Research article

Blends of nitrophenylmaleimide isomers with carboxymethylcellulose for the preparation of supramolecular polymers

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A B S T R A C T

Novel water-compatible supramolecular polymers (WCSP) based on the non-covalent interaction between carboxymethylcellulose (CMC) and o, m, and p-nitrophenylmaleimide isomers are proposed. The non-covalent supramolecular polymer was obtained from high viscosity CMC with a degree of substitution 1.03 with o, m, and p-nitrophenylmaleimide molecules that were synthesized from maleic anhydride and its corresponding nitroaniline. Subsequently, blends were made at different nitrophenylmaleimide concentrations, stirring rate, and temperatures, with 1.5% CMC, to select the best conditions for each case and to evaluate the rheological properties. The selected blends were used to form films and analyze spectroscopic, physicochemical, and biological properties. Then, the interaction between a CMC monomer and each isomer of nitrophenylmaleimide was investigated using quantum chemistry computational calculations with the B3LYP/6-311 + G (d,p) method, providing a detailed explanation of their intermolecular interactions. The supramolecular polymers obtained exhibit an increase in viscosity of blends between 20% and 30% compared to CMC, a shift in the wavenumber of the OH infrared band by approximately 66 cm^{-1}, and the first decomposition peak at the glass transition temperature occurring between 70 and 110 °C. These changes in properties are attributed to the formation of hydrogen bonds between the species. However, the degree of substitution and the viscosity of the CMC affects the physical, chemical, and biological properties of the polymer obtained. The supramolecular polymers are biodegradable regardless of the type of blends made and are easily obtainable. Notably, the CMC with m-nitrophenylmaleimide yields the polymer with the best properties.

1. Introduction

Maleimides are a class of organic compounds that have recently gained significant attention due to their unique physicochemical and biochemical properties. These small, reactive molecules contain a distinctive CO–N-(R)-CO functional group, where R can be an alkyl, aryl, or hydrogen atom group. Maleimides are categorized into two main types: N-alkyl maleimides and N-aryl maleimides. The

latter is particularly noteworthy for its low toxicity and commercial availability, which provides significant advantages over aliphatic species, depending on the specific substituent used, N-aryl maleimides offer a broad range of potential applications in various fields. It has been shown that the reactivity and photochemical properties of these compounds depend on the substituent group and the torsion angle between the two rings (aromatic and imide), with the molecules being more active as the angles approach perpendicularity. Substituted N-phenyl maleimides are used as free radical initiators during polymerization and act as copolymers in copolymerizations induced by exposure to light or heat [1,2].

N-phenylmaleimides are fundamental building blocks in the design of various materials, such as thermally reactive adhesives, composites, and metal adsorption. Moreover, they endow polymers with high flame retardancy, excellent structural rigidity, good dielectric properties, and enhanced thermal stability [3]. The double bond present in the imide ring acts as a dienophile (acceptor) in Diels-Alder cycloaddition reactions and is often used in synthesizing new organic compounds [4,5]. Additionally, N-phenylmaleimides have demonstrated good fungicidal properties against human pathogenic fungi [6,7], and have been found to be effective and selective in differential cytotoxicity against hematopoietic cancer cells, thus showing promise in cancer treatment [7,8].

On the other hand, carboxymethyl cellulose (CMC) is an ether obtained from cellulose and monochloroacetic acid or by the addition of alkaline cellulose to sodium monochloroacetate [9,10]. Polymer chains of CMC monomers are formed by linking them through 1,4-glycosidic bonds. Each unit within the chain features free hydroxyl groups that can undergo substitution by carboxymethyl groups, with a maximum of three such substitutions possible. The degree of substitution (DS) on CMC corresponds to the number of carboxymethyl groups present in the polymer chain. The degree of substitution (DS)provides different properties and utilities to carboxymethylcellulose. However, it has been demonstrated through kinetic control that the substitution is favored at position 6 [11]. Commercially, CMC is supplied as a sodium salt that is odorless, tasteless, non-toxic, and soluble in water at low concentrations (typically less than 2% by mass) [12]. Some of the macromolecules that include CMC can be classified as water-compatible supramolecular polymers (WCSP) due to their water compatibility and the reversible non-covalent interactions with other molecules, as demonstrated in this research. WCSPs have a wide range of applications, including photocatalysis, biomaterials, molecular recognition, and drug delivery. These polymers can be classified into five categories based on the type of interaction: hydrogen bonding (as seen in the polymers studied here), electrostatic interactions, p-conjugated components, host-guest interactions, and peptide-based systems [13].

The CMC in an aqueous solution can present different types of viscosities (low, medium, and high). Moreover, studies have demonstrated that the value of viscosity can vary within the same type of viscosity depending on the distribution of molecular weight [14]. This makes it necessary to always verify the viscosity values of the CMC solutions and compare the results to perform a statistical analysis. CMC possesses various such as elasticity, innocuousness, and excellent behavior as an adhesive protective colloid, thickener, among others, which make it an attractive option for different applications. In industry, CMC is used in paper products, construction materials, textile manufacturing, food products, pharmaceuticals, cosmetics, etc. [15,16]. Additionally, CMC solutions can be evaporated to form films characterized by biodegradability, biocompatibility, and non-toxicity, making CMC attractive for synthesizing, or blending biodegradable polymers that do not harm ecosystems [17,18].

The different molecular weights of CMC make supramolecular polymers obtained from it viable for a wide range of applications in the field of polymeric materials [19,20]. The presence of hydroxyl groups on CMC facilitates interaction with different molecules and allows chemical modifications, conferring important rheological and water solubility properties to the polymers. CMC finds several important applications in the field of biomedical and pharmaceutical sciences [19,21].

Many research papers on supramolecular polymers are currently being published; however, the interaction between CMC and nitrophenylmaleimide isomers, as potential biodegradable materials with better mechanical and thermal properties than those provided by phenylmaleimides, has not been reported. For this reason, this research has shown the obtention of new water-compatible supramolecular polymers (WCSP) [14]. These polymers are reversible and biodegradable, which are important properties in the design of new materials. The polymers were obtained from blends of CMC with nitrophenylmaleimide isomers in an aqueous solution. The behavior of the blends was evaluated with variation in temperature, agitation, and concentration of the nitrophenylmaleimide isomers, in relation to viscosity measurements. Based on the highest viscosity differences observed between the blends and the CMC solution, better blends were selected to produce polymeric films. The experimental results reveal differences in shear rate, viscosity, increased consistency index, and viscous molecular weight of the blends compared to CMC. Additionally, the properties of the films show resistance to acidic and basic solutions as well as different solvents. Furthermore, the first glass transition temperature of the blends increased between 70 °C and 100 °C, and there were additional decomposition points for some blends compared to CMC. These differences in the results can be explained by the interaction via hydrogen bonding between the studied systems, which is supported by computational calculations. This novel type of polymer is a proposal as an easily obtainable, biodegradable material with high thermal resistance, making it suitable for potential applications in industries such as packaging or biodegradable plastics.

2. Experimental

2.1. Precursor synthesis

2.1.1. Synthesis of o-nitrophenylmaleimide

The synthesis of o-nitrophenylmaleimide was carried out following the methodology [1]. 1.008 g (10.282 mmol) of maleic anhydride (Aldrich Chemical Co., 98% purity), was dissolved in 25 mL of anhydrous diethyl ether (Merck, 99.98% purity). Then, 1.400 g (10.148 mmol) of o-nitroaniline (Merck, purity 99.8%) was added to 10 mL of anhydrous diethyl ether, and the solutions were mixed with stirring at room temperature for 2 h. The solvent was allowed to evaporate for 24 h, and after several washes with anhydrous

diethyl ether, 1.692 g (yield 76.5%) of a yellow solid was obtained. The melting point was determined to be 127 ± 1 °C, using a BI. Barnstead 9100 electrothermal model.

2.1.2. Synthesis of m-nitrophenylmaleimide

The synthesis of m-nitrophenylmaleimide was conducted following the methodology [22]. Firstly, 1.008 g (10.282 mmol) of maleic anhydride and 1.400 g (10.148 mmol) of m-nitroaniline (Merck, 99.5% purity) was dissolved in 40 mL of nitrobenzene (Aldrich Chemical Co., 99.98% purity). The mixture was then refluxed at 200 °C for 3 h. After completion of the reaction, it was cooled and allowed to settle for 48 h, then filtered and washed with anhydrous diethyl ether to obtain 0.996 g (45% yield) of a pale-yellow solid with a melting point of 123 ± 1 °C.

2.1.3. Synthesis of p-nitrophenylmaleimide

The synthesis of p-nitrophenylmaleimide was conducted following the methodology described in Ref. [2]. Maleic anhydride (1.008 g, 10.282 mmol) and p-nitroaniline (1.400 g, 10.148 mmol, Merck, 99.5% purity) were dissolved in 40 mL of nitrobenzene (Aldrich Chemical Co., 99.98% purity) and refluxed for 3 h at 200 °C. After cooling and allowing to settle for 48 h, the product was filtered, washed with anhydrous diethyl ether, and obtained as a pale-yellow solid with a melting point of 165 ± 1 °C and a yield of 41% (0.907 g).

2.1.4. Analysis of nitrophenylmaleimide isomers by IR

The compounds obtained from each isomer of nitrophenylmaleimide were analyzed via infrared (IR) spectroscopy using a Thermo Nicolet Avatar Model 320. This was done by preparing 1 mg pellet of each compound with 100 mg of anhydrous KBr and compressing them using a 15000-psi die. The obtained results were compared with the reported IR spectra.

2.1.5. Mass spectrometry analysis of nitrophenylmaleimide isomers

The nitrophenylmaleimide isomers were subjected to mass spectrometry analysis using a GCMS-QP2010 Shimadzu instrument with an HP-5ms capillary column. For each compound, 10 mg was dissolved in 5 mL of acetone (Merck, 99.95% purity), and 10 μL of the resulting solution was injected directly into the instrument.

2.2. Preparation and evaluation of CMC blends with and without nitrophenylmaleimide

2.2.1. Preparation of carboxymethylcellulose (CMC) solutions

Solutions were prepared by dissolving 3 g of CMC (Profinas, purity 96.49%, degree of substitution 1.03) in 200 mL of distilled water. The solutions were prepared under different conditions, including various temperatures (20, 30, and 40 °C) and stirring rates (204, 306, and 417 rpm).

2.2.2. Preparation of carboxymethylcellulose blends with o, m, and p-nitrophenylmaleimide

The Blends were prepared as described in the previous step by adding 1, 5, 10, 20, 50, and 100 mg of o, m, and p-nitrophenylmaleimide in 5 mL of acetone (Merck, 99.95% purity) to each CMC solution. Each solution was prepared in triplicate. The amounts added were selected based on the LD_{50}.

2.2.3. Determination of solution and blend densities

The Densities of the solutions and blends were measured by the pycnometer method using a Metter AE 100 + 0.00001 g balance. The real volume of 5.02 mL was previously calibrated with distilled water. Each measurement was performed in triplicate at room temperature.

2.2.4. Viscosity measurements of solutions and blends

The viscosity of the solutions and blends was measured using a rotational viscometer (J. P. Selecta S.A., ST 2010) with the L4 spindle and a temperature probe. The measurements were performed for triplicate, and the viscosity values were obtained in centi-Stokes (mm^2/s).

2.2.5. Properties of carboxymethylcellulose (CMC) and nitrophenylmaleimide blends

The statistical analysis results helped us evaluate the best blends, and we determined their average molecular masses and consistency index by rheology.

2.2.6. Rheological curves

The rheology curves were performed in a measuring disk where 1 mL of the CMC solution or blends containing o, m and p-nitrophenylmaleimide were added. Shear rate readings were obtained between $0.01 \, s^{-1}$ and $10^5 \, s^{-1}$ with a constant 1 mm gap at 20 °C using a Kinexus rotational rheometer.

2.2.7. Degree of substitution

The degree of substitution of the solutions was determined using the ASTM D- 1439-03 methodology [23].

2.2.8. Statistical analysis

The Experimental design was performed using multifactorial analysis (2-factor ANOVA) with a 95% confidence level, correlating the effects of temperature, agitation, and concentration on the viscosity responses. The optimal relationships between the variables for each mixture were determined using STATGRAPHICS Plus Version 5.1 software.

2.3. Preparation and evaluation of CMC films with and without nitrophenylmaleimide

2.3.1. Evaluation of physical and chemical properties of polymeric films

Initially, films of CMC and nitrophenylmaleimide isomers were obtained by adding the previously prepared solutions into a refractory. The refractory was then placed in an oven at 120 °C for 2 h to obtain thin films approximately 1 mm thick. Resistance to chemical agents of the obtained films was evaluated by using 1 × 2 cm squares, which were immersed in solutions of sulfuric acid (Merck, purity 96%, P.E. 1.84) at concentrations of 96%, 80%, 70%, 60%, and 40% by mass; nitric acid (Merck, purity 65%, P.E. 1.40) at a concentration of 65% by mass; hydrochloric acid (J. T. Baker, purity 37%, P. E. 1.19) at a concentration of 37% by mass; glacial acetic acid (Merck, purity 100%, P.E. 1.05); potassium hydroxide (Merck, purity 85%) at a concentration of 22% by mass-volume; sodium hydroxide (Merck, purity 99%) at a concentration of 24% mass-volume and hydrogen peroxide (Carlo Erba Reagents, purity 30%, P. E. 1.122) at concentrations of 30%, 20%, 10%, 5%, and 1% by mass. Each evaluation was performed in triplicate and left for 24 h. To evaluate the solubility of the films, 0.5 × 0.5 cm squares were introduced into solvents including hexane (Mallinckrodt chemical, purity 98.5%); petroleum ether (Mallinckrodt chemical, boiling range of 30–75 °C); ethyl ether (Merck, purity 99.7%); ethyl acetate (J. T. Baker, purity 99.92%); isopropyl alcohol (J. T. Baker, purity 99.9%); acetone (J. T. Baker, purity 99.8%); acetonitrile (Mallinckrodt chemical, purity 99.9%); methanol (J. T. Baker, purity 99.9%), and absolute ethanol (Mallinckrodt chemical, purity 99.9%). Each evaluation was performed in triplicate and left for 24 h.

2.3.2. FTIR-ATR spectra

Films of CMC and blends with o, m, and p-nitrophenylmaleimide were placed onto a universal ATR device (DiCompTM crystal), which consisted of a diamond ATR device with a zinc selenide focusing element on direct contact with the diamond, on a PerkinElmer Spectrum 100 spectrophotometer (PerkinElmer Cetus Instruments, Norwalk CT, USA).

2.3.3. Thermogravimetric analysis (TGA)

The measurements of thermogravimetric analysis for CMC and blends with o, m, and p-nitrophenylmaleimide were carried out using a TGA Netzsch TG 209 F1 with a heating ramp of 10 °C/min in a nitrogen atmosphere (60 mL/min).

2.3.4. Intrinsic biodegradability

Agar-agar culture medium was prepared by dissolving 3.4 g of agar in 250 mL of distilled water and sterilizing at 121 °C for 20 min and was taken as the blank. Then, the aforementioned process was repeated using 1 mL of CMC solution or blends of CMC with o-nitrophenylmaleimide, m-nitrophenylmaleimide, and p-nitrophenylmaleimide blends. Each of the assays was performed in quintuplicate. The culture media were exposed to the environment for 20 min and then incubated at 37 °C for 48 h, after which the number of colonies formed was counted [18].

2.4. Computational calculations

Computational quantum chemistry calculations were performed for the nitrophenylmaleimide isomers and carboxymethyl-β-glucopyranose using the density functional theory (DFT) method and the B3LYP functional [24,25], along with the 6-311 + G (d,p) basis set of orbitals [26,27]. The Gaussian 16 quantum chemistry software was employed [28]. The molecular geometries were fully optimized with a threshold of 10^{-5} a.u. for the RMS forces. The optimized structures were confirmed to be true local minima by estimating the normal vibrations within the harmonic approximation.

3. Results and discussion

3.1. Precursor synthesis

The compounds obtained reported melting points like those obtained by Cortes and Valencia [1] and Moreno et al. [2,22], with a variation of ±1 °C. The range of variation in melting points indicates the purity of the synthesized nitrophenylmaleimide isomers.

Table 1
Comparison of the most important bands of o, m, and p-nitrophenylmaleimide.

Band Type	o-nitrophenylmaleimide	m-nitrophenylmaleimide	p-nitrophenylmaleimide
C–H sp^2 aromatic	3072.67 cm^{-1}	3054.84 cm^{-1}	3089.56 cm^{-1}
C=O (imide)	1712.56 cm^{-1}	1716.42 cm^{-1}	1708.71 cm^{-1}
NO$_2$ Strain	1585.28 and 1353.85 cm^{-1}	1550.56 and 1371.51 cm^{-1}	1542.85 and 1338.42 cm^{-1}
C=C maleimidic Ring	1585.28 cm^{-1}	1596.85 cm^{-1}	1600.71 cm^{-1}

Additionally, the infrared spectra of the precursors (nitroaniline isomers) [29–31] and the synthesized compounds (Fig. S1 in the supplementary file) were compared. The absence of a band corresponding to the primary amine hydrogens near 3500 cm^{-1} suggests the absence of nitrophenyl maleamic acid intermediate. The presence of the secondary amine hydrogens and the carboxylic group formed would give a frequency of 3300 to 3500 cm^{-1}, which is not evident in the obtained compounds [32,33].

Table 1 compares the most relevant bands of the nitrophenylmaleimide isomers obtained, showing a close similarity in their vibrational bands. The observed variation is due to the position of the nitro group and the torsion angle between the maleimide ring and the aromatic ring, as studied by Cortés and Castro [34]. The molecules were verified by mass spectrometry (Fig. S2 in the supplementary file).

3.2. The viscosity of CMC and its blends with nitrophenylmaleimide isomers

Table S1 in the supplementary file shows the average densities of the prepared blends of CMC with o, m, and p-nitro-phenylmaleimide. The results indicate that the densities of the CMC blends with nitrophenylmaleimide varied from 0.27% (o-nitro-phenylmaleimide) to 0.82% (p-nitrophenylmaleimide). The low variation in densities is attributed to the incorporation of nitrophenyl maleimide molecules into the CMC matrix, which affects the molecular volume, as reported in theoretical studies [32]. Furthermore, the position of the nitro group in the aromatic ring of the *n*-phenylmaleimides enables us to predict a trend in the intermolecular attractions that these two species can generate. This type of supramolecular interaction is currently being studied by computational methods.

Tables S2, S3, and S4 in the supplementary file present the average values of kinematic viscosity for variation in concentration, temperature, and stirring rate of CMC and blends with o, m, and p-nitrophenylmaleimide. The data trends show an increase in the viscosity of the blends when the isomers of nitrophenylmaleimides are added compared to CMC. The variation observed corresponds to an increase in intermolecular forces through hydrogen bonding between CMC and nitrophenylmaleimide isomers, resulting in more viscous blends. The isomers impart greater resistance to flow in the blends, thereby requiring higher shear stress to displace them.

Then, A multifactorial ANOVA was conducted to select the best blends of CMC with nitrophenylmaleimide derivatives, using viscosity as the response variable and categorical variables or factors such as agitation rate, temperature, and concentration. The null hypothesis (H_0) proposed that sample variances between factors are equal, while the alternative hypothesis (H_1) proposed that the sample variances between the factors are different [35]. A detailed statistical analysis of each blend is presented below.

In the supplementary file, Fig. S3 shows that stirring rate is not a variable that affects viscosity (p-value >0.05). However, temperature and concentration (p-value <0.05) were variables that affect the viscosity of CMC blends with (O) and without (B) o-nitrophenylmaleimide. A high difference between B and O is observed for temperature, which may be related to the intermolecular attractions that *ortho*-nitrophenylmaleimide generates with CMC to increase viscosity. Fig. S4 shows that the value of the stirring rate is not significant and that concentrations of 1, 10, and 20 mg are similar in viscosity results, but differ from 5, 50, and 100 mg, with 100 mg having the best effect on viscosity. On other hand, the different temperatures are significant in relation to viscosity, so the preparation temperature is considered an important factor. The better temperature for preparation is 40 °C.

Table S5 in the Supplementary file summarizes the results of the analysis of variance for viscosity in CMC blends with and without o-nitrophenylmaleimide, with and without concentration, temperature, and agitation interactions. The F-statistic and p-value indicate that the alternative hypothesis is accepted [36]. The F-statistic and p-value also show that temperature, concentration, and the interaction between them are significant factors in the variation of viscosity. Therefore, these variables are essential for the preparation and comparison of results.

The selection of the better blend conditions was carried out by considering the significant variables from the statistical analysis, such as temperature and concentration. Fig. S5 in the supplementary file summarizes the viscosity difference between CMC mixtures without (B) and with (O) o-nitrophenylmaleimide. It can be observed that the greatest viscosity difference (710 cSt or 781 cP) occurs when the conditions are at 20 mg concentration, 30 °C temperature, and 417 rpm stirring rate. This indicates that the chosen conditions favor non-covalent crosslinking between o-nitrophenylmaleimide and CMC polymeric chains.

In Fig. S6 in the supplementary file, the evidence shows that agitation is not a significant variable for the preparation of the blends (p-value >0.05). Temperature and concentration (p-value <0.05) affect the viscosity of CMC with (M) and without (B) m-nitro-phenylmaleimide. Fig. S7 in the supplementary file indicates that there are significant differences between concentrations and temperatures for CMC blends with (M) or without (B) m-nitrophenylmaleimide (M). Both variables do not report any range of similarity between the compared values.

Table S6, like S5 in the supplementary file, presents a summary of the analysis of each factor and their interactions for CMC blends with or without m-nitrophenylmaleimide. The P-value and F-statistic data confirm that variations in viscosity are significant for temperature and concentration, as well as their interaction.

To select the better blend, the factor interaction plot was used (Fig. S8 the in supplementary file), which shows that the system with the greatest difference (379.1 cSt or 414 cP) from the CMC solution is the one with 50 mg, 20 °C, and 417 r. p. m. The selected blend has higher non-covalent crosslinking for the formation of the m-nitrophenylmaleimide supramolecular polymer due to the mass used.

The last compound to be evaluated was p-nitrophenylmaleimide. Like its isomeric counterparts, blends of CMC were prepared with and without p-nitrophenylmaleimide. Fig. S9 in the supplementary file shows that the significant factors for the blends are temperature and concentration (p-value <0.05). Stirring does not affect the preparation (p-value >0.05). Fig. S10 of the supplementary file reflects the heterogeneity of concentrations (in this case more noticeable than its isomers) and temperatures between the blends of CMC (B) and CMC with p-nitrophenylmaleimide (P).

The p-value and F-statistic data in Table S7 of the supplementary file confirm that temperature and concentration, as well as their

interaction, are significant factors for the variation in viscosity in CMC blends with and without p-nitrophenylmaleimide.

Fig. S11 in the supplementary file compare the effects of concentration and temperature on the viscosity of CMC system with and without p-nitrophenylmaleimide. It is evident that the combination of 10 mg, 20 °C, and 417 r. p. m results in the largest variation of 516.8 cSt or 562.3 cP. This blend contains the smallest amount of nitrophenylmaleimide used for the formation of the supramolecular polymer.

3.3. Rheological curves of CMC and blends of CMC with nitrophenylmaleimide isomers

The rheological properties of CMC and its blends with nitrophenylmaleimide derivatives are illustrated in Fig. 1. The shape of the CMC solution plot is consistent with those reported by other authors, showing viscosity as a function of shear rate [37,38]. The plot shows three regions for the CMC solution (Fig. 1a). In region I, a significant decrease from 450 to 20 Pa s is observed due to the typical shear thinning behavior of pseudoplastic fluids such as CMC. This phenomenon is attributed to a higher orientation of the polymer chains in the direction of flow [37]. Next, a slower descent to a Newtonian zone with a near-constant viscosity (μ_0) of 10 Pa s at a velocity limit of 0.25 s^{-1} follows. After exceeding this velocity, region II of Fig. 1a is displayed, showing a gradual decrease generated by the breaking of the intermolecular hydrogen bonding attractions between the CMCs. This process is induced by unthreading the chains to finally align completely with the flow [39,40], resulting in a decrease in resistance to flow (pseudoplastic zone) [41]. Finally, region III is exhibited, at high velocities above 2700 s^{-1}, showing a constant value (Newtonian fluid).

Blends with o, m, and p-nitrophenylmaleimide (Fig. 1b–d) exhibit a similar trend to the CMC solution, with pseudoplastic fluids, but differ in viscosity and shear rate. For o-nitrophenylmaleimide (Fig. 1b), a decrease from 900 to 20 Pa s is evident in the region I, with a μ_0 of 9 Pa s and a limit velocity of 0.65 s^{-1}. Region III presents a value of 0.1 Pa s at 4200 s^{-1}. For m-nitrophenylmaleimide (Fig. 1c), a region I presents a decrease from 950 to 20 Pa s, with a μ_0 of 9 Pa s at a limiting velocity of 0.63 s^{-1}. Region III exhibits a value of 0.11 Pa s at 4900 s^{-1}. For p-nitrophenylmaleimide (Fig. 1d), a region I exhibit a decline from 100 to 12 Pa s, with a μ_0 of 10 Pa s at a limit velocity of 0.4 s^{-1}. Region III reveals a value of 0.11 Pa s at 4100 s^{-1}.

The differences in the supramolecular polymer blends of the maleimide systems, compared to the CMC solution, indicate that intermolecular attractions produced by the nitrophenylmaleimide cause the initial solutions to be more crosslinked. Non-covalent interaction favors a high initial viscosity value for the *ortho* and *meta* isomers, unlike the *para* isomer. Similarly, the boundaries of the pseudoplastic regions help to predict that more external force is needed to overcome the intermolecular attractions that cause the resistance to the flow of the blends. This demonstrates that N-phenylmaleimide isomers help to increase the resistance to flow of the
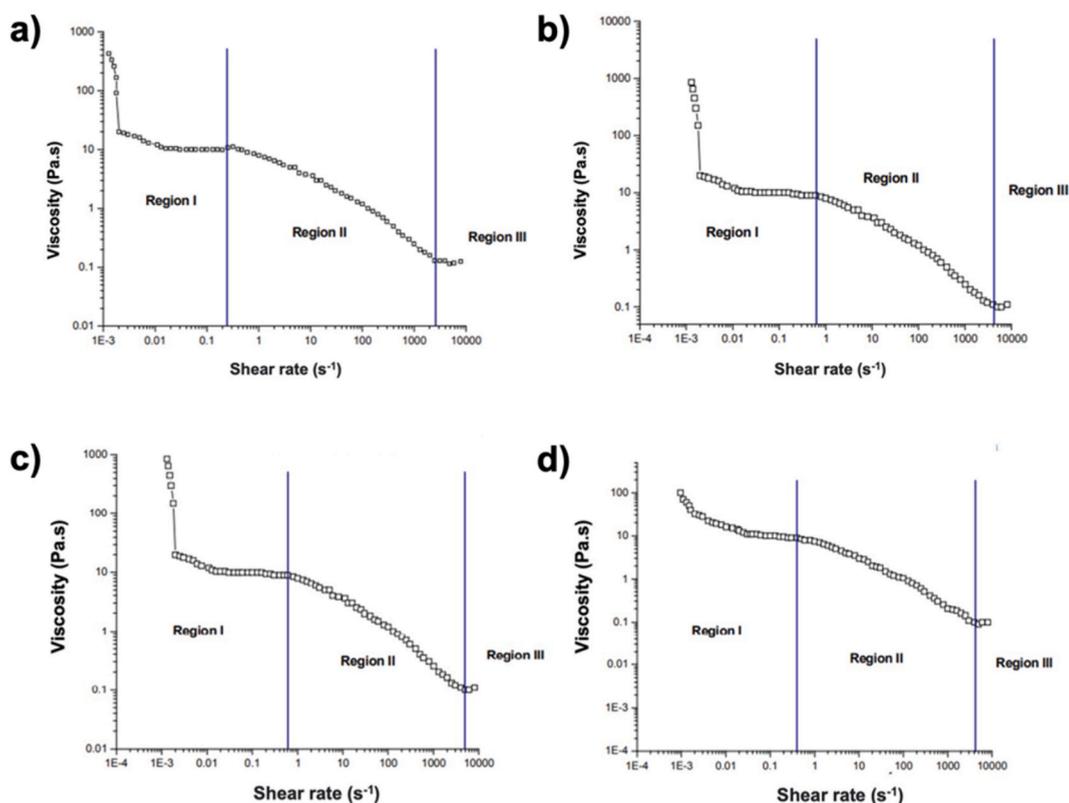
Fig. 1. Variation of viscosity vs shear stress for CMC blends with **(a)** o-nitrophenylmaleimide **(b)**, m-nitrophenylmaleimide **(c)**, and p-nitro-phenylmaleimide **(d)**.

solution.

Fig. 2 shows the pseudoplastic profile of the solutions, with differences in the viscosity values explained above. As these systems follow a non-Newtonian fluid type, the Ostwald-de Waele power law model [39], which is suitable for pseudoplastic fluids, was applied. Fig. S12 in the supplementary file illustrates the absence of a yield stress value, indicating that the solution does not exhibit a yield stress. This characteristic applies to Bingham plastics.

Table 2 shows the data obtained from Fig. S12 in the supplementary file, which have been linearized by a power law. The coefficient of determination values obtained is nearly 1.0, indicating that the data conforms to the Ostwald-de Waele model. The values of n are lesser than 1, demonstrating that the fluids behave as pseudoplastic, as expected in CMC solutions [37,39]. Although the type of fluid does not change significantly (variations of about 2%) when solutions with nitrophenylmaleimide derivatives are mixed, the flow behavior index value decreases from 65 to 62%, resembling that of a Newtonian fluid. The consistency index value is higher than that of CMC, especially for blends with m-nitrophenylmaleimide, suggesting a more significant effect of this isomer. These values indicate that the blends increase the viscosity of the solutions due to intermolecular attractions, which generate greater resistance to flow.

Using the Huggins method, the intrinsic viscosity value (134.78 mL/g) was determined from the CMC solution. Then, the Mark-Houwink-Sakurada equation was applied to this value, resulting in a K value of 2.10×10^{-3} mL/g and α values of 0.83 (constants for the polymer-solvent-temperature system) [10,42]. Table 3 presents the values of intrinsic viscosities (η) and approximate molecular masses in viscosity (Mv) for the CMC solutions with and without phenylmaleimide. The results indicate an increase in molecular mass distribution and intrinsic viscosity due to the entry of nitrophenylmaleimide molecules into the polymeric network, with m-nitrophenylmaleimide showing higher values and p-nitrophenylmaleimide demonstrating lower values.

3.4. Physical and chemical properties of CMC films and blends CMC with nitrophenylmaleimide isomers

After forming films of the supramolecular polymer blends, their resistance to chemical agents was evaluated (Table S8 in the supplementary file), and the maximum concentration that they could withstand in complete immersion was observed. They showed tolerance to a 40% solution of sulfuric acid, 65% nitric acid, 37% hydrochloric acid, and 100% acetic acid. For sodium hydroxide at 22 g/100 mL and potassium hydroxide at 24 g/100 mL, no dissolution or destruction of the sample was observed. However, only hydrogen peroxide dissolves them, except for the CMC film with m-nitrophenylmaleimide, which was unaffected at 1%, demonstrating the molecular stability of CMC and its blends with maleimide.

Table 4 shows the evaluation of some physicochemical properties of CMC films with and without blends of nitrophenylmalemide isomers. The incorporation of nitrophenylmaleimide molecules into the CMC matrix leads to an increase in the percentage of humidity in the films, which was demonstrated in the degree of substitution (DS) of CMC (1.03), where 21, 46, and 15 units are more substituted by *ortho-*, *meta-,* and *para*-nitrophenylmalemide, respectively, per 100 monomeric units. The type of substitutions between these systems is intermolecular. Moreover, the films obtained with the three isomers do not dissolve in petroleum ether (polarity index, i.p., 0.0), hexane (i.p. 0.0), diethyl ether (i.p. 2.8), isopropyl alcohol (i.p. 3.9), ethyl acetate (i.p. 4.4), acetone (i.p. 5.1), methanol (i.p. 5.1), ethanol (i.p. 5.2) and acetonitrile (i.p. 5.8).

The insolubility of the films was attributed to the polarity of the systems and the strong interactions that can occur within the systems.

Fig. S13 in the supplementary file, shows the infrared spectra of CMC and blends of CMC with nitrophenylmaleimide isomers, and the wavenumbers of highest intense bands are summarized in Table 5. The observed wavenumbers of CMC are in agreement with reported literature [43]. The films showed a broad band between 3200 and 3400 cm^{-1}, which corresponds to the tension vibration of OH in CMC. This band presents a greater frequency shift with nitrophenylmaleimide isomers compared to CMC. For the *meta* and *para* isomers, it increases by 66 cm^{-1}, and for *ortho* isomers, it increases by 61 cm^{-1}, which is an approximate increase of 2%. The OH band shift is due to the intermolecular attractions generated through hydrogen bonding between H of OH in CMC with C=O in the
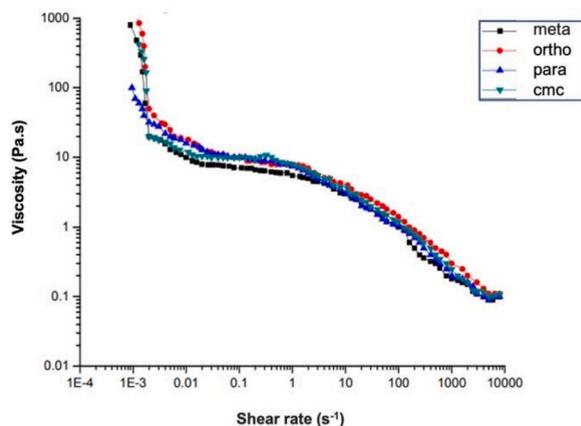
Fig. 2. Comparison of viscosity and shear stress for CMC solutions and blends with nitrophenylmaleimides.

Table 2
Coefficients k and n of the Ostwald-de Waele equation for CMC solutions and CMC blends with nitrophenylmaleimide isomers.

Solution	n	k	r^2
CMC	0.65248 ± 0.01396	4.31042 Pa s$^{0.35}$	0.97066
Blend CMC with o- nitrophenylmaleimide	0.64834 ± 0.01200	5.18872 Pa s$^{0.35}$	0.97887
Blend CMC with m- nitrophenylmaleimide	0.65158 ± 0.01303	5.42013 Pa s$^{0.35}$	0.97429
Blend CMC with p- nitrophenylmaleimide	0.62421 ± 0.01114	4.39026 Pa s$^{0.38}$	0.97909

Table 3
Viscous molecular weight and intrinsic viscosity of CMC solutions with and without nitrophenylmaleimides.

Solution	Mv (g/mol)	η (mL/g)
CMC	619520	134.78
Blend CMC with o-nitrophenylmaleimide	695381	148.342
Blend CMC with m-nitrophenylmaleimide	733058	154.983
Blend CMC with p-nitrophenylmaleimide	653087	140.814

Table 4
Humidity values and degree of substitution for CMC and blends with nitrophenylmaleimides.

Sample	Humidity (Percentage)	Degree of substitution (D.S)
CMC	3.01	1.03
Blend CMC with o-nitrophenylmaleimide	8.14	1.21
Blend CMC with m-nitrophenylmaleimide	23.89	1.46
Blend CMC with p-nitrophenylmaleimide	20.85	1.06

maleimide ring and O of OH on CMC with H in the maleimide ring (as shown in the computational study below). This finding corroborates the affinity between the compounds and the entry into their molecular network. The other bands, such as the shoulder around 2920 cm^{-1}, due to stretching of C–H; 1585 cm^{-1} due to stretching of carboxyl group; and 1412 cm^{-1} of bending of C–H corresponding to CMC, do not show significant changes between the formed films. This agrees with the proposed interaction between the systems that affects the vibration of OH and not the other bands. The other peaks found in the spectrum are related to bonding (C–O–C and C–O), typical of CMC. The typical vibration bands of nitrophenylmaleimide isomers overlap with CMC, due to the low amount of these compounds used relative to the mass of CMC for film formation.

Supplementary file Table S9 summarizes the results of TGA analysis of CMC films and CMC blends with nitrophenylmaleimide isomers. The table shows the decomposition temperatures, the residual jumps, and the final mass at 780 °C. The first loss is due to the evaporation of free water molecules or volatile molecules found in the films. Additionally, the blends increase this first temperature by approximately 70 °C (*ortho* isomer), and 100 °C (*meta* and *para* isomers). This increase is consistent with the shift of the OH band in the IR and the computational study (below), which predicts how hydrogen bonding between molecules increases and may affect free water due to possible interactions with both molecules. The second point of loss is very close for all the films (approximately 295 to 320). It has been reported as chain transitions in the CMC, degradation of the main cellulose chain, and decarboxylation of the carboxyl group, eliminating CO_2 [44,45]. At the second inflection, the greatest mass loss in relation to the first point shows the following trend: CMC (48%) > *ortho*-mix (44%) > *para*-mix (25%) > *meta*-mix (23%). These values demonstrate that the interaction with the nitrophenylmaleimides affects the CMC chain transition and decarboxylation due to new intermolecular attractions of hydrogen bonding formed in the systems.

It is important to highlight that the films with *para* and *meta* nitrophenylmaleimides showed one (416 °C, −20%, with respect to the second point) and two additional decomposition points (408 °C, −17.1%, concerning the second point and 548 °C, −9.3% with respect to the third point), respectively. This demonstrates how the position of the nitro group in the structure can affect interactions due to the low angle of torsion between the maleimide and benzene rings for *meta* and *para* isomers [34], which is reflected in additional points of mass loss.

The type of degradation mechanism and the structural explanation of the inflections are the subject of current research in the group.

Table 5
I.R. bands for CMC and blends with nitrophenylmaleimides.

Sample	B and (cm^{-1})			
	O–H Strain	C–H Strain	C=O Strain	C–H Flexion
CMC	3276	2922	1585	1412
Blend CMC with o-nitrophenylmaleimide	3337	2922	1586	1412
Blend CMC with m-nitrophenylmaleimide	3344	2920	1586	1412
Blend CMC with p-nitrophenylmaleimide	3344	2923	1585	1412

The results obtained, although not reported, have the same trend as those obtained in other similar studies [46,47]. This demonstrates that blends with nitrophenylmaleimide isomers increase the thermal stability of the supramolecular polymers obtained.

3.5. Biodegradability of CMC films and CMC blends with nitrophenylmaleimide isomers

Bacteria (*Bacillus, Pseudomonas, Staphylococcus,* and *Legionella*) as well as fungi (*Penicillium, Aspergillus,* and *Alternaria*) [48] are among the most common environmental microorganisms that can grow on CMC substrate enriched with o-nitrophenylmaleimide. This was demonstrated by the presence of 5 colonies, two of which had a high number of spores, as shown in Fig. S14c in the Supplementary file. In contrast, blends with m-nitrophenylmaleimide (Figure S14 d) showed two colonies, while p-nitrophenylmaleimide (Figure S14 e) exhibited only small growth sites. The CMC substrate alone did not show a considerable increase in microbial growth (Figure S14 b). Comparison with the blank solution, which did not support any growth (Figure S14 a), suggests that the blends can serve as a nutrient for airborne organisms. The blend of *ortho* isomers showed the highest degree of biodegradability in the environment.

3.6. Computational analysis of the CMC monomer with o, m, and p-nitrophenylmaleimides

To demonstrate the interaction sites of the molecules and observe the most favorable positions, the NBO populations, molecular orbitals, and electrostatic potential were analyzed using the B3LYP/6-311 + G (d,p) level of theory. Fig. S15 in the supplementary file shows the charge analysis for the nitrophenylmaleimide isomers and the CMC (6-carboxymethylglucopyranose) monomer with a degree of substitution of 1.0.

For the former, it is shown that the highest charge deficiency is found in the imide ring, specifically in the carbonyl carbons and the hydrogens of the double bond. On the other hand, the regions with the highest charge are located in the nitro group's oxygens and the carbonyl oxygen. Regarding the CMC monomer, the most electrophilic sites are the hydrogens attached to the hydroxyl group's oxygens, and the most nucleophilic sites are the OH oxygens of the pyranose ring and the carboxylic group's carbonyl.

In supplementary file, Fig. S16, the boundary molecular orbitals reveal that the nitrophenylmaleimide isomers can attack any part of the molecule (HOMO) but can only interact with another molecule through the imide ring (LUMO), regardless of the position of the nitro group. The 6-carboxymethylglucopyranose can attack through any part of the molecule (HOMO), but it can only interact through the carboxymethyl group (LUMO). Similarly, in Fig. S17 in the supplementary file, the electrostatic potential map confirms the NBO population analysis for the studied structures. The hydrogens of the imide ring are the most deficient in charge (blue chroma) in nitrophenylmaleimide, and the OH oxygens (red chroma) are the most charged in the CMC 1.0 monomers. These results agree with those of Cortés and Castro [34]. Therefore, the intermolecular interaction occurs through a hydrogen bond with the C–H of the imide ring (acidic hydrogens) with the OH oxygens of the pyranose ring, which is induced by the spatial arrangement of the compounds.

Table 6 shows the interaction energy values at the theoretical level B3LYP/6-311 + G (d,p). In all cases, there is an interaction between species, with the interactions being more favorable for the *meta > para » ortho* isomers. The values for the hydrogen bonds obtained can be classified as moderate (*meta* and *para*) and weak (*ortho*), according to Jeffrey's scale [49]. Therefore, the blends of the study systems generate new supramolecular polymeric materials through hydrogen bonding (as shown in Fig. 3a–c), between the maleimide ring and the OH groups of the pyranose ring.

4. Conclusion

The films formed by blending CMC with small amounts of nitrophenylmaleimide isomers created a new type of water-compatible supramolecular polymer. This new supramolecular polymer was easily obtained and exhibited resistance to different acids and strong bases at various concentrations but was not resistant to oxidant solutions such as peroxide. In addition, it did not present solubility in different polar and nonpolar solvents, making it a very stable material with chemical resistance. In thermal analysis, an increase from 70 to 100 °C was observed, in the first point of degradation, and a decrease in the loss of mass in the second point was noted, indicating that the mixtures of nitrophenylmaleimide isomers exhibit thermal stability in comparison with CMC.

Likewise, the films demonstrated biodegradability with respect to the growth of bacteria and fungi from the environment, indicating that the blends with nitrophenylmaleimide isomers do not affect the degradation of CMC. The effect on the change of properties is evidenced by computational calculations and the IR band shift of the OH strain, which shows moderate intermolecular hydrogen bonding interactions between the OH group of CMC and the maleimide ring of the nitrophenylmaleimide. It is important to highlight that the mixture with the best properties is the one obtained with *meta*-nitrophenylmaleimide, possibly due to the low torsion angle and new interactions with the nitro group that it can form. On the other hand, in solution, the mixtures with the nitrophenylmaleimide isomers maintain the same pseudoplastic profile as CMC, but an increase in viscosity, consistency index, and the viscous molecular weight is observed, which is affected by temperature and the concentration of the maleimide isomers. The effect in solution is caused

Table 6
Energy values of the interaction of the nitrophenylmaleimide isomers with 6-carboxymethylglucopyranose.

Interaction	Electronic energy difference (kJ/mol)	Energy difference of ZPE (kJ/mol)	Energy difference with enthalpy (kJ/mol)
o-NFM -Glucopyranose	−6.547997	−5.3323905	−1.3258775
m-NFM - Glucopyranose	−23.907803	−20.116581	−17.512085
p-NFM - Glucopyranose	−23.3013125	−19.3998195	−16.8530845
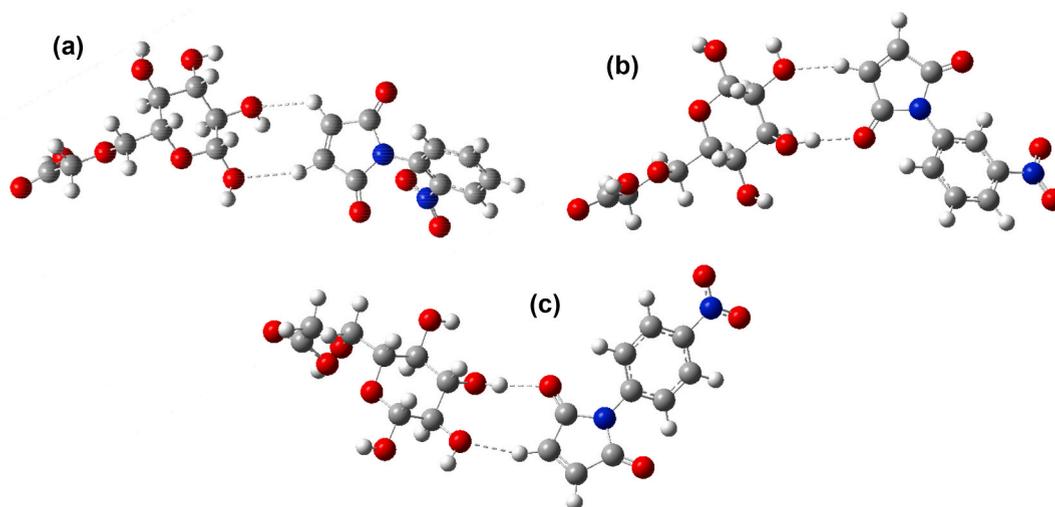
Fig. 3. Interactions between 6-carboxymethyl glucopyranose and *ortho* **(a)**, *meta* **(b)**, *para* **(c)** – nitrophenylmaleimide.

by intermolecular attractions that generate crosslinking between the CMC chains and the nitrophenylmaleimide system that enters the polymer network.

This new material developed by supramolecular polymers compatible with water continues to be a research topic in our group. Some of the ongoing studies involve mechanical properties, permeability tests, and application tests of plastics. Additionally in another research, the group looked for other degrees of substitution, the viscosity of CMC, and different maleimide compounds.

Author contribution statement

Maribel Montoya García, Hector Fabio Cortés: Performed the experiments; Analyzed and interpreted the data; Wrote the paper.
Pedro Nel Martínez: Conceived and designed the experiments.
Hoover Albeiro Valencia: Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data.

Data availability statement

Data included in article/supp. material/referenced in article.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.heliyon.2023.e16108.

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