

Preparation of Galactomannan-based Materials Compatibilized with Ionic Liquids

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ABSTRACT This paper reports the preparation of galactomannan/ionic liquid composite materials from the corresponding ion gels. Three kinds of galactomannans, that is, fenugreek gum (FG), guar gum (GG), and locust bean gum (LBG) and an ionic liquid of 1-butyl-3-methylimidazolium chloride (BMIMCl) were used. When the galactomannan/BMIMCl gels were immersed in ethanol, followed by dryness under reduced pressure, the galactomannan/BMIMCl composite materials were obtained. The crystalline structures of galactomannans in the materials were evaluated by the powder X-ray diffraction measurement. The mechanical property of the FG/BMIMCl composite material under compressive mode was superior compared with the GG and LBG/BMIMCl composite materials. Then, FG films compatibilized with polymeric ionic liquids (PILs) were also prepared by in-situ radical polymerization of polymerizable ionic liquids, 1-(3-acryloyloxypropyl)-3-vinylimidazolium bromide and 1-methyl-3-vinylbenzylimidazolium chloride by AIBN in mixtures of FG with BMIMCl. The mechanical properties of the resulting films were affected by the FG/PIL ratios as well as the unit ratios in PILs.

Keywords Composite; Galactomannan; Film; Ionic liquid

Introduction

Abundant natural polysaccharides such as cellulose, starch, and chitin have received much attention for the use as biomass resources to provide new green and sustainable materials because of their eco-friendly and biodegradable properties [1]. Besides the abundant polysaccharides, many kinds of natural polysaccharides from various sources such as plants, animals, seaweeds, and bacteria have been known [2]. For example, some polysaccharides are used as hydrocolloids for a stabilizer, a viscous agent, and a structure provider in food industries [3]. Galactomannans, which are representative food hydrocolloids, consist of a (1→4)-linked β -D-mannopyranose main-chain with a branched α -D-galactopyranose unit at the 6-position [5]. The proportions of galactose and mannose residues in galactomannans are dependent on the source. Three major galactomannans, fenugreek gum (FG) from *Trigonella foenum-graecum*, guar gum (GG) from *Cyamopsis tetragonoloba*, and locust bean gum (LBG) from *Ceratonia siliqua*, have the average galactose/mannose ratios of *ca.* 1:1, 1:1.8, and 1:3.5, respectively (Fig. 1) [5-8].

To provide new polysaccharide-based materials, we have noted ionic liquids [9,10], which are low-melting point salts and form liquids at a temperature below the boiling point of water. Because ionic liquids have been recently found to be used as good solvents for natural polysaccharides such as cellulose [11-14], and accordingly, can be considered to have a specific affinity for polysaccharides, efficient methods to produce new polysaccharide-based materials compatibilized with ionic liquids have the potential to lead to the practical use of natural polysaccharides as the promising biomass resources. On the basis of these viewpoints, we have reported the facile preparation of gel materials not only of abundant polysaccharides such as cellulose, starch, and chitin [15-18], but also of hydrocolloid polysaccharides such as GG, carrageenans, and xanthan gum [19-23], which include ionic liquids as disperse media in the polysaccharide network matrixes, so-called ion gels. For example, we reported that functional ion gels of GG with an ionic liquid, 1-butyl-3-methylimidazolium chloride (BMIMCl), were obtained when 10 – 30% (w/w) solutions of GG in BMIMCl were left standing at room temperature for 30 min [19,23]. Furthermore, the resulting gels were converted into the GG/BMIMCl composite films by compression with hot-pressing equipment. To provide another type of polysaccharide materials with

ionic liquids, we have also focused on polymeric ionic liquids (PILs), *i.e.*, the polymer forms of ionic liquids, which are prepared by polymerization of polymerizable ionic liquids [24,25], as components of composite materials with such polysaccharides [26-30]. The composite materials were facilely prepared by in-situ radical polymerization of polymerizable ionic liquids in the presence of the polysaccharides.

In this paper, we extensively report the preparation of galactomannan-based materials using not only GG, but also FG and LBG compatibilized with ionic liquids. We first performed the fundamental studies on the preparation and characterizations of galactomannan/BMIMCl composite materials. The materials were prepared via the formation of ion gels of FG, GG, or LBG with BMIMCl, followed by removing appropriate volumes of BMIMCl from the gels. Because FG gave the composite material, which exhibited the better mechanical property compared with other two galactomannans, then, the approach was extended to the preparation of FG/PIL composite films by in-situ radical polymerization of polymerizable ionic liquids in mixtures of FG with BMIMCl, followed by the appropriate procedure. As the polymerizable ionic liquids, 1-(3-acryloyloxypropyl)-3-vinylimidazolium bromide (AVIMBr) was used, which had two polymerizable groups, and thus was polymerized by a radical initiator to produce a cross-linked insoluble PIL (PAVIMBr, Scheme 1a). In-situ copolymerization of AVIMBr with other polymerizable ionic liquid, that is, 1-methyl-3-vinylbenzylimidazolium chloride (MVIMCl), was also conducted to produce FG/P(AVIMBr-*co*-MVIMCl) composite films (Scheme 1b).

Experimental

Materials

Galactomannans, GG and LBG, were purchased from Wako Pure Chemical Industries and Sigma-Aldrich Chemical Co., respectively. A commercial FG powder with contents of > 86% was purchased from Air Green Co., Ltd. and purified according to the literature procedure [31]. An average galactose/mannose ratio of the purified FG was evaluated by the ¹H NMR measurement in D₂O to be *ca.* 1:1. An ionic liquid, BMIMCl, was purchased from Sigma-Aldrich Chemical Co. Polymerizable ionic

liquids, AVIMBr and MVIMCl, were prepared according to the literature procedures [27,28]. Other reagents were used as commercial grade without further purification.

Preparation of Galactomannan/BMIMCl Composite Materials

A typical experimental procedure was as follows (Runs 4-6, Table 1). A mixture of galactomannan (FG, GG, or LBG, 0.20 g) with BMIMCl (1.0 g) was heated at 100 °C for 5 h. The resulting homogeneous solution was left standing at room temperature for 3 h to give a galactomannan/BMIMCl gel (20% (w/w)). The gel was immersed in ethanol (10 mL for FG gel, 12 mL for GG gel, and 6 mL for LBG gel) for 5 d. The product was dried under reduced pressure for 2 d to give the galactomannan/BMIMCl composite material.

Preparation of FG/PIL Composite Films

A typical experimental procedure was as follows (Run 5, Table 2). A mixture of FG (0.31 g, 0.95 mmol) in BMIMCl (1.6 g) was vigorously stirred to give a suspension. To the suspension, a solution of AVIMBr (0.064 g, 0.21 mmol), MVIMCl (0.048 g, 0.20 mmol), and AIBN (0.0007 g, 0.0043 mmol, 1.0 mol% for AVIMBr + MVIMCl) in methanol (0.20 mL) was added with stirring. After the resulting mixture was thinly casted on a Petri dish, it was heated at 100 °C for 9 h and then left standing at room temperature for 3 h. The obtained **gel-like** material was subjected to Soxhlet extraction with ethanol for 6 h, followed by dryness under reduced pressure for 2 d to give a FG/PIL composite film.

Measurements

The powder X-ray diffraction (XRD) measurement was conducted using a Rigaku Geigerflex RADIIB diffractometer with Ni-filtered CuK α radiation ($\alpha = 0.15418$ nm). The ^1H NMR and IR spectra were recorded on a JEOL ECX-400 and a Shimadzu FTIR8400, respectively. The thermal gravimetric analysis (TGA) was performed using SII TG/DTA 6200 at a heating rate of 10 °C/min. The stress-strain curves were measured using a tensile tester (Little Senster LSC-1/30, Tokyo Testing Machine). **All tests**

were performed on a single film with a length of *ca.* 10 mm and the crosshead speed was set at 2 mm/min.

Results and Discussion

Preparation of Galactomannan/BMIMCl Composite Materials

As previously reported [19,23], a solution of GG in BMIMCl was totally turned into the GG/BMIMCl gel by standing it at room temperature. In this study, we also obtained the FG and LBG gels with BMIMCl (20% (w/w)) from the corresponding solutions by the same procedure. However, the resulting gels were hygroscopic and gradually excluded BMIMCl as the similar phenomena appeared for the GG/BMIMCl gel in 2 d. Therefore, suitable amounts of BMIMCl were removed from the gels by immersing them in ethanol under appropriate conditions to yield the stable composite materials (Fig. 2). The weight ratios of BMIMCl and water to galactomannan in the material were calculated by a weight change from the gel to the composite material and the TGA analysis, respectively (Table 1). The gels (1.2 g) were first immersed four times in ethanol (6.0 mL each) for 5 d, 2 d, 2 d, and 1 d to remove BMIMCl as much as possible. However, the amounts of remained BMIMCl in the resulting FG, GG, and LBG composite materials were different as decreased in this order (galactomannan : BMIMCl = 1 : 0.41 (FG), 1 : 0.36 (GG), and 1 : 0.13 (LBG)). This was probably owing to the different galactose/mannose ratios in galactomannans. It was considered that the lower ratio in LBG favorably constructed looser network structure in the gel compared with FG and GG, causing the exclusion of larger amounts of BMIMCl by immersing in ethanol. To adjust the weight ratios of BMIMCl to galactomannans in the three kinds of composite materials identically, the gels were appropriately immersed in the different volumes of ethanol. Consequently, when the FG, GG, and LBG/BMIMCl gels were immersed in ethanol of 10, 12, and 6 mL, respectively, for 5 d, followed by dryness under reduced pressure, the composite materials with the similar weight ratio of BMIMCl were obtained (Runs 1-3, Table 1). Then, these galactomannan/BMIMCl composite materials were subjected to the detailed characterizations.

Fig. 3 shows the XRD profiles of the composite materials in comparison with those of the original gels and galactomannan powders. The XRD patterns of FG and GG powders exhibited several crystalline peaks (Figs. 3c and f), whereas such peaks were not mostly detected in the XRD pattern of a LBG powder (Fig. 3i). The XRD patterns of all the gels did not show obvious crystalline peaks (Figs. 3a, d, and g), but some crystalline peaks were observed in the XRD patterns of the FG and GG composite materials (Figs. 3b and e). These results indicated that certain crystalline structures of FG and GG, which had been disrupted by gelation with BMIMCl, were regenerated in the composite materials.

Fig. 4 shows the stress-strain curves of the composite materials under compressive mode. Both the fracture stress and strain values decreased in the order of FG, GG, and LBG (Fig. 4a; 5.5 MPa and 35.4%, Fig. 4b; 3.1 MPa and 29.6%, Fig. 4c; 0.9 MPa and 26.1%). The presence of the crystalline structures of galactomannans in the composite materials probably enhanced their mechanical properties. The above XRD results and mechanical properties indicated the galactose/mannose ratios somewhat affected crystallinities of galactomannans in the composite materials, which also influenced their mechanical properties. Because it can be considered that the mechanical properties are probably affected by other factors such as chain lengths of galactomannans, the detailed study is under way in our group.

Preparation of FG/PIL Composite Films

Because FG gave the composite material with BMIMCl, which exhibited the better mechanical property compared with other galactomannans, an attempt to prepare FG films compatibilized with PILs was made by means of in-situ radical polymerization of polymerizable ionic liquids in mixtures of FG with BMIMCl (Fig. 5). First, a polymerizable ionic liquid, AVIMBr, which had two polymerizable groups, and accordingly, gave a cross-linked insoluble PIL (PAVIMBr) by its radical polymerization (Scheme 1), was employed. A suspension of FG and AVIMBr (1:0.5 w/w, Run 1, Table 2) with AIBN (1.0 mol% for AVIMBr) in BMIMCl was thinly casted on a Petri dish. Then, the suspension was heated at 100 °C for 9 h simultaneously for the dissolution of FG with BMIMCl and the progress of radical polymerization of AVIMBr. The resulting homogeneous material was left standing at room temperature for 3 h for the

gelation. The gel-like product was subjected to Soxhlet extraction with ethanol to remove BMIMCl and unreacted AVIMBr, followed by dryness under reduced pressure to give a FG/PAVIMBr composite film. As a control experiment, a FG film was also prepared from a mixture of FG with BMIMCl according to the same procedure as above. From the elemental analysis data by the SEM-EDX measurement of this film, Cl element was not detected, suggesting the absence of BMIMCl in the FG film. On the basis of this result, we evaluated that BMIMCl was mostly removed from the FG/PAVIMBr composite film by Soxhlet extraction with ethanol. The presence of PAVIMBr in the composite film was then confirmed by the IR measurement. Fig. 6b shows the IR spectrum of the composite film in comparison with that of a FG powder (Fig. 6a). The C=O absorption due to the ester linkage of PAVIMBr, which was not detected in the IR spectrum of a FG powder, was observed at 1713 cm^{-1} in Fig. 6b. This data indicated that in-situ radical polymerization of AVIMBr progressed in the system to produce the insoluble PAVIMBr, which was not washed out by Soxhlet extraction and thus was present in the composite film. The weight ratio of PAVIMBr to FG in the composite film was estimated by a weight of the Soxhlet extract and its ^1H NMR analysis using 1,4-dimethoxybenzene as an internal standard to be 1:0.23. Similarly, the composite films with the different FG/PAVIMBr weight ratios were prepared by varying the FG/AVIMBr feed weight ratios in the preparation procedure. As understood from the data in Table 2, the half or one-third of AVIMBr used were polymerized.

Fig. 7 shows the XRD profiles of the obtained composite films in comparison with those of a FG powder and the FG film. These results indicated that the crystalline peaks of FG at around 21° (indicated with shadow) gradually appeared with decreasing the ratios of PAVIMBr to FG in the composite films (Fig. 7c \rightarrow Fig. 7f). To evaluate the mechanical properties of the composite films, the stress-strain curves were obtained by the tensile testing, which were shown in Fig. 8. Both the fracture stress and strain values of the composite film with the higher PAVIMBr ratio (Fig 8b; 27.0 MPa and 1.1% for Run 1, Table 2) were smaller than those of the FG film (Fig. 8a; 38.7 MPa and 2.5%). With decreasing the PAVIMBr ratios in the composite films, the fracture stress and strain values increased, as an example of Fig. 8c (34.2 MPa and 2.3% for Run 2, Table 2). Furthermore, the fracture strain values in the composite

films with FG/PAVIMBr ratios of 1:0.046 and 1:0.022 (Runs 3 and 4, Table 2) were a little beyond those of the FG film with the comparable fracture stress values (Fig. 8d; 32.2 MPa and 2.8%, Fig. 8e; 36.1 MPa and 3.1%). These results suggested that the presence of higher ratio of PAVIMBr in the composite film caused the brittle nature, whereas a little amount of PAVIMBr present in the composite films induced to show high elongation ability although the effect was limited. In addition to the ratios of PAVIMBr to FG, the crystallinities of FG in the composite films, which were evaluated by the XRD analysis (Fig. 7), probably somewhat affected the mechanical property.

The FG/P(AVIMBr-*co*-MVIMCl) composite films were also prepared by in-situ radical copolymerization of AVIMBr with MVIMCl (Scheme 1) according to the procedure of Fig. 5. The unit ratios in the PILs of the composite films, which were estimated by the ¹H NMR analysis of the Soxhlet extracts using 1,4-dimethoxybenzene as an internal standard, relatively accorded to the feed molar ratios in the copolymerization (Runs 5 and 6, Table 2). Figs. 9c and d show the stress-strain curves of the resulting two composite films under tensile mode in comparison with those of the FG/PAVIMBr composite film (Fig. 9b) with the relatively identical FG/PIL molar ratio (*ca.* 1:0.05, Run 3, Table 2) as well as the FG film (Fig. 9a). The fracture strain values increased with increasing the unit ratio of MVIMCl in PILs, whereas the fracture stress values decreased. These data indicated the incorporation of the MVIMCl units in PILs affected higher elastic modulus of the composite films.

Conclusions

In this study, we performed the preparation of galactomannan/BMIMCl composite materials. When the 20% (w/w) FG, GG, and LBG/BMIMCl gels were immersed in ethanol, followed by dryness under reduced pressure, the galactomannan/BMIMCl composite materials with the appropriate ratios were obtained. The XRD results of the materials indicated that the certain crystalline structures of FG and GG, which had been mostly disrupted in the gels, were regenerated in the composite materials. The mechanical property of the FG/BMIMCl composite material was better than that of other materials, probably because of the higher galactose/mannose ratio in FG. Furthermore, the FG/PIL composite films

were prepared by in-situ radical polymerization of AVIMBr or copolymerization of AVIMBr with MVIMCl by AIBN in mixtures of FG with BMIMCl. The higher ratios of PAVIMBr to FG in the composite films gave brittle nature, whereas the presence of a little amount of PAVIMBr affected to show high elongation abilities of the films. Furthermore, the higher unit ratios in P(AVIMBr-co-MVIMCl)s affected higher elastic modulus of the films. The present materials will have potential to apply to the bio-based functional materials such as conductive materials in the future. Therefore, the more detailed studies on the properties and functions as well as the suitable applications of the present films are now in progress.

References

1. Berg JM, Tymoczko JL, Stryer L (2006) Biochemistry. WH Freeman & Co., New York, 6th ed, Chap 11
2. Schuerch C (1986) Polysaccharides. In: Mark HF, Bilkales N, Overberger CG (eds) Encyclopedia of polymer science and engineering, 2nd ed. John Wiley & Sons, New York, Vol 13, pp 87-162
3. Stephen AM, Philips GO, Williams PA (1995) Food polysaccharides and their applications. Taylor & Francis, London
4. Dea I. CM, Morrison A (1975) Chemistry and interactions of seed galactomannans. Adv Carbohydr Chem Bio-Chem 31:241–242
5. McDougall GJ, Morrison IM, Stewart D, Hillman JR (1996) Plant cell walls as dietary fiber: Range, structure, processing and function. J Sci Food Agric 70:133–150
6. Garti N (1999) Hydrocolloids as emulsifying agents for oil-in-water emulsions. J Disper Sci Tech, 20:327–355

7. Dakia PA, Blecker C, Roberta C, Watheleta B, Paqueta M (2008) Composition and physicochemical properties of locust bean gum extracted from whole seeds by acid or water dehulling pre-treatment. *Food Hydrocoll* 22:807–818
8. Bourbon AI, Pinheiro AC, Ribeiro C, Miranda C, Maia JM, Teixeira JA, Vicente AA (2010) Characterization of galactomannans extracted from seeds of *Gleditsia triacanthos* and *Sophora japonica* through shear and extensional rheology: Comparison with guar gum and locust bean gum. *CarbohydrPolym* 24:184-192
9. Kadokawa J (2011) Preparation of polysaccharide-based materials compatibilized with ionic liquids. In: Kokorin A (ed) *Ionic liquids, Application and perspectives*. InTech, Rijeka, Chap 6, pp 95-114
10. Kadokawa J (2012) Preparation of functional Ion gels of polysaccharides with ionic liquids. In: Mun J, Sim H (eds) *Handbook of ionic liquids: Properties, applications and hazards*. Nova Science Publishers, Hauppauge, Chap 18, pp 455-466
11. Seoud OAE, Koschella A, Fidale C, Dorn S, Heinze T (2007) Applications of ionic liquids in carbohydrate chemistry: A window of opportunities. *Biomacromolecules* 8:2629-2647
12. Feng L, Chen ZI (2008) Research progress on dissolution and functional modification of cellulose in ionic liquids. *J Mol Liq* 142:1-3
13. Liebert T, Heinze T (2008) Interaction of ionic liquids with polysaccharides 5. Solvents and reaction media for the modification of cellulose. *BioResources* 3:576-601
14. Pinkert A, Marsh KN, Pang S, Staiger MP (2009) Ionic liquids and their interaction with cellulose. *Chem Rev* 109:6712-6828
15. Kadokawa J, Murakami M, Kaneko Y (2008) A facile preparation of gel materials from a solution of cellulose in ionic liquid. *Carbohydr Res* 343:769–772

16. Kadokawa J, Murakami M, Takegawa A, Kaneko Y (2009) Preparation of cellulose–starch composite gel and fibrous material from a mixture of the polysaccharides in ionic liquid. *Carbohydr Polym* 75:180–183
17. Prasad K, Murakami M, Kaneko Y, Takada A, Nakamura Y, Kadokawa J (2009) Weak gel of chitin with an ionic liquid, 1-allyl-3-methylimidazolium bromide. *Int J Biol Macromol* 45:221-225
18. Takegawa A, Murakami M, Kaneko Y, Kadokawa J (2010) Preparation of chitin/cellulose composite gels and films with ionic liquids. *Carbohydr Polym* 79:85-90
19. Prasad K, Izawa H, Kaneko Y, Kadokawa J (2009) Preparation of temperature-induced shapeable film material from guar gum-based gel with an ionic liquid. *J Mater Chem* 19:4088–4090
20. Izawa H, Kaneko Y, Kadokawa J (2009) Unique gel of xanthan gum with ionic liquid and its conversion into high performance hydrogel. *J Mater Chem* 19:6969-6972
21. Prasad K, Kaneko Y, Kadokawa J (2009) Novel gelling systems of κ -, ι - and λ -carrageenans and their composite gels with cellulose using ionic liquid. *Macromol Biosci* 9:376–382
22. Izawa H, Kadokawa J (2010) Preparation and characterizations of functional ionic liquid-gel and hydrogel materials of xanthan gum. *J Mater Chem* 20:5235-5241
23. Mine S, Prasad K, Izawa H, Sonoda K, Kadokawa J (2010) Preparation of guar gum-based functional materials using ionic liquid. *J Mater Chem* 20:9220-9225
24. Green O, Grubjesic S, Lee S, Firestone MA (2009) The design of polymeric ionic liquids for the preparation of functional materials. *J Macromol Sci, Part C: Polym Rev* 49:339-360
25. Mecerreyes D (2011) Polymeric ionic liquids: Broadening the properties and applications of polyelectrolytes. *Prog Polym Sci* 36:1629-1648

26. Murakami M, Kaneko Y, Kadokawa J (2007) Preparation of cellulose-polymerized ionic liquid composite by in-situ polymerization of polymerizable ionic liquid in cellulose dissolving solution. Carbohydr Polym 69:378–381
27. Kadokawa J, Murakami M, & Kaneko Y (2008) A facile method for preparation of composites composed of cellulose and a polystyrene-type polymeric ionic liquid using a polymerizable ionic liquid. Comp Sci Tech 68: 493–498
28. Takegawa A, Murakami M, Kaneko Y, Kadokawa J (2009) A facile preparation of composites composed of cellulose and polymeric ionic liquids by in situ polymerization of ionic liquids having acrylate groups. Polym Comp 30:1837-1841
29. Prasad K, Kadokawa J (2010) Preparation of composite materials composed of *ι*-carrageenan and polymeric ionic liquids. Polym Comp 31:799-806
30. Prasad K, Mine S, Kaneko Y, Kadokawa J (2010) Preparation of cellulose-based ionic porous material compatibilized with polymeric ionic liquid. Polym Bull 64:341-349
31. Brummera Y, Cuib W, Wang Q (2003) Extraction, purification and physicochemical characterization of fenugreek gum. Food Hydrocoll 17:229-236

Scheme and Figure Captions

Scheme 1. Radical polymerization of AVIMBr (a) and radical copolymerization of AVIMBr with MVIMCl (b).

Fig. 1. Structures of fenugreek gum, guar gum, and locust bean gum.

Fig. 2. Procedure for preparation of galactomannan/BMIMCl composite materials.

Fig. 3. XRD profiles of FG/BMIMCl gel (a), FG/BMIMCl composite material (b, Run 1, Table 1), FG powder (c), GG/BMIMCl gel (d), GG/BMIMCl composite material (e, Run 2, Table 1), GG powder (f), LBG/BMIMCl gel (g), LBG/BMIMCl composite material (h, Run 3, Table 1), and LBG powder (i).

Fig. 4. Stress-strain curves of FG, GG, and LBG composite materials of Runs 1, 2, and 3 in Table 1 (a, b, and c, respectively) under compressive mode.

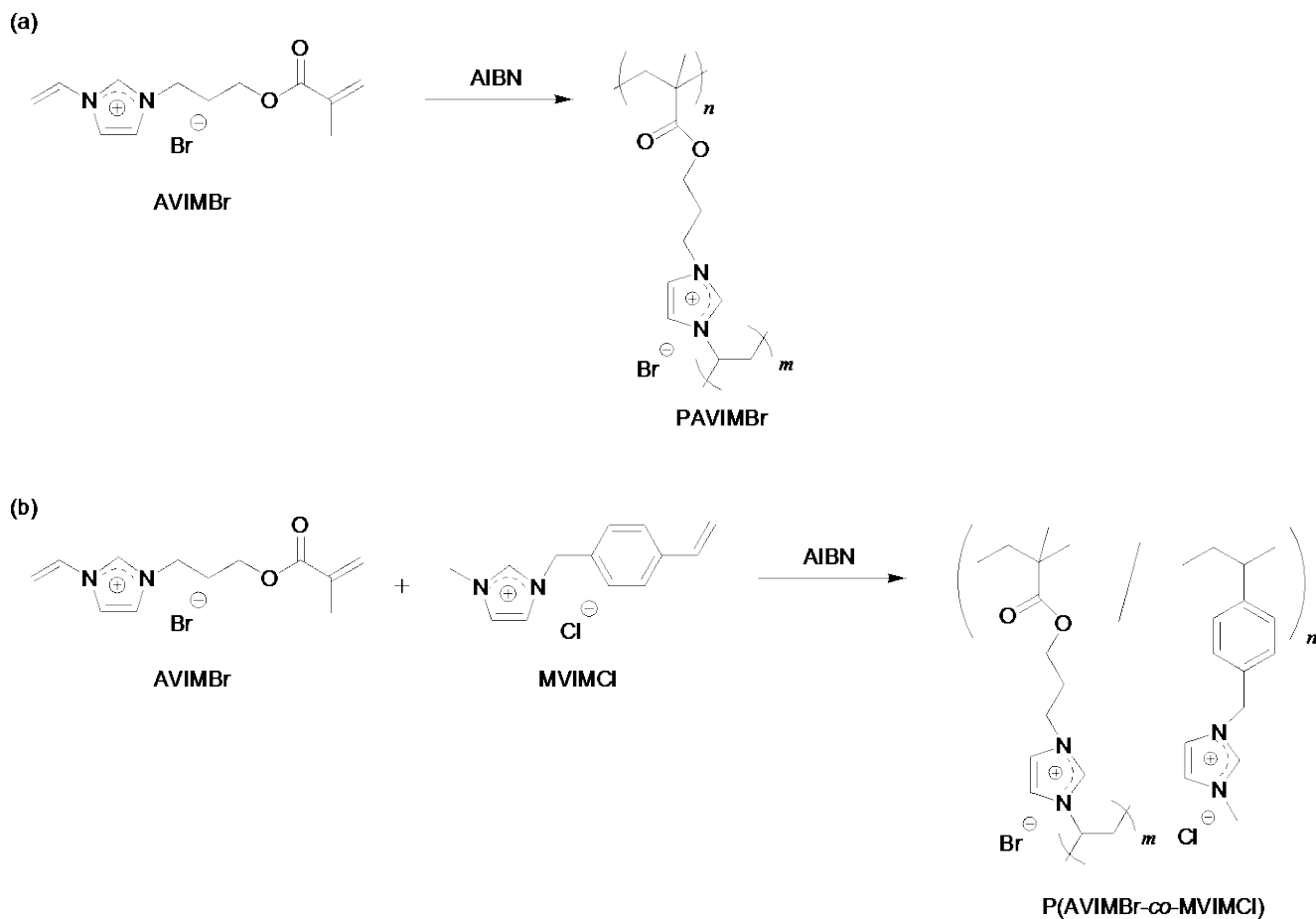
Fig. 5. Procedure for preparation of FG/PIL composite film.

Fig. 6. IR spectra of FG powder (a) and FG/PAVIMBr composite film (b, Run 1, Table 2).

Fig. 7. XRD profiles of FG powder (a), FG film (b), and FG/PIL composite films of Runs 1, 2, 3, and 4 in Table 2 (c, d, e, f, respectively).

Fig. 8. Stress-strain curves of FG film (a) and FG/PIL composite films of Runs 1, 2, 3, and 4 (molar ratios of FG to PIL = 1 : 0.25, 1 : 0.14, 1 : 0.050, and 1 : 0.024) in Table 2 (b, c, d, e, respectively) under tensile mode.

Fig. 9. Stress-strain curves of FG film (a) and FG/PIL composite films of Runs 3, 5, and 6 (molar ratios of FG to PIL = 1 : 0.050, 1 : 0.041, and 1 : 0.045) in Table 2 (b, c, d, respectively) under tensile mode.



Scheme 1. Radical polymerization of AVIMBr (a) and radical copolymerization of AVIMBr with MVIMCl (b).

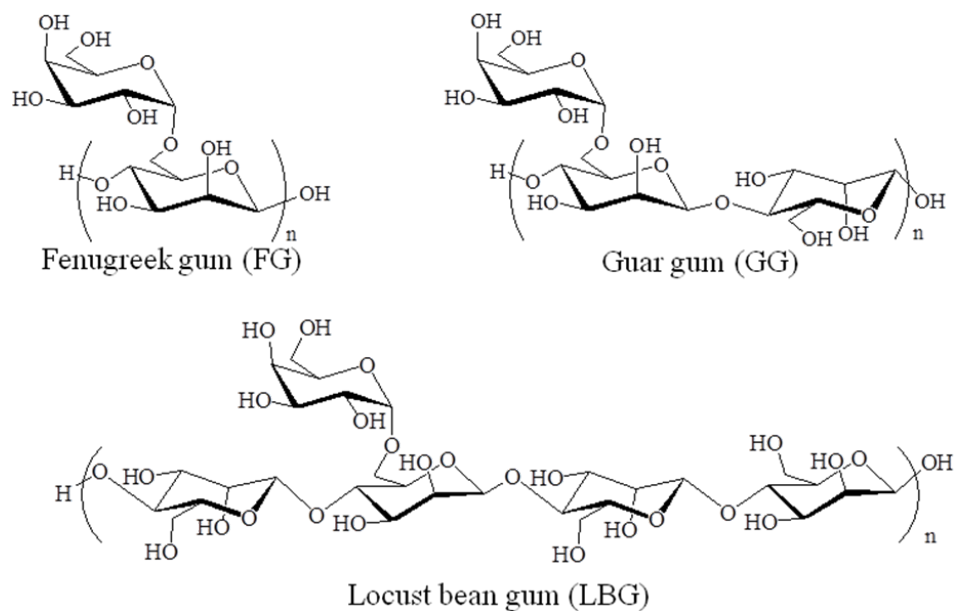


Fig. 1. Structures of fenugreek gum, guar gum, and locust bean gum.

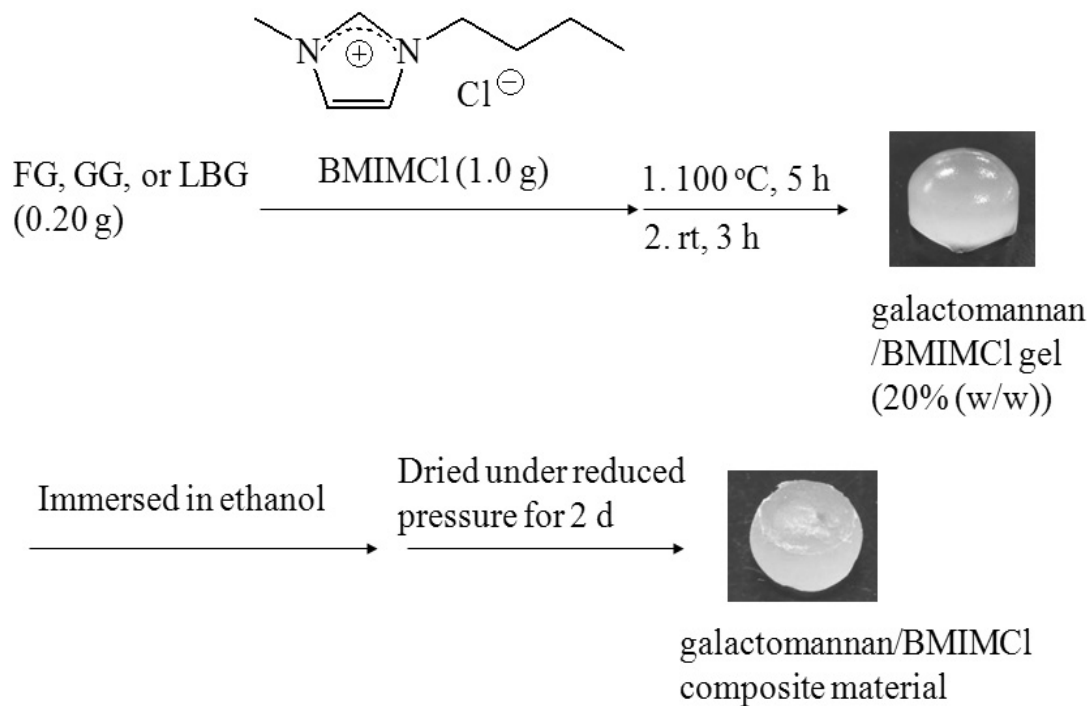


Fig. 2. Procedure for preparation of galactomannan/BMIMCl composite materials.

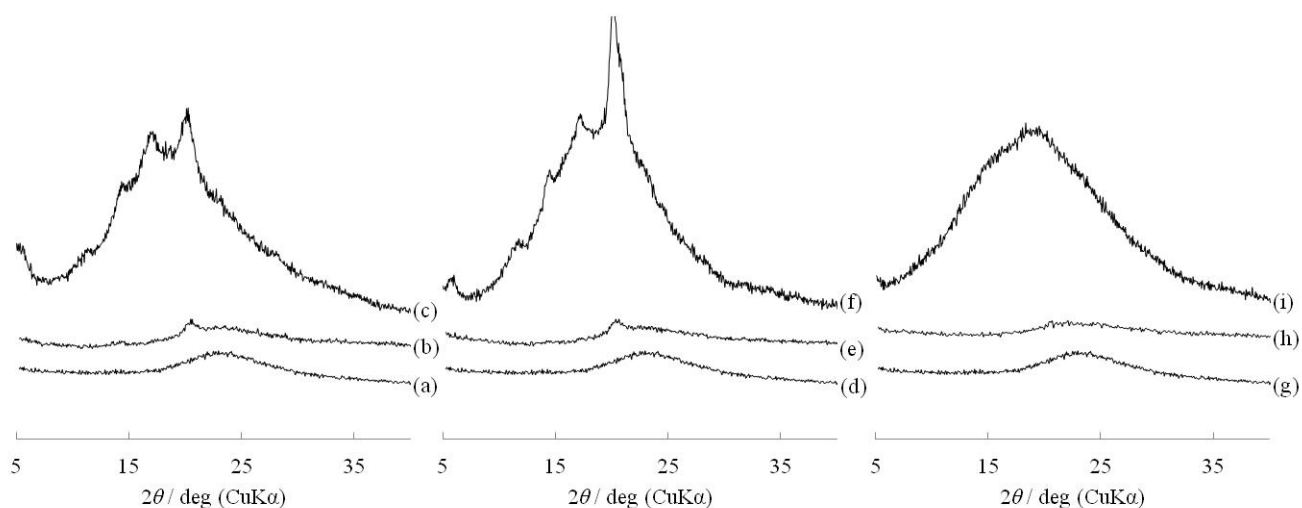


Fig. 3. XRD profiles of FG/BMIMCl gel (a), FG/BMIMCl composite material (b, Run 1, Table 1), FG powder (c), GG/BMIMCl gel (d), GG/BMIMCl composite material (e, Run 2, Table 1), GG powder (f), LBG/BMIMCl gel (g), LBG/BMIMCl composite material (h, Run 3, Table 1), and LBG powder (i).

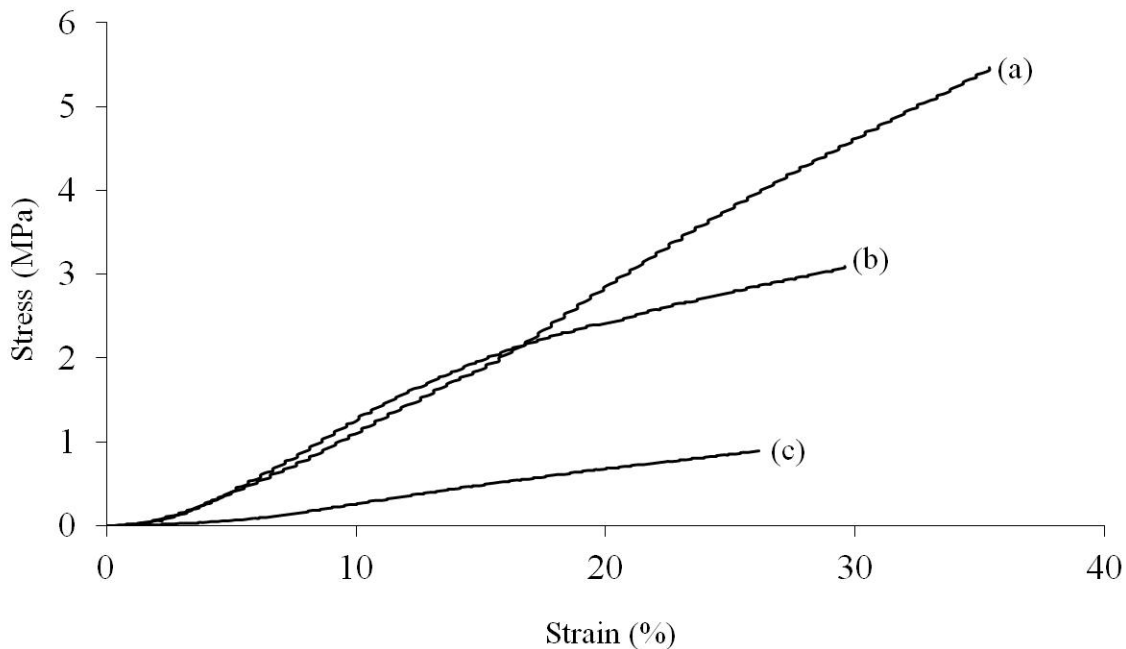


Fig. 4. Stress-strain curves of FG, GG, and LBG composite materials of Runs 1, 2, and 3 in Table 1 (a, b, and c, respectively) under compressive mode.

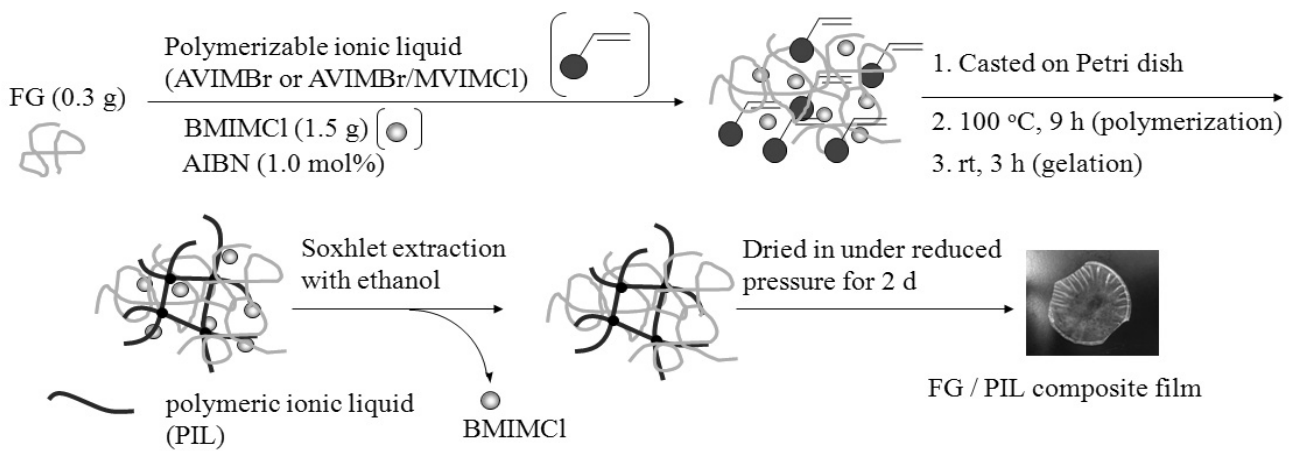


Fig. 5. Procedure for preparation of FG/PIL composite film.

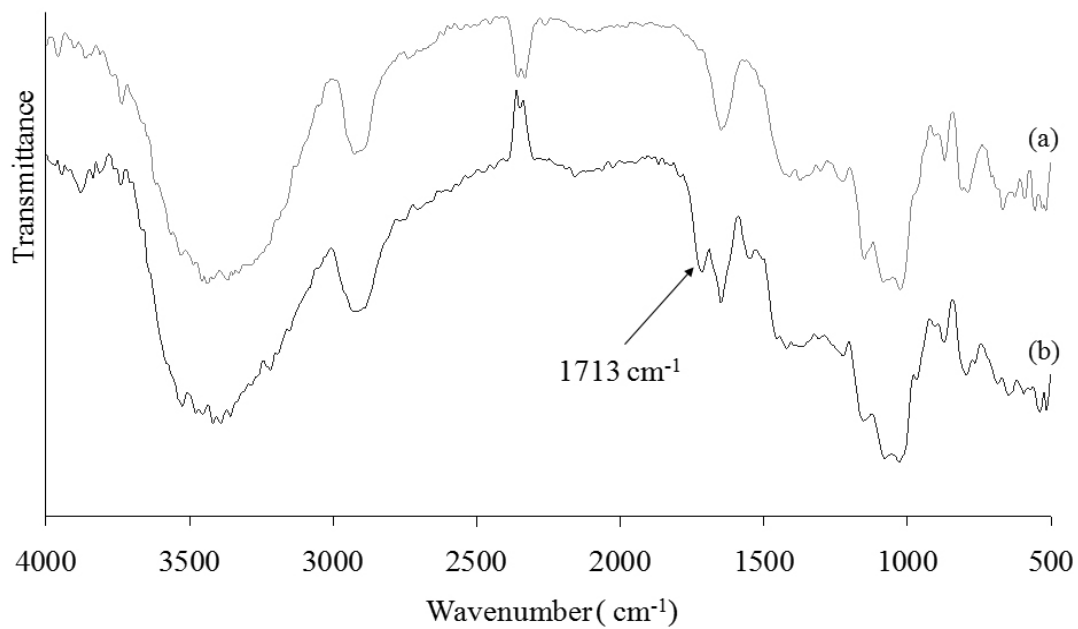


Fig. 6. IR spectra of FG powder (a) and FG/PAVIMBr composite film (b, Run 1, Table 2).

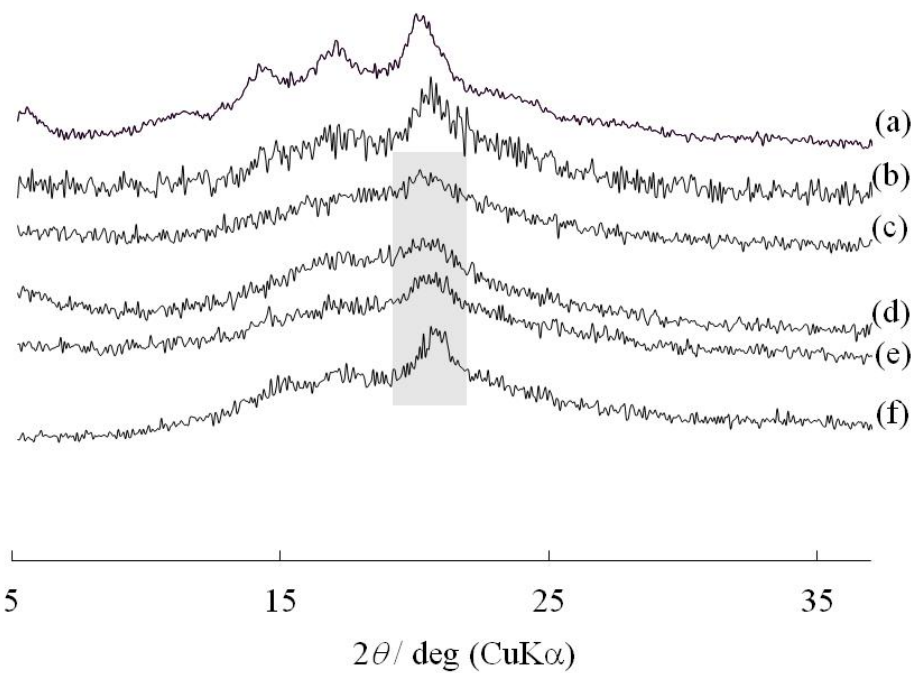


Fig. 7. XRD profiles of FG powder (a), FG film (b), and FG/PIL composite films of Runs 1, 2, 3, and 4 in Table 2 (c, d, e, f, respectively).

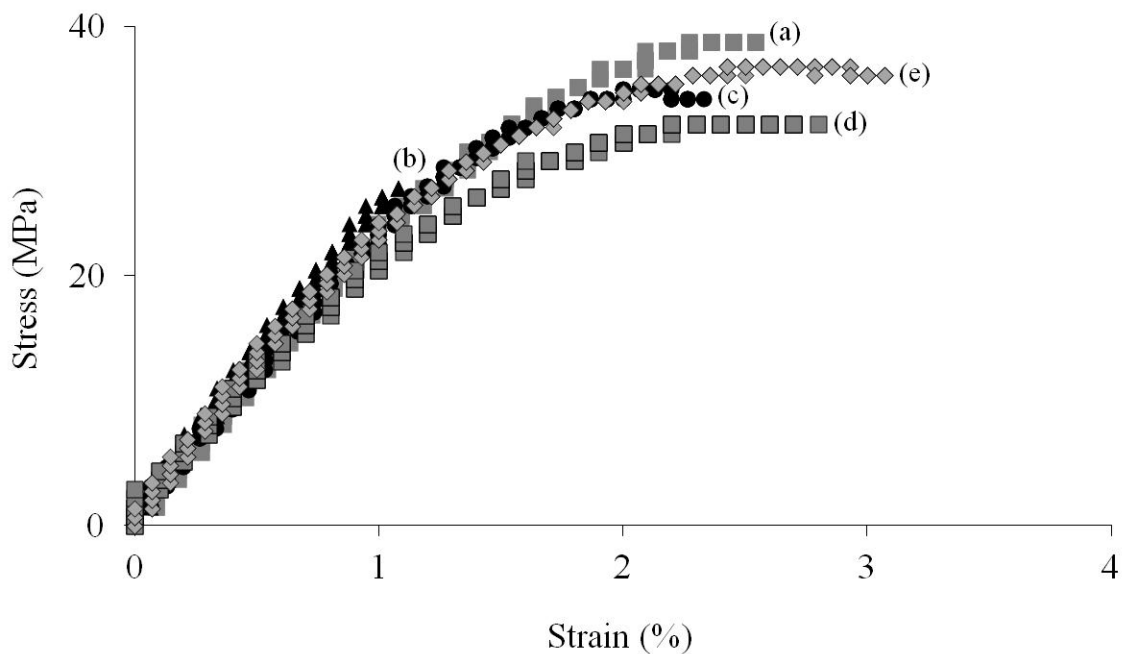


Fig. 8. Stress-strain curves of FG film (a) and FG/PIL composite films of Runs 1, 2, 3, and 4 (molar ratios of FG to PIL = 1 : 0.25, 1 : 0.14, 1 : 0.050, and 1 : 0.024) in Table 2 (b, c, d, e, respectively) under tensile mode.

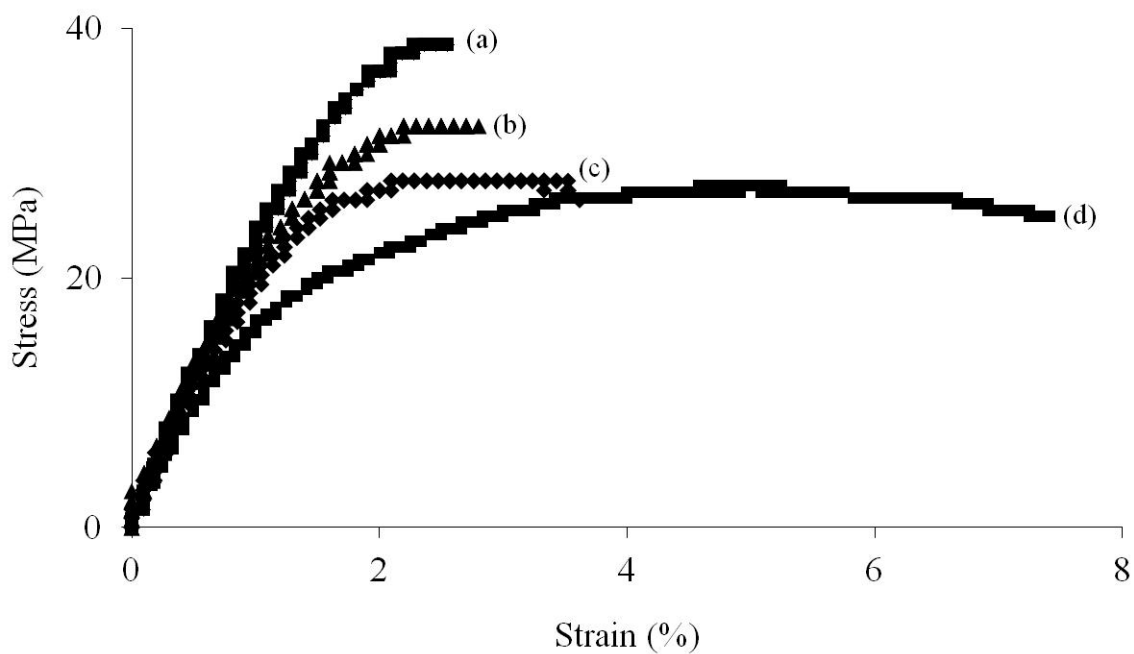


Fig. 9. Stress-strain curves of FG film (a) and FG/PIL composite films of Runs 3, 5, and 6 (molar ratios of FG to PIL = 1 : 0.050, 1 : 0.041, and 1 : 0.045) in Table 2 (b, c, d, respectively) under tensile mode.

Table 1 Preparation of galactomannan/BMIMCl composite materials

Run	Galactomannan	Volume of ethanol (mL)	Weight ratio in material
			Galactomannan : BMIMCl ^a : water ^b
1 ^c	FG	10	1 : 0.75 : 0.26
2 ^c	GG	12	1 : 0.72 : 0.19
3 ^c	LBG	6	1 : 0.76 : 0.11

^a Determined by weight change from gel to composite material.

^b Determined by TGA.

^c 20% (w/w) Galactomannan/BMIMCl gel (1.2 g) was immersed in ethanol for 5 d.

Table 2 Preparation of FG/PIL composite film

Run	Feed		Film	
	Weight ratio	Molar ratio	Weight ratio ^a	Molar ratio ^a
	FG : polymerizable ionic liquid	FG : AVIMBr : MVIMCl	FG : PIL	FG : AVIMBr : MVIMCl
1	1 : 0.50	1 : 0.54 : 0	1 : 0.23	1 : 0.25 : 0
2	1 : 0.25	1 : 0.27 : 0	1 : 0.13	1 : 0.14 : 0
3	1 : 0.13	1 : 0.14 : 0	1 : 0.046	1 : 0.050 : 0
4	1 : 0.071	1 : 0.076 : 0	1 : 0.022	1 : 0.024 : 0
5	1 : 0.36	1 : 0.22 : 0.22	1 : 0.035	1 : 0.022 : 0.019
6	1 : 0.18	1 : 0.021 : 0.22	1 : 0.033	1 : 0.0032 : 0.042

^a Determined by weight of Soxhlet extract and its ¹H NMR analysis.