

Preparation of tamarind gum based soft ion gels having thixotropic properties



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ABSTRACT

Tamarind gum was used to prepare ion gels using both synthetic ionic liquids (ILs) namely 1-butyl-3-methylimidazolium chloride and 1-butyl-3-methylimidazolium bromide and bio-based ionic liquids (Bio-ILs) namely choline acrylate, choline caproate and choline caprylate by heating cooling process. The gels were found to have good thermal stability and exhibited thixotropic behaviour. Upon relaxation after applied breaking strain, the recovery of gel structures after ten consecutive cycles was observed. The hydrogel of the gum prepared using ethanol aqueous solution had much inferior quality in terms of viscosity, viscoelasticity, thermal stability and thixotropy when compared with the ion gels. The ion gels also showed very good adherence to human finger muscles and skin. The ion gels thus prepared may find application in electrochemistry, sensors, actuators and the gels prepared with Bio-ILs could even be useful in biomedical applications.

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1. Introduction

Tamarind gum (TG) is a natural polysaccharide, extracted from the endosperm of the seeds of *Tamarindus indica* Linn (Glicksman, 1986). Chemically TG is composed of β -(1,4)-D-glucan backbone substituted with side chains of α -(1,4)-D-xylopyranose and (1,6) linked [β -D-galactopyranosyl-(1,2)- α -D-xylopyranosyl] to glucose residues (Fig. 1), where glucose, xylose, and galactose units are present in the ratio of 2.8:2.25:1.0 as the monomer units (Gidley et al., 1991). TG is widely used as a thickening, stabilizing, emulsifying and gelling agent in food and pharmaceutical industries (Zhang, Zeng, Zhang, Wang, & Wang, 2006). Besides high thermal and chemical stability, it also possesses properties like non-carcinogenicity, biocompatibility, mucoadhesivity, non-toxicity and high drug holding capacity (Burgalassi, Panichi, Saettone, Jacobsen, & Rassing, 1996; Kulkarni, Dwivedi, Sarin, & Singh, 1997; Saettone et al., 2000; Sano et al., 1996; Sumathi & Ray, 2002).

Generally TG is insoluble in most of the organic solvents, however it is dispersible in hot water and formed a viscous mucilaginous gel solution with wide range of pH tolerance and adhesivity (Khanna, Dwivedi, & Singh, 1997; Kulkarni et al., 1997). Picout, Ross-Murphy, Errington, and Harding (2003) have reported the

“pressure cell” heating method suitable to improve the TG solubility in water by reducing molecular aggregation (Picout et al., 2003). Although in presence of gellan gum, TG forms gel materials, it is reported that TG itself is reluctant to form gel and thus regarded as non-gelling polysaccharide (Nitta & Nishinari, 2005). It has been reported that enzymatic degradation of TG led to formation of gel at higher temperature through removal of galactopyranosyl residues (Shirakawa, Yamatoya, & Nishinari, 1998). Yamanaka et al. (2000) have also reported that TG form gel in the presence of 15% (v/v) ethanol in water at 80–100 °C (Yamanaka et al., 2000). Thus it is very little known in the literature about the gelation of TG and hence formation of gel of TG is a challenging goal.

Recently, ionic liquids (ILs) are getting attention for their extraordinary ability to dissolve many natural polysaccharides including DNA (Lacroix, Sultan, Fleury, & Charlot, 2012; Mukesh, Mondal, Sharma, & Prasad, 2013; Prasad, Kaneko, & Kadokawa, 2009; Rogers & Seddon, 2003; Swatloski, Spear, Holbery, & Rogers, 2002) and possess properties suitable to be used as a novel platform for the design of new materials (Lodge, 2008). Besides synthetic ionic liquids, biodegradable non-toxic bio-based ionic liquids composed of only biomaterials are also being developed and termed as bio-ionic liquids (Bio-ILs) (Fukaya, Iizuka, Sekikawa, & Ohno, 2007; Meera, Sankar, Jaisankar, & Mandal, 2011). These new class of ionic liquids due to their unusual solvation characteristics are considered as unique solvent systems for bio-molecules such as proteins (Fujita, MacFarlane, & Forsyth, 2005). Considering the above merits of the ILs, it is envisaged to manipulate the properties of TG using the ILs. Although ILs are used to prepare ion-gels of agarose,

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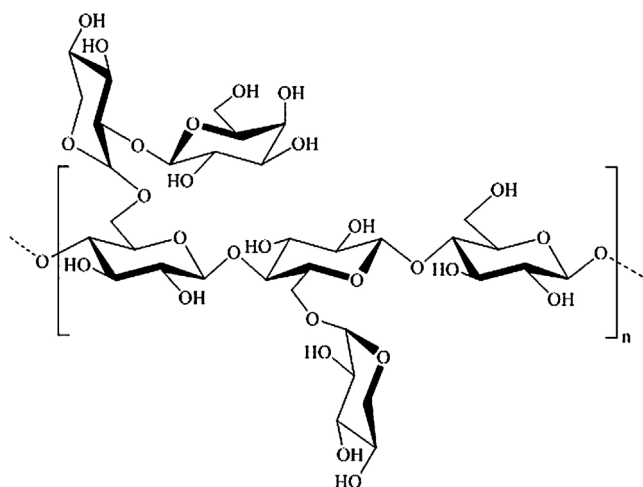


Fig. 1. The repeating units in tamarind gum.

carrageenan, cellulose, etc. (Mine, Prasad, Izawa, Sonoda, & Kadokawa, 2010; Prasad, Izawa, Kaneko, & Kadokawa, 2009) but no significant research endeavours are made so far to prepare ion gel of TG in ILs. Herein, we report the preparation of TG based ion gel using both synthetic ILs namely 1-butyl-3-methylimidazolium chloride and 1-butyl-3-methylimidazolium bromide and Bio-ILs namely choline acrylate, choline caproate and choline caprylate by heating-cooling process. Moreover, induction of thixotropic behaviour in gel matrices is a very challenging task and chemical modification of the substrates need to be done to induce this property. Recently we were able to induce thixotropicity in a sodium alginate based hydrogel by chemical modification of the polysaccharide (Chattbar, Prasad, Chejara, & Siddhanta, 2012) and we too demonstrated self-healing and solvent responsive healing behaviour of a guar gum based gel prepared in an ionic liquid (Sharma, Mondal, Mukesh, & Prasad, 2013a, 2013b). The ion gels reported in this paper showed very good thixotropic behaviour without any chemical modification of the gum and there is no report on the preparation of thixotropic ion gel of tamarind gum. Apart from the thixotropic nature, the presence of ILs makes these gels thermally stable and long term structural stability when stored at room temperature unlike their hydrogel counterparts.

2. Experimental

2.1. Materials

Tamarind gum (tamarind seed polysaccharide) extracted from the seed of *T. indica* was purchased from TCI chemicals, Tokyo, Japan. The molecular weight of tamarind gum was reported to be in the range of $2.5\text{--}6.5 \times 10^5$ Da (Gidley et al., 1991; Lang & Kajiwara, 1993; Zhang et al., 2006). Choline bicarbonate (80% aqueous solution) was purchased from Sigma–Aldrich, USA. BmimCl and BmimBr were procured from Merck & Co., Germany. Acrylic acid, caproic acid and caprylic acid were purchased from SRL chemicals, Mumbai, India. All chemicals were used as received without further purification.

2.2. Syntheses of ionic liquids

The bio-ionic liquids containing choline caproate/caprylate/acrylate were synthesized by metathesis reaction as described by Petkovic et al. (2010). In a typical reaction, corresponding acid was added drop wise into the aqueous choline bicarbonate (80% aqueous solution) (molar ratio 1:1) under stirring at

ambient temperature and pressure followed by refluxing at 100°C for 24 h under vigorous stirring. The ionic liquids were finally washed with ethyl acetate to remove the unreacted components and remaining ethyl acetate and water were then removed under reduced pressure using a rotary evaporator (e.g. 60°C , 2 h) (Supporting information, Scheme S1). Structure of the synthesized ionic liquids was confirmed by ^1H NMR and electro spray-mass spectrometry (ESI-MS).

2.3. Preparation of the TG-ionic liquid gel

The gelation of TG (10%, w/w) was achieved by heating-cooling process (Mine et al., 2010; Prasad, Izawa, et al., 2009). In a typical procedure, TG (0.10 g) was dissolved in the ILs (1.0 g) by heating at $80\text{--}100^\circ\text{C}$ for 1 h under an inert atmosphere. After the respective solutions were cooled to room temperature, it gave formation of the gels (Fig. 2A–E).

2.4. Preparation of the TG hydrogel

Tamarind gum does not form a gel itself in water. Yamanaka et al. (2000) have reported a method of preparation of TG gel in water in the presence of ethanol (Yamanaka et al., 2000). In a typical procedure for the preparation of hydrogel of TG, the solution was prepared by dissolving 0.10 g TG in 1.0 g of 15% (v/v) ethanol aqueous solution at $80\text{--}100^\circ\text{C}$. After that solution was cooled to room temperature and it gave formation of gel (Fig. 2F).

2.5. Measurements

Powder X-ray diffraction patterns were recorded at 298 K on a Phillips X'pert MPD system using $\text{Cu K}\alpha$ radiation ($\lambda = 0.15405$ nm) with 2θ range from 5° to 80° at a scan speed of 0.1°s^{-1} . Thermo gravimetric measurements (TGA) were carried out on a Mettler Toledo TGA system, Greifensee, Switzerland, machine with pristine and recovered tamarind gum powders (10 mg) using a temperature programme $30\text{--}450^\circ\text{C}$ at a heating rate 5°C min^{-1} under a nitrogen atmosphere. FT-IR analyses were carried out on a Perkin-Elmer FT-IR machine (Spectrum GX, USA) using KBr disc (2 mg sample in 600 mg KBr).

2.6. Rheological measurements

Rheological measurements were done on an Anton Paar, Physica MCR 301 rheometer USA, using parallel plate PP50/P-PTD200 geometry (49.971 mm diameter; 0.75 mm gap). Temperature was maintained by Anton Paar, Viscotherm VT2 circulating water bath. The dynamic viscosities were determined varying the shear rate at 25°C e.g. $0.1\text{--}200\text{ s}^{-1}$ and $0.1\text{--}1.0\text{ s}^{-1}$. For thixotropy measurement, the shear rates applied were varied from 0.1 to 1000 s^{-1} in an upward sweep immediately followed up by a downward sweep. Area under the upstream data points (A_{up}) and the downstream data points (A_{down}) as well as the hysteresis (thixotropic) area ($A_{up} - A_{down}$) was obtained using Rheoplus software. The percentage of relative thixotropic area (A_r) was calculated using Eq. (1) as described by Dolz, González, Delegido, Hernández, and Pellicer (2000).

$$A_r = \left(\frac{A_{up}}{A_{up} - A_{down}} \right) \times 100 \quad (1)$$

The time, frequency and strain dependence of the storage and loss moduli (G' and G'') for the TG gels were measured at 25°C and temperature dependent G' and G'' were measured with the temperature range from 20°C to 100°C . To investigate the time dependent recovery of elastic modulus, G' and loss modulus, G''

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