

Tetramethylguanidine-based gels and colloids of cellulose



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ABSTRACT

Novel and stable gels of cellulose were produced. These gels are prepared at room temperature by combination of cellulose and tetramethylguanidine (TMG) in different ratios (1:1, 1:2, 1:3 in equivalents of alcohol groups of cellulose per number of molecules of TMG). Detailed NMR, SEM, rheological and XRD studies of these gels were carried out. The concentration of cellulose in the gel, temperature, frequency of oscillation and shear rate were used as variables in order to understand the fundamentals and optimize operational conditions, considering their possible use as matrices for CO₂ capture. Cellulose recovery from a specific gel was performed using ethanol as precipitating agent, leading to a lower crystallinity, which permits to consider this polymer in further studies associated to physical/chemical modification of cellulose.

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1. Introduction

Cellulose, the most abundant organic compound on earth obtained from renewable resources, has enormous applications in the pharmaceutical and fine chemical industries, in the development of new materials and as an alternative energy resource. Nevertheless, the processing of this polysaccharide is a challenge due to the strong intra- and intermolecular hydrogen-bonds between the different –OH groups present in the polymeric chain, which precludes an effective solubilisation in most solvents.

We found in our labs, initially by serendipity, that cellulose forms homogeneous gels using a single component, commercially available and cheap tetramethylguanidine (TMG), an organic superbase.

In fact, other authors tested systems containing organic superbases in the context of cellulose solubilization. As examples (King, Asikkala, Mutikainen, Järvi & Kilpeläinen, 2011) tested diverse protic ionic liquids, with basic anions, in order to obtain fast dissolution of moderated quantities of cellulose at high temperatures and, with

a judicious choice of anion and temperature, control the degree of polymerization of cellulose as well as the recyclability of the system. Additionally, the authors highlight the importance of basic moieties able to disrupt, by hydrogen bond, the strong intra- and inter-molecular interactions among cellulose polymeric chains. A different system (Wang, Xue, Yan, Li & Mu, 2016) consists on the use of an organic superbase in DMSO to solubilize cellulose under an atmosphere of CO₂. The concept follows the principle of reversible ionic liquid/molten salt (with CO₂ as element of reversibility) previously applied in our labs. In concrete, we have reported the use of organic superbases, such as TMG and DBU, in combination with amines, aminoacids, mono- and oligosaccharides, as reversible CO₂ capture systems (Carrera, Jordão, Branco & Nunes da Ponte, 2015a,b; Carrera, Nunes da Ponte & Branco, 2012; Carrera, Jordão, Santos, Nunes da Ponte & Branco, 2015).

In this context, and in order to capitalize the very high values of cellulose uptake by TMG, we carried out a detailed spectroscopic, rheological, SEM and XRD evaluation. Such studies are essential to understand the intermolecular interactions ruling the Cellulose/TMG system, as well as to find optimized operational conditions to use these mixtures as films and membranes for CO₂ capture. Other possible applications reported in the literature consist in novel material preparation, (Frey, Chan & Carranco, 2005) or chemical, (Zhou, Zhang, Deng & Wu, 2004) and physical (Gavillon

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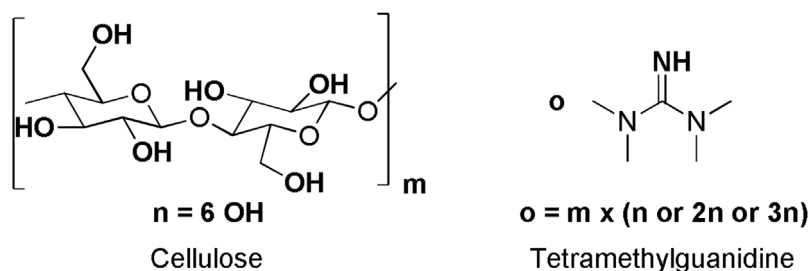


Fig. 1. Components of the prepared gels: cellulose and tetramethylguanidine.

& Budtova, 2007; Xia, Patchan, Maranchi & Trexler, 2015) modification of this polymer.

From the diverse cellulose/solvent systems, the concept of gel of cellulose is thoroughly studied, mostly in aqueous-based systems and different combinations of additives. As an example, it is important to highlight the work (Roy, Budtova & Navard, 2003) focused on the rheological properties and gelation of aqueous/NaOH/cellulose solutions, where the temperature effect on aggregation of cellulose chains, separation from solvent matrix and irreversibility of the gels were reported. Those found contrast with methylcellulose hydrogel-based properties, (Li et al., 2001) with intermediate degree of substitution of the hydroxyl groups by methoxides, where no additive is required for solubilisation in water and reversibility of gelification. Additional studies were carried out using water/NaOH as solvent, with inclusion of additives such as thiourea (Ruan, Lue & Zhang 2008) and urea, (Cai & Zhang 2006) presenting similarly an irreversible behaviour on gelification with variation of temperature. The inverse relation between concentration of cellulose and temperature of gelification is stated in these studies to be a strong indication that, at higher concentrations of this polymer, lower temperatures are required to promote disruption of hydrogen bond-based interactions between the solvent system and cellulose, and the consequent entanglement between the different polymer chains, leading to aggregation and formation of a gel.

Different kinds of rheological measures on cellulose-based gels can give valuable structural insights, such as G' (storage modulus), which represents the elastic behavior of the material, as a measure of the deformation energy stored during the shear process, and G'' (loss modulus), the viscous component of the material, a measure of the energy used to flow, and therefore lost, during the shear process. (Angioloni & Collar, 2009) Both parameters are measured as functions of stress, frequency and temperature, stimuli that promote or disrupt phase separation between solvent matrix and cellulose chains as well as aggregation between polymer chains. Another relevant parameter is the flow behaviour in steady shear tests, (Burchard, 2001; Lue & Zhang, 2009; Zhang, Ding, Huang, Chen & Yang, 2014) (viscosity η) as a function of temperature and shear rate. A more complete picture of the structural organization of these gels, responsible for a specific behavior, can be given by spectroscopic characterization, in order to aid in the interpretation of results, it is important to highlight the work of (Vitorino et al., 2014), where the X-ray structure of tetramethylguanidinium nitrate and the hydrogen bond-based interactions between the different motifs are reported. The preparation conditions of the mixtures are another important parameter, where period and rate of stirring are essential to obtain an effective mixing between the intervening components. (Qin, Lu & Zhang, 2012) These studies support some of the experimental results hereby presented. The simplicity of the preparation of these gels, the low associated cost and the potential applications are characteristics that convert these gels in systems worth to investigate from a fundamental point of view.

2. Materials and methods

2.1. Materials

1,1,3,3 Tetramethylguanidine (TMG) was supplied from Sigma-Aldrich (99%) and water was removed using molecular sieves. Microcrystalline cellulose was purchased from Alfa-Aesar (Degree of polymerization <350) and Ethanol (Carlo Erba, p.a.).

2.2. Methods

2.2.1. Preparation of gels

The gels were prepared by adding 3 g of TMG to the proper amount of cellulose, 0.465 g, 0.698 g, and 1.395 g, corresponding to 1:3, 1:2 and 1:1 Cellulose:TMG ratios in equivalents of alcohol groups per number of molecules of TMG, respectively, and continuously stirring the mixtures for approximately 48 h at the rotational speed of 750 rpm. After completion of the mixing period, the samples were stored in a freezer.

2.2.2. Thermal ^1H NMR spectra

The prepared gels were characterized, from 25 to 100 °C, by thermal ^1H NMR spectra (in a capillary inside an NMR tube containing d_6 -DMSO as the reference solvent), recorded on a Bruker AMX400 spectrometer. Chemical shifts are reported downfield in parts per million from a tetramethylsilane reference.

2.2.3. Rheological characterization

Small amplitude oscillatory system (SAOS) measurements of storage (G') and loss (G'') moduli were performed in a controlled-stress rheometer (Haake, Mars III Germany), using a serrated parallel plate geometry (PP20 Ti – 20 mm diameter) with 0.3 mm of gap. Temperature was controlled by an EHEIM circulating water bath (Germany) coupled with a Peltier system. Thermal study was carried out on three consecutive steps: heating (5–90 °C) in 2700 s, cooling (90–5 °C) in the same period of time and maturation (5 °C) during 1800s. Stresses of 100, 10 and 0.1 Pa, under the linear viscoelastic region, were considered after carrying out the respective stress sweeps from the highest to the lowest concentration of cellulose. The oscillation frequency considered was 1 Hz in all the situations.

Another study was carried out using oscillation frequency as the variable (0.001–100 Hz) in five steps at 5 °C, considering the same stress values used in the thermal studies.

Moreover, two different steady shear flow studies were performed. The first considering shear rate as a variable ($1 \times 10^{-8} \text{ s}^{-1}$ – 500 s^{-1}) in 660 s (20 steps) at 20 °C with a serrated parallel plate geometry PP20 Ti (20 mm diameter) with 0.3 mm of gap. In the second study the temperature was considered as the variable: heating (5 °C–90 °C) in 600 s (10 steps), considering a constant shear rate of 1 s^{-1} using the same geometry and gap.

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