Modification and extrusion coating of polylactic acid films

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ABSTRACT: Polyethylene (PE) extrusion coating on paper substrates are the traditional packing material for coffee cups and take-out food containers. It is difficult to recycle the PE/paper laminates and the thin polymer films remain in landfills after the decomposition of their paper substrates. Disposal of plastic materials is causing serious effects on our environment and wildlife. Demand for compostable or biodegradable plastic packaging products is increasing because of consumer pressure and legislation. Biodegradable polylactic acid (PLA) is regarded as one of the most promising biopolymers with a large market potential, but its applications are limited by poor thermal stability, mechanical properties and processibility. We utilize modified gelatin as additives to improve PLA's performance without compromising the biomass origin and compostable properties of the material. Extrusion coating, or extrusion casting, of polylactic acid (PLA) films onto paper substrates to form PLA/paper laminates was achieved by modification of the polymer with a plant or animal gelatin. Various paper substrates with thin PLA coatings were prepared using a conventional extrusion coating equipment for the fabrication of take-out food containers and coffee cups. Melt rheology of PLA and adhesion of the resulting thin film were greatly improved in the presence of a small amount of gelatin in the polymer matrices. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 42472.

INTRODUCTION

The use of light weight, convenient packaging to facilitate food storage and transportation, as well as increasing the shelf life of food has become very important because of pressure from a high population growth rate and the resulting food shortage. Approximately 31% of municipal solid waste (MSW) was from packaging-related materials in the US in 2005.[1] The rise of plastic packaging material closely relates to the change of general lifestyle.[2] Petroleum-based polyethylene (PE), polypropylene (PP), and polyethylene terephthalate (PET) are being widely used in the packaging industry for food, snacks, and drinks.[3] The plastic packaging materials remain in landfills for decades without decomposing and cause serious environmental problems.[4,5] Combustion of contaminated plastics invisibly causes air pollution and other environmental loading. Recycle or reuse of food packing materials is limited because discarded items often consist of multilayers difficult to separate.[6] Generally speaking, treatment and recycling of plastics used in disposable applications after use is not economic and imposes a greater impact on the environment. In 2010, plastics accounted for 12% of the 250 million tons of trash in the United States.[7] Development of biodegradable packaging materials provides a

solution for plastic wastes management. A biodegradable polymer has been generally defined as a material that, under conditions with sufficient water, oxygen, and suitable nutrients and temperature, is capable of being decomposed into carbon dioxide and water by microbes. Polylactic acid (PLA) is compostable, biodegradable, and derived from renewable resources.[5,8–10] Superior optical transparency and reasonable mechanical strength render the polymer a potential candidate to replace petroleum-based polymers for a wide range of packaging applications. Industrial processing techniques for PLA include extrusion coating, blown extrusion, and biaxial orientation for films, blown molding for bottles, thermoforming for cups as well as injection molding for plastic objects.[5,11–20] Brittleness, however in some degree, limits PLA applications in the packaging industry.[21–23]

Flexibility of PLA is often enhanced by blending with an oligomer, a second polymer or a plasticizer.[24–29] Studies suggest that modification of PLA with poly (butylene succinate) (PBS), Poly (ethylene glycol) (PEG) and ricinoleic acid increases the polymer ductility while the tensile strength and modulus decrease slightly.[25] Incorporation of PEG-400 into PLA decreases free volume in the polymer matrices and thus reduces

oxygen permeability of the casting films.[26] On the other hand, Yuniarto et al. suggest that enhanced crystallization in the presence of the plasticizer, < 5%, lowers oxygen permeability of the modified PLA film.[30] Oxygen transmission rate (OTR) increases if the PEG content exceeds 5%. PLA has comparable mechanical properties of polyethylene terephthalate (PET) and polystyrene (PS) that fulfil the food industry's requirements for rigid containers. Plasticizers, on the other hand, are needed for the fabrication of flexible packaging PLA films. Small molecules tend to migrate to the surface and may contaminate foods in contact with the packaging material. Alternatively, PLA has been blended with a second polymer, such as polyhydroxyl butyrate, polyvinyl acetate, polycaprolactone, PBS, and polyethylene oxide, to render flexibility. Performance of modified PLA strongly depends on compatibility of the plasticizer and the polymer matrices. Pillin et al. studied thermal and mechanical properties of modified PLA using PEG, poly(1,3-butanediol), dibutyl sebacate, or acetyl glycerol monolaurate as a plasticizer.[42] Differential scanning calorimetry (DSC) investigations indicated a single glass transition curve at temperatures above 0°C and thus suggested miscible of PLA and all of the above plasticizers. This is in contradiction with the Hoy solubility calculation results that suggest PLA/PEG is the only miscible blend among the series studied. The authors suggest the miscibility improvement observed for the other plasticizers is because of the dipole/dipole interactions that are not accounted for the Hoy model estimation. High molecular scale miscibility in PLA/PEG blends enhances PLA chain mobility, thus promoting crystallization of the polymer at relatively low temperatures. At high plasticizer content, >20%, high degree of crystallization causes phase separation.

Industrial applications of plastic packaging films are typically prepared by means of extrusion, stretching, blown extrusion, and extrusion coating processes.[11–16,31–36] Uniaxial-oriented PLA films are used for shrink sleeves, window envelops, and floral wraps, while biaxial-oriented films are applied to metalizing and laminations products that require dimensional stability. Transparent PLA films with high crystallinity and low shrinkage at 120°C were obtained by suitable control of stretching condition and heat setting temperature.[37] The low melt index and strength of PLA present challenges to the preparing of blown films. Studies are focused on modifying the polymer with chain extenders and plasticizers.[38–40] Our everyday use of carry out food paper containers, wraps, and coffee cups are made of PE-coated papers. Polyethylene/paper laminates were made to be heat sealable and to improve moisture and grease barrier properties.[41] Thin PE films for water and oil barriers remain in landfills after decomposition of their paper substrates. Plasticizers for PE film processing may contaminate food and cause health issues. Demand for compostable and nontoxic plastic paper laminates for food packaging is increasing. At present, manufacturers are modifying extrusion coating facilities to accommodate the poor melt rheology and adhesion properties of PLA. This results in increased capital investment and production cost. Our work on PLA product development focuses on modification of PLA for film fabrication with existing biaxial orientation, blown extrusion, and extrusion coating machines. Physical properties

of PLA films were improved without compromising biomass origin of the polymer by using additives from renewable resources. To our knowledge, there are few articles describing fabrication processes and performance of PLA/paper laminates.[13–15]

The extrusion coating (or extrusion casting) process is preferred over that of solvent-based coating in industrial production lines to produce composite or multilayer structures. This is because solvent-based coatings often require energy-intensive evaporation and drying steps; furthermore, they tend to generate large amounts of volatile organic compounds (VOCs). In extrusion coating, the melt rheology of a polymer affects the coating speed while adhesion and melt strength govern coating efficiency. Therefore, the PLA extrusion coating process requires specifically designed machinery to accommodate the relatively low melting index and poor adhesion of the polymer. Modification of PLA with a plant or animal gelatin improves its adhesion and facilitates thin film and lamination fabrication processes. PLA thin films were successfully laminated onto paper substrates using conventional polyethylene extrusion coating machines. Melt flow rheology of PLA was improved for thin film fabrication processes by modifying the polymer with a gelatin-based plasticizer. Introducing a small amount of functionalized gelatin to PLA matrices not only increases the melting index of the resulting modified polymer but also improves adhesion of the polymer film to substrates. Production of PLA/paper laminates with existing extrusion coating machines without modification decreases manufacture costs and improves production flexibility. PLA-coated papers were evaluated for the fabrication of paper cups and lunch boxes.

EXPERIMENTAL

Plant gelatin (vegetable hard shell capsule #0) and animal gelatin were purchased from Dah Feng Capsule Industry, Taiwan, and Buildmore Enterprise, Taiwan, respectively. Lactic acid was purchased from Purac. All chemicals and materials were used as received without further purification. A commercial grade polylactic acid was purchased from UNIC Technology. The PLA pellets were dried at 80°C for 4 hours before use.

Modification of PLA: The first step is to prepare a gelatin-based plasticizer using a plant or animal gelatin. As a typical procedure, a mixture of 5 g gelatin and 5 g lactic acid was placed in a round-bottom flask and heated to 130°C for 4 hours. For comparison, 5 g gelatin was mixed with 5 g water and heated to 80°C for 1 hour. A 10 L round-bottom flask or a 200 L stainless steel reactor was used for the scale-up production of the gelatin-based plasticizer. A master batch of modified PLA was prepared by blending the above plasticizer with PLA (NatureWorks) in a kneader. The master batch was then diluted to a desired concentration of the natural plasticizer with PLA using a conventional PE extrusion coating machine for the fabrication of PLA/paper laminates. A DSM Xplore MC 15 Micro-Compounder was used in our laboratories to blend-modified gelatin and PLA for evaluations. We used the ZENIX ZPT-32HT twin-screw extruder for production of the plasticized PLA for on-line extrusion coating evaluations.

Differential Scanning Calorimetry (DSC) characterization was performed at a heating rate of 10°C/minute between 30°C and
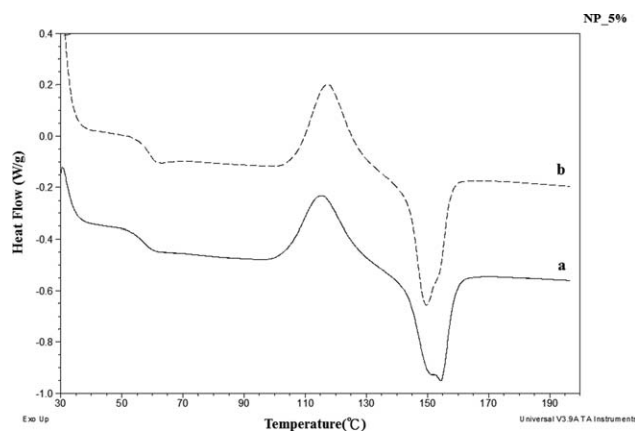
Figure 1. DSC thermograms of modified PLA containing 5 wt % modified gelatin (a) first heating and (2) second heating.

Figure 2. DSC thermograms of pristine PLA: (a) first heating and (2) second heating.

200°C under a nitrogen blanket using the TA Instruments DSC Q20. The software provided by the manufacturer was used for analyzing the thermal transitions. PLA crystallinity (χ_c) was estimated according to the following equation:

$$\chi_c = (\Delta H_m - \Delta H_c)/\Delta H^0 \times 100\%$$

where ΔH_m : enthalpy of melting; ΔH_c : enthalpy of cold crystallization; ΔH^0 : 93 J/g.

Melting index of PLA and plasticized PLA was measured at 190°C for samples containing less than 5% modified gelatin or 160°C for those with higher plasticizer content and both at 2160 g load according to ASTM D1238 using the Tinius Olsen Melt Indexer. Molecular weight of pristine PLA and modified PLA were determined by WATER 1515 size exclusion chromatography (SEC) equipped with a WATER 2414 refractive index detector using polystyrene standard and THF as the eluent under 1 mL/min flow rate at 40°C.

RESULTS AND DISCUSSION

Foreign substances introduced to PLA need to be uniformly distributed in the matrix to render the polymer with improved performance and processability. A strong interfacial interaction is critial for uniform dispersion of an additive in the polymer matrices. It is critical to select a molecule structure to enhance bonding between the selected biomolecules and PLA. Chemicals selected for the surface modification of gelatins consist molecule structures resembling that of PLA or reacting with the polymer. This leads to improved dispersion of the additives in PLA matrix through enhancing interfacial interaction between the two components. Uniform mixing and strong interfacial interaction of key components facilate property enhancement of the resulting products. Direct compounding of gelatin and PLA resulted in the formation of gelatin granules in the PLA matrix. On the other hand, gelatin was uniformly blended with PLA after heat treated with lactic acid. A master batch containing 40–90% modified gelatin was first prepared and then diluted to a desired concentration for laminates fabrication to ensure uniform mixing. Depending on extrusion coating facilities, concentration of the gelatin-based plasticizer can be adjusted to meet specific requiremts of film thickness and adhesion strength. The
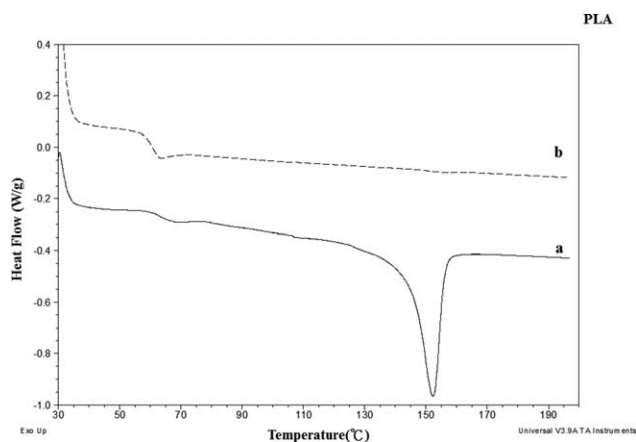
weight average molecular weight (MW) of pristine PLA is 103,700 and it decreases to about 89,600 for a modified PLA containing 2.26% gelatin-based plasticizer. It is critical to ensure uniform dispersion of the plasticizer while minimizing the blending temperature and the number of dilution processes to prevent PLA degradation. DSC thermogram, Figure 1(a), of a modified PLA containing 5% of the gelatin-based plasticizer indicates a glass transition temperature, T_g, at about 57°C and a cold crystallization temperature, T_{cc}, at about 116°C followed by multiple melting peaks at about 151°C and 154°C. The intensity ratio of the two main peaks are clearly dependant on thermal histry. A DSC thermogram of the modified PLA is rather different from that of a pristine PLA, Figure 2 a, which shows a glass transition temperature at about 63°C and a single melting peak at about 152°C.

Thermal Transitions of the Plasticized PLA

Multiple melting behavior was observed for PLA annealed at temperatures between 100°C and 120°C.[43,44] The difference between FTIR spectra between PLA crystallized at the temperatures above 120°C and below 100°C suggests the presence of different crystalline structure. Polymorphism represents the presence of more than one form of crystalline structure in a polymer. There are α-, β- and γ-forms of crystals in PLA, depending on the preparation conditions. The α-form is the most common type of PLA crystal that develps from melt, cold crystallization or solution casting.[43,44] A crystalline structure resembles a hexagonal packing of helices. Interchain interactions between methyl groups may force a distortion of the helix conformation. The arrangement and packing of molecular chains in the crystalline structure play an important role in the polymorphism transitions. The α′-form crystal of PLA is considered to be a disordered modification of the α-form.[43–51] Wide-angle X-ray diffraction (WAXD), FTIR spectroscopy and DSC studies indicate that α′-form crystal was obtained for PLA annealed at the temperatures below 100°C.[43] The α′-form crystals were transformed into their counterparts upon annealing at elevated tempratures of 120–160°C.

PLA pellets are often produced with various degrees of crystallinity for enhancing thermal stability and to prevent colligation

Table I. Thermal Transitions of First Heating for Pristine PLA and Modified PLAs Obtained by DSC Measurements

No.	T_g (°C)	T_c (°C)	ΔH (J/g)	χ_c (%)	T_{m1} (°C)	T_{m2} (°C)	ΔH (J/g)
a	**62.84**				**152.36**		**26.52**
b	57.32	115.98	27.99	31.68	151.03	154.39	27.88
c	56.00	112.60	30.06	35.91	147.76	153.25	30.36
d	54.68				152.69	155.83	38.47
e	52.48				149.18	154.73	42.63
f	51.76				147.49	155.26	35.56
g	52.64					155.59	33.36

of pellets during thermal drying. As shown in Figure 2(a), the polymer melts at the temperatures below 160°C. Typical extrusion coating temperature was set between 180°C and 230°C to ensure complete melting of PLA pellets. PLA film uniforminity and adhesion to the paper substrate strongly depend on the temperature setting. Operation temperature, concentration of gelatin-based plasticizer and equipment setting are corelated factors in controlling the qualities of PLA/paper laminates. The composition and content of the plasticizer will not only affect the melt rheology of the PLA but also the physical properties of the resulting thin films. Upon reheating of the pristine PLA after melting, the second heating curve, Figure 2(b), does not show a melting peak at temperatures below 200°C. This suggests the crystallization kinetic of pristine PLA is sluggish and does not crystallize at the cooling and heating rate of 10°C/minute. Under the same conditions, modified PLA does not crystallize during cooling but does crystallize upon the second heating at about the same temperature range, Figure 1(b). Previous isothermal investigations of a commercial grade PLA at 110°C and 120°C indicated that crystallization kinetics are always faster from the glassy state than from the molten state.[52] Enthalpy values of cold crystallization and following melting are about the same for the first and second heating cycles, 28 and 29 J/g, respectively. These results suggest the plasticized PLA is stable at the temperature range. Although the plasticized PLA recrystallized upon heating, it did not crystallize during cooling, which is a critical factor for extrusion coating processes. If a polymer crystallizes too rapidly during cooling, it will be difficult for a polymer film to adhere properly onto a paper substrate. Post-thermal treatment after extrusion coating, however, renders PLA paper laminates with improved physical properties because of crystallization.

The degree of crystallinity, Tables I and II, increases as the concentration of gelatin-based plasticizer increases as observed in the previous studies.[30] The increase of PLA crystallinity can be attributed to enhanced chain mobility in the presence of plasticizer.[53] It is interesting to note that at high gelatin-based plasticizer concentration, ≥ 15 wt %, modified PLAs do crystallize at self-cooling conditions after melting. As shown in Figure 3(d–g), there is no cold crystallization peak on the first heating curves but there are melting peaks between 140°C and 160°C. This suggests the PLA crystallized during cooling after melt blending with modified gelatin. At these concentrations, the plasticizer facilitates melt crystallization of PLA. Thus, high con-

centration of plasticizer may have adverse effects on laminate quality, particularly adhesion, and film uniformity. DSC thermograms of the modified PLA reveal multiple melting peaks as shown in Figure 3. Compared to melt transitions of the modified PLA containing less than 15% gelatin-based plasticizer, Figures 3(b,c), most of the crystals generated upon cooling of the PLA melt tended to melt at temperatures slightly higher than that of a pristine PLA, Figures 3(d–g). Upon heating to temperatures above 120°C, the disordered α′-form PLA crystals convert to their α-counterparts.[44] The α′ to α transformation involves a direct solid-solid transition with slight rearrangement of the polymer chain packing within the unit cell. The process leads to the more energy-favorable state and to a reduction of lattice dimensions. These crystals transfer to α-form and melt at a slightly higher temperature.[44] The α′ to α transformation depends on thermal history, molecular weight, and additives in the polymer matrices. Crystalline structure formed upon cooling of the PLA melt is less compacted and larger in size. The gelatin-based plasticizer facilitates melt crystallization of PLA. Most of the PLA chains do not have enough time to align in order before the polymer solidified under the self-cooling condition. The low temperature melting peak intensity increases in relation to the high temperature one for all modified PLA during the second heating, Figure 4(b–g). The polymer chain may maintain a certain degree of alignment after melting because of
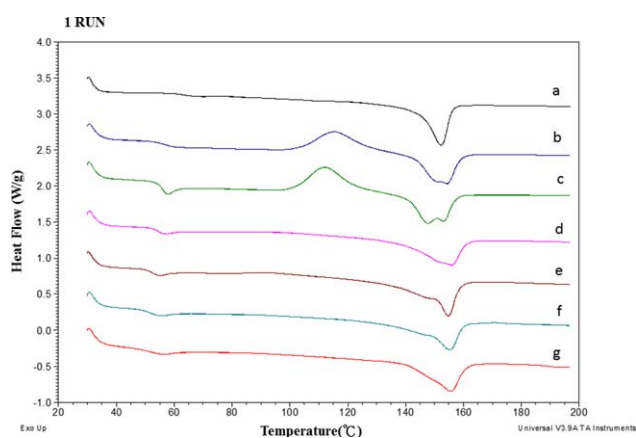

Figure 3. First heating DSC thermograms of: (a) pristine PLA and modified PLA containing, (b) 5 wt %, (c) 10 wt %, (d) 15 wt %, (e) 20 wt %, (f) 30 wt %, as well as (g) 40 wt % modified gelatin. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
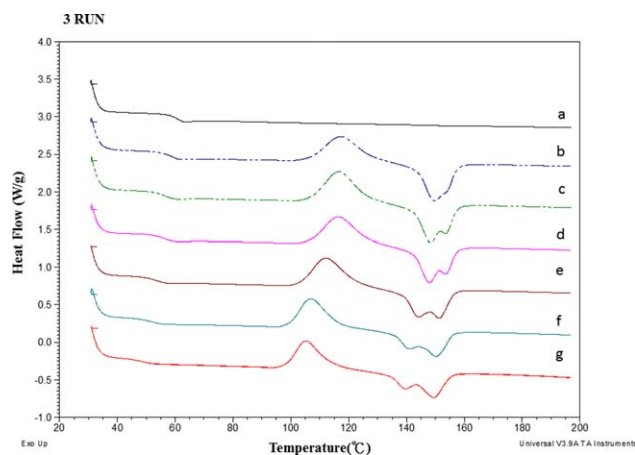
Figure 4. Second heating DSC thermograms of (a) pristine PLA and modified PLA containing (b) 5 wt %, (c) 10 wt %, (d) 15 wt %, (e) 20 wt %, (f) 30 wt %, as well as (g) 40 wt % modified gelatin. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary. com.]

Figure 5. Melting Index (MI) of modified PLAs obtained at 190°C and 2160 g loading.

rigid nature of its structure. Thus, there is an increase in ordered α-form crystals generated upon reheating. The other noticeable feature of the plasticizer's effect is gradual decrease of glass transition temperature as concentration increases, Table II. For the second heating curves, Figure 4, all modified PLAs show cold crystallization peaks. Since enthalpy values are the same for cold crystallization and melting in all cases, modified PLAs do not crystallize at the controlled cooling rate of 10°C/minute. The cold crystallization temperature decreases as the concentration of gelatin-based plasticizer increases, Table II. Again, as shown in Figure 4, PLA crystals are less compact at high concentrations of plasticizer even if they are formed upon heating. The melt behavior of PLA depends on crystallization temperature. The previous isothermal melt crystallization studies of PLLA using DSC, X-ray diffraction, and FTIR indicated an abrupt change in crystallization kinetic and crystalline form at about 110°C.[43] The α-form tends to form at temperatures higher than 110°C while there is more α'-form generated at lower temperature. Dynamic heating and cooling of modified PLA resulted in the same conclusion. As the concentration of the gelatin-based plasticizer increases, cold crystallization cure shifts below 110°C and there is more of the α'-form produces. For modified PLA with plasticizer content greater than 15 wt %, both melt crystallization, Figure 3(d–g), and cold crystalliza-
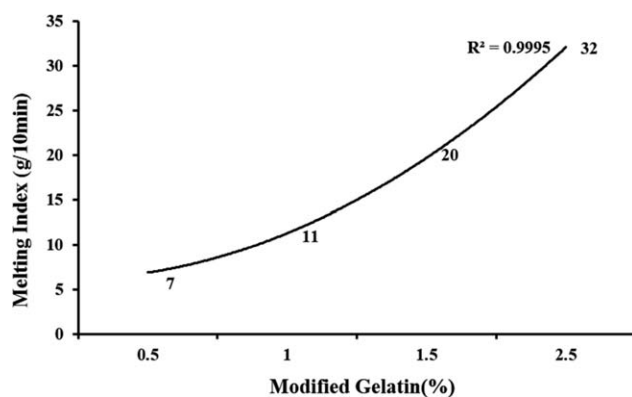
tion, Figure 4(d–g), processes resulted in higher frequencies of α'-form than of α-form. On the other hand, low temperature melt peak intensity is stronger than that of the high temperature for modified PLAs with the plasticizer concentration less than 15 wt %.

An endothermic peak in the glass transition region which can be ascribed to the enthalpy relaxation of PLA was observed for samples containing more than 10% of the gelatin-based plasticizer, Figures 3(c–g). This endothermic peak cannot be observed in the second heating process for all the samples. This suggests that enhancement of the segmental mobility of PLA in the presence of 10% or greater plasticizer causes volume relaxation at room temperature. An aged sample with reduced free volume has lower enthalpy and potential energy than those of an unaged sample and thus needs more energy for the glass transition.[54] However, the endothermic peak intensity decreases as the plasticizer content is increased to greater than 15%. This is because of the presence of crystals which restrict the segmental mobility at the temperatures below the glass transition temperature.

Melt Flow Rheology

Because of poor melt flow rheology of pristine PLA, high power equipment is required for shaping PLA products during manufacture. In the presence of a small quantity of modified biomolecules, such as protein or plant gelatin, PLA's melt index (MI) increases from about 3.5 to greater than 10 depending on the concentration of the gelatin-based plasticizer in the polymer matrices (Figure 5). The melt flow rate of a plasticized PLA

Table II. Thermal Transitions of Second Heating for Pristine PLA and Modified PLAs Obtained by DSC Measurements

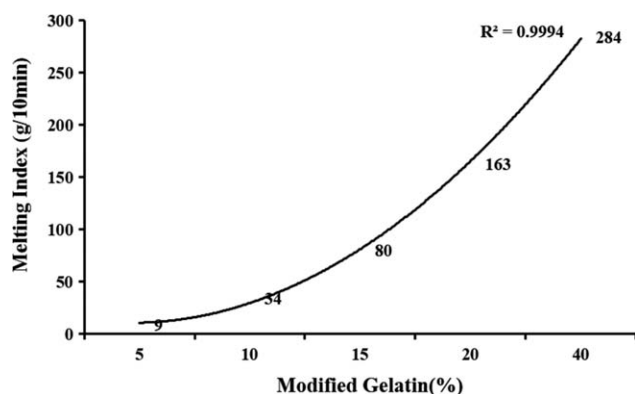| No.	T_g (°C)	T_c (°C)	ΔH (J/g)	χ_c (%)	T_{m1} (°C)	T_{m2} (°C)	ΔH (J/g)
a	61.28						
b	59.16	117.17	29.71	33.63	149.71	153.60	29.18
c	56.80	116.93	31.72	37.90	148.29	153.42	31.73
d	56.80	116.82	29.36	37.14	147.95	153.59	29.78
e	53.81	112.31	30.20	40.59	144.21	151.27	30.78
f	51.80	107.10	27.14	41.69	140.97	150.12	27.08
g	52.64	105.30	25.54	45.77	139.77	149.40	25.46

Figure 6. Melting Index (MI) of modified PLAs obtained at 160°C and 2160 g loading.

Figure 7. Modified PLA melt curtain. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

containing more than 5 wt % is too fast for MI measurement at 190°C. Melting index data of these samples was collected at 160°C and shown in Figure 6. Typical concentration of the gelatin-based plasticizer for on-line extrusion coating evaluation is in the range between 0.5-2.5 wt % depending on the machine and paper used as well as specific laminate requirements. Once the concentration is selected, the operation temperature setting is critical to obtain a thin uniform film from a narrow slit die
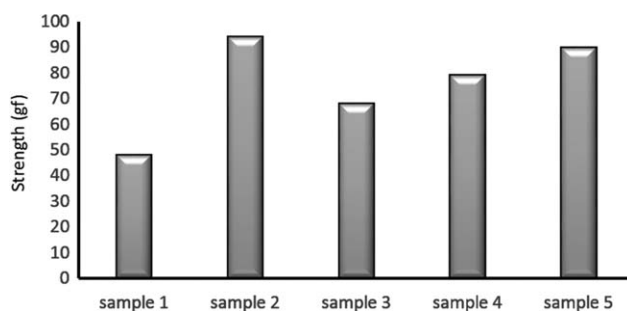

Figure 9. Bonding strength of modified PLA on printing paper.

without neck-in. Uniform films, as shown in Figure 7, were fabricated using conventional polyethylene (PE) extrusion coating machines. The thin modified PLA film was then laminated with a paper substrate between a chill roll and a pressure roll, Figure 8. Previously, because of poor melt flow rheology of pristine PLA, commercial manufacturing equipment required for shaping PLA products cannot be used. Machines generally used to process polyolefins or polyesters must be modified to process conventional PLA. Once the equipment is modified, it can only produce PLA products. The high conversion cost and the risk of completely losing conventional production line, discourage manufacturers to switch from conventional polymers to PLA. This is no longer the case.

Adhesion Strength and Surface Properties

The gelatin-based plasticizer also promotes adhesion of modified PLA to paper, wood, metal, and glass. When used in extrusion coating applications, PLA film adheres strongly on the surface of paper. PLA/paper strips in the center of a 98 cm width laminate were sampled in every hundred-meter intervals form the production line for adhesion evaluation. Typical peeling strength for a half-inch width PLA strip on a paper substrate is 70 g or higher on average (Figure 9). Sample 1 has relatively lower adhesion strength compared to those of the later ones. This may be because the coating system had yet to reach the optimal conditions at the early stage of production. After this, samples 2–5 have much higher adhesion strength. The results suggest that uniform PLA films adhere strongly on paper
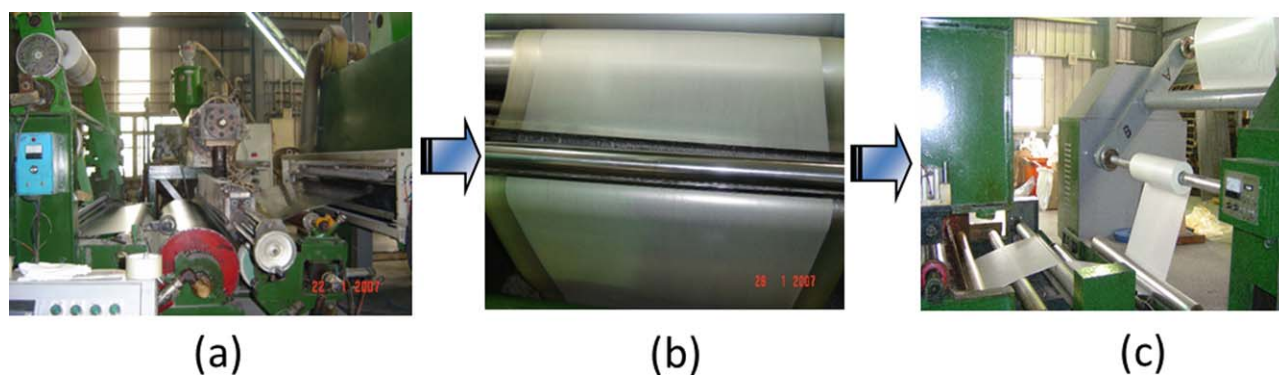

Figure 8. Extrusion coating process: (a) extrusion and lamination, (b) modified PLA/paper laminate, and (c) windup. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
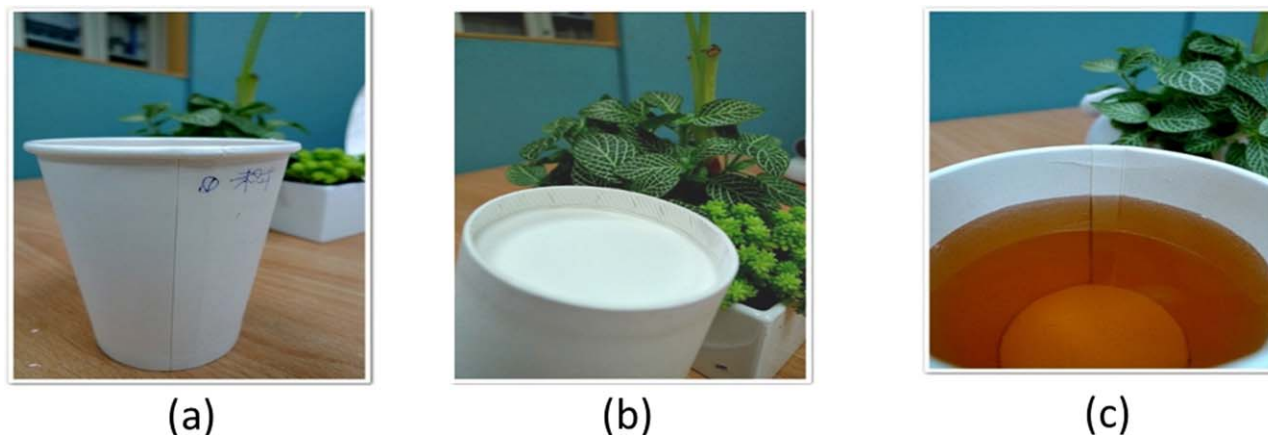
Figure 10. Coffee cup made of the modified PLA/paper laminate (a) side and (b) bottom after filling with hot coffee, and then (c) refilling with hot tea. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

substratea. A low adhesion strength on one of the edges may be because of the rapid cooling of the PLA film at that specific area. When used for food packaging, the containers may be subjected to microwave heating and freezer storage. To evaluate the adhesion performance of PLA/paper laminates, paper lunch boxes with PLA coatings containing 2 wt % modified animal gelatin underwent microwave heating and freezer cooling cycles. Lunch boxes with and without steamed rice or Chinese fried dumplings were microwaved for 3 minutes at 750 W microwave power, and no peeling-off of the PLA thin film was observed. Afterwards, water was added to 80% confluence of the lunch box without steamed rice, then placed in a freezer for 4 hours, defrosted at room temperature, and again no peeling-off of the thin film was observed. After the tests, PLA coatings were peeled off the paper substrate, and some fiber residue was observed on the paper surface, which shows that the adhesion between the polymer film and the paper remain strong after the heating and cooling cycles. Coffee cups made of the PLA/paper laminate can also stand repeat fillings of hot coffee and tea without leakage from the edge or the bottom, Figure 10.

In some cases, wood panels were laminated with plastic coated glassine paper to make wooden boxes for food or gift packaging. For this application, a PLA thin film containing 2 wt % modified animal gelatin is sandwiched between glassine paper and wood panel (glassine paper/PLA/wood). Adhesion strength of the PLA thin film in the sandwiched was evaluated using the JIS K5400 testing standard. In the control case, glassine paper/LDPE/wood was tested under the same conditions. The adhesion test result for LDPE is 4, and 8 for PLA containing gelatin. The plastic coating serves as a water barrier for the wood substrate. Contact angle of a water droplet on a substrate was performed to evaluate the barrier efficiency of PLA coating. Without surface modification of the glassine paper, the contact angle is 40.25 degrees, and it is elevated to 70.89 degrees when the surface is rod-coated with modified PLA. In the data control study, the contact angle of a glassine paper coated with low density polyethylene (LDPE) is 60.93 degrees. A small amount of water soluble gelatin in the polymer matrices does not affect hydrophobicity natural of PLA. Plasticized PLA coating increases the hydrophobicity of glassine paper surface.

CONCLUSIONS

Compostable polylactic acid/paper laminates were made of polylactic acid modified with gelatin-based plasticizer using conventional polyethylene extrusion coating machines. Animal and plant gelatin were functionalized with lactic acid to improve compatibility with the polymer matrices. Melting index of PLA was adjusted by varying the concentration of the plasticizer for the fabrication of laminates using a few different models of existing machines. Adhesion of PLA thin film on paper or wood substrates was improved in the presence of the gelatin-based plasticizer. Lunch boxes made of PLA/paper or Paper/PLA/wood laminates can stand microwave heating and freezer cooling cycle without delamination. Coffee cups with a thin PLA coating can be used for filling hot coffee or tea without leakage. Use of the biomass derived plasticizer to modify biodegradable PLA for the fabrication of laminates reduces capital investment for manufacturers and resolves plastic debris problems to some degree.

The gelatin-based plasticizer facilitates crystallization of PLA by introducing the less ordered α'-form crystals. Glass transition temperature and cold crystallization temperature decrease while the degree of crystallinity and the melting index of PLA increase as the plasticizer concentration increases.

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