

Cellulose/Acrylic Acid Copolymer Blends for Films and Coating Applications

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ABSTRACT: Enzymatically treated cellulose was dissolved in a NaOH/ZnO solvent system and mixed together with poly(ethylene-*co*-acrylic acid) (PE-*co*-AA) or poly(acrylamide-*co*-acrylic acid) (PAA-*co*-AA) polymers, in order to improve the properties of dissolved cellulose and to prepare homogeneous cellulose-based blends for films and coatings. The solution stage properties of the blends were evaluated by rheological methods and the precipitated dry blends were characterized by dynamic mechanical analysis, differential scanning calorimetry, and scanning electron microscopy. Paperboard coating tests done at laboratory scale showed dissolved cellulose/acrylic acid copolymer-based blends function well as coating materials. All of the tested blends showed a good resistance against grease in the coating trials, having grease resistance from 60 to 69 days despite a very thin ($\sim 2 \mu\text{m}$) coating layer. In addition, cellulose/PE-*co*-AA coating showed improved water vapor and oxygen barrier properties when compared with neat dissolved cellulose-coated paperboard. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40286.

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INTRODUCTION

The development of packaging materials from renewable resources, looking for alternative materials for petroleum-based polymers has been pursued for a long time. Cellulose and cellulose-based materials have become one of the most important bio-based substances when developing new types of polymeric materials.¹ Although cellulose is the most abundant natural polymer on earth, its processability has been limited. Strong hydrogen bonding between cellulose chains and fibers are the main reason why cellulose degrades, rather than becomes deformed when heated and the reason why cellulose is insoluble in most common solvents. However, new approaches to use cellulose have been developed during recent years. One way to overcome the processability problem of the cellulose is to dissolve it in a suitable solvent, such as NaOH in water. The first reported dissolutions of cellulose in NaOH/water were done in 1934 by Davidson² even though Sobue et al.³ are often mentioned as the finders of this discovery. In NaOH-based solvent systems cellulose can be dissolved with NaOH concentrations ranging from 6 to 18 wt % at a temperature of +5 to -6°C ³⁻⁹ or through a freeze-melting procedure.^{4,10} Based on aqueous sodium hydroxide, several solvent systems, for example, NaOH/

urea,^{9,11,12} NaOH/thiourea,^{9,13} NaOH/urea/thiourea,¹⁴ and NaOH/ZnO^{10,15} have been developed during recent years. The additives such as zinc oxide or urea have been reported to help the cellulose dissolution process by stabilizing the solution against gelation. In addition to NaOH-based solvents, ionic liquids (IL) such as, 1-*N*-allyl-3-methylimidazolium chloride (AmimCl) or 1-butyl-3-methylimidazolium chloride (BmimCl) have arisen as new types of promising environmentally friendly solvents for dissolution of cellulose.^{16,17} Also direct solvents, like *N*-methylmorpholine-*N*-oxide (NMMO),^{18,19} have been developed to dissolve cellulose. At the moment NMMO is the only cellulose solvent that is used for industrial scale production of regenerated cellulose fibers.

In order to prepare new feasible polymeric materials the importance of polymer blending has increased during recent years. Blending of polymers is a relatively efficient way to produce materials that have properties unattainable with single components. The properties of natural polymers can be significantly improved by blending them with synthetic polymers. Desired properties can be achieved through blending different polymers by physical or chemical blending techniques such as melt mixing, powder mixing, and solution mixing.¹ The main

requirement in order for the properties of polymers to combine within the blend is to get homogeneous morphology. When considering this, the disadvantages of cellulose mentioned earlier and the different characteristics of blended polymers make the preparation of well-mixed cellulose-based blends highly demanding.

One proper way to prepare a cellulose/polyolefin blend is to use poly(ethylene-*co*-acrylic acid) (PE-*co*-AA) as the polyolefin. The advantage of PE-*co*-AA is that when the polymers, for example, cellulose (for instance in NaOH/ZnO solvent) and PE-*co*-AA are in an alkaline water phase, they precipitate simultaneously by acidic treatment. The blending of cellulose with PE-*co*-AA is introduced in articles by Saarikoski et al.²⁰ and Lipponen et al.²¹

As mentioned above, blending is an important procedure to improve and modify the physical properties of the polymers. The mechanical properties of cellulose films can be enhanced by blending, for instance, poly(acrylamide-*co*-acrylic acid) (PAA-*co*-AA) with cellulose. Acrylic acid- or acrylamide-based water-soluble polymers are widely used as: adhesives, flocculating, and viscosity-control agents or drainage/retention aids in paper making.²² Because of hydrophilic $-\text{COOH}$ and $-\text{NH}_2$ groups belonging to PAA-*co*-AA it has the capability to absorb large amounts of water and therefore has been used to produce, for instance, super-absorbent hydrogel nanocomposites²³ and used in controlled drug release applications.²⁴ When PAA-*co*-AA is compared with PE-*co*-AA, the advantage is that it can form strong hydrogen bonds with cellulose due to its amide groups. This could exhibit better compatibility and mechanical properties for film and coating applications.

Recently there has been an increasing demand for alternatives to fossil-based packaging applications due to the increasing oil prices, growing packaging markets, and growing environmental concerns.²⁵ However, many packaging applications require a good resistance against grease, oxygen, and water, but to meet all of these requirements is extremely demanding.

A low oxygen transmission rate (OTR) is one of the main requirements for many packaging applications, especially in food packaging. To meet the demand for low oxygen permeability, the coated polymer must meet a number of general criteria. Polymer film properties that reduce oxygen permeability are high crystallinity, low mobility of the local polymer segments, and a dense polymer matrix.²⁶ For instance, chitosan has been used to achieve an oxygen barrier on greaseproof paper, because of its hydrogen bonding ability and high crystallinity.²⁷

Similar to oxygen barrier properties, the water vapor permeability plays a key role in food packaging. In food packaging, the shelf-life of food is influenced by the presence of moisture and oxygen. For instance, when developing new polymeric materials from renewable resources for the food packaging industry, hydrophobicity of the materials is crucial and hence a low water vapor transmission rate (WVTR) is a very desirable property.²⁸ The water barrier properties of paper or board can be improved by coating the paper or board with hydrophobic materials or by changing the wettability of the paper surface with sizing agents.²⁹

Commercially there are a number of techniques in order to obtain oil/grease resistant paper. In general, to obtain a good oil/grease resistance, a high mechanical treatment (beating) of the furnish is often used in the manufacturing process, resulting in a dense paper with very fine pores.³⁰ In addition to the mechanical treatments, the grease resistant paper is normally coated with film forming polymers. For instance, starch, carboxymethyl cellulose (CMC), or polyvinyl alcohol (PVOH) are used in combination with fluorochemicals or sodium alginate as sizing agents in size press coating technique to improve the barrier properties of the greaseproof paper.³⁰ One of the most commonly used greaseproof papers is vegetable parchment paper. Vegetable parchment is prepared by feeding a paper manufactured from chemical pulp through a bath of sulfuric acid. By this treatment, the acid dissolves the surface layers of the paper and the cellulose fibers become almost fused together. As an outcome, a paper with dense structure, low porosity, and good greaseproof characteristics is achieved.³¹

In this study, blends of cellulose and PE-*co*-AA or PAA-*co*-AA were prepared by the solution mixing method. To characterize the miscibility and viscosity profiles of the blends studies were carried out by rotational rheometry. The final dry blends were characterized by dynamic mechanical analysis (DMA), differential scanning calorimetry (DSC), optical microscopy (OM), and scanning electron microscopy (SEM). Finally, the surface coating approach was used to prepare barrier coatings in a laboratory scale and the barrier properties of the coated paperboards were measured and evaluated. Previous studies by Saarikoski et al.²⁰ and Lipponen et al.²¹ have proved that the solution mixing procedure is an effective and easy way of preparing blends from dissolved cellulose and PE-*co*-AA. Dissolved cellulose with its dense and crystalline structure when regenerated, has potential especially in textile fiber applications.^{10,32} However, the potential of dissolved cellulose in coating and film applications has not yet been fully identified. By combining cellulose with acrylic acid polymers it is possible to prepare materials with a wide range of advantageous properties for film and coating purposes.

EXPERIMENTAL

Materials

Alkaline cellulose water solution (3 wt % cellulose, 6.5 wt % NaOH, and 1.3 wt % ZnO) was received from Tampere University of Technology. Softwood (spruce-pine) sulfite cellulose pulp from Domsjö Fabriker AB (intrinsic viscosity 520 mL/g) was shredded mechanically and thereafter treated with commercial enzyme preparation (dosage 250 nkat/g). The enzyme-treated pulp was dissolved in NaOH/ZnO through a freeze-melting procedure as published previously by Vehviläinen et al.¹⁰ The preparation of this solution is described in the patent application of Vehviläinen et al.³³ and the dissolution process is presented in Figure 1. After the dissolution, the cellulose solution was stored in a freezer (-20°C). An alkaline sodium salt water solution of PE-*co*-AA (20 wt % of PE-*co*-AA, pH ~ 10) was obtained from BIM Finland Oy and it was stored in a refrigerator ($+5^\circ\text{C}$). Both solutions (cellulose and PE-*co*-AA) were allowed to warm up to room temperature prior to usage. Partial

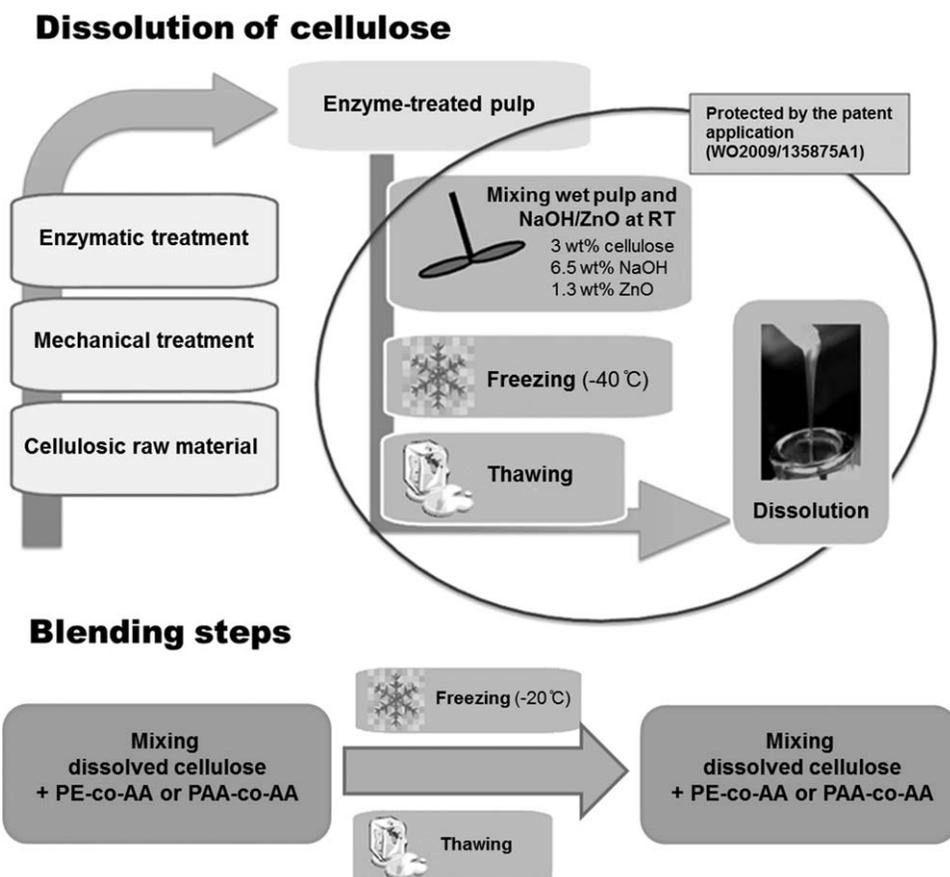


Figure 1. Process chart of the blending process.

sodium salt powder of PAA-*co*-AA (Mw 520,000, acrylamide ~80 wt %) was obtained from Sigma-Aldrich.

All the preparation steps were made at 23°C unless otherwise mentioned. The solutions and polymers mentioned above were mixed vigorously in a 100 mL glass vessel with a magnetic stirrer (cellulose batch ~50–100 mL). Dosing of the PE-*co*-AA solution was done with a syringe by feeding it slowly into the vortex of the cellulose solution. Dosing of PAA-*co*-AA was done similarly, but with a metal spoon instead of syringe. The formed dispersion was mixed directly for 24 hr. After mixing the dispersion for 24 hr it was cooled to –20°C and kept in a freezer

overnight, after which it was slowly warmed back to room temperature and mixed for another 24 hr (slow melting with vigorous stirring). This freeze–melting method between the mixing steps was done in order to dissolve any cellulose which may have gelled during mixing. The effect of this procedure is explained in more detail in an article by Saarikoski et al.²⁰ The blending process is presented in Figure 1. The polymer compositions of the blend dispersions are represented in Table I.

After the mixing steps, film samples for DMA, DSC, and SEM were prepared as follows: 2 mL of the dispersion were flattened between two glass plates where the polymer dispersions were

Table I. The Polymer Compositions of the Blend Dispersions and the Neat Cellulose Reference Sample (Cell 100)

ID	Polymer content (wt %)	Cellulose (wt %)	PE- <i>co</i> -AA (wt %)	PAA- <i>co</i> -AA (wt %)	Mixing (hr)	Freeze-melted
Cell/PE- <i>co</i> -AA 95/5	3.1	95	5	–	24 + 24	Yes
Cell/PE- <i>co</i> -AA 90/10	3.3	90	10	–	24 + 24	Yes
Cell/PE- <i>co</i> -AA 75/25	3.8	75	25	–	24 + 24	Yes
Cell/PAA- <i>co</i> -AA 95/5	3.0	95	–	5	24 + 24	Yes
Cell/PAA- <i>co</i> -AA 90/10	3.1	90	–	10	24 + 24	Yes
Cell/PAA- <i>co</i> -AA 75/25	3.2	75	–	25	24 + 24	Yes
Cell 100	3	100	–	–	–	No

The samples were freeze-melted in the middle of 48 hr of mixing.

regenerated by immersing the layers in acidic solution (20 wt % H_2SO_4). After complete regeneration, the glass plates became loose and the sample was washed carefully with water until neutral. The wet film sample was placed between two polyimide films with a small weight on top and allowed to dry at room temperature. The thicknesses of the films were between 20 and 40 μm .

Characterization

All the analyses were performed at 23°C unless otherwise mentioned. The rheological characterization of the solutions and dispersions were done using a Physica MCR 301 rotational rheometer (Anton Paar GmbH, Austria) equipped with DIN concentric cylinders geometry (CC 27) with a bob (\varnothing 26.67), and a stainless steel cup (\varnothing 28.92 mm). In order to estimate the changes in the dispersion structure during the mixing and to obtain the viscosity profiles of the coatings, steady shear flow rotational measurements (0.1–1000 1/s) were performed for all of the blend dispersions and solutions.

Changes in the dispersion structure during the mixing were also estimated with an Olympus BH-2 optical microscope equipped with a digital camera. Photomicrographs of precipitated dispersions were taken with a 100 \times magnification. The morphology of the films and coated samples were observed using a SEM (Zeiss Sigma VP) with an acceleration voltage of 3.5 kV. The exposed surfaces were coated with a thin layer (\sim 1–2 nm) of gold/palladium by sputtering to promote conductivity before SEM observation. In addition, samples of coated paperboards were cut with a Microm HM 325 microtome and cross-section photomicrographs were taken with a Zeiss Axioskop 40 upright microscope with polarization contrast.

The thermal behavior of the dry blends was measured with a Mettler Toledo DSC 821e under nitrogen atmosphere. The thermal history of the blends was destroyed by heating the samples to 150°C at 20°C/min. The crystallization behavior was then determined from the peak temperature of the crystallization exotherm (T_C), which was obtained at a cooling rate of 10°C/min (from 150°C to -30°C). After the cooling step, the glass transition temperatures (T_g) of the blends were measured by reheating the sample at 10°C/min to 150°C. The sample amounts varied between 4.5 and 6 mg with the film samples. A 10 mg sample amount was used with the neat polymer samples.

The mechanical properties of the film samples (thickness \sim 20–40 μm) were analyzed with DMA (TA instruments Q800) at 23°C (relative humidity 25%) using a film/tension measuring head. Stress sweeps for the samples were done from 0 to 30 MPa or until they broke down. Three parallel measurements were performed for each sample with the exception of the Cell/PE-co-AA 75/25 and Cell/PE-co-AA 90/10 samples on which it was possible to do only two measurements due to the brittleness of the films.

The coating application trials were made with an Erichsen film applicator Coatmaster 510 (Erichsen GmbH & Co., Germany) with spiral rods on the coated side of the carton board (Stora Enso Performa Natura 210). The coating speed was 24 mm/s.

The coatings were dried in a circulating air oven at 105°C for 5 min. The target weight for the dry coating was 10 g/m². The uniformity of the coating layers (pinholes) were observed with isopropanol.

OTRs were measured using an Oxygen Permeation Analyzer Model 8001 (Sys-tech Instruments Ltd, Thame, UK) according to a modified ASTM D-3985 procedure at 23°C and 50% relative humidity. Two to three parallel measurements were performed per sample. WVTRs were determined gravimetrically according to the modified ISO 2528:19958E standard at 23°C and 50% relative humidity. Two parallel measurements were performed per sample. The water contact angle of the coated samples was measured with an optical contact angle meter CAM 200 (KSV Instrument Ltd).

Grease resistance was determined according to the ASTM F119-82 standard test method for the rate of grease penetration of flexible barrier materials (rapid method). Six parallel measurements per sample were examined as function of time (days). The penetration time of olive oil through the samples determined the grease barrier value. In addition to the ASTM F119-82 standard test method, Tappi 507 T cm-09 method was used to test the grease resistance. In Tappi 507 T method the test is done at 60°C and 50% relative humidity for 4 hr. The tests with this method were performed 2 weeks after application. Rapeseed oil was applied in five parallel specimens per sample. Numerical values for the oil penetration through the measured area were calculated using customized software after specimen scanning.

RESULTS AND DISCUSSION

Solution Stage Properties

Rheological properties, including viscosity profiles are one of the key matters to be considered when preparing new types of blends and coatings. Rheological properties of the blend dispersions were studied and compared to find out the influence of the solution stage properties on the final dry films and coatings. The effect of mixing time and procedure on the dispersions was visible in rheological behavior in the solution stage and in optical microscopy micrographs of the precipitated films after each mixing step. Poor solubility (soluble vs. gel vs. aggregate) of cellulose/PE-co-AA dispersion is observed at the early stages of mixing. This appears not only as aggregated particles in OM micrographs of precipitated blends [Figure 2(a,b)] but also in rheological results as slightly increased viscosity values (see Figure 3). However, like expected, as the mixing proceeds and the freeze–melting procedure was between the mixing steps, the viscosity values decreased and the dispersion quality became more uniform. Furthermore, better mixing is seen in the form of more homogeneous film quality after precipitation, that was also confirmed by SEM micrographs of the precipitated films (Figure 4).

After the mixing steps, rheological properties remained approximately the same when a low polymer content was used (95/5 and 90/10 dispersions; Figure 5), regardless of the added polymer (PE-co-AA or PAA-co-AA). Although, a slightly decreased viscosity value for the Cell/PE-co-AA 90/10 dispersion was seen

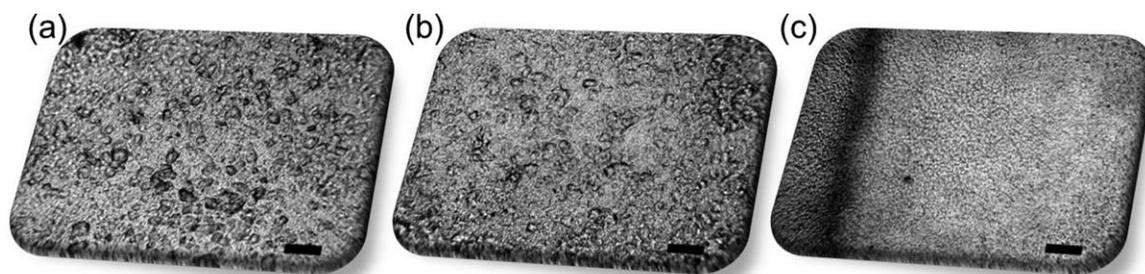


Figure 2. OM-photomicrographs of precipitated cellulose/PE-*co*-AA 95/5 films after (a) 3 hr, (b) 24 hr, and (c) 24 + 24 hr of mixing. The 24 + 24 hr sample was freeze-melted between the mixing steps. Scale bar 100 μm .

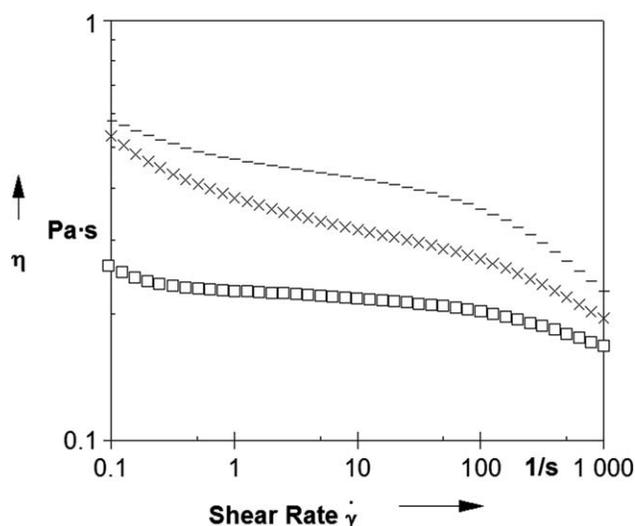


Figure 3. Viscosity as function of shear rate for Cell/PE-*co*-AA 95/5 dispersion after 3 hr (-), 24 hr (x), and 24 + 24 hr (\square) of mixing. The 24 + 24 hr sample was freeze-melted between the mixing steps.

due to the diluting effect of PE-*co*-AA water solution. The differences between the added polymers (PE-*co*-AA and PAA-*co*-AA) did not show until higher amounts of polymer were used in the dispersion, showing especially increased viscosity value for the PAA-*co*-AA dispersion (75/25 dispersions; Figure 5) when compared with 75/25 cellulose/PE-*co*-AA dispersion. This type of flow behavior of cellulose/PAA-*co*-AA dispersion results from the water absorbing capability of PAA-*co*-AA due to the hydrophilic $-\text{COO}^- \text{Na}^+$ and $-\text{NH}_2$ groups, leading to gel-

type rheological behavior and an increase in viscosity when more polymer is added. The shear rate-viscosity profile is also strongly dependent on the polymer concentration. Intrapolymer interaction may dominate at low polymer concentrations, whereas interpolymer interaction becomes remarkable at higher polymer concentrations.³⁴ As concluded in our previous article by Saarikoski et al.²⁰ evolution in viscosity of the dispersions is the sum of several different phenomena, that is, the solubility levels (soluble vs. gel vs. aggregate) of cellulose, PE-*co*-AA and PAA-*co*-AA as well as the size and amount of these different phases during mixing.

Mechanical and Thermal Properties

Mechanical properties of the precipitated films were analyzed with DMA in order to find out the effect of added PAA-*co*-AA and PE-*co*-AA compared with pure cellulose film (Figure 6; Table II). In general, the variances between the mechanical properties of the film samples were relatively large due to the small number of parallel samples. For this reason the results are indicative. DMA results showed the plasticizing effect of PE-*co*-AA as an increase in strain values. As the PE-*co*-AA content increases, the viscose component in the blend increases, improving the cellulose film. In comparison between neat cellulose (Cell 100) film and cellulose/PE-*co*-AA films, a 90/10 ratio gave the best results, that is, approximately 1.4 times higher tensile strength and strain compared with neat cellulose film, but decrease in Young's modulus [Figure 6(a,b)] due to the plasticizing effect of added PE-*co*-AA. On the other hand added PAA-*co*-AA increased both, Young's modulus and tensile strength levels [Figure 6(c,d)]. The best results were obtained with a 95/5 cellulose/PAA-*co*-AA ratio, giving approximately 0.6

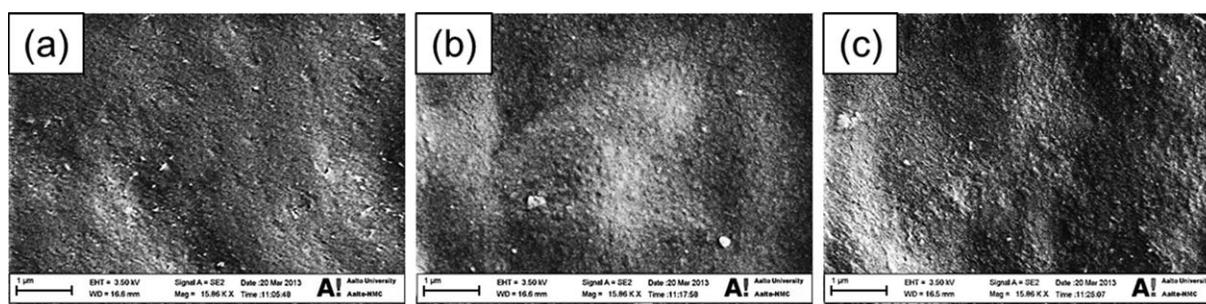


Figure 4. SEM-micrographs of precipitated films after 24 + 24 hr of mixing. (a) Cell 100, (b) Cell/PE-*co*-AA 90/10, and (c) Cell/PAA-*co*-AA 95/5. Scale bar 1 μm . The freeze-melting procedure was done between the mixing steps.

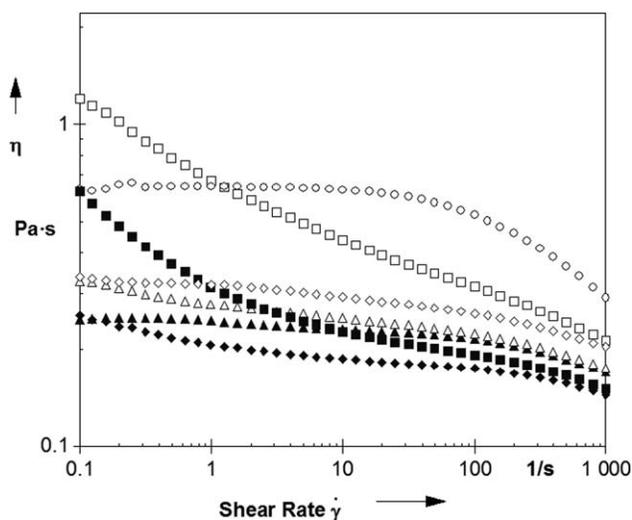


Figure 5. Viscosity as a function of shear rate for neat cellulose solution (\circ), Cell/PE-*co*-AA 95/5 (\blacktriangle), Cell/PAA-*co*-AA 95/5 (\triangle), Cell/PE-*co*-AA 90/10 (\blacklozenge), Cell/PAA-*co*-AA 90/10 (\lozenge), Cell/PE-*co*-AA 75/25 (\blacksquare), and Cell/PAA-*co*-AA 75/25 (\square). Samples were mixed for 24 + 24 hr with the freeze–melting procedure between the mixing.

times higher Young's modulus, approximately 2.8 times higher tensile strength, and approximately 1.1 times higher tensile strain compared with pure cellulose film (Cell100). This effect is due to amide groups of PAA-*co*-AA, that form strong hydrogen bonds with cellulose, and work with small amounts positively. However, as more polymer is added, the effect also vanishes. When the PAA-*co*-AA content of the blend is increased, its capability to absorb high amounts of water becomes notable.

High water absorption may lead to a gel type of behavior in the solution stage, leading to a situation where mixing the polymers becomes more demanding, which is reflected directly in film properties as decreased modulus and strength when the PAA-*co*-AA content of the film is increased over a certain limit.

The thermal behavior of the blends were analyzed with DSC. From the Figure 7 it can be seen how the crystallization temperature of the PE-*co*-AA phase was clearly observed in cellulose/PE-*co*-AA blends. When compared with neat PE-*co*-AA, the T_C 's of the blend samples were clearly higher [Figure 7(a) $T_C = 66^\circ\text{C}$ vs. Figure 7(b,c) $T_C = 69^\circ\text{C}$]. This same phenomenon was observed in the earlier studies (Saarikoski et al.²⁰ and Lipponen et al.²¹) which clearly indicated that the polymers were mixed. Rigid/solid cellulose was able to act as a strong nucleation agent for the molten PE-*co*-AA phase during the cooling. Good mixing enables a large interfacial area between cellulose and PE-*co*-AA which was able to intensify any weak nucleation effects.

Glass transition temperatures (T_g) of the blends were measured with DSC in order to see the influence of added polymers on the neat cellulose. The results are reported in Figure 8 and Table II. The glass transitions of cellulose and cellulose-based materials are quite difficult to determine using DSC analysis, because the drop of heat capacity change is quite minimal at the glass transition. Due to this aspect and melt point overlapping effects of the PE-*co*-AA in the thermographs, the T_g values of cellulose/PE-*co*-AA blends could not be evaluated with DSC. However, the T_g of neat cellulose was found at 84°C [Figure 8(a); Table II] which correlates well with the T_g for dehydrated cellulose reported in literature (Roig et al.³⁵). When the T_g values of cellulose/PAA-*co*-AA blends [Figure 8(c,d); Table II] were

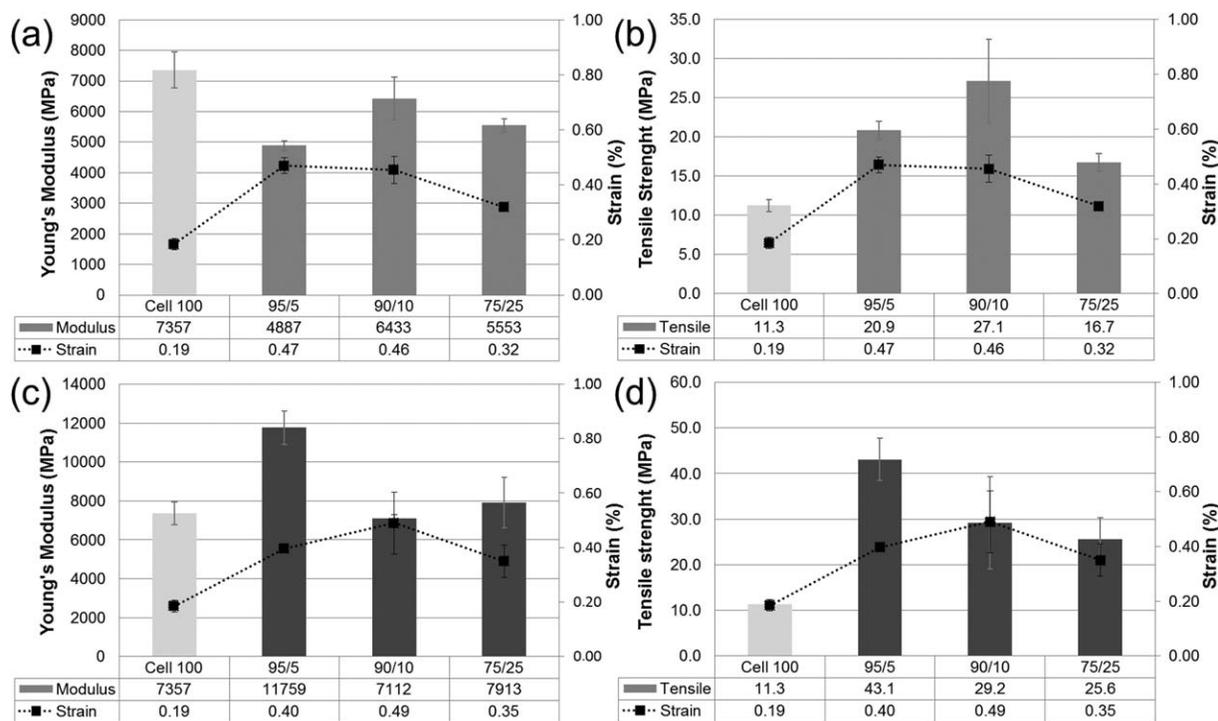


Figure 6. Young's modulus and tensile strengths of (a, b) Cell/PE-*co*-AA and (c, d) Cell/PAA-*co*-AA blends with different cellulose/polymer compositions compared with a neat cellulose reference sample Cell 100.

Table II. Mechanical Properties and thermal transition Temperatures of Precipitated Blend Films and Neat Cellulose Film (Cell 100) with the Thermal Transition Temperatures of Neat PE-*co*-AA and Neat PAA-*co*-AA

ID	Young's modulus (MPa)	Tensile strength (MPa)	Strain (%)	T_c ($^{\circ}\text{C}$)	T_g ($^{\circ}\text{C}$)
Cell/PE- <i>co</i> -AA 95/5	4887 \pm 162	20.9 \pm 1.1	0.47 \pm 0.028	69	-
Cell/PE- <i>co</i> -AA 90/10	6433 \pm 699	27.1 \pm 5.3	0.46 \pm 0.050	69	-
Cell/PE- <i>co</i> -AA 75/25	5553 \pm 215	16.7 \pm 1.1	0.33 \pm 0.014	72	-
Cell/PAA- <i>co</i> -AA 95/5	11759 \pm 873	43.1 \pm 4.6	0.40 \pm 0.006	-	69
Cell/PAA- <i>co</i> -AA 90/10	7112 \pm 192	29.2 \pm 10.1	0.49 \pm 0.113	-	70
Cell/PAA- <i>co</i> -AA 75/25	7913 \pm 1292	25.6 \pm 4.7	0.35 \pm 0.060	-	69
Cell 100	7357 \pm 588	11.3 \pm 0.8	0.19 \pm 0.021	-	84
PE- <i>co</i> -AA	-	-	-	66	-
PAA- <i>co</i> -AA	-	-	-	-	79

compared with the T_g values of neat cellulose and pure PAA-*co*-AA (T_g 79 $^{\circ}\text{C}$), a clear decrease in glass transition temperatures was seen with all of the blend compositions. The T_g values of cellulose/PAA-*co*-AA blends (69 $^{\circ}\text{C}$ and 70 $^{\circ}\text{C}$) were even lower than with the pure PAA-*co*-AA. This atypical behavior can be an indication that a low addition of PAA-*co*-AA into the cellulose causes irregularity to the cellulose chain structure, weakening the intermolecular forces between the chains and thus increasing the chain mobility. For these reasons mentioned above, a clear shift of the T_g to the lower value can be considered as an indication of good mixing between the polymer phases.

Coating Trials

Aiming for high bio-content in the coatings, two different dispersion compositions with 95/5 cellulose/polymer ratio and a cellulose reference sample were chosen for laboratory coating tests. Sheets of paperboard were coated with a target coat weight of 10 g/m². However, this target coat weight was not

self-evident due to the low-viscosity levels (see Figure 5) and therefore a double coating was used for the Cell 100 solution and the Cell/PE-*co*-AA 95/5 dispersion. As a result, a coat weight between 10.0 and 11.0 g/m² was achieved for all of the tested dispersions and the Cell 100 solution. The cross-section photomicrographs of the coated sheets (Figure 9) showed that, as a consequence of the low viscosity values despite of the coat weight and double coating, the coating layer was very thin (1.35–2.02 μm , average 1.69 μm) for every sample, but with no pinholes. SEM micrographs (Figure 10) revealed that most of the ZnO and part of the NaOH is on the surface of the paperboard. However, it is important to note that because there was the same amount of NaOH and ZnO in the dispersions and in the solutions, these two components could not have any impact on the barrier properties when compared with each other. Although, it is important to take into account the fact that nanosize ZnO has a self-crosslinking effect on carboxy functional polymers.³⁶ Therefore, it is possible that cross-links are

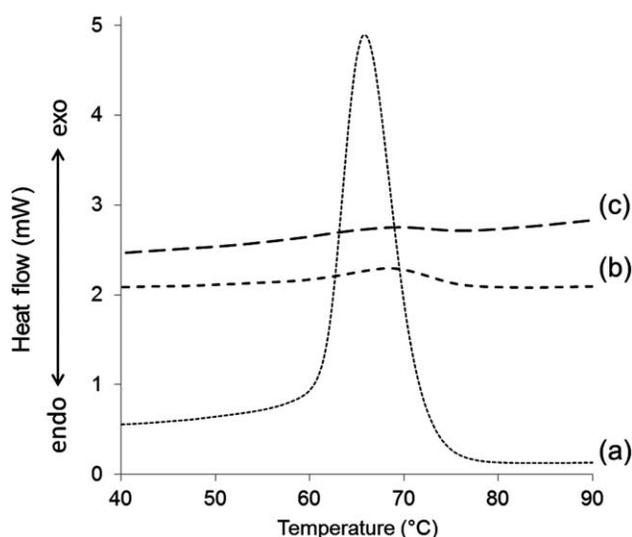


Figure 7. DSC-crystallization curves of (a) neat PE-*co*-AA, (b) Cell/PE-*co*-AA 90/10, and (c) Cell/PE-*co*-AA 95/5 samples obtained at cooling rate of 10 $^{\circ}\text{C}/\text{min}$. Sample amounts between 4.5 and 6 mg were used for the film samples and 10 mg for the neat PE-*co*-AA.

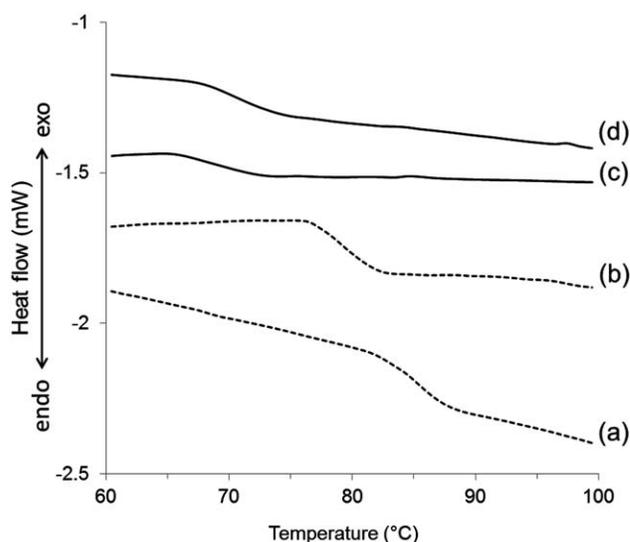


Figure 8. DSC-thermograms of (a) Cell 100, (b) neat PAA-*co*-AA, (c) Cell/PAA-*co*-AA 95/5, and (d) Cell/PAA-*co*-AA 90/10 samples obtained at heating rate of 10 $^{\circ}\text{C}/\text{min}$. Sample amounts between 4.5 and 6 mg were used for the film samples and 10 mg for the neat PAA-*co*-AA.

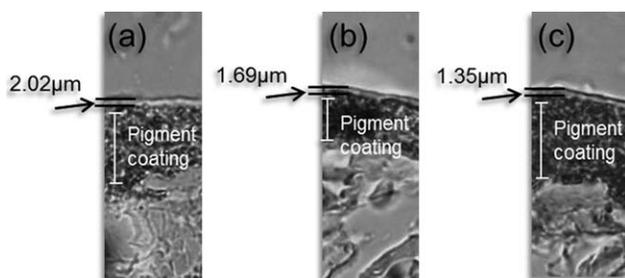


Figure 9. Cross-section photomicrographs of (a) Cell 100, (b) Cell/PE-co-AA 95/5, and (c) Cell/PAA-co-AA 95/5 dispersion coated paperboards. Magnification 400 \times .

formed between the used polymers in the coatings, and thus in consequence affecting the properties of the coatings. The WVTR and OTR results for the pure cellulose and both blend samples have been normalized to a coating thickness of 2 μm based on average coating thicknesses observed in the cross section images (shown in Figure 9).

The barrier results of the coated paperboards are represented in Table III. From the results it can be concluded that the coating layer of regenerated cellulose (Cell 100) works well as an oxygen barrier. This may result mainly from the crystalline and dense structure of cellulose. In addition, the coating results show that added PE-co-AA improves slightly water vapor barrier

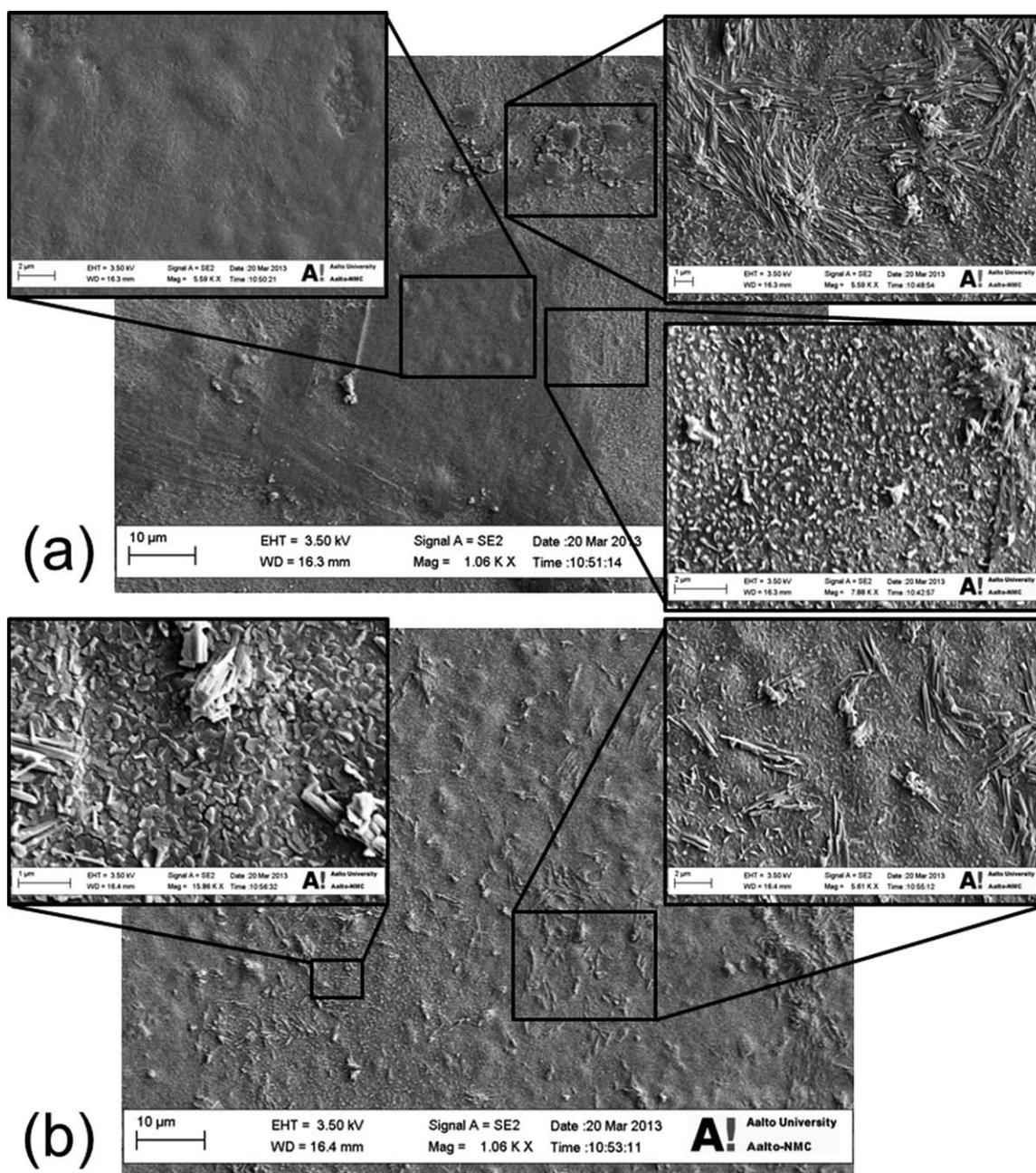


Figure 10. SEM micrographs of (a) Cell 100 and (b) Cell/PE-co-AA 95/5 dispersion-coated paperboards.

Table III. Barrier Properties of Cell/PE-*co*-AA 95/5-, Cell/PAA-*co*-AA 95/5, and Neat Cellulose (Cell 100)-Coated Paperboards

ID	Coat weight (g/m ²)	Rods (μm)	Norm. WVTR to 2 μm (g/m ² d)	Norm. OTR to 2 μm (mL/m ² d bar)	Grease 507T (%)	Grease F119 (d)
Cell/PE- <i>co</i> -AA 95/5	11 ± 1	30 + 30	49 ± 9	179 ± 157	0	60
Cell/PAA- <i>co</i> -AA 95/5	11 ± 1	60	58 ± 4	7853 ± 4989	0	60
Cell 100	11 ± 0.5	30 + 30	54 ± 4	2855 ± 2603	0	69

Double coating was used due to low viscosity with Cell/PE-*co*-AA 95/5 and Cell 100 samples. The grease resistance was tested according to ASTM F119-82 and Tappi 507 T cm-09 standards. WVTR and OTR values are normalized to 2 μm coating layers.

properties due to good WVTR properties of polyethylene when compared with WVTR results of pure cellulose (Cell 100). SEM-micrographs of Cell 100 and Cell/PE-*co*-AA 95/5 coatings (Figure 10) reveal the uniformity of the coatings in more detail. The micrographs show that the coating layer of Cell/PE-*co*-AA 95/5 blend [Figure 10(b)] is mainly very uniform, having PE-*co*-AA evenly dispersed throughout the blend. In addition, when SEM images are examined in more detail, it seems that with the Cell/PE-*co*-AA 95/5 blend, a layer of PE-*co*-AA is formed on the surface of the coating [Figure 10(b)], thus explaining the slightly improved WVTR results. Added PE-*co*-AA may have also affected the OTR results. It may be possible that the added PE-*co*-AA makes a hybrid coating structure with cellulose, having regenerated cellulose at the bottom and PE-*co*-AA on the top, thus, showing better WVTR and OTR values than the pure cellulose. In order to find out the differences between the degree of wetting of the coated boards, contact angle measurements were conducted. The contact angle results are represented in Table IV. These measurements confirmed that part of the PE-*co*-AA can be on the surface of the coating layer, giving hydrophobicity to the coating and thus increasing the advancing angle by 25.2° and the receding angle by 36.9° compared with the pure cellulose (Cell 100) sample. In comparison between the pure cellulose and cellulose/PAA-*co*-AA coatings; PAA-*co*-AA has a negative effect on the barrier properties as can be seen from Table III. Adding a small amount of PAA-*co*-AA to the cellulose solution may lead to a discontinuity in the formed cellulose surface. This is seen as a slight decrease in the WVTR properties and a bigger decrease in OTR values. On the other hand, when compared with Cell 100 and Cell/PE-*co*-AA 95/5 coated paperboards, the desired coat weight was achieved already in the first coating with PAA-*co*-AA. Without double coating, the coating layer with PAA-*co*-AA may have been weaker and thereby one of the reasons behind the weaker barrier results.

In addition to OTR and WVTR testing, grease resistances of the coated sheets were evaluated (see Table III). First, the coated

Table IV. Contact Angle Measurements of Cell/PE-*co*-AA 95/5, Cell/PAA-*co*-AA 95/5, and Neat Cellulose (Cell 100)-Coated Paperboards

ID	Advancing angle (°)	Receding angle (°)
Cell/PE- <i>co</i> -AA 95/5	79.6	56.6
Cell/PAA- <i>co</i> -AA 95/5	61.8	48.5
Cell 100	54.4	19.7

sheets were tested with the Tappi 507 T cm-09 testing method at 60°C and 50% relative humidity for 4 hr. However, the differences between the samples did not come out with the Tappi 507 T method. Therefore, in order to test the penetration time of olive oil through the samples, the ASTM F119-82 testing method was used. With this testing method coated sheets showed grease resistance from 60 to 69 days. As mentioned earlier, grease resistance properties of the paper sheets result mainly from the density of the coating layer. In other words, the dense structure of the precipitated cellulose has a major influence on the grease barrier properties. Due to this fact, adding a small amount of polymer such as PE-*co*-AA to the coating actually decreases the grease resistance ability, from 69 to 60 days.

CONCLUSIONS

In this study, enzymatically treated cellulose was dissolved, in a NaOH/ZnO solvent system and blended with acrylic acid copolymers PE-*co*-AA or PAA-*co*-AA by a solution mixing method. A wide variety of analyses were conducted in order to determine the properties of the blends and their suitability for film and coating applications. Rheological studies, with the results from microscopic images (OM and SEM) and from the DSC analyses of the dried blends, indicated that the polymers were well mixed and dispersed in the blends. The DMA of the precipitated cellulose/PE-*co*-AA and cellulose/PAA-*co*-AA films showed improved mechanical strength when compared with the neat cellulose films with only small amounts of added polymer in the blends. Furthermore, in spite of the low viscosity levels at the dispersion stage, leading to a very thin coating layer of approximately 2 μm in coating trials, the dissolved cellulose/acrylic acid copolymer blends demonstrated a grease resistance of 60 days and improvements in oxygen and water vapor barrier properties. As an outcome, this study has shown that by blending dissolved cellulose with the right type of acrylic acid copolymers, it has potential in barrier coating applications especially for grease barrier purposes and therefore could be considered as interesting alternative for completely fossil-based barriers in the future.

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