Polysaccharide-based biodegradable films for agricultural mulching

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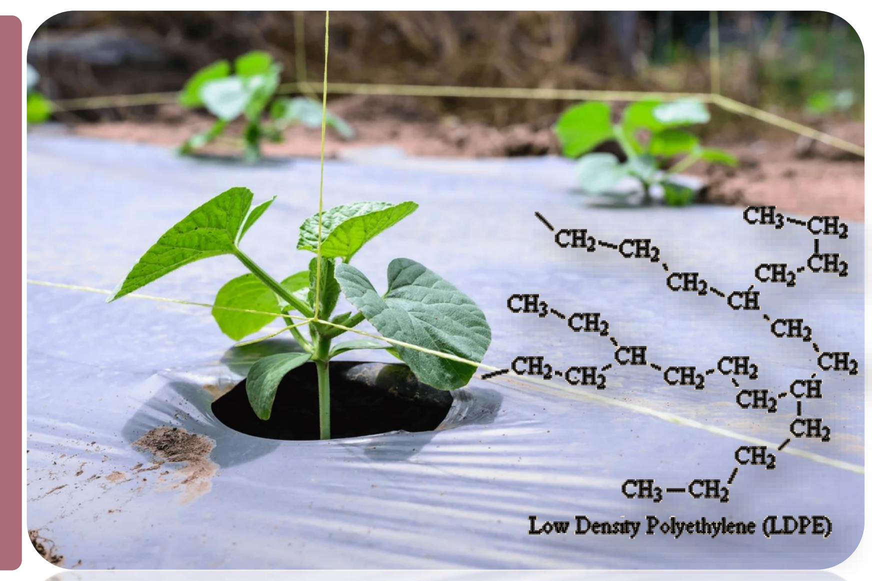
Introduction

Over the past 20 years, the world's population has grown exponentially. Consequently, food shortage has drawn attention, and the demand for agricultural products has increased annually. To meet this need, the excessive and prolonged use of low-density polyethene **(LDPE)-based mulching films** has resulted in significant **environmental pollution** events, leading to serious side effects even on human health. Based on the above issues, there is a great interest in developing **biodegradable bio-based polymeric films** that can be tilled directly into the soil after use to guarantee greater environmental sustainability.



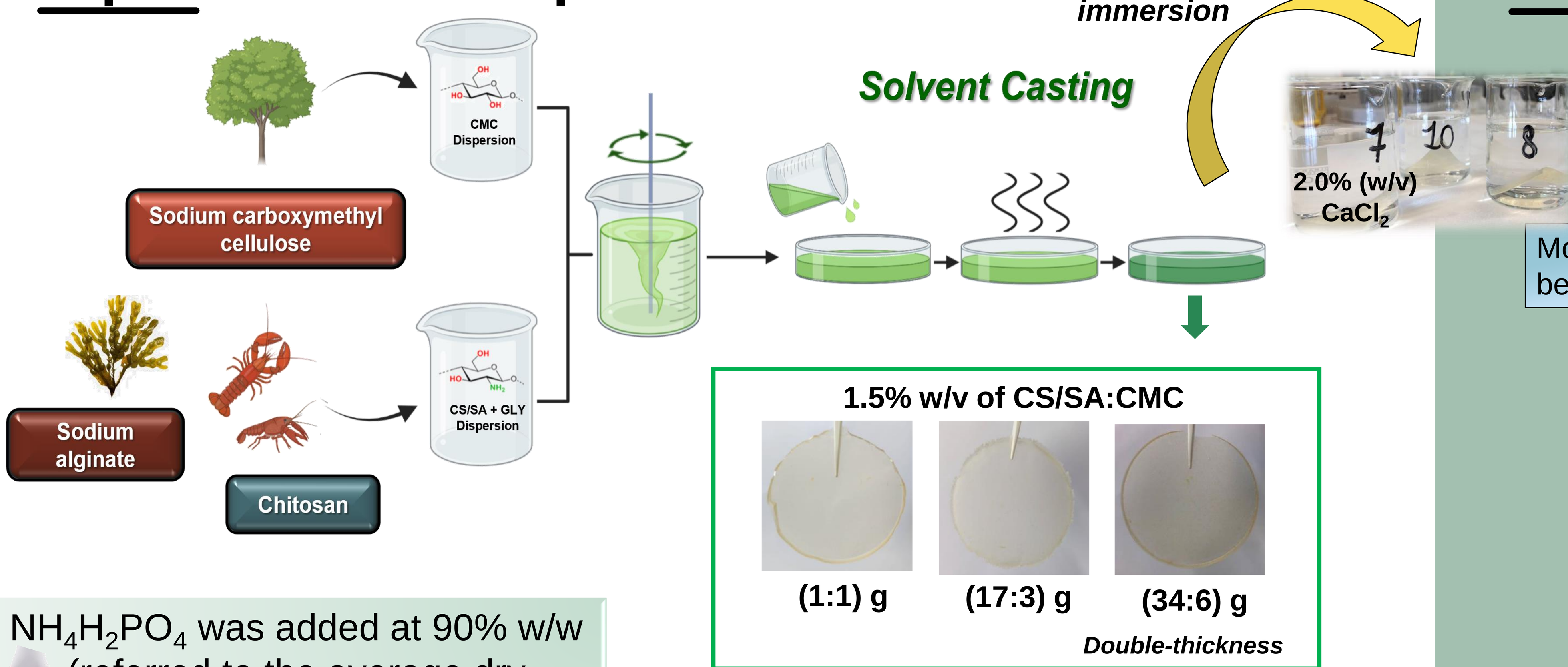
Objectives

In this study, we present (i) the preparation and characterization of biodegradable sodium carboxymethyl cellulose (**CMC**), chitosan (**CS**) and sodium alginate (**SA**)-based composite films in the presence of glycerol (**GLY**) as a plasticizer and calcium chloride (**$CaCl_2$**) as cross-linker, (ii) their enrichment with the $NH_4H_2PO_4$ (**AP**) inorganic salt, and (iii) the study of its release kinetics into the water. The latter aspect is of great importance as the release of **N** and **P** helps to improve the nutrient supply to the soil during film usage and degradation and provides an added **innovative benefit** to the film to be applied as mulch on the agricultural soil.

Composition (i.e., mass ratios between the precursors) and cross-linking agent effects on films' properties were evaluated, as well as water-interaction properties (degree of swelling and solubility in water) and thermal and mechanical properties to predict possible industrial applications.

Preparation of composite film

Cross-linking by immersion



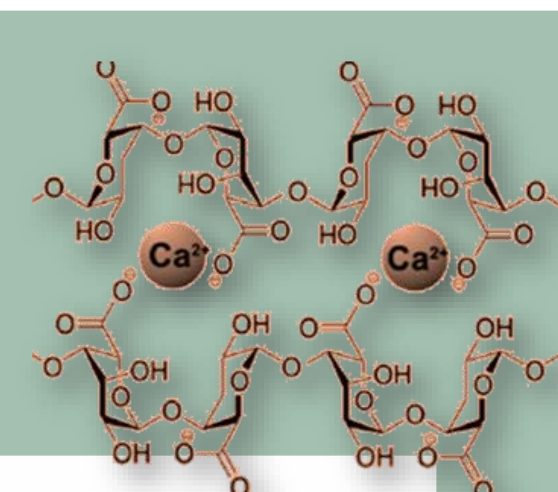
$NH_4H_2PO_4$ was added at 90% w/w (referred to the average dry polymer weight) during the film preparation.

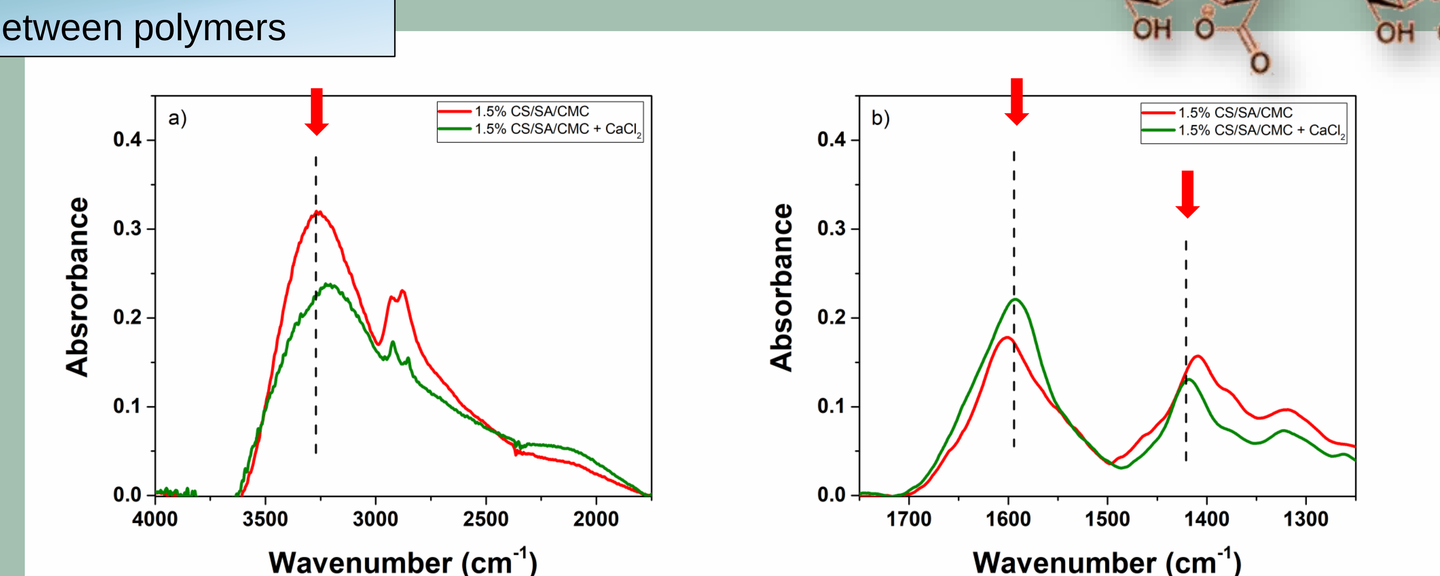
Results

CROSSLINKER EFFECT

Crosslinking between the polysaccharide **-COO⁻** groups and **Ca^{2+}** ions

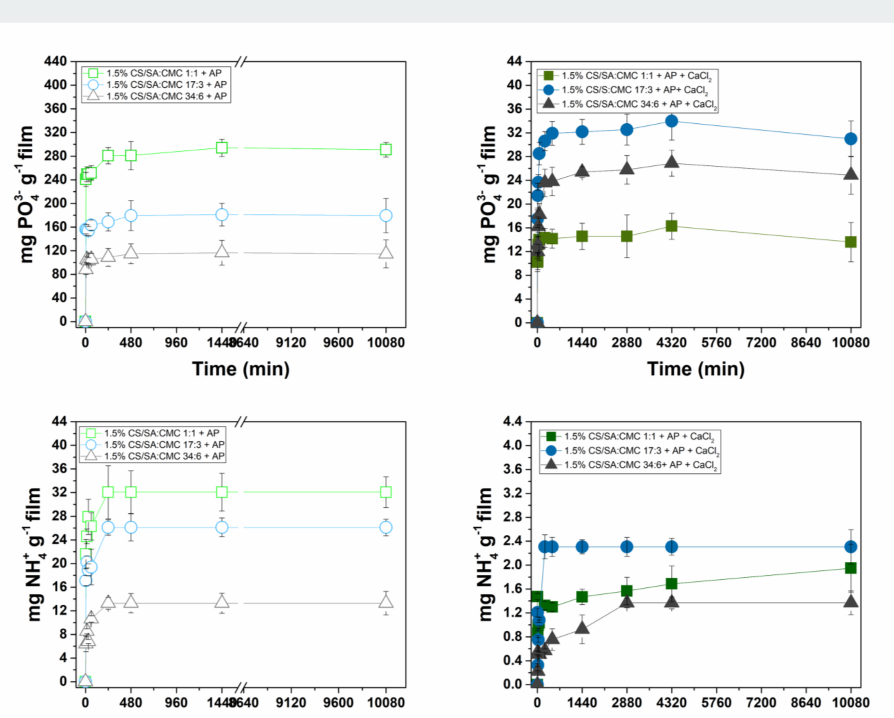
More **H-bonds** between polymers





Overlapping of the ATR-FTIR spectra of 1.5% CS/SA_CMC films before and after the addition of $CaCl_2$ in the spectral region from a) 4000 to 2500 cm^{-1} b) 1750 to 1250 cm^{-1}

Release kinetics of PO_4^{3-} and NH_4^+ ions



$CaCl_2$ minimises the initial sudden release (*bursting effect*) common to all non-crosslinked films and slows the salt release rate.

The amount of ions released decreases with film thickness.

Korsmeyer-Peppas Model

$$Q = kt^{n}$$

Q amount of analyte released,
k release velocity constant,
n exponent of release
t time

Release exponent (n) and correlation coefficient (R^2) are derived by fitting the log-log trends

0 < n < 0.5 → *Fickian model*

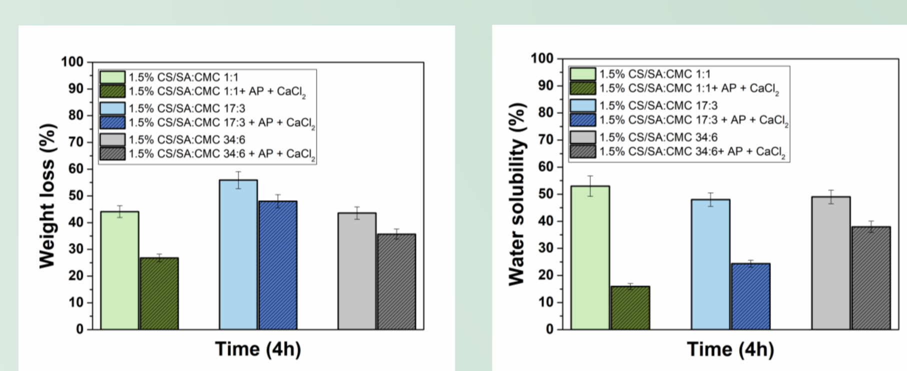
The release mechanism of $NH_4H_2PO_4$ is governed by the diffusion of salt through the polymeric matrix.

CS/SA:CMC	PO_4^{3-}		NH_4^+	
	n	R^2	n	R^2
1:1 + AP + $CaCl_2$	0.13 ± 0.04	0.84	0.11 ± 0.01	0.98
17:3+ AP + $CaCl_2$	0.17 ± 0.01	0.99	0.57 ± 0.10	0.95
34:6+ AP+ $CaCl_2$	0.18 ± 0.02	0.98	0.27 ± 0.05	0.95

WATER INTERACTION PROPERTIES

Results of the swelling test

CS/SA:CMC	Degree of swelling (%)
1:1	1968.5 ± 39.4
1:1 + AP + $CaCl_2$	**74.6 ± 2.2**
17:3	1524.4 ± 30.7
17:3 + AP + $CaCl_2$	**80.1 ± 2.4**
34:6	1410.3 ± 28.2
34:6 + AP + $CaCl_2$	**76.3 ± 3.3**



The Degree of Swelling (%), Weight Loss and Solubility in water of the crosslinked film drastically decreases.

Crosslinking hinders water penetration into the films, likely by forming a semi-interpenetrating polymer network.

The cross-linking with Ca^{2+} improves the **water resistance** of the composite film, justifying their retarded release of salt.

PHYSICAL-CHEMICAL PROPERTIES

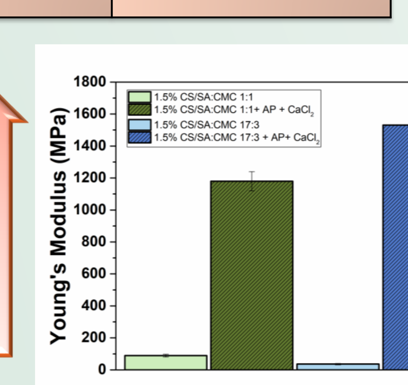
Results of thermogravimetric analysis

CS/SA:CMC	Decomposition temperature (°C)
1:1	234.4
1:1 + AP + $CaCl_2$	**243.2**
17:3	238.5
17:3 + AP + $CaCl_2$	**248.5**

Results of mechanical tests

Tensile strength (MPa)	Elongation at break (%)
15.9 ± 0.5	**79.8 ± 2.4**
15.7 ± 0.5	**1.9 ± 0.1**
7.9 ± 0.2	43.6 ± 1.3
36.5 ± 1.0	**3.7 ± 0.1**

Cross-linked films have a **higher thermal resistance**. Cross-linking limits chains' mobility and gives the film a more compact structure and a **higher resistance to mechanical stress.**



However, the elongation at break decreases in cross-linked films. The crosslinking probably disrupts the films' H-bond network, blocking the chains' entanglement and making the film less deformable.

Conclusions

The effect of introducing $NH_4H_2PO_4$ as a fertiliser into polymeric films based on CS, SA and CMC cross-linked with $CaCl_2$ could lead to the development of **novel films for agricultural mulches**. Positively, the cross-linked films (**1**) reduced the H_2O interaction, (**2**) increased the thermal stability of the films, and (**3**) slowed the rate of salt release. The films achieved the tensile strength parameter (**16 MPa**) for its function, but not the elongation at break parameter (**150%**) required by **EN 17033**. Therefore, the results reported here can be considered *a good starting point* for designing research activities that can improve the mechanical properties of films to make them suitable for agricultural applications.

Mulching+
PRIN 2020