



# Improvements in the melt and solid-state properties of poly(lactic acid), poly-3-hydroxyoctanoate and their blends through reactive modification



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## ABSTRACT

Poly(3-hydroxyoctanoate) (PHO), poly(lactic acid) (PLA) and PHO/PLA blends were reactively modified in the melt state, using dicumyl peroxide (DCP) and triallyl trimellate (TAM) trifunctional coagent. The viscosity and elasticity of PHO and PLA increased substantially following reactive modification. The processability of the partially cross-linked PHO was improved, whereas coagent-modified PLA displayed strain hardening and enhanced crystallization. Reactive compounding of PLA and PHO in the presence of DCP and TAM resulted in blends with enhanced strain hardening, indicative of high melt strength, and improved crystallinity compared to the unreacted blend. Furthermore these blends had a finer morphology, which was attributed to a compatibilizing effect possibly arising from copolymer formation at the interface. The elongation at break and impact properties of the blends were improved compared to the neat PLA, while the heat deflection temperature remained unaffected.

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## 1. Introduction

Among the key challenges to more wide-spread acceptance of biopolyesters, such as poly(lactic acid) (PLA) and poly-3-hydroxyalkanoates (PHA), in engineering applications are their high production costs, often brittle nature, slow crystallization rates and low melt strength, which restrict their processability under common polymer processing operations. The advantages and drawbacks of PLA and PHAs, as well as the current state-of-the-art of various modification methods that have been employed to overcome their limitations, have been reviewed extensively [1–6]. Blending with ductile polymers and addition of plasticizers are commonly used to improve the properties and processability of PLA [1,2] and poly(3-hydroxybutyrate) (PHB) [5,7], the most common PHA. Blends of biopolymers have been studied extensively [5,8,9] in

efforts to achieve fully bio-based formulations. PHAs and their copolymers have been used to enhance the toughness of PLA through solution blending [10] or melt blending [10–12]. As shown previously [13], medium chain length (MCL) PHAs can serve as impact modifiers for PHB due to their low crystallinity and elastomeric character [9,14,15].

To address the lack of melt strength and poor rheological properties of biopolyesters, reactive modifications in the melt state have been employed to achieve chain extension. Various approaches to the modification of PLA have been summarized by Pilla et al. [15] and Yu et al. [9]. These include chain extension of PLA in the presence of glycidol [16] and introduction of long chain branching via functional group reactions with pyromellitic dianhydride and triglycidyl isocyanurate [17]. Furthermore chain extenders, such as tris (nonylphenyl) phosphite, polycarbodiimide and epoxy-functionalized oligomeric acrylic copolymer (trade name Joncryl® from BASF) have been considered to counteract degradation in PLA and introduce chain extension [18–20]. In situ cross-linked, hyperbranched polymers have been used to improve

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the toughness of PLA [21,22]. Reactive extrusion of PLA using organic peroxides and coagents has also been undertaken [3,23–27], while cross-linking of MCL PHAs has been achieved using peroxides, radiation, or sulfur cures [28–30].

Reactive blending of biopolyesters has been employed to produce in situ compatibilized blends with improved properties. Examples of blends reacted with peroxides include PHB and poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) with polybutylene succinate (PBS) [31], as well as PLA with polycaprolactone (PCL) [32], PBS [33], polybutyrate adipate terephthalate (PBAT) [34] and PHB [35]. Chemical modification using diisocyanate chain extenders, which are highly toxic, has also been proposed for reactive blending of PLA with MCL-PHAs [36]. PLA–PHA block copolymers have been introduced in MCL PHA to react with the hydroxyl groups of PLA, thus increasing the interfacial interaction and improving the blend morphology and compatibility [10].

In our previous work [37] we employed a simple reactive modification approach, utilizing solvent-free peroxide-initiated grafting of a multi-functional coagent, to introduce branching and achieve substantial improvements in the strain hardening characteristics of PLA. This approach resulted in faster crystallization kinetics, both under isothermal and non-isothermal conditions. In the present work, we investigate chain extension of PHO and PLA using this technique, as well as reactive blending of PLA with PHO, and compare their properties to the unmodified blends.

## 2. Experimental methods

### 2.1. Materials

PHO containing ~98 mol% of 3-hydroxyoctanoate and ~2 mol% of 3-hydroxyhexanoate was produced from glucose and octanoic

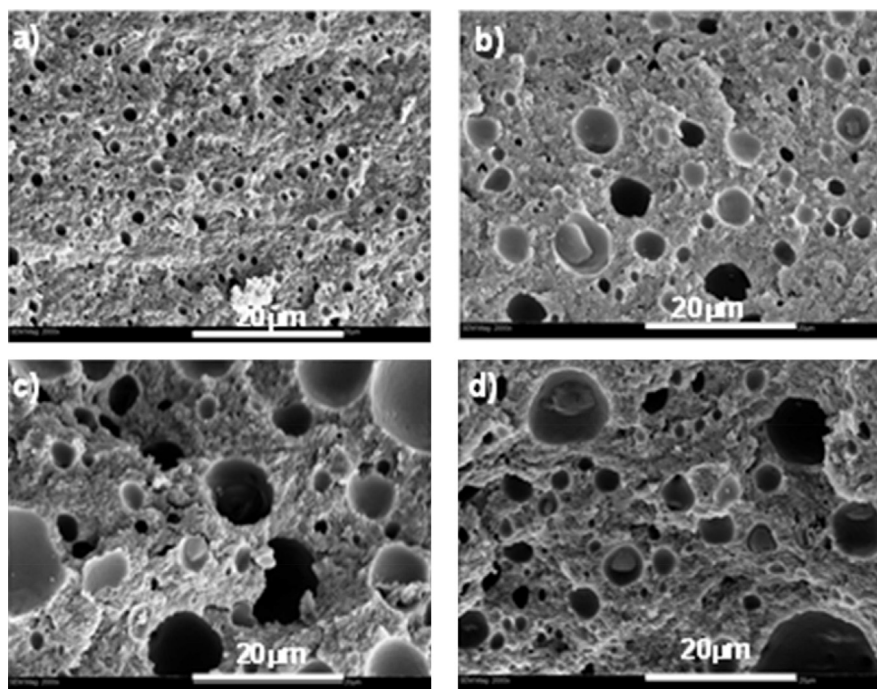
**Table 1**  
Mechanical properties of PLA/PHO blends.

PHO (wt.%)	Tensile stress (MPa)	Young's modulus (MPa)	Elongation at break (%)	Unnotched impact (KJ/m <sup>2</sup> )	Crystallinity (%)
0	74 (±3)	670 (±74)	14 (±1)	32 (±5)	24
5	56 (±4)	582 (±68)	24 (±10)	63 (±6)	17
10	50 (±4)	696 (±29)	35 (±15)	65 (±5)	16
15	45 (±3)	571 (±22)	47 (±10)	53 (±9)	16
20	34 (±3)	442 (±34)	24 (±3)	40 (±5)	16

acid using bacterial fermentation as described by Jiang et al. [38,39]. The weight average molecular weight of the PHO, determined by triple-detector size exclusion chromatography, was 172,000 Da with a dispersity of 1.75 [40]. PLA (grade 3251D, MFI 35 g/10 min at 190 °C/2.16 kg) was obtained from Natureworks®. Triallyl trimetate (TAM, 98%, Monomer Polymer Inc.), dicumyl peroxide (DCP, 98%, Sigma–Aldrich) and chloroform (Sigma–Aldrich) were used as received.

### 2.2. Compounding

PLA and PHO were dried in a vacuum oven at 100 °C and room temperature, respectively, to remove moisture as per standard manufacturer recommendations. PLA/PHO blends containing 0–20 wt.% PHO were compounded in a DSM microcompounder at 180 °C for 3 min at a screw speed of 100 rpm. The compounder was operated under nitrogen blanket to limit polymer degradation. After compounding the strands were quenched in cold water before chopping into pellets. The neat materials were compounded under the same conditions for comparison.



**Fig. 1.** Scanning electron microscope images of PLA blend containing a) 5 wt.%, b) 10 wt.%, c) 15 wt.% and d) 20 wt.% of PHO. The magnification is  $\times 2000$ .

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