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Wall-slip Velocity As A Quantitative Measure Of Powder-Binder Separation During Powder Injection Moulding

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This paper tends to point out the specific features of PIM compounds which should be taken into account in their rheological characterization as a necessary approach to optimize moulding step of the process. A lot of effort has been paid to describe the powder-binder separation during the flow through the mould channels in the quantitative way. Flow curves of the materials undergoing the structural changes during shearing are not a monotonically decreasing, but instead they exhibit minima/maxima upon increasing shear rate. Therefore, the multi-parameter rheological model, describing the flow peculiarities of PIM compounds, must be firstly developed and approved on reliable experimental data. Further, it is supposed that wall slip can serve as a quantitative parameter directly connected to the powder-binder separation. As it depends not only on material and processing parameters, but also on the microscopic nature of a channel wall, rheometer with special roughened plates was designed to carry out wall slip measurement.

Problem formulation

Powder injection moulding (PIM) represents an ongoing topic for both basic and applied research due to rather complex processing chain, where each step has its own quality issues, which in some cases cannot be identified until the final sintering stage is reached, thus resulting in material, time and energy losses.

A fundamental quality influencing issue is the flow of PIM feedstocks into a mould cavity during injection moulding, where separation of binder and feedstock might occur. The mechanism of phase separation occurrence has still not been fully understood.

Recently, Thornagel [1] demonstrated that local shear rate gradients are the driving forces initiating phase separation as they force powder particles to leave areas of high gradients. Assuming no slip condition, i.e. good adhesion of the feedstock to the wall of the channel, a significant shear rate peak occurs close to the wall, while a plateau at much lower shear rate level is observed in the middle of the flow domain. Then, particles flowing in the peak area experience a non uniform shear rate resulting in their rotation, which becomes severe as the shear stress gradients increase. Such rotating particles try to leave areas of high shear gradients. Therefore, the area of the highest shear rate is characterized by high binder content, while the plateau of the lower shear rate accommodates a powder rich material [1]. To predict the situation, where a separation pattern changes continuously during moulding would require a multi-phase simulation, considering the particular feedstocks components. Instead, Thornagel [1] proposes a simplified simulation with modelling the feedstock as a bulk and extending currently used 3D Navier Stokes equations in a way that powder and binder concentrations and their variations can be predicted depending on the shear rate history. If validated, such an approach might be a breakthrough in PIM computer aided support.

In another approach Jenni et al. [2] compared the influence of injection moulding parameters on separation appearance with a current software simulation based on the balance model of the flow of rigid, spherical particles in a Newtonian fluid. Differential scanning calorimeter (DSC) was selected to quantify the local powder content. To compare different materials and processing parameters used for injection moulding, three testing moulds were used. The experimental runs were performed with the dependent variable for the mouldability - flow length and the input variables (nozzle and mould temperatures and injection speed). It has been demonstrated that powder content decreases to some extent with increasing number of corners in cavity geometry.

To quantify the separation, the results from the software simulation using the balance model were compared with experimental findings obtained using radiography, computer tomography and DSC [2]. The authors demonstrated that the balance model gives a clear picture of migration of particles for simple geometries, but the irregularities of the feedstock flow such as slip effects at the wall and the fountain flow are not intercepted by this model [2].

The practical output of the ongoing research should be an easy approach linking directly the factors responsible for powder-binder separation during injection moulding to the quality defects appearing on final sintered products. However, we are still far from this target. This paper tends to open discussion on several detailed approaches which should be considered to proceed with investigation of assembly and mechanism of powder-binder separation.

Although often disregarded from simulations, unstable rheological phenomenon – wall slip – accompanies the flow of PIM compounds, and could be considered as a qualitative parameter indicating powder-binder separation absence/occurrence. The conditions at which the highly filled materials slip at the wall, resulting in a plug flow (and thus no separation), are not only material characteristics and processing parameters, but the most important is an interfacial adhesion between the channel walls and PIM feedstock, depending on the material of the channel, its roughness and surface treatment.

Discussion

Query 1 - Testing moulds

Currently used testing moulds, designed mainly for investigating the mouldability of plastics, should be replaced with a testing specimen, particularly designed to evaluate the disposition of PIM feedstocks to the phase separation. In order to understand the mechanism of phase separation and its influence on the shape retention during debinding and sintering, the testing mould should include inner and outer corners, radical thickness changes, weld lines and a thin film part. Such a testing mould geometry (based on idea of dr T. Hartwig and developed in cooperation with IFAM, Bremen) allows us to observe the phase separation progression during mould filling by including elements with different cross sections, and analyze them with SEM.

SEM pictures depicting phase separation (Fig.1) are then distributed into meshes, where analysis of chemical elements can be done for particular mesh windows (for examples see Fig.1, where window 1 represents no separation area and 2 stands for separated binder area). The EDX analysis of SEM windows then gives distribution of elements typical for powder (Fe, Cr, Si, Cu) and binder (O and C), and thus provides a quantitative picture of the powder-binder separation (Table 1).

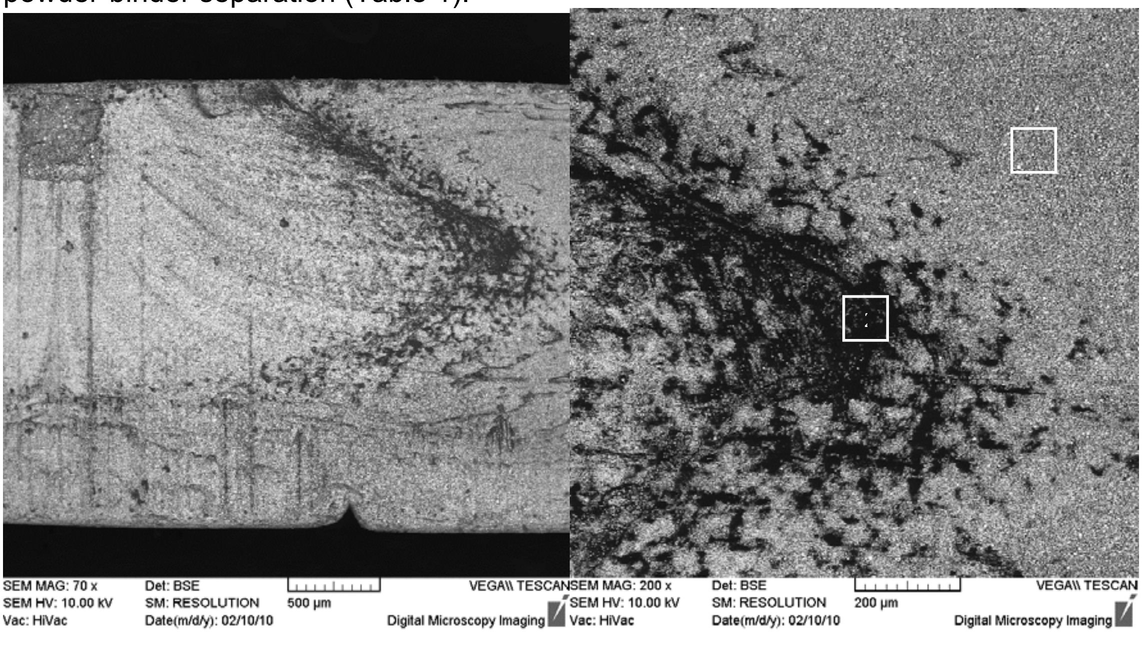

Fig.1 Evidence of powder-binder separation obtained using testing mould.

Table 1 Quantitative analysis of powder-binder separation from SEM analysis.

Element (wt. %)	1- no separation	2- binder rich
C	23.07	58.23
O	3.80	32.17
Fe	64.37	9.60
Cu	1.41	-
Si	0.30	-
Cr	7.05	-
Total	100	100

Query 2 - Rheological models for PIM compounds

Rheological models implemented to software programmes at present were also developed for polymer melts; their relevance is rather limited for PIM feedstocks. Therefore, they should be replaced with models describing the specific features of flow behaviour of PIM feedstocks in the broad shear rate range and validated on reliable rheological data. It might be speculated that often researches conducting rheological measurements consider the structural changes of PIM compound upon shearing as a test artefact due to local inhomogeneities within a feedstock, and disregard them from the flow data presented. In this respect, five independent measurements on fresh material are recommended to interpret the results correctly.

The viscosity values of a PIM feedstock are usually about three to two orders of magnitude higher in comparison to binder viscosity at the corresponding shear rates. It has been widely accepted that the turn to non-Newtonian behaviour arises from the disruption of agglomerates formed by particles [3]. An apparent yield appearing at low shear rates is often considered as an indicator of temporary particle network structure within melt (e.g. [4]). The Casson method [5] based on an energy dissipation mechanism or the empirical Herschel-Bulkley model [6] are usual approaches to yield stresses evaluation.

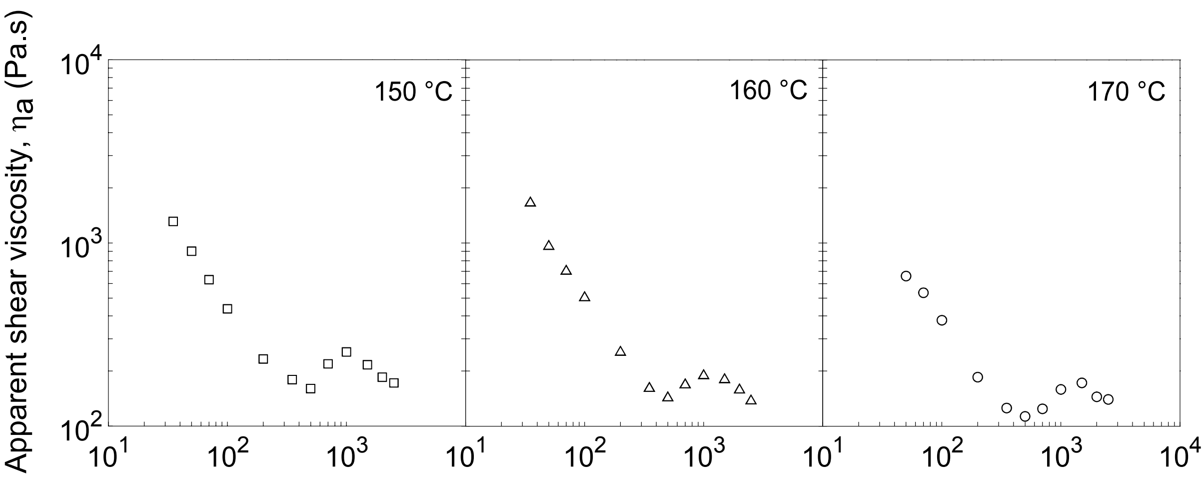

Fig. 2 Viscosity of the alumina feedstock as a function of shear rate at three different temperatures.

Generally, for particle filled systems, two mechanisms causing shear thinning can be discerned. First, the destruction of particle network during shearing results in a decay of amount of suspending fluid trapped among particles and a drop of effective volume fraction of powder [7]. Second, viscosity decrease is related to the dissipation energy rising from the rotation and distortion of particle agglomerates [e.g. 5]. Upon further increase of shear rates, particles and polymer orientate and order in the flow direction allowing interparticle motion, and the viscosity is dominated by hydrodynamic interactions resulting in shear thinning.

For PIM compounds the situation can be even more complicated [8]. As demonstrated on ceramic feedstock based on commercially available binder and fine aluminium oxide powder (Fig.2), at lower shear rates (up to 500 1/s) the viscosity of feedstock decreases with increasing shear rate, suggesting particle and binder chains orientation and ordering with flow. When the shear rate reaches about 500 1/s, particles do not have enough time to form layers and slide over each other, and the flow turns into a thickening as firstly reported by Hoffman [9]. There is still considerable uncertainty about the source of such behaviour. Jansma and Qutubuddin [10] showed, using different viscometers, that it could not be an experimental artefact due to wall slip. The mechanism proposed by Barnes [11] is that with increasing shear stress (rate) the layers formed in the pseudoplastic flow region become disrupted, and at a certain shear stress (rate) are fully eliminated. It implies that every highly concentrated suspension exhibits dilatant flow if proper parameters as powder concentration, its particle size distribution and binder viscosity are selected.

For the alumina feedstock, this structure restructuralization appears repeatedly. Both Herschel-Bulkley [6] and Casson [5] models applied to the rheological data resulted in similar parameters, however they could not describe the flow properties of alumina feedstock in the whole range of the measured data, because classical rheological models are primarily determined for characterization of monotonous dependence of viscosity on shear rate or stress.

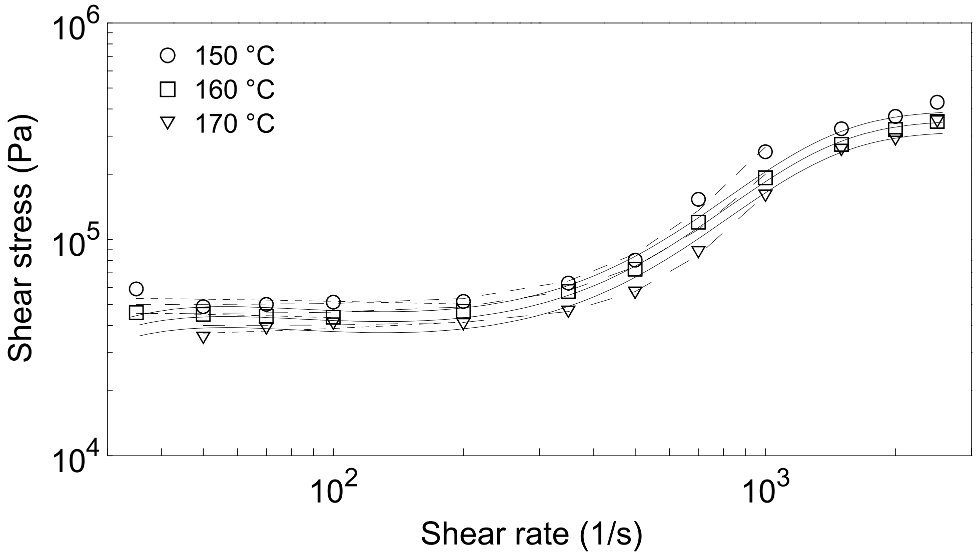

Fig. 3 Shear stress as a function of shear rate of the alumina feedstock at three different temperatures. Lines represents the fitting with Herschel-Bulkley (— — —), Casson (- - - - -), and proposed PIM model (solid line).

As the flow curve of alumina feedstock is consecutively shear thinning, shear thickening and again shear thinning, a model with the increased number of empirical parameters has to be applied. For materials lacking their 'symmetry' Roberts et al. [12] used so-called generalized Ellis model with eight parameters. For the non-monotonous behaviour presented we applied a model with the same number of parameters (published in Filip et al. [13]):

$$\eta = \frac{\eta_1 \exp(-f_1)}{b_1 + \exp(f_1) + \exp(-f_1)} + \frac{\eta_2 \exp(f_2)}{b_2 + \exp(f_2) + \exp(-f_2)}$$

where

$$f_1 \equiv f(\dot{\gamma}; c_1, p_1) = \log(c_1\tau)^{p_1} \quad ; \quad f_2 \equiv f(\dot{\gamma}; c_2, p_2) = \log(c_2\tau)^{p_2} .$$

The proposed model relates viscosity to shear stress instead of shear rate because the stress (contrary to the deformation) is continuous across the interface for two phase materials [14]. It could be noted that the same applies for calculation of maximum packing fractions of a powder/binder system from the relative viscosity vs. shear stress (not shear rate) curves.

If the flow curves are transformed to the viscosity vs. shear stress relation, the problem with a seeming discontinuity is eliminated, which is in accordance with the interpretation of rheological data in Hoffman [9]. The results of the fitting the experimental data with this model are shown in Fig. 3, where the results obtained with Casson and Herschel-Bulkley models are depicted as well for comparison.

It should be stressed that six out of eight parameters are fixed and the same for all temperatures, the remaining two depend on the identical temperature-dependent function. It is supposed that the empirical parameters should be further linked to the materials characteristics when the corresponding database will be created.

Query 3 – Determination of wall slip

As already pointed out, practical approach to avoid powder-binder separation is to set up conditions, where PIM compounds flow as a plug, exhibiting slippage at the wall. Occurrence of wall slip depends on material characteristics as the type of powder and polymer binder, the size and particle size distribution of powder, concentration of the powder and its surface treatment. These parameters can be easily simulated during rheological evaluation. Nevertheless, slip depends also on processing parameters as temperature, pressure, and shear rate, and most important on the microscopic nature of the channel wall, which is usually different during processing and rheo-testing. For this purpose roughened rheometer with plates made of the most often employed mould-construction steels with different surface modifications (nitride, titanic nitride) and surface roughness (0.025 – 1.6 of arithmetic average of absolute values) were designed at the Polymer Centre (TBU in Zlin) to study breakdown of the feedstocks-mould interface and wall slippage.

The relevance of this method has been tested on two 50 vol.% carbide powder feedstocks differing in their particle size distributions: BC10U prone to wall slip, having a broad particle size distribution and relatively high portion of small particles (diameter at 10%: 0.45 µm, at 50%: 1.11 µm, at 90%: 3.75 µm, average diameter: 1.24 µm) and BC75H based on larger particles (diameter at 10%: 2.19 µm, at 50%: 15.38 µm, at 90%: 28.06 µm, average diameter: 7.38 µm) without the disposition to wall slip. As demonstrated on viscoelastic functions (Figs. 4 and 5), the surface roughness affects not only the values of viscoelastic properties, but also their disposition to wall-slip.

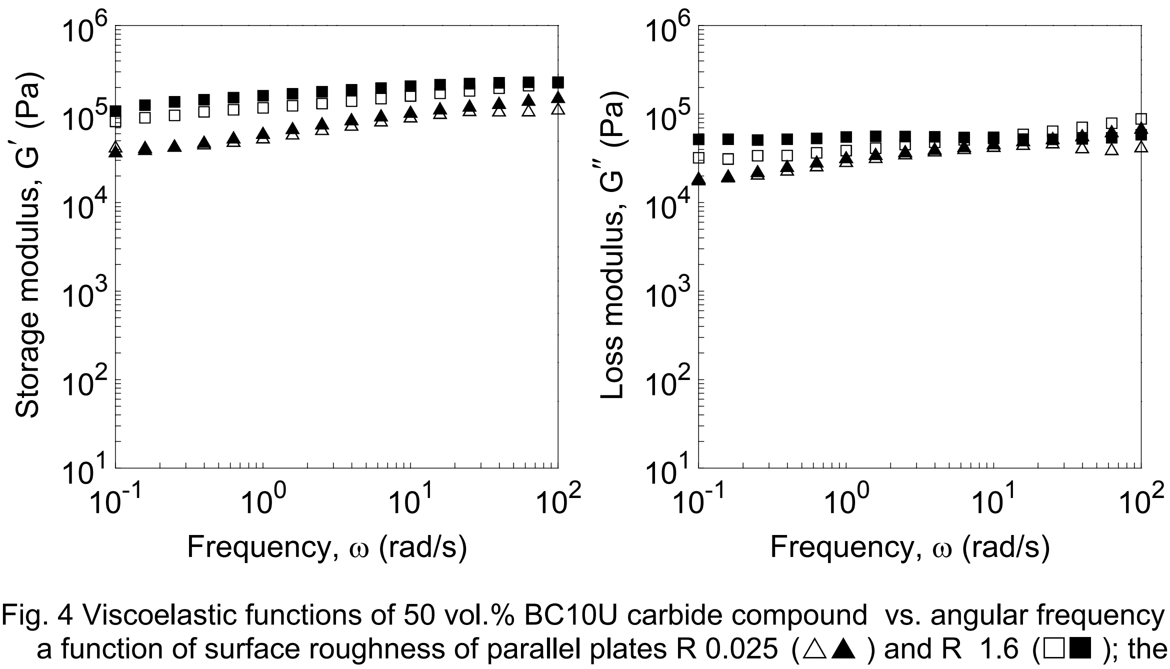

Fig. 4 Viscoelastic functions of 50 vol.% BC10U carbide compound vs. angular frequency as a function of surface roughness of parallel plates R 0.025 (△▲) and R 1.6 (□■); the distance between plates: 0.6 mm (open symbols) and 1 mm (full symbols).

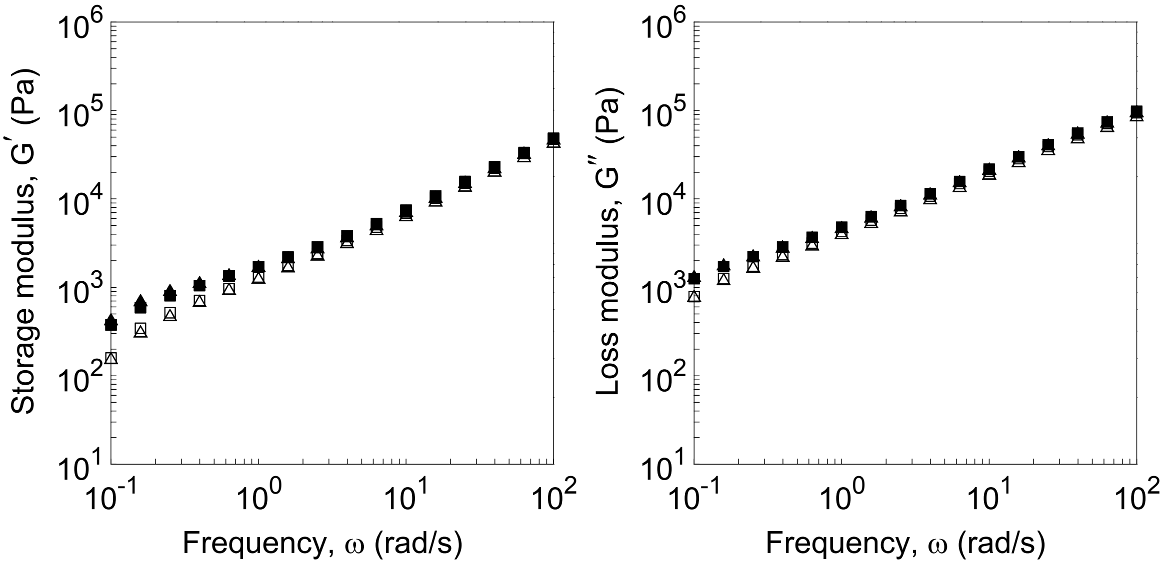

Fig. 5 Viscoelastic functions of 50 vol.% BC75H carbide compound vs. angular frequency as a function of surface roughness of parallel plates R 0.025 (△▲) and R 1.6 (□■); the distance between plates: 0.6 mm (open symbols) and 1 mm (full symbols).

Conclusion

The critical step of the PIM process is the flow of highly filled feedstocks into a mould cavity accompanied by separation of binder and powder components. In order to prevent such quality limiting issue, simulation software approved on reliable experimental data must be created. Wall slip as a possible measure of the separation onset has to be evaluated at the conditions reproducing the processing ones. Then, a rheological model taking into account the specific features of flow behaviour of PIM feedstocks in the broad shear rate range has to be developed. Finally, the flow data can be related to the powder-binder separation quantified from SEM chemical elements analysis obtained from the special design testing mould.

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References:

[1] M. Thornagel, *Euro PM2009*, 135 (2009).
[2] M. Jenni, L. Schimmer, R. Zauner, J. Stampfl, J. Morris, *PIM International*, **2**, 50 (2008).
[3] S. Kurzberck, J. Kaschta, H. Münstedt, *Rheol. Acta*, **35**, 446 (1996).
[4] A.B. Metzner, *J. Rheol.*, **29**, 739 (1985).
[5] N. Casson, In: C.C. Mill (ed) *Rheology of disperse systems*, Pergamon Press, New York (1959).
[6] W.H. Herschel and R. Bulkley, *Proc. ASTM*, **26**, 621 (1926).
[7] C.R .Wildemuth and M.C. Williams, *Rheol. Acta*, **23**, 627 (1984).
[8] B. Hausnerova, L. Marcanikova, P. Filip, P. Saha, *Polym. Eng. Sci*. (submitted 2010)
[9] R.L. Hoffman, *T. Soc. Rheol.*, **16**, 155 (1972).
[10] J.B. Jansma and S. Qutubuddin, *J. Rheol.*, **39**, 161 (1995).
[11] H.A Barnes, *J. Non-Newtonian Fluid Mech.*, **56**, 221 (1995).
[12] G.P. Roberts, H.A. Barnes, and P. Carew, *Chem. Eng. Sci.*, **56**, 5617 (2001).
[13] P. Filip, J. David, and R. Pivokonsky, *Acta Technica CSAV*, **51**, 349 (2006).
[14] P. Lomellini and D. Ferri, In: D.M. Binding, N.E. Hudson, J. Mewis, J.M. Piau, C.J.S. Petrie, P. Towsend, M.H. Wagner, and K. Walters (eds), *Proc. 13th Int. Congress on Rheology*, Cambridge (2000).