

Aqueous polymer dispersions from long chain cellulose fatty acid ester for coating of paperboard

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ABSTRACT: Fiber-based substrates are coated with aqueous polymer dispersions to obtain the necessary barrier properties for, e.g., food service, takeaway, and other packaging applications. There is interest to replace non-renewable substances driven by the concerns over the price stability and depletion of fossil resources, environmental and safety issues, and legislative actions.

In this study, we demonstrated that stable aqueous polymer dispersions with solids content of at least 35% can be prepared from a long chain cellulose fatty acid ester (cellulose octanoate) using both solvent-based and thermomechanical processes. In the solvent-based process, water and additives were mixed with a polymer dissolved in chloroform followed by solvent removal. In the thermomechanical method, water and stabilizers were added into polymer melt under mixing in a pressurized reactor.

Dispersions were tested as coatings on paperboard and assessed for their grease resistance and water and oil barrier. Oil barrier was clearly improved with most of the dispersions. In addition, proper film formation was necessary for achieving improved water barrier. However, the stabilizing system had a clear impact on the dispersion stability and the water barrier performance of these coatings.

Application: This study demonstrates that aqueous polymer dispersions can also be prepared from preformed cellulose-based polymers using different techniques. These dispersions can be applied, for example, as barrier coatings for different fiber-based packaging materials.

Aqueous polymer dispersions are used in paints, binders, adhesives, primers, and sealants for numerous applications, and they can be processed further into toners, powders, and foams [1-7]. Polymer dispersions are also used as barrier coatings for paper, paperboard, molded pulp products, and other fiber-based materials to provide protection against grease, oil, water, water vapor, and gases [8]. Dispersions can be applied using printing and on-machine and off-machine coating methods, and compared to extrusion coatings of a similar polymer, they enable, for example, thinner coatings [4,9,10].

Aqueous polymer dispersions are defined as stabilized colloidal polymer particles in water [11]. However, preformed water-insoluble polymers are not amenable to polymerization in aqueous systems [9,12-14]. Techniques of interest here for preparing aqueous dispersions based on such polymers can be divided roughly into solvent and thermomechanical processes.

Solvent-based techniques involve the use of a solvent containing the dissolved polymer and an aqueous medium with additives [12,13,15-24]. These are combined under mixing, and the solvent is removed. The mixing process and dispersion components have a major impact on the particle size distribution and the solids content of the dis-

persions. While these methods enable small particles with little thermal stress on the polymer, the main challenges include safety concerns and an additional process required for recycling and recovering the solvent.

Thermomechanical methods utilize mixing polymer and water with additives at elevated temperatures in an extruder, reactor, or batch mixer [2-7,9,10,16,25-32]. The process parameters and the rheological properties of the polymer have a strong impact on the particle size distribution, and polymers prone to hydrolyses require special attention. These methods typically result in a higher solids content and larger particles than the solvent-based techniques.

While such dispersions can be produced from petroleum-based preformed polymers [4,5,9,21,28,31], there has also been interest in using these techniques for biopolymers [1,2,6,7,10,12,13,16-20,22,25,27,30,32]. However, there are only few cases where dispersions have been prepared from cellulose or starch esters, especially those with a substituent length exceeding six carbon (C6) atoms. These long chain fatty acid esters of abundant natural polymers are hydrophobic and thermoplastic, enabling melt processing [33-36]. Tanaka et al. [37] provided methods for preparing dispersions from starch esters (C2-C18) with a high degree of substitution, while a thermomechanical method has

been suggested for cellulose esters consisting of ester groups up to C18 [38].

Additives are necessary for producing stable dispersions, adjusting their properties for a specific coating or printing technique, and optimizing the final coating performance. Plasticizers are often needed for efficient melt mixing [1,5,16,29,38]. Additives also include surfactants and colloidal stabilizers [1,2,4,5,16,27,28]. Polyvinyl alcohol (PVOH) has frequently been used as a stabilizer [1,2,6,10,15-18,25,27,30,32,37,38]. Besides the base polymer, the choice of the stabilizing system depends on the production process. For example, elevated temperatures used in the thermomechanical process can impair the efficiency of surfactants [1,9].

Our main objective for this study was to test whether long chain cellulose fatty acid ester can be processed into aqueous dispersions using solvent and thermomechanical methods. We also wanted to evaluate water and oil barrier properties of paperboard coated with such dispersions as a base for further development.

MATERIALS AND METHODS

Materials

The cellulose used for preparing the fatty acid ester was softwood dissolving pulp produced by Domsjö Fabriker AB (Örnsköldsvik, Sweden). All reagents and solvents were purchased from commercial sources and used as received.

Partially saponified polyvinyl alcohol (PVOH) grades were obtained from Kuraray Europe Nordic (Vantaa, Finland); anionic and non-ionic surfactants were from Croda Nordica (Malmö, Sweden); and defoamers were from Kemira (Helsinki, Finland). Dibutyl sebacate (plasticizer) was purchased from Sigma-Aldrich (St. Louis, MO, USA).

Fully pigment coated bleached folding boxboard, Prime FBB Bright 210 g/m², was obtained from Metsä Board (Espoo, Finland). The multiple pigment coated top side was used for the coating tests. This substrate was chosen to enable an even coating layer and to minimize interactions between the fiber network and water from the dispersion coatings.

Synthesis of cellulose octanoate (CFAE)

We used the same octanoyl cellulose fatty acid ester (CFAE) produced in pilot scale as reported in our recent study [39]. Pulp was first treated enzymatically prior to a homogenous esterification with the method presented by Willberg-Keyriläinen et al. [35,40] using a 500 L enamel Büchi reactor (Büchi AG; Uster, Switzerland). Ten kilograms of cellulose was dissolved in lithium chloride/N,N-dimethylacetamide (LiCl/DMAc) solution (12.5 kg LiCl/250 kg DMAc), and then anhydrous pyridine, 3.6 equivalents to cellulose anhydroglucose unit (AGU), was mixed with the cellulose solution. After this, octanoyl chloride, 3.0 equivalents to AGU, was added dropwise to the cellulose mixture followed by stirring for 16 h at 80°C. The obtained CFAE was precipitated

with water using a Seitz filter unit (Pall Corp.; Port Washington, NY, USA) and washed once with water and twice with ethanol. Finally, the CFAE material was dried.

Preparing CFAE dispersions

In the solvent method, the CFAE was first dried and dissolved into chloroform while mixing overnight with a magnetic stirrer. Chloroform has also previously been used to dissolve long chain cellulose fatty acid esters [34,35,40]. Appropriate safety precautions should be followed when using solvents such as chloroform. We transferred the solution to a beaker and subjected it to continuous mixing. Additives were added with water into the solution dropwise. Mixing was then intensified followed by treatment with a Dispermat (VMA-GETZMANN; Reichshof-Brüchermühle, Germany) device for 15 min at 5000 rpm, and water was added as required for the final solids content. The mixture was transferred to a round-bottom flask and installed in Rotavapor to extract the solvent. To ensure complete solvent removal, the pressure was reduced during the solvent extraction from 700 mbar to 100 mbar.

In the thermomechanical method, the CFAE and a plasticizer were first melted in a 0.5 L reactor (Büchi AG) heated with an oil bath, and mixing was initiated. The reactor was closed and pressurized with nitrogen. Mixing was increased, and additives and warm water were fed into the reactor in a controlled manner. Mixing was continued for 10 min, after which the temperature setting was decreased while mixing was continued. After the reactor had cooled down, pressure was released carefully and the resulting dispersion was filtered. Post treatment with Ultra Turrax (IKA; Breisgau, Germany) was tested with some of the dispersions.

Coating with CFAE dispersions

Dispersions were applied onto paperboard using an Erichsen Coatmaster 510 (Erichsen GmbH & Co. KG; Hemer, Germany) at a speed of 3 m/min. Thickness of the coating layer was adjusted with the size of the metering rod. The coated samples were dried in a laboratory oven for 5 min at 105°C, 130°C, and 160°C. Some of the coated sheets were hot pressed (~3.5 kPa) between siliconized label backing papers using a L&W Rapid Dryer (ABB/Lorenzen & Wette; Kista, Sweden) for 5 min at 160°C. Coated samples were conditioned at 23°C and 50% relative humidity prior to testing.

Characterization of CFAE polymer, dispersions, and coatings

Fourier-transform infrared spectroscopy (FTIR) analysis was carried out to confirm a successful synthesis of the CFAE. The CFAE polymer with and without a thermal treatment in a laboratory oven at 160°C for 1 h was analyzed with a Nicolet iS50 FTIR spectrometer (Thermo Fisher Scientific; Waltham, MA, USA) with an attenuated total re-

flectance (ATR) diamond. Both spectra were obtained from 32 scans with a resolution of 4 cm⁻¹ in absorption mode between 400 cm⁻¹ and 4000 cm⁻¹.

Thermogravimetric analysis was done to evaluate thermal stability and degradation temperature of the CFAE polymer. Analysis was done with NETZSCH STA 449F1 (Erich NETZSCH GmbH & Co. Holding KG; Selb, Germany). Heating range was from 40°C to 800°C with heating rate of 10°C/min. The test atmosphere was synthetic air (80/20 mixture of nitrogen and oxygen). The same CFAE samples were analyzed as mentioned previously.

The melting temperatures (T_m) and crystallization temperatures (T_c) were determined for the same CFAE samples with and without a thermal treatment by a Mettler Toledo differential scanning calorimeter (DSC) Model DSC2 (Mettler Toledo GmbH; Greifensee, Switzerland). Samples (5–10 mg) were placed in sealed 40- μ L aluminum crucibles with pierced lids. The temperature profile with the following steps was used: (1) cooling phase from 25°C to -60°C; (2) first heating phase from -60°C to 200°C; (3) cooling phase to -60°C; and (4) second heating phase from -60°C to 200°C. Heating and cooling rate of 10°C/min was used in all cases.

Particle size distribution (PSD) for the CFAE dispersions was measured with a Mastersizer 3000 particle size analyzer (Malvern Panalytical; Malvern, UK). A minimum of three parallel runs were carried out for each sample. Both number and volume-based PSD were reported. For some of the dispersions, the PDS was also assessed with an optical microscope from a drop of diluted dispersion placed between microscope slides.

Solids content of the dispersions was measured by drying a specific amount of dispersion in a laboratory oven at 105°C until dry and calculating the ratio of dried polymer to the original wet sample. Also, pH of some of the dispersions was measured.

Stability of the dispersions was assessed visually. Dispersions without an obvious separation of the aqueous phase after several days from the dispersion production were regarded as stable.

Coating thickness was measured using Micrometer Model 51 (Lorenzen & Wettre) from multiple points and sheets. Thickness of the uncoated sheet was subtracted from that of the coated samples to obtain the coating thickness.

Water absorption (TAPPI Standard Test Method T 441 “Water absorptiveness of sized [non-bibulous] paper, paperboard, and corrugated fiberboard [Cobb test]”) was determined by exposing the sample to water at room temperature inside a Cobb apparatus (Gurley Precision Instruments; Troy, NY, USA) for 30 min. The excess water was removed by pressing the sample between blotting papers. The initial mass of the sample was subtracted from that of the sample exposed to water to obtain the water absorption (g/m²).

The KIT test (TAPPI T 559 “Grease resistance test for paper and paperboard”) was used to assess the grease re-

sistance of the coated samples. Originally developed for evaluating oil and grease resistance in paper with fluorochemical sizing agents, the test applies drops of reagents (KIT No. 1–12) to the sample. The highest numbered reagent that stays on the surface for 15 s without staining the sample is recorded as the “KIT number.” Tests were performed using mixtures of castor oil, n-heptane, and toluene, with higher solvent content indicating greater aggressiveness and higher reagent number. Results were averaged over five measurements for each sample.

Oil barrier test was based on measuring the size of the area stained by a red dyed virgin olive oil (Borges; Spain) on the reverse side of the coated sample as a function of time [41]. Five square pieces of each sample were placed on a glass plate with the coated side up. Circular discs of blotting paper were placed onto the samples and saturated with 200 μ L of oil. Weights of 50 g were placed onto the saturated discs. The reverse side of the samples was scanned through the glass plate after preselected time intervals, and the stained area was analyzed from the scanned images. Between the scans, the test setup was kept in a laboratory oven at 40°C. Three characteristics were determined from the data: the breakthrough time, defined as the point at which at least two squares indicated a stained area of 2%; the average relative area (%) stained by oil after one day of testing; and the average relative stained area (%) after one week of testing.

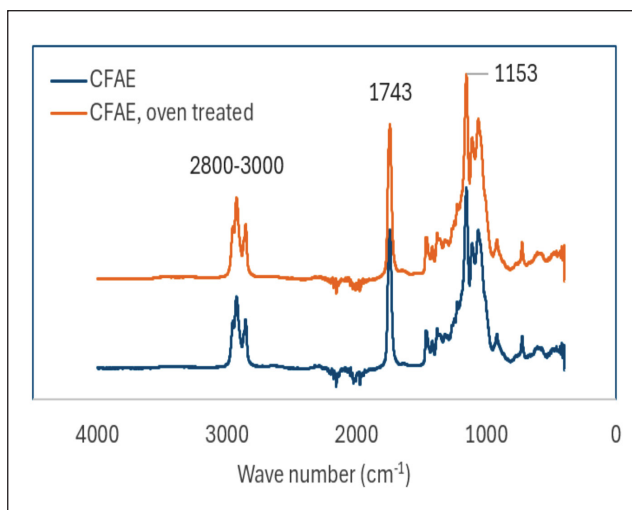
RESULTS

Cellulose octanoate polymer (CFAE)

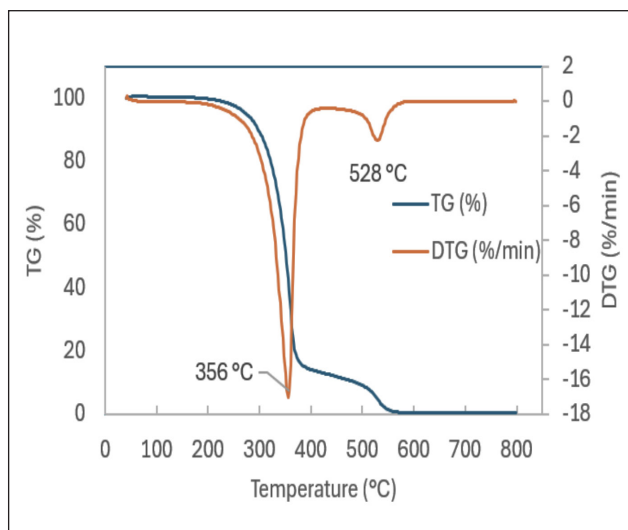
As reported previously [39], the degree of substitution (DS) for this cellulose octanoate determined by quantitative ¹³C NMR was 3.0, which means that all the cellulose OH groups were substituted by the ester groups. In addition, melt flow rate (MFR) of the CFAE polymer increased from 51 g/10 min to 143 g/10 min when temperature was increased from 120°C to 130°C, indicating an obvious drop in melt viscosity with increased temperature.

A clear absorption peak around 1743 cm⁻¹ was observed in the FTIR spectra for both CFAE samples (**Fig. 1**). This is due to stretching vibration of the carbonyl groups in the CFAE indicating that fatty acid has reacted with cellulose [35,42]. No peaks at 1650 or between 3300–3470 cm⁻¹ were present. These correspond to absorbed water and cellulose hydroxyl groups, respectively [35,42,43]. This cellulose ester is thus hydrophobic in nature and has a high DS. The peak around 1153 cm⁻¹ is linked to the oxygen bridge between the cellulose rings [43], and peaks around 2800–3000 cm⁻¹ arise from the aliphatic chain of the fatty acid and CH bonds in the cellulose [42,43]. This, together with the previous nuclear magnetic resonance (NMR) results, shows that the synthesis of the CFAE was indeed successful. Thermal treatment did not have an obvious impact on the absorption spectra.

The thermogravimetric (TG) and DTG (differential TG)



1. Absorption Fourier transform infrared (FTIR) spectra for the cellulose octanoate fatty acid ester (CFAE), with and without treatment in an oven at 160°C.



2. Thermogravimetric (TG) and differential TG (DTG) curves for the CFAE polymer.

curves for the CFAE polymer are shown in **Fig. 2**. There are two degradation steps. The first one is linked to the ester itself, and it is broader than typically reported for cellulose as such. The polymer lost 0.5%, 5%, and 10% of its weight at 210°C, 274°C, and 298°C, respectively. Although not directly comparable, decomposition temperatures of 208°C–234°C for the first 0.5% have been observed previously under nitrogen for cellulose esters with a high DS [44,45]. The first maximum degradation rate occurred at a relatively high temperature (356°C), likely affected by a high DS [46]. The second step with a maximum decomposition temperature of 528°C is due to the oxidation of the formed cellulose char [47]. In addition, weight loss due to the removal of, e.g., water is practically absent. No differences could be observed between samples with or without the oven treatment, indicating a thermally stable polymer, at least under no shear.

The thermal behavior of the synthesized cellulose esters was studied by DSC (**Table I**). No clear glass transition temperature was detected, whereas melting and crystalli-

Sample	T_m ^a , °C	Melting Enthalpy, J/g	T_c ^b , °C	Crystallization Enthalpy, J/g
CFAE	66	6	58	5
CFAE, oven treated	67	7	58	5

CFAE: cellulose octanoate fatty acid ester;

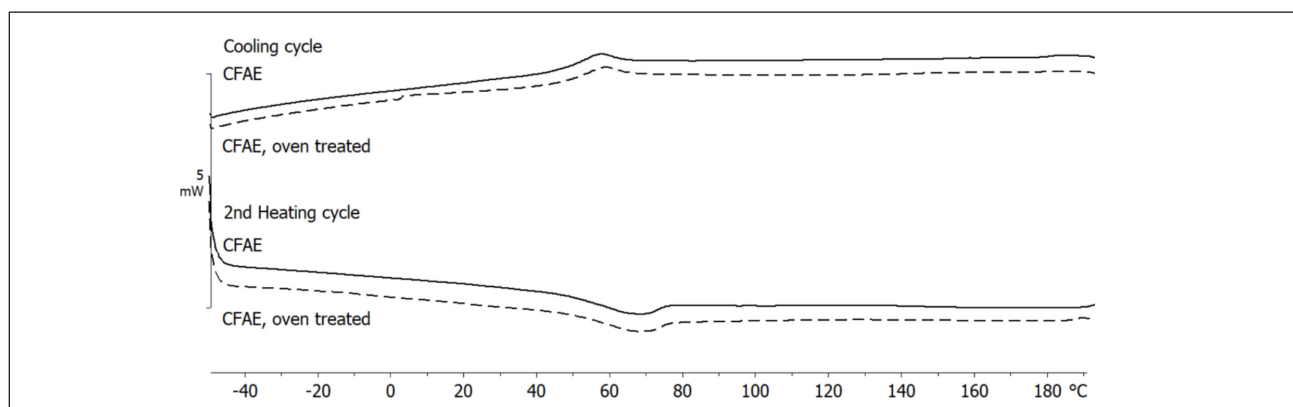
T_m : melting temperature;

T_c : crystallization temperature.

^a Side-chain melting temperature (2nd heating cycle), standard deviation $\pm 2^\circ\text{C}$ (DIN 53765 "Testing of plastics and elastomers; thermal analysis; DSC-method").

^b Side-chain crystallization temperature, standard deviation $\pm 2^\circ\text{C}$ (DIN 53765).

1. Thermal properties of cellulose esters measured with differential scanning calorimeter (DSC).



3. Cooling cycle and 2nd heating cycle of cellulose esters. Heating/cooling rate 10°C/min.

COATING

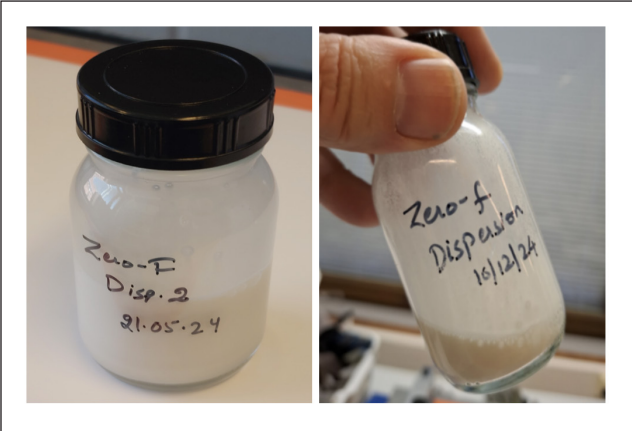
zation peaks were observed (Fig. 3). Because long chain cellulose esters are amorphous materials, primary cellulose chain melting cannot be observed. Therefore, the detected melting and crystallization is due to the side chains [35,48]. No differences were observed between the two samples.

Dispersions by solvent method

Dispersions produced by the solvent-based method were creamy white and of low viscosity, as Fig. 4 shows. In total,

11 dispersions were produced, out of which four are presented in Table II. No solvent residues could be detected olfactorily from any of the dispersions or observed during drying of the dispersion coated paperboard samples. Possible residual solvent entrapped in the polymer matrix needs to eventually be assessed using an appropriate analytical method.

The first dispersion (SD1) was prepared from a 7% solution of CFAE in chloroform. This dispersion was visually



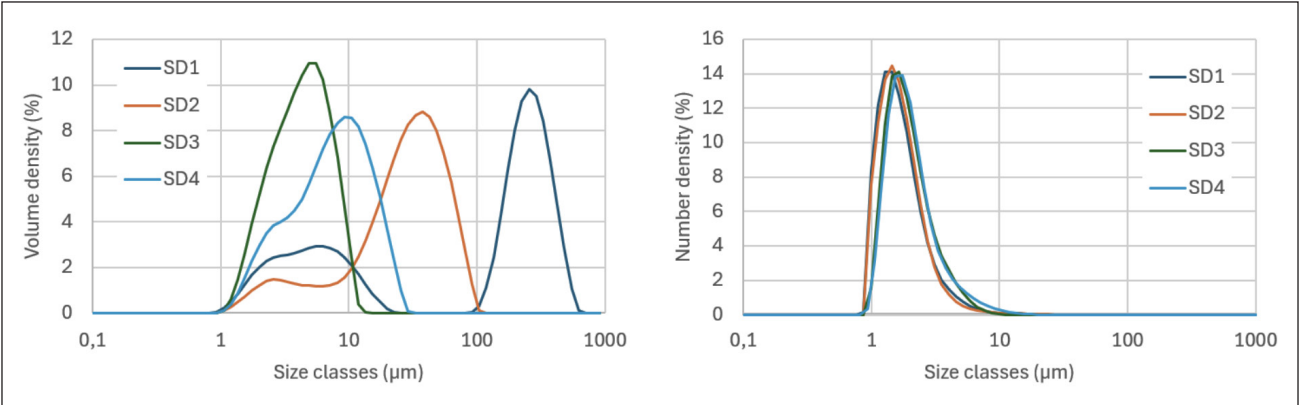
4. Dispersions SD3 (left) and SD4 produced with the solvent-based method.

Dispersion	Additives		Solids Content
	Type	Amount	
SD1	POVAL 32-80	20%	15%
SD2	POVAL 32-80	5%	19%
SD3	POVAL 32-80	20%	27%
SD4	POVAL 32-80	3%	35%
	ZEPHYRM 3300B-LQ-(MV)	5%	

II. Dispersions produced with the solvent-based method.

Dispersion	Volume-Based			Number-Based		
	D _V (10%)	D _V (50%)	D _V (90%)	D _N (10%)	D _N (50%)	D _N (90%)
SD1	1.75 μm	4.50 μm	10.7 μm	1.14 μm	1.67 μm	3.08 μm
SD2	4.58 μm	29.0 μm	61.9 μm	1.02 μm	1.50 μm	2.64 μm
SD3	2.04 μm	4.33 μm	7.95 μm	1.16 μm	1.71 μm	3.22 μm
SD4	2.44 μm	7.61 μm	16.5 μm	1.18 μm	1.75 μm	3.46 μm

III. Volume (D_V)- and number (D_N)-based particle size distribution (PSD) of dispersions produced with the solvent-based method.



5. Volume-based PSD for dispersions produced with the solvent-based method.

stable. Most of the spherical polymer particles were smaller than 10 μm in diameter (**Table III, Fig. 5**). However, there were also large air bubbles created during the solvent extraction and subsequent mixing steps, which explains a second separate peak present in the volume-based PSD graph. This secondary peak was omitted from the particle size analyses.

To decrease foaming and water absorption, we tested the impact of decreasing the amount of PVOH from 20% to 5% (SD2) based on the polymer. Unfortunately, phase separation was already obvious within couple of days due to large polymer particles containing a significant part of the polymer.

Another option is to replace part of the PVOH with a co-surfactant. For this purpose, two anionic and two non-ionic surfactants were first tested for creating a stable dispersion out of a finely ground cellulose palmitate powder. Based on this test, a combination of PVOH and an anionic surfactant, ZEPHRYM 3300B-LQ-(MV) (ZEPHRYM) from Croda Nordica, was used for producing dispersion sample

SD4. This dispersion was stable and had only slightly larger particles compared to, e.g., SD3.

For dispersion SD3, we increased the overall target solids content and the concentration of the CFAE in chloroform from 7% to 10% to test the possibility for decreasing the amount of solvent by 32% for a specific amount of polymer. This resulted in a stable dispersion with all the particles smaller than 20 μm . As indicated by the number-based PSD, most of the particles were actually smaller than 4 μm , similar to the other three dispersions.

While the use of solvents remains the main challenge of this process, the main benefit is a lower process temperature needed, especially with amorphous or temperature sensitive polymers.

Dispersions by thermomechanical method

In total, 14 tests were carried out. **Table IV** provides composition, oil bath temperature and reactor pressure setting, solids content, and pH for the more successful dispersions. These dispersions were more viscous and brownish com-

Dispersion	Additives		Process Settings		Solids Content	pH
	Type	Amount	Oil Bath Temperature	Reactor Pressure		
TD1	POVAL 40-88	20%	170°C	8 bar	33%	4.5
	Dibutyl sebacate	20%				
TD2	POVAL 40-88	10%	170°C	8 bar	29%	N/A
	Dibutyl sebacate	20%				
TD3	POVAL 35-80	10%	165°C	8 bar	36%	4.0
	ZEPHRYM 3300B-LQ-(MV)	5%				
	Dibutyl sebacate	20%				
TD4	POVAL 35-80	10%	165°C	8 bar	30%	3.6
	ZEPHRYM 3300B-LQ-(MV)	5%				
	Dibutyl sebacate	20%				
	FennoTech 6042	0.1% *				
TD5	POVAL 35-80	8%	165°C	8 bar	38%	N/A
	ZEPHRYM 3300B-LQ-(MV)	3%				
	Dibutyl sebacate	10%				
	FennoTech 6042	0.1% *				

* Based on total dispersion; otherwise based on cellulose octanoate fatty acid ester (CFAE).

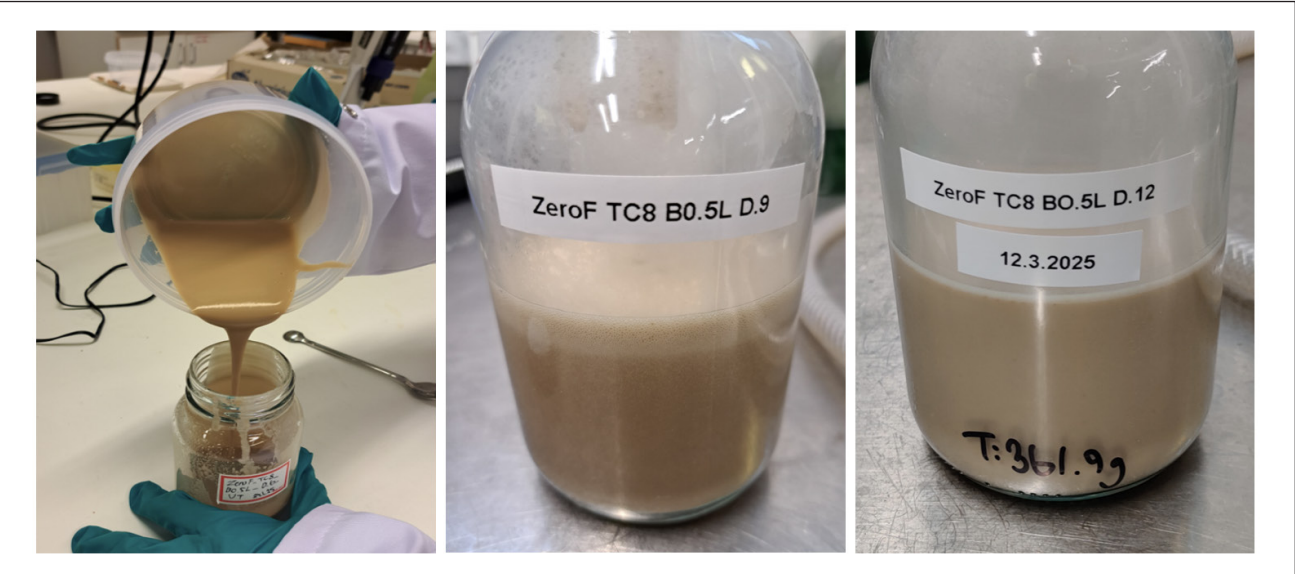
IV. Dispersions produced with the thermomechanical method.

COATING

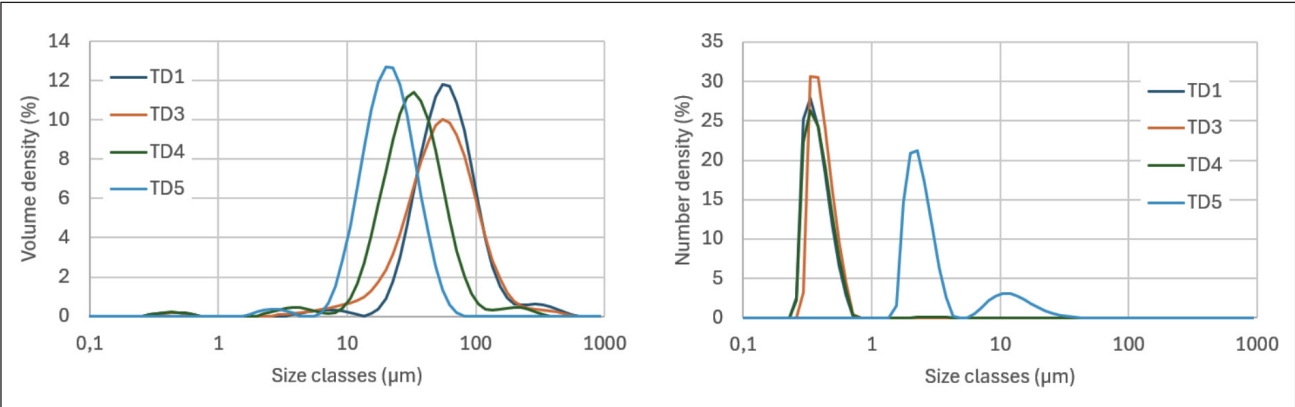
pared to those produced by the solvent-based method, as demonstrated in **Fig. 6**, likely due to polymer degradation during the thermomechanical process. Initially, oil bath temperature up to 195°C was also tested, but this led to a deep dark polymer. Low pH measured for some dispersions indicated hydrolysis. To confirm this, we dispersed CFAE powder into water and followed pH as a function of time

at 23°C and 80°C; pH decreased from 7.4 to 5.0 and 3.6, respectively, after 1 h.

Initial tests without a plasticizer resulted in large spherical particles. While most of the particles in TD1 were smaller than 1 µm, there were also large particles present containing most of the polymer (**Fig. 7, Table V**). The microscope images (**Fig. 8**) revealed that the large particles were actually



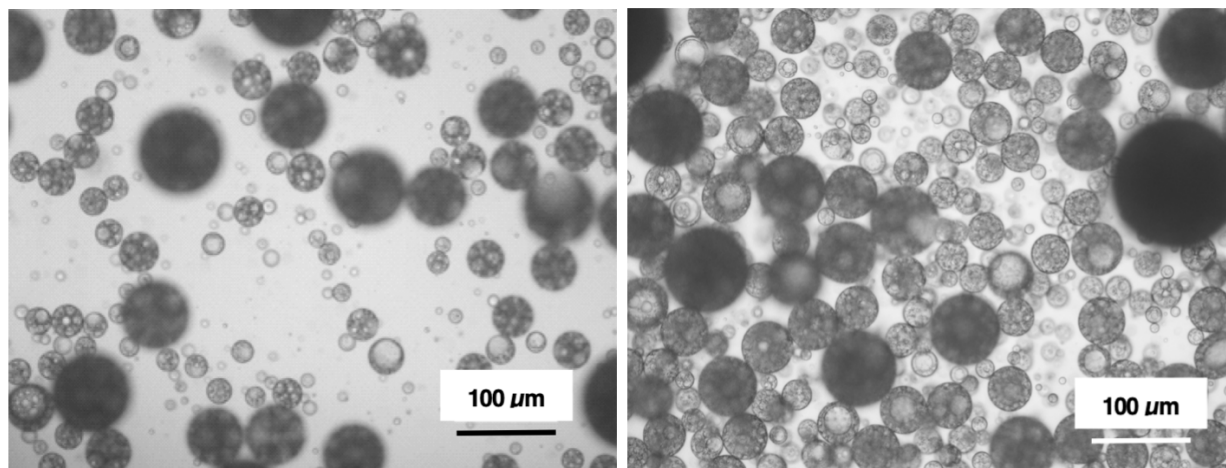
6. Dispersions TD1 (left), TD3 (middle), and TD4 (right) produced with the thermomechanical method. Image of dispersion TD1 is after Ultra Turrax treatment.



7. Volume-based (left) and number-based (right) PSD for dispersions produced with the thermomechanical method.

Dispersion	Volume-Based			Number-Based		
	D _V (10%)	D _V (50%)	D _V (90%)	D _N (10%)	D _N (50%)	D _N (90%)
TD1	29.6 µm	58.1 µm	115 µm	0.29 µm	0.36 µm	0.51 µm
TD3	21.6 µm	53.4 µm	112 µm	0.33 µm	0.40 µm	0.54 µm
TD4	15.5 µm	32.0 µm	63.5 µm	0.29 µm	0.37 µm	0.52 µm
TD5	11.3 µm	20.8 µm	37.5 µm	1.82 µm	2.44 µm	11.9 µm

V. Volume (D_V)- and number (D_N)-based particle size distribution (PSD) for the thermomechanical dispersions.



8. Optical microscope images of TD1 (left) and TD3 (right).

aggregates of smaller particles. This was not observed with the dispersions prepared using the solvent-based method.

Tests both with a low viscosity PVOH (POVAL 5–74) or a reduced amount of PVOH (TD2) did not result in proper dispersions but rather in large soft polymer particles that eventually clogged the filter. Based on the learnings with the solvent-based method, we also tested a combination of ZEPHYRM and PVOH for TD3. In addition, dibutyl sebacate was chosen as a water-insoluble plasticizer based on pre-screening (not reported here) and as suggested previously by others [38]. The PSD was quite similar to TD1. The largest particles were most probably air bubbles not observed with the optical microscope. Air bubbles were also observed within the polymer particles.

Foaming was likely due to both PVOH and release of pressure from the reactor. Gas within the dispersion tends to expand, thus creating foam. Two defoamers were added into a previously prepared TD3, and after dilution both samples were shaken vigorously to create foam. FennoTech 6042 (Kemira) was able to break the foam immediately, and this product was therefore chosen for the subsequent dispersion tests.

Dispersion TD4 with the defoamer had a clearly lower foaming tendency than the previous dispersions, as shown in Fig. 6, and the size of the largest particles or particle aggregates was reduced. The final filtering step was carried out with a 450 μm sieve.

Dispersion TD5 had a similar composition as TD4, but the amount of both the stabilizers and the plasticizer was reduced, and the final filtering step was carried out through a 200 μm sieve. A higher portion of the polymer was transferred to the dispersion. The overall particle size distribution became narrower; while the majority of particles were somewhat larger than in the other dispersions, the size of the large particles was also reduced.

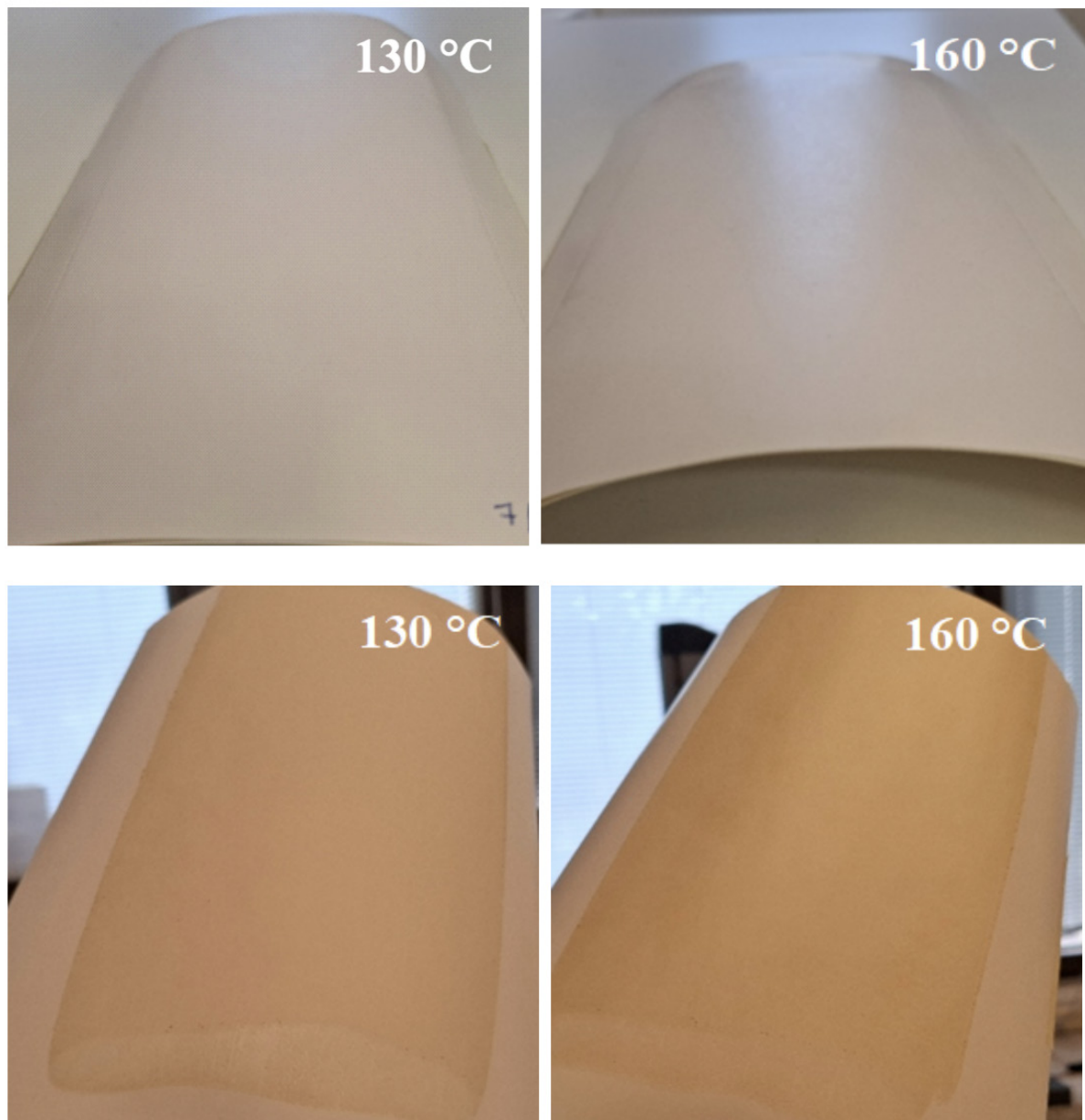
The relative increase in the solids content compared to

the materials used for dispersion preparation was 11%–17% for the dispersions TD1, TD3, and TD5 due to water evaporation, while for TD4, the relative decrease in the solids content was 9% due to a lower yield in filtration.

A post treatment with Ultra Turrax was tested with several dispersions. However, this had no significant impact on the particle size distribution, indicating that the particles were strong enough to resist the shear forces. Cellulose fatty acid esters are thermoplastic polymers with the original crystalline structure of cellulose destroyed during the esterification process [49]. Amorphous polymers are in general regarded as difficult to process with the thermomechanical method as these do not necessarily exhibit a sharp melting point [5]. However, a more dynamic process with a fast cooling step might reduce both the polymer degradation under shear in contact with water and the tendency of the small primary particles to form larger aggregates observed in this study.

Dispersion coating and coated samples

Four dispersions produced with the solvent-based method (SD1–SD4) and two of the thermomechanical dispersions (TD4 and TD5) were tested as laboratory coatings. Coating tests were carried out within 1–4 days after the production of the dispersions. Dispersions with large particles led to a high apparent coating thickness (e.g., SD2), and increasing drying temperature increased the coating gloss with both types of dispersions (**Fig. 9**), indicating improved film formation. Similar to the dispersions, coatings based on the thermomechanical dispersions were brownish, and an increased drying temperature caused a slight color change. No coating defects were visually observed with SD1–SD3, indicating that some of the larger particles observed were indeed air bubbles. Dispersion SD4, on the other hand, had few crater-type defects. Only a few characteristic streaks caused by large particles were observed with TD4 and TD5.



9. Examples of coatings obtained with dispersions produced with the solvent-based (upper) and the thermomechanical (lower) methods after drying at 130°C and 160°C.

As the viscosity was on the high side, some rod marking was also present.

Water barrier was improved with an increased drying temperature (**Table VI** and **Table VII**). In addition, a hot pressing step used to improve film formation and to mimic the molding step used for the 3D fiber products had a positive impact on water barrier, especially in the case of lower drying temperatures. Although not reported here, we also noticed that the relative impact of hot pressing on water absorption was more profound with thinner coatings. However, the lowest water absorption was clearly obtained with

the dispersion SD4 with a co-surfactant and the lowest amount of PVOH. While being a good dispersion stabilizer, PVOH is water soluble and hydroscopic, which is a challenge when aiming for good water barrier, as observed earlier [10]. Although the base substrate was different, these values were higher than those obtained for the CFAE powder coatings [39]. These powder coatings were hydrophobic and did not contain any additives. The same polymer has also provided an excellent water barrier below 5 g/m² when applied as thin coatings directly from chloroform.

Grease resistance was poor, and hot pressing did not

Sample	Drying/ Pressing	Water Absorption (30 min)	KIT	Oil Barrier			Thickness
				Breakthrough	Staining After 1 Day	Staining After 7 Days	
BOARD	—	130 ± 2 g/m ²	1	3–4 h	34 ± 9%	89 ± 23%	—
SD1	105°C	117 ± 2 g/m ²	0	6–24 h	6 ± 8%	29 ± 8%	37 µm
	+ hot pressing	51 ± 0 g/m ²	—	6–24 h	4 ± 6%	33 ± 5%	36 µm
SD2	105°C	98 ± 5 g/m ²	0	54–72 h	0%	13 ± 9%	66 µm
	+ hot pressing	21 ± 4 g/m ²	3	48–54 h	0%	22 ± 18%	63 µm
SD3	130°C	101 ± 1 g/m ²	2	25–30 h	1 ± 3%	32 ± 12%	41 µm
	160°C	86 ± 2 g/m ²	0	30–48 h	1 ± 2%	30 ± 5%	39 µm
SD4	130°C	19 ± 2 g/m ²	1	48–55 h	0%	29 ± 11%	31 µm
	+ hot pressing	16 ± 2 g/m ²	0	55–73 h	0%	21 ± 12%	25 µm

VI. Barrier properties of coatings based on the solvent-based method.

Sample	Drying/ Pressing	Water Absorption (30 min)	KIT	Oil Barrier			Thickness
				Breakthrough	Staining After 1 Day	Staining After 7 Days	
BOARD	—	130 ± 2 g/m ²	1	3–4 h	34 ± 9%	89 ± 23 %	—
TD4	130°C	113 ± 2 g/m ²	0	30–48 h	0%	19 ± 11%	30 µm
	+ hot pressing	85 ± 4 g/m ²	0	72–77 h	0%	14 ± 11%	23 µm
	160°C	66 ± 14 g/m ²	0	48–55 h	0%	21 ± 8%	32 µm
	+ hot pressing	67 ± 7 g/m ²	0	30–48 h	0%	26 ± 7%	30 µm
TD5	130°C	128 ± 2 g/m ²	0	55–72 h	0%	17 ± 8%	33 µm
	+ hot pressing	56 ± 3 g/m ²	0	48–55 h	0%	16 ± 15%	31 µm
	160°C	76 ± 8 g/m ²	0	55–72 h	0%	14 ± 8%	33 µm
	+ hot pressing	50 ± 10 g/m ²	0	55–72 h	0%	20 ± 8%	35 µm

VII. Barrier properties of coatings based on the thermomechanical method.

have a systematic impact. The CFAE with a high number of nonpolar groups is oleophilic in contrast to fluorochemicals, and castor oil can wet the surface and enter the surface structure. Low KIT values were also obtained for CFAE powder coatings, with a slight improvement with increased coating thickness and post hot pressing due to a more closed and smooth coating [39]. Rod marking with the thermomechanical dispersion coatings could also therefore contribute to the low KIT values. Additives, such as PVOH, did not provide grease resistance. Although designed for fluorochemical treated papers, the KIT test is

widely used to test dispersion coatings [50]. However, absorption of the test liquids into coated surfaces does not provide similar stains as with porous papers, and analyzing stains on coated surfaces is affected by the differences in the coating structure, color, and gloss. In addition, the solvents can evaporate quickly from the coated surfaces, leaving behind a stain of oil, and interactions between the dispersion components and the test liquids can be different compared to actual oils [51,52].

Unlike grease resistance assessed with the KIT test, olive oil barrier was clearly improved with the CFAE coat-

ings compared to the pigment coated base board. Oil breakthrough time for the coated board was prolonged from just a few hours to 1–3 days, and on average, the thermomechanical dispersions performed slightly better when looking at staining as a function of time. Poorer performance of SD1 was likely due to persistent air bubbles present in the dispersion. Increased drying temperature or hot pressing did not have a systematic impact. There is also clearly room for optimizing the dispersion composition without impairing the oil barrier.

CONCLUSIONS

We verified a successful pilot-scale synthesis of a long chain (octanoyl) cellulose fatty acid ester and demonstrated that stable aqueous polymer dispersions can be prepared from this preformed, predominately amorphous cellulose derivative in laboratory scale using both solvent-based and thermomechanical methods.

Dispersions based on the solvent method were creamy white and had a low viscosity, but the thermomechanical dispersions produced using a pressurized reactor were brownish and more viscous, most likely due to polymer degradation due to, e.g., hydrolysis. A solids content of 35% was achieved in both cases. The solvent-based method enabled a narrow particle size distribution, while dispersions consisting of both small particles and larger particle aggregates were produced with the thermomechanical method.

We coated paperboard sheets with selected dispersions in laboratory scale and evaluated the grease resistance and water and oil barrier of the resulting coatings. Oil barrier was clearly improved, with most of the dispersions with oil breakthrough time extending to 1–3 days. While water barrier was also improved with increased drying temperature and an additional hot pressing step due to a better film formation, the stabilizing system had a profound impact.

Although we were able to optimize the composition and to decrease the particle size of the polymer dispersions during this study, the results indicate there is also need for further research and development regarding the additives, the dispersion preparation process, and the process parameters used.

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ABOUT THE AUTHORS

We studied this topic because there is a need for alternatives to petroleum-based plastics and fluoroalkyl substances. Cellulose is an abundant natural polymer providing interesting options for modification. To be industrially viable, these derivatives have to be applicable with relevant coating techniques. Dispersion coating is one option for creating barrier properties for fiber-based materials.

We have backgrounds both in developing aqueous polymer dispersions and modifying cellulose through esterification. Cellulose esters can be melt processed into various products, and recently we demonstrated the possibility to also use these for powder coating. However, there are only a few cases where these have been processed into aqueous polymer dispersions.

The most difficult aspect of this study was adjusting properties of dispersions with various additives. In addition, a relatively small amount of dispersion could be produced at a time in lab scale, and timing of the subsequent tests was critical. We had to focus on the most critical additives and choose a specific paperboard for the initial coating tests.

It was fascinating to learn that such preformed polymers can be processed into aqueous dispersions. Of particular interest was the discovery that to

utilize the full potential of the base polymer(s), both the process parameters and the additive system in particular have to be chosen carefully to enable stable dispersions with good barrier performance.

Such dispersions as those in this study can be used to create, for example, barrier coatings for fiber-based materials. Although our focus was on paperboard and food service and takeaway applications, these could also have potential for, e.g., molded fiber products and other packaging applications.

This study provided insight in how to further develop and upscale the concept of both of the involved processes, as well as the additives used. This would also enable optimizing the coating method and thickness to reach the required barrier performance.

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