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Influence of 1-Butyl-3-Methylimidazolium Chloride ([BMIM] Cl) Reaction Temperatures to the Toxicity and Biodegradation of Kapok Cellulose Film

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Abstract:

The influence of the 1-butyl-3-methylimidazolium chloride ([BMIM] Cl) reaction temperature to the toxicity and biodegradation of kapok cellulose film were studied. In this study, ([BMIM] Cl) acted as a solvent to dissolve kapok cellulose by partial ionic dissolution method. The kapok cellulose films were produced by dissolving cellulose at various reaction temperature ranged from 60 ^{o}C to 100 ^{o}C. The toxicity of ([BMIM] Cl) has been related directly with the length of the butyl chain in the solvent. According to the Fourier Transform Infrared Spectroscopy (FTIR), the intensity of the peak which represented butyl chain (2800 – 3000 cm^{-1}) decreased as the reaction temperature increased. This might be due to the butyl chain that has been vaporized at high temperature. Based on the biodegradation results, kapok cellulose film E degraded at fastest rate among other films. This film exhibited 93.56 % weight loss while the lowest was film A with 91.63 %. These results were in agreement with the previous study that stated the rate of degradation is enhanced as the reaction temperature increased. For moisture uptake test, moisture uptake continuously increased with the increasing time from day 1 to day 7 for all reaction temperatures. The percentage of moisture uptake drop subsequently after day 5 due to the moisture water uptake has reached the equilibrium in all samples.

Keywords: ([BMIM] Cl), Partial ionic dissolution, Toxicity, Biodegradation

Introduction

Cellulose has been widely used as a source of biopolymers and has been known to provide undeniable benefits for the development in polymer industry. Cellulose consists of three components such as cellulose, hemicelluloses and lignin (Xiao et al., 2012). Cellulose exhibited many advantages such as high biodegradability, high mechanical performance, easy to recycle, low cost, not depending on petroleum source, available from renewable sources and able to replace synthetic polymers (Liu et al., 2011). Recently, there are many products that have been widely derived from cellulose source such as fiber, paper, films, polymer and paint (Liu et al., 2011). Kapok or its scientific name (*Ceiba pentandra*) is a non-edible and draught resistance plant which abundantly found in Southeast Asia countries such as India, Sri Lanka and Malaysia. Kapok fiber or kapok linter which is yellowish seed-hair fiber is obtained from the fruit pod of the kapok tree (Yunus Khan et al., 2015). Kapok fiber is the lightest natural fiber and it's eight times lighter than the cotton. It has the very thin wall and a huge hollow region full of air (Tye et al., 2015). Kapok fiber has been chosen as a source of cellulose fiber due to its high cellulose content. Single kapok fiber consists of cellulose (64%), lignin (13%) and polysaccharide (23%) (Zheng et al., 2015). In recent years, many researchers are focusing on fabricating 'green' composite which made from cellulose fibers. 'All-cellulose composite' which has been designed by 100 % cellulose source has drawn so much attention due to its unique properties such as excellent mechanical and optical properties and low toxicity (Duchemin, Mathew, & Oksman, 2009). 'All-cellulose composite' is rather preferred compare to synthetic polymer derived composite due to its recyclability property as the fiber and matrix come from the same source which are cellulose (Duchemin et al., 2009). Many researches regarding 'All cellulose composite' have been reported

so far as these research have gave positive impact in creating new 'green' composite replacing synthetic derived composite. Ionic liquids (ILs) are organic salts having liquid phase below boiling temperature (<100 ^{o}C). ILs consist of ions, usually large organic cations and small inorganic anions (Gulhane, Gomashe, & Deo, 2014). ILs have some properties such as high thermal stability, lack of inflammability, low volatility, chemical stability, and excellent solubility with many organic compounds (Gibril et al., 2012). ILs are considered as potential substitutes of environment friendly green solvent in a sustainable process based on their biodegradability property (Zadegan et al., 2011). There are several types of ILs, such as, 1-ally-3-methylimidazolium chloride (AMIM [Cl]), 1-ethyl-3-methylimidazolium acetate (EMIM [OAc]), 1-butyl-3methylimidazolium chloride ([BMIM] Cl), and 1-ethyl-3-methylimidazolium diethyl-phosphate ([EMIM] DEP). Among all ILs, ([BMIM] Cl) is chose as a common solvent to dissolve cellulose as it can dissolve cellulose even at low temperature. Many researches have been reported regarding the capability of ([BMIM] Cl) for dissolving cellulose from different type of sources. Other study by Liu et al., (2011), proven that the dissolution and regeneration of cotton pulp has been successfully conducted by using ([BMIM] Cl) as solvent. Other study by Jin et al., (2010) proven that the novel cellulose packaging films were successfully prepared through the phase inversion in ([BMIM] Cl) as ionic liquid solvent. The film prepared by using ionic liquid technology would be used in food packaging or other fields as a kind of green packaging material. Although ILs is claimed to be 'green' solvent for dissolving cellulose but some other previous work argued that ILs still exhibited certain degree of toxicity (Lozano et al., 2011). The toxicity of ILs has been related directly with the length of the alkyl substituent in the imidazolium cation structure. It is claimed that the toxicity of the ILs increase with the number of carbon at the side chain and the chain branching (Zhang et al., 2011). Apart from that, the anion structure in ILs has a low effect on the toxicity parameter (Lozano et al., 2011). ([BMIM] Cl) is a type of ILs that exhibited certain degree of toxicity. Gulhane, Gomashe & Deo (2014) concluded that the application of ([BMIM] Cl) in their research influenced the micro-ecological of soil. According to the previous research, there was a little attention on studying the relationship between the ([BMIM] Cl) reaction temperature and the toxicity and biodegradation of cellulose film produced. Biodegradation is a chemical degradation of materials and substances that triggered by the action of microorganisms such as bacteria, algae and fungi. It is also considered as a type of degradation that involves biological activity (Leja & Lewandowicz, 2010). From previous study of Liu et al., (2011), the rate of degradation is also enhanced as the reaction temperature of the medium increased. The regenerated film degraded apparently as the temperature of the reaction increased. In this work, an attempt has been made to fabricate the cellulose film from kapok fiber by using ([BMIM] Cl) as a solvent. The effect of ([BMIM] Cl) reaction temperatures and the relationship to the toxicity and biodegradation of cellulose film were studied. Hypothesis has been made due the toxicity in the ([BMIM] Cl) can be diminished at high temperature.

Methodology

Materials

Kapok linter from Kampung Jelempok, Perlis was used as a raw material in this research. Kapok linter is a source of cellulose fiber for preparing cellulose film. The chemicals that have been used in this research include 1-butyl-3methylimidazolium chloride ([BMIM] Cl), sodium hydroxide (NaOH) and hydrogen peroxide (H_2O_2). All of these chemicals are purchased from SIGMA ALDRICH Malaysia.

Preparation of raw material

Kapok linter was collected from kapok tree. All the seeds were separated from its linter. Then, the kapok linter was shredded into small sizes. After that, kapok linter was immersed in the water for 2 hours to make sure all the impurities were removed. After 2 hours, kapok linter was put in the oven for drying process at 60 ^{0}C for 24 hours. Then, the kapok was put in a desiccator until further used (Abdul Rahman, Abd Rahim, & Din, 2014).

Chemical pre-treatment

Lignin, hemicelluloses and the other organic compound was eliminated or removed from kapok linter by alkaline treatment. The kapok linter was put in the 10 % of NaOH solution and was heated at 60-70 ^{0}C for 4 hours. After the treatment, the pre-treated kapok linter was filtered. The sample was thoroughly washed with distilled water for several times. Wet red litmus paper was used to check the alkalinity of the sample. If the red color of litmus paper remain unchanged, it proof that all the alkali has been removed from the sample. Next, the sample was dried in an oven at 60 ^{0}C for 24 hours to obtained cellulose fiber. Then, the bleaching process was carried out by put the cellulose fiber in 10 % H_2O_2 solution at 60-70 ^{0}C for 3 hours. It was allowed to cool at room temperature. Then, the slurry was

filtered and washed with distilled water. Finally, the samples were re-dried in oven at 60 °C for 24 hours to obtain bleached cellulose fiber (Abdul Rahman, Abd Rahim & Din, 2014).

Preparation of kapok cellulose film

The kapok cellulose film was produced by dissolving the bleached cellulose fiber at various ([BIMIM] Cl) temperatures ranging from 60 ^{0}C - 100 ^{0}C. Based on Zhang *et al*., (2012) has stated that the temperature range of 60 ^{0}C- 100 ^{0}C is suitable to dissolve cellulose with ILs. The dissolved cellulose was stirred by magnetic stirring to form a homogeneous and transparent cellulose/ ([BMIM] Cl) solution. The solution was placed into a petri dish and dried in oven at 70 ^{0}C for 6 hours. For preparation of regenerated cellulose film, it was immersed in water bath at 35 ^{0}C for 2 minutes. Finally, it was dried in oven at 70 ^{0}C for 4 hours. All the dried kapok cellulose films were stored in desiccators for further test and characterization.

Table 1: Various reaction temperature of ([BMIM] Cl)

Samples	Temperature (^{o}C)
Kapok A	60
Kapok B	70
Kapok C	80
Kapok D	90
Kapok E	100

Characterization

FTIR

The effect of ([BMIM] Cl) reaction temperatures to the toxicity and biodegradation of kapok cellulose film was investigated using FTIR. In our study, the toxicity effects of the ([BMIM] Cl) can be determined by the butyl chain exists in its structure. The butyl peak of pure BMIM Cl was used as references. The level of toxicity of kapok cellulose film at different reaction temperature can be determined by the intensity of the alkyl peak observed.

Biodegradability test

The biodegradability test was conducted according to the method as described by Wan et al., (2009). This test was carried out at room temperature under moisture controlled condition for about 30 days. Triplicate sample of each kapok cellulose film were placed in petri dish containing moisturized soil. The samples about 30 mm x 10 mm were buried in 100 mm beneath the surface of soil. Then, the sample was regularly moistened with distilled water. At predetermined time point, the sample was removed and the sample was washed with distilled water for a several times in order to stop the degradation. Then, the sample was dried at room temperature in the oven to a constant weight. The sample was weighed on analytical balance in order to determine the average weight losses. The amount of weight loss in kapok cellulose composite film was determined by following equation:

$$Percentage\ weight\ loss\ (\%) = \frac{Wo - Wt}{Wo}\ x\ 100\%$$

Where W_o is the initial mass of the sample and W_t is the remaining mass at any given time, t. All results were the average of triplicates (Wan et al., 2009).

Moisture uptake test

The moisture uptake was conducted according to the method as described by Soykeabkaew et al., (2012). The sample used for moisture uptake testing is a thin rectangular of kapok cellulose film. The dimension of the strips was 30 mm x 10 mm. This test was conducted for 7 days. The kapok film strips were dried at 60 ^{0}C for 24 hours. The strips were cool down to room temperature in desiccator. After that, all the samples were weighed and put back in the desiccator which contains a saturated NaCl. For every 24 hours, the strips were taken out from the desiccator and weighed using an analytical balance. The moisture uptake for every 24 hours was calculated as follows:

$$Moisture\ uptake = \frac{Wt - Wo}{Wo}\ x\ 100\%$$

Where W_t is the weight of the samples after 24 hours exposure and W_o is the weight of the samples before exposure to moisture content. All results were average of triplicates samples.

Results and discussion

FTIR of kapok cellulose fiber

Figure 1 showed the FTIR spectra of untreated, alkaline treated and bleached kapok cellulose fiber. All spectra showed the strong and broad peak in the region between 3000 to 3500 cm^{-1} corresponding to the hydroxyl (O-H) stretching vibration and hydrogen bonded –OH. This peak is shifted to the lower wavenumber from untreated to bleached kapok cellulose fiber. This is due to the breaking down of hydrogen bond and the increment of cellulose hydroxyl group in fiber wall, the wax and lignin are removed from the surface of kapok cellulose fiber. The intensities of peak decreased and became broader than

untreated kapok cellulose fiber. Whereas, the strong peak at region 2914.86 cm^{-1} is assigned to asymmetric and symmetric stretching vibration in CH_2 and CH_3 that represent the surface wax in untreated and this peak is also shifted to the lower wavenumber for alkaline kapok and bleached kapok. For absorption peak at 1734.45 cm^{-1}, it was due to C=O stretching vibration of ketones, ester and carboxylic groups in lignin. The intensity of this peak was decreased in alkaline and bleached kapok due to the removal of lignin compound during chemical pretreatment. Besides, the absorption peak at 1503.72 and 1638.84 cm^{-1} were attributed to the aromatic ring skeletal stretching in untreated kapok cellulose fiber. The peaks around 1371.08 cm^{-1} and 1242.86 cm^{-1} were within the range of C-H and C-O bending vibration. In addition, remarkable reduction of band intensity observed at 1646.22 cm^{-1} and 1159.97 cm^{-1} occurs for alkaline kapok. The strong alkali can result in de-esterification of kapok fiber and all the ester linked with aromatic ring of lignin is almost completely removed (Wang et al., 2012).

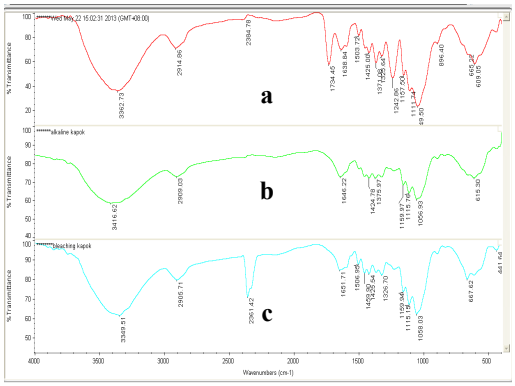

Figure 1: FTIR spectra for a) untreated kapok, b) alkaline kapok and c) bleached kapok

FTIR of kapok cellulose film for different ([BMIM] Cl) reaction temperature

Figure 2 showed the FTIR spectra of kapok cellulose film at different reaction temperature of ([BMIM] Cl) ranging from 60 ^{0}C to 100 ^{0}C. It can be seen that the all peaks were quite similar and no new peak appeared in the kapok cellulose film. These indicated that no chemical reaction occurred during dissolution process of the cellulose in ([BMIM] Cl). Thus, it can be proofed that ([BMIM] Cl) was a direct solvent for cellulose (Zadegan et al., 2011). The pure peak of ([BMIM] Cl) spectrum was used as a reference. For pure ([BMIM] Cl) spectrum, broad absorption band was observed at 3300 - 3500 cm^{-1} corresponds to the stretching vibration of the OH groups. In contrast, the band at 2800 to 2900 cm^{-1} is attributed to the vibration of CH_2 groups. While the peak at 1639.02 cm^{-1} corresponds to the C-O stretching vibration of C-O-H. Additionally, the peaks at 1370-1379.99 cm^{-1} were attributed to the O-H bending vibration and a peak appearing at 1215 cm^{-1} is attributed to C-O bond stretching vibration. For absorption peaks at 2960.05 cm^{-1} to 3066.34 cm^{-1} corresponds to the stretching of C-H group (Liu et al., 2011). Peak at 3141.76 cm^{-1} correspond to the CH-stretching mode of imidazolium ring band (Jeon et al., 2008). Beside, a strong and new peak at 760.39 cm^{-1} represented imidazolium structure was observed. While a peak at 1379.99 cm^{-1} and 1568.76 cm^{-1} were indicated the imidazolium ring stretching (Shi, Peng, & Deng, 2003). Absorption peak at 1169.83 cm^{-1} indicated the C-O-C stretching and the peak around 1568.76 cm^{-1} represent C=C stretching (Solomons & Fryhle, 2000). The butyl chain was observed in the range of 2800 to 3000 cm^{-1}. Beside, two peaks at 621.10 and 654.01 cm^{-1} represented the peaks of gauche and trans forms of the butyl chain. For pure ([BMIM] Cl) samples, the ratio of these two peaks were different, the trans peak was much bigger compared to gauche formation. This indicated the bulks structural difference due to the type of anion is reflected in the conformation of the butyl chain attached to the imidazolium core of the cation (Jeon et al., 2008). Besides, from the Figure 2, the FTIR spectrum of the kapok cellulose film were similar to that original kapok fiber, indicating that all cellulose composite have no chemical reaction occur besides breakage of hydrogen bond during the process dissolution and regeneration. All kapok celluloses films (Kapok A to E), showed obvious peak at 3300-3500 cm^{-1} correspond to the stretching vibration of O-H group. This peak is shifted to the lower wavenumber and broadens as reaction temperature of ([BMIM] Cl) increased. We can see that, the highest broadening peak is corresponding to kapok E that represents the highest reaction temperature of ([BMIM] Cl) (Liu *et al*., 2011). The peak at 2700-2900 cm^{-1} is corresponding to the vibration of CH_2 groups. We can see that the intensity of this peak is decreasing from kapok A to kapok E. Besides, peak at 1500 cm^{-1} to 1600 cm^{-1} also decrease as the reaction temperature increased compare to the pure ([BMIM] Cl) spectra. The peak which represented toxicity of ([BMIM] Cl) is the peak which located at 2800 to 3000 cm^{-1}. This peak represented butyl chain which exhibit toxicity characteristic of the ([BMIM] Cl). The intensity of the peak keeps decreasing and became broaden as the reaction temperature increased. This peak exhibited highest intensity for kapok A which has reaction temperature at 60 ^{o}C. At reaction temperature of 100 ^{0}C, the peak of butyl chain is more broaden and exhibited lowest intensity compared to others. So it is proved that as the reaction temperature increased, it will decrease the toxicity of kapok

cellulose film because the entire toxicity element has been vaporized along with the vapor.

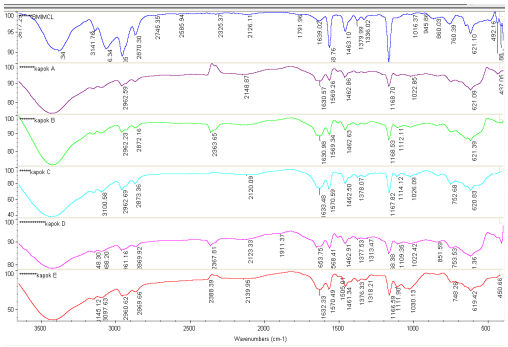

Figure 2: FTIR spectra of kapok cellulose film in BMIM Cl at different reaction temperature

Biodegradability Test

Figure 3 showed the percentage weight loss of the samples as the function of time at different reaction temperature. Based on the overall results, we can conclude that the percentage weight loss showed an approximately linear relationship with the degradation time for all kapok cellulose films (Wan *et al*., 2009). After 2 days, we can see all kapok A, B and C slowly degraded by time. In contrast, kapok D was degraded faster than kapok A, B, and C. For kapok E, the degradation rate was the highest among others. The degradation rate was observed based on the percentage weight loss because percentage weight loss is directly proportional to the degradation rate of certain sample. It is observed that the percentage weight loss of kapok A is the lowest while kapok E exhibit highest percentage weight lost. The weight loss was affected by increasing the reaction temperature of ([BMIM] Cl) to the kapok cellulose film. This is in agreement with previous study of Liu *et al*., (2009), in which the rate of degradation is enhanced as the reaction temperature increased. To conclude, we can say that at reaction temperature of 100 ^{0}C, the kapok cellulose film degraded faster than the others. Apart from that, all kapok cellulose films can be concluded as fully biodegradable material as they can degrade in soil medium either fast or slow.

Moisture uptake test

Moisture uptake process is a type of process which involved water molecules diffused through the polymeric structure's inherent microvoids or any porosity or micro-cracks (Grammatikos, Zafari, Evernden, Mottram, & Mitchels, 2015). From Figure 4, we can observe that the moisture uptake for all reaction temperature is decreasing after 5 days. However, if we compare for all kapok samples, Kapok E exhibit highest moisture uptake. This is because when the reaction temperature was increased, the cellulose chain is expected to degrade slowly. Hence, the diffusion of the water molecules into the film increased. Kapok A which has reaction temperature at 60 ^{o}C exhibit lowest moisture uptake compare to others. In other words, Kapok A is less sensitive to moisture attack.

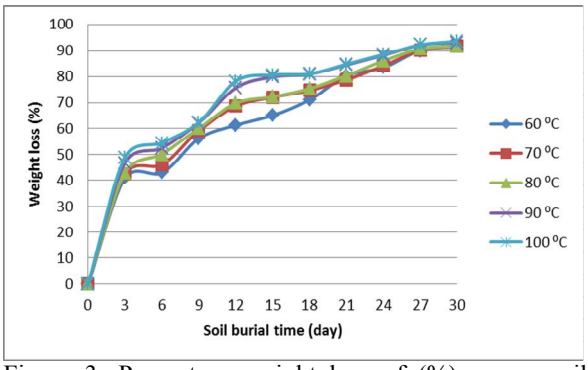

Figure 3: Percentage weight loss of (%) versus soil burial time (day) for every reaction temperature.

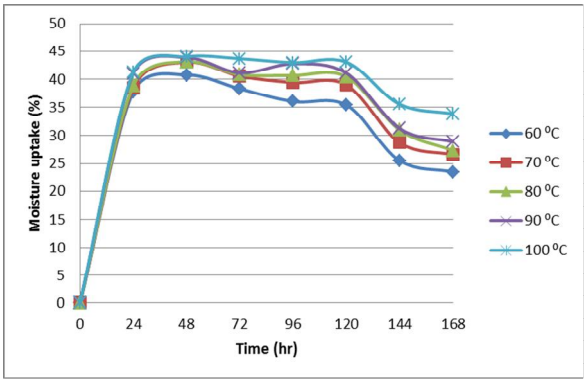

Figure 4: Percentage of moisture uptake versus time.

Conclusion

In this research, 'All cellulose composite' film from kapok cellulose fiber have been successful prepared via partial ionic dissolution method by using ([BMIM] Cl). From the FTIR result, we can conclude that the peak which represents butyl group which indicated the toxicity of the ([BMIM] Cl) decreased as the reaction temperature increase. This is due to the solvent of ([BMIM] Cl) which vaporized when the temperature of the solvent is increased. When the solvent vaporized, the alkyl compound is also vaporized and diminishes along with the vapor. From the biodegradability test, it showed that the degradation of the kapok cellulose film increased as the reaction temperature increase and it is

supported by the previous study of Liu *et al*., (2011). According to moisture uptake test, kapok cellulose film at all reaction temperature exhibited decreasing trend after 5 days. Kapok A showed lowest moisture uptake compare to Kapok E. Kapok A is expected to be less sensitive to moisture attack compare to Kapok E.

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References

Abdul Rahman, W., Abd Rahim, N., & Din, S. N. (2014). Novel Cellulose Composite Film Of Durian Rind/Kapok Linter By NaOH/Urea Solvent System. *Proceedings of 5th International Conference on Science and Technology*.

Duchemin, B. J., Mathew, A. P., & Oksman, K. (2009). All-cellulose composites by partial dissolutio in the ionic liquid 1-butyl-3-methylimidazolium chloride. *Composites Part A: Applied Science and Manufacturing, 40*(12), 2031-2037.

Gibril, M. E., Yue, Z., Da, L. X., Huan, L., Xuan, Z., Feng, L. H., & Muhuo, Y. (2012). Current status of applications of ionic liquids for cellulose dissolution and modifications: review. *International Journal of Engineering Science and Technology, 4*(7).

Gulhane, P. A., Gomashe, A. V., & Deo, N. V. (2014). Influence of Ionic Liquid 1-butyl-3-Methylmidazolium Chloride on the Soil Micro-Ecological System. *International Journal of Current Microbiology and Applied Sciences, 3*, 805-813.

Grammatikos, S. A., Zafari, B., Evernden, M.C., Mottram, J. T., & Mitchels, J. M. (2015). Moisture uptake characteristics of a pultruded fibre reinforced polymer flat sheet subjected to hot/wet aging. *Polymer Degradation and Stability, 121*, 407-419.

Jeon, Y., Sung, J., Seo, C., Lim, H., Cheong, H., Kang, M., Kim, D. (2008). Structures of ionic liquids with different anions studied by infrared vibration spectroscopy. *The Journal of Physical Chemistry B, 112*(15), 4735-4740.

Jin, Z., Wang, S., Wang, J., Zhao, M., & Gao, S. Effect of Coagulation Bath Conditions on the Properties of Cellulose Packaging Films From Ionic Liquid [BMIM] Cl.

Leja, K., & Lewandowicz, G. (2010). Polymer biodegradation and biodegradable polymers—a review. *Polish Journal of Environmental Studies, 19*(2), 255-266.

Liu, Z., Wang, H., Li, Z., Lu, X., Zhang, X., Zhang, S., & Zhou, K. (2011). Characterization of the regenerated cellulose films in ionic liquids and rheological properties of the solutions. *Materials Chemistry and Physics, 128*(1), 220-227.

Lozano, L., Godinez, C., De Los Rios, A., Hernandez-Fernandez, F., Sanchez-Segado, S., & Alguacil, F. J. (2011). Recent advances in supported ionic liquid membrane technology. *Journal of Membrane Science, 376*(1), 1-14.

Shi, F., Peng, J., & Deng, Y. (2003). Highly efficient ionic liquid-mediated palladium complex catalyst system for the oxidative carbonylation of amines. *Journal of Catalysis, 219*(2), 372-375.

Shi, F. Peng,

Solomons, T. G., & Fryhle, C. Organic chemistry, 2000: John Wiley & Sons, Inc., USA.

Soykeabkaew, N., Laosat, N., Ngaokla, A., Yodsuwan, N., & Tunkasiri, T. (2012). Reinforcing potential of micro-and nano-sized fibers in the starch-based biocomposites. *Composites Science and Technology, 72*(7), 845-852.

Tye, Y. Y., Lee, K. T., Wan Abdullah, W. N., & Leh, C. P. (2015). Effects of process parameters of various pretreatments on enzymatic hydrolysability of Ceiba pentandra (L.) Gaertn. (Kapok) fibre: A response surface methodology study. *Biomass and Bioenergy, 75*, 301-313.

Wan, Y., Luo, H., He, F., Liang, H., Huang, Y., & Li, X. (2009). Mechanical, moisture absorption, and biodegradation behaviours of bacterial cellulose fibre-reinforced starch biocomposites. *Composites Science and Technology, 69*(7), 1212-1217.

Wang, J., Zheng, Y., & Wang, A. (2012). Effect of kapok fiber treated with various solvents on oil absorbency. *Industrial Crops and Products, 40*, 178-184.

Xiao, W., Yin, W., Xia, S., & Ma, P. (2012). The study of factors affecting the enzymatic hydrolysis of cellulose after ionic liquid pretreatment. *Carbohydrate Polymers, 87*(3), 2019-2023.

Yunus Khan, T. M., Atabani, A. E., Badruddin, I. A., Ankalgi, R. F., Mainuddin Khan, T. K., & Badarudin, A. (2015). Ceiba pentandra, Nigella sativa and their blend as prospective feedstocks for biodiesel. *Industrial Crops and Products, 65*, 367-373.

Zadegan, S., Hosainalipour, M., Rezaie, H., Ghassai, H., & Shokrgozar, M. (2011). Synthesis and biocompatibility evaluation of cellulose/hydroxyapatite nanocomposite scaffold in 1-n-allyl-3-methylimidazolium chloride. *Materials Science and Engineering: C, 31*(5), 954-961.

Zadegan, S., Hosainalipour, M., Rezaie, H. R., Ghassai, H., & Shokrgozar, M. A. (2011). Synthesis and biocompatibility evaluation of cellulose/hydroxyapatite nanocomposite scaffold in 1-n-allyl-3-methylimidazolium chloride. *Materials Science and Engineering: C, 31*(5), 954-961.

Zhang, J., Liu, S.-S., Dou, R.-N., Liu, H.-L., & Zhang, J. (2011). Evaluation on the toxicity of ionic liquid mixture with antagonism and synergism to Vibrio qinghaiensis sp.-Q67. *Chemosphere, 82*(7), 1024-1029.

Zheng, Y., Wang, J., Zhu, Y., & Wang, A. (2015). Research and application of kapok fiber as an absorbing material: A mini review. *Journal of Environmental Sciences, 27*, 21-32.