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Biodegradable Agricultural Mulch Films from Wastepaper Pulp and Calcium Alginate

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ABSTRACT

The survival of 8 billion people on the planet depends on agriculture, the cultivation of crops and the raising of livestock. In agricultural crop production, rather than organic mulches, plastic mulch films, usually made of low-density polyethylene (LDPE), are the most popular choice, because of their superior weed and pest prevention as well as their longevity. However, traditional plastic mulch films depend on non-renewable resources and are nonbiodegradable, accelerating plastic pollution with deadly environmental ramifications. Existing biodegradable mulch films are too expensive to be used commercially; this research proposes a more economically viable biodegradable mulch film consisting of wastepaper pulp, sodium alginate, and calcium chloride. Globally, 400 million tons of paper waste are produced yearly, with nearly 30% unrecycled and sent to the landfill. Thus, this wastepaper/alginate film turns something that would otherwise be trash into a useful tool. Films with different amounts of wastepaper pulp, sodium alginate, and calcium chloride were synthesized to determine an optimal combination. Wastepaper/alginate films without calcium chloride had little water resistivity and only had a lifespan of only a few days. Calcium ion crosslinking was found to significantly increase the water resistance and mechanical strength of the films. In addition, the field test proved that the films effectively prevented weeds and reduced required irrigation by half. It is concluded that these wastepaper/alginate mulch films have satisfactory performance and are cheap enough to replace LDPE films in agricultural applications, and a sodium alginate to wastepaper pulp weight ratio of between 1:9 and 2:8 is recommended.

Introduction

Agriculture, the cultivation of crops and the raising of livestock, is extremely important because it is how food is produced for the over 8 billion people on the planet. Mulch is used in agriculture to promote plant growth by stopping weed growth, conserving water, and reducing soil erosion.[1] The dominance of conventional plastic mulch films in crop production over organic mulches, which are made of natural materials like leaves and tree bark, is fueled by plastic films' long-lasting nature, effectiveness in suppressing weeds, and pest prevention. However, plastic films have limited end-of-life options and are dependent on non-renewable resources, sparking increased interest in more eco-friendly alternatives, such as biodegradable mulch films. Thermoplastic biodegradable films made from natural and synthetic polymers like starch, polylactic acid (PLA), and polyvinyl alcohol (PVOH)[2, 3] offer a sustainable alternative to traditional low-density polyethylene (LDPE) films, but the high costs of these biodegradable films make it impossible for them to be used commercially.

Globally, there are approximately 400-500 million tons of paper and paperboard waste each year.[4] In 2018, the U.S. generated 67.4 million tons of paper and paperboard waste, accounting for around 23% of total municipal solid waste, with 30% of paper waste remaining unrecycled and sent to the landfill.[5] By transforming low-cost wastepaper into biodegradable mulch films, landfill waste and greenhouse gas emissions are reduced, as well as helping to make global food security a reality while being considerate of the environment.

Because of its sensitivity to water, paper pulp must first be integrated with other biodegradable materials to turn it into useful biodegradable mulch films. Sodium alginate is a natural polysaccharide derived from seaweed, serving as a polymer used to cast biopolymeric films. It is a linear unbranched polymer consisting of β-(1,4)-linked *D*-mannuronic acid (M) and α-(1,4)-linked *L*-guluronic acid (G) moieties, as illustrated in Figure 1.[6] Sodium alginate is a cell wall component of marine brown algae and contains approximately 30 to 60% alginic acid. The conversion of alginic acid to sodium alginate grants it solubility in water, which aids in its extraction.[7]

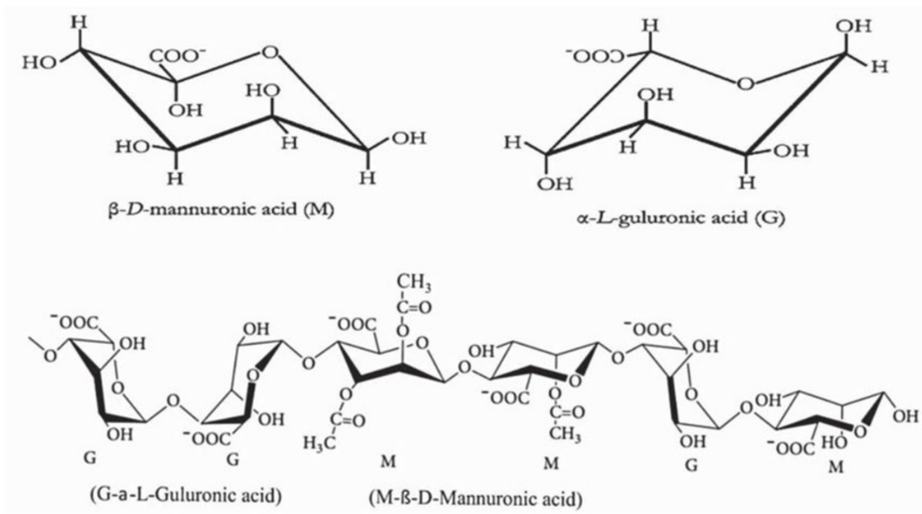

Figure 1. Chemical structure of sodium alginate with containing β-(1,4)-linked D-mannuronic acid (M) and α-(1,4)-linked L-guluronic acid (G) moieties.[6]

Alginate forms transparent, uniform, and good oxygen barriers but it has poor water resistivity due to hydrophilic nature. Alginate belongs to the polyuronates group and is a typical example of natural ionic polysaccharides undergoing chain–chain association and forming hydrogels on addition of divalent cations (e.g. Ca^{2+}), the mechanism of which is demonstrated in Figure 2.[8] The crosslinked alginate (i.e., calcium alginate) can significantly improve its mechanical strength and water resistance. The combination of sodium alginate and wastepaper pulp with the aid of crosslinking chemistry provides a promising approach toward the fabrication of biodegradable agricultural mulch films.

The goal of this research is to develop biodegradable agricultural mulch films made of wastepaper pulp, alginate, and calcium ions that are environmentally friendly alternatives to conventional non-biodegradable plastic mulch films. There are a few key properties that the wastepaper pulp/alginate film must have for it to be a viable alternative to existing solutions.

- The film must have low water vapor permeance to reduce water evaporation, save water usage, and help reduce the water fluctuations in the soil.
- The film must not be water-soluble: it needs to stay intact when it rains instead of dissolving. Also, the film must not allow liquid water to pass through.
- The film must prevent weed growth.
- The film must be durable for at least one crop season but must decompose eventually for it to be biodegradable.

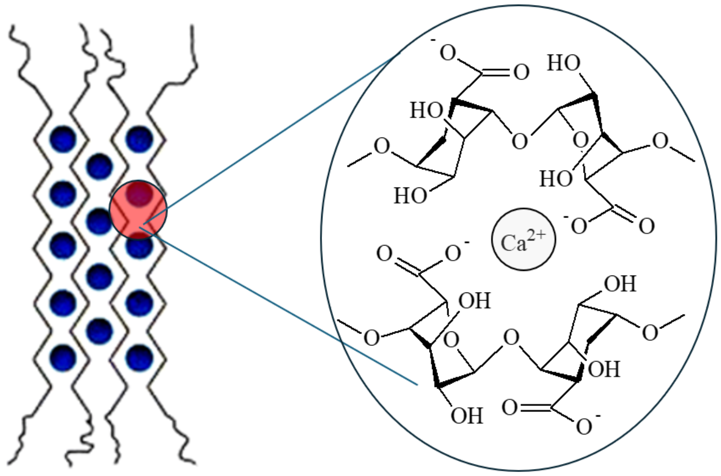

Figure 2. Fundamental mechanism of crosslinking reaction of sodium alginate with Ca^{2+} ions: ionic interactions and egg-box junction model.[8]

Materials and Methods

Food grade sodium alginate powder (Fit Lane) and calcium chloride (Cape Crystal, E509) were purchased from Amazon.com, and wastepaper pulp (bleached) was sourced from Etsy.

Procedure for Making Wastepaper Pulp/Alginate Agricultural Mulch Films

Sodium alginate powder was weighed using weighing paper on a balance, and then transferred to a beaker. Then, deionized water was added to the beaker and a metal spoon was used to mix the solution. A microwave was employed to heat the solution to 90-100°C and then a metal spoon was applied on the undissolved particles to facilitate the dissolution process. This procedure was repeated a few times before sodium alginate was completely dissolved in water. A predetermined amount of wastepaper pulp was weighed and dispersed in sodium alginate solution using a hand mixer. The well-mixed wastepaper pulp/alginate solution was poured into a metal tray (20 cm x 20 cm), and then it was placed on a flat surface. An electrical fan was used to accelerate the drying rate of the solution. When most of the water was evaporated, the mixture was turned into a film.

Calcium chloride was weighed and added to a predetermined amount of water in an Erlenmeyer flask with a magnetic stirring bar. Then, the flask was placed on a magnetic stirring plate, and the solution was stirred until calcium chloride was fully dissolved in water. The calcium chloride solution was loaded onto the top of wastepaper pulp/alginate film, allowing it to crosslink overnight. Subsequently, the film was removed from calcium chloride solution and rinsed with water. The crosslinked film was finally dried by an electrical fan or in an oven at 60°C overnight. Hereafter, SA is referred to as sodium alginate, and PA denotes wastepaper pulp. Different SA/PA ratios were evaluated in this study, for example, SA/PA (1:9, wt%) represents 10 wt% sodium alginate and 90 wt% wastepaper pulp. On the other hand, SA/PA (1:9, wt%)-Ca means that the SA/PA (1:9, wt%) film is crosslinked with Ca^{2+} ions.

Fourier Transform Infrared (FTIR) Spectroscopy Measurement

A Fourier transform infrared spectrometer (Nicolet iS50, ThermoScientific) with a single reflection diamond Attenuated Total Reflectance (ATR) sampling module was used to measure the extent of crosslinking in wastepaper pulp/alginate films. A small specimen was cut from the film and the FTIR spectrum was obtained at room temperature. Spectral resolution was maintained at 4 cm^{-1}, and the wavenumber was set between 400 and 4400 cm^{-1}.

Tensile Tests

Tensile tests were performed on the films using an MTS Insight 5 Tensile Tester following ASTM D638. A minimum of five specimens were tested per sample, and the specimen dimensions including thickness and width were measured before the test. Specimens were evenly punched out across the width of the film using a dogbone-shaped JDC Precision Sample Cutter. During the tensile test, the specimen was pulled at a rate of 5 mm/min. The stress-strain curve was recorded, and the tensile strength in units of MPa along with elongation at break (%) was reported.

Water Vapor Permeance (WVP) Testing

The wet cup water vapor permeance was determined according to ASTM E96/E96M. Specimens with a diameter of 76.2 mm were prepared. After the pocket of a dish was filled with distilled water, a specimen was fit into the dish right above the pocket with a metallic plate exposing a section of the specimen with a diameter of 63.5 mm to the environment. The entire setup was placed in a controlled chamber operating at constant temperature (23 ± 0.6)°C and relative humidity (50 ± 2)%. The entire setup was weighed periodically. The data was reported in units of $g/(24h\cdot m^2)$.

Water Resistance Testing

To test the water resistance of wastepaper pulp/alginate mulch film, 5 g liquid water was applied onto one side of the film. Photos were taken before and after one hour to observe whether the film remained intact and liquid water did not appear on the other side of the film.

Water Retention Testing by Weight Loss

The same amount of soil/water, which included approximately 200 g soil and 100 g water, was added to two cups. As indicated in Figure 3, the testing cup on the left-hand side was covered by a wastepaper pulp/alginate agricultural mulch film, whereas the one on the right-hand side did not have the film cover. Both testing cups were weighed daily, and the weight loss was calculated by the change from the initial weight.

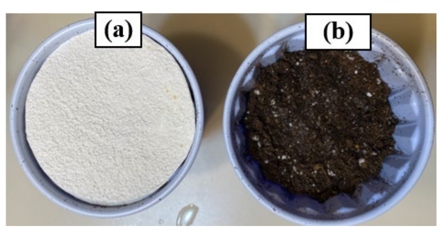

Figure 3. Photographs of testing cups containing soil/water (a) with and (b) without a wastepaper pulp/alginate agricultural mulch film.

Water Retention Testing by Moisture Content

Two testing cups were filled with the same amount of soil and water, and a Romaine lettuce was planted in each cup, as given in Figure 4. A grove moisture sensor was inserted into the soil of each testing cup and connected with Arduino

Mega 2560 R3 as shown in the left-hand side of Figure 4. The moisture content data was collected using custom code written in Arduino IDE 2.3.2.

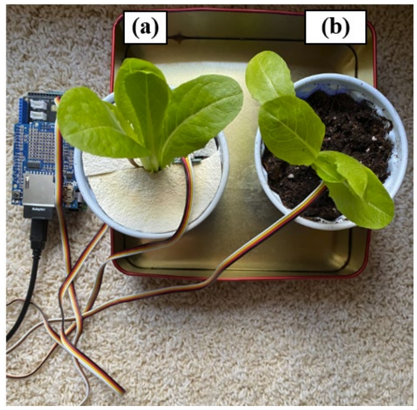

Figure 4. Photograph of experimental setup for testing water retention of testing cups, which grew Romaine lettuce, by moisture sensors: (a) with and (b) without wastepaper pulp/alginate agricultural mulch film.

Field Testing of Wastepaper Pulp/Alginate Agricultural Mulch Films

The field test of wastepaper pulp/alginate agricultural mulch film was conducted on *Allium schoenoprasum* (chives), which was planted in a garden pot. 3 pieces of film were used to cover the pot, and the weed growth and moisture retention were monitored. After an extended period of time, some of the films were taken to measure the tensile properties to determine biodegradability.

Results

Pure wastepaper pulp is unable to properly form a film. After going through the above film synthesis procedure, only small individual pieces of wastepaper pulp were able to be manufactured in the absence of alginate polymer. Moreover, pure wastepaper pulp has low structural strength, and is easily saturated with water, making it unsuitable for use as an agricultural mulch film.

In contrast, pure sodium alginate formed a better film than pure wastepaper pulp, as shown in Figure 5a. However, it was extremely brittle and had no resistance to liquid water; as a matter of fact, it would swell and re-dissolve in liquid water. Nevertheless, sodium alginate film became very resistant to liquid water, once it was cross-linked with Ca^{2+} ions. Furthermore, the crosslinked film exhibited reasonable mechanical strength. However, cross-linking also resulted in significant shrinkage and warpage in the film (Figure 5b). Also, sodium alginate by itself is more expensive than LDPE, so it is imperative to develop a new technology based on alginate polymer for agricultural mulch film application.

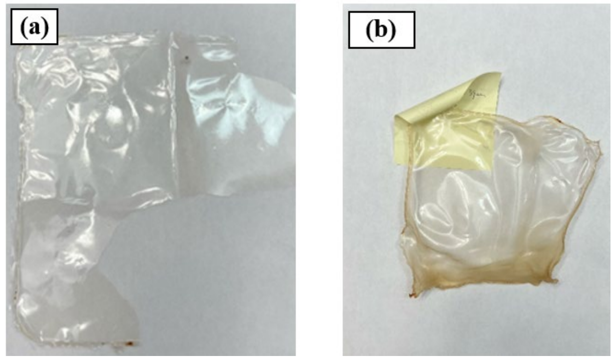

Figure 5. (a) Uncrosslinked pure sodium alginate film and (b) pure sodium alginate film crosslinked by Ca^{2+} ion.

The combination of wastepaper pulp with sodium alginate, along with the crosslinking chemistry by divalent or trivalent ions, opens a new avenue toward the production of affordable agricultural mulch films. This not only overcomes the shortcomings of both materials but also significantly reduces the cost of finished products.

At lower $CaCl_2$ solution concentrations (e.g. 1 wt%), the wastepaper pulp/alginate films appeared to have weak mechanical strength. In order to simplify the experimental design, all crosslinked samples (unless otherwise specified) were treated with 5 wt% $CaCl_2$ solution for at least 12 hours (left overnight) to ensure that the film was fully crosslinked. To fully dissolve sodium alginate in water, excess water (about 100 g water per 1 g sodium alginate) was added. If 5 wt% $CaCl_2$ solution was added right after the solution casting, the film shrank significantly. As a result, it was decided to remove excess water from the cast solution before adding $CaCl_2$ for the other samples.

Effect of Composition on the Formation of Wastepaper Pulp/Alginate Films

Figure 6 shows that the film shrinkage and warpage became more and more significant as the amount of sodium alginate increased. SA/PA (1:9, wt%) and SA/PA (2:8, wt%) samples exhibited smooth/flat films without warpage. Since wastepaper pulp is much cheaper than sodium alginate, these results indicate that by using cheaper materials (more wastepaper pulp than sodium alginate), films with larger surface areas are produced. Thus, low SA/PA ratios (e.g. 1:9 or 2:8, wt%) are more economically efficient.

Figure 6. Photograph of wastepaper pulp/alginate agricultural mulch films synthesized using different SA/PA ratios, all of which were crosslinked with Ca^{2+} ions. In the photograph, the amount of wastepaper pulp increases from left to right. The SA/PA (2:8, wt%) and SA/PA (1:9, wt%) films experienced the least shrinkage and warpage.

FTIR Spectra of Wastepaper Pulp/Alginate Agricultural Mulch Films

By comparing the FTIR spectra of the control samples (Figure 7), the extent of crosslinking in the films can be determined (Figure 8). According to Papageorgiou et al., the most important bands of the FTIR spectra of metal carboxylates are "a strong asymmetric COO stretching vibration (i.e., $v_{asym}(COO^-)$ and a somewhat weaker symmetric COO stretching vibration (i.e., $v_{sym}(COO^-)$)".[9] $\Delta v(COO^-)$ is the difference between the $v_{asym}(COO^-)$ and $v_{sym}(COO^-)$ bands and is a way to quantify the relationship between these two values and determine the metal-carboxylate coordination type ($v_{asym}(COO^-) = v_{asym}(COO^-) - v_{sym}(COO^-)$), as summarized in Table 1.

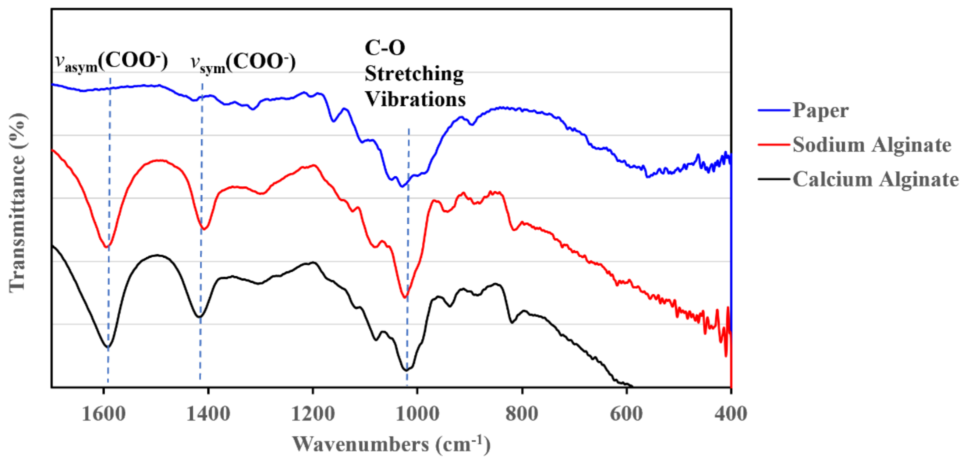

Figure 7. FTIR spectra of control samples in the wavenumber region of 400-1750 cm^{-1}.

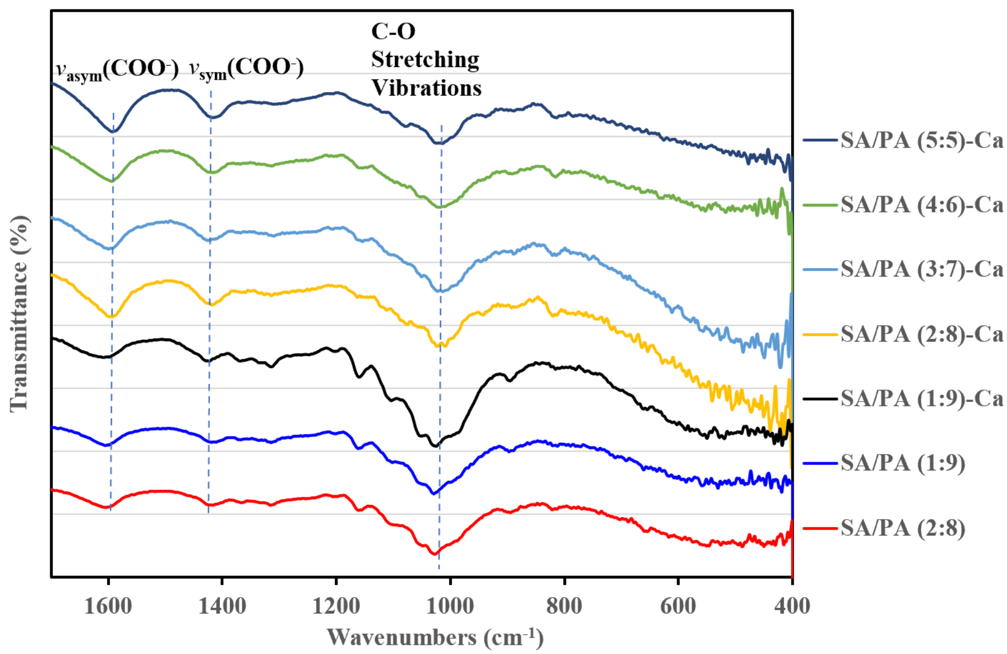

Figure 8. FTIR spectra of various film samples in the wavenumber region of 400-1750 cm^{-1}.

Table 1. FTIR key absorption band peaks (cm^{-1}) of wastepaper pulp, sodium alginate, calcium alginate and SA/PA films with/without being crosslinked by Ca^{2+} ions.

	v_{asym}(COO$^-$)	v_{sym}(COO$^-$)	Δv(COO$^-$)	C-O Stretching Vibrations
Wastepaper Pulp	1638.4	1428.1	210.3	1028.9
Sodium Alginate	1595.5	1407.9	187.6	1024.6
Calcium Alginate	1592.3	1418.2	174.1	1021.3
SA/PA (5:5, wt%)-Ca	1592.9	1416.9	176.0	1013.7
SA/PA (4:6, wt%)-Ca	1594.0	1414.9	179.1	1018.5
SA/PA (3:7, wt%)-Ca	1594.1	1416.4	177.7	1019.2
SA/PA (2:8, wt%)-Ca	1592.6	1418.2	174.4	1023.6
SA/PA (1:9, wt%)-Ca	1599.4	1421.1	178.3	1025.0
SA/PA (1:9, wt%)	1605.3	1419.2	186.1	1029.2
SA/PA (2:8, wt%)	1605.2	1417.2	188.0	1027.6

Even though the uncrosslinked SA/PA (1:9, wt%) and (2:8, wt%) films are primarily composed of wastepaper pulp, their Δv(COO$^-$) values were much closer to the Δv(COO$^-$) value of sodium alginate than paper. A proposed explanation for this observation is that in the preparation of the film, sodium alginate is completely dissolved in solution, allowing it to participate in extensive hydrogen bonding with insoluble cellulose fibers, with the surface of each fiber covered with multiple alginate molecules. Because ATR-FTIR spectroscopy (the method used in this experiment) has very low penetration depth (only a few μm), most of the IR radiation will hit the alginate molecules on the surface of the fiber and be reflected away, resulting in the uncrosslinked $\Delta\nu(COO^-)$ values to be closer to the value of sodium alginate despite it only being 10-20% of the film. However, it is notable that for both SA/PA (1:9) and (2:8) films, their $\nu_{asym}(COO^-)$ and $\nu_{sym}(COO^-)$ values were in between the sodium alginate and wastepaper pulp values, indicating that IR radiation does still reach the cellulose fibers, just not to the extent that was first expected given the SA/PA ratio.

The calcium alginate and SA/PA crosslinked $\Delta\nu(COO^-)$ values are less than the corresponding sodium alginate value. This is consistent with the findings in Papageorgiou et al., who propose a "pseudo bridged" unidentate coordination for the crosslinking interactions resulting from hydrogen bond interactions between an oxygen atom from a COO^- not bonded to Ca^{2+} and an adjacent hydroxyl group from a different alginate strand (see Figure 9).[9]

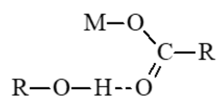

Figure 9. Proposed "pseudo bridged" unidentate coordination of carboxylate-metal (M) complexes in calcium alginate.[9]

For the crosslinked films, their $\Delta\nu(COO^-)$ values are all closer to that of pure calcium alginate and considerably lower than the values of their uncrosslinked counterparts and pure sodium alginate. This is consistent with the earlier conclusion on uncrosslinked SA/PA films: the $\Delta\nu(COO^-)$ values are closer to the value of alginate than the value of wastepaper pulp because of the coating of alginate molecules onto the surface of cellulose fibers. The same applies for crosslinked SA/PA films: the only difference is that the $\Delta\nu(COO^-)$ value is closer to the value of calcium alginate instead because of the "pseudo-bridged" bonding structure of calcium alginate discussed above.

Theoretically, a larger SA/PA ratio means that more alginate will be bonded the surface of cellulose fibers, resulting in a smaller $\Delta\nu(COO^-)$ value; However, the results do not show a clear trend. The most probable explanation for this observation is that the film composition is not perfectly consistent throughout (e.g. some sections of the film could have cellulose strands with more alginate polymers bonded to them while others could have fewer alginate), causing small deviations in the FTIR spectra.

Tensile Strength of Wastepaper Pulp/Alginate Agricultural Mulch Films

As shown in Figure 10 and Figure 11, crosslinking significantly increased both the tensile strength and elongation at break of the wastepaper pulp/alginate films. Crosslinked films increased tensile strength by 250% for SA/PA (1:9, wt%)-Ca films and 138% for SA/PA (2:8, wt%)-Ca films. For elongation at break, crosslinked SA/PA (1:9, wt%)-Ca films experienced a 95% increase, and SA/PA (2:8, wt%)-Ca films showed a 97% increase compared to their uncrosslinked counterparts. Furthermore, higher sodium alginate content results in higher mechanical performance, for both tensile strength and elongation at break. Higher tensile strength means a film is more durable, and higher elongation at break means that the film is more flexible and less prone to ripping. After 1-month of field testing, there was about 30% decrease in tensile strength for both SA/PA (1:9, wt%)-Ca film and SA/PA (2:8, wt%)-Ca film, while elongation at break only exhibited slight reduction. This may be attributed to UV radiation from the sun, and can be fixed by introducing ultraviolet (UV) stabilizers in the films. The reduction in mechanical strength may aid in the biodegradation process after the crop season, provided it is strong enough to provide protection for the necessary duration.

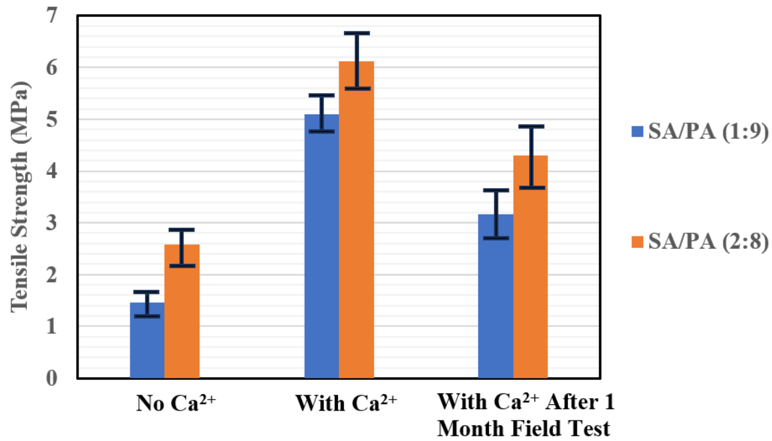

Figure 10. Tensile strength of wastepaper pulp/alginate film with/without crosslinking by Ca^{2+} ions for different film compositions: SA/PA (1:9, wt%)-Ca and SA/PA (2:8, wt%)-Ca films, as well as their corresponding samples after 1 month field test.

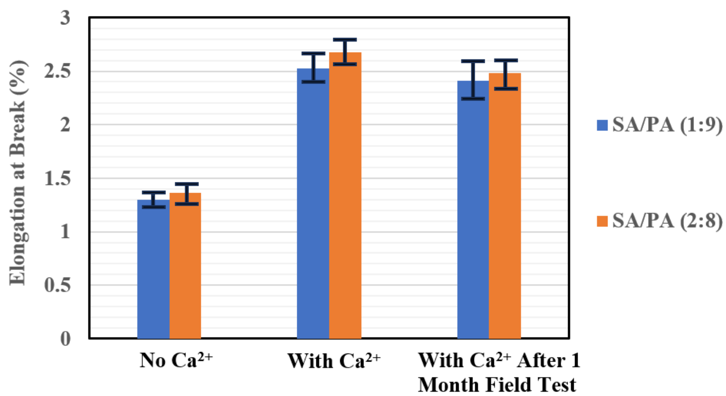

Figure 11. Elongation at break of wastepaper pulp/alginate film with/without crosslinking by Ca^{2+} ions for different film compositions: SA/PA (1:9, wt%)-Ca and SA/PA (2:8, wt%)-Ca, as well as their corresponding samples after 1 month field test.

Water Resistance and Water Vapor Permeance of Wastepaper Pulp/Alginate Agricultural Mulch Films

Neither pure sodium alginate nor pure wastepaper pulp could hold liquid water without leakage. Indeed, as noted earlier, pure sodium alginate re-dissolves in water. Uncrosslinked wastepaper pulp/alginate agricultural mulch films also let water pass through. Only Ca^{2+} crosslinked wastepaper pulp/alginate mulch films could prevent liquid water from passing through them, as illustrated in Figure 12.

Figure 12. Water resistance test for crosslinked wastepaper pulp/alginate film. Left: Top side of the film loaded with water. Right: Bottom side of the film. No water has passed through.

Water vapor permeance (WVP) describes a material's ability to allow water vapor to pass through it. It can be seen from Figure 13 that the water vapor permeance of wastepaper pulp/alginate agricultural mulch films decreases with increasing sodium alginate content, indicating the possibility of achieving even lower water vapor permeance. Specifically, SA/PA (1:9, wt%)-Ca and SA/PA (2:8, wt%)-Ca films had a water vapor permeance of 312.6 g/(24h·m^2) and 227.4 g/(24h·m^2), respectively. In contrast, the water vapor permeance of LDPE is 0.6 g/(24h·m^2).[10] As a consequence of the extremely low water vapor permeance of LDPE mulch films, they run the potential of accumulating too much moisture in the soil, which can cause root rot and kill the crops. Therefore, the higher water vapor permeance of wastepaper pulp/alginate agricultural mulch films can be an advantage.

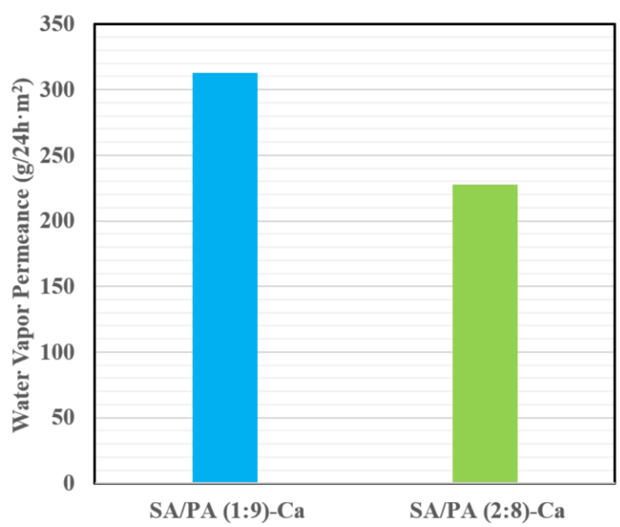

Figure 13. Water vapor permeance of different film compositions: SA/PA (1:9, wt%)-Ca and SA/PA (2:8, wt%)-Ca.

Water Retention of Wastepaper Pulp/Alginate Agricultural Mulch Films

Figure 14 gives plots of water loss versus testing time for testing cups containing soil/water with and without SA/PA (2:8, wt%)-Ca mulch film. As stated previously in Figure 3, both testing cups have about the same amount of soil and water. The test cup covered by SA/PA (2:8, wt%)-Ca mulch film dramatically decreased the water loss by 39.3% after 2 weeks, compared to the one without wastepaper pulp/alginate agricultural mulch film.

Furthermore, Figure 15 gives plots of moisture content versus field testing time for testing cups, which grew Romaine lettuce, with/without SA/PA (2:8, wt%)-Ca mulch film. Grove moisture sensors were employed to measure the moisture content in the soil. At the beginning, both testing cups exhibited a moisture content of approximately 75%. After 2 weeks, the moisture content in the testing cup covered by SA/PA (2:8, wt%)-Ca mulch film remained above 70%, whereas the moisture content in the one without SA/PA (2:8, wt%)-Ca mulch film decreased below 25%.

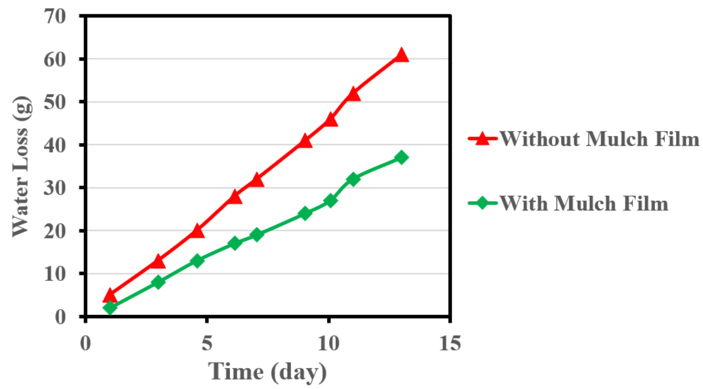

Figure 14. Plots of water loss versus testing time for testing cups containing soil/water with and without SA/PA (2:8, wt%)-Ca agricultural mulch film.

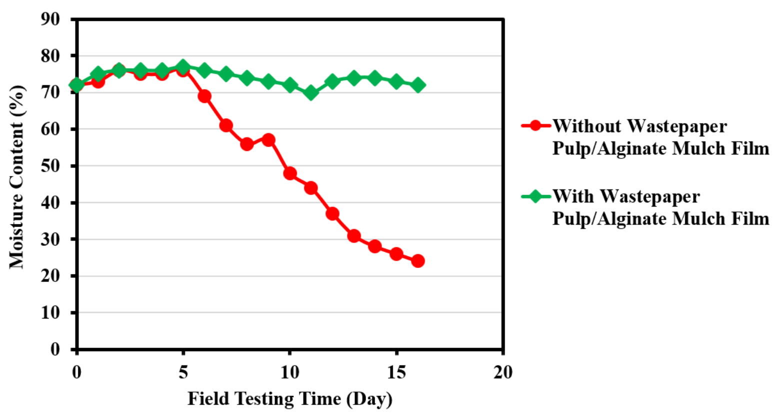

Figure 15. Plots of moisture content versus field testing time for testing cups, which grew Romaine lettuce, with/without SA/PA (2:8, wt%)-Ca agricultural mulch film.

Field Testing Results of Wastepaper Pulp/Alginate Agricultural Mulch Films

Figure 16 shows photographs of field-testing results after 1 month, 3 months, 5 months, and 9 months for SA/PA (2:8, wt%)-Ca mulch films, which covered a garden pot. Chives were planted in this garden pot, and the test began from July 2023. Over the growing season, SA/PA (2:8, wt%)-Ca agricultural mulch films effectively suppressed weeds and retained enough moisture in the soil that the required irrigation was reduced by about half from qualitative observations, which supported the water retention testing data present in Figure 14 and Figure 15. The control group consisting of other chives without the mulch film grew weeds weekly even after pulling them out regularly. After 3 months, the film visibly began to degrade (Figure 16b). After 5 months, the chives died, but SA/PA (2:8, wt%)-Ca agricultural mulch films were still able to cover the pot (Figure 16c). During the winter season, snow pushed these films deeper in the soil, causing more degradation after 9 months (Figure 16d). This effect may be attributable to the degradation effect of microorganism in the soil.[11]

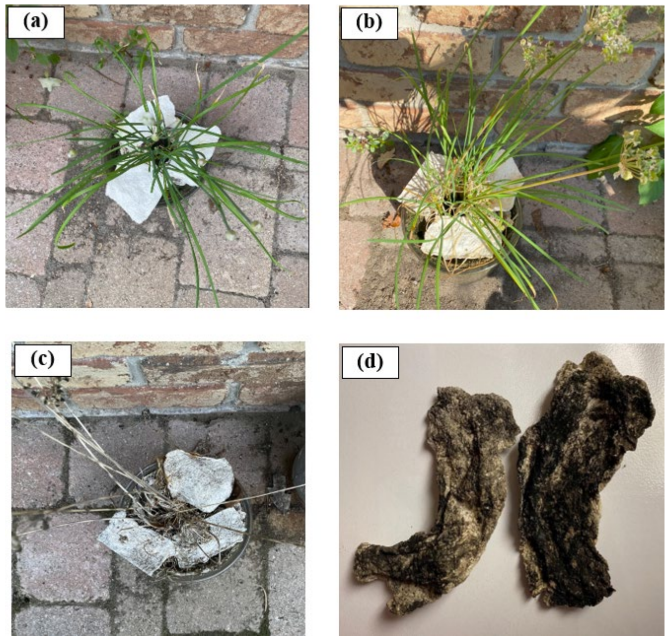

Figure 16. Photographs of field-testing results after (a) 1 month, (b) 3 months, (c) 5 months, and (d) 9 months for SA/PA (2:8, wt%)-Ca mulch films, which covered a garden pot. Chives were planted in this garden pot.

Discussion

It has been demonstrated that wastepaper pulp/alginate films crosslinked by Ca^{2+} ions can meet most of product design criteria required for application as agricultural mulch films. Uncrosslinked films, which are water soluble, only last a few days before decomposing, and they are a breeding ground for mold and pests as they consist of entirely organic material. On the other hand, as shown in the field test, Ca^{2+} crosslinked films can last for multiple months, enough for one crop season. Crosslinking significantly improves tensile strength and elongation at break, allowing for a more durable film. Moreover, the biodegradability of the film can be finely tuned by adjusting the SA/PA ratio, degree of crosslinking, and thickness. A higher degree of crosslinking means that the film is more strongly bonded and thus takes longer to degrade. Additionally, a higher SA/PA ratio means that more alginate polymer can participate in crosslinking, also increasing the bonding strength of the film and lengthening the lifespan of the film. Furthermore, a thicker film means that more material must decompose for the film to decompose, taking more time to biodegrade. The opposite of the above changes can be made to make the film more biodegradable. Thus, since different crops have different growing season durations, films with different biodegradabilities can be custom designed for different crops.

It was found that a lower SA/PA ratio results in a crosslinked film with larger surface area (less film shrinkage), and since wastepaper pulp is much cheaper than sodium alginate or calcium chloride, a low SA/PA ratio is the cheapest way to make wastepaper pulp/alginate agricultural mulch films. For comparison to LDPE films, the cost of raw materials should be compared. Wastepaper pulp is practically worthless, so its cost is negligible. Sodium alginate costs about \$3000 per metric ton, while calcium chloride costs about \$300 per metric ton.[12, 13] On the other hand, LDPE costs about \$1200 per metric ton.[14] Since sodium alginate and calcium chloride are only minor components of a film with a low SA/PA ratio, the film will be cheaper and should compare favorably to the cost of LDPE mulch films. A custom cost analysis model created in Excel supports this conclusion, calculating a raw material cost of \$0.020/m^2 for SA/PA (1:9, wt%) films (basis weight = 50g/m^2) versus \$0.033/m^2 for LDPE mulch films. One thing to note is that if the wastepaper pulp/alginate agricultural mulch films begin manufacturing at high quantities, more alginate suppliers (the most expensive part of the film is alginate) would enter the market, and combined with the fact that alginate is a renewable resource, occurring naturally in seaweed, which grows very fast, the price of alginate would lower drastically, further ensuring commercial viability.

Regarding the optimal SA/PA ratio, there is a tradeoff between stronger and less water vapor permeable films produced from higher SA/PA ratios and cheaper and more biodegradable films produced from lower SA/PA ratios. The recommendation is to use low SA/PA ratios (e.g. (1:9, wt%) or (2:8, wt%)) for most applications because cost is the limiting factor: it is the reason why existing biodegradable mulch films have not seen widespread commercial use. Also, in humid climates, a higher water vapor permeance is preferred as it prevents moisture oversaturation in soil. Only in special cases, such as in extremely dry regions without much access to water, should higher SA/PA ratios be used.

Conclusion

This research demonstrates that it is feasible to produce biodegradable agricultural mulch films from wastepaper pulp and calcium alginate with tensile strengths of up to 6 MPa. The FTIR spectra shows the completion of the crosslinking reaction between Ca^{2+} and COO^{-} groups on alginate. Tensile testing reveals the considerable increase in strength and flexibility that results from Ca^{2+} crosslinking, as well as the positive correlation between sodium alginate content and mechanical performance. In addition, increasing sodium alginate content was found to lower water vapor permeance. On a similar note, crosslinked films displayed remarkable water resistance and performed exceptionally well for retaining water in soil and preventing weeds. For most use cases, an SA/PA ratio of (1:9, wt%) or (2:8, wt%) is recommended; only in rare situations should higher ratios be used.

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