



Starch-poly(vinyl alcohol) barrier coatings for flexible packaging paper and their effects of phase interactions



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ABSTRACT

Starch and poly(vinyl alcohol) based barrier coatings for flexible packaging papers were studied. Both octenyl succinate modified and hydroxypropylated corn and potato starches were blended with regular and ethylene modified poly(vinyl alcohol) to increase the water vapor barrier properties and enhance the flexibility of the starch coatings, in order to accomplish superior barrier performance. Phase separation between starch and poly(vinyl alcohol) was studied in detail, both in the solution and in dry draw-down coatings on paper. The barrier performance of the coated paper was evaluated with respect to water vapor transmission rate. Conditions for the creation of a thin surface layer consisting of only one of the pure polymers were identified and discussed in terms of phase separation in solution migration of poly(vinyl alcohol) to the uppermost surface layer. The phase separation promoted low water vapor transmission rates also with a rather high fraction of starch in the coatings.

1. Introduction

Various packaging applications currently utilize flexible paper for a diversity of food packaging solutions such as baked goods, fast foods and flours. Most of these solutions rely on petroleum derivatives to create the barrier properties needed. Production of petroleum based products furthers to the emission of greenhouse gases and significant amounts of used packages will not become recycled. In order to advance the sustainable development of packaging materials, development of manufacturing processes is needed to provide flexible packaging paper from renewable resources with competitive barrier properties.

For creating sustainable, biodegradable and re-pulpable products, raw materials with comparatively low cost and high natural availability are important. Starches are attractive biopolymer candidates for replacing a part of synthetic polymers in paper coatings, since starch will increase the biodegradability of the final products and lower the material costs. The starch component of the blended coating will be consumed by micro-organisms and the remaining synthetic component skeleton structure will subsequently be subjected to natural elements attack such as UV photo-degradation and thermal oxidation [1].

In the US and Europe, the most commonly used starches are wheat, potato, corn and tapioca starches which all have different properties and compositions due to differences in amylose and amylopectin content. Varieties of waxy starches contain little or no amylose: for instance, waxy corn starch contains < 1% amylose whereas waxy

barley starch can contain up to 8% amylose [2].

Octenyl succinate (OSA) modification of starch is prepared by esterification reaction where the cyclic dicarboxylic acid anhydride and starch suspended in water are mixed under alkaline conditions resulting in a starch derivative with balanced hydrophobic and hydrophilic groups with capability of stabilizing emulsions by forming strong films at the oil/water interphase. OSA modification of starch increases the viscosity in aqueous suspensions, decreases the gelatinization temperature and OSA-modified starches have a lower retrogradation tendency compared to unmodified starch [3]. OSA modified starches improve paper properties by increasing the surface strength and the resistance to wetting [4]. FDA has approved OSA modified starches up to 3% treatment level (D.S. ~ 0.02) for food contact use [5].

Poly(vinyl alcohol), PVOH, is a water-soluble synthetic linear polymer with hydrophilic character which leads to poor water and water vapor barrier properties. Barrier properties for oxygen and other gases are however high [6]. The degree of hydrolysis of PVOH can be adjusted and it is denoted as fully hydrolyzed at > 98 mol%. Fully hydrolyzed grades are only soluble in hot water and form less stable solutions than partially hydrolyzed grades [7,8]. Previous studies have shown that PVOH is compatible [9] with starches and blends have been created to form biodegradable films [10].

Previous research has proven that good film forming properties of starches are fundamental in order to achieve coatings with adequate mechanical flexibility and water resistance [11]. The film forming properties and effects of a super-hydrolyzed ethylene modified poly

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(vinyl) alcohol blend with hydrophobically modified potato starch have been investigated and results indicated that ethylene modified PVOH gave higher film flexibility compared to standard PVOH grade in the presence of plasticizer [12].

During the last four decade's phase separation research concerning polymers has included many aspects like liquid–liquid phase studies with thin polymer films confined between two impenetrable plates [13–15]. Studies on polymer thin film coatings with deformable polymer–air interface have shown that surface tension has a strong influence on the shape of the boundary, the flexibility of the interphase can lead to unique pattern formation on the film surface which follows the process of underlying phase separation [16–23]. Studies of phase separation and rheological properties of biopolymer systems have been done with xanthan/amylose and xanthan/starch [24], starch/galactomannan [25], and extruded plasticized starch/PVOH blends [26]. From the blended melts of plasticized starch and PVOH processed with extruder and pelleted, the observation was made that the starch component formed a continuous phase while PVOH formed a discrete, network-like phase especially on the surface area [27]. Javed et al. [28] presented results from mechanical testing of starch/PVOH films that indicated a stratified structure in starch/PVOH paper coating layers. Recent computational modelling combined with experimental FTIR has been used to confirm the compatibility and stability of PVOH/cassava starch blends in water-based solution by investigating the nature of hydrogen bonding between the starch and PVOH [9].

The aim of this study is to investigate the possibility to improve the water vapor barrier properties of a starch coating by adding a small amount of PVOH, to create water-based coatings for flexible packaging paper based mainly on renewable materials. Liquid coating properties like turbidity, phase separation and viscosity were studied. Dry coating barrier properties were investigated in terms of water vapor transmission rate (WVTR) and the coating structure was analyzed with x-ray photoelectron spectroscopy (XPS). The hypothesis was that addition of PVOH could lead to a phase separation that decreases the water vapor transmission rate could decrease the water vapor transmission rate by reducing the moisture sensitivity of the coating layer.

2. Materials and methods

An OSA-modified thinned waxy corn starch (98% amylopectin), denoted C-OSA, and a hydroxypropylated and acid thinned native corn starch (76% amylopectin), denoted C-HP, both supplied by Cargill Deutschland GmbH (Krefeld, Germany) were used. In addition, a thinned OSA-modified potato starch, denoted P-OSA, with similar composition and degree of substitution as the corn starch counterpart, and a commercial hydroxypropylated, oxidized potato starch, denoted P-HP were used, the latter two supplied by Solam (Kristianstad, Sweden).

A fully hydrolyzed (saponified) standard poly(vinyl alcohol), Mowiol 4–98, with degree of hydrolysis (DH) 98.4 mol% (here denoted as PVOH_{st}) and an ethylene modified poly(vinyl alcohol), Exceval AQ-4104, with DH 98.5 mol% (here denoted as PVOH_{et}) were used. Both grades were supplied by Kuraray Europe GmbH (Frankfurt a.M., Germany). The viscosity of a 4% aqueous solution at 20 °C was about 4.0 mPas for both grades according to data supplied by the manufacturer, indicating similar molecular weight. Glycerol (ReagentPlus®, ≥99%) was supplied by SIGMA-Aldrich.

Aqueous starch solutions were prepared in a water bath held at > 95 °C under continuous stirring for 90 min (corn starches) and for 60 min (potato starches). The final solution concentration was 20% or 25% by weight, depending on the type of experiment to be performed. PVOH's were dissolved in hot water (> 95 °C) for 60 min under continuous stirring and the final concentration was 20% or 25% by weight, depending on the type of experiment to be performed. The starch and PVOH solutions were mixed at starch:PVOH ratios ranging from 100:0 wt% to 0:100 wt% on dry basis, in gradual increase of

Table 1

The pH values of freshly prepared 20 wt% stock solutions and their 50:50 wt% blends measured at 65 ± 2.5 °C.

Starch or Poly(vinyl alcohol)	pH	50:50 wt% blend of stock solutions			
		Blend		pH	
C-OSA	5.3	C-OSA:PVOH _{et}	5.2	C-OSA:PVOH _{st}	5.3
C-HP	6.7	C-HP:PVOH _{et}	6.0	C-HP:PVOH _{st}	6.0
P-OSA	4.2	P-OSA:PVOH _{et}	4.0	P-OSA:PVOH _{st}	4.4
P-HP	5.2	P-HP:PVOH _{et}	4.8	P-HP:PVOH _{st}	5.4
PVOH _{st}	5.4				
PVOH _{et}	4.0				

PVOH concentration by steps of 10% by weight. pH of 20 wt% stock solutions and their 50:50 wt% blends are presented in Table 1. The polymer solutions were cooled down to 62.5 ± 2.5 °C before subsequent experiments. The polymer solutions were used immediately after they had reached 62.5 ± 2.5 °C or shortly stored at this temperature before use if not otherwise stated. The impact of a plasticizer was studied for the combination of C-OSA and PVOH_{et} by adding 20 parts glycerol per hundred parts of total polymer (starch + PVOH_{et}), final solution concentration 23 wt%.

One-side pigment coated flexible packaging paper with a grammage of 50 gsm (Ahlstrom, France) was used as substrate. The polymer solutions were applied onto the uncoated backside by a laboratory bench coater (K-Control Coater Model 202, RK Print Coat Instruments Ltd., Royston, UK) equipped with a wire-wound metering bar giving a nominal wet film deposit of 50 µm. The speed of the metering bar was 4 m/min. The temperature of all polymer solutions was 62.5 ± 2.5 °C when applied onto the paper substrate. This temperature mimics industrial paper coating conditions, where the recommended size press and storage temperature of a starch solution normally is in the range from 62 °C to 65 °C [3]. The dry solids content of the applied polymer solutions was 20% by weight. The coated paper sheets were clamped to a metal plate, dried in an air-circulated laboratory oven for 90 s at 105 °C and subsequently coated with the same solution in a second layer followed by constrained drying at 105 °C for 90 s. The final coat weight of the double-coated backside was 20 ± 1 g/m². After the drying procedure, all coated sheets were stored in a climate room at 23 °C and 50% RH for 7 days prior to further evaluation of properties.

All error limits presented in this paper have been calculated as standard deviations based on the given number of replicates. In figures presenting WVTR (Figs. 2 and 3), turbidity (Figs. 4 and 5), and viscosity curves (Fig. 1), standard deviations have been calculated for each measuring point but have been left out in order to enhance the readability of the diagrams (see Table 3. for examples of standard deviations).

The water vapor transmission rate (WVTR) for six replicates per coating was measured by the gravimetric cup method according to ISO 2528 at constant conditions of 23 °C and 50% RH using silica gel as desiccant.

Viscosity (η) measurements were performed with a controlled shear stress rheometer MCR 300 (Physica Messtechnik GmbH, Stuttgart, Germany) equipped with a coaxial standard measuring system CC17 and Physica Viscoterm VT2 thermostat. Measurements were performed in duplicates at 60 °C. The samples were pre-sheared at 50 s^{-1} for 5 s and then ramped logarithmically with 60 points between 3–4000 s^{-1} . The dry solids content was 20% by wt. A comparison the viscosities of pure polymer solutions at shear rate 103 s^{-1} , showed that C-OSA had a viscosity of 24 ± 1 mPas and C-HP 50 ± 2 mPas which were significantly lower than the corresponding potato starch viscosities; 107 ± 0 mPas (P-OSA) and 134 ± 5 mPas (P-HP); Fig. 1. The viscosity of PVOH_{et} was 130 ± 4 mPas and PVOH_{st} 87 ± 3 mPas respectively at the same shear rate.

Electron Spectroscopy for Chemical Analysis (ESCA), also known as

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