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International Journal of Pharmaceutics 216 (2001) 147–157

international journal of pharmaceutics

www.elsevier.com/locate/ijpharm

Use of a capillary rheometer to evaluate the rheological properties of microcrystalline cellulose and silicified microcrystalline cellulose wet masses

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Received 21 August 2000; received in revised form 2 January 2001; accepted 10 January 2001

Abstract

The influence of microcrystalline cellulose (MCC) type and water content on the rheological properties of the wet powder masses were studied using two different MCC grades (Avicel and Emcocel) and silicified microcrystalline cellulose (SMCC, Prosolv). A ram extruder was used as a capillary rheometer and unique flow curves for each cellulose grade and moisture content were derived. In addition, the elastic parameters of recoverable shear and compliance were determined. From different flow curve models evaluated, it was not possible to obtain clear evidence, which model best described the rheological properties of each cellulose grade at each water level. Furthermore, the residuals were shear rate dependent, which indicates that the models do not perfectly agree with physical properties of the wet masses. The elastic properties of wet masses increased with increasing water content and decreased with increasing shear stresses. SMCC grade proved to be more elastic than the simple MCC grades at each moisture content. Thus, the rheological properties of MCC and SMCC wet masses were different and changed with water content. Consequently, it was not possible to achieve similar rheological properties between different grades of cellulose by altering the water content of the wet mass. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Microcrystalline cellulose; Silicified microcrystalline cellulose; Ram extruder; Capillary rheometer; Rheological properties; Elastic parameters

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1. Introduction

Microcrystalline cellulose (MCC) is an essential excipient in extrusion/spheronisation to achieve the required rheological characteristics of the wet mass. MCC is also used in conventional granulations, at water levels lower than used in extrusion/spheronisation. Since MCC has the ability to hold

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PII: S0378-5173(01)00585-3

large amounts of water in the internal structure, it controls the movement of water through the wet powder mass (Fielden et al., 1988). Raines et al. (1989) observed that the various grades of MCC have different rheological properties when mixed with water and lactose. In addition, Newton et al. (1992) showed that in the formulation of spherical particles by extrusion/spheronisation it is not possible to interchange brands of MCC without changing water content. Thus grades which are considered equivalent do not function always in an equivalent manner.

Silicified microcrystalline cellulose (SMCC) is a combination of co-processed MCC and colloidal silicon dioxide (CSD). Tobyn et al. (1998) found that the silicification process produces a material, which is chemically and physically very similar to standard MCC. On the other hand, SMCC has been claimed to be more resistant to wet granulation than conventional MCC grades, since SMCC maintains compaction properties after wetting and drying (Sherwood and Becker, 1998). Luukkonen et al. (1999) compared the rheological properties of SMCC with those of standard grades of MCC using a mixer torque rheometer (MTR). They observed that the silicification process affected the swelling properties and, furthermore, the mixing kinetics of water and MCC.

The ease of extrusion depends on the excess of the liquid present over that is required to fill the interparticle space between the particles (Benbow and Bridgwater, 1993). Jerwanska et al. (1995) suggested that a nearly complete filling of the pore space with a liquid component is a prerequisite for the wet mass to yield and thus to extrude. Powders, which have a large particle size distribution, pack closely requiring less liquid to fill the spaces between particles than powders having a narrow particle size distribution (Benbow et al., 1987; Chen et al., 2000). Because of this behaviour, the particle size distribution has a large effect on packing, and hence on flow parameters. In addition, the interaction of MCC with water is complicated and several theories have been proposed on how water is bound to cellulose (Froix and Nelson, 1975; Zografi and Kontny, 1986; Fielden et al., 1988; Kleinebudde 1997). Li et al. (1992) attributed water in the cellulose samples to the bulk water between fibres and to water in pores within the fibres. In the interaction the cellulose particles swell, and unlike non-porous materials, MCC is capable of retaining large amounts of water in the internal structure.

In addition to particle size and size distribution, particle shape and its surface state exert significant influence on the extrusion behaviour of pastes (Chen et al., 2000). Edge et al. (1999) found that CSD is mainly located on the surface of MCC particles. CSD is known to improve the flowability and increase the specific surface area of dry SMCC particles compared to MCC particles. Li et al. (2000) suggested that the physical reason for the difference between MCC and SMCC wet masses may be caused by the presence of silicate particles that strengthen the interparticulate interactions. Strong interparticulate interactions has been suggested to cause also the stronger tensile strength of SMCC tablets in direct compression (Edge et al., 2000). However, the mechanism behind this behaviour is still unknown.

According to Ovenston and Benbow (1968), the parameters necessary to characterise the flow of a material through a die during extrusion can be measured directly only using a capillary rheometer, whereas Landín et al. (1995) claims that it is possible to determinate shear stress/shear rate curves and yield stresses also from MTR measurements. The capillary rheometer, however, represents the more usual approach to the characterisation of rheological properties. Numerous extrusions of pharmaceutical pastes by the ram extruder have indicated that whilst slip has been observed, the flow is dominated by wall adhesion. Although the capillary rheometer has been used previously to study MCC containing systems (Harrison et al., 1985; Raines et al., 1989; Fielden et al., 1992), it has not been used to compare system, which contains only MCC or SMCC and water.

The extrusion of pastes can result in the phenomenon of liquid migration, which causes changes in fluid content within the wet mass as measurements are made (Chen et al., 2000). The aim of this study was to evaluate whether there is adequate stability in the water/MCC systems to allow the use of capillary rheometry at wide water range, and to evaluate the influence of MCC type and water content on the rheological properties of the wet powder masses.

2. Materials and methods

2.1. Materials

Three different materials were studied; Avicel PH 101 manufactured by FMC Corp. (Co. Cork, Ireland) and Emcocel 50 and Prosolv 50 from Penwest Pharmaceuticals Co. (Nastola, Finland). Avicel PH 101 and Emcocel 50 are two different grades of MCC, whereas Prosolv 50 is SMCC with a 2% w/w silicon dioxide concentration. The particle size distributions of cellulose grades studied have been determined earlier by Luukkonen et al. (1999). The mean diameter of the cellulose particles varied between 58.6 and 59.7 μm, and there were no significant differences between particle size distributions of cellulose samples. Hence, in this study, the influence of particle size distribution will be negligible.

2.2. Extrusion

The materials were mixed with six different water contents (0.8–1.5 ml g^{-1}) in a planetary mixer (Hobart, London, UK) for 10 min. The wet masses were allowed to equilibrate overnight in plastic bags before extrusion. The wet masses were extruded using a ram extruder designed by Ovenston and Benbow (1968). The barrel (diameter 2.54 cm) was fitted with a die of 1.5 mm diameter with different lengths (3–12 mm). The ram extruder was driven downwards by a mechanical press (Lloyds MX-50, Southampton, UK).

The materials were extruded at five different ram speeds (400, 200, 100, 50 and 25 mm min^{-1}) with one filling of the barrel. Starting at the highest speed and moving to lower speeds enables the measurements at different speeds to be made with a single barrel of wet mass (Benbow and Bridgwater, 1993). Furthermore, starting with the highest speed restricts the potential water migration. The disadvantage of using different speeds during one extrusion is that the ram pressure may decline as the wetted area of the barrel decreases or the ram pressure may exhibit overshoot in the beginning of extrusion. Thus, the system was operated manually to ensure that a steady state pressure had been achieved before the next barrel speed setting was selected. The results are the mean of three extrusions.

2.3. Capillary rheometry

The steady state extrusion pressure values were calculated by cross sectional dividing the steady state extrusion forces by the surface area of the piston face (5.067 cm^2). The pressure values were plotted as a function of the die length to radius ratio (4–16) to construct the graphs proposed by Bagley (1957). The intercept on the pressure axis at zero L/R ratio is called entrance pressure (i.e. upstream pressure loss). The die wall shear stresses were derived from the Bagley plots by dividing the slopes by two. The die wall shear rates were calculated as previously reported by Harrison et al. (1987). The die wall shear stresses were then plotted against the die wall shear rates to construct a flow curve, which provides a representation of the rheological properties of a given material.

2.4. Flow curve models

The simplest rheological model is the Newtonian flow model (Eq. 1), which relates the die wall shear stress (τ_w) to the shear rate $\dot{\gamma}_A$ by the viscosity (η). This model is unable to represent the flow of complex systems.

$$\tau_w = \eta \dot{\gamma}_A \tag{1}$$

The Bingham Body model (Eq. 2), describes plastic flow where a yield stress (τ_y) precedes Newtonian flow. η_P is the plastic viscosity.

$$\tau_w = \tau_y + \eta_P \dot{\gamma}_A \tag{2}$$

The Power Law model (Eq. 3), describes materials that flow as non-Newtonian systems, i.e. the viscosity of the material is changed when a shear stress is applied. This type of flow curve becomes linear when plotted logarithmically. The value of k_P is the Power Law viscosity constant which describes the consistency of the wet mass and n is the power law index, which describes the deviation from Newtonian behaviour. When the value of n is greater than one, the type of flow is shear thickening and when n is less than one, the type of flow is shear thinning.

$$\tau_w = k_P \dot{\gamma}_A^n \tag{3}$$

The Herschel–Bulkley (H–B) model (Eq. 4), is used to describe a material, which has a Bingham type yield stress followed by non-Newtonian flow of the Power Law type. The model was developed for concentrated dispersions of rubber in benzene (Herschel Von and Bulkley, 1926).

$$\tau_w = \tau_y + k_{HB} \dot{\gamma}_A^n \tag{4}$$

A further model proposed for solid dispersions is that of Casson (Eq. (5)) described to represent the behaviour of flocculated pigment particles in suspension (Casson, 1959).

$$\tau_w^{1/2} = \tau_y^{1/2} + k_C^{1/2} \dot{\gamma}_A^{1/2} \tag{5}$$

The non-linear curve fittings of mathematical models (Casson, H–B and Power law) were made to flow curves using the program SigmaPlot 5.0 (SPSS Inc., Chicago).

2.5. Elastic properties of the materials

During extrusion material has to undergo flow reorganisation when going from the wider cross-section barrel to the small cross-section die. A pressure drop, known as upstream pressure loss or entrance pressure, is required for the material to flow through this entrance region. Chohan (1994) and Chohan and Newton (1996) used the entrance pressure (P) and shear stress (τ) to calculate the recoverable shear and the compliance, which should indicate a measure of elasticity of molten polymers (Chohan, 1994) and wet masses (Chohan and Newton, 1996) at low flow rates.

The definitions for recoverable shear and compliance are the following:
Recoverable shear, RS:

$$\mathrm{RS} = \frac{P}{4\tau}. \tag{6}$$

Compliance, C:

$$C = \frac{P}{4\tau^2}. \tag{7}$$

3. Results and discussion

3.1. Flow curves

The water contents used were chosen to be the same than previously used in MTR experiments (Luukkonen et al., 1999). In spite of the wide water range, all wet masses could be extruded without any evidence of water migration. This is unusual for water powder mixtures of this type of ratio. Polymers are often added to pastes to restrict water movement and even then systems are stable only over a narrow range of water contents. Thus all the cellulose grades showed unusual behaviour. The typical Bagley plot is shown in Fig. 1. The steady state extrusion pressure increased both with increasing L/R ratio of the die and with increasing ram speed. These results are consistent with previous findings (Harrison et al., 1985; Raines et al., 1989). The flow curves of the MCC and SMCC grades for each moisture content are shown in Fig. 2(a)–(f). The derived flow curves show shear thinning behaviour indicating that the materials realign or reorientate themselves or there is appreciable water movement so that there

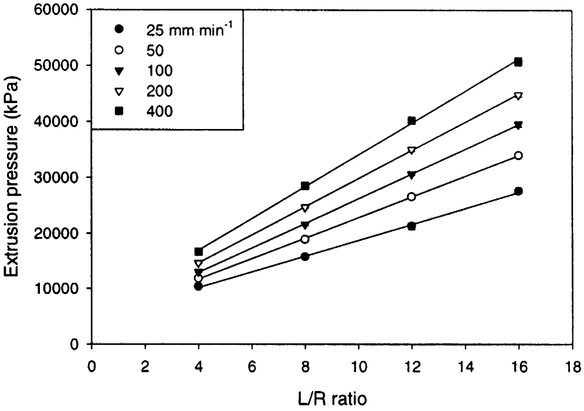

Fig. 1. Bagley plot of Avicel PH 101 at 0.8 ml g^{-1}. Standard deviations are so small that they can not be seen behind the symbols.

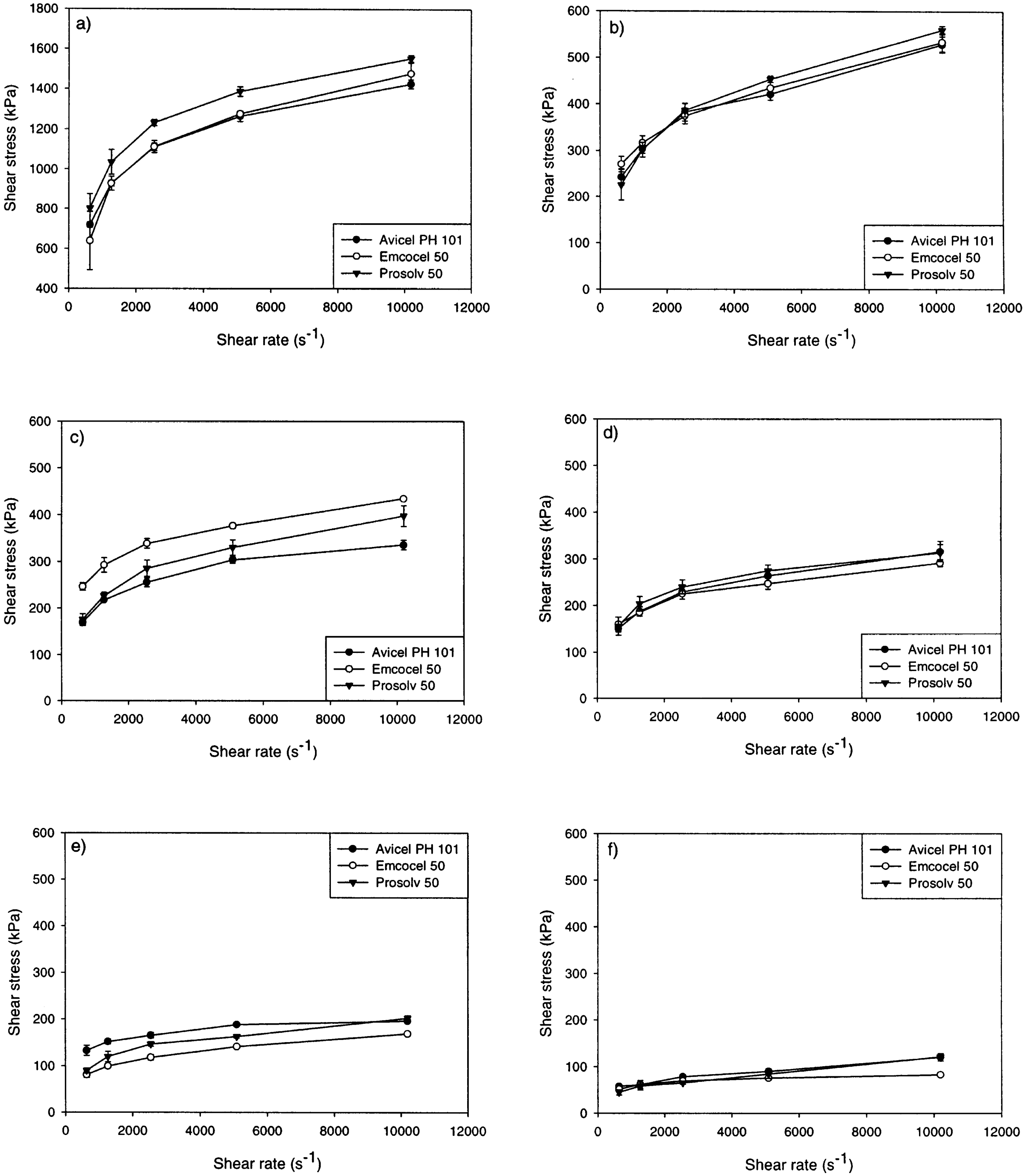

Fig. 2. Flow curves of Avicel, Emcocel and Prosolv; (a) 0.8 ml g^{-1} (b) 1.1 ml g^{-1} (c) 1.2 ml g^{-1} (d) 1.3 ml g^{-1} (e) 1.4 ml g^{-1} (f) 1.5 ml g^{-1}.

is less resistance to flow at higher shear rates. At the lowest water content (0.8 ml g^{-1}) the flow curves of Avicel and Emcocel are very similar, whereas Prosolv shows larger shear stresses throughout the whole flow curve (Fig. 2(a)). At 1.2 ml g^{-1} the flow curves are different for each cellulose grade, Emcocel showing the largest shear stresses (Fig. 2(c)). At 1.4 ml g^{-1}, the largest shear stresses are shown by Avicel (Fig. 2(e)). In addition, Avicel has the least variation of shear stress with shear rate. At the largest moisture content (1.5 ml g^{-1}) the flow curves of Avicel and Prosolv are almost identical (Fig. 2(f)). Generally, the shear stresses decreased with increasing water content with all cellulose grades. Furthermore, the variation of shear stress with shear rate decreased when the water content increased.

The different water contents affected the rheological properties of cellulose grades studied differently. This can be an indication that different cellulose grades react with water in a different way. The results agree with those reported by Raines et al. (1989). Variations in the performance of different sources of MCC have been associated with the different interactions between the particular grade of MCC and water due to different pore structures (Ek and Newton, 1998).

3.2. Flow curve models

The majority of mathematical models used in rheology express a non-linear relationship between shear stress and shear rate in terms of a small number of parameters which may then be measured to determine the variations between materials of formulations. The model that reveals the most significant trends in the flow parameters is usually the model of choice. Results for the rheological models are shown in Table 1. The Power Law viscosity constants (k_P) decrease with increasing water content for all cellulose grades (Fig. 3(a)). Minor deviations from this behaviour can be seen at 1.4 ml g^{-1} for Avicel, at 1.2 ml g^{-1} for Emcocel and at 1.3 ml g^{-1} for Prosolv. The results appear logical as the value of k_P describes the consistency of the wet mass by which it resists permanent change of shape, i.e. the rigidity of the wet mass. The degree of non-Newtonian flow (n) is almost constant at all water contents for all cellulose grades. In general, the lowest values are seen at the same level of water contents at which the k_P values have the maximum values. Exceptions to this are the highest water contents where the values of n are the largest for Avicel and for Prosolv. Since the value of n describes the degree of non-Newtonian flow, the wettest masses are approaching the Newtonian flow model.

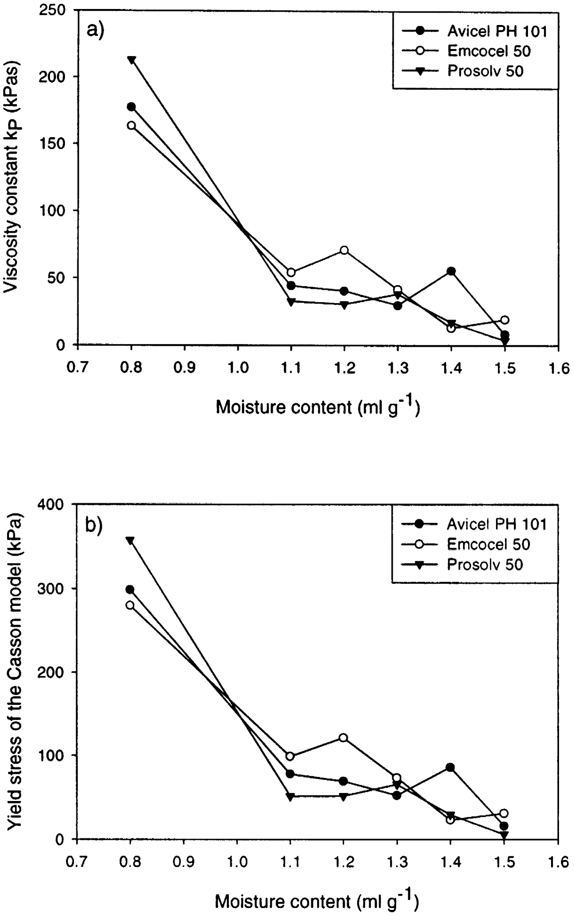

Fig. 3. Effect of cellulose grade and moisture content on (a) the Power Law viscosity constant (b) the yield stress of the Casson model.

When non-linear iteration of the H–B equation was performed also negative yield stresses were observed. Marquardt et al. (1997) eliminated this error by estimating a substitute value $\tau_{0.1}(\dot{\gamma}_A = 0.1$

Table 1
Results for flow curve models

Moisture content (ml g^{-1})	Rheological parameters	Avicel			Emcocel			Prosolv		
		Power law	H–B	Casson	Power law	H–B	Casson	Power law	H–B	Casson
0.8	Yield value (kPa)	–	0	299	–	0	280	–	0	358
	k (kPa s)	177	177	4.5	163	163	4.9	213	213	4.5
	n	0.23	0.23	–	0.24	0.24	–	0.22	0.22	–
	R^2	0.976	0.976	0.955	0.990	0.990	0.976	0.972	0.972	0.949
	RMS%	3.4	3.4	2.5	2.3	2.3	2.0	3.5	3.5	2.5
1.1	Yield value (kPa)	–	0	77	–	126	99	–	0	51
	k (kPa s)	45	45	2.0	54	14	1.7	33	33	2.8
	n	0.27	0.27	–	0.25	0.37	–	0.31	0.31	-
	R^2	0.985	0.985	0.979	0.996	0.998	0.999	0.991	0.991	0.982
	RMS%	3.1	3.1	1.9	1.4	0.9	0.5	2.6	2.6	2.1
1.2	Yield value (kPa)	–	0	69	–	0	121	–	0	51
	k (kPa s)	41	41	1.1	71.03	71.03	1.0	31	31	1.7
	n	0.23	0.23	–	0.20	0.20	–	0.28	0.28	–
	R	0.978	0.978	0.961	0.995	0.995	0.984	0.991	0.991	0.980
	RMS%	3.3	3.3	2.3	1.3	1.3	0.4	2.4	2.4	1.9
1.3	Yield value (kPa)	–	0	52	–	0	73	–	0	65
	k (kPa s)	30	30	1.13	42	42	0.7	39	39	1.0
	n	0.26	0.26	–	0.21	0.21		0.23	0.23	–
	R^2	0.995	0.995	0.986	0.985	0.985	0.980	0.978	0.978	0.958
	RMS%	1.8	1.8	1.5	2.4	2.4	1.5	3.1	3.1	2.4
1.4	Yield value (kPa)	–	0	86	–	0	23	–	0	29
	k (kPa s)	56	56	0.25	13	13	0.68	17	17	0.79
	n	0.14	0.14	–	0.28	0.28	–	0.27	0.27	–
	R^2	0.975	0.975	0.954	0.999	0.999	0.996	0.981	0.981	0.969
	RMS%	2.2	2.2	1.5	0.7	0.7	0.9	3.3	3.3	2.4
1.5	Yield value (kPa)	–	46	16	–	0	31	–	38	6
	k (kPa)	8	0.14	0.46	19	19	0.14	4	0.06	0.68
	n	0.29	0.68	–	0.16	0.16	–	0.37	0.78	–
	R	0.970	0.992	0.977	0.965	0.965	0.936	0.972	0.992	0.977
	RMS%	4.7	2.4	2.0	2.8	2.8	2.1	5.4	2.9	2.6

s^{-1}) instead of obtaining τ_y by iteration. Due to the fact that in this study no measured values were available at low shear rates, constraint $\tau_y > 0$ was used in the final iteration. The results of the H–B model show that in general there is no yield stress before the flow begins (Table 1). There are only three exceptions when a yield stress was detected and the H–B model fitted better than the Power Law model. In all other cases, the H–B model gives the same values for k_{HB} and n as the Power Law model.

In contrast to the H–B model, the Casson model gives yield stresses for every flow curve. The value of the yield stress decreases with increasing water content. Interesting thing is that the yield stress of the Casson model shows identical behaviour with the Power Law viscosity constant (k_P) (Fig. 3(a) and (b)). The values of k_C decrease with increasing water content as well, but are much smaller than those for the other models. The values of the Power Law index (n) for this model are not shown in Table 1, since the Casson model presumes that n is always 0.5. The H–B model seems to give better curve fittings for the materials with a yield stress, and thus the Casson model is not regarded as a convenient fitting form for pseudoplastic materials (Marquardt et al., 1997; Ceulemans et al., 1999). Since there are no values supporting either the H-B or the Casson model at the low shear rates, the existence of real yield stresses remains unclear.

R^2 and RMS% values for all rheological models are shown in Table 1. In general, R^2 values are better for the Power Law and the H–B model, whereas RMS% values are smaller for the Casson model. The residual plot for the Power Law and the Casson model is shown in Fig. 4. If the rheological model is appropriate for the experimental data, the residuals should be normally distributed. The residuals are, however, shear rate dependent, which reveals that the models do not perfectly agree with physical properties of the wet masses.

3.3. Mixer torque rheometer versus capillary rheometry

Landín et al. (1995) compared logarithmic, Casson and H–B models when they attempted to relate the torque measurements from MTR directly to the rheological parameters, such as yield stress and kinematic viscosity. They reported that the data generated by the MTR compare favourably with those measured by capillary rheometry and that the H–B model was the model of choice. In the later studies Rowe (1995, 1996) used the Casson model, which is easier to apply since it does not require iteration to solve the equation. He observed that as water content of the wet mass was increased both the yield stress and kinematic viscosity increased (Rowe, 1995). Since in the capillary rheometer studies the viscosity constant (k) decreases when water content increases, Rowe's results are in contrast to the results obtained in this and other studies by capillary rheometer (Harrison et al., 1985; Raines et al., 1989; Fielden et al., 1992), and therefore must cast doubt on the suitability of the MTR for the measurement of classical rheological parameters.

The source of this difference is presumably to be found in the different measuring systems included. The mixer torque rheometer has two intermeshing paddles, and the sample is compressed and expanded between contrarotating blades with a changing gap. In the MTR experiments the material exhibits an increase in torque with increasing water content as consistency of the wet mass rises to maximum, thereafter decreasing as

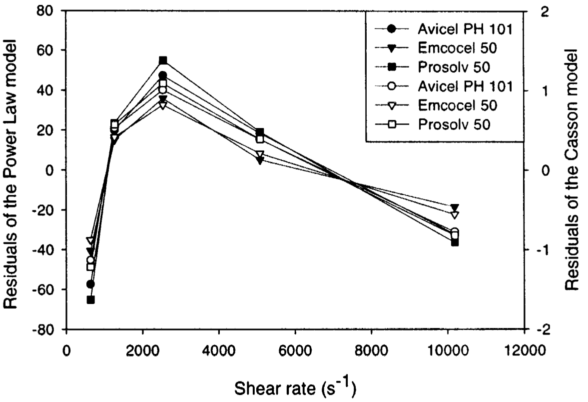

Fig. 4. Residual plot for the Power Law (filled) and the Casson models (open) at water content 0.8 ml g^{-1}.

the material becomes overwetted. Alleva (1984) and Rowe and Sadeghnejad (1987) have suggested that this behaviour is consistent with the different states of liquid saturation defined by Newitt and Conway-Jones (1958). In the case of the capillary rheometer, the resistant to movement involves two components; the convergent flow from the wide barrel to the narrow capillary and the flow through the capillary. The air is expelled during the compression stage, and the system consists of liquid and solid particles only. Because of consolidation of the wet mass the possible differences in liquid saturation are diminished. Thus the material is in a very different state in these two systems and one would not expect an identical behaviour. Consequently, MTR has been traditionally used in wet granulation studies, while the information obtained by capillary rheometry has been related to extrusion. The flow curves and parameters derived from the rheological models were quite similar between different MCC and SMCC grades, and the differences seen earlier in MTR studies by Luukkonen et al. (1999) could not be observed.

3.4. Elastic properties of the materials

The compliance (C) is shown as a function of shear stress in Fig. 5(a)–(c). The recoverable shear (RS) exhibited the same behaviour than C, and hence is not shown. The C values of wet masses increased with increasing water content and decreased with increasing shear stresses. The value of C of Avicel was greater than that of Emcocel at 1.2 and 1.3 ml g^{-1}, whereas Emcocel proved to be more elastic at higher water contents (Fig. 5(a)–(c)). The C values of SMCC masses were greater than the C values of MCC masses at each water content studied, indicating that the SMCC masses were more elastic than MCC masses.

It has been suggested that there appears to be an optimal elasticity for the formation of satisfactory spheres in the spheronisation stage (Chohan and Newton, 1996). Wet powder masses with high elasticity or low plasticity may resist the spheronisation by restoring the original shape. Chohan and Newton (1996) found that relatively inelastic

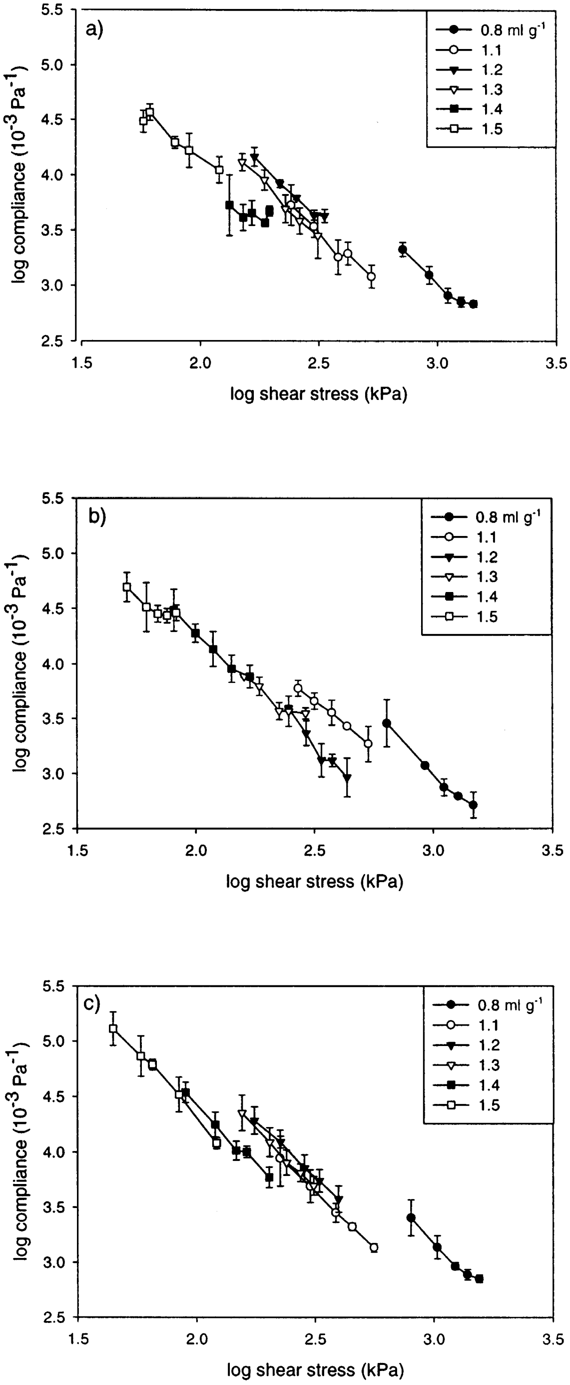

Fig. 5. Effect of cellulose grade and moisture content on the compliance of wet powder masses; (a) Avicel PH 101 (b) Emcocel 50 (c) Prosolv 50.

materials, such as the colloidal grades of MCC tend not to round during the spheronisation. The RS values of colloidal grades were of the same magnitude as those reported for Avicel, Emcocel and Prosolv in this study. However, the effect of higher elasticity of SMCC wet masses on the sphericity of pellets has not yet been studied.

4. Conclusions

In spite of the wide water range used, all wet masses could be extruded without any evidence of water migration. From the different rheological models evaluated, it was not possible to indicate, which model best described the rheological properties of each cellulose grade at each water level. In addition, the residuals were shear rate dependent, which reveals that the models do not perfectly agree with physical properties of the wet masses. It was shown that the MTR results were in contrast to the results obtained by capillary rheometer, which indicates that MTR does not measure the classical rheological parameters, only liquid saturation. In capillary rheometer the air is expelled during the compression stage, and the possible differences in liquid saturation are diminished. The elastic properties of wet masses increased with increasing water content and decreased with increasing shear stresses. The SMCC grade proved to be more elastic than the simple MCC grades at each moisture content. Thus the rheological properties of MCC and SMCC wet masses were different and changed with water content. Consequently, it is not possible to achieve similar rheological properties between different grades of cellulose by altering the water content of the wet mass.

Acknowledgements

This study was supported by The Finnish Cultural Foundation and The Finnish Pharmaceutical Society.

Appendix A. Nomenclature

τw	shear stress
$\dot{\gamma}_A$	shear rate
τy	yield stress
η	viscosity
ηP	plastic viscosity
n	Power law index
$k P$	viscosity constant for Power Law model
$k HB$	viscosity constant for Herschel–Bulkley model
$k C$	viscosity constant for Casson model

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