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Cellulose/phosphorus combinations for sustainable fire retarded polylactide

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ABSTRACT

In the present work, sustainable flame retardant polylactide (PLA) compositions, containing cellulose–phosphorus combinations, have been studied. The effect of combining MicroCrystalline Cellulose (MCC) or NanoCrystalline Cellulose (NCC) with phosphorus, on thermal stability and flame retardant properties of PLA was investigated by thermogravimetric analysis (TGA), cone calorimeter and UL-94 tests. Phosphorus was introduced either by chemical grafting on cellulose or by coadditive melt blending by using a bio-based phosphorous agent, i.e., aluminum phytate. In both cases, the charring effect of cellulose was enhanced.

The phosphorylation process used allowed grafting 16.5 wt% of P as determined by Inductively Coupled Plasma analysis (ICP). However, this process led to the generation of water soluble cellulose and to the loss of the nanometric particle shape. For this reason, the phosphorylation of cellulose has been performed only on the microcrystalline particles. Using 20 wt% of phosphorylated MCC (MCC-P) allowed reaching V0 at UL-94 test but did not result in significant reduction of pHRR. Significant pHRR reduction was obtained only when aluminum phytate was combined with phosphorylated MCC (P-MCC). As far as NCC was concerned, the use of a phosphorylated-NCC was not required since the simple combination of aluminum phytate and NCC allowed reaching significant decrease of the pHRR actually at the level of the value found when MCC-P was used in combination with aluminum phytate. The high specific surface area of NCC proved very useful to promote the formation of a better insulating charred layer.

1. Introduction

Polymeric materials play a significant role in our daily life owing to their wide range of advantages such as versatile mechanical properties, ease of processing and recycling capability. With the growing concern on environmental impact, a great interest is devoted to find sustainable solutions for the development of new classes of polymers produced from renewable resources. Bioplastics, characterized by the presence of renewable carbon (instead of fossil carbon), are considered as "carbon sequester" polymers for technical and durable applications [1,2]. Among those polymers, poly(lactide) (PLA), initially developed for low volume biomedical applications and more recently single use short-term applications [3,4],

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represents one of the most promising biobased polymers. However, to be used in technical and durable applications, new grades with improved properties are required. The need to confer new properties to PLA in order to obtain engineering plastics is also dependent on the improvement of its thermal stability and fire performances.

Among others, halogenated flame retardant compounds have been widely used to improve fire properties of polymeric materials. Unfortunately, these products, considered as harmful agents to both the environment and human beings (toxic), are gradually forsaken to the benefit of halogen-free flame retardant additives [5–9], preferably developed from renewable resources [10–15].

On another hand, cellulose, the most abundant raw organic material in the nature, presents interesting char forming properties. Dorez et al. [16] studied the pyrolysis and combustion of natural fibers and they found out that a low content of lignin with a high content of cellulose lead to charring by affecting the degradation pathway of cellulose. Similarly, Fox et al. [17] have recently reported on the performances of cellulose materials used in its nanofibrillated form as a carbon source in intumescent flame retardant system for PLA. The introduction of 15% of ammonium polyphosphate (APP)/polyoligosilsesquioxane (POSS)-modified nanofibrillated cellulose (3:1) into PLA improved its fire behavior by reducing the peak of heat release rate (pHRR) as efficiently as the introduction of 15% of APP/pentaerythritol (PER). Moreover, when associated with other compounds that interfere with its thermal degradation mechanisms, cellulose exhibits higher char forming potential. The presence of these additional compounds gives rise to longer residence time of the volatiles generated from cellulose degradation in the condensed phase that in turn undergoes secondary reactions to form char. The lower the temperature and heating rate are, the higher the residual carbonaceous char production is [18–20]. Several publications reported on the influence of the addition of inorganic compounds on the cellulose thermal degradation mechanisms. It was shown that a significant catalytic effect resulting in a decrease of the first degradation temperature and in an increased char amount was obtained by combining cellulose and inorganic compounds [21–24]. More particularly, the use of phosphorous compounds in combination with cellulosic materials proved to be an efficient flame retardant treatment for polymers [25–28]. The improvement of fire performances lies on the capacity of treated cellulose to form carbonaceous char along the combustion step. Dobele et al. [29] reported on the impregnation of cellulose with phosphoric acid and they found out that during pyrolysis the yield of levoglucosenone, a dehydrated cyclic structure of cellulose, was dependent on the amount of phosphoric acid.

The present study aims at focusing on the evaluation of the flame retardant properties of micro-/nano-crystalline cellulosic (MCC/NCC) particles associated or not with phosphorous compound in PLA. Three different pathways were considered to combine cellulose with phosphorus keeping the bio-based characteristic of the flame retardant system: (i) an additive approach by combining untreated cellulose particles (MCC and NCC) with aluminum phytate, (ii) a reactive approach by chemical grafting of phosphorus on microcrystalline cellulose, and (iii) a combination of additive and reactive routes. The second and third approaches were considered only in the case of microcrystalline cellulose particles since the phosphorylation process used in the present study leads to the formation of highly phosphorylated but water soluble cellulose. The crystallinity of the particles and the shape of the resulting phosphorylated cellulose were thus expected to be totally different from the shape of native particles.

The combination of cellulose particles with aluminum phytate salt was motivated by its bio-based nature, and because this phosphorous compound was shown to present the most effective flame retardant effect among different metallic phytate salts in PLA [30]. Aluminum phytate (Al-Phyt) exhibited better flame retardant behavior than sodium, iron and lanthanum phytate salts owing to a synergistic effect between aluminum and phosphorus. Introduction of 20 wt% of Al-Phyt into PLA resulted in a significant improvement of fire behavior related to an effective barrier effect thanks to the fast formation of homogenous char layer at the surface of the burning sample. Cellulose nanoparticles, unmodified and modified cellulose microparticles were characterized by Fourier transform infrared spectroscopy (FTIR), ICP and thermogravimetric analysis (TGA). The effect of the incorporation of these additives and their combinations on both thermal and flammability properties of PLA was evaluated by using TGA, UL-94 vertical burning test and cone calorimetry.

2. Experimental

2.1. Materials

PLA resin (3051D) with an average molecular weight of 100,000, a dispersity of 2.1% and 4.3% of D-lactide content was purchased from NatureWorks. Microcrystalline cellulose (MCC), phosphorous acid solution $\geqslant$50%, and urea (purity > 98%) were purchased from Sigma Aldrich. Dimethyl formamide was purchased from VWR. MCC is a white, crystalline powder obtained by the partial depolymerization of cellulose with mineral acids. The degree of polymerization of MCC is typically less than 400. The particle size distribution of MCC particles was determined by using the Mastersizer 3000 (from Malvern) in ethanol (after 10 min of sonication). Results indicate a mean particle size (d_{50}) value of around 30 μm.

2.2. Nano-crystalline cellulose preparation

Nano-crystalline cellulose (NCC) was extracted from ramie fibers as described in the literature [31]. First, small pieces of ramie fibers were treated two times with a 4 wt% NaOH solution at 60 °C for 3 h for the first step, and overnight for the sec-