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Mechanical Properties of Films Based on Blends of Starch-Coumarin Complex and Other Polymers Reinforced with Microcrystalline Cellulose

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Abstract: This research aimed to develop scented plastic materials based on cassava starch, coumarin, microcrystalline cellulose (MCC), and other polymers such as xanthan gum, karaya gum, gum arabic, poly(vinyl alcohol) (PVA), and poly(lactic acid). The films were made by solvent casting, focusing on using starch-coumarin (SC) complex as the base material. The SC complex was prepared by mixing starch and coumarin using water as a dispersion medium. The amount of coumarin was 5% (w/w), based on total weight of starch and coumarin. Several variations were used, such as types of plasticizers, stirring and sonication times to disperse MCC, types of added polymers, and the mass ratio between the added polymer and the starch-coumarin complex. The results showed that the films made of plasticizers 20% (w/w), consisting of poly(ethylene glycol) (PEG200) and glycerol with a mass ratio of 1:1, prepared by implementing 30 minutes stirring and 50 minutes sonication times of dispersing MCC of 4% (w/w), with the mass ratio of added polymer:complex of 1:2, resulted in the most optimum mechanical properties. Using this procedure and composition, added polymers of xanthan gum, karaya gum, and PVA produced homogenous films with tensile strength of 1.5-6.7 MPa, elongation of 9.5-189.7%, and Young's modulus of 2.3-7.9 MPa. Amongst these added polymers, PVA showed the best compatibility in the blend, resulting in a film with a tensile strength of 3.9 MPa, an elongation of 189.7%, and Young's modulus of 2.3.

Keywords: blend, coumarin, microcrystalline cellulose, plastic, starch

***Abstrak*:** *Penelitian ini mengarah untuk pengembangan material komposit plastik beraroma berbasis pati dari singkong dengan selulosa mikrokristalin (microcrystalline cellulose, MCC) dan molekul beraroma kumarin. Pati belum mampu sepenuhnya menggantikan bahan plastik non biodegradable karena sifat mekaniknya yang rendah. Kelemahan tersebut dapat diatasi dengan memodifikasi melalui penambahan polimer kompatibilitas tinggi yaitu selulosa. Selain itu, dilakukan juga peningkatan kristalinitas dan memperbaiki struktur pati melalui pembentukan kompleks inklusi antara pati dengan molekul tamu yaitu kumarin. Penggunaan molekul kumarin dalam kompleks inklusi merupakan metode enkapsulasi yang menawarkan fungsi tambahan yaitu menghasilkan plastik beraroma. Polimer lain yang digunakan dalam komposit kompleks pati− kumarin dan selulosa mikrokristalin yaitu karaya gum, xantan gum, dan poli(vinil alkohol) (PVA). Optimasi fabrikasi film diharapkan menghasilkan bioplastik yang bersifat unggul minimal sesuai dengan standar kemasan mudah terurai (BSN, 2014) dan plastik konvensioanal (SNI). Optimasi yang dilakukan yaitu variasi jenis pemplastis, waktu pengadukan dan sonikasi, jenis polimer tambahan, dan perbandingan polimer tambahan dengan kompleks. Teknik pembuatan film menggunakan proses basah yaitu pencetakan larutan (casting solution). Analisis hasil optimasi berdasarkan sifat mekanik antara lain kuat tarik, regangan dan modulus Young diperoleh kesimpulan pembuatan film komposit menggunakan pemplastis poli(etilen glikol) (PEG) 200 dan gliserol pada perbandingan massa 1:1 dengan kadar 20% (b/b), durasi pengadukan selulosa mikrokristalin (MCC) selama 30 menit dan sonikasi 50 menit. Komposisi film komposit pati–kumarin dengan MCC beserta penambahan polimer pendukung yang digunakan yaitu xanthan gum, karaya gum dan poli(vinil alkohol), pada perbandingan polimer pendukung dan kompleks sebesar 1:2.*

Kata kunci: *film komposit, kumarin, pati, selulosa mikrokristalin.*

INTRODUCTION

The limitations of starch for industrial applications are due to its low mechanical properties, low resistance to water, and poor water vapor barrier (Rodriguez-Garcia *et al*. 2011). These limitations can be overcome by modifying starch physically (heat, gelatinization, high pressure, radiation, sonication) and chemically (cross-linking, substitution, acid

hydrolysis, oxidation/bleaching, and enzymatic). Physical modification can be conducted by blending starch with other compatible polymers such as cellulose, polyvinyl alcohol, and gum polymers. The process involves heat, high pressure, sonication, and gelatinization.

Another noncovalent modification to increase the crystallinity of starch can be done via complexation by adding coumarin as a guest molecule to form complexes with starch (Gao *et al.* 2020). The use of coumarin can also result in scented plastics. However, including aromatic compounds by another molecule requires proper modification methods, significantly reducing the aromatic compounds' volatility during processing and storage. The complexation method offers several advantages, such as minimizing and delaying the evaporation. This is expected to enhance consumer perception and acceptance of scented plastic products. In addition, polymers combined with coumarin can interact through cross-linking to improve mechanical properties. This was shown by the attachment of coumarin to thermoplastic silicone polymers with π build up from head to tail of coumarin on the main chain of silicone, forming a complex with a ratio of 1:1 (Fawcett *et al.* 2014). In this case, as the research on a combination of starch and coumarin is still limited, it opens the opportunity for broader research, especially on their bioplastic applications.

Coumarin is a low molecular weight organic compound that produces a sweet vanilla-like aroma (Huda *et al.* 2022). The benzo-α-pyrone group on coumarin is hydrophobic with a relatively small chemical structure that makes it easy to occupy the cavity of the amylose helix. This makes coumarin suitable to be applied as a guest molecule in inclusion complexes. In addition, the inclusion complex between the host and guest molecules produces a more crystalline compound that minimizes the interaction of amylose with water. This method can improve starch's structure and properties, reducing water absorption, retrogradation, and enzymatic digestibility (Shi *et al*. 2021; Kong *et al*. 2014).

Related to application, plastic films are expected to have high flexibility, optical transparency, thermal stability, mechanical strength, biodegradability, and good gas barrier properties (Bedane *et al*., 2015). The films are also expected to meet the BSN standards for biodegradable packaging (minimum tensile strength of 14.7 MPa) and the SNI for conventional plastics (tensile strength of 24–302 MPa and strain of 21–220%). Additional modifications are made by adding hydrophilic biopolymers expected to increase biodegradability, improve mechanical properties, and produce compatible and homogeneous blends (Chen *et al*. 2020[a]; Nazrin *et al*. 2020). In this research, the additional polymers included poly(vinyl alcohol) (PVA) (Cazón *et al*. 2017), xanthan gum, gum arabic, and karaya gum. In addition, to increase the mechanical properties of the films, a strong supporting compatible polymer (Gunawardene *et al*. 2021), such as cellulose (Chen *et al*. 2020[a]; Nazrin *et al*. 2020) was used.

The starch dissolution process requires water with a concentration of more than 90% (w/w) to form a homogeneous solution. According to Gabriel *et al*., (2021), small starch sizes require high gelatinization temperatures due to stronger intermolecular bonds that require higher energy. Therefore, the complexation between starch and coumarin in this research was conducted using water as a medium at 80−85 ºC in a closed vessel. The high temperature and water vapor pressure were expected to ease the complexation between amylose in starch and coumarin (Shi *et al*. 2021). In this case, heating will disrupt the intermolecular interactions in starch to help water molecules diffuse and interact with starch hydroxyl groups. This starch gelatinization occurred at 65–90 ºC (Cazón *et al*. 2017). Starch that had been heated at high temperature and pressure in water was in the form of random coils. Under these conditions, coumarin then interacted with the amylose in starch to form inclusion complexes, which induced the formation of a crystalline structure called V-amylose.

The solvent-casting method used to make plastic films in this research included a wet process, which began with the dissolution of the polymer under the influence of temperature, then manually pouring the mixture into the mold and drying (Singh *et al*. 2022). Using microcrystalline cellulose as a matrix filler requires good handling as it can also reduce tensile strength in polymer blends with poor dispersion (Nazrin *et al*. 2020). The optimum conditions were studied to produce homogenous mixtures, which lead to homogenous films.

MATERIALS AND METHODS

Materials

The materials used were isolated cassava starch (amylose content of 19.7% (w/w), moisture content of 8.0% (w/w)), coumarin (Sigma Aldrich, C4261), microcrystalline cellulose (MCC, $[C_6H_{10}O_5]n$, Avicel PH 101, Merck), poly(ethylene glycol) (PEG200) (Sigma Aldrich, P3015), glycerol ($C_3H_8O_3$, Merck, 1.04094), KBr (Merck, 1.04907), xanthan gum from Xanthomonas campestris (Sigma Aldrich, 43708), karaya gum (Sigma Aldrich, G0503), gum arabic from acacia tree (Sigma Aldrich, G9752) poly(vinyl alcohol) (PVA, MM 72000 g/mol, Merck, 8.21038), tetrahydrofuran (C_4H_8O, THF, Merck, 1.09731), and poly(lactic acid) (PLA, Aldrich, GF45989881).

Optimization of Films' Composition

Types of Plasticizers

Microcrystalline cellulose (MCC) 4% (w/w) was dissolved in aqua DM in a closed glass bottle at 80−85 ºC and stirred for 30 minutes. Starch and aqua DM were added to the mixture and stirred for 20 minutes until the starch was gelatinized, resulting in a homogeneous mixture. This mixture of MCC and

starch was then sonicated for 50 minutes with a frequency of 40 kHz at a temperature of 75−80ºC. Coumarin was added at 5% (w/w total complex) and stirred constantly for 2 hours. The mixture was subsequently sonicated for 10 minutes at 75−80 ºC. Glycerol plasticizers of 20% and 30% concentrations (w/w) and poly(ethylene glycol) (PEG200)−glycerol, with 1:1 and 1:9 mass ratios, were added at 85ºC for 20 minutes. The resulting mixture was poured into a 6.5 x 6.5 cm silicone mold and dried in a ventilation oven at 45 ºC for 24 hours (Chen *et al*. 2019).

Stirring and Sonication Times

Microcrystalline cellulose (MCC) 4% (w/w) was dissolved in aqua DM in a closed glass bottle at 80−85 ºC and stirred with a time variation of 30 minutes (Talebi *et al*. 2022) and 60 minutes (Othman *et al*. 2019). Starch and aqua DM were added to the mixture and stirred for 20 minutes until the starch was gelatinized and the mixture became homogeneous. This mixture of MCC and starch was then sonicated with a variation of 10 minutes (Othman *et al*. 2019) and 50 minutes (Maulida *et al*. 2016) with a frequency of 40 kHz at a temperature of 75−80 ºC. Coumarin was added at 5% (w/w total complex) and stirred constantly for 2 hours. The mixture was then sonicated for 10 minutes at 75−80 ºC. Next, PEG200:glycerol (mass ratio of 1:1) with a concentration of 20% (w/w) was added at 85ºC and stirred for 20 minutes (Chen *et al*. 2019). The resulting mixture was poured into a 6.5 x 6.5 cm silicone mold and dried in a ventilation oven at 45 ºC for 24 hours.

Added Polymers

Microcrystalline cellulose (MCC) 4% (w/w) was dissolved in aqua DM in a closed glass bottle at 80−85 ºC and stirred for 30 minutes. Starch and aqua DM were added to the mixture and stirred for 20 minutes to gelatinize the starch, resulting in a homogeneous mixture. This mixture of MCC and starch was then sonicated for 50 minutes with a frequency of 40 kHz at a temperature of 75−80 ºC. Coumarin was added at 5% (w/w total complex) and stirred constantly for 2 hours. The mixture was then sonicated for 10 minutes at 75−80 ºC. PEG200:glycerol (mass ratio of 1:1) with a concentration of 20% (w/w) was added at 85 ºC and stirred for 20 minutes (Chen *et al*. 2019). Added polymers such as xanthan gum, karaya gum, and gum arabic, as well as poly(vinyl alcohol) (PVA) and poly(lactic acid) (PLA), each was added with a mass ratio of 1:1 for the starch–coumarin complex and another polymer. The mixture was poured into a 6.5 x 6.5 cm silicone mold and dried in a ventilation oven at 45 ºC for 24 hours.

Mass Ratio of Starch–Coumarin Complex and Another Added Polymer

Microcrystalline cellulose (MCC) 4% (w/w) was dissolved with aqua DM in a closed glass bottle at 80–85ºC and stirred for 30 minutes. Starch and aqua DM were added to the mixture and stirred for 20 minutes until the starch was gelatinized, resulting in a homogeneous mixture. The mixture was then sonicated for 50 minutes with a frequency of 40 kHz at a temperature of 75−80 ºC. Coumarin was added at 5% (w/w total) and stirred constantly for 2 hours. The resulting complex was sonicated for 10 minutes at 75−80ºC. PEG200:glycerol with a mass ratio of 1:1 with a concentration of 20% (w/w) was added at 85ºC and stirred for 20 minutes (Chen *et al*. 2019). Another polymer, such as xanthan gum, karaya gum, or PVA, was added to the mixture. The mass ratio between the starch–coumarin complex and another polymer was varied as 1:1, 1:2, and 2:1. The mixture was poured into a 6.5 x 6.5 cm silicone mold and dried in a ventilation oven at 45ºC for 24 hours.

2. Characterizations

Mechanical Test

The thickness of the film was measured using a digital micrometer at the part that would be exposed to tension (center). The mechanical strength of the film was determined using a Tensile Strength Tester (Instron H1324). The film was cut into a rectangular form with a 10 mm × 50 mm dimension and placed on the apparatus with a clamp distance of 2 cm. The initial grip separation and film stretching speed were set to 80 mm/min with a load cell of 50 g−50 kg. Each data was obtained from the measurements of 5 films.

Fourier Transform Infrared (FTIR) Spectroscopy

FTIR analysis was conducted to investigate the changes in the vibration of functional groups that might occur due to complexation and plasticization. The spectra were analyzed with an ATR and KBR FTIR Spectrophotometer. The samples were measured at wave number 515–4000 cm^{-1} with a resolution of 4 cm^{-1} and 32 scans.

RESULTS AND DISCUSSION

1. Effects of Types of Plasticizers on the Properties of the Films

Optimization of plasticizers in the films was carried out by varying the amount with 20% and 30% (w/w) concentration and using two different mass ratios of poly(ethylene glycol) (PEG200) and glycerol (1:1 and 1:9). The plasticizers were expected to overcome the brittle properties of starch films (Cazón *et al*. 2017) and improve mechanical properties, reduce deformation, hardness, and density, and increase the flexibility of polymer chains in the films (Vieira *et al*. 2011). In this case, the plasticizers could reduce network cohesion so that the intermolecular forces of adjacent polymer chains were weakened (Espitia *et al*. 2014; Marcos *et al*. 2010).

Visually, all composite films showed a homogeneous and translucent appearance (Figure 1). The surface of the PEG200:glycerol (1:1) film was

smoother and more flexible than the others. The effect of adding PEG200−glycerol plasticizers showed the highest tensile strength compared to glycerol plasticizers (Table 1). Film with the highest strain was obtained when a 20% (w/w) glycerol plasticizer was used. However, the film with the highest tensile strength, which used PEG200:glycerol at a 1:1 mass ratio and 20% (w/w) mixture concentration, was chosen as the optimum condition to achieve the standard of biodegradable plastic bags (BSN 2014). The use of 20% (w/w) concentration of plasticizers followed Lubis *et al*. (2018), who reported that the addition of glycerol higher than 20% disrupted the cohesiveness of starch. This could decrease hydrogen bond interactions in the hydrophile groups of starch and reduce the intermolecular attraction of adjacent polymer chains, thereby increasing polymer mobility.

The decrease in flexibility and increase in tensile strength of the blend film (Table 1) was due to the ability of plasticizers to maintain crystallinity by forming plasticizer crystals in the film (Lubis *et al*. 2018). According to Bocqué *et al*. (2016), plasticizers with linear chains (glycerol and PEG) function as spacers between polymer chains. The length of the plasticizer chain should not be too short to avoid volatilization and not too long to facilitate interaction. Glycerol has shorter chains with low molecular weight and fewer polar groups than PEG, making it easier to diffuse. Using PEG as a plasticizer could cause the starch chain to be more branched, thus increasing the plasticization effect.

2. Effects of Stirring and Sonication Times on the Properties of the Films

Optimization of the stirring time and additional homogenization using ultrasonic allowed the MCC to be more well dispersed. This step was important because the homogeneity of all components played an important role, affecting the resulting film's properties. Cellulose structures with high molecular weight and crystallinity were difficult to dissolve in water. Therefore, additional sonication was required to disperse the micro-sized cellulose into the film matrix (Talebi *et al*. 2022). In this case, sonication could reduce particles' sizes by causing the deformation of granules, loosening intermolecular bonds, resulting in smaller sizes, improving molecular distribution, and increasing thermal stability (Liu *et al*. 2023). In this research, to study the effects of the stirring and sonication times, the films were prepared using the previously optimized plasticizers' composition, which was PEG200:glycerol with a mass ratio of 1:1 at 20% (w/w) concentration. Visually, the films did not show significant differences characterized by similar transparency and few bubbles (Figure 2).

The mechanical test results (Table 2) showed that the 30 min stirring and 50 min sonication times to disperse MCC resulted in a film with the highest tensile strength and strain of 3.3±1.6 MPa and 31,7±17,5%, respectively. In this variation, MCC had the best level of homogeneity and flexibility

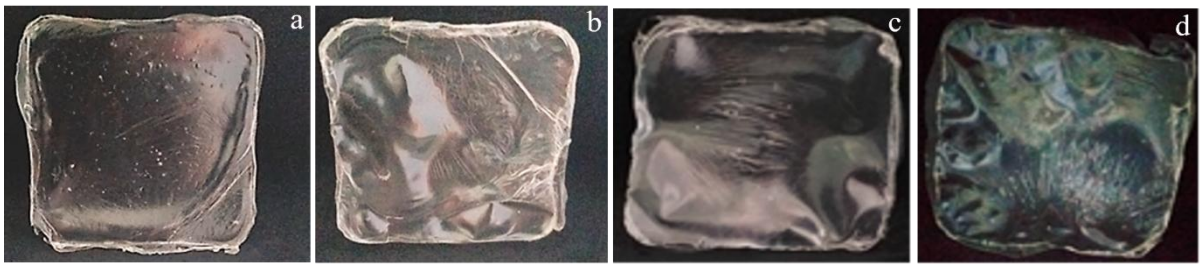

Figure 1. Films made using single and double plasticizers: PEG200:glycerol (mass ratio 1:1, 20% (w/w)) (a), PEG200:glycerol (mass ratio 1:9, 30% (w/w)) (b), glycerol 20% (w/w) (c), and glycerol 30% (w/w) (d)

Table 1. Mechanical test results of films with varying amounts and compositions of plasticizers

Sample*	Mass ratio of PEG200:Glycerol		Concentration of plasticizer (%)	Film thickness (mm)	Tensile strength (MPa)	Elongation (%)	Young's modulus (MPa)
	PEG200	Glycerol					
PG 20 (1:1)	1	1	20	0.3±0.02	4.0±1.2	6.2±1.8	8.3±4.7
PG 30 (1:9)	1	9	30	0.3±0.04	2.0±1.1	2.3±0.3	15.8±2.8
Glycerol (20% w/w)	0	1	20	0.3±0.06	0.4±0.1	43.0±16.2	1.2±1.0
Glycerol (30% w/w)	0	1	30	0.2±0.02	0.8±0.2	25.3±10.9	2.3±1.5

*****_PG = film made using PEG200 and glycerol as plasticizers_
PG 20 = PEG200:glycerol with a total concentration of 20% (w/w)
PG 30 = PEG200:glycerol with a total concentration of 30% (w/w)

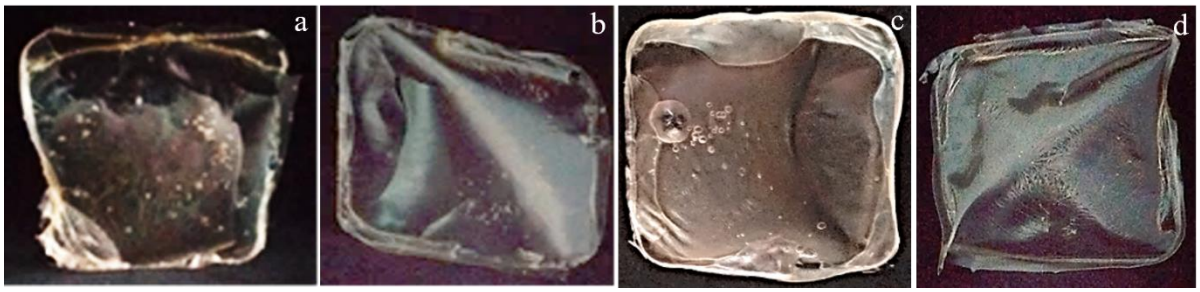

Figure 2. Films made by varying stirring and sonication times: 30 min stirring, 10 min sonication (a), 30 min stirring, 50 min sonication (b), 60 min stirring, 50 min sonication (c), and 60 min stirring, 10 min sonication (d)

Table 2. Mechanical test results of films with varying stirring and sonication times to disperse MCC

Variation		Thickness (mm)	Tensile Strength (MPa)	Elongation (%)	Young's Modulus (MPa)
Stirring (min)	Sonication (min)				
30	10	0.3±0.10	1.5±0.5	30.5±1.8	10.2±1.2
30	50	0.3±0.08	3.3±1.6	31.7±17.5	2.5±1.1
60	50	0.3±0.50	1.8±0.7	25.3±12.4	11.6±7.4
60	10	0.2±0.01	1.7±1.0	14.5±12.0	13.2±9.7

compared to the others. This film had Young's modulus value of 2.5±1.1 MPa, which showed that 30 min stirring and 50 min sonication led to the lowest stiffness. In this case, a longer sonication increased the dispersion homogeneity of microcrystalline cellulose (MCC) in water (Nazrin *et al*. 2020; Talebi *et al*. 2022), leading to stronger intermolecular bonds and higher tensile strengths. From this observation, 30 min stirring and 50 min sonication times were used as the optimum time and dispersion methods in this research.

3. Effects of the Types of Added Polymers on the Properties of the Films

To study the effects of the added polymers on the mechanical properties of the films, the films were prepared using the mass ratio of supporting polymer and complex of 1:1, mass ratio of PEG200:glycerol of 1:1 with 20% (w/w) concentration, and MCC dispersing methods using 30 min stirring and 50 min sonication times. The added polymers in this study are biodegradable polymers able to form intermolecular interactions with starch and MCC, to have a homogenous mixture and prevent the evaporation of organic substances (aroma compounds) (Cazón *et al*. 2017). Figure 3 shows the resulting films made of different types of added polymers. Adding either xanthan gum or PVA produced a transparent film (Figure 3(a) and (c)), while adding karaya gum produced a light brown film (Figure 3(b)). These three films were perfectly dry. In comparison, adding gum arabic resulted in a transparent film with a sticky texture (Figure 3(d)). Adding PLA was conducted using a pretreatment to dissolve PLA. When NaOH solution was used, the resulting film was orange-ish with a slight stickiness (Figure 3(e)), while using THF produced an inhomogeneous film (Figure 3(f)). Gum arabic and PLA produced sticky films. Therefore, xanthan gum, karaya gum, and PVA were used in subsequent studies.

The results showed that the presence of additional polymers affected the properties of the resulting films, such as color, homogeneity, texture, and mechanical and thermal properties. Film morphology is closely associated with transparency and color (Othman *et al*. 2019). Generally, films with high transparency have broader applications because they can help present the product's visuals while containing them. Meanwhile, the color of the film can affect the level of consumer acceptance of a product. As xanthan gum and poly(vinyl alcohol) (PVA) were the added polymers that resulted in transparent and translucent films, they are expected to be used in biofilm material blends for various applications.

Table 3 shows the mechanical properties of the films made by varying the types of the added polymers. Films with the highest to the lowest tensile strength values were made by adding PVA, xanthan gum, karaya gum, and gum arabic, respectively. The film's tensile strength produced by adding karaya gum was close to that of using gum arabic. This was likely due to the abundant carboxyl and hydroxyl groups that might provide active sites that enabled crosslinking (Bie *et al*. 2017). The lowest elongation was obtained for the film made by adding karaya gum. The solubility of karaya gum was not good as the swelling properties were so high that it formed a gel in water (Bie *et al*. 2017), which led to an inhomogeneous mixture. In this case, the small value of elongation was obtained because the stress was not

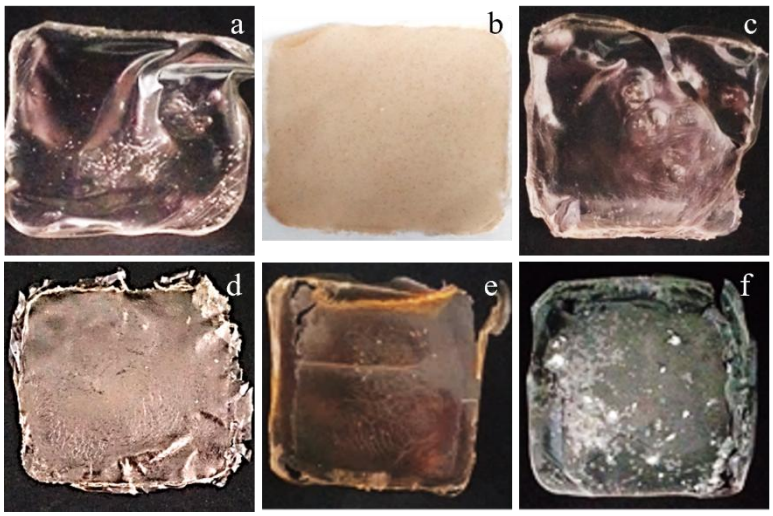

Figure 3. Films made by varying the types of added polymers: xanthan gum (a), karaya gum (b), PVA (c), gum arabic (d), PLA, using NaOH solution (e), and PLA, using THF (f)

Table 3 Mechanical test results of composite films varying supporting polymer types

Added Polymer	Thickness (mm)	Tensile Strength (MPa)	Elongation (%)	Young's Modulus (MPa)
Xanthan gum	0.3±0.1	3.4±2.2	18.8±6.3	7.1±2.6
Karaya gum	0.3±0.1	1.6±1.3	9.5±4.3	12.0±4.9
Gum arabic	0.3±0.1	1.5±0.3	17.4±9.9	12.5±4.8
PVA	0.3±0.0	3.9±1.1	189.7±31.5	2.3±1.4

effectively distributed throughout the polymer chain between the starch−coumarin complex, MCC, and the karaya gum (Talebi *et al*. 2022). The film made by adding PVA had the highest elongation with the lowest Young's modulus. In this case, the intermolecular forces of PVA with other components in the films caused elasticity to increase, thus decreasing the film's stiffness as Young's modulus was influenced by structure and crystallinity (Talebi *et al*. 2022). Based on Figure 3 and Table 3, as gum arabic produced an incompatible texture for large-scale production and had a low tensile strength value, thus xanthan gum, karaya gum, and PVA were selected as the added polymers for further investigations

Effects of the Composition and Types of Added Polymers on the Properties of the Films

The homogeneity and number of fillers influence the transparency and properties of composite films (Lee *et al*. 2008). Therefore, it is necessary to investigate the types and composition ratios of added polymers with starch−coumarin complex. Variations in the ratio of supporting biopolymers and complexes were carried out using a fixed procedure using the results of the previous optimization, namely the double plasticizer using PEG200:glycerol at 1:1 mass ratio (20% w/w), MCC (4% w/w) with 30 min stirring and 50 min sonication times. The added polymers used were xanthan gum, karaya gum, and poly(vinyl alcohol) (PVA) with mass ratios of added polymer:complex of 1:1, 1:2, and 2:1.

The visuals of the films made by varying the composition and types of added polymers are shown in Figure 4. The controls, made of starch−coumarin complex, MCC, and plasticizers, produced films with low transparency, especially the control films with mass ratios of MCC:complex at 1:1 and 2:1. In this case, eventhough MCC could serve as a filler, a high number of MCC could reduce the transparency of starch-based films (Othman *et al*. 2019). In addition, a higher amount of MCC was relatively not applicable as the MCC was not evenly distributed, resulting in agglomeration.

In general, films made by adding another polymer, with a mass ratio of added polymer:complex at 1:2, had higher transparency, with some still having several visible MCC particles. A higher amount of added polymer (mass ratio of 2:1) using xanthan gum and PVA did not significantly increase the transparency of the films. In contrast, the one with karaya gum clearly showed less transparency with several inhomogeneous particles. Films with the addition of xanthan gum in the mass ratio of added polymer:complex of 1:1 and 2:1 experienced clumping during filmmaking. They were not homogeneous and had many bubbles compared to the ratio of 1:2. The results of the study were in line with the results from Tako *et al*. (1984), which showed that the maximum dynamic modulus was obtained at a ratio of xanthan gum to locust-bean gum of 1:2.

The films containing xanthan gum, karaya gum, and PVA looked more homogeneous at the mass ratio of added polymer:complex of 1:2 than 1:1 and 2:1. Therefore, the 1:2 ratio was used as the composition ratio of added polymer to be blended with starch–coumarin complex. The clumping phenomenon of xanthan gum might be due to the formation of intramolecular bonds and conformational transition to the double helix of anionic side chains (pyruvate and acetate) (Chen *et al*. 2020[b]; Kumar *et al*. 2018). In this case, the xanthan gum chain had the ability to form a physical network with bivalent cations involving two disaccharides then united in the main chain. In this case, solubilization of xanthan gum in either hot or cold water required intensive stirring to minimize lump formation.

Table 4 shows the mechanical properties of the control films. Two types of controls were made: no-MCC and no-coumarin films. The no-MCC films were made of starch–coumarin complex, added polymer, and plasticizers (PEG200-glycerol). In contrast, the no-coumarine films were made of starch, MCC, added polymer, and plasticizers (PEG200-glycerol). The results showed that the control films without MCC had a tensile strength of 1.5–3.7 MPa with elongation of 9.2–109.0%, while the ones without coumarin (without complex formation) had a tensile strength of 1.3–3.2 MPa with elongation of 10.9–30.8%.

In the control films (Table 4), the MCC addition decreased the elongation of the film containing either karaya gum or PVA. Still, it slightly increased the elongation of the one containing xanthan gum. As for tensile strength, the MCC addition decreased the tensile strength of films containing either xanthan gum or karaya gum but slightly increased the one containing PVA. In this case, MCC has the best compatibility with PVA regarding the increase in the mechanical properties of the films.

Adding polymers to the blends of starch–coumarin complex and MCC produced films with increased tensile strength and elongation compared to the control films, as shown in Table 5. The film containing karaya gum (SCMKG) had the highest tensile strength and the lowest elongation.

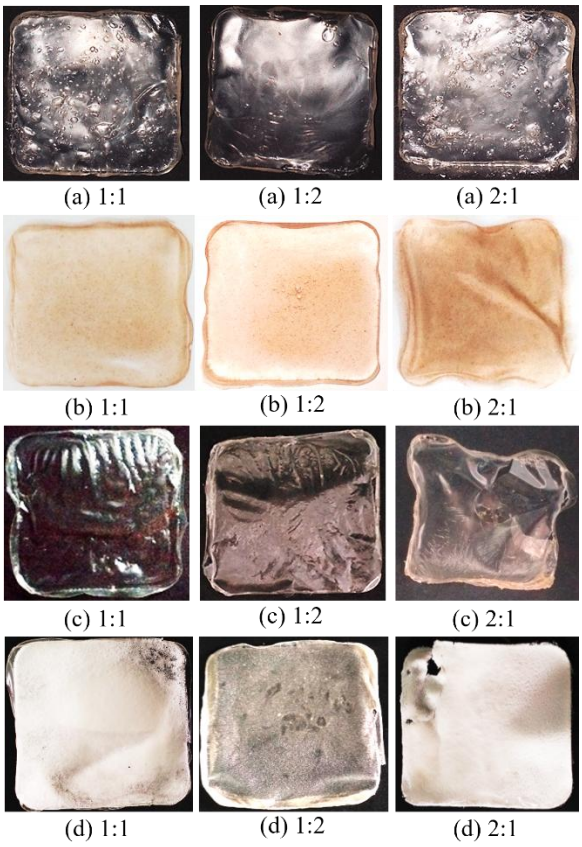

Figure 4. Films of polymer blends with varying types of added polymers: xanthan gum (a), karaya gum (b), poly(vinyl alcohol) (PVA) (c), and without added polymer (control film) (d). The films were made of starch–coumarin complex, MCC (4% w/w) with 30 min stirring and 50 min sonication times, and plasticizers of PEG200:glycerol at a 1:1 mass ratio (20% w/w). The mass ratios of added polymer:complex were 1:1, 1:2, and 2:1. The control films were prepared utilizing the same procedur, using PEG200:glycerol plastisizers at a 1:1 mass ratio (20% w/w), with mass ratios of MCC:complex of 1:1, 1:2, and 2:1.

Table 4. Mechanical properties of control films

Sample*	Condition of control	Mass ratio	Thickness (mm)	Tensile Strength (MPa)	Elongation (%)	Young's Modulus (MPa)
SCXG	no-MCC	added polymer: complex = 1:2	0.4±0.06	3.7±0.2	9.2±3.3	11.2±6.5
SCKG			0.3±0.01	1.5±0.1	48.0±5.7	2.9±0.8
SCPVA			0.3±0.09	2.4±0.8	109.0±24.1	2.5±1.1
SMXG	no-coumarin	added polymer: starch = 1:2	0.4±0.09	3.2±0.6	10.9±2.6	9.0±2.5
SMKG			0.4±0.05	1.3±0.4	29.1±7.8	7.3±3.9
SMPVA			0.3±0.10	2.8±0.9	30.8±7.2	9.3±1.5

*SCXG = starch–coumarin complex, xanthan gum, PEG200-glycerol
SCKG = starch–coumarin complex, karaya gum, PEG200-glycerol
SCPVA = starch–coumarin complex, PVA, PEG200-glycerol
SMXG = starch, MCC, xanthan gum, PEG200-glycerol
SMKG = starch, MCC, karaya gum, PEG200-glycerol
SMPVA = starch, MCC, PVA, PEG200-glycerol

Table 5. Mechanical test results of films with varying ratios of complexes and added polymers

Sample*	Mass ratio of added polymer:complex	Thickness (mm)	Tensile Strength (MPa)	Elongation (%)	Young's Modulus (MPa)
Control	1:1	0.30±0.01	1.2±0.6	19.2±8.7	9.2±3.3
SCMXG	1:2	0.27±0.08	1.5±0.4	48.9±4.8	7.9±2.6
SCMKG		0.28±0.01	6.7±0.2	9.5±2.6	4.4±0.8
SCMPVA		0.28±0.02	3.9±1.1	189.7±31.5	2.3±1.4

*Control = starch, MCC, PEG200-glycerol; mass ratio of starch:MCC was 1:1
SCMXG = starch–coumarin complex, MCC, xanthan gum, PEG200-glycerol
SCMKG = starch–coumarin complex, MCC, karaya gum, PEG200-glycerol
SCMPVA = starch–coumarin complex, MCC, PVA, PEG200-glycerol

This low elongation was likely due to the low solubility of karaya gum in water, causing an inhomogeneous mixture. This led to the stress not being effectively distributed throughout the polymer chain between starch–coumarin complex, MCC, and added polymer (Talebi *et al*. 2022).

Related to the use of MCC in the films, the combination of starch–coumarin complex, MCC, and added polymer generally produced blends with minimal agglomeration of MCC. This shows that the components in the mixture had good intermolecular interactions, which increased the mechanical properties of the films. As shown in Table 5, for films containing MCC with a mass ratio of added polymer:complex of 1:2, the use of PVA and karaya gum led to an increase in the tensile strengths of the films. This shows that the total interactions in the components in the films increased. Films containing xanthan gum (SCMXG) and PVA (SCMPVA) had a higher elongation percentage than the control films. In this case, as a filler, MCC molecules might also contribute to spacing the intramolecular interactions of the molecules, leading to flexibility increases (Othman *et al*. 2019), which was related to the rise of free volume in the film matrix (Ma *et al*. 2008).

The interaction of MCC in the film matrix could be more dominant than the added polymer in affecting the mechanical properties of the films. The increase in strain or elongation properties was due to stress being effectively distributed throughout the polymer chain (Talebi *et al*. 2022). As karaya gum had a low solubility with a substantial swelling property, it formed a gel in water (Bie *et al*. 2017). This phenomenon caused the strain of the film containing karaya gum (SCMKG) to decrease. The increase in tensile strength in SCMKG and SCMPVA was due to the interaction between MCC and the added polymers, which was strong and more dominant despite the low solubility of MCC.

MCC could act as a filler, forming hydrogen bonds and producing a rigid network (Sung *et al*. 2017). This resulted in a higher crystallinity (Gabriel *et al*. 2021), encouraging heterogeneous nucleation and lowering the free energy barrier by forming crystals (Frone *et al*. 2013). The addition of MCC had no significant effect on tensile strength because the dispersion of MCC was not uniform, thus forming aggregations, causing structural inhomogeneity, thereby reducing intermolecular interactions (Sung *et al*. 2017) and inhibiting crystal formation (Gao *et al*. 2020). Interactions between MCC molecules could also occur so that competition occurred and reduced the interactions between the matrix and starch (Lani 2014). In this case, improving cellulose compatibility

could be done by melting and compression molding to improve cellulose distribution, maximize the function as a filler, and increase crystallinity (Kargarzadeh *et al*. 2018). MCC decreased the tensile strength of SCMXG, likely due to the thickening properties of xanthan gum, which caused bubbles and made it more challenging to form interactions between soluble MCC and polymers. Compounds with polar groups and linear alkyl chains tended to form aggregations due to the interaction of head groups (hydrophilic) with water and aliphatic tails in the canal (Gao *et al*. 2020).

The presence of coumarin molecules, which formed complexes with starch, also contributed to the increase in tensile strength (Table 5) compared to the data of Table 4 (without coumarin) for films containing karaya gum (SCMKG) and PVA (SCMPVA). Starch−coumarin complex decreased the elongation of the film containing karaya gum (SCMKG) from 29.1±7.8% to 9.5±2.6%. In this case, the interaction of starch−coumarin complex with MCC and karaya gum was likely too rigid, or it might be due to the low solubility of karaya gum and MCC, causing the elasticity to decrease. The most significant increase of elongation was observed for film containing PVA (SCMPVA), from 30.8±7.25 to 189.7±31.5%. In this case, coumarin, as a hydrophobic molecule, was able to enter the amylose canal to form complexes. PVA formed hydrogen bonds with the hydroxyl groups on the surface of the complex, producing a non-rigid structure and making it more elastic. In this case, the effect of adding MCC to the composite film with PVA increased flexibility compared to the control sample but not significantly more than the effect of adding coumarin. Under these circumstances, the three-dimensional network formed by MCC increased the strength of the film compared to the interaction of coumarin with the amylose canal, so the flexibility of the chain was weaker after the addition of MCC. Here the mechanical properties of starch composite films with MCC were significantly influenced by interactions between the matrix and MCC (Chen *et al.* 2020[a]).

5. *Fourier Transform Infrared Spectroscopy* (FTIR) Analysis

FTIR spectra were used to analyze the vibrations of functional groups and correlate them to the possible intermolecular interactions between the film's components. As shown in Figure 5, the measurements were conducted for starch, heated starch, MCC, coumarin, xanthan gum, karaya gum, PVA, and the blend films. Heated starch was starch

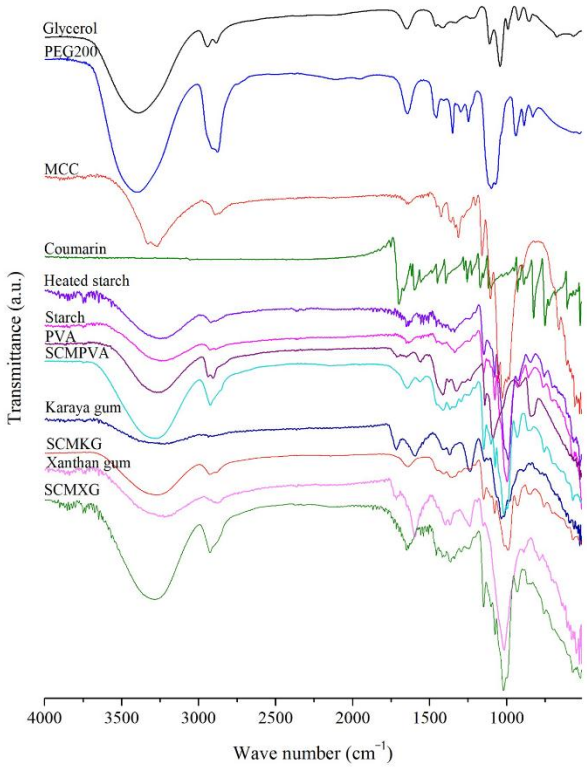

Figure 5. FTIR spectra of glycerol, PEG200, MCC, coumarin, heated starch, starch, PVA, and blend films. The blend films were prepared by mixing starch, coumarin (5% (w/w) based on the total weight of starch−coumarin complex), PEG200:glycerol with a mass ratio of 1:1 (20% (w/w)), MCC (4% (w/w)), and added polymer with a mass ratio of 1:1 (added polymer:complex). The resulting blend contained an added polymer of either PVA (SCMPVA), karaya gum (SCMKG), or xanthan gum (SCMXG).

processed using the procedure to form starch−coumarin complex but without the addition of coumarin. In this case, the heating process broke the hydrogen bonds between the starch chains. At the same time, water acted as a dispersion medium, facilitating the hydration of the starch molecules, thereby increasing chain mobility. In this case, water caused starch to swell, thus providing a larger movement space (Chang *et al*. 2021). As shown in Figure 5, starch and heated starch showed the presence of OH groups at 3200–3400 cm^{-1} and C-O-C bond at 1000–1200 cm^{-1} (Bergel *et al*. 2018). In general, the peaks from coumarin were not visible in the spectra of the blend films, indicating that coumarin was included inside the amylose canal (Anisa *et.al*. 2023), making its vibration not appear as a free molecule. MCC as a filler (amount of 4% (w/w)), and the plasticizers (PEG200 and glycerol, total amount of 20% (w/w)) were difficult to distinguish in the spectra of the blends, as they have similar functional groups to other components with higher amount in the blend

The added polymer and the starch−coumarin complex (mass ratio of 1:2) account for 76% (w/w) of the film's weight. PVA had peaks at 1095 and 1141 cm^{-1}. In the corresponding blend (SCMPVA), these two peaks shifted to 1100 and 1145 cm^{-1}, respectively, with an additional peak at 1078 cm^{-1} from starch. Karaya gum and xanthan gum showed a vibration peak of carbonyl groups at 1713 and 1720 cm^{-1}, respectively. Another peak close to this carbonyl peak was seen at 1597 cm^{-1} in karaya gum and 1591 cm^{-1} in xanthan gum. These two peaks in each karaya gum and xanthan gum were no longer in the corresponding blends (SCMKG and SCMXG). Instead, a peak was observed at 1638 cm^{-1} in SCMKG and at 1649 cm^{-1} in SCMXG. The vibrations of C-O-C (between 1000–1200 cm^{-1}), C-H (around 2900 cm^{-1}), and -OH (3400−3200 cm^{-1}) in the added polymers were also seen fused with the corresponding vibrations from starch. This indicated that interactions happening between these functional groups, thus affecting the coupling of the bond vibration, such as the -OH band in the region at 3200–3400 cm^{-1} (Wang *et al*. 2013). The shift in wave number, the appearance and disappearance of peaks, and the change in relative intensity of the peaks suggested that the intermolecular interactions between the component molecules in the blend film affected the vibration of some functional groups.

CONCLUSION

The encapsulation method in the form of starch−coumarin complex was successfully used to prepare starch-based film blends, with the addition of MCC as a filler, PEG200 and glycerol as plasticizers, and mixed with an additional polymer, such as xanthan gum, karaya gum, arabic gum, PVA, and PLA. MCC helped as a filler and reinforcement in the film. However, it faced challenges in homogenizing it when the MCC's amount was higher. In the case of the polymer blend based on starch−coumarin complex as the main polymer, the use of plasticizer was not enough to increase the flexibility of the polymer chains in the film significantly. Additional polymer was still required to help increase the elongation of the film. Based on tensile strength, strain, Young's modulus, and physical appearance, the optimum composite film was obtained using PEGb200 and glycerol plasticizers (mass ratio of 1:1), and stirring and sonication times of microcrystalline cellulose (MCC) for 30 min and 50 min, respectively. The components of the blend included starch, coumarin (5% (w/w), based on the total weight of starch and coumarin), plasticizers of 20% (w/w), MCC of 4% (w/w), and the mass ratio of the added polymer and starch−coumarin complex of 1:2. From the five added polymers tried in this research, xanthan gum, karaya gum, and PVA produced acceptable blend films, with tensile strength of 1.5–6.7 MPa, elongation of 9.5–189.7%, and Young's modulus of 2.3–7.9 MPa. The results showed that to produce a homogenous film with good mechanical properties, all components in the film, such as the main polymer, filler, plasticizer, and added polymer, must be able to form intermolecular interactions with one another. Strong intermolecular interactions within components with high compatibility will result in a film with high tensile strength. Amongst the blends studied in this research, the one using PVA as the added polymer resulted in a film with the most homogeneous visual, with a tensile strength of 3.9 MPa, an elongation of 189.7%, and Young's modulus of 2.3 MPa.

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