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Incorporation of cellulose with adsorbed phosphates into poly (lactic acid) for enhanced mechanical and flame retardant properties

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ABSTRACT

We have engineered an environmentally sustainable, biodegradable, and flame retardant poly (lactic acid) (PLA) based composite by introducing resorcinol bis (diphenyl phosphate) (RDP) coated cellulose fibers at a mass fraction of only 8%. Mechanical testing showed that formation of the composite significantly improved the impact strength, dynamic and elastic moduli, and tensile strength relative to neat PLA. The composite self-extinguished in less than 2 s and had greatly reduced dripping, hence easily passing the UL-94 V0 criteria. Fourier Transform Infrared Spectroscopy (FTIR) was used to elucidate the chemical mechanism responsible for these effects, which were interpreted in terms of a dehydration process of cellulose in the presence of RDP. This has an overall cooling effect and reduction of the combustion, which can be observed in the reduction of heat release rate (HRR) by cone calorimetry and increase in limiting oxygen index (LOI) value.

1. Introduction

Using biodegradable polymers to replace or partially replace conventional polymers has been considered as an effective way to minimize the impact of plastic products disposal on the environment. Poly (lactic acid) (PLA), which has been commercialized and produced [1–3] on a large-scale, is the most common conventional polymer substitute due to its good mechanical properties and non-microbial degradation process [4]. In order to be able to use PLA for the electronics, construction and automotive industries, as well as prototype 3D printing, and textile manufacturing, it must also meet various flame retardant standards. Neat PLA homopolymer ignites easily, supports continued combustion, and does not form a char. Hence before the polymer can be widely applicable as a substitute for non-biodegradable materials, its flame retardant properties must be improved [5].

A great deal of effort has been invested in finding appropriate fillers and formulation to render PLA flame retardant [6–20]. However, most of the fillers had high environmental persistence and harmful bioaccumulation, which contradicted to the original purpose of making “environmentally benign” polymer materials. Biodegradable “natural” polysaccharide fillers such as starch, cyclodextrin and chitin were effective in making PLA flame retardant but severely embrittled the polymer matrix [21–26], making it difficult to mold, process, and especially draw the composite into fibers required for printing. Recently, cellulose, another polysaccharide, has attracted a great deal of interest due to its abundance, renewable nature, and potential to act as the good mechanical enhancer. Numerous schemes have been reported in the literature [27–34] to obtain cellulose based PLA composites with enhanced mechanical properties. Mixing cellulose fibers with water/acetone and extruding them together with PLA resulted in a significant enhancement of the Young's modulus and tensile strength of PLA [28]. Processing the cellulose with amine and organic solvents such as acetone or toluene yielded surface functionalized cellulose nanofibrils, which were shown to increase the crystallinity and tensile strength of the polylactide system by more than 30% and 100%, respectively [31]. Several other studies have investigated the effect of cellulose surface modification on the flame retardancy of the PLA composites [35–40]. Using cellulose fibers with surface grafted by phosphorus compounds significantly

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improved the flame retardancy of PLA composites [35]. Modifying cellulose with polyoligosilsesquioxane (POSS) enabled them to act as a carbon source in an intumescent flame retardant system for PLA [39,40]. However, the organic solvents used in achieving the enhanced mechanical and flame retardant properties are highly toxic, and their introduction into the soil as the PLA matrix degrades raises additional problems regarding their safety. In addition, in order to achieve the desired flame retardancy, other flame retardant agents need to be added in conjunction with the surface modified cellulose. These flame retardant agents tend to have weak compatibility with polymer matrix, disturbing the internal entanglement structure, promoting crack propagation, and embrittling the composites.

Here we show that processing the cellulose with a single liquid flame retardant agent, resorcinol bis (diphenyl phosphate) (RDP) (Chemical formula shown in Fig. 1), provides an uncomplicated alternative method which does not degrade the mechanical properties and yet produces a composite which passes the stringent UL-94 V0 test for flame resistance. RDP has been proposed as an alternative for halogenated compounds, since it has been shown by several agencies to pose a significantly lower risk to human health and environment as summarized in a recent report by the New York Task Force on Flame Retardant Safety [41,42]. RDP is liquid at room temperature and acts as a plasticizer when mixed directly into a polymer melt. Furthermore, since its mobility is high, it is also known to bloom to the surface when a material is processed. Pack et al. [43] have found that RDP can be strongly adsorbed onto fillers with hydroxyl groups on the surface such as MMT-clay, Halloysite nanotubes and starch. When compounded together with the fillers, RDP retained its flame retardant properties, but was immobilized and no longer segregated to the surface or plasticized the compounds [23,43]. Guo et al. has shown that PLA wetted RDP coated surfaces, and successfully used RDP to disperse MMT-clay and Halloysite nanotubes in a PLA matrix [44,45]. In this study, we show that the same methodology can be used to absorb RDP onto cellulose and achieve a flame retardant PLA composite, which maintains its ductility and could be processed into filaments and other structures.

2. Experimental

2.1. Materials

Poly (lactic acid) (PLA) used in this experiment as the polymer matrix was purchased from the Natureworks LLC with a density of 1.24 g/cm^3 and molecular weight of 120,000 g/mol. Resorcinol bis(diphenyl phosphate) (RDP) utilized in this experiment as flame retardant additive was from ICL Industrial Products with its brand name Fyrolflex RDP®. Cellulose fibers (CF) used in this study were α-cellulose fibers (C8002) purchased from Sigma-Aldrich. The average length of the CF is 50 μm.

2.2. RDP coated cellulose (CF-RDP) preparation

CF and RDP (3:1 weight ratio) were poured into a 200 mL beaker on a hotplate at 70 °C. The mixture was then stirred manually with a 0.5 cm metal rod until the liquid was completely absorbed onto the cellulose fibers. After heating and blending, mixture was removed from the stirring hotplate and placed in a Thinky Conditioning Mixer for further homogenization. The speed of the mixer was set at 1000 rpm for 8 min and defoaming at 2000 rpm for 20s. The beaker containing the mixture was then placed in a vacuum oven at 70 °C for 24 h to remove moisture.

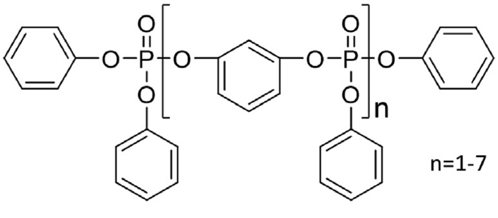

Fig. 1. The chemical formula of RDP.

2.3. Composites preparation

Samples with different composition of additives were prepared via melt blending at 180 °*C* using a C.W. BRABENDER® Plasti-Corder. The rotor speed was first set to 20 rpm for feeding materials; after the feeding, the rotor speed was set up to 100 rpm for 15 min. Then the mixtures were fed in the standard molds with standard patterns to cast the specimens which were utilized for further testing and characterization. The formulations of the composites used in this study were summarized in Table 1.

2.4. Characterization methods

2.4.1. UL94 vertical burning test

UL-94 is one of two types of pre-selection test programs conducted on plastic materials to measure flammability characteristics. The standard geometry of the specimen is 127 mm long by 12.7 mm wide by 3.2 mm thick. Those specimens were tested in accordance with ASTMD 3801 standards. In the test, a flame was applied to the sample for 10 s and removed. The time that the sample took to self-extinguish was recorded as t_1. The flame was then reapplied for 10 s and the time to self-extinguish was recorded as t_2. Furthermore, a piece of cotton was placed beneath the sample to detect if the sample generated flaming drips during burning.

2.4.2. Cone calorimetry and limiting oxygen index (LOI) test

Cone calorimetry was performed at ICL Industrial Products using a Stanton Redcroft Cone Calorimeter with the heat flux of 40 kW/m^2. The time to ignition (TTI), effective heat of combustion (EHC), peak heat release rate (PHRR) and average heat release rate (AHRR) were recorded during the test. The LOI of each sample was measured according to ASTM D 2863.

2.4.3. Thermogravimetric analysis (TGA)

Thermal stability of the composites was studied using a Mettler Toledo TGA851. A small sample piece (about 10 mg) in a crucible was heated from 40 °C to 800 °C at the rate of 20 °C/min under nitrogen flow. Weight loss profiles are analyzed for the amount or percentage of weight loss at any given temperature.

2.4.4. Scanning electron microscopy (SEM)

A JEOL JSM7600F SEM with a Schottky electron gun was conducted with CF, CF-RDP and specimens obtained after impact test. A gold layer with thickness around 10 nm was applied onto the surface of the samples to enhance electrical conductivity.

Table 1
Composition of PLA composites used in this study.

Sample	PLA (wt%)	RDP (wt%)	CF (wt%)	CF-RDP (wt%)
100PLA	100	0	0	0
98PLA2RDP	98	2	0	0
94PLA6CF	94	0	6	0
92PLA8CF-RDP	92	0	0	8