Convertability and Oil Resistance of Paperboard with Hydroxypropyl-Cellulose-Based Dispersion Barrier Coatings

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ABSTRACT

The convertability and barrier properties of paperboard coated with hydroxypropyl-cellulose (HPC) based dispersions were studied via tray pressing trials, oil resistance measurements and microscopic analyses. To improve the oil resistance of the HPC-based coatings and to maximize their convertability, talc, gelatin and latex were used as additives in coating formulations. The oil resistance of the coatings improved to some extent with these additives, but scanning electron micrographs revealed the existence of pinholes particularly in coatings with a high HPC content. The coated paperboard samples were pressed into rectangular trays and the convertability of the paperboards was evaluated with a microscope. Thereafter, the oil resistance of the trays was determined in order to clarify how the tray pressing process affected the oil resistance. Pure HPC coating did not provide appreciable oil resistance to the paperboard, but the composite coatings resisted oil up to 11 minutes at the tray corners, which were considered the most demanding regions in the tray. The pure HPC coating was sticky and tended to stick to the converting tools in the press forming. Adding talc to the coating dispersion reduced this problem. By applying a thin pre-coating layer, it was possible to raise the blank holding force in the pressing process from 1.16 kN to 1.55 kN without causing rupture in the tray corner areas or compromising the quality of the creases. With commercial polyethylene-terephthalate-coated reference paperboard, the use of such a high force resulted in long rupture and opened creases, which confirms the excellent applicability of the developed dispersion-coating recipes for the tray-pressing process. These observations suggest that convertibility is not necessarily a major problem with bio-based dispersion barrier coatings and that more attention should be paid to their barrier properties and particularly to the prevention of pinholes being formed during the coating process.

Key Words*:*

hydroxypropyl-cellulose, composite coating, press forming, oil and grease resistance, formability

INTRODUCTION

The continuously growing packaging market, changing consumer habits worldwide [1] and demands for a greater utilization of sustainable packaging materials require new barrier materials with good convertability for food products such as bakery goods, microwavable instant meals and fast food. During recent years, there has been a growing interest in composite-type dispersion barrier coatings with a high proportion of bio-based components. The importance of oil resistance is emphasized in such applications due to the typically high fat content of packaged foods. Fiber-based packaging materials coated with plastics such as polyethylene (PE) or polyethylene terephthalate (PET) by extrusion and surface treatment with fluorocarbon chemicals have been shown to possess good functionality for many applications. The plastic coatings provide a physical barrier against oils and the fluorocompounds inhibit the wetting of the fibers [2]. However, neither of these approaches is trouble-free. Increasing environmental awareness means that the use of oil-based plastics should be reduced, and this means that new environment-friendly, ideally biodegradable barrier coatings must be developed. At the same time, the poor biodegradability, potential toxicity, and accumulation in human tissue and blood are considered serious drawbacks for the use of fluorocompounds [3, 4], and this has already led to a substantial decrease in their use.

Dispersion coatings can be repulped, composted or burned at a waste burning plant [5], which means that dispersion coatings have certain environmental benefits over plastic coatings. Several attempts to use bio-based coatings as barriers have recently been reported [6−11]. Aqueous dispersions used for barrier coating can be either oil- or bio-based, or mixtures thereof. Mixing of biopolymers with inorganic pigments and synthetic polymers, i.e. preparing composite dispersion coatings, has been reported to improve grease resistance [6, 7]. Due to their sensitivity to water, bio-based coatings require in practice an additional protective layer of a hydrophobic agent, although hydrophobization of biopolymers is also possible [11]. In addition, barrier films made from bio-based polymers are typically more brittle than oil-based films [8], although the addition of a small amount of synthetic polymer [7] or gelatin [9] to a bio-based polymer dispersion improves its flexibility and convertibility. Hydroxypropyl cellulose (HPC) is the only edible (and thus also safe) film-forming thermoplastic and biodegradable cellulose derivative [12], and this makes it particularly interesting as a main component for multi-component dispersion coatings.

Another typical drawback of biopolymer dispersions is their high viscosity, i.e. challenging rheological properties, which makes it difficult to use dispersions with a high dry solids content. Filling the dispersions with an optimized amount of pigments, however, has been shown not only to improve the barrier properties but also to reduce runnability problems [13]. Such an approach may enable dispersions to be prepared with a higher dry solids content, thus decreasing the energy consumption in the drying phase of the coating process. The ability of high shape factor pigments in dispersions to improve barrier properties is founded on increasing tortuosity, but the critical pigment volume concentration should not be exceeded [13]. Large clay flakes with a high aspect ratio have been reported to improve the barrier properties more than small flakes with a low aspect ratio [14]. However, aqueous coatings containing naturally hydrophobic talc not only have a higher resistance to oil and grease than clay-containing coatings but their resistance to water is also better [15]. The unique properties of talc make it an interesting component in bio-based coating dispersions, since the moisture resistance of biopolymers is not usually sufficient for packaging applications [16].

Press-forming is a process whereby fiber-based materials can be formed into three-dimensional shapes, but with paperboards defects such as cracks, pinholes or visual blemishes can occur. The formability and the quality of formed products has been evaluated by different methodologies. Tanninen et al. [7] compared the lengths of the ruptures that appear during forming. In another method, wrinkles are counted and it has been proposed that number of the wrinkles describes the quality of the formed product [17]. Leminen et al. [18] compared trays formed with different blank-holding forces, and it was found that a higher blank-holding force (until breakage occurs) resulted in better end-product quality. Microscopic analysis to investigate the formability of creases in the rim area where surface quality is critical has also been used [19].

The aim of the present work was to study bio-based dispersion barrier coatings loaded with pigment in order to increase their resistance to oils. The coatings consisted of hydroxypropyl cellulose, gelatin, talc and a synthetic styrene-butadiene latex at different ratios. To our knowledge, there is no earlier literature concerning either the oil barrier properties of HPC/talc-based composite dispersion coatings or their convertability in tray pressing processes. The results provide experimental data concerning these questions and demonstrate that the convertability of bio-coated paperboard is not necessarily a major problem, although more attention must be paid to the barrier properties of such coatings.

MATERIALS AND METHODS

Coating Dispersions

Two types of dispersion (i. pre-coating dispersions, and ii. barrier dispersions) were used in the coating process. In the preparation of the dispersions, barrier-grade talc (Finntalc C15B, Mondo Minerals B. V., Finland) with a mean aspect ratio of 0.6, hydroxypropyl cellulose (Klucel J-Ind, Ashland), styrene-butadiene latex (Styronal D517, Basf, Germany), and gelatin (Meira, Finland) were used. The pre-coating dispersion consisted of carboxymethyl cellulose (CMC; Finnfix 30, CP Kelco, Finland), microfibrillated cellulose (MFC; Nano Novin Polymer Co, Iran), and gelatin. The latex and gelatin additions were calculated on the basis of the total dry matter content of the other components. The nominal compositions of the coatings, given as relative amounts of the dry mass, are given in Table 1. The order of addition in the preparation of the barrier dispersions was: talc – latex – HPC – gelatin. In the case of the pre-coating dispersion, gelatin was added to the mixture of CMC and MFC. All the dispersions were prepared with a Diaf mixer using a mid-size rotor (Pilvad Diaf, Denmark).

The rheological properties of HPC placed a limit to the dry solids content of the barrier dispersions. To reduce the number of variables in the coating process, the dry solids content of all the barrier dispersions was adjusted to 12% with tap water, which was also the highest reasonable dry solids content of HPC in the blade coating process. The dry solids content of the pre-coating dispersion was 8%. Pre-coating was tested only with barrier dispersion #5.

Coating Process

Commercial SBS paperboard (Stora Enso Oyj, Imatra) with a grammage of 350 g/m2 was used as the substrate. The substrate was coated with a carbide-tipped blade in a pilot coater from DT Paper Sciences with a machine speed of 10 m/min. The blade with a carbide tip was selected rather than the regular bent-blade and soft-tip blade, with which it was more difficult to obtain the targeted coat weight, indicating that a hard-tipped blade is more suitable for low-solid-contents coating dispersions at least with regard to achieving the maximum coat weight. The coat weight for a single barrier layer was 5 g/m2 and the targeted total coat weight for two barrier

Table 1: Composition (pph) of the coating dispersions.

	Pre-coating*	Barrier dispersions / Test point				
Chemical	**0**	**1**	**2**	**3**	**4**	**5**
CMC	90	-	-	-	-	-
Gelatin	10	-	5	5	5	-
HPC	-	100	100	90	80	70
Latex	-	-	-	-	-	10
MFC	10	-	-	-	-	-
Talc	-	-	-	10	20	30

* Only coating dispersion 5 was applied on pre-coated paperboard.

layers was thus 10 g/m². The targeted coat weight for the pre-coating layer was 2 g/m². Coated samples were dried in-line with a combination of an infrared dryer with a heating power of 6 kW and an air dryer (1.5 kW).

Converting of Materials

The trays were prepared using the press-forming process, which is explained in [19]. The forming parameters were: forming force 135 kN, male mould temperature 20°C, female mould temperature 140°C, forming speed 130 mm/s, and dwell time 1 s. The blank-holding force was varied from 0.97 kN to 1.55 kN. The dimensions of the tray were 265x162x38 mm.

Paperboard and Tray Characterization

Coat weight was calculated by subtracting the grammage of the uncoated paperboard from the grammage of the coated material. Grammages were determined in accordance with ISO 536:2012. Air permeability was measured in accordance with ISO 5636-3:2013. Scanning electron microscope (SEM) images of the surfaces of the samples were taken with a Jeiotech JEOLJSM-5800 SEM using a secondary SEI-detector with an acceleration voltage of 15 kV. The rim areas of the trays were studied with a stereomicroscope (Olympus Tokyo) in order to compare the crease forming between the commercial PET-coated reference sample and the experimental paperboard.

The oil resistance of non-converted samples was determined using palm kernel oil dyed with Sudan red in accordance with standard ISO 16532-1 at 60°C. The volume of pipetted palm kernel oil was 200 µl. Only the coated sides of the samples were tested. The oil resistance of the material at the tray corners was also determined. The tray was positioned at an angle of approx. 45° when the corner areas were tested (Figure 1 next page). Due to the shape of a tray, no weight of 50 g was placed on the oil drop for this measurement.

The surface free energies of the samples were determined with a Theta optical tensiometer (Biolin Scientific AB). The probe liquids were deionised water, ethylene glycol (VWR S.A.S. International, France) and diiodomethane (Alfa-Aesar GmbH & Co KG, Germany). The drop volumes were 3 µl for water and ethylene glycol and 1 µl for diiodomethane. The contact angle value (θ) was read 1 s after dispensing the drop. The average value of three independent measurements was reported. The surface free energy (SFE, γ) was calculated using the acid-base approach, which allows closer inspection of solid (s) surfaces [20]. The calculation is based on summing the three SFE components, Lifshitz-van der Waals (LW), electron-acceptor (+), and electron-donor (-) components:

$$(1+cos\theta_i)\gamma_{li} = 2\left(\sqrt{\gamma_{li}^{LW}\gamma_s^{LW}} + \sqrt{\gamma_{li}^{+}\gamma_s^{-}} + \sqrt{\gamma_{li}^{-}\gamma_s^{+}}\right)$$

Figure 1: Positioning of trays in OGR testing (left) and a close-up of an oil stain at a tray corner

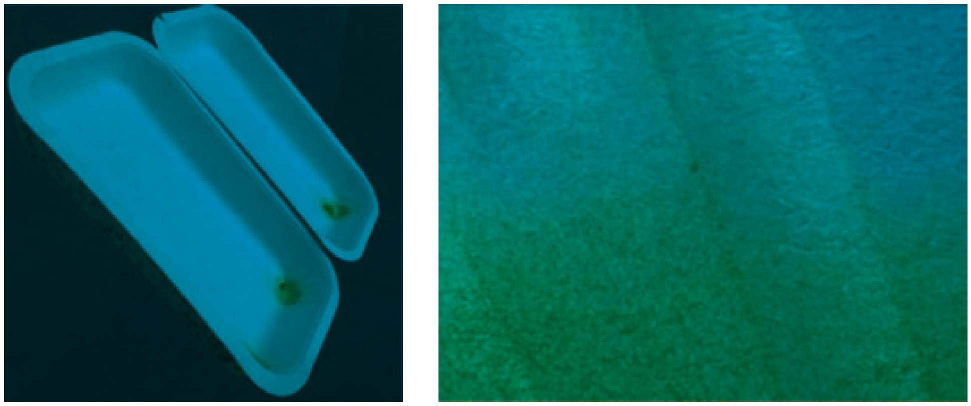


Table 2: Coat weights (g/m^2), surface free energies (mN/m), and water contact angles (°).

Test point	Coat weight, (g/m^2)	Air permeance, (ml/min)	SFE, (mN/m)	CA_{water}, [°]
Uncoated ref.	-	184 ± 53	37.5	99.8 ± 0.7
1	10.0	15 ± 2	45.4	67.5 ± 2.2
2	12.5	14 ± 3	45.3	67.4 ± 1.0
3	9.0	15 ± 1	41.6	62.5 ± 2.4
4	10.5	13 ± 1	43.1	69.0 ± 0.9
5	11.5	10 ± 1	42.5	69.2 ± 2.5

RESULTS AND DISCUSSION

Properties of the Barrier Coatings

The coat weight and the air permeance of the samples were primarily taken to be measures of the successfulness of achieving coating coverage (see Table 2 above). Since all the coatings led to a decrease in the air permeance of the paperboard, approx. 90%, the coverage appeared to be adequate. The results were very similar, regardless of whether the dispersion contained talc, gelatin, latex, or a combination of thereof, confirming that HPC has relatively good film-forming properties. The SEM images, however, revealed that pinholes were scattered in the coating particularly with high HPC concentrations, probably due to a non-optimized drying process (Figure 2). Due to the configuration of the pilot coater and the relatively low dry solids content of the dispersion (12%), the use of milder drying settings would have resulted in inadequate drying and this, in turn, would have led to blocking problems. Increasing the proportion of talc in the dispersion reduced the prevalence of pinholes in the coatings but, at the same time, the fibers in the paperboard surface became more visible, indicating that the coat weight should be increased if it is desired to control pinhole formation by pigment addition. Pinhole formation could also be controlled by adding synthetic polymer in the coating dispersion, since latex-containing composite dispersion barrier coatings have been reported to have self-healing properties when exposed to heat [6], as in the tray-pressing process.

The surface free energy of the coatings was determined in order to see whether the observed stickiness of coatings in the tray-pressing process

Figure 2: SEM images (400x magnification) of test points 3 (left) and 5 (right). A pinhole with a diameter of approximately 55 µm can be seen in the lower right-hand corner of the left-hand figure. The bar size in the figures is 50 µm.

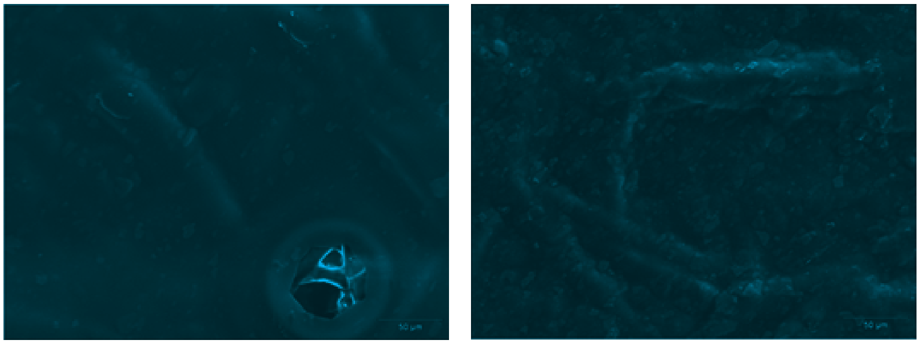


Table 3: Oil resistance (min) of non-converted and converted paperboards.

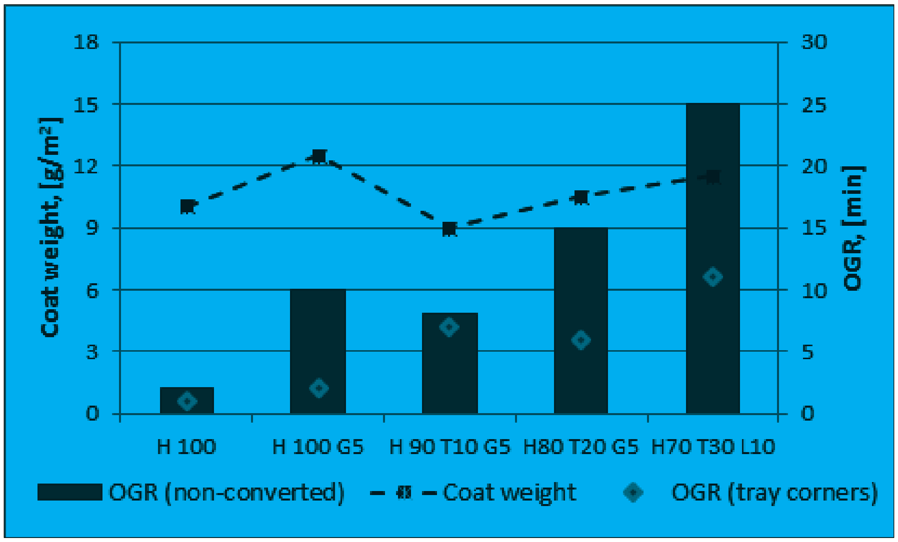
Test point	OGR (non-converted), (min)	OGR (tray corner), (min)
Uncoated ref.	0 ± 0	0 ± 0
1	2 ± 1	1 ± 0
2	10 ± 3	2 ± 1
3	8 ± 3	7 ± 2
4	15 ± 3	6 ± 1
5	25 ± 5	11 ± 4

could be related to a change in surface energy. Coatings with 100 pph HPC stuck to the converting tools particularly severely, but the stickiness was substantially reduced with increasing pigment content, indicating that the convertability can be improved by using composite coatings. The surface free energies of all the coatings where higher than that of the uncoated reference paperboard, obviously due to the presence of HPC. The presence of gelatin in the coating (test point 2) had practically no effect on the surface free energy, but a minor decrease in surface energy was observed when the coating contained talc, latex or a blend thereof (test points 3-5), and this agrees well with an earlier study of the surface energies of coatings comprising hydroxypropylated starch, talc and latex were studied [6]. However, the changes in the surface energy in the present study were only moderate and the difference between talc-containing and talc-free materials was so small, that the surface energy value is definitely not an explanation of tray sticking problems in converting. Contact angle determinations with water also revealed only minor differences between the experimental coatings, indicating fairly identical wetting properties, which was surprising since the hydrophobicity of talc should have increased the contact angle for water [15]. It is possible that the proportion of talc in the coatings was not sufficient to have this effect, but heat-induced pigment movement towards the baseboard may also explain the behavior [6].

Oil Resistance

Oil resistance was determined on both tray corners (converted samples) and non-converted paperboards. As seen in Table 3, converting had very little effect on the oil resistance in most cases, but this was obviously due to an insufficient initial oil

Figure 3: Coat weight (g/m2) of experimental coatings and oil resistance (min) of non-converted paperboards and trays corners. H denotes HPC, G gelatin, T talc, and L latex.



barrier. Billmers et al. [9] reported that the addition of gelatin improves both oil resistance and flexibility of starch films, providing better convertability, and this agrees with the present observations, although the differences in oil penetration times were small between the various materials. On the other hand, the addition of a synthetic polymer to starch also provides a similar effect on the convertability and grease resistance [7]. Comparing test point 5 with other materials partly confirms the positive effect of adding a synthetic polymer, but the effect of greater tortuosity cannot be ruled out since the paperboard was pre-coated and the talc content of test point 5 was 30 pph, the highest among these experimented materials.

It can be seen in Figure 3 that the variation in coat weight may partly explain the variation in oil penetration time. One should, however, note that the difference in coat weight was rather small and, when comparing talc-containing samples with paperboard with pure a HPC coating, it seems that the slight increase in penetration time can also be a consequence of a greater coating tortuosity.

Converted samples, in particular, did not benefit from an increase in coat weight, as far as their oil resistance was concerned, which may indicate a too thick dispersion barrier coating. Tanninen et al. [7] have reported a decrease in grease resistance with increasing coat weight when the proportion of synthetic polymer in the dispersion coating is high, indicating that there is an optimal coat weight and an optimal proportion of synthetic polymer. In the present study, however, the proportion of synthetic polymer was significantly lower and the oil resistance was not determined by the KIT-test as in the case of the earlier work.

In summary, the experimental coatings did not provide sufficient oil resistance regardless of whether or not the material was converted. Bearing in mind that all the experimental coated paperboards used in this study are suitable for organic recycling due to their very high renewable raw material content [21], such dispersion barrier coatings might have a potential in applications where the lifetime in use of the package is short, as in the case of fast food packaging.

Figure 4: A crease formed in the experimental paperboard with a flat surface.

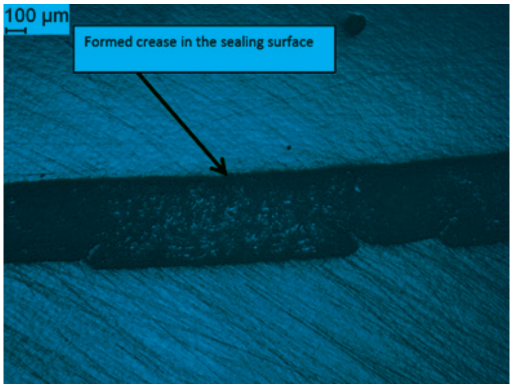
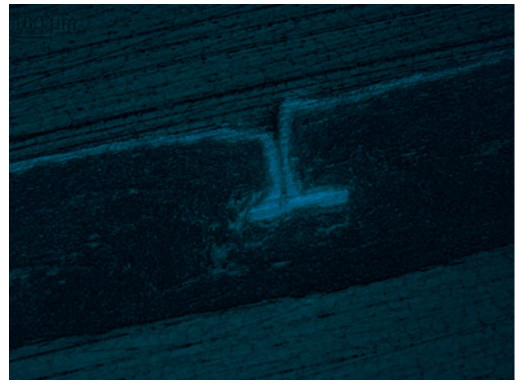


Figure 5: A crease in the commercial PET-coated paperboard.



Convertability of Samples

The formability of the experimental coated paperboards in converting was found to be good. A blank-holding force up to 1.55 kN was used without breaking the coated paperboard (test point 5). This is 25 % more than is used with a commercial reference paperboard coated with 40 g/m^2 of PET or than the other experimental coated paperboards. An example of the surface flatness can be seen in Figure 4. This kind of formability can considered excellent since with press-formed trays there are very often creases or wrinkles up to 150 µm deep, while in the figure it is hard to even locate the crease. For comparison, Figure 5 shows a stereomicrograph of the formed crease in a PET-coated reference paperboard, in which case the creases were mostly visible to the naked eye. A flat surface on the rim area of the tray improves the visual quality and the functionality of the package in the heat-sealing of a lid [18, 19]. No ruptures in trays were reported with the forming parameters used.

CONCLUSIONS

The dispersion-coating formulations developed may have a potential in sustainable packaging applications where excellent convertability is needed together with a moderate grease barrier. Potential uses may include fast food packages and disposable paperboard plates. The oil resistance and convertability of hydroxypropyl-cellulose-coated paperboard can be improved by various additives. Inorganic pigments, such as talc, not only reduce the stickiness of the coating layer, but also slightly improve the oil resistance. The presence of talc or latex in the coating had no substantial impact on coating hydrophobicity, which leaves a topic for further research in order to reduce the water-sensitivity of the packaging material. Gelatin has earlier been found to improve starch film flexibility and grease resistance, and similar observations were made with HPC-based coatings.

By adding a pre-coat layer, the convertability of dispersion-barrier-coated board was significantly improved and the addition of a pre-coat layer enabled the rim tool pressure in the pressing process to be increased from 1.16 kN to 1.55 kN without any rupture at the sensitive corner areas of trays or deterioration in the quality of creases. The pre-coated sample also exhibited the best grease resistance. However, it is not possible to draw reliable conclusions as to whether or not the pre-coating alone increased the grease penetration time, because the composition of the barrier layers did not completely match those of experimented coatings in that case.

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