

IONIC LIQUID-MEDIATED SYNTHESIS OF CELLULOSE/MONTMORILLONITE NANOCOMPOSITE

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Cellulose regeneration is a facile approach to produce biopolymer/clay composites with improved physical properties. In this study, a cellulose/montmorillonite nanocomposite was prepared using a novel ionic liquid, 1-butyl-3-ethylimidazolium bromide ([BEIm]Br). Montmorillonite clay was modified using cetyltrimethylammonium bromide (CTAB) and was characterized using X-ray diffraction (XRD) analysis, which revealed the substitution of cetyltrimethylammonium (CTA⁺) cations in the clay gallery. The exfoliation-adsorption method was used to prepare the cellulose/montmorillonite nanocomposites, and scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS) and X-ray diffraction (XRD) analyses confirmed the successful dispersion of cellulose into the clay matrix. Thermogravimetric analysis (TGA) further revealed the optimum thermal stability of the nanocomposite was achieved with 4 wt% montmorillonite, which provided a white cellulose/montmorillonite nanocomposite.

Keywords: cellulose, clay, nanocomposite, ionic liquid, thermal property

INTRODUCTION

The impetus to utilize available bioresources has prompted the design, development, and use of bio-based polymer composites for a wide array of applications. The continuous production of synthetic polymers is harmful to the environment because of the generation of persistent hazardous wastes.¹ The use of polymers from renewable sources and the development of a method that is environmentally friendly have been subjects of recent research interest. Cellulose, being the most abundant polymer on earth, is an interesting candidate for such developments. Nanocomposite materials render polymers from renewable sources to acquire additional, improved properties that can often match, if not surpass, the properties or performance of mainstream materials. Cellulose, for example, can have improved thermal and mechanical properties upon the addition of nanoparticles as fillers.²⁻³

Cellulose is a linear homopolysaccharide, consisting of β -D-glucopyranose as its monomer unit, and is the structural component of the cell wall of plants. Cellulose can be derived from plant fiber, wood pulp, tunicate, algae and

bacteria.⁴ The industrial sources of cellulose are wood pulp (40-50% cellulose) and cotton (90% cellulose). Cellulose and cellulose-based composite materials have attractive properties, such as biodegradability, renewability, biocompatibility, low toxicity and low cost.²

The characteristic properties of the polymer matrix, such as cellulose, can be improved through the addition of nanomaterials as fillers. Nanomaterials that can serve as reinforcement fillers can be metal and metal oxide nanoparticles, clay nanoparticles, carbon nanofibers, carbon black nanoparticles, and carbon nanotubes.⁵ Layered silicate materials, such as montmorillonite, have been widely used as clay fillers in preparing nanocomposites. There have been a number of studies on the application of clay materials due to the cost-effectiveness of clay, the wide range of applicability to polymers, the well-established clay intercalation chemistry, and the performance enhancement of the end-product.⁶ Clay fillers are usually incorporated within the polymer matrix through the exfoliation-adsorption technique.⁷⁻⁹ Here, the clay

and the polymer are dispersed in the solvent. A commercially used solvent for the preparation of cellulose composites is N-methyl-morpholine-N-oxide (NMMO).⁴ However, the use of this solvent has also its drawbacks, because of its innate toxicity, difficulty in recycling, limited dissolving capability, high cost, and the side reaction of the solvent itself, among others.^{2,10-11}

To address these concerns, new methods have been reported using other ionic liquids. Ionic liquids (or room temperature molten salts) are ionic systems that take the liquid state at room temperature. They are usually composed of molten salts of nitrogen in organic cations and inorganic anions, and represent a promising new class of solvents, especially for cellulose dissolution and regeneration.¹⁰ The application of ionic liquids, particularly 1-butyl-3-methylimidazolium chloride ([BMIm]Cl), as a dissolving medium for cellulose regeneration was first reported by Swatloski *et al.*^{6,10-14} With this discovery, ionic liquids are now used as solvents in the preparation of cellulose composite materials. The advantage of ionic liquids, over the organic and other inorganic solvent systems, aside from being eco-friendly solvents, are their good chemical and thermal stability, low flammability and melting point, and ease of recycling.^{2,11}

The use of a novel ionic liquid is promising in the preparation of cellulose and cellulose-based nanocomposite materials. To the best of our knowledge, no study has been reported to utilize 1-butyl-3-ethylimidazolium bromide ([BEIm]Br) as dissolving medium for the preparation of cellulose nanocomposites. The novelty of the study consists in presenting a facile approach in cellulose/montmorillonite nanocomposite

synthesis, mediated by 1-butyl-3-ethylimidazolium bromide (ionic liquid).

The synthesized [BEIm]Br was used as solvent for the preparation of a cellulose/montmorillonite nanocomposite. The morphology of the regenerated cellulose and cellulose/montmorillonite nanocomposite was evaluated using scanning electron microscopy (SEM), X-ray diffraction (XRD), and energy dispersive X-ray spectroscopy (EDS) analyses. In addition, the thermogravimetric properties of both the pristine cellulose and the cellulose/montmorillonite nanocomposites were also evaluated.

EXPERIMENTAL

Materials

Montmorillonite K10 powder (Sigma, A.R.) hexadecyltrimethylammonium bromide (Sigma, A.R., ≥98%) powder, and α-cellulose powder (Sigma, A.R.) were purchased from Belman, Philippines. 1-butylimidazole (Sigma, A.R., >98%) and 1-bromoethane (Sigma, A.R., >98%) were also purchased and used without further purification.

Synthesis of 1-butyl-3-ethylimidazolium bromide

The synthesis of 1-butyl-3-ethylimidazolium bromide ([BEIm]Br) was performed according to a previous study.¹⁵ In a 250 mL round bottom flask, 1 equivalent of 1-butylimidazole (1) and 1.25 equivalent of 1-bromoethane (2) with 30 mL of ethyl acetate were refluxed for 4 h at 90 °C. Two layers were formed after the mixture was cooled down to room temperature. The mixture was washed three times with 15 mL of ethyl acetate and the organic layer was removed from the mixture. Ethyl acetate was completely removed through freeze-drying and a viscous and light yellow-tinted product was isolated.

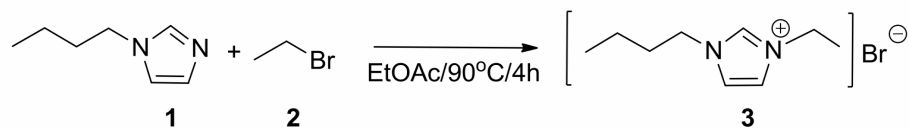


Figure 1: Synthesis of 1-butyl-3-ethylimidazolium bromide (3)

Modification of montmorillonite clay

Modification of montmorillonite clay (MMT) with quaternary alkylammonium salts was also done according to a previously published study.¹⁶ An amount of 2.0 g of montmorillonite was dispersed initially in a 500 mL Erlenmeyer flask and was stirred for 2 h. 100 mL of 0.5M of aqueous cetyltrimethylammonium bromide (CTAB) solution was added to the clay dispersion and was magnetically

stirred for 48 h at room temperature. The centrifugate was recovered through four cycles of washing and centrifugation using distilled water at 3500 rpm for 3 min each. The recovered clay was dried and was ground into powder. X-ray diffraction spectroscopy was used to characterize and evaluate both the pristine and the modified montmorillonite.

Preparation of regenerated cellulose/montmorillonite nanocomposite

Regenerated cellulose/montmorillonite (RC/MMT) nanocomposites were prepared via the exfoliation-adsorption method.⁴ The α -cellulose was oven-dried for 3 h at 70 °C. The pre-dried cellulose (8% w/w) was dissolved in [BEIm]Br and was stirred/heated for 2 h at 60 °C. Meanwhile, montmorillonite clay (MMT), in a varying amount of clay loading (2-8% w/w), was also dispersed in [BEIm]Br, using a sonicator for 40 min, and was stirred for 15 min at 60 °C. The two solutions were mixed and stirred for another 2 h at 60 °C. The solution was cast on a glass slide and immersed immediately in a water bath. The obtained nanocomposite was dried at 40 °C and stored in a desiccator.

Characterization of regenerated cellulose/montmorillonite nanocomposite

Powder X-ray diffraction (PXRD) was performed using a Siemens Kristalloflex 760 X-ray Generator, with a copper X-ray tube ($\lambda = 1.545 \text{ \AA}$) and a Philips 1080 Goniometer with a high voltage of 34 kV and a current of 20 mA. The XRD pattern was recorded with a step-size of 0.02° in the 2θ range of $5\text{--}85^\circ$. The surface morphology (SEM) of the pristine RC and RC/MMT nanocomposite samples was also recorded using a JEOL JSM 5310, equipped with a Canon digital camera, in the super macro mode at 1000x, 5000x, and 10000x magnification. Thermogravimetric analysis (TGA-50 Shimadzu) was used to evaluate the thermal stability of the samples. Tests were performed in a nitrogen environment and with a step-up rate of $10^\circ\text{C}/\text{min}$.

RESULTS AND DISCUSSION

Modification of montmorillonite clay

Montmorillonite (MMT) clay contains Na^+ and Ca^+ cations in its interlayer spacing.^{7,17-18} To impart organophilic properties to the MMT clay and increase its interlayer spacing, modification with quaternary alkylammonium ions is usually

performed.^{12,19-21} Through the cation exchange process, Na^+ cations from the interlayer spacing of the clay are replaced by the cetyltrimethylammonium (CTA^+) cations.¹⁶ Figure 2 presents the XRD pattern for both the pristine montmorillonite clay and CTA-MMT (organo-modified) clay.

The decrease in the crystallinity of the montmorillonite clay, as presented by the amorphous crystalline pattern of the CTA-modified MMT (CTA-MMT), suggests its modification. There is an accompanying decrease in intensity of the characteristic peak of montmorillonite clay (at $2\theta = 8.62^\circ$), suggesting the substitution of CTA^+ cations in the clay gallery. The main indication of the surface modification of the clay is the increase in the basal spacing (d-spacing) on the 001 plane. The calculated d-spacing of the pure montmorillonite is 5.03 \AA , using Bragg's equation. However, upon modification with CTAB, the characteristic peak ($2\theta = 8.84^\circ$) shifted to a lower diffraction angle ($2\theta = 8.62^\circ$); as a result, the calculated basal spacing (d-spacing) increased to 5.15 \AA , which indicates the swelling of the crystals as a result of the substitution. The small increase in the basal spacing is attributed to the orientation of the modifier in the gallery.¹⁶

Preparation of pristine regenerated cellulose and cellulose/montmorillonite nanocomposite

α -Cellulose did not dissolve immediately in the [BEIm]Br solution upon addition, rather it just absorbed the ionic liquid (Fig. 3a). After heating the mixture to 60 °C, cellulose started to dissolve, and the mixture formed a clear and viscous solution (Fig. 3b).

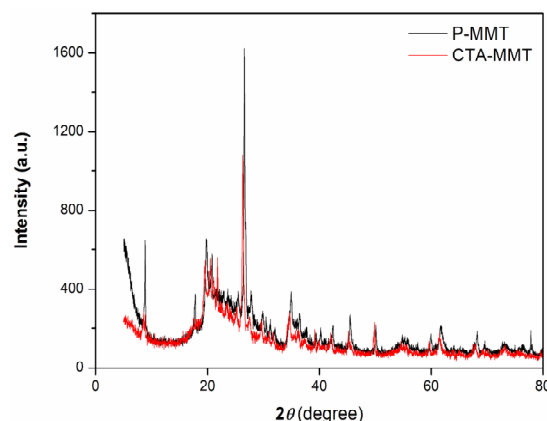


Figure 2: XRD pattern of (P-MMT) pristine montmorillonite and (CTA-MMT) modified montmorillonite clay

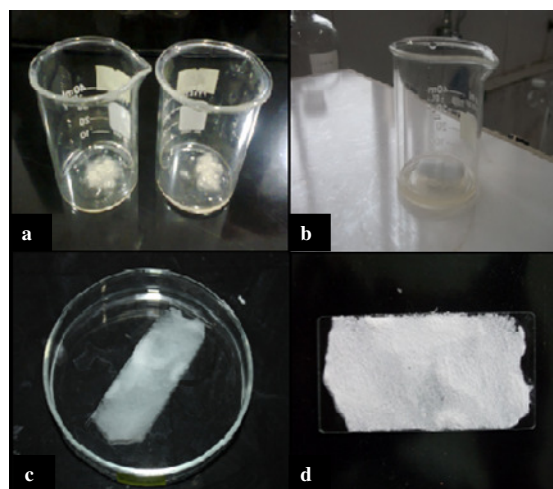


Figure 3: Cellulose regeneration: (a) cellulose before dissolution; (b) dissolved cellulose; (c) cellulose during coagulation and (d) cellulose after oven drying

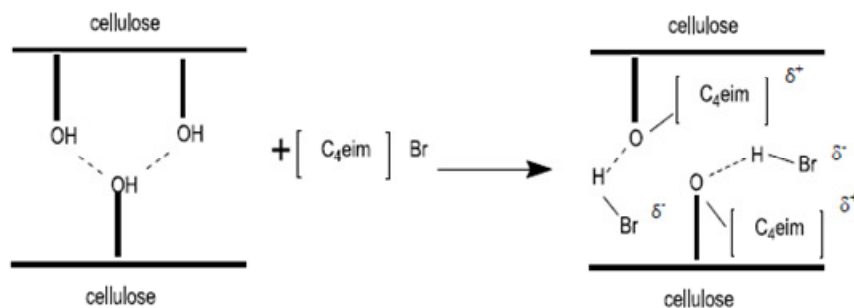


Figure 4: Proposed dissolution mechanism of cellulose in [BEIm]Br (3)

After casting, the glass slide was immersed in distilled water and a white precipitate was immediately formed on the slide (Fig. 3c). Oven drying the sample removed the excess water from the glass slide, producing a flaky precipitate (Fig. 3d).

The ionic liquid, in this case, 1-butyl-3-ethylimidazolium bromide ([BEIm]Br), disrupts the H-bonding of the hydroxyl group (-OH) of cellulose.¹⁰ Through the electron donor-electron acceptor mechanism (EDA), the oxygen atom and the hydrogen atom of the hydroxyl groups interact with the [BEIm]Br.¹⁰ The oxygen atom serves as electron donor and interacts with the imidazolium cation of the [BEIm]Br. The Br anion of the [BEIm]Br interacts with the hydrogen of the

hydroxyl groups through H-bonding. The breaking of the inter- and intra- H-bonding within the α -cellulose resulted in the opening of the chains and consequently dissolution of cellulose in the ionic liquid.¹⁰⁻¹¹ Figure 4 presents the proposed dissolution mechanism of cellulose in [BEIm]Br (3).

The immersion and coagulation of the sample in distilled water removes the BEImBr from the [BEIm]Br-cellulose system. Since [BEIm]Br – which is highly polar – interaction with water molecules is highly favored, they are liberated from the [BEIm]Br-cellulose system. As the [BEIm]Br solution is dispersed in water, α -cellulose is regenerated through H-bonding.

The cellulose/montmorillonite nanocomposites were prepared by dissolving α -cellulose (8% w/w) in [BEIm]Br solution. Montmorillonite clay, in varying loading (2-8% w/w), was also dispersed in a separate [BEIm]Br. The two mixtures were further mixed at 60 °C for 4 h. The ionic liquid has two roles in the preparation of the cellulose/montmorillonite nanocomposite via the exfoliation-adsorption method. First, it caused the swelling and exfoliated the clay, and second, in another set-up, it dissolved the α -cellulose. As the [BEIm]Br is removed from the system through coagulation in distilled water, the clay sheets of

MMT organized themselves back, and in the process intercalated the α -cellulose.³

Morphological assessment of cellulose/montmorillonite nanocomposite

The surface topography of the regenerated cellulose (RC) and the cellulose/montmorillonite nanocomposites (RC/MMT) is revealed in the SEM micrographs. The micrographs for RC showed a smooth surface (Fig. 5 a, b and c). However, the RC/MMT nanocomposite exhibited a rough surface with fiber-like structures (Fig. 5 d, e, and f).

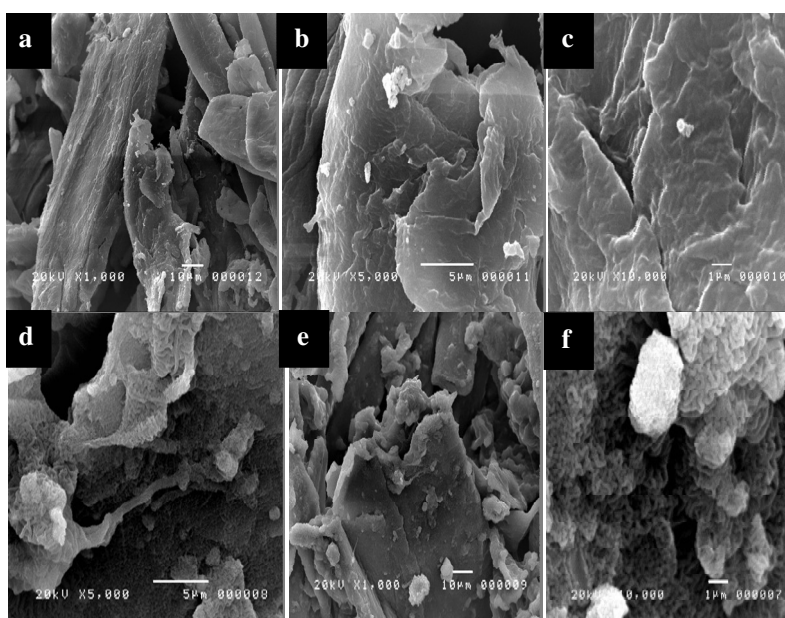


Figure 5: SEM micrographs of cellulose: (a) 1000x, (b) 5000x, (c) 10000x magnification; and RC/MMT nanocomposite: (d) 1000x, (e) 5000x and (f) 10000x magnification

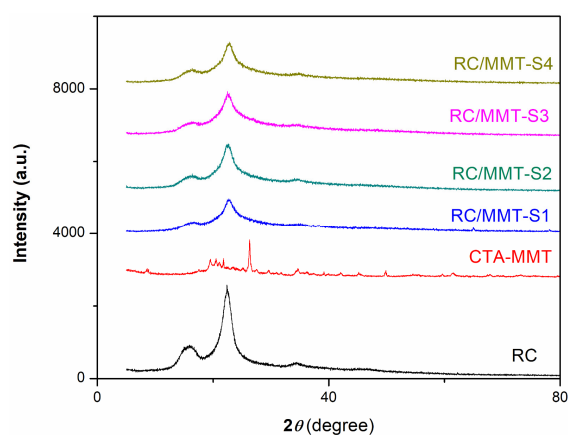


Figure 6: XRD patterns for montmorillonite, regenerated cellulose and cellulose/montmorillonite nanocomposite

The XRD patterns of the montmorillonite clay and cellulose are shown in Figure 6. The organo-modified clay (CTA-MMT) exhibited a diffraction peak at $2\theta = 8.62^\circ$, while RC exhibited diffraction peaks at $2\theta = 16^\circ$ and 23° , which are characteristic peaks for cellulose 110 and 220 lattice planes.²² As seen by their crystal patterns, the RC/MMT nanocomposites (RC/MMT-S1, RC/MMT-S2, RC/MMT-S3, and RC/MMT-S4)

exhibited a diffraction peak similar to the crystal pattern of RC. The characteristic peak for MMT was not observed in any of the crystal patterns of the synthesized nanocomposite. This suggests that MMT had been well dispersed in the polymer matrix. Previous studies² also showed the absence of the montmorillonite peak, which further suggests the intercalation/exfoliation of clay in the cellulose matrix.

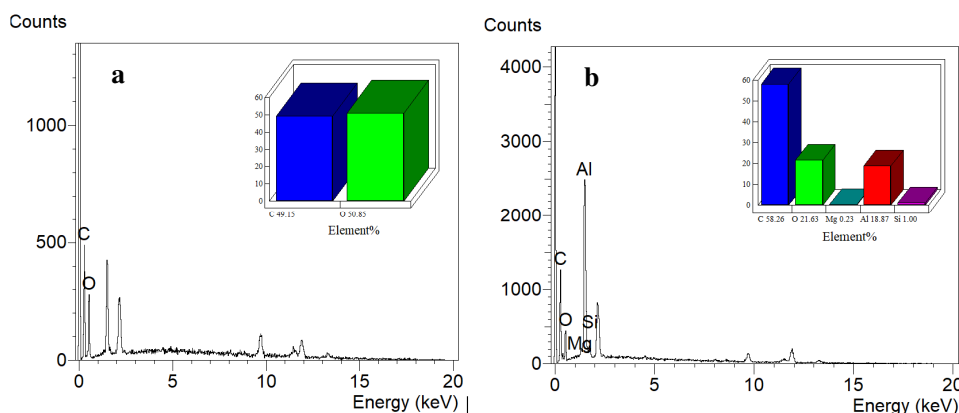


Figure 7: EDS graphs for regenerated cellulose (a) and cellulose/montmorillonite nanocomposite (b)

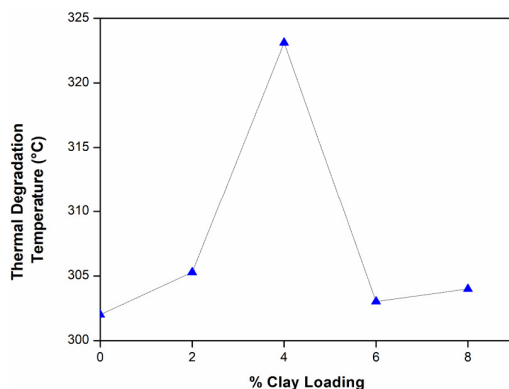


Figure 8: Thermal stability graph for RC/MMT nanocomposite as a function of clay loading

The dispersion of MMT into the α -cellulose matrix was revealed by EDS analysis. The RC showed only two peaks, which are explained by the presence of C and O atoms, with a percentage composition of 49.15% and 50.85%, respectively. However, the RC/MMT nanocomposite exhibited 5 peaks due to the presence of C, O, Mg, Al, and Si atoms. Their percentage composition is reported as follows: 58.26%, 21.63%, 0.23%, 18.87% and 1.00%, respectively. The presence of Mg, Al and Si atoms suggests that the nanocomposite sample contains MMT on its surface. Figure 7 shows the EDS profile of both RC and RC/MMT nanocomposite.

Thermal stability analysis of cellulose/montmorillonite nanocomposite

The comparative thermal stability analysis of RC and RC/MMT nanocomposites showed a relationship between the thermal decomposition temperature of the RC/MMT nanocomposite and the clay loading (Fig. 8). The highest decomposition temperature of the RC/MMT nanocomposite was achieved upon the addition of 4% clay loading. The thermal stability of the RC/MMT nanocomposite increased from 302 °C to 323 °C. The increase in the thermal stability of the cellulose is due to the clay, such as montmorillonite, which prevented the diffusion of gases in the polymer matrix; thus, retarding the

decomposition rate of the compound.² However, at higher clay loading, the thermal decomposition of the nanocomposite decreased, which is attributed to the poor dispersion of the clay into the polymer matrix, possibly caused by aggregation, increasing the amorphous character and porosity of the material. A previous study² had also shown that at 4-6% clay loading, the thermal stability of RC/MMT nanocomposites was optimum.

CONCLUSION

A cellulose/montmorillonite nanocomposite was successfully prepared using a synthesized ionic liquid, 1-butyl-3-ethylimidazolium bromide ([BEIm]Br). First, montmorillonite clay was modified using CTAB. The amorphous crystal pattern and the increase in the basal spacing (d-spacing) of the CTA-MMT (organo-modified) clay indicated a decrease in the crystallinity, compared to the pristine montmorillonite clay. The SEM micrographs and the XRD pattern of the cellulose/montmorillonite nanocomposite suggested that the montmorillonite clay was dispersed in the cellulose matrix, which was further verified using EDS analysis. The presence of Si, Mg and Al peaks in the EDS graph strongly suggested the presence of clay in the nanocomposite produced. As the addition of clay into the cellulose matrix was increased, the thermal stability of the RC/MMT nanocomposite also increased. The highest thermal stability of the RC/MMT nanocomposite was achieved upon the addition of 4% MMT clay loading and shifted the thermal degradation temperature from 302 to 323 °C.

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