Aqueous polyolefin dispersion for packaging boards and papers

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Abstract

Various types of polyolefins are used in many industrial applications due to the combination of attractive performance attributes they offer. Extrusion coating has traditionally been the main technology for achieving relatively thin polyolefin coatings on a moving web.

Recently Dow introduced aqueous dispersions of polyolefins. The dispersions are produced by a proprietary mechanical dispersion technology. The delivery of polyolefins in a water-based dispersion enables the use of a variety of new coating application techniques available today for water or solvent borne systems. The delivery of polyolefins as aqueous dispersions introduces polyolefins into new application areas where current emulsions and binders are limited by their performance and where extrusion coating cannot be used or may not the most efficient coating method.

Aqueous dispersions of polyolefins offer the characteristics of polyolefins such as chemical resistance, thermoform ability, recyclability and adhesion to polyolefins in combination with a waterborne fabrication advantage. This presentation introduces the aqueous polyolefin dispersion technology with examples of application areas for the packaging industry where aqueous polyolefin dispersions provide synergies as well as new opportunities beyond extrusion coating of polyolefins.

Introduction

Today over 8 million tons of paper and board products are coated via polyolefin extrusion coating processes. Globally the largest application segments are liquid packaging and flexible packaging where the purpose of the polyolefin coating is mainly to protect the packaged goods. In addition, polyolefins provide ease of processing, low off-taste, low odor and heat sealability.

In the paper industry waterborne barrier coating is often the term utilized in the context of increasing barrier properties of paper or board. In recent years various technologies have been developed to enable waterborne barrier coatings for paper and board. Still currently the waterborne barrier paper market is a nascent segment of the total barrier coating market in paper and paperboard. Main barrier products used in the paper industry are extruded polyethylene (PE), fluoropolymers and aluminum foil. These incumbent barriers or barrier coatings are being targeted by the paper industry for replacement due multiple reasons. Replacement of extrusion coated PE with waterborne coatings can enable value chain integration with online coating utilizing the existing waterborne coating equipment on paper or paperboard machine. Fluoropolymers are used often as grease resistant coatings but environmental and health concerns have been driving the industry to find better alternatives. Aluminum based oxygen barriers extend the shelf life of products, but recovery of raw materials is made challenging since the aluminum is often combined with PE layers and thus resulting to metal polymer mixture rather than monomaterial.

In waterborne barrier coatings research a large number of studies focused on styrene-butadiene latex based formulations, ethylene vinyl alcohol, polyvinylidene chloride, polyethylene waxes, and emulsions of polyethylene terephtalate to understand the water vapor barrier performance, but the water vapor properties were generally inferior to those achieved with extruded PE; in-reel blocking was often a challenge as well [1,2,3,4,5]. To further improve water vapor barrier properties and to reduce the inherent blocking tendency of typical waterborne coatings, mineral fillers have been explored in many studies [2,6]. However, the water vapor barrier performance did not always show the expected improvement, presumably due to incompatibilities between the polymer and pigment interfaces and due to the density increase and consequent lower coating thickness at equal coat weight. High mineral filler levels can also result in brittle coating layers and lead to cracking in creasing and folding operations and subsequent loss of barrier performance. The research in waterborne barrier coatings does generally not discuss the organoleptic properties, which are an important aspect in food packaging applications and may limit the commercialization even if all the other performance criteria are achieved.

It the area of waterborne barrier coatings many studies have also focused on the use natural polymers, such as starch, pectin and xylan [7,8,9,10,11]. From the barrier performance perspective the natural polymers are typically targeted for oxygen barrier and oil and grease barrier. It has to be noted that for oxygen barrier the bar is set high by aluminum in most of the applications where true oxygen barrier is required. The limited moisture resistance of natural polymers requires moisture protection in order to maintain the oxygen barrier. Most of the natural polymers targeted for barrier applications are brittle and thus require a significant amount of plasticizer to improve the mechanical properties, which negatively impact the barrier performance. From a coating process perspective a challenge with natural polymers in the waterborne coating process is that they require a high water concentration to maintain low enough viscosity for industrial applications.

The here discussed novel approach of using mechanical dispersion technology has enabled production of polyolefin dispersions that are not available via emulsion polymerization of conventional dispersion technologies. This route enables high solids and low viscosity dispersion polyolefins. The first products made via this route are ethylene and propylene co-polymers delivering olefinic properties in waterborne dispersions. These aqueous polyolefin dispersion show moisture resistance, oil and grease resistance, heat sealability and adhesion to both polyolefins and non-polar cellulose based materials. The oxygen barrier performance is limited as expected based on the polymer choice. The mechanical dispersion process is solvent-free and the use of selected polyolefin resins enables very low VOC and good organoleptic properties enabling use in food packaging applications. This unique combination of processing and performance attributes overcomes many of the limitations of previous waterborne barrier coatings described above.

The use of an aqueous processing technology in the aqueous dispersion of polyolefins delivers new options for the industry that are not viable by melt processing of polyolefins. Examples of new coating options include low coat weights (even in the sub micron range), impregnation of paper, coat in pattern, low temperature processing, high speed coating and use of current aqueous coating technologies at paper mills to enable on-line coating.

The above mentioned characteristics of aqueous polyolefin dispersions and their application benefits allow the use of these products in various applications in paper and board and especially in packaging and specialty paper grades, which can be categorized by their coat weights;

1. Low coat weight (0.1- 3 gsm): Adhesion priming and sizing effect to paper
2. Medium coat weight (4-7 gsm): Heat seal coatings and improved sizing effect
3. High coat weight (7-15 gsm): Improved water vapor barrier and oil and grease resistance.

Fundamentally the same dispersions can be applied in all these three application segments. However, the final product selection for each of the category depends on the application requirements. The coat weights given above are only indicative since the final coat weight requirements are highly dependent on the substrate roughness, the coating technology, the number of coating layers as well as final performance targets.

Experimental

Aqueous Polyolefin Dispersions

Table 1 describes the aqueous polyolefin dispersion (POD) products used in this work. In addition, the dispersion POD Standard was modified in this work by reducing the polar content in order to improve water vapor barrier and water resistance. The solids portion of all the described products contain 100% polymer. The solids content of all the dispersions used in this work were between 44% and 50%. The average particle size was below 2 µm for all the dispersions.

Table 1. *Description of blocking test evaluation*

Product designation	Target performance	Polymer composition	Functional groups	Polymer melting point [˚C]	Polymer glass transition point [˚C]
POD Primer	Primer	Ethylene-Copolymer	Medium	63	-53
POD Standard	Standard	Ethylene-Copolymer	Low	63	-53
POD BI	Barrier Improvement	Ethylene-Copolymer	Low	63	-53
POD BR	Blocking Reduction	Propylene-copolymer	Medium	80	-26

Paper Coating
The paper coating for the adhesion priming work was done at a pilot coater. The coating method was pre-metering size press (PMSP) and coatings were applied at a speed of 500 m/min. Grooved rods were used in PMSP application to control the coat weight. The paper (60 g/m^2) was coated on the side that did not have any prior surface treatment, i.e. no coating nor sizing.

In the blocking study the same pilot coater was used but a bent blade application head was used. In the blocking study a paperboard with 370 g/m^2 basis weight was coated. The coating speed of the paperboard was 250 m/min. The coated side of the paperboard did not have coating nor sizing.

Laboratory coatings for the barrier work were applied to paper sheets using an automated lab rod drawdown coater. The depth of the grooved rod, coating speed, formulation solids, and caliper of the rod holder were adjusted to obtain the target coat weight. After coating, the sheet was immediately dried in a preheated forced air oven of 1 minute at 150ºC (300ºF) and conditioned for 24 hours at 50% relative humidity at 23º C before testing. The paper in the laboratory studies had 54 g/m^2 basis weight. This paper did not have sizing or coating treatment prior to the laboratory coating with polyolefin dispersions.

Extrusion Coating
Extrusion coatings were applied on a Dow extrusion coating/laminating pilot line in Horgen, Switzerland. Extrusion coatings of 20 g/m^2 coat weight were applied at 200 m/min line speed at set melt temperatures of 280 and 300 °C with and without corona pre-treatment of the substrate web. Extrusion coating polymer was ELITE™ 5800G, which is enhanced polyethylene (EPE) resin from Dow. This EPE coating resin is characterized with its density of 0.911 g/cm^3 and melt index of 12 dg/min. The resin is an ethylene-octene copolymer.

Water Vapor Transmission Rate Test
A gravimetric determination was made of the water vapor transmission rate (WVTR) of sheet materials at various temperatures and humidities on one side and a desiccant on the other. The WVTR of a sheet material was measured in grams per meter squared per day under specified steady conditions. Measurements were done at two different temperature and humidity conditions, namely 23°C and 50% RH (room condition) and 38°C and 90% RH (jungle condition). The lower the WVTR the less water has penetrated through the barrier coating to the desiccant below.

Blocking Test
The blocking was conducted according to the following method. Two press platens were preheated. The test was done at both 60ºC and 45ºC. Two test samples (6” x 6”) were positioned between two pieces of blotter paper (6” x 6”) to form a composite. The composite was placed between the preheated press platens, and subjected to 1500 psi (pounds per square inch) of pressure for the total sample area at 60ºC and 45ºC for approximately 3 minutes. After 3 minutes, the sample was removed from the press, and it was allowed to cool for approximately 15 seconds. Subsequently, the blotter sheets were pulled manually apart under a uniform and rapid force. The samples were inspected for their blocking properties, and ranked according to the scale displayed in Table 2. The percent of fiber tear was also determined and recorded.

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Table 2. *Description of blocking test evaluation*

Value	Description
0	Sample sheets fall apart without effort
1	Sample sheets come apart with slight resistance
2	Sample sheets come apart with slight stickiness
3	Sample sheets show noticeable stickiness, but no material transfer between sheets. Coated sample sheet appears similar to untested sample
4	Sample sheets show noticeable stickiness but with some slight picking or material transfer between sheets. Coated sample sheet appears different than untested sample
5	Sample sheets show noticeable stickiness and can not be completely separated without fiber tear (complete transfer of some or the entire sample sheet to the other) Note: Amount of fiber tear was estimated and expressed as a percentage. Example: 5%, 10%, 75% etc

Hot Bar Sealing Test
Hot bar sealing was performed with a Kopp SGPE-20 instrument. The contact time was 3s and pressure was 50 N/cm^2. The sealing bar temperatures ranged from 85˚C to 170˚C. The sealing performance was evaluated by opening the seal and analyzing the percentage of fiber tear.

Adhesion Rating – Panel Test
A panel of six individual members pulled the samples apart. Each reported rating is the average of at least 6 manual ratings per sample. The adhesion rating scale was 1 (no adhesion) to 10 (strong adhesion), and the failure classification was as follows: 1 = D delamination; 2 = FT fiber tear; 3 = FB film break or paper break.

Standard Tests
Water absorption was tested by using a Cobb test via Tappi method T-441. The duration of the test was set to 2 minutes. Grease resistance was tested (Kit test) as described in Tappi method T-559. The test was performed for both flat and folded samples.

Results and Discussion

Adhesion priming with low coat weights

In general, adhesion of fundamentally incompatible polyethylene (PE) to paper is often a limitation in extrusion coating of paper. Adhesion between polyolefin and paper can be improved by pretreatment techniques such as corona or flame treatment. However, corona treatment is a high-energy process creating high temperatures and UV-radiation that can cause substrate degradation and increased odor. Adhesion can be also increased by oxidation of the polyolefin by increasing the melt temperature or applying ozone treatment to the molten web, but this is known to increase the potential for decomposition products that can lead to poorer organoleptic characteristics. Often the only viable option to improve adhesion is to limit the line speed.

Enhanced polyethylene (EPE) resins can deliver better performance than traditional low density PE (LDPE) and thus allow down gauging. However, significant reduction in their adhesion to paper is a major drawback that can limit the extrusion coating to relatively low line speeds (see Figure 1).

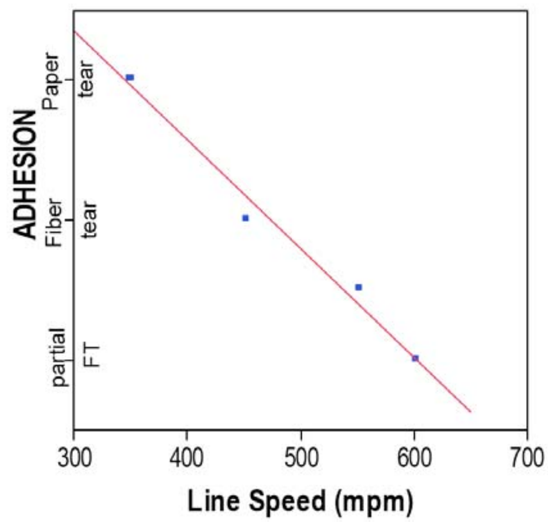

Figure 1. *Adhesion of EPE resin to paper as a function of line speeds [12].*

Aqueous polyolefin dispersions were evaluated for their performance as an adhesion primer to improve the adhesion of EPE resins to paper. The dispersion POD Primer was applied as the priming layer. The results displayed in Figure 2 show the adhesion data for different POD Primer coat weights and extrusion coating conditions (melt temperature and pre-treatment). The reference surface without any surface treatment showed very poor adhesion even with corona treatment and at high extrusion temperature. The paper with 0.8 g/m^2 polyolefin dispersion coating showed a significant improvement in adhesion when compared to the reference paper. It is worth noting that the difference between the two coat weights in this case is minor suggesting further down gauging potential. One might postulate that only a very thin layer is required on the cellulose surface to achieve the adhesion improvement. From these results it is apparent that significant improvement in adhesion can be achieved with functionalized polyolefin dispersion, POD Primer, which acts as a link between two inherently incompatible layers.

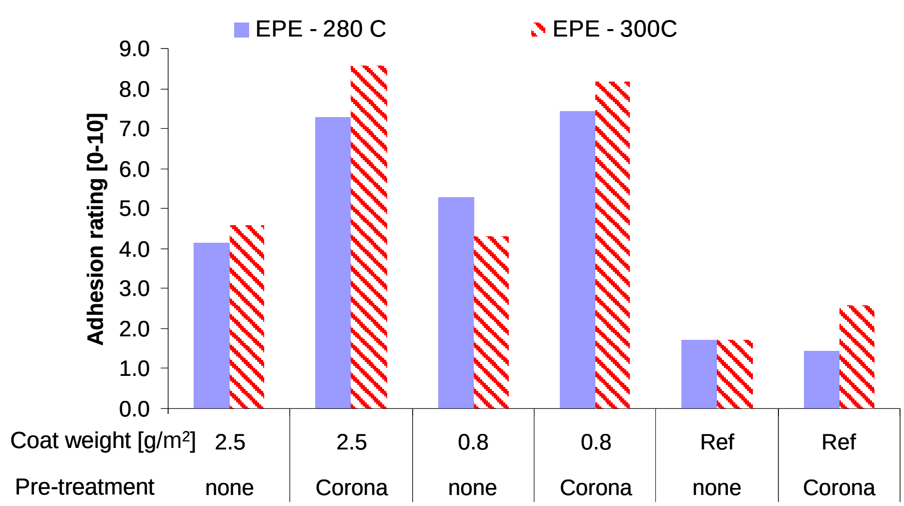

Figure 2. *Manual adhesion rating for paper surface primed with POD Primer vs. reference without any surface treatment. The extrusion coating polymer was EPE resin, which was coated at two different extrusion coating temperatures. The primed surface was extrusion coated on paper surface without corona pre-treatment and with corona pre-treatment.*

Barrier applications with high coat weight

A key benefit of using semi-crystalline polyolefins in aqueous polyolefin dispersion is that fundamentally both water and oil resistance can be achieved with a single product. However, incorporation of polar components is necessary to make a stable aqueous dispersions of polyolefins. An early hypothesis was that reduction of the polar content should improve the water and water vapor barrier properties. The results displayed in Figure 3 and 4 confirm the hypothesis and demonstrate significant improvement in the water vapor and water resistance as the polar content is reduced. In the early stage of the development high level of polar components were used and dispersion POD Standard has a normalized polar content or 100%. The high polar content led to a limited water and water vapor barrier performance. Optimization of the mechanical dispersion process allowed development of stable dispersions at significantly reduced polar content, which has resulted in dispersions with significantly improved water vapor barrier performance and reduced water absorption behavior.

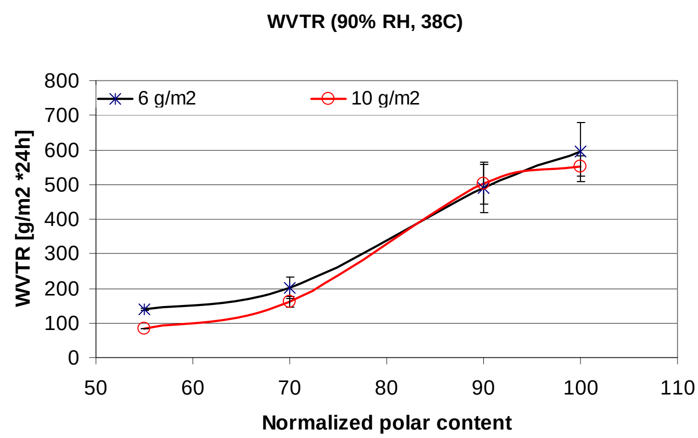

Figure 3. *Water vapor barrier (WVTR 90% RH 38˚C) for product POD Standard as a function of the polar content. The laboratory coated paper had coat weights of 6 g/m² and 10 g/m².*

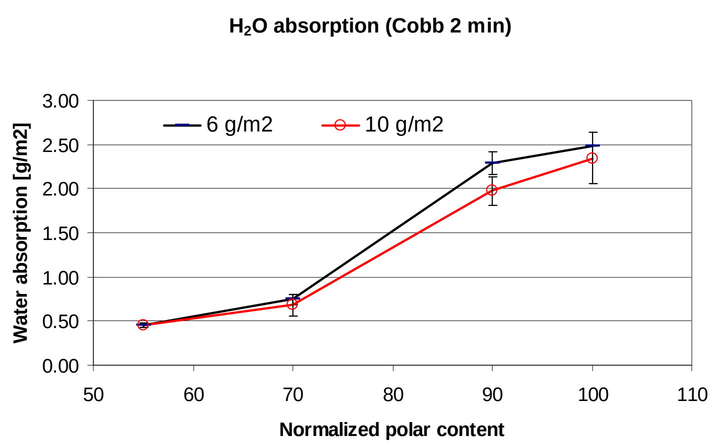

Figure 4. *Water absorption values (Cobb, 2 min) for product POD Standard as a function of the polar content. The laboratory coated paper had coat weight of 6 g/m² and 10 g/m².*

Table 3 displays the barrier results together with blocking and heat seal performance. The dispersion POD BI show the possibility to obtain water vapor barrier, water resistance and grease barrier. This product also is heat sealable at low heat seal initiation temperatures. However, in-reel blocking may become a problem with POD BI, if the web temperature exceeds 45˚C in rewinding. To demonstrate the possibility to reduce the blocking behavior the product POD BR was developed and tested for its blocking resistance. Table 3 shows that low in-reel blocking performance can be achieved with POD BR by changing the polyolefin backbone. The low blocking was also tested in the pilot coater where the rewind temperature was set to 48˚C and the coat weight was 14 g/m^2. No blocking was observed immediately after the coating application. In addition, the reel was left on a pallet for 3 days and no indication of blocking was observed along the pressure line. Further, the fact that the POD BR allows heat sealing provides interesting options to develop specialty paper and board grades by using an on-line coating unit.

Table 3. *Performance balance of aqueous polyolefin dispersion.*

Test results	**POD BI – Barier improved dispersion**	**POD BR - Blocking reduced dispersion**
Barrier test results		
WVTR AVG (90%,RH 38C) [$g/m^2/24h$]	54	185
WVTR STD (90%RH, 38C) [$g/m^2/24h$]	*1*	*5*
WVTR AVG (50%RH, 23C) [$g/m^2/24h$]	13	9.5
WVTR STD (50%RH, 23C) [$g/m^2/24h$]	*0.2*	*0.4*
Cobb 2 min AVG [g/m^2] [$g/m^2/24h$]	0.1	0.6
Cobb 2 min STD [g/m^2] [$g/m^2/24h$]	*0.2*	*0.1*
Grease resistance (Kit test) flat sample	12	11.8
Grease resistance (Kit test) folded sample	12	12
Blocking test results		
Blocking rating / fiber tear % (45˚C, 1500 psi)	3 / 0%	3 / 0%
Blocking rating / fiber tear % (60˚C, 1500 psi)	5 / 83%	4 / 0%
Heat seal performance		
Heat seal initiation temperature (˚C)	<70	<100

Conclusions

The novel mechanical dispersion process and further optimizations of the process have lead to an offering of aqueous dispersions of polyolefins with wide application potential in paper and board applications. This paper demonstrated the clear performance benefits in

1) Providing adhesion between inherently incompatible paper and polyolefin surface, allowing higher extrusion coating speeds and use of higher performance polyolefins for extrusion coating of paper.
2) Delivering significantly improved water and water vapor resistance by reducing the polar content of the dispersion.
3) Achieving grease barrier with balance of water and water vapor barrier.

Most importantly, the developed polyolefin dispersion with low in-reel blocking enables on-line coating of 100% polyolefin based coating at a paper or board machine and thus allows to make a product that is heat sealable and delivers both water and oil resistance.

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