Journal of Cleaner Production 161 (2017) 257–266

Contents lists available at ScienceDirect

Journal of Cleaner Production

journal homepage: www.elsevier.com/locate/jclepro

Ionic liquids pretreatment for fabrication of agro-residue/thermoplastic starch based composites: A comparative study with other pretreatment technologies

Hamayoun Mahmood [a], Muhammad Moniruzzaman [a, **], Suzana Yusup [a, *], Nawshad Muhammad [b], Tanveer Iqbal [c], Hazizan Md. Akil [d]

[a] Department of Chemical Engineering, Universiti Teknologi PETRONAS, 32610, Bandar Seri Iskandar, Perak Darul Ridzuan, Malaysia
[b] Interdisciplinary Research Center in Biomedical Materials, COMSATS Institute of Information Technology, Lahore, Pakistan
[c] Department of Chemical Polymer & Composite Material Engineering, University of Engineering & Technology, KSK Campus, Lahore, Pakistan
[d] School of Materials and Mineral Resources Engineering, Universiti Sains Malaysia, Nibong Tebal, Penang, Malaysia

ARTICLE INFO

Article history:
Received 12 October 2016
Received in revised form
15 May 2017
Accepted 20 May 2017
Available online 23 May 2017

Keywords:
Lignocellulosic waste
Ionic liquid pretreatment
Biocomposite board
Sustainable composite
Thermoplastic starch
Pretreatment energy consumption

ABSTRACT

Ionic liquids (ILs) pretreatment has emerged as a promising technology toward environmentally benign conversion of lignocellulosic residues into high value cellulosic fiber as sustainable raw material for biocomposite fabrication. This study presents a comparison of ILs-assisted pretreatment of oil palm fronds (OPF) fiber with dilute acid, alkaline, and hot compressed water pretreatments on the mechanical and thermal properties of their fabricated thermo-molded biocomposites with thermoplastic starch as a biopolymer binder. A comparison of energy consumption for ILs pretreatment with other pretreatment methods was also performed and the comparative impact of ILs pretreatment on OPF fiber was investigated by lignocellulosic composition, crystallinity and thermal stability analysis for untreated and all pretreated fibers. Results indicate that ILs pretreatment is superior in terms of delignification of OPF and produces cellulose rich fiber (CRF) with 48–50% reduced crystallinity as compared to those of acidic, alkaline, and hot water pretreated fibers. However, the flexural strength of the IL [emim][dep] treated composite (13.8 MPa) was significantly improved over that of untreated composite with value of 5.3 MPa, but was slightly higher than acidic and hot water pretreatments which were 13.5 MPa and 10.8 MPa, respectively. ILs pretreatment consumed about 0.5–2.0 folds more energy per kg of OPF residue as compared to other methods. In the premises of the present findings, we believe that ILs-based pretreatment could be a new, clean and promising alternative processing approach for conversion of a wide variety of agro-based lignocellulosic waste materials into cellulose-rich fibers for manufacturing of engineered biocomposite panels.

1. Introduction

The quest for sustainable and alternative raw material resources for the composite industry is of critical importance with ever-increasing demand for plastics together with the growing environmental and economic concerns such as the accumulation of atmospheric CO_2 and the high prices of oil, respectively (Väisänen et al., 2017). Natural fibers derived from agricultural residues benefit the environment as they can be biodegradable, renewable, recyclable, compostable, and abate greenhouse gas emissions (Spiridon et al., 2016). Biocomposite panels made from lignocellulosic residues exhibit lower environmental impacts regarding the consumption of non-renewable resources as compared to those manufactured from wood particles mainly due to transportation distance as implied by a comparative life cycle assessment study (dos Santos et al., 2014).

However, use of lignocellulosic fibers in composite manufacturing is not a problem-free alternative due to certain shortfalls in their properties. During the manufacturing of lignocellulosic composites, fiber-binder interfacial conglutination is the most critical factor which identifies the mechanical properties of the composites. The presence of non-cellulosic impurities over the

* Corresponding author.
** Corresponding author.
E-mail addresses: m.moniruzzaman@utp.edu.my (M. Moniruzzaman), drsuzana_yusuf@utp.edu.my (S. Yusup).

http://dx.doi.org/10.1016/j.jclepro.2017.05.110
0959-6526/

fiber surface such as lignin, pectin, hemicellulose etc., promotes weak fiber-polymer interfacial bonding throughout the interface of composite and imparts poor mechanical properties (Kalia et al., 2009). Moreover, lower resistance to thermal degradation of lignocellulosic materials is another critical issue during the development of biocomposites in both manufacturing and materials in service. The poor thermal stability of non-cellulosic constituents in lignocellulose is one of the major technological drawbacks of biocomposites which impedes their processing and practical "window-use" (Vilaplana et al., 2010). Numerous pretreatments have been developed to address the aforementioned issues that can eliminate non-cellulosic constituents and enhance the fiber dispersibility in and adhesion with polymeric phase during molding process. Presently, chemical (e.g., dilute acid and alkaline delignification) (Hou et al., 2014; Li et al., 2010), physical (e.g., mechanical comminution) (Lin et al., 2010), hydrothermal (e.g., steam explosion and hot water extraction) (Baskaran et al., 2013; Jumhuri et al., 2014), and biological methods (Financie et al., 2016) have been studied for extraction of cellulosic fiber at laboratory and pilot-plant scales. Most of these technologies need extreme temperature and pressure conditions as well as highly concentrated chemicals for the fiber cooking process. Sulfite and sulfates pulping methods provoke severe environmental hazards. Although biological reactions can be conducted under mild conditions, this approach requires very long pretreatment time mainly because of the poor solubility of lignin and the difficulties in enzyme accessibility to the solid substrate (Kalia et al., 2009). Development of a new and environmentally benign pretreatment method for efficient conversion of lignocellulosic residues into cellulose-rich fiber remains challenging.

Ionic liquids (ILs) have attracted augmented attention as a new class of 'green solvents' for the dissolution and homogeneous processing of wide variety of lignocellulosic materials for biocomposite manufacturing under relatively mild operating conditions (Mahmood et al., 2017). Ionic liquids represent thermally stable, nonvolatile, nonflammable, and tunable designer solvents that can replace highly volatile organic solvents (VOSs) in a broad range of applications (Crowhurst et al., 2003). Shibata et al. (2013) prepared the thermo-molded biocomposite after pretreatment of hinoki lumber with IL [bmim][Cl] at 100° C and an increase in tensile modulus of the biocomposite after IL pretreatment was reported. Two imidazolium-based ILs ([bmim][Cl] and [dmim][$MeSO_4$]) were used to dissolve various lignocellulosic materials to form composite films. Cellulose contents in the regenerated films were mainly responsible to enhance the flexibility of films especially at low lignin content (Abdulkhani et al., 2013). A recent report (Chen et al., 2015) describes the novel use of ILs in production of wood-plastic composites. Ball-milled mulberry wood was first kneaded in the IL [bmim][Cl] and [emim][OAc] with the help of co-solvent DMSO. Manufacturing of composite samples was achieved by injection-molding after the structural destruction of the wood cell wall in the presence of ILs. Ionic liquids pretreatment enhanced the thermal flowability and mechanical properties of the fabricated biocomposites. Fabrication of lignocellulosic based thermo-molded biocomposite board with improved mechanical properties after pretreatment and regeneration of oil palm fiber with imidazolium based ILs prior to compounding with polymer binder has also been reported (Mahmood et al., 2016).

Several research articles describe the efficacy of ILs pretreatment of lignocellulosic biomass by comparing it with leading pretreatment technologies in terms of cellulose recovery and subsequent enzymatic saccharification to produce biofuels (Uppugundla et al., 2014). However, to date, no report has been published that compares the impact of ILs pretreatment of lignocellulosic fiber with existing pretreatment methods in terms of different properties of the fabricated fiber-reinforced polymeric composite. Comparison of different pretreatment methods by investigating the impact of pretreatment on final product properties at commercially viable operating conditions helps to focus the attention on improved process development and contributes to minimize the cost of biocomposite production. The palm oil industry is the backbone of the Malaysia's economic growth and this industry is estimated to produce 100 Mt dry weight of oil palm lignocellulosic waste per year (Umar et al., 2013). In the present study, the performance of two immidazolium based ILs having chloride and ethylphosphate anions has been compared with leading pretreatment methods including dilute acid, alkaline and hot-compressed water for pretreatment of oil palm frond (OPF) fiber prior to fabricate thermo-molded biocomposite board with thermoplastic starch as a binder polymer. In addition, the lignocellulosic characterization, crystallinity and thermal properties of untreated and all treated fiber samples were investigated and compared in detail. A comparison for impact of ILs pretreatment on the mechanical and thermal properties of the fabricated biocomposites with respect to acidic, alkaline, and hot water pretreatments was conducted.

2. Materials and methods

OPF residue samples (70–80 cm strands) were collected from nearby plantation around Universiti Teknologi PETRONAS, Bandar Seri Iskandar, Perak, Malaysia. Ionic liquids 1-ethyl-3-methylimidazolium diethylphosphate [emim][dep] and 1-butyl-3-methylimidazolium chloride [bmim][Cl] were acquired from Sigma-Aldrich, Germany. Commercial corn starch (moisture contents 12%), plasticizing agent glycerol (99+%), co-solvent dimethyl sulfoxide (DMSO) and other chemicals were received from R & M Marketing, Essex, U.K. All reagents were of analytical grade and utilized as received.

2.1. Pretreatment of OPF fiber

Oil palm frond samples were cut into 3–4 cm chips by a knife (Supplementary Information Fig. S1) , grinded in a Retch SM 100-series grinder, and then subjected to sieve analysis to ensure particle size in the range of 250–300 μm. Pretreatment of OPF fiber with ILs and other solvents was conducted in a small-scale stainless-steel reactor (Premex Reactor AG, Switzerland) fitted with an electrically heating jacket in a double-shell design and a magnetic-driven variable-speed stirrer as shown in Fig. 1. In a typical experiment, IL ([bmim][Cl] or [emim][dep]) and co-solvent DMSO were mixed in a ratio of 1:1 at 90° C for 30 min with vigorous stirring to get a homogeneous phase. Oven-dried OPF fiber was then added into IL solvent with 15% biomass concentration, and pretreatment was performed at 90° C and 600 rpm for 3 h. After completion, a precipitating solvent comprising an equal volume of acetone/water mixture (10 mL/1 g IL) was instantly poured into the pretreated mixture and stirred vigorously (Sun et al., 2009). The regenerated cellulose-rich fiber was precipitated out by decantation, separated, and washed with distilled water several times to ensure complete removal of residual IL. Subsequently, rotary evaporator was used to remove precipitating solvent from supernatant phase to get the IL/DMSO/lignin-rich phase. Finally, IL/DMSO was separated from lignin by using vacuum filtration. Besides, dilute acid, alkaline, and hot compressed water pretreatments were performed under optimized conditions (Yu et al., 2014). Briefly, a 25 g of dried OPF fiber was added into 160 mL of dilute acid solution of H_2SO_4 (1.82% w/w) in the autoclave reactor and the pretreatment was proceeded at 140° C for 20 min with 400 rpm. Alkaline pretreatment was conducted with dilute NaOH solution (2% w/w) in the autoclave reactor