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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 thixotropicity 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.

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 extra ordinary 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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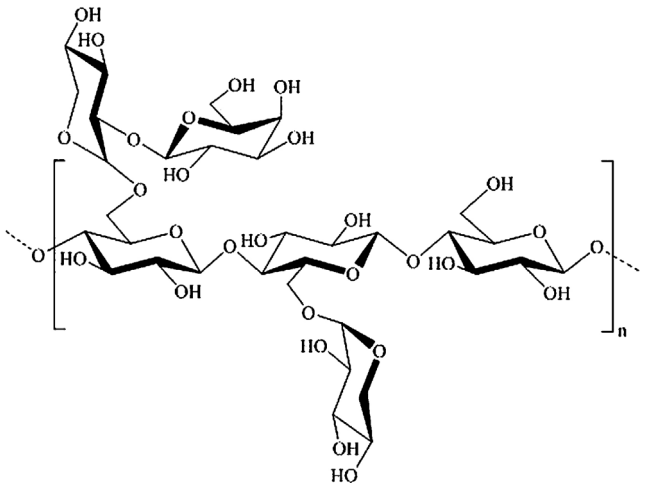

Fig. 1. The repeating units in tamarind gum.

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 $2.5–6.5 \times 10^5$ 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 ^{1}H 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 80–100 °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 80–100 °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 Cu K_α 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 30–450 °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. 0.1–200 s^{-1} and 0.1–1.0 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''

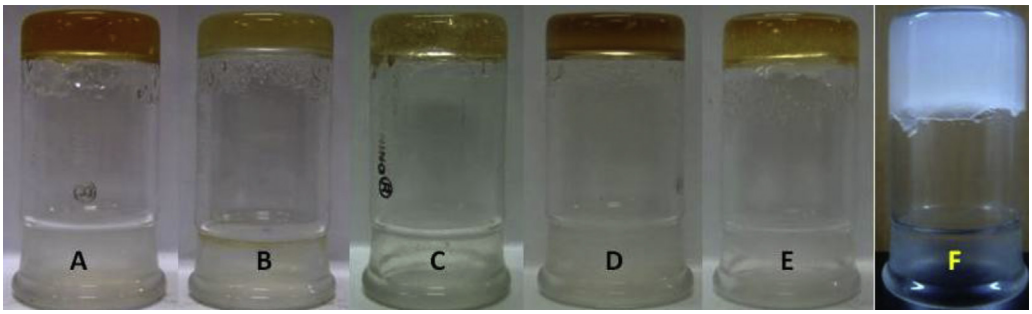

Fig. 2. Tamarind gum ion gels prepared in various room temperature ionic liquids (A) BmimCl, (B) BmimBr, (C) choline acrylate, (D) choline caproate, (E) choline caprylate and (F) tamarind gum hydrogel prepared in presence of 15% ethanol.

were recorded during deformation using strain 1% (linear viscoelastic range) for 300 s at frequency of 1 Hz followed by deformation of the gel employing higher strain (outside linear viscoelastic region) for 100 s at frequency of 1 Hz. The cycle was repeated for thirteen times for the GG-BmimCl ion gel. The recovery of G' was monitored during the entire deformation-restoration process. All rheological experiments e.g. shear viscosity flow as well as dynamic viscoelasticity measurements were also investigated for the 10% (w/v) TG hydrogel in 15% (v/v) ethanol aqueous solutions under the similar rheological parameters.

3. Results and discussion

Prior to optimization of 10% (w/w) TG ion gels, TG of concentration 3–12% (w/w) was solubilized in different ionic liquids viz., BmimCl, BmimBr, Choline acrylate, choline caproate and choline caprylate by heating at 80–100 °C for 1 h under nitrogen gas atmosphere. After the respective solutions were cooled to room temperature, it gave formation of the gels. The ion gels obtained from 10% (w/w) TG were very stable in nature, while the TG of lower concentrations gave formation of softer unstable iongels with ILs leaching out from the gel matrices. The 12% (w/w) TG gel was too tough. All the ion gels thus obtained were soft in nature (Fig. 2). The time required to form the ion gels of TG was similar to guar gum ion gels prepared in BmimCl (Sharma et al., 2013a, 2013b) and much lesser in comparison to the ion gels of carrageenan and cellulose in the IL (Prasad, Kaneko, et al., 2009; Rogers & Seddon, 2003). The physical appearance of the TG hydrogel is shown in Fig. 2F. The ion gels thus obtained were washed with IPA to recover the TG and the regenerated gum was investigated for their various properties.

The XRD profiles of pristine TG and TG recovered from the ion gels were recorded and are shown in Fig. 3. The pristine TG powder showed a broad peak at 2θ of 20° and similar peak was observed for all the TG samples regenerated from the ILs indicating preservation of structural integrity of the gum during dissolution in the ILs. The FT-IR spectra of pristine TG powder showed characteristic carbonyl (—HC=O) stretching band at 1649 cm^{-1}. It may be explained due to the fact that each monosaccharide of tamarind gum has two isomers, comprising of a ring and a linear structure. The linear structure contains the residues of glucose, xylose and galactose units resulting in the appearance of the carbonyl absorption band (H—C=O). The position and intensity of the bands remained a bit altered in the regenerated TG from the ionic liquids, indicating formation of hydrogen bonds between the gum and the ILs. A sharp band at 1730 cm^{-1} in the TG recovered from choline acrylate/caproate/caprylate was observed (Fig. 4d–f) due to the ester group of the ILs in the recovered gum indicating stronger interaction of these ILs with the gum in comparison to imidazolium based ILs, where the ILs got washed out during the regeneration process. However, the band was more predominant in case of TG recovered from choline acrylate (Fig. 4c). A sharp band at 2300 cm^{-1} due to atmospheric CO_2 was also observed in the recovered TG. Fig. 5 shows the TGA thermograms of the pristine TG powder and TG recovered from the ion gels. The TG powder showed three step mass losses, the first step (about 10%) near 100–150 °C was due to the absorbed moisture in the sample followed by mass loss (about 20%) near 320 °C due to the breaking of weak bonds (preferably the glycosidic bonds) present in the side chains. The major mass loss (about 80%) was perhaps due to the breaking of glycosidic bonds of the backbone leading to formation of water and carbon dioxide. The trend of mass loss was bit different in the recovered TG samples. The TG recovered from ion gels prepared in BmimCl showed much lower loss for moisture and the mass loss due to breaking of side chains is also took place at lower temperature (290 °C) and the major mass loss took place about 310 °C. All the other recovered samples also showed different thermal behaviour when compared with pristine tamarind gum indicating influence of the ILs on the

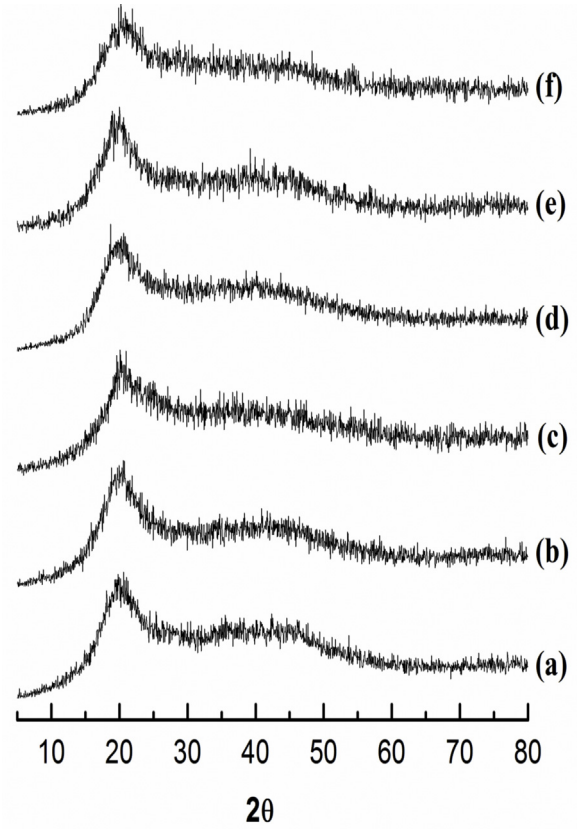

Fig. 3. XRD spectra of pristine tamarind gum (a), regenerated tamarind gum from TG-BmimCl iongel (b), TG-BmimBr ion gel (c), TG-choline acrylate ion gel (d), TG-choline caproate ion gel (e) and TG-choline caprylate ion gel (f).

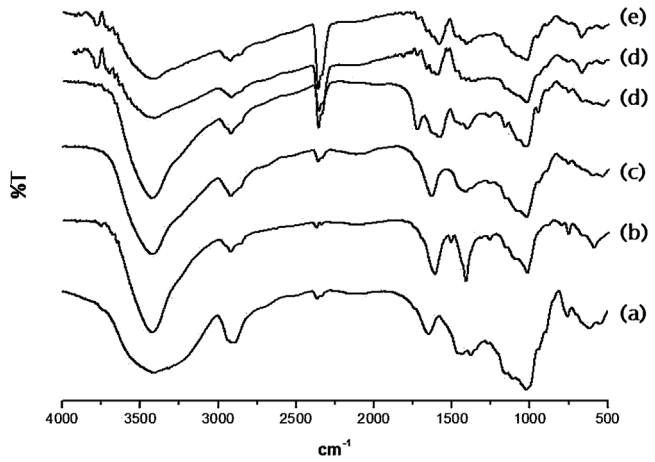

Fig. 4. FT-IR spectra of pristine tamarind gum (a) and regenerated tamarind gum from TG-BmimCl ion gel (b), TG-BmimBr ion gel (c), TG-choline acrylate iongel (d), TG-choline caproate ion gel (e) and TG-choline caprylate ion gel (f).

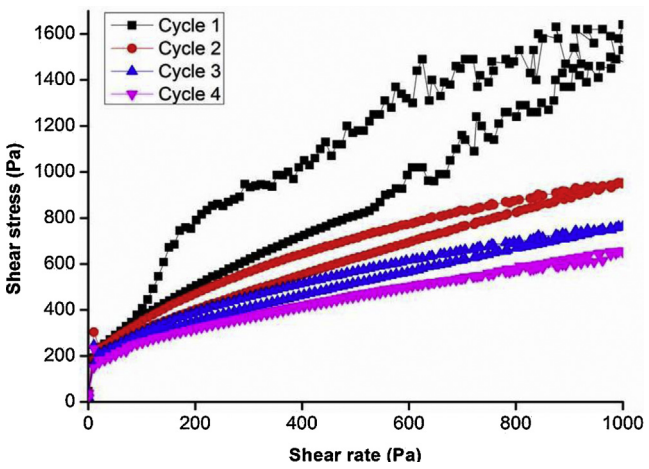

Fig. 6. Thixotropic behaviour of ion gel of TG prepared in BmimCl assessed by hysteresis loop experiment.

thermal behaviour of the gum during formation of the ion gels. The elemental analyses of the recovered TG showed presence of trace amount of ionic liquids, which is due to the strong interactions of the ILs with the gum (evident from the FT-IR spectra) and these influenced the thermal behaviour of the recovered TG.

The detailed rheological properties of the ion gels (10%, w/w) of TG prepared in all the ILs were evaluated and compared with the properties of the hydrogel. The TG ion gel prepared in choline caprylate showed the highest shear viscosity followed by the gels prepared in BmimBr, choline acrylate, BmimCl and choline caproate. The TG hydrogel showed much lower viscosity as shown in Figure S1 (supporting information). Ionotropic gelation involving IL/IL interactions (including Van der Waals and coulombic interactions) and multiple TG/IL and hydrogen bonds in TG contributed to form a more stable associative system having higher life time of the interactions. The ILs have a dual functionality since they behaves both as solvent and as a junction promoter that ties TG chains leading to a network structure similar to physical gels. These crosslinkings are not regular but rather form extended junction zones due to the cooperative effect giving strength to the structure (Sharma et al., 2013a, 2013b). This type of effect is not present in case of the hydrogel and is the reason behind the lower shear viscosity. In order to study the temperature dependency of the loss and storage modulus of the ion gels, the representative ion gel of TG prepared in BmimCl was chosen and the property was

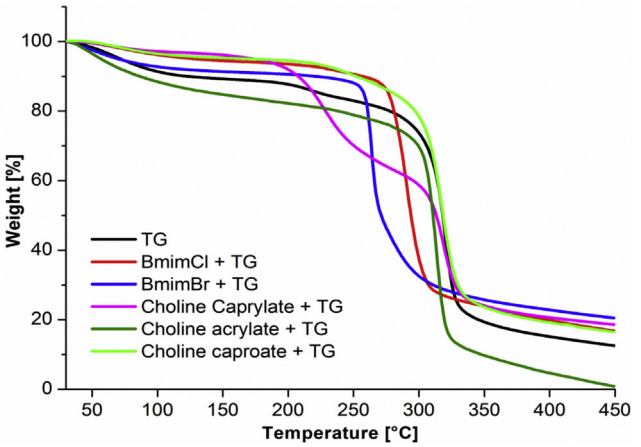

Fig. 5. TGA thermogram of pristine tamarind gum and the gum recovered from the ion gels prepared in different ionic liquids.

evaluated and compared with the TG hydrogel. Both the moduli for the hydrogel was found to cross over at 50 °C, on the other hand for the ion gel both the moduli has much higher values and they did not cross over till 100 °C indicating solid like behaviour of the later (supporting information, Fig. S2). The variation of both the moduli with time also confirmed the solid like behaviour of the ion gel (supporting information, Fig. S3). Frequency dependent viscoelastic measurements of the ion gels showed signature of typical viscoelastic material with predominance of storage modulus (G') on the whole frequency range (supporting information, Fig. S4). Ionotropic gelation involving BmimCl/BmimCl interactions (including Van der Waals and coulombic interactions) and multiple tamarind gum/BmimCl and hydrogen bonds among the tamarind gum contributed to form a more stable associative system having higher life time of the interactions. All the ionic liquids had played a dual functionality, both as solvent and as a junction promoter that ties tamarind gum chains leading to a network structure similar to physical gels. These crosslinkings are not regular but rather form extended junction zones due to the cooperative effect. Dynamic rheology is the most suitable technique to quantify the restoration ability of gel networks after their fracturation (Terech et al., 2013). The three dimensional network upon application of mechanical strain (higher shear rate) was disturbed but upon release of the force reconstitution of the three dimensional structure took place responsible for the thixotropic nature of the ion gels. For the evaluation of thixotropic behaviour, the samples were subjected to thinning under increasing shear rate (upward curve) immediately followed by dropping the applied shear rate (downward curve) (Fig. 6). The area of the loop thus formed gave an idea of the extent of thixotropy present in the samples calculated employing Eq. (1). The ion gel prepared in BmimCl showed a very good thixotropic loop and the thixotropic nature could be sustained for three consecutive cycles (Fig. 6). Further the area under the loops decreases upon increase of cycles due to the expulsion of ionic liquids from the gel matrices with time making the gels less viscoelastic. It should be noted that the hydrogel did not exhibit any thixotropic behaviour (supporting information, Figure S5).

In order to investigate recovery of storage modulus (G') of the gels upon relaxation, the gels were fractured employing high strain followed by relaxation. The ion gel prepared in BmimCl was initially subjected to 1% strain at 1 Hz frequency for 300 s and G' and G'' were monitored during the process followed by fracturing of the gels employing very high strain at 1 Hz for 100 s. It was observed that storage modulus for TG-BmimCl gel recovered the original value upon relaxation (Fig. 7). The cycle could be repeated for 10 consecutive times. The hydrogel did not show structure recovery

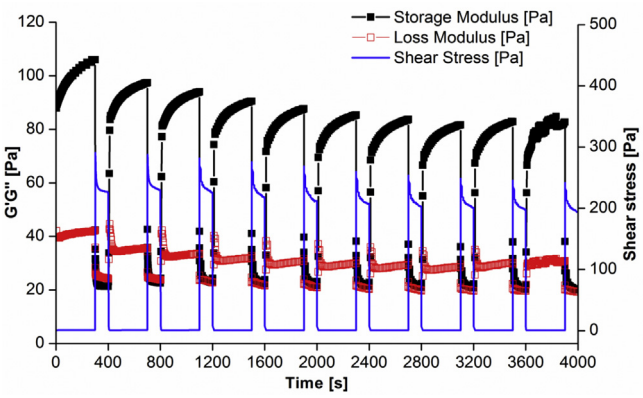

Fig. 7. Thixotropic behaviour of tamarind gum-BmimCl ion gel as characterized by dynamic recovery of the storage modulus (G') upon induced relaxation.

upon relaxation indicating absence of thixotropic nature (supporting information, Fig. S6).

Apart from the above properties, the TG ion gels prepared in the ILs showed very good adherence to human finger muscles as well as clean and de-haired human skin as shown in supporting Figures S7 and S8 similar to the properties of guar gum ion gels prepared in 1-butyl-3-methylimidazolium chloride recently reported by us (Sharma et al., 2013a, 2013b). It should be noted that the hydrogel of TG did not exhibit this type of properties. Since the ionic liquids are known to interact with amino acids (Tomé et al., 2009) and the adhesive property perhaps due to the interaction.

4. Conclusions

In summary, we have demonstrated a simple approach to prepare ion gels of tamarind gum 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. Upon investigations employing various analytical tools, interaction between tamarind gum and the ionic liquids found to influence the thermal as well rheological properties of the ion gels. The rheological property measurement showed formation of viscoelastic ion gels with thixotropic nature. The gels also showed excellent ability to adhere on human finger muscles and skin. This type of gels may find application in electrochemistry, sensors and actuators and the gels prepared in bio-ionic liquids would be useful even for biomedical applications.

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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.2013.11.063.

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