

Application and Performance of Maleated Thermoplastic Starch–Poly(Butylene Adipate-co-Terephthalate) Blends for Films

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ABSTRACT: In this work, we studied the effect of the percentage of maleated thermoplastic starch (MTPS) in MTPS–poly(butylene adipate-co-terephthalate) (PBAT) blends that were used to produce extruded films. The materials were characterized by their mechanical properties (tensile and puncture tests), their barrier properties (carbon dioxide, oxygen, and water-vapor permeability tests), and microstructural analysis [transmission electron microscopy (TEM)], and the biobased content of the materials was determined. The results of the testing show that increasing the MTPS content decreased the tensile strength (from 19.7 to 8.6 MPa in the machine direction and from 15.3 to 7.1 MPa in the transverse direction) and puncture force (from 42.5 to 30.3 N) of the films; however, the elongation was not significantly affected. The permeability of

the films to oxygen and carbon dioxide decreased with increasing MTPS content. The oxygen permeability decreased from 1.68×10^{-17} to 6.0×10^{-18} kg m m⁻² s⁻¹ Pa⁻¹, whereas the carbon dioxide permeability decreased from 3.0×10^{-16} to 1.1×10^{-16} kg m m⁻² s⁻¹ Pa⁻¹. However, the permeability to water vapor increased from 5.0×10^{-15} to 1.04×10^{-14} kg m m⁻² s⁻¹ Pa⁻¹. Finally, TEM showed that PBAT was the continuous phase and MTPS was the dispersed phase. As the amount of MTPS in the samples increased, the dispersed phase became finer and more regularly spaced. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

Key words: biodegradable; blends; films; mechanical properties; microstructure

INTRODUCTION

Starch has been considered for many years as a polymer with a high potential for packaging applications because of its low cost, renewability, and biodegradability. Several studies have been done to analyze the properties of starch-based films.^{1–6} Edible and/or biodegradable films are not able to replace all synthetic packaging films; however, they do have the potential to replace conventional packaging in some applications.

The hydrophilic nature of starchy polymers makes them sensitive to environmental humidity, and the presence of high levels of glycerol strengthens this behavior.⁷ Blending thermoplastic starch (TPS) with biodegradable polymers that are less hydrophilic is one option for producing film materials that are more water resistant.

One such biodegradable polymer is poly(butylene adipate-co-terephthalate) (PBAT). PBAT is a biodegradable, hydrophobic, aromatic/aliphatic copolyester that is easily processable and exhibits no

adverse effects on the environment.⁸ By blending PBAT with starch, one has the opportunity to produce materials that are much better suited for making consumer products than with starch alone, while having the added benefit of decreasing the price compared to using PBAT alone.

Modification is often necessary to allow better compatibility between hydrophilic and hydrophobic materials in a blend. Different methods of modification include maleation, silanization, acetylation, and acrylation.⁹ In the maleation process of reacting maleic anhydride with starch, it has been shown that maleated thermoplastic starch (MTPS) has a lower molecular weight than TPS that has not been modified. This lower molecular weight causes a lower melt viscosity for MTPS and allows for better dispersion of the starch fraction within a polymer matrix.¹⁰

Some work has been performed to look at films of starch and PBAT. Bilck et al.¹¹ produced blown films of thermoplastic cassava starch and PBAT, whereas Raquez et al.¹⁰ produced blown films of maleated thermoplastic corn starch and PBAT. The maleation of the starch was shown to yield graft copolymers, and the films exhibited an increased tensile strength.

This work was performed to better understand the effect of the percentage of MTPS in MTPS–(PBAT) blends used to produce extruded films containing

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high-amylose corn starch. Preliminary studies showed high-amylose corn starch to have improved processability over regular corn starch. The materials were characterized by mechanical properties (tensile and puncture tests) testing, barrier properties (carbon dioxide, oxygen, and water-vapor permeability tests) testing, and microstructural analysis [transmission electron microscopy (TEM)].

EXPERIMENTAL

Materials

High-amylose corn starch, containing 70% amylose, was purchased from National Starch and Chemicals (Indianapolis, IN). PBAT was purchased from BASF Chemicals (Ludwigshafen, Germany) under the trade name Ecoflex. Anhydrous glycerol (99.9% assay) was purchased from J. T. Baker (Phillipsburg, NJ). Maleic anhydride was purchased from Sigma-Aldrich, Inc. (St. Louis, MO). The initiator, 2,5-bis(*tert*-butylperoxy)-2,5-dimethylhexane, also referred to as Luperox 101, was purchased from Sigma-Aldrich.

Equipment

A Century CX-30 corotating twin-screw extruder, having a length/diameter ratio of 42 and a screw diameter of 30 mm was used to prepare the TPS and MTPS and to blend these materials with PBAT. A pelletizer was used to cut the extrudate strands into small pellets. The blended material was then extruded through a Killion single-screw extruder, having a length/diameter ratio of 24 and a screw diameter of 1 in. The extrudate exited the extruder in the form of a film of material and was collected on a roller.

Procedure

Production of the modified TPS (MTPS)

MTPS was produced in the CX-30 corotating twin-screw extruder. The temperature profile of the extruder was set to 25/95/125/145/160/165/165/165/150/145°C from the feed throat to the die. Maleic anhydride was ground into a fine powder with a mortar and pestle and preblended with the high-amylose corn starch, which had been acclimatized to ambient conditions for 1 day. The starch and maleic anhydride mixture were fed into the feed port of the extruder from an external feeder. Luperox 101 was pumped into the feed throat of the extruder with a peristaltic pump. The concentrations of maleic anhydride and Luperox 101 used were 2 and 0.1 wt % with respect to the total mass, respectively. Glycerol, which was warmed in a water bath, was pumped into the extruder with a peristaltic pump. The feed

TABLE I
Composition of the Films of Blends of MTPS with PBAT

Sample	Blend composition	
	MTPS (%)	PBAT (%)
1	—	100
2	10	90
3	20	80
4	30	70
5	40	60
6	50	50

rates of the external feeder and the peristaltic pump for the glycerol were set so as to accomplish compositions of 80 wt % starch and 20 wt % glycerol and a total flow rate of material through the extruder of 11 kg/h. The screw speed was set to 125 rpm. A vacuum was pulled on the vent port of the extruder to remove unreacted maleic anhydride and moisture. The extruded strand was air-cooled and pelletized in line. The pellets were dried for 2 days in an oven at 65°C before they were blended with PBAT.

Blend production of MTPS with PBAT

Blends of MTPS/PBAT were produced in the CX-30 corotating twin-screw extruder. Pellets of MTPS were premixed with PBAT in 10 : 90, 20 : 80, 30 : 70, 40 : 60, and 50 : 50 weight ratios of MTPS to PBAT (Table I) and fed into the feed port of the extruder with an external feeder. The temperature profile of the extruder was set to 25/125/135/140/145/150/150/150/145/135°C from the feed throat to the die. The screw speed was set to 100 rpm. The extruder's vent port was opened to remove any moisture. The extruded strand was air-cooled and pelletized in line. The pellets were dried for 1 day in an oven at 65°C before they were extruded into films.

Film production

The extruded films of the blended material and of the neat PBAT were produced in the single-screw extruder. The pellets were gravity-fed into the extruder at the feed throat. The temperature profile of the extruder was 160/160/160/160/154°C for zones 1, 2, and 3, the clamp ring, and the die, respectively. The screw speed was set to 65 rpm. The extruded sheet was cooled on a chill roller set at 21°C and then collected on an auxiliary roller. The speed of the chill roller was adjusted to produce a film with a thickness of 150 μm .

Determination of the biobased content

Samples of MTPS and the 50 : 50 MTPS:PBAT blend were sent to Beta Analytic, Inc. (Miami, FL) for

biobased content analysis. This analysis was run according to standard method ASTM D 6866 method B.¹² In this testing, the amount of radiocarbon (¹⁴C) in a test sample is compared to that of a modern reference sample. The ratio of the unknown to the standard is reported as a percentage, having units of percentage modern carbon. A sample that is a mixture of fossil carbon (i.e., contains no radiocarbon) and present-day radiocarbon will have a percentage modern carbon value that correlates directly to the amount of biobased content in the sample.

It should be noted that the results of the biobased content analysis give a value for the percentage of carbon that is radiocarbon, out of the total amount of carbon in the sample, not the total weight of the sample.

Mechanical properties

Tensile tests. Tensile specimens of the MTPS and MTPS/PBAT blends were conditioned as recommended in standard method ASTM D 4332¹³ in a constant environment room at $23 \pm 1^\circ\text{C}$ and $50 \pm 2\%$ relative humidity for at least 40 h before testing. The tensile tests were measured in accordance with standard method ASTM D 882.¹⁴ Specimens ($100 \times 25 \text{ mm}^2$) of the extruded films of each formulation, cut along the machine direction and along the transverse direction, were clamped between the grips. Force–extension curves were recorded. Values for the tensile strength and elongation were determined for each sample, in both the machine and transverse directions. Seven specimens were tested for each blend and direction.

Puncture tests. Puncture tests were performed on the film samples to determine puncture strength (newtons) and deformation (millimeters) with a TA TX2i Stable Micro Systems texture analyzer (Surrey, England). Specimens ($40 \times 40 \text{ mm}^2$) were fixed on the plate of the equipment with a hole 20 mm in diameter with the help of tape. A cylindrical probe 5 mm in diameter was moved perpendicularly to the film surface at a constant speed of 1 mm/s until the probe passed through the film. Force–deformation curves were recorded. At the rupture point, the force and deformation were determined. Each data point represents an average of 10 specimens.

Barrier properties

Carbon dioxide permeability. Carbon dioxide (CO_2) permeability tests were performed with a Mocon Permatran-C model 4/41 carbon dioxide permeability instrument. Testing was run per ASTM standard F 2476.¹⁵ For the CO_2 permeability tests, specimens of each formulation were cut from the films that were extruded. Aluminum masks (4 mil thick) were

used to ensure that the area of the specimen tested was 1.41 cm^2 . The carrier gas used was nitrogen. Permeability tests were run at a flow rate of 50 sccm for carbon dioxide and nitrogen. All tests were run at 23°C and 0% humidity. Once the specimens were loaded into the Permatran-C, they were conditioned for 2 h. Permeability data was then collected for 30 min for each specimen (one cycle each). The Permatran-C had two cells and could test two specimens at once. After every two cycles, the test module was zeroed. Each test was run until steady-state conditions were achieved. Values for the permeability of CO_2 for each specimen were determined by multiplication of the average thickness of the specimen area tested by the average steady-state transmission rate. The Permatran-C compensated the transmission data to 1 atm of barometric pressure. Each value reported is an average of four specimens for each sample.

Oxygen permeability

Oxygen (O_2) permeability tests were performed with an Illinois Instruments model 8001 oxygen permeability instrument. Testing was run per ASTM standard D 3985.¹⁶ For the O_2 permeability tests, the specimens that were used to test the carbon dioxide permeability were tested. Aluminum masks (4 mil thick) were used to ensure that the area of the specimen tested was 1.41 cm^2 . The carrier gas used was nitrogen. The permeability tests were run at a flow rate of 10 sccm for oxygen and nitrogen. All tests were run at 23°C and 0% humidity. Once the specimens were loaded into the test equipment, the gas lines and cells were purged. Permeability data was then collected for 5 min for each sample (one cycle each). The Illinois Instruments instrument had two cells and could test two specimens at once. Each test was run until steady-state conditions were achieved. Values for permeability of O_2 for each specimen were determined by multiplication of the average thickness of the specimen area tested by the average steady-state transmission rate. The Illinois Instruments instrument acquired the data at atmospheric pressure. The permeability data presented were compensated to 1 atm of barometric pressure. Each value reported is an average of four specimens for each sample.

Water-vapor permeability. Water-vapor (H_2O) permeability tests were performed with a Mocon Permatran-W model 3/33 water-vapor permeability instrument. Testing was run per ASTM standard F 1249.¹⁷ For the H_2O permeability tests, the specimens that were used to test carbon dioxide and oxygen permeability were tested. Aluminum masks (4 mil thick) were used to ensure that the area of the specimen tested was 1.41 cm^2 . The carrier gas used was nitrogen. Permeability tests were run at a flow rate of 100

sccm. All tests were run at 37.8°C and 100% humidity. Once the specimens were loaded into the Permatran-W, they were conditioned for 2 h. Permeability data was then collected for 15 min for each specimen (one cycle each). The Permatran-W had two cells and could test two specimens at once. After every two cycles, the test module was rezeroed. Each test was run until steady-state conditions were achieved. Values for the permeability of H₂O for each specimen were determined by multiplication of the average thickness of the specimen area tested by the average steady-state transmission rate. The Permatran-W acquired the data at atmospheric pressure. The permeability data presented was compensated to 1 atm of barometric pressure. Each value reported is an average of four specimens for each sample.

TEM

A transmission electron microscope (JEOL-100CX) was used to make observations of the morphology of the blends. Samples of PBAT and the extruded blends were cryogenically frozen with liquid nitrogen and microtomed. The samples were mounted on TEM grids and then viewed with the transmission electron microscope.

Statistical analysis

One control sample, PBAT, was tested to evaluate the effects of the blends of MTPS with PBAT on the mechanical and barrier properties of the films. Analysis of variance and Tukey mean comparison tests ($p \leq 0.05$) were performed with Minitab 15 software (Minitab, Inc., State College, PA).

RESULTS AND DISCUSSION

Determination of the biobased content

The results of the biobased content analysis show that MTPS had a mean biobased result of $96 \pm 3\%$, whereas the 50 : 50 blend had a mean biobased result of $32 \pm 3\%$. That is, $96 \pm 3\%$ of the carbon in the MTPS was biobased carbon, whereas $32 \pm 3\%$ of the carbon in the 50 : 50 blend was biobased carbon.

It should be noted that PBAT is a synthetic biodegradable polyester that has no biobased carbon content.

To maintain the greatest amount of biocontent in a material, the least amount of PBAT should be used that will provide the required material properties for a specific application.

Mechanical properties

Tensile tests

The tensile properties of the different samples provided performance metrics for these materials. The

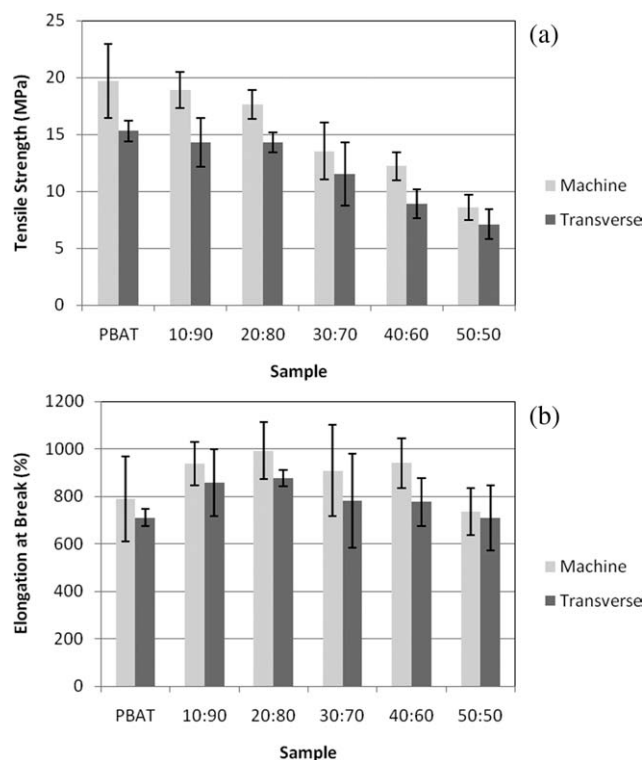


Figure 1 Mechanical properties (determined by tensile tests) of the films of blends of MTPS with PBAT: (a) tensile strength and (b) elongation at break.

effect of the ratio of MTPS/PBAT of the blends and the effect of the direction from which the specimens were cut are discussed here. Figure 1 and Table II present the tensile strength (megapascals) and break elongation (percentage) for the samples.

The tensile strength values for the samples tested in the machine direction were greater than those of samples tested in the transverse direction. Also, as the amount of MTPS in the samples increased, the tensile strength decreased. The addition of MTPS to the material decreased the tensile strength of the resulting films.

For the elongation at break of the samples, there was not a statistical difference between the samples when we compared the composition and the direction. The addition of MTPS to PBAT did not radically change the elongation exhibited. We also observed that all of the samples showed elongations greater than 700%. These materials could deform greatly before breaking.

In a comparison of these materials to other biodegradable materials, we noted that the values for the tensile strength and elongation of films containing 20% MTPS were greater than those of Parulekar and Mohanty,¹⁸ in which extruded cast films of 50 wt % poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV), 30 wt % PBAT, 12 wt % high-amylose corn starch, and 8 wt % glycerol exhibited tensile strength and elongation values of 15 MPa and 368%, respectively.

TABLE II
Thickness and Mechanical Properties (Determined by Tensile Tests) of the Films of Blends of MTPS with PBAT

Sample	Direction	Thickness (μm)	Tensile strength (MPa)	Elongation at break (%)
PBAT	Machine	148.8 ± 6.51 ^A	19.7 ± 3.27 ^A	789.0 ± 179.08 ^A
PBAT	Transverse	146.4 ± 3.45 ^A	15.3 ± 0.90 ^B	709.6 ± 35.79 ^{A,B}
10 : 90	Machine	150.4 ± 5.63 ^A	18.9 ± 1.59 ^A	937.5 ± 90.11 ^{A,B}
10 : 90	Transverse	154.7 ± 7.79 ^{A,B}	14.3 ± 2.14 ^{B,C}	857.5 ± 141.60 ^{A,B}
20 : 80	Machine	152.1 ± 9.96 ^A	17.6 ± 1.26 ^{A,B,D}	991.8 ± 121.00 ^{A,C}
20 : 80	Transverse	170.9 ± 3.14 ^C	14.3 ± 0.90 ^{B,D,E}	877.4 ± 34.00 ^{A,B,C}
30 : 70	Machine	155.8 ± 4.59 ^{A,D}	13.5 ± 2.50 ^{B,F}	908.6 ± 192.09 ^{A,B,C}
30 : 70	Transverse	154.8 ± 6.95 ^{A,E}	11.5 ± 2.79 ^{C,E,F,G}	781.3 ± 196.92 ^{A,B,C}
40 : 60	Machine	152.8 ± 5.97 ^{A,F}	12.2 ± 1.22 ^{B,C}	940.0 ± 104.64 ^{A,B,C}
40 : 60	Transverse	163.3 ± 5.26 ^{B,C,D,E,F,G}	8.9 ± 1.25 ^{G,H}	776.0 ± 102.23 ^{A,B,C}
50 : 50	Machine	144.9 ± 4.52 ^A	8.6 ± 1.12 ^{G,I}	736.9 ± 99.54 ^{A,B}
50 : 50	Transverse	157.1 ± 6.93 ^{A,G}	7.1 ± 1.32 ^{H,I}	709.0 ± 138.81 ^{A,B}

Means in the same column with different superscript letters are significantly different ($p \leq 0.05$).

However, Otey et al.¹⁹ reported blown films consisting of 20% corn starch and 80% poly(ethylene-co-acrylic acid) having tensile strength and elongation values of 28.5 MPa and 120%, respectively. Furthermore, poly(ethylene-co-acrylic acid) is not biodegradable. The films that were produced in this work were biodegradable.

From the data presented in this work, one would expect the tensile strength of starch films to be lower than those of the MTPS–PBAT blends. This was shown by Zamudio-Flores et al.,²⁰ who reported values for the tensile strength of native and acetylated banana starch films of approximately 2.5 and 3 MPa, respectively.

The tensile strength and elongation of the 50 : 50 blend was greater than those reported by Brandelero et al.,²¹ in which films containing 50% cassava TPS and 50% PBAT (with thicknesses of $147 \pm 58 \mu\text{m}$) exhibited tensile strength and elongation values of 5–6 MPa and 340%, respectively. The tensile strength and elongation values of the 30 : 70 blend were greater than those reported by Bilck et al.,¹¹ in which films containing 30% cassava TPS and 70% PBAT (with thicknesses of $123 \pm 12 \mu\text{m}$) exhibited tensile strength and elongation values of $8.4 \pm 1.1 \text{ MPa}$ and $537 \pm 89\%$, respectively. These improved results of the tensile strength and elongation of the films in this work could be related to the modification of TPS by maleic anhydride, which better compatibilized starch and polyester.²²

Puncture tests

The results of the puncture tests on the film specimens are shown in Table III. The thickness, force, and deformation of the samples are given. Each entry is an average of 10 specimens.

One can see that as the amount of MTPS in the samples increased, the maximum force achieved before rupture decreased. This phenomenon was

observed for the tensile tests. The addition of MTPS to PBAT decreased the amount of force that could be withstood both in a tensile-type loading and a puncture-type loading. One would expect starch films to exhibit a lower puncture strength than MTPS–PBAT films. Aguilar-Mendez et al.²³ observed that the gelatine–corn starch films had, on average, a lower puncture strength and deformation than what is reported here.

With regard to the deformation, we observed that the blends containing 10, 20, 30, and 40% MTPS had the highest deformation before rupture, but the PBAT sample and the 50 : 50 blend sample had lower values for deformation. However, all of the samples exhibited puncture deformation values between 17.9 and 25.2 mm.

Barrier properties

A main function of packaging, especially food packaging, is often to avoid or at least decrease the transfer of gases such as oxygen, carbon dioxide, and water vapor between the contents of the package and the surrounding environment. Thus, the permeabilities of the packaging material to oxygen, carbon dioxide, and water vapor should be as low as

TABLE III
Puncture Test Results of the Films of Blends of MTPS with PBAT

Sample	Thickness (μm)	Force (N)	Deformation (mm)
PBAT	155 ± 6.6 ^A	42.5 ± 3.22 ^A	17.9 ± 1.74 ^A
10 : 90	150 ± 8.4 ^{A,B}	42.1 ± 3.21 ^A	24.2 ± 1.78 ^B
20 : 80	152 ± 7.4 ^{A,B}	40.9 ± 2.93 ^A	23.5 ± 1.32 ^B
30 : 70	148 ± 10.1 ^{A,B}	38.2 ± 6.04 ^A	25.2 ± 3.09 ^B
40 : 60	151 ± 8.5 ^{A,B}	32.2 ± 1.18 ^B	24.8 ± 2.14 ^B
50 : 50	143 ± 3.9 ^B	30.3 ± 1.72 ^B	20.3 ± 2.04 ^A

Means in the same column with different superscript letters are significantly different ($p \leq 0.05$).

TABLE IV
Barrier Properties of the Films of Blends of MTPS with PBAT

Sample	Carbon dioxide permeability ($\text{kg m}^{-2} \text{s}^{-1} \text{Pa}^{-1}$) $\times 10^{16}$	Oxygen permeability ($\text{kg m}^{-2} \text{s}^{-1} \text{Pa}^{-1}$) $\times 10^{18}$	Water-vapor permeability ($\text{kg m}^{-2} \text{s}^{-1} \text{Pa}^{-1}$) $\times 10^{15}$
PBAT	3.0 ± 0.33^A	16.8 ± 1.77^A	5.0 ± 0.50^A
10 : 90	$2.5 \pm 0.10^{A,B}$	$14.5 \pm 1.27^{A,B}$	5.9 ± 0.24^A
20 : 80	$2.1 \pm 0.17^{B,C}$	$12.2 \pm 0.70^{B,C}$	6.7 ± 0.12^B
30 : 70	$1.8 \pm 0.31^{C,D}$	$10.0 \pm 1.79^{C,D}$	$8.1 \pm 1.10^{B,C}$
40 : 60	$1.3 \pm 0.10^{D,E}$	$8.0 \pm 0.67^{D,E}$	$10.4 \pm 0.74^{C,D}$
50 : 50	1.1 ± 0.12^E	6.0 ± 0.39^E	10.4 ± 0.80^D

Means in the same column with different superscript letters are significantly different ($p \leq 0.05$).

possible.²⁴ The values of the carbon dioxide, oxygen, and water-vapor permeabilities of the film samples are shown in Table IV.

One can see that when the amount of MTPS in the sample was increased, the carbon dioxide and oxygen permeability values decreased. For carbon dioxide, the permeability value decreased from $3.0 \times 10^{-16} \text{ kg m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ for PBAT to $1.1 \times 10^{-16} \text{ kg m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ for the 50 : 50 blend, although, for oxygen permeability, the values decreased from $1.68 \times 10^{-17} \text{ kg m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ for PBAT to $6.0 \times 10^{-18} \text{ kg m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ for the 50 : 50 blend. This could have been due to the fact that a second phase was added to the material, which caused the transport of the gases through the films to be hindered.

However, for water-vapor permeability, we observed that the values increased from $5.0 \times 10^{-15} \text{ kg m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ for PBAT to $1.04 \times 10^{-14} \text{ kg m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ for the 50 : 50 blend. Starch is a hygroscopic material and, thus, has a greater affinity for water than PBAT. This causes an increase in the permeability of water vapor through films with higher starch contents.

One would expect the starch films to have carbon dioxide and oxygen permeability values that were lower than the values for the 50 : 50 blends reported in this work. In fact, this was the case. Biliaderis et al.²⁵ observed carbon dioxide and oxygen permeability values of 1.60×10^{-18} and $5.46 \times 10^{-19} \text{ kg m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$, respectively, for polyol- and water-plasticized pullulan-starch blend films. Bae et al.²⁶ reported an oxygen permeability value for mungbean starch films of $9.22 \times 10^{-20} \text{ kg m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$.

One would also expect the starch films to have water-vapor permeability values that were higher than the value for the 50 : 50 blends reported in this work. This was also the case. Bae et al.²⁶ reported a water-vapor permeability value of $1.8 \times 10^{-12} \text{ kg m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ for mungbean starch films, whereas Thirathumthavorn and Charoenrein²⁷ reported a value of $3.08 \times 10^{-13} \text{ kg m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ for films of tapioca starch plasticized with sorbitol.

With regard to other polymers, Avella et al.²⁸ reported carbon dioxide and oxygen permeabilities for isotactic polypropylene of approximately $7.4 \times$

10^{-17} and $1.7 \times 10^{-17} \text{ kg m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$, respectively. These values were lower and slightly higher, respectively, compared to the permeabilities of the blends reported in this work. Also, the blends reported in this work exhibited oxygen permeability values that were higher than those reported by Frounchi and Dourbash²⁹ ($3.4 \times 10^{-19} \text{ kg m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$) for films of poly(ethylene terephthalate). Shellhammer and Krochta³⁰ reported values for the water-vapor permeability for low-density polyethylene, cellophane, and whey protein plasticized with glycerol of 3.6×10^{-16} , 8.4×10^{-14} , and $5.3 \times 10^{-13} \text{ kg m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$, respectively. In this work, the water-vapor permeability values for the MTPS/PBAT blends were lower than those of cellophane and whey protein plasticized with glycerol but higher than those of low-density polyethylene.

TEM

Images of the samples of taken with the transmission electron microscope are shown in Figure 2. PBAT was the continuous phase, whereas MTPS was the dispersed phase. One can see that with an increasing amount of MTPS in the samples, the dispersed phase became finer and more regularly spaced.

For all of the blends, the MTPS phase was dispersed and was not significantly agglomerated. This demonstrated that the extrusion process of the blending of MTPS and PBAT resulted in a well-mixed material. This was most likely due to the fact that MTPS made it more compatible with PBAT, and this resulted in a more consistent blend. This regularity will help to provide consistent properties for films produced with these materials.

CONCLUSIONS

Blends of MTPS and PBAT were produced and formed into films. Mechanical tests of the films showed that the tensile strength decreased with increasing MTPS in the samples; however, the elongation of the samples was not significantly affected by the addition of MTPS to the PBAT. Also, the puncture force decreased as the amount of MTPS in

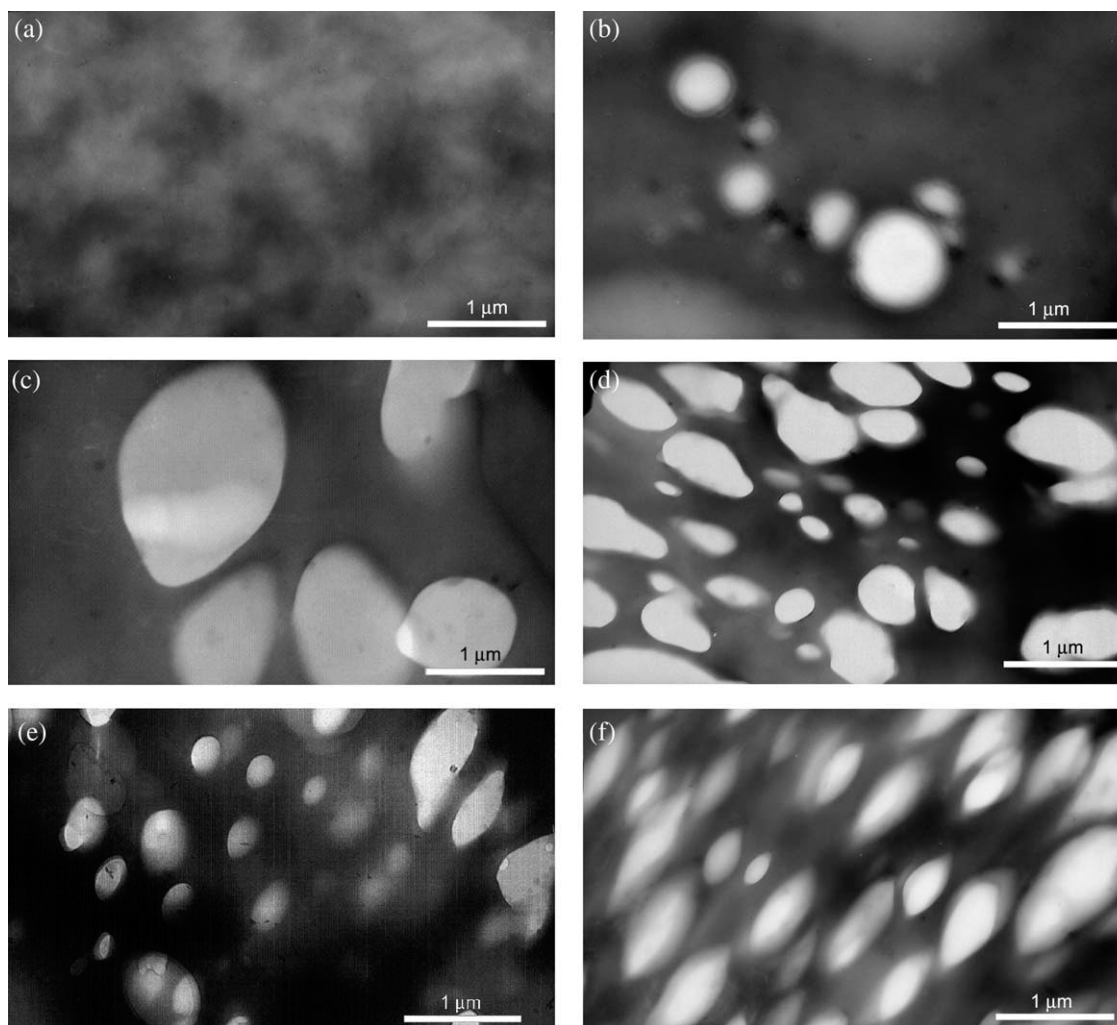


Figure 2 TEM images of the samples at 20,000 \times magnification (1- μ m scale bar): (a) PBAT, (b) MTPS:PBAT (10 : 90), (c) MTPS:PBAT (20 : 80), (d) MTPS:PBAT (30 : 70), (e) MTPS:PBAT (40 : 60), and (f) MTPS:PBAT (50 : 50).

the samples increased. As a barrier to carbon dioxide and oxygen, the addition of MTPS to PBAT improved the performance of the films. The permeability of carbon dioxide and oxygen decreased as the amount of MTPS in the materials increased. However, for water-vapor permeability, the opposite was true. With increasing MTPS in the samples, the permeability of water vapor increased because of the hygroscopic nature of starch. Images of the samples, with TEM, showed that MTPS was the dispersed phase and PBAT was the continuous phase. Also, as the amount of MTPS in the samples increased, the dispersed phase became finer and more regularly spaced. To use these materials for specific film applications, one must determine the necessary trade-off between mechanical properties and barrier properties. One should also keep in mind that when the amount of PBAT is increased in the material, the percentage biocontent decreases. To maintain the maximum amount of biocontent in the material, the minimum amount of PBAT should be used that

will still give the required material properties for the specific application.

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