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Reactive functionalization of poly(lactic acid), PLA: Effects of the reactive modifier, initiator and processing conditions on the final grafted maleic anhydride content and molecular weight of PLA

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ABSTRACT

A response surface methodology (RSM) design was used to analyze the effects of maleic anhydride (MA) and 2,5-bis(*tert*-butylperoxy)-2,5-dimethyl hexane (Luperox or L101) content, and TSE screw speed on the degree of grafted MA (MA_g) and number average molecular weight (M_n) of maleated PLA (PLA-g-MA), which can be used as a reactive compatibilizer in production of PLA blends with various components. PLA-g-MA's FTIR peaks indicated that MA was grafted onto the PLA backbone and oligomeric MA was also present. A maximum of 0.52 wt% MA_g determined by titration was achieved at the expense of a 50% reduction of M_n and an increase in the polydispersity index to around 2.0. Generally, increasing L101 increased the degree of grafting and decreased M_n. L101 and MA_g had a large effect on the stability of PLA-g-MA's M_n during storage. Nominally, amounts of MA equal to 4.5 wt%, L101 between 0.45 and 0.65 wt%, and screw speed of 20 rpm provided the optimal conditions for grafting MA onto PLA.

1. Introduction

The research, development, and commercial use of poly(lactic acid) (PLA) have exponentially increased due to its unique advantages such as being produced from biobased resources, biodegradable and compostable, and recyclable [1]. Although PLA has many advantages such as transparency and good mechanical properties, some of its drawbacks such as low heat deflection temperature and fragility have led to concerted efforts from researchers to improve PLA's limitations by blending with non-biodegradable and biodegradable polymers, elastomers, and rubbers, as well as with annually renewable biodegradable materials including thermoplastic starch (TPS), reinforcement with fibers, and blending with micro and/or nano-composites [2–5]. The main challenge to enhancing PLA's desirable properties by these routes lies in increasing its compatibility and/or surface adhesion to those other materials.

Hence, production of biobased, biodegradable compatibilizers for PLA has been investigated and extensively studied using free-radical melt grafting, initiated by different peroxide initiators, of maleic anhydride (MA), the most used monomer for commercial maleated polyolefins and polystyrene (PS), by reactive extrusion or melt-solution [6,7]. MA is approved as a food grade additive. Improvement of compatibility, surface adhesion, and mechanical properties by using maleated PLA has been reported [8–10], and research continues for comprehensively understanding and improving the properties of maleated PLA. Additionally, one of the most used peroxide initiators is 2,5-bis(*tert*-butylperoxy)-2,5-dimethylhexane (Luperox 101 or L101), which is extensively used in acrylic paints and coatings, adhesives, composites, food additives and thermoplastic applications.

Among the grafting techniques, free-radical melt grafting performed during extrusion has been considered as one of the most practical and cost-effective methods [11,12] since it offers a better degree of mixing, is solvent-free, has shorter production time, and is suitable for mass production. However, by itself free radical grafting is very complex and has many concurrent side reactions that limit the degree and quality of grafting [13]. There are many

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interrelated factors involved to improve the degree of grafting, minimize side reactions, and obtain the right microstructure of grafts, including MA concentration, type and amount of peroxide initiator, processing conditions (*i.e.*, temperature, residence time, pressure), and screw/extrusion design including venting and mixing efficiency [13,14]. Furthermore, interactions and synergism between these factors are also very important. Consistent information demonstrating the effects of the maleation parameters, and especially the effects of interacting variables on maleation of PLA and its side reactions, are scarce.

Thus, the aim of this research work was to use design of experiments (DOE) response surface methodology (RSM) to obtain a statistical and mathematical model to identify the important parameters affecting grafting of MA onto PLA and provide a predictive model for the grafting. RSM is an effective and widely used statistical tool for determining the optimum conditions for a process, selecting operating conditions to fulfill specifications, or mapping a response surface over a specific region of interest [15]. In this work, RSM was used to investigate the influences of three of the main factors affecting the amount of MA in PLA (*i.e.*, MA concentration, peroxide initiator concentration, and screw speed of the twin screw extruder – TSE) and their effects on percentage of grafted MA (MA_g) onto PLA grafted MA (PLA-*g*-MA), molecular weight of PLA-*g*-MA (an indicator of the main side reaction), and molecular weight stability during storage, to set up the boundary conditions for optimizing production of PLA-*g*-MA compatibilizer.

2. Materials & methods

2.1. Materials

Ingeo™ Biopolymer 2003D poly(96% L-lactic acid), (PLA) was provided by NatureWorks LLC (Minnetonka, MN). Maleic anhydride (MA, 95%) and 2,5-bis(*tert*-butylperoxy)-2,5-dimethylhexane (Luperox 101 or L101, 90%) were obtained from Sigma–Aldrich Chemical Company, Inc. (Milwaukee, WI). All materials and/or chemical agents were used as received or as later specified.

2.2. Response surface experimental design

A uniform precision central composite design (CCD) of RSM was initially performed in this study using JMP® 10.0.0 software program SAS Institute Inc. (Cary, NC). Three factors (input variables), X_1 = MA content (weight percent, wt%, on PLA basis), X_2 = L101 content (wt% on PLA basis), and X_3 = screw speed of the twin-screw extruder (TSE) (revolutions per minute, rpm) were investigated. An initial α for rotatability of 1.6818 was used for the CCD. Factors and levels of each factor were determined from preliminary work conducted by the authors. The experimental design was initially composed of twenty experimental trials, which were six center-full factorial points, eight full factorial points, and six axial factorial points. Table 1 lists the coded and actual levels of variables. The levels of the coded variables (X_j) were defined as follows:

$$X_j = \frac{\text{Actual level} - \frac{\text{High level}+\text{Low level}}{2}}{\frac{\text{High level}+\text{Low level}}{2}} \tag{1}$$

2.3. Reactive functionalization of PLA-g-MA

PLA resins were vacuum dried at 90 °C for 6 h, premixed with mixtures of ground MA and L101, and fed into the feed throat of a 32-mm counter-rotating conical TSE having a length to diameter (L/D) ratio of 13:1 (C.W. Brabender® Instruments, Inc., South Hackensack, NJ). The barrel temperatures from the feed throat to the die were set at 165/185/185/165 °C. The two zones of the extruder were set at 185 °C as a compromise between extensive thermal degradation of PLA and half-life time ($t_{1/2}$) of L101 ($t_{1/2}$ = 69 s @ 180 °C) [17]. The screw speeds (10, 18, 25 and 30 rpm) corresponded to approximate residence times at 185 °C of 6.5 ± 0.1, 4.5 ± 0.2, 3.5 ± 0.2, and 2.3 ± 0.2 min, respectively, which were measured by a simplified carbon black residence time methodology modified from Agur, 1986 [18], to get complete decomposition of organic peroxide with no residuals [19].

Table 1
Coded levels and concentrations of MA, L101, and screw speed of the uniform precision of rotatable CCD with three factors.

Run	Pattern	Type	Coded levels			Actual levels		
			X_1, MA	X_2, L101	X_3, TSE screw speed	X_1, MA (wt%)	X_2, L101 (wt%)	X_3, Screw speed[a] (rpm)
1	−	F	−1	−1	−1	2	0.2	10
2	−++	F	−1	1	1	2	0.65	25
3	+−+	F	1	−1	1	7	0.2	25
4	++−	F	1	1	−1	7	0.65	10
5	000	C	0	0	0	4.5	0.425	18
6	000	C	0	0	0	4.5	0.425	18
7	−−+	F	−1	−1	1	2	0.2	25
8	−+−	F	−1	1	−1	2	0.65	10
9	+−−	F	1	−1	−1	7	0.2	10
10	+++	F	1	1	1	7	0.65	25
11	000	C	0	0	0	4.5	0.425	18
12	000	C	0	0	0	4.5	0.425	18
13	a00	A	−1.6818	0	0	0.296	0.425	18
14	00a	A	0	0	−1.6818	4.5	0.425	5
15	0a0	A	0	−1.6818	0	4.5	0.047	18
16	0A0	A	0	1.6818	0	4.5	0.803	18
17	A00	A	1.6818	0	0	8.704	0.425	18
18	00A	A	0	0	1.6818	4.5	0.425	30
19	000	C	0	0	0	4.5	0.425	18
20	000	C	0	0	0	4.5	0.425	18

F, C, and A types indicate representation of factorial, center, and axial factorial points, respectively. '−' and '+' indicate the lowest and highest values of the factorial terms, respectively. 'a' and 'A' indicate the lowest and highest values of the axial terms, respectively. Runs 14, 16, 17, and 20 were not used for the parameter evaluations. The statistical analysis was conducted as an incomplete CCD RSM, based on the adjustment of α, and missing information as previously explained by Akhtar and Prescott (1986) [16].

[a] The calculated actual screw speed levels of 17.5, 4.9, and 30.1 rpm were adjusted to 18, 5, and 30 rpm, respectively, to fit the actual capacity of the TSE.

The extrudates were cooled by air blowing, pelletized, and kept in an aluminum container at 23 ± 2 °C and 50 ± 10% RH until further testing. The controls (extruded PLA labeled as ePLA) were prepared from PLA resins that were processed at similar conditions without MA and L101. For example, ePLA 10R indicates neat PLA extruded at a screw speed of 10 rpm and so on. PLA-*g*-MA and ePLA resins were vacuum dried at 130 °C for 24 h to evaporate unreacted MA and also to complete cyclization (transform any diacid into the cyclic anhydride form) before characterization of the samples [20].

2.4. Characterization

Approximately, 5 g of resin was vacuum dried at 130 °C for 24 h as mentioned and fabricated into thin film using an M CARVER compression molder (Carver Laboratory Press, Menomonee Falls, Wisconsin). The dried resin was placed between poly(tetrafluoroethylene) (PTFE) sheets and preheated at 160 °C for 20 min, then molded at 680 kg for 5 min, removed from the compression molder, placed between PTFE sheets with new metal plates, double wrapped