig. 4),

370 and also enables the results of different shear rates to be correlated on a single curve (Figs. 5-  
371 6), we can integrate with respect to  $W_s$  rather than time.

$$372 \quad \eta = \eta_0 e^{bW_s} \quad (5)$$

373 where  $\eta_0$  is viscosity before significant work thickening,  $\eta$  is viscosity at time  $t$  or shear work  
374  $W_s$  during work thickening and  $a$ ,  $b$  are work thickening constants.

375 Equation 5 is in exactly the form of the equations on Figs. 6 and 7c for apparent viscosity  
376 versus shear work. The results give  $b$  values at 150 rpm of 0.05 kg/kJ for full fat cheese, 0.03  
377 kg/kJ for nonfat cheese and 0.01 kg/kJ for full fat cheese with added TSC (Fig. 7c).

378 An alternative approach to explain the exponential nature of work thickening with time or  
379 shear work arises from the nature of the laminar mixing process occurring in the Blentech  
380 with the extremely viscous cheese (Szalai, Alvarez & Muzzio, 2004). In the chaotic flow  
381 occurring in laminar mixing the stretching of a fluid element,  $\lambda$ , from length  $l_0$  to length  $l_n$   
382 after time  $t$  is given by

$$383 \quad \lambda = l_n/l_0 = e^{\Lambda t} \quad (6)$$

384 where  $\Lambda$ , the Lyapunov exponent of the flow, represents the average rate of stretching after a  
385 given time. The stretching and folding action in laminar mixing not only gives an alternative  
386 theoretical basis for the exponential nature of work thickening, but also forms the structural  
387 basis for the creation of striated cheese microstructures such as those observed in Mozzarella  
388 cheese.

389 Torque versus time curves similar to those in Fig. 1 occur during mechanical development of  
390 dough which is a structurally similar food system where work thickening behaviour has been  
391 well explored (Zheng, Morgenstern, Campanella & Larsen, 2000; Peressini,  
392 Peighambardoust, Hamer, Sensidoni & van der Goot, 2008; Peighambardoust, van der Goot,  
393 van Vliet, Hamer & Boom, 2006). During mechanical development of dough a fibrous gluten  
394 network is formed during the mixing process and moisture is also distributed uniformly  
395 within the developed protein network (Bloksma & Bushuk, 1988; Zheng et al., 2000). During  
396 dough development torque reaches a peak value indicating maximum resistance to  
397 deformation and subsequently declines possibly indicating depolymerisation of the gluten  
398 network or some solubilisation of the gluten proteins (Hoseney, 1998; Bekes, Gras, Gupta,  
399 Hickman & Tatham, 1994). The chemistry of dough development is very different to that of

400 cheese with S-H to S-S interchange reactions forming new covalent bonds between two  
401 adjacent gluten chains but there are many parallels in physical behaviour. Supramolecular  
402 polymer networks also display work thickening behaviour above a critical shear rate with the  
403 critical shear rate being experimentally correlated with the lifetime of crosslinking bonds  
404 (Xu, Hawk, Loveless, Jeon & Craig, 2010).

405 With large shear work inputs (>70 kJ/kg) work thickening became more extreme and along  
406 with the changes in rheological properties other major changes in cheese properties occurred  
407 including loss of stretch (Fig. 3), syneresis leading to liquid exudation (Fig. 2) and loss of  
408 melt (Fig. 8, 10b). All three of these changes are caused by very strong casein-casein  
409 interactions meaning that attractive forces have become dominant over repulsive forces.  
410 Stretch can be regarded as the ability of the casein network to maintain its integrity, i.e. not  
411 break, upon continuous application of tensile stress to molten cheese. It requires flexibility of  
412 interactions between casein molecules enabling them to relax applied stresses within the time  
413 scale of deformation. Loss of stretch is an indication that casein-casein interactions have  
414 become too strong (Lucey et al., 2003).

415 Liquid exudation upon prolonged working is likely to be caused by a change in the structure  
416 of the cheese. Various micro-structural models proposed the presence of fat-serum channels  
417 within the fibrous casein network of Mozzarella cheese (McMahon et al. , 1999). Working of  
418 Mozzarella cheese allows coalescence of proteins to form larger strands (fibres) that are  
419 oriented in the direction of deformation. The rearrangement of casein fibres results in  
420 redistribution of water and fat during working with larger protein strands being separated by  
421 channels containing water, water soluble substance, bacteria and fat globules. These  
422 channels not only improve the water holding capacity of cheese matrix but also contribute to  
423 the melting behaviour of cheese (McMahon et al., 1999). It is apparent that prolonged  
424 working increases casein-casein interactions leading to a more compact structure with  
425 diminished fat-serum channels so leading to exudation of liquid and poor melting. After  
426 prolonged working the fat globule size is small (results not shown – fat size distribution and  
427 microstructure will be covered in a subsequent paper) so the fat is well locked into the protein  
428 structure and the fat content of the exuded liquid is very small (Table 1).

429 The modified Schreiber melt test assesses the ability of cheese to lose individual shred  
430 identity and then flow and spread. For optimum melting a balance of attractive and repulsive  
431 casein-casein interactions is required (Lucey et al., 2003). The decreasing tendency to melt

432 after prolonged working is another strong indication of excessive associative protein-protein  
433 interactions either from increased hydrophobic interactions or from absence of repulsive  
434 (electrostatic) interactions or both (Lucey et al., 2003).

435 Overall the results suggest that the protein phase is dominant in the work thickening process  
436 and in the resulting changes in rheological and melt behaviour, though the fat phase also  
437 makes a contribution. Nonfat cheese showed similar though smaller changes in rheological  
438 behaviour (Fig. 7) and melt score (Fig. 9) to full fat cheese, and in the nonfat cheese it is  
439 clearly the protein phase that is changing. Comparing melting behaviour in Fig. 10b  
440 (excessively worked cheese) with Fig. 10c (excessively worked cheese with vegetable oil on  
441 the surface) indicated that excessive shear work had changed the protein phase and it was not  
442 just poor fat migration to the surface that was preventing melting.

443 Some aspects of the results are not yet well understood. First, torque versus time curves at  
444 150 and 250 rpm (Fig. 1) show a maximum torque implying a maximum in cheese viscosity  
445 whereas the rheological measurements (Figs. 5-6) show no maximum. We suggest this is  
446 caused by wall slip in the Blentech as liquid exudation begins – the rheological methods used  
447 in the rheometer were chosen to minimise or eliminate wall slip (Sharma et al., 2015).  
448 Second, although rheological measurements (Figs. 5-6) and melt score (Fig. 8) versus shear  
449 work fitted reasonably well on one line the points for 250 rpm are further right than those at  
450 150 rpm suggesting that shear work at 250 rpm is less damaging, i.e. more shear work is  
451 needed at 250 rpm to cause a given change in rheology or melt score. Similarly the maximum  
452 torque in Fig. 1 occurs at 66 kJ/kg for 150 rpm and at 129 kJ/kg for 250 rpm. We suggest that  
453 this is related to the viscoelasticity of the material and the time scale of the deformation.  
454 Shear rates are higher at 250 rpm so the material behaves more elastically and less energy  
455 goes into viscous flow which is probably more important for changing the structure. Pulling  
456 Mozzarella cheese slowly causes stretching and effective interactions between the fibres  
457 whereas pulling it fast tends to break the cheese instead (Lucey et al., 2003). An alternative  
458 explanation is that the flow pattern in the Blentech is somewhat different at 250 rpm with  
459 build up of cheese against the wall at the discharge end of each screw so that some cheese  
460 stays out of the shearing zone for a time. Third, it is puzzling that the melt behaviour of  
461 nonfat cheese was less impacted by excessive shear work than that of full fat cheese (Figs. 9  
462 & 10) and that nonfat cheese work thickened less than full fat cheese (Fig. 7). A possible  
463 explanation is that maybe a filled gel such as full fat cheese work thickens more than a single  
464 phase gel such as nonfat cheese. Fourth, the manual rolling process of Bast et al. (2015)



465 caused huge work thickening in just 18 s of rolling, i.e. an increase in tensile fracture stress of  
466 5.7 times parallel to the fibres and 2.1 times perpendicular to the fibres. However, shearing in  
467 the Blentech at 50 rpm for 4000 s caused only small changes in steady shear viscosity. We  
468 suggest that the one dimensional elongational flow caused by rolling is far more effective  
469 than shear flow at causing work thickening. Another possible explanation is that the shearing  
470 process in the Blentech causes repeated rupture of any new casein-casein interactions that are  
471 formed whereas the rolling operation is a slow and gentle process where the new structure  
472 formed remains intact. The four features of the results described in this paragraph warrant  
473 further study.

## 474 **5 Conclusions**

475 Shear work input significantly increased steady shear viscosity and decreased melt score of  
476 model Mozzarella cheese. The rheological changes indicate very significant work thickening.  
477 The work thickening process showed unusual isothermal kinetics in that the viscosity  
478 increased exponentially with either time or shear work input. At shear work inputs > 70 kJ/kg  
479 expulsion of serum liquid and loss of cheese stretch were also observed. All these changes are  
480 caused by increasingly strong, calcium-mediated, attractive casein-casein interactions after  
481 prolonged working. An inverse relationship was found between melt score and apparent  
482 viscosity. Nonfat cheese also work thickened suggesting that shear induced changes in the  
483 protein phase of the cheese are a major contributor to the effects.

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594

**Figure Captions**

**Fig. 1.** Evolution of torque with time during mixing of model Mozzarella cheese in the Blentech cooker at 70 °C and three screw speeds.

**Fig. 2.** Visual appearance of model Mozzarella cheese in the Blentech cooker after various levels of shear work input at 70 °C and 150 rpm; a. 3.3, b. 6.6, c. 58.2 d. 73.7 kJ/kg

**Fig. 3.** Stretch appearance of model Mozzarella cheese after working in the Blentech cooker at 70 °C and 150 rpm. a. Optimum melt functionality after shear work input of 6.6 kJ/kg; b. Damaged texture after excessive shear work input of 73.7 kJ/kg

**Fig. 4.** Changes in Consistency coefficient (K from power law model) and meltability of model Mozzarella cheese versus time (a,c) and shear work (b,d). Model Mozzarella cheese was manufactured in the Blentech cooker at 150 rpm screw speed and 70 °C. Error bars represent one standard deviation

**Fig. 5.** Effect of shear work on flow behaviour index (n from power law model) of model Mozzarella cheese at 70 °C. Error bars represent one standard deviation.

**Fig. 6.** Effect of shear work on apparent viscosity of model Mozzarella cheese at 0.01 s<sup>-1</sup> shear rate and 70 °C. Error bars represent one standard deviation.

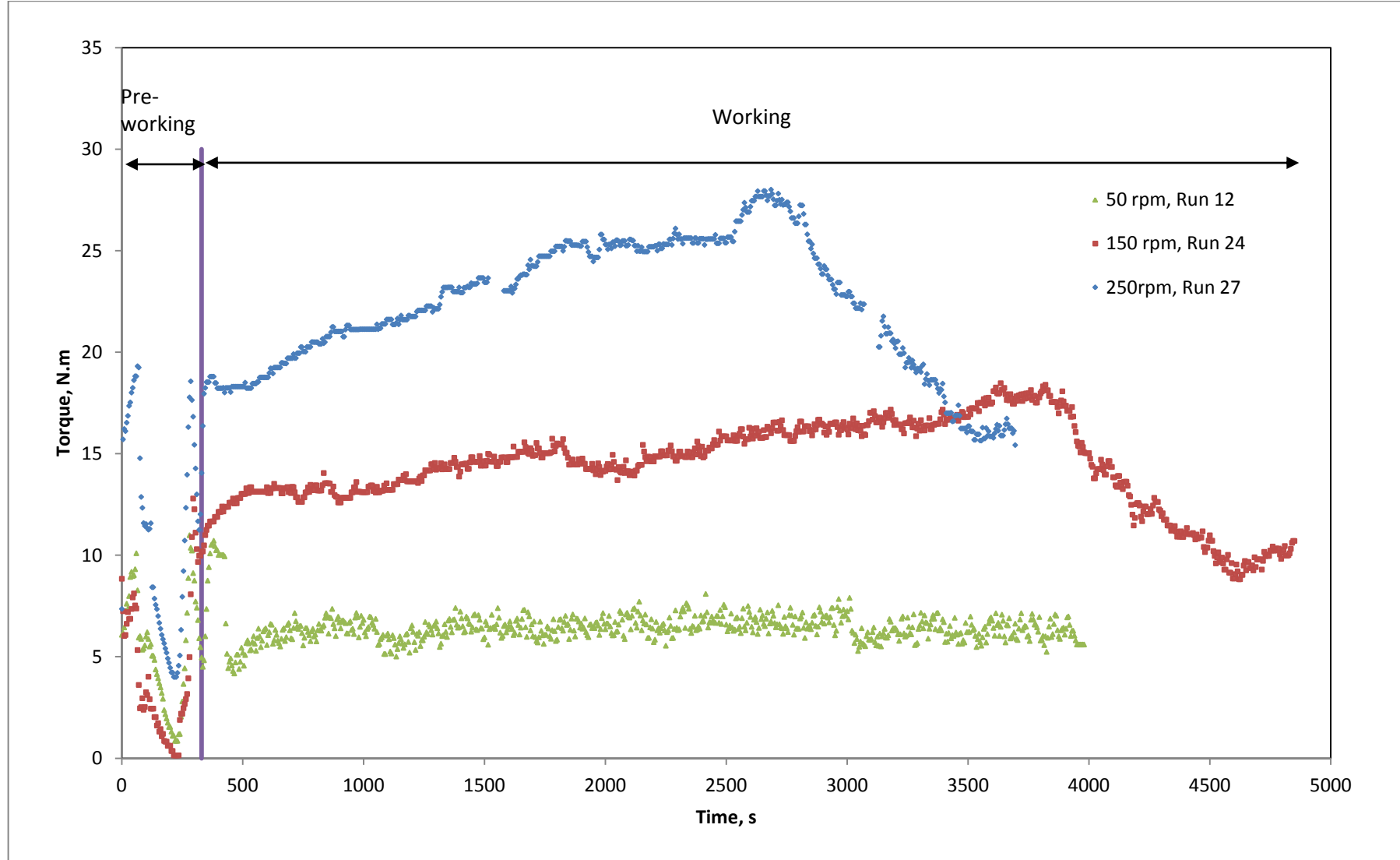
**Fig. 7.** Effect of shear work on (a) consistency coefficient (K from power law model); (b) flow behaviour index (n from power law model) and (c) apparent viscosity at 0.01 s<sup>-1</sup>, all at 70 °C, for three model Mozzarella cheeses prepared in the Blentech cooker using 150 rpm screw speed.

**Fig. 8.** Effect of shear work on meltability of model Mozzarella cheese prepared at 70 °C in the Blentech cooker. Error bars represent one standard deviation.

**Fig. 9.** Melt score versus shear work input for model Mozzarella cheeses prepared in the Blentech cooker using 150 rpm screw speed.

**Fig. 10.** Photographs of cooled model Mozzarella cheese after the modified Schreiber melt test. a. Optimum functionality full fat cheese after 6.6 kJ/kg shear work input, melt score 7.5; b. Full fat cheese after excessive shear work input 166 kJ/kg, melt score 0.2; c. Full fat cheese after excessive shear work input 166 kJ/kg and with vegetable oil sprayed on the surface before melting, melt score 0.5; d. Nonfat cheese after 6.75 kJ/kg shear work, melt score 5.7; e. Nonfat cheese after 128 kJ/kg shear work, melt score 3.7; f. Nonfat cheese after 128 kJ/kg shear work and with vegetable oil sprayed on the surface before melting, melt score 4. Melt score given is the mean of the quadruple tests for each batch.

**Fig. 11.** Correlation of consistency coefficient (K from power law model) and apparent viscosity at  $0.01 \text{ s}^{-1}$  with melt score for the model Mozzarella cheese at  $70 \text{ }^\circ\text{C}$ .

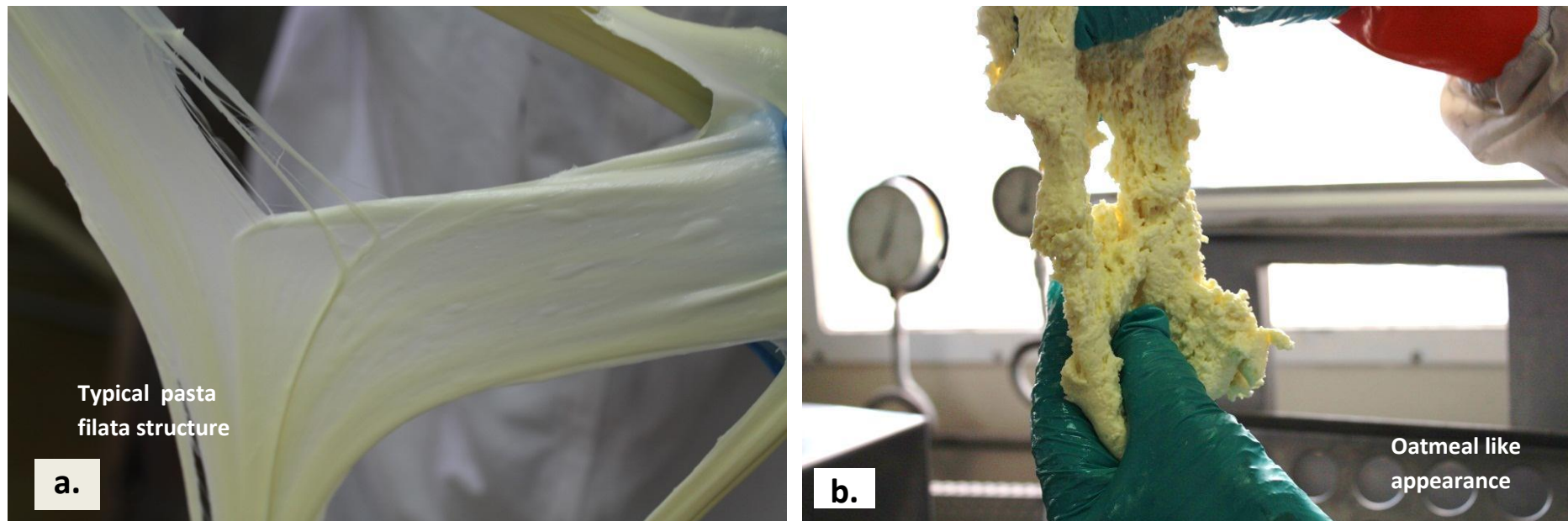


**Fig. 1.** Evolution of torque with time during mixing of model Mozzarella cheese in the Blentech cooker at 70 °C and three screw speeds.

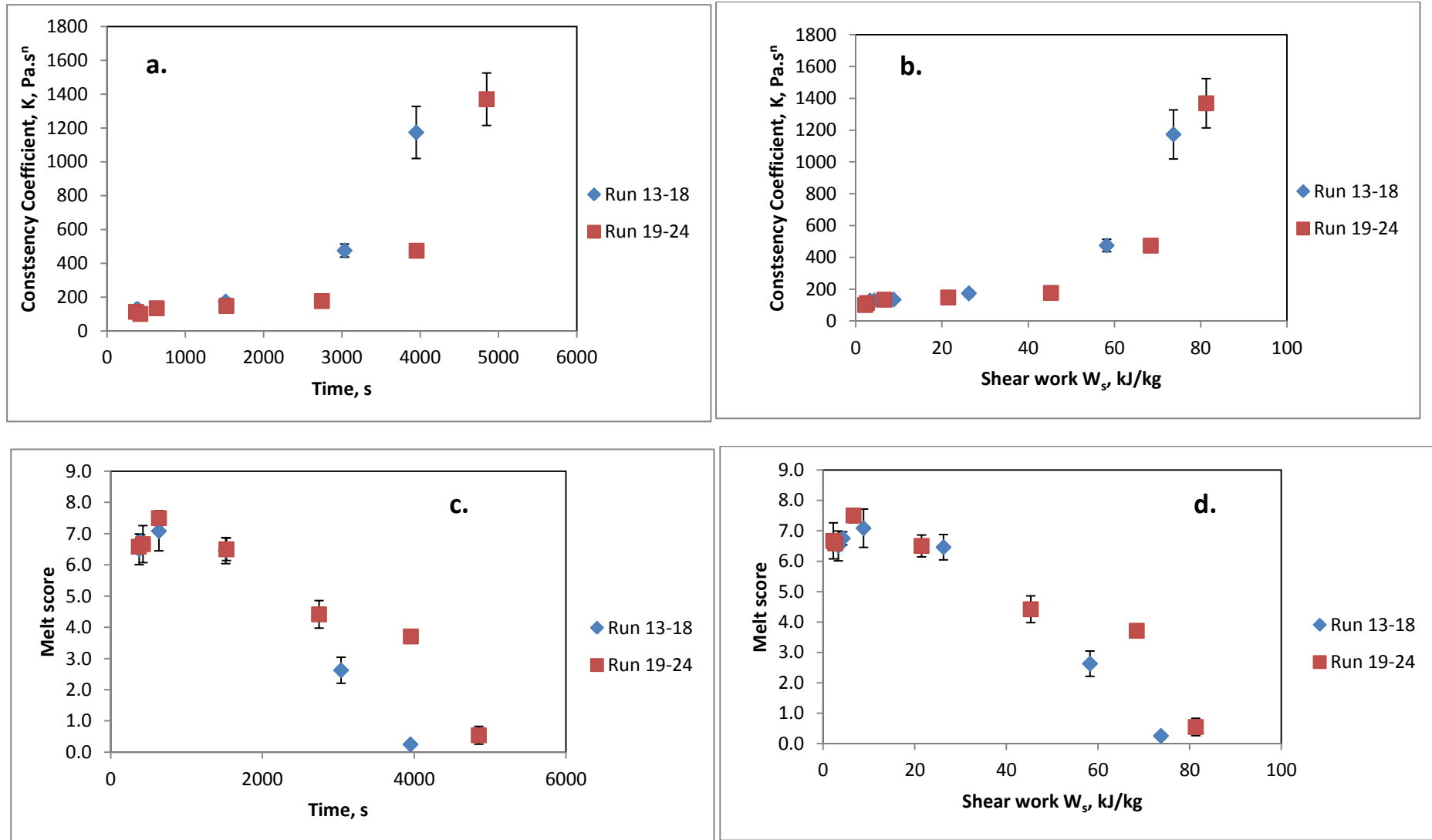




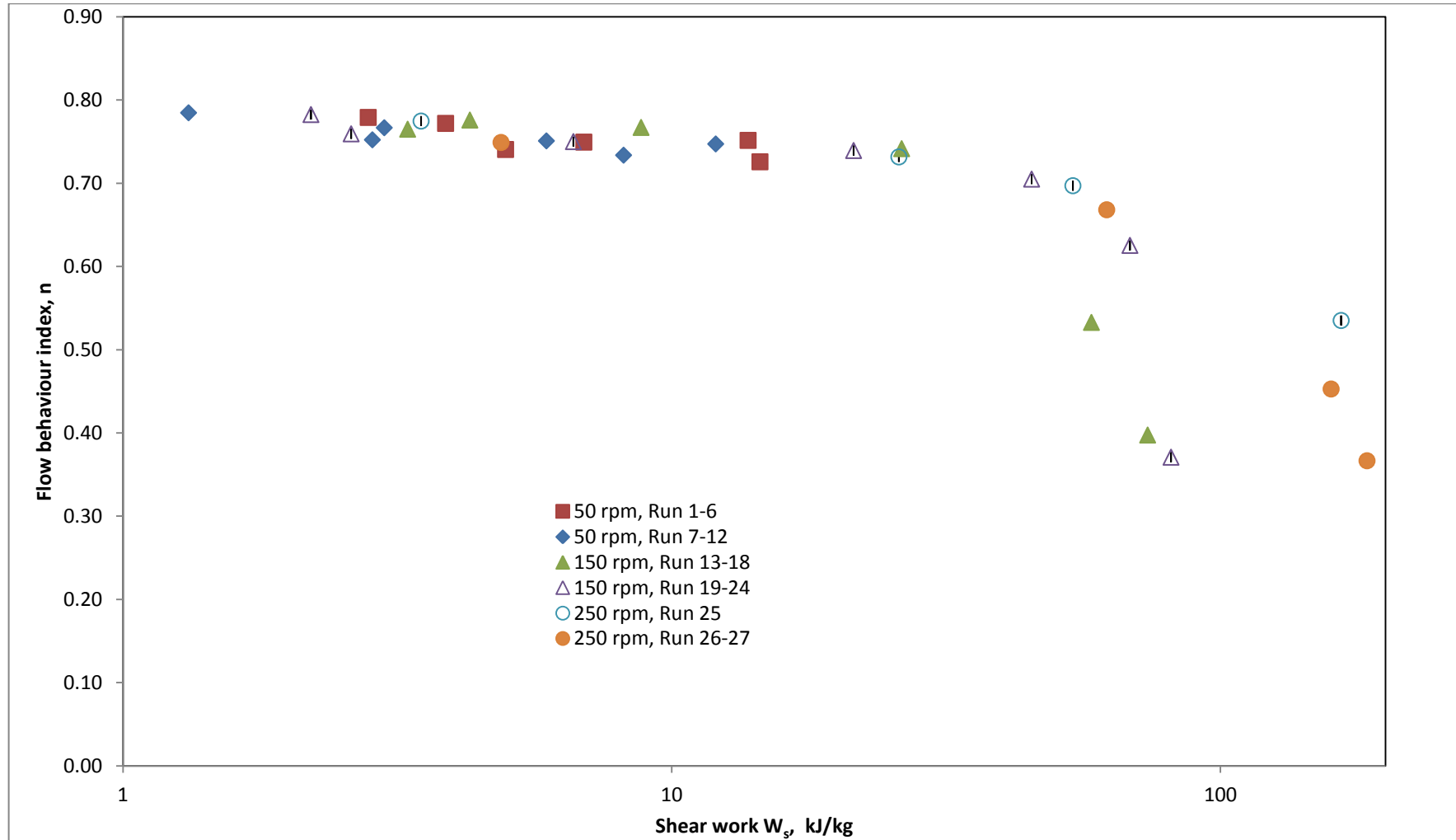
**Fig. 2.** Visual appearance of model Mozzarella cheese in the Blentech cooker after various levels of shear work input at 70 °C and 150 rpm; a. 3.3, b. 6.6, c. 58.2 d. 73.7 kJ/kg



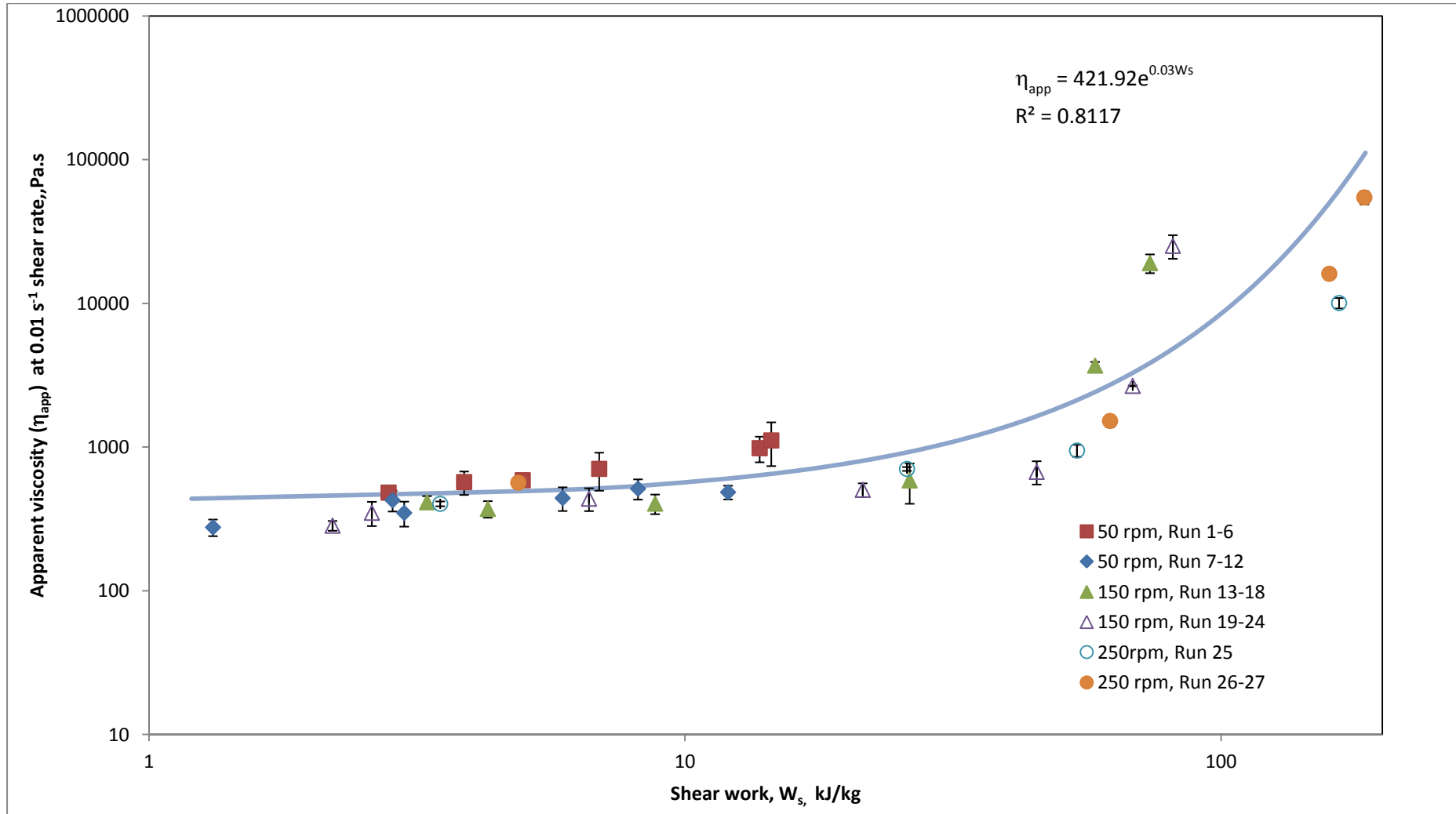
**Fig. 3.** Stretch appearance of model Mozzarella cheese after working in the Blentech cooker at 70 °C and 150 rpm. a. Optimum melt functionality after shear work input of 6.6 kJ/kg; b. Damaged texture after excessive shear work input of 73.7 kJ/kg



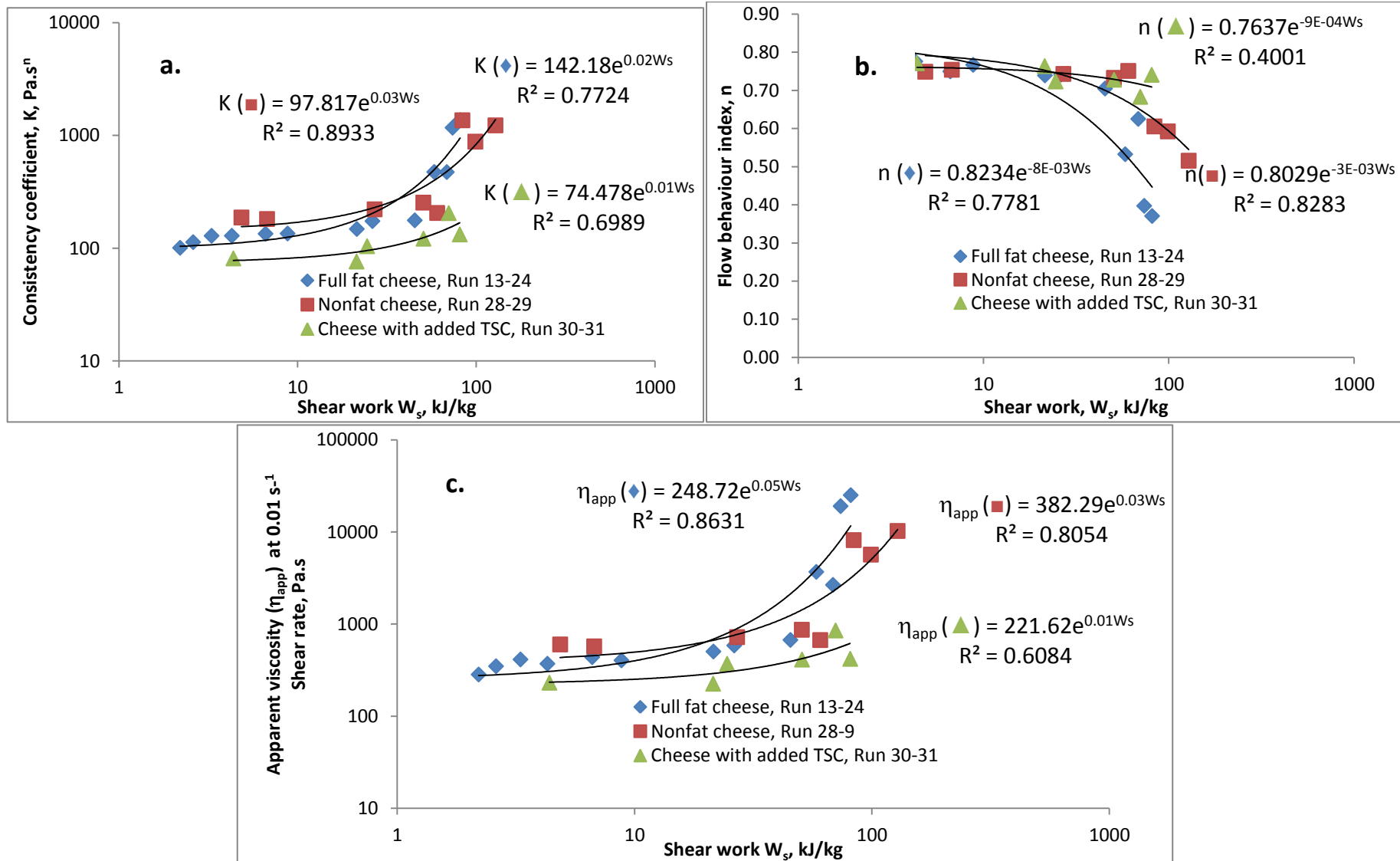
**Fig. 4.** Changes in Consistency coefficient ( $K$  from power law model) and meltability of model Mozzarella cheese versus time (a,c) and shear work (b,d). Model Mozzarella cheese was manufactured in the Blentech cooker at 150 rpm screw speed and 70 °C. Error bars represent one standard deviation



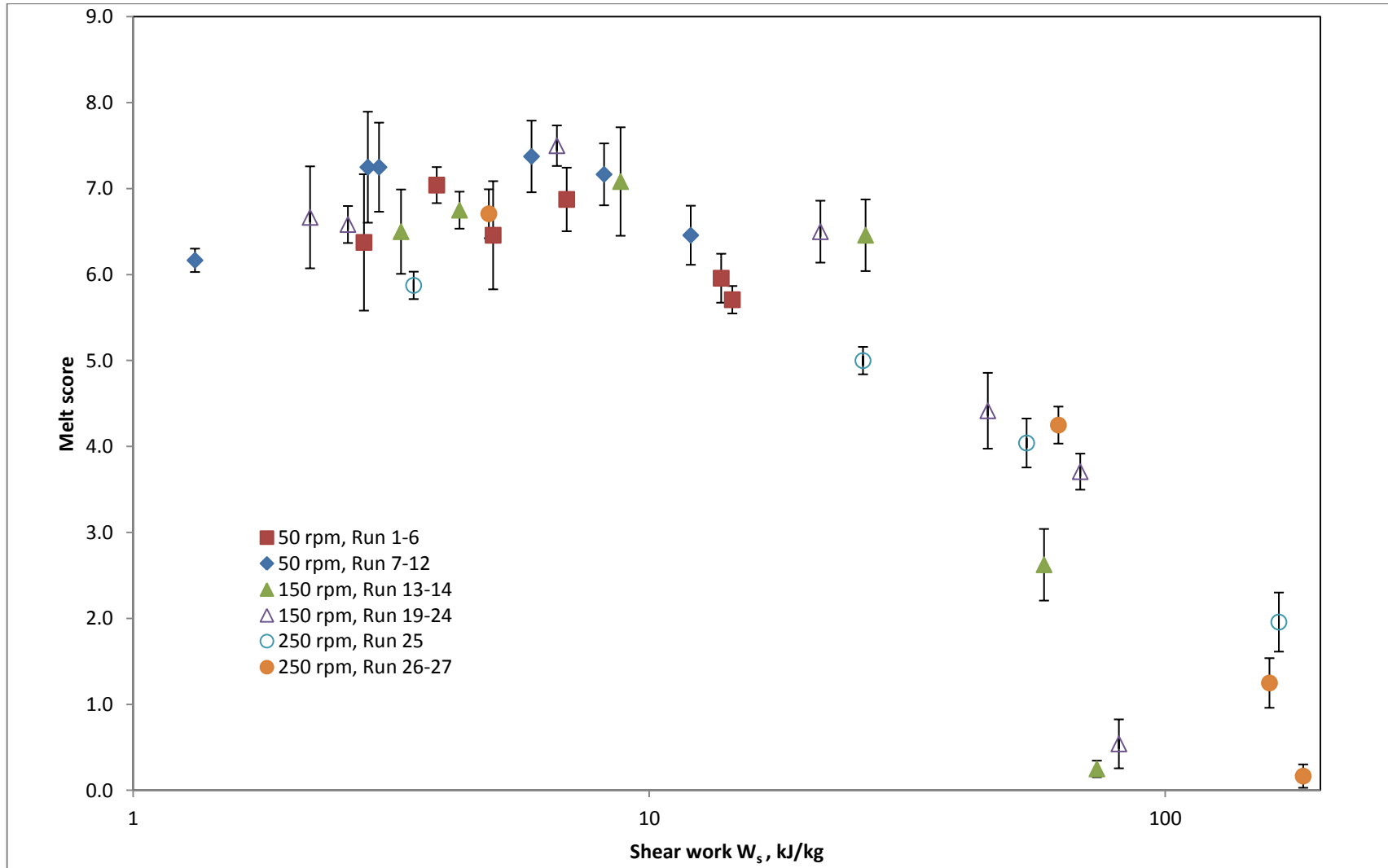
**Fig. 5.** Effect of shear work on flow behaviour index ( $n$  from power law model) of model Mozzarella cheese at 70 °C. Error bars represent one standard deviation.



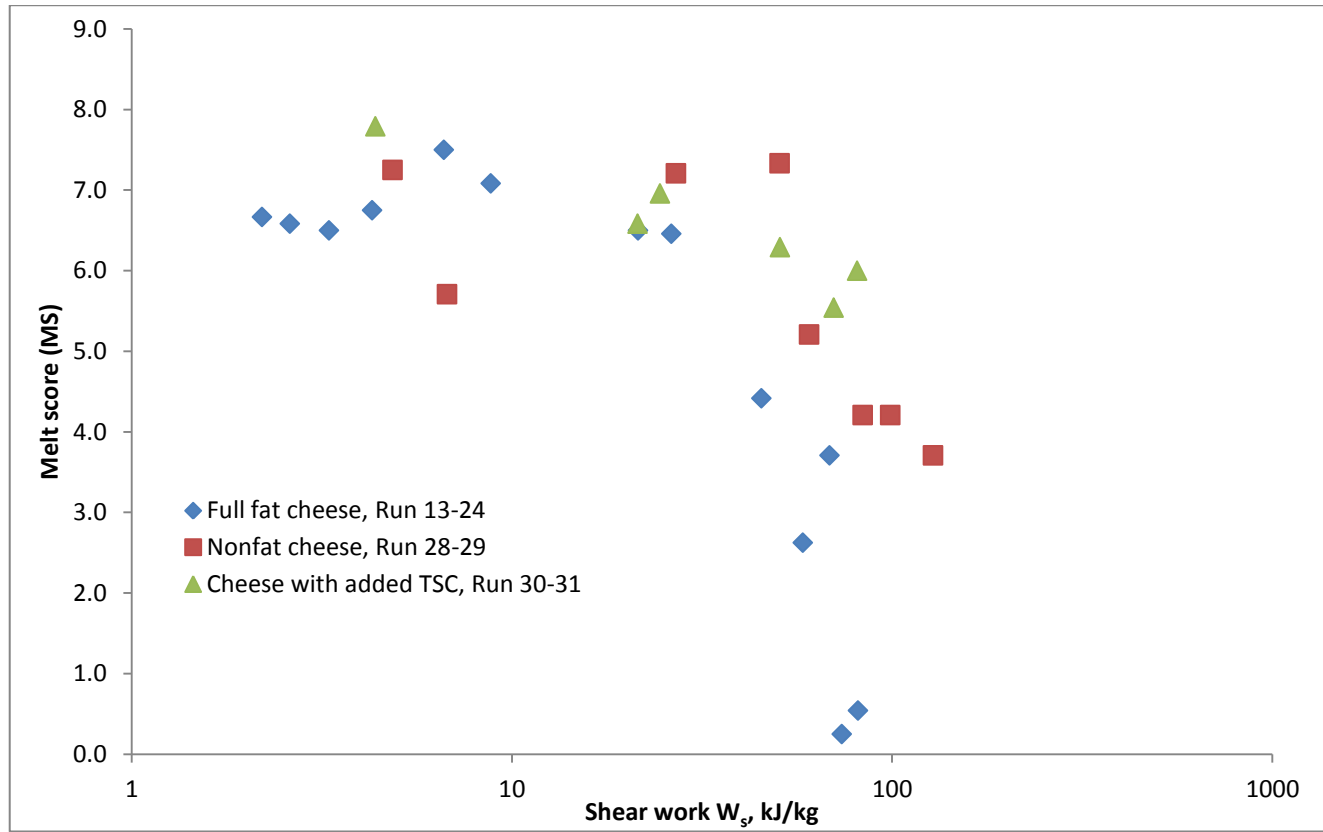
**Fig. 6.** Effect of shear work on apparent viscosity of model Mozzarella cheese at  $0.01 \text{ s}^{-1}$  shear rate and  $70 \text{ }^\circ\text{C}$ . Error bars represent one standard deviation.



**Fig. 7.** Effect of shear work on (a) consistency coefficient ( $K$  from power law model); (b) flow behaviour index ( $n$  from power law model) and (c) apparent viscosity at  $0.01 \text{ s}^{-1}$ , all at  $70 \text{ }^\circ\text{C}$ , for three model Mozzarella cheeses prepared in the Blentech cooker using 150 rpm screw speed.

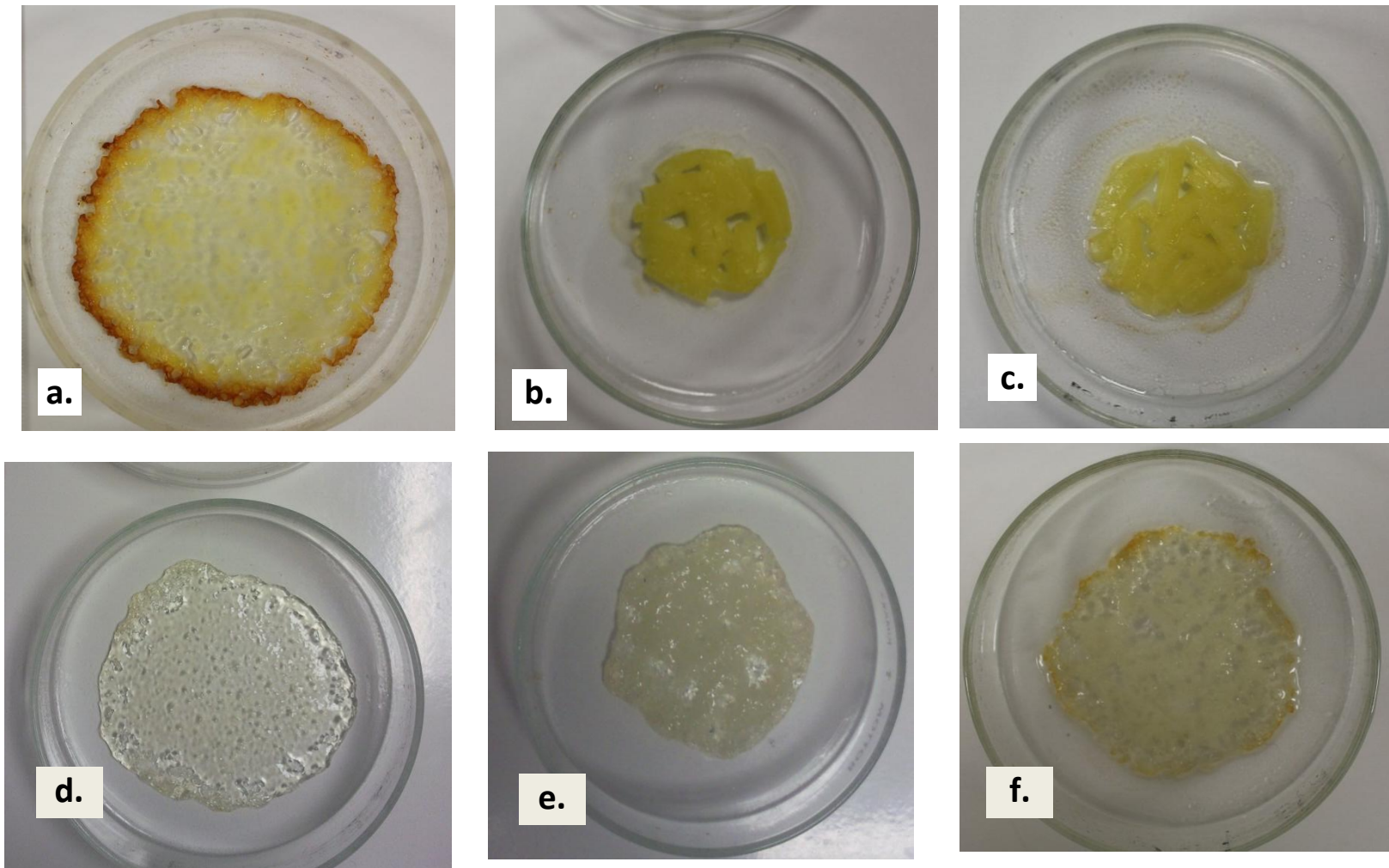


**Fig. 8.** Effect of shear work on meltability of model Mozzarella cheese prepared at 70 °C in the Blentech cooker. Error bars represent one standard deviation.

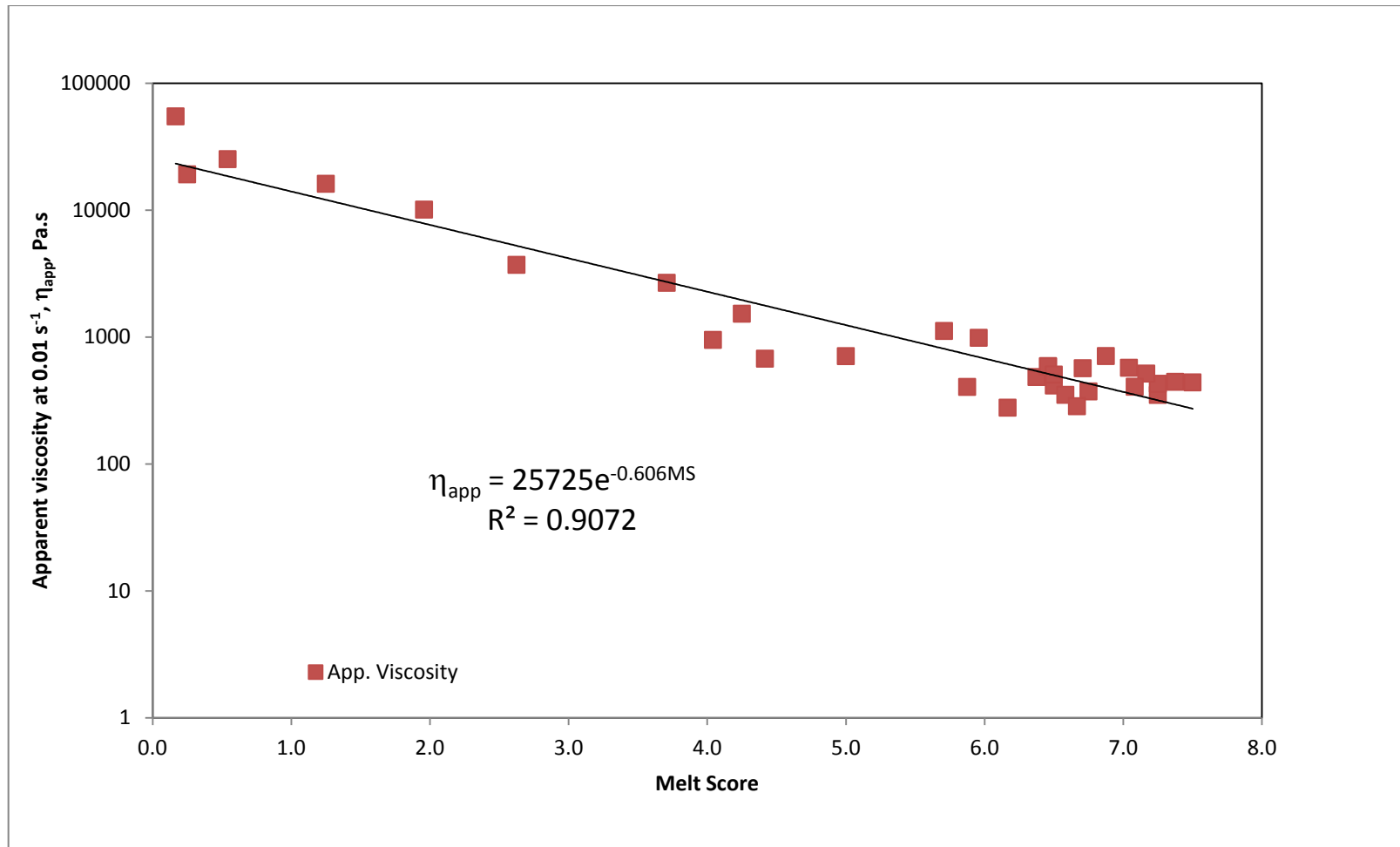


**Fig. 9.** Melt score versus shear work input for model Mozzarella cheeses prepared in the Blentech cooker using 150 rpm screw speed.





**Fig. 10.** Photographs of cooled model Mozzarella cheese after the modified Schreiber melt test. a. Optimum functionality full fat cheese after 6.6 kJ/kg shear work input, melt score 7.5; b. Full fat cheese after excessive shear work input 166 kJ/kg, melt score 0.2; c. Full fat cheese after excessive shear work input 166 kJ/kg and with vegetable oil sprayed on the surface before melting, melt score 0.5; d. Nonfat cheese after 6.75 kJ/kg shear work, melt score 5.7; e. Nonfat cheese after 128 kJ/kg shear work, melt score 3.7; f. Nonfat cheese after 128 kJ/kg shear work and with vegetable oil sprayed on the surface before melting, melt score 4. Melt score given is the mean of the quadruple tests for each batch.



**Fig. 11.** Correlation of apparent viscosity at 0.01 s<sup>-1</sup> with melt score for the model Mozzarella cheese at 70 °C.

## Table Captions

### Table 1

Blentech cooker run conditions and product compositions.

The table illustrates processing conditions e.g. screw speeds and composition of experimental model Mozzarella cheese. The compositions given in the table were not different for most of the runs except for nonfat cheese. Sampling time during the manufacture of the cheeses are also given.

**Table 1**

Blentech cooker run conditions and product compositions.

| Run no.         | Screw speed rpm     | Date       | Sampling time <sup>e</sup> s | Shear work kJ/kg | Moisture g/100g | Fat g/100g | Protein g/100g | Salt g/100g | Ash g/100g |
|-----------------|---------------------|------------|------------------------------|------------------|-----------------|------------|----------------|-------------|------------|
| 1               | 50                  | 17-10-2013 | 520                          | 2.80             | 54.3            | 20.6       | 20.61          | 1.4         | -          |
| 2               | 50                  | 17-10-2013 | 650                          | 3.87             | 53.6            | 22.6       | 20.93          | 1.4         | -          |
| 3               | 50                  | 17-10-2013 | 780                          | 4.98             | 53.4            | 22.9       | 21.31          | 1.41        | -          |
| 4               | 50                  | 17-10-2013 | 1680                         | 6.92             | 52.6            | 24.0       | 20.16          | 1.39        | -          |
| 5               | 50                  | 17-10-2013 | 3180                         | 13.78            | 53.1            | 23.1       | 21.12          | 1.41        | -          |
| 6               | 50                  | 17-10-2013 | 4185                         | 14.49            | 52.9            | 23.4       | 20.80          | 1.42        | -          |
| 7               | 50                  | 2-7-2014   | 315                          | 1.32             | 54.0            | 22.4       | 20.67          | 1.4         | 2.22       |
| 8               | 50                  | 2-7-2014   | 430                          | 2.99             | 53.9            | 22.6       | 20.80          | 1.4         | 2.18       |
| 9               | 50                  | 2-7-2014   | 640                          | 2.85             | 54.1            | 22.5       | 20.86          | 1.39        | 2.2        |
| 10              | 50                  | 2-7-2014   | 1590                         | 5.91             | 53.5            | 23.1       | 20.92          | 1.42        | 2.24       |
| 11              | 50                  | 2-7-2014   | 2735                         | 8.17             | 53.6            | 23.1       | 21.05          | 1.42        | 2.21       |
| 12              | 50                  | 2-7-2014   | 3980                         | 12.03            | 53.4            | 23.1       | 20.86          | 1.41        | 2.22       |
| 13              | 150                 | 23-1-2014  | 375                          | 3.30             | 53.7            | 22.7       | 20.8           | 1.40        | 2.13       |
| 14              | 150                 | 23-1-2014  | 395                          | 4.29             | 52.9            | 23.2       | 20.9           | 1.42        | 2.18       |
| 15              | 150                 | 23-1-2014  | 635                          | 8.80             | 52.8            | 23.2       | 20.7           | 1.43        | 2.21       |
| 16              | 150                 | 23-1-2014  | 1515                         | 26.26            | 52.5            | 23.5       | 20.9           | 1.42        | 2.19       |
| 17              | 150                 | 23-1-2014  | 3035                         | 58.23            | 53.1            | 23.3       | 20.7           | 1.41        | 2.20       |
| 18              | 150                 | 23-1-2014  | 3950                         | 73.71            | 52.5            | 23.7       | 20.6           | 1.43        | 2.21       |
| 19              | 150                 | 29-5-2014  | 370                          | 2.61             | 53.7            | 23.0       | 20.93          | 1.39        | 2.20       |
| 20              | 150                 | 29-5-2014  | 425                          | 2.20             | 53.9            | 22.9       | 20.74          | 1.41        | 2.21       |
| 21              | 150                 | 29-5-2014  | 635                          | 6.62             | 53.8            | 23.1       | 20.74          | 1.40        | 2.21       |
| 22              | 150                 | 29-5-2014  | 1525                         | 21.46            | 53.7            | 23.3       | 20.67          | 1.41        | 2.21       |
| 23              | 150                 | 29-5-2014  | 2745                         | 45.30            | 53.6            | 23.4       | 20.48          | 1.43        | 2.17       |
| 24 <sup>a</sup> | 150                 | 29-5-2014  | 3955                         | 68.44            | -               | -          | -              | -           | -          |
|                 | 150                 | 29-5-2014  | 4850                         | 81.32            | 54.0            | 23.0       | 20.48          | 1.38        | 2.19       |
|                 | Liquid <sup>d</sup> | 29-5-2014  | 4850                         |                  | 93.6            | 1.27       | 0.76           | 2.69        | 3.02       |

|                   |                     |           |      |        |      |      |       |      |      |
|-------------------|---------------------|-----------|------|--------|------|------|-------|------|------|
| 25 <sup>a</sup>   | 250                 | 31-7-2014 | 380  | 3.49   |      |      |       |      |      |
|                   | 250                 | 31-7-2014 | 1020 | 25.95  |      |      |       |      |      |
|                   | 250                 | 31-7-2014 | 1645 | 53.87  | -    | -    | -     | -    | -    |
|                   | 250                 | 31-7-2014 | 3685 | 166.05 | 50.6 | 23.2 | 23.54 | 1.47 | 2.46 |
| 26                | 250                 | 3-9-2014  | 335  | 4.89   | 53.6 | 22.7 | 21.37 | 1.41 | 2.31 |
| 27 <sup>a</sup>   | 250                 | 3-9-2014  | 1520 | 62.08  | -    | -    | -     | -    | -    |
|                   | 250                 | 3-9-2014  | 3080 | 159.21 | -    | -    | -     | -    | -    |
|                   | 250                 | 3-9-2014  | 3690 | 185.09 | 53.3 | 23.0 | 21.56 | 1.42 | 2.30 |
|                   | Liquid <sup>d</sup> | 3-9-2014  | 3690 |        | 95.4 | 0.22 | 0.49  | 2.75 | 2.92 |
| 28 <sup>a,b</sup> | 150                 | 31-7-2014 | 470  | 6.75   | -    | -    | -     | -    | -    |
|                   | 150                 | 31-7-2014 | 3025 | 60.49  | -    | -    | -     | -    | -    |
|                   | 150                 | 31-7-2014 | 4400 | 98.88  | -    | -    | -     | -    | -    |
|                   | 150                 | 31-7-2014 | 5285 | 128.10 | 63.8 | 0.06 | 32.86 | 1.79 | 2.56 |
|                   | Liquid <sup>d</sup> | 31-7-2014 | 5285 |        | 95.8 | -    | 0.54  | 2.82 | 3.05 |
| 29 <sup>a,b</sup> | 150                 | 3-9-2014  | 330  | 4.85   | -    | -    | -     | -    | -    |
|                   | 150                 | 3-9-2014  | 1480 | 27.01  | -    | -    | -     | -    | -    |
|                   | 150                 | 3-9-2014  | 2680 | 50.59  | -    | -    | -     | -    | -    |
|                   | 150                 | 3-9-2014  | 3920 | 83.68  | 66.2 | 0.28 | 30.81 | 1.85 | 3.08 |
|                   | Liquid <sup>d</sup> | 3-9-2014  | 3920 |        | 95.7 | 0.19 | 0.52  | 2.84 | 3.06 |
| 30 <sup>a,c</sup> | 150                 | 31-7-2014 | 430  | 4.37   | -    | -    | -     | -    | -    |
|                   | 150                 | 31-7-2014 | 1570 | 24.52  | -    | -    | -     | -    | -    |
|                   | 150                 | 31-7-2014 | 2775 | 50.69  | -    | -    | -     | -    | -    |
|                   | 150                 | 31-7-2014 | 3970 | 80.90  | 52.6 | 22.7 | 21.95 | 1.35 | 3.08 |
| 31 <sup>a,c</sup> | 150                 | 3-9-2014  | 1570 | 21.40  | -    | -    | -     | -    | -    |
|                   | 150                 | 3-9-2014  | 3965 | 70.76  | 53.7 | 22.9 | 20.99 | 1.41 | 2.56 |

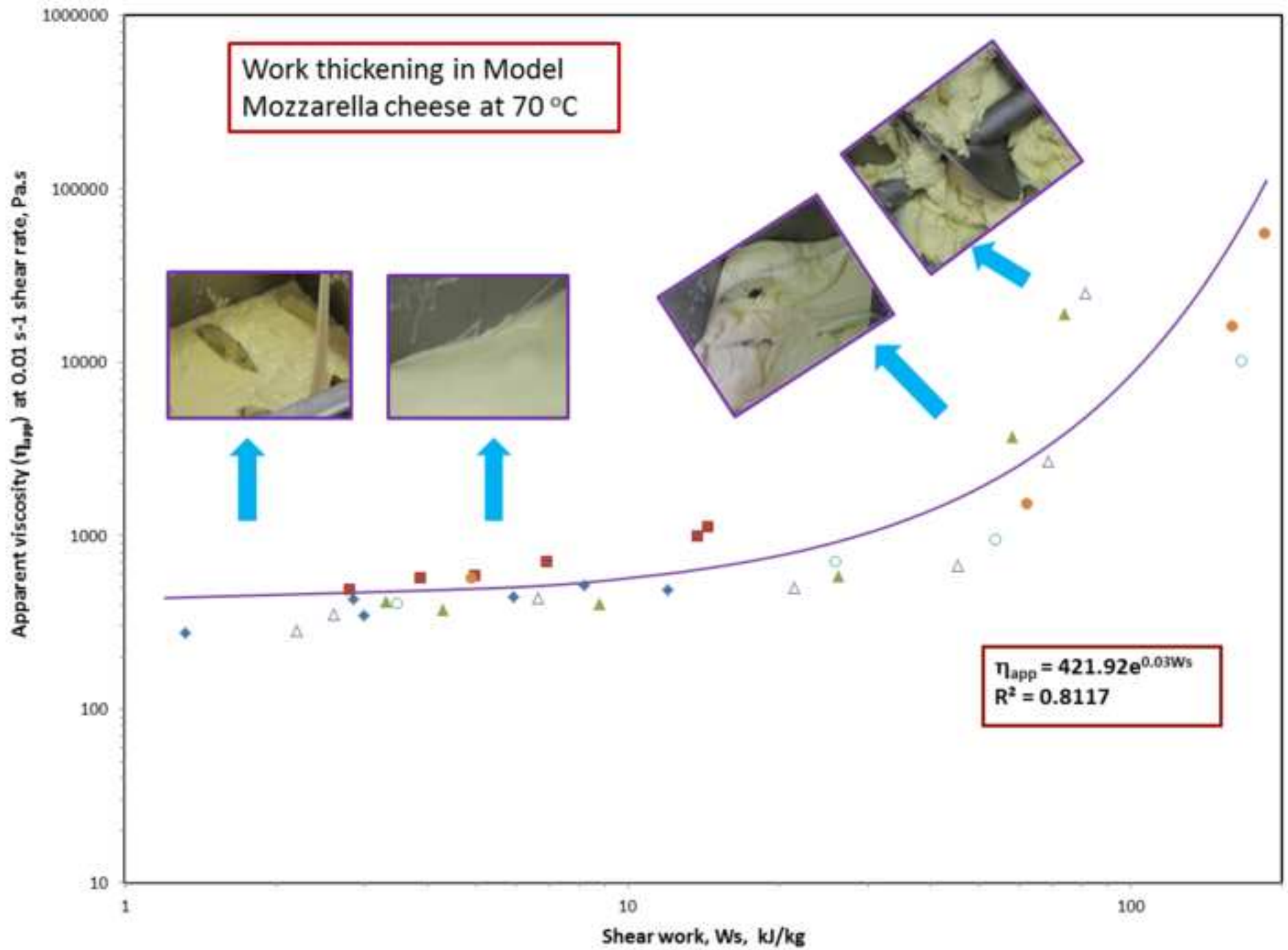
<sup>a</sup>Samples taken for rheological and functionality measurement during the run. Shear work calculation was corrected for the reduced mass later in the run.

<sup>b</sup>These runs were for nonfat cheese.

<sup>c</sup>Trisodium citrate was added to these runs.

<sup>d</sup>Exuded liquid sample at end of run.

<sup>e</sup>Cheese samples unless noted as liquid.



## **Highlights**

We found rheology and melt functionality of Mozzarella type cheeses strongly dependent on total shear work input

We observed work thickening of cheese during making of Mozzarella type cheeses.

We propose an exponential work thickening equation to describe work thickening behaviour.

We found protein matrix as the dominant contributor to the changes in properties with increased shear work.