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Green Composites from Ionic Liquid-Assisted Processing of Sustainable Resources: A Brief Overview

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Abstract

The massive use of synthetic, petroleum-based polymeric composites has disturbed the fragile environmental equilibrium of our planet. Composites made solely from polysaccharides can offer unique intrinsic properties such as renewability, biodegradability, easy availability, eco-friendliness, facile processing, flexibility, and exciting physico-mechanical characteristics. The development of green processing of lignocellulosic materials and bio-based polymers such as cellulose, starch, chitin, and chitosan, the most abundant biorenewable materials on earth, is urgent from the perspectives of both environmental protection and sustainability in materials industries. Recently, the enormous potential of ionic liquids (ILs) as an alternative to ecologically harmful conventional organic solvents has been well recognized. Presently, a wide range of pronounced approaches have been explored to further improve the performance of ionic liquid-based processing of polysaccharides for green composite manufacturing. This review presents recent technological developments in which the advantages of ionic liquids as a dissolution medium for polysaccharides for production of plethora of green composites have been gradually realized.

Keywords: ionic liquids, polysaccharides, biocomposites, biofilms, biofiber, plasticization, biopolymer, lignocellulose

1. Introduction

Ionic liquids (ILs) are termed as “liquid salts” and entirely composed of ions. Most of these materials are liquids at ambient or far below ambient temperature and have been widely used as a potential alternative to toxic, hazardous, volatile, and highly flammable organic solvents

[1–3]. Various unique and attractive physicochemical properties of ILs, such as remarkable thermal and chemical stability [4, 5], extremely low vapor pressure [6], high solvation interactions with inorganic and organic compounds [7], broad electrochemical window, and sharp ionic conductivity, make ILs promising candidates for the replacement of volatile organic compounds (VOCs) for polysaccharide dissolution and modification [8]. ILs have been accredited as “designer solvents” as their properties can be tailored by appropriate combinations of anions and cations [9]. The combination of all these unique properties has triggered the use of ILs as environmentally benign dissolution media for lignocellulose and various biopolymers for the manufacturing of different composite products [10].

The extensive use of petroleum-based polymers and composites and their existing anti-natural processing methods has disturbed the fragile environmental equilibrium and exhausting limited petroleum reserves [11]. A fierce public debate regarding the future of the earth and the need for transition toward a CO₂ neutral bio-based economy was emphasized in the UN conference on climate change [12]. To this end, polymeric carbohydrates, e.g., starch, cellulose, chitin, inulin, chitosan, lignin, etc., are natural polymers found abundantly in nature as structural building elements and could be potential alternatives for petroleum-based nonbiodegradable polymers [13].

Manufacturing of sustainable composites demands not only the assortment of renewable or biodegradable resources for their manufacturing but also the utilization of mild pretreatment methods that avoid the use and production of hazardous by products [14, 15]. The strong inter- and intramolecular hydrogen bonding and the highly recalcitrant nature of the biopolymers and lignocellulose offer a critical challenge to extend the novel applications of these materials in composite industries [16, 17]. In this regard, various pretreatment technologies were developed to reduce the recalcitrance of lignocellulosic polymers, which apply chemical or hydrothermal treatments after mechanical comminution. However, most of the current pretreatment methods exhibit several drawbacks. Some pretreatments have to be tailored to the specific biopolymer material and or may cause decomposition of biopolymer constituents to side products, which can severely hinder downstream processing of these materials [18]. Further, some pretreatment technologies require strong acids or bases and extreme conditions of temperatures and pressures for which special equipment are necessary. Therefore, the development of alternative processing techniques for widespread potential applications of bio-based polymeric carbohydrates and lignocellulosic agricultural waste for fabrication of biocomposite material still remains challenging [19, 20].

Ionic liquids have attracted numerous interest as a new and highly effective solvent for a plethora of biodegradable polymers and lignocellulosic materials. Thus, the technological utilization of such materials for biocomposite manufacturing could be enhanced remarkably by their dissolution in ILs rather than the use of conventional organic solvents [5, 21]. Various reports on dissolution of a wide variety of polysaccharides in ILs over the past 10–15 years suggested that by using ILs, efficient selective extraction of the components is also feasible [22]. The main purpose of the present work is to depict a short overview of the state of the art on the current role of ILs as dissolution medium to explore polysaccharide-based sustainable raw materials for engineered green materials applications.

2. Ionic liquids and their properties

Typical ionic liquids consist of an organic cation with an inorganic anion with melting point usually below 100°C, and they persist in liquid state for a wide temperature range (typically <400 °C). ILs could be capable of having a broad range of intermolecular interactions with biopolymers including hydrogen bonding, dispersive, ionic, and dipolar [23]. Some ILs are considered as highly polar solvents due to their excellent solvation properties. A number of techniques could be used to predict the polarity of ILs, such as solvatochromic dyes [24], partition [25], and fluorescence probe methods [26]. Generally, ILs are immiscible with most of the organic solvents like hexane and ether but miscible with most of the polar solvents, such as ketones, lower alcohols, and dichloromethane [27]. Furthermore, ILs can also be classified into two categories: hydrophilic and hydrophobic based on their solubility in water. Usually, ILs exhibit higher viscosities in comparison with ordinary molecular solvents which significantly impede the dissolution of polysaccharide materials in ILs. Different organic cosolvents such as dimethylformamide, dimethylsulfoxide, and 1, 3-dimethyl-2-imidazolidinone have been successfully applied to cope with higher viscosities [28].

3. A comparison of ILs with conventional organic solvents for polysaccharide dissolution and modification

In addition to the greener aspects and the excellent physicochemical properties, some important merits of the ILs over conventional organic solvents for bio-based polymers could be summarized as follows:

- Ionic liquids are tunable solvents, and hence they can be designed by appropriate selection of cations and anions for particular application which is generally not possible using conventional organic solvents [29].
- ILs can dissolve biopolymers under relatively mild conditions of temperature and time and at normal atmospheric pressure which offer remarkable benefit to ILs in comparison with other molecular solvents. The dissolution of cellulose at the temperature of 45 °C for 30 min in the alkyl-substituted imidazolium-based ILs was reported [30, 31].
- ILs have also been proved to be highly effective solvents for lignocellulosic materials under solid biomass loadings of as high as 50 % in a continuous pretreatment reactor [32]. Thus, the feasibility of high-throughput continuous pretreatment could enhance the potential for use of IL-based pretreatment as a cost-effective and highly invaluable technology for fabrication of sustainable composite materials from polysaccharide raw materials.

4. Ionic liquid-assisted processing of polysaccharides for biocomposites

Composites are engineered materials fabricated from two or more components usually referred as reinforcement and matrix. However, for the composites fabricated from polysac-

charide materials, the end-product properties could be fitted without strict distinction for reinforcement and matrix. The present section briefly describes the IL-based preparation of different composite products from polysaccharides or their sources. Keeping in view the ethical standards, the sources may include plant cell walls or some sort of living species.

4.1. Biofilms and biofibers

Although petroleum-based synthetic polymer products have offered excellent services to modern society, their extensive use has become a serious threat to the environment. Therefore, interest has been focused for the exploitation of natural biopolymers. Cellulose is a linear polysaccharide, which exhibited outstanding characteristics and broad range of applications as engineering material. Generally, it does not melt or dissolve in ordinary solvents, which makes its processing extremely difficult. Recently, the capabilities of ILs to dissolve cellulose have significantly impacted its processing for fabrication of biodegradable plastic films [9, 22].

Dissolution and regeneration of cellulosic biofilms from IL [bmim][Cl] by using cotton pulp as raw cellulose source was reported by Liu et al. [33]. It was observed that solubility of cellulose could reach up to 13 wt% at 90°C in 7 h. Takegawa et al. [34] fabricated the bicomponent biopolymer film with cellulose and chitin each dissolved separately in the ILs [amim][Br] and [bmim][Cl], respectively, at 100 °C. The biofilms became more elastic by decreasing the relative ratio of chitin to cellulose in the final product. Further, **Figure 1** depicts the scheme of successful dissolution and regeneration of the native skin collagen in IL [bmim][Cl] [35]. The possible mechanism of dissolution of collagen in IL was also suggested which was based mainly on the hydrogen bond breaking.

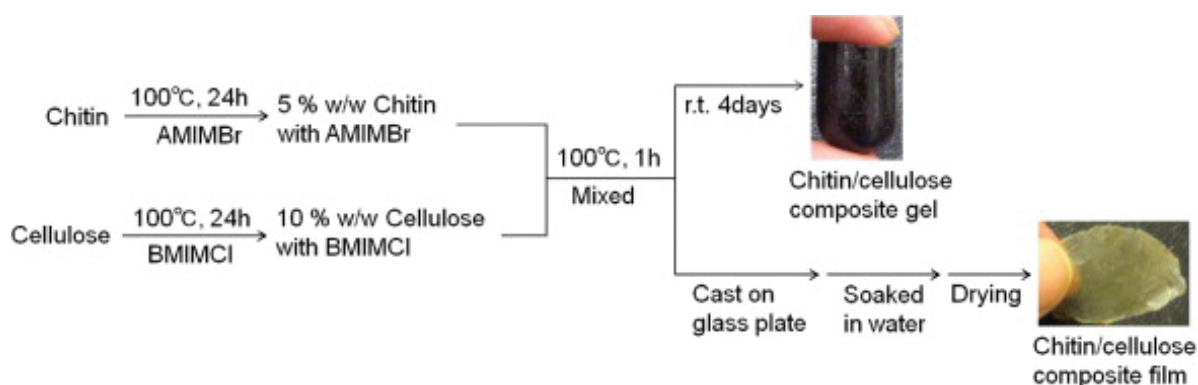


Figure 1. Schematic representation for preparation of collagen/cellulose composite materials using IL [bmim][Cl].

Electrospinning of polymer solution has turned up as a dominant technology for the preparation of fibrous materials with high specific surface area, controllable compositions, and high porosities for various applications. Particularly, the electrospinning of biopolymers for fabrication of biofiber has attracted numerous interests not only because of the renewable resources but also due to the advantageous characteristics of these biomacromolecules such

as biocompatibility, biodegradability, and significant specificity [5]. With the aim to replace commonly used noxious solvents, ILs have been investigated as new, nonvolatile, and nonflammable media for the electrospinning of biopolymers. A typical electrospinning apparatus based on IL-assisted dissolution and regeneration of cellulose is shown in **Figure 2**.

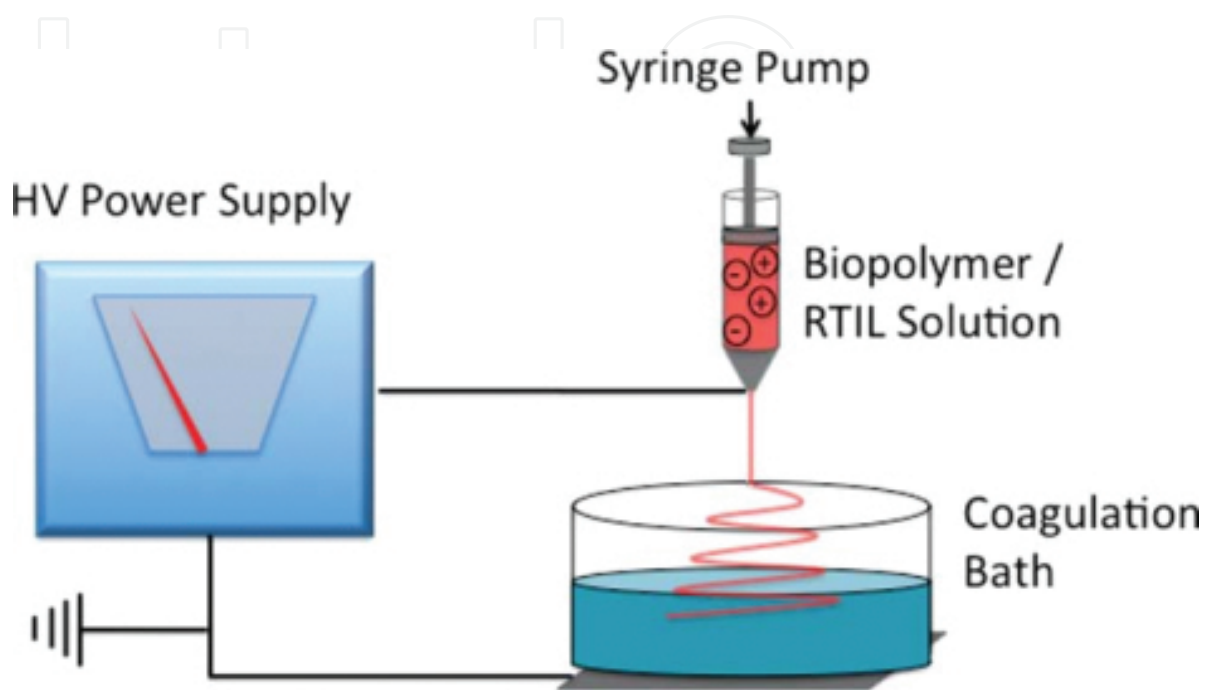


Figure 2. A typical electrospinning apparatus for IL-based processing of biofibers.

Polaskova et al. [36] dissolved raw pine wood in IL [emim][OAc] and utilized wet electrospinning technique to transform it into microfibers (1–4 μm). It was noted that 5% wood loading in IL was the most appropriate concentration for electrospinning, and further increase in the biomass loading up to 10% could complicate the process due to significant increase in the viscosity of solution. Similarly, electrospinning technology was utilized to obtain nonwoven nanoscale fibers from regenerated cellulose in the IL [bmim][Cl] [37]. The influence of the viscosity of biopolymer solution IL on the structure and size of the resulting biofiber was explored. Besides, Qin et al. [38] noted that high-molecular-weight and high purity chitin powder could be recovered after complete dissolution of raw crustacean shells in IL [emim][OAc] (**Figure 3**). The direct fabrication of chitin fibers and films from the extract solution was also reported. The conversion of cellulose and starch into fibrous material by making their homogeneous solution in IL [bmim][Cl] was described [39]. As explained in **Figure 4**, the fine linear material was obtained by raising the viscous biopolymer mixture with the help of a spatula and subsequently soaked into acetone to remove IL and then vacuum dried. The fabricated fiber showed the compatibilized fibrous structure of ca. 100–200 μm with higher thermal stability than that of gel made from the same biopolymers in [bmim][Cl]. Branched fibers with the size range of micro- to nanometer were extruded from 10% (w/w) of cellulose-heparin solution in the IL by using electrospinning technique [40].

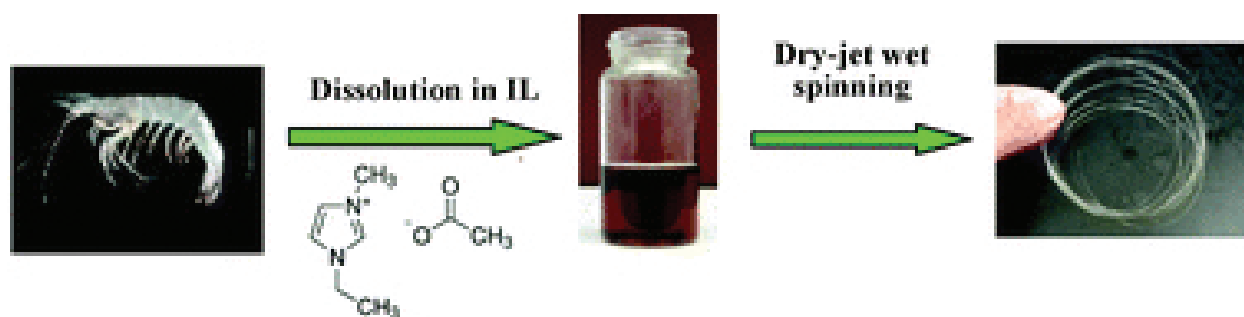


Figure 3. Preparation of chitin fiber from IL solution of crustacean shells.

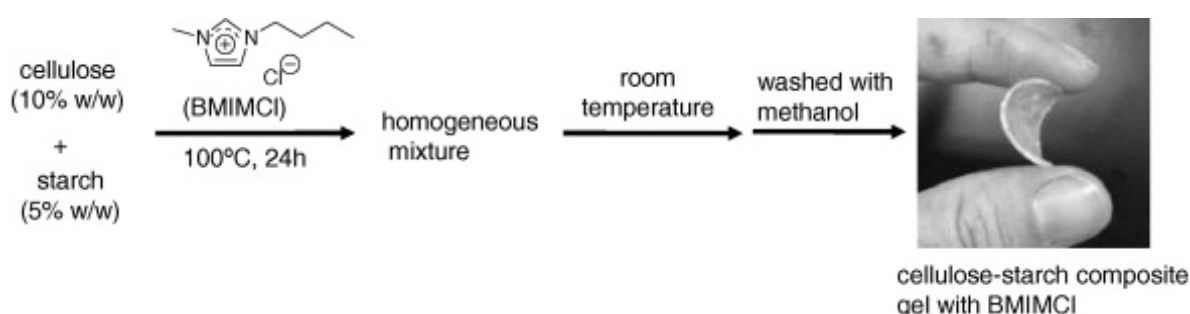


Figure 4. Cellulose-starch composite gel (a) and fiber (b).

4.2. Role of ionic liquids to provide alternative raw materials for wood composite industry

Although woody biomass has been the most promising raw material for production of composite panels, the excessive deforestation and at the same time increasing demand for wood composite panels has evoked a critical raw material issue in the wood composite industry [41]. Therefore, extensive research has been focused for the possibilities of using lignocellulosic residues of agro-industries as a direct substitute for wood fiber for the manufacturing of products such as fiberboard, particleboard, plywood, and so on [42]. Every year, about 184.6 million tons of lignocellulosic solid waste is being generated worldwide only from the oil palm industry [43]. The effective utilization of these lignocellulosic materials for manufacturing of industrial products would be highly helpful for development of agricultural-based economy in the rural areas.

Recently, we have reported the pretreatment of oil palm biomass with imidazolium-based ILs to produce cellulose-rich fiber (CRF) which was subsequently compounded with thermoplastic starch biopolymer binder to fabricate thermo-molded “green” composite board [44, 45]. Oil palm frond (OPF) samples were ground into particle size below 250 μm and pretreated with IL 1-butyl-3-methylimidazolium ([bmim][Cl]) or 1-ethyl-3-methylimidazolium diethyl phosphate ([emim][dep]) prior to mix with thermoplastic starch biopolymer. Finally, the compounded mixture was hot-pressed at 170°C and 25 MPa in a 30 ton Carver Laboratory Machine (CARVER, Inc., USA) [44].

During dissolution of lignocellulose particle in IL, some bonds between major biopolymer components are broken down leading to the swelling of plant cell wall. Separation of hydrogen and oxygen atoms occurs as a result of interaction of IL with lignocellulose which causes it to dissolve due to the disruption in the intermolecular and intramolecular hydrogen bonds. A fraction of hemicellulose and lignin is decreased in the pretreated material due to partial removal of these components. The results of lignocellulosic characterization of OPF samples before and after pretreatment showed that untreated OPF contained 26.4 %, 47.6 %, and 26 % of cellulose, hemicellulose, and lignin, respectively. This composition was changed to, respectively, 48%, 38%, 14% for pretreatment with IL [bmim][Cl], and 41% cellulose, 49% hemicellulose, and 10% lignin were achieved for IL [emim][dep]-treated fiber [44, 45].

Investigation of the thermal properties of lignocellulosic materials is important to explore their suitability for thermo-mechanical processing of biocomposite where the glass transition temperature of certain thermoplastic polymers is above 200°C. The thermal decomposition profiles obtained by TGA for untreated IL-treated OPF fibers are sketched in **Figure 5a**. These measurements clearly indicated that the thermal stability of the fiber was increased after pretreatment with IL. Indeed, treatment with both ILs [bmim][Cl] and [emim][dep] had a significant impact on the thermal decomposition profiles of the OPF fibers, raising the temperature at which the thermal degradation was initiated. This increase in the thermal stability of lignocellulosic fiber could be due to the removal of some constituents with lower thermal stability than cellulose. Besides, the thermal decomposition profiles of the composites fabricated from both treated and untreated fibers are provided in **Figure 5b**. It could be noted that the modifications occurred in the thermal properties of the fibers as a result of ILs pretreatment embarked a positive influence on the thermal properties of the fabricated composite as implied by their relatively higher thermal stability. It was observed that IL pretreatment increased the 10 % loss temperature (T_{10}) from 206°C to 225°C and 223°C for biocomposites manufactured from ILs [bmim][Cl] and [emim][dep] treated fibers, respectively. In fact, the improved thermal properties of the IL-treated biocomposites indicated that IL pretreatment was capable to increase the interfacial adhesion of the OPF fiber with polymer binder so that a higher amount of thermal energy was essential to break these fiber-binder linkages [44].

Furthermore, mechanical testing of the fabricated biocomposite panels before and after IL pretreatment in the flexural mode was also conducted to find the properties such as bending strength and bending modulus. **Figure 6** schematically depicts the details of the bending test. The obtained results plainly indicated that pretreatment of OPF fiber with both ILs [bmim][Cl] and [emim][dep] had a noteworthy impact on the bending strength and bending modulus. The bending strength of the untreated composite was found to be 4.9 MPa, which was increased to 8.3 and 8.9 MPa after the pretreatment with ILs [emim][dep] and [bmim][Cl], respectively. It could be possible that IL pretreatment reconstituted the lignocellulose structure by providing a more accessible interfacial area for thermoplastic binder flow during the thermo-molding step. This could lead to the improved fiber-matrix interfacial adhesion which consequently increased the bending properties [44].

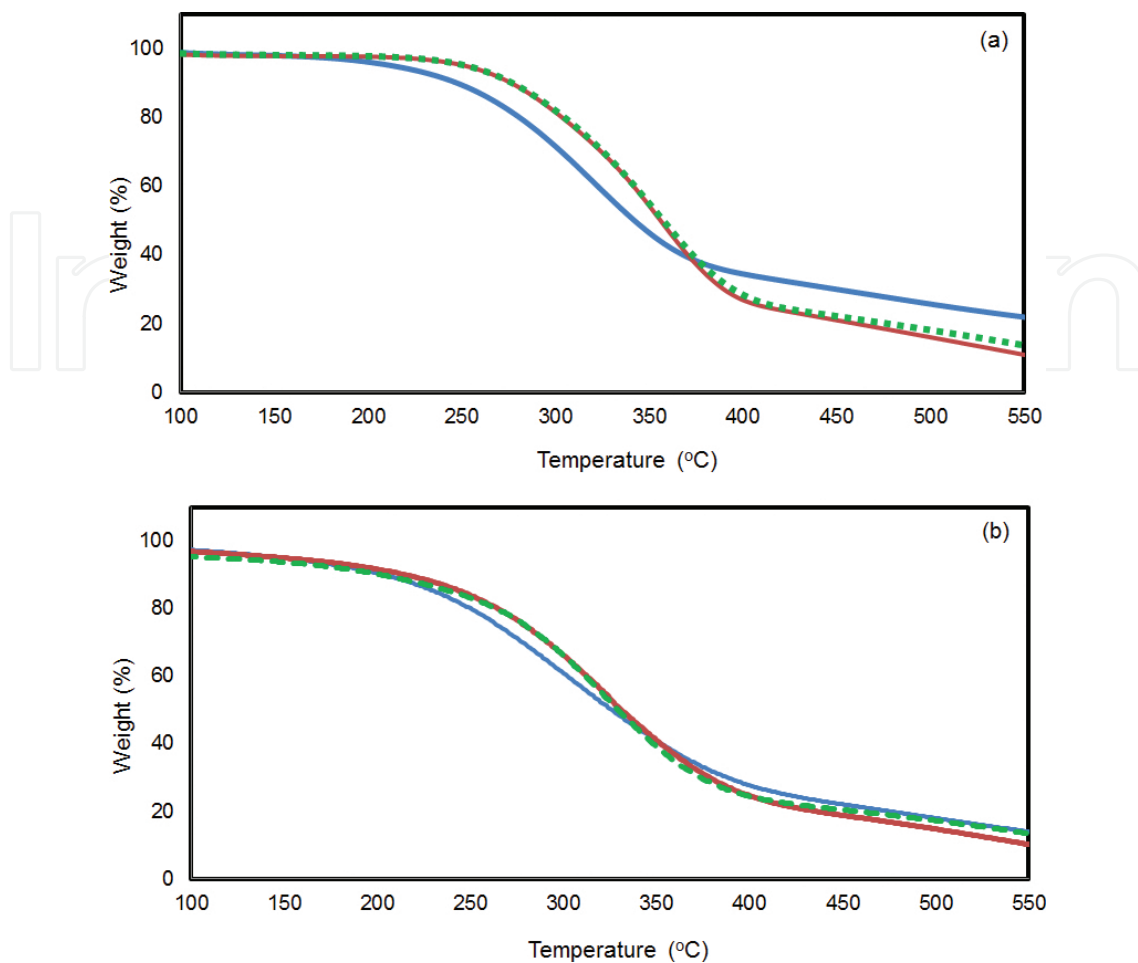


Figure 5. TGA profiles for untreated and IL-treated OPF fibers (a) and the fabricated composites (b).

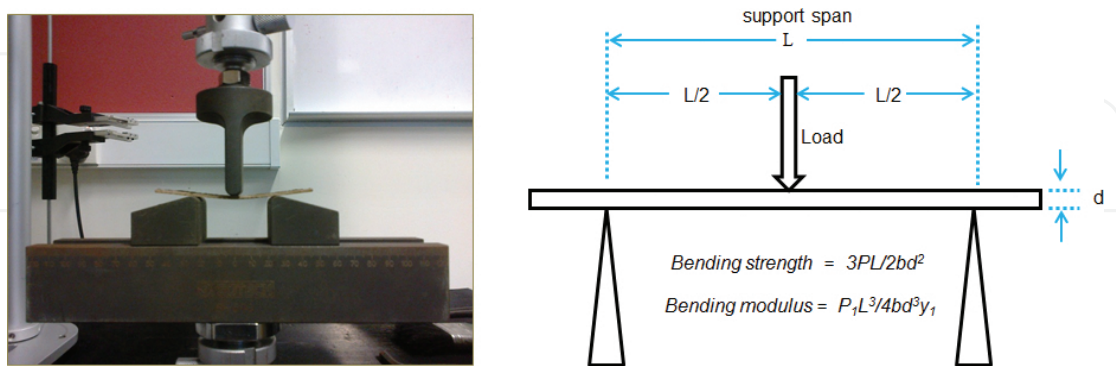


Figure 6. Schematics of the flexural test of composite board. P = peak load, P_1 = load at proportional limit, y_1 = deflection at proportional limit, and L , b , and d = length, width, and depth of specimen.

Thus, ionic liquid-treated composite panels exhibited superior mechanical and thermal properties because of partial removal of noncellulosic impurities from the lignocellulosic fiber after IL pretreatment. These studies demonstrated that IL-facilitated pretreatment technology

could be highly promising and green alternative route for efficient utilization of lignocellulosic biomass in the wood composite industries.

5. Future prospects

Processing of natural fiber reinforcements and a wide variety of biopolymer materials with IL for manufacturing of various biocomposite products would achieve commercial success only if the advantages of ILs outweigh its limitations, the most important of which is prices of ILs as compared to the value of the material processed [46]. In general, the design of a certain pretreatment process and selection of appropriate conditions for efficient and economical processing of biocomposite materials would need an adjustment between conflicting objectives which could be restrained by the use of multi-objective optimization tool in design and selection of particular pretreatment process [47].

Process modeling for the pretreatment operation could be highly beneficial to estimate thermal energy consumption for dissolution step and the associated cost so that the comparison with other conventional pretreatment technologies would be made. Additionally, molecular-level simulation could be helpful to better understand the interaction mechanism of ILs with biological molecules [48, 49]. Furthermore, the physicochemical characteristics of IL may also be tuned by optimized selection of both cation and anion, and the careful selection of processing conditions may allow the more efficient utilization of ILs in the production of green composite materials from lignocellulosic and biopolymer-based sustainable raw materials [50].

Table 1 provides a cost comparison for ILs with conventional organic solvents. Although the cost of ILs has always been one of the major issues, all ILs are not expensive, particularly, when considered at large scale [51]. Recently, the ILs derived from “low-cost” feedstock or from renewable raw materials may open new pathways for synthesis of cost-effective and competitive ILs for pretreatment of natural fibers and polymers for biocomposite manufacturing [52, 53].

	Pretreatment solvent	Price (\$/g)
Ionic liquid	[bmim]Cl	0.262
	[emim]Cl	0.325
	[bmim][OAc]	0.696
	[amim]Cl	6.250
Solvent	MeOH	0.041
	DMSO	0.453
	NMMO	2.010
	DMF	0.094
	H ₂ SO ₄	0.574

Table 1. Price comparison of some ILs used for lignocellulose dissolution with ordinary biomass pretreatment solvents.

The major aspects that should be focused for the future research work in IL-based processing of various biofibers and biopolymers could be summarized as:

- “Dry” pretreatment under high biomass loading
- Development of low-cost ILs
- Applicability to a wide range of raw materials
- Minimum dissolution time
- Optimization of IL recycling to reduce losses
- “Greenness” of ILs (environmental and health impact)

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