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High-solid-loading ionic-liquid pretreatment of lignocellulosic particles for biocomposites

Hamayoun Mahmood, Muhammad Moniruzzaman, Suzana Yusup, and Hazizan M. Akil

A novel and environmentally friendly pretreatment approach is used for the production of cellulose-rich fibers as reinforcements for thermoplastic-starch-based bioplastics.

In the last 25 years, the use of lignocellulosic biomass-based composite materials, in place of petro-materials, has received an increasing amount of attention for a number of reasons, i.e., growing environmental awareness, concerns for environmental sustainability, the increasing global waste problem, and the depletion of fossil fuels. Indeed, the research paradigm in composite production and consumption has been shifting toward the use of natural polysaccharide-based raw materials.[1] However, there are still some associated problems with such biobased composites that need to be addressed. For instance, it has previously been demonstrated that biobased composites exhibit limited thermal stability at the required temperatures (i.e., for processing and service life). Low-molecular-weight volatiles may thus be generated from these materials (because of the degradation of either the lignocellulosic component or the polymeric binder), which may in turn significantly impede the suitability of these materials for indoor applications.[2]

As part of the production of engineered composite panels, effective pretreatment of the lignocellulosic biomass is therefore an important (and challenging) task. With the aim of achieving sustainable composites, ionic liquids (ILs)—because of their excellent solvation powers for a variety of lignocellulosic materials—are thought to be a good option for widening the range of raw materials that can be used in such composites. ILs, which consist entirely of ions, melt below 100°C and are a new class of non-volatile, thermally stable, nonflammable, and tunable designer solvents that have high polarities. There is thus a great potential for ILs to replace highly volatile organic solvents in a broad range of applications.[3,4] Furthermore, the concept of a high-solid-loading (i.e., biomass/IL ratio of 1) pretreatment for lignocellulosic biomass has recently been shown to have advantages over lower-solid loading. Such advantages include improved process efficiency, reduction in capital cost, lower energy consumption, and being more environmentally friendly (because less wastewater is generated when the residual IL is washed out from the pretreated material).[5]

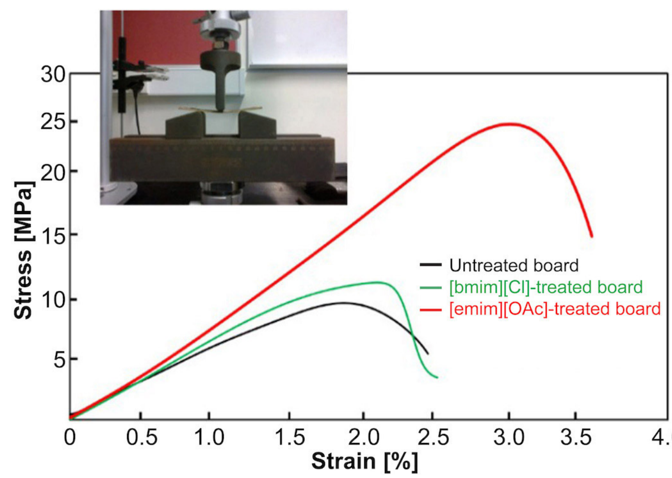

Figure 1. Stress–strain analysis (experimental setup is shown in the inset) of the untreated and the ionic-liquid-treated composite panels. Results are shown for boards fabricated with organic palm frond particles pretreated with either 1-butyl-3-methylimidazolium chloride, [bmim][Cl], or 1-ethyl-3-methylimidazolium acetate, [emim][OAc].

In our work,[6] we have therefore explored the feasibility of using an IL-assisted pretreatment technique for lignocellulosic biomass in the manufacturing of thermomolded composite panels. In particular, we have studied the effect of a high-biomass-loading IL pretreatment of a thermomolded biocomposite board that we fabricated from oil palm frond (OPF), and from thermoplastic starch (TPS) as the biopolymer matrix. We used a variety of techniques (e.g., scanning electron microscopy, x-ray diffraction, thermogravimetric analysis, and chemical composition analysis) to characterize the properties of our samples made with both our IL-treated and untreated OPF particles.

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In our fabrication methodology, we first pretreated the OPF particles with ILs—1-butyl-3-methylimidazolium chloride, [bmim][Cl], and 1-ethyl-3-methylimidazolium acetate, [emim][OAc]—in a stainless steel stirred-type vessel at 90°C.[6] We then recovered the ILs by rinsing with an acetone-water mixture. To preserve the biodegradability of the product, we also prepared a biobased TPS polymer as the binder material. For this purpose, we plasticized commercial cornstarch by mixing it with 30wt% glycerol and 20wt% water, at a temperature range of 70–80°C.[7] Lastly, we compounded the untreated or the IL-treated OPF particles with the polymer binder (at a 1:1 ratio) and used a compression molding technique to manufacture the composite plates.

Our results indicate that the composite samples made with the IL-pretreated OPF fibers possess better properties than those of the untreated composites. For example, we find that the flexural properties of the composite panels were strongly affected by the pretreatment of the OPF particles, i.e., the flexural strength increased from 10MPa for the untreated composite to 12 and 25MPa for the [bmim][Cl]-treated and [emim][OAc]-treated composites, respectively (see Figure 1). These results are important because the flexural properties of lignocellulosic-fiber-based composites are one of their most beneficial engineering properties for many applications (e.g., when biocomposites are used as structural or load-bearing components in the construction and furniture industries).

The results of our thermal stability analysis (see Figure 2) indicate that the peak temperature (which corresponds to the fastest degradation rate) for the untreated composite was 310°C. This increased to 320 and 321.5°C for the [bmim][Cl]-treated and [emim][OAc]-treated composites, respectively. We suggest that the high-solid-loading IL pretreatment caused restructuring of the lignocellulosic particles by changing its chemical composition and thus providing a more accessible surface area for polymer–binder interactions during the thermal molding step.[3]

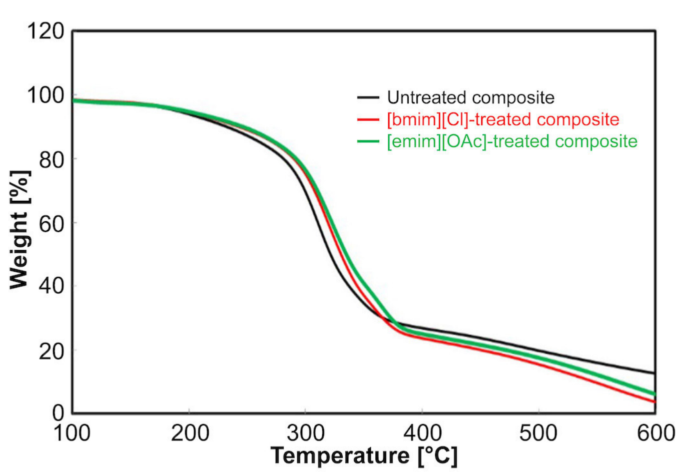

Figure 2. Thermal stability analysis of the untreated and IL-treated composite panels.

In summary, we have investigated the effect of a high-solid-loading IL pretreatment for oil palm frond fibers used in thermoplastic starch composite boards. Our mechanical and thermal analysis results clearly demonstrate that IL-assisted pretreatment is an effective and green approach for the production of cellulose-rich fibers as reinforcements in thermoplastic biopolymers. Although ILs are starting to find their way into a wide variety of industrial applications, several aspects of their use need to be explored further (e.g., their optimized structure, loading, recycling, and co-products).[8] Indeed, our future research will be directed toward the screening of optimized ILs for selective removal of hemicellulose or lignin from biomass feedstock, to achieve an efficient reinforcing effect during biocomposite manufacturing. Furthermore, the selection of appropriate pretreatment conditions is of prime importance from environmental and economic perspectives. IL pretreatment of lignocellulosic residues for commercial-scale manufacturing of composite products is only feasible if its advantages outweigh its limitations. In particular, we will therefore explore the critical issues of recycling and re-use of ILs. We also plan to investigate how different biomass/IL ratios, and the use of co-solvents, affect our pretreatment process.

Author Information

Hamayoun Mahmood, Muhammad Moniruzzaman, and Suzana Yusup
Deparment of Chemical Engineering
Universiti Teknologi PETRONAS
Ipoh, Malaysia

Muhammad Moniruzzaman received his MSc and PhD in biochemical engineering from Kanazawa University, Japan. In 2007, he moved to Kyushu University as a Japan Society for the Promotion of Science postdoctoral fellow. His current research interests focus on the application of ionic liquids as alternative 'green' solvents for the design of bioconversion processes.

Hazizan M. Akil
School of Materials and Minerals Resources Engineering
Universiti Sains Malaysia
Nibong Tebel, Malaysia

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