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

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Abstract

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

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

1. Introduction

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

The rheology, stretch and melt functionality of cheeses at higher temperatures is determined by the strength and number of casein-casein interactions (Park, Rosenau & Peleg, 1984) mainly hydrophobic, calcium cross-linking, electrostatic interactions and hydrogen bonds. The overall effect of increasing temperature on these interactions is weakening of the cheese matrix. Lucey et al. (2003) reviewed the chemistry and physics of cheese stretching which is relevant both to the stretching stage during manufacture and to stretch functionality during application on a pizza. There is a critical level of energy storage and dissipation that enables melt and stretch of a casein network. This energy level is related to the relaxation times of casein-casein interactions. If the interactions are too strong then internal stresses generated in the cheese during stretching are not easily released and the fibres are more likely to break rather than stretch or flow. If the interactions are too weak then the cheese will not stretch but will act as a viscous liquid. For cheese to stretch well the casein molecules must interact closely but the bonds must relax and reform very quickly.

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

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

2. Materials and methods

2.1 Materials

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

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

2.2 Manufacture of model Mozzarella cheeses

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

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

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

2.3 Shear work calculation

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

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

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

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

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

2.4 Meltability of Mozzarella cheese

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

2.5 Steady shear rheology

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

2.6 Statistical analysis

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

3 Results

3.1 Processing characteristics and physical properties of model Mozzarella cheese

Table 1 shows the total mixing times and compositions of all samples and the corresponding values of shear work. Torque-time curves during mixing at three screw speeds are presented in Fig. 1. The end of the preworking period when the temperature reached 70 ^{o}C is indicated by a vertical straight line. Accumulated shear work during the preworking period varied between runs but was always in the range 1.2-2.0 kJ/kg. Post-preworking, the torque at 50 rpm remained relatively constant for the whole working time, accumulating shear work in the range of 12 kJ/kg (run 12) to 14.5 kJ/kg (run 6). In contrast at 150 and 250 rpm the torque progressively increased with time to a maximum, then decreased steeply and finally increased a second time after prolonged working. The rate of increase of torque with time was higher at 250 rpm. The increase of torque with time indicates work thickening of the cheese mass while the steep decline coincided with rapid changes to the macroscopic cheese structure. The maximum values of torque for 150 and 250 rpm occurred at 3820 s and 2685 s (Fig. 1) corresponding to shear work inputs of 66 and 129 kJ/kg respectively. An earlier start of torque decline at 250 rpm indicates earlier onset of macroscopic structural breakdown. Throughout the working time, torque values were highest for 250 rpm followed by 150 rpm and then 50 rpm. At short times this may be attributed to higher inertial forces at higher speeds, but at longer times the higher work thickening at higher speeds also makes a contribution. Manski, van der Zalm, van der Goot and Boom (2008) reported similar changes in torque with time as a result of structure formation and breakdown during prolonged shearing of fat-containing Ca-caseinate dispersions.

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

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

Cheese prepared at 150 rpm with the addition of TSC showed uniform torque versus time with less fluctuation than the curves in Fig. 1. El-Bakry et al. (2010 a, b; 2011a, b, c) also reported relatively stable torque readings after attaining a homogenous mass during mixing at constant temperature for cheeses with added chelating salts. The typical fibrous structure of Mozzarella cheese was absent and the cheese showed a grainy visual appearance instead. TSC would be expected to chelate some calcium resulting in reduced casein-casein interactions (Mizuno & Lucey, 2005). This may result in dispersion of caseins (Brickley, Govindaswamy-Lucey, Jaeggi, Johnson, McSweeney & Lucey, 2008). Cheese with TSC added was very sticky. It stuck to plastic bags, rubber gloves and stainless steel. This could be attributed to the tendency of para-casein to stick to hydrophobic materials such as nylon gloves (Paulson, McMahon & Oberg, 1998). Brickley et al. (2008) attributed this stickiness to a decrease of hardness upon addition of TSC as a result of weakening of the casein matrix because of sequestering of calcium and increase of pH resulting in increased electrostatic repulsion.

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

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

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

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

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

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

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

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

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

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

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

Nonfat cheese with low shear work input melted and flowed well (Fig. 10d). These melting results for nonfat cheese were surprising given the explanation above of the role of fat in preventing surface drying and skin formation and contrast with the pizza baking results of Rudan & Barbano (1998), who reported that low fat Mozzarella cheeses had limited melting. The melt of nonfat cheese was less impacted by excessive shear work (Fig. 10e) than that of full fat cheese. Again coating with vegetable oil spray had only a small positive effect on melt score (Fig. 10f). This suggests that there is a significant contribution of the fat phase to the poor melting properties of excessively worked full fat cheese. Changes to the protein matrix alone cannot explain the results. Molten nonfat cheese was white in appearance while still hot but transformed into a transparent plastic like sheet upon cooling to room temperature (Fig. 10d). Pastorino, Dave, Oberg and McMahon (2002) reported increased opacity of nonfat Mozzarella cheese upon heating from 10 ^{o}C to 50 ^{o}C and attributed this to heat induced changes in protein interactions as manifested by structural changes in the cheese. Heating would favour hydrophobic interactions and would possibly allow re-association of β-casein and calcium within the protein matrix, causing enhanced protein-protein interactions (Pastorino et al., 2002). Translucency of nonfat Mozzarella cheese in the presence of salt has also been attributed to limited light scattering from pockets of free serum distributed in the protein matrix (Paulson et al., 1998). Translucency of cheese has been attributed to the formation of a fine stranded protein network that allows light to pass through (Brickley et al., 2008).

3.4 Relationships between melt functionality and steady shear rheology

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

4 Discussion

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

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

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

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

$$d\eta/dt \;\alpha\; \eta \qquad (3)$$

Rearranging and integrating between limits

$$\eta = \eta_o e^{at} \qquad (4)$$

As we have found that shear work input (W_s) as an independent variable is a stronger predictor than time of the outcome with respect to rheology and melt functionality (Fig. 4), and also enables the results of different shear rates to be correlated on a single curve (Figs. 5-6), we can integrate with respect to W_s rather than time.

$$\eta = \eta_o e^{bW_s} \qquad (5)$$

where η_o is viscosity before significant work thickening, η is viscosity at time t or shear work W_s during work thickening and a, b are work thickening constants.

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

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

$$\lambda = l_n / l_o = e^{\Lambda t} \qquad (6)$$

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

Torque versus time curves similar to those in Fig. 1 occur during mechanical development of dough which is a structurally similar food system where work thickening behaviour has been well explored (Zheng, Morgenstern, Campanella & Larsen, 2000; Peressini, Peighambardoust, Hamer, Sensidoni & van der Goot, 2008; Peighambardoust, van der Goot, van Vliet, Hamer & Boom, 2006). During mechanical development of dough a fibrous gluten network is formed during the mixing process and moisture is also distributed uniformly within the developed protein network (Bloksma & Bushuk, 1988; Zheng et al., 2000). During dough development torque reaches a peak value indicating maximum resistance to deformation and subsequently declines possibly indicating depolymerisation of the gluten network or some solubilisation of the gluten proteins (Hoseney, 1998; Bekes, Gras, Gupta, Hickman & Tatham, 1994). The chemistry of dough development is very different to that of cheese with S-H to S-S interchange reactions forming new covalent bonds between two adjacent gluten chains but there are many parallels in physical behaviour. Supramolecular polymer networks also display work thickening behaviour above a critical shear rate with the critical shear rate being experimentally correlated with the lifetime of crosslinking bonds (Xu, Hawk, Loveless, Jeon & Craig, 2010).

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

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

The modified Schreiber melt test assesses the ability of cheese to lose individual shred identity and then flow and spread. For optimum melting a balance of attractive and repulsive casein-casein interactions is required (Lucey et al., 2003). The decreasing tendency to melt after prolonged working is another strong indication of excessive associative protein-protein interactions either from increased hydrophobic interactions or from absence of repulsive (electrostatic) interactions or both (Lucey et al., 2003).

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

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

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

5 Conclusions

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

Acknowledgements

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Figure Captions

Fig. 1. Evolution of torque with time during mixing of model Mozzarella cheese in the Blentech cooker at 70 ^{o}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 ^{o}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 ^{o}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 ^{o}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 ^{o}C. Error bars represent one standard deviation.

Fig. 6. Effect of shear work on apparent viscosity of model Mozzarella cheese at 0.01 s^{-1} shear rate and 70 ^{o}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^{-1} , all at 70 ^{o}C, for three model Mozzarella cheeses prepared in the Blentech cooker using 150 rpm screw speed.

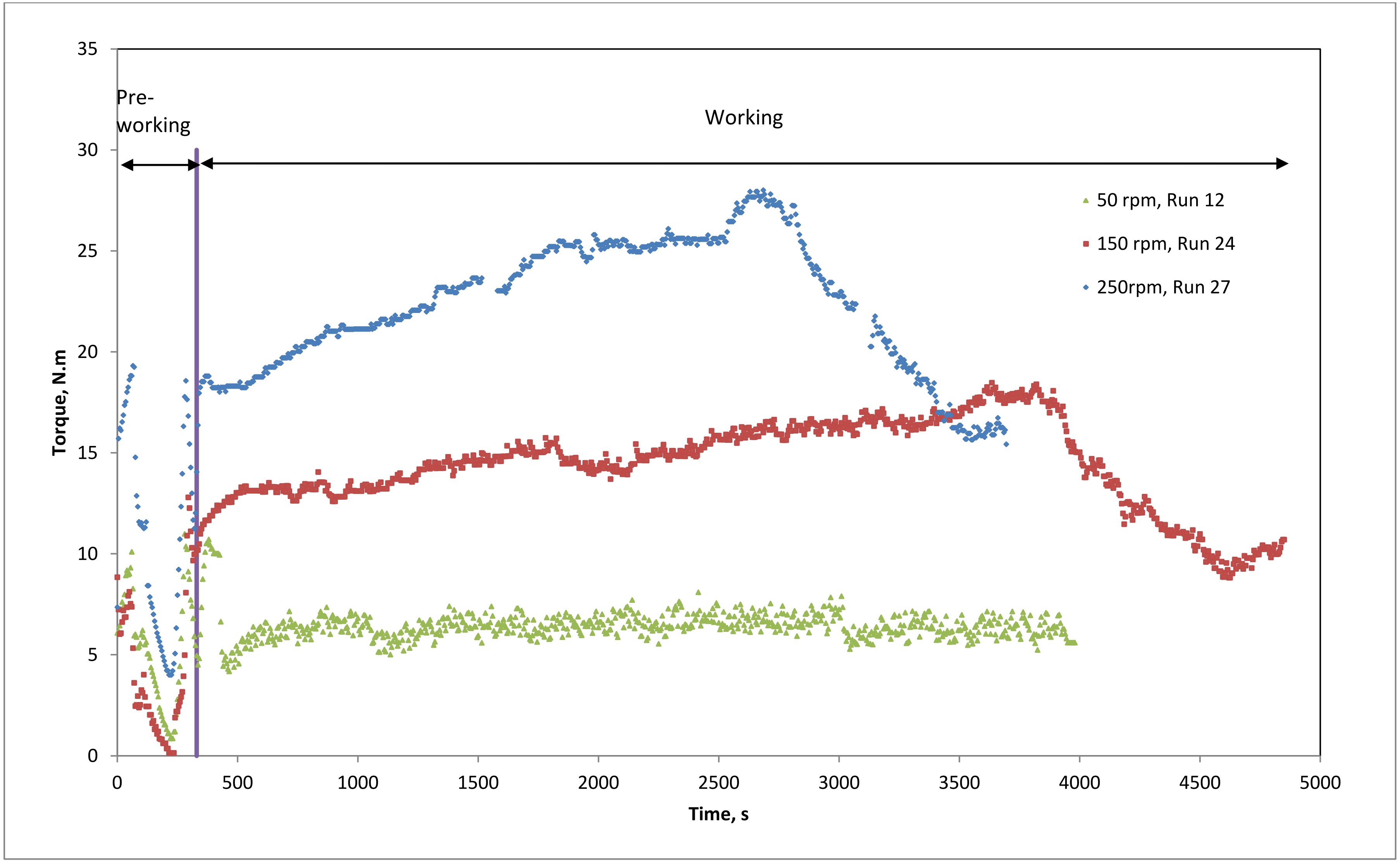
Fig. 8. Effect of shear work on meltability of model Mozzarella cheese prepared at 70 ^{o}C in the Blentech cooker. Error bars represent one standard deviation.

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 s^{-1} with melt score for the model Mozzarella cheese at 70 ^{o}C.

Figure



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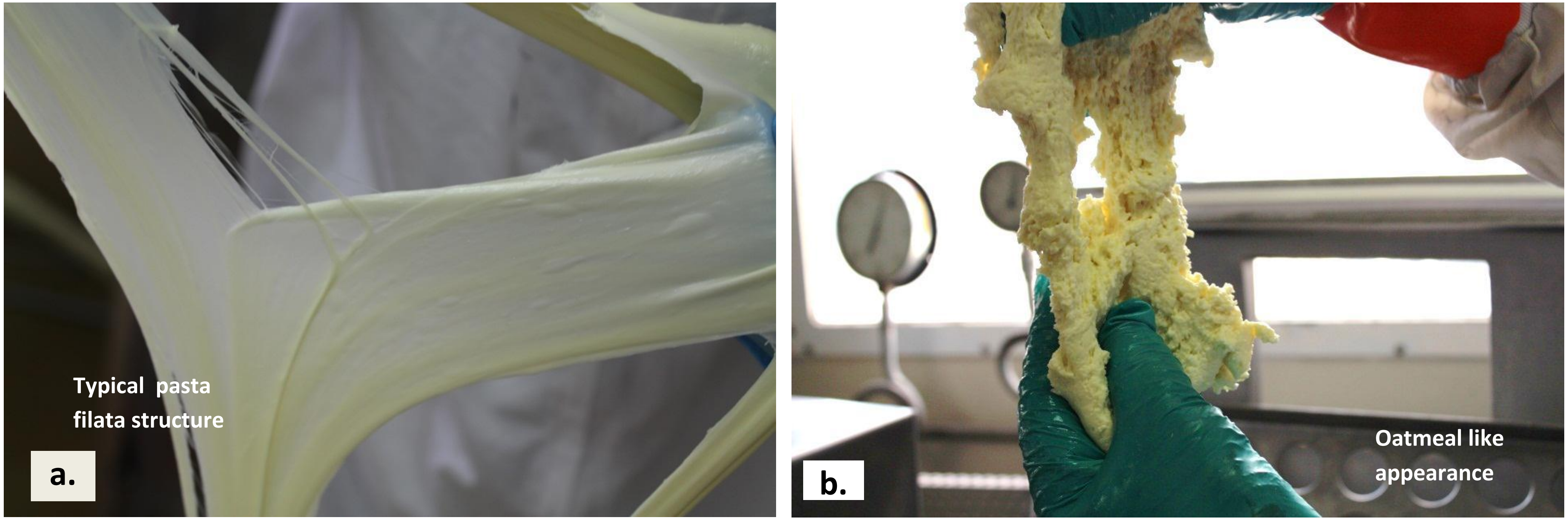

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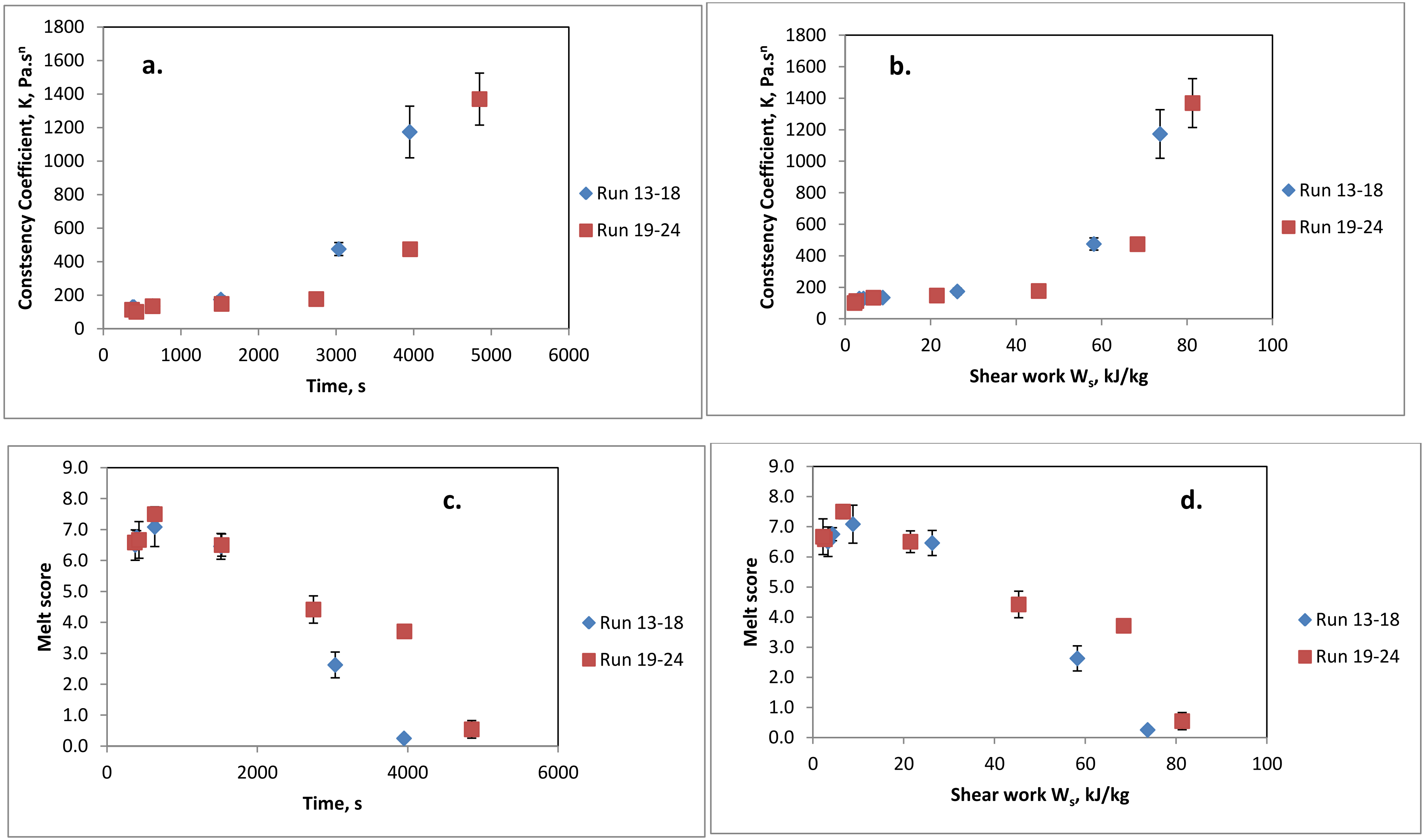

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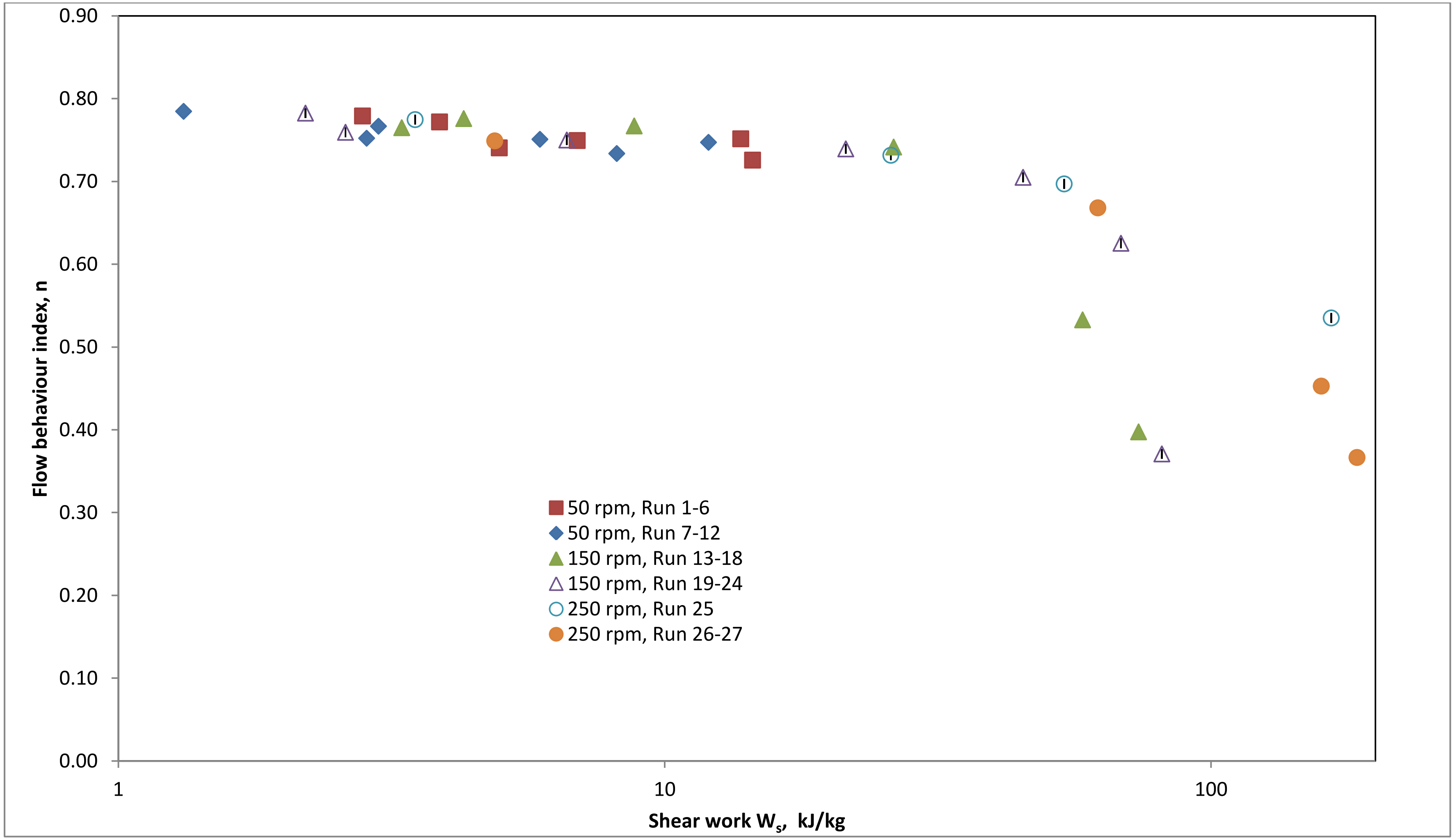

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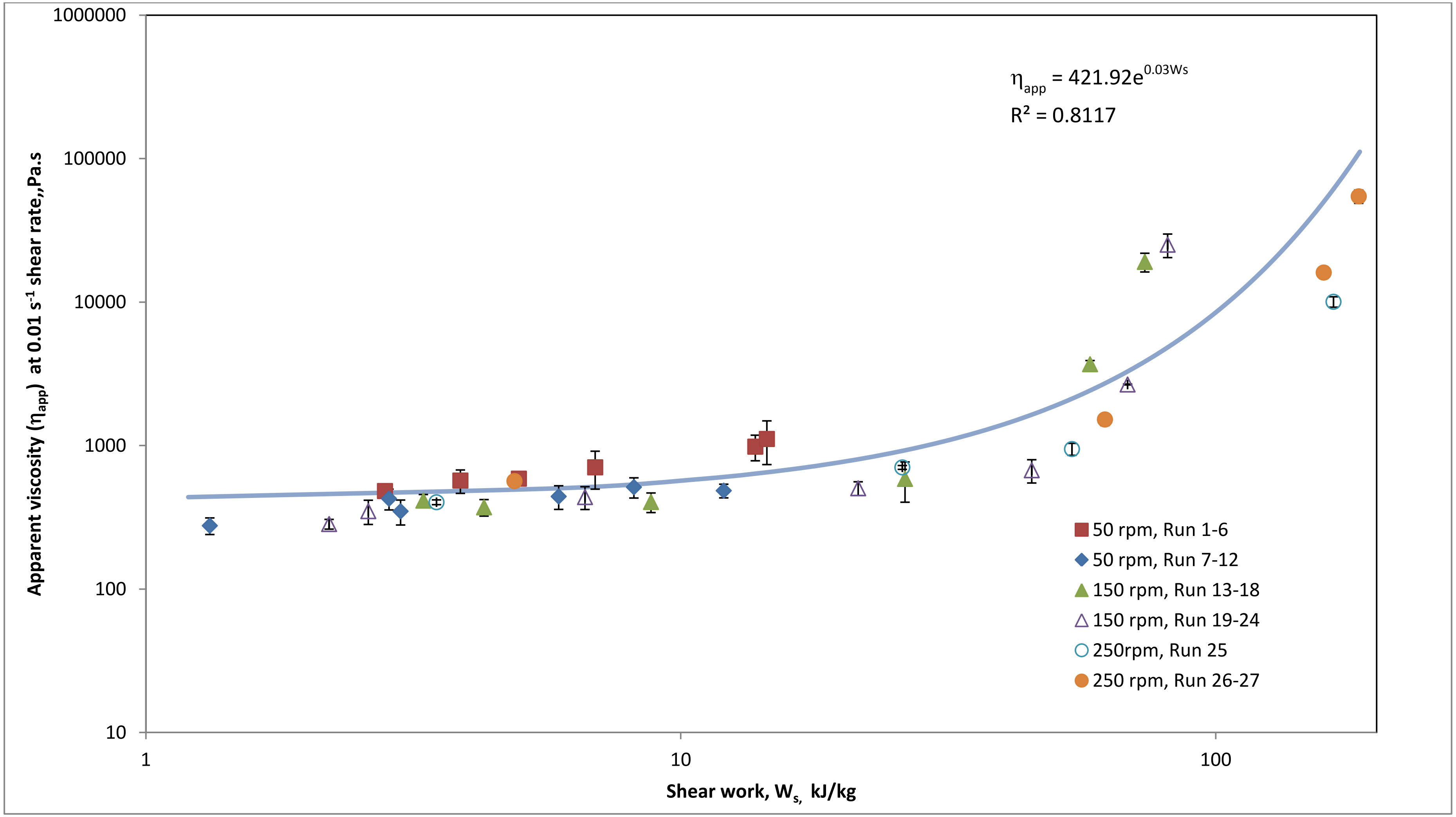

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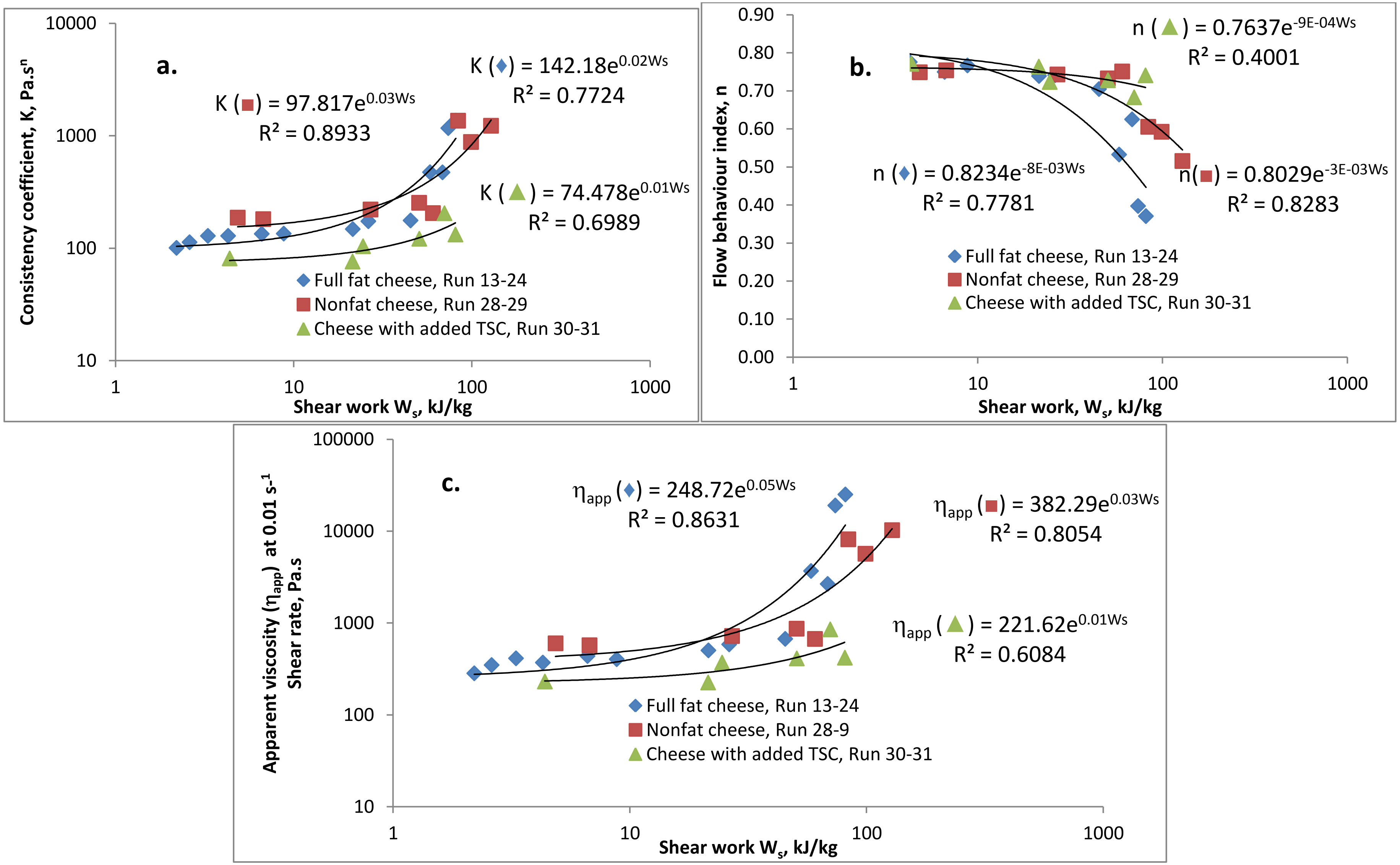

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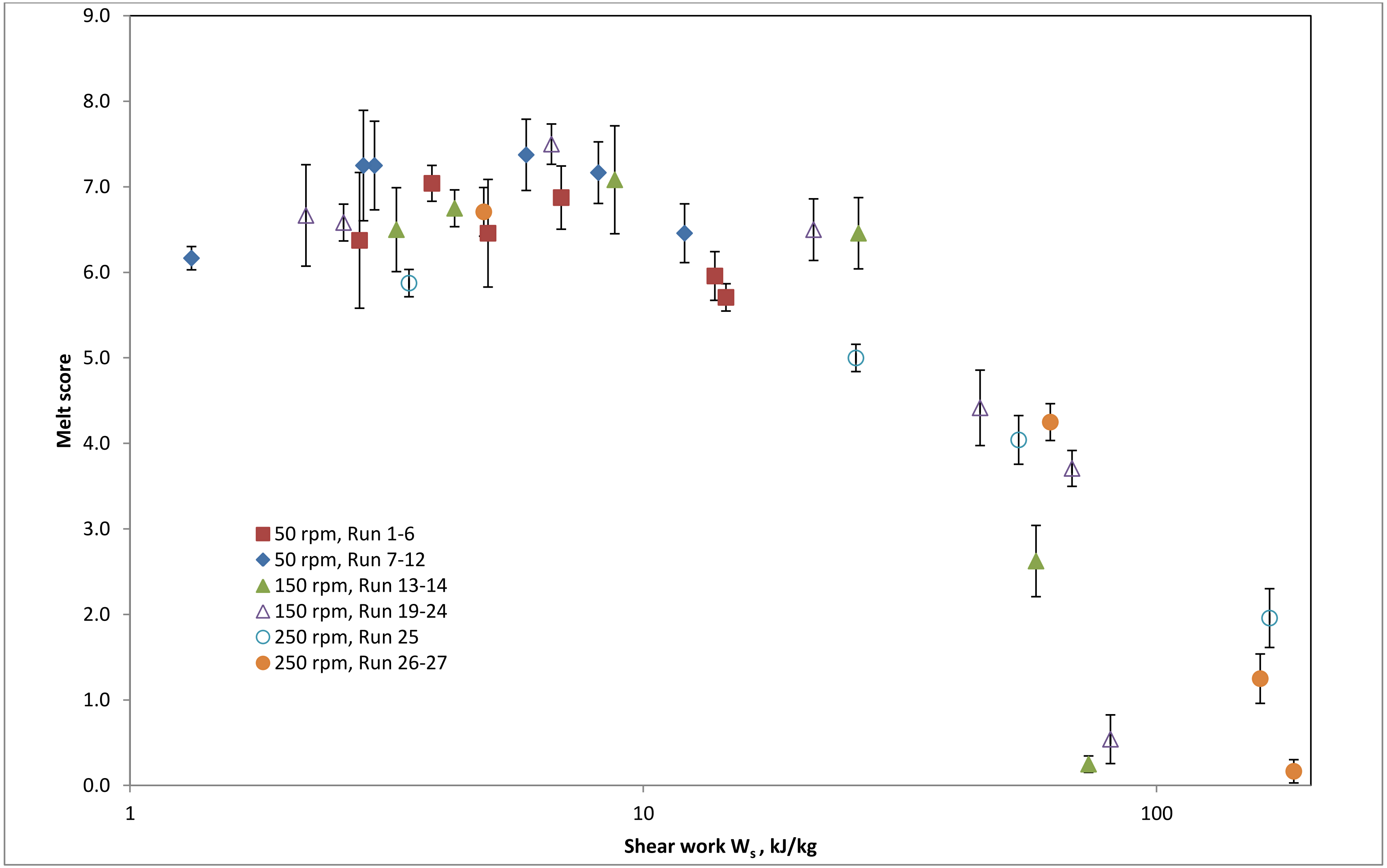


Fig. 8. Effect of shear work on meltability of model Mozzarella cheese prepared at 70 °C in the Blentech cooker. Error bars represent one standard deviation.

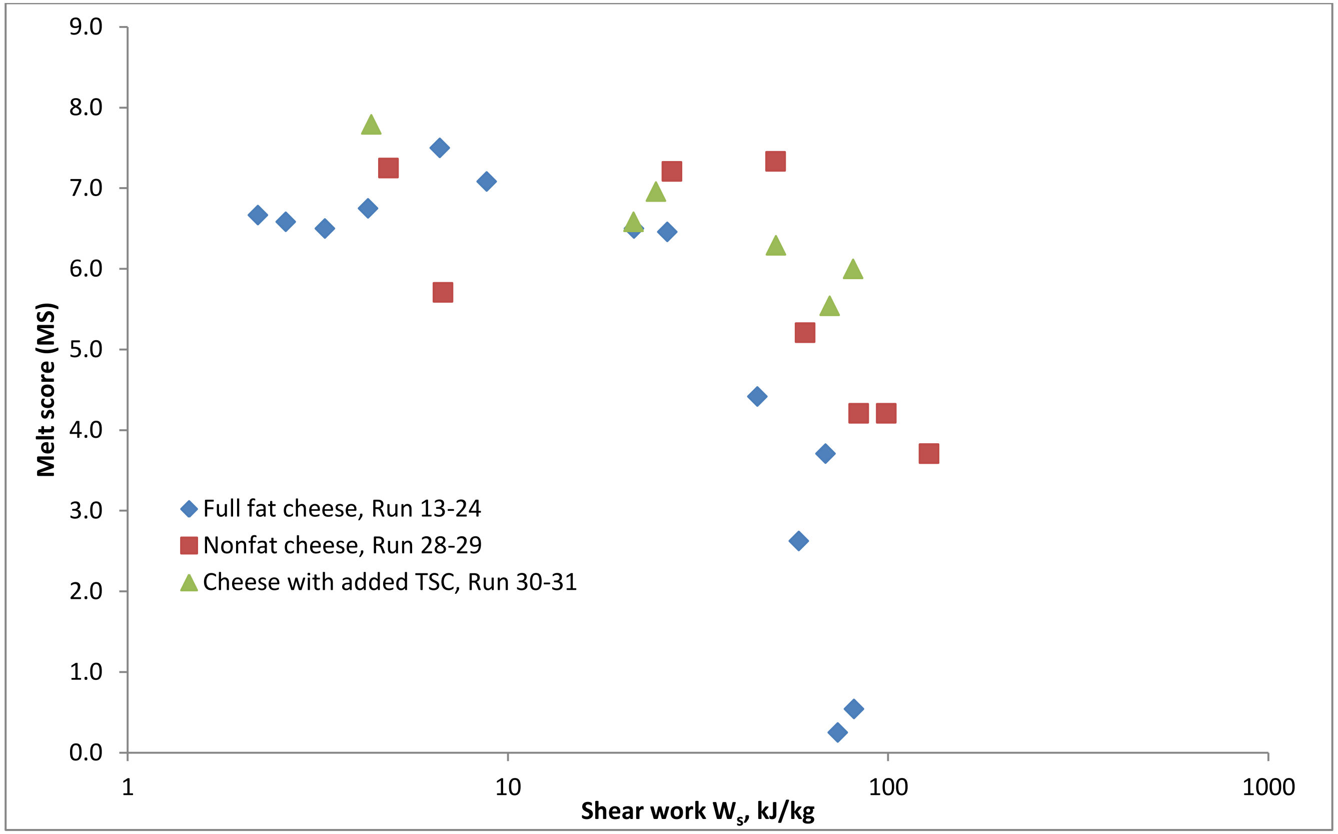
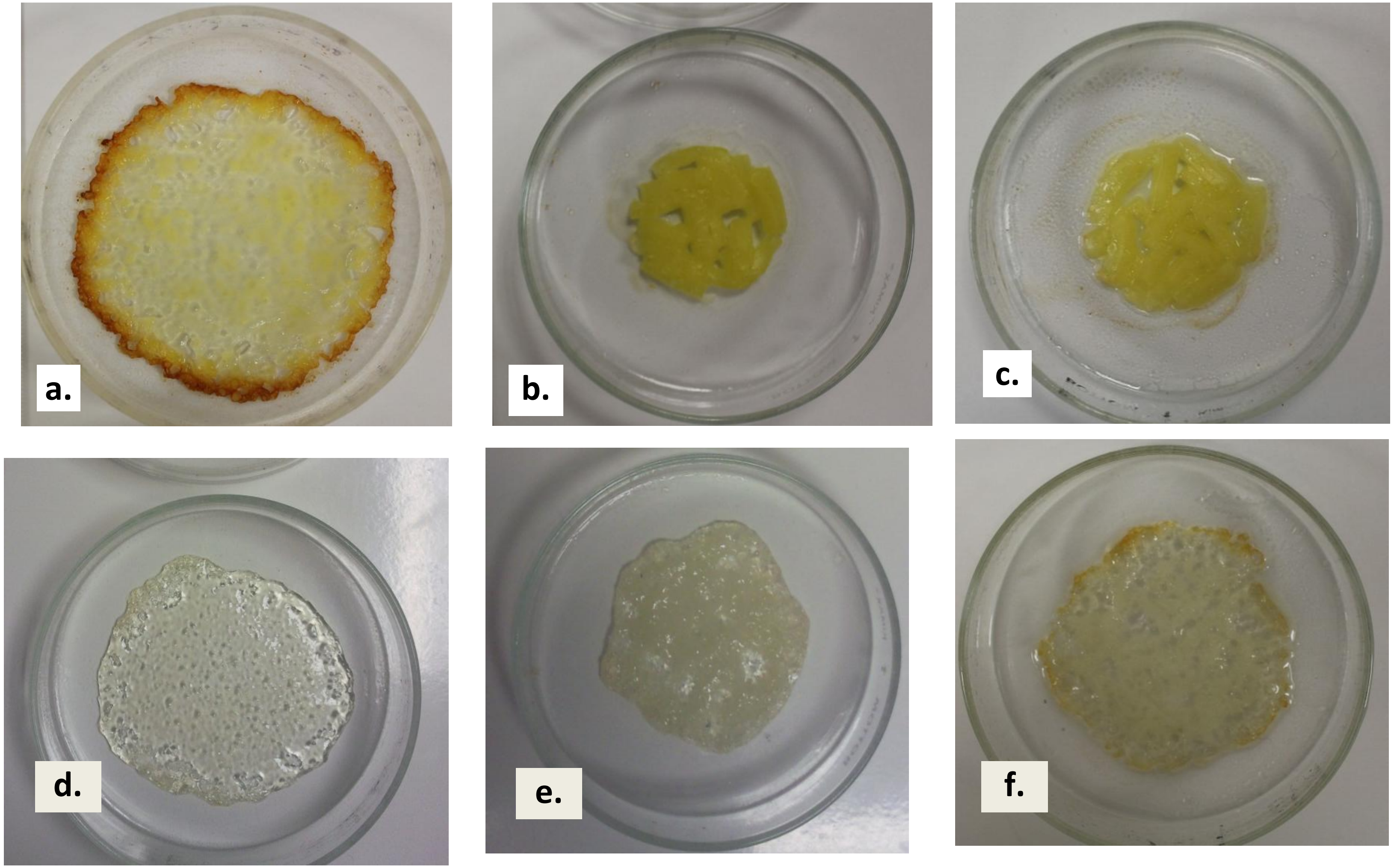


Fig. 9. Melt score versus shear work input for model Mozzarella cheeses prepared in the Blentech cooker using 150 rpm screw speed.



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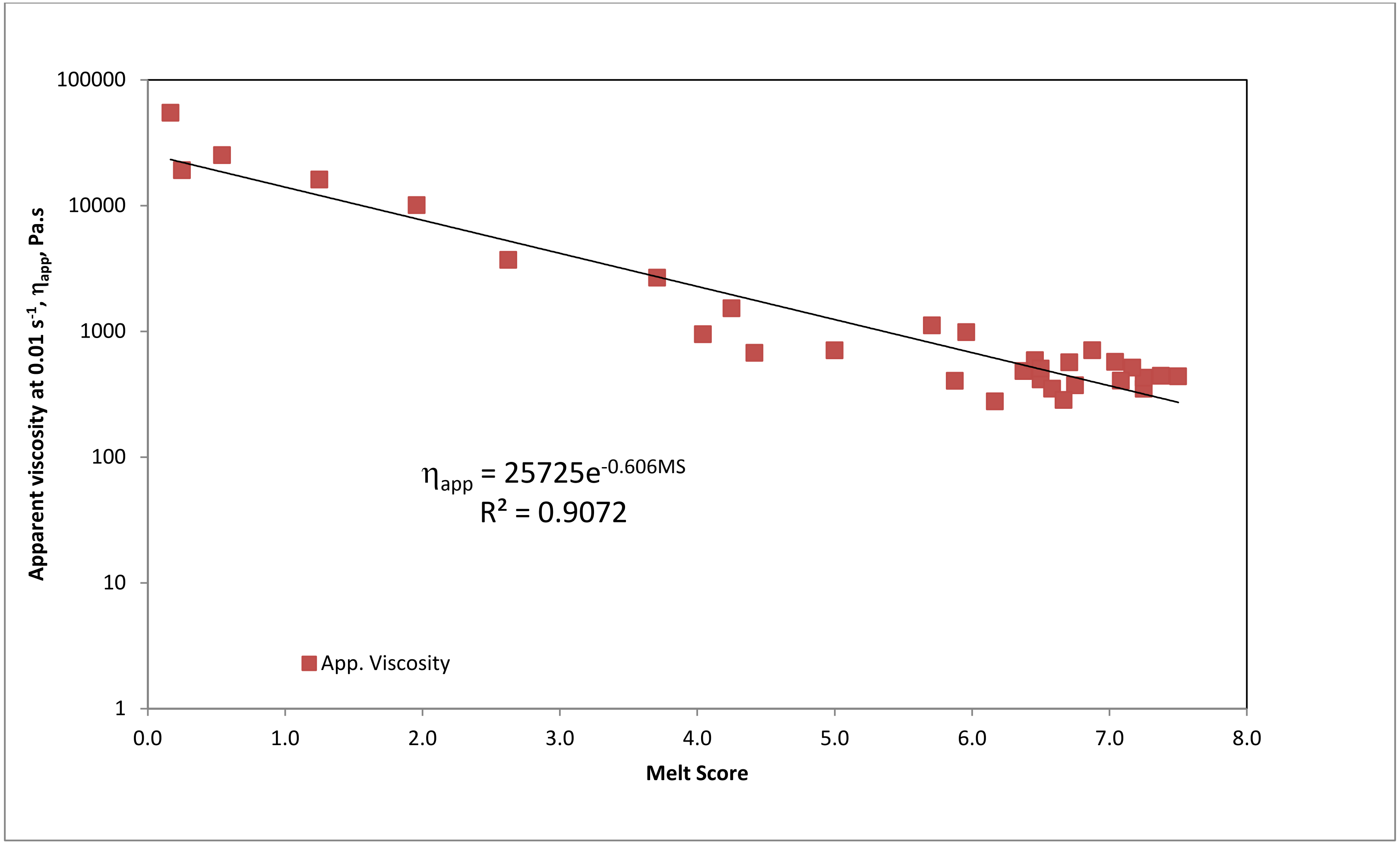


Fig. 11. Correlation of apparent viscosity at 0.01 s^{-1} with melt score for the model Mozzarella cheese at 70 °C.

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

Table 1

Blentech cooker run conditions and product compositions.

Run no.	Screw speed rpm	Date	Sampling time[e] 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[a]	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[d]	29-5-2014	4850		93.6	1.27	0.76	2.69	3.02

25[a]	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[a]	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[d]	3-9-2014	3690		95.4	0.22	0.49	2.75	2.92
28[a,b]	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[d]	31-7-2014	5285		95.8	-	0.54	2.82	3.05
29[a,b]	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[d]	3-9-2014	3920		95.7	0.19	0.52	2.84	3.06
30[a,c]	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 [a,c]	150	3-9-2014	1570	21.40	-	-	-	-	-
	150	3-9-2014	3965	70.76	53.7	22.9	20.99	1.41	2.56

---

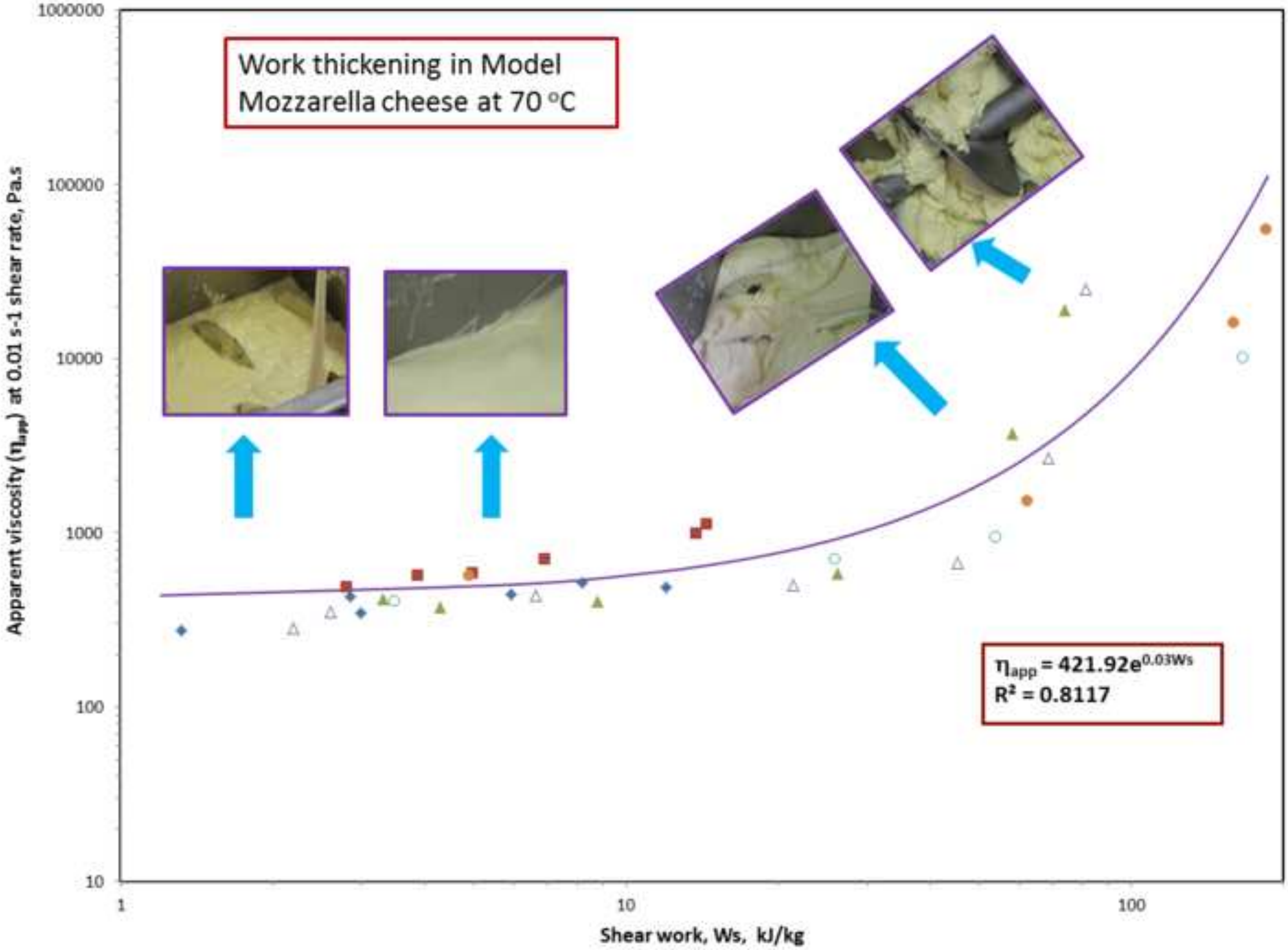
[a] Samples taken for rheological and functionality measurement during the run. Shear work calculation was corrected for the reduced mass later in the run.

[b] These runs were for nonfat cheese.

[c] Trisodium citrate was added to these runs.

[d] Exuded liquid sample at end of run.

[e] Cheese samples unless noted as liquid.


Work thickening in Model Mozzarella cheese at 70 °C
η_{app} = 421.92e$^{0.03Ws}$
R² = 0.8117
Apparent viscosity (η_{app}) at 0.01 s-1 shear rate, Pa.s
1000000
100000
10000
1000
100
10
1
10
100
Shear work, Ws, kJ/kg

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.