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REINFORCED PECTIN-DES BIOPLASTIC WITH DIFFERENT CONCENTRATION OF CITRIC ACID

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Abstract: The constant demand for synthetic plastics has led to the accumulation of plastic waste in nature due to its non-biodegradable attributes. In this study, the properties of pectin as biodegradable bioplastic were enhanced using Deep Eutectic Solvent (DES) as a plasticiser with concentrations of citric acid as a crosslinker that was ranged from 1% to 4%. The physical characteristic and mechanical properties of bioplastics were determined using the thickness test and the tensile test. The sample with 3% citric acid showed the highest thickness value (0.25±0.01 mm). The results showed that the increase in the concentration of citric acid increased the film's flexibility, thereby influencing the properties of the bioplastic film obtained. The highest citric acid concentration at 4% showed the highest flexibility with 29.02±2.99 MPa, 2.73±0.38% and 10.14±0.88 MPa for tensile strain, tensile stress and Young's Modulus values, respectively. The presence of peak OH, C=O and C-O from Fourier Transform Infrared (FT-IR) spectroscopy outlined the formation and showed the interactions between the pectin, DES and citric acid in the bioplastic that was produced. In conclusion, the properties of bioplastic/pectin/DES were altered with the different concentrations of citric acid either as a crosslinker or as a plasticiser to become a new green alternative to synthetic plastics.

Keywords: Pectin based-bioplastic, plasticizer, deep eutectic solvent, crosslinker, citric acid.

Introduction

Plastics are undoubtedly useful materials used in nearly every aspect of human life and the research into and production of this material has become the fastest-growing industrial field (Urbanek *et al.*, 2018; Walker & Rothman, 2020). Most daily use products are packaged in plastics, leading to an accumulation of plastic packaging waste. Unmanaged plastic waste has become a threat to the environment and marine and other ecosystems (Walker & Rothman, 2020). Consequently, more than half (58%) of the plastic waste is disposed of in landfills and only 18% is recycled throughout the world (Zheng & Suh, 2019). The most commonly used plastic packages are fossil-based plastics derived from petro-chemical as polymer sources (Ahmed *et al.*, 2018) which has a large carbon footprint and depletes non-renewable resources.

With regard to the environment, an innovative application of technology has sparked a transition away from fossil-based plastics towards bio-based polymers (Spierling *et al.*, 2018). The use of bio-based plastics is a promising prospect that leans towards a cleaner environment, increasing the demand for more for research into the industrial uses of such materials (Taufik *et al.*, 2020).

The capacity of bio-based plastics to sustain the desired performance standards is usually prioritised in developing bioplastics for future use. A bioplastic is a polymer made up of renewable or bio-based resources, which depending on their end-of-life disposal options are either biodegradable or recyclable (Álvarez-Chávez *et al.*, 2012; Samantaray *et al.*, 2020).

Polysaccharides are one of the biopolymers derived from biomass, which has the characteristics of being a biodegradable material base sustainable for producing bioplastics. Among the polysaccharide groups, pectin can potentially be used as an alternative to the conventional polymers (Mellinas *et al.*, 2020). Instead of natural bioplastic materials, pectin has numerous advantages, including being renewable, biodegradable and biocompatible.

The linear 1,4-galacturonic acid chain found in pectin allows it to be a tough, flexible and transparent bioplastic film (Vieira *et al.*, 2011). On the other hand, pectin tends to be brittle, highly water-soluble and has poor mechanical characteristics, making it a difficult polymer resource to deal with (Gouveia *et al.*, 2019). Therefore, the physical properties of pectin-based bioplastic can be enhanced by using additives such as plasticisers and crosslinkers. The use of plasticiser via a casting method potentially enhanced the mechanical and barrier properties of pectin. Besides, the biopolymer properties of pectin can be improved through the use of crosslinkers, which help to modify its intra and intermolecular bonding capabilities (Bátori *et al.*, 2019).

Compatibility between the plasticiser and polymer is of major significance for effective plasticisation to increase its flexibility, workability or distensibility (Vieira *et al.*, 2011). Plasticisers function to enhance the plasticity and mechanical characteristics of a material by forming hydrogen bonds that disrupt the strong inter and intramolecular bonds of the material (Krishnamurthy & Amritkumar, 2019). In line with the current trend towards green chemistry, a new group of plasticisers known as Deep Eutectic Solvents (DES) has been discovered. Recent studies showed the potential of DES as a plasticising agent in polysaccharide-based materials (Häkkinen, 2020; Jakubowska *et al.*, 2020). DES possess several advantages, including its sustainability, cost-savings and the fact that it is non-toxic. The modified plastic showed enhancements in its overall morphology, conductivity, thermal and chemical properties (Tomé *et al.*, 2018). Thus, DES has become the preferred component for bio-based packaging materials.

Furthermore, the addition of crosslinker in bioplastics has played an important role in the components. The crosslinker uses covalent bonds to link two or more polymer molecules together, promoting rigidity and molecular mass of the material (Krishnamurthy & Amritkumar, 2019; Nugroho *et al.*, 2020). Citric acid is a type of carboxylic acid that is considered a natural source since it can be extracted from citrus fruits. In recent years, there has been a surge of interest in its usability as a crosslinking agent due to its low-cost, non-toxicity and efficiency in reacting with and stabilising polysaccharide sources (Wu *et al.*, 2019). The citric acid can crosslink with polysaccharides, thus, improving the bioplastic's physical and mechanical characteristics (Uranga *et al.*, 2020).

This study aims to evaluate the mechanical properties and physical characteristics of the pectin-DES reinforced with citric acid at different concentrations of 1%, 2%, 3% and 4%, respectively. On the results obtained, it can be deduced following a comparison with previous literature and works on the subject that these bio-based plastics have the potential to be used as material substitutes for synthetic plastic packaging.

Materials and Methods

Synthesis of DES

The DES (ChCl:EG) was synthesised by heating choline chloride (ChCl) and ethylene glycol $(CH_2OH)_2$ as the hydrogen bond acceptor and donor, in a 1:2 moles ratio at 80°C until the colourless liquid was formed. Both chemicals were bought from Acros, Belgium with 99% purity.

Pectin-DES Bioplastic Preparation

About 2.7 g of 3% w/w citrus pectin and 0.9 mL of 1% ChCl:EG were prepared at a 1:2 moles ratio. Then, DES was added into a beaker to obtain a pectin:DES volume ratio of 3:1. Afterward, citric acid was added to the mixture, ranging from 1%, 2%, 3% and 4% v/v (0% was used as a control).

Distilled water was then added to give a volume of 90 mL and stirred using a magnetic stirring hotplate at room temperature for 2 hours. 30 mL of the solution was poured into a cast and allowed to sit for a few minutes to reduce air bubbles. The samples were dried for 43 hours in Memmert UNE 400 hot-dry oven at 40°C. The bioplastics were prepared in triplicate for each citric acid concentration (Azman *et al.*, 2020).

Thickness Test

The thickness of each bioplastics produced was 7 cm x 1 cm measured using digimatic thickness gauge (Model 547-301, Mitutoyo, Japan). The thickness of the bioplastic was measured six times throughout the sample length and the average thickness was recorded (Galvis-Sánchez *et al.*, 2018).

Tensile Test

The tensile properties of bioplastic were tested at room temperature using an Instron Universal Testing Instrument (Instron 3365, Instron, USA) based on the tensile stress, tensile strain and Young's Modulus analysis. The pectin-DES bioplastics were cut into strips of 7 cm long and 1 cm wide. The specifications of the tensile test were set to 5 cm test area, 5 cm/min crosshead speed and 1 kN cell load according to method ASTM D882-02 (ASTM, 1992).

Fourier Transform Infrared (FT-IR) Spectroscopy

The FT-IR spectroscopy was carried out using an FT-IR spectrometer to determine the functional groups within pectin-DES bioplastic. The spectra was recorded in the range of 4000 to 500 cm^{-1} at room temperature (Truong & Kobayashi, 2020).

Results and Discussion

Pectin-DES bioplastics produced were translucent with smooth appearances. Figure 1 shows the developed bioplastics.

The thickness of the bioplastics was measured, and their average thickness was determined to compare their properties. Table 1 shows the thickness of each pectin-DES bioplastic sample. The bioplastic with 3% citric acid had the highest average thickness, which was 0.25±0.01 mm while the control sample had the lowest average thickness, which was 0.11±0.01 mm. Furthermore, the average thickness of modified pectin-DES bioplastics showed an increasing trend up to 3% citric acid sample, then slightly decreased for the 4% citric acid sample (0.23±0.04 mm).

The result shows that up to a concentration of 3%, citric acid increased the thickness of pectin-DES bioplastics. The increase in thickness can be explained by the total solid content of the modified pectin-DES bioplastic. According to Wu *et al.* (2019), in film formation, citric acid contributes to the amount of solid content of the polymer films, hence, increasing their thickness.

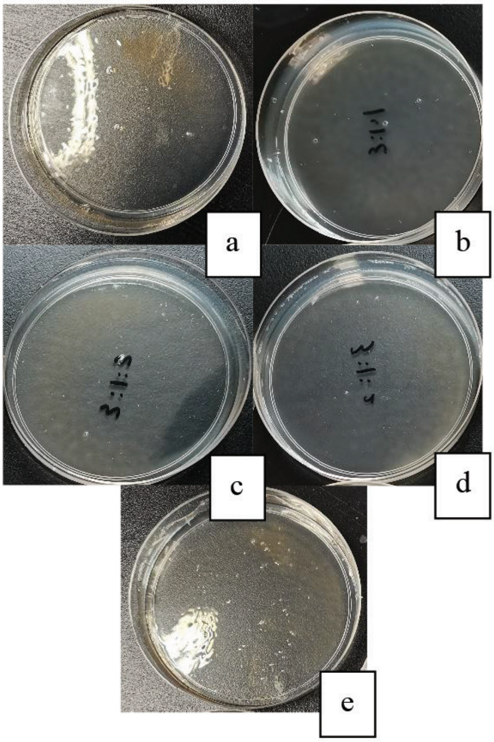

Figure 1: Developed pectin-DES bioplastic with different concentration of citric acids (a) control, (b) 1% citric acid, (c) 2% citric acid, (d) 3% citric acid and (e) 4% citric acid

The effect of citric acid content on tensile stress, strain and Young's Modulus of pectin-DES bioplastics was presented in Table 2. The addition of 1% citric acid in the pectin-DES bioplastics had the highest tensile stress and Young's Modulus.

However, increasing citric acid from 2% to 4% has reduced the tensile stress and Young's Modulus of pectin-DES bioplastic. The tensile strain values increased with the increasing concentration of citric acid. As a result, pectin/DES/4% citric acid appeared as the highest to elongate at 29.02±2.99% compared with the control sample, which had the lowest strain at 2.03±0.61%. The citric acid at 1% increased the mechanical properties due to the improvement of the interaction and crosslinking among the chain.

On the other hand, the citric acid acts as a plasticiser when it became a residue, which is when the crosslink between pectin and citric acid becomes saturated. This caused a decrease in the interaction between the chain and resulted in a reduction of tensile strength and Young's Modulus. Hence, the flexibility properties of the polymer films are enhanced. The flexibility of pectin-DES bioplastics is significantly changed with higher concentrations of citric acid.

This is due to the ability of citric acid to hydrolyse the polymeric chains in high concentrations (Simões *et al.*, 2020). Figure 2 shows the schematic diagram of pectin/DES linkages with addition of citric acid in developed bioplastic.

Table 1: Thickness of pectin-DES bioplastics

Sample	Thickness (mm)*	P-value
Control (pectin/DES)	0.11±0.01	0.00*
Pectin/DES/1% citric acid	0.16±0.01	
Pectin/DES/2% citric acid	0.18±0.03	
Pectin/DES/3% citric acid	0.25±0.01	
Pectin/DES/4% citric acid	0.23±0.04	

Data are presented in mean±SD; n=6
*p<0.05 indicates significant difference by Welch test of One-way ANOVA

Table 2: Tensile strain and stress of pectin-DES bioplastics

Sample	Tensile Stress (MPa)	P-value	Tensile Strain (%)	P-value	Young's Modulus (MPa)	P-value
Control (pectin/DES)	4.48±2.01	0.013*	2.03±0.61	0.00*	455.57±216.10	0.004*
Pectin/DES/1% citric acid	8.65±3.07		4.11±2.54		584.31±88.00	
Pectin/DES/2% citric acid	5.14±0.43		9.16±0.86		135.54±25.85	
Pectin/DES/3% citric acid	3.79±0.53		17.71±0.45		30.05±4.96	
Pectin/DES/4% citric acid	2.73±0.38		29.02±2.99		10.14±0.88	

Data are presented in mean±SD; n=3

*p<0.05 indicates significant difference by Welch test of One-way ANOVA

Ghanbarzadeh *et al.* (2011) had reported that different functions of citric acid were observed either as a crosslinker or plasticiser according to their concentrations used in biopolymers. The role of citric acid as a plasticiser was reported by Wang *et al.* (2014). As a plasticiser, citric acid increases the mobility of the polymer's macromolecules and its interstitial volume, leading to lower intermolecular forces and less dense polymeric networks.

Hence, a decrease in tensile strength and modulus value but increased elongation properties of pectin were observed as more citric acid was added into the solution. Moreover, citric acid may have increased the flexibility of the modified pectin-DES bioplastics because of its ability to increase the molecular space between polymer chains while reducing the hydrogen bonds (Mohamed *et al.*, 2017).

The pectin/DES and pectin/DES/citric acid bioplastics were analysed with FTIR to observe the effect of additions of citric acid to the bioplastic matrix (Figure 3).

There were three main peaks observed in the spectra, which are OH, C=O and C-O. The OH bond vibrations, which depict the presence of hydroxyl groups were observed in the spectra range of 3339.26 cm^{-1} to 3379.70 cm^{-1} to represent the alcohol group in pectin and DES. The OH vibrations became less intense with the increase of citric acid concentration.

According to Wu *et al.* (2019), the cross links that result in the esterification of alcohol from pectin and citric acid causes a decrease in free OH resulting in more ester bonds. The production of the ester group can be seen from the carbonyl peak of C=O around 1739.88 cm^{-1} to 1714.92 cm^{-1}, which proved that crosslinking had taken place between citric acid and pectin.

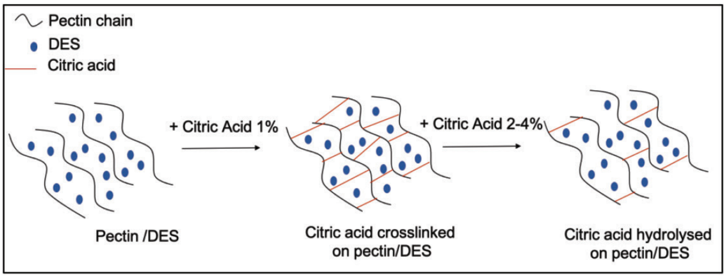

Figure 2: Schematic diagram of pectin/DES linkages with addition of citric acid in developed bioplastic

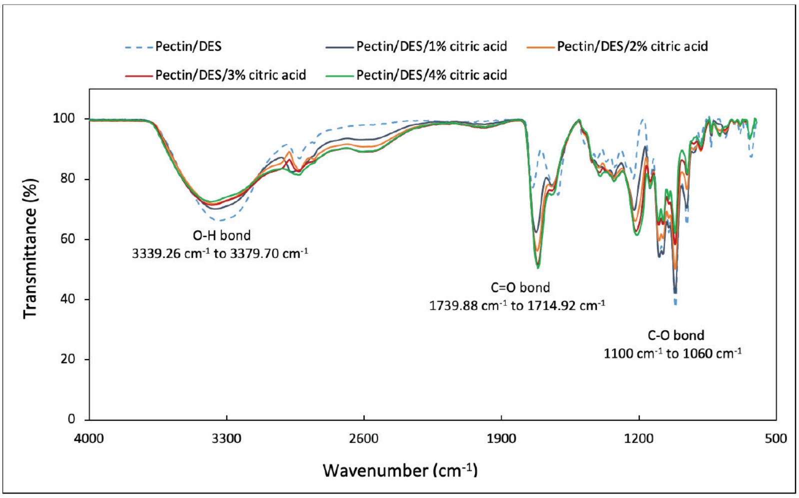

Figure 3: FT-IR spectra of pectin-DES bioplastic samples

The C-O bond that appeared in a spectra range of 1100 cm^{-1} to 1060 cm^{-1} was attributed to the alcohol in DES and the ester bonds produced. The presence of all these peaks confirmed the crosslinking between pectin/DES and citric acid in modified pectin/DES/citric acid. The increased concentration of citric acid has slightly shifted the frequencies of spectra bands, which changed the interactions within the bonds and the resulting properties of the bioplastics produced.

Conclusion

The addition of citric acid to pectin as biopolymer can help to improve the plastic properties. Pectin-DES bioplastics were modified with different concentrations of citric acid and the proceeding tests showed statistically significant effects of citric acid as a crosslinker at 1% for the plastic properties of the biofilm.

The flexibility of modified pectin-DES was also improved with increasing concentrations of citric acid, with 4% citric acid modified sample being most flexible by being less brittle (2.73±0.38 MPa), having an increased elongation value (29.02±2.99%) and lower Young's Modulus (10.14±0.88 MPa).

FT-IR analysis depicted interactions, mainly via esterification and hydrogen bonds formation, between pectin, DES and citric acid through OH, C=O, C-O and C-H stretch vibrations. The results suggest that an increase of the citric acid concentration as plasticiser led to a significant decrease of Young's Modulus values and an increase of tensile strain, which indicate the flexibility of the bioplastic produced. Thus, it makes as an excellent biodegradable alternative for food packaging applications such as food wrappers.

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