

Reactive modification and compatibilization of poly(lactide) and poly(butylene adipate-co-terephthalate) blends with epoxy functionalized-poly(lactide) for blown film applications

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ABSTRACT: Biodegradable blown films comprising of poly(lactide) (PLA) and poly(butylene adipate-co-terephthalate) (PBAT) were produced using epoxy functionalized-poly(lactide) (EF-PLA) reactive modifiers for rheological enhancement and compatibilization. The epoxy groups on the EF-PLA modifiers react with PBAT forming an in situ copolymer that localizes at the blend interphase resulting in compatibilization of the polymer blend components. The EF-PLA modified polymer blends have improved melt strength and the resultant films showed better processability as seen by increased bubbled stability. This allowed for blown films with higher PLA content (70%) compared to the unmodified control films (40%). The static charge build-up typically experienced with PLA film blowing was decreased with the inclusion of EF-PLA yielding films with better slip and softness. The compatibilization effect of the EF-PLA modifiers resulted in significant improvement in mechanical properties. For example, dart test performance was up to four times higher than the control, especially at higher PLA concentrations. Therefore, the rheological enhancement and compatibilization effects of the EF-PLA reactive modifiers make them ideally suited to create high PLA content films. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43310.

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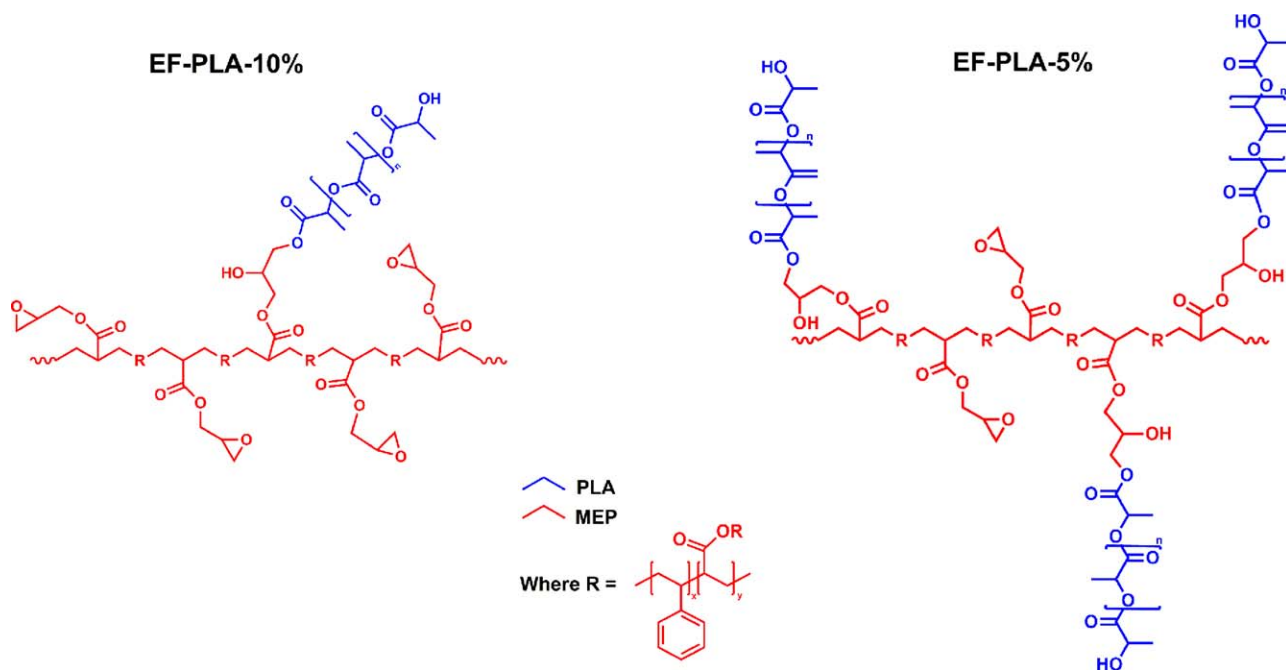
INTRODUCTION

Poly(lactide) (PLA) is a biobased and biodegradable/compostable polymer derived from corn that is continuing to find increasing applications.¹ Some of these include injection molded and thermoformed products, especially packaging, and disposable one time use products like plastic cutlery.² PLA exhibits excellent strength properties and is therefore a good candidate for applications like wrapping films, waste bag/bin liners, and carry out bags. However, PLA's weak melt strength due to its highly linear structure hinders its use in blown film applications.³ Polymers that are ideal for film blowing have high melt strength and exhibit nonlinear viscoelastic properties like strain hardening. Another inherent weakness of PLA is its ductility and toughness.⁴ Typical PLA exhibits ~3% elongation to failure, which limits its potential applications unless modified through plasticization or blending with other polymers.

Rheological Enhancement of PLA

The rheological behavior of PLA can be easily enhanced using reactive modifiers, allowing for easier production of blown films. Incorporating long chain branching and a small fraction

of high molecular weight polymer can increase the strain hardening and melt strength of PLA, respectively. Chain extension is a common method to boost the rheological properties in polyesters, where the chain extender either reacts with the polymer's carboxyl or hydroxyl groups. Reactive functional groups on these chain extenders can include isocyanate, peroxide, and epoxide groups. Isocyanates undergo the chain extension reaction readily however their toxicity greatly limits their use, especially in films, where a major application is food packaging.⁵ Peroxide chain extenders also have been shown effective at increasing the rheological properties, however their high reactivity causes gels at concentrations as low as 0.7 wt %.⁶ Multifunctional epoxy polymers (MEP) can function as rheology modifiers through reaction of the carboxyl and/or hydroxyl groups with the epoxy groups of MEP. This increases molecular weight and imparts branching leading to an improvement in properties.⁷⁻¹¹ In our previous work, high concentrations of MEP were reacted with PLA to produce epoxy functionalized-poly(lactide) (EF-PLA) reactive modifiers.¹² Controlling the reaction temperature below 200°C resulted in the epoxy's preferential reaction with the carboxyl group of PLA leading to no gel



Scheme 1. A schematic comparison of the EF-PLA reactive modifiers based on molecular weight characteristics. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

formation. We observed a significant increase in the molecular weight, melt strength, and strain hardening properties for EF-PLA modified materials, even compared to traditional MEP modified PLA processing. Therefore, modifying PLA with EF-PLA is an extremely effective and efficient method for enhancing the rheological behavior of PLA, making it more suitable for blown film applications.

Compatibilization of PLA/PBAT Blends

Melt blending PLA in an extruder with other flexible polymers is an excellent method to increase the elongation and toughness of the resulting material and is a highly economical and efficient production method. A common polymer combined with PLA in melt blending is poly(butylene adipate-co-terephthalate) (PBAT). It is also a biodegradable polymer that possesses excellent ductility, around 700%. Blends of these polymers are still biodegradable and can theoretically possess both the strength and ductility of PLA and PBAT, respectively. By incorporating PBAT into PLA, it has been observed that the ductility of the blended product is increased with increasing PBAT concentration.¹³ The addition of PBAT also decreases the rate of hydrolytic degradation, which is another issue plaguing PLA.¹⁴ However PLA and PBAT are immiscible, so the properties of the blends are highly dependent on the morphology.¹⁵ As the PBAT content in the blend is increased from 20 to 50 wt %, the blend becomes heterogeneous leading to decreased properties.¹⁶ Therefore, for manufacturing high performance PLA/PBAT blown film materials, a compatibilizer is an essential requirement.

Literature reports the use of MEP for compatibilizing PLA/PBAT blends, resulting in improved mechanical properties.^{17–19} However, very few papers report the use of these materials for blown film applications.^{6,20} As discussed earlier, EF-PLA is a highly effective rheology modifier of PLA. EF-PLA is a high

molecular weight branched PLA polymer, in which its molecular weight and reactive epoxy percentage can be tailored. It can function as an effective compatibilizer in PLA/PBAT blends because the unreacted epoxy groups on the EF-PLA can react with PBAT forming EF-PLA-g-PBAT copolymers. This copolymer localizes at the interphase and provides for compatibilization resulting in more stable and smaller dispersions of PLA in the PBAT matrix. In turn, this results in improved mechanical properties. This makes EF-PLA not only an excellent rheological modifier but also an efficient compatibilizer as well, resulting in a final product that has significantly improved processability (improved melt strength and strain hardening) and performance properties (dart strength).

Based on the discussion above, we report the use of EF-PLA as a rheology modifier and compatibilizer to produce blown films of PLA/PBAT blends with enhanced ease of processing and excellent mechanical properties compared to unmodified control films. Two different EF-PLA modifiers were used containing different MEP concentrations (5% and 10%). Physical characteristics and processing of the films are discussed with emphasis on bubble stability and texture while mechanical properties of the films were determined by tensile and dart impact testing. Molecular weight and epoxy content characterizations were used as a method of monitoring the reactivity of EF-PLA in the film blends. The morphology of the resulting films was studied and used as a comparative tool for the change in mechanical and physical properties.

EXPERIMENTAL

Materials

PLA resin pellets (Ingeo 3052D) were purchased from NatureWorks, LLC (NE, USA) with a weight average molecular weight of ~175,000 and 4% D-lactide (8% meso-lactide) content. The

MEP (Joncryl 4368C), PBAT (Ecoflex F Blend C1200), and a PBAT masterbatch containing an erucamide slip agent (Ecoflex Batch SL 1) were obtained from BASF (IL, USA). The PBAT had a weight average molecular weight of $\sim 90,000$ and the slip agent masterbatch had a 10% loading of erucamide.

Reactive Extrusion of EF-PLA

The PLA resin pellets were dried for a minimum of 6 hours at 60°C in a vacuum oven. PLA and MEP pellets were carefully weighed and physically blended to obtain mixtures containing various percentages of each (5 and 10% MEP in PLA). The physical blend was then fed into a 26 mm diameter LabTech (Thailand) co-rotating, twin screw extruder with an L/D ratio of 44:1. All samples were compounded at a throughput of ~ 6 kg/h, cooled in a water bath, and then pelletized (LZ-120, LabTech, Thailand). The screw speed was held constant at 140 rpm for all compounding, as it was shown to provide the greatest reaction in previous testing where the speed was adjusted. The temperature profile used for all compounding was:

143–154–171–177–177–177–185–185–185–185 $^{\circ}\text{C}$

The EF-PLA compounds that were created consisted of 5% (EF-PLA-5%) and 10% (EF-PLA-10%) of MEP by weight.

Production of PBAT/PLA Based Films

All resin pellets were dried a minimum of 6 hours at 60°C in a vacuum oven to remove any residual moisture. This is crucial when dealing with PLA because it can hydrolytically degrade through extrusion processes as a result of hydrolysis, backbiting, and intermolecular transesterification reactions, which can result in decreased properties.²¹ The various materials were carefully weighed to determine accurate weight percentages, which also included an additional 2% of the slip masterbatch to enhance the ease of handling after production. The films produced had PLA content ranging from 20 to 70% and for each concentration three different films were made; a control sample containing neat PLA and PBAT, and two samples modified with EF-PLA so that the total MEP content in the films was 1%. To get to 1% total MEP in the films, 20% of EF-PLA-5% and 10% of EF-PLA-10% are needed. Therefore, all modified films, regardless of PLA or PBAT content, had 1% MEP in the system. Since the reactive content is the same for all films, the differences in the film's properties are due to how the MEP is incorporated with the different EF-PLA reactive modifiers. The preweighed mixture of pellets was added to the hopper of a LabTech (Thailand) Extrusion Blown Film Line. The single extruder (Type LE20-30/C) had a 20 mm diameter with an L/D ratio of 30:1, and the attached blown film unit (LF250) had a 2-inch die diameter.

The processing parameters of films such as the Blow-up Ratio (BUR) and nip roller speed have a large effect on the resulting properties of the films and therefore all conditions were held constant. BUR is the ratio of the diameter of the blown film bubble to the diameter of the extrusion die. It can be difficult if not impossible to accurately measure the diameter of the inflated bubble, so instead it can be calculated using the width of the bubble after it has been flattened (Layflat Width) through

the nip rollers according to the equation below. The Layflat Width is half of the circumference of the bubble, therefore relating the bubble diameter to Layflat Width is done through the factor of $2/\pi = 0.637$.

$$BUR = \frac{0.637 * \text{Layflat Width}}{\text{Die Diameter}}$$

The temperature of the extruder across all heating zones and the die was held at 185°C and maintained at a consistent screw speed of 40 rpm, which resulted in a residence time of ~ 5 minutes. The nip roller speed was held constant and pulled the film at 5.3 ft/min and the bubble was blown to a consistent Layflat Width of 7.5 inches. These processing parameters resulted in an average film thickness of ~ 1 mil (25.4 μm) and a BUR of 2.4.

Mechanical Properties Characterization

Tensile Properties. The tensile properties of the films were characterized in both the machine direction (MD) and transverse direction (TD) following ASTM D882-12: Standard Test Method for Tensile Properties of Thin Plastic Sheeting.²² Films were conditioned for at least 24 hours prior to testing in a temperature and humidity controlled environment. The testing specimens were cut from the blown film using a parallel blade sample cutter with a fixed width of 1 inch. Specimens were long enough to ensure that at least 1 inch of additional material was on each side of the gage length, to prevent any slippage. The testing apparatus was an Instron 5544 (MA) testing machine using Bluehill 2 software. The ultimate strength and elongation data were determined with a grip separation rate of 20 in/min (508 mm/min) in accordance with the ASTM for films with elongations at break greater than 100%. For determination of modulus of elasticity, a grip separation rate of 1 in/min (25.4 mm/min) was used. A minimum of six specimens were tested for each orientation of the film samples. The properties recorded were max load, max stress and strain, elastic modulus, and thickness.

Dart Impact Properties. The impact resistance of the films was determined with testing following ASTM D1709-09: Standard Test Methods for Impact Resistance of Plastic Film by the Free-Falling Dart Method.²³ This test method determines the energy needed to cause a plastic film to fail 50% of the time under specified conditions by a free-falling dart. The energy needed for failure is expressed as a weight (mass) of the dart. Method A was employed for this testing utilizing the standard testing technique, the staircase method.

The blown film samples were cut and separated lengthwise so that only a single layer of film could be tested at a time. Prior to testing, the thicknesses of the films throughout the tested area were measured to ensure consistent film thicknesses. Sections of the films that did not possess uniform and consistent thickness were not subjected to testing.

Gel-Permeation Chromatography

The molecular weights characteristics of all raw and manufactured materials were determined by gel-permeation chromatography (GPC). The intensity was measured by a Refractive Index Detector (RID-10A, Shimadzu, Japan) using a combination of

columns (Waters Co., MA). Tetrahydrofuran was used as the mobile phase with a flow rate of 0.500 mL/min at 40°C. Polystyrene standards were used as a reference for molecular weight calculations.

Epoxy Content Titrations

Titration was performed to determine the remaining reactive epoxy groups present in the reactive modifiers and the films. The procedure used is outlined in ASTM D1652-11: Standard Test Method for Epoxy Content of Epoxy Resins.²⁴ In this method, the titration is done using perchloric acid solution in the presence of an excess of tetraethylammonium bromide. The combination of perchloric acid and tetraethylammonium bromide generate hydrogen bromide in situ, which with the quaternary ammonium halide rapidly opens the oxirane ring. The epoxide weight percent, E , is determined by the equation:

$$E = F \times \frac{V}{W_e}$$

where F is the perchloric acid solution reagent factor, determined through standardization with potassium hydrogen phthalate, V is the volume of the perchloric acid solution needed to reach the equivalence point, and W_e is the weight of the sample used in grams.

Differential Scanning Calorimetry

Differential Scanning Calorimetry (DSC) was used to determine any differences in thermal properties of the films created. Samples of film (~5 mg) were placed in a Tzero aluminum pan and heated from room temperature to 200°C, then cooled to -50°C, and reheated to 200°C at 10°C/min using a Discovery DSC from TA Instruments (DE).

Scanning Electron Microscopy

The morphologies of the films were studied using a JEOL 6610LV (Japan Electron Optics Laboratories, Japan) Scanning Electron Microscope (SEM). The samples were cut from the films and cryofractured using liquid nitrogen. They were mounted vertically to look at the fractured cross-section followed by coating with approximately 8 nm platinum.

RESULTS AND DISCUSSION

Blown Film Processing and Physical Characteristics

Modification with EF-PLA resulted in different physical characteristics and processability compared to the control films. EF-PLA modified films resulted in improved bubble stability, as observed by less popping and tearing of the bubble. Due to this, it was possible to blow PLA/PBAT films with higher PLA concentrations than the control films. The highest PLA concentration that could be blown for the control films was 40% PLA, whereas with EF-PLA modification a 70% PLA film was produced. The control films at these high PLA concentrations were not able to achieve the same BUR outlined in the procedure due to overstretching and tearing. The reason the bubble instability occurs for the control samples is because neat PLA possesses very weak melt strength and little to none strain hardening, both of which are critical for film blowing. By incorporating EF-PLA, PLA has higher melt strength and can strain harden which makes the film blowing more effective and efficient. The free epoxy groups on EF-PLA continue to react with

neat PLA and PBAT, thereby enhancing its ability to be blown into a film by further increasing melt strength and strain hardening. This allows EF-PLA to not only act as a rheological modifier but as a compatibilizer as well, making more stable films.

The control films were also more difficult to process because they possessed a lot of static charge. Due to the static, once the nip rollers flattened the bubble it became difficult to separate the layers, regardless of how much slip additive was in the film, resulting in a poor quality final product. The EF-PLA modified films did not possess this static charge, which resulted in a film with much better slip (i.e. the layers were easier to separate).

There were also physical differences observed between the modified and control films, most notably texture and color. The EF-PLA modified films had a much softer texture, which probably correlates with better slip. This occurs because EF-PLA acts as a compatibilizer for PLA and PBAT resulting in better dispersion. For the lower PLA content samples (20% and 30%), PLA is the dispersed phase and by decreasing the sizes of these dispersed particles, it decreases the overall rigidity of the film resulting in a softer feel. The other physical difference between the films was the color, or more correctly, transparency. Both films were white in color but the control samples were translucent while the modified films were more opaque. This is indicative of films with higher crystallinity and can also be affected by morphological differences, which will be discussed later.

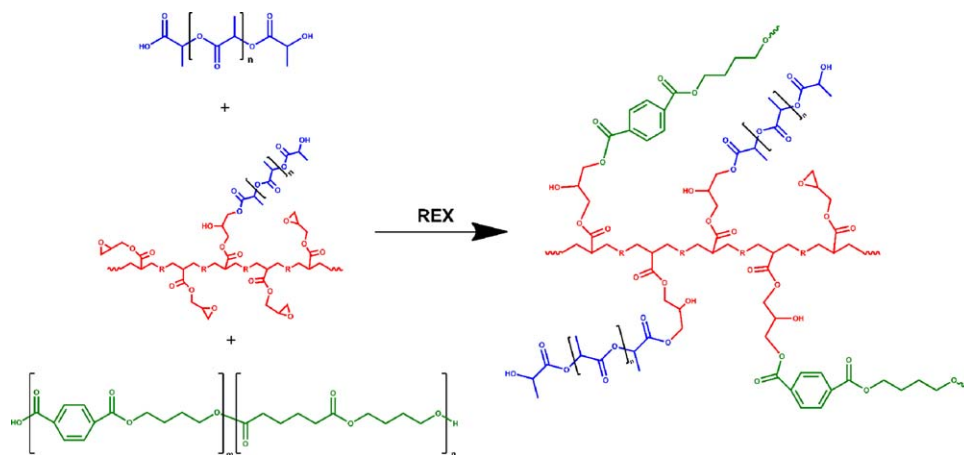
Molecular Weight Characteristics

The different EF-PLA reactive modifiers possess different starting characteristics, which should have different effects on the resulting molecular weights of the films. The molecular weight characteristics of the films produced should give insight into the property differences from the various reactive modifiers used, as well as the controls. First, we look at the neat resins and the EF-PLA reactive modifier compounds (5% and 10%).

Table I shows that the neat PLA has a higher molecular weight than neat PBAT. So as more PLA is introduced into the films, the molecular weights of the films will increase, even for the controls. EF-PLA-5% is a higher molecular weight modifier than EF-PLA-10%, however, it possesses less unreacted epoxy groups, which makes EF-PLA-10% the more reactive molecule. In comparing the molecular weights, it is clear that EF-PLA-5% on average has 2–3 PLA chains connected to one MEP molecule.¹² This results in a higher molecular weight, and more branched structure. EF-PLA-10%, however, shows molecular weight characteristics close to 1 PLA chain per MEP, yielding a

Table I. Molecular Weight Characteristics of Neat Resins and Reactive Modifiers

	$M_w (10^3)$	$M_n (10^3)$	PDI
Neat PLA	175	105	1.67
Neat PBAT	115	55	2.09
EF-PLA-5%	300	170	1.76
EF-PLA-10%	210	120	1.75



Scheme 2. The reaction of neat PLA and PBAT with EF-PLA-10% to yield a high molecular weight, branched copolymer. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

more linear structure with higher reactivity from the additional epoxy groups available (Scheme 1).

Figure 1 shows the weight average molecular weights of the films produced. As expected, when the PLA content in the films is increased, the molecular weight increases. In comparing the EF-PLA modifiers, EF-PLA-5% results in films with higher weight average molecular weights (M_w) than seen in modification with EF-PLA-10%. However, there is no significant difference observed in number average molecular weight (M_n) or polydispersity (PDI). This leads to the conclusion that the differences in M_w are due to the creation of ultra-high molecular weight species, which would have a large effect on M_w , but a small effect on M_n . EF-PLA-5% starts at a higher M_w and further reaction during film blowing results in formation of high molecular weight species resulting in the higher M_w .

The reactive epoxy groups on the EF-PLA modifiers are capable of reaction with both neat PLA and PBAT, since they are both polyesters containing carboxylic acid end groups. The resultant chemical species is a branched copolymer of PLA and PBAT, with an MEP center as shown in Scheme 2. These copolymers are created in situ and aid in compatibilization of the blends by localizing at the interphase between the two phases. This results in better dispersion as well as smaller dispersed particles.

Table II. Residual Epoxide Content in the Modified Films (\pm Standard Deviation)

Film sample	Epoxide %	% Increase over EF-PLA-5%
20% PLA (EF-PLA-5%)	0.116 \pm 0.003	-
20% PLA (EF-PLA-10%)	0.121 \pm 0.009	3.87
30% PLA (EF-PLA-5%)	0.102 \pm 0.009	-
30% PLA (EF-PLA-10%)	0.111 \pm 0.008	8.32
40% PLA (EF-PLA-5%)	0.127 \pm 0.011	-
40% PLA (EF-PLA-10%)	0.137 \pm 0.006	7.87

Epoxide Content Analysis

The molecular weight and property differences observed in the films made with reactive modifiers containing different epoxide content can be understood by reviewing the epoxide content analysis and molecular structure. EF-PLA-5% is a higher molecular weight, highly branched material with less reactivity (unreacted epoxide content of 0.30 wt %). In comparison, EF-PLA-10% is lower molecular weight, more linear structure, and higher reactivity (epoxide content of 0.95 wt %). The total MEP content in all of the films was kept at 1%, but the structure and epoxy content of the modifier used accounts for the property differences.

The reactive epoxide content (weight percent of unreacted epoxy groups in the polymer) is shown in Table II. In comparing the EF-PLA modifiers, the data clearly shows that the film samples with the EF-PLA-10% modifier have more residual unreacted epoxy groups than the films from EF-PLA-5%. EF-PLA-10% with its lower molecular weight and linear structure would be a more effective compatibilizer. EF-PLA-5% with its higher molecular weight and branched structure would be more effective as a rheology modifier.

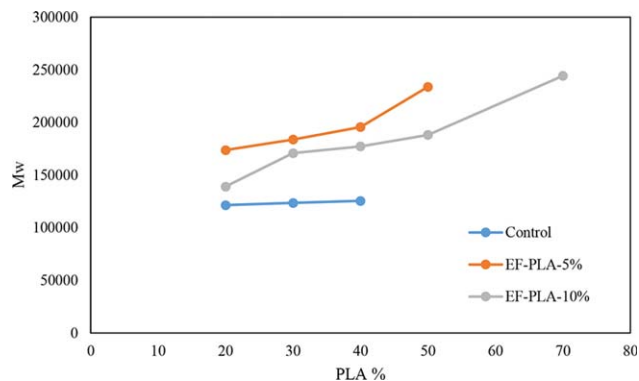


Figure 1. Weight average molecular weight as a function of reactive modifier and PLA content. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

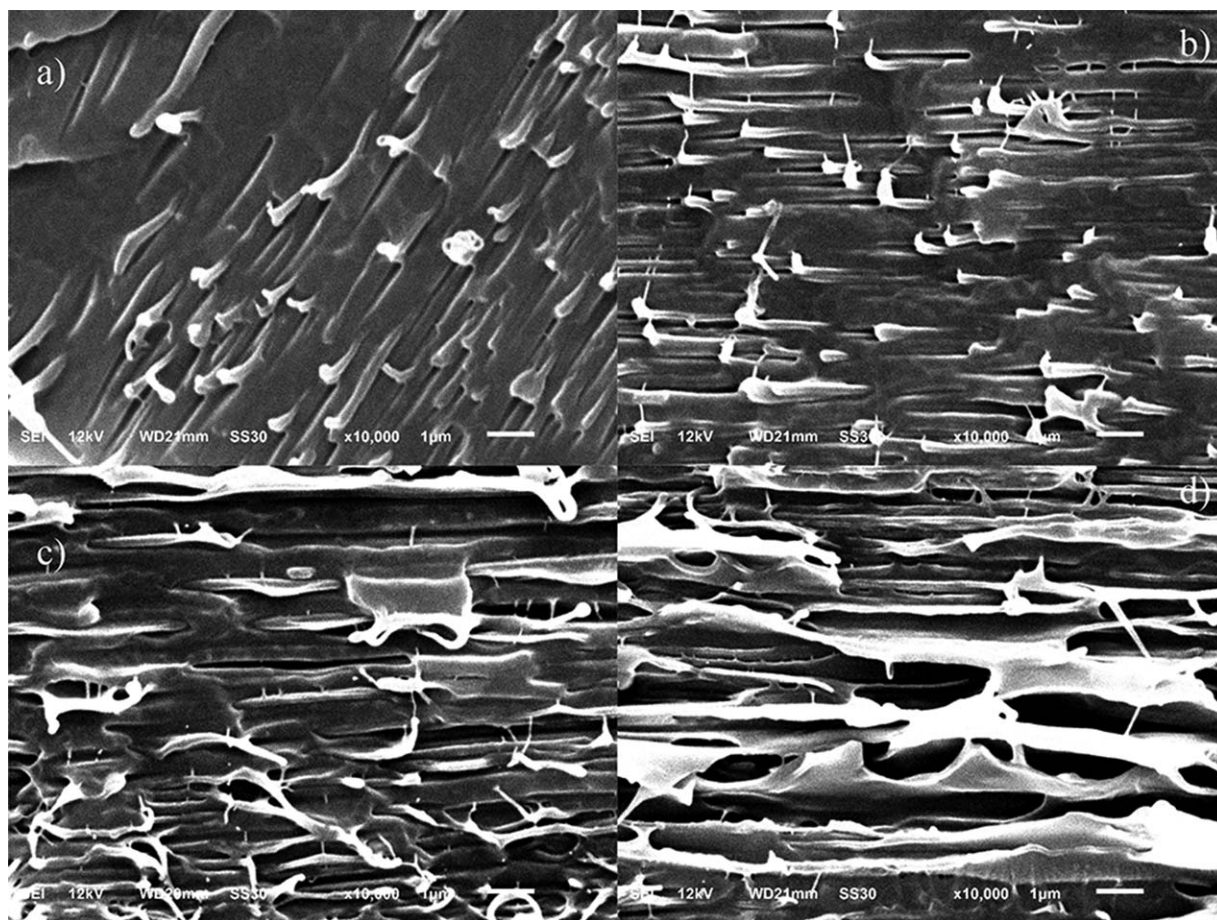


Figure 2. SEM micrographs of modified films, (a) 30% PLA with EF-PLA-10%, (b) 30% PLA control, (c) 40% PLA with EF-PLA-10%, and (d) 40% PLA control.

Morphological Comparison

The cryofractured surfaces of the films were analyzed using SEM to determine the effect of modification on the resultant morphology and to give explanation for the differences in mechanical properties. Since the TD properties best predict the overall film quality, discussed later, SEM micrographs of the TD cross-sections are shown in Figure 2. Figure 2(a,b) show the 30% PLA films modified with EF-PLA-10% and control, respectively. At this PLA concentration, PBAT is the continuous phase with PLA fibrils dispersed in it. See Figure 2(a,b) where the PLA fibrils can be seen dispersed in the dark PBAT matrix. The SEM shows that the interface for the control film, Figure 2(b), is sharply defined and separated indicating poor compatibility between the two blend components. The addition of the EF-PLA provides compatibilization of the two phases and one can see better dispersion of the PLA fibrils in the PBAT matrix in Figure 2(a). This is observed as a diffused interface in the SEM demonstrating compatibilization. Increasing the PLA content of the films to 40% results in a change in morphology for the control samples with the white PLA fibrils beginning to connect and forming the continuous phase with PBAT becoming the dispersed phase [Figure 2(d)]. This morphology change at 40% PLA in PLA/PBAT blends was also noted by Arruda *et al.*²⁰ The EF-PLA-10% modified film seen in Figure 2(c) shows smaller

and better dispersed fibrils than those in the control film. The interface is diffused showing better compatibilization. The increased compatibility from the EF-PLA results in better and more stable dispersion at this high PLA content. Indeed, the EF-PLA modified films exhibit superior dart properties of these films, discussed next, because of the morphology change to the continuous PLA matrix and incompatibility of the two phases in the control film. Therefore, EF-PLA modifiers can be used to create high PLA content films (40%) with superior mechanical properties compared to control blends.

Mechanical Properties of Films

Dart. The impact resistance of the films were tested through the free-falling dart method in which varying weights are dropped onto the samples in a consistent manner. The results are measured in the weight (in grams) of the dart required for failure 50% of the time. However, it is actually a determination of the energy required to puncture the film. Therefore, a higher failure weight results in a more impact/puncture resistant film. This resistance is a combination of the film's strength and ductility in its ability to deform and absorb the energy. Therefore, dart testing is a good measure of the overall performance of a film because it is a dynamic test that is a combination of mechanical properties.

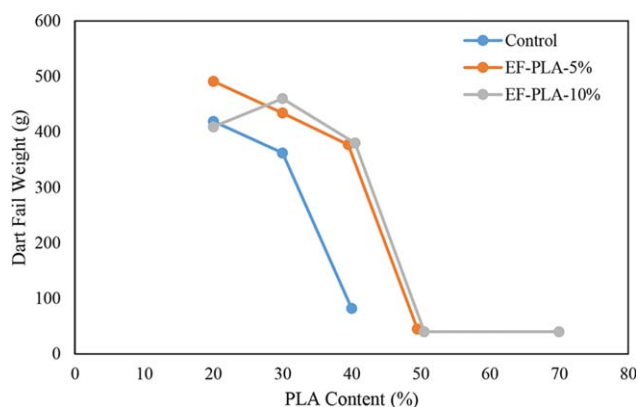


Figure 3. Dart impact performance as a function of reactive modifier and PLA content. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

EF-PLA modification resulted in an increase in dart performance. The EF-PLA modified film samples showed failure at much higher weights than the control samples at all PLA concentrations. The EF-PLA enhances the molecular weight and branching of the polymers, which increases the number of chain entanglements. This leads to more strain hardening and therefore an increase in toughness. The EF-PLA modifiers also act as

a compatibilizer between PLA and PBAT, which can increase miscibility allowing for better dispersion, increasing properties. The films modified with EF-PLA-5% showed a maximum dart weight at 20% PLA content while films with EF-PLA-10% reached a maximum at 30% PLA (Figure 3). This supports the earlier discussion that the lower molecular weight and linear structure of EF-PLA-10% provides more compatibilization compared to EF-PLA-5% modifiers, resulting in better properties for the high PLA content films. The most significant result is seen in films containing 40% PLA, where the failure weight of the EF-PLA modified films is >4 times that of the control film. At this high PLA content without compatibilization, immiscibility occurs and the two components are phase separated, as previously shown in Figure 2.

A significant decrease in the failure weight is seen once the PLA content reaches 50% for the modified films and at 40% for the controls. This sudden drop off in impact resistance can be attributed to the change in morphology of the films. At lower PLA concentrations, PLA is dispersed in the continuous PBAT matrix. The PBAT provides good flexibility to the film while the dispersed PLA imparts strength and stiffness, resulting in a film with high dart properties. The EF-PLA modification provides for better dispersion and a more stabilized morphology resulting in more improved properties. As the PLA content is

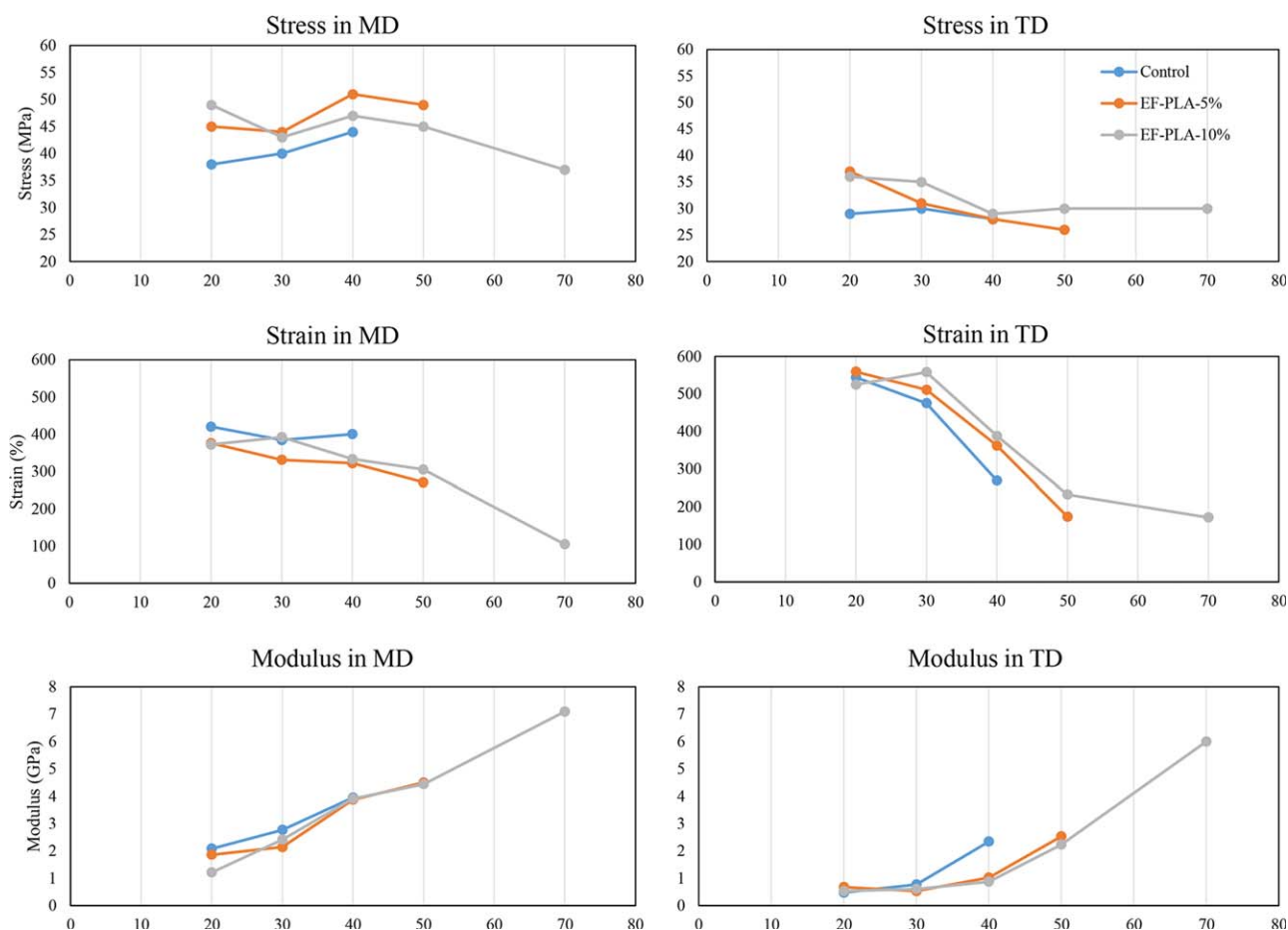


Figure 4. Tensile properties of modified and unmodified PLA/PBAT films. The x-axis on all graphs is PLA content (%). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table III. Thermal Properties of Modified and Unmodified PLA/PBAT Films

Film sample	$T_{m,PBAT}$	$X\%,_{PBAT}$	$X\%,_{PLA}$
20% PLA Control	120.63	3.8	2.6
20% PLA (EF-PLA-5%)	123.76	5.4	0.0
20% PLA (EF-PLA-10%)	123.96	6.3	0.0
30% PLA Control	110.56	2.9	5.8
30% PLA (EF-PLA-5%)	123.35	5.3	0.2
30% PLA (EF-PLA-10%)	122.29	6.1	0.2
40% PLA Control	109.26	3.4	11.0
40% PLA (EF-PLA-5%)	123.00	4.8	0.3
40% PLA (EF-PLA-10%)	122.01	5.0	0.5
50% PLA (EF-PLA-5%)	123.04	2.9	1.3
50% PLA (EF-PLA-10%)	120.52	4.2	1.5
70% PLA (EF-PLA-10%)	-	0.0	9.6

increased, a morphological change occurs resulting in a continuous PLA phase being formed. Figure 2 shows the white PLA fibrils connecting to form a continuous fibrillar matrix and phase separation from the dart PBAT matrix. The continuous PLA matrix properties dominate, and its inherent brittleness greatly detracts from the films properties, as seen by the drastic reduction in dart performance. The EF-PLA modifiers hold off this morphology change until higher PLA content allowing for significantly better dart performance than control films at 40% PLA. The EF-PLA modified films show only a 17% decrease in dart properties from 30% to 40% PLA films. In contrast, the control films with no EF-PLA added, showed a 77% decrease in dart performance.

Tensile. Film blowing involves biaxial stretching of the polymer melt, therefore the resultant films tend to be anisotropic. Because of this, the film samples were tested in both the machine direction (MD) and the transverse direction (TD). The tensile properties of the films for the most part followed the rule of mixtures, where an increase in the PLA content resulted in an increase in modulus and a decrease in ductility (Figure 4). However, the maximum stress achieved for the films did not occur at the highest PLA content, as would be expected. This maximum typically occurred around 30–40% PLA, most likely due to immiscibility issues. The tensile properties for the EF-PLA-10% films exhibited a slightly different trend than the other films. It is probable that the more unreactive EF-PLA-10% does not fully utilize its reactivity until there is 30% PLA, which is why it exhibits different local minima and maxima.

The strength of the films modified with EF-PLA was higher than that of the control films, especially in the MD. The addition of high molecular weight branched polymer chains in the sample increases the number of chain entanglements, which allows the film to withstand a higher stress prior to failure. An interesting result was observed in the fracture strain behavior. The MD fracture strain of the control films was higher than the EF-PLA modified films, while the opposite trend occurred in the TD with the modified films experiencing higher strain.

The most significant result of tensile testing was observed for the TD modulus. At 40% PLA, the TD modulus of the control film showed a dramatic increase. This was the same concentration when the dart performance significantly decreased. The TD modulus appears to show an inverse correlation with the dart performance of the films. This is also seen for the EF-PLA modified films at 50% PLA and higher. The TD moduli of these films increases at a more rapid rate and this is accompanied by the drastic decrease in dart performance. The modulus significantly increases when the PLA goes from a dispersed phase to a co-continuous phase in the blend. As PLA becomes the matrix it more greatly affects the moduli of the films, and therefore its inherent brittleness decreases the dart properties.

Thermal Properties of Films

The films were analyzed with DSC to determine any effects that EF-PLA modification had on crystallinity and crystallization behavior, and the results are shown in Table III. No significant trend was observed for T_g and T_c of PLA and PBAT in the films, however T_m and crystallinity ($X\%$) were affected by the reactive modifiers. The control films showed a lower melting temperature (T_m) than the EF-PLA modified films, potentially indicating that the crystallites in the control films were smaller.²⁵ When EF-PLA is reactively blended into the film, there is a drastic decrease in PLA crystallinity along with an increase in PBAT crystallinity. The incorporation of the high molecular weight branched PLA structure makes it difficult for PLA to crystallize, hence lower PLA crystallinity is observed. The higher PBAT crystallinity in the modified films could be due to the formation of larger crystallites rather than more crystallites, which would coincide with the increase in T_m .

Even amongst samples modified with EF-PLA there is a slight difference in the crystallinity depending on the EF-PLA modifier used. The samples created with EF-PLA-10% have slightly higher crystallinities than those created with EF-PLA-5% due to the molecular weight difference of these materials. EF-PLA-10% is lower molecular weight than EF-PLA-5% and therefore is capable of more and quicker crystallization. This trend occurs for both the crystallinity of PBAT and PLA in the films.

CONCLUSIONS

Modification of the PLA/PBAT films with EF-PLA reactive modifiers resulted in films with superior physical and mechanical properties. The rheological and compatibilization enhancement allowed for films of higher PLA content being efficiently produced without bubble instability and tearing compared to control films. No significant difference in film properties was observed for the two EF-PLA reactive modifiers, however the higher epoxy content of EF-PLA-10% resulted in improved compatibility at high PLA concentrations. An added benefit of the EF-PLA-10% modifier is that since it is more reactive, less modifier is needed making it more economical. The increase in compatibilization resulted in improved dart performance especially at higher PLA content where the control films experienced a significant decrease in properties. This was due to the change in morphology from a continuous ductile PBAT phase, to the brittle PLA phase coupled with phase incompatibility. Addition

of EF-PLA reactive modifiers provided for better and more stable dispersion of the two phases with a more diffused and compatibilized interface.

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