Epoxy functionalized poly(lactide) reactive modifier for blown film applications

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ABSTRACT: Epoxy functionalized poly(lactide) (EF-PLA) was synthesized by reacting PLA with a multifunctional epoxy polymer (MEP) using reactive extrusion processing. These polymers can function as a rheology modifier for PLA and a compatibilizer for other biopolyesters in blown film and foam applications. Model compound studies show that the epoxy functional group on the MEP reacts selectively with the carboxylic acid chain-ends of PLA at processing temperatures below 200°C. An EF-PLA containing up to 10% MEP was prepared without gel formation and reactively extruded with neat PLA to obtain three different product formulations containing MEP (0.25, 0.5, and 1.0%). These products showed significantly enhanced rheological properties compared to what has been reported by other groups and is currently used in the PLA blown film industry, the blending of MEP with PLA in a single step. These benefits are a result of how the MEP gets distributed in the material, and can lead to improved properties even at lower MEP concentrations. Our new materials showed significant strain hardening rheological behavior demonstrating that they can be readily blown into films and foams. A statistical simulation was developed to provide a fundamental understanding of the reaction as well as provide information on the molecular weight characteristics and reactivity of the EF-PLA. The EF-PLA molecule shows good potential for use as a rheology modifier and compatibilizer. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 42243.

INTRODUCTION

Poly(lactide) (PLA) is a biobased and biodegradable polyester made by ring-opening polymerization of lactide.[1] PLA has found major applications in thermoformed and molded packaging as well as disposable products. It is also used in paper coatings as a biobased and compostable alternative to polyethylene. PLA has been used in fiber applications such as clothing and textiles where its breathability and insulation outperforms traditional polyethylene terephthalate (PET) fabrics.

PLA is an excellent candidate for blown film products such as carry-out bags, wrapping films, and waste bags/bin liners. The blown film process requires polymer melts to exhibit a certain level of melt strength as well as nonlinear viscoelastic properties like strain hardening. However, PLA exhibits low melt strength and does not show strain hardening behavior. Long-chain branching or a small fraction of high-molecular-weight polymer can be introduced to neat PLA to improve these rheological properties.[2,3] Chain extenders have been widely used to improve the rheological properties of polyesters by reacting with either the carboxylic acid and/or hydroxyl end groups. For example, diisocyanates have proven to be an effective chain extender of PLA and improve its rheological properties.[4,5] However, the toxicity of isocyanates as well as the high propensity to form gels have limited its application. Epoxy-based chain extenders, like the one used in this study, can increase the molecular weight of polyesters and introduce long-chain branching.[6–12] These chain extenders can be available in both solid and liquid forms allowing for easier processing. They show low toxicity and can be introduced via reactive extrusion. The chemistry involves reaction of the carboxylic acid or the hydroxyl chain ends of PLA with its epoxy groups to form an ether or an ester linkage.[13–16] Very few studies have focused on the reactivity difference between the hydroxyl and carboxylic acid chain ends. In the need to prevent undesirable cross-linking, previous studies have "avoided" using high concentrations of chain extenders. The epoxy-based chain extender used in this study is a copolymer consisting of styrene, acrylic, and glycidyl methacrylate blocks. There are multiple poly(glycidyl methacrylate) blocks per polymer chain and these blocks contain primary epoxide rings

which make it an excellent modifier for fast processes such as reactive extrusion.

In this study, we exploit the reactivity difference between the carboxylic acid and the hydroxyl end groups of PLA to synthesize epoxy functionalized PLA (EF-PLA) molecules by reaction with a multifunctional epoxy polymer (MEP). Model compound studies helped establish the reactivity difference between the end groups, and the process parameters driving the chemistry. A series of EF-PLA compounds containing 1–10% MEP content were prepared with no gel formation. These new epoxy modified PLA polymers function not only as chain extenders but also as rheology modifiers and compatibilizers in PLA and other biodegradable polyesters to give resin formulations that have the required melt strength and strain hardening properties to be blown into films and foams. Molecular weight and rheological studies are presented to help understand and establish the improved properties and processability. A statistical simulation was created to model the properties of the EF-PLA materials at various MEP content, to support the results presented.

EXPERIMENTAL

Reagents
PLA 3051D resin pellets with a molecular weight of ∼130,000 and 8% meso-lactide content were purchased from Nature-Works, LLC (NE, USA). The MEP (Joncryl 4368F) was purchased from BASF (MI, USA). Reagent grade stearic acid and Poly(ethylene glycol) with a molecular weight of 400 were purchased from Sigma-Aldrich (MO, USA).

Compounding
The PLA resin pellets were dried overnight at 70°C prior to compounding. The MEP was powdered using a mortar and pestle to ensure differences in pellet size did not affect distribution. The PLA and MEP (1, 5, or 10 wt %) were fed into a ZSK 30 twin-screw extruder (Werner Pfleiderer, NJ, USA) with an L/D ratio of 30 using two separate gravimetric feeders. All samples were compounded at a throughput of 4.8 kg/h, cooled in a water bath, and then pelletized. After drying overnight at 70°C, the 5 wt % MEP (EF-PLA-5%) sample was used as a rheology modifier to further compound with neat PLA resin pellets and extruded again to obtain diluted specimens with 0.25, 0.5, and 1 wt % MEP. The temperature profile for all compounding was 140, 165, 170, 175, 175, and 170°C while the screw speed was kept constant at 125 rpm. The screw configuration included three major kneading zones, which were included to impart additional mechanical energy into the extrusion system helping the reaction proceed. These zones also increase the distributive mixing and the residence time of the extruder, allowing for enhanced reactive blending and additional time for the reaction to occur.

Model Compound Reaction Study
The model compound reaction kinetics were monitored by differential scanning calorimetry (DSC). Stearic acid and PEG were used as the model compounds for this reaction because they contain terminal carboxylic acid and terminal hydroxyl groups, respectively. The model compounds were premixed with powdered MEP at 1 : 1 weight ratio. Samples (∼10 mg) were

sealed in a Tzero aluminum pan and heated from room temperature to 220°C at 10°C/min in the furnace of a Q20 Differential Scanning Calorimeter (TA Instruments, DE, USA). The heat flow from the exothermic transition of the epoxide ring opening reaction was recorded.

Characterization of EF-PLA Compounds
Soxhlet extraction was performed for 72 h using dichloromethane as the solvent. The weight of dried cellulose thimbles before and after the extraction was recorded for gel content analysis. For each Soxhlet extraction experiment, at least 1 g of the compounded resin was used and each experiment was repeated twice.

The molecular weight characteristics of all the materials and final products were determined by gel permeation chromatography (GPC) (Shimadzu, Japan, RID-10A) using a combination of three columns (Waters Co., Israel). 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 the molecular weight calculations.

Complex viscosity was measured by dynamic rotational experiments using an ARES rheometer (TA Instruments, DE, USA) with a parallel-plate geometry and a plate separation of 1.05 mm. A frequency sweep was performed using a frequency range of 1–100 rad/s. When testing with frequencies lower than 1 rad/s (e.g., 0.1–100 rad/s), severe degradation of PLA was observed due to the long testing time at elevated temperature. Four temperatures (170, 180, 190, and 200°C) were used.

The extensional viscosity was also measured on the ARES rheometer equipped with an EVF fixture at 180°C.[14,17] The test specimens were compression molded into dimensions of 18 × 10 × 1 mm prior to testing. Four different Hencky strain rates (0.1, 0.5, 1.0, and 5.0 rad/s) were tested. Equation (1) was used to calculate the extensional viscosity of the PLA melt at steady strain rate:

$$\eta_E^+ = \frac{(T)}{2R\,\varepsilon_H^{\cdot}\,A_0 \left(\rho_s / \rho_m\right)^{2/3} \exp\left(-\varepsilon_H^{\cdot}(t)\right)} \qquad (1)$$

where η_E^+ is the value of tensile stress growth, $\varepsilon_H^{\cdot}$ is the applied Hencky strain rate, T is the torque, R is the drum radius, A_0 is the initial area of the sample measured in the solid state, and t is the time in seconds. The density of PLA in the solid state, ρ_s, was assumed to be 1.25 g/cm³, and the density for PLA melt at 180°C, ρ_m, was 1.115 g/cm³.[13]

RESULTS AND DISCUSSION

Model Compound Reaction Study
Previous researchers have discussed the possible reaction between PLA and epoxy-based chain extenders.[6,8,16] However, there is still some uncertainty related to the reactivity of the two major functional groups present in PLA, hydroxyl, and carboxyl groups. These previous studies have not created high MEP content samples for fear of cross-linking or gelation. It is well known that PLA has the tendency to hydrolytically degrade through extrusion processes as a result of back-biting and intermolecular transesterification reactions.[18] To counteract this, triphenylphosphine can be added to suppress/delay these
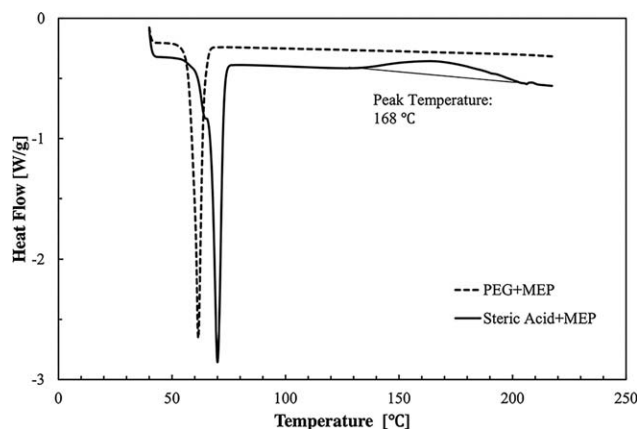
Figure 1. DSC of PEG–MEP and stearic acid–MEP mixtures.

degradation phenomena. However, the slight degradation caused by the reactive extrusion is not an issue in this study since the reaction with MEP results in a dramatic increase in molecular weight. A series of experiments was designed with two different model compounds to study the chemistry and the effect of temperature on the reaction between MEP and the functional groups of PLA. Stearic acid and low-molecular-weight PEG were used as the model compounds to represent the carboxyl and hydroxyl functional groups, respectively. The exothermic signal from the epoxide ring-opening reaction was monitored in the DSC.

In the case of stearic acid, an exothermic signal was observed which indicates that a reaction had occurred between the carboxyl group of PLA and the MEP (Figure 1). The reaction temperature was between 130 and 200°C with a peak temperature of 168°C. In contrast, no exothermic signal was seen in the spectra of PEG/MEP at these temperatures, indicating that there was no reaction between the hydroxyl functional groups and MEP in the processing temperature range of PLA, typically between T_m and 200°C. The absence of an exothermic signal with the hydroxyl model compound and a signal observed with the carboxyl model compound indicates that MEP only reacts with carboxyl functional groups under the typical processing temperatures seen with PLA. It has been reported that at higher temperatures, around 250°C, the hydroxyl end group of PLA reacts with the epoxide ring. Therefore, by staying in the correct processing range, we can ensure no gelation occurs.

The gel formation reported in previous studies is due to improper processing conditions. Either the processing temperature used was too high or the screw configuration resulted in areas of extreme high shear. These high shear zones can result in a dramatic increase in the temperature of the melt locally, which can lead to the formation of gels caused by the hydroxyl group reaction.

Synthesis and Characterization of EF-PLA
The results of the DSC model compound study indicated that only the carboxyl chain end of PLA reacts with the MEP under typical PLA processing conditions. Thus, only branched PLA structures form instead of a cross-linked network (gel), irrespective of the MEP content. Utilizing specific processing condi-

tions, materials can be made without fear of gelation. In order to verify this conclusion, two samples of EF-PLA with high MEP content (EF-PLA-5% and EF-PLA-10%) were synthesized by REX and subjected to soxhlet extraction to determine if any gel was formed. As expected, no gels were found, indicating no cross-linking during the REX process.

There are multiple epoxy groups present in each MEP, which on average has a molecular weight of 6800 g/mol and an epoxy equivalent weight of 285 g/mol. Reactive compounding with higher molecular weight PLA (∼100,000 g/mol) results in more epoxy groups present than the carboxyl groups, even at low total weight percent of MEP. If all PLA chains reacted with epoxy groups during the reactive extrusion of EF-PLA, the resulting material would still be capable of further reaction since it still possesses unreacted epoxies. This potential for further reaction makes the EF-PLA good modifier compounds.

The concentration of MEP in the reaction with PLA to make EF-PLA has a dramatic impact on the structural architecture of the polymer (Figures 2 and 3) as shown through the molecular weight and molecular weight distribution analysis. At lower concentrations of MEP, less than ∼5%, there are multiple PLA chains grafting onto one MEP molecule as shown schematically in Figure 2. This occurs because at these ratios, there are more PLA carboxylic chain ends available for grafting than MEP molecules. Therefore, on average, there will be more than one PLA chain reacting with each MEP. This is shown by the observed increase in molecular weight values (M_w and M_n) and the polydispersity index (PDI). Very interestingly, as the concentration
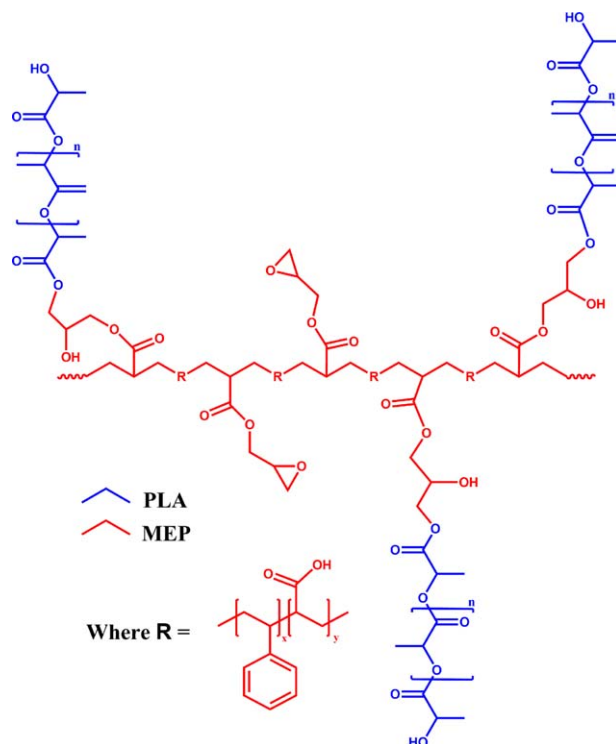

Figure 2. Molecular structure of EF-PLA modifier at low MEP concentrations. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
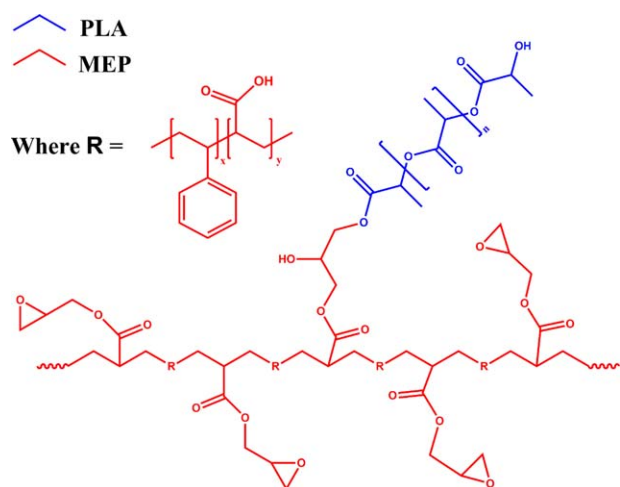
Figure 3. Molecular structure of EF-PLA modifier at high MEP concentrations. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

of MEP was increased from 5 to 10%, the molecular weight and PDI decreased (Table I). This can be explained on the basis that there are more MEP molecules than PLA chains for grafting, and therefore generate the structure in Figure 3. In this material, there is one PLA chain per MEP molecule, as opposed to structure in Figure 2 with multiple PLA chains per MEP molecule. This suggests that as the MEP concentration in the reaction with PLA in increased, the structure from Figure 3 forms with more unreacted epoxy groups available in the EF-PLA modifier, increasing its overall potential reactivity.

Synthesis of EF-PLA-Modified PLA Resins

The EF-PLA modifier formed by reactive extrusion of 5% MEP in PLA has been reactively blended with neat PLA to obtain resin formulations containing MEP concentrations of 0.25, 0.5, and 1.0 wt %. The molecular weight of these modified PLA formulations increased with increasing MEP content (1.84×10^5 to 3.61×10^5). As discussed earlier, the EF-PLA modifier has additional epoxy groups available for reaction. These react with PLA chains to give branched, high molecular weight products (Table II) with suitable rheological properties (discussed in a later section) for blown film operations.

The value of using EF-PLA as a reactive modifier in neat PLA is clearly observed when comparing samples containing 1 wt % MEP. Higher PDI and molecular weight were observed in the PLA samples modified with EF-PLA to give 1 wt % MEP ($M_w = 3.61 \times 10^5$, PDI = 2.98) compared with a sample containing 1 wt % MEP obtained by directly blending PLA with 1

Table I. Effect of MEP Content on Molecular Weight of EF-PLA

MEP [wt. %]	M_w [10^3]	M_n [10^3]	PDI
0	139	95	1.46
1.0	248	143	1.73
5.0	327	171	1.91
10.0	211	115	1.83

Table II. Molecular Weight Characteristics of EF-PLA-Modified PLA

MEP [wt. %]	M_w [10^3]	M_n [10^3]	PDI
0.25	184	77	2.39
0.5	250	102	2.45
1.0	361	121	2.98

wt % MEP ($M_w = 2.48 \times 10^5$, PDI = 1.73). With the same total amount of MEP in the samples, modification with EF-PLA utilizes the material present in a much more effective way. Rather than just mixing the MEP throughout the neat PLA, making the sample a slightly higher molecular weight as is seen in the direct blending method, modification with EF-PLA creates a portion of the sample that is highly branched with ultra high molecular weight. This is seen by the introduction of a shoulder in the GPC curves.

GPC curves of these samples and the original PLA resin used in this study are shown in Figure 4. The presence of a high molecular weight shoulder is clearly observed in the samples modified with EF-PLA. This high molecular weight fraction is clearly the result of the epoxy ring-opening reaction connecting multiple PLA chains to a single MEP. The data further indicates that the amount of the high molecular weight fraction increased as the total concentration of MEP in the sample was increased, at these low concentrations.

Rheological Properties

Branched polymers exhibit more pseudoplastic behavior than linear polymers of the same molecular weight due to their more compact structure.[19] As the MEP content in the samples increased, a more significant shear thinning behavior was observed (Figure 5) indicating that a branched structure was obtained via reaction with EF-PLA. There was a dramatic difference between the 1% MEP samples synthesized through reactive blending with EF-PLA and the sample synthesized by direct blending with 1 wt % MEP. This direct blending method is what has been done in previous studies and what is currently used for industrial processes involving PLA films. The sample
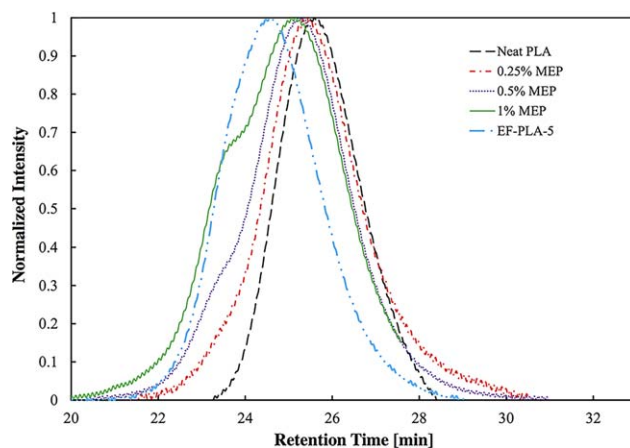

Figure 4. GPC traces of neat PLA, PLA modified with EF-PLA-5%, and EF-PLA-5%. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
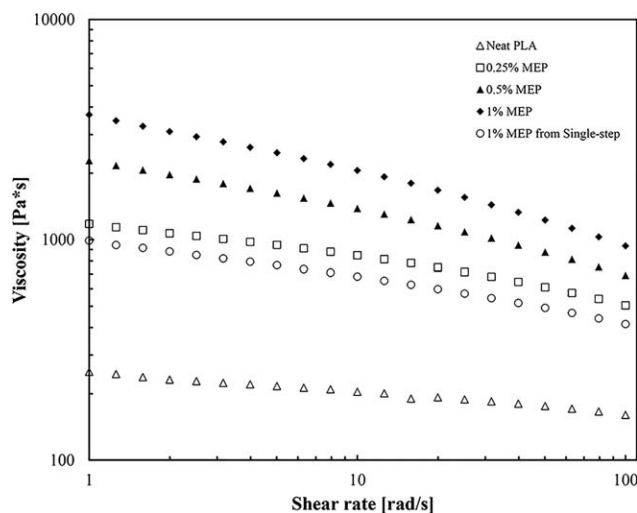
Figure 5. Comparison of complex viscosity frequency sweep at 180°C between neat PLA, PLA modified with EF-PLA-5%, and 1% MEP from direct blending.

modified with EF-PLA showed a complex viscosity ~4 times greater than direct blending with 1 wt % MEP. This is due to the distribution of the MEP in the samples made from the different processing conditions. As mentioned earlier, by modification with EF-PLA, a branched high molecular weight fraction is created in the sample, as opposed to an even distribution in the direct blending which just account for a slight increase in molecular weight evenly. This high molecular weight fraction has a much more substantial effect on the viscosity of the sample, as seen by the large increase in melt strength. Even with higher MEP content, the complex viscosity of the 1% MEP sample obtained through direct blending was lower than that of the sample containing 0.25% MEP prepared through modification with EF-PLA. Again, this shows how the distribution of MEP can show large effect on the properties. This phenomenon can be used to create either better blown films or the similar rheological properties with much less MEP.
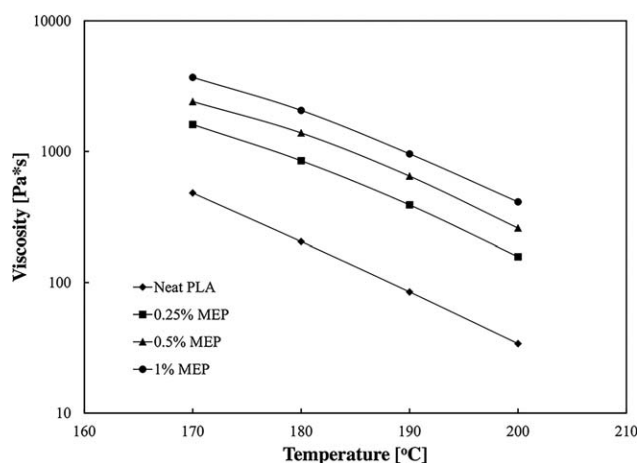

Figure 6. Complex viscosity at 10 rad/s at various temperatures for neat PLA, and EF-PLA-5% modified PLA.
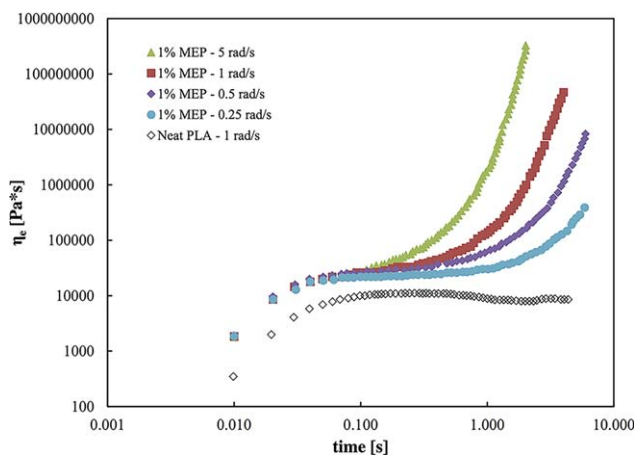

Figure 7. Comparison of extensional viscosity at 180°C between neat PLA at 1 rad/s and EF-PLA modified PLA (1% MEP) at varying strain rates. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

A complex viscosity–temperature correlation study was conducted to compare the rheological properties of the EF-PLA-modified materials. Four temperatures (170, 180, 190, and 200°C) were studied (Figure 6). A significant viscosity decrease was observed as the temperature was increased for all formulations. However, when the temperature was ~180°C, the modified PLA (1% MEP) showed a comparable complex viscosity to LDPE, which could be used as a guide for the viscosity needed for effective film blowing.

Extensional Viscosity

Extensional viscosity is an important property for polymer processing, especially for film blowing and foaming operations. The extensional viscosity of a polymer can be increased by increasing the molecular weight as well as the number of entanglements, which can be done through branching. The extensional viscosity of the EF-PLA-modified PLA products was tested at 180°C (which is a common PLA processing temperature) at varying strain rates (in rad/s). In Figure 7, the extensional viscosity of neat PLA was compared to that of the EF-PLA-modified PLA products containing 1 wt % MEP. The modified PLA exhibited over 1000 times higher extensional viscosity at the same strain rate compared with neat PLA due to an increase in melt strength and dramatic strain hardening. Also pictured is varying strain rates for the 1% MEP sample through EF-PLA modification. Note that as the strain rate is increased, the strain hardening and therefore extensional viscosity increases. It should be noted that increasing the MEP content resulted in both an increase in extensional viscosity as well as strain hardening (for the low MEP content modified samples), again resulting in rheological properties similar to that of LDPE. Strain hardening is a crucial property in film blowing and foaming operations as it impacts bubble stability and size of the foam cells.

Statistical Modeling of EF-PLA

The synthesis of EF-PLA and reactive blending with PLA can be statistically modeled to provide more fundamental understanding of the reaction and experimentally observed properties. The

model is based on random interaction and reaction of the polymer chains. The molar percentages of the components are calculated using the relative mass percentages of the components in the reactive blends and the molecular weight data of provided by the suppliers. The molecular weight data was experimentally validated using GPC. The molar % is needed to determine how PLA and MEP interact in the synthesis of EF-PLA. At a specific MEP concentration, there exist different extents to which the materials react. For example, 1 PLA chain can be grafted onto an MEP molecule, or 2 PLA chains can attach, and so on. There can also exist free/unreacted PLA and MEP depending on the relative molar ratios used. Each of these combinations of PLA and MEP has a theoretical molecular weight (e.g., the molecular weight of 2 PLA chains grafted on 1 MEP molecule = $2 \times MW_{PLA} + MW_{MEP}$). The probability of each of these species occurring at a specific MEP concentration can be calculated based on the molar % using Standard Probability Theory. Much similar to the example where there is a bag of red and blue marbles. Of the marbles, 60% are red and 40% are blue. The probability that if two marbles are picked from the bag and they are both red would be $0.60 \times 0.60 = 0.36$ or 36%. Thus, probabilities for each of the PLA/MEP species existence can be calculated, and that coupled with their theoretical molecular weights can lead to molecular weight characteristics being calculated. Weight and number average molecular weights can be calculated by determining the theoretical molecular weight and probability of each species existing using the following equations.

$$M_w = \frac{\sum p_i M_i^2}{\sum p_i M_i}$$

$$M_n = \sum p_i M_i$$

where M_i is the theoretical molecular weight of each PLA and MEP combination and p_i is the probability of its occurrence. A factor in the simulation that needed to be experimentally determined was the maximum number of PLA chains that can react with a given MEP, which is equivalent to the maximum number of epoxy groups that can react on an MEP molecule. If there were 10 active epoxy groups present on each MEP, then a small percentage of the MEP molecules would contain 10 PLA chains. This would significantly increase the theoretical weight average molecular weight of EF-PLA compared to the assumption that only 5 epoxies are active. Figure 8 shows the simulated weight average molecular weights at varying MEP mass content assuming three different number of maximum epoxy groups per MEP molecule. The experimental weight average molecular weight data obtained for EF-PLA by GPC nicely fits the curve of 5 reactive epoxy groups per MEP in the simulation model.

The following assumptions were made for the statistical simulation to operate correctly: 1) all epoxy groups have equal probability to react with PLA (Markovian behavior); 2) only the carboxyl groups of PLA react (experimentally validated using model compounds); 3) MEP does not react with MEP; 4) when [mol % PLA] > [mol % MEP], all MEP reacts (there is no free MEP left in the blend); 5) when [mol % PLA] < [mol % MEP], all PLA reacts (there is no free PLA left in the blend); and 6) a
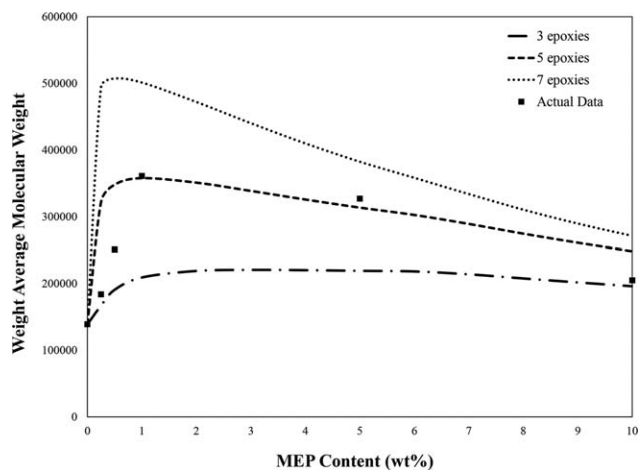

Figure 8. Comparison of actual data with simulated weight average molecular weight of PLA compounds modified with EF-PLA assuming different number of epoxy groups per MEP.

maximum of 5 epoxy groups per MEP molecule can react (validated by experimentally by measuring M_w values using GPC results). This model can be used as a tool to tailor properties of the EF-PLA modifier for specific applications.

As can be seen from Figure 8, the simulation shows good fit with the actual data except at the extreme ends, high and low MEP concentrations. This is because the model assumes that at high MEP concentrations, there is no free PLA because it has all reacted with epoxy groups (Assumption 5). Hundred percent reaction is difficult to achieve in practice and the experimental data shows that there is free PLA remaining which down the molecular weight of the sample. Conversely, the simulation shows more rapid molecular weight increase at very low MEP concentrations compared to the actual data. This is due to Assumption 4 requiring every MEP molecule to react. Assuming 100% reaction shifts the maximum molecular weight to lower MEP concentration than observed experimentally because in practice 100% reaction is not obtained.

The model can also be used to determine the percentage of unreacted epoxy groups remaining on the MEP molecules in the EF-PLA compounds. The model shows good fit between predicted unreacted epoxy content and the experimentally determined epoxy content following ASTM D1652. The epoxide weight percentage of the 5 and 10 MEP wt % EF-PLA compounds from the theoretical model were 0.33 and 0.94 epoxide wt % remaining, respectively. The experimental titration data showed unreacted epoxide wt % of 0.299 and 0.95 for the same MEP wt % samples. This is good indication that the theoretical model does a good job in determining the remaining epoxide content of the EF-PLA modifiers. Epoxy titrations were also done on the EF-PLA-modified resins containing 0.25, 0.5, and 1.0 MEP wt %. However, due to the very low amount of unreacted epoxy groups remaining, it proved difficult to get accurate values as the variance in these samples was high.

EF-PLA molecules containing higher MEP concentrations are capable of more reaction than molecules containing lower

concentrations, and could potentially be better used as compatibilizers and precursors for copolymer synthesis. Physically, this is seen as a material that has more unreacted epoxy groups present and is capable of further reaction with the carboxyl groups of PLA or other polymers. Large potential for further reactivity combined with the fact that PLA is covalently bonded to the material makes this high MEP content EF-PLA an excellent compatibilizer, in addition to the processing benefits due to rheological property modifications. The statistical model developed can be used as an excellent guide for tailoring the properties of the EF-PLA compounds for targeting specific applications as the model shows a good fit with respect to both molecular weight and epoxide content.

CONCLUSIONS

The reaction mechanism between MEP and PLA was investigated and reveals that only the carboxyl end groups of PLA react with the epoxy groups of MEP under typical PLA processing conditions (below 200°C). We have synthesized an EF-PLA rheology modifier through reactive extrusion containing a relatively high concentration of MEP (up to 10 wt %) without gel formation. Reactive blending of EF-PLA with neat PLA provided significant rheological property improvements, such as increased viscosity and strain hardening characteristics that are necessary for blown film and foam applications. These improvements cannot be achieved by directly blending the MEP polymer with PLA in a single-step blending process as has been studied by other groups and what is used in the PLA blown film industry. This is due to how the MEP is distributed through the material, which allows for EF-PLA-modified materials to exhibit much better rheological properties even at lower MEP concentrations. Films of this material were successfully blown and were capable of blow-up ratios much higher than that used for neat PLA due to the improved properties, such as melt strength and strain hardening. A statistical model was developed to simulate the molecular weight effects of PLA modified with EF-PLA as well as calculating unreacted epoxide content at varying MEP concentrations.

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