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The Counter Ions of Calcium on The Properties of Thermal Processed Agar Film

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ABSTRACT: This study investigates the fabrication of agar-glycerol films via compression moulding, a scalable thermal processing technique. The objective is to investigate the properties of thermally processed agar films by varying the type of calcium counter ions: adding calcium stearate (CS) to increase hydrophobicity, while calcium chloride ($CaCl_2$) to promote its degradation. The study includes different types of films with varying glycerol amounts, along with different levels of CS and $CaCl_2$ represented by these codes (HGCS25Ca5, HGCa25CS5, LGCS25Ca5 and LGCa25CS5) refer to the specific film samples used in this study. The impact of these compositional variations on thermal behaviour, surface characteristics and degradation profiles is rigorously assessed. The highest melting peak (T_{peak}) observed was 140°C, achieved by the formulation containing high $CaCl_2$ (HGCa25CS5), indicating the crosslinking of $CaCl_2$ with agar contributes to an increase in the melt transition temperature. The LGCa25CS5 and HGCa25CS5 have higher residual char, approximately 28.42% and 23.37% compared with agar films without CS and $CaCl_2$ (7.49%–8.97%), which implies that the material decomposes less, indicating better thermal stability. The highest contact angle (110.053°) was observed in low glycerol formulations containing high CS, which contributes to enhanced surface hydrophobicity. Conversely, $CaCl_2$, while contributing to the structural integrity of the film, exhibited a less pronounced effect on surface hydrophobicity. High glycerol (HG) sample showed a weight loss of 15.80%, while the thermal compressed agar film incorporating CS and $CaCl_2$ exhibited the highest weight loss of 90%, indicating that CS and $CaCl_2$ promote oxidative degradation of agar chains, enhancing the film's susceptibility to microbial degradation and resulting in increased weight loss during soil burial tests. The weight loss of all films in the vermicompost condition is more pronounced than in the soil condition. These findings highlight the potential of compression moulding to produce agar-based films

with adjustable properties by carefully adding CS and $CaCl_2$. This approach offers a useful understanding of how these additives influence thermal stability, surface hydrophobicity and degradation behaviour in agar-glycerol systems.

Keywords: agar, thermal processed, melt-compressed, degradation, hydrophobicity

1. INTRODUCTION

The pervasive use of single-use plastics presents a significant environmental challenge, contributing to the growing issue of plastic pollution worldwide. The global issue of single-use plastics and their environmental impact have prompted the exploration of various alternatives, including biodegradable materials. These alternatives aim to reduce plastic pollution by offering sustainable options that can decompose naturally. Research on bioplastics made–from natural polymers like starch, chitosan and seaweed is gaining attention.[1–4] These materials are derived from renewable resources and can be composted, offering an eco-friendly solution to plastic waste.[5] Starch is a widely used biodegradable material due to its abundance and renewability. It is often combined with other polymers to enhance its properties.[6] Polylactic acid (PLA) is also a popular biodegradable polymer made from fermented plant starch. It is used in packaging and disposable items due to its compostability.[7] Chitosan's antimicrobial properties make it ideal for applications requiring bacterial inhibition, such as wound dressings and food packaging.[8] Among these, agar-glycerol bioplastics have emerged as a promising solution due to their biodegradability and environmental benefits.

Agar, derived from red seaweed, presents a promising biodegradable alternative to conventional plastics like starch-based, PLA and chitosan-based plastics. Its environmental benefits are primarily rooted in its biodegradability, renewable sourcing and potential to reduce plastic pollution. Agar-based bioplastics exhibit excellent biodegradability, decomposing completely in soil within a short period, which significantly reduces environmental pollution compared to conventional plastics that persist for decades.[9] The biodegradation process of agar-based materials results in non-toxic byproducts, such as carbon dioxide and water, which are harmless to the environment.[10] The cultivation of seaweed for agar production can contribute to carbon sequestration and does not require arable land, making it a more sustainable option compared to land-use intensive crops used for PLA and starch production.[11]

Agar, a natural polysaccharide derived from red algae, has gained attention as a film-forming agent due to its gel-like properties and biodegradability. Agar's ability to form films is due to its gel-forming properties, which are effective at concentrations as low as 1.0% to 10.0%.[12] The addition of plasticisers like glycerol can significantly enhance the flexibility and mechanical properties of agar-based films. Glycerol, in particular, acts by disrupting intermolecular forces, thereby increasing the film's elasticity and reducing brittleness. This interaction between agar and glycerol is crucial for developing films

with desirable properties for various applications. Thermal compression moulding is emerging as a viable alternative to solution casting, particularly in the production of composite materials. This method involves the application of heat and pressure to form materials, offering several advantages over traditional solution casting, such as enhanced mechanical properties and reduced solvent use. One of the significant advantages of thermal compression moulding is the elimination of solvents, which are typically required in solution casting. This not only reduces the environmental impact but also simplifies the production process and lowers costs.[13]

To further improve the performance of agar-glycerol films, additives such as calcium stearate (CS) and calcium chloride ($CaCl_2$) can play a crucial role. CS has long hydrocarbon chains that are non-polar and hydrophobic; these chains orient themselves outward, creating a barrier that repels water when applied to surfaces. This, enhances the hydrophobicity of the films, providing resistance to moisture and improving their utility for single-use applications. In contrast, $CaCl_2$ acts both as a catalyst for degradation and as a structural modifier that enhances the breakdown process. This dual functionality is particularly beneficial in creating materials that are not only effective during their use but also environmentally responsible after disposal.[14] $CaCl_2$ influences the physical properties of films by affecting the crosslinking density and molecular entanglement. For instance, in alginate films, varying the concentration of $CaCl_2$ alters the gelation process, which in turn affects the film's tensile strength and flexibility. This controlled modification allows for a balance between durability during use and breakdown after disposal.[15]

This study aims to explore properties of agar-glycerol films developed via thermal compression moulding, focusing on their thermal properties, hydrophobicity, and degradation rate as types of calcium counter ions are varied, stearate from CS and chloride from $CaCl_2$. By addressing the interplay between the formulation components and processing method, this research contributes to the development of eco-friendly alternatives to conventional plastics that can be easily disposed of and degrade post-use.

2. EXPERIMENTAL

2.1 Materials

The commercial agar powder of HmbG Chemicals brand, glycerol (Systerm), CS, $C_{36}H_{70}CaO_4$ and $CaCl_2$ were purchased from BG Oil Sdn. Bhd., Penang, Malaysia. The agar film was fabricated using a stainless-steel mould measuring 120 mm × 120 mm × 0.5 mm, purchased from Su Hai Thong Foundry Sdn. Bhd., Penang, Malaysia.

2.2 Thermal Processed Agar Film Preparation

The mixing components were divided into two parts: solid (referred to later as MS) and liquid. The MS consisted of agar, CS and $CaCl_2$ whereby the agar content is fixed at 12.72 cm^3 per gram for all formulations, while the liquid part is glycerol. The MS were premixed using a blender and later mixed with the glycerol as shown in Table 1. In this study, the term "parts per hundred" (pph) is used to describe the composition of the agar films. This unit is expressed in terms of weight, where the total weight of all components in the mixture is considered as 100 parts. This ensures that the proportions of agar and the additives are accurately maintained for achieving the desired properties of the film.

Table 1: Samples with different formulations with different content of CS and $CaCl_2$ in thermal compressed agar films

Formula name	Agar (pph)	Glycerol (pph)	CS (pph)	$CaCl_2$ (pph)
HG	Low	High	–	––
LG	High	Low	–	–
HGCS25Ca5	30	40	25	5
HGCa25CS5	30	40	5	25
LGCS25Ca5	40	30	25	5
LGCa25CS5	40	30	5	25

Premixed mixtures (MS and glycerol) were placed between two stainless-steel plates that were wrapped in PET film within a mould. PET film acts as a release agent and structural support, preventing the agar film from sticking to the mould and helping it maintain its shape and integrity during the hot compression process so that the agar film can be easily removed without damage. Each formulation was thermal compressed in a hydraulic press at 150°C, 1,000 psi for 5 min. The hot polymer film was allowed to rest between plates for 24h before being separated from the stainless-steel plates, as seen in Figure 1.

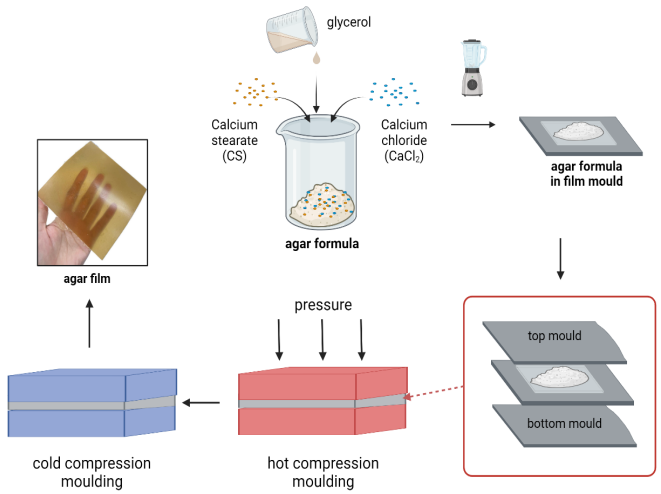


Figure 1: Process flow of fabricating thermal compressed agar film.

2.3 Characterisation of Thermal Compressed Agar Films

2.3.1 Thermogravimetric analysis (TGA)

TGA thermograms were used to determine degradation temperatures such as T_{max} and mass residue at 800°C TGA measurements of raw materials were conducted using a thermogravimetric analyser (Mettler Toledo TGA/Differential Scanning Calorimetry (DSC) 1, Schwerzenbach, Switzerland) under a nitrogen atmosphere over a temperature range of 30°C–800°C, with a heating rate of 10°C/min.

2.3.2 Differential scanning calorimetry

DSC analysis was conducted using a differential scanning calorimeter with model of DSC Q200 (TA Instruments, New Castle, Delaware, USA) under dry nitrogen gas. Approximately 5 mg–10 mg of samples were weighed and sealed. Samples were subjected to heating–cooling cycle at a rate of 10°C/min from 30°C to 320°C. During the heating cycle, the melting temperature (T_m) were determined.

2.3.3 Contact angle

Surface hydrophobicity was checked via contact angle measurement based on ASTM D5946-04. Water contact angles of the films were measured using the static sessile drop method by the Attension (Theta Tensiometer) from Biolin Scientific, Espoo,

Finland, under ambient conditions. Water droplets (approximate 7 μL) were dropped onto the film surface (1 cm × 1 cm). Three different measurement points of the sample surface were carried out to determine the average static contact angle.

2.3.4 Soil burial test

The soil burial test was carried out by the method described by Hasan M. et al., with slight modification.[16] Four samples (20 × 20 × 0.6) mm from different formulations were weighed for determination of initial weight. Samples were placed 7 cm deep in a container of soil at room temperature under two different conditions; (1) soil only; (2) vermicompost. The soils were regularly moistened with distilled water every alternative day for 15 days. Metal mesh was used to wrap the samples before burying into the soil to facilitate removal of the degraded samples while maintaining the access of moisture and microorganism. After 15 days of burial, the films were collected and recorded as their final weight.

3. RESULTS AND DISCUSSION

3.1 Thermal Properties

The DSC thermograms provide valuable insights into the peak characteristic and thermal stability range in the thermal compressed agar films with different formulations as seen in Figure 2. The pure agar sample exhibits an endothermic peak at 112.86°C, consistent with the expected thermal behaviour of pure agar.[17] In Figure 2, the thermal compressed agar films of high glycerol (HG) with high $CaCl_2$ demonstrates a shift to higher melt transition temperatures than agar. The crosslinking of $CaCl_2$ with agar contributes to an increase in the melt transition temperature through the formation of ionic bonds between calcium ions and the O^- in the hydroxyl groups of the agar chains. These ionic interactions enhance structural stability and resistance to thermal disruption. As a result, more thermal energy is required to break these bonds and facilitate the transition from solid to liquid phase, leading to a shift to higher melt transition temperatures compared to pure agar, which lacks such ionic crosslinking. This increased thermal stability reflects the stabilising effect of calcium-induced crosslinks within the agar structure.

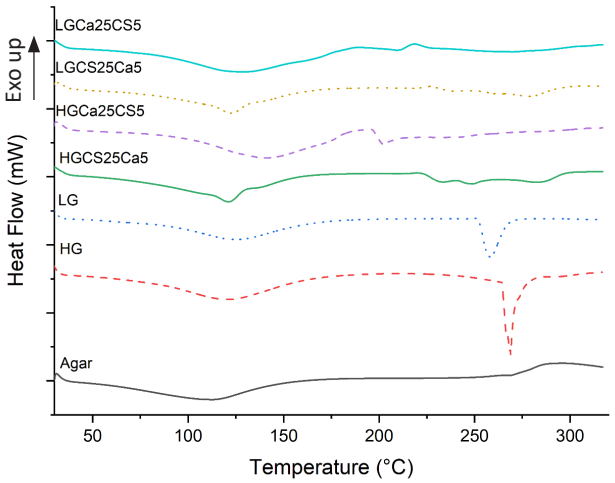


Figure 2: Thermogram of thermal compressed agar films with high and low glycerol content at various CS and $CaCl_2$ content by DSC analysis.

Table 2 shows the melting parameters of thermal compressed agar films with high and low glycerol (LG) content at various CS and $CaCl_2$ content. The highest T_{peak} (140°C) is achieved when both high glycerol high $CaCl_2$ (HGCa25CS5) is in the film. It shifted way higher than agar (112.85°C), low glycerol high CS films; (LGCS25Ca5, 122.26 °C) and low glycerol high $CaCl_2$ (LGCa25CS5, 128.61°C). It suggests that both hydrogen bonding between the hydroxyl groups of agars with glycerol, as well as ionic bonding between Ca^{2+} in $CaCl_2$ and O^- in the hydroxyl groups of agars, contributed to delay sliding between agar chains, thus increasing melting temperature.[18]

Even at low glycerol and elevated levels of $CaCl_2$ (LGCa25CS5, 128.61°C), the observed T_{peak} is higher compared to samples with high glycerol content but high CS (HGCS25Ca5, 120.73°C). This suggests that, despite the increased presence of glycerol that may increase hydrogen bonding between hydroxyl groups in glycerol and agar, the counter ion of calcium in CS (that is stearate) may inhibit the crosslinking process facilitated by Ca^{2+} ions from $CaCl_2$. Consequently, CS appears to interfere with the bonding interactions between agar chains, thereby affecting the overall thermally induced transition behaviour.

Table 2: Melting parameters of thermal compressed agar films with high and low glycerol content at various CS and $CaCl_2$ content

Samples	Melting steps	T_{onset} (°C)	T_{peak} (°C)	Δ T (°C)	Enthalpy (J/g)
Agar	1	48.16	112.86	64.7	359.1
HG	1	75.58	121.83	46.25	382.5
	2	264.46	267.80	3.34	163.3
LG	1	78.29	125.67	47.38	384.8
	2	252.52	257.79	5.27	113.7
HGCS25Ca5	1	94.53	120.73	26.2	397.9
	2	224.64	231.22	6.58	11.44
	3	241.42	248.51	7.09	9.907
	4	268.87	283.58	14.71	28.98
HGCa25CS5	1	95.44	140.86	45.42	391.6
	2	196.84	202.03	5.19	25.34
LGCS25Ca5	1	97.11	122.26	25.15	340.0
	2	228.81	278.51	49.70	115.7
LGCa25CS5	1	73.99	128.61	54.62	542
	2	195.19	209.88	172.69	22.50
	3	219.48	261.57	97.68	121.8

The thermal degradation characteristic of thermoplastic agar must be analysed to understand the material constraint in further processing. The TGA thermograms in Figure 3 presents the weight losses of thermal compressed agar films during heating. According to Figure 3, LGCa25CS5 and HGCa25CS5 has higher residual char, approximately 28.42% and 23.37% compared to thermal compressed agar films with high CS (LGCS25Ca5 and HGCS25Ca5) which have lower residual char, 17.47% and 15.37%. A higher residual weight implies better thermal stability.[19] These results may indicate that 1) ionic bonding between Ca^{2+} in $CaCl_2$ and O^- in hydroxyl groups of agars has more pronounce effect in holding the agar chain together than hydrogen bonding between OH in glycerol and in agar and 2) stearate in CS may hindered the ionic bonding between Ca^{2+} in $CaCl_2$ and O^- in hydroxyl groups of agars, similarly indicated by DSC result previously.[20]

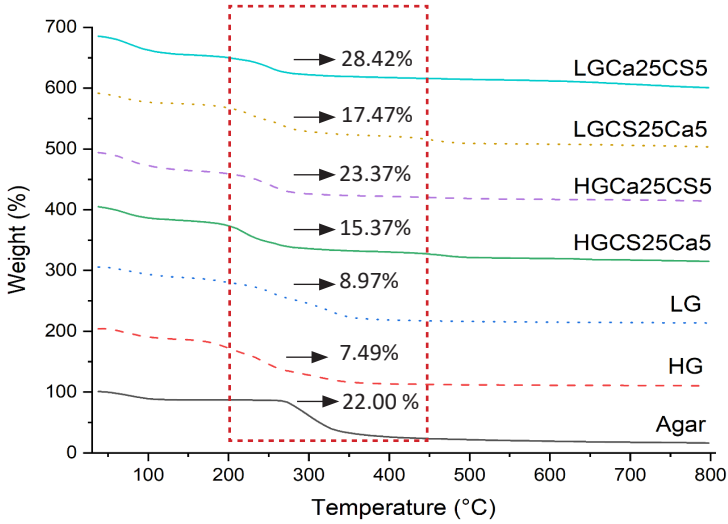


Figure 3: Thermogravimetric analysis/TGA of thermal compressed agar films with high and low glycerol content at various CS and $CaCl_2$ content.

The DTG thermograms in Figure 4 shows four steps of thermal degradation were observed for thermal compressed agar films while only two peaks for pure agar. This change is attributed to the complex interactions and decomposition pathways introduced by glycerol. Glycerol, a polyol with three hydroxyl groups, can undergo various dehydration and decomposition reactions, leading to additional thermal events that are detected as separate peaks in DTG. The presence of glycerol alters the thermal stability and decomposition mechanisms of the agar-glycerol mixture, resulting in a more complex thermal profile.[21]

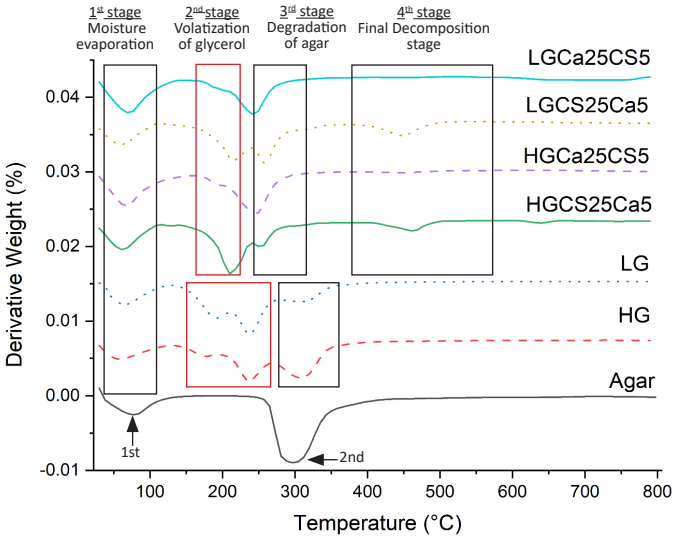


Figure 4: Derivative thermogravimetry/DTG of thermal compressed agar films with high and low glycerol content at various CS and $CaCl_2$ content.

The stages of decomposition can be explained by the various decomposition temperatures of the essential elements found in thermal compressed agar film samples in Table 3.

As shown, the pure agar and thermal compressed agar films demonstrate the first weight loss stage at the temperature of 61.33°C–77°C, which correspond to the moisture evaporation from the bioplastic material.[22] The water molecules within agar-glycerol films will evaporate when subjected to temperatures spanning from 50°C–100°C, attributable to the disruption of hydrogen bonds. The second stage, are the subsequent peaks of thermal decomposition pertains to the volatilisation of glycerol, which transpires within the range of 171°C–249.33°C. As shown, when glycerol is combined with CS and $CaCl_2$, it shows a single decomposition peak, whereas glycerol with agar only, typically shows two peaks. The ionic character calcium influences the thermal stability and decomposition behaviour of glycerol by stabilising certain intermediate products or altering the energy barriers of decomposition reactions.[23] CS, for instance, has been shown to have a zero-order decomposition kinetics, which can lead to a more uniform decomposition process, resulting in a single peak in TGA analysis. In contrast, the presence of agar, a polysaccharide, can lead to multiple decomposition pathways due to its complex structure and interaction with glycerol. This can result in two distinct peaks in the TGA analysis, representing different stages or mechanisms of decomposition.[24] The overlapping processes typical in polymer degradation, as seen with agar, can lead to multiple peaks due to the presence of various decomposition stages.

Table 3: Thermogravimetric data of thermal compressed agar films with high and low glycerol content at various CS and $CaCl_2$ content

Samples	Degradation steps	T_{onset} (°C)	T_{max} (°C)	Residual char (%)
Agar powder	1	54.72	77.000	87.00
	2	272.27	296.330	22.69
HG	1	45.60	61.330	83.59
	2	167.28	171.000	28.27
	3	225.81	233.670	7.81
	4	292.53	304.000	7.49
LG	1	47.22	61.330	83.15
	2	165.30	186.580	45.83
	3	229.31	233.720	8.97
	4	295.90	312.000	8.97
HGCS25Ca5	1	52.07	61.170	79.46
	2	131.92	194.500	42.81
	3	255.94	249.330	27.46
	4	444.13	460.830	15.37
HGCa25CS5	1	56.81	69.170	69.27
	2	176.59	194.500	28.79
	3	222.83	249.200	23.37
LGCS25Ca5	1	52.65	61.330	84.55
	2	198.58	218.000	56.70
	3	259.44	257.170	31.08
	4	428.70	445.167	17.47
LGCa25CS5	1	56.01	69.170	69.38
	2	186.67	221.300	31.64
	3	230.14	250.500	28.42

The third stage of thermal decomposition peaks took place at approximately 249°C–312°C which is in accordance with the deterioration of the crosslinked network involving $CaCl_2$ and agar, as well as the decomposition of covalent bond of the agar backbone. The thermal degradation peaks result obtained agreed with previous work carried out by Fransiska et al.[25] Finally, the final decomposition stage occurred due to the deterioration of excessive CS occurred above 400°C. This decomposition involves the breakdown of CS into calcium carbonate and further into calcium oxide, which aligns with the observed TGA peak. CS decomposes in two main stages, with the first stage occurring between 361°C and 402°C, matches the result in this study.[26]

3.2 Hydrophobicity

As shown in Figure 5, very small contact angle was detected in HG film while the contact angle of LG and thermal compressed agar films was obtained in the range between 26.31°C–110.05°C. Very low contact (0.30°) contact angle was detected in control films HG due to the water droplet freely moved on the surface. In high glycerol formulations, the glycerol content is abundant, leading to a more flexible and mobile polymer network. This increased fluidity can disrupt the hydrogen bonding between agar chains and result in a less defined surface.[25] Consequently, the ability to form stable contact angles with water droplets diminishes, often rendering the contact angle nearly undetectable. In low glycerol formulations, the agar retains more of its inherent structure, with fewer plasticiser-induced disruptions. The lower glycerol content allows the agar molecules to maintain stronger hydrogen bonds, leading to a more defined surface that can resist water penetration and achieve contact angles up to 70°.

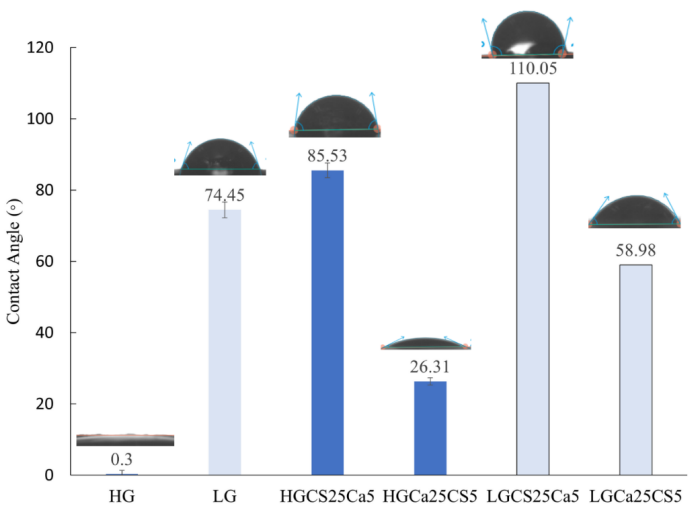


Figure 5: The contact angles of thermal compressed agar films with high and low glycerol content at various CS and $CaCl_2$ content.

In general, thermal compressed agar films with high CS (LGCS25Ca5, 110.05°; HGCS25Ca5, 85.53°) has higher contact angles than films with high $CaCl_2$ (LGCa25CS5, 58.98°; HGCa25CS5, 26.31°). The contact angle tests reveal a significant enhancement in the hydrophobicity of thermal compressed agar films through the incorporation of CS. Figure 6 schematically proposes a mechanism for hydrophobicity between agar chains in the presence of CS and $CaCl_2$.

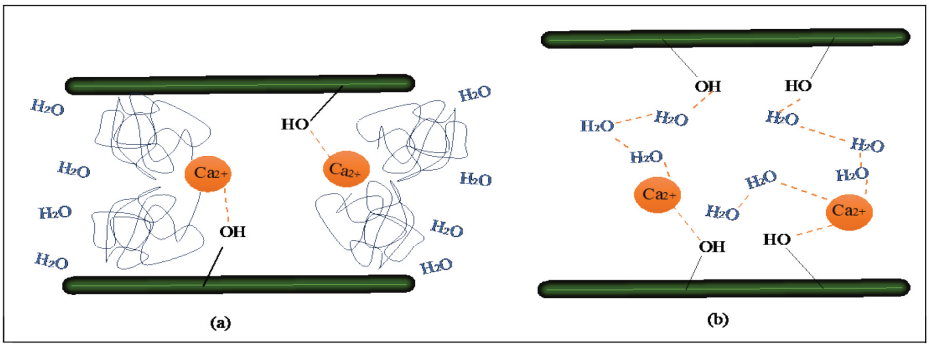


Figure 6: Proposed mechanism for hydrophobicity between agar chains in the presence of (a) CS; (b) $CaCl_2$.

CS, a long-chain fatty acid salt, improves hydrophobicity due to its hydrophobic hydrocarbon tail, which promotes non-polar interactions at the film surface, thus repelling water molecules as seen in Figure 6(a). This enhancement is further pronounced in the low glycerol formulations, suggesting that higher concentrations of CS facilitate greater alignment and packing of hydrophobic domains, effectively increasing the contact angle and reducing the film's wettability. $CaCl_2$, however, has an adverse effect on hydrophobicity. $CaCl_2$ initially promotes the crosslinking of agar polymers by forming ionic bonds between Ca^{2+} and O^- in hydroxyl groups in the agar structure. However, as water enters the film, the water is attracted to the $CaCl_2$, causing the agar chains to become more separated as more water is absorbed, as shown in Figure 6(b). This results in a decrease in the contact angle in films with higher levels of $CaCl_2$.[27] In addition, it is important to note that $CaCl_2$ can also attract moisture from the atmosphere due to its hygroscopic nature, which might increase the hydrophilic properties of the film.

It is also worth noting that the formulation with high glycerol (HGCa25CS5, 26.31°) shows a lower contact angle than the film with low glycerol (LGCa25CS5, 58.98°), indicating an attraction of glycerol to water, which produces films with a lower contact angle.

3.3 Degradability

The weight loss data presented in Figure 7(a) and 7(b) provides insights into the degradation behaviour of thermal processed agar films with varying compositions of CS and $CaCl_2$ under soil and vermicompost conditions. In soil only condition, bioplastic degradation primarily occurs through enzymatic action by soil microorganisms. Vermicompost is a condition where the gut mucus from the earthworm provides

good conditions for a microbial population to flourish by increasing the surface area of the microplastics for further degradation by microbial activity after excreting them through their vermicast.[28] Weight loss serves as a direct indicator of the extent of degradation, where higher weight loss percentages generally correspond to greater degradation of the film.

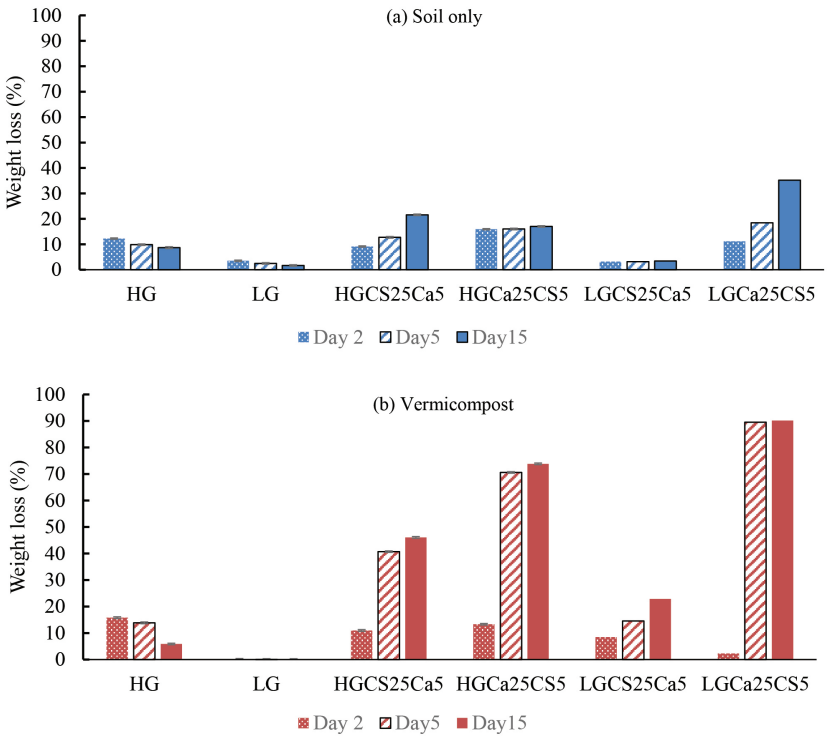


Figure 7: Weight loss of thermal compressed agar films with high and low glycerol content at various CS and $CaCl_2$ content retrieved from (a) soil only and (b) vermicompost after 2, 5, and 15 days.

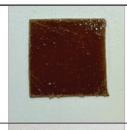
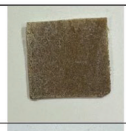
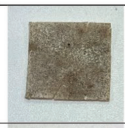
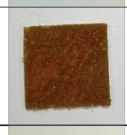
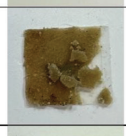
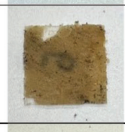
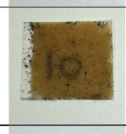
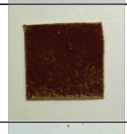
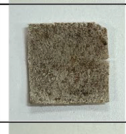
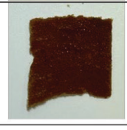
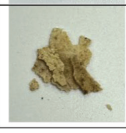
From Figure 7, the degradation rate of thermal compressed agar films without CS and $CaCl_2$ (HG and LG) are slower than thermal compressed agar film with CS and $CaCl_2$. The weight loss observed in the HG sample, approximately 15.80%, whereas the thermal compressed agar film containing CS and $CaCl_2$ demonstrated the highest

weight loss, reaching 90%. This indicates that CS and $CaCl_2$ can act as pro-oxidant agents, which facilitate the breakdown of agar chains by promoting oxidation. This process increases the film's susceptibility to microbial degradation, leading to higher weight loss during soil burial tests.[29] Also shown in Figure 7, the thermal compressed agar films with high $CaCl_2$ exhibited higher weight loss than films with high CS in both soil and vermicompost conditions. This can be explained by the highly hygroscopic nature of $CaCl_2$, which increases the films' water absorption capacity by absorbing moisture from the environment that can facilitate microbial activity and hydrolysis, enhancing the breakdown of biodegradable films.[30] In contrast, the hydrophobic characteristic of CS limits microbial colonisation and activity, further contributing to the slower degradation rate.

However, the degradation rate of all thermal compressed agar films is more pronounced in vermicompost as shown in Figure 7(b) compared to in soil condition as depicted in Figure 7(a). In vermicompost, the films generally exhibit a rapid initial degradation phase between days 2 and 5, followed by sustained degradation leading to the highest overall weight loss by day 15. This accelerated initial degradation is attributed to the presence of earthworms that can significantly affect the physical characteristics of thermal compressed agar films by increasing the films' surface area through ingestion and can contribute to further degradation. Vermicompost also provided favourable conditions to accelerate the decomposition of organic material, which is lacking in soil conditions.[28] The degradation patterns observed in this study underscore the potential of strategically manipulating the properties of agar films through the incorporation of CS and $CaCl_2$. While CS enhances hydrophobicity, slowing down degradation under certain conditions, $CaCl_2$ promotes degradation by increasing water absorption and microbial accessibility.

Figure 8(a) and Figure 8(b) show digital images of samples buried in soil only and in vermicompost, which revealed the significant deterioration of the thermal compressed agar samples across all formulations monitored over a period of 2, 5 and 15 days. Films with high $CaCl_2$ exhibited noticeable fragmentation after day 2 when handled in both conditions. At high CS, the once smooth and uniform surface had become irregular and pitted, indicating the progressive degradation of the agar film in the vermicompost environment after day 5. However, the films remain intact in soil, particularly those with a high concentration of CS. This observation highlights the slower degradation rate for these materials.

(a) Soil only

Sample	Day 0	Day 2	Day 5	Day 15
HGCS25Ca5				
HGCa25CS5				
LGCS25Ca5				
LGCa25CS5				

(b) Vermicompost

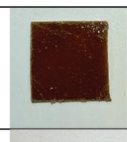
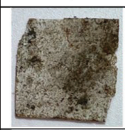
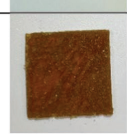
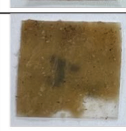
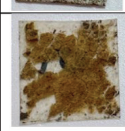
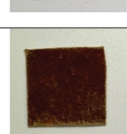
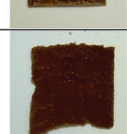
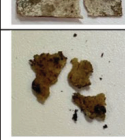
Sample	Day 0	Day 2	Day 5	Day 15
HGCS25Ca5				
HGCa25CS5				
LGCS25Ca5				
LGCa25CS5				

Figure 8: Digital images of thermal compressed agar films with high and low glycerol content at various CS and $CaCl_2$ content retrieved from (a) soil only and (b) vermicompost after 2, 5 and 15 days.

4. CONCLUSION

This study demonstrates that the addition of different calcium counter ions from CS and $CaCl_2$ significantly improves the thermal properties, hydrophobicity and degradation of the thermal compressed agar films. $CaCl_2$ induced different thermal performance than CS, as evidenced by higher increases in both melting and degradation temperatures in $CaCl_2$ films. The higher hydrophobicity of the film was induced by stearate's long alkyl chains in CS compared to $CaCl_2$. Additionally, the thermal compressed agar films with high $CaCl_2$ exhibited higher weight loss than films with high CS in both soil and vermicompost conditions, but the degradation rate of all thermal compressed agar films in the vermicompost condition are more pronounced than in the soil condition. It is also worth noting that formulation with high glycerol in thermal compressed agar film shows high thermal stability, low contact angle and high degradation rate compared to formulations with low glycerol in thermal compressed agar film. This research has successfully demonstrated the production of thermal compressed agar films using thermal compression moulding. This achievement not only underscores the versatility of agar as a biopolymer but also challenges the conventional notion that solution casting is the sole method for producing agar films. This study explores the potential of agar as a viable alternative to petroleum-derived polymers manufactured via compression moulding with a focus on its thermal processing capabilities to assess the effect of CS and $CaCl_2$ on thermal properties, surface hydrophobicity and degradation of the thermal compressed agar film. These findings open new avenues for the utilisation of agar in various industries, particularly in those requiring efficient and scalable film production methods. It is hoped that this study serves as a stepping stone for further research into the potential applications of agar and other biopolymers in the realm of thermal melt processing.

5. ACKNOWLEDGEMENTS

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6. REFERENCES

1. Nasir, N. N. & Othman, S. A. (2021). The physical and mechanical properties of corn-based bioplastic films with different starch and glycerol content. *J. Phys. Sci.*, 32(3). https://doi.org/10.21315/jps2021.32.3.7
2. Yeng, C. M., Husseinsyah, S. & Amirudin, M. A. A. A. (2016). Tensile and thermal properties of crosslinked chitosan/empty fruit bunch biofilms by phthalic anhydride. *J. Phys. Sci.*, 27(2). https://doi.org/10.21315/jps2016.27.2.6
3. Masbah, M. S. et al. (2024). Microwave crosslinked chitosan/green fluorescent carbon nanoparticles film: Comprehensive characterisation and antimicrobial performance. *J. Phys. Sci.*, 35(2). https://doi.org/10.21315/jps2024.35.2.4
4. Abdul Khalil, H. P. S. et al. (2019). Techno-functional properties of edible packaging films at different polysaccharide blends. *J. Phys. Sci.*, 30, 23–41. https://doi.org/10.21315/jps2019.30.s1.2
5. Sable, S. et al. (2024). Bioplastic from agar powder: Preparation and its characterization. *Sci. Adv. Mater.*, 16(10), 1040–1046. https://doi.org/10.1166/sam.2024.4713
6. Raghunathan, R. et al. (2025). Biodegradable products from renewable sources: impact on replacing single-use plastic for protecting the environment. *Int. J. Environ. Sci. Technol.*, 22(7), 6181–6208. https://doi.org/10.1007/s13762-024-06104-7
7. Samuel, H. S., Ekpan, F. D. M. & Ori, M. O. (2024). Biodegradable, recyclable, and renewable polymers as alternatives to traditional petroleum-based plastics. *Asian J. Environ. Res.*, 1(3), 152–165. https://doi.org/10.69930/ajer.v1i3.86
8. Favian, E. & Nugraheni, P. S. (2023). Effect of carrageenan addition on the characteristic of chitosan-based bioplastic. *IOP Conf. Ser.: Earth Environ. Sci.*, 1289(1), 012039. https://doi.org/10.1088/1755-1315/1289/1/012039
9. Wagh, P., Vaidya, V. & Nawani, N. (2024). Physical characterization of agar-based biodegradable films derived from nonhazardous laboratory waste. *Energy Environ.*, 36(5), 2152–2173. https://doi.org/10.1177/0958305X241282606
10. Patil P.D. (2022). Production of agar-agar and sago based bioplastic: A review. *Int. J. Sci. Technol. and Eng.*, 10(4), 2378–2380. https://doi.org/10.22214/ijraset.2022.41749
11. Nivetha, A. et al. (2023). Dissolvable and biodegradable packaging with agar agar using design thinking approach. *Int. J. Multidiscip. Res.*, 5(6). https://doi.org/10.36948/ijfmr.2023.v05i06.8786
12. Osovskaya, I. I. & Baranova, A. E. (2023). Optimization of conditions for the formation of stable gel from agar-agar. *Chem. Plant Raw Mater.,* 2, 71–78. https://doi.org/10.14258/jcprm.20230211723
13. Dumont, P., Martoïa, F. & Orgéas, L. (2023). Compression moulding. In H. Lee & C. Mike (Eds). *Design and manufacture of structural composites*. Oxford, United Kingdom: Woodhead Publishing, 273–300.

14. Viktoriya, S. K. (2023). Investigation of the effect of volumetric hydrophobization on the kinetics of mass transfer processes occurring in cement concretes during corrosion. *Materials,* 16(10), 3827. https://doi.org/10.3390/ma16103827
15. Jiwei, L. et al. (2016). A new insight to the effect of calcium concentration on gelation process and physical properties of alginate films. *J. Mater. Sci.*, 51, 5791–5801. https://doi.org/10.1007/s10853-016-9880-0
16. Hasan, M. et al. (2019). Micro crystalline bamboo cellulose based seaweed biodegradable composite films for sustainable packaging material. *J. Environ. Polym. Degrad.*, 27, 1602–1612. https://doi.org/10.1007/s10924-019-01457-4
17. Cooke, D., Gidley, M. J. & Hedges, N. D. (1996). Thermal properties of polysaccharides at low moisture: II. Molecular order and control of dissolution temperature in agar. *J. Therm. Anal. Calorim.*, 47(5), 1485–1498. https://doi.org/10.1007/BF01992841
18. Mohamad Haafiz, M. K. et al. (2016). Exploring the effect of cellulose nanowhiskers isolated from oil palm biomass on polylactic acid properties. *Int. J. Biol. Macromol.*, 85, 370–378. https://doi.org/10.1016/j.ijbiomac.2016.01.004
19. Weng, L. & Elliott, G. D. (2014). Polymerization effect of electrolytes on hydrogen-bonding cryoprotectants: Ion–dipole interactions between metal ions and glycerol. *Phys. Chem. B*, 118(49), 14546–14554. https://doi.org/10.1021/jp5105533
20. Boral, S. & Bohidar, H. B. (2012). Effect of water structure on gelation of agar in glycerol solutions and phase diagram of agar organogels. *J. Phys. Chem. B,* 116(24), 7113–7121. https://doi.org/10.1021/jp3022024
21. Shin, M., Kim, T. & Suh, Y. W. (2017). Effect of glycerol on coke characteristics in the aromatization of aqueous glycerol solution. *Top. Catal.*, 60, 658–665. https://doi.org/10.1007/s11244-017-0773-5
22. Federica, R. et al. (2021). Degradation of film and rigid bioplastics during the thermophilic phase and the maturation phase of simulated composting. *J. Environ. Polym. Degrad.*, 29, 3015–3028. https://doi.org/10.1007/s10924-021-02098-2
23. Mehrotra, K. N. & Upadhyaya, S. K. (1989). Thermogravimetric, X-Ray and Infrared Studies on Calcium Soaps in Solid State. In Mittal, K. L. (Ed.). *Surfactants in Solution.* Boston: Springer US, 411–415. https://doi.org/10.1007/978-1-4615-7990-8_30
24. Ramón, A. et al. (2005). Separation of overlapping processes from TGA data and verification by EGA. *J. ASTM Int*. Retrieved 9 June 2025 from https://dl.astm.org/stps/book/178/chapter-abstract/59111/Separation-of-Overlapping-Processes-from-TGA-Data
25. Dina, F. et al. (2024). Impact of agar–glycerol ratios on the physicochemical properties of biodegradable seaweed films: A compositional study. *Int. J. Biol. Macromol.*, 280,135855–135855. https://doi.org/10.1016/j.ijbiomac.2024.135855
26. Guangbao, W., Shangsuo, Y. & Jijun, X. (2020). Thermal degradation kinetics of calcium stearate/PVC composite. *Res. Mater.*, 8, 100123. https://doi.org/10.1016/j.rinma.2020.100123
27. Rokhati, N., Hapsari, F. D. & Prasetyaningrum, A. (2023, February). The influence of calcium chloride and potassium chloride cross-linking agent on the physical properties of chitosan-carrageenan composite film. *AIP Conf. Proc.,* 2667(1), 050004. https://doi.org/10.1063/5.0129789

28. Shahad, K. et al. (2022). A review on the role of earthworms in plastics degradation: Issues and challenges. *Polymers*, 14(21), 4770. https://doi.org/10.3390/polym14214770
29. Liu, M., Huang, Z. B. & Yang, Y. J. (2010). Analysis of biodegradability of three biodegradable mulching films *J. Environ. Polym. Degrad.*, 18(2),148–154. https://doi.org/10.1007/S10924-010-0162-7
30. Letendre, M. et al. (2002). Physicochemical properties and bacterial resistance of biodegradable milk protein films containing agar and pectin. *J. Agric. Food Chem.,* 50(21), 6017–6022. https://doi.org/10.1021/jf011688h