

## Engineering biodegradable polymer blends containing flame retardant-coated starch/nanoparticles

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### ABSTRACT

We have shown that the addition of resorcinol di(phenyl phosphate) (RDP)-coated starch can improve the compatibility to either Ecoflex or poly(lactic acid) (PLA). The increased compatibilization enhanced the tensile properties such as yield strength and impact toughness. In particular, we examined the effect of addition of RDP-coated starch on thermal responses of a blend of Ecoflex/PLA. We found that the combination of RDP-coated starches with nanoclays could render the blends self-extinguishing since they are formed as a shell-like chars on the exposure surface against heat, which can prevent the melt polymers against dripping. With an examination on the scanning transmission X-ray microscopy (STXM) images of the blends, the Ecoflex domains were well dispersed in the PLA matrix, while the domains became smaller when the RDP-coated starch was added. Moreover, we demonstrated that the introduction of either flat-like or tube-like clays could provide an increase of interfacial area on the RDP-coated starch surfaces, where each polymer chain preferentially segregates to either the starch or the clay surface. Thus, large complex in-situ grafts with polymers can be formed at the interfaces. Additionally, the complex in-situ grafts could influence flammability of the blends. We have shown that the addition of RDP-coated clays can decrease the mass loss rate of Ecoflex/Starch blends, while a lot of nanofiber are formed on the chars surface, which are entangled each other with the clay platelets. The mechanical properties of the chars structures were examined by nano-indentation, where a good elastic chars formation could keep the internal pressures built up with decomposed gases from melt polymers as well as ductility of the chars could play an important role on releasing the internal gases through small vents on its surface, steadily where a good elastic and ductile chars formation could require keeping the internal pressures built up with decomposed gases from melt polymers.

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### 1. Introduction

Environmental concerns are rapidly growing regarding the large amounts of waste which is accumulating. As a result, interest in biodegradable polymers has been also risen sharply both in academia and industry [1–8]. The replacement of conventional polymers with biodegradable alternatives though, poses a significant challenge since the mechanical, thermal, and electronic properties of the original material have to be reproduced. For

example, biodegradable polymers tend to absorb water more readily, are not easily compatibilized with other polymers, and the mechanical properties may be more difficult to control. To overcome those problems, biodegradable polymers have to be modified by either chemical/physical treatments on the polymers or the addition of compatibilizer. For instance, polylactic acid (PLA) is a biodegradable polymer, which can be produced by synthetic methods [3], has good mechanical properties and many potential applications as packing materials and automotives parts [4]. Although the biodegradable polymer can be applied to the commodity products, the PLA should need to be rendered flame retardant because it is highly flammable. Reti et al. demonstrated that addition of 40% flame retardant formulation (FRs) containing 30%

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**Table 1**  
Polymers were used in this study.

Polymer	MW or grade	Manufacturer
Starch	Melojel	National Starch
Ecoflex	F BX 7011	BASF
Poly(lactic acid) (PLA)	2002D	NatureWorks Co. Ltd.

ammonium polyphosphate (APP) and either 10% starch or 10% lignin in the PLA matrix could achieve the vertical flammable designation [5]. Since PLA is non-charring polymer the addition of intumescent FRs have been used to pass the stringent flammable test. Zhan et al. showed that 25% intumescent FRs containing bisphosphate diphosphoryl melamine was added in a PLA matrix [6]. Another method to achieve the self-extinguishing designation with PLA is to mix it with another biodegradable polymer, which can produce chars when heated. Starch is a good example of a thermally stable, charring polymer, where the carbonization process is known [5]. However, it is also well known that starch crystallizes easily and is difficult to blend with other materials [7,8].

Recently, researchers in NIST have studied that the addition of nanoclays resulted in the synergistic effects in producing more char formations when the Cloisite 20A was blended with the catalyst containing ammonium phosphomolybdate hydrate in poly(styrene-co-acrylonitrile) [9]. However, since the di-tallow surfactants on the clays have been considered as a toxic substance in the environmental community, an alternative surfactants have seek out in nanocomposite Pack et al. showed that montmorillonite (MMT) clays coated with resorcinol di(phenyl phosphate) (RDP) were very effective in the compatibilization of highly immiscible polymer blends [10]. Since RDP is a biodegradable compound with good thermal stability, we describe in this manuscript how it can play a role in improving the compatibility of starch with biodegradable polymers. In Ref. [11] Pack et al. also pointed out that in order to impart a polymer blend with multiple properties, such as high impact strength and good thermal response, a single nanoparticle was not sufficient to achieve the proper response. They showed that combination of nanoparticles with different surface interactions or morphologies was needed to achieve the synergy, which is necessary to simultaneously optimize multiple properties. Here we describe the use of clay tubes or platelets, coupled with starch nanoparticles, all coated with RDP surfactant, in optimizing the polymer blends of Ecoflex and PLA for both mechanical as well as flame retardant properties. To characterize the degree of the compatibility and flame retardancy, we used complementary techniques such as dynamic mechanical analysis (DMA), electron microscopy, a scanning transmission X-ray microscopy (STXM), and cone calorimetry on 1.5 mm molded

samples, and determined relationships of the structure property of chars which resulted in blends that could have a good mechanical properties.

## 2. Experimental section

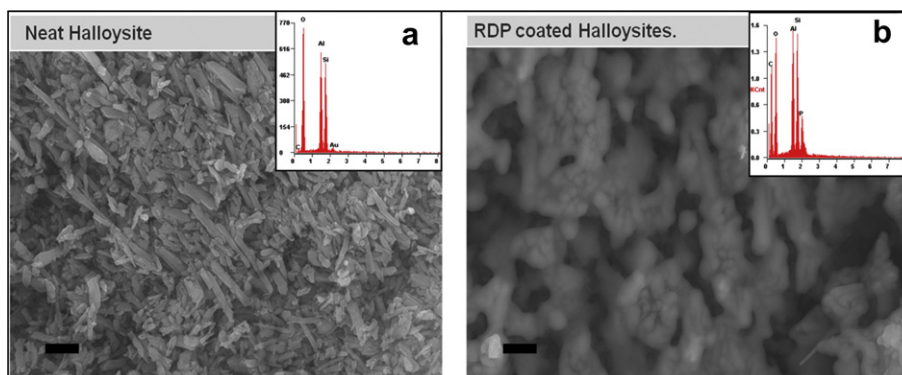
### 2.1. Materials

Halloysite nanotubes (HNTs), tubular-like clays were provided from NaturalNano, Inc. The length of the HNTs was 0.5–1  $\mu\text{m}$  and the diameter was  $\sim 500$  nm. Cloisite  $\text{Na}^+$  was provided by Southern Clay Products, INC. Three biodegradable polymers were used in this study: a corn-based starch, known as Melojel, was supplied by National Starch. A poly(lactic acid) (PLA) was a commercial grade provided by Amco Plastic Inc. Ecoflex (grade F BX 7011) A commercial grades of biodegradable polymers was an aliphatic-aromatic co-polyester, (Ecoflex, F BX 7011), provided from BASF. The properties of the biodegradable polymers using in this study are tabulated in Table 1. Resorcinol di(phenyl phosphate) (RDP) was used as an absorbent, which was provided by ICL-Supresta Inc.

### 2.2. Preparation of the RDP-coated starch, MMT clay and Halloysite nanotube

To obtain the FR-coated particles, 20 wt% of RDP was first poured into a 200 ml beaker and then the beaker was placed on a hotplate stirrer at a temperature of 80  $^{\circ}\text{C}$ . Once the viscosity of the RDP in the beaker becomes decreased to the point where it can easily be stirred manually or with a magnetic stirring bar, 80 wt% of starch, MMT clays, or Halloysite tubes were poured into the beaker while stirring mildly. The mixture was continuously stirred for an additional 15–20 min at 80  $^{\circ}\text{C}$  in order to ensure the complete absorption of the RDP into the respective particles. The beaker was inserted in a vacuum oven at 100  $^{\circ}\text{C}$  for 24 h to remove any unabsorbed liquid. The final RDP-coated particles were placed in a storage room before blending with the biodegradable polymers.

The RDP coated MMT clays were characterized with atomic force microscopy and X-ray diffraction, as described in Ref. [10], which showed a uniform coating of 2.23 nm thick forming around individual platelets. The Halloysite tubes were also thoroughly coated with RDP as shown in Fig. 1, where we show SEM images of the neat and coated nanoclay tubes. Here, as well we see a thick uniform layers forming with no exposed clay surfaces. EDAX spectroscopy inserted in the figure confirms that the composition of the coating contains phosphorous.



**Fig. 1.** SEM images and EDAX spectra: (a) Neat HNTs (b) RDP-coated HNTs (The scale bar is 1  $\mu\text{m}$ ).

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