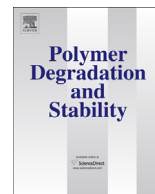




Contents lists available at ScienceDirect

Polymer Degradation and Stability

journal homepage: www.elsevier.com/locate/polydegstab

Chemical modification of lignin by phosphorus molecules to improve the fire behavior of polybutylene succinate

L. Ferry*, G. Dorez, A. Taguet, B. Otazaghine, J.M. Lopez-Cuesta

Ecole des Mines d'Alès, Centre des Matériaux des Mines d'Alès (C2MA), 6 Avenue de Clavières, F-30319 Alès Cedex, France

ARTICLE INFO

Article history:

Received 3 June 2014

Received in revised form

23 November 2014

Accepted 15 December 2014

Available online xxx

Keywords:

Lignin

Polybutylene succinate

Flame retardancy

Thermal degradation

Grafting

Phosphorus

ABSTRACT

Lignin was used as flame retardant for polybutylene succinate (PBS) biopolyester. Lignin was first demonstrated to weakly contribute to material flammability due to a high charring ability and a low heat release when burning. Alkali lignin was proved to be more interesting than organosolv lignin due to the release of sulfur dioxide during decomposition. When incorporated at a 20%wt loading in PBS, alkali lignin significantly reduces pHRR and promotes a thick charring behavior. Alkali lignin was successfully surface modified by grafting molecular or macromolecular phosphorous compounds. When blended with PBS, modified lignin was highlighted to further increase the barrier effect. Char promotion is accelerated and the resulting charred layer exhibits a higher cohesivity. Modified lignin appears as an interesting biobased flame retardant component.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

Recent years have seen the development of plastics made from renewable resources (bioplastics). These materials represent an interesting alternative to traditional polymers due to their independence towards oil and, in some cases, they offer a different end of life scenario (biodegradation). Ten years ago, bioplastics were essentially used for short life products (packaging for example). Now durable applications can be envisaged. However to penetrate some industrial sectors, a set of functional properties, like mechanical properties, ageing resistance or reaction to fire, have to be improved. Generally, functional properties of plastics are modified by using additives (antioxidant, colorant, flame retardant ...). To get a completely "green" material, these additives should be also bio-based. Until now, this domain has been only poorly studied, particularly with regard to flame retardant additives (flame retardant).

Lignin is an abundant polyphenolic compound that can be extracted from biomass (plant fibers in particular). Lignin exhibits a good thermal stability with a degradation peak temperature around 350 °C in nitrogen atmosphere. Moreover its aromatic chemical structure results in a very high char yield after

decomposition (around 40% at 900 °C) [1]. Thus, advantage could be taken from this char forming ability to use lignin as flame retardant additive [2]. Until now, a limited number of papers have been published on fire behavior of polymers containing lignin. Canetti et al. used lignin in polypropylene (PP) [2] and in polyethylene terephthalate (PET) [3]. They showed an increase in the PP thermal degradation temperature with increasing lignin content. Interactions between PP and lignin lead to a protective surface layer. In the case of PET, lignin influences the overall crystallization of the polymer due a nucleating effect. Lignin was also incorporated in polyhydroxybutyrate (PHB) by Mousavioun et al. [4] and Bertini et al. [5]. It was highlighted that soda lignin decreases the onset of degradation but brings thermal stability on a wider range of temperature. Lignin was observed to be well dispersed in PHB due to interaction between the functional groups of lignin and the carbonyl group of PHB. Song et al. [6] studied the reactive compatibilization of lignin in acrylonitrile butadiene styrene (ABS). They showed that compatibilization can further reduce the flammability of ABS due to an improved char layer.

Lignin has been also used in combination with traditional flame retardant salts. De Chirico et al. [7] used lignin in synergism with aluminum hydroxide, poly(vinyl alcohol), melamine phosphate, monoammonium phosphate and ammonium polyphosphate. They revealed that these flame retardants increase the thermal degradation temperature, the combustion time and the char yield of PP, and decrease the rate of heat release. Réti [8] has utilized lignin as

* Corresponding author.

E-mail address: laurent.ferry@mines-ales.fr (L. Ferry).

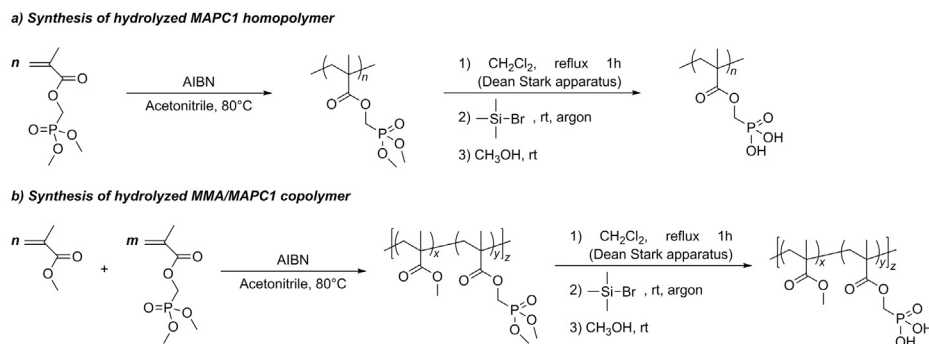


Fig. 1. Synthesis of (a) homopolymer P(MAPC1(OH)₂) and (b) copolymer P(MMA-co-MAPC1(OH)₂).

substituent of the charring source in an intumescent system for PLA. V0 UL94 rating was obtained, however the cone performance was better by using pentaerythritol or starch as charring agent. One recent paper [9] mentions the functionalization of lignin with phosphorus and nitrogen in order to improve thermal stability and flame retardancy of PP. The authors succeeded in increasing the char yield and improving the fire behavior.

In this paper, we tried to improve the fire behavior of a biopolymer, polybutylene succinate (PBS), by grafting of phosphorous compounds onto lignin, to promote a stable char during combustion. A first part is focused on the effect of unmodified lignin on the thermal and fire properties of PBS. A second part is dedicated to the fire behavior of PBS containing the functionalized lignin. Two lignins (alkali and organosolv) obtained from different extraction processes have been compared.

2. Experimental

2.1. Materials

Poly(1,4-butanediol succinate) (PBS film grade 1903 F, from Xinfu Pharm) was used as matrix. Two lignins were used in this study: an alkali lignin (Lig Alk) with a low sulfonate content (4% of sulfur), from Sigma Aldrich and an organosolv lignin (Lig Org) kindly supplied by the Centre de Mise en Forme des Matériaux (CEMEF-Mines ParisTech at Sophia Antipolis, France). Methyl methacrylate (MMA) (Sigma Aldrich, France), dimethyl(methacryloxy)methyl phosphonate (MAPC1) (Specific Polymers, France), 2,2'-azobis(2-methylpropionitrile) at 98% (AIBN) (Sigma Aldrich, France), bromotrimethylsilane (Sigma Aldrich), dihydrogen ammonium phosphate (DHAP) (Prolabo, France) were used as received.

Table 1
Content of PBS, Lig Org or Alk and treatment agent for all samples.

Designation	PBS (wt%)	Lig X ^a (wt%)	DHAP (wt%)	P(MAPC1(OH) ₂) (wt%)	P(MMA-co-MAPC1(OH) ₂) (wt%)
Lig X		100			
Lig X-DHAP		90	10		
Lig X-homoP		90		10	
Lig X- copoP		90			10
PBS-z%Lig X	100-z	z ^b			
PBS-20%Lig X-DHAP (only X = Alk)	80	18	2		
PBS-20%Lig X-homoP (only X = Alk)	80	18		2	
PBS-20%Lig X-copoP	80	18			2

^a X = Org or Alk.

^b z = 5, 10 15 wt%.

2.2. Synthesis of treatment agent

The polymers P(MAPC1(OH)₂) and P(MMA-co-MAPC1(OH)₂) were prepared by a two-step synthesis described in Fig. 1.

2.2.1. Synthesis of P(MMA-co-MAPC1(OH)₂) (75/25 mol%)

The first step consisted in a radical copolymerization of MMA and MAPC1. Into a 100 mL flask with a condenser, 21.6 g (2.16×10^{-2} mol) of MMA, 15 g (7.2×10^{-2} mol) of MAPC1, 0.47 g (2.9×10^{-3} mol) of AIBN and 22 g of acetonitrile were introduced. The mixture was then stirred and heated at 80 °C for 15 h. After reaction the polymer was purified by precipitation in diethylether.

The second step consisted in a hydrolysis of the phosphonate groups of the copolymer obtained from the first step. Into a 100 mL two-necked flask equipped with a Dean Stark apparatus, 10 g of copolymer P(MMA-co-MAPC1) (75/25 mol%) and 40 mL of dichloromethane were introduced, under inert atmosphere. The mixture was then degassed by bubbling argon for 15 min, stirred at dichloromethane reflux for 1 h (water was eliminated by the Dean Stark apparatus). The mixture was then cooled at room temperature and 6.6 g (4.3×10^{-2} mol) of bromotrimethylsilane was added dropwise. After 15 h the solvent was eliminated under vacuum and 80 mL of methanol was then added. Finally, the mixture was stirred for 3 h before precipitation of the copolymer P(MMA-co-MAPC1(OH)₂) in diethylether [10–12].

The same procedure was used to synthesize the homopolymer P(MAPC1(OH)₂).

2.3. Lignin treatment

In a one-necked round-bottom flask (500 mL) equipped with a condenser, 27 g of lignin, 3 g of treatment agent and 250 mL of

Download English Version:

<https://daneshyari.com/en/article/5201604>

Download Persian Version:

<https://daneshyari.com/article/5201604>

[Daneshyari.com](https://daneshyari.com)