Maleation of Polylactide (PLA) by Reactive Extrusion

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ABSTRACT: Free-radical-initiated grafting of maleic anhydride (MA) onto a polylactide (PLA) backbone was performed by reactive extrusion. A concentration of 2 wt % MA in the presence of 2,5-dimethyl-2,5-di-(*tert*-butylperoxy)hexane (Lupersol 101) as the free-radical initiator was used for all experiments. Two reaction temperatures were studied (180 and 200°C) with a peroxide initiator concentration between 0.0 and 0.5 wt %. Under these conditions, between 0.066 and 0.672 wt % MA was grafted onto the PLA chains. Triple-detector size-exclusion chromatography (TriSEC), melt flow index (MFI), and thermal gravimetric analysis (TGA) were used to characterize the maleated PLA polymers. Increasing the initiator concentration resulted in an increase in the grafting of MA, as well as a decrease in the molecular weight of the polymer. The maleation of PLA proved to be very efficient in promoting strong interfacial adhesion with corn native starch in composites as obtained by melt blending. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 477–485, 1999

Key words: polylactide; free-radical branching; maleation; reactive extrusion

INTRODUCTION

Polylactide (PLA) is an important biodegradable polymer which has been used in such established applications as medical implants,[1] sutures,[2,3] and drug-delivery systems.[4] As the need for biodegradable polymers in the context of designing materials for the environment opens up new market opportunities,[5] PLA polymers are finding commercial use in single-use disposal items. Combining PLA with natural materials and synthetic polymers provides ways of cost reduction and combined properties. Unfortunately, simple PLA composites with natural materials and polyblends have poor properties because of the lack of interfacial adhesion. Introducing new functional groups onto the PLA backbone paves the way to prepare composites, laminates, coated items, and blends/alloys with improved properties and cost effectiveness. Functionalizing the matrix polymer and the fiber/filler with highly reactive groups is perhaps the most successful strategy, leading to a variety of commercial composites and alloys made by reactive processing.

Functional groups such as isocyanate, amine, anhydride, carboxylic acid, epoxide, and oxazoline are often introduced during reactive extrusion with a short residence time. Combinations of hydroxyl/isocyanate,[6] amine/anhydride,[7–9] amine/epoxide, anhydride/epoxide, amine/lactam,[10] and amine/oxazoline[11] provide practical routes for re-

Table I   Temperature Settings for Maleation

Temperature (°C)	Temperature Type	Temperature (°C)			
		Zone 1	Zone 2	Zone 3	Die
180	Set	170	170	190	160
	Melt	148	184	180	162
200	Set	170	190	210	155
	Melt	146	201	199	175

active processing. Such coupling reactions provide interfacial bondings in composites, laminates, and coated items,[12,13] and in immiscible polymer blends, they provide better control of the phase size and strong interfacial adhesion. The reactive extrusion technique has also been used to introduce a variety of functional groups onto the surface of natural polymers.[14,15]

The objective of this article was to investigate the results of the grafting of maleic anhydride (MA) onto a PLA backbone at temperatures of 180 and 200°C with an initiator concentration ranging from 0 to 0.5 wt %. The samples were titrated to determine the quantity of MA which was grafted. These maleated samples were characterized by several analytical techniques including size-exclusion chromatography, melt flow index (MFI) measurement, and thermogravimetric analysis (TGA). Scanning electron microscopy (SEM) of surface fractures was also investigated to compare the interfacial adhesion of starch blends of PLA previously maleated or not.

EXPERIMENTAL

Materials

PLA (96% L-lactide) was provided by Cargill Central Research, Minneapolis, MN. 2,5-Dimethyl-2,5-di-(*tert*-butylperoxy)hexane organic peroxide (Lupersol 101) was provided by Elf Atochem, King of Prussia, PA. MA was purchased from Aldrich Chemical Co, Bornem (Belgium). Commercial industrial corn starch having a particle size of about 10 microns was dried in a forced convection oven at 90–140°C for 20 h.

Reaction Conditions

PLA, MA, and Lupersol 101 (L101) were mixed in zip-lock plastic bags before extrusion on a Baker

Perkins corotating intermeshing twin-screw extruder. The diameter of each screw was 3 cm, and the length, 42 cm. Each screw had two sets of six mixing paddles and a camelback discharge screw at the end. The die which was used had two 3-mm-diameter holes. The temperature was measured at three points on the barrel, at the point on the die, and at four points inside the barrel (melt temperature) defining the zones 1–3 and the die (zone 4). Table I shows the zone temperatures used in the extrusion reaction. The barrel could be cooled by adjusting the flow rate of the cooling water supply which was manually controlled by four valves. The extruder shafts were composed of slip-on screws, kneading paddles, and orifice plug segments. The transversely neighboring paddles were always kept at 90° to each other, while the axially kneading paddles could take on a number of orientations depending on the amount of forwarding action desired in each mixing zone. The amount of cross-sectional area available for axial flow was controlled by the barrel valves and orifice plugs. Screw speed was set at 100 rpm with a feed rate of 5 wt %. Samples of 350 and 400 g of PLA were used for purging and collection. The percentage of L101 added is on a PLA weight basis, and 2 wt % MA (PLA basis) was chosen for this maleation study.

MFI

A Ray-Ran melt flow indexer was used to characterize melt viscosity. Material was first pelletized before analysis. ASTM standard test D-1238 was used at the conditions of 190°C and a 2.16-kg load.

Size-exclusion Chromatography

Molecular weights and molecular weight distributions were determined using triple-detector size-exclusion chromatography (TriSEC) operating in

Figure 1 Weight percent maleation as a function of initiator concentration.

THF at 25°C. The samples were dissolved in degassed THF and then filtered with a 0.45-micron filter before injection to remove undissolved contaminants which may block the system. The TriSEC system consists of (1) a Viscotek model 600 RALLS (right-angle laser light-scattering) detector, (2) a differential viscometer/refractometer, and (3) a size-exclusion chromatograph. The total injection volume was 242 μL with a flow rate of 1 mL/min. At least three injections of each sample were done. Each injection resulted in a different refractive index (n). The refractive indices for each sample were averaged and a new sample concentration was back-calculated. Molecular weight analysis was then done. The computer software used an iterative algorithm to correlate all three detector values.

Characterization of the Extent of Maleation

The extent of maleation for samples grafted with MA can be determined by titration. Since the initial percent of MA reacted is quite low (2 wt %), it can be assumed that the actual percent grafted onto the PLA backbone is very small. A direct titration of these samples would probably be inaccurate as a small discrepancy such as a contaminant could result in a large error; therefore, a back titration of the sample is necessary. A back titration consists of adding a known excess of base

and then titrating the base with acid. The base reacts with both the maleated sample and the acid. The amount of anhydride attached to the PLA backbone can then be determined.

A potentiometric titration was done using an Orion 960 Autochemistry System. A first-derivative analysis was used to determine the equivalence point of the sample. The following titration method which was used is a modified version of Johnson and Funk's[16] method: (1) remove unreacted MA by drying in a vacuum oven at 130°C for 24 h; (2) dissolve ~ 1 g of the sample (containing a maximum of 2 wt % MA) in 20 mL of THF–MeOH (5 : 1); (3) after 1 h or when the samples are completely dissolved, add 2.0 mL of morpholine solution ($0.05N$ in MeOH); (4) let mixture react for 10 min; and (5) titrate samples with $0.01N$ HCl using the autotitrator. The HCl solution was titrated against a known NaOH standard. The morpholine solution was then titrated against the HCl to get a blank reading.

The calculation for determining the quantity of grafted anhydride is as follows:

$$\% \text{ Anhydride} = (V_{\text{mor}} N_{\text{mor}} - V_{\text{HCl}} N_{\text{HCl}})$$
$$\times \frac{98.06 \text{ g/mol}}{W_{\text{sample}}} \times 100$$

Table II Maleation of PLA: MP Load %, Size-Exclusion Chromatography, and % Maleation

	PLA Samples				TriSEC				
ID No.	T (°C)	Wt % L101	MP Load %	MFI (g/10 min)	M_{peak}	M_n	M_w/M_n	IV_w	Wt % Maleation
1[a]	Pure PLA		—	12.8	134,500	121,000	1.41	1.04	—
2[b]	180	0.00	59–61	31.92	85,900	81,000	1.30	0.83	—
3	180	0.00	58–60	27.8	86,900	81,200	1.25	0.92	0.066
4	180	0.10	61–64	60.0	100,900	95,300	1.27	0.95	0.227
5	180	0.25	59–61	83.6	96,200	89,000	1.30	0.84	0.475
6	180	0.50	56–58	83.4	92,500	85,100	1.31	0.77	0.653
7	200	0.10	61–63	32.8	103,000	100,100	1.25	0.88	0.280
8	200	0.25	55–57	67.9	81,400	76,500	1.30	0.88	0.464
9	200	0.50	50–52	134.9	90,200	83,200	1.30	0.73	0.672

[a] Not extruded.
[b] No MA added to the reaction.

where V is the volume in liters; N, the normality (mol/equivalent); and W, the weight in grams.

Thermogravimetric Analysis

A thermogrametric analyzer (DuPont TGA module 951 and Hi-Res TGA 2950) was used to measure the change in weight of the sample due to decomposition. Analysis was performed at 20°C to about 20 wt % volatilization.

SEM

A scanning electron microscope (JEOL JSM-6400 SEM) was used to observe the surface

Figure 2 DV chromatogram of 180°C maleated series showing molecular weight distribution (normalized to concentration).

DV Chromatogram

Figure 3 DV chromatogram of 200°C maleated series showing molecular weight distribution (normalized to concentration).

RESULTS AND DISCUSSION

The grafting of MA onto PLA was performed in an attempt to produce functional groups which would improve the interfacial adhesion of PLA polymer blends. A concentration of 2% MA was used for all experiments.

Effect of Extrusion Temperature

Based on the free-radical branching results previously obtained,[17] the extrusion temperature was not expected to play a large role in the maleation of PLA. Two temperatures were selected (180 and 200°C) for this study with an initiator

concentration ranging from 0 to 0.5% L101. Figure 1 shows that for the same initiator concentration there is little or no difference in the grafting content of MA.

Effect of Initiator Concentration

At 180°C

With no peroxide, the addition of 2% MA has virtually no effect on the extruded PLA. M_n and M_{peak} are approximately the same as the PLA which has been extruded alone (compare entries 2 and 3 in Table II). The addition of 0.1% L101 slightly increases both M_n and M_{peak}. TriSEC chromatographs for samples extruded at 180°C are shown in Figure 2 (sample code: temperature/wt % MA/wt % L101). Further addition of L101, 0.25 and 0.5%, had a slight negative effect on the molecular weight of the samples (see entries 3–6 in Table II). This decrease in molecular weight may be due to the competition between branching (which increases as initiator concentration increases and also increases molecular weight[17]) and grafting of MA (which also in-

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morphology of PLA/starch composites fractured at room temperature. All samples were mounted on aluminum stubs and gold-coated with a sputter coater. PLA (maleated or not) was blended with starch in a Haake mixer. The mixer chamber had a volume of 300 cc and was operated at 80% capacity to ensure thorough mixing.

Figure 4   MFI of maleated samples (with 2% MA).

creases as initiator concentration increases, but results in little or no molecular weight change). Chain scission may also occur at this temperature. A proposed reaction mechanism will be discussed later. Figure 1 further shows that an increase in the free-radical initiator results in an increase in the percent of MA which is grafted (percent maleation).

At 200°C

Results similar to the 180°C series are seen at 200°C. The sample with 0.1% L101 has slightly higher M_n and M_{peak}, while the samples with 0.25 and 0.5% L101 are slightly lower (see entries 7–9 in Table II). Figure 3 is the corresponding TriSEC chromatograph of the 200°C series.

Table II also shows the reduction of MP load % at increasing amounts of peroxide. The presence of MA appears to cause the chain scission of PLA. A melt flow analysis was done at both temperatures (see Fig. 4 and Table II), indicating that the addition of increasing quantities of initiator result in higher MFIs (i.e., lower melt viscosity). The observation of increased melt viscosity in the presence of peroxide[17] and of reduced melt viscosity in the presence of both peroxide and MA is different from what is found in the modification of polyolefins. For example, in the modification of polyethylene (PE), the addition of peroxide causes branching and gelation; the presence of MA further promotes branching and gelation.[18] In the modification of polypropylene (PP), the addition of peroxide causes chain scission

Table III   Maleated Decomposition Temperatures from TGA

ID No.	Temperature (°C)	Wt % L101	Onset Value (°C)	Max Value (°C)
1	PurePLA	—	320.0	321.2
2	180	0.0	311.7	316.4
3	180	0.1	317.3	322.5
4	180	0.25	313.8	318.3
5	180	0.5	309.2	314.6
6	200	0.1	314.9	319.0
7	200	0.25	314.5	319.1
8	200	0.5	309.2	314.9

Figure 5 TGA analysis for 180°C maleated series showing decomposition temperatures.

of PP, the presence of MA causes further chain scission of the PP chain.[19]

Results of the TriSEC analysis further show that the addition of peroxide and MA does increase the chain scission of PLA. Table II also shows that the weight-average intrinsic viscosity (IV_w) of the maleated samples is between 0.73 and 0.95, whereas the IV_w for pure PLA is 1.04 (much higher). A further indication of reduced chain size, probably by chain scission, is the de-

crease in the radius of gyration for the maleated samples (Rg between 13.6 and 15.4 nm) from the pure PLA sample ($Rg = 17.85$ nm).

TGA

An increase in the decomposition temperature results in a more thermally stable product. The maleated samples have decomposition tempera-

Figure 6 SEM micrograph of 60% PLA and 40% starch blend showing poor interfacial adhesion.

Figure 7 SEM micrograph of 30% starch and 70% maleated PLA showing good interfacial adhesion.

Scheme 1

tures which range from 2 to 7°C below that of PLA (shown in Table III). This is to be expected as the maleated samples, in general, are of lower molecular weight. An exception to this is the 180°/0.1 sample which has a slightly higher decomposition temperature. This may be explained by the fact that the 180°/0.1 sample is of a higher molecular weight than that of the other samples. Figure 5 is a plot of the TGA analysis for the 180°C series. The 200°C series follows a similar trend.

PLA/Starch Blends

Only small amounts of anhydride grafted to a polymer backbone are needed to improve the interfacial adhesion in PLA blends. To verify this statement,

several experiments were carried out to compare the interfacial adhesion properties between starch and PLA, which has been previously maleated or not. Figure 6 is an SEM micrograph of a 40% starch/60% PLA blend showing poor interfacial adhesion. Figure 7 is an SEM micrograph of a 30% starch/70% maleated PLA blend. The maleated PLA consists of PLA, 2% MA, and 0.5% L101. Clearly, the interfacial adhesion has been improved substantially.

Thus, the addition of even a small amount of MA onto the PLA backbone can improve the interfacial adhesion of PLA-based blends and composites. Investigation on the resulting mechanical properties will be the topic of a forthcoming article. These blends may be incorporated into single-use biodegradable disposable items in the future.

Proposed Maleation Reaction Mechanism

The formation of a radical is the first step in the maleation of PLA. The radical formation is the same as it was for the branching of PLA.[17] Once the radical is formed, hydrogen abstraction can occur, producing a PLA which may react with the MA. Note that such an hydrogen abstraction on the PLA backbone was recently reported by Malincolino et al. in the case of radical polymerization of butyl acrylate in the presence of preformed PLA.[20] The resulting polymer radical may then combine with another radical (MA, peroxide, or polymer radicals or hydrogen) and further undergo a β-scission as shown in Scheme 1. Chain scission by either back-biting or thermohydrolysis may also occur as shown in Scheme 2.[17]

The homopolymerization of MA is considered by many to be another significant reaction when grafting MA onto polymer backbones.[21,22] Recently; however, Russell[23] discussed a thermodynamic argument based on the ceiling temperature of poly(MA) in which the formation and grafting of poly(MA) during maleation in the melt (at temperatures greater than 160°C) would not occur. Since no explicit experimental evidence was given to prove one case over the other, we must assume that there is a possibility that MA might oligomerize.[25]

CONCLUSIONS

To our best knowledge, this is the first report of the functionalization of PLA chains with MA. These initial results are very encouraging. In addition, this functionalization is performed by reactive extrusion, resulting in little degradation of the PLA

Back-biting

Thermohydrolysis

Scheme 2

backbone (i.e., M_n and M_w/M_n are relatively unchanged). It is worth mentioning that the synthesis and characterization of anhydride-functionalized poly(ε-caprolactone) was recently reported. The MA grafting was also performed by reactive extrusion using dicumylperoxide as the free-radical initiator.[25] Such maleated PLA should be of prime interest in order to promote good adhesion between inorganic fillers and PLA resins. Further applications may include PLA blends, alloys, and/or composites.

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