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# **New Generation of Controlled Release Phosphorus Fertilizers based on Biological Macromolecules: Effect of Formulation Properties on Phosphorus Release**

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## **Abstract**

The main objective of this work was to study the possibility of using polysaccharides and lignin as a coating material for water-soluble triple superphosphate (TSP) granular fertilizers. In this study, composites based on three polysaccharides (sodium alginate (alginic acid sodium salt): AL, kappa-carrageenan: CR and carboxymethyl cellulose sodium salt: CM) and lignin (LG) were prepared. The lignin used was extracted from olive pomace (OP) biomass using the alkali method. The morphological, mechanical, and surface properties as well as the thermal behavior of the coatings were characterized and compared. Their morphology and thickness revealed by scanning electron microscopy (SEM) showed good adhesion between the fertilizer and coating materials. The results showed that the lignin-carrageenan formulation (LGCR) exhibited the highest water absorbency and elastic modulus. Release tests showed the effect of the TSP/biopolymer mass ratio and that the slowest P release was obtained with the LGCR@TSP formulation composite within 3 day. In addition, 59.5% and 72.5% of P was released after 3 days with the TSP/biopolymer mass ratios of 5/1 and 15/1, respectively, compared to 100% P release with the uncoated TSP.

**Keywords:** Polysaccharide, Lignin, Biomass, Phosphorus Fertilizer, Coating, Controlled Release

## 1. Introduction

Recently, much attention has been paid to fertilizers with slow release and water retention properties due to their essential roles in the development of sustainable agriculture and horticulture [1]. Plant growth and yield mainly rely on the nutrients available in soil and water. When soil nutrients are missing or in short supply, fertilizers, mostly of chemical origin, are applied. Their use is open to criticism because of their price, their negative impact on the environment (water and air pollution) and the fossil origin of phosphorus fertilizers. Phosphorus fertilizers are one of the most highly demanded because P is often the most limiting plant nutrient.<sup>3</sup> This is not because the amount of total P in soil is low but rather because the P in soils is in chemical forms that are not available to plants [2,3]. The world phosphate fertilizer demand is expected to reach 45.858.000 tons ( $P_2O_5$ ) in 2020, while it was 41.151.000 tons in 2015 [4]. However, due to the low efficiency of soil P fertilizers, only 10-20% of this P is taken up by plants [1,5,6]. The currently available forms of P fertilizers require further improvements to increase their bioavailability in soils. Controlled-release fertilizers (CRFs) may improve the efficiency of P fertilizers while reducing their negative environmental effects [7,8]. CRFs employ either coating or encapsulation of mineral fertilizers in polymeric matrices. CRFs use is a new trend and a good alternative to conventional fertilizer to reduce fertilizer consumption and loss and to alleviate the negative environmental effects of chemical fertilizers. In most cases, the fertilizer granule is encapsulated inside an inert material [9]. The coating layer acts as a physical barrier that controls nutrient release [7]. The release behavior of water-soluble fertilizers depends on many parameters, including the porosity and structure of the coating material, coating thickness, granule size and form, soil temperature and pH, humidity and microbial activity [7,10–12]. The coating materials applied most frequently are sulfur [13,14], waxes [15], polystyrene [16], polyethylene [15,17,18], poly(N-isopropylacrylamide) [19,20], polyurethane

[19], polysulfone [21–24], polyacrylonitrile [23,24], etc. However, the combination of fertilizer and polymeric coatings has some disadvantages. The majority of synthetic polymers require organic solvents (e.g., N-dimethylformamide [24], chloroform [25]) for solubilization, which are harmful to the environment. In addition, the polymers remain in the soil when the nutrients are exhausted. According to Trenkel [26], the use of polymeric materials in coatings could lead to an undesirable accumulation of plastic residues of up to 50 kg/ha/year. The development of environmentally friendly CRFs using biodegradable polymers derived from biomass, agricultural and agro-industrial waste (carbohydrates, lignin, etc.) is a much better solution. Compared to synthetic polymers, biological macromolecules are relatively inexpensive [27], biodegradable, nontoxic for soil organisms and contribute to the improvement of soil properties [28,29]. In addition, biological polymers appear to be a potential alternative to synthetic polymers for CRFs coatings [30] and could contribute significantly to organic waste recycling and the circular economy. Lignin is a cheap and natural polymer available as a waste material, as it is recovered mainly as a byproduct from wood pulping processes, with approximately 100 million tons produced annually worldwide [31]. Moreover, compared to other polymers, lignin is a renewable, biodegradable, amorphous, relatively hydrophobic biopolymer that is rich in recalcitrant carbon, which could contribute to increasing the soil organic matter content [9]. Studies using commercial lignin blended with additives as a coating agent (rosins and linseed oil [8,9], alkenyl succinic anhydride [32]) showed its efficiency at decreasing the release rate of nutrients from fertilizers. Polysaccharides are also used in coating formulations. However, these compounds have never been tested alone. They are always mixed with other polymers or other components, such as clays [33]. Wan et al [34] reported that k-carrageenan-Na-alginate and k-carrageenan-g-poly(acrylic acid)/celite composite superabsorbents were used as inner and outer coating materials, respectively, for nitrogen fertilizer. This double-coated fertilizer had

slow-release behavior and improved the water-holding capacity and water-retention properties of the soil.

This work is a continuation of the investigations of new biobased formulations for CRF production, initiated in our previous work recently published [30]. This study for objective to use extracted lignin from olive pomace (OP) biomass and some commercial polysaccharides (alginates (AL) from brown algae, carrageenan (CR) from red algae and carboxymethyl cellulose (CM) from wood pulp) for the preparation of different formulations composites for TSP fertilizer coating. The choice of these polysaccharides is based on the availability and dissimilarity of their basic materials (algae and wood), their ability to form films and their high water absorption capacity [34]. The main objective of this research was to evaluate the influence of different biopolymers coatings on the P release behavior of CRF granules.

## **2. Experimental Section**

In this study, OP was used for lignin extraction. OP was provided from a Moroccan olive press (*Tadla* region). Kappa carrageenan (CR) (CAS: 1114-20-8), sodium alginate (AL) (CAS: 9005-38-3), sodium carboxymethyl cellulose Mw~700.000 (CM) (CAS: 9004-32-4), potassium carbonate  $K_2CO_3$  (CAS: 584-08-7), sodium hydroxide NaOH (CAS: 1310-73-2) and phosphorus pentoxide ( $P_2O_5$ ) (CAS: 1314-56-3) were purchased from Sigma-Aldrich. Triple superphosphate (TSP), a granular phosphate fertilizer (46%  $P_2O_5$ ), was produced and offered by OCP group, Morocco.

### ***2.1. Lignin polymer extraction from OP biomass***

The lignin polymer used in this study was extracted from OP biomass using the alkali method. Details of the lignin (LG) alkali extraction and the chemical and structural analysis of the OP and LG were presented and discussed in our previous work [30]. The elementary composition of the LG biomass was estimated to be  $58.24 \pm 0.01\%$  C,  $7.89 \pm 0.03\%$  H, and  $28.05 \pm 0.07\%$  O, and the C/N ratio was 32.54.

## 2.2. Preparation of formulations and polymer-based films

Formulations and composite films were prepared using lignin solution (LG), alginate (AL), carboxymethyl cellulose (CM), and carrageenan (CR) in different ratios (**Table 1**). Black liquor (33.34 g/L) was used directly without stirring for lignin formulation and film preparation. Polysaccharide solutions (AL, CM, CR) were prepared separately in water (0.5 w/w%) under constant stirring for 2 h at ambient temperature (**Table 1**). The lignin-polysaccharide-based composites were prepared as follows: 80% lignin was mixed with 20% polysaccharides (w/w). All solutions were stirred overnight at room temperature. The same formulations were used for composite film preparation and TSP fertilizer coating. For the film preparation, the mixtures were deposited onto square Petri dishes (12 cm), and the water was evaporated by drying overnight at 40 °C. Films were made in triplicate.

**Table 1:** Composition of prepared formulations. LG: lignin, AL: alginate, CM: carboxymethyl cellulose, CR: carrageenan, LGAL: lignin-alginate, LGCM: lignin-carboxymethyl cellulose, LGCR: lignin-carrageenan

Polymers-based formulations	LG (%)	AL (%)	CM (%)	CR (%)
LG	100	0	0	0
AL	0	100	0	0
CM	0	0	100	0
CR	0	0	0	100
LGAL	80	20	0	0
LGCM	80	0	20	0

LGCR	80	0	0	20
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## ***2.3.Characterization of lignin-polysaccharide composite films***

### ***2.3.1. Contact angle***

The hydrophobicity of the composite films was evaluated by analyzing the behavior of water drops injected onto their surfaces. Before contact angle measurements, films were cut into small rectangles (0.5 cm\*2 cm), and their support sides were glued to glass slides using double-sided tape. Samples were equilibrated for 5 days at 46% relative humidity (RH) in a desiccator in the presence of K<sub>2</sub>CO<sub>3</sub>-saturated solution. A humidity detector was used to verify the obtained humidity. Contact angle measurements were realized with a goniometer (Digidrop, GBX, France) equipped with a diffuse light source and a CCD camera (25 frames/sec). A droplet of ultrapure water (~3 µL) was deposited on the film surface with a precision syringe (Teflon needle, 0.82 mm external diameter). The method is based on image processing and curve fitting for the contact angle. The video was analyzed frame-by-frame with GBX software to determine the contact angle as a function of time [35,36]. Three measurements were performed on each sample.

### ***2.3.2. Mechanical properties***

The film elasticity (tensile modulus EM), tensile strength (TS) and elongation at break (EB) were studied using tensile tests. Tests were performed on films using a texture analyzer (TA. XT plus). The tensile specimens were cut into rectangles (80 mm in length and 10 mm in width). The gauge length was fixed at 30 mm, and the speed of the moving clamp was 5 mm/min [37]. Measurements were carried out at room temperature. Three replicates were characterized, and the results are reported as average values with standard deviations.

### ***2.3.3. Thermogravimetric analysis (TGA)***

The different formulations were analyzed using TGA. TGA was conducted under nitrogen (with a flow rate of 50 mL/min) using a TGA instrument (Mettler Toledo) with a 5 °C/min heating rate from 25 to 900 °C. Ash content was determined under air (with a flow rate of 50 mL/min) with an isothermal segment (900 °C for 1 h).

#### ***2.4. Preparation and characterization of TSP fertilizer coatings***

Granules of TSP fertilizer were sieved to select homogeneous granules with diameters of 2-3 mm and then placed into a rotary drum (12 rpm, capacity of 11 L) developed in our laboratory. The distance between the spray nozzle and the center of the rotary drum was 25 cm. Fifty grams of TSP granules were covered with a layer of different formulations (3.33 g) based on lignin and polysaccharides by spraying at regular time intervals. The mass ratio of TSP/polymer was 15/1. Then, the coated TSP granules were continuously dried in the rotary drum by a hot air stream (65°C). To study the effect of the solution concentration on coating thickness and phosphorus release behavior, the mass concentration of the coating solutions was tripled (the ratio of TSP/polymer was 5/1).

##### ***2.4.1. Morphology and thickness of the coating layer***

The morphology of the coated TSP was evaluated by a tabletop scanning electron microscopy (SEM) (Phenom ProX, Phenom-World) using a backscattered electron detector (acceleration voltage of 10 kV, mode image). Three granules of each type of coated TSP fertilizer were randomly chosen. These granules were cut in half with a razor blade and fixed on a support using double-sided tape. To measure the thickness of the coating layers, the drawing rule option of the SEM was used, and three measurements were performed on different areas of each granule.

##### ***2.4.2. Hygroscopicity of uncoated and coated TSP***

Coated TSP granules were dried at 50°C in a vacuum oven in the presence of P<sub>2</sub>O<sub>5</sub>. Samples were weighed to a constant weight (complete drying). Then, they were conditioned in

humidity-controlled rooms at three relative humidities: 35, 60 and 80%. The water absorbency of the coated TSP was monitored for 3 days [8]. Samples were weighed every 24 h, and the water absorption was determined by the weight difference between dried and conditioned samples. All the determinations reported here are triplicate results with standard deviations.

### **2.5. Slow release behavior of coated TSP in water**

For release experiments, uncoated and coated fertilizers were equilibrated for 3 days at 60% RH. Then, 0.25 g of each type of coated TSP was immersed in 50 ml of distilled water in glass bottles. The bottles were conditioned at a constant temperature of 25°C. After 1 and 6 h, and 1, 2, 3, 4 and 5 days, 1 ml of the different solutions was sampled for phosphorus concentration determination, and an additional 1 ml of distilled water was added to the bottles to maintain a constant volume. All release experiments were carried out in triplicate. The phosphorus concentration was determined using the colorimetric molybdenum vanadate method [24]. The phosphorus release at each time was obtained by **Equation 1**, which was proposed by Rashidzadeh et al [38], and expressed in relation to the phosphorus concentration and total weight of phosphorus contained in the TSP fertilizer. All the determinations reported here are triplicate results.

$$\text{CR (\%w/w)} = \frac{V_e \sum C p_i + V_0 C p_n}{m p_0} * 100 \quad \text{Equation 1}$$

where CR is the cumulative amount of phosphorus released (%) from the TSP fertilizer,  $V_e$  is the sampling volume,  $V_0$  is the initial volume of the release media,  $C p_i$  and  $C p_n$  are the phosphorus concentrations (mg/ml),  $i$  and  $n$  are the sampling times, and  $m p_0$  is the total weight of phosphorus contained in the TSP fertilizer.

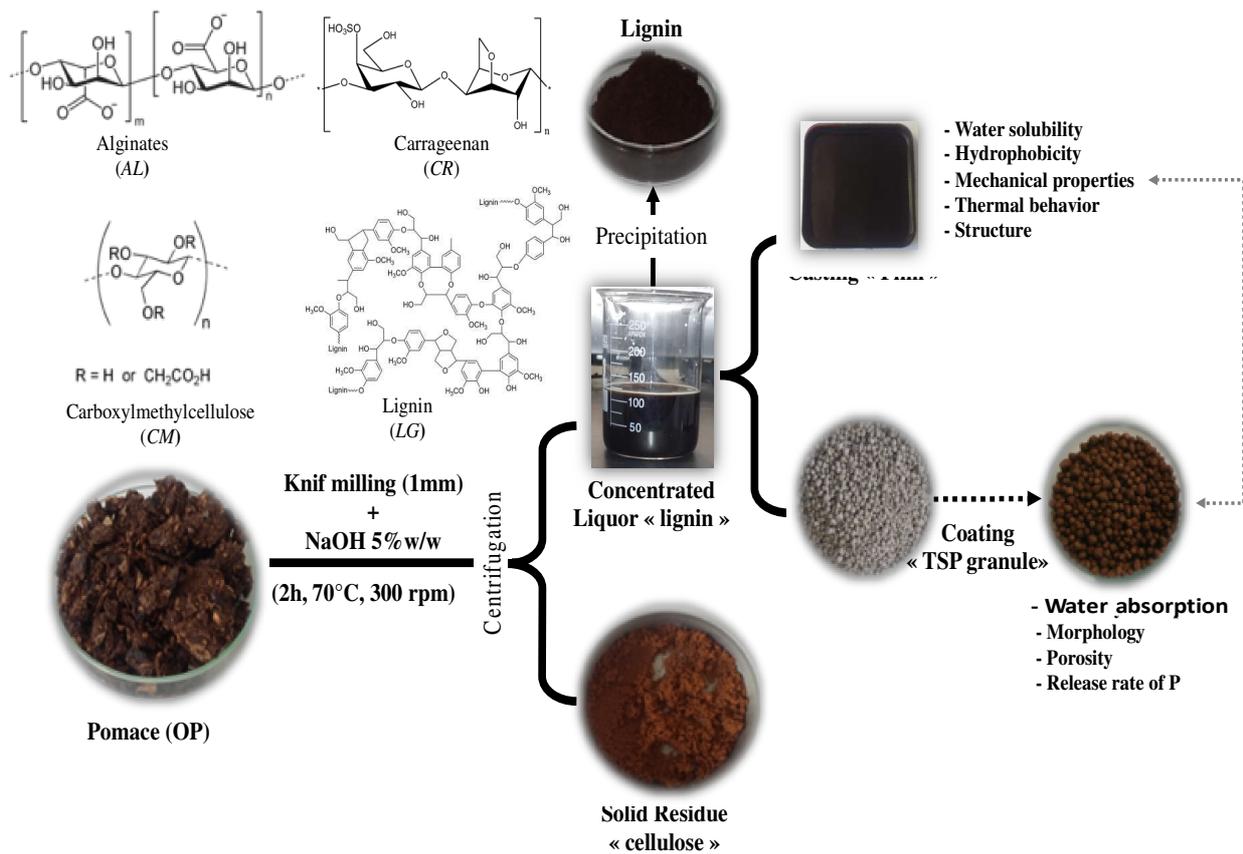
### **2.6. Data analyses**

The average values were calculated for each treatment. Analysis of variance (ANOVA), mixed models and correlation matrixes among treatments were performed using R version 3.4.2. The effect of formulation on contact angle (CA), Young's modulus (EM), tensile strength (TS), elongation at break (EB), and thickness of the coating agent was tested by one-way ANOVA. Mixed models ((Package: lme4) were performed to analyze the effect of formulation and time and on P release with formulation and time as fixed effects and the bottle (containing fertilizer and water) as a random effect. If significant, Tukey's (for ANOVA) and Emmeans (for mixed models) post hoc tests were used for pairwise multiple comparisons ( $p < 0.05$ ). Correlations between films and coated TSP characteristics (treated with lignin and lignin-polysaccharides) were analyzed using a correlation matrix.

### **3. Results and discussion**

Different lignin-polysaccharide formulations were prepared using alkali extracted lignin from OP residue (**Scheme 1**). The objective of this study was to develop a new generation of coating formulations based on lignin and polysaccharides and to study the effect of the biopolymers type on the formulation properties. Finally, this study sought to correlate the physicochemical properties of different composite formulations on the P release behavior. For this purpose, we utilized two strategies (**Scheme 1**):

- i) Preparation of composite films and study of their surface, mechanical and thermal properties.
- ii) Coating of TSP granules using the same formulations and study of their water absorption, morphology and P release.



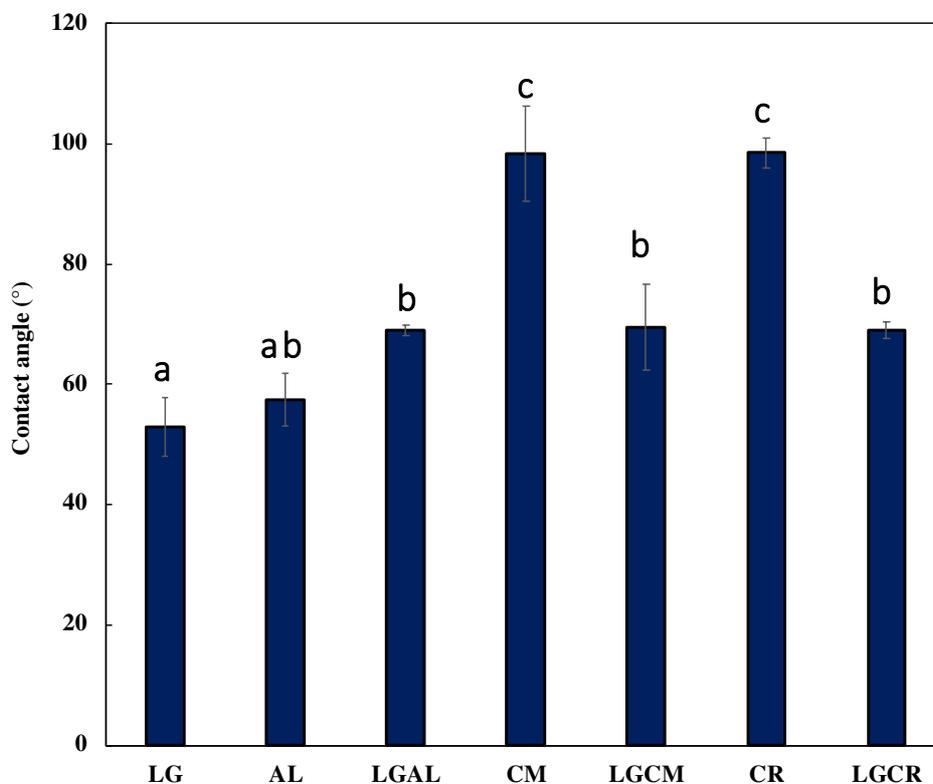
**Scheme 1:** Extraction details of lignin from OP and strategies used to coat TSP fertilizer and to characterize the coating agents

### 3.1. Lignin-polysaccharide composite formulations

#### 3.1.1. Surface properties (contact angle)

The hydrophobic surface corresponds to a contact angle  $> 60^\circ$ , while a contact angle  $< 60^\circ$  corresponds to a hydrophilic surface [36]. A significant difference in contact angle was observed between different formulations ( $p$ -value  $< 0.05$ ) (**Fig. 1**). The hydrophobicity of formulation composites decreased in the following order:  $\text{CM} = \text{CR} \gg \text{LGCM} = \text{LGAL} = \text{LGCR} > \text{AL} = \text{LG}$ . No significant difference was observed between CM ( $98^\circ$ ) and CR ( $98^\circ$ ) films, which are more hydrophobic than alginate and lignin film composites with contact angles of  $57^\circ$  and  $53^\circ$ , respectively. The low contact angle of the lignin film could be

attributed to the presence of  $\text{HO}^-\text{Na}^+$  groups in lignin (after solubilization in NaOH) (Schema 1).



**Fig. 1.** Contact angle of composite films, LG: lignin, AL: alginate, CM: carboxymethyl cellulose, CR: carrageenan, LGAL: lignin-alginate, LGCM: lignin- carboxymethyl cellulose, LGCR: lignin-carrageenan. Different letters between treatments indicate significant differences ( $P < 0.05$ ,  $n=3$ ).

Notley and al [39] reported that the contact angles of softwood kraft lignin and softwood milled wood film (thickness: 50-60 nm) were 46, 52.5 and 55.5°, respectively. Norgren [40] also reported that softwood lignin films with a thickness of 20-140 nm had a contact angle of 46°, which is in good agreement with our study. In another study, Ramirez et al [41] reported that the contact angle of CM was estimated to be 83, compared to 98° obtained for CM in this study. This difference could be due to the difference in the total solid content, the thickness of

the CM composite film and the surface roughness. Lijun Yang et al [42] obtained for alginate film a contact angle of approximately 59° compared to 53° obtained in this study. They attributed this value to the hydrophilic surface of this material due to hydrophilic hydroxyl functional groups in the AL polymer (**Scheme 1**). The contact angle obtained for CR was 98° in agreement with Karbowiak et al [36] The contact angle of iota-carrageenan ranged between 88.3°-115.2°. The authors attributed this hydrophobic behavior of the iota-CR film to the three-dimensional helical structure of the carrageenan polymer, with strong intramolecular hydrogen bonding beneath the film surface and no orientation of polar groups at the surface. Jayasekara et al [43] also observed this phenomenon with starch composite film. We also observed that the addition of lignin (LG) to the polysaccharide formulation with a mass ratio of 4/1 (LG/polysaccharides) modified the hydrophobicity of the composite formulations (**Fig. 1**). The presence of lignin in the formulation tends to decrease the surface hydrophobicity of lignin-polysaccharide composites. Shankar et al [44] observed the same phenomenon. They reported that the contact angle of agar-lignin films was lower than that of agar films, and this reduction in contact angle might be due to the roughness of the film after the addition of lignin.

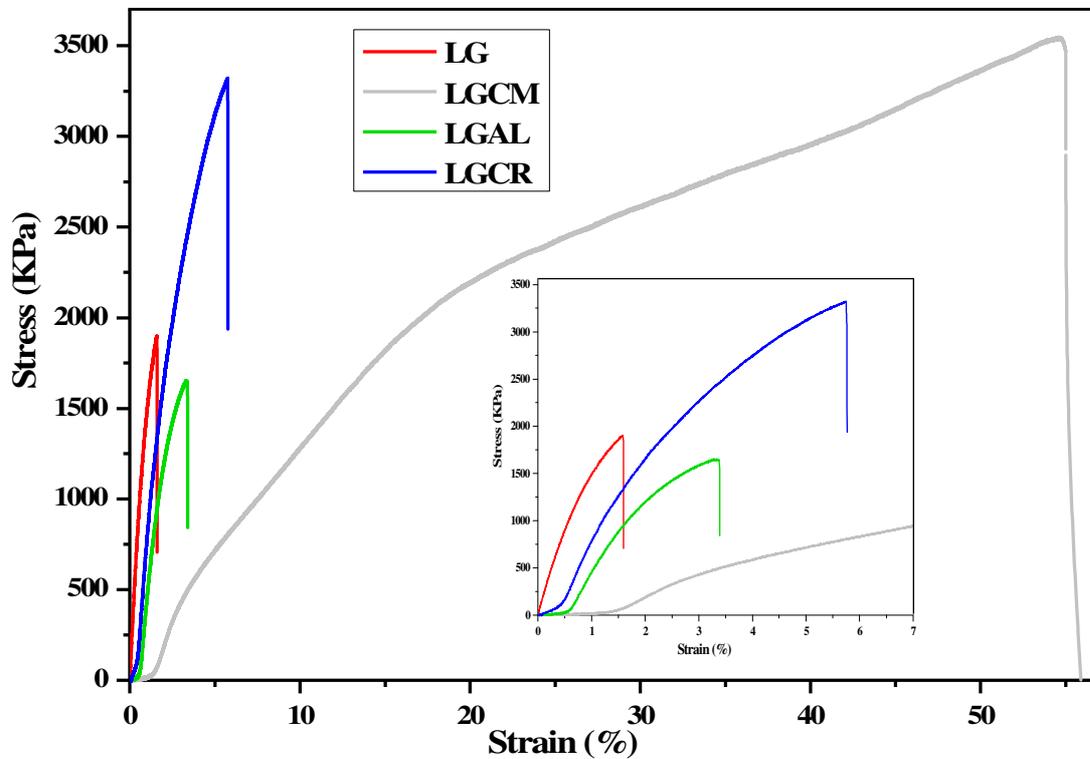
### 3.1.2. Mechanical properties of composite films

**Table 2:** Tensile modulus (EM), tensile strength (TS) and elongation at break (EB) of composite films. LG: lignin, LGAL: lignin-alginate, LGCM: lignin-carboxymethyl cellulose, LGCR: Lignin-carrageenan, n=3

Formulation	EM (KPa)	TS (KPa)	EB (%)
LG	786,93 ± 385 <sup>ab</sup>	1135.09 ± 766 <sup>a</sup>	1.46 ± 0.11 <sup>a</sup>
LGCR	1191,51 ± 356 <sup>a</sup>	3674.11 ± 318 <sup>b</sup>	9.37 ± 1.99 <sup>b</sup>
LGCM	225.49 ± 96 <sup>b</sup>	2510.98 ± 754 <sup>ab</sup>	43.94 ± 15.99 <sup>c</sup>

LGAL	$612.53 \pm 65^{ab}$	$1653.57 \pm 261^a$	$2.79 \pm 0.43^a$
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Within a column, means followed by the same letter are not significantly different



**Fig. 2.** Typical stress-strain curves of film composites: LG: lignin, AL: alginate, CM: carboxymethyl cellulose, CR: carrageenan, LGAL: lignin-alginate, LGCM: lignin-carboxymethyl cellulose, LGCR: lignin-carrageenan,  $n=3$

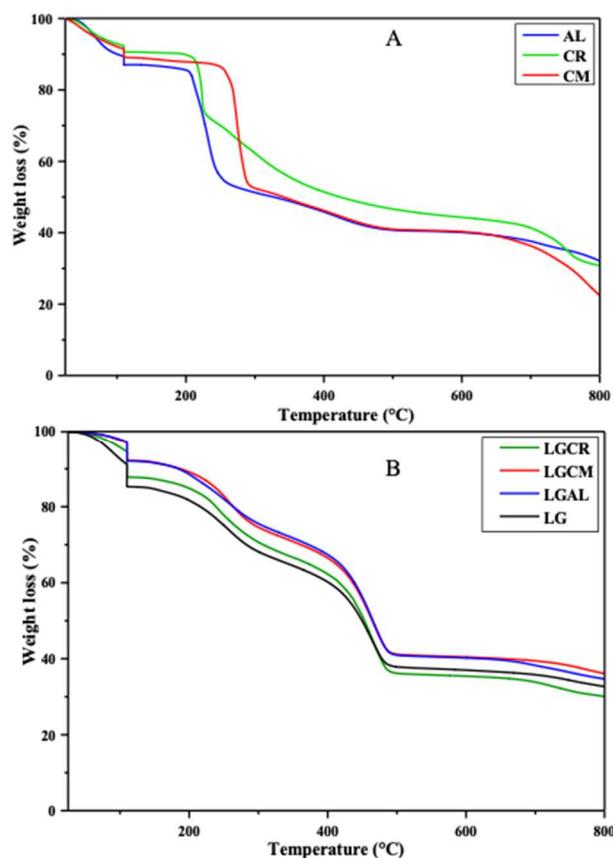
**Fig. 2** shows the typical stress-strain curves of different composite films. The elastic modulus (EM), tensile strength (TS) and elongation at break (EB) depends on the type and structure of the polysaccharides in the composites ( $p$ -value < 0.05) (**Table 2**). The EM, TS and EB of the obtained composite films varied between 225-1191 KPa, 1135-3674 KPa and 1.5 - 44%, respectively. The TS of the lignin (LG) film was  $1135.09 \pm 766$  KPa, which is lower than that of the polysaccharide-incorporated composite films (**Table 2**). Aadil et al [36] reported that the tensile strength of lignin films extracted from acacia wood and blended with alginate was

413 ± 2 KPa, while the tensile strength increased to 625 ± 7, 569 ± 12, 466 ± 6 KPa with the addition of the different plasticizers, glycerol, epichlorohydrin and PEG 4000, respectively. Lignin extracted from OP (this study) has a greater tensile strength than acacia wood lignin, even when blended with alginate and plasticizers. This is probably due to the presence of fatty acids in lignin from OP, as discussed in our previous work [30]. Fatty acids are usually used as plasticizers in composite formulations [45], and their presence can play a role in natural plasticizers in different lignin formulations. The lignin-carrageenan (LGCR) composite exhibited higher EM (1191 KPa) and TS (3674 KPa) than the LGAL and LGCM composite films. We can also see from the results that TS and EB were significantly increased by 224% and 542%, respectively, with the addition of CR compared to LG, while the addition of CM significantly increased the EB by 2910%. This increase in EB compared to LG film can be explained by the hygroscopicity of polysaccharides. These compounds are more hygroscopic than LG polymers; hence, water uptake could explain the plasticization behavior [46]. However, in the case of lignin loaded with alginate, no strong effect on mechanical properties was observed compared to the LG film. The lignin polymer has a tridimensional and porous surface structure that might aid in compatibility with the polysaccharides. These phenomena have also been observed in the plant cell wall, confirming the lignin-polysaccharide interaction [48,49].

### **3.1.3. Thermogravimetric analysis (TGA)**

The thermal stability and degradation behavior of polysaccharides and lignin-polysaccharide composites were assessed using TGA and weight loss curves. **Fig. 3A** presents the TGA analysis of the polysaccharide films. From these curves, we can observe that the thermal degradation of all polysaccharides occurs in three steps. The first step at 25-105 °C corresponds to water desorption, with approximately 9-13% overall weight loss due to dehydration. The second decomposition stage starts at 192°C for the AL and CR films and

230°C for the CM film. This step is attributed to the thermal degradation of polysaccharides. In the last step, the AL and CM films lost approximately 50% of their weight at 340°C, while the CR film had to reach 422°C to lose the same percentage of weight. This mass loss is related to the formation of byproducts of polysaccharides during the thermal degradation process [50]. Based on the TGA analysis (**Fig. 3B**) of LG and composite films, the lignin film had fast thermal degradation compared to the lignin-polysaccharide blended film. The thermal behavior of the LGAL and LGCM composites seemed to be similar. These films exhibited the slowest thermal degradation, followed by the LGCR and LG films. The 50% weights of LG and LGCR were lost at 450°C and 454°C, respectively, while LGCM and LGAL lost 50% of their initial mass at 464°C.

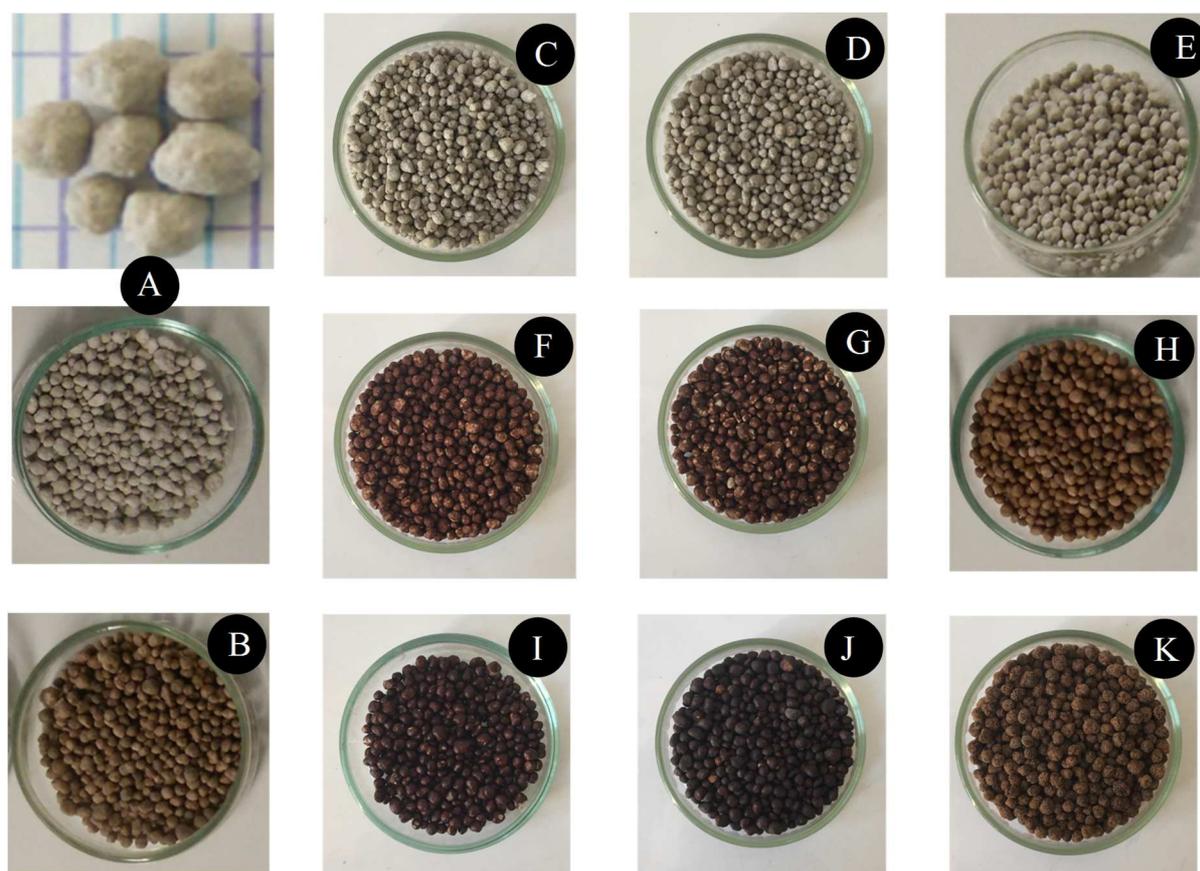


**Fig. 3.** TGA of (A) polysaccharide films (AL: alginate, CM: carboxymethyl cellulose, CR: carrageenan) and (B) LG and composite films (LG: lignin, LGAL: lignin-alginate, LGCM: lignin- carboxymethyl cellulose, LGCR: lignin-carrageenan)

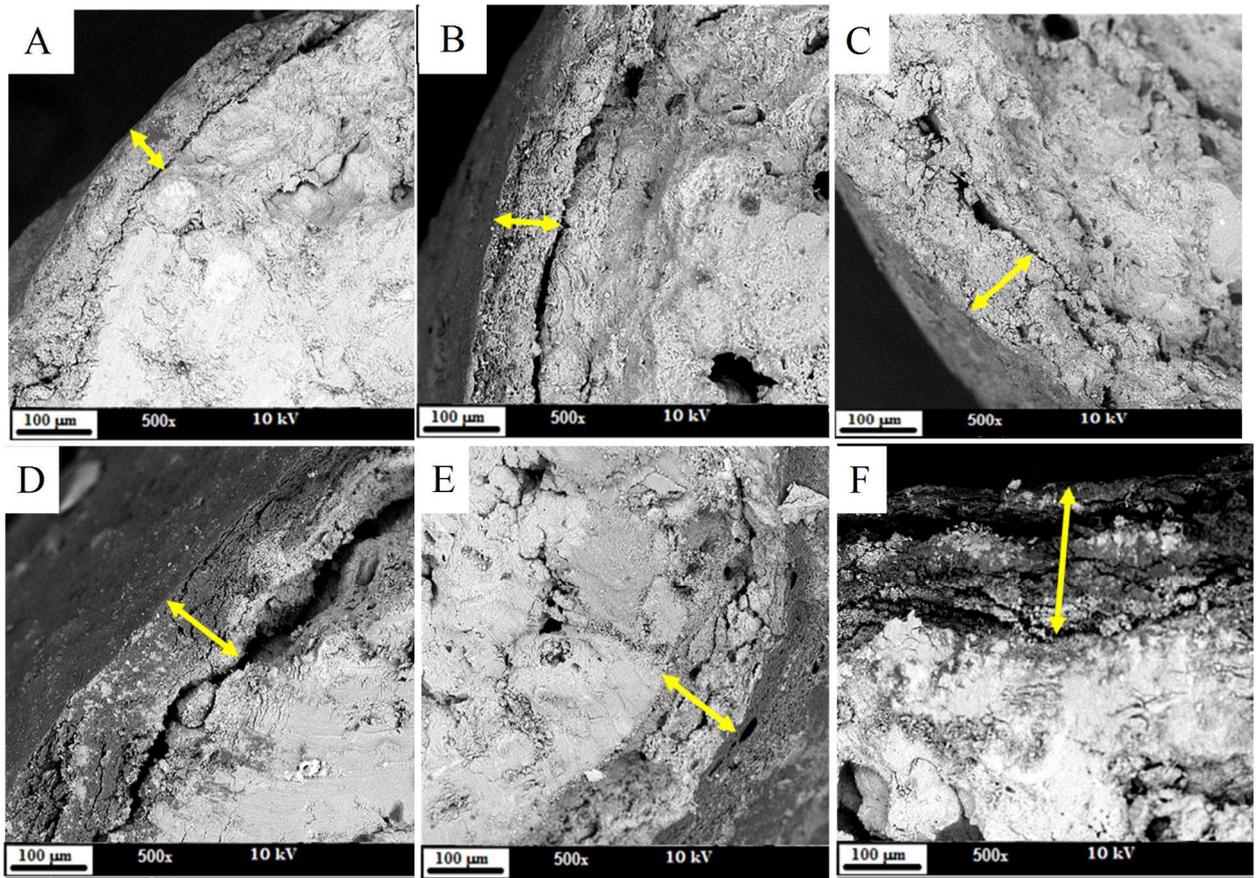
The blending of lignin with polysaccharides enhanced the thermal stability of the three materials. LG, CM and CR films underwent the active weight loss step at 25-290 °C, while this step occurred at 25-500°C with the addition of lignin. In general, the mass loss of composite-polymer films occurred between 25 and 500°C [51,52]. Changhua Liu [51] reported similar intervals of degradation temperatures of lignin-poly (4-vinylpyridine) films.

### 3.2. Coated TSP fertilizer properties

#### 3.2.1. Morphological characterization of coated TSP fertilizers

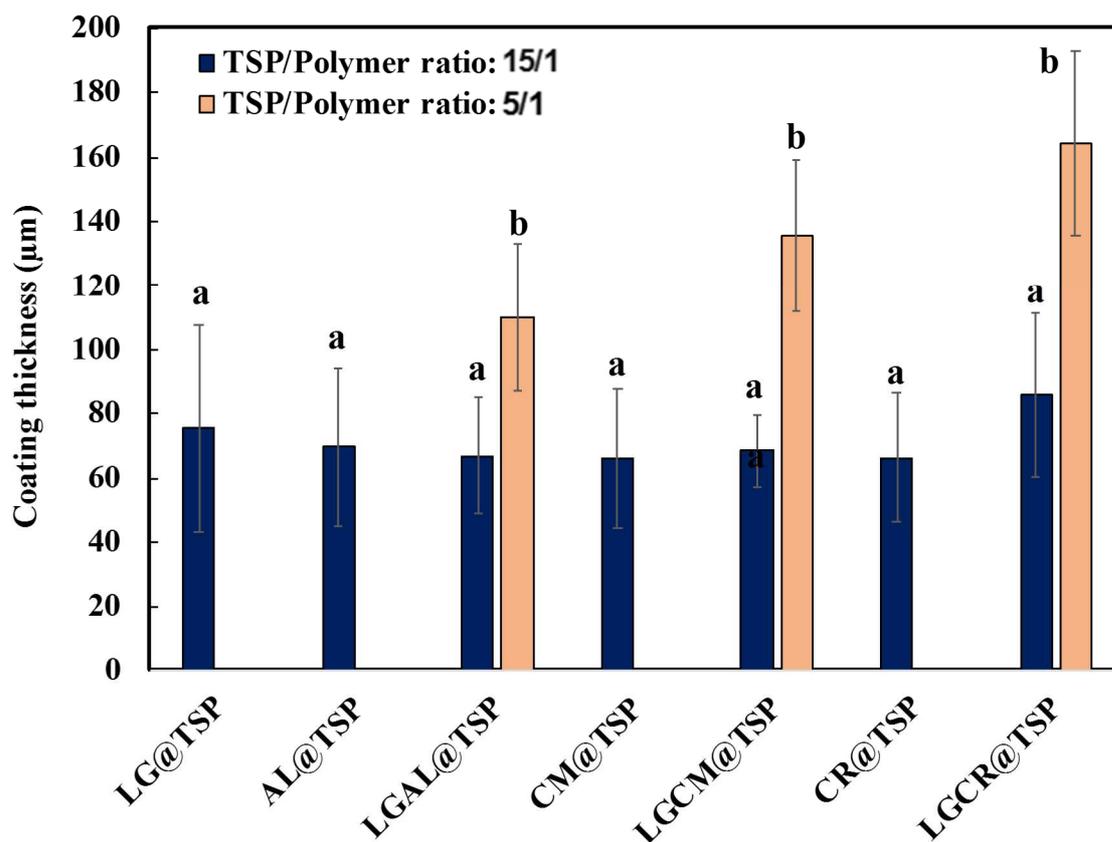


**Fig. 4.** Real image of noncoated TSP (A) and coated TSP at the TSP/polymer ratio of 15/1 with (B) LG (lignin), (C) AL (algininate), (D):CM (carboxymethyl cellulose), (E) CR (carrageenan), (F) LGAL, (G) LGCM and (H) LGCR, and at the TSP/polymer ratio of 5/1 with (I) LGAL, (J) LGC and (K) LGCR



**Fig. 5.** SEM of cross-section of the coated TSP fertilizer at the TSP/polymer mass ratio of 15/1 with (A) LGAL (lignin-alginate, (B) LGCM (lignin- carboxymethyl cellulose and (C) LGCR (lignin-carrageenan) and at the TSP/polymer ratio of 5/1 with (D) LGAL, (E) LGCM and (F) LGCR

**Fig. 4** presents pictures of coated TSP. The interactions of TSP granules and coatings were observed using SEM (**Fig. 5**). The thickness of the coating layers was determined for the coated TSP fertilizers. The thickness of the layers (TSP/polymer ratio of 15/1) was  $71.3 \pm 23.6 \mu\text{m}$  on average. The coating formulation has no significant effect on coating thickness (p-value > 0.05).



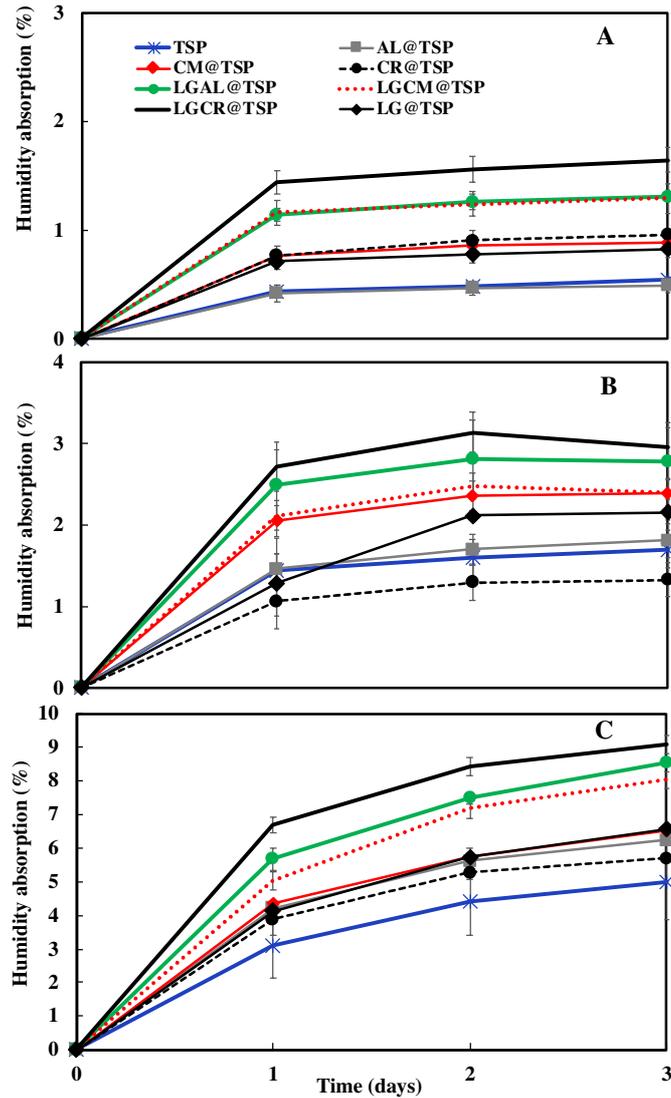
**Fig. 6.** Thickness of coating layers on TSP granules coated with LG (lignin), AL (alginate), LGAL (lignin-alginate), CM (carboxymethyl cellulose), LGCM (lignin- carboxymethyl cellulose), CR (carrageenan) and LGCR (lignin-carrageenan). Different letters between treatments indicate significant differences ( $P < 0.05$ ,  $n=9$ ).

The coating thickness is an important parameter that can control the nutrient release rate [24,53]. The effect of two ratios of TSP/polymers (15/1 and 5/1) on the coating agent thickness was studied, and the results are shown in **Fig. 6**. A significant effect on coating agent thickness was observed between ratios for the granules coated with the three formulations. The coatings formed with a higher polymer concentration exhibited higher thickness ( $135.6 \pm 20.9 \mu\text{m}$ ) for the TSP/polymer ratio of 5/1 than the  $71.3 \pm 23.6 \mu\text{m}$  observed for the TSP/polymer ratio of 15/1. This result is in agreement with the previous report of

Anna Jarosiewicz et al [24], suggesting an increase in the thickness with increasing polymer concentration in the coating solution.

### **3.2.2. *Hygroscopicity of uncoated and coated fertilizers***

**Fig. 7.** illustrates the water absorption of uncoated and coated TSP within 3 days at different RHs (35%, 60% and 80%). The water absorption of all formulations increased with increasing air humidity and with time. LGCR@TSP, LGAL@TSP and LGCM@TSP exhibited the highest hygroscopicity in the following order: LGCR@TSP > LGAL@TSP > LGCM@TSP. According to Liang et al [54], the water absorption of coating polymers depends on many factors, such as the amount of hydrophilic groups and elasticity of the polymer networks. As previously mentioned in **Table 2**, LGCR exhibited the highest elastic modulus (EM) ( $1191.51 \pm 356$  KPa), followed by LGAL ( $612.53 \pm 65$  KPa) and then LGCM ( $225.49 \pm 96$  KPa). The major result was that the water absorption of the coating increased when the elasticity increased, which could improve the swelling properties of the coated fertilizers. It is noteworthy that a coated fertilizer with swelling and slow release behavior could effectively improve the utilization of both fertilizer and water resources [54].



**Fig. 7:** Water absorption (WA) of uncoated and coated fertilizers over time at different relative humidities: (A) 35%, (B) 60% and (C) 80% RH with LG (lignin), AL (alginate), CM (carboxymethyl cellulose, CR (carrageenan) LGAL (lignin-alginate), (G) LGCM (lignin-carboxymethyl cellulose) and LGCR (lignin-carrageenan), n=3.

**3.3.Slow-release behavior of phosphorus from coated TSP fertilizers**

**Table 3:** Release behavior of TSP and coated TSP with different polymers in water, TSP coated with LG: lignin, AL: alginate, CM: carboxymethyl cellulose, CR: carrageenan, LGAL: lignin-alginate, LGCM: lignin- carboxymethyl cellulose, LGCR: lignin-carrageenan, n=3.

Formulation	TSP/	P-release in water (%) over time (h)
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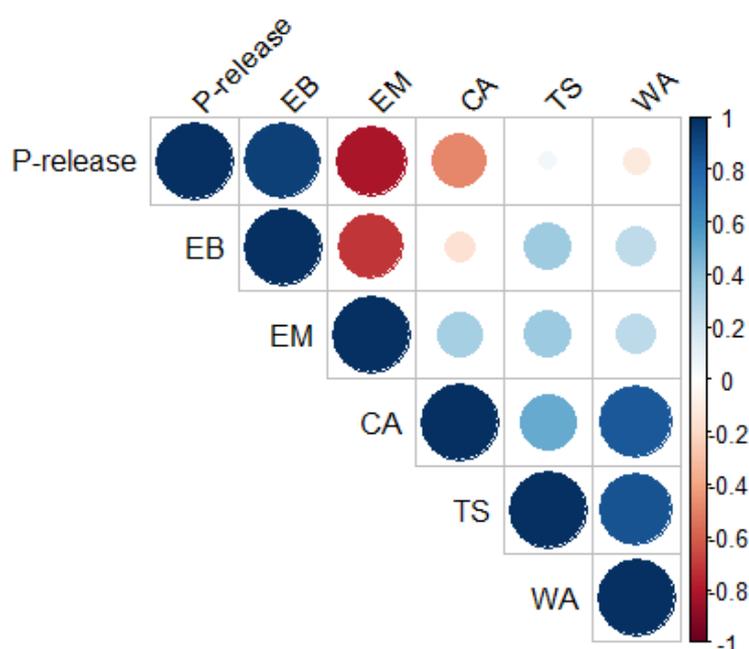
Polymer		6	24	48	72	96	120
ratio							
<b>TSP</b>	-	72.0 ± 0.4 <sup>a</sup>	85.0 ± 14 <sup>a</sup>	95.0 ± 2.7 <sup>a</sup>	99.5 ± 4.3 <sup>a</sup>	-	-
<b>LG@TSP</b>	15/1	34.3 ± 4 <sup>ab</sup>	55.5 ± 6.4 <sup>a</sup>	64.1 ± 1 <sup>bc</sup>	65 ± 9.8 <sup>bcd</sup>	71.6 ± 1.8 <sup>abcd</sup>	76 ± 0.7 <sup>a</sup>
<b>CR@TSP</b>	15/1	44.9 ± 4.9 <sup>ab</sup>	60.9 ± 0.7 <sup>a</sup>	69.5 ± 7.8 <sup>ab</sup>	78.1 ± 5.7 <sup>abcd</sup>	84.7 ± 15 <sup>a</sup>	90.2 ± 3.8 <sup>b</sup>
<b>CM@TSP</b>	15/1	39.7 ± 7.6 <sup>ab</sup>	77.1 ± 0.1 <sup>a</sup>	73.8 ± 4.7 <sup>bc</sup>	79.5 ± 3.5 <sup>abc</sup>	75.1 ± 1.7 <sup>abc</sup>	73.7 ± 1.1 <sup>a</sup>
<b>AL@TSP</b>	15/1	19.3 ± 13 <sup>b</sup>	76.7 ± 0.1 <sup>a</sup>	77.9 ± 6.6 <sup>abc</sup>	80.6 ± 10 <sup>ac</sup>	77.3 ± 5.5 <sup>ac</sup>	75.3 ± 4.4 <sup>a</sup>
<b>LGCR@TSP</b>	15/1	28.2 ± 4.8 <sup>ab</sup>	52.0 ± 6.5 <sup>a</sup>	59.0 ± 8.9 <sup>abc</sup>	72.5 ± 1.2 <sup>abcd</sup>	78.8 ± 2.0 <sup>abcd</sup>	75.3 ± 4.0 <sup>abcd</sup>
<b>LGCM@TSP</b>	15/1	55.7 ± 9.4 <sup>ab</sup>	66.7 ± 0.8 <sup>a</sup>	73.1 ± 4.8 <sup>bc</sup>	71.9 ± 0.5 <sup>bcd</sup>	69.6 ± 0.9 <sup>abcd</sup>	68.5 ± 1.1 <sup>ad</sup>
<b>LGAL@TSP</b>	15/1	51.7 ± 9.9 <sup>ab</sup>	74.5 ± 0.1 <sup>a</sup>	67.1 ± 1.7 <sup>bc</sup>	68.3 ± 3.1 <sup>bcd</sup>	68.7 ± 3.1 <sup>abcd</sup>	64.9 ± 0.5 <sup>acd</sup>
<b>LGCR@TSP</b>	5/1	-	59.1 ± 1.9 <sup>a</sup>	60.0 ± 1.0 <sup>c</sup>	59.5 ± 1.9 <sup>bd</sup>	60.4 ± 3.0 <sup>bcd</sup>	59.3 ± 1.6 <sup>cd</sup>
<b>LGCM@TSP</b>	5/1	-	59.9 ± 1.8 <sup>a</sup>	59.0 ± 1.4 <sup>c</sup>	58.9 ± 2.4 <sup>d</sup>	57.4 ± 0.8 <sup>bd</sup>	59.2 ± 2.2 <sup>cd</sup>
<b>LGAL@TSP</b>	5/1	-	56.3 ± 3.3 <sup>a</sup>	61.7 ± 3.9 <sup>bc</sup>	57.9 ± 5.5 <sup>d</sup>	55.1 ± 3.7 <sup>d</sup>	55.8 ± 3.5 <sup>c</sup>

Within a column, means followed by the same letter are not significantly different

As shown in **Table 3**, the untreated TSP released approximately 72±0.4, 85±140 and 99.5±4.3% of P within 6, 24, and 72 h, respectively. In contrast, the fertilizers coated with only lignin or only polysaccharides or with lignin-polysaccharides (the TSP/polymer ratio of 15/1) released only 19.3-55.7%, 52-77.1% or 68.3-80.6% within 6, 24, and 72 h, respectively. Statistical analysis showed a significant effect of coating formulation and time on the delay of P release ( $p < 0.05$ ). The slowest P release was observed with the LGCR@TSP formulation within the first and second days.

To understand the relationship between P release behavior and the physicochemical properties of film composites of coated TSP discussed previously in this work, a correlation matrix was constructed (**Fig. 8**). P release is strongly negatively correlated with EM ( $R = -0.81$ ), while it is strongly positively correlated with EB ( $R = 0.93$ ). The young modulus (EM) represents the elastic deformation. When the coating material is elastic, the shell is able to resist the internal pressure created inside the core upon contact with water, and the P is released slowly without the shell being destroyed. A moderate negative correlation between P release and CA was also

revealed ( $R = -0.49$ ). This phenomenon could be explained by the fact that, when the contact angle is large, the coating material is hydrophobic, and then the affinity between the layer and water is weak. This lack of affinity prevents the penetration of large quantities of water inside the fertilizer core and then decreases the dissolution of TSP. For TS and WA, a weak or no correlation was observed with P release ( $R < 0.11$ ). From these data and discussion, we concluded that the LGCR formulation is the most efficient coating for mineral fertilizer due to its high elastic modulus, high CA, high water absorption and, as a consequence, slow release of P.



**Fig. 8.** Correlation matrix between the properties of composite films and coated TSP. Film properties: EM (elastic modulus), TS (tensile strength), EB (elongation at break) and CA (contact angle). Coated TSP properties: P release within 1 day and WA (water absorption at RH 35% within 1 day). Positive correlations are displayed in blue, and negative correlations are displayed in red. Color intensity and circle size are proportional to the correlation coefficient, R. On the right side of the correlogram, the legend color shows the correlation coefficients and the corresponding colors.

The release behaviors of TSP coated with LGCR, LGCM and LGAL formulations at TSP/biopolymer ratios of 15/1 and 5/1 are shown in **Table 3**. A statistical study showed a significant effect of TSP/biopolymer ratios (the effect of coating thickness) on the release response from LGAL@TSP and LGCM@TSP ( $p$ -value $<0.05$ ) but not LGCR@TSP. As previously presented in **Fig. 5B**, a high TSP/biopolymer ratio resulted in a high thickness. A higher polymer coating concentration decreased the P release of coated TSP granules due to the increase in coating layer thickness. After 3 days, TSP coated with LGCR, LGCM and LGAL formulations at the TSP/biopolymer ratio of 15/1 (thickness= $71.3\pm 23.6\mu\text{m}$ ) released 72.5%, 71.9% and 68.3% of P, respectively, while TSP coated with the same formulations using a TSP/biopolymer ratio of 5/1 (thickness= $135.6\pm 20.9\mu\text{m}$ ) released only 59.5, 58.9 and 57.9% of P. These results are in accordance with other studies in the literature. Lubkowski et al [55] showed that the release of phosphate from uncoated fertilizer was very fast and that all phosphates were released within 50 min, while coated NPK with different thicknesses (0.047–0.5425 mm) revealed a smaller release of phosphate in comparison with the initial NPK. Jarosiewicz et al [24] showed that the release rate of NPK can be controlled by adjusting the thickness of the coating. They argued that NPK granules with double or triple-layered coatings (high thickness) released nutrients much slower than granules coated with one layer. NPK granules coated with one layer of 17% polyacrylonitrile (thickness  $\approx 0.2$  mm) released 93.7% of  $\text{K}^+$  within 5 h, while granules with three layers of the same formulation (thickness  $\approx 0.49$  mm) released only 11.7%. Behin et al [56] confirmed that the release of nitrogen depends strongly on the thickness of the coating. They reported that the dissolution rate decreases with increasing coating percentage. For urea coated with acetylated kraft lignin and sulfite lignin, dissolution rates of 88 and 97%, respectively, were obtained after 24 h for the sample with a 5.0% coating, whereas only 43 and 72% were obtained for the sample with a 15.0% coating.

**Table 4:** Comparative studies of different works using lignin as a coating material to control nutrient release

Coating materials	Fertilizer	Granule size (mm)	T drying (°C)	Coating methods	Thickness (µm)	Release rate(%)	Ref	
Lignin + Polysaccharides	TSP	2-3	65	Rotating pan	77-211	Noncoated Coated	100% after 3 d 57-58% after 3d	This work
Commercial lignin + rosins	TSP	2		Rotating pan	83-106	Noncoated Coated	80% after 3days 20% after 3 days	Garcia et al [8]
Commercial lignins + plasticizers + hydrophobic compounds	Urea	-	70	Rotating pan	-	Noncoated Coated	>80% after 30min 60-80%after 30min	Mulder et al [32]
Commercial lignin	Urea	0.5-5	-	Matrix	-	Non-treated Matrix	100% after <5h 40-90% after 1h	Perez et al [57]

**Table 4** provides a comparative study of the results obtained in this work and those from previous studies using lignin as a coating material. It can be deduced from the work of Perez et al [57] that using lignin alone does not improve the delayed release of urea in water, which can be explained by the presence of the polar groups on its surface and the resulting good affinity with water. Mulder et al [32] also employed lignin coupled with plasticizers and some other hydrophobic compounds and reported that complete nitrogen release through these coating materials still occurred within 1 h. To improve its coating properties, lignin has also been mixed with rosins as a coating system for soluble fertilizers such as phosphate fertilizer [8] According to Garcia et al [8], only 20% of P was released was this method. In comparison

with these previous works, it can be concluded that our study is interesting in that we used low-cost materials based on OP, which can potentially be a good candidate for coating fertilizers and slowing the release rate of nutrients; however, our materials remain less efficient in this regard than synthetic polymers.

#### **4. Conclusion**

This work reports the valorization of lignin extracted from OP biomass with polysaccharides as a new coating material for water soluble TSP fertilizer. Films containing lignin and carrageenan show the best mechanical properties. The blending of lignin with polysaccharides reduced the hydrophobicity of the composites compared to that of the pure polysaccharide films but still showed higher hydrophobicity than the lignin film. The coating materials based on lignin and polysaccharides appear to have a good interaction and adhesion with the mineral fertilizer surface, confirming the effect of different formulations on the delay of P release. The results showed that more than 95% of P was released from uncoated TSP within 48 h, and 100% of P was released within 72 h, while the release of P with the lignin-polysaccharides@TSP formulations decreased to approximately 60% within 72 h with a TSP/polymer ratio of 5/1.

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### Graphical abstract

