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Development of a Melt-Extrudable Biobased Soy Flour/Polyethylene Blend for Multilayer Film Applications

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ABSTRACT: Monolayer and multilayer films from biobased linear low-density polyethylene and milled soy flour were produced through cast film coextrusion processes using conventional thermoplastic processing equipment. Films containing 10 and 20% by weight of soy flour milled to maximum particle sizes of 8, 11, and 22 μm were extruded and characterized as a packaging film material. Water resistance, tensile properties, and gas permeability were measured on each film and analyzed with respects to the soy particle size, soy loading, and layer configuration in the multilayer film structure. Mechanical properties results indicated that ultimate elongation of the soy-containing films decreased by as much as 14% compared to the control, while tensile strength and maximum load testing did not reveal any identifiable trends. Monolayer soy-containing film showed high moisture sensitivity, as measured by contact angle and absorption testing, while the multilayer films demonstrated a more hydrophobic nature as indicated by higher contact angle measurements. This increase in hydrophobic properties is due to protective polyolefin skin layers, which are more hydrophobic. Oxygen transmission rates of the multilayer films decreased by 38% due to the presence of soy flour as compared to the control that did not contain any soy flour. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40707.

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INTRODUCTION

Soybean farming is a global industry in which the major producers include the United States, Argentina, Brazil, China, and India. These five countries combine for more than 90% of the world's current soybean supply.[1] Estimates for the 2011 soybean crop show that the United States harvested over 73 million acres of soybean farmland, which produced roughly 3.1 billion bushels of soybeans, yielding over 22 billion pounds of soybeans. Domestic annual use of soybeans within the United States is estimated at 18 billion pounds, with the remaining 4 billion pounds exported to various countries.[2] Soybeans provide a sustainable source of protein and oil worldwide. Soybean's properties allow its use in a variety of applications from animal feed and human consumption, to road fuel and other industrial uses.[3]

The development of biobased and biodegradable materials for use in applications such as coatings, packaging, agriculture, and medicine has proven to be of high-interest in recent years. The development of these materials from natural sources helps to reduce the carbon footprint of these materials and reduces negative effects on the environment from the production of such materials.[4] Along with the environmental benefits that materials of this nature would provide, the development of new-uses for soybeans is a primary goal of the United Soybean Board whose mission is to effectively invest and leverage soybean check-off resources to maximize profit opportunities for US soybean farmers. Increasing demand for soybeans through new-uses helps develop market growth and supports, the roughly, 681,000 domestic soybean producers.[5]

Melt-extrusion of thermoplastics containing soybean products has been a challenge, as the degradation/decomposition of soy-proteins containing 1% moisture, typically occur around 190°C and even lower at higher moisture content.[6] Chemical modification of soy protein has been a popular area of research to promote processing improvement and mechanical properties. Chemical modification with monomers such as maleic anhydride, glycidyl methacrylate, and styrene has shown to be successful in altering the denaturation temperature of soy protein as well as mechanical properties.[7] Other modifications that have been examined include crosslinking, thermal treatments, and blends with easier flowing thermoplastics.[8,9]

Flexible food packaging is a particularly interesting area of research for biobased polymers as much of the petroleum-based trash found in landfills is from food packaging. Several materials have demonstrated favorable properties that may prove useful for packaging specific food items.[10] Moisture sensitivity of soy proteins remains to be a critical element in the design and development of flexible soy-based packaging. Enhancing the water stability of soy plastics has been an exciting research area for the development of new uses for soy proteins. Examples of this research include modifications to the soy molecule using acid anhydrides as well as blending with other more stable bioplastics and starches.[11,12] One of the most important limiting properties of polymeric materials in the food packaging field is their inherent permeability to low molecular weight substances, including permanent gases, water, and organic vapors. This has boosted the interest for developing new resins or blends with higher barrier properties and to carry out research aimed at the understanding of the structure/barrier properties relationship.[13] Initial research on barrier performance of soy-based films mainly focus on samples based on expensive soy-protein isolate or solvent casted/coated systems, which contain high protein contents.[14–16] Very few publications discuss the successful use of soy flour in flexible films, especially those that are produced through a continuous melt-extrusion operation. Mohanty and coworkers[17,18] investigated the use of glycerol-plasticized soy flour in composites with modified polyesters for fiber and molded applications. Biodegradable and edible pectin/soy flour films were investigated by Di Pierro et al.[19] as drug coatings, but would not perform well as a packaging film due to their moisture sensitivity. Defatted soy-flour dispersed in styrene–butadiene latex to form an elastomeric material was investigated by Jong,[20] but this was done through a solution batch process and not produced through continuous melt extrusion.

The use of defatted soy flour in packaging materials has advantages over soy concentrates and soy isolates. Soy flour prices are typically around \$0.40/lb while soy concentrates and soy isolates can cost anywhere from \$1.00 to \$2.00/lb.[21] Given the cost of most commodity thermoplastics used in packaging are less than \$1.00/lb, an additive such as soy flour will help keep material costs down. Another advantage of soy flour is its low protein content as compared to soy concentrate and isolate. Protein content of soy flour is about 53% and the content of soy concentrate and soy isolate is 69 and 90%, respectively.[22] Denaturation of soy proteins often occurs during extrusion, which leads to a reduction in protein solubility, and the creation of cross-linking reactions and covalent bonding in the extrudate.[23] The mere presence of a denatured protein should not negatively affect the film, but decomposition and degradation of the soy protein must be avoided to avoid undesirable affects in the extrusion process such as discoloration, foul odors, and smoke generation. Minimizing these effects will aid in creating a more homogeneous and acceptable film material.

The work discussed in this article focuses on the development of a melt-compounded blend of soy flour and biobased polyethylene for flexible film/packaging applications.

EXPERIMENTAL

Materials

Defatted soy flour (Soy Flour 7B) containing 53% protein was supplied by Archer Daniels Midland with a maximum particle size of 210 μm. SCLAIR 8107 linear low density polyethylene (LLDPE) (density: 0.925 g/cc, melt flow index: 4.8 g/10 min) was supplied in granular form by Entec Polymers. LLDPE grades Braskem SLL218 (density: 0.918 g/cc, melt flow index: 2.3 g/10 min), and Braskem SLH118 (density: 0.916 g/cc, melt flow index: 1.0 g/10 min) were supplied by FKUR Plastics Corporation. Both grades of Braskem polyethylene are considered “green polyethylene” and are made from sugarcane versus petroleum-based feed-stocks.

Soy Milling

To incorporate the as-received soy flour into flexible film and fiber applications, the 210-μm soy flour 7B particles were milled into smaller diameter particles. Milling operations were conducted at Custom Processing Services (Reading, PA) using a laboratory-scale fluid-bed jet mill. Once milling was completed, 2–3 kg batches of milled soy flour were provided for compounding. Particle size analysis conducted at the milling location indicated a Gaussian distribution of particle sizes with dv100 values of 8, 11, and 22 μm. A microtrac S3000/S3500 particle size analyzer was used to confirm these sizes.

Extrusion Processing—Particle Size Optimization

To determine how the particle size of the flour affected the properties of the polymer, three compounds were produced using a Thermo-Prism TSE-16 twin-screw extruder with an L/D ratio of 24:1 and a screw diameter of 16 mm. The SCLAIR 8107 LLDPE and milled soy flour were fed into the feed port of the twin-screw extruder using two volumetric feeders at a soy flour loading level of 20 wt % to make a LLDPE/soy flour masterbatch. The materials were compounded at a screw speed of 100 rpm, producing a melt temperature of 140°C. The extruded strand was pulled through a water bath and pelletized into 2-mm long cylindrical pellets. Three batches were made using the three different particle sizes of soy flour. Each batch was dried to 0.1% moisture in a two-bed desiccant hot air dryer at 90°C for 10 h.

The dried compounds were extruded into 100 mm wide films using a ThermoHaake Rheomex single screw extruder with a 20 mm, three-zone general purpose screw. Cooling rolls were set to 30°C and films were produced with an average thickness of 150 μm. A control LLDPE film along with three soy-containing films were collected and prepared for characterization.

Characterization

Thermal analysis characterization of the soy flour and blend materials was conducted by means of a TA Instruments Q500 thermogravimetric analyzer (TGA) under a nitrogen gas purge. Samples were heated at a ramp rate of 20°C/min from 0 to 800°C and analyzed using TA Universal Analysis software. Initial weight loss indications around 100°C were attributed to water loss from the sample on heating.

Mechanical properties of all films were measured using an Instron tensile testing machine according to ASTM D882.[24] Film samples were dried for 48 h in a recirculating desiccant drying oven at a temperature of 80°C prior to testing. Samples were tested on removal of the sample from the oven to minimize any moisture affects on the tensile properties of the films.

The hydrophilic properties of the films were determined through contact angle measurements of the film surface using distilled water at intervals of 0, 5, and 10 min. Water retention

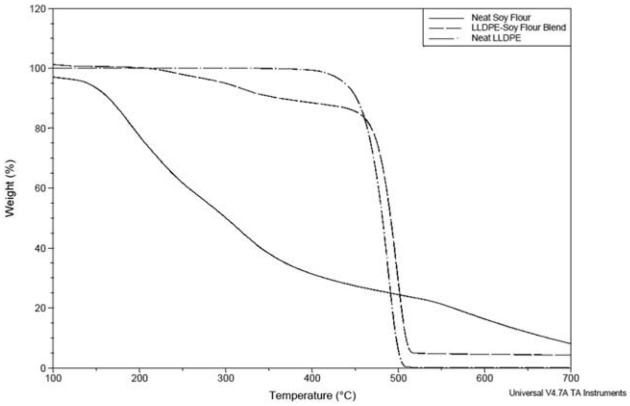

Figure 1. TGA generated curve of "as-received" soy flour and LLDPE-soy flour blends.

measurements were also taken to determine moisture sensitivity of the films as the soy component of the films is hydrophilic while the polyethylene component is not. Samples were submerged in distilled water for 48 h and the percentage change in weight was recorded.

Barrier property testing of the films to both oxygen and water vapor was conducted. Oxygen transmission testing was carried out in accordance with ASTM Standard D3985-06 and water vapor permeation testing was performed according to ASTM F1249. Oxygen transmission was measured using a MOCON Ox-Tran 2/20 with an oxygen flow rate of 20 cm^3/min at 23°C and 50% relative humidity. Oxygen transmission testing was carried out at atmospheric pressure using both oxygen and nitrogen. Water vapor transmission testing was measured using a MOCON Perma-Tran at a temperature of 37.8°C and 90% relative humidity.

Light microscopy of the film's cross-section was conducted by preparing a 20-μm thick sample using a Leica RM2265 microtome. Samples were then imaged using an Olympus BX51 polarizing light microscope and measured using Studio Measure™ software from Studio86 Designs.

Multilayer Film Extrusion

Multilayer film coextrusion was conducted using a Dr. Collin GmbH multilayer Teach-Line coextrusion system. three-layer film coextrusions were produced in an A–B–A structure using two 20-mm single screw extruders connected to a feed-block and a 250 mm-wide flat film die with a flex-lip adjustment. Extruder 1 produced the skin "A" layers while Extruder 2 produced the core "B" layer. All films were produced with a target average thickness of 65 μm during extrusion processing as this was a common film thickness for packaging applications. A Dr. Collin GmbH Type 136P chill roll system, cooled to 20°C was used to form and collect the extruded film at a line speed of 3.5 m/min. The temperature profile of extruder 1 was set at 180–190°C, while the profile of extruder 2 was set at 145–155°C. The feed-block and die temperature for all trials was 160°C.

RESULTS AND DISCUSSION

Thermal Analysis

Determination of the degradation temperature of the soy flour during the extrusion processes was conducted via TGA. This was conducted to determine the maximum temperatures that the soy should be subjected to during processing to avoid degradation problems. Figure 1 illustrates the curve generated during testing of the "as-supplied" soy flour as well as the soy-LLDPE blends in the TGA.

The results from the TGA indicate that a high rate of weight loss begins at a temperature of 170°C. This is the degradation associated with the protein component of the soy flour[25] and explains why melt extrusion at higher temperatures is more difficult with higher protein-containing soy materials. The remaining components of the soy flour (carbohydrates, fats, and fibers) are degraded at higher temperatures, also shown in Figure 1. A lower degree of weight loss (5%) occurs prior to 170°C and can be associated to absorbed water in the soy sample, which is lost on heating. Based on these results, melt temperatures of processing were maintained below 170°C to avoid degradation in the melt.

Monolayer Film

A series of monolayer films containing various levels and particle sizes of soy flour along with LLDPE SCLAIR 8107 were produced through single screw extrusion. The percentages of soy flour desired for each sample were achieved by dry-blending the 20% soy flour master-batch with the proper amount of neat LLDPE prior to film extrusion. A list of these samples is presented in Table I along with the sample identification letter that will be used throughout this section.

TGA results of the neat LLDPE and the blended LLDPE/soy flour at a concentration of 10% soy flour are illustrated in Figure 1 along with the "as-received" soy flour as previously mentioned. As it is observed in Figure 1, protein weight-loss begins around 210°C in the LLDPE–soy flour blend. The increase in weight-loss temperature in the blend over the neat soy flour can be attributed to a combination of the previously heat-treated soy flour that occurred during the compounding step and the presence of the polymer matrix, which has been reported to delay onset degradation in composites.[26]

Mechanical testing of each film sample was conducted to determine the effect of the particle size on the physical properties of the films so that a determination could be made as to which particle size would be the most efficient for packaging applications. Presented in Figure 2 is the tensile yield strength and elongation at break values for each of the film samples listed in

Table I. Monolayer LLDPE/Soy Flour Film Samples

Sample	Soy flour loading (%)	Maximum particle size (μm)
A	0	N/A
B	10	8
C	20	8
D	10	11
E	20	11
F	10	22
G	20	22

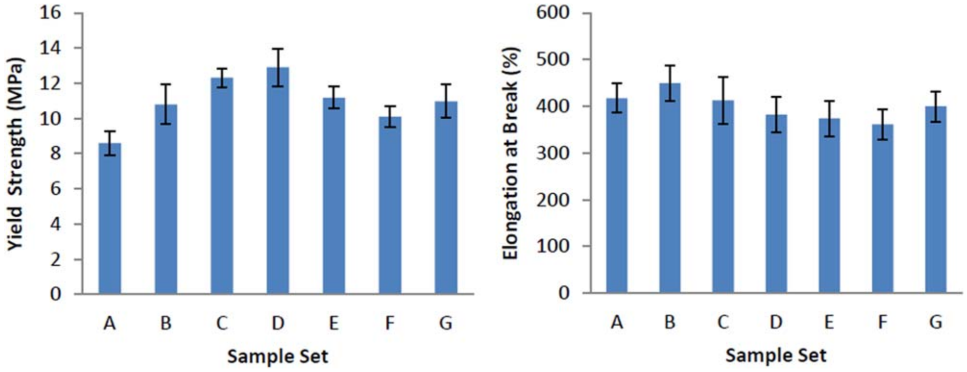

Figure 2. Tensile property measurements of monolayer LLDPE/soy flour films. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table I. Sample names in the figure refer to the samples identified in Table I.

The data presented in Figure 2 indicates that the soy flour particles in the monolayer samples acted as reinforcing agents to the LLDPE matrix and increased the tensile yield strength of the films. In the finest particle size (8 μm), the extent of reinforcement increased with the amount of soy flour up to the 20 wt % level with a low standard deviation. The highest yield strength increase was observed with the 11-μm particle size soy flour at a 10% loading level. This reinforcing effect did not continue in this sample with increasing soy percentage. In fact, a significant drop in yield strength was observed when increasing the loading of 11 μm soy flour from 10 to 20%. Finally, the yield strengths of the films loaded with 22-μm soy flour were similar to the films produced with the 8 μm particles. Examination of the elongation at break values, indicated that the smallest particle size (8 μm) soy filler had a similar elongation value to that of the control, within the margin of error. This result indicated that elongation at break was not affected by the use of the 8-μm soy flour. Larger soy flour particle size (11 and 22 μm) had a more significant affect on the ultimate elongation as they acted as stress concentrators within the film. These results indicated that the smallest particle size soy flour did not increase the yield strength of the films to a level that would warrant the extra milling time and expense needed to produce particle sizes that small for an application involving a film of this thickness (150 μm). The negative effect of the larger particle sizes on the film's elongation will need to be considered based on the type of application intended for the film. As the overall film thickness decreases, it is expected that the particle size will play more of an effect on the mechanical properties of the film.

Contact angle and water absorption measurements were taken on each film to determine the water sensitivity of the films as well as the quality of the soy flour dispersion in the LLDPE matrix. Higher contact angles would indicate more soy flour in the center of the film and away from the film surface. Table II lists the measured contact angles and water absorption percentages for each film sample.

The data presented in Table II compares the hydrophilic behavior of the soy-based films against the LLDPE control (Sample A). The data indicates that the LLDPE control film is hydrophobic and is only minimally affected by water. Comparison of the contact angle measurements of this control sample to the samples containing the 8-μm soy flour (Samples B and C) show no significant differences in the 10-min testing time. Knowing that soy is hydrophilic, these results indicate that the soy particles are well contained within the LLDPE matrix and there is minimal surface affect. A significant difference is observed when examining the water absorption percentage as the soy-containing samples have much higher water absorption amounts compared to the control. This data indicates that there is very little affect of water on the films in the short-term, but over time, the water penetrates the surface of the film and is absorbed by the soy flour particles. Examination of the remaining soy-containing films indicates that the samples containing the larger size soy particles have higher hydrophilic properties in the short-term, but similar long-term water absorption. Although LLDPE is known to demonstrate low moisture permeability,[27] moisture vapor can still permeate LLDPE allowing absorption of the water by the soy particles.

Coextrusion Processing

To control the water-sensitivity of the soy materials for longer periods of time, coextrusion of multilayer films was conducted as described previously. Given the interest of the researchers to examine biobased materials for packaging applications, two different grades of LLDPE were used for the multilayer film production. These materials were supplied by Braskem under the

Table II. Contact Angle and Water Absorption Measurements

Sample	θ (0 min)	θ (5 min)	θ (10 min)	Maximum water absorption (%)
A	96	93	87	0.24
B	94	91	84	1.3
C	98	94	85	2.4
D	64	57	50	2.2
E	55	49	43	2.8
F	73	70	66	2.7
G	60	57	53	5.2

Table III. Multilayer Film Coextrusion Samples

Sample	Skin layer 1 thickness (μm)	Core layer description	Skin layer 2 thickness (μm)
MA	11	44-μm thick SLL218	11
MB	11	44-μm thick SLL218 + 10% 22-μm soy flour	11
MC	8	50-μm thick SLL218 + 10% 22-μm soy flour	8
MD	11	44-μm thick SLL218 + 20% 11-μm soy flour	11
ME	8	50-μm thick SLL218 + 20% 11-μm soy flour	8

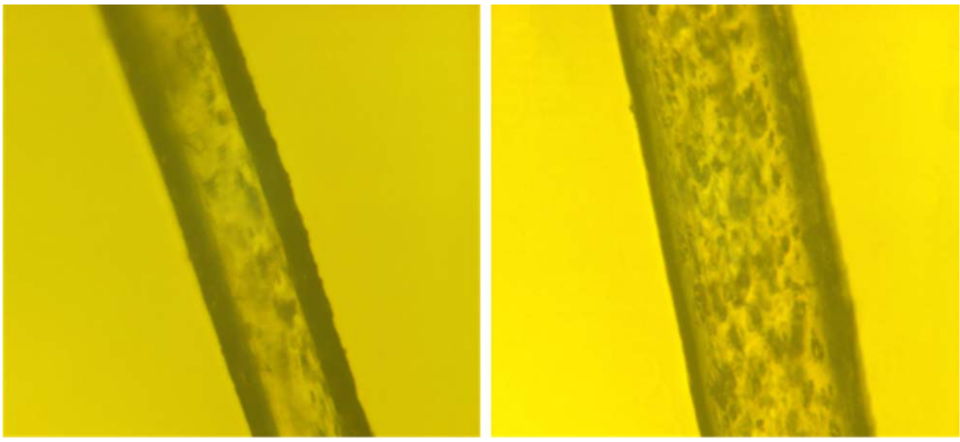

Figure 3. Cross-sectional image of (left) multilayer soy film sample "MB" and (right) multilayer soy film sample "MC". [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

grade names SLL218 and SLH118. The melt-flow behaviors of these LLDPE grades provided for improved melt-rheology in coextrusion processing and would ultimately produce high quality multilayer films. Table III lists the multilayer films, which were produced using these materials. The total thickness of each film sample was targeted at 66 μm. SLH 118 was used as the polymer for all skin layers and did not contain any soy flour. The "M" used in the sample name indicates that these are multilayer structures.

Verification of these changes in thicknesses was accomplished using optical light microscopy on microtome-cut samples of the film cross-sections. Presented in Figure 3 are example images of the cross-sections of samples MB and MC, displaying the soy-containing core layer and the neat skin layers. Also, listed in Table IV are the contact angle and water absorption results as measured using the same method that was used for the monolayer film samples.

The images in Figure 3 indicate that the thickness of the skin and core layers changed from sample to sample as the screw speed was altered. This was done to determine how the thickness of the skin layers would affect the moisture sensitivity of the films. The contact angle measurements and water absorption data from Table IV show that both the thick and thin skin layers were quite effective in protecting the water-sensitive core layer from outside moisture at the lower soy level (10%). As the soy content of the core layer was raised to 20% (samples MD and ME), the samples became more sensitive to water as shown by the decrease in contact angle and increase in water absorption percentage. In addition to water sensitivity testing, mechanical strength testing was carried out in both the machine and transverse directions with the results presented in Figure 4. All samples were dried prior to testing according to the procedure described previously to remove any moisture affects on the mechanical properties of the films.

From Figure 4, it is apparent that the ultimate elongation and the yield strength of the films were decreased by the addition of the soy particles. This is common with particulate additives such as this as the soy particles act as stress-concentrators and are typically the point of failure for a tensile rupture or break during tensile testing. The unfilled control sample had the highest tensile elongation and yield strength before failure of all the samples. The soy-containing films all demonstrated elongation

Table IV. Contact Angle and Water Absorption Measurements for Multilayer Films

Sample	θ (0 min)	θ (5 min)	θ (10 min)	Maximum water absorption (%)
MA	89	83	79	0.00
MB	88	82	80	0.50
MC	92	83	81	0.29
MD	85	79	76	0.81
ME	82	77	73	1.00

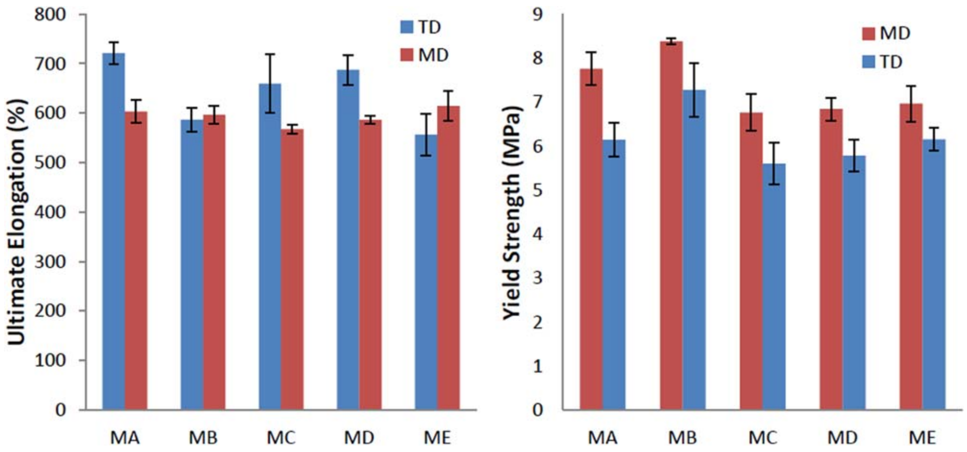

Figure 4. Ultimate elongation (left) and yield strength (right) test results for multilayer soy-containing films in both the machine and transverse directions. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

and yield strength values that were less than that of the control, but no real trend could be seen to correlate the thickness of the core and skin layers to the ultimate tensile elongation. Elongation and yield strength values in the machine direction were all higher than those measured in the transverse direction. This is due to the fact that the films were all processed using cast-film extrusion, which produced less isotropic films than that which would be produced using blown film or other biaxial processing methods.

The oxygen transmission of the multilayer soy films was tested according to the procedure outlined earlier. Figure 5 illustrates the results of the oxygen transmission testing on the control and soy-containing multilayer films.

Examination of the oxygen transmission data in Figure 5 reveals that the soy multilayer structure exhibited reduced oxygen transmission when compared to the neat control. The enhanced gas barrier properties exhibited by the soy-containing films were expected as additives such as clay nanoparticles,[28] cellulose,[29] and graphite flakes[30] have been reported to improve barrier properties of polymer films by creating a tortuous path through which gas molecules must travel to permeate through a film membrane. If the surface area of the additives is large enough and the dispersion of the additive is of a high quality, permeability of gases can be reduced in polymer membranes. A number of publications in the literature discuss oxygen permeability of protein-based films and the effect of humidity and temperature on those results.[31,32] These publications typically focus on edible films which contain plasticizing agents and are based on protein and cellulosic materials. Given the results from these publications, it is difficult to determine whether the gas permeability differences measured in the LLDPE/soy flour blends are the result of particle distribution or a property of the soy flour itself. Analysis of the water vapor transmission rate data indicates only small changes in the water vapor transmission rate were observed as a result of the added soy flour and the minor changing of the core and skin layer thicknesses. This result tends to indicate that the hydrophilic soy flour had reached its moisture absorption capacity and was not influencing water vapor barrier any longer. These results will be investigated

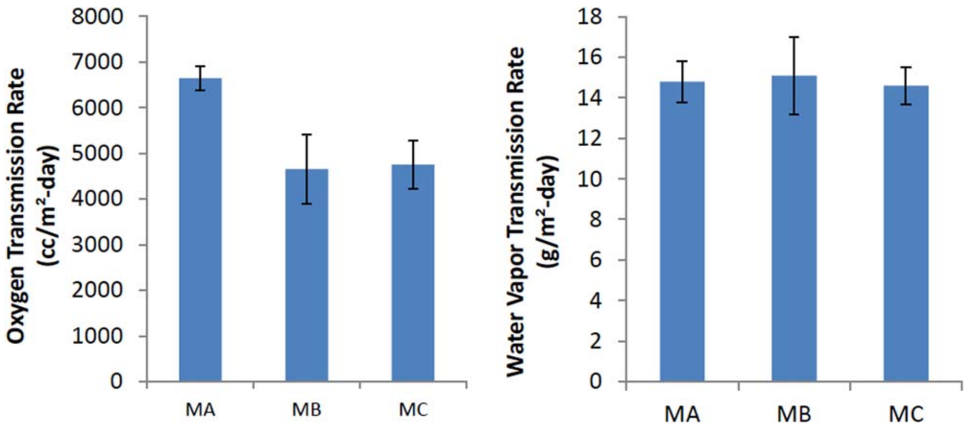

Figure 5. Oxygen and water vapor transmission testing results for control and soy-containing multilayer films. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

further to determine why oxygen transmission rates of the sample films were affected by the soy flour but the water vapor transmission rates were not.

CONCLUSIONS

The use of milled soy flour as an additive for flexible film packaging applications has been shown to have a significant effect on the mechanical properties of films as well as moisture sensitivity and permeability of oxygen and water vapor. In the monolayer film set of experiments, the milled soy flour acted as a reinforcing agent to the polyethylene-based film. Data showed that the flour milled to a particle size of 11 μm demonstrated the highest degree of reinforcement to the LLDPE-based films, increasing the yield stress of the film by 53%. The moisture sensitivity of the monolayer films were also drastically affected by the addition of the larger particle-size soy flour (22 μm) as the contact angle was shown to decrease by as much as 34° in these samples. The smaller particle size soy flour (8 μm) proved to have better short-term water resistance, but still absorbed a considerable amount of moisture (2.4%) in the longer water absorption test. Although less permeable to water vapor than other common polymers, water vapor will still permeate LLDPE and be absorbed by any soy within the polymer.

Multilayer film samples made from coextrusion processing was used as a method of creating films that contain the water-sensitive soy within the core structure and protected by skin layers of neat LLDPE polymer for enhanced moisture protection. The varying soy particle size (11 and 22 μm) in the multilayer films along with the varying soy loading level had a direct effect on film properties. The films containing 20% of soy flour were more hydrophilic than the films containing only 10% soy flour and this effect was observed in the contact angle and moisture absorption tests. Ultimate elongation was decreased with soy content, which is a common occurence with particulate fillers in a polymer matrix. The permeability testing of the samples to both oxygen and water vapor provided data indicating that both were affected differently by the soy flour. The oxygen permeability of the LLDPE films decreased by 38% with the addition of the 22 μm size soy flour particles in the core of the three-layer structure. Water vapor permeation rates were only affected to a small degree and no significant trends or patterns were observed in this data.

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