

Physicochemical Properties of Low Transition Temperature Mixtures in Water

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A new generation of designer solvents, low transition temperature mixtures (LTTMs) could be the ideal solvent for the separation of the main biopolymers in lignocellulosic biomass such as lignin, cellulose and hemicellulose. The separated biopolymers have prospective to be converted into high valuable products. LTTMs can be synthesized from two natural high melting point materials through hydrogen bonding interactions. The objective of this research was to study the effects of water in the physicochemical properties of LTTMs such as hydrogen bonding, thermal stability and lignin solubility. LTTMs were prepared in the presence and absence of distilled water with malic acid as the hydrogen bond donor (HBD) and sucrose as hydrogen bond acceptor (HBA). The molar ratio of malic acid to sucrose was fixed at 1:1. Based on the fourier transform infrared spectroscopy (FTIR) analysis, the FT-IR spectra of all the LTTMs shown representative peak of carboxylic acid group of malic acid turned broader at $1,710\text{ cm}^{-1}$ for the C=O group. Nevertheless, the peaks involved in the H-bonding due to the formation of LTTMs shifted and became broader within $2,500 - 3,600\text{ cm}^{-1}$ for the OH groups of carboxylic acid and alcohols in the presence of water. The degradation temperature of LTTM was not affected by the addition of water which remained at 400 K. In addition, the LTTM with water had increased the lignin solubility from 6.22 to 6.38 wt% without affecting the thermal behaviour of LTTMs.

1. Introduction

Nowadays, the manufacturing of raw materials resulted from chemicals obtained mainly from fossil resources are in the process of exhaustion. Tuck et al. (2012) highlighted the use of renewable raw materials as alternatives to fossil resources for the generation of energy and as starting materials for industrial chemical processes gain great attention. Biomass is the most abundant renewable resource with an estimated global production of around 1.0×10^{11} tons per year. Cellulose is the most abundant biopolymer on earth, thus it is a valuable source of raw materials for chemical and fuel industries (Mäki-Arvela et al., 2010). The lignin, cellulose and hemicellulose in lignocellulosic biomass are congregated in a complicated three-dimensional structure which causes resistant against chemicals and microbial attack that makes it hard to be hydrolysed. An efficacious separation of these components and their subsequent separation are the requirement for the production of high value products from lignocellulosic biomass (Hamzeh et al., 2013).

To realize the aim of dissociating the lignocellulosic biomass, the development of ideal green solvents with high sustainability which are safe for both human and environment is critical (Moity et al., 2012). Sheldon (2005) stated that the most popular green solvents are water which includes aqueous phase, supercritical carbon dioxide and ionic liquids. Initially, ionic liquids were classified as new generation of green solvents with the properties of negligibly low vapour pressure, good structural tunability, high heat capacity, density and conductivity. Somehow, most of the ionic liquids failed to satisfy the sustainability requirement of ideal green solvent due to their petroleum-based starting materials and poor bio-compatibility.

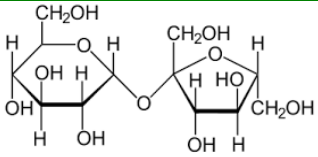
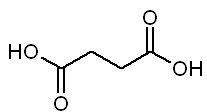
Protic ionic liquids were used as biomass pretreatment for the production of ethanol (Enio de Azevedo Rocha et al., 2014). Ionic liquids show restrictions in terms of recoverability and cost for large scale applications in the early stages (Sun et al., 2011). Nonetheless, the recoverability and commercialization potential of ionic liquids had been evaluated and improved recently (Chen et al., 2014). Hence, new green approaches towards the substitution of volatile organic solvents were taken into consideration. In recent years, deep eutectic solvents (DES) have evolved as new substitution of green solvents for ionic liquids as they are bio-compatible and easy to prepare in which some bio-based chemicals represented as a major part of the final mixtures (Avalos et al., 2006). DES have significant advantages over conventional solvents as their structures can be tuned by changing the nature and the ratio of the hydrogen-bonding components. Thus, their properties are straightforwardly influenced by the molar composition of the compounds in the mixture. Choi et al. (2011) reported the disclosure of 30 combinations with natural carboxylic acids, sugars, choline chloride and water which formed viscous liquids known as "natural deep-eutectic solvents" (NADESs). NADESs had been utilized in dissociating the metabolites in plants. This technique was applied by other authors (Maugeri and Domínguez de María, 2012) for the synthesis of new green solvents. Besides, low transition temperature mixtures (LTTMs) and 26 new solvents have been proposed by combining choline chloride, amino acids, carboxylic acids and other environmentally benign starting materials as most of the DESs show glass transition points instead of eutectic melting points (Francisco et al., 2012). LTTMs comprise of at least one hydrogen bond donor (HBD) and one hydrogen bond acceptor (HBA) counterpart that result in the formation of liquid mixture showing an unusually low freezing point. The hydrogen bonding interaction lead to some of the promising characteristics of ionic liquid as solvents are shared by DESs. The HBA can be an amino-acid, a salt, carbohydrates, an organic salt or a natural salt whereas urea, an organic acid, an alcohol, a polyol or an aldehyde can be the HBD. Natural carbohydrates are the most abundant class of organic compounds found in living organisms. They were considered as promising starting materials to sustain the revolution in chemical synthesis. Some attention has been paid to the potential applications of carbohydrates due to their ability in value-added conversions (Kubik et al., 1996) and the growth of research on this field has been noticed in the past few years (James et al., 2010). The potentials of LTTMs to dissociate the lignocellulosic biomass structure were evaluated. Preliminary experiments were performed to examine the solubility of real wheat straw biomass samples in choline chloride-lactic acid (LC 2:1) and malic acid-proline mixtures (MP 1:3) where less biomass particles can be noticed after the pretreatment with MP 1:3 mixtures. Therefore, malic acid had been selected as a hydrogen bond donor for the synthesis of LTTMs as the malic acid combinations were found to show much higher solubility in lignin when comparing with other hydrogen bond donors (Francisco et al., 2012). This work focused on the effect of water in the synthesis of LTTMs by using L-malic acid as HBD and sucrose as HBA. The physicochemical properties of the LTTMs prepared in the presence of water such as hydrogen bonding, degradation temperature and biopolymers solubility were analysed and discussed.

2. Experimental Section

2.1 Materials

Starting materials for the synthesis of LTTMs such as L-malic acid and sucrose were obtained from Wako Pure Chemical Industries Ltd. Their molecular structures and melting points are shown in Table 1.

Table 1: Molecular structure and melting point of the starting materials

Raw Material	Molecular Structure	Melting Point (°C)
Sucrose		186
L-malic acid		130

Cellulose microcrystalline was obtained from Merck, Germany and starch (corn) was purchased from Wako Pure Chemical Industries Ltd for the screening of biopolymers solubility. The lignin (alkaline) was bought from Tokyo Kasei Kogyo Co., Ltd with the specification as shown in Table 2.

Table 2: Product Specification of Lignin Sample

Name	Lignin (alkaline)
Methyl group	10.0 to 12.0 %
Ignition residue (sulfate)	20.0 to 29.0 %
Water	max. 10.0 %
pH	8.0 to 10.0 (50 g/L)

2.2 Synthesis of LTTMs

Both the starting materials (HBD and HBA) were blended completely at 1:1 molar ratio in a three-neck round bottom flask with magnetic stirring to develop contact between the solid crystals. The flask was heated up gradually in an oil bath and the heating process was stopped when all the solid particles can no longer be observed. The experiment was repeated in the presence of 1 ml of distilled water.

2.3 Freeze drying of LTTMs

Freeze-drier (EYELA FDU-1200) was acquired to remove the excessive water content in the LTTMs. The vacuum pump operation was started its auto-mode function after the trap temperature was cooled to -45 °C. The drying process was stopped once the samples have constant weight.

2.4 Physicochemical properties tests

Frontier FT-IR Spectrometer (PerkinElmer) equipped with attenuated total reflectance (ATR) was used to analyse the fourier transform infrared spectroscopy (FTIR) spectra of starting materials and LTTMs. The existence of hydrogen bond between the starting materials was proven by comparing the data collected. Thermogravimetric analysis (TGA) was performed using EXSTAR 6000 TG/DTA6300 from 35 °C to 300 °C with heating rate of 20 K/min to determine the degradation temperature of starting materials and LTTMs. The carrier gas used was nitrogen with flow rate of 250 mL/min.

2.5 Biopolymers solubility tests

Cloud point method was applied to examine the biopolymers solubility such as lignin, starch and cellulose. Vials containing 2 g of LTTMs were placed into an oil bath at constant temperature of 60 °C and 0.2 – 1 mg of sample was added continuously with vigorous stirring. The sample was kept for 24 h after complete dissolution of solutes in LTTMs was observed. The solubility (wt %) was recorded if the biopolymers did not dissolve into the solvents.

3. Results and Discussion

Transparent colour LTTM was obtained in molar ratio of 1:1 for malic acid and sucrose with the presence of water (MSW 1:1:1). Introduction of water avoided the caramelisation of sucrose at high temperature and yielded clear LTTM which reduced the temperature for synthesis of LTTM from 90 to 60 °C while the reaction time was reduced from 10 to 5 min. Adding small amount of water to a mixture reduced preparation time, temperature and viscosity as the water was strongly bound with the mixture formed (Dai et al., 2013). The heating process was terminated once clear mixtures formed and the excessive water content in LTTMs was eliminated by using freeze drier. Further analysis such as FTIR, thermal stability and biopolymers solubility were performed and discussed to study the effects of water on the physicochemical properties of LTTMs.

3.1 FTIR spectra analysis

Figure 1 shows the broad band with strong intensity in the wavenumber region of 2,500 to 3,700 cm^{-1} as a result of the O-H bond stretching vibration of the alcohol groups. In addition, the stretching vibration of C=O group resulted in the broaden peak at 1,710 cm^{-1} . Based on the works of Francisco et al. (2012), these peaks demonstrated the existence of hydrogen bond in the mixtures. The spectra for LTTMs synthesized from sucrose as HBA appeared very similar with the presence of water in the synthesis of LTTMs. There is a slight difference in terms of band intensities within the wavenumber of 2,500 to 3,700 cm^{-1} which might be due to the increased ratio of symmetric and asymmetric H_2O stretching vibrations. The main bands for peak shifts and malic acid peaks were separated by using the dotted red lines. Therefore, removal of excessive water content from the LTTMs through freeze drying was critical as hydration of compounds will lead to an enormous consequence on the spectrum and generally produces a lot of complexity in the form of additional absorption bands and structure to existing band.

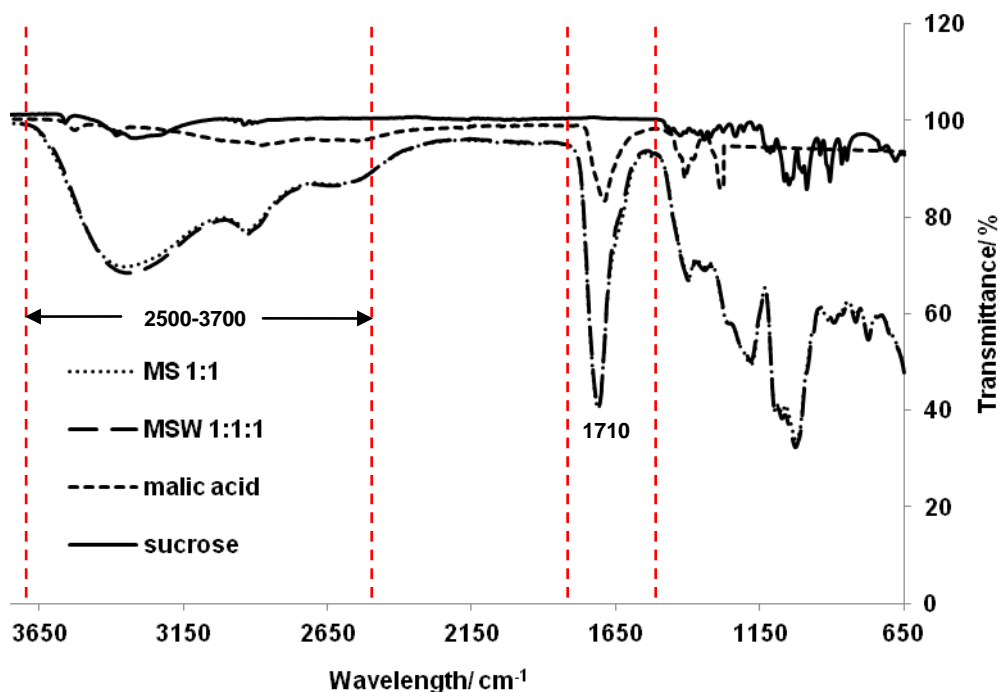


Figure 1: FT-IR spectra of malic acid, sucrose and LTTMs (MS 1:1, MSW 1:1:1)

3.2 Thermogravimetric analysis

The thermal behaviour of LTTMs prepared in the absence and presence of water were analysed to determine their degradation temperatures. The comparison of the TGA curves of LTTMs with the presence and absence of water is shown in Figure 2. The TGA curves of LTTMs were similar to each other at the degradation temperature of 400 K. Besides, the remaining water in LTTMs had formed part of the mixture as there was no reduction of mass at 373 K. In addition, the degradation temperature of starting materials was higher than the LTTMs which presumably due to the potential scattered structure during the synthesis of LTTMs that generated the high amorphous fraction and further decreased the heat-resistivity of LTTMs to decompose at lower temperature (Ramesh et al., 2012).

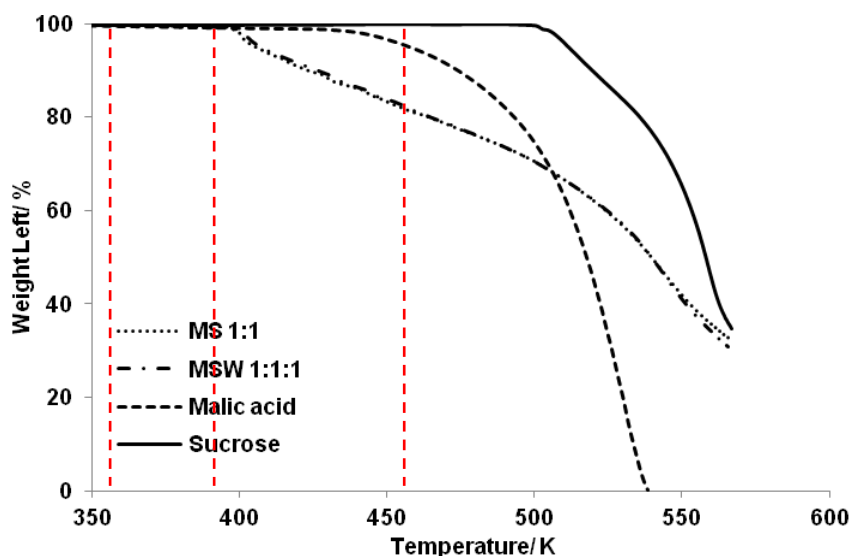


Figure 2: TGA curves of malic acid, sucrose and LTTMs (MS 1:1, MSW 1:1:1); the vertical line indicates the transition temperature of the constituents

The high polarity of water makes it be the abundant natural substance that acts both as donor and acceptor. Water was assumed to form part of the LTTMs without affecting their properties (Francisco et al., 2013). It is crucial for LTTMs to have stable degradation temperature after the addition of water as thermal properties regulate the range of temperature at which the LTTMs can sustain their liquid state and its range of function. In this context, the maximum temperature used for the study of biopolymers solubility was based on the degradation temperature of LTTMs. In future works, it will also be used as the pretreatment temperature for the delignification of lignocellulosic biomass by using LTTMs.

3.3 Screening of biopolymers solubility

This screening is very vital to estimate the capability of LTTMs to extract the lignin from lignocellulosic biomass. The most abundant renewable polymers in lignocellulosic biomass are cellulose and lignin while starch is used to replace the polysaccharide in our study (Francisco et al., 2012). Table 3 shows LTTMs had higher solubility for lignin compared to starch and cellulose. There was no solubility of cellulose was found for the synthesized solvents and formed opaque liquid after stirring for 24 h. Solvents with high selectivity are preferable for separating lignin from cellulose and starch which indicated the mixtures had a high potential to be applied for the delignification of lignocellulosic biomass (Francisco et al., 2012).

Table 3: Biopolymers Solubility of the Synthesized LTTMs

Name	T _{test} (°C)	Lignin (wt %)	Starch (wt %)	Cellulose (wt %)
MS 1:1	60	6.22	0.14	0.00
MSW 1:1:1	60	6.38	0.16	0.00

The solubility's efficiency of LTTMs was improved with the addition of water which shows the trend of MS 1:1 < MSW 1:1:1. Therefore, the solubility capacity of the solvents was varied accordingly to the amount of water added during preparation. Nevertheless, extended dilution would result in the loss of existing hydrogen bonds and resulted in the rupture of unique structures in mixtures (Gutiérrez et al., 2010). Thus, optimum amount of water should be taken into consideration for the preparation of LTTMs.

4. Conclusions

In this work, LTTMs were prepared in the presence and absence of distilled water with malic acid as the HBD and sucrose as the HBA. The FT-IR spectra of all the LTTMs shown representative peak of carboxylic acid group of malic acid turned broader at 1,710 cm⁻¹ for the C=O group due to the hydrogen bonding between the starting materials. However, the peaks involved in the H-bonding as a result of the formation of LTTMs shifted and became broader within 2,500-3,600 cm⁻¹ for the OH groups in the presence of water due to the increased ratio of symmetric and asymmetric H₂O stretching vibrations. The degradation temperature of LTTMs with the absence and presence of water were in vicinity to each other. Besides, the addition of water during the synthesis of LTTMs also enhanced the biopolymers solubility capacity without affecting the thermal behaviour of LTTMs.

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