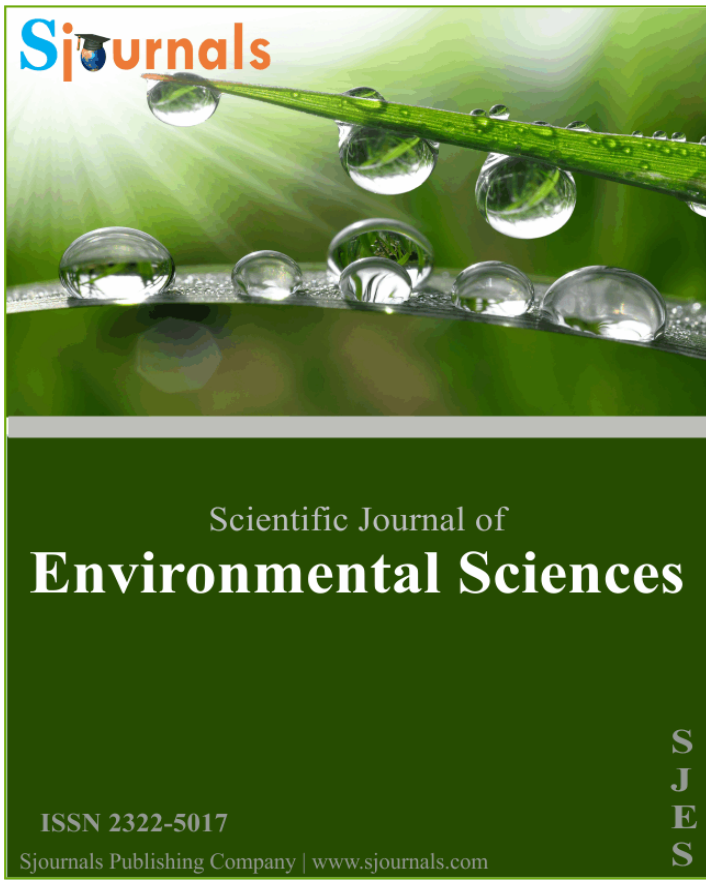

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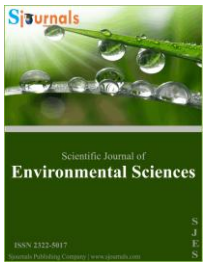

Original article

Synthesis of biodegradable cellulose-chitin polymer film using recycled N,N-dimethylacetamide

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ABSTRACT

The current laboratory-scale synthesis of chitin-based bioplastics involves the immediate disposal of lithium chloride/N,N-dimethylacetamide (LiCl/DMAc) solvent after use, making the process wasteful, harmful to the environment and expensive. In this study, DMAc was recovered via conventional distillation of liquid waste solvent from previous chitin-based plastic syntheses. The effectivity of the recovery process was confirmed through FTIR analysis and pH measurements. The recovered DMAc was then used in the dissolution of commercially-available chitin and chitin extracted chitin from the shell of *Portunuspelagicus* to successfully synthesize 80:20 wt% cellulose-chitin blend films. Tensile tests following the ASTM D882-10, UTM tensile testing results showed that the films synthesized using extracted chitin have higher tensile strength than those synthesized using commercial chitin. Analysis of variance showed that the source of DMAc i.e. (fresh or recovered), is not a significant factor affecting the UTS tensile strength of the films. SEM images also showed that the surface morphology of the films synthesized using extracted chitin and recovered DMAc is similar to the one synthesized using extracted chitin and fresh DMAc. The comparable properties of films produced using fresh and recovered DMAc indicate that solvent recovery of DMAc is indeed a viable step in the greener production of biodegradable cellulose-chitin polymer film.

1. Introduction

Chitin, known to be the second most abundant naturally-occurring renewable biodegradable, polymer, may be extracted from these shells of crustaceans such as the *P. Pelagicus*, a species abundant in the Philippines (Luckachan and Pillai, 2011; Zhang et al., 2009). Upon extraction, chitin must be converted into a more useable form, such as film. In order to do this, it must first be dissolved to obtain a solution then cast into a film. For this study, the lithium chloride/N,N-dimethylacetamide (LiCl/DMAc) solvent system was used as it was found to be non-degrading and non-derivatizing, i.e. does not form chemical bonds with the chitin molecules (Zhang et al., 2009). The dissolution in the said solvent system was also found to be faster, easier and more reproducible (Striegel, 2003). The current set-up, however, requires that the solvent system be only used once, thus making the process wasteful and defeats the purpose of creating an environment-friendly material. With this, the study aims to produce a biodegradable film from extracted chitin and recovered DMActhat is of comparable properties with the commercially-available counterparts.

2. Materials and methods

2.1. Chemicals and reagents

Technical grade methanol, ethanol and isopropanol were bought from BE Laboratory Supplies. Waste LiCl/DMAc solvent, lithium chloride, commercial chitin, chitin extracted from *P. pelagicus* and cellulose were provided for by the Green Materials Group of the Department of Mining, Metallurgical and Materials Engineering (UP DMMME).

2.2. Solvent recovery

Waste LiCl/DMAc system was recovered using a conventional distillation apparatus to recover DMAc, improvised using a Corning PC 620D Digital Hot Plate, Erlenmeyer flasks and a bent Pyrex glass tubing. The temperature of the solution was measured every 5 minutes, as the temperature on the hot plate was ramped up 50^{o}C per 10 minutes.Fourier transform infrared (FTIR) analysis using a Thermo Scientific Nicolet 6700 apparatus was performed on the recovered DMAc at the Department of Chemical Engineering, UP Diliman. The pH values of 20% aqueous solution of the recovered DMAc were also obtained using a pH meter.

2.3. Film forming

2.3.1. Design of experiment

The study followed the 2^{k} factorial design having the source of chitin, either commercial or extracted and type of DMAc, fresh or recovered, as factors. The response variable considered was the tensile strength of the resulting films.

2.3.2. Chitin and cellulose dissolution

The 5% (w/v) lithium chloride-N,N–dimethylacetamide (LiCl/DMAc) solvent for chitin dissolution was prepared. The covered mixture was stirred at room temperature until all LiCl dissolved in the separate vessels of fresh and recovered DMAc. Then, 0.5% (w/v) of commercial and extracted chitin was added to different solutions, and agitated until homogenous (Dupont, 2003). Unlike chitin, cellulose fibers underwent activation stage, prior to actual dissolution. One percent (w/v) of cellulose was stirred for one hour at 40°C in distilled water, and twice in both methanol (CH_3OH) and DMAc for 45 minutes at room temperature. The filtrate and precipitate were separated using the vacuum filtration set-up, between each step (Phonwong et al., 2000). After swelling, cellulose was added to 8% LiCl/DMAc and stirred until a clear solution was obtained (Dupont, 2003).

2.3.3. Polymer blending and forming

Different amounts of the solutions were measured based on the 80:20 cellulose:chitin ratio by mass. These were then mixed in covered containers for 1 hour. The resulting solutions were then poured into a glass mold, covered with pin-holed aluminum foil, and allowed to set for 24 hours. The formed gels were soaked in isopropyl and methyl alcohol. These were then cold pressed between filter papers, glass plates, and binder clips, then oven-dried for 18 hours at 60°C. The dried films were again soaked in isopropyl and methyl alcohol, then cold-pressed for another 48 hours. The final films were characterized (Yusof et al., 2004).

2.4. Film characterization

Following a modified version of the ASTM Standard Test Method for Thin Plastic Sheeting (D882-10), films were cut accordingly and mounted on a jig. The films' ultimate tensile strength were then measured with an Instron 3366 universal testing machine (UTM) using a 1 kN load cell at a crosshead speed of 1 mm/min at the Department of Mechanical Engineering, UP Diliman. On the other hand, surface morphology of the films was observed under a Hitachi TM3000 scanning electron microscope (SEM) at 15 kV filament voltage at the Analytical Services Laboratory, University of Santo Tomas. Prior to electron microscopy, samples were gold-coated via sputter coating using a JEOL Ion Sputter JFC-1100 for 3 minutes at the Department of Mining, Metallurgical and Materials Engineering, UP Diliman.

3. Results

3.1. Distillation characterization

Distillate that evaporated at the temperature range of 165^{o}C to 180^{o}C was taken to be recovered DMAc. It can be noted that FTIR peaks of the recovered DMAc in Figure 1 corresponded with literature DMAc peaks. However, the peaks present at around 3300-3400 cm^{-1} and 1600-1700 cm^{-1} still indicates the presence of water in the recovered DMAc. Thus, the recovered solvent may still benefit from another round of distillation to further improve its purity.

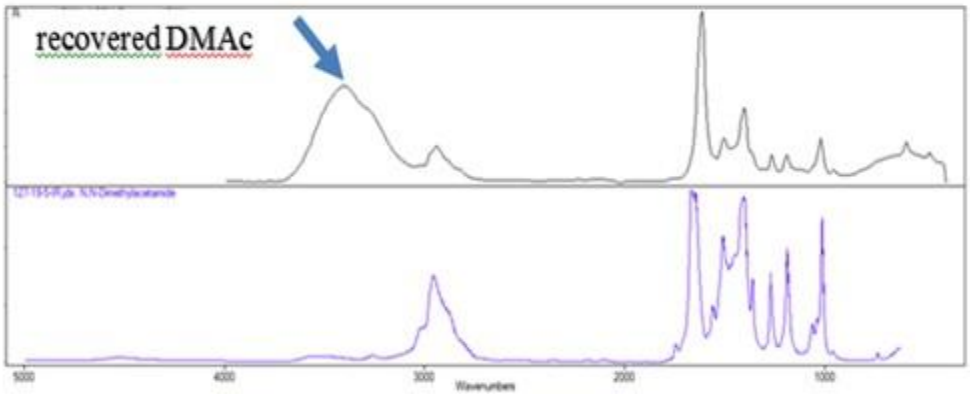

Fig. 1. FTIR absorption spectra of recovered DMAc (top) and literature DMAc (bottom).

The pH values of 20% aqueous solution of the recovered DMAc were measured to be 5.30. This value complies with the industry standard DMAc pH range set by DuPont. Thus, DMAc was successfully recovered via conventional distillation of waste LiCl/DMAc mixture disposed of from previous syntheses of chitin-based plastics.

3.2. Mechanical properties by uniaxial tensile test

Figure 2 shows representative stress-strain profiles of the polymer blend films from recovered DMAc. It can be observed for both commercial and locally extracted chitin that the films extended to the yield point followed by strain softening and decrease in measured stress, until fracture. This indicates ductile failure typical of polymeric materials.

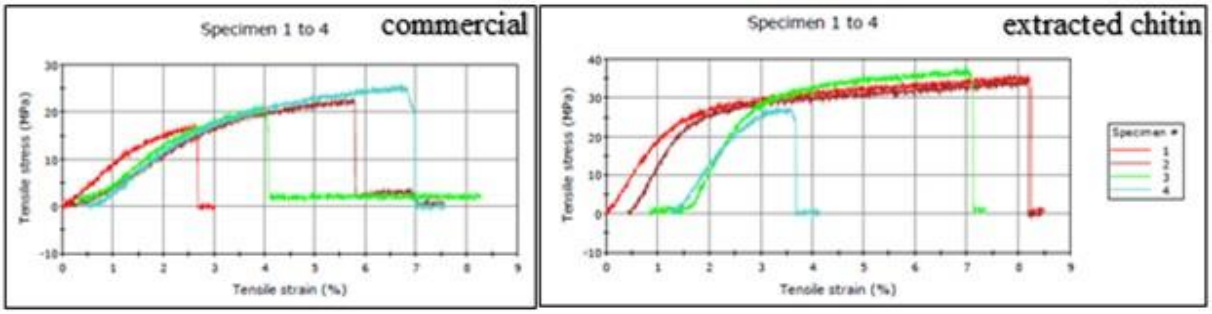

Fig. 2. Representative stress-strain profiles for commercial chitin-cellulose film (left) and extravted chitin-cellulose filme (right).

The best sample in terms of tensile strength at 34.035 MPa was that of locally-extracted film formed from recovered DMAc, while the worst was that of commercially-available – recovered DMAc combination, having 20.66 MPa. The results may be explained by the SEM images shown in Figures 4 and 5.

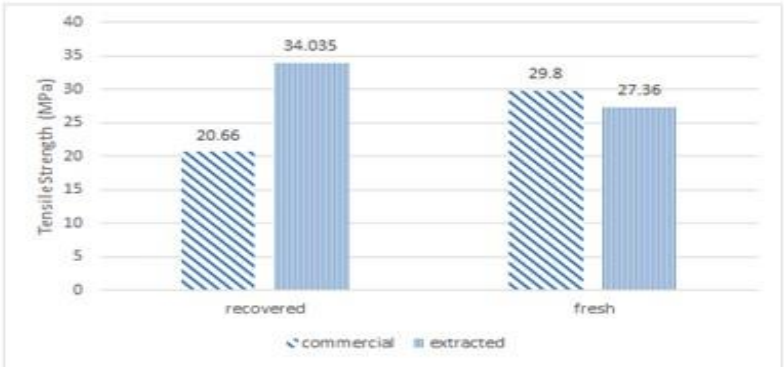

Fig. 3. Ultimate tensile strength of the samples.

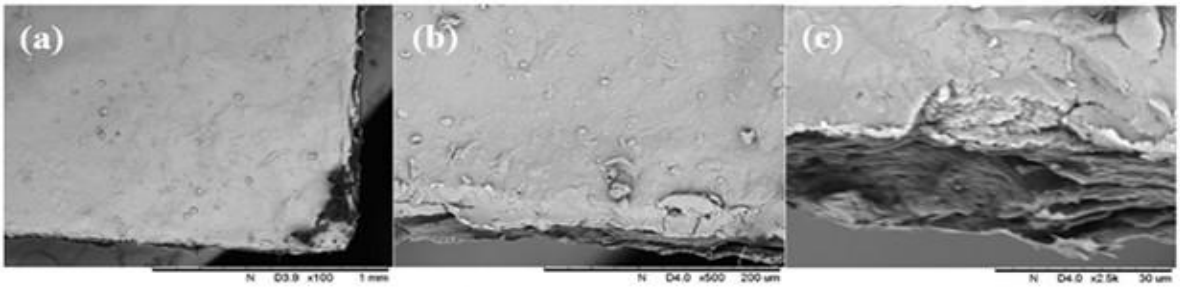

Fig. 4. SEM images of 80:20 cellulose-chitin film synthesized using extracted chitin and recovered DMAc at (a) 100x, (b) 500x and (c) 2500x magnification.

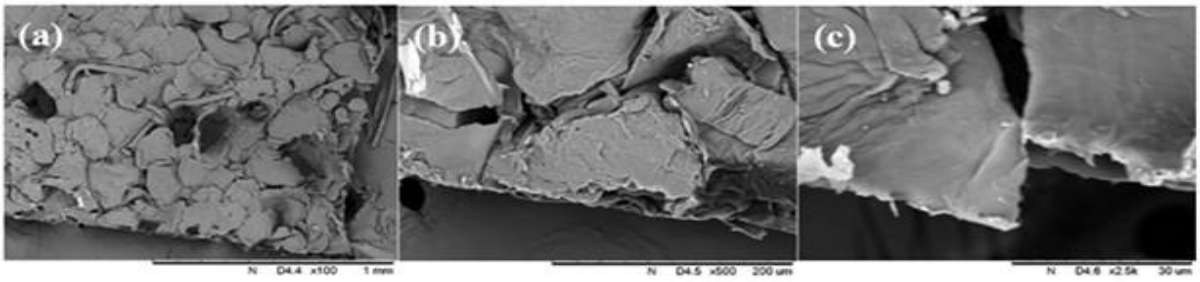

Fig. 5. SEM images of 80:20 cellulose-chitin film synthesized using extracted chitin and commercial DMAc at (a) 100x, (b) 500x and (c) 2500x magnification.

Upon comparison, films synthesized using commercial chitin and recovered DMAc have a rougher surface and suggests incomplete dissolution. This can be considered as a defect, which acted as stress concentrators and weakened the sample in tensile, thus the lower UTS value measured.

3.3. Comparison of films synthesized using fresh and recovered DMAc

Two-way ANOVA was performed to compare UTS data obtained for films synthesized using recovered and fresh DMAc. It was determined that the chitin source and the interaction between the chitin source and DMAc source are significant model terms. The DMAc source, on the other hand, is determined to be an insignificant factor. Therefore, the DMAc source will not significantly affect UTS values of the chitin-cellulose films.

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References

Dupont, A.L., 2003. Cellulose in lithium chloride/N,N-dimethylacetamide, optimisation of a dissolution method using paper substrates and stability of the solutions. Polymer (Guildf)., 44(15), 4117–4126.

Dupont, A.L., 2003. Gelatine sizing of paper and its impact on the degradation of cellulose during aging: A study using size-exclusion chromatography. University of Amsterdam.

Fisheries, S., 2012. Philippine blue swimming crab fishery improvement project. [Online]. Available: http://www.sustainablefish.org/fisheries-improvement/crabs/philippines-blue-swimming-crab.

Luckachan, G.E., Pillai, C.K.S., 2011. Biodegradable polymers- A review on recent trends and emerging perspectives. J. Polym. Environ., 19(3), 637–676.

Phonwong, A., Rujiravanit, R., Hudson, S., 2000. Preparation and characterization of chitin cellulose blend films. J. Met. Mater. Miner., 10(1), 1–22.

Striegel, A.M., 2003. Advances in the understanding of the dissolution mechanism of cellulose in DMAc/LiCl. J. Chil. Chem. Soc., 48(1).

Yusof, N.L.B.M., Lim, L.Y., Khor, E., 2004. Flexible chitin films: Structural studies. Carbohydr. Res., 339(16), 2701–11.

Zhang, S., Li, F.X., Yu, J., 2009. Preparation of cellulose/chitin blend bio-fibers via direct dissolution. Cellul. Chem. Technol., 43(9–10), 393–398.

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