

Preparation and Characterization of Pectin-Starch Hydrogel Modified with Urea and Lactic Acid-Based Deep Eutectic Solvent for Soil Water Retention

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ABSTRACT

Hydrogels are 3D polymeric networks that can absorb and retain large amounts of water and benefit many industries, including agriculture. However, most hydrogels nowadays are synthetic, negatively affecting the environment and human health. In this study, two biodegradable hydrogels were prepared using natural polymers of pectin and starch with the addition of deep eutectic solvent (DES) of choline chloride: urea (ChCl: urea) and choline chloride: lactic acid (ChCl: LA) to increase the water absorption through the casting method. The hydrogel has been optimized using different concentrations of crosslinking agent and different concentrations of DES to obtain their highest water sorption. The properties of hydrogels, such as swelling ratio, water retention, mechanical strength, biodegradability, and seed germination, have been investigated using standard methods. The results showed that the optimized and pectin-starch-ChCl: urea, and pectin-starch-ChCl: LA successfully absorbed water up to 108.70% and 120.80% within one hour, respectively, compared to the control, pectin-starch hydrogel without DES (97.86%). The hydrogels were found to be biodegradable with a rate of degradation of 100% for pectin-starch-ChCl: urea and 95.75% for pectin-starch-ChCl: LA, which was better than the control of 90.25% after 20 days in soil. The germination seed testing showed that hydrogel with ChCl: LA significantly promoted the growth of bean seeds and could maintain soil moisture for 20 days. In conclusion, it is proven that hydrogel with DES is better than hydrogel without DES,



considering the higher water sorption of hydrogel and the ability to release water in dry areas. Hence, the hydrogel developed with DES showed high potential for agriculture by maintaining soil moisture, reducing irrigation water consumption, and increasing seed germination.

Keywords: Hydrogel; Pectin-starch; Biodegradable; Water Retention; Deep Eutectic Solvent

INTRODUCTION

In Malaysia, the demand for crop products has grown significantly due to the country's increasing population. Thus, the need for water in agriculture will also increase substantially. In Southeast Asia countries, including Malaysia, irrigation is essential for improving crop yields, particularly in areas with little rainfall, to ensure that crops receive enough water for growth and development. Hence, efficient water management is important, as conventional irrigation methods often lead to water wastage and soil degradation. Agriculture uses more than 70% of freshwater resources, but much of that water is lost due to evaporation, runoff, or leaching. This inefficiency calls for advanced materials that can improve water retention in soil and reduce irrigation frequency, particularly in drought-prone areas.

Nowadays, green agriculture technology is popular since it boosts production and sustainability. Hydrogels have garnered significant attention in agriculture due to their ability to absorb and release water gradually, making them valuable for improving water retention in soil, aiding seed germination, and enabling the controlled release of agrochemicals. Hydrogels are three-dimensional (3D) networks of hydrophilic polymers capable of absorbing large amounts of water while maintaining their structure, making them ideal for agricultural applications. A wide range of natural and synthetic polymers have been used to produce hydrogels. Natural polymers like pectin, chitosan, agar, alginate, and carrageenan are particularly attractive for hydrogel synthesis due to their biocompatibility, biodegradability, and availability from renewable resources [1].

Some hydrogel investigations have shown promise in agriculture, but limits remain. According to Bahram *et al.* [2], after over 50 years of

development, hydrogels are widely used across biological and industrial sectors. Despite their advantages, most commercially available hydrogels are made from non-biodegradable synthetic polymers such as poly(acrylic acid), poly(vinyl alcohol) and polyacrylamide which can absorb more water and show higher mechanical strength than natural polymers. The water absorption capacity of cross-linked polyacrylates is 400 times its weight [3]. However, these synthetic hydrogels pose environmental risks, including soil contamination and the potential to harm human health when residues accumulate [4]. The poor water sorption capacity in many existing hydrogels, particularly those made from natural polymers, is the result of limited cross-linking flexibility, weak hydrophilicity, slow swelling kinetics, environmental sensitivity, and structural instability [5-6].

Previously, researchers have made efforts to overcome the problem of poor water sorption in natural polymers. In 2018, Hasiya *et al.* [7] successfully grafted the acrylic acid over agar and gum Arabic to produce hydrogels using microwave irradiation for soil conditioning material for agriculture. The hydrophilicity of hydrogel increases when the acrylic acid increases as more monomer is accessible for propagation with agar and gum Arabic. Meanwhile, Bora and Karak [8] reported on the use of itaconic acid, which can self-polymerize to form poly(itaconic acid) (PIA) in starch base hydrogel, which reported a faster water absorption on higher itaconic acid content of gel, which suitable for agricultural application. Hence, it proves that hydrophilicity plays a role in improving the rate of swelling in hydrogels.

This study focuses on developing a biodegradable and environmentally friendly hydrogel using natural polymers of pectin and starch, incorporating hydrophilic green solvents called deep eutectic solvent (DES) to enhance water sorption properties. The hydroxyl groups of components in DES interact with the hydrophilic sites on pectin and starch, increasing the number of water-bound sites and potentially improving the hydrogel's water absorption capacity. This research investigates the swelling ratio, water retention, mechanical strength, and biodegradability of developed hydrogels. Additionally, seed germination testing was conducted to evaluate the hydrogel's ability to maintain moisture in soil, ensuring consistent water availability for plants. This approach aims to develop a sustainable hydrogel that overcomes the limitations of synthetic materials while offering a viable

solution for improving water management in agriculture.

EXPERIMENTAL

Materials

Commercial pectin from citrus peel (purity \geq 74.0%) and starch from Sigma-Aldrich were used as a primary base of hydrogel. Calcium chloride (CaCl_2), (purity \geq 94 %) obtained from Bendosen Laboratory Chemicals was used as a crosslinking agent. In preparation for DES, choline chloride (ChCl) from Sigma-Aldrich, with a purity of 95% was used as a hydrogen bond acceptor, while urea and lactic acid which obtained from Merck were used as hydrogen bond donors. The soil and green beans were purchased from Mart in Arau, Perlis.

Preparation of DES

The method to prepare DES was adapted from Shi *et al.* [1]. ChCl and urea were weighed at a mole ratio 1:2, placed in a vial to be heated at 80 °C, and stirred at 800 rpm until a homogeneous solution formed. A solution labeled ChCl : urea was kept in a desiccator before use. The same steps were repeated to prepare another DES, ChCl with lactic acid (ChCl : LA) at a mole ratio of 1:2 were mixed, heated, and stirred to produce ChCl : LA.

Preparation of pectin-starch-DES hydrogel

Separately, 5.0 g of pectin and 5.0 g of starch were dissolved in 100 mL of distilled water. The mixtures were stirred at 800 rpm and heated thoroughly at 80 °C for 1 hour to ensure even distribution [9]. 50 mL of pectin solution was mixed with 50 mL of starch solution, followed by adding CaCl_2 as a cross-linking agent into the mixture at different concentrations. The heated and stirred process was continuous for 30 minutes to produce a homogeneous mixture. Then, DES was added into the mixture under constant stirring at a certain volume. The heating and stirring processes were stopped when a homogeneous mixture was formed. The mixture was poured (100 mL) into a petri dish and cooled at room temperature. The control, pectin-starch hydrogel, was prepared without DES for comparison. A prepared hydrogel

was taken to determine the swelling ratio. The optimization of the hydrogel was studied using three parameters: the concentration of the crosslinking agent, CaCl_2 , and the concentration of two different DES.

Optimization of concentration crosslinking agent

The method to optimize the hydrogel's condition was adapted from Rizwan *et al.* [10]. A 0.25 g of CaCl_2 (0.5% (w/v)) was added to the pectin-starch solution by stirring and heating for up to 15 minutes. The mixture was poured into a petri dish and allowed to cool at room temperature. The same step was repeated by using 0.5 g (1.0 % (w/v)), 0.75 g (1.5%(w/v)), and 1.0 g (2.0% (w/v)) of CaCl_2 to produce hydrogels.

Optimization of concentration of DES

The different concentrations (1.0%, 2.0%, 3.0%, and 4.0% (v/v)) of two different types of DES (ChCl: urea and ChCl: LA) were used for optimization. 0.75 g of CaCl_2 (1.5% w/v) was added to the pectin-starch solution by considering the highest swelling ratio from the previous optimization. After 15 minutes, 500 μL (1.0% (v/v)) of ChCl: urea was added to the mixture and continuously heated for another 15 minutes. Then, the mixture was poured into a petri dish and cooled to room temperature. The same step was repeated to produce other hydrogels using 1000 μL (2.0% v/v), 1500 μL (3.0% v/v), and 2000 μL (4.0% v/v)) of ChCl: urea. The method was continued using the same step by replacing ChCl: urea with ChCl: LA.

Characterization properties of hydrogel

Swelling ratio

A swelling test was conducted to measure the ability of a hydrogel to absorb and retain water. The hydrogels were dried in a vacuum oven (Memmert VO400) at 50 °C for 18 hours before testing. Approximately 0.20 g of dry hydrogel was weighed, soaked in 10 mL of distilled water, and recorded as W_d . After 1 hour, the hydrogel was removed, and excess water was filtered using filter paper. Then, the swollen hydrogel was weighted and recorded as W_s . The measurement was conducted in triplicate. According

to Sousa *et al.* [11], the swelling ratio was calculated using Equation (1).

$$\text{Swelling ratio(\%)} = \frac{W_s - W_d}{W_d} \times 100 \quad (1)$$

W_s (g) and W_d (g) are the weights of swollen and dry hydrogels.

Fourier Transform Infrared Spectroscopy (FTIR)

The functional groups of pectin, starch, prepared DES, and hydrogels were tested using Fourier transform infrared spectroscopy (FTIR, Perkin Elmer, Frontier) over a scanning number range of 400 cm^{-1} to 4500 cm^{-1} and a resolution of 4 cm^{-1} . 0.02 g of prepared samples were placed directly on a sample holder and pressed until it touched the sample. A detector reads the signal and converts the signal to a spectrum. The spectrum shows the percentage transmittance of the sample as a function of wavenumber [12].

Mechanical properties

Tensile stress, tensile strain, and Young Modulus were used to assess the hydrogels' mechanical characteristics. These tensile behaviors were tested at room temperature using a testing machine (Instron 3365) following the ASTM D882-02 standard. The hydrogel was cut into rectangular specimens utilizing a scalpel, with $1.5 \text{ cm} \times 6.0 \text{ cm}$ dimensions, and the machine was operated at a cross-head speed of 0.1 mm/s . The measurements were conducted in triplicate. The Young Modulus was determined from the linear slope of the stress versus strain curves, while the tensile stress and tensile strain were calculated using Equation (2) and (3), respectively [13].

$$\text{Tensile stress (MPa)} = \frac{F_{\max}}{A} \quad (2)$$

F_{\max} (N) and A (mm^2) were the maximum force and the initial cross-sectional area, respectively.

$$\text{Tensile strain(\%)} = \frac{\Delta L}{L_o} \times 100 \quad (3)$$

where ΔL (mm) and L_o (mm) were the change in length and the initial length of the hydrogel, respectively.

Biodegradability

The degree of degradation was used to evaluate the performance and ability of the hydrogel to break down. The method was adapted from Fabian *et al.* [14]. Approximately 0.20 g of dry hydrogel was weighed and recorded as W_i . Then, the dry hydrogel was planted into the soil at 2 cm from the pot's surface. The sample was left at room temperature for 20 days. During this period, 15 mL of distilled water was added every three days to overcome soil drying through evaporation. The hydrogel was removed every two days, cleaned, and dried at 45 °C for 1 hour. After 1 hour of drying, the weight of the hydrogel was recorded as W_f . The test was conducted in triplicate. The degree of degradation (D) was calculated using Equation (4).

$$\text{Degree of Degradation, } D (\%) = \frac{W_i - W_f}{W_i} \times 100 \quad (4)$$

W_i is the initial weight of the hydrogel, and W_f is the hydrogel's weight after specific time intervals of biodegradation.

Water retention in soil

Soil water retention was conducted to evaluate the effectiveness of the hydrogel in improving soil moisture retention. This method was adapted by Ahmad *et al.* [15]. The soil was dried in a vacuum oven (Memmert VO400) at 45 °C for 20 minutes, followed by soil moisture measurement using a digital soil moisture meter (Extech Instruments-MO750). Then, 50 g of soil was transferred into two pots; one pot containing 0.20 g of hydrogel and the other without hydrogel was used as the control. Then, 10 mL of distilled water was added to both pots, followed by the soil moisture measurement. The samples were stored at room temperature. After seven days, the soil moisture in both pots was measured and recorded. The measurement was conducted in triplicate.

Seed germination

The seed germination test was conducted to observe the rate of bean seed (*Vigna radiata*) germinating with and without hydrogel. The germination measurement method was modified by Kolya and Kang [12]. Approximately 0.20 g of hydrogel and 50 g of soil were weighed. After that, the hydrogel and soil were transferred into a pot, and five green bean

seeds were planted. About 10 mL of distilled water was poured into the pot. The pot containing 50 g of soil, five green bean seeds, and 10 mL of distilled water without hydrogel was prepared as a control. After five days, plant germination was observed in both pots. The test was conducted in triplicate. The rate of germination (G) was calculated using Equation (5).

$$\text{Rate of Germination(\%)} = \frac{\text{Numbers of germination seeds}}{\text{Total seeds}} \times 100 \quad (5)$$

RESULTS AND DISCUSSIONS

Preparation of DES

Two different DES, ChCl: LA and ChCl: urea, were produced at a mole ratio 1:2 as a modifier in the hydrogel. The eutectic mixture is a homogenous, colorless, transparent liquid at room temperature. Figure 1 shows the produced eutectic mixtures that were used to prepare gels.



Figure 1: Eutectic mixture of ChCl: LA (left side) and ChCl: urea (right side).

Preparation of hydrogel through optimization

Optimization was performed on the hydrogel to obtain the maximum swelling ratio. The pectin starch solution was prepared and modified with two prepared DES, ChCl: urea and ChCl: LA, to produce pectin-starch-ChCl: urea hydrogel and pectin-starch-ChCl: LA hydrogel. The optimization was conducted on different concentrations of crosslinker and DES. The pectin-starch hydrogel without DES was prepared as a control.

Effects of crosslinker concentration

Calcium chloride (CaCl_2), a crosslinking agent, is added to the hydrogel matrix to bind polymer chains to provide structural stability and prevent the gel from dissolving or disintegrating in water. Thus, the concentration of the crosslinker is a crucial factor in determining the best hydrogel prepared. The pectin-starch hydrogel with different concentrations of CaCl_2 (i.e., 0.5, 1.0, 1.5, and 2.0 (w/v%)) was successfully prepared. From the results obtained, the best concentration of CaCl_2 is 1.5%, based on the highest swelling ratio obtained at 103.77%. The concentration was chosen as the optimized concentration of CaCl_2 . As observed in Figure 2, the swelling ratio of hydrogel increased from 30.21% to 103.77%, with the concentration of CaCl_2 increased from 0.5 to 1.5%. However, at 2.0% of crosslinkers, the swelling ratio dropped significantly to 70.12% due to the excess crosslinking agent that caused the polymer network to become too dense and unable to expand well [16]. Therefore, at 1.5% CaCl_2 , the polymer network is sufficiently spaced, promoting efficient water binding, and this concentration has been selected as the perfect concentration of CaCl_2 . This suggests that the ideal balance is needed for the hydrogel to successfully retain water without dissolving, which is essential for intended applications such as agricultural and biomedical usage. Figure 2 shows the swelling ratio of hydrogel with different concentrations of crosslinking agents.

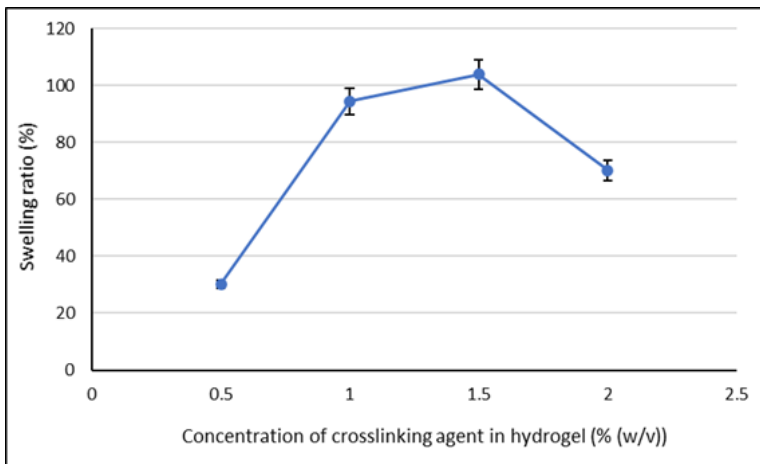


Figure 2: Swelling ratio of hydrogel with different crosslinking agents.

The trend of increasing swelling ratio with concentration of CaCl_2 and decreased when it reached at higher level was similar to study conducted by Amiruddin *et al.* [17]. According to their study, when the concentration of the CaCl_2 crosslinker in the gel are too high, the ionic bond strength increased and lead to more cross-links that caused the network are more compact and cause the degree of swelling to decrease.

Effects of DES concentration

The pectin-starch-DES hydrogels have successfully been prepared using different concentrations of DES (1.0%, 2.0%, 3.0%, and 4.0% (v/v)). The effect of different concentrations of DES on the swelling ratio is shown in Figure 3.

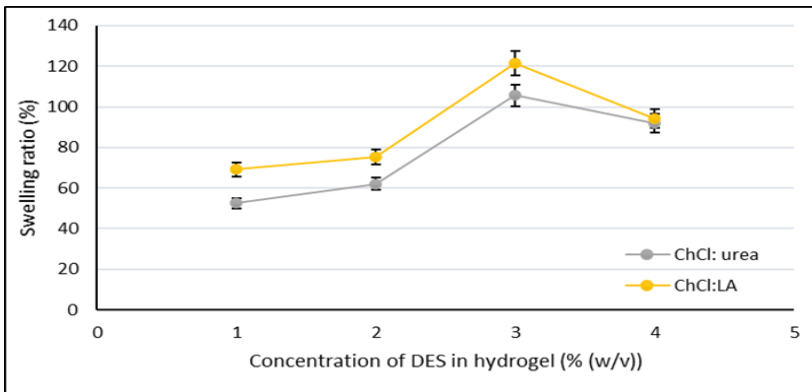


Figure 3: Swelling ratio of hydrogel with different concentrations of DES.

The hydrogels containing both DES exhibit a consistent pattern: the swelling ratio progressively increases from 1 to 3% but undergoes a reduction at 4% DES concentration. Figure 3 demonstrates that the swelling ratio of the pectin-starch-ChCl: LA hydrogel (121.52%) is greater than that of the pectin-starch-ChCl: urea hydrogel (105.74%) when the DES concentration is optimized. Lactic acid's O-H bond is more polar than urea's N-H bond, making hydrogen bonding with water molecules stronger and raising the hydrogel's swelling ratio [18].

The swelling ratio of optimized hydrogels

The improved hydrogels containing 1.5% CaCl_2 and 3% DES

concentration was successfully developed, and their capacity to swell for an extended period (50 minutes) at room temperature was examined. Generally, a hydrogel with DES absorbs more water than the hydrogel without DES (control), proving the ability of DES to act as a water binder in a gel. When DES comes into contact with water, these hydrophilic groups interact with water molecules, allowing the DES to effectively bind and absorb water [19]. From Table 1, the pectin-starch-ChCl: LA hydrogel exhibited the greatest swelling ratio (120.80%) at 25 mins in comparison to the pectin-starch-ChCl: urea hydrogel (108.70%) at 40 mins and pectin-starch hydrogel (97.86%) at 30 mins. Each hydrogel shows a different time to reach the maximum level. Hydrogel with ChCl: LA shows the fastest in absorbing more water than other hydrogel because carboxylic acid-based DES can form more hydrogen bonds to water molecules via the carboxyl group (-COOH) and the hydroxyl group (OH), resulting in multiple hydrogen bonds and increasing their affinity for water. On the other hand, a hydrogel with ChCl: urea needs a longer time to fully swollen as the water can only make hydrogen bonds to urea through the carbonyl group (C=O) and the ammonia group (NH₂), which is less polar compared to in lactic acid. Hence, it slows the water sorption of pectin-starch-ChCl: urea. Control took the longest time to reach the highest swelling ratio as the DES was not added.

Table 1: The swelling ratio of optimized hydrogel with and without DES over 50 minutes.

Time (min)	Swelling ratio (%)		
	Pectin-starch (Control)	Pectin-starch-ChCl: urea	Pectin-starch-ChCl: LA
5	55.78	63.68	80.00
10	68.77	83.95	114.34
15	75.03	95.00	115.57
20	84.31	97.60	117.56
25	90.35	100.03	120.80
30	97.86	102.71	116.57
35	89.31	106.36	114.71
40	80.77	108.70	113.80
45	79.89	107.92	112.82
50	78.03	105.32	112.00

Characterization of hydrogel

The optimized developed hydrogels (at 1.5% CaCl_2 and 3% ChCl : LA and ChCl : urea) were sent for characterization. Generally, all the hydrogels are soft, smooth surfaces and are brittle. As shown in Figure 4, control is the most opaque, followed by pectin-starch- ChCl : LA and pectin-starch- ChCl : urea.

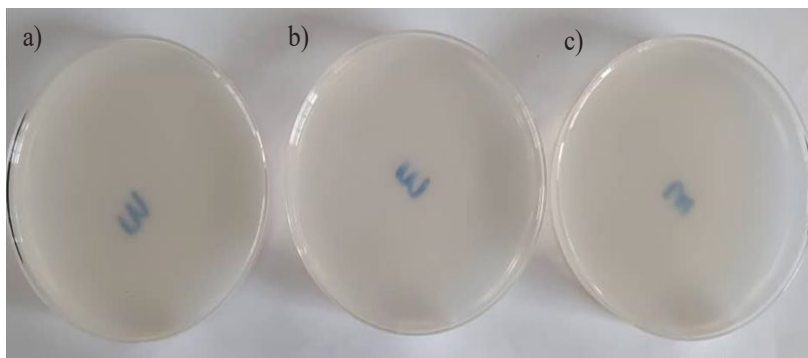


Figure 4: The hydrogels prepared for testing: a) pectin-starch hydrogel (control), b) pectin-starch- ChCl : LA, c) pectin-starch- ChCl : urea.

FTIR spectra

The FTIR spectra of commercial starch, commercial pectin, prepared DES, and prepared hydrogel with and without DES were analyzed to confirm the molecular interactions and functional groups within the gels. Figure 5 shows the FTIR spectra of commercial pectin and starch. The O-H stretching at a peak of 3330 cm^{-1} in the pectin and starch spectra indicates the presence of a hydroxyl group. According to Sulianto *et al.* [9], the C-H stretching peaked at 2937 cm^{-1} in pectin and 2929 cm^{-1} in starch, indicating the existence of methylene ($-\text{CH}_2$). C=O stretching at 1733 cm^{-1} in pectin is due to ester carbonyl group stretching, which is not found in starch. The C-O stretching was seen in pectin and starch at peak values of 1002 cm^{-1} and 998 cm^{-1} , respectively.

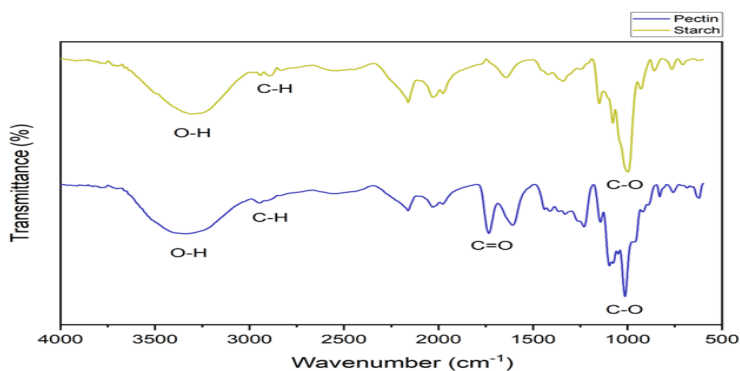


Figure 5: FTIR spectra of commercial pectin and starch.

The FTIR spectra of DES are shown in Figure 6. The C-H stretching was found in both DES at 2888 cm^{-1} for ChCl: urea and 2944 cm^{-1} for ChCl: LA, which was contributed by the quaternary ammonium cation from the choline chloride, $(\text{CH}_3)_3\text{N}+\text{CH}_2\text{CH}_2\text{OH}$. The C-H bonds in the methyl group (CH_3) and the methylene group (CH_2) can give rise to C-H stretching, around $2800\text{--}3000\text{ cm}^{-1}$. In ChCl: urea, the N-H stretching was found at 3320 cm^{-1} , which indicates the urea peak in DES. The C=O stretching was observed at 1662 cm^{-1} , indicating the carboxyl group that forms in the urea molecule. The C-N stretching and C-O stretching were found at peaks of 951 cm^{-1} and 1278 cm^{-1} , respectively. This two-stretch structure comes from the choline chloride structure. Meanwhile, C=O and C-O stretching were found in the lactic acid molecule at peaks 1728 cm^{-1} and 1201 cm^{-1} , respectively. The O-H stretching in ChCl: LA is broad from 2800 to 3800 cm^{-1} , indicated of carboxylic acid. The C-N stretching was observed at 952 cm^{-1} due to choline chloride mixed with lactic acid.

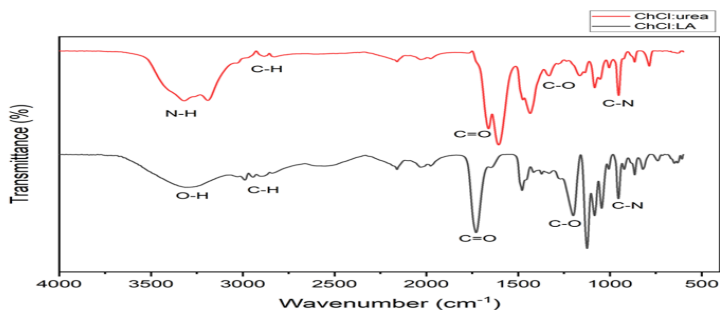


Figure 6: FTIR spectra of prepared two different DES.

Figure 7 shows the peak of hydrogel mixed with pectin, starch, and DES. The peak O-H stretching at 3325 cm^{-1} was found in a pectin-starch hydrogel that slightly shifted to the lower frequency at 3330 cm^{-1} in pectin and starch. This indicates the hydrogen bonding interaction between these polymers. The C=O stretching of pectin at 1733 cm^{-1} was slightly shifted to the lower frequency at 1727 cm^{-1} , along with a reduction in the peak intensity. This is due to the occurrence of the esterification process [20]. Meanwhile, the C-O stretching at 1016 cm^{-1} of pectin-starch hydrogel was found to be shifted to a higher frequency than pectin at 1002 cm^{-1} and 998 cm^{-1} in starch.

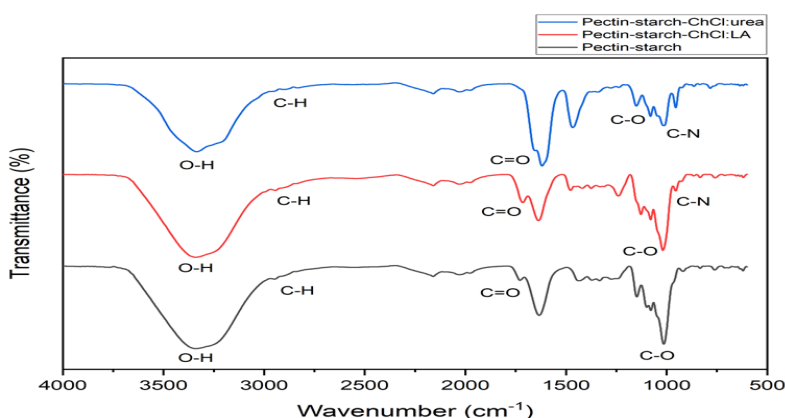


Figure 7: FTIR spectra of different hydrogels.

In the meantime, a new peak indicating OH stretching was seen at 3333 cm^{-1} in the pectin-starch-ChCl: urea hydrogel, confirming the integration of ChCl into hydrogel. The C-N stretching in this hydrogel shifted to a higher frequency at 1014 cm^{-1} than in its DES, ChCl: urea at 950 cm^{-1} due to the interactions between compounds. The N-H stretching in this hydrogel was discovered to overlap with the O-H stretching at 3300 cm^{-1} . The peak of OH stretching was observed at 3336 cm^{-1} in pectin-starch-ChCl: LA. The C=O peak in the hydrogel with lactic acid shows a significant reduction of wavenumber at 1650 cm^{-1} compared to its DES, ChC: LA at 1750 cm^{-1} . When the carboxyl groups dissolve in simple water, COO^- ions are created, which can then mix with Ca^{2+} ions to produce a hydrogel [21]. Thus, the variations in these peaks' wavenumbers provide more evidence of the interaction between pectin, starch, and DES.

Mechanical strength

The tensile strain, tensile stress, and modulus of hydrogels were successfully tested and measured, as shown in Table 2.

Table 2: The value of tensile stress, tensile strain, and modulus for hydrogel without DES (control) and with DES.

Hydrogel	Tensile stress (MPa)	Tensile strain (%)	Modulus (MPa)
Pectin-starch (Control)	0.87 ± 0.15	4.02 ± 0.33	31.19 ± 3.00
Pectin-starch-ChCl:urea	0.67 ± 0.09	4.51 ± 0.11	17.72 ± 1.16
Pectin-starch-ChCl:LA	0.45 ± 0.12	4.76 ± 0.12	12.94 ± 1.55

The tensile stress was analyzed to determine the maximum stress that hydrogels can withstand before fracturing [22]. The control pectin-starch hydrogel, without DES, has the highest tensile stress (0.87 MPa) compared to the hydrogels with DES. Meanwhile, a hydrogel with DES, pectin-starch-ChCl: urea, and pectin-starch-ChCl: LA exhibit reductions to 0.67 MPa and 0.45 MPa, respectively. Tensile strain is the elongation or deformation of a solid object caused by applying a tensile load or stress. DES has increased the tensile strain of pectin-starch-ChCl: urea and pectin-starch-ChCl: LA at 4.51 % and 4.76%, respectively. When DES is added to the pectin-starch network, it lowers intermolecular contact between polymer chains and improves mobility, allowing the hydrogel to elongate before breaking. Hydrogel with ChCl: LA has a higher strain than hydrogel with ChCl: urea because lactic acid is larger than urea, taking up more space in the gel network and reducing pectin-starch contact, resulting in increased elongation. As a result, the hydrogel's deformability rises while its tensile stress decreases. The modulus measurement further confirmed the results, which proved the hydrogel's flexibility. The hydrogels containing ChCl: LA had the lowest modulus value of 12.94%, indicating that this hydrogel is more flexible and can change its shapes considerably. According to Sapula *et al.* [23], DES can reduce the intermolecular tensions in the polymer network as plasticizing agents, increasing the material's flexibility, decreasing its stiffness, and eventually resulting in a lower modulus.

Biodegradability

The hydrogels were buried in moist soil for 20 days and assessed for weight reduction, with measurements taken every two days. The hydrogel pectin-starch-ChCl: urea was the quickest to break down 100%, taking 18 days. Meanwhile, during the same period (18 days), the degradation rates for pectin-starch-ChCl: LA and control hydrogel only reached 86.62% and 81.11%, respectively. The control hydrogel without DES was the slowest to disintegrate compared to hydrogel with DES, demonstrating that DES aided the breakdown process. The rate of degradation over time for each hydrogel is shown in Figure 8.

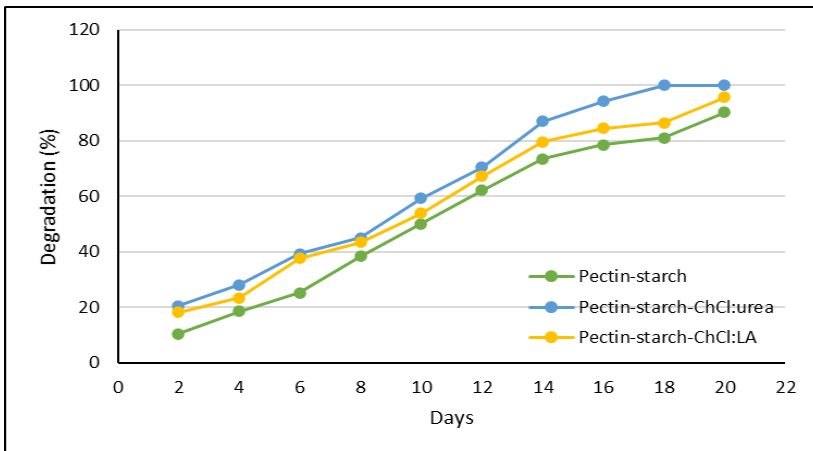


Figure 8: Degradation rate of each hydrogel by times.

From the findings, hydrogel with ChCl-urea is more easily degraded than hydrogel with ChCl: LA. This happens because urea is hydrolyzed by the enzyme urase found in the soil. Urease is an enzyme that catalyzes urea hydrolysis into ammonia (NH₃) and carbon dioxide (CO₂). The fast-moving reaction is one of the nitrogen cycle's processes that accelerates degradation. Meanwhile, the lactic acid does not have a specific enzyme to catalyze its decomposition in the soil. The degradation of lactic acid usually involves a more complex and slower set of microbial pathways compared to the rapid hydrolysis of urea [24]. In conclusion, material with urea was degraded more quickly in soil than material with lactic acid because it has a simpler chemical structure, is readily used by soil microorganisms, and

has the urease enzyme. The increased microbial activity can break polymer chains and ultimately lead to more efficient hydrogel biodegradation. Urea can also function as a fertilizer, which is advantageous for plant growth.

Water retention in soil

Water retention allows the hydrogel to contain water in its three-dimensional structure for extended periods and release it slowly when needed. When hydrogels are placed into soil, they absorb rainwater and produce a water reservoir over time. This water later gets absorbed by the plant's root systems, minimising the requirement for regular irrigation. As a result, hydrogels can help to reduce water irrigation [25]. Due to the pectin-starch-ChCl: LA hydrogel exhibiting the greatest swelling ratio (120.80%) compared to other hydrogels, water retention in soil was conducted on this hydrogel. Table 3 demonstrates the changes in soil moisture before and after adding 10 mL of water, as well as over seven days, as measured by a soil moisture meter.

Table 3: The value of soil moisture measured by soil meter.

Soil	Soil moisture (%)		
	Before added water	After added water	After seven days
With pectin-starch-ChCl: LA hydrogel	19	41	28
Without hydrogel (control)	19	57	9

The initial soil moisture before watering is similar, 19% for both pots. After adding 10 mL of water, the soil moisture immediately increased to 41% and 57% for hydrogel with DES and hydrogel control, respectively. However, the soil with hydrogel shows a lower moisture percent (41%) than soil without hydrogel (57%). This is because the hydrogel in the soil absorbed a portion of the water that was introduced, whereas, without the hydrogel, the water would have come into direct contact with the soil. After seven days, the soil moisture with hydrogel was 28%, significantly greater than soil without hydrogel (9%). The hydrogel in the soil has slowly released water into the soil, keeping the moisture at a reasonable level. This is due to

the ability of the developed hydrogel to retain and discharge water slowly.

Seed germination

The seed germination test was successfully carried out by sowing five green bean (*Vigna radiata*) seeds into two pots, one containing hydrogel (pectin-starch-ChCl: LA) and the other without hydrogel. The test was analyzed on days 5 and 20 to measure the height of seeds growing and the ability of plants to grow freshly in both pots. The condition of plants is shown in Figure 9 and Figure 10, respectively.

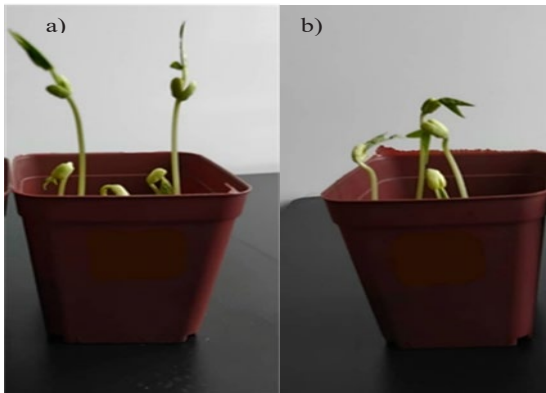


Figure 9: The condition of plants after five days a) plants with hydrogel b) plants without hydrogel.

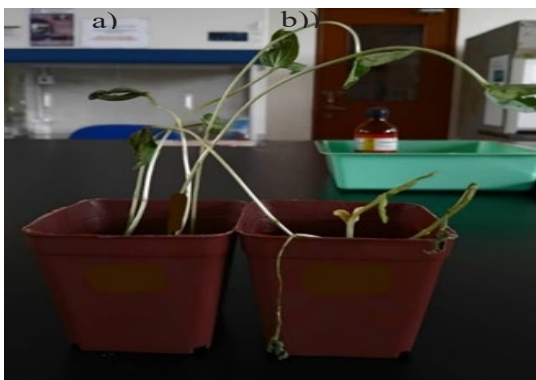


Figure 10: The condition of plants after 20 days a) plants with hydrogel b) plants without hydrogel.

The seeds of the plants began to sprout after five days (Figure 9). The germination rate of seeds treated with hydrogels is 100%, whereas the germination rate without hydrogels is 80%, with one seed failing to germinate out of five beans. After 20 days of growth, it is evident that the plants with hydrogel are still growing fresh, whereas the plants in the pot without hydrogel have begun to wither. This proved that hydrogels considerably retain soil moisture, allowing plants to grow properly with enough water to germinate. DES's lactic acid in the hydrogel could serve as a carrier in the soil, facilitating the transport of nutrients such as iron, zinc, and calcium, thereby promoting plant growth [26]. The plant could also benefit from the ability of lactic acid to maintain a lower pH. This proves that DES-modified hydrogel is essential for accelerating seed germination and preserving plant fertility over time without requiring regular irrigation.

CONCLUSION

Pectin-starch modified with DES hydrogels were successfully prepared and optimized by varying crosslinker and DES concentration. FTIR result confirmed that the pectin-starch-DES hydrogel was performed successfully. Pectin-starch-ChCl: LA exhibited the greatest swelling ratio (120.80%) at 25 mins with an ability to retain and release water slowly to keep soil moisture which enhance seed germination and maintain plant fertility without frequent irrigation. In conclusion, the pectin-starch hydrogels with DES have a larger swelling ratio, were more biodegradable, and had better mechanical properties than the pectin-starch control hydrogels. The hydrophilic structure of DES act as a water binder in a gel, while making an interaction with the pectin and starch. When water was added, hydrogel with DES effectively bind and absorb more water due to more sites for interaction. Therefore, incorporating DES into hydrogels shows promising potential as a future agricultural technology by enhancing soil water retention capabilities.

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