Thermal precipitation or gelling behaviour of dissolved methylcellulose (MC) derivatives—Behaviour in water and influence on the extrusion of ceramic pastes. Part 1: Fundamentals of MC-derivatives

Roland Bayer*, Matthias Knarr

Dow Wolff Cellulosics GmbH, August Wolff Str. 13, D-29699 Bomlitz, Germany

Dedicated to Dr. Walter Bayer on the occasion of his 87th birthday.

Abstract

Methylcelluloses dissolved in water show a temperature dependent gelling behaviour. The gel temperatures depend mainly on the degree of substitution with methyl groups. The behaviour of methylcellulose containing pastes is of high importance in various applications. The paper describes the influence of the degree of substitution on the thermal characteristics of methylcelluloses in water and in ceramic pastes. The gelation temperature of the methylcellulose in both systems is increasing with decreasing degree of substitution. This enables a broader temperature window in the ceramic extrusion process. Extrusion near the gelation temperature normally leads to many defects in the extrudate. However, close to the gelation temperature the extruded profiles show more defects with methylcelluloses having a higher degree of substitution. Methylcelluloses having a low degree of substitution also enable a paste extrusion above the gelation temperature (up to 90 °C). This is not possible with currently commercially available methylcelluloses.
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1. Introduction

Cellulose ethers (CE) are derived from cellulose, the most widespread polysaccharide in nature. Cellulose forms the primary structural component of plants and is made of repeated units of the anhydroglucose monomer. The cellulose molecule is a very regular, rigid and straight chain without any branching. Each anhydroglucose unit contains three functional groups—the hydroxyl groups on carbon atoms 2, 3 and 6 (see Fig. 1).

These hydroxyl groups form a highly ordered network of hydrogen bonds and ensure the secure linkage of the cellulose molecules in each elementary fibre of the plant's cell wall. Cellulose is therefore not soluble in water or other commonly used solvents.[1] After reaction with different chemicals the cellulose backbone can carry different functional groups. Depending on the type and amount of functional side groups (methyl-, hydroxypropyl- and other groups) the solubilisation temperature of the cellulose ether can be varied between temperatures of 60 down to 30 °C. At the solubilisation temperature a suspension of MC-particles in water starts dissolving when cooling down. Moreover, many water soluble cellulose ethers show a thermo reversible gelation or precipitation at elevated temperatures.[2]

Water soluble cellulose ethers are mainly used as thickeners and water retention agents in many cement or gypsum based dry mortars,[3] for tablet coating in the pharmaceutical industry,[4] as thickeners and gelling agents in various food applications,[5] in extruded cement based and ceramic pastes, as a rheology

* Corresponding author. Tel.: +49 5161 442906; fax: +49 5161 44142906.
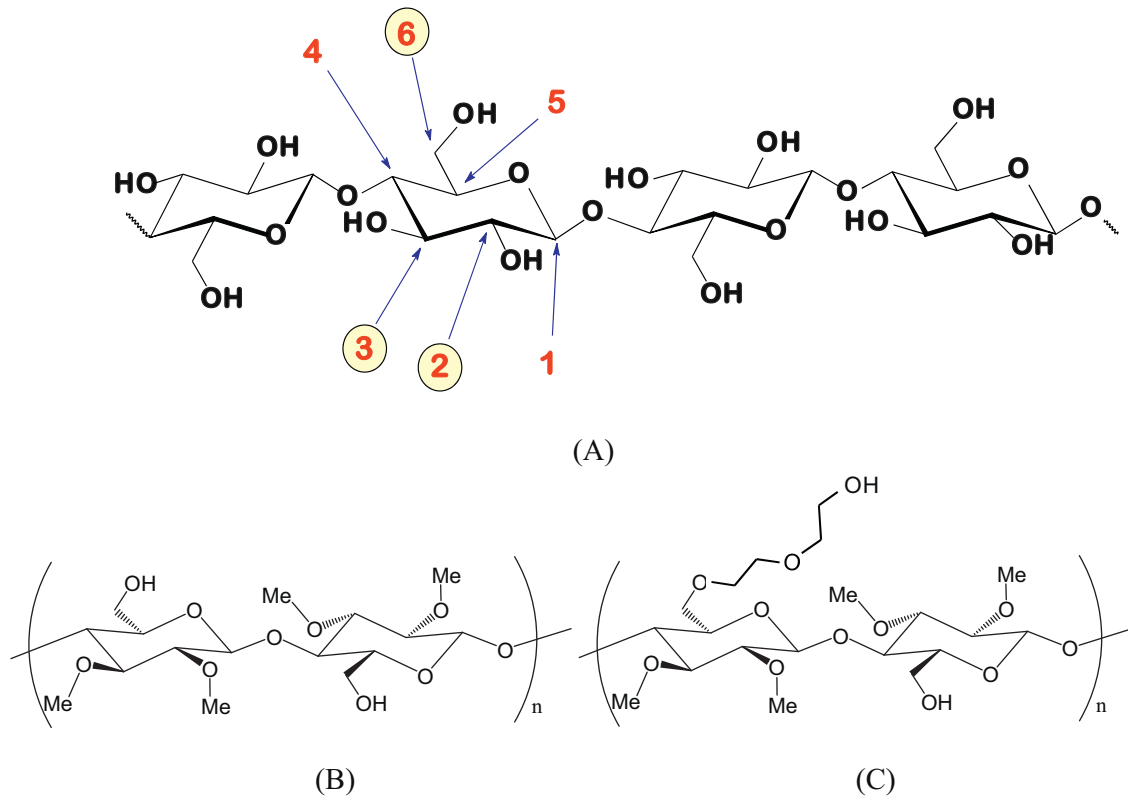*E-mail address:* rbayer@dow.com (R. Bayer).

Fig. 1. Repeating anhydroglucose as cellobiose (dimer units) with (A) the three reactive OH-groups in 2-, 3- and 6-position, (B) a DS (Me) of 2, (C) a DS (Me) of 2 and a MS (HP) of 0.5.

modifier in water-borne paints, household use and many other industries.

This paper focuses on the thermal behaviour of dissolved methyl-group containing cellulose ethers in pure water and in ceramic pastes. Ceramic pastes, plastified with methylcellulose ethers, are extruded in large amounts for honeycomb ceramics (see Fig. 2).
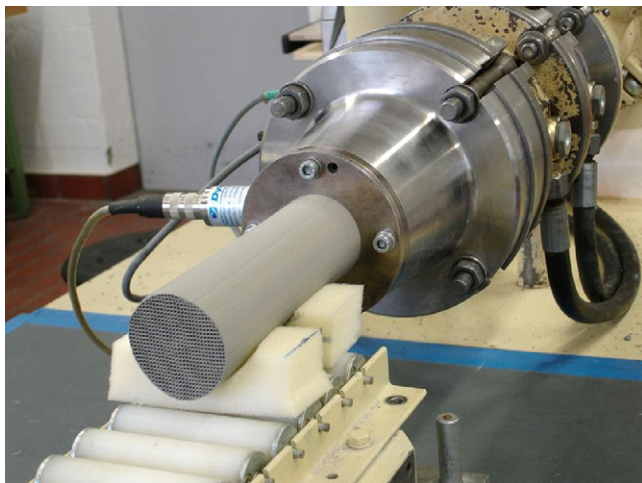

Fig. 2. SiC extrusion with a single screw extruder and an auto honeycomb die.

1.1. Basic properties of cellulose ethers in solutions and pastes

1.1.1. Viscosity

Cellulose ethers form clear to opaque solutions in water. The viscosities in water vary from water-like (a few mPa s) to jellylike (several ten thousands mPa s) depending on the concentration and on the chain length of the cellulose raw material. Cellulose ethers are specified according to their viscosity measured at 1 or 2% aqueous solution. Different producers use different methods and apparatus to specify the viscosity of their CE-solutions: the Haake Rotovisco, Höppler and Brookfield methods are mainly in use. The viscosity of cellulose ethers is shear rate dependent.[6] As different methods are applied under different shear rates same solutions can lead to different results in viscosity. This should be taken into consideration when comparing viscosities of methylcelluloses being specified with different techniques. Fig. 3 shows a comparative scale of viscosities measured with the apparatus commonly used for the viscosity determination of cellulose ethers.

Mixing cellulose ethers with different kinds of ceramic powders, with gypsum or cement based building materials, with food ingredients or other materials leads to pasty or stiff mixtures, depending on the amount of water used. Rheological properties of those mixtures like pseudoplasticity (shear thinning) or thixotropy (time dependent change of viscosity under mechanical stress) are largely affected by the rheological properties of the
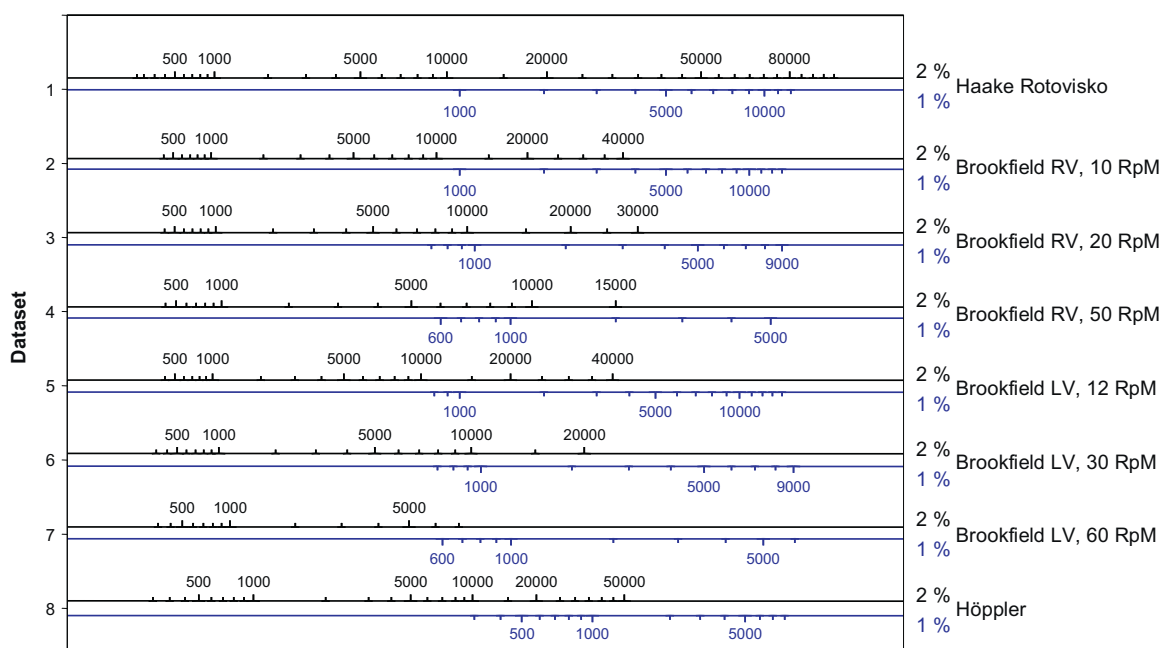
Fig. 3. Viscosity scale, comparing the eight commonly used different measurement techniques for cellulose ethers in 1 and 2% solution (1: Haake Rotovisco, 2–7: Brookfield, 8: Höppler).

cellulose ether solution itself. In ceramic pastes, cellulose ethers also affect properties like lubrication, cohesion between the dispersed particles, wet and dry green properties of the formed body, water retention and others.

1.1.2. Thermogelation of cellulose ethers

As explained above, many water soluble cellulose ethers solutions show a thermoreversible gelation or precipitation at elevated temperatures.[2] The thermal behaviour of an MC-solution differs from that of an HPMC- or HEMC-solution. On heating up, aqueous MC-solutions form stable gels, whereas aqueous HPMC and HEMC solutions precipitate and form weak gels (see Fig. 4).

The thermal gelation of methylcellulose solutions with increasing temperatures was first observed by Heymann.[7] The turbidity during the phase transition was at that time explained by a dehydration of the methylcellulose chains at high temperatures. Since that time, the thermoreversible phase transition of MC in aqueous solutions has been extensively investigated by various techniques.[8–15] Haque et al. investigated the presence of crystalline structures in solutions at low temperatures which melt out during heating and allowing the development of a different structure at higher temperatures.[16]

According to Sarkar water at relatively low temperatures forms an ice-like structure around the hydrophobic groups, such as the methyl substitution of the methylcellulose polymers. When the solutions are heated, the ice-like structure breaks down with an increase of entropy, thus allowing the hydrophobic groups to interact and causing gelation.[17]

Kobayashi found evidence of a weak supermolecular association or clustering at 20 °C of semi dilute methylcellulose solutions. This clustering was significantly enhanced as the

temperature increased based on a hydrophobic association. At higher temperatures a strong local segregation of polymer-rich and polymer-lean regions occurs.[18]

Desbrieres, Hirrien et al. describe heterogeneities in solutions to become more and more important with increased
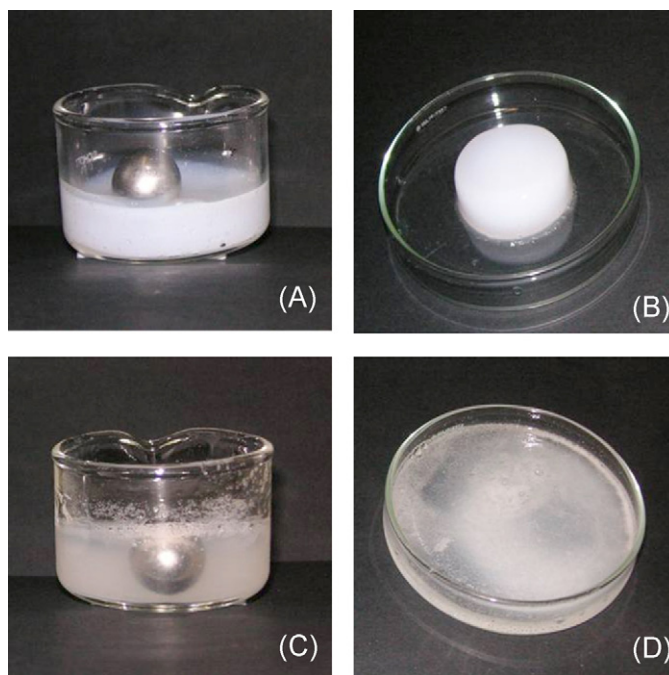

Fig. 4. (A) and (B) 2% MC solution, forming strong gels above the gelation temperature. (C) and (D) 2% HPMC and HEMC solutions, forming weak gel structures above the precipitation temperature. In the case of an HPMC and HEMC a steel ball sinks to the bottom, in the case of an MC the steel ball is held by the gel.

temperatures. Further, it was suggested that gelation is mainly driven by hydrophobic interactions between highly substituted zones and that the presence of tri-substituted units is compulsory for gelation.[19,20] The presence of tri-methyl glucose units in the methylcellulose gel was also observed and that the gel network is formed of crystalline junction points out of these.[21]

Li et al. reported the concept of hydrophobic effective units based on the dispersity in the degree of substitution along the cellulose chain. Therefore, the thermodynamic mechanism involved in the hydrophobic association during gelation has been explained as an entropy-driven process that is mainly controlled by the thermally induced destruction of hydrogen bonds formed between water molecules and methylcellulose chains.[22–24]

In order to characterise the temperature dependent properties of precipitation or gelation, the oscillation shear flow experiment is commonly used. The complex viscosity η^* is obtained from this experiment. In the low temperature region the viscosity slightly decreases at increasing temperature, a well known behaviour for liquids.

If precipitation at elevated temperatures takes place, the complex viscosity drops, further increasing temperatures lead to an increase in viscosity, representing the formation of a weak gel. If gelation takes place, no strong decrease of the complex viscosity can be found. In these cases η^* has a minimum after the slight decrease and is increasing directly afterwards. An example for these characteristics is given in Fig. 5.

The gelation or precipitation temperature is mainly dependent on the chemical substitution of the cellulose backbone (DS/MS), on the concentration and on additional ingredients (e.g. salts or other solvents) present in the mix.

The repeating unit in the cellulose chain is the anhydroglucose unit which contains three reactive OH-groups (in 2-, 3- and 6-position). All OH-groups are able to react both with methyl chloride resulting in methyl groups and with ethylene oxide or propylene oxide resulting in hydroxyethyl or hydroxypropyl groups during the synthesis process. The average "degree of substitution" (DS) indicates how many hydroxyl groups of an anhydroglucose unit are etherified.

For that reason the DS-values can vary between 0 and 3. The "molar degree of substitution" (MS) quantifies the average number of hydroxyethyl (HE) or hydroxypropyl (HP) groups per anhydroglucose unit. The MS, in contrast to DS, can have values above 3 due to a possible oligomerisation of ethylene oxide or propylene oxide starting on the OH-side group.

However, from a technical perspective, there are two general limitations to reach all theoretical DS and MS values:

1. below a certain DS (Me) cellulose ethers are insufficient or not water soluble and
2. for HEMC a separation of the slurry resulting from production via a thermal separation is only possible below a certain MS (HE) (see Fig. 6). However, the borderlines of solubility and thermal separation introduced in Fig. 6 are smooth transitions and depend upon the synthesis pathways.

1.2. Extrusion of ceramic pastes and "temperature sweep measurements" at the extruder

Extrusion is one of the main processes for shaping ceramic products. We differentiate between thermoplastic extrusion with thermoplastic polymers as the binder and plastic paste extrusion with a liquid dissolving the polymeric binder. In paste extrusion with water as the liquid, a non-self-lubricating ceramic material, unlike clay, requires a cellulose ether thickener as plasticiser and binder. The main segment with cellulose ethers as extrusion aid in the technical ceramic is the auto honeycomb market. We estimate this segment to be about 150,000 tons (2010). The dry ceramic raw material is mixed with a cellulose ether, optionally other additives and water. After mixing and kneading a plastic material is formed. This can be extruded as a stiff paste and even very complex shapes such as honeycombs (see Fig. 2) can be obtained. After extrusion, the profile is cut, dried and sintered. The extrusion of ceramics plasticised with cellulose ether has been well-known for many years.

There has, however, been no systematic study on the impact of different cellulose ethers with various substitutions on the process properties and extrusion behaviour of extrudable aqueous ceramic pastes. In lieu thereof, today extrusion normally is performed with cellulose ether substitution degrees which originally had been developed for requirements in other applications.

The goal of this study was to investigate the thermal properties of the whole range of technically producible methylcellulose ethers in solution as well as in a ceramic paste under real extrusion conditions. This paper deals with methylcelluloses without any hydroxyalkyl side chains.

When extruding a ceramic mixture containing a methylcellulose like Methocel[TM] A4M (see Fig. 11, samples 1 and 2), there is an upper temperature limit, beyond that no defect free extrusion is possible. A further increase in the extrusion temperature leads to a ceramic mass which continuously becomes more brittle; the cohesion between the ceramic particles decreases, cracks appear and at the same time the extrusion pressure sharply increases. In this temperature range the MC in the ceramic paste gels. The gelation temperature decreases on increasing the MC-concentration in the aqueous solution[8] as well as in the water based ceramic paste.[25] Depending upon the conditions, the gelation temperature can be at or near room temperature, which often leads to a very narrow temperature frame for a safe extrusion process. Trials with novel methylcelluloses were performed to test whether it is possible to solve this problem. The novel MC's ought to show a higher gelation temperature than those well-known so far.

Extrusion trials are normally performed at a constant temperature. In the ceramic industry many efforts are made to keep the processing temperature constant. The goal of our study was to investigate the extrudability of pastes at different temperatures in order to get a deeper understanding of the binder's temperature dependent performance. Instead of running dozens of single extrusion trials, we continuously heated-up the extruder jacket and the screw and measured the resulting paste temperatures in the profile extruded. The extrusion pressure, extrusion speed and the extrudate quality were investigated as a function of the
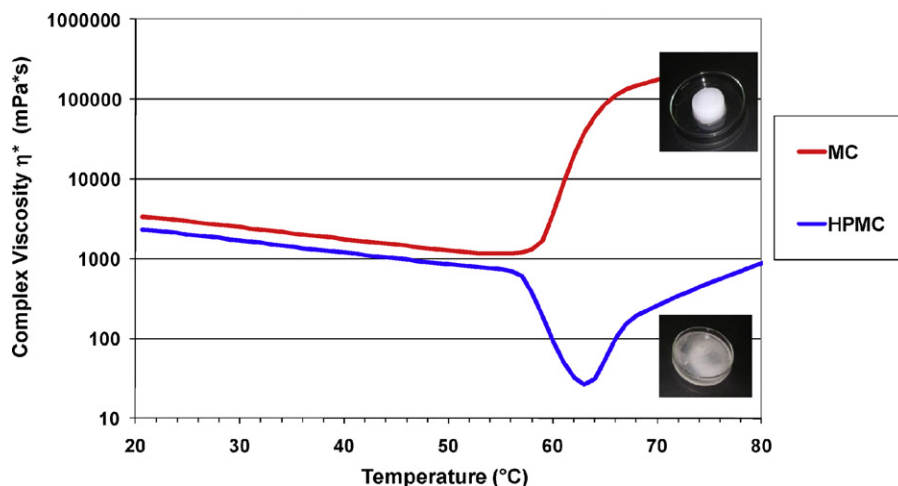
Fig. 5. Determination of gelation or precipitation of a 2% solution: MC and HPMC (HEMC behaves similar to HPMC).

temperature in the profile. The paste extruded was continuously returned into the feeder screw and returned in a circle. The heating speed in the thermostat does, however not fully correlate with the heating speed in the profile extruded due to a heat transfer delay which increases at higher temperatures (see Section 3).

2. Materials and methods

2.1. Synthesis of the methylcelluloses

Six MC's were synthesised under comparable conditions, of which two were inside the commercially available specification of DS (Me) and four were below this range (DS (Me) 1.41–1.59). The detailed synthesis conditions of these MC's are given in Ref. 27, whereas the general procedure for the synthesis of cellulose ethers is described in Ref. 28.

2.2. Preparation of methylcellulose solutions

2% solutions of the cellulose ethers are prepared by adding a specific amount of cellulose ethers to tap water (water

hardness 1.99 mmol/l according to DIN 38409-6, 11.1°dH) at room temperature, stirring the solutions with an overhead lab stirrer at 1000 rpm for an hour and cooling these solutions with an ice/water mixture. These solutions are then stored in a refrigerator at 5 °C overnight right to the beginning of the measurements.

2.3. Viscosity measurements

The investigations of the shear rate dependency of the viscosity were performed with an Anton Paar Physica MCR 501 rheometer with a cone and plate geometry (diameter 50 mm, angle 1°, CP50-1°) at a constant temperature of 20 °C in a steady shear rate experiment. The shear rate applied was varied from 1 to $1000\,\mathrm{s}^{-1}$. Further details regarding the measurement principles are given in Ref. 29.

2.4. Temperature sweep measurements

The temperature depending properties were investigated with the help of the temperature sweep experiment. The heating rate
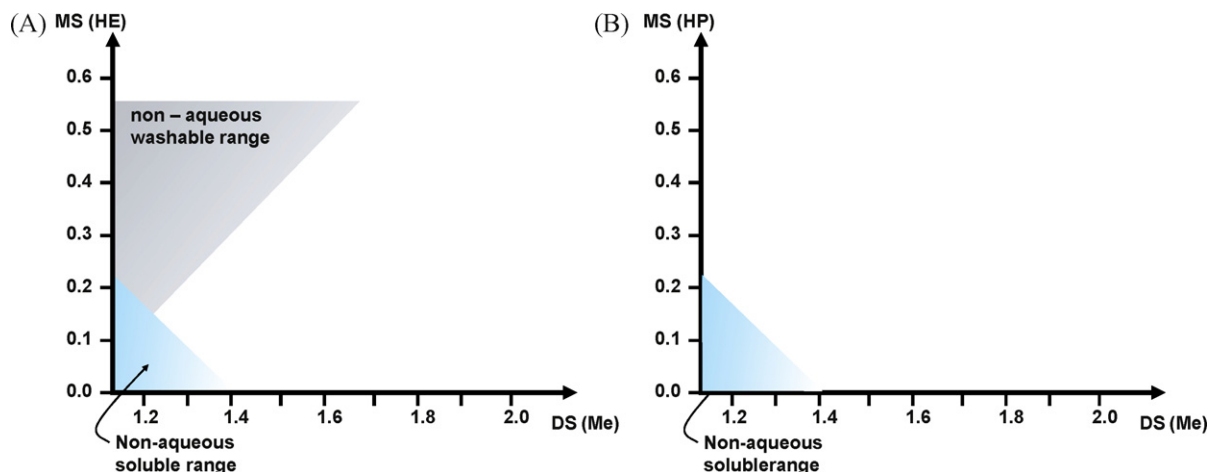

Fig. 6. Schematic illustration showing the fundamental limits of aqueous solubility and washability according to production limits of (A) HEMC and (B) HPMC as well as MC (at MS = 0).

was 3 °C/min. An Anton Paar Physica MCR 501 rheometer with Peltier system was used in small deformation oscillation shear flow using 2% MC solutions. The cup and bob geometry (CC-27) was used due to the possibility to investigate higher fluid volumes compared to cone and plate geometry and therefore to avoid significant evaporation of the fluid at higher temperatures. The measurements were performed at a constant frequency of 2 Hz and a constant strain (deformation) of 0.5% from 20 °C to 85 °C with a heating rate of 3 C/min. These measurements were performed in the linear visco-elastic region, so that the resulting properties could not be influenced by the applied strain. The material functions storage modulus G', loss modulus G'' and complex viscosity $\eta*$ were investigated. Further details regarding these measurement principles are given in Ref. [30].

2.5. Paste preparation for extrusion trials

100 parts by weight (equivalent to 5.5 kg in all trials) of a spray dried cordierite (CP 820M, Imerys Tableware, Neustadt, Germany; properties: moisture content: 1.8%, bulk density: 996 g/l, surface area: 18 m^2/g, primary particles showing 50% < 10 μm and 100% < 60 μm) and 2 parts by weight of the cellulose ether were mixed dry for 3 min in a fluidised-bed mixer (20 l mixer M 20 MK with 1.5 kW engine, shaft rotating speed 230/min, producer Lödige, Germany) until a homogeneous mixture was formed. Than 30.5 parts of water (water hardness 1.99 mmol/l per DIN 38409-6, 11.1°dH) at 20 °C are subsequently sprayed into the batch for further 2 min. The wet paste is mixed for further 20 s. The paste was transferred to a kneader (AMK IIU, engine 2 × 1.5 kW, usable vol. 20 l, total vol. 35 l, producer AMK, Aachen, Germany) and kneaded for 15 min. The completion of mixing was reached when the best plastification or texture occurred in the paste. This was defined when the paste reached the largest possible clod like shape in the kneader and when further kneading (more than 15 min) did not increase the size of the clods.

2.6. Preparation and procedure of the temperature sweep trials at the extruder

After kneading, the paste was immediately introduced into the feed trough of a water-cooled single-screw extruder (PZVE 8 D from Händle GmbH, Mühlacker, inner screw diameter 80 mm, feeder screw speed 12 rpm, auger screw speed 15 rpm). The paste was pressed through a perforated plate and passed through a vacuum chamber for degassing under a pressure of 300–350 mbar at room temperature, then strained (i.e. pressed through a screen that had a mesh size of 0.3 mm in order to free the paste of aggregates and to enable easier homogenisation) for 30 min, whilst the material was continuously returned in a circle. Subsequently, the material was extruded through a honeycomb profile with a cell density of 47 cells/cm^2 (300 cells/in.^{2}) and slot width 0.26 mm and returned in a circle for 9 min until the extrusion pressure drop reached a constant level. After 9 min the absolute pressures never differed more than 2 bar from the first value measured and the temperature sweep measurement at the extruder was started by heating up the water in the extruder jacket with a thermostat

(Julabo SL6), programmed to an upper limit of 90 °C, heating speed 3 °C/min. The material was extruded through the die described above. During all the process the material was discharged onto a conveyor belt and returned in a circle into the feeder screw until the temperature reached 90 °C or the extruded cordierite paste lost its plasticity, got brittle or gave significant defects. The extrusion pressure was measured with a pressure sensor (Dynisco ID370-1C, operation range 0–100 bar, installed close to the die). The resulting temperature in the extrudate was measured with two different methods: an infra-red thermometer (Dostmann electronic, type: Scan Temp 0-1351) was used in the temperature range below approx. 67 °C, a needle thermometer (Testo 925 from Testo AG) was used in the temperature range above approx. 67 °C. The difference measured between both scales was between 0.2 and 0.4 °C when the thermometers were changed. All given "extrusion temperatures" refer to the measured temperatures in the profile. The extrusion discharge speed was calculated by measuring the required time to extrude a profile of 50 cm length. During the temperature sweep experiment the water loss was measured in some exemplary cases (see Section 3).

3. Results and discussions

3.1. Rheological measurements in water

In general, the viscosity of cellulose derivatives in water is shear rate dependent. This shear rate dependency of the viscosity of the samples 1–6 at a concentration of 2% in water at a constant temperature of 20 °C is given in Fig. 7. The used concentration of cellulose ether in a typical ceramic extrusion formulation is significantly higher compared to that used in our aqueous model system. However, general technical limitations in rheometers do not allow to handle cellulose ether solutions with solution viscosities being equivalent to their concentration in a ceramic paste.

With increasing shear rate, the viscosity decrease is increasing. This shear thinning behaviour can be explained by disentanglements of the polymer coils in solutions and increased orientation of the polymer coils in the direction of the flow.[6] According to Clasen et al. the disentanglements of the polymer coils in moderately concentrated network solutions without intermolecular interactions are the main driver for the decrease in viscosity at high shear rates.[30]

A comparison of the samples 1–6 with different DS (Me) shows a similar shear rate—viscosity dependency. Samples 1–2 with the highest DS (Me) value have the highest viscosity and the samples with the lowest DS (Me) (samples 5 and 6) show slightly lower viscosities.

We assume that all cellulose raw materials (same specification) have equal intrinsic viscosities and therefore equal molar masses. Besides raw material influence and processing, there are the two following viscosity-influencing parameters for a decrease of viscosity: a low DS (Me) leads to polymers near to the limit of solubility (see Fig. 6). A minor part of the polymer chains is not able to participate in the entanglement network of the polymer coils in solution which are responsible for
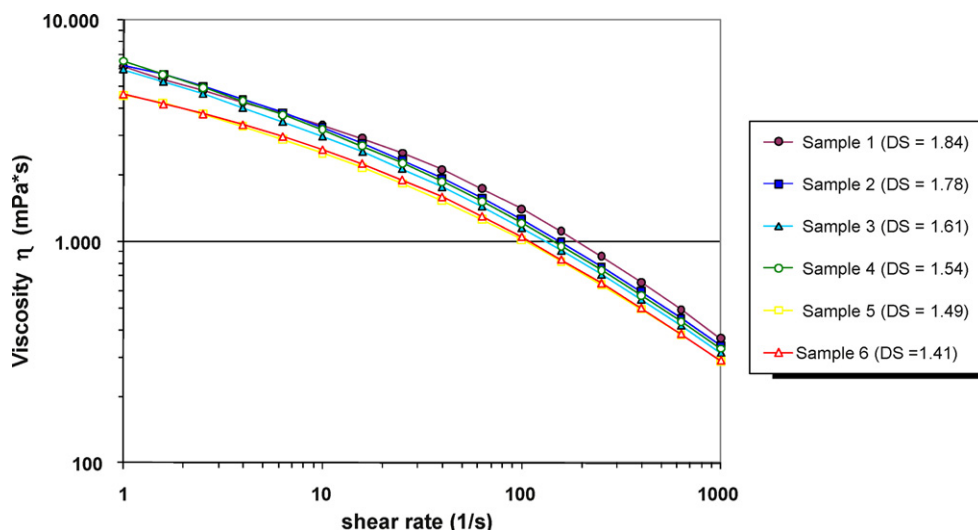
Fig. 7. Viscosity shear rate dependence of the samples 1–6 at $c = 2\%$ in water at 20 °C.

Table 1
Viscosities of samples 1–6 at 2% and 20 °C in water.

	DS (Me)	Viscosity ($c = 2\%$) at 2.55 s^{-1} (mPa s)	Viscosity ($c = 2\%$) at 10 s^{-1} (mPa s)
Sample 1	1.84	4810	3350
Sample 2	1.78	5000	3280
Sample 3	1.61	4640	2980
Sample 4	1.54	4950	3200
Sample 5	1.49	3760	2500
Sample 6	1.41	3770	2600

viscous properties. A high DS (Me) represents a high amount of methyl groups per gram of polymer leading to a lower amount of cellulose chains per weight. The methyl groups on the cellulose backbone do not lead to any significant viscosity increase. This means a high DS (Me) leads to a lower viscosity. Table 1 shows that the low DS (Me) effect overbalances one of the high DS (Me).

As introduced in Figs. 4 and 5, the MC derivatives in solution show a gelation or precipitation behaviour at enhanced temperatures. This temperature depending phase (sol ⇔ gel) transition of the six materials has been investigated by a rheological small amplitude oscillatory approach. The results of the temperature depending complex viscosity are given in Fig. 8.

Each curve can be divided into three zones. Below 60 °C the viscosity decreases with temperature. The polymers are highly entangled. With increasing temperatures the Brown motion of the polymers increases and more entanglements are disengaged leading to a decreasing viscosity.

At temperatures above 58 °C the viscosity increases strongly. At these temperatures methylcellulose starts to build up a gel network based on the hydrophobic association of the cellulose ethers' methyl groups.[23] The network structure further increases which leads to a viscosity increase.

In the region of higher temperatures only a slight viscosity increase is detected for some solutions. In this region the formation of the hydrophobic network structure is mostly completed and only minor changes take place.

Up to the gelation temperature all six solutions show the same temperature dependence of the viscosity. Above 60 °C the samples with the highest DS (Me) (samples 1 + 2) show the highest slope of the viscosity. For the samples with lower DS (Me) this viscosity increase is slightly shifted to higher temperatures and the slope is lower. The minimum viscosity is used as one metric of the gelation temperature (Table 2).
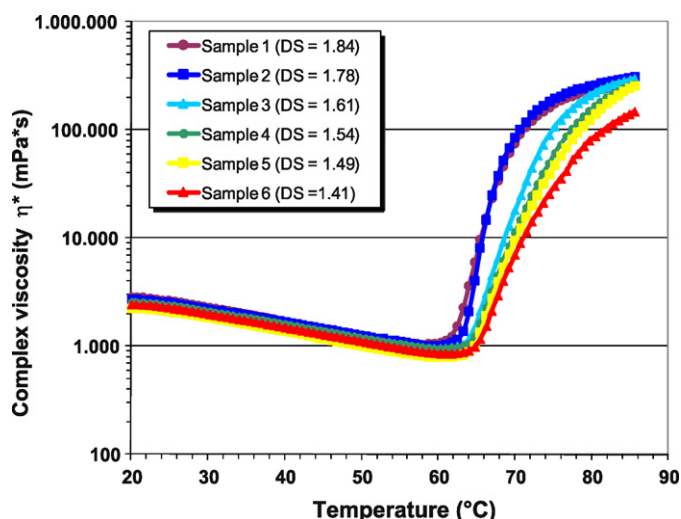

Fig. 8. Temperature dependence of the complex viscosity of samples 1–6 at $c = 2\%$ in water.
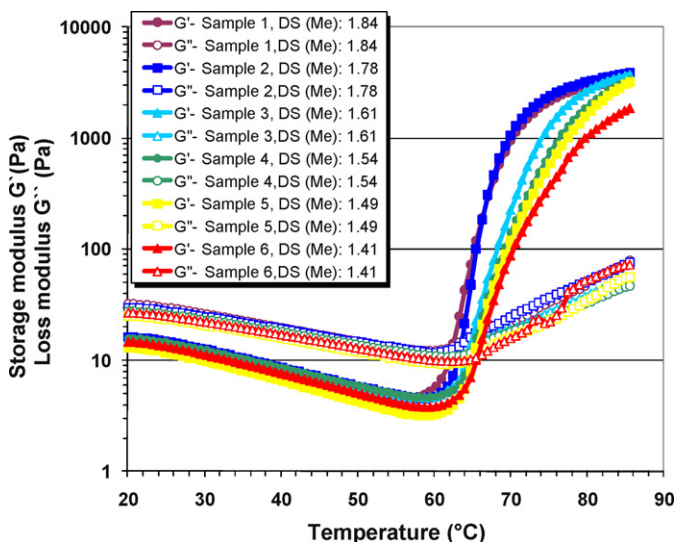
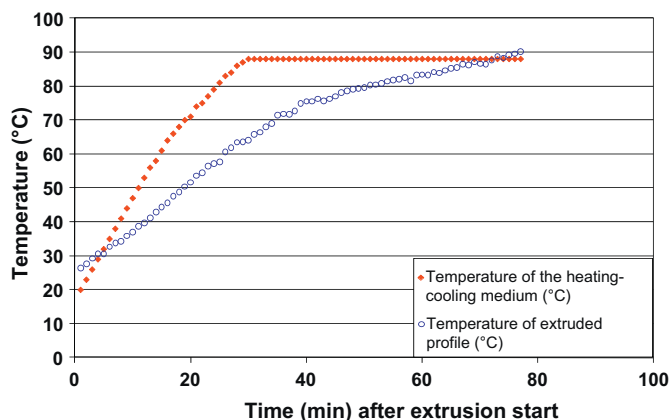Fig. 9. Temperature dependence of the storage and loss modulus of the samples 1–6 at $c = 2\%$ in water.

Fig. 10. Time delay of heat transfer between the temperature in the thermostat (for heating the extruder jacket and the auger screw) and the extruded profile: water temperature measured in the jacket (solid symbols), temperature measured in the profile (hollow symbols) ($t = 0$: start of temperature sweep measurement at the extruder).

Samples with a high DS (Me) show a plateau like behaviour at high temperatures, those with a lower DS (Me) only indicate the beginning of the plateau-like region at high temperatures. The viscosities show a descending trend with decreasing DS (Me).

The plot of the storage modulus G' and the loss modulus G'' vs. temperature is another way to analyse the gelation performance of MC solutions. This plot is given in Fig. 9 where the storage modulus represents the elastic parts and the loss modulus the viscous parts of the material. At low temperatures the viscous parts are dominant over the elastic parts. With increasing temperatures both moduli decrease due to the increasing Brownian motion of the polymers and the decreasing entanglements between the polymer coils.

At temperatures above 60 °C the storage modulus G' shows a strong increase and due to the gel formation its values become dominant over the loss modulus. The cross-over of the storage modulus G' and loss modulus G'' is another definition of the gelation temperature (values see Table 2).

The gel structure increases with increasing temperatures. This is also shown by the further increase of the storage modulus vs. the loss modulus. Like it has been shown in the viscosity temperature dependency, the storage modulus reaches a plateau in the high temperature range. The hydrophobic network formation is nearly completed and only minor changes are taking place. The comparison of the six samples with various DS (Me) show comparable storage and loss modulus values in the lower

temperature range due to their comparable viscosities. With further enhancing temperatures, the samples with the highest DS (Me) (samples 1 + 2) show the highest slope of storage modulus increase and therefore the low cross-over temperature between the storage modulus G' and the loss modulus G''. For the samples with lower DS (Me) this storage modulus increase is slightly shifted to higher temperatures and the slope of this storage modulus increase is lower. A plateau-like behaviour at high temperatures for the storage modulus is only obtained for the samples with high DS (Me). The samples with lower DS (Me) show the beginning of the plateau-like range at high temperatures and the storage modulus shows a descending trend with decreasing DS.

3.2. General measurement of temperature sweep in the ceramic paste

During the trials the paste stiffness and the pressure were not only influenced by the gelation of the cellulose ether, but also by the drying process itself: above approximately 65 °C the paste heats up slower than below 65 °C (see Fig. 10). Due to the slow temperature increase and the higher evaporation rate at elevated temperatures; there is a higher paste water loss at higher temperatures than at lower temperatures. At a paste temperature of approximately 65 °C, the water in the heating–cooling jacket is close to reaching its maximum temperature of 88 °C. We expect a slight additional increase in pressure and stiffness above 65 °C

Table 2
Gelation performance of samples 1–6 at 2% in water.

	DS (Me)	Gelation temperature (min η^*) (°C)	Gelation temperature (cross-over G'/G'') (°C)
Sample 1	1.84	58 ± 0.5	63 ± 0.5
Sample 2	1.78	60 ± 0.5	64 ± 0.5
Sample 3	1.61	60 ± 0.5	65 ± 0.5
Sample 4	1.54	60 ± 0.5	66 ± 0.5
Sample 5	1.49	62 ± 0.5	66 ± 0.5
Sample 6	1.41	62 ± 0.5	66 ± 0.5

originating from the evaporation. However, this system immanent error does not have a significant influence on the gelation or precipitation behaviour and temperature. Fig. 10 shows the delay in heat transfer from heating water to the extrudate in a typical trial. At the beginning of the trial the extrudate temperature is normally higher than the water temperature in the jacket due to the fact that the paste had already been heated up due the friction coming from the afore trial (extrusion and recirculation in order to reach a constant pressure level)—something that has to be done before starting the temperature sweep trial. The heating–cooling water in the jacket comes directly from the thermostat and heats up faster than the profile. The heat transfer to the environment leads to a delayed temperature increase in the profile, but at the end of the trial temperatures above 90 °C could be reached due to high friction in the extruded material.

As explained in Section 2, the extrusion trial started with a straining step, where the paste typically loses 0.1–0.4% of humidity. Subsequently, a measurement of the wet green paste properties was done where another loss of up to 0.3% of humidity occurred.[31] On performing the measurements with the honeycomb die (first the run for a constant extrusion pressure, then the temperature sweep trial), a further water loss could be observed which was dependent on the processing time. A temperature sweep trial at the extruder up to 45 °C led to a water loss of 0.4%, whereas a trial of up to 90 °C led to a water loss of 2.8–4.4%. The described water losses in the paste are leading to higher extrusion pressures, this phenomenon becomes more significant at higher temperatures. However, the water loss will not impact the gelation phenomena of the MC in the paste and only slightly the resulting gelation temperatures. The largest part of water evaporation happens significantly above the gelation temperatures as the heating speed is not the same all over the temperature range; at higher temperatures the heating speed decreases significantly.

In this investigation the MCs listed in Table 1 with different DS (Me) were compared according to their extrusion behaviour. As a reference, two of them (samples 1 and 2) were used in the well known level of the currently marketed methylcelluloses like Methocel[TM] A types (available from Dow Wolff Cellulosics). Their specification is equivalent to a DS (Me) ranging between 1.64 and 1.92. Samples 3–6 are MCs with a DS (Me) between 1.61 and 1.41. All six samples lie in the same range of viscosity (see Table 1).

3.2.1. Dependency of the extrusion pressure on the extrusion temperature

With a changing DS (Me) the six curves show a continuous change in their behaviour. Generally, the curves can be divided into three segments. In the first segment (up to 45 °C), the pressure in most cases develops linear with increasing temperature and shows a negative slope or a temperature independency. At 44 °C all curves cross each other. Above this temperature the behaviour of the curves with a higher DS (Me) differs from the behaviour of the curves with a DS (Me) of 1.54 and below. Whereas the extrusion must be stopped for higher DS (Me) values at a certain temperature due to a large defect formation and paste brittleness, lower DS (Me) samples prove an extrudability in a larger temperature range, the defect formation is less

significant and the paste is much more plastic. The defect formation happens close after the gelation of the MC-chains in the aqueous paste. Curves from MCs with lower DS (Me) show a significant lower pressure increase until a maximum is reached. From the maximum the slope turns downwards to a minimum close to 78–79 °C. In the third curve segment the pressure in all remaining curves raises up sharply. All curves show a large overlap.

3.2.1.1. The three temperature regions. All pressure curves (temperature sweep) were started slightly above room temperature (25–27 °C) and at different extrusion pressure levels. With a decreasing DS (Me) the starting pressure increases whilst the slope of the curve decreases. At a DS (Me) of 1.84 (sample 1) the pressure is temperature independent. We assume that in the case of sample 1 the upcoming gelation of the MC in the paste already has some impact on the pressure evolution significantly below 44 °C.

Surprisingly, all curves cross at an "isobaric extrusion temperature" of 44 °C and a pressure of 34–35 bar. At this temperature all different MC samples lead to the same paste extrusion pressure, independent of their individual specified DS (Me). This could be of importance in plant process control when it comes to running a process under the same and stable conditions.

In the range between 44 °C and 77–79 °C the extrusion pressure increases with the extrusion temperature due to the gelation of the methylcellulose in the aqueous paste. On the molecular level the phenomenon of gelation is based on hydrophobic interactions between hydrophobic methyl groups coming from the same or different cellulose chains. The MC with the highest DS (Me) shows a paste gelation at the lowest extrusion temperature (38.8 °C). Schuetz[25] (binder A[a]) reported curves similar in shape to curves of samples 1 and 2 in Fig. 11. He made an investigation with an alumina paste in a torque-rheometer using a methylcellulose trade product with a typical DS (Me) specification as mentioned above. By reducing the DS (Me) in Fig. 11 the gelation temperature increased (see Table 3). There are different methods of determining the gelation temperature. In this investigation the gelation temperature is defined as the temperature with the lowest extrusion pressure, before the extrusion pressure increases due to the gelation of the MC in the paste. As it is very important for industrial extrusion processes to maintain a stable extrusion pressure over the whole processing time, the gelation temperature defines the maximum operation temperature for stable processing. As can be seen in Table 3, extrusion defects usually appear a few degrees above the gelation temperature. Normally, the defects start with a profile deformation. In the case of auto honeycomb extrusion (see Section 2) this always means a cone formation between the thinner core and

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[a] Today the cellulose ethers mentioned in this study carry different trade names: binder A (Methocel[TM] 20-231): today Methocel[TM] A4M; binder B (Methocel[TM] 20-223): today Methocel[TM] F4M; binder C (Methocel[TM] 20-223): today Methocel[TM] K15M; binder D (Methocel[TM] 20-213): today Methocel[TM] K4M. Binder A is the only methylcellulose from this study. Samples 1 and 2 of our study fall into the specification of the cited binder A. The mentioned binders B–D are hydroxypropyl methylcelluloses.

Table 3
Paste gelation temperature, defect formation and pressure maximum of the six extrusion trials presented in Fig. 12.

|	Gelation temperature (°C) in the paste	Temperature range of defect formation	Pressure maximum in the gelation area (°C)	Remarks
Sample 1	38.8	Above 46 °C	–	No evaluation possible, paste not extrudable at gelation temperature
Sample 2	40.4	Above 46 °C	–	Like sample 1
Sample 3	43.2	Above 55 °C	(Estimated) 57–59	Like sample 1
Sample 4	47.8	56–70 °C	64–65	
Sample 5	50.2	62–70 °C	66	
Sample 6	60.8	68–86 °C: def.	67–68	
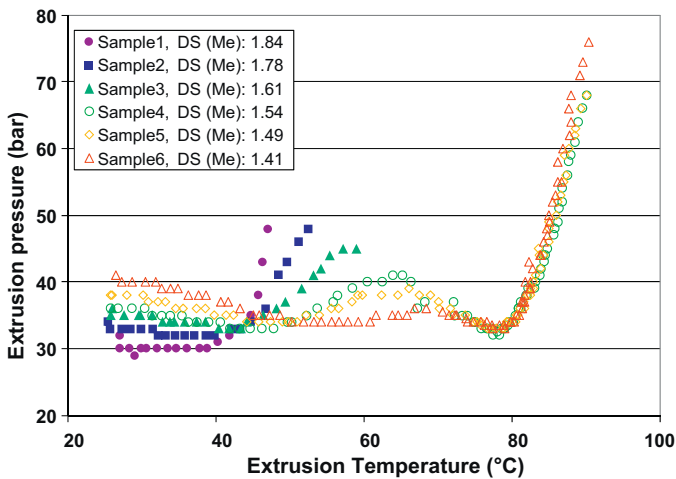
Fig. 11. Extrusion pressure as a function of the extrusion temperature for different methylcelluloses with varying DS (Me), all tested in a cordierite based paste containing the same amount of water.

the thicker shell (outer cover) of the honeycomb profile indicating a weaker cohesion in the paste, at higher temperatures followed by a delaminating profile and larger crack formation. Finally, in cases of higher DS (Me) extrusion becomes

impossible above a certain temperature and no further data could be determined. However, in cases of a lower DS (Me), surprisingly the cohesion in the ceramic paste never significantly decreases and again little defects disappear at higher temperatures.

The three samples with lower DS (Me) show a pressure maximum, than a decreasing extrusion pressure until the minimum is reached at 78–79 °C. With decreasing DS (Me) the temperature of the pressure maximum is shifted to higher temperatures, the pressure maximum itself and the area under the curve decreases with decreasing DS (Me). The peak area under the curve indicates the paste's gel strength which decreases with decreasing DS (Me).

Above 78–79 °C all extrudable compositions show a sharp increase in extrusion pressure. There are two reasons for the pressure growth above 78–79 °C to be discussed: first, due to the higher Brown's motion of the water molecules at higher temperatures, the cellulose ether chains lose their water molecules surrounding. As a result, the MC-chains lose their lubrication effectiveness. Second, as already discussed above, paste drying and a too slow increase of paste temperature in the higher temperature region could lead to artificially increased extrusion pressure data. Due to difficult experimental conditions above 90 °C no further data were determined.
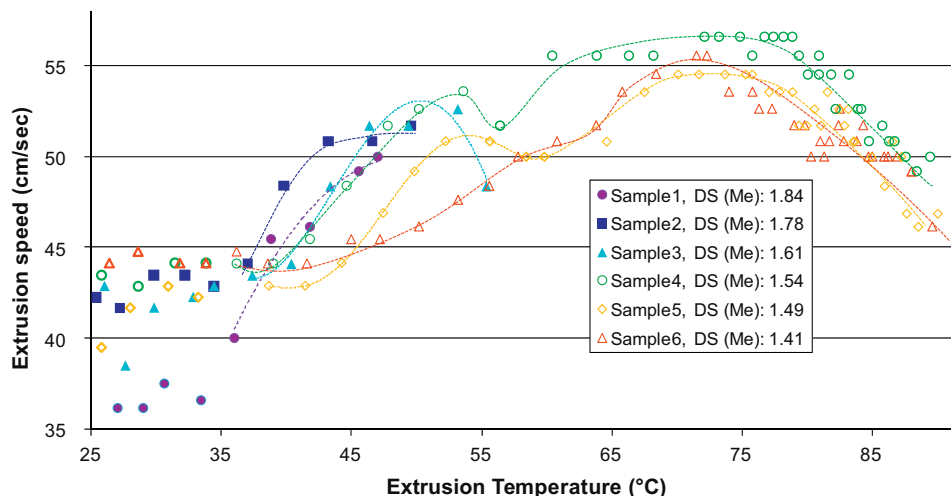

Fig. 12. Extrusion speed as a function of the extrusion temperature for different methylcelluloses with varying DS (Me), all tested in a cordierite based paste containing the same amount of water. The auger screw rotation speed was held constant at 15/min. Below 35 °C no lines were drawn through the data points.

3.2.2. Dependency of the extrusion speed on the extrusion temperature

Increasing the extrusion temperature leads to an increase of discharge speed until reaching a maximum between 70 and 78 °C. Between 52 and 61 °C the extrusion speed decreases significantly (samples 3–5) before growing again. Fig. 12 shows, that the size of this effect is growing with the DS (Me). The temperature range of the transient speed minimum lies at the beginning of the temperature range of defect formation as indicated in Table 3. This leads to the conclusion that the transient speed minimum is caused by the increased paste brittleness and decreased paste lubricity which comes close after the gelation of the paste.

4. Conclusions

Various methylcelluloses with different DS (Me) were analysed concerning their rheological performance in water based model systems and their applied material characteristics in ceramic extrusion systems based on cordierite.

The rheological data in aqueous solution showed an increasing gelation temperature with decreasing DS (Me). Furthermore, the detected gel strength in the high temperature region is decreased with decreasing DS (Me). Both findings can be confirmed in the ceramic paste: the gelation temperature (T_{onset}) increases with decreasing DS (Me) and is indicated by an extrusion pressure increase. The pressure increase as well as the peak area indicating the gel strength is getting smaller with a lower DS (Me).

44 °C was found to be an isobaric extrusion temperature where all curves are crossing at the same pressure. In the temperature range of thermal gelation the paste increases in brittleness and decreases in plasticity as indicated by an extrusion with many defects. MCs with a high DS (Me) lead to a higher paste brittleness when coming close to the gelation temperature which makes extrusion at even higher temperatures impossible. This is caused by the hydrophobic interactions between the Me-groups. A lower DS (Me) offers the possibility to extrude the material even up to significantly higher temperatures where no extrusion with methylcelluloses has been performed before. This also enables increased production rates as a larger heat evolution due to higher friction might not lead to the risk of paste gelation during processing. We assume that extrusion above the gelation temperature is only possible because the gel strength of the MCs with lower DS (Me) near the gelation temperature is significantly lower and the material behaves more plastic than materials plasticised with MCs of a higher DS (Me). Also the extrusion speed at constant auger screw rotation speed is temperature dependent. Before reaching a maximum, most samples show a speed drop close to the gelation temperature.

Authors' contributions

M.K. initiated the rheological measurements in water. R.B. conceived the method of temperature sweep trials in ceramics and designed the paste experiments. All authors analysed the results and contributed to writing the manuscript.

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