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Dual guar/ionic liquid gels and biohybrid material thereof: Rheological investigation

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ABSTRACT

Polysaccharide-based ion gels were prepared by mixing biosourced guar gums with imidazolium ionic liquid (IL) molecules that act as crosslinking agents. The in-depth investigation of the rheological properties of the guar/IL solutions emphasized that the shear viscoelastic properties can be finely tuned by IL chemical structure, concentration and molecular weight of guar chains as well as by temperature changes. Under suited conditions, highly elastic physical ion gels were formed as a result of multiple guar/IL, guar/guar and IL/IL interactions. Such synergistic associations were usefully exploited to elaborate films dually composed of guar chains and entrapped IL molecules. Their thermomechanical properties, which revealed a solid-state behavior, were closely controlled by the structural parameters of the constituents. This straightforward approach, which requires no chemical derivatization step, provides a facile way to design physical gels with a large applicative potential.

1. Introduction

The rarefaction of Earth's fossil fuel reserves in conjunction with the unique combination properties of natural polymers in terms of hydrophilicity, biodegradability, biocompatibility, renewable and sustainable character, have encouraged a plethora of research groups to develop polysaccharide-based gels, which are suitable for a wide range of applications (Gandini, 2008; Tizzotti, Charlot, Fleury, Stenzel, & Bernard, 2010a; Tizzotti et al., 2010b). Gels can be chemically or physically bounded (Hennink & Van Nostrum, 2002). Except for dynamical chemical reactions, covalent junctions in chemically crosslinked networks are difficult to be remodeled and tuned. Such adverse effects can be circumvented by the use of physical networks for which junctions arise from non-covalent interactions (Hennink & Van Nostrum, 2002; Rinaudo, 2006). Different kind of interactions were exploited such as hydrogen bonds (Braccini, Rodriguez-Carvajal, & Perez, 2005; Goycoolea, Milas, & Rinaudo, 2001; Masakuni, 2009), stereocomplexation (De Jong et al., 2000), ionic (Chung et al., 2002; Lee, Park, & Ha, 1997) or hydrophobic interactions (St. Dennis et al., 2011; Tizzotti, Charlot, et al., 2010; Tizzotti, Creuzet, et al., 2010), and host-guest molecular recognition (Charlot & Auzély-Velty, 2007; Charlot, Auzély-Velty, & Rinaudo, 2003). In most cases, a chemical modification of the polysaccharide was required to introduce along the chain the right functionalities able to develop the specific non-covalent interactions. Therefore, the formation of physical gels simply based on polysaccharide/solvent mixture according to a non-degrading approach is highly desirable. In view of generating high-performance bio-based materials, guar gum is a relevant building-block due to its availability, hydrophilicity and the possibility to access to high molecular weights. Guar is a neutral biopolymer extracted from the seeds of the leguminous shrub *Cyamopsis tetragonolobus*. This galactomannan is constituted of a β-1.4 mannose backbone bearing α-1.6 galactose moieties which are randomly distributed in C-6 position. The mannose/galactose (M/G) ratio of guar is generally comprised between 1.3 and 1.8 (Cheng, Brown, & Prud'homme, 2002). It is widely employed as a co-gelling, thickener, stabilizer agent in the food industry (Whistler & BeMiller, 1993) and for applications in the field of paper, textile, petroleum (Cheng & Prud'homme, 2000; Prud'homme, Constien, & Knoll, 1989) personal care and biomaterials (Coviello, Alhaique, Dorigo, Matricardi, & Grassi, 2007; Cunha, Castro, Rocha, & Feitosa, 2008; Mercuri et al., 2008; Tayal, Pai, & Khan, 1999). However, despite its inherent advantages, hydrogen bonds between hydroxyl groups limit its dissolution in common solvents and water. Recently, we have shown that imidazolium ionic liquids (IL) efficiently solubilize guar gums of

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high molecular weight without jeopardizing the chain integrity (Lacroix, Sultan, Fleury, & Charlot, 2012). Ionic liquids, defined as organic salts at low melting temperature, present a lot of assets such as negligible vapor pressure, nonflammability, high thermal and chemical stability (dependently of the nature of the anion) (Huddleston et al., 2001) as well as exceptional ionic conductivity (Erdmenger, Guerrero-Sanchez, Vitz, Hoogenboom, & Shubert, 2010; Wilkes, 2002). Besides, their particular potential to behave as functional structuring additives enabled the development of ion gels. The most widely studied polymer for the preparation of such gels is poly(vinylidene fluoride-*co*-hexafluoropropylene) and a large number of works reported on mixtures with various imidazolium salts (Carlin & Fuller, 1997; Jansen, Friess, Clarizia, Schauer, & Izak, 2011; Yeon, Kim, Choi, Cha, & Lee, 2005). Other homopolymers as poly(vinyl)alcohol (Lewandowski & Swiderska, 2004) or copolymers such as poly(styrene-*b*-ethylene oxide-*b*-styrene) (Zhang, Lee, Sun, Frisbie, & Lodge, 2011), poly(styrene-*b*-methylmethacrylate-*b*-styrene) (Zhang, Lee, Frisbie, & Lodge, 2011) have also been used (Lu, Yan, & Texter, 2009). The applications targeted catalytic membranes or electrochemical actuators. Regarding the use of natural polymers, the team of Kadokawa was particularly interested in combining polysaccharides (Izawa & Kadokawa, 2010; Kadokawa, Murakami, & Kaneko, 2008; Kadokawa, Murakami, Takegawa, & Kaneko, 2009; Prasad, Kaneko, & Kadokawa, 2009a; Prasad et al., 2009b; Takegawa, Murakami, Kaneko, & Kadokawa, 2010) with ionic liquids, including guar gum (Mine, Prasad, Izawa, Sonoda, & Kadokawa, 2010; Prasad, Izawa, Kaneko, & Kadokawa, 2009). In the latter work, the authors submitted guar/1-butyl-3-methylimidazolium chloride mixtures to heating-cooling process followed by a compression manipulation by using a hot-pressing equipment. The ionic liquid acted as an aid-processing and was then totally extracted to obtain guar materials.

However, in order to combine the attributes of natural polymers with the inherent properties of IL molecules in particular their high conductivity, gels dually composed of both guar chains and IL appear as suitable candidates. The development of high performance guar/IL materials with targeted functional properties requires a detailed understanding of the rheological behavior through the study of the influence of various parameters, which was not reported so far. In this frame and in quest for "biohybrid" materials through a simple approach, we present a comprehensive rheological investigation of guar gum/imidazolium salts solutions through dynamic shear and creep measurements based on the impact of the IL chemical structure, guar molecular weight, temperature, time and guar chain concentration. Moreover, by following a simple experimental approach, the resulting guar/IL gels were processed under the form of self-supported films, which were characterized in terms of thermomechanical properties.

2. Experimental

2.1. Materials

Three guar gums from seeds of *Cyamopsis tetragonolobus* with three different weight average molecular weight ($\overline{M_w} = 126$ kDa, $I_p = 1.92$; $\overline{M_w} = 299$ kDa, $I_p = 1.82$; $\overline{M_w} = 566$ kDa, $I_p = 1.91$) were provided by Rhodia. The mannose/galactose (M/G) ratio of these samples was found to be equal to 1.33 as determined by ^{1}H NMR spectroscopy. Polysaccharides were dried before use (80 °C under vacuum overnight). 1-allyl-3-methylimidazolium (AMIMCl) (>97%) mp 50 °C, 1-butyl-3-methylimidazolium chloride (BMIMCl) (>99%) mp 75 °C were purchased from Aldrich and 1-ethyl-3-methylimidazolium methylphosphonate (EMIMMP) (>98%) mp <20 °C was purchased from Solvionic. All ionic liquids were dried (80 °C under vacuum overnight) before use.

2.2. Preparation of guar gum/IL systems

2.2.1. Guar/IL solutions or gels

As a typical procedure for the preparation of a guar/IL solution, an appropriate weight amount of dried polysaccharide, as a powder, was progressively added in dried IL, without addition of co-solvent, under continuous stirring with a magnetic stirrer, during 12 h under inert atmosphere (nitrogen or argon). Solubilisations in AMIMCl, EMIMMP were conducted at 50 °C and the one in BMIMCl was performed at 80 °C. Temperatures of 50 and 80 °C allowed for decreasing the viscosity and for ensuring an efficient stirring. Concentrations in weight percent (wt.%) were varied, dependently on the performed analysis. The resulting solutions were macroscopically transparent.

2.2.2. Guar/IL gelled films

The films were prepared by a casting of a guar/IL gel between two glass sides, which were manually pressed. The assembly was cooled down at 4 °C for three days and was recovered as a free-standing film (with a thickness around 2.5 mm, determined by a mechanical sensor). It was then subjected to washings with ethanol by an exposure during around 30 s to jets provided by an ethanol plastic wash bottle. This procedure allows for expelling IL molecules located at the surface of the film, which are not strongly embedded in the network. The films were further dried at 60 °C overnight.

The guar gum concentration inside the films was ascertained by taking into account the weight of IL leached out in ethanol during the washing (19–24 wt.%). This value was determined by the measurement of the weight difference.

Given the hydrophilic nature of both guar gum and imidazolium IL molecules, the films are hygroscopic and the maximum amount of adsorbed water after storage at room temperature under air for several months was estimated at around 14 wt.% by thermogravimetric measurements (Fig. S1).

2.3. Instrumentation and methods

2.3.1. Viscoelastic measurements under shear mode

Dynamic viscoelastic properties of guar/IL solutions were carried out by using a AR1000 controlled stress rheometer (TA Instruments Inc., UK) with an aluminum cone/plate geometry (diameter 60 mm, angle 2°, gap 2 μm). All dynamic rheological data were checked as a function of strain amplitude to ensure that the measurements were performed in the linear domain. It results that the applied strain during the dynamical measurements was settled at 1% for guar/IL solutions (and gels) and at 5% for pure BMIMCl. The temperature was precisely controlled by a Peltier system. A particular care was taken in order to prevent the moisture uptake during measurements by using a homemade cover. Creep and recovery measurements were also performed with a AR1000 rheometer by using the same geometry. Creep tests were recorded at settled stress amplitude (1 Pa) for 15 min. The recovery properties were monitored after removal of stress.

2.3.2. Thermomechanical properties measurements under tensile mode

Tensile tests at a frequency of 1 Hz of guar/IL films were performed on a Triton Technology apparatus. Specimens with an effective length of 10 mm (distance between the clamps), a width of 5 mm were analyzed at a displacement of 0.001 mm to remain in the linear regime.

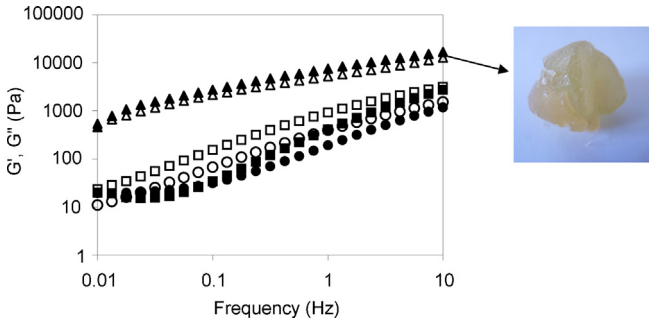


Fig. 1. Frequency-dependence of G' (filled symbols) and G'' (open symbols) moduli of guar (126 kDa, 15 wt.%)/BMIMCl (△), guar (126 kDa, 15 wt.%)/EMIMMP (□) and guar (126 kDa, 15 wt.%)/AMIMCl (○) solutions at 25 °C.

2.3.3. Thermogravimetric analysis

TGA measurements were performed under nitrogen using a TA Instruments TGA Q500 apparatus at a heating rate of 10 °C/min.

3. Results and discussion

3.1. Shear viscoelastic properties of guar gum/imidazolium ionic liquid solutions

As previously demonstrated in our recent article (Lacroix et al., 2012), imidazolium-based ionic liquids act as efficient and mild solvents of guar gums without any alteration of the chain integrity. Whereas significant efforts have been devoted to rheological properties of cellulose/IL solutions spanning from dilute to concentrated regime (Gericke, Schlufter, Liebert, Heinze, & Budtova, 2009; Haward, Sharma, Butts, McKinley, & Rahatekar, 2012; Horinaka, Yasuda, & Takigawa, 2011; Kuang, Zhao, Niu, Zhang, & Wang, 2008; Lv et al., 2012; Sammons, Collier, Rials, & Petrovan, 2008; Song et al., 2011), only one work reported on shear viscoelastic properties of concentrated solutions of galactomannan in BMIMCl (Horinaka, Yasuda, & Takigawa, 2012). In this contribution, Horinaka et al. were interested in analyzing the rheological behavior of guar (only by using one molecular weight)/BMIMCl in order to determine the molecular weight between entanglements in view of accessing to the spacing between entanglements in the molten state. From their interesting works, the authors concluded that galactomannan chains adopt a random coil conformation in BMIMCl but the influence of experimental and structural parameters on the viscoelastic properties was not investigated.

3.2. Influence of the ionic liquid type

Fig. 1 reveals the influence of the imidazolium chemical structure on solutions based on guar 126 kDa solubilized at 15 weight percent (wt.%) on the evolution of the storage (G') and loss (G'') moduli as a function of the frequency. The selected ionic liquids: 1-ethyl-3-methylimidazolium methylphosphonate (EMIMMP), 1-allyl-3-methylimidazolium chloride (AMIMCl) and 1-butyl-3-methylimidazolium chloride (BMIMCl) differ in the nature and the length of the alkyl side chain of the cation as well as in the type of the counterion. All are polar, as quantified by their high π^* Kamlet-Taft parameter around 1.1 (Jessop, Jessop, Fu, & Phan, 2012).

From Fig. 1, it can be seen that the viscoelastic behavior is closely dependent on the IL structure. For guar/EMIMMP and guar/AMIMCl solutions, G'' modulus is higher than G' on the whole frequency range, which is typical of a fluid behavior. We can note that for both guar/EMIMMP and guar/AMIMCl systems, G' is initially almost independent of frequency and a plateau is observed, subsequently followed by a typical G' increase, as already reported for microcrystalline cellulose solubilized in 1-ethyl-3-methylimidazolium acetate (Song, Niu, Wang, & Zhang, 2011) and silk fibroin in AMIMCl (Wang, Yang, Chen, & Shao, 2012). This plateau may arise from the presence of a weak network mainly constituted of ionic liquid molecules (AMIMCl or EMIMMP), which do not interact (or less) with guar chains. Unfortunately, due to the rheometer sensitivity, it was impossible to measure the viscoelastic properties of pure AMIMCl and EMIMMP at such low frequency range (from 0.01 to 0.1 Hz). Conversely, guar gum in BMIMCl does not exhibit any plateau at low frequencies and displays higher moduli with a G' modulus superior to G'' on the entire frequency range reflecting a more solid-like behavior, contrary to pure BMIMCl (Fig. S3.). In all cases, contrary to chemical networks, viscoelastic properties are affected by the time scale due to (i) the reversible breakage of the non covalent interactions and (ii) the guar chain reptation. Literature dealing with cellulose solubilization in ionic liquid mentioned that the solvation process is essentially governed by hydrogen bonds developed between carbohydrate backbone and IL (Pinkert, Marsh, Pag, & Staiger, 2009). More precisely, studies by NMR spectroscopy and molecular dynamics revealed that cellulose dissolution involves the formation of hydrogen bonds between the imidazolium salt anion and the hydroxyl group protons of the sugar (Feng & Chen, 2008; Remsing, Swatloski, Rogers, & Moyna, 2006; Remsing et al., 2008; Youngs, Hardacre, & Holbrey, 2007). The IL molecules used herein all possess a strong H-bond accepting ability, as reflected by the high β Kamlet-Taft parameters (0.87 for BMIMCl and 1 for EMIMMP) (Jessop et al., 2012). Moreover, in our previous work, we have shown by Infrared spectroscopy that hydrogen bonds are formed in guar/IL solutions (Fig. S2). Thus, it is reasonable to assume that, as for cellulose, H-bonds are developed between the conteranion (chloride or methylphosphonate) of the IL and hydroxyl groups of guar gums. Moreover, we cannot exclude the possibility for the acidic proton at the C2 position of the imidazolium ring to develop interactions with oxygen of guar backbone. Ionic liquid has a dual functionality since it behaves as solvent and junction promoter that ties guar chains, leading to a kind of percolating network structure similar to physical gels.

The enhanced viscoelasticity for the guar/BMIMCl combination may arise from (i) more numerous and stronger physical interactions developed between BMIMCl and guar chains and from (ii) the properties inherent to BMIMCl. Indeed, as reflected by its higher melting temperature and viscosity BMIMCl is more organized than AMIMCl and EMIMMP. Not only electrostatic interactions and hydrogen bonds are developed in BMIMCl (Heinze et al., 2008; Wang, Li, & Han, 2006) but additional attractive Van der Waal between butyl chains tethered to the cation might contribute to promote the rheological properties of the corresponding guar/IL system (Huddleston et al., 2001). Thus, the interesting rheological properties originate from the development of physical interactions, such as IL/IL, IL/guar and guar/guar interactions as well as guar chains entanglements (present at the used polymer chain concentration), which all contribute to the final elasticity. We can note that the crystalline character of BMIMCl disappears when it is mixed with guar gum (see DSC thermogram in Fig. S4). Indeed, BMIMCl has been shown to exhibit an efficient solubilization ability of guar gums, which means that in guar/BMIMCl solutions, BMIMCl/BMIMCl interactions are unfavored and partially dissociated, while physical interactions between BMIMCl and guar are predominant (Lacroix et al., 2012). The phase diagram of pure BMIMCl is completely shifted in binary system. Consequently, guar/BMIMCl solutions present neither demixion nor solidifying (due to a possible BMIMCl recristallisation) with time (picture in Fig. 1). The rheological properties were shown to be stable, as demonstrated by shear measurements collected one day after the solubilization (Fig. S5).

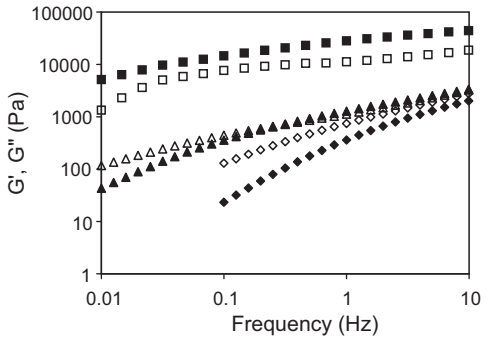


Fig. 2. Frequency-dependence of G' (filled symbols) and G'' (open symbols) moduli of a guar (5 wt.%)/BMIMCl solution, with a guar $\overline{M_w}$ equals to 566 kDa (□), 300 kDa (△) and 126 kDa (◇) at 25 °C.

3.3. Influence of the guar molecular weight

The influence of the chain molecular weight ($\overline{M_w}$) was evaluated on the viscoelastic properties of a guar (5 wt.%)/BMIMCl solution (Fig. 2).

It appears that the $\overline{M_w}$ value strongly affects the rheological behavior since while viscoelastic fluid behaviors are obtained for molecular weights of 126 and 300 kDa, a gel-like state results from the highest guar $\overline{M_w}$. For a mass of 566 kDa, no crossover between G' and G'' moduli is observed on the frequency range and G' modulus exhibits a plateau at high frequency, which indicates that guar chains have difficulties to overcome the energy barrier to diffuse inside the network. This restriction of mobility is mainly caused by the guar chain entanglements in addition to the physical junctions between guar chains mediated by IL molecules, which both are widely enhanced by a high guar molecular weight. It is worth mentioning that the maximum G' value reaches a value of 45 000 Pa for a low chain concentration (5 wt.%) which reflects a strongly elastic physical gel compared to some polysaccharide-based networks ($G' < 300$ Pa) reported in the literature (De Jong et al., 2000; Goycoolea et al., 2001; Rinaudo, 2006).

3.4. Influence of the guar chain concentration

Rheological properties are expected to be impacted by the chain concentration, as observed for more conventional polysaccharide solutions. Guar (126 kDa)/BMIMCl solutions were investigated at guar gum concentrations (C_{guar}) ranging from 5 to 25 wt.% (Fig. 3).

Up to a chain concentration of 7 wt.%, G'' is much greater than G' within the entire detected frequency range indicating that the mixtures exhibit a viscoelastic fluid-like state with a viscously dominated behavior. At a concentration of 9 wt.%, G' and G'' moduli are of similar magnitudes and follow relatively close frequency dependence (G' and $G'' \sim f^{0.51}$), which is typical of a transition between liquid-like and solid-like behavior. When the guar concentration increases, the response exhibits an elastic dominant behavior and the terminal cross-over point, which is related to the intra and inter-forces and to the longest relaxation time τ_d (Mours & Winter, 1996; Soltero, Puig, & Manero, 1996) is shifted to lower frequencies. This dynamics slowing down, reflected by a τ_d increase, is constricted by the formation of a large number of guar/BMIMCl hydrogen interactions and guar/guar entanglements. Even at 25 wt.%, G' and G'' moduli are not totally constant and decrease at low frequencies, which highlights the transient character of the network and the overall relaxation of the system with time. At 7 wt.% and low frequencies, G' scales approximately with frequency (f) by $G' \sim f^{1.25}$, which deviates from the terminal relaxation slope of 2 expected for polymer solutions. The deviation becomes more and more pronounced when the concentration increases and the slope of the storage modulus in the terminal region gradually decreases. This slope deviation can be ascribed to the organized character of the guar/BMIMCl system due to the presence of strong guar/IL physical interactions, which already exist at low concentration and which are reinforced and strengthened with the guar concentration increase. The existing models are commonly applied to synthetic flexible and linear polymers solubilized in solvent with low viscosity (De Gennes, 1976). Guar gum is a natural semi-rigid and pseudo-ramified polymer, which develops peculiar and strong interactions with IL molecules. Moreover, BMIMCl solvent is a structured and organized solvent with high viscosity (Fig. S5). For all these reasons, it seems to be difficult to predict the dynamics of such systems with models established from synthetic polymers, which adopt a conformation in solution totally different than the one of polysaccharides such as guar gums with high molecular weight. The variation of the complex viscosity $|\eta^*|$ is also an important rheological data (Fig. S6). A Newtonian plateau followed by a shear-thinning behavior is observed for all concentrations (even at 5 wt.%). Such a viscosity decrease highlights the frequency-induced dissociation of both (i) guar/guar entanglements and (ii) guar/IL and IL/IL non-covalent interactions. The onset of the shear-thinning behavior is shifted to lower frequencies when polymer concentration increases, as observed by various authors for cellulose dissolved in ILs when the concentration raises (Haward et al., 2012; Kuang et al., 2008). At 25 wt.%, a remarkable shear-thinning behavior is observed, which highlights a highly entangled and associated system due to the formation a gelling guar/IL network (Montalvo, Valiente, & Rodenas, 1996; Song et al., 2011).

For guar molecular weight of 300 kDa, the gelation concentration value was shown to be around 5.5 wt.% (Fig. S7).

3.5. Influence of the temperature

Fig. 4 represents the G' and G'' evolution for a 5 wt.% concentration solution at different temperatures ranging from 10 to 60 °C.

Fig. 4(A) shows that a temperature increase leads to a G' and G'' decrease as well as a shortening of the longest relaxation time. At 25, 35, 45 and 60 °C, G'' is much higher than G' modulus, reflecting a viscous fluid behavior. At 10 °C, a quasi-superimposition of G' and G'' moduli is observed, which is related to a global decrease of the mobility. The time–temperature superimposition principle was successfully applied to guar/BMIMCl solutions and master plots of storage and loss modulus of a guar (126 kDa, 5 wt.%)/BMIMCl solution was built (Fig. 4(B)). This emphasizes the homogeneity of the solution under the used experimental conditions and shows that guar gum at 5 wt.% in BMIMCl behaves as a classical polymer solution. At low frequency G' and G'' scale with frequency by $G' \sim f^{1.32}$ and by $G'' \sim f^{0.82}$ and at high-frequency the exponents tend to 0.55. As previously mentioned, the exponent values diverges from classical exponent of 2 for G' and 1 for G'' expected in the terminal region for Rouse-like behavior (Kuang et al., 2008).

For both curves, the same horizontal shift factor a_t was applied and no vertical shifting was required. Temperature changes affect the dynamics of the gel by promoting the guar chain and BMIMCl mobility, which disturbs the IL/guar interactions. The curve of Ln (a_t) *versus* the inverse of temperature obeys Arrhenius law, as displayed by the linearity variation in Fig. 4(C). Similar behavior was recently reported for cellulose acetate in 1-ethyl-3-methylimidazolium acetate (Rudaz & Budtova, 2013). The slope of Fig. 4(C) can be used to calculate an activation energy (E_a) since $a_t = \exp[(E_a/R)(1/T - 1/T_{ref})]$, where R is the ideal gas constant, T is temperature in °K and T_{ref} the reference temperature. E_a is a measure of the energy required to overcome intra- and intermolecular forces, allowing for guar chain motion. The resulting E_a of guar/BMIMCl (at 5 wt.%), which was not reported in the

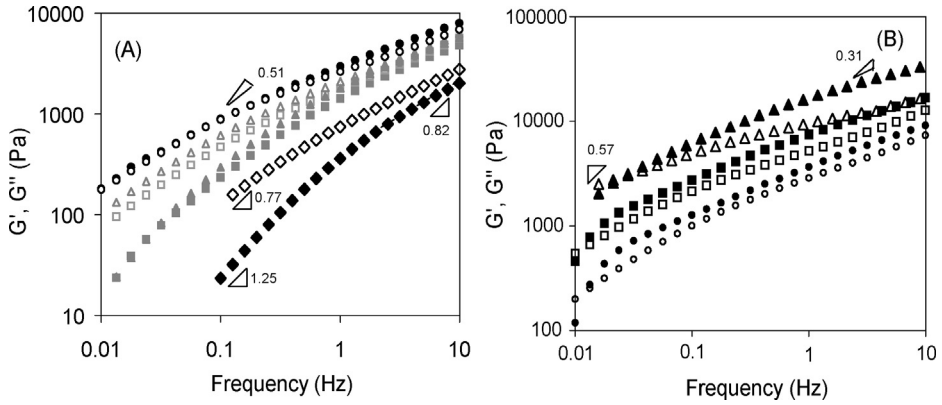


Fig. 3. Frequency-dependence of G' (filled symbols) and G'' (open symbols) moduli of a guar (126 kDa)/BMIMCl solution, with a guar concentration equals to 5 wt.% (◊), 6 wt.%, (□), 7 wt.% (△), 9 wt.% (○) (A), 10 wt.% (○), 15 wt.% (□) and 25 wt.% (△) (B) at 25 °C.

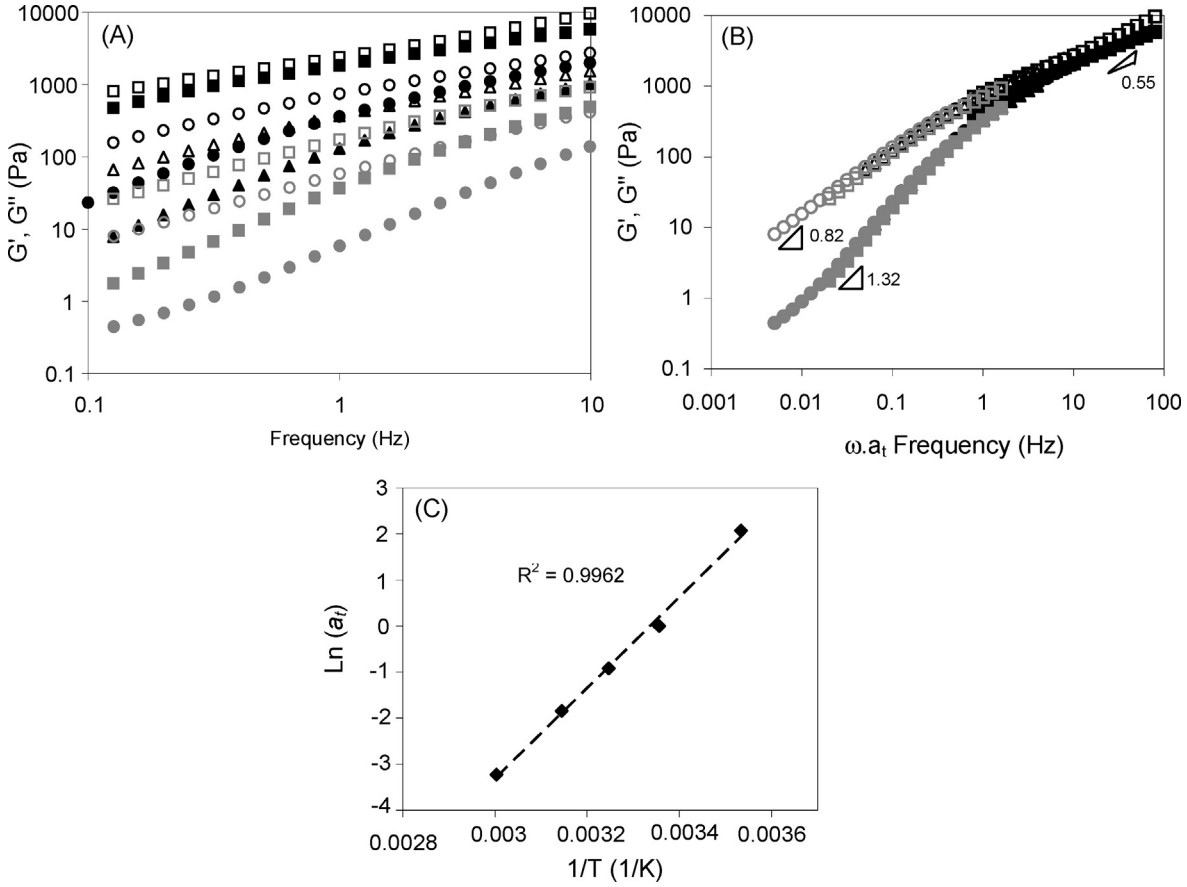


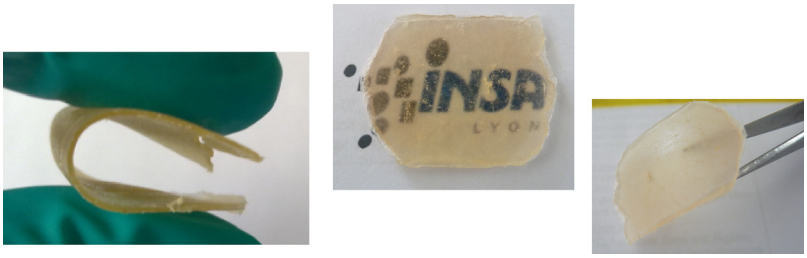
Fig. 4. (A) Frequency-dependence of G' (filled symbols) and G'' moduli (open symbols) of a guar (126 kDa, 5 wt.%)/BMIMCl solution at 10 °C (□), 25 °C (○), 35 °C (△), 45 °C (□), and 60 °C (○). (B) Master curves of G' and G'' moduli as a function of reduced frequency (25 °C is the reference). (C) Evolution of $\ln(a_t)$ *versus* temperature, where a_t is the horizontal temperature-dependant shift factor.

literature so far, is equal to 81.8 kJ/mol (≈32 kT). This high energy highlights (i) a strong temperature dependence and (ii) the presence of numerous physical interactions (H-bonds, electrostatic and Van der Waals interactions). We can notice that this value is quite similar to the one obtained from steady-state viscosity measurements (73.4 kJ/mol) performed on the same system, namely guar (126 kDa, 5 wt.%)/BMIMCl solution (Lacroix et al., 2012).

The thermo-dependant behavior of the solution was also monitored by the evolution of G' and G'' as a function of the temperature ranging from 10 to 90 °C, which emphasized a progressively G' and G'' decrease with the temperature (Fig. S8). Similar G' and G'' values, upon heating and cooling ramp with no hysteresis, point out the reversible character of the physical interactions with the temperature.

3.6. Creep properties

To further characterize and quantify the influence of the guar chain concentration and the IL type on the viscoelastic properties, creep and recovery experiments were undertaken on



Scheme 1. Example of guar/BMIMCl-based films.

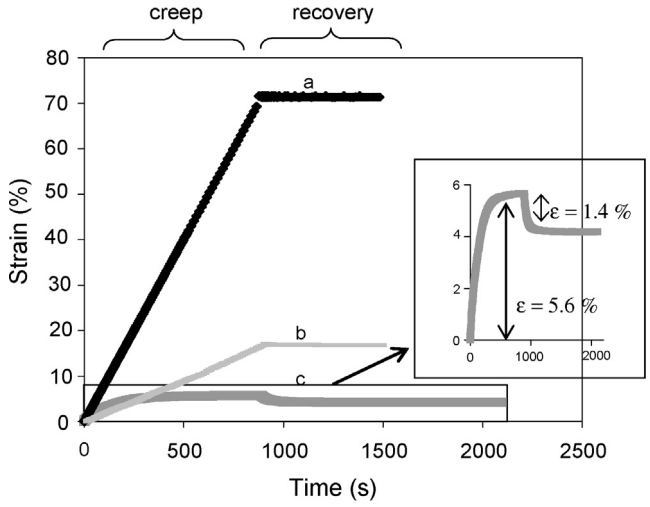


Fig. 5. Creep and recovery curves at 25 °C of guar (126 kDa, 10 wt.%)/AMIMCl (a), guar (126 kDa, 8 wt.%)/BMIMCl (b) and guar (126 kDa, 10 wt.%)/BMIMCl (c) solutions at 25 °C.

guar (126 kDa)/BMIMCl (at 8 and 10 wt.%) and guar (126 kDa, 10 wt.%)/AMIMCl systems (Fig. 5). During the creep experiment, the same constant stress (1 Pa) was applied to all samples for a duration of 15 min. The stress was then removed and the solutions were allowed to relax.

As depicted in Fig. 5, the strain response of guar (126 kDa, 8 wt.%)/BMIMCl and guar (126 kDa, 10 wt.%)/AMIMCl solutions during the creep experiment is linear and no elastic recovery is observed, which is a response typical of materials with liquid-like behavior (Rayment, Ross-Murphy, & Ellis, 1998; Warhier & Grinstaff, 2010). Interestingly, while the guar (126 kDa, 8 wt.%)/BMIMCl sample is rather weakly deformed (18%) (Fig. 5(b)), the guar/AMIMCl combination is definitely much more deformed (71%) (Fig. 5(a)). These differences are due to stronger interactions developed in the guar/BMIMCl system, which lead to a lower propensity to be deformed.

Conversely, for guar chains at 10 wt.% in BMIMCl, the creep curve progressively increases up to a strain of 5.6%, which is characteristic of a more organized solid-like physical network. The induced deformation is not irreversible since a recovery of 25% of the maximal deformation is observed, which underlines a more elastic behavior for this system.

3.7. Preparation of guar/imidazolium ionic liquid gelled films

The procedure developed to prepare films is straightforward and based on simple laboratory equipment. It consists in casting and manually compressing guar/IL gels between glass slides that are subsequently subjected to a cooling down. The thickness can be controlled by the amount of deposited mixtures and the pressure applied to the glass slide. It was checked that reproducible film can be obtained and thermomechanical properties are not impacted by the film thickness (Fig. S9).

Washings with ethanol (and not immersion in a bath) allow for expelling IL molecules located at the film surface, which are not strongly entrapped in the network. As indicated in the experimental part, this washing procedure leads to a removal of 19–24 wt.% of IL. Such brief and superficial washings do not lead to any guar aggregation or coagulation at the surface of the film, as verified by Scanning Electron Microscopy analysis collected onto guar/BMIMCl cross-sections, which exhibit a morphology similar all along the thickness of the sample (data not shown). All casted gels take the form of self-supported flexible and optically transparent films with sufficient mechanical resistance to be handled without difficulties (Scheme 1).

Macromolecular and/or molecular rearrangements occurring during the thermal treatment yield the formation of a solid material containing confined ionic liquid molecules. These guar-based films are different from the ones developed by the team of Kadokawa, which used a more complex experimental process to prepare guar-based films from guar/BMIMCl mixtures (Mine et al., 2010; Prasad, Murakami, et al., 2009). In their report, BMIMCl acted as a template to generate guar films and IL molecules were removed from the material. Such an approach was also exploited for the preparation of cellulose-heparin and cellulose fibers (Viswanathan et al., 2006; Yousefi, Nishino, Faezipour, Ebrahimi, & Shakeri, 2011) and lignocellulose aerogel (Li et al., 2011), for which ionic liquid played the role of aid-processing.

3.8. Thermal properties

The films were characterized by thermogravimetric analysis. An example of guar (566 kDa, 18.5 wt.%)/BMIMCl film is given in Fig. 6. These analytical data confirms that the gel is a "hybrid" material composed of guar chains as well as BMIMCl, as reflected by the thermal decomposition which occurs through two main stage weight losses (see derivative weight) extended on a large temperature window spreading from 220 to 350 °C. Moreover, this temperature range indicates that the thermal stability of both BMIMCl molecules and guar chains are not affected when mixed together (Fig. S10 for TGA of single components). Such a wide thermal decomposition profile is representative of a broad size and number distribution of physical interactions between BMIMCl and guar backbone. We can assume that different association states exist due to the insertion of IL molecules between the guar chains. Moreover, as reported for other polysaccharide/IL mixtures (Mine et al., 2010; Prasad, Kaneko, et al., 2009), the thermogram indicates that the film, stored at ambient conditions under air, contains water (6.3% after a storage of one week (Fig. 6(b) and 7% after four weeks (Fig. 6(c)) due to the hygroscopic nature of IL and guar chains. A drying at 80 °C overnight under vacuum allows for an elimination of most of uptaked water (Fig. 6(a)).

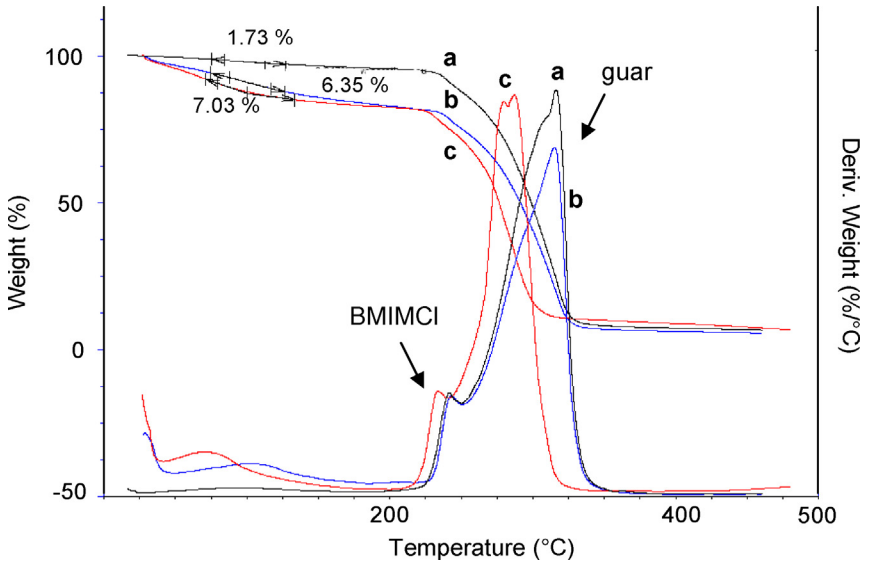


Fig. 6. TGA thermograms of films based on guar (566 kDa, 18.5 wt.%)/BMIMCl dried at 80 °C overnight under vacuum (a), stored for one week (b) and stored for four weeks (c) at ambient condition under air.

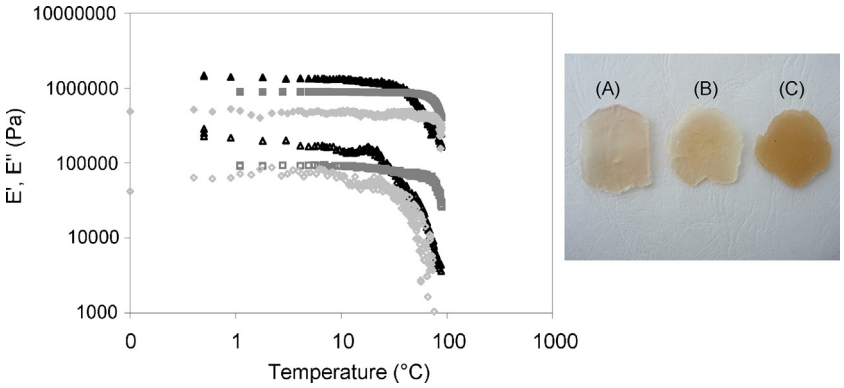


Fig. 7. Evolution of E' (filled symbols) and E'' (open symbols) as a function of the temperature of films based on guar (566 kDa, 18.5 wt.%)/BMIMCl (△) (picture (A)), guar (566 kDa, 19.2 wt.%)/EMIMMP (□) (picture (B)) and guar (566 kDa, 19.8 wt.%)/AMIMCl (◊) (picture (C)). *Important: Note that the guar concentration indicated between brackets are calculated by taking into account the weight of IL leached out during the washing (see experimental part).*

3.9. Elongational thermomechanical properties

Guar/IL films were characterized by dynamical mechanical analysis (DMA) under uniaxial tensile mode and the evolution of the elongational storage (E') and loss (E'') moduli was monitored as a function of the temperature.

The impact of the IL type was evaluated by comparing films composed of guar (566 kDa) in BMIMCl, EMIMMP and AMIMCl (Fig. 7).

Whatever the ionic liquid nature and the temperature, the films exhibit an E' modulus higher than E'' with an E' value around 10^6 Pa. The E'/E'' ratio for guar/BMIMCl, guar/EMIMMP and guar/AMIMCl is equal to 8, 11 and 6, respectively, which is typical of a solid state. The elongational moduli are constant on a large range of temperature and then sharply decrease from a critical value, as the result of a thermo-induced softening of the material. This can be explained by the promotion of guar chains and IL molecules mobility that induces a progressive disruption of hydrogen, Van der Waals and electrostatic interactions. At high temperatures, IL exudates appear as droplets on the surface of the film as a consequence of the IL diffusion. The BMIMCl-based film exhibits superior E' and E'' moduli compared to films based on EMIMMP or AMIMCl. The propensity of BMIMCl to generate superior materials in terms of mechanical properties confirms the shear response of guar/BMIMCl mixtures. As previously

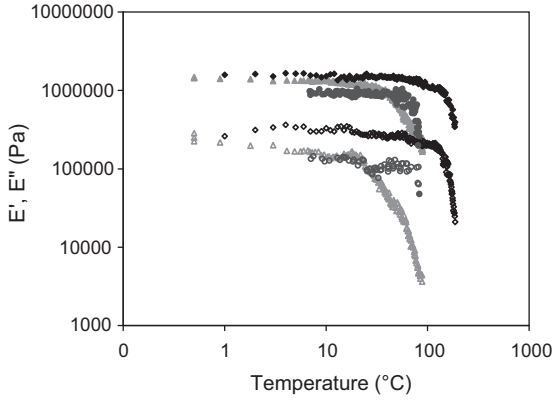


Fig. 8. Evolution of E' (filled symbols) and E'' (open symbols) as a function of the temperature of films based on guar (126 kDa, 26.6 wt.%)/BMIMCl (○), guar (300 kDa, 19.2 wt.%)/BMIMCl (△) and guar (566 kDa, 18.5 wt.%)/BMIMCl (◊).

mentioned, this can be reasonably explained by the capacity of BMIMCl to behave as strongly organized liquid. However, the critical temperature from which the moduli begin to drop is slightly increased by using EMIMMP or AMIMCl. These results reveal that thermomechanical properties of such biohybrid materials

can be finely tuned by both the experimental conditions and parameters inherent to the components' structure.

Three guar/BMIMCl gel films with different guar molecular weight (126 kDa, 300 kDa and 566 kDa) were analyzed. For all guar $\overline{M_w}$, the guar concentration is above the gelation one (determined by shear measurements).

Fig. 8 highlights that a molecular weight increase conducts to an enhanced thermal stability since the E' modulus of the system elaborated from a $\overline{M_w} = 300$ kDa begins to drop at 50 °C, while a thermal stability up to 150 °C results from the use of a $\overline{M_w} = 566$ kDa. A high molecular weight restricts the IL diffusion due to the presence of additional guar entanglements. Also, the influence of the moisture uptake was assessed on the thermomechanical properties of guar/BMIMCl materials. The results evidence that the presence of water (up to 7 wt.%) does not affect the mechanical properties, which is a very promising asset for further applications (Fig. S11).

4. Conclusion

A simple approach, which does not require any chemical polysaccharide modification to generate physical ion gels by mixing guar gums with IL molecules was described. The influence of the IL chemical structure, the molecular weight and concentration of guar chains as well as the temperature was investigated. It results that these parameters play an important role on interactions developed within such systems. IL molecules act as physical crosslinkings and solid-like behavior can be obtained as a result of the formation of guar/IL hydrogen bonds. The use of BMIMCl imparts the highest elastic properties on account of its stronger organized character (IL/IL interactions). The sol-gel transition can be tuned by the concentration and molecular weight of guar gum. The thermodependence of the viscoelastic response allowed for providing an activation energy, which was shown to be very high. The synergistic interactions between guar gum and IL molecules were then exploited to prepare self-supported films composed of guar chains in which IL molecules were strongly confined, according to a straightforward experimental process. Again, thermomechanical properties evidenced solid-like behavior, which can be tuned by the IL type and guar molecular weight. Finally, the water adsorbed in guar/IL films does not alter the thermomechanical properties. Such materials that synergize the advantageous features of polysaccharide-based physical gels and conductive organic molecules present a large applicative potential in the field of energy devices. Further studies in particular in soft matter conductive devices are now in progress.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carbpol.2013.10.043.

References

Braccini, I., Rodriguez-Carvajal, M. A., & Perez, S. (2005). Chain-chain interactions for methyl polygalacturonate: Models for high methyl esterified pectin junction zones. *Biomacromolecules*, *6*, 1322–1328.

Carlin, R. T., & Fuller, J. (1997). Ionic liquid–polymer gel catalytic membrane. *Chemical Communications*, 1345–1346.

Charlot, A., & Auzély-Velty, R. (2007). Novel hyaluronic acid-based supramolecular assemblies stabilized by multivalent specific interactions: Rheological behavior in aqueous solution. *Macromolecules*, *40*, 9555–9563.

Charlot, A., Auzély-Velty, R., & Rinaudo, M. (2003). Specific interactions in model charged polysaccharide systems. *Journal of Physical Chemistry B*, *107*, 8248–8254.

Cheng, Y., Brown, K. M., & Prud'homme, R. K. (2002). Characterization and intermolecular interactions of hydroxypropyl guar solutions. *Biomacromolecules*, *3*, 456–461.

Cheng, Y., & Prud'homme, R. K. (2000). Enzymatic degradation of guar and substituted guar galactomannans. *Biomacromolecules*, *1*, 782–788.

Chung, T. W., Yang, J., Akaibe, T., Cho, K. Y., Nah, J. W., Kim, S. I., et al. (2002). Preparation of alginate/galactosylated chitosan scaffold for hepatocyte attachment. *Biomaterials*, *23*, 2827–2834.

Coviello, T., Alhaique, F., Dorigo, A., Matricardi, P., & Grassi, M. (2007). Two galactomannans and scleroglucan as matrices for drug delivery: Preparation and release studies. *European Journal of Pharmaceutics and Biopharmaceutics*, *66*, 200–209.

Cunha, P. L. R., Castro, R. R., Rocha, F. A. C., & Feitosa, J. P. A. (2008). Hydrogel of guar gum in experimental osteoarthritis in rats. *Macromolecular Symposia*, *266*, 48–52.

De Jong, S. J., De Smedt, S. C., Wahls, M. W. C., Demeester, J., Van Den Bosh, K., & Hennink, W. E. (2000). Novel self-assembled hydrogels by stereocomplex formation in aqueous solution of enantiomeric lactic acid oligomers grafted to dextran. *Macromolecules*, *33*, 3680–3686.

De Gennes, P. G. (1976). Dynamics of entangled polymer solutions. I. The Rouse Model. *Macromolecules*, *9*, 587–593.

Erdmenger, T., Guerrero-Sanchez, C., Vitz, J., Hoogenboom, R., & Shubert, U. S. (2010). Recent developments in the utilization of green solvents in polymer chemistry. *Chemical Society Reviews*, *39*, 3317–3333.

Feng, L., & Chen, Z. (2008). Research progress on dissolution and functional modification of cellulose in ionic *liquid*. *Journal of Molecular Liquids*, *142*, 1–3.

Gandini, A. (2008). Polymers from renewable resources: A challenge for the future of macromolecular materials. *Macromolecules*, *41*, 9491–9504.

Gericke, M., Schlufter, K., Liebert, T., Heinze, T., & Budtova, T. (2009). Rheological properties of cellulose/ionic liquid solutions: From dilute to concentrated states. *Biomacromolecules*, *10*, 1188–1194.

Goycoolea, F., Milas, M., & Rinaudo, M. (2001). Associative phenomena in galactomannan-deacetylated xanthan system. *International Journal of Biological Macromolecules*, *29*, 181–192.

Haward, S. J., Sharma, V., Butts, C. P., McKinley, G. H., & Rahatekar, S. S. (2012). Shear and extensional rheology of cellulose/ionic liquid solutions. *Biomacromolecules*, *13*, 1688–1699.

Heinze, T., Dorn, S., Schoebitz, M., Liebert, T., Koehler, S., & Meister, F. (2008). Interactions of ionic liquids with polysacchrides-2: Cellulose. *Macromolecular Symposia*, *262*, 8–22.

Hennink, W. E., & Van Nostrum, C. F. (2002). Novel crosslinking methods to design hydrogels. *Advanced Drug Delivery Reviews*, *54*, 13–36.

Horinaka, J-i., Yasuda, R., & Takigawa, T. (2011). Entanglement properties of cellulose and amylose in an ionic liquid. *Journal of Polymer Science Part B: Polymer Physics*, *49*, 961–965.

Horinaka, J-i., Yasuda, R., & Takigawa, T. (2012). Rheological properties of concentrated solutions of galactomannans in an ionic liquid. *Carbohydrate Polymers*, *89*, 1018–1021.

Huddleston, J. G., Visser, A. E., Reichert, W. M., Willauer, H. D., Broker, G. A., & Rogers, R. D. (2001). Characterization and comparison of hydrophilic and hydrophobic room temperature ionic liquids incorporating the imidazolium cation. *Green Chemistry*, *3*, 156–164.

Izawa, H., & Kadokawa, J-i. (2010). Preparation and characterizations of functional ionic liquid-gel and hydrogel materials of xanthan gum. *Journal of Materials Chemistry*, *20*, 5235–5241.

Jansen, J. C., Friess, K., Clarizia, G., Schauer, J., & Izak, P. (2011). High ionic liquid content polymeric gel membranes: Preparation and performance. *Macromolecules*, *44*, 39–45.

Jessop, P. G., Jessop, D. A., Fu, D., & Phan, L. (2012). Solvatochromic parameters for solvents of interest in green chemistry. *Green Chemistry*, *14*, 1245–1259.

Kadokawa, J-i., Murakami, M-a., & Kaneko, Y. (2008). A facile preparation of gel materials from a solution of cellulose in ionic liquid. *Carbohydrate Research*, *343*, 769–772.

Kadokawa, J-i., Murakami, M-a., Takegawa, A., & Kaneko, Y. (2009). Preparation of cellulose–starch composite gel and fibrous material from a mixture of the polysaccharides in ionic liquid. *Carbohydrate Polymers*, *75*, 180–183.

Kuang, Q.-L., Zhao, J.-C., Niu, Y.-H., Zhang, J., & Wang, Z.-G. (2008). Celluloses in an ionic liquid: The rheological properties of the solutions spanning the dilute and semidilute regimes. *Journal of Physical Chemistry B*, *112*, 10234–10240.

Lacroix, C., Sultan, E., Fleury, E., & Charlot, A. (2012). Functional galactomannan platform from convenient esterification in imidazolium-based ionic liquids. *Polymer Chemistry*, *3*, 538–546.

Lee, K. Y., Park, W. H., & Ha, W. S. (1997). Polyelectrolyte complexes of sodium alginate with chitosan or its derivatives for microcapsules. *Journal of Applied Polymer Science*, *63*, 425–432.

Lewandowski, A., & Swiderska, A. (2004). New composite solid electrolytes based on a polymer and ionic liquids. *Solid State Ionics*, *169*, 21–24.

Li, J., Lu, Y., Yang, D., Sun, Q., Liu, Y., & Zhao, H. (2011). Lignocellulose aerogel from wood-ionic liquid solution (1-allyl-3-methylimidazolium chloride) under freezing and thawing conditions. *Biomacromolecules*, *12*, 1860–1867.

Lu, J., Yan, F., & Texter, J. (2009). Advanced applications of ionic liquids in polymer science. *Progress in Polymer Science*, *34*, 431–448.

Lv, Y., Wu, J., Zhang, J., Niu, Y., Liu, C.-Y., He, J., et al. (2012). Rheological properties of cellulose/ionic liquid/dimethylsulfoxide (DMSO) solutions. *Polymer*, *53*, 2524–2531.

Masakuni, T. (2009). Studies on the gelation mechanism of polysaccharides, and development and application of fucoidan from commercially cultured *Cladosiphon okamuranus*. *Journal of Applied Glycoscience*, *47*, 17–27.

Mercuri, D., Leone, G., Barbucci, R., Favaloro, R., Facchini, A., Signori, F., et al. (2008). An artificial disc: Chemical and biomechanical analysis. *Macromolecular Symposia*, *266*, 74–80.

Mine, S., Prasad, K., Izawa, H., Sonoda, K., & Kadokawa, J-i. (2010). Preparation of guar gum-based functional materials using ionic liquid. *Journal of Materials Chemistry*, *20*, 9220–9225.

Montalvo, G., Valiente, M., & Rodenas, E. (1996). Rheological properties of the L phase and the hexagonal, lamellar and cubic liquid crystals of the CTAB/benzyl alcohol/water system. *Langmuir*, *12*, 5202–5208.

Mours, M., & Winter, H. H. (1996). Relaxation patterns of nearly critical gels. *Macromolecules*, *29*, 7221–7229.

Pinkert, A., Marsh, K. N., Pag, S. S., & Staiger, M. P. (2009). Ionic liquids and their interaction with cellulose. *Chemical Reviews*, *109*, 6712–6728.

Prasad, K., Kaneko, Y., & Kadokawa, J-i. (2009). Novel gelling systems of κ-, ι- and λ-carrageenans and their composite gels with cellulose using ionic liquid. *Macromolecular Bioscience*, *9*, 376–382.

Prasad, K., Murakami, M-a., Kaneko, Y., Takada, A., Nakamura, Y., & Kadokawa, J-i. (2009). Weak gel of chitin with ionic liquid, 1-allyl-3-methylimidazolium bromide. *International Journal of Biological Macromolecules*, *45*, 221–225.

Prasad, K., Izawa, H., Kaneko, Y., & Kadokawa, J-i. (2009). Preparation of temperature-induced shapeable film material from guar gum-based gel with an ionic liquid. *Journal of Materials Chemistry*, *19*, 4088–4090.

Prud'homme, R. K., Constien, V., & Knoll, S. (1989). Polymers in aqueous media: Performance through association. *Advances in Chemistry*, *223*, 89–112.

Rayment, P., Ross-Murphy, S., & Ellis, P. R. (1998). Rheological properties of guar galactomannan and rice starch mixtures II. Creep measurements. *Carbohydrate Polymers*, *35*, 55–63.

Remsing, R. C., Hernandez, G., Swatloski, R. P., Masseski, W. W., Rogers, R. D., & Moyna, G. (2008). Reply to "Comment on 'NMR spectroscopic studies of cellobiose solvation in EmimAc aimed to understand the dissolution mechanism of cellulose in ionic liquids". *Journal of Physical Chemistry B*, *112*, 11071–11078.

Remsing, R. C., Swatloski, R. P., Rogers, R. D., & Moyna, G. (2006). Mechanism of cellulose dissolution in the ionic liquid 1-n-butyl-3-methylimidazolium chloride: A ^{13}C and 35/37Cl NMR relaxation study on model systems. *Chemical Communications*, 1271–1273.

Rinaudo, M. (2006). Non-covalent interactions in polysaccharide systems. *Macromolecular Bioscience*, *6*, 590–610.

Rudaz, C., & Budtova, T. (2013). Rheological and hydrodynamic properties of cellulose acetate/ionic liquid solutions. *Carbohydrate Polymers*, *92*, 1966–1971.

Sammons, R. J., Collier, J. R., Rials, T. G., & Petrovan, S. (2008). Rheology of 1-butyl-3-methylimidazolium chloride cellulose solutions. I. Shear rheology. *Journal of Applied Polymer Science*, *110*, 1175–1181.

Song, H., Niu, Y., Wang, Z., & Zhang, J. (2011). Liquid crystalline phase and gel–sol transitions for concentrated microcrystalline cellulose (MCC)/1-ethyl-3-methylimidazolium acetate (EMIMAc) solutions. *Biomacromolecules*, *12*, 1087–1096.

Soltero, J. F. A., Puig, J. E., & Manero, O. (1996). Rheology of the cetyltrimethylammonium tosilate–water system. 2. Linear viscoelastic regime. *Langmuir*, *12*, 2654–2662.

St. Dennis, J. E., Meng, Q., Zheng, R., Pesika, N. S., McPherson, G. L., He, J., et al. (2011). Carbon microspheres as network nodes in a novel biocompatible gel. *Soft Matter*, *7*, 4170–4173.

Takegawa, A., Murakami, M-a., Kaneko, Y., & Kadokawa, J-i. (2010). Preparation of chitin/cellulose composite gels and films with ionic liquids. *Carbohydrate Polymers*, *79*, 85–90.

Tayal, A., Pai, V. B., & Khan, S. A. (1999). Rheology and microstructural changes during enzymatic degradation of a guar–borax hydrogel. *Macromolecules*, *32*, 5567–5574.

Tizzotti, M., Charlot, A., Fleury, E., Stenzel, M., & Bernard, J. (2010). Modification of polysaccharides through controlled/living radical polymerization grafting-towards the generation of high performance hybrids. *Macromolecular Rapid Communications*, *31*, 1751–1772.

Tizzotti, M., Creuzet, C., Labeau, M. P., Hamaide, T., Drockenmuller, E., Charlot, A., et al. (2010). Synthesis of temperature responsive biohybrid guar-based grafted copolymers by click chemistry. *Macromolecules*, *43*, 6843–6852.

Viswanathan, G., Murugesan, S., Pushparaj, V., Nalamasu, O., Ayayan, P. M., & Linhardt, R. J. (2006). Preparation of biopolymer fibers by electrospinning from room temperature ionic liquids. *Biomacromolecules*, *7*, 415–418.

Wang, Y., Li, H., & Han, S. (2006). The chemical nature of the C–H–X (X = Cl or Br) interaction in imidazolium halide ionic liquids. *Journal of Chemical Physics*, *124*, 044504/1

Wang, Q., Yang, Y., Chen, X., & Shao, Z. (2012). Investigation of rheological properties and conformation of silk fibroin in the solution of AmimCl. *Biomacromolecules*, *13*, 1875–1881.

Warhier, M., & Grinstaff, M. W. (2010). Synthesis and creep-recovery behavior of a neat viscoelastic polymeric network formed through electrostatic interactions. *Macromolecules*, *43*, 9529–9533.

Whistler, R. L., & BeMiller, J. N. (1993). *Industrial gums: Polysaccharides and their derivatives*. San Diego, CA: Academic Press.

Wilkes, J. S. (2002). A short history of ionic liquids-from molten salts to neoteric solvents. *Green Chemistry*, *4*, 73–80.

Yeon, S. H., Kim, K. S., Choi, S., Cha, J. H., & Lee, H. (2005). Characterization of PVdF(HFP) gel electrolytes based on 1-(2-Hydroxyethyl)-3-methyl imidazolium ionic liquids. *Journal of Physical Chemistry B*, *109*, 17928–17935.

Youngs, C. T. G. A., Hardacre, C., & Holbrey, J. D. (2007). Glucose solvation by the ionic liquid 1,3-dimethylimidazolium chloride: A simulation study. *Journal of Physical Chemistry B*, *111*, 13765–13774.

Yousefi, H., Nishino, T., Faezipour, M., Ebrahimi, G., & Shakeri, A. (2011). Direct fabrication of all-cellulose nanocomposite from cellulose microfibers using ionic liquid-based nanowelding. *Biomacromolecules*, *12*, 4080–4085.

Zhang, S., Lee, K. H., Frisbie, C. D., & Lodge, T. P. (2011). Ionic conductivity, capacitance, and viscoelastic properties of block copolymer-based ion gels. *Macromolecules*, *44*, 940–949.

Zhang, S., Lee, K. H., Sun, J., Frisbie, C. D., & Lodge, T. P. (2011). Viscoelastic properties, ionic conductivity, and materials design considerations for poly(styrene-*b*-ethylene oxide-*b*-styrene)-based ion gel electrolytes. *Macromolecules*, *44*, 8981–8989.