## Special Issue: Bio-based Packaging

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# Applied Polymer

# Bio-based multilayer barrier films by extrusion, dispersion coating and atomic layer deposition

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**ABSTRACT:** A single biopolymer film rarely has a competitive edge against synthetic films. One solution is to combine several layers with different properties into multilayer structures. In this way, for example, the barrier properties of bio-based materials can be improved. In this study, the multilayer films are produced by combining three different techniques/materials: 1) dispersion coating (cellulose nanofibrils, CNF), 2) atomic layer deposition ($Al_2O_3$; aluminum oxide), and 3) extrusion coating (polyglycolic acid, PGA). Especially the CNF and PGA-containing multilayer films show promising oxygen barrier improvements at different humidities. Thin inorganic coatings are brittle and sensitive toward stresses during converting, which may limit their use in such specific multilayer structures. The developed bio-based films largely fulfill the barrier requirements of fresh food packaging. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 42260.

## INTRODUCTION

There is a trend in packaging industry toward more sustainable packaging materials not interfering with the end-of-life or recovery schemes and helping to avoid plastic waste accumulation. Simultaneously, there is interest in bio-based materials, which could open up possibilities for various biopolymers.[1] Roughly 40% of all plastics are used in packaging, which puts a particular pressure on the packaging industry to adopt such materials. New approaches are, however, needed to improve the functional properties of biopolymers for more demanding packaging applications. Moisture resistance of hydrophilic polymers, such as many conventional biopolymers, is in many cases inadequate, and excessive water vapor transmission through packaging impairs the quality of foods resulting in shorter shelf-lives, increased costs, and eventually more waste.

The classical biopolymers include polylactic acid (PLA), polyhydroxyalkanoates (PHA), polyhydroxybutyrates (PHB), and starch and cellulose derivatives. However, the strongest growth among biopolymers will likely take place within specific "drop-ins," especially bio-based polyester (bio-PET) and polyolefins. For example, different types of bio-based polyethylenes (bio-PE) have been recently produced from sugarcane and commercialized in, e.g., extrusion coatings for frozen food and liquid packaging cartons. These drop-ins have similar functional and processing properties as their petroleum-based counterparts.

Also excellent gas barrier polymers, such as polyglycolic acid (PGA), can be prepared from renewable raw materials. PGA is a biodegradable, thermoplastic and also the simplest of the linear aliphatic polyesters. It can be prepared from glycolic acid by means of polycondensation or ring-opening polymerization. Glycolic acid can in turn be produced via a natural metabolic route using the glyoxylate cycle.[2]

Another intensively studied material is nano-sized cellulose. Cellulose nanofibrils (CNF), also commonly referred to as nanocellulose, are typically generated by mechanical grinding or high-pressure fluidization. CNF consists of very thin (~20 nm) and long (several micrometers) fibrils, and in low concentrations (<2%), it forms a gel-like transparent material which can be used for producing biodegradable and environmentally safe, homogenous, and dense films.[3,4] CNF can be produced from various raw materials, such as banana, sugar beet, hemp, softwood, and hardwood pulps. Films plasticized with 30% of sorbitol had some promising properties including good grease and oxygen barriers, especially at dry conditions.[5] Recently, a semi-industrial roll-to-roll pilot line has been utilized to produce CNF films. The developed method is up-scalable and brings CNF film production one step closer to commercialization.[6]

Atomic layer deposition (ALD) technique is a surface-controlled layer-by-layer deposition process based on repeated self-limited gas–solid reactions.[7–9] It is well suited for producing inorganic
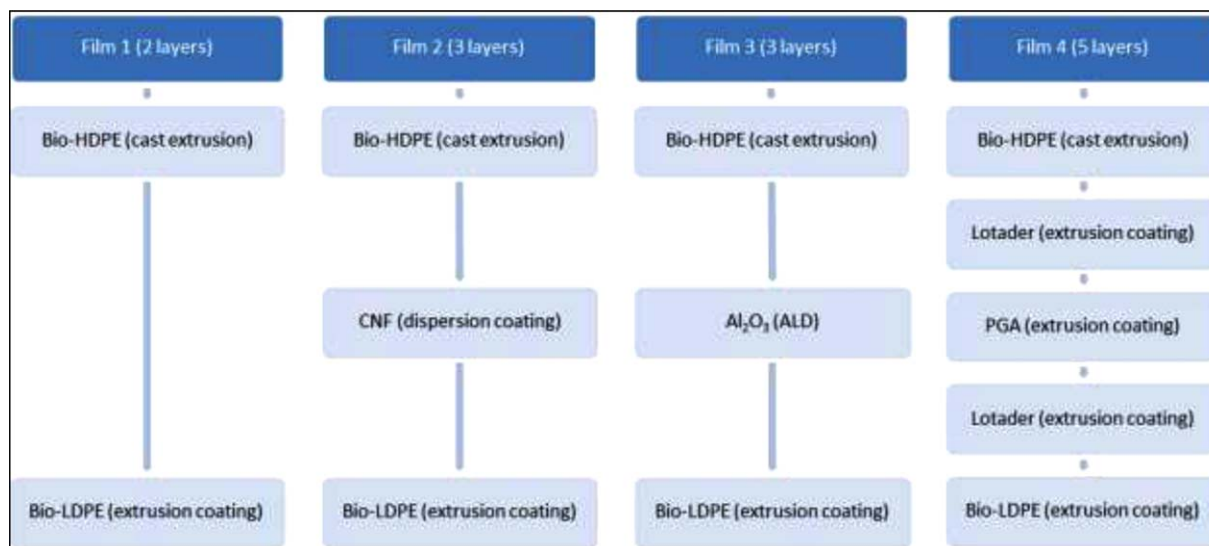
**Figure 1.** Experimental matrix: (1) bio-HDPE/bio-LDPE, (2) bio-HDPE/CNF/bio-LDPE, (3) bio-HDPE/Al$_2$O$_3$/bio-LDPE, and (4) bio-HDPE/tie/PGA/tie/bio-LDPE. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

moisture and gas barrier coatings, such as Al$_2$O$_3$, SiO$_2$, and ZnO, onto petroleum- and bio-based polymers.[10–17] However, inorganic oxide coatings with thickness of tens of nanometers are sensitive toward mechanical stresses, and they in most cases require tailored inorganic/organic hybrid multilayer structure preferably with a protective polymer coating layer.[18–22] A protective heat sealing layer can, for example, be applied in a subsequent extrusion coating process. ALD thin films have typically been produced with single wafer or batch processes at low pressures, which limits its throughput on large area applications. However, recently there have been an increasing number of activities related to roll-to-roll and atmospheric ALD processes.[23–27] A thin ALD coating does not impair disintegration of PLA film or coated board in compost, and polymer granules deposited with such coatings have been melt processed into composites indicating certain level of recyclability.[20,28]

There are also various other means, such as nano-sized fillers and different polymer blends and cross-linking, to improve the functional and processing properties of biopolymers. For example, nano-sized clays have been used to improve mechanical and barrier properties of various polymers including PLA.[29–32] Nano-sized clays and cross-linking with polyacrylic acid have also been used successfully to improve the barrier properties of CNF films.[33] Although some clay–polymer composites have reached the commercial state in high-barrier films and beverage bottles, the improvements in barrier properties are in most cases relatively weak and it is sometimes challenging to fully disperse the organic or inorganic fillers during melt processing. In addition, there have been safety-related concerns related to nano-sized particles.

Single-layer biopolymer films rarely have a competitive edge against synthetic films, thus combining several individual layers or films into multilayer packaging materials becomes necessary. In this way, good properties of several materials can be combined and, for example, the overall barrier properties may be improved.

## EXPERIMENTAL

### Materials
Figure 1 shows the different material combinations.

**Base High-Density Polyethylene (HDPE) Film.** Bio-based HDPE (Braskem SGE7252) film was produced using Extruder EX-35 (Extron Engineering) with a screw diameter ($D$) of 35 mm, a length-to-diameter ratio ($L/D$) of 30, and a cavity transfer mixer. A melt filter (50/325/50 mesh sieves) was used with a 300-mm-wide die (gap 0.7 mm). An air knife (90 kPa) and a nip roll (100 kPa) were used to enhance the contact between the film and the chill roll. Temperature profile within the extruder varied from 170 to 210°C. Temperature settings were as follows: 190°C (melt filter and connector), 200°C (die), and 80°C (chill roll). Extruder throughput was 5.0 kg/h and line speed 8 m/min. Bio-HDPE film with a thickness of 48 μm was finally collected to a core.

**Three-Layer Barrier Structures with CNF and Al$_2$O$_3$.** CNF was obtained from UPM, Finland. The material contained approx. 2 wt % cellulose in water. Tempo-oxidized CNF was produced as follows: 0.1 mmol/g pulp (2,2,6,6-Tetramethylpiperidin-1-yl)oxy (Tempo) and 1 mmol/g pulp NaBr were dissolved in water. Solution was mixed with pulp in 1% consistency. Oxidation was initiated by adding 5 mmol/g pulp NaClO and adjusting pH to 10 with HCl. During oxidation, the pH was kept at 10 with NaOH. Oxidation was continued until pH of solution did not change, and reaction was quenched by adding ethanol. Oxidized pulp was then washed thoroughly with excess water and passed through a high-pressure homogenizer (M-110EH-30, Microfluidics Inc., USA) twice. The final consistency was approximately 1 wt %. Tempo-oxidized CNF was further diluted to 0.5 wt %, and mixed first with Diaf dissolver for 1 h (500 rpm) and then with SpeedMixer (DAC 110.1 VAC-p, Hauschild) for 2 min at 1500 rpm under vacuum to prevent formation of air bubbles.

Bio-HDPE film was atmospheric plasma-activated with argon/nitrogen gas mixture for increasing the surface energy prior to

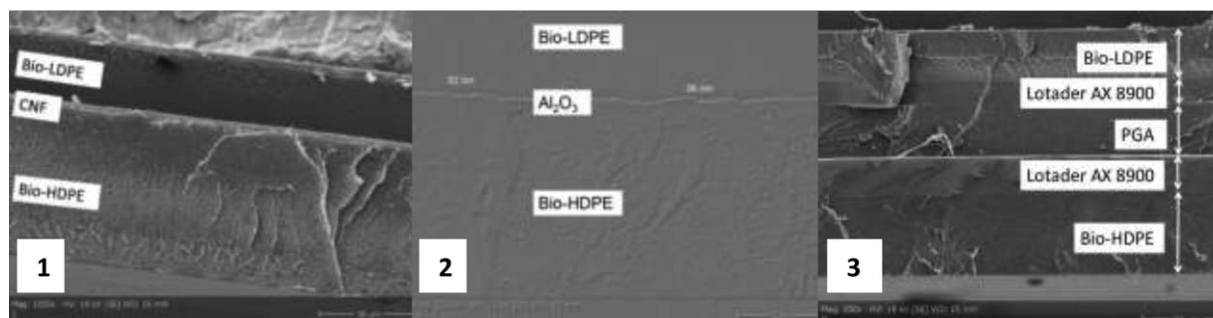**Figure 2.** Multilayer films: (a) bio-HDPE/CNF/bio-LDPE, (b) bio-HDPE/Al2O3/bio-LDPE, and (c) bio-HDPE/tie/PGA/tie/bio-LDPE.

being coated with CNF. Coating was performed with SutCo pilot-line using line speed of 1 m/min and dried at ambient conditions overnight due to the low dry content and a thick wet deposit (0.5 mm).

$Al_2O_3$ thin coating (35 nm) was deposited onto a corona-treated bio-HDPE film in Picosun SUNALE[TM] batch ALD reactor at 70°C. Trimethyl aluminum, TMA (Strem Chemicals Inc., >98%), was used as a precursor and water as an oxygen source. High-purity nitrogen (99.9999%) was used as both the carrier and the purge gas. A deposition cycle for $Al_2O_3$ was 0.1/10/0.1/10 s ($TMA/N_2/H_2O/N_2$).

Both two-layer films (bio-HDPE/CNF and bio-HDPE/$Al_2O_3$) were finally extrusion-coated with bio-based low-density polyethylene (bio-LDPE; Braskem SPB681) using Dolci extruder with a screw diameter ($D$) of 45 mm, $L/D$ of 27, and a Maddock-type mixing head. A die was 300 mm wide (gap 0.7 mm). Both CNF and $Al_2O_3$ surfaces were pre-activated by corona treatment. Temperature profile within the extruder varied from 120 to 250°C. Other temperature settings were as follows: 250°C (die) and 40°C (chill roll). Extruder throughput was 3.0 kg/h and line speed 7.5 m/min.

**Five-Layer Barrier Structure with PGA.** PGA (Kuraray 100R35) was co-extruded into a multilayer film using two Dolci extruders, first (I) one with a screw diameter ($D$) of 45 mm, $L/D$ 27, and a Maddock-type mixing head, and a second (II) one with a screw diameter ($D$) of 45 mm and $L/D$ 22. Lotader AX8900 (a terpolymer of ethylene, acrylic ester, and glycidyl methacrylate) was used as a tie layer between the PGA and polyethylene layers in order to improve the interlayer adhesion. A five-layer film was prepared on the bio-HDPE film with two sequential trials, first tie-layer and PGA were extruded onto the bio-HDPE film and then tie-layer and bio-LDPE were extruded onto the bio-HDPE/tie/PGA film.

Processing parameters at the first trial were as follows: temperatures in extruder I (PGA) were from 220 to 250°C, and in extruder II (Lotader AX8900) from 70 to 250°C. Temperature setting for the die and chill roll was 250 and 40°C, respectively. Parameters at the second trial were varying from 120 to 250°C for extruder I (bio-LDPE), from 70 to 250°C for extruder II (Lotader AX8900), 250°C for the die, and 40°C for the chill roll. Line speeds were 8 and 7.5 m/min, respectively.

**Test Methods**

Scanning electron microscope (SEM; JEOL JSM-6360LV) with accelerating voltage control of 10 kV was used to visualize the cross-section and interlayer adhesion of the multilayer structures.

Oxygen transmission rates (OTR) were determined according to standard ASTM D3985 using Ox-Tran 2/21 Oxygen Transmission Rate System (Mocon, Modern Controls Inc., USA). The tests were carried out at 23°C temperature and 0, 50, and 80% relative humidities using samples with a test area of 50 $cm^2$.

Water vapor transmission rates (WVTR) of the films were determined according to standard ASTM F-1249 using Permatran-W 3/33 MG Plus (Mocon, Modern Controls Inc., USA). The tests were carried out at 23 and 38°C temperatures and 90% relative humidity using samples with a test area of 50 $cm^2$.

Heat sealability of the films was determined using the sealing strength tester (Labormaster HTC 3000, Willi Kopp, Germany). The sealing strength was measured after sealing at 140°C with a sealing force of 300 kPa, a sealing time of 1.2 s, a delay time of 10 s, and a peeling rate of 12 m/min. Width of the sample strips was 2 cm. In each case, the bio-HDPE surfaces were sealed against each other.

## RESULTS AND DISCUSSION

Multilayer films were successfully produced by using different methods, such as extrusion coating, dispersion coating, and atomic layer deposition (ALD) (Figures 1 and 2; Table I). Sufficient bonding between layers is needed in order to minimize the delamination tendency. The main mechanisms in adhesion include mechanical interlocking, diffusion, electron transfer, and adsorption.[34,35] Adsorption theory is considered one of the most important causes in creating strong adhesion. When intimate contact is formed at the interface, both primary and secondary chemical bonds can be formed. Sufficient wetting is a precondition for good adhesion, and defects, such as air entrapment, can decrease the effective area participating in bonding. Physical surface activation treatments, such as atmospheric plasma or corona, were used to enhance wettability of surfaces and to increase the interlayer bonding. There were also adequate methods for improving the interlayer bonding between bio-polyethylenes, $Al_2O_3$, and CNF. However, PGA needed special

**Table I.** Multilayer Film Structures

| Multilayer structure | Middle layer thickness ($O_2$ barrier) [μm] | Total thickness [μm] |
|---|---|---|
| bio-HDPE (48 μm)/bio-LDPE (28 μm) | – | 76 |
| bio-HDPE (48 μm)/CNF (2 μm)/bio-LDPE (28 μm) | 2 | 78 |
| bio-HDPE (48 μm)/$Al_2O_3$ (35 nm)/bio-LDPE (28 μm) | 0.035 | ∼76 |
| bio-HDPE (48 μm)/tie (21 μm)/PGA (29 μm)/tie (13 μm)/bio-LDPE (28 μm) | 29 | 139 |

tie layers for ensuring the sufficient adhesion between the layers. Bio-HDPE and bio-LDPE were rather nonpolar, whereas $Al_2O_3$, Tempo-oxidized CNF, and PGA surfaces had comparable polar and dispersive components, and thus the total surface free energies were higher compared to polyethylene. The lack of polar component in polyethylenes limited their interactions with the polar materials, unless they were treated with plasma or corona, or otherwise oxidized. The middle layer providing the oxygen barrier was added using three different coating techniques: 1) dispersion coating (CNF), 2) atomic layer deposition ($Al_2O_3$), and 3) extrusion (PGA).

Polyethylenes are thermoplastic polymers consisting of long nonpolar hydrocarbon chains. The solubility of nonpolar oxygen molecules in polyethylene is proportional to the volume of the amorphous phase.[36] OTR of bio-HDPE/bio-LDPE film was similar to petroleum-based polyethylenes, i.e., relatively high (∼2100 $cm^3$/($m^2$ × 24 h)) and independent on the relative humidity. Oxygen barrier properties of semicrystalline polymers are mainly due to the crystalline regions which are considered to be gas impermeable.

CNF coatings have low OTR due to relatively high crystallinity and the ability to form a dense network via cellulose nanofibrils.[37–40] Close packing of fibrils reduces the free volume and efficiently prevents the oxygen transmission, as also observed earlier with coated high-density papers.[41,42] High surface area and polarity of nano-sized fibrils result in enhanced fibril-to-fibril attraction especially at low humidity. Indeed, CNF-containing multilayer films had the lowest OTR (0.6 $cm^3$/($m^2$ × 24 h)) of all tested films at dry condition. Due to the hydrogen bonds, the movement of fibrils was restricted efficiently preventing the oxygen permeation. Typically the barrier properties of most bio-based films are very sensitive to moisture variations. Water molecules enter the polymer and break the hydrogen bonds that keep the chains together. At high humidity conditions, the CNF coatings tend to swell, which resulted in an impaired oxygen barrier with the CNF-containing multilayer films at high humidities (Table II).

Thin $Al_2O_3$ layers are typically excellent and humidity-independent oxygen barriers. Also in this study, the two-layer structure of bio-HDPE/$Al_2O_3$ had relatively low OTR between 10 and 12 $cm^3$/($m^2$ × 24 h) at all tested moisture conditions (0–80% RH). However, after coating the upper bio-LDPE layer by extrusion, the good barrier properties were almost completely lost. Extrusion coating of bio-LDPE with high melt temperatures and low coating speed can have a detrimental effect on the bio-HDPE surface onto which the thin $Al_2O_3$ coating was deposited. Different thermal expansion between the layers or even melting of the bio-HDPE surface may have damaged the oxide film, which also explains why in some cases ALD-coated polyethylene surfaces can be heat sealed against each other.[20] In most cases, dry or solvent-free lamination would actually be a more feasible laminating process typically used for metallized and other metal oxide coated plastic films. As also pointed out earlier, inorganic coatings are brittle and sensitive toward several process steps including nip contacts, bending, line tensions, and other mechanical stresses. The batch ALD-coated samples were also quite small making their further processing challenging.

PGA-containing five-layer films had excellent oxygen barrier properties within a wide range of humidities (0–80% RH). Unlike CNF, PGA did not suffer a dramatic fall-off in barrier performance under high humidity. Barrier layer thickness of PGA (29 μm) was, however, considerably higher compared to CNF (2 μm) and $Al_2O_3$ (35 nm).

Polyethylene is the most widely used moisture barrier plastic nowadays. Its inherently good water vapor barrier properties were only slightly improved by using the additional barrier layers. Temperature had a more distinctive effect on the water vapor transmission rates. At 23°C and 90% relative humidity max., 25% improvement in the water vapor barrier was obtained by using CNF and $Al_2O_3$-containing multilayer films, whereas at 38°C and 90% RH, >33% decrease in transmission rates was attained with CNF and PGA layers (Figure 3).

**Table II.** Oxygen Transmission Rates of Multilayer Films at 23°C and 0, 50, and 80% Relative Humidity Expressed as $cm^3$/($m^2$ × 24 h).

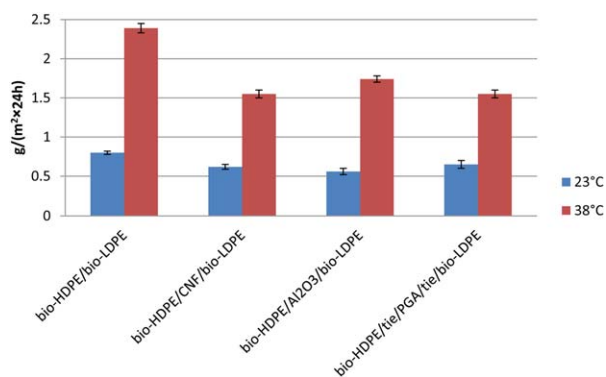| Multilayer structure | 0% RH | 50% RH | 80% RH |
|---|---|---|---|
| bio-HDPE/bio-LDPE | 2140 ± 40 | 2130 ± 30 | 2120 ± 30 |
| bio-HDPE/CNF/bio-LDPE | 0.6 ± 0.1 | 8 ± 3 | 490 ± 20 |
| bio-HDPE/$Al_2O_3$/bio-LDPE | 730 ± 30 | 650 ± 40 | 670 ± 30 |
| bio-HDPE/tie/PGA/tie/bio-LDPE | 1.0 ± 0.1 | 0.9 ± 0.1 | 1.9 ± 0.1 |

**Figure 3.** Water vapor transmission rates of multilayer films at 23 and 38°C, 90% relative humidity expressed as g/(m$^2$ × 24 h). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary. com.]

**Table III.** Heat Seal Strength of Multilayer Films Expressed as N/m

| Multilayer structure | N/m |
|---|---|
| bio-HDPE/bio-LDPE | 220 ± 100 |
| bio-HDPE/CNF/bio-LDPE | 510 ± 90 |
| bio-HDPE/Al$_2$O$_3$/bio-LDPE | 230 ± 140 |
| bio-HDPE/tie/PGA/tie/bio-LDPE | 690 ± 160 |

All multilayer films were easily heat-sealed at 140°C. In each case, the bio-HDPE surfaces were sealed against each other, and the peeling strength was measured after 10 s delay time. However, there were significant variations in sealing strengths of different samples, which may have been due to different failure modes. During the peeling the failure may occur, if the multilayer structure first separates into monolayers and then the strength of the layer structure is lower than both the strength of the interlayer bond and the strength of the heat seal.[43] CNF films are well-known for their mechanical properties,[5,40] thus both bio-HDPE/CNF/bio-LDPE and bio-HDPE/tie/PGA/tie/bio-LDPE films had considerably higher heat seal strength as compared to the other films (Table III). However, all the values were at acceptable level (>200 N/m).

## CONCLUSIONS

For extending the shelf-life and maintaining quality of fresh foods, food packaging films typically consist of multiple layers with specific functions, such as barrier layers against oxygen, moisture, grease, aromas, and UV light. As single-layer bio-based films have typically very limited technical properties, such as moisture resistance and sealability, the multilayer structures need to be produced for pushing them toward more demanding commercial applications. Multilayer films were produced by combining three different techniques and materials: 1) dispersion coating (CNF), 2) atomic layer deposition (Al$_2$O$_3$), and 3) extrusion (PGA). Especially the CNF and PGA containing multilayer films showed promising oxygen barrier improvements at different humidity conditions. Thin Al$_2$O$_3$ coatings, on the other hand, were brittle and sensitive toward thermal and

mechanical factors which may limit their use in the type of multilayer structures produced in this study. The developed bio-based multilayer films largely fulfilled the barrier requirements of fresh food packaging.

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