The effect of choline chloride: acetamide deep eutectic solvent to physicochemical and mechanical properties of pectin-based bioplastic

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Abstract. The rapid increment of synthetic plastic wastes in our environment has triggered in production and development of new biomaterial for resolving problems such as pollution as well as weak mechanical properties. Pectin polysaccharides are recognized as a new potential biomaterial in developing bioplastic. The main purpose of this study is to develop and characterize citrus pectin bioplastic using deep eutectic solvents (DES) of choline chloride: acetamide (1:2), CC:Ac as a plasticizer. The potential of produced bioplastic (BP-CC:Ac) was studied through investigation of their physicochemical and mechanical properties which include pH, thickness, opacity, solubility, tensile strain, tensile stress and Young Modulus. A citrus pectin-based bioplastic without the plasticizer (C1) and with the conventional plasticizer of pure acetamide (C2) were prepared as controls. The produced BP-CC:Ac showed a higher value of thickness (0.2658±0.0015mm), opacity (0.492±0.02A), and solubility (23.26±0.03%) than the control, C1 (0.1963±0.0032mm, 0.407±0.01A, and 16.42±0.01% respectively) and C2 (0.1833±0.001mm, 0.447±0.01A, and 17.88±0.05% respectively). The high acidity of BP-CC:Ac (pH 3.21) provide a strong inhibition toward bacteria which is highly demanding for medical purposes. The tensile strain, tensile stress and Young Modulus of BP-CC:Ac were measured at 5.080 ± 0.04 %, 2.221 ± 0.08 MPa and 113.946 ± 0.08 MPa, respectively. It was found the BP-CC:Ac was more flexible and have smooth surface texture than both controls, C1 and C2 which suitable for plastic wrapping. Other than being natural and biodegradable, the addition of CC:Ac DES had improved the physicochemical and mechanical properties of pectin based-bioplastic. In conclusion, the addition of CC:Ac DES has enhanced the properties of BP-CC:Ac and increased the potential of plastic as an ecofriendly and sustainable future material.

1 Introduction

The everyday uses of petrochemical-based plastic have led to large-scale demand for mass-produce product, which then rapidly accumulated and ends up as non-biodegradable trash in landfills and the ocean for centuries [1]. The generic growth of these unsustainable products
was continuously damaging the environment and human while researchers were struggled in finding the solution to the problems.

There is still a lot of sustainable material that can be used to encounter the problem, such as polysaccharide from sugar cane or potato[2]. The development of the bioplastic for future applications is normally focused on the ability of bioplastic to sustain. One of the material bases for producing a sustainable bioplastic is a polysaccharide which can be disposed of in the environment and can easily degrade through the enzymatic actions of microorganisms[2]. The presence of enzymes in bacteria known as *Ideonella sakaiensis* have converted the plastics into an intermediate substance and also plastic building blocks[3].

A common additive such as phthalate used in plastic production has become one of the causes of health problem, which leaking of this endocrine disruptors can cause cancerous tumour and other development disorders[4]. Therefore, a green solvent has been introduced to replace the conventional and toxic additive, which is known as deep eutectic solvent (DES). DES is a better extension of the ionic liquid model that made up from the formation of two or more compounds; a quaternary ammonium salt and either a metal salt or a hydrogen bond donor[5]. Previous studies have shown the abilities of DES as a solvent in various fields such as organic reactions[6], extraction of metals, polyaromatic hydrocarbons and DNA[7]–[9], electrochemistry [10] and bioplastic development[11]–[13].

Hence, this study was conducted to investigate the role of DES as a plasticizer in the production of pectin-based bioplastic by characterizing their physicochemical and mechanical properties. The effect of addition DES to the produced plastic were evaluated according to the changes observed in both physicochemical and mechanical properties. The unique properties of DES itself such as low cost of components, easy to prepare, tuneable physicochemical properties, negligible vapour pressure, non-toxicity, non-reactive with water, non-flammability, high conductive, bio renewability and biodegradability have promised great potential for enhancing the bioplastic properties[5], [14]–[16].

2 Method

2.1 Synthesis of DES

The DES (CC:Ac) was synthesized by heating choline chloride (CC) (20.1g) and acetamide (Ac) (17.72g) in 1:2 moles ratio at 60 to 80 °C until the colourless liquid was formed. Both chemicals were bought from Acros, Belgium with 99% purity.

2.2 Bioplastic preparation

30 ml of 2% of w/w citrus pectin solution were poured in a cast. The sample of bioplastic BP-CC:Ac was added with 3% of DES CC:Ac. Two controls were prepared; which were the pectin bioplastic without plasticizer as control one (C1) and pectin bioplastic with acetamide as control two (C2). The bioplastics were prepared in triplicates for each test [17].

2.3 Physicochemical characterization of DES

2.3.1 pH measurement of bioplastic

The pH of pectin-DES mixtures was measured using a pH meter (EL20-Kit Benchtop, Mettler Toledo, USA). The pH probe was immersed into the non-solidified bioplastic prior to casting in the beaker. The pH measurements were conducted in triplicates.
2.3.2 Thickness determination of bioplastic

The thickness of each produced bioplastic was measured using digimatic thickness gauge (Model 547-301, Mitutoyo, Japan). The thickness of the bioplastic was measured at the centre and the reading was repeated for three times.

2.3.3 Opacity of bioplastic

The opacity of each bioplastic was measured using UV visible spectrometer (SPECTRONIC™ 200 Spectrophotometer, ThermoFisher Scientific). The light transmittance value for each bioplastic was recorded three times. The highest and lowest value of absorbance were taken for the indication of high and low opacity of bioplastic[18].

2.3.4 Solubility (S) of bioplastic

Each of the bioplastics was cut into a standard size of 2 cm x 2 cm. Thus, the bioplastic was incubated in a drying and sterilization oven (Fisherbrand™ Isotemp™). Then the sample was weighed ($W_i$), immersed and stirred in a beaker filled with 50 ml of distilled water at 175 rpm for 6 hours. The solubility of the bioplastic was measured based on weight loss after 6 hours. The samples were then removed from the water and the dry mass ($W_f$) was determined under the same described conditions to obtain the initial dry mass. The solubility in water was expressed as a percentage of solubilized material, calculated from the results in triplicate, as shown in Eq. (1).

\[ S = \frac{W_i - W_f}{W_i} \times 100 \quad (1) \]

2.4 Mechanical characterization of DESs

The tensile properties of bioplastic which include tensile stress, tensile strain and Young modulus analysis were measured at room temperature using Instron Universal Testing Instrument (Instron 3365, Intron, USA) equipped with a 1kN load cell according to method ASTM D882-02 (ASTM, 1992).

3 Results and Discussion

3.1 Physicochemical properties

Fig. 1 shows the results obtained from the testing conducted on three produced bioplastics, BP-CC:Ac, C1 and C2. It can be observed that all of the produced bioplastics were relatively acidic (pH 2.98 to 3.28) and the most acidic bioplastic is the bioplastic made of pure pectin without aceticamide, C1 at pH 2.98±0.05. The acidity of pectin bioplastic was influenced by the depolymerization through a treatment with sodium hydroxide and hydrochloric acid in the extraction of pectin process. Besides that, pectin is a low ester compound that has a pH range from 2.6 to 7.0[17]. Both of BP-CC:Ac and C2 show a small increase of pH than C1 due to the presence of substances other than pectin which changed the concentration of proton and reduced the acidity of solution. The acidic properties of all produced bioplastics showing that they can provide a strong inhibition toward bacteria which suitable as a material for medical application, such as anti-microbial appliance.
Thus, in Fig. 1 a linear effect of the DES on the thickness was observed where the width of BP-CC:Ac (0.2658±0.0015 mm) was measured thicker than controls (C1:0.1963±0.0032 mm; C2: 0.1833±0.001 mm). The increase in the thickness of BP-CC: Ac was caused by the interaction of plasticizer added to the pectin solution. This results can be related to the study done by Cabello et al., [19] who reported that the interaction between the ion pairs of the carboxylic group on pectin with amine from chitosan produced a diminution, which resulted for reducing numbers of hydroxyl groups and cause d the hydrophilicity followed by swelling of the membranes. Hence, since the result of the study have shown a similar trend with the past research, it can be concluding the size of the plastic with DES become thicker than controls due to the interaction of plasticizer with pectin structures.

BP-CC:Ac was found to have the lowest opacity with the absorbance of 0.492±0.02A, which is lower than the controls. The additional of DES add up the number of components in the bioplastic structure; thus it decreases the space for light to be transmitted [20]. The high value of absorbance reading proves the number of particles that can absorb light were higher in BP-CC:Ac.

The solubility of the bioplastics was ranged from 16.42 to 23.26%. The solubility rates for BP-CC:Ac was the highest when compared to the controls. The hygroscopic choline chloride from DES has increased the rate of solubility as it easily absorbs water [21]. The addition of DES plasticizer increases the solubility rates of the bioplastic as the two hydrogen atoms that were bonded to the nitrogen in acetamide carbonyl group able to form hydrogen bonding with water. However, all the produced bioplastics are considered to have high solubility rates. From the other point, this result has shown with the addition of DES; the produced bioplastic was more easily to degrade and the sustainability of bioplastic was not disturbed.
3.2 Mechanical properties

Fig. 2 shows the tensile strain of BP-CC:Ac (6.77±0.23%) was higher than control (C1: 2.15±0.15%; C2: 5.06±0.16%). The tensile strain of the bioplastic was increased when adding the plasticizer and having a greater thickness. In general, tensile strain is the relative length of deformation exhibited by bioplastic when a force applied. According to Shafie et al., [11], there was an interruption of the polymer chains interactions when the plasticizer added. Besides that, the complex structures between pectin and plasticizer created when the plasticizer was added and its eventually increased the strength of the bioplastic thus increase the tensile strain percentage.

The tensile stress was analysed to measure the maximum stress of bioplastics can stand before it breaks. As depicted in Fig. 2, the tensile stress of BP-CC:Ac and C2 were lower than C1 as the added plasticizers in both BP-CC:Ac and C2 caused the interaction of hydrogen bonding in the bioplastics. The added of DES (CC:Ac) and acetamide have decreased the contact between the polymer matrix and the adjacent segments of polymer chains, therefore increasing the segmental mobility and free volume[11]. Meanwhile, a very high value of tensile stress (20.87±0.132 MPa) in C1 caused the bioplastic with pure pectin was too stiff and easily broken.

Hence, the addition of plasticizer could cause the larger inter-molecular area between the polymer chains, thus preventing them from gathering close to each other. Consequently, it restricted the compactness and cohesive strength of the molecular chains in bioplastic with plasticizer. The trend of Young modulus was found to be similar with tensile stress. The interaction of plasticizer was beneficial in reducing the stiffness of polymeric materials which allow it to be more flexible.

Conclusion

The bioplastics were successfully characterized and developed by measuring physicochemical and mechanical properties. The addition of DES as plasticizer into bioplastic had overcome the brittleness and enhance the structures of the bioplastic. Apart from that, the addition of DES also retains the sustainability of BP-CC:Ac as it was easily...
dissolved in water. Therefore, based on the results of the physicochemical and mechanical properties in this study BP-CC:Ac can be suggested as new sustainable material to be used in multiple types of application such as food packaging materials

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