

Storage stability of spray-dried flaxseed oil powders protected by wood hemicelluloses – Part 1: Physical properties and initial stage oxidation

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ABSTRACT

Polyunsaturated fatty acids, abundant in flaxseed oil (FO), easily oxidize, requiring stabilization preferably through encapsulation. Wood hemicelluloses, including galactoglucomannans (GGM) and glucuronoxylans (GX), effectively protect FO during spray drying, but temperature initiated radical reactions may induce oxidation during long-term storage. Additionally, spray-dried FO powders are prone to physical instability under fluctuating storage conditions, such as particle agglomeration and structural collapse, which can further accelerate oil oxidation. Understanding these changes and reactions is essential to ensure good quality and stability of spray-dried FO powder. Here, we investigated the physical properties of spray-dried GGM and GX encapsulated FO powders at relative humidity (RH) levels of 11–75% (22 °C) and assessed how these properties and storage conditions influenced the oxidative stability of encapsulated FO. The results indicated that, for both GGM and GX microcapsules, storage RH conditions did not affect their amorphous structure; however, powder aggregation, along with increases in particle size and water activity, was observed at high RH levels. In GX microcapsule powders, FO oxidized significantly within the first week of storage at all RH levels. In contrast, FO in GGM microcapsule powders remained stable, showing no signs of hydroperoxide formation for two months, which even surpassed the bulk FO. Increasing storage RH reduced the susceptibility of GGM powders to primary oxidation. This study demonstrates that GGM effectively protects highly unsaturated oils from oxidation at high temperature processing and long-term storage, making it an excellent material for producing healthy and functional products.

1. Introduction

Health benefits, especially those related to non-communicable diseases, associated with the consumption of adequate amounts of polyunsaturated fatty acids (PUFAs), which are abundant in marine and vegetable oils, have been well documented (Astrup et al., 2011; Ganesan et al., 2014; Li, 2015; Simopoulos, 2008). These benefits, along with their role in energy supply and as carriers of lipid soluble nutrients, have led to high consumer demand for food products and supplements containing PUFAs to maintain good health and wellbeing. Flaxseed oil (FO) is one of most abundant plant-based sources of PUFAs, containing 4.9–8.0 % palmitic acid, 2.2–4.6 % stearic acid, 13.4–19.4 % oleic acid, 39.9–60.4 % linolenic acid and 12.3–17.4 % linoleic acid (Goyal et al., 2014). Due to the high degree of unsaturation in the molecular chemical

structure of PUFAs in FO, it is easily oxidized under processing conditions and environmental stressors. This oxidation leads to the formation of unpleasant flavors and compounds that can deteriorate nutritional values and potentially cause adverse health effects (Guillén and Ruiz, 2005; Holstun and Zetocha, 1994). Microencapsulation of FO to prevent its direct contact with environmental stressors is a widely used strategy to improve its oxidative stability, and enhance its water dispersibility and handling properties. This method subsequently facilitates PUFA fortification into many food products (Gallardo et al., 2013; Gowda et al., 2018; Goyal et al., 2016, 2017; Rubilar et al., 2012) and pharmaceutical supplements (Ganesan et al., 2014; Goyal et al., 2014).

Over the past decades, many studies have focused on encapsulating FO by spray drying (Elik et al., 2021; Fioramonti et al., 2019; Gallardo et al., 2013; Tonon et al., 2012; Wang et al., 2022). However, the wall

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materials used in these studies are costly (e.g., guar gum) and/or derived from unsustainable sources (e.g., bovine milk-based ones). This necessitates the search for alternatives that are sustainable, natural, economical, and provide additional nutritional value to the final microcapsule powders. In our recent study (Ho et al., 2023), we investigated wood hemicelluloses, including softwood galactoglucomannans (GGM) and hardwood glucuronoxylans (GX), obtained from forest industry side-streams via pressurized hot water extraction (Kilpeläinen et al., 2014), as wall materials for spray-dried microencapsulation of FO. GGM consists of a β -(1→4)-linked D-glucopyranosyl and D-mannopyranosyl backbone, with α -(1→6)-linked D-galactopyranosyl side chains attached to the mannose units, which are partially acetylated at the C-2 and C-3 positions (degree of acetylation: 0.28–0.37). GX has a β -(1→4)-linked D-xylopyranosyl backbone branched with (1→2)-linked 4-O-methyl- α -D-glucopyranosyluronic acid and O-acetyl groups. Both hemicelluloses comprise about 20 % of wood mass and are reported to have good emulsifying capacity, low viscosity, high thermal stability, and strong antioxidant and prebiotic properties due to residual lignin content (Mikkonen et al., 2016; Mikkonen, 2020; Lehtonen et al., 2016; Deloule et al., 2020; Kynkänniemi et al., 2022). These characteristics make them promising wall materials for spray-dried microencapsulation. We found that depending on the ratios of wall materials to oil (1:1, 3:1 and 5:1), the oil encapsulation efficiency of GGM was 88–96 %, and that of GX was 63–98 %, both of which were higher than that of gum Arabic (49–92 %). Additionally, GGM and GX demonstrated a greater ability to protect the oil from oxidation during spray drying than gum Arabic. However, high temperatures during spray drying introduce a significant risk to the oxidative stability of FO microencapsulated powders, potentially initiating the formation of free radicals (precursors of oil oxidation). During storage, the formed free radicals could react with oxygen forming hydroperoxides, propagate the chain (increasing the rate of radical turnover) and undergo recombination and scission to form secondary products such as hydroxides, epoxides, aldehydes and polymers (Schaich, 2005). In powder form, microencapsulated FO capsules have considerably large in the surface area, thus their rate of oxidation and stability during storage could be governed by their contact and mass transfer with the surroundings, where reactants such as oxygen, radicals, relative humidity (RH) and metal catalysts exist (Damerau et al., 2014). An understanding of these changes of micro-encapsulated FO powders coated by GGM and GX could provide insight about their quality and storage stability, which subsequently orientates their potential applications. Given the high antioxidant activities of GGM and GX, which are attributed to phenolic residues composed mainly of lignin partially covalently bound with wood hemicelluloses (de Carvalho et al., 2021; Lahtinen et al., 2019), it is expected that GGM and GX could retard the oil oxidation of FO microcapsules during storage.

This study aimed to investigate the physicochemical properties and oxidative stability of spray-dried FO powders coated with GGM and GX, focusing on their ability to enhance FO oxidative stability and the impact of physicochemical changes in the powders on FO oxidation under varying RH conditions during long-term storage. To reflect practical storage environments, samples were stored at 11, 33, 55, and 75 % relative humidity (RH) at 22 °C for up to 34 weeks. The results were compared to those of bulk FO stored under the same conditions. During storage, samples were withdrawn and analyzed to assess how moisture uptake, structural changes, and molecular interactions between FO and GGM/GX contribute to the mechanisms underlying the physical stability of the powder over time. Additionally, oxidation of FO was investigated by monitoring primary oxidation products (hydroperoxides), secondary products (volatile and non-volatile compounds) and recombination products (polymers). To provide a thorough understanding of the relationship between physicochemical properties and FO oxidation in microcapsule powders, particularly the impact of changes in physicochemical properties on oil oxidation, the research results were reported in two distinct parts: part 1 focused on physicochemical

properties and initial stage of oxidation, while part 2 addressed a more in-depth understanding of FO oxidation pathways under the studied conditions. For this manuscript, we present the research results related to part 1. The study results facilitate the assessment of whether wood hemicelluloses can effectively protect highly unsaturated oils against oxidation, potentially serving as excellent wall materials in the production of stable and functional products in the food, pharmaceutical, and cosmetic industries.

2. Materials and methods

2.1. Materials

Spray-dried GGM powders were bought from Boreal Bioproducts (Espoo, Finland). Spray-dried GX powders were obtained from the Natural Resources Institute Finland (Luke). Both GGM and GX extracts were recovered by pressurized hot water extraction, followed by spray drying to obtain the powders. The main characteristics of GGM and GX powders were reported in our previous study (Ho et al., 2023). FO mainly consisting of 59 % (w/w) α -linolenic acid, 15 % (w/w) linoleic acid, and 14 % (w/w) oleic acid was obtained from Elixia Oil company (Somero, Finland).

Chemicals, reagents, and solvents used for oil extraction and analyses of primary oil oxidation products were of HPLC grade. These included iron(III) chloride (Tritisol®; Merck) and iron(II) chloride-4-hydrate (Fluka Chemie) as catalysts for oxidation, ammonium thiocyanate (Sigma-Aldrich) for colorimetric analysis, 1-decanol (≥ 95 %; Merck) as an internal standard, ethanol (99.5 %; Altia, Rajamäki, Finland) and heptane (Honeywell) as solvents for extraction and chromatography. Lithium chloride (≥ 99.0 %; Thermo Scientific), magnesium chloride hexahydrate (≥ 99.0 %; Fisher Bioreagents), magnesium nitrate hexahydrate (Thermo Scientific), and sodium chloride (≥ 99.5 %; Fisher Bioreagents) were used to establish and maintain RH levels inside the storage cabinets at 11, 33, 55 and 75 %, respectively.

2.2. Preparation of flaxseed oil microcapsules

The conditions for preparing FO microcapsules, including feed emulsion formulation and spray drying, were based on our previous study (Ho et al., 2023). These conditions yielded microcapsules with the highest encapsulation efficiency and stability against oil oxidation during spray drying. Feed emulsions were prepared with a 10 % (w/w) total solid concentration, using a GGM/GX-to-FO ratio of 3:1, dispersed in distilled water and stirred at 400 rpm for at least 24 h. After adding FO, the mixture underwent homogenization using an Ultra-Turrax homogenizer (T-18 basic, IKA, Staufen, Germany) at 12,000 rpm for 2 min, followed by a high-pressure homogenizer (Microfluidizer 110Y, Microfluidics, Westwood, MA, USA) at 800 bars for three cycles. The homogenized feed emulsions were immediately spray-dried using a laboratory scale spray drier (B-290, Buchi Labortechnik GmbH, Essen, Germany) with inlet/outlet air drying temperatures at 150/70 °C and flow rate of drying air at 32 m³/h. Throughout the preparation of feed emulsions and spray drying, sample containers were consistently covered with aluminum foil to shield the samples from direct light exposure, preventing potentially initiate oil oxidation. The powders collected from the sample containers and cyclone were stored for investigation into their stability.

2.3. Storage conditions for flaxseed oil microcapsules

Four cabinets (Fisherbrand™ acrylic desiccator cabinets, 4 shelves, 30.5 × 30.5 × 45.7 cm³) were prepared to maintain RH levels at 11, 33, 55 and 75 % with oversaturated solutions of lithium chloride, magnesium chloride, magnesium nitrate, and sodium chloride, respectively. To prevent direct exposure of the samples to light during storage, the cabinets were wrapped with aluminum foil. Before commencing the

storage experiment, the RH level in each cabinet was verified using a handheld humidity meter (HygroPalm 22, Rotronic AG, Bassendorf, Switzerland). Additional oversaturated salt solutions were added as needed to ensure that the targeted RH levels were reached and maintained.

After spray-drying, four batches of either GGM or GX microcapsules were immediately well mixed. Approximately 8 g of each powder was evenly spread in a 1-cm layer on a petri dish ($1.6 \times 9.0 \text{ cm}^2$, Thermo Scientific™). For each RH level (11, 33, 55, and 75 %), 12 petri dishes of either GGM or GX microcapsules were prepared and placed inside the respective desiccator cabinets. Control samples consisting of 8 g of bulk FO were also stored in petri dishes under the same conditions as the microcapsules. All cabinets were maintained at room temperature (22 °C). This temperature was chosen to represent controlled room conditions commonly used in stability studies (typically 20–25 °C) (Jiménez-Martín et al., 2016; Saga et al., 2011; Shen et al., 2010).

At specified time intervals (week 1, 2, 3, 5, 8, 12, 16, 22, 28, and 34), one petri dish from each sample set was withdrawn for physicochemical characterization and oxidative status determination. Freshly-prepared GGM and GX microcapsules, along with fresh bulk FO, were similarly analyzed for comparative purposes.

2.4. Determination of physicochemical properties of microcapsules

The analytical methods used to determine the physicochemical properties of the microcapsules were detailed in our previous study (Ho et al., 2023), thus we provide a brief overview here. Water activity (a_w) at 22 °C was measured using a water activity meter (LabMaster-AW, Novasina AG, Lachen, Switzerland). Particle size distribution was analyzed with a laser light scattering analyzer (Mastersizer Hydro 3000 SM, Malvern Instruments Ltd., Worcestershire, UK) integrated into an Aero S dry powder disperser. For these analyses, each sample was measured three times ($n = 3$) and the results are expressed as mean values (\pm standard deviation). The amorphous/crystalline structure was assessed using X-ray powder diffraction (XRD) with an Empyrean Alpha 1 X-ray diffractometer (Malvern Panalytical, Malvern Worcestershire, UK) equipped with copper radiation ($\lambda_{K\alpha 1} = 1.541 \text{ \AA}$) ($n = 2$). The samples were placed in plastic holders and secured with Kapton tape (Elgood Ltd., Vantaa, Finland). Measurements were conducted at 40 mA and 45 kV, over a 20 range of 5–50°, with a step size of 0.01°/s. Morphological characteristics were examined using a field emission scanning electron microscope (FESEM, S-4800, Hitachi, Tokyo, Japan), with two replications for each sample and images taken of at least five different locations for each replicate ($n = 2 \times 5$). The samples were mounted on double-sided carbon tape pre-fixed to the specimen holders, then flushed with dry N₂ gas to remove loose particles. They were then coated with gold/palladium (4 nm per cycle, two cycles) using a rotating sputter coater (208HR, Cressington Scientific Instruments, Watford, UK) for uniform coverage. SEM imaging was performed at 10 kV accelerating voltage, 10 μA emission current, 10 mm working distance. For thermal analysis, the samples were used without any pretreatment. Samples (5–10 mg) were sealed in 40 μL aluminum crucibles (ME-51,119,870, Mettler Toledo AG, Greifensee, Switzerland) with hermetic lids (ME-51, 119,871) and scanned using a differential scanning calorimetry (DSC823e, Mettler Toledo AG, Greifensee, Switzerland) under a dry nitrogen purge (50 mL/min), with a heating rate of 5 °C/min from 20 to 200 °C ($n = 3$). For structure and morphology analyses, one representative measurement was selected to illustrate in the figures due to the similarity across replications.

2.5. Determination of the oxidative status of flaxseed oil

2.5.1. Peroxide value

In our previous study (Ho et al., 2023), we described in detail the procedure for total oil extraction and analysis of primary oil oxidation products, determined as peroxide value (PV). Therefore, we briefly

outlined these methods in this study. These analyses were conducted immediately after withdrawing the microcapsules and bulk FO from the storage cabinets.

For total oil extraction, 0.2 g of microcapsules or 120 mg of bulk FO were dispersed in 2.0 mL of MilliQ water after which the hemicelluloses were precipitated by adding 2 mL of ethanol. The oil released was then extracted by 2 mL of heptane. To ensure proper separation of the organic layer, the samples were centrifuged at 2000 g for 5 min. Each sample was extracted in duplicate ($n = 2$). PV was determined as duplicates from each of the extracts ($N = 2 \times 2$) following the ferric thiocyanate method (Lehtonen et al., 2018, 2016) and obtained results were expressed as milliequivalents per kilogram of extracted oil (mEq/kg oil).

2.5.2. Fourier transform infrared spectroscopy (FTIR)

FTIR was employed to indicate oil oxidation and to reveal possible interactions between FO and GGM/GX. Infrared transmittance spectra of microcapsule powders and bulk FO were obtained using a Fourier transform infrared spectrometer (PerkinElmer, Waltham, MA, USA). After the background of clean crystal in the air was obtained, the samples were scanned with a frequency range of 4000–700 cm⁻¹, a spectra resolution of 4 cm⁻¹ and a scan number of 32. Each of the measurements were performed as triplicates ($n = 3$).

3. Results and discussion

To understand how storage RH affects the physicochemical properties of the FO microcapsules and how these changes impact oil stability, the FO microcapsules were monitored at intervals (e.g., week 1, 2, 3, 5, 8, 12, 16, 22, 28, and 34) until oxidation progressed beyond the propagation stage. This was indicated first by a significant increase in PV followed by a marked decrease. Hence, GX microcapsules were analyzed for up to 8 weeks, by which time they had become highly oxidized, while GGM microcapsules were observed over the entire 34-week storage period. Additionally, the morphology (SEM) and structure (XRD) of the FO microcapsules were reported only for freshly prepared samples, those stored for one week, those showing notable changes, and those at the end of the storage period.

3.1. Effects of RH on physicochemical properties of microcapsule powders during storage

3.1.1. Water activity

Water activity is the key factor affecting the physical, chemical, and microbial stability of dehydrated powders, including the oil oxidation of oil-containing products (Barbosa-Cánovas et al., 2020). Due to similarity in the spray drying conditions (170/50 °C), freshly-prepared GGM and GX microcapsules had a similar a_w value (~0.2). During storage, their a_w alteration followed a similar trend (Fig. 1), slightly decreasing at 11 % RH, but significantly increasing at 33–75 % RH, especially during the first week of storage. The changes in the microcapsule a_w result from water vapor exchange with environmental RH (Phosanam et al., 2021), driven by differences between water content in the microcapsules and surrounding storage RH (Ho et al., 2023; Li et al., 2011). Thus, higher RH levels led to a greater increase in the a_w of the microcapsules. At each RH level, there was almost no change in the a_w values of GX microcapsules after week 3 of storage, and of GGM microcapsule after week 8 – 12 of storage, indicating a moisture equilibrium between the microcapsules and storage RH.

3.1.2. Structure of microcapsules

XRD analysis was conducted to assess whether storage RH conditions induce structural changes, such as crystallization, in the microcapsules, which could lead to the release of encapsulated oil and subsequently accelerate oil oxidation (Drusch et al., 2006). As shown in Fig. 2, freshly-prepared GGM and GX microcapsules (day 1) had a completely amorphous structure, as indicated by the large humps observed on their

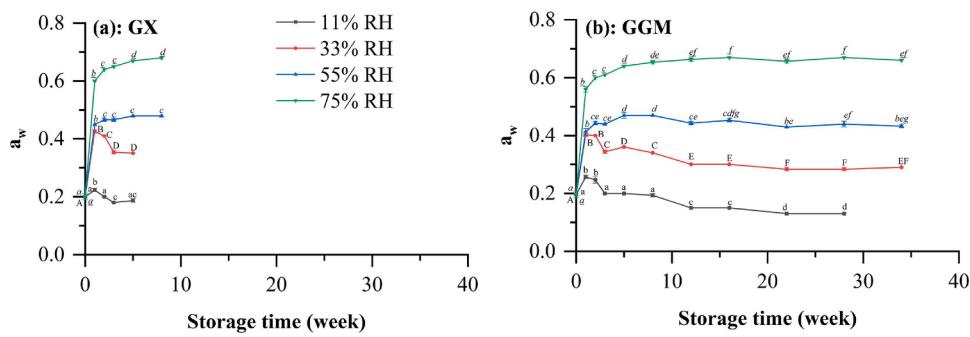


Fig. 1. Water activity (a_w) of GX and GGM microcapsule powders as a function of storage time under various RH levels. Different letters within each wall material and RH level indicate statistically significant differences in mean values ($p < 0.05$).

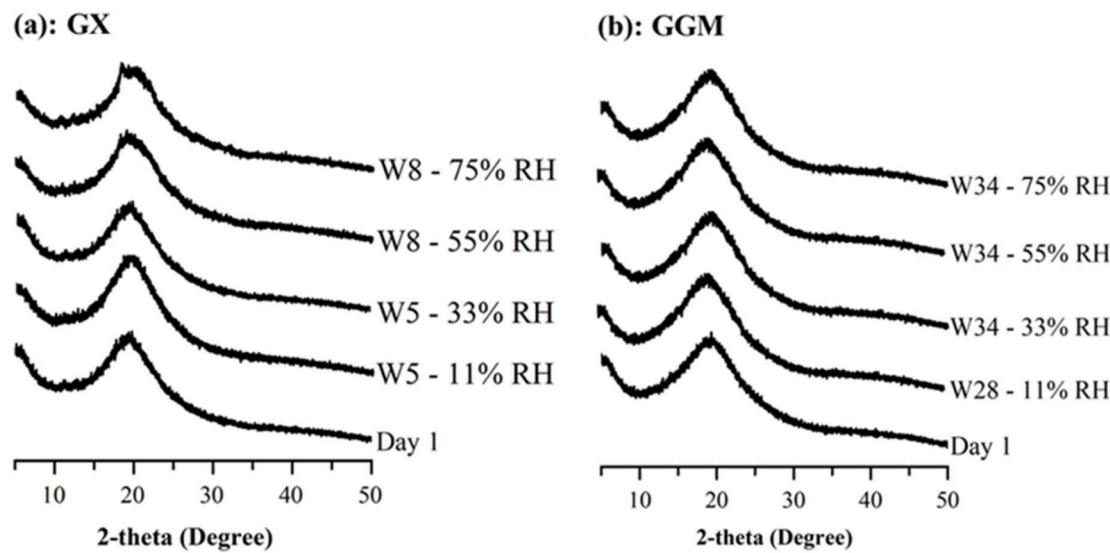


Fig. 2. Similarity in XRD spectra of GX and GGM microcapsules at the freshly-prepared stage (day 1) and at the end of the storage period (weeks 5 and 8 for GX microcapsules; and weeks 28 and 34 for GGM microcapsules).

XRD spectra. This amorphous structure of all microcapsule powders did not change during storage, regardless of RH levels. These results indicate that GGM and GX microcapsules are very stable against structural transformation. Crystallization of amorphous powders mainly depends on water content (governed by surrounding RH), temperature and molecular mass (Chiou and Langrish, 2007). Despite water uptake during storage at 33–75 % RH, the absorbed water could not be sufficient to act as a lubricant for molecular rearrangement into a crystalline structure. Therefore, all GX and GGM microcapsules can maintain their structural integrity.

3.1.3. Morphology

Given the high dependence of the functional properties of dehydrated powders on their surface structure, characterizing the surface morphology of microcapsule powder particles provides a deeper understanding of the mechanisms related to their reactivity when exposed to different environments such as air or water (Burgain et al., 2017). The freshly-prepared GGM and GX microcapsules were characterized by spherical-shaped particles with a wrinkled and uneven surface, devoid of apparent cracks or fissures, and exhibiting variations in size along with slight agglomeration (Fig. S1 – Supplementary materials). These characteristics are typical of amorphous spray-dried oil powders containing polymers (Vehring et al., 2007), and are consistent with findings reported in our previous study (Ho et al., 2023).

According to Fig. 3, both GX and GGM microcapsules stored at 11–55 % RH exhibited no apparent changes in their morphology and surface

structure throughout the storage period. In contrast, at 75 % RH, GX microcapsules began to clump and cake by week 2, whereas GGM microcapsules showed this phenomenon starting around week 5. Additionally, scratching and cracking were also observed on the surface of GX and GGM microcapsules at these respective time points, indicated by (*) symbols, after which this deterioration became more pronounced in both types of microcapsules. These results are consistent with visual observations, showing that aggregation and/or caking of microcapsule powders stored at 75 % RH was evident by week 2. However, the aggregates were fragile and easily broken during powder handling in containers and sample preparation for SEM imaging.

With their amorphous structure, both GGM and GX microcapsules are highly hygroscopic and metastable, making them particularly vulnerable to caking when exposed to high RH environments (Bhandari and Ho, 2020). Caking of the microcapsules at 75 % RH could be due to the formation of liquid bridges between the powder particles, resulting from the dissolution of the outer particle surface and/or the condensation of capillary moisture within the powder. This is caused by high water absorption from the storage environment, which aligns with the a_w results. At the same RH level, GX microcapsules were reported to have a much higher water absorption capacity than GGM microcapsules (Ho et al., 2023), which explains the difference in the time points at which their caking was observed. Despite the caking of microcapsules stored at 75 % RH, their amorphous structure remained intact, indicating that the physical changes caused by caking affected only the powder particle surface. Surface oil was reported to cause oil

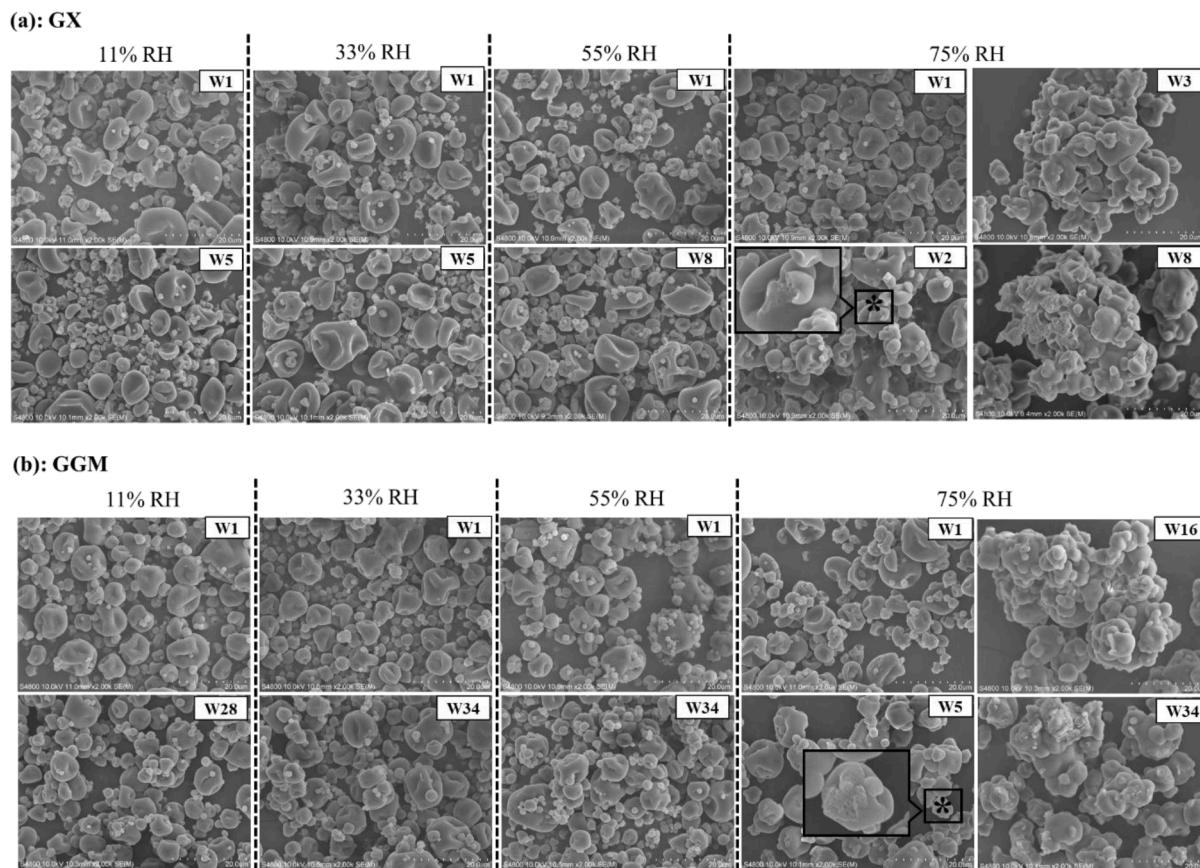


Fig. 3. Changes in the morphology of GGM and GX microcapsules during the storage period at various RH levels. SEM images are shown for samples taken at week 1 and at the end of the storage period, or at time points where significant changes in morphology were observed. The symbols (*) indicated scratching and cracking on the surface of the microcapsules.

microcapsules to adhere together (Binsi et al., 2017). However, despite the presence of surface oil in GX and GGM microcapsules i.e. 0.9–1.3 % (Ho et al., 2023), it is not the primary cause of caking. This phenomenon was observed only in microcapsules stored at 75 % RH, indicating that water adsorption from storage conditions is the main factor responsible.

3.1.4. Particle size distribution

The amount of powder surface exposed to environmental oxygen and the length of the oxygen diffusion path, both of which have been reported to govern the rate of oil oxidation (Linke et al., 2020a). The changes in volume-based ($D[4,3]$) and surface area-based ($D[3,2]$) particle diameters, as well as surface area, of GGM and GX microcapsule powders during storage are shown in Fig. 4, while their corresponding particle size distribution (PSD) curves are illustrated in Fig. S2. The particle diameters, i.e., $D[4,3]$ and $D[3,2]$ values, of freshly-prepared GGM microcapsules were 15.97 μm and 8.02 μm , respectively, which were larger than those of the corresponding GX microcapsules (9.04 μm and 6.15 μm). However, both types exhibited similar PSD curves — mono-modal distributions with peaks around 10 μm .

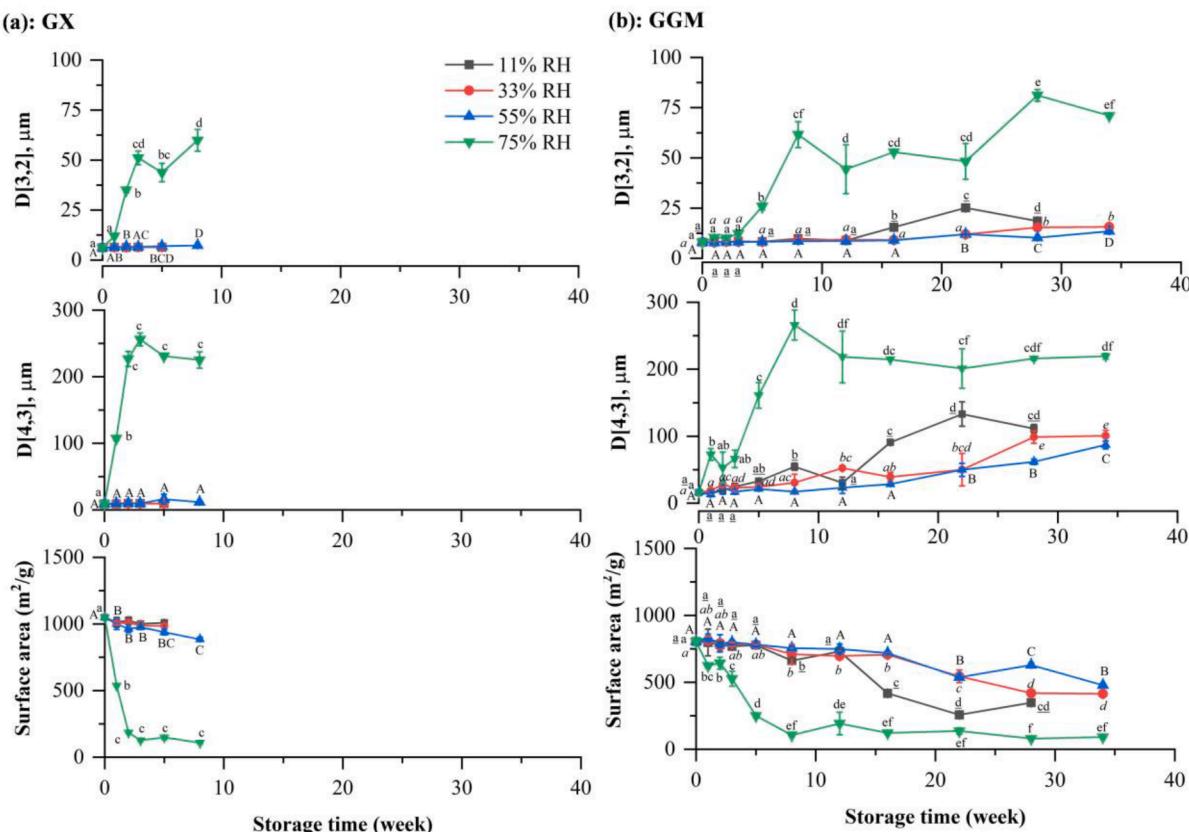
During storage, RH significantly influenced the changes in particle diameters of GX and GGM microcapsules. At 11–55 % RH, both $D[4,3]$ and $D[3,2]$ values of GX samples remained unchanged throughout the storage period, with nearly identical PSD curves. In contrast, for GGM microcapsules at the same RH levels, $D[3,2]$ remained nearly constant during the first 12 weeks, followed by a gradual increase, particularly noticeable at 11 % RH. $D[4,3]$ values began to increase after week 5. The results indicated that GGM microcapsules formed a proportion of large particles after 5 weeks of storage at 11–55 % RH. This was clearly observed in their PSD curves, which showed new peaks around 50–60 μm and an increase in intensity with prolonged storage (Fig. S2). At 75 %

RH, both types of microcapsule powders showed a drastic increase in particle diameters ($D[4,3]$ and $D[3,2]$) and the appearance of new peaks at large particle sizes ($>50 \mu\text{m}$) on their PSD curves within the first week of storage. However, these changes in particle diameters leveled off after 3 weeks for GX microcapsules and 8 weeks for GGM microcapsules. These observations of particle size changes due to RH are consistent with SEM analysis, which revealed the particle aggregation. Larger particle sizes result in smaller surface areas. The freshly-prepared GGM and GX microcapsules had surface areas of 804 and 1049 m^2/kg , respectively. It is noticed that the changes in surface area of the microcapsule powders during the storage period were inversely proportional to their $D[3,2]$ values.

3.1.5. Thermal properties

Determining the thermal properties, especially the glass transition temperatures (T_g), of oil microcapsules with an amorphous structure under different RH levels can help select suitable storage conditions to minimize oil oxidation. In our previous study (Ho et al., 2023), we found that the T_g of FO microcapsules ($a_w \approx 0.1$) coated with GX was 72–74 °C, while those coated with GGM had a T_g of 112–120 °C. However, in this study, freshly prepared GX microcapsules exhibited two thermal events at the onset points of the endothermic transition peaks at 72 and 118 °C, likely corresponding to T_g (Fig. 5). Meanwhile, freshly prepared GGM microcapsules showed a thermal event at 97.7 °C (Fig. S3), also corresponding to T_g . The inconsistency in T_g of GX and GGM microcapsules between studies is possibly due to differences in DSC scanning conditions and water activity of microcapsules.

During storage, water exchange between the microcapsules and the surrounding environment alters their water content and consequently T_g . Notably, T_g decreases with increasing water content (Roos and



3.2. FO oxidation in microcapsule powders and in bulk oil

3.2.1. Primary oxidation

Regardless of the excellent physical properties, FO oxidation was apparent both in GX and in GGM microcapsule powders. Storage conditions influenced some of the physicochemical properties affecting the rate of hydroperoxide formation and decomposition. At low RH, the formation and decomposition rates were greatest while both rates decreased along with the increasing RH.

Oxidation of FO was initiated already during spray drying: PV of FO in freshly prepared GX and GGM microcapsules was 9.4 and 5.2 mEq/kg oil, respectively, both being higher than that of bulk oil (3.4 mEq/kg oil). GGM demonstrated greater antioxidative properties than GX during powder preparation, which is consistent with our previous study (Ho et al., 2023). Also, during long-term storage, FO in GX microcapsules oxidized at a higher rate than in GGM microcapsules or as bulk oil (Fig. 6). The initial oxidation rate was greatest in the powder stored at RH 75% and having highest a_w . PV continued increasing reaching the highest values (180–300 mEq/kg oil) after two weeks of storage. For FO in GGM microcapsules, a significant increase in PV was observed only after 5 weeks at RH 11%, 12 weeks at RH 33%, 16 weeks at RH 55% and 34 weeks at RH 75%. Also, the rate of oxidation was opposite to a_w values.

Observed differences in the lag phase and in the rate of oxidation between GX and GGM powders are most likely originating to the surface area of initial powder particles but also to the residual lignin contents and their compositional differences (de Carvalho et al., 2021; Lahtinen et al., 2019). Smaller particle size (i.e., larger surface area) of GX microcapsule powders increased the exposure of FO to air. Also, the

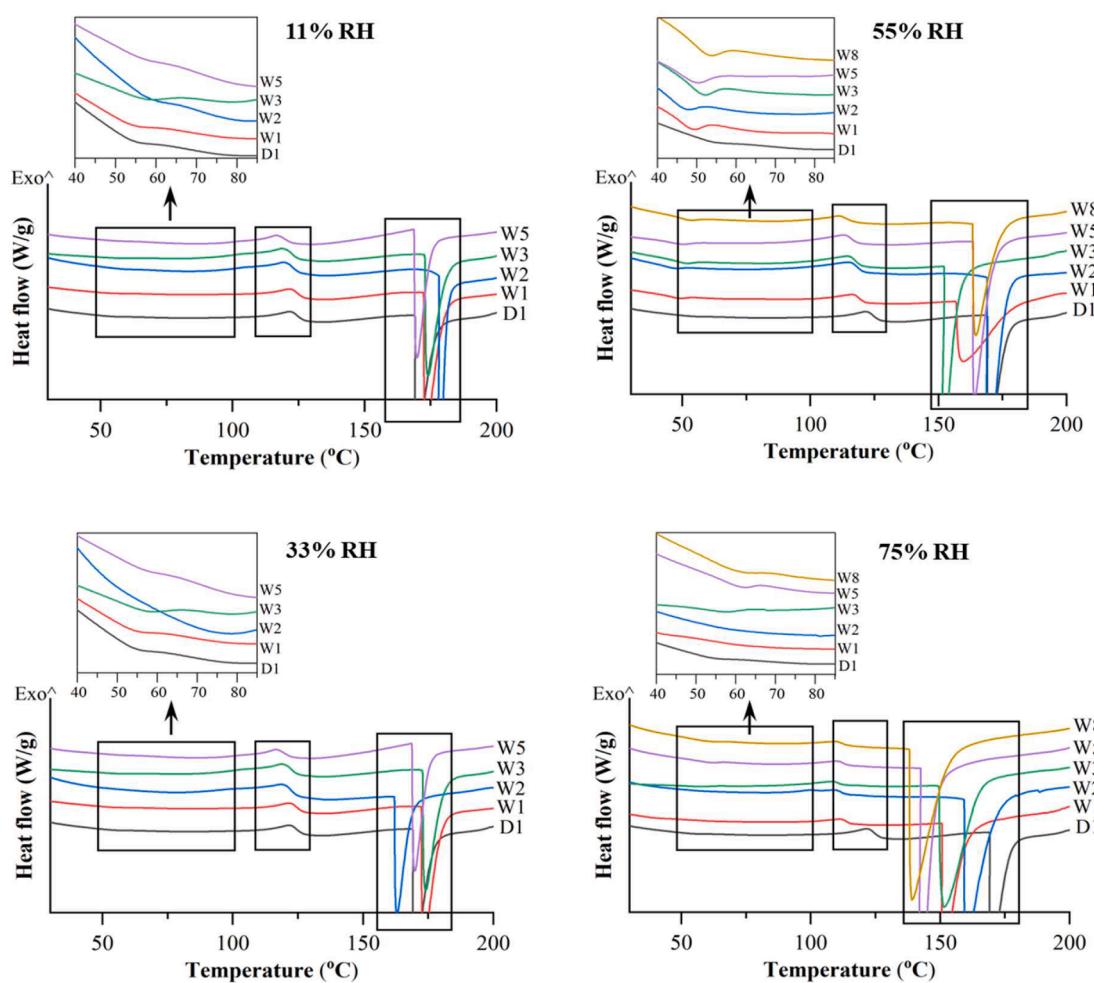


Fig. 5. DSC curves showing three endothermic thermal events of GX microcapsules during storage at various RH levels.

effect of exposure to heat and metallic surfaces within the machinery during spray drying cannot be overseen. These external factors potentially initiated and promoted FO oxidation more in GX than in GGM. Changes in the particle sizes during storage at various RH could not explain the observed differences in the oxidation behavior as they showed opposite effects in GX and GGM microcapsules. As previously shown in oil-in-water emulsions, the content and composition of lignin residues alter the oxidation rates and pathways of unsaturated lipids (Lehtonen et al., 2016, 2018). Interestingly, these antioxidative compounds functioned in the studied dry systems even though their movement was restricted. Their actions most likely took place both during powder preparation and storage. Phenolic compounds scavenge lipid radicals formed for example during heat treatment and bind transition metals readily present in crude emulsions prepared for spray-drying. During storage, higher RH resulted in the increased content of a_w enabling greater mobility of the wall material. This in turn enables physicochemical structures where oxygen permeability is decreased, and the action of phenolic compounds may be elevated. Both actions likely explain the obtained prolonging of the lag phase and decrease in the peroxide formation rate.

As radical reactions progress, hydroperoxides decompose into alkoxy radicals and volatile aldehydes and ketones (Schaich, 2005). When the decomposition becomes greater than the formation, a decrease in the PV is observed. For GX microcapsules, the decomposition rate was greatest for powders with the lowest a_w and least for those with the highest a_w (Fig. 6). This observation addresses that the higher the a_w is the more stable the powder becomes. Though the surface area of the

powder at RH 75 % decreased significantly during storage, the increased stability could not be explained by the surface area. For GGM powders, the observed decreases in the surface areas did not correlate with the stability. This is likely due to the same underlying factor responsible for the prolonged lag phase and reduced oxidation rate: Physicochemical structures enable efficient antioxidant action of lignin residues. When transition metals which catalyze decomposition of hydroperoxides into alkoxy and other secondary radicals are chelated the decomposition of hydroperoxides is suppressed. Also, phenolic compounds not only scavenge primary lipid radicals but also alkoxy and other secondary radicals formed during the decomposition of hydroperoxides.

For bulk FO, the rate of oxidation was similar regardless of storage RH levels. The lag phase lasted for eight weeks, followed by a very slow increase in PV throughout 28 weeks. After 34 weeks of storage, a significant increase in PV (570–840 mEq/kg oil) was observed for oils stored at RH 11, 33, and 75 %. At this point, the oil stored at RH 55 % was polymerized to an unmeasurable level. Comparing the oxidation behavior in bulk FO to that in the microcapsule powders is not straightforward because the surface area of the microcapsules is much higher, and the oxygen concentration at the oil interface is likely reduced in the solid-liquid interface (microcapsules) compared to the gas-liquid interface (bulk oil) (Partanen et al., 2008). Similar observations have been reported for fish oil (Kolanowski et al., 2006), soy oil (Sarkar et al., 2016) and sunflower oil (Hernández Sánchez et al., 2016). These factors provide part of the explanation for the higher oxidative stability of bulk FO compared to FO in GX and GGM microcapsules. Also, bulk oil was not exposed to heat treatment comparable to spray-drying

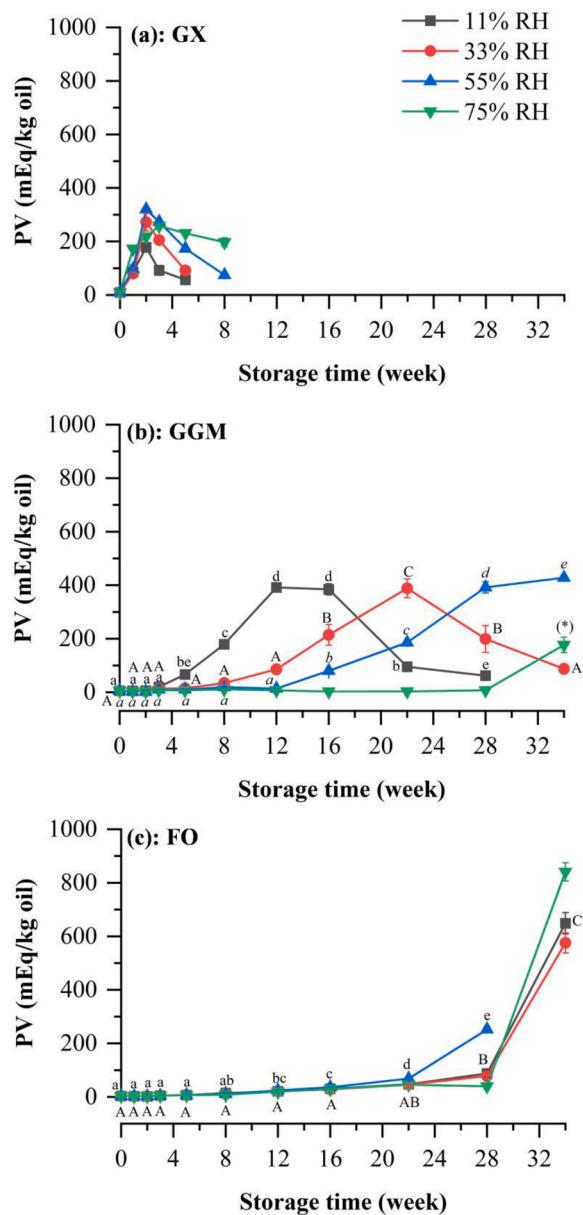


Fig. 6. Peroxide values (PV) of GX and GGM microcapsule powders (a and b, respectively) and bulk FO (c) as a function of storage time and RH. For GX microcapsules (a), significant differences in mean values ($p < 0.05$) were observed across storage times within each RH level, except between W1–W3 at 11 % RH, W1–W5 at 33 % RH, and W2–W5 at 75 % RH ($p > 0.05$). For bulk FO (c), no significant differences ($p > 0.05$) were observed across storage times within each RH level, except at W28 (31 % RH) and W34 (75 % RH), where significant differences were detected ($p < 0.05$). Statistical results for other comparisons are shown in the figure. Different letters within each wall material and RH level indicate statistically significant differences in mean values ($p < 0.05$).

conditions and therefore the potential initiation was omitted.

During storage, surface oil (non-encapsulated oil) in microcapsules is exposed to the environmental oxygen and has been reported to oxidize significantly faster than encapsulated oil (Aghbashlo et al., 2012; Shiga et al., 2017). However, as reported in our previous study (Ho et al., 2023), GX microcapsules had similar surface oil content as GGM microcapsules (0.9 % vs. 1.3 %), and yet the FO oxidation occurred more rapidly in GX microcapsules compared to GGM ones. Nevertheless, the majority of the oxidation in powders is explained by the oxidative status of the encapsulated oil due to its significantly higher proportion.

Environmental oxygen is able to penetrate through the wall material and participate in oxidation reactions (Linke et al., 2020a, 2020b).

These obtained results deserve more thorough investigation which will be presented in Part II. The degree of oxidation and potential mechanistic oxidation behavior differences between GX and GGM powders and between these powders and bulk oil will be further elaborated and discussed.

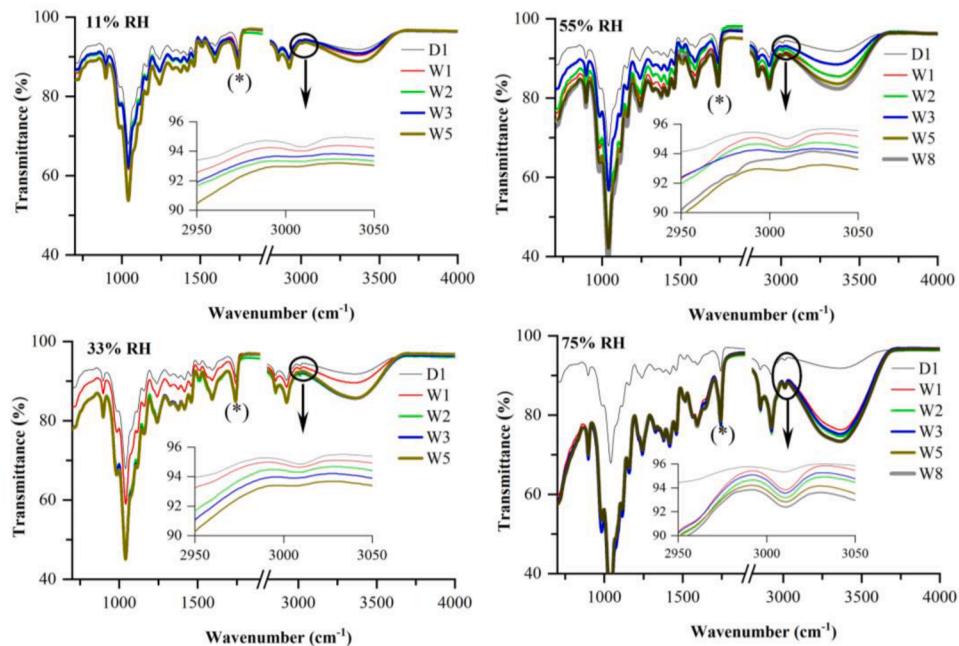
3.2.2. Oil oxidation investigated by FTIR

The FTIR spectroscopy has been used as a nondestructive and rapid analytical method to investigate the oxidative stability of oils and their products (Belhaj et al., 2010; Daoud et al., 2019; Hayati et al., 2005; Rohman and Che Man, 2013; Vlachos et al., 2006). The progress of oil oxidation is evaluated based on the increase in peak intensity at the wavenumber range of 3600–3100 cm⁻¹, which originates either from hydroxyl groups in water, hydroperoxides (R-OOH), or their breakdown products such as alcohols (R-OH) (Belhaj et al., 2010; Rohman and Che Man, 2013). In our study, the change in this peak was observed for all investigated microcapsules (Fig. 7). However, due to water exchange between the microcapsules and the storage environment, indicated by a significant increase in a_w , moisture content in the microcapsules increased. Thus, this region (3600–3100 cm⁻¹) could not be used to explain oil oxidation in the microcapsules. Similarly, the high water content of fish oil emulsion (>80 %) restricted the use of the FTIR region to record oil oxidation of the emulsion (Daoud et al., 2019). For microcapsules stored at 11 % RH, there was a reduction in a_w . Thus, an increase in the intensity of this peak (especially for GX microcapsules) during storage could be attributed to oil oxidation, which is consistent with the analytical results for PV indicating the formation of hydroperoxides. For all bulk FO samples, despite oxidation, changes in this peak were not clearly observed in their FTIR spectra, except for the samples kept at 55 % RH in week 34, where an increase in peak intensity was noted (indicated by the (*) symbol in Fig. S4). This suggests that FTIR may not directly detect lipid oxidation but rather captures changes in functional groups or secondary products that correlate with the progression of oxidation. It was visually observed that only the bulk FO samples at 55 % RH among investigated samples, formed a plastic-like film at week 34, indicating extensive polymerization of the oil. The oil polymerization was also confirmed by SEC-RI analytical results (data not shown). Guillén and Cabo (2000) reported that for edible oils, peak at 3600–3100 cm⁻¹ remained unchanged during the initial stage of oxidation and increased in intensity as hydroperoxides became present in significant proportions.

It was reported that as oil is oxidized, the cis-double bonds (C=CH) rearrange to trans-double bonds, resulting in the reduction or even disappearance of the peak at 3012–3006 cm⁻¹ (Belhaj et al., 2010; Daoud et al., 2019). For GX microcapsules (Fig. 7a), the intensity of this peak gradually decreased with extended storage time, and almost disappeared by week 2 at 11 % RH, week 3 at 33–55 % RH, and week 8 at 75 % RH, indicating RH-dependent oil oxidation. For GGM microcapsules (Fig. 7b), the changes in this peak were more complex and highly dependent on RH. At 11 and 33 % RH, this peak disappeared at weeks 16 and 28, respectively, while at 55 and 75 % RH, the peak fluctuated in intensity and shifted in position throughout the storage period. It was suggested that a reduction in the intensity of this peak could indicate the onset of an oxidation reaction — the lower the intensity values, the more advanced the oxidation of the sample (Guillén and Cabo, 2002). However, changes in the intensity of this peak were not consistently observed for GX and GGM microcapsules at various RH levels, or even for bulk FO (Fig. S4). A reduction in peak intensity was noted for the sample stored at 55 % RH in week 34, where the oil had already formed a plastic-like film. The results indicated that changes in this peak are more closely associated with polymerization of the oil and highlight differences in the storage stabilization of GX and GGM microcapsules, which warrants further investigation.

During oxidation, the peak near 1747 cm⁻¹, attributed to the

(a): GX



(b): GGM

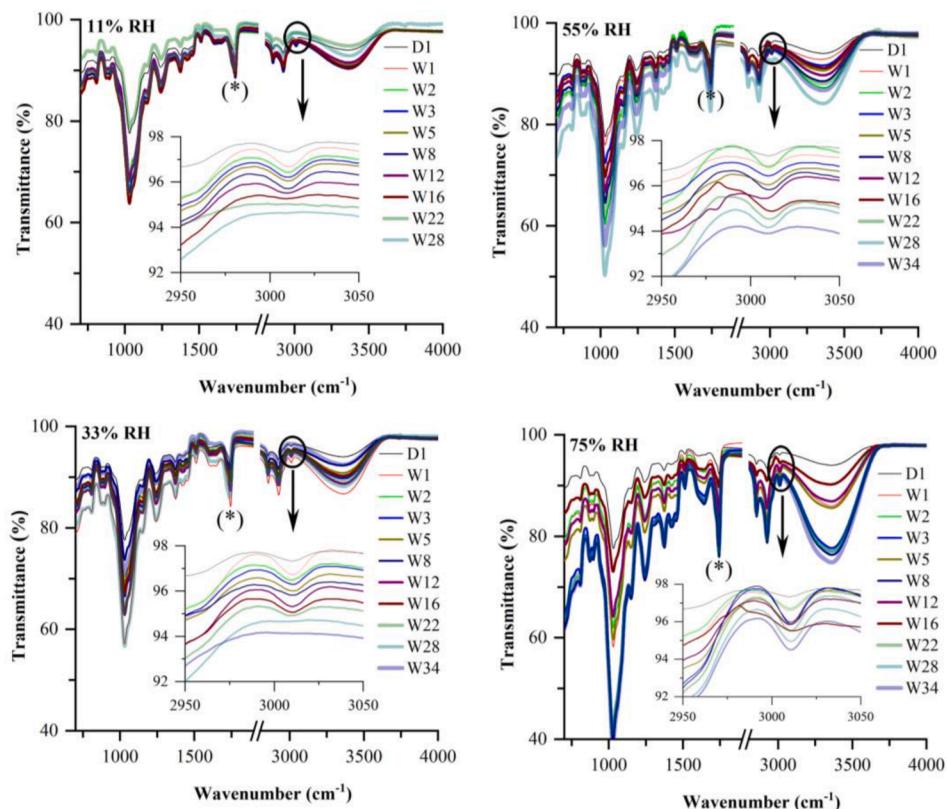


Fig. 7. FTIR spectra of GX and GGM microcapsule powders during storage under various RH levels. The small figures indicated the changes in the FTIR peaks at 3012–3006 cm⁻¹.

stretching vibrations of carbonyl groups in triglyceride esters (C=O), and the peaks at 1725 and 1705 cm⁻¹, related to aldehydes and ketones, should increase in intensity (Daoud et al., 2019). However, as oxidation advances, the peaks at 1725 and 1705 cm⁻¹ may overlap with the peak at

1747 cm⁻¹, reducing their intensity. In our study, the peak near 1747 cm⁻¹ (indicated by the (*) symbol in Fig. 7) increased with increasing PV and shifted to smaller values in both GX and GGM microcapsules during storage. However, these changes in the peak were not obvious for bulk

FO due to its high stability during storage. Results indicate that the microcapsules with frequency values below 1746 cm^{-1} are undergoing oxidation — the more advanced the oxidation, the lower the frequency value. Similar findings were also reported for edible oils (Guillén and Cabo, 2000) and oil emulsions (Hayati et al., 2005).

Another important peak for evaluating the formation of secondary oil oxidation products is at 972 cm^{-1} , representing the C-H out-of-plane deformation vibration of *trans*-double bonds. During oil oxidation, the *cis*-double bonds of unsaturated fatty acids undergo isomerization to the *trans*-form, leading to the appearance of this peak and/or an increase in its intensity (Daoud et al., 2019). In our study, this peak was observed only for bulk FO at week 34 across all RH levels, particularly evident in the sample at 55 % RH due to the polymerization. However, this peak was not observed for the microcapsules, likely because it was overlapped with the finger regions (800 and 1200 cm^{-1}) of polysaccharides (Guo et al., 2018). Therefore, this peak could not be utilized for studying oil oxidation in the FO microcapsules coated by GGM and GX.

FTIR analysis showed that FO oxidation in the microcapsules was greatly influenced by storage RH and interactions with the encapsulating materials. GX microcapsules exhibited more pronounced spectral changes, particularly the reduction of *cis*-double bonds, indicating reduced oxidative protection, possibly due to less effective encapsulation, greater oil exposure, and weaker oil-matrix interactions. In contrast, GGM microcapsules showed more variable changes, suggesting a different interaction pattern and potential stabilizing effect. While peaks related to primary and secondary oxidation products (e.g., 3012 – 3006 cm^{-1} and 1747 cm^{-1}) served as useful indicators, their interpretation was limited by moisture uptake and spectral overlap. These results highlight the complex role of wall material composition in controlling FO oxidation and the need for complementary methods to fully assess lipid stability in encapsulated systems.

3.3. Overall impact of physicochemical properties on oxidative stability of FO microcapsules

Overall, the physicochemical properties of spray-dried FO microcapsules, particularly water activity, particle size, morphology, and surface area, played a central role in governing lipid oxidation during storage. Smaller particles with larger surface areas, as observed in GX microcapsules, facilitated greater exposure of FO to oxygen, heat, and metallic surfaces during spray drying and storage, accelerating initial oxidation. In contrast, GGM microcapsules demonstrated greater oxidative stability, retaining a prolonged lag phase and delayed hydroperoxide formation even at elevated RH levels. Despite being hygroscopic and structurally amorphous, both GGM and GX microcapsules maintained their structural integrity across RH conditions, indicating that crystallization was not a contributing factor to oil oxidation. Notably, water uptake and particle aggregation at high RH (e.g., 75 %) contributed to changes in surface reactivity, but did not directly correlate with oxidation trends. This highlights the complexity of the oxidation mechanisms and the influence of encapsulation efficiency and wall material matrix composition. From a production and application perspective, these findings emphasize the importance of selecting suitable wall materials and optimizing processing parameters to ensure the long-term stability of encapsulated FO. GGM demonstrated superior performance as a wall material for FO encapsulation, effectively mitigating oxidative degradation, even under elevated RH conditions. This makes GGM microcapsules highly suitable for functional food, nutraceutical, or cosmetic formulations where product's shelf-life and FO integrity are critical. The observed physicochemical and oxidative stability of GGM microcapsules further indicate their capacity to endure industrial processing and fluctuating storage environments, supporting their potential in the development of stable, health-enhancing products enriched with FO.

4. Conclusion

We report the first part of our study on the storage stability of spray-dried FO microcapsules coated with GGM and GX at 11–75 % RH, focusing on physical characterization and early stage oil oxidation. During storage, GX and GGM microcapsules exhibited similar physicochemical changes, maintaining their amorphous structure across all RH levels, with aggregation and size increase observed specifically at 75 % RH. FO in GX microcapsules was less stable than in GGM microcapsules. In the second part of our study, we will elaborate further the influence physicochemical properties and storage conditions have on the degree of oxidation and potential mechanistical differences in the oxidation behavior between GX and GGM powders. As compared to the oxidation of bulk FO, microencapsulation of FO by GX and GGM did not improve its storage stability, except for the GGM microcapsules stored at 75 % RH, which showed comparable stability to bulk FO. However, the purposes of FO microencapsulation are not only to improve its storage stability but also to facilitate its fortification into various products, thereby developing stable, functional food products containing polyunsaturated fatty acids. The study results highlight the robust nature of GGM in preserving the structural stability of encapsulated FO, making them promising candidates for use in various industrial applications where moisture exposure is a concern.

Future research should focus on evaluating the functionality of GGM-based FO microcapsules in real food systems with diverse physicochemical environments, such as varying pH levels, water activity, and thermal or mechanical processing conditions. It is essential to assess how the microcapsules perform during typical food manufacturing steps (e.g., mixing, heating, freeze-drying) and to examine their compatibility with a range of ingredients and food textures. Additionally, comprehensive studies on sensory attributes, oxidative protection under complex food matrix conditions, the release behavior of encapsulated fish oil, and compliance with food safety and regulatory standards are critical for practical applications in the functional food and nutraceutical sectors. Safety assessments should include toxicological evaluations, such as *in vitro* and *in vivo* assays, to confirm the absence of harmful effects from the products or their degradation and oxidation byproducts, in line with guidelines from regulatory authorities such as the European Food Safety Authority. Moreover, to better simulate storage conditions in warmer climates, future studies should investigate the storage stability of these microcapsules at elevated temperatures above $22\text{ }^{\circ}\text{C}$. These initiatives will help position GGM as a high-performance, bio-based encapsulation system capable of delivering stable, health-promoting fish oil across a variety of food products.

Ethical statement - ethical statement - studies in humans and animals

The research presented does not involve any human or animals.

CRediT authorship contribution statement

Thao M. Ho: Writing – review & editing, Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Conceptualization. **Mari Lehtonen:** Writing – review & editing, Methodology, Investigation, Formal analysis, Conceptualization. **Heikki Räikkönen:** Writing – review & editing, Formal analysis. **Abedalghani Halahlah:** Writing – review & editing, Formal analysis. **Kirsi S. Mikkonen:** Writing – review & editing, Supervision, Methodology, Funding acquisition, Conceptualization.

Declaration of competing interest

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

improvement.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.fufo.2025.100744](https://doi.org/10.1016/j.fufo.2025.100744).

Data availability

Data will be made available on request.

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