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Real-time monitoring of radical grafting of poly(lactic acid) with itaconic anhydride in melt

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ABSTRACT

Poly(lactic acid) (PLA) was functionalized with itaconic anhydride (IAH) via radical grafting in melt initiated by 2,5-dimethyl-2,5-bis(tert-butylperoxy)hexane (L101). The main interest was the real-time monitoring of grafting reaction using oscillatory rheology which was considered as an effective tool for monitoring radical grafting. It was found that low concentration of IAH and high concentration of L101 leads to the high grafting efficiency while further increase of IAH concentration does not lead to the proportional increase of grafting degree due to predomination of β-scission. Nevertheless, high grafting efficiency is accompanied by PLA crosslinking as evidenced from both rheology data. Therefore,

2,6-di-tert-butyl-4-methylphenol (BHT) was applied at different L101/BHT molar ratio with potential to reduce the extent of crosslinking. The effect of BHT was real-time evidenced during the reaction performed by internal mixer and rotational rheometer. The kinetics of the PLA grafting/crosslinking was studied using differential scanning calorimetry (DSC) which confirmed both rheological data and the difference in kinetics parameters for radical reaction with/without BHT. Both techniques proved desired effect of BHT at L101/BHT molar ratio greater than 1/0.5 which makes BHT promising agent for better control of grafting process and suppression of undesired collateral reactions.

1. Introduction

PLA is biodegradable, thermoplastic, aliphatic polyester produced from renewable resources which seems to be potential substituent of petroleum-based polymers [1,2]. Although PLA represents promising material in the field of biodegradable polymers, some of its properties do not allow its wider applicability such as poor thermal stability or brittleness. To overcome this disadvantage, PLA can be modified in different ways, basically by ring opening polymerization (ROP) of substituted lactides or post-polymerization techniques of poly(lactic acid). Since ROP of substituted lactides requires strict reaction conditions and reaches low yields [3,4], the post-polymerization modifications of native PLA is the most promising modification technique.

In this study, PLA was functionalized with IAH via radical grafting in melt which represents cost effective and environmentally friendly post-polymerization technique. Generally, radical grafting is a sequence of reactions leading to covalent bonding of monomer units onto polymer backbone whereas the reaction mechanism was sketched in many works [5–10]. Because of the different nature of radical species generated by thermal decomposition of L101 used in our study, undesired side reactions occur simultaneously with the main reaction which results in the decrease of grafting yield and change of the polymer structure, e.g. due to β-scission, branching or crosslinking. Some of these reactions can be avoided by optimization of reaction conditions such as reaction temperature or concentration of reagents. This approaching is typical for radical grafting of polypropylene (PP) [11–13]. On the other hand, radical grafting of PLA cannot be successfully controlled by change of reaction parameters as described above. Domenichelli et al. [14] pointed out the specific reactivity of tertiary carbon of PLA backbone which may be responsible for lower number of grafted moieties compared to PP. In addition, back-biting reaction and thermos-hydrolysis occur independently on the reaction conditions due to the presence of water traces. According to this conclusion, application of specific co-agents has been suggested by several authors in order to control the incidence of secondary reactions and enhance the grafting yield.

The function of proposed co-agents is based on the rapid reaction with polymer macro-radicals generating resonance-stabilized macro-radicals that successfully prevent polymer degradation by β-scission. For example, butyl 3-(2-furyl)propenoate can be used for the

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modulation of grafting degree and molecular weight evolution during the maleic anhydride grafting of polypropylene [15,16]. Compared to that, functional nitroxides are able to modulate the insertion of unsaturated monomers as well as control of radical crosslinking through the reversible nitroxide–carbon radical coupling reaction. For example, European patent EP 0837080 describes the avoiding of crosslinking by addition of 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) during the grafting of maleic anhydride onto a thermoplastic polymer [17]. The reaction mechanism takes the advantage of the selectivity of TEMPO for radical termination with carbon-centered radicals before radical-initiated crosslinking. Moreover, the concentration of free-radicals is kept low through their trapping by TEMPO radicals which also limits secondary reactions.

The main objective of our study is to avoid crosslinking of PLA during the radical grafting of PLA with IAH. Although the high concentration of initiator gives susceptible grafting efficiency, incidence of high extent of PLA crosslinking complicates both grafting process and further processability. In addition, functional properties of crosslinked PLA as well as solubility get worse, e.g. elongation. To overcome this issue, 2,6-di-tert-butyl-4-methylphenol (BHT) as a co-agent towards better control of radical grafting of PLA with IAH. This scheme is motivated by the fact that BHT can act as a free radical scavenger suppressing radical reactions such as polymerization and crosslinking [18–20].

Except of the application of BHT for optimization of PLA grafting, oscillatory rheology and differential scanning calorimetry techniques were chosen in order to real-time control of the grafting process. This approaching can be an effective tool for more precise experimental description of radical reaction.

2. Experiments

2.1. Materials

PLA 2003D grade (NatureWorks, Minnetonka, USA) was dried in vacuum oven at 60 °C for 12 h to remove residual moisture. Itaconic anhydride (IAH; purity > 95%) was purified by recrystallization from toluene as described in patent EP 0070142 and dried under vacuum at ambient temperature. Grafting reaction was initiated by 2,5-dimethyl-2,5-bis(tert-butylperoxy)hexane (L101) purchased from Sigma-Aldrich and stored at 4 °C to prevent its decomposition. Sterically hindered phenolic antioxidant 2,6-di-tert-butyl-4-methylphenol (BHT; Sigma-Aldrich) was used in order to suppress undesired side reactions and was used without any treatment as well as other chemicals.

2.2. Reaction methodology and samples preparation

2.2.1. Radical grafting of PLA with IAH in internal mixer

Radical grafting of PLA with IAH was achieved in internal mixer at feed composition summarized in Table 1. The reaction temperature 190 °C (m. p. of PLA ~155 °C) was calculated according to Arrhenius equation including activation energy (E_a = 155.7 kJ·mol^{-1}) and pre-exponential parameter (A = 8.7·10^{15} s^{-1}) of L101 [21]. Reaction time 6 mins equals to 10 × $\tau_{1/2}$ of L101 and ensures complete decomposition of L101 after 6 mins of reaction period (see Fig. 5 in Section 3.4.1).

Table 1
Concentration of reagents applied for radical grafting of PLA with IAH in melt.

	$[L101]_0$ [wt.%]				
$[IAH]_0$ [wt.%]	0	0.1	0.5	1	2
0.5	PLA05g0	PLA05g01	PLA05g05	PLA05g1	PLA05g2
1	PLA1g0	PLA1g01	PLA1g05	PLA1g1	PLA1g2
5	PLA5g0	PLA5g01	PLA5g05	PLA5g1	PLA5g2
10	PLA10g0	PLA10g01	PLA10g05	PLA10g1	PLA10g2

Table 2
Concentration of reagents applied for radical grafting of PLA with IAH in melt in the presence of BHT.

Sample designation	$[IAH]_0$ [wt.%]	$[L101]_0$ [wt.%]	X = L101/BHT = A or B or C [mol. ratio]	Investigated reaction
PLA0g2X	0	2	A = 1/0.5; B = 1/1; C = 1/2	Crosslinking
PLA05g2X	0.5	2		Crosslinking/grafting

Grafting procedure consisted of loading desired amount of PLA into the reaction chamber and plasticization for 2 mins. As soon as PLA was melted, IAH was added and homogenized continuously for 1 min. In the case of samples with BHT, both IAH and BHT were loaded simultaneously. Finally, L101 was injected and the reaction continued for 6 mins at 60 rpm. Torque of reaction mixture was recorded during grafting reaction.

Unreacted monomer was removed by dissolving raw PLA-g-IAH in hot dichloromethane and precipitating in methanol. Powdered product was filtered and purified PLA-g-IAH was vacuum dried at 60 °C for 12 hrs.

Since an effort of grafting process is to reach high grafting efficiency, the effect of BHT was evaluated for sample PLA05g2 prepared at feed composition giving highest reaction conversion but also high extent PLA crosslinking as a collateral reaction as discussed in Sections 3.2 and 3.3. For comparison, the effect of BHT was simultaneously studied for sample PLA0g2. The concentration of BHT ($[BHT]_0$) was expressed as L101/BHT molar ratio as proposed in Table 2.

2.2.2. Real-time monitoring of radical grafting of PLA with IAH

High shear stress applied for the grafting process in internal mixer affects the melt behavior of PLA which lowers sensitivity to the detection of change of PLA structure. Therefore, the modification of PLA was also investigated in linear viscoelastic region for more precise study of grafting mechanism. For this purpose, radical grafting was real-time monitored using dynamic rheological measurement performed by controlled-stress rheometer (AR-G2, TA Instruments, USA) equipped with parallel-plate geometry (25 mm diameter, gap between upper and bottom plate 250 μm). Polymer films were prepared for measurement by dissolving PLA in dichloromethane (10% w/v) with defined amount of reagents (i.e., IAH, L101 and BHT) at ambient temperature for 24 h under stirring. Then THF was evaporated at room temperature under atmospheric pressure and prepared PLA films were dried in vacuum oven at ambient temperature for 12 hrs.

Isothermal (190 °C, 6 min) and dynamic (160–220 °C, heating rate 5 °C·min^{-1}) measurement mode was applied in order to simulate reaction conditions in internal mixer and evaluate kinetics of reaction, respectively. PLA films were used for each measurement and the oscillatory time/temperature sweep was performed at constant strain 5% and angular frequency 10 rad·s^{-1} for both modes.

2.3. Characterization methods

Change in PLA structure due to radical grafting was detected by Fourier transform infrared spectroscopy (FTIR, Bruker Tensor 27, USA) using ATR measuring mode (32 scans, resolution 4 cm^{-1}) in the wavenumber range 4000–600 cm^{-1}.

For quantitative analysis FTIR spectra of PLA films (thickness of ~100 μm) were measured in the transmittance mode in the wavenumber range 4000–400 cm^{-1} (32 scans, resolution 4 cm^{-1}).

Grafting yield was determined by acid-base titration of purified PLA-g-IAH samples. Approximately 0.2 g of purified PLA-g-IAH was dissolved under stirring in 20 mL of THF for 1 h and after complete dissolving the solution 6–8 drops of 1% thymol blue in ethanol were added. The acid-base titration was carried out with 0.005 M aqua-free

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