The shear dependence of the methylcellulose gelation phenomena in aqueous solution and in ceramic paste

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ABSTRACT

The gelation temperature of methylcellulose (MC) in aqueous solutions as well as in aqueous ceramic paste depends on the applied shear. Rheological investigations in oscillation vs. shear mode show lower gelation temperature at low shear rates as for the corresponding angular frequencies. Above a critical shear rate the gelation temperature is shifted to higher temperatures. The paste extrusion process uses MC as a plasticizer and runs under high shear conditions. When extruding close to the gelation temperature of the MC in the paste, crack formation and other defects can occur. The upwards shift of the gelation temperature with increasing applied shear gives a larger temperature window during the extrusion process. The understanding of the shear influence on the gelation temperature is important to design the optimal process conditions.

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1. Introduction

Cellulose ethers (CE), like methylcellulose (MC), are derived from cellulose, the most widespread polysaccharide in nature. Cellulose forms the primary structural component of plants and is made of repeat units of the anhydroglucose monomer. The cellulose molecule is a 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. These hydroxyl groups form a highly ordered network of hydrogen bonds. Cellulose itself is insoluble in water and in most organic solvents.

The insolubility in water is often referred to strong intermolecular hydrogen bonding between cellulose molecules. Medronho, Romano, Miguel, Stigsson, and Lindman (2012) revisited some fundamental polymer physicochemical aspects of the polymer and postulated, cellulose is significantly amphiphilic and hydrophobic interactions play also an important role with regard to the solubility. These findings are currently under debate especially while considering previous publications (Glasser et al., 2012).

Methylcellulose is one of the most important commercial cellulose ethers that has been used in food (Floury, Desrumaux, Axelos, & Legrand, 2003; Kandasamy, Varadharaju, Kalemullah, & Maladhi, 2012; Knarr, Adden, Anderson, & Hübner-Keese, 2012), pharmaceutical (Ford & Mitchell, 1995; Ford, 1999; Rogers & Wallick, 2012) as well as non-regulated applications like ceramic extrusion (Schuetz, 1986), fuel cells (Church, Sanders, Speyer, & Cochran, 2007; Pusz, Smirnova, Mohammadi, & Sammes, 2007), nano particle synthesis (Bhui & Misra, 2012; Bhui, Pyne, Sarkar, Bar, Sahoo, & Misra, 2011) and construction applications (Akthar & Evans, 2010; Ou, Ma, & Jian, 2012). One of the most important features is the thermo-reversible gelation performance strongly influenced by the degree of substitution (Bayer & Knarr, 2012).

From all classes of cellulose ether that contain methyl groups MC has the lowest gelation temperature. This can be a hindrance in some applications e.g. reduced water retention in dry mortars when applied at higher temperatures or extruded ceramic pastes with a high concentration of methylcellulose in the paste (Bayer & Lang, 2012a), however it can be an advantage in some like food applications (hindrance of boil-out of fruit fillings in baked and hot-served pastry).

The synthesis of MC was already described by Lilienfeld (1912a,b,c) and independently by Dreyfus (1912), the cold water solubility, the coagulation and precipitation by heating, was also

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described by Lilienfeld. In 1913, Denham and Woodhouse (1913) published a similar process to achieve methylcellulose derivatives. First systematic studies of the "inverse" sol–gel transformation of MC with increasing temperatures were conducted by Heymann (1935). The turbidity during the phase transition at that time was explained by a dehydration of the methylcellulose chains at high temperatures. Since then the thermo-reversible phase transition of MC in aqueous solutions has been extensively investigated by various techniques like Sarkar (1979) with rheological investigations, Desbrieres, Hirrien, and Rinaudo (1998) with calorimetric experiments on heterogeneous (commercial) vs. homogenous lab synthesized MC, Takahashi, Shimazaki, and Yamamoto (2001) via micro-differential scanning calorimetry & small-angle X-ray scattering. Wang and Li (2005) studied the impact of MC with different molar mass with DSC and rheology as well as the influence of a magnetic field, which showed slightly lower gelation temperatures (Wang, Li, Chen, & Yang, 2007). Funami et al. (2007) investigated the thermal aggregation of methylcellulose by static light scattering technique to trace the transition of its molecular size and shape upon heating, Nishida and Takahashi (2008) with polarized optical microscope (POM) and wide angle X-ray scattering (WAXS) and Takeshita, Saito, Miya, Takenaka, and Shiomi (2010) with small-angle X-ray scattering (SAXS) and light scattering (LS) techniques and applied speckle analysis on the LS profiles and found the observed gelation and phase separation are strongly coupled to each other.

Haque and Morris (1993) investigated the presence of crystalline structures in solutions at low temperatures which dissociated during heating and allowed the development of a different structure at higher temperatures.

According to Sarkar (1995), water at relatively low temperatures forms an ice-like structure around the hydrophobic groups, such as the methyl substituents. When the solution is heated, the water structure breaks down with an increase of entropy, thus allowing the hydrophobic groups to interact and cause gelation.

Kobayashi, Huang, and Lodge (1999) found out evidence of the weak supermolecular association or clustering at 20 °C of semi dilute methylcellulose solutions. This clustering was significantly enhanced as the temperature increased based on hydrophobic association. At higher temperatures, strong local segregation of polymer-rich and polymer-poor regions occurred.

Hirrien, Chevillard, Desbrières, Axelos, and Rinaudo (1998) and Desbrières, Hirrien, and Ross-Murphy (2000) described heterogeneities in solutions which become more and more important with superimposed temperatures. It has been further suggested that the gelation is mainly driven by hydrophobic interactions between highly substituted zones and the presence of trisubstituted units that are essential for gelation.

By X-ray diffraction patterns of MC gels Kato, Yokoyama, and Takahashi (1978) proved the network junction points of gels are crystalline and consist of trimethyl glucose units.

Li et al. (2001, 2002), Li (2002) 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 the 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.

Previous studies have proved the effect of decreasing gelation temperatures with increasing MC concentrations (Kobayashi et al., 1999; Sarkar, 1979). Additionally, co-ingredients like salts according to the Hofmeister series (Hofmeister, 1888) or sugar and sugar alcohols in aqueous solutions decrease the gelation temperature, whereas alcohols as co-ingredients in aqueous solutions lead to higher gelation temperatures (Bain et al., 2012; Heymann, 1935;

Iso and Yamamoto, 1970; Kundu & Kundu, 2001; Levy & Schwarz, 1958; Xu, Li, Zheng, Lam, & Hu, 2004).

One of the drawbacks of the previous investigations has been the absence of an applied shear during the gelation process which is often present in industrial application processes. Therefore, it has been the aim of this study to investigate whether there is an influence of an applied shear on the gelation properties of the MC, on the one hand dissolved in an aqueous solution and on the other hand in a ceramic paste extrusion formulation.

Aqueous ceramic paste extrusion with cellulose ethers like MC, is the main method to produce ceramic profiles for automotive and industrial applications like filters, catalysts, insulation tubes and others. It is well known that the gelation temperature of the methylcellulose in the paste is dependent on the same parameters as in solution (Schuetz, 1986; Bayer & Knarr, 2012). To date however, prediction of the paste gelation temperature without the effect of an applied shear remains imprecise.

2. Experimental part

Aqueous MC solutions were prepared by adding the MC (Methocel™ A4M, Dow Chemical Company) to water, stirring the solutions with an overhead lab stirrer at 1000 rpm for one hour while cooling the solutions with an ice/water mixture. These solutions were stored in a refrigerator at 5 °C overnight.

Rheological investigations were performed with an Anton Paar Physica MCR 501 rheometer, with a cup and bob geometry (CC-27). Oscillatory measurements were made at 20 °C for $\omega = 100–0.1$ rad s^{-1} with 5 data points each decade. The strain (deformation) γ was been held constant at 2%, which is within the linear visco-elastic region.

Steady shear flow experiments were performed at 20 °C for $\dot{\gamma} = 0.1 - 1000$ s^{-1} with 5 data points each decade. Only the MC solution at a concentration of 3% was investigated with a cone and plate geometry (CP50-1°).

Temperature sweep investigations were performed with a heating rate of 1 °C min^{-1} at the given angular frequencies of 0.1, 1, 10 & 100 rad s^{-1} and shear rates of 0.1, 1, 10 & 100 s^{-1} with 4 data points each minute.

Pastes were prepared in a 30 ml kneading cell W30 of a Brabender Plasti-Corder PL 2000 torque rheometer with metallic cover head and were cooled down to 4 °C. A homogeneous mixture of 40 g of cordierite precursor material (Imerys cordierite CP820M) and MC (Methocel™ A4M, Dow Chemical) was introduced into the cell and mixed with water dosed in portions with a syringe. Further homogenization was done at 20 rpm until a constant torque was reached. After a break of 5 min, the temperature ramp was started at a defined shear rate (counter rotating kneading blades rotation speed) and a heating rate of 3 °C min^{-1} (programmed at the thermostat).

For the extrusion trials the paste preparation was started by mixing the cordierite precursor material and MC in the dry state, spraying in water, and kneading at room temperature. For details see Bayer and Knarr (2012). After kneading, extrusion through a water-cooled single-screw extruder with inner screw diameter of 80 mm took place using a honeycomb profile with a cell density of 47 cells cm^{-2} (300 cells per square inch) following the temperature sweep method described in Bayer and Knarr (2012). During all trials, the feeder screw speed was kept slightly lower than the auger screw speed. The temperature sweep measurement was started by heating up the water in the extruder jacket with a thermostat, programmed to an upper limit of 97 °C (heating rate 3 °C min^{-1}). The material was extruded through the die, discharged onto a conveyor belt and recycled into the feeder screw until the temperature reached 90 °C or the extruded cordierite paste lost its plasticity,