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Effects of Different Processing Techniques and Sol-Gel Coating on Physical Properties of Starch and Clay-Based Biocomposite Material

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ABSTRACT

This study investigated the effects of different processing techniques and sol-gel coating on the physical properties of biocomposite material. Two dispersion series from corn starch, clay, and sorbitol were prepared by conventional and microwave-assisted processing, and casting technique. One film from each series was sol-gel coated by immersion. All the samples were subjected to moisture content (MC), water solubility (WS), water absorption (WA), FT-IR, DSC, and SEM/digital microscopy tests. The results showed that the coated films contained higher MC (11.5±0.5%) than the non-coated films (5.3±0.6%) and absorbed less water (44.7±12.4%), compared to the non-coated ones (166.3±2.5%). Non-coated films exhibited less solubility in water (26.1±0.2%) than the coated ones (51.0±0.7%). FT-IR test detected cross-linking (1723 cm^{-1} ester) in the microwave-assisted coated film. The sol-gel coating increased the latent heat of melting and specific heat values by 14.9% and 19.4% for conventionally fabricated samples, and 22.3% and 25.3% for microwaved films, respectively, whereas it reduced the temperature of melting by 23.1% for conventionally fabricated ones, and 6.6% for microwaved ones. Microscopic tests revealed that microwaved compact morphology indicated better gelatinization of starch. Overall, microwaving and sol-gel coating need further investigation to improve the physical properties of biocomposite materials for food packaging.

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Introduction

Food packaging is a tool for storing, transporting, distributing, retailing, and protecting foods at an optimal cost with a minimum environmental impact (Abdullah et al., 2022). Plastics have the largest market share (37%) in food packaging among paper and board (34%), glass (11%), and metal (9%) packaging materials. Polypropylene (PP) is the most used plastic in food packages in Europe (19.3%), followed by low-density polyethylene (LDPE) and linear low-density polyethylene (LLDPE) (17.5%), and polyethylenterephthalat (PET) (7.4%). In 2018, 39.9% of all manufactured plastics in Europe (61.8 million tons) were used for packaging. Globally, 350 million tons of plastics are produced annually, corresponding to 6% of all produced oil. Only 1% of the globally produced plastics is bio-based; the rest is fossil-derived, with a large carbon footprint equivalent to the aviation sector (Halonen et al., 2020).

Packaging food products is critical in preventing them from deteriorating and extending their shelf-life and stability (Campardelli et al., 2021). Due to the growing demand for eco-friendly biomaterials, research into alternative active packaging materials is significantly gaining attention (Reshmy et al., 2021). The global biomaterial market is estimated to be worth 3.6 billion dollars in 2022 and is expected to reach 6.5 billion dollars by 2027. By application, the packaging segment is witnessing a fast-growing food-packaging industry. By end-user, the food and beverages segment contribute to 51% of the biomaterials market globally. Therefore, valorizing new commercial biomaterials ensures food products' safety and quality (Kunam et al., 2022).

In Europe, food contact materials are regulated under EU Framework Regulation EC 1935/2004 on materials and articles intended to engage with food (Deshwal et al., 2019). Barrier coatings made of naturally renewable biopolymers have the potential to replace synthetic paper with petroleum-based ones in paper packing materials. According to The Future of Functional & Barrier Coatings for Paper & Board Packaging Report, the global demand for functional barrier coating applications in paper

packaging reached 3 million tonnes in 2018, with a market potential of 7.8 billion dollars. By 2024, it is estimated to be almost 4 million tonnes with a market potential of 11 billion dollars. Additionally, alternative, and new areas of innovation include the development of biodegradable coatings and a continual focus on weight reduction for resource efficiency (Adibi et al., 2022).

The advances in this field of research are challenging the improvement of physiochemical characteristics, barrier stability, and biodegradable nature of typical packaging through lightweight, durable, and non-toxic packaging material for food safety and stability without generating waste of petroleum-based hazardous materials (Reichert et al., 2020). Among the coating deposition technologies, sol-gel assisted ones are highly promising solutions. This process have some advantages, including the ability of producing pure materials at low synthesis temperatures and with no purifying process, resulting in the minimization of the environmental impact. Additionally, the sol-gel process is highly suitable: for the synthesis of hybrid organic-inorganic materials. Additionally, these coatings can be applied to a wide range of substrates using cost-effective, easy and viable techniques such as dip-coating (Suárez-Vega et al., 2024). The sol-gel technique is as an alternative method to develop packaging under extraordinary thermal conditions by providing high surface area and mechanical and barrier characteristics (Razavi et al., 2020). Among different biological methods, sol gel approach is easily used as effective method (Rout and Pradhan, 2024). For instance, sol-gel method has been used to encapsulate bioactive compounds in packaging materials. At the present time, multiple methods are combined for more practical and effective active packaging applications (Lu et al., 2024).

Native starch can be chemically or/and physically modified and used for food or non-food applications. Heat gelatinizes it with high water content, also so-called destructuring agent. Depending on the level of destructurization, it can be obtained for various products and applications (Avérous and Halley, 2009). A high compatibility occurs between starch matrix and fillers and the high improvement of the performances, including mechanical properties and water sensitivity because of the 3D hydrogen bonds network formed between different components (Y. Lu et al., 2005). For instance, montmorillonite is the most commonly used natural clay, and it is sued as a filler in starch-based materials. However, starch-clay combination generally suffers from poor dispersion and miscibility. Therefore, organic cations and plasticizers are important factors to improve this challenge (Chung et al., 2010).

The research on environment-compatible and biodegradable biomaterials, including high-barrier bio-based material in food packaging applications, highlights many other multidisciplinary topics in the field of food packaging, including active ingredients, surface chemistry, aspiring physicochemical properties, edible coating, characterization techniques, biopolymer matrix, nanotechnology, antioxidant, and antimicrobial finishing enables packaging for food biopreservation, environmental impact, and biodegradability, new regulatory issues and risk assessment, safety and health toxicokinetic modeling, end-user acceptance, manufacturing technologies, and processing, and so on (Yusuf and Khan, 2022).

Overall, biomaterials are promising for food science and technology, other disciplines of science such as materials, business and commercial applications, saving our planet, and the sustainability goals, environmental protection and climate change mitigation, as well as beyond . This study aimed to investigate the effects of different processing techniques and sol-gel coating on the physical properties of starch- and clay-based biocomposite material.

Materials and Methods

Materials

Corn starch (EDEKA Zentrale, Hamburg), clay (Rayher, Laupheim), sorbitol (Caelo 2620, Hilden), lecithin (Vitaquell, Hamburg), olive oil, gelatin (Aptei OP Pharma, Marienmünster), and glycerol 85% (Merck 1.04094.1000, Darmstadt) were purchased in Ansbach, Germany.

Methods

Fabrication of biocomposite films

The casting technique was used in the preparation of the biocomposite films. Four g of corn starch (4% w/w) and 4 g of clay (4% w/w) were dispersed in 92 g of distillate water and stirred for 10 min at room conditions. Two sampling series, i.e., conventionally (Dispersion 1) and microwaved assisted (Dispersion 2) were prepared separately (Figure 1).

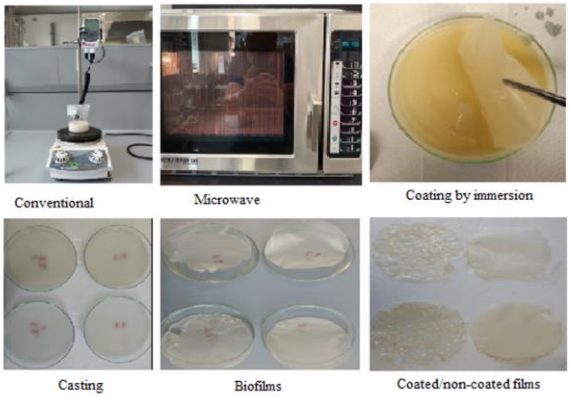


Figure 1. Fabrication of biocomposite materials

Conventional fabrication

The dispersion 1 was heated to 85℃ for 45 min by continuously stirring. Following that, 1.44 g of sorbitol (36% w/w of the starch) was added as a plasticizer, and the dispersion was kept at this temperature for 30 min. Finally, the solution was cast equally, i.e., 50 g each, onto two glass Petri dishes, i.e., conventionally processed non-coated (Sample 1.1) and coated (Sample 1.2) with a diameter of 120 mm and dried in a climatic chamber (Kambic KK-105 CHLT, Semic, Slovenia) at 50℃ and 60% relative humidity (RH) for 20 h. The dried films were then peeled off the petri dishes and kept in a desiccator for a few days before further testing (D'hooge et al., 2017).

Microwave-assisted fabrication

The dispersion 2 was heated to 85°C for 45 s by a microwave oven (Menumaster Commercial MFS 1200, Iowa, USA) at defrosting mode (with the output power of 360 W). Following that, 1.44 g of sorbitol (36% w/w of the starch) was added as a plasticizer, and the dispersion was again microwaved at this temperature for a further 20 s. Finally, the solution was casted equally, i.e., 50 g each, onto two glass Petri dishes, i.e., microwave-assisted non-coated (Sample 2.1) and coated (Sample 2.2) with a diameter of 120 mm and dried in a climatic chamber (Kambic KK-105 CHLT) at 50°C and 60% RH for 20 h. The dried films were then peeled off the Petri dishes and kept in a desiccator for a few days before further testing (Ballesteros-Mártinez et al., 2020; Tarique et al., 2021).

Sol-gel coating by immersion

Amongst the fabricated films, one from each series, i.e., conventionally and microwave assisted films were sol-gel coated by immersion. The sol-gel was prepared by dispersing 4 g lecithin, 2 g olive oil, and 1.1 g gelatin in 50 g glycerol and 42.9 g distillate water at 70°C until completely dissolved. After cooling down the solution at room conditions, it was subjected to high-speed homogenization by centrifuging at 12,000 rpm for 8 min. The samples were then immersed into this coating solution for 30 s. After that, the coated films were kept in a climatic chamber (Kambic KK-105 CHLT) at 50°C/60% RH for 24 h. Finally, they were stored in a desiccator for another 24 h (Hazrati et al., 2021).

Characterization and Testing Methodology

Moisture content (MC), water solubility (WS), and water absorption (WA) tests

The MC was determined by taking each sample's initial weight (W_i) via digital weighing scale. The film samples were then allowed for drying in an oven for 24 h at 105°C (W_f). Eq. (1) was used to calculate each film's MC (Hazrati et al., 2021).

$$MC\ (\%) = (W_i - W_f) \times 100 / W_i \quad (1)$$

Oven drying for the film samples was carried out at 105°C for 24 h. The initial dry matter of each specimen was fixed by examining the sample's weight and described as (W_i). This was supported by immersing each specimen in a beaker containing distilled water (100 mL). The beaker was then affixed, and the beaker was continuously stirred under constant stirring for 6 h at a temperature of 23 ± 2°C. Finally, the sample fraction that did not dissolve was isolated, allowed to dry for 24 h in an oven at 105°C temperature, and subsequently weighed (W_o). Using Eq. (2), the WS was determined (Figure 2) (Hazrati et al., 2021).

$$WS\ (\%) = (W_i - W_o) \times 100 / W_i \quad (2)$$

The WA was investigated by implementing the ASTM D 570-98 (1998) approach. The films were oven-dried at 50°C for 24 h and then cooled in a desiccator to ensure consistent weight. Then, the specimens were weighed at room temperature and immersed in distilled water. The soaked samples were cleaned with a clean cloth and reweighed. Using the recorded initial and final masses, the mass difference was calculated using Eq. (3) (Hosseinihashemi et al., 2011).

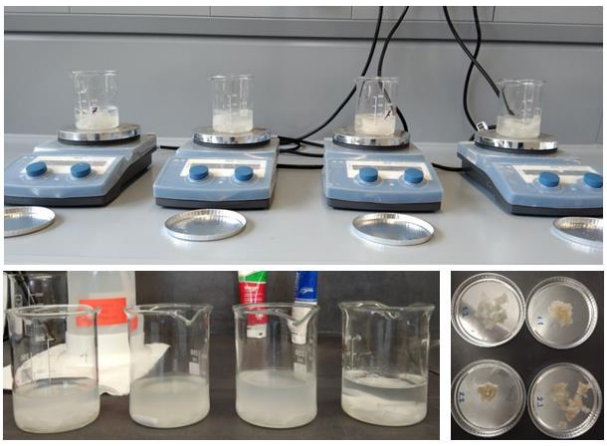


Figure 2. Water solubility test

$$WA\ (\%) = (M_f - M_i) \times 100 / M_i \quad (3)$$

Each measurement of the MC, WS, and WA tests was repeated five times.

Fourier transformed infrared (FT-IR) test.

The films were subjected to FT-IR analysis (Thermo Scientific Nicolet iS50 FT-IR, Dreieich, Germany) to examine the functional groups' existence. All FT-IR spectra were recorded at room temperature between 4000 and 600 cm^{-1} after 32 scans with a spectral resolution of 4 cm^{-1} using Thermo Fisher Scientific OMICS software (Medina et al., 2012).

Differential scanning calorimetry (DSC) test

The heat flow was measured using Mettler Toledo DSC (Greifensee, Switzerland). The specimens of 5 to 10 mg mass were heated from 20 to 200°C at a rate of 10°C min^{-1} and then cooled at the same rate to 20°C, waited at 20°C for 5 min, and finally reheated to 200°C. The Mettler Toledo STARe 17 software was used for thermal analysis [Latent heat of melting (LHM) in Jg^{-1}, melting temperature (T_m) in°C, specific heat (C) in $Jg^{-1}K^{-1}$] (Mettler Toledo, 2022).

Morphological Test

The microstructure of the uncoated samples was studied using Tescan Clara GMU Scanning Electron Microscope (SEM) (Bruno, Czech Republic). To improve conductivity and image contrast, all the samples were initially subjected to surface treatment at 0.30 mbar/3 min for cleaning, etching, and activating the samples by Diener Tetra 30-LF-PC (Nagold, Germany). Subsequently, they were coated with a layer of Pt/Pd in an argon atmosphere (30 mA, 0.1 mbar, 30 s) to sputter conducting layers to prevent Cressington 108 Auto Sputter Coater (Watford, UK) charging effects. The acceleration voltage used in SEM was 2 keV, the beam current was 5×10^{-9} mA, and the working distance was 10 mm. The samples were viewed and photographed at a magnification of 700x (Liu et al., 2015).

The morphological properties of the coated films were photographed at a magnification of 500x using a Digital Microscope (Keyence VHX-900F, Neu-Isenburg, Germany).

Statistical Evaluation

The mean (M) and standard deviation (SD) of the collected dataset of MC, WS and WA were calculated in Excel. One-way Anova including Tukey HSD test was applied to test for differences in all sample pairs (in-group and between-group) with a significance level of 0.05 ($P<0.05$) using SPSS 19 software (IBM Corporation, New York, USA).

Results and Discussion

This study investigated the effects of different processing techniques and sol-gel coating on the physical properties of biocomposite material. The results showed that the coated films had higher MC (11.5±0.5%) than the non-coated films (5.3±0.6%) and absorbed less water (44.7±12.4%), compared to the non-coated ones (166.3±2.5%). Non-coated films were less solubility in water (26.1±0.2%) than the coated ones (51.0±0.7%). FT-IR test indicated that there was a cross-linking (1723 cm^{-1} ester) in the microwave-assisted coated film. The sol-gel coating increased LHM (14.9%) and C (19.4%) values for conventionally fabricated samples, while 22.3% and 25.3% for microwaved films. On the other hand, the sol-gel coating decreased T_m by 23.1% for conventionally fabricated ones, and 6.6% for microwaved ones. Microscopic scanning showed that microwaved compact morphology exhibited better gelatinization of starch. Overall, microwaving and coating needs further investigation to enhance the physical properties of starct and clay-based biocomposite films for food packaging applications.

Moisture Content (MC), Water Solubility (WS), and Water Absorption (WA) Data

This study fabricated the biofilms using corn starch, clay, and sorbitol plasticizer dried at 50°C and 60% RH overnight. The sol-gel coating increased the MC of conventionally fabricated coated and non-coated films from 5.7% to 11.2% (by 126.5%), while it raised that of microwaved-assisted coated and non-coated specimens from 4.9% to 11.7% (by 137.9%), respectively (Table 1, Figure 3). Biofilm development is a challenging research area in the food sector (Paixão et al., 2019). The water resistance is the most widely studied property of biofilms (Perera et al., 2023). Properties of the starch-based films are affected by many factors, such as type of starch, processing time, temperature, type of plasticizer, storage conditions, and co-biopolymers (Thakur et al., 2019). Biomacromolecules generally show a strong hydrophilic character, and this drawback restricts their applications as the packaging material for food with high water activity. The efforts to improve the biopolymers' water-resistance ability include adding waxes and lipids as moisture barriers (Abdullah et al., 2022). Paraffin, waxes, or shellac resins have apolar characteristic with high content of long-chain fatty alcohols and alkanes in their structure, resulting in good moisture protectors (Goslinska and Heinrich, 2019). In the literature, some works present the MC of the starch-based materials at different temperatures and RHs, such as 6.62 to 11.85% at normal conditions (Oluwasina et al., 2021), 2.37 to 12.24% at 43 to 95% RH (Othman et al., 2019), 8.10 to 4.78% at 10 to 50°C (Mostafa and Sourell, 2009), respectively. RH influences MC, and the films stored at high RH conditions contain more moisture or water (Othman et al., 2019). Briefly, film drying temperature, air humidity and drying time influence the physicochemical state of the amylose matrix, influencing its degree of crystallinity (Frangopoulos et al., 2023). According to Marichelvam et al. (2019), corn starch is one of the most suitable materials for food packaging applications. An increase in the MC of the corn-starch film decreases the mobility of the starch molecules causing an increase in the rearrangement of crystal structure. For instance, the crystallinity of the starch films at 84% RH was found to be lower than that of the films at 22% and 54% RH (Suh et al., 2020). Temperature influences the binding characteristic of water molecules in biofilm matrix (Lei et al., 2014). In addition, in the presence of plasticizers (water and polyols), heat, and under shear stresses or in their absence, starch behaves as a thermoplastic. However, plasticizers have hydrophilic property, such as sorbitol and glycerol, which increase the water susceptibility to the moisture in the environment (Paixão et al., 2019). To reduce the disadvantage of moisture sensitivity; starch can be chemically modified, such as microwave-assisted cross-linking (García-Guzmán et al., 2022). The MC of corn starch-based films varied between 11.7 and 13.9% (Marichelvam et al., 2019), 10.64 and 13.63% with fructose-glycerol plasticizer, and 14.7 to 16.55% with sorbitol-plasticizer (Abotbina et al., 2021), respectively. The films with higher starch and glycerol content had higher MC due to the hydroxyl groups of glycerol and starch's hydrophilicity (Frangopoulos et al., 2023). In this study, the MC between the coated samples ($P=0.371813$) was insignificant, however remained significant for all other pairwise comparisons, i.e., conventionally fabricated non-coated and coated ($P=0.000033$), microwave-assisted coated and non-coated ($P= 0.00001$), and conventionally and microwave fabricated non-coated ($P=0.02479$) films, indicating that MC is mainly a process-driven property and influenced from film's composition, RH, and drying temperature in line with the literature.

The conventionally- and microwave fabricated non-coated films (Sample 1.1 and Sample 2.1) exhibited less solubility in water (25.9±0.2% and 26.3±0.7%, compared to the coated ones (Sample 1.2 and Sample 2.2) (51.5±0.2% and 50.5±0.1%). The WS of a biofilm is a critical property, especially for food packaging applications where water insolubility and resistance are required (Basiak et al., 2018). In the literature, starch film solubility is reported as 0.208 g dissolved/g dry films, almost equal to 20.8%. The aqueous medium for packaging and storage needs low solubility values for good stability (Onyeaka et al., 2022). Punia et al. (2022) demonstrated that the WS of the rice starch modified with heat-moisture treatment was decreased by 19.50%. Abotbina et al. (2021) showed that the WS of the corn starch-based films with fructose-glycerol plasticizers ranged from 37.99 to 51.26%. Ballesteros-Mártinez et al. (2020) reported that the starch-based films plasticized with 10% sorbitol exhibited WS between 18.15 and 28.68%. Shanbhag et al. (2023) revealed that the WS of the edible corn-starch film was the lowest one (23.25 ± 0.23%) amongst various blends of arrowroot powder, refined wheat flour, pectin, glycerol, and vinegar, and the plasticizer, i.e., glycerol, might be responsible for the increasing WS because of its hydrophilic nature through weakening the connections between polymer molecule chains, leading to more free space between chains available for water's diffusion into

polymer matrix. However, the lower degree of WS is regarded as one of the most desirable properties in food packaging applications (Tafa et al., 2023). In this study, the conventionally- and microwave fabricated coated films exhibited higher solubility in water (51.5±0.2% and 50.5±0.1%). These results show that the coated materials are not suitable for food packaging applications, particularly liquid food products, as previously indicated by Tarique et al. (2021). Additionally, Désiré et al. (2018) showed that the addition of glycerol (25 to 30%), oil (5 to 10%), and lecithin (0 to 5%) increased the WS of the starch-based films from all varieties. In this work, olive oil, lecithin, and glycerol also were used in the sol-gel coating dispersion, and the coated samples had the highest WS levels, as compared to the non-coated ones, in line with the literature. Another detail is the addition of clay to the biocomposite films. Slavutsky et al. (2012) argued that the stronger hydrogen bonds formed between the clay and starch chains with water decreased the film's WS solubility in the solvent. This study obtained similar results with Slavutsky et al. (2012). Another study by Zailani et al. (2022) revealed that microwave treatment of sago starch for 15 min exhibited more excellent solubility than native starch. The findings showed that the effect of microwaving was not significantly influential on the WS, compared to the conventionally fabricated films, in opposite to the work by Zailani et al. (2022). The statistical analysis revealed that the WS between non-coated samples (P = 0.309078) was insignificant, however remained significant for all other pairwise comparisons, i.e., conventionally fabricated non-coated and coated (P = 0.00001), microwave-assisted coated and non-coated (P=0.00001), and conventionally and microwave fabricated coated (P=0.00001) films, indicating that WS is independent from type of processing and mainly affected from sol-gel composition in line with the literature.

The coated films (Sample 1.2 and Sample 2.2) absorbed water (53.4±2.4% and 35.9±0.7%) less than the non-coated ones (Sample 1.1 and Sample 2.1) (168.0±1.7% and 164.5±0.9%). The WA ability is also a critical property for starch-based films due to the significant role of water in a plasticizer (Khan et al., 2019). In the literature, there are previously conducted studies on the WA property of starch-based biofilms with different plasticizers, such as ethylene vinyl alcohol reduced the amount of WA from 250% to about 100% during a 1 h soaking period (Glenn et al., 2007), 10% of corn starch with 20% of glycerol had the lowest WA (65%) (Nasir and Othman, 2021), biofilms immersed in water for 120 min had WA (194.3%) (Khan et al., 2019), corn-starch-based film with sorbitol-plasticizer exhibited WA (112%) (Hazrol et al., 2021), respectively. In this study, sorbitol (0.56 g sorbitol/g corn starch) was added as a plasticizer. Sorbitol affects the water barrier property of the films because it has a great affinity for water. Müller et al. (2008) determined that sorbitol over the concentration range 0.25–0.35 g sorbitol/g starch had less effect on the equilibrium water content, compared to that of glycerol. Similarly, Islam et al. (2020) reported that sorbitol has lower WA capacity and mixing of clay with starch also decreased the WA property in starch-based films. In contrary, the non-coated samples exhibited higher WA activity (168.0±1.7% and 164.5±0.9%), that are significantly greater than that of Hazrol et al. (2021) and other previous works. Briefly, the water molecules could diffuse to H-bonds with OH-groups of glucosyl units along the polymer chains in the starch/clay composite films, as previously described by Wilhelm et al. (2003). In this study, four g of corn starch (4% w/w) and 4 g of clay (4% w/w) were dispersed in water, including the plasticizer. Slavutsky et al. (2012) used 10 g of clay in 100 g of starch and reported the WA value between 13.0 and 14.5%. The WA results in this study ranged between 164.5 and 168.0%, which were significantly higher than the results obtained by Slavutsky et al. (2012). The statistical evaluation showed that the WA between all pairwise comparisons remained significant (P=0.00001), indicating that WA characteristic of starch- and clay based biocomposite material includes complicated physico-chemical interactions in the film matrix, that are difficult to control.

Microwaving was used to fabricate the biocomposite film to gelatinize starch quickly by saving time and energy, compared to other the conventional processing. The dispersions were heated to 85°C for 45 s by a microwave oven at defrosting mode (with the output power of 360 W). The sol–gel technique simplifies fabrication and provides film uniformity and the capacity to cover surfaces of any size and over vast areas at low processing temperatures (Butt, 2022). In addition, the microwave technique has been an alternative heating operation during polymer processing. It mixes the material with blowing agents such as water, expands the material by microwave radiation, and stabilizes the foam structure during drying. Microwave processing reduces heating time and enables homogeneous heating (Amaraweera et al., 2022). Microwave processing can alter the physicochemical properties of starch, such as gelation and rheology. Among chemical modifications, microwave radiation is preferred for oxidation and esterification of starch (Lewicka et al., 2015). Zhu et al. (2016) processed the starch dispersions from 30°C to 100°C within 1 min, 3 min, 5 min and 10 min using microwaving (maximum power 1000 W) and demonstrated that microwaving had an important role on the subsequent plasticizer migration and water permeation, compared to conventional heating. In this work, microwaving together with sol-gel coating increased MC and WS, while it decreased WA, in line with the findings of Zhu et al. (2016), particularly for the WA results of the microwaved assisted films.

Table 1. MC, WS and WA results of the biocomposite films

Sample no*	MC (%)	WS (%)	WA (%)
Sample 1.1	5.7 ± 0.3^{a}	25.9 ± 0.2^{b}	168.0 ± 1.7^{c}
Sample 1.2	11.2 ± 1.2^{a}	51.5 ± 0.2^{b}	53.4 ± 2.4^{c}
Sample 2.1	4.9 ± 0.6^{a}	26.3 ± 0.7^{b}	164.5 ± 0.9^{c}
Sample 2.2	11.7 ± 0.4^{a}	50.5 ± 0.1^{b}	35.9 ± 0.7^{c}
Sample 1.1 & Sample 2.1	5.3 ± 0.6^{a}	26.1 ± 0.2	166.3 ± 2.5^{c}
Sample 1.2 & Sample 2.2	11.5 ± 0.5	51.0 ± 0.7^{b}	44.7 ± 12.4^{c}

a, b, c < 0.05; Sample 1.1: Conventionally-fabricated non-coated film; Sample 1.2: Conventionally-fabricated sol-gel coated film; Sample 2.1: Microwave-assisted non-coated film; Sample 2.2: Microwave-assisted sol-gel coated film

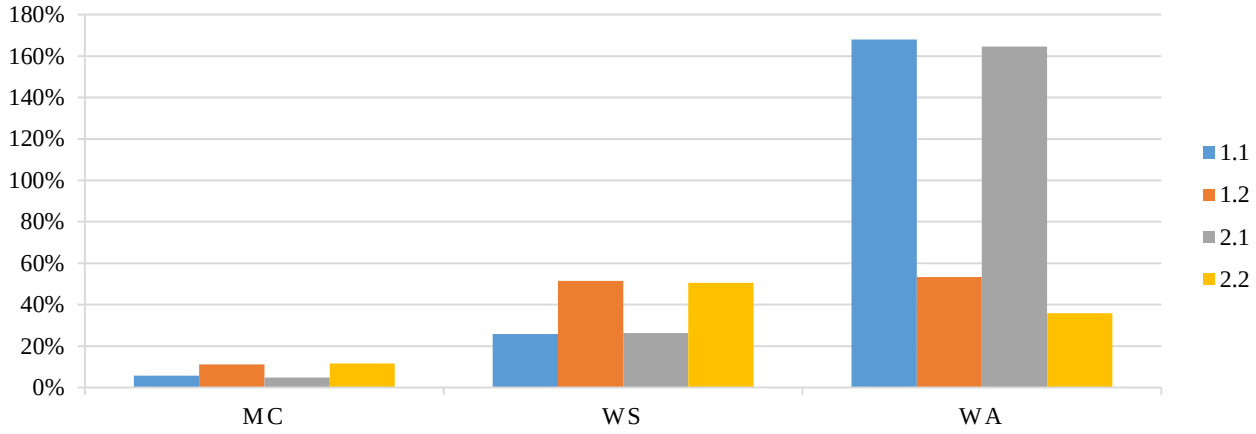


Figure 3. MC (%), WS (%) and WA (%) results of the biocomposite films

Sample 1.1: Conventionally-fabricated non-coated film; Sample 1.2: Conventionally-fabricated sol-gel coated film; Sample 2.1: Microwave-assisted non-coated film; Sample 2.2: Microwave-assisted sol-gel coated film

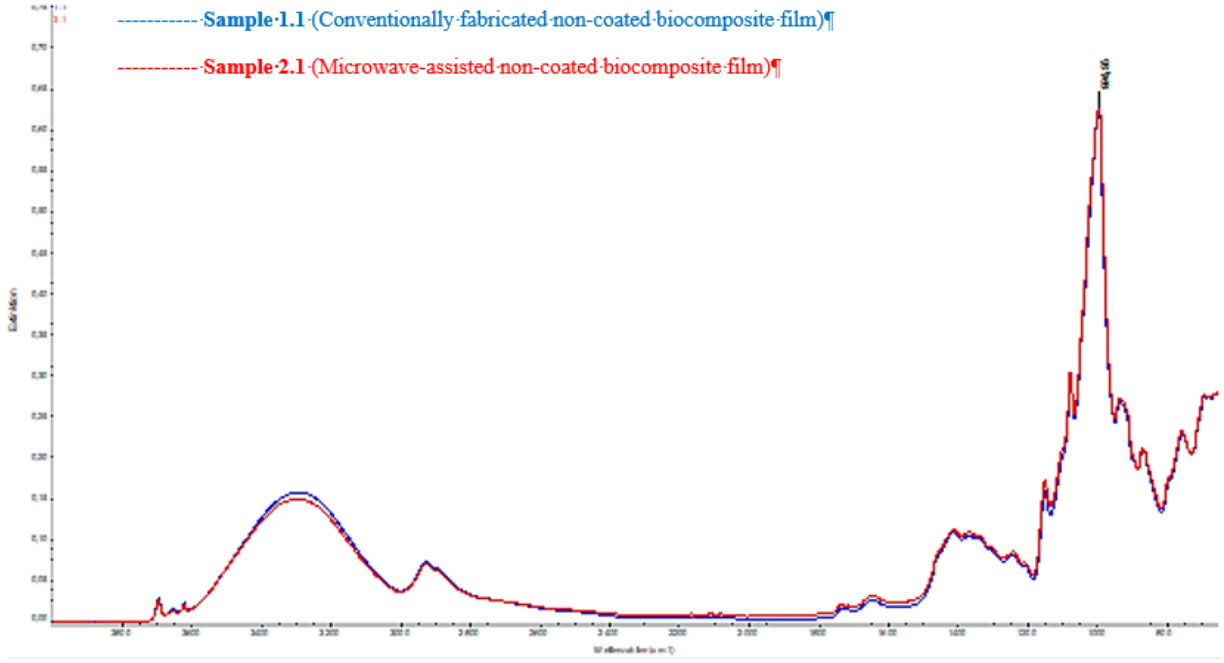


Figure 4. FT-IR spectra of the non-coated biocomposite films

Fourier Transformed Infrared (FT-IR) Spectrum

The FT-IR spectrum indicated the distinct changes to the chemical structure of the microwave-assisted sol-gel coated film, compared to the conventionally fabricated coated and other non-coated films. The most distinctive peak was at 1723 cm^{-1}, corresponding to the cross-linking, i.e., ester band (Figure 4, Figure 5). FT-IR spectroscopy is used to examine the chemical structure and composition of starch-based films (Onyeaka et al., 2022). The characteristic IR bands of starch at 3000–3600 cm^{-1}, 2800–3000 cm–1, 1630–1643 cm^{-1}, 1323–1332 cm^{-1}, and 1450–1469 cm^{-1} correspond to the O–H stretching vibrations of absorbed water present in starch, the band of flexion of the CH_2 deformation, the bending vibration of O–H bonds of absorbed water molecules in the amorphous region of starch, the C–O–H bending and C–O–C bending vibrations, and the $-CH_2$ symmetric scissoring, respectively (Amaraweera et al., 2022). Starch cross-linking is a technique of modification in which linear or branched chains are covalently interconnected by enhancing the hydrophobicity (García-Guzmán et al., 2022). Polar materials, like starch, can absorb microwave energy. Heat provided by microwave radiation may lead to significant changes in starch functionality even at a very short microwaving time of less than 1 min (Oyeyinka et al., 2021). This peak can explain the lower WA value of the microwaved-coated sample, in line with Gerezgiher and Szabó (2022) and Amaraweera et al. (2021). In addition, FT-IR peaks of the sol-gel coated biofilms at 3300 cm^{-1}, 2850 and 2950 cm^{-1}, and 1650 cm^{-1} are attributed to the O–H stretching vibrations of absorbed water present in starch, the band of flexion of the CH_2 deformation, and the bending vibration of O–H bonds of absorbed water molecules in the amorphous region of starch, respectively. Wang et al. (2016) prepared a starch polymer with clay, forming an organic-inorganic hybrid material with the assistance of a microwave oven. With the addition of clay, new peaks appear at 3618 cm^{-1} at the FT-IR spectrum, in line with the findings.

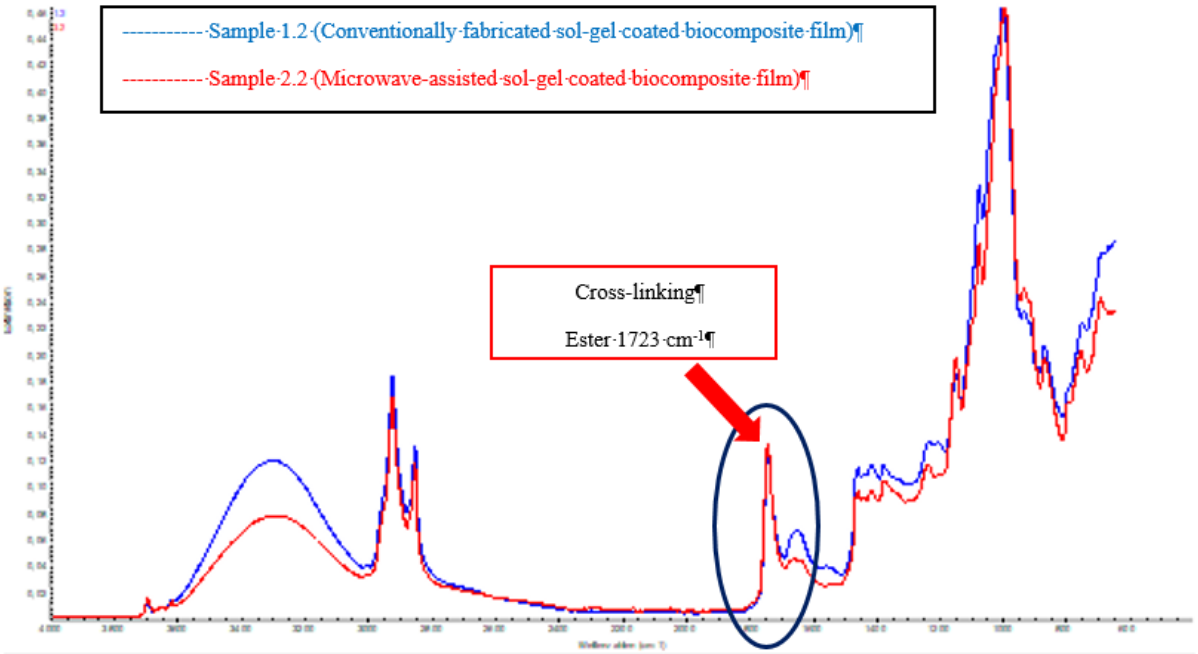


Figure 5. FT-IR spectra of the the sol-gel coated biocomposite films

Esterification happens under the influence of organic and inorganic acids and their derivatives (Lewicka et al., 2015). We did not add organic and inorganic acids and their derivatives. However, corn starch may include proteins, lipids, water, and very small amounts of phosphorus, magnesium, and calcium compounds. However, we did not see these peaks in FT-IR spectra of the conventionally fabricated coated and non-coated films. In other words, the microwave-assisted coated sample is cross-linked, which means the technique followed favors cross-linking to realize, as previously indicated by Molina et al. (2020) and Liu et al. (2018).

Differential Scanning Calorimetry (DSC) Thermographs

The DSC thermographs showed that the LHM, T_m, and C values of the conventional and microwave-fabricated non-coated films (Sample 1.1 and Sample 2.1) were found to be 118.64 and 100.95 Jg^{-1}, 109.58, and 134.90°C, and 0.72 and 0.58 $Jg^{-1}K^{-1}$, respectively. In contrast, the values for the coated samples (Sample 1.2 and Sample 2.2) were determined to be 120.11 and 93.27 Jg^{-1}, 95.46 and 101.77°C, and 0.83 and 0.62 $Jg^{-1}K^{-1}$, respectively (Table 2, Figure 6, Figure 7). The cross-linked film (Sample 2.2) exhibited lower LHM and T_m values than the conventional-fabricated samples, whereas the microwave-assisted coated- and non-coated films showed lower C values. Briefly, there were slight differences between the LHM values of the films.

In the literature, it is given that the cross-linked starch exhibits higher LHM (10.70 to 14.20 Jg^{-1}), compared to native starch (9.47 Jg^{-1}) (Shogren and Biswas, 2006; Punia et al., 2022). Another study reports that microwaved starch generally increases T_m and decreases process enthalpy (Lewicka et al., 2015). The findings showed that the cross-linked biofilm had lower T_m in opposite to Punia et al. (2022) and Lewicka et al. (2015), whereas its process enthalpy data was in line with Lewicka et al. (2015). The T_m of the crystalline structure is considered as a thermal stability indicator in the biocomposite films (Gazonato et al., 2019). For instance, Gazonato et al. (2019) reported 149.41°C to 155.48°C for the T_m of the crystalline structure of the corn starch-based biofilm. Similarly, Shapi'i et al. (2022) also indicated that the thermal stability of the starch-based biofilms decreased slightly whereby the T_m reduced from 316.32 to 289.11°C with the addition of chitosan filler. In this study, the highest T_m value was determined for the microwaved-assisted coated film (Sample 1.2) to be 134.90°C, and this finding might indicate the existence of strong interactions between clay particles and starch molecules under microwaving without sol-gel coating. On the other hand, T_m was 101.77°C for the microwaved-assisted coated film (Sample 2.2), with 1723 cm^{-1}, corresponding to the cross-linking.

In this study, the C values of the conventionally fabricated films (Sample 1.1 and Sample 1.2) were found to be 0.72 and 0.58 $Jg^{-1}K^{-1}$, respectively, whereas the values for the microwave-assisted films (Sample 2.1 and Sample 2.2) were 0.83 and 0.62 $Jg^{-1}K^{-}1$, respectively. It is seen that the microwaved films had higher C values than those of the conventionally fabricated ones by 15.3% and 6.9%. On the other hand, the sol-gel coating reduced the C values of the films by 19.4% for the conventionally fabricated sample and 25.3% for the microwave-assisted ones. The C measures the ability of a biocomposite material to conduct heat and is useful for the control of the multiple changes during food processes. The apparent C value of starch dispersions raises with temperature, and strongly dependent on the temperature and moisture content (Aklouche et al., 2019). The C value of native starch was 1.638 $Jg^{-1}K^{-1}$ whereas it was 1.87 $Jg^{-1}K^{-1}$ for the pregelatinized cornstarch (Mariam et al., 2008). Tan et al. (2004) reported the C value of the starch-water (50%) - glycerol (20%) dispersion at 85°C as 2.75 $Jg^{-1}K^{-1}$. However, the C values of the films manufactured in this study were lower than the values presented by Tan et al.

(2004) and Mariam et al. (2008). At this point, the effect of the clay should be considered. According to Islam et al. (2020), all types of clays can significantly improve the thermal stability. Accordingly, the lower C values of the films obtained in this work can be linked to the presence of the clay in the recipes. Additionally, clay's thermal conductivity is higher than starch (Wang et al., 2016), and therefore clay can retard the heat transfer in the material in co-operation with the role of the coating process. Briefly, these two factors would play a dominant role in the lower C values.

Table 2. DSC results of the biocomposite films

Parameter/Sample no*	Conventionally-fabricated		Microwave-assisted	
	Sample 1.1	Sample 1.2	Sample 2.1	Sample 2.2
Mass (mg)	3.45	3.68	1.55	2.53
Integral (mJ)	409.31	371.49	186.17	235.97
Latent heat of melting (Jg^{-1})	118.64	100.95	120.11	93.27
Melting temperature (T_m, °C)	109.58	134.90	95.46	101.77
T_f (°C)	185.82	196.51	167.19	173.39
T_i (°C)	21.92	23.17	21.73	22.80
C ($Jg^{-1}K^{-1}$)	0.72	0.58	0.83	0.62

* Sample 1.1: Conventionally-fabricated non-coated film; Sample 1.2: Conventionally-fabricated sol-gel coated film; Sample 2.1: Microwave-assisted non-coated film; Sample 2.2: Microwave-assisted sol-gel coated film

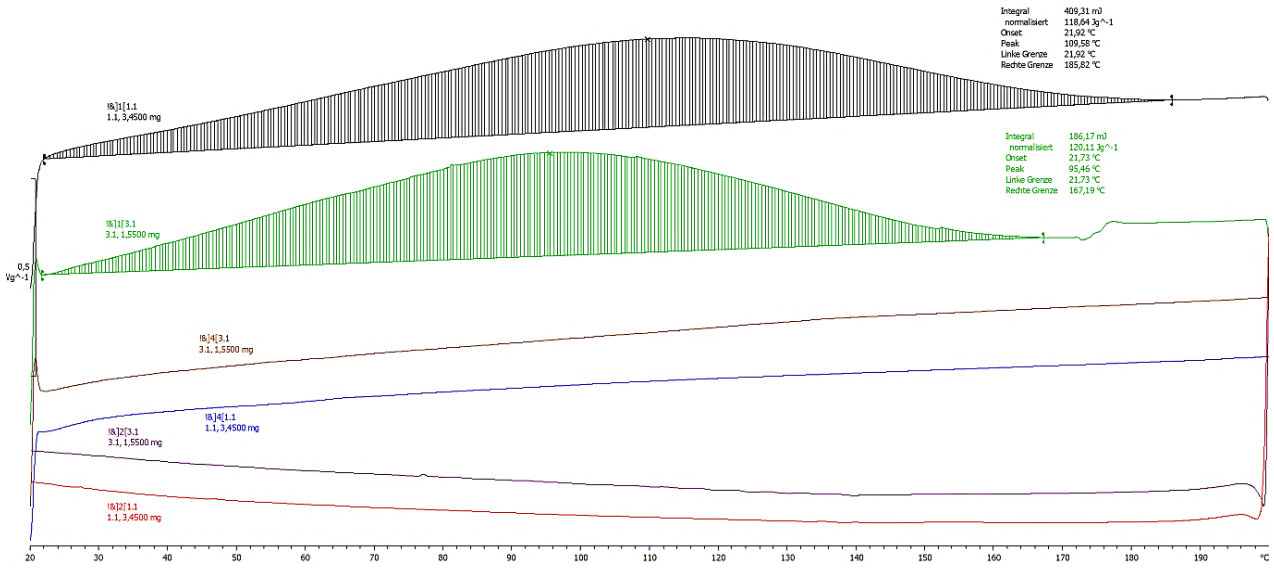


Figure 6. DSC graphs of the non-coated biocomposite films

Sample 1.1: Conventionally-fabricated non-coated film; Sample 2.1: Microwave-assisted non-coated film

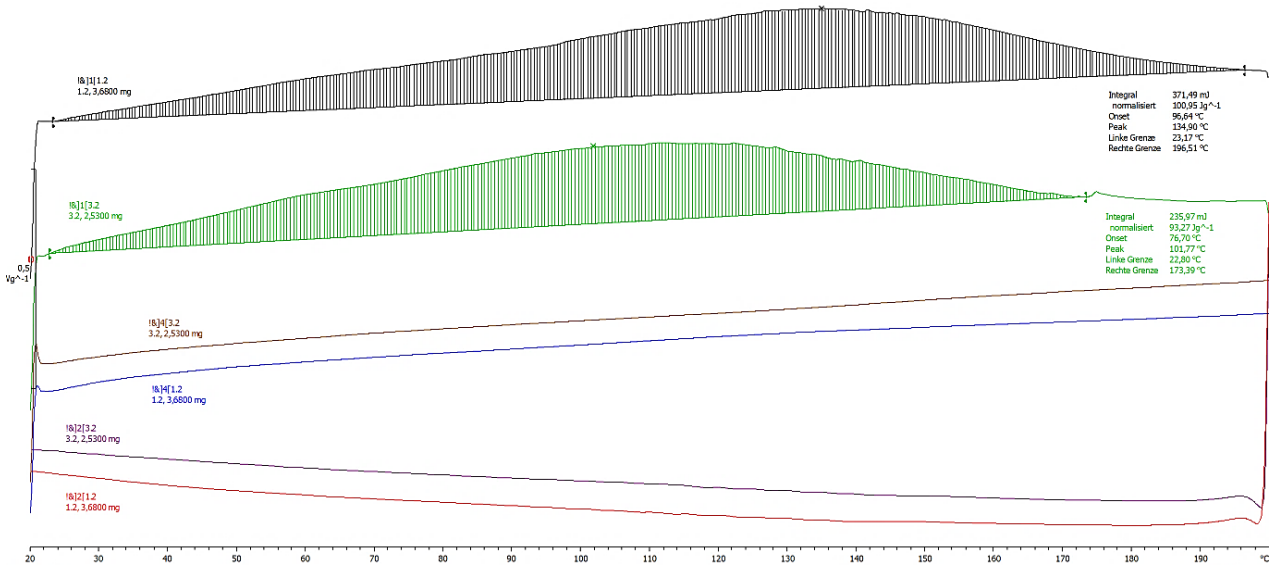
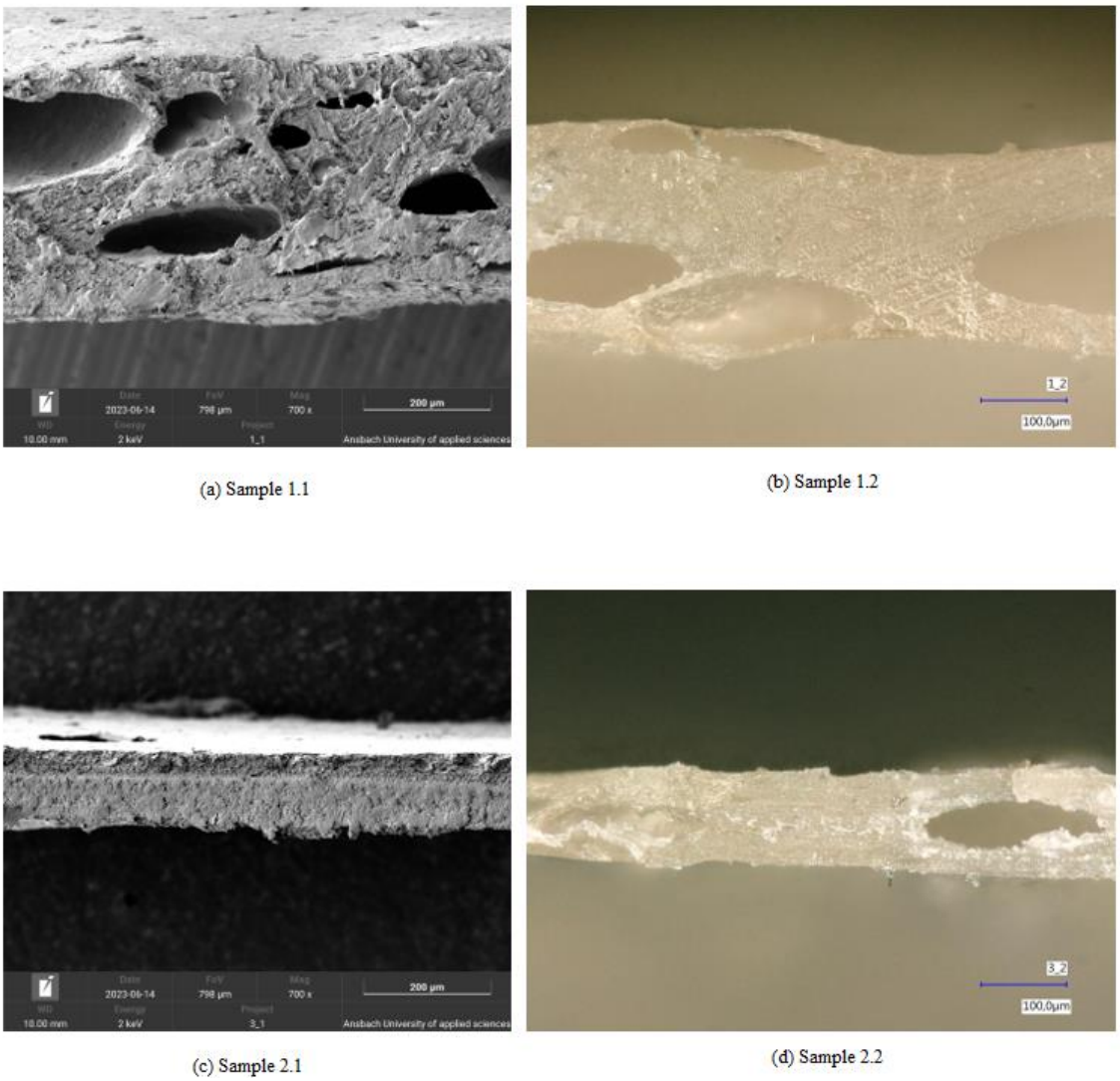


Figure 7. DSC graphs of the sol-gel coated biocomposite films

Sample 1.2: Conventionally-fabricated sol-gel coated film; Sample 2.2: Microwave-assisted sol-gel coated film



(a) Sample 1.1 (b) Sample 1.2

(c) Sample 2.1 (d) Sample 2.2

Figure 8. SEM and digital microscopy images of the biocomposite films

Sample 1.1: Conventionally-fabricated non-coated film; Sample 1.2: Conventionally-fabricated sol-gel coated film; Sample 2.1: Microwave-assisted non-coated film; Sample 2.2: Microwave-assisted sol-gel coated film

Morphology

The SEM images of the biocomposite films are shown in Figure 8. In this study, the conventionally fabricated films exhibited a thicker and more porous morphology than the microwave-assisted ones. The porous structure in the conventionally fabricated films might be due to the lack of gelatinization during heating (Amaraweera et al., 2022). On the other hand, upon the microwave treatment, the morphology changed into a thinner and more compact morphology. It could be evident that microwaving caused the better gelatinization of the starch. Further microwaving may lead to the formation of surface cracks (Łukasiewicz and Kowalski, 2011). The morphological findings in this study did not exhibit such defects.

Conclusion

Environmentally sustainable packaging prepared with green biocomposites is pivotal in the emerging sustainable food packaging industry. To meet consumer safety, quality, and convenience, food packaging incorporates various multidisciplinary activities, including materials science, food science, information technologies, and socioeconomics. In this manner, biopolymers and naturally occurring minerals such as native starch and clay can exhibit a significant synergy in food packaging applications with the involvement of various processing and coating techniques. Higher moisture barrier and absorption properties of the biodegradable packaging materials are the challenging factors restricting the efficient utilisation of this input. Thus, this study focused on understanding the effects of different processing techniques and sol-gel coating on the starch- and clay-based biocomposite films' physical properties. Overall, microwaving and sol-gel coating, compared to conventional fabrication without cost, could play an important role in developing natural biofilms for packaging implications. Further studies are needed to reveal the chemical mechanisms of the action of different processing techniques and coating operations that influence the physical performance of the biocomposite films.

Conflict of Interest

The author reports no conflict of interest.

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