

Accelerating Reactive Compatibilization of PE/PLA Blends by an Interfacially Localized Catalyst

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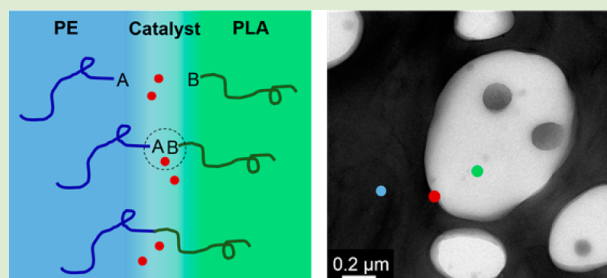
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S Supporting Information

ABSTRACT: We show catalyst localized at the interface can compatibilize polyethylene (PE) and polylactide (PLA) blends. Telechelic hydroxyl functional PE was synthesized by ring opening metathesis polymerization, which reacted with PLA in melt mixing (shown by adhesion and droplet size reduction). Lewis acid tin catalysts were examined as interfacial reaction promoters, with the goal of interfacial localization. Stannous octoate was shown to localize at the interface by transmission electron microscopy with energy dispersive X-ray spectroscopy and improved dispersion of PLA in PE as compared to uncatalyzed materials and a nonlocalized tin chloride dihydrate.



Immiscible blends represent a growing fraction of advanced polymeric materials but require compatibilizers to achieve stable morphologies and superior mechanical properties.^{1,2} Reactive compatibilization is the preferred approach, as block or graft copolymers are formed in situ, thereby avoiding loss of compatibilizer to micellization. However, few reactions (e.g., primary amine plus cyclic anhydride) are sufficiently rapid without a catalyst. Suitable catalysts could greatly expand the palette of accessible reactive groups, but to be efficient, they should be localized at the interface. In this report we demonstrate directly that interfacial localization is crucial by preparing novel blends of biorenewable polylactide (PLA) in a majority polyethylene (PE) matrix using esterification of hydroxyl-functionalized PE.

Reactive compatibilization leads to improvements in adhesion,^{3,4} processing stability,⁵ and bulk mechanical properties (impact,^{6,7} tensile,^{8,9} hardness,¹⁰ and scratch resistance^{11,12}). Interfacial coupling kinetics determines the amount of copolymer formed and, therefore, final material properties. Past work has identified variables that strongly affect coupling kinetics, including Flory–Huggins interaction parameter,¹³ flow,^{14,15} coupling reaction type,¹⁶ and catalyst. Several reports have utilized catalysts to improve conversion to copolymer, but results have been mixed.^{17–26} Most studies select catalysts based on their activity toward analogous small molecule reactions and stability at melt processing temperatures, with little regard for surface activity or localization. The sole report of catalyst localization came from Legros et al.,²³ where tin distannoxane catalyst preferentially localized in poly(butylene terephthalate) (PBT) portions of PE/PBT reactive blends.

However, in that work a relationship between localization and compatibility was not determined. Guegan et al. reported that *N,N*-dimethyldodecylamine catalyst had no effect on conversion in acid functional polystyrene (PS-COOH)/epoxy functional polystyrene miscible blends, but adding the same catalyst to an analogous immiscible blend, PS-COOH/epoxy end-functional poly(methyl methacrylate), resulted in a 250% increase in reaction rate.²⁴ This suggests that the presence of an interface, or localization, might be critical for catalyst performance. This concept finds a precedent in small molecule chemistry with catalyst-combined surfactants from Kobayashi and co-workers.^{27–29}

Reactive groups on PLA homopolymers have recently been used in catalyzed reactive compatibilization schemes. PE-*co*-ethyl acrylate-*co*-glycidyl methacrylate (EMA-GMA)/PLA blends catalyzed with *N,N*-dimethylstearylamine resulted in higher conversion to graft copolymer, finer dispersion, and increased impact strength of PLA.²⁵ Sadik et al. also compatibilized poly(ethylene-*co*-vinyl alcohol) (EVOH) and PLA with stannous octoate catalyst, demonstrating copolymer formation with NMR, SEC, and rheology.²⁶ However, these studies used undiluted functional PE copolymers with many functional groups per chain in order to obtain improved properties and conversion. Also, the miscibility of these functional PE copolymers with neat PE may limit applications.

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In this work, compatibilized blends of HDPE (high density PE) and PLA are created using modest amounts of hydroxyl functional PE. PLA is chosen to blend with PE for its high modulus (~ 3 GPa) and renewable nature.⁷ This particular PLA/PE system may have applications in food packaging since stannous octoate catalyst is FDA approved³⁰ and the chemistry is less hazardous than maleic anhydride or epoxy functional PEs. The effect of catalyst localization on blend compatibility and adhesion is examined. This work develops a method of finding catalyst location in reactive polymer blends and, thereby, expands the number and types of interfacial reactions with sufficient rates for applications.

Telechelic α,ω -hydroxyl functional PE (HO-PE-OH) was synthesized using ring opening metathesis polymerization with a chain transfer agent, followed by hydrolysis and hydrogenation, as pioneered by Pitet and co-workers.³¹ This serves as a high density PE analog to commercial EVOH. HO-PE-OH was diluted with commercial HDPE (DMDA 8904 NT-7, Dow Chemical Company) and reacted with PLA (Natureworks 2003D) during compounding. Polymer characteristics are shown in Table 1. Tin chloride dihydrate (SnCl_2 ; Sigma-Aldrich) and stannous octoate (SnOct_2 ; Sigma-Aldrich) were used to promote interfacial reaction.

Table 1. Polymer Characteristics

polymer	M_n (kg/mol)	D	η_0^c (Pa s)	T_m^d ($^\circ\text{C}$)
HDPE	32 ^a	2.4 ^a	2600	132
PLA	190 ^b	1.5 ^b	5700	150
HO-PE-OH	27 ^a	1.7 ^a	190	130

^aMeasured with high temperature SEC and an RI detector, relative to PS standards at 135 $^\circ\text{C}$. ^bMeasured with 30 $^\circ\text{C}$ chloroform SEC with RI and LS detectors. ^cMeasured by 180 $^\circ\text{C}$ dynamic frequency sweep, from Cross model fit and Cox–Merz rule. ^dMeasured with DSC on second heating with 10 $^\circ\text{C}/\text{min}$ ramp rate.

Catalysts were screened for activity toward esterification and ester exchange using model small molecule reactions. Kinetic rate constants from small molecule reactions compare well to those found for homogeneous polymer blends, in terms of ranking relative rates.² Hexadecanol was reacted with either methyl stearate (ester exchange) or hexadecanoic acid (esterification) at 180 $^\circ\text{C}$. Conversion with and without catalyst was monitored with ^1H NMR spectroscopy. SnCl_2 and SnOct_2 showed similar, significant activity toward both esterification and ester exchange (see Supporting Information for more details).

Melt mixing was performed in a Minimax cup and rotor mixer (Custom Scientific Instruments) with two 1/4" diameter ball bearings added to improve mixing.^{32,33} Samples were blended at 180 $^\circ\text{C}$ and 310 rpm for 5 min, then removed and quenched in liquid nitrogen. All blends contained 90 wt % PE, 10 wt % PLA, and 0.01 M catalyst (0.4 wt % SnCl_2 or 0.8 wt % SnOct_2) for 0.50 g total material.

Blends were cryo-microtomed at -160 $^\circ\text{C}$, washed with acetone overnight to remove PLA, coated with 50 \AA Pt, and imaged on a JEOL 6500 scanning electron microscope (Figure 1). Droplet sizes were measured using ImageJ software (NIH) and are compared in Table 2. Formation of copolymer reduces surface tension in mixing, resulting in decreased droplet size.^{34–36} The reduction in droplet size with addition of HO-PE-OH suggests interfacial reaction. Addition of SnCl_2 did not appreciably reduce droplet size, despite evidence from small

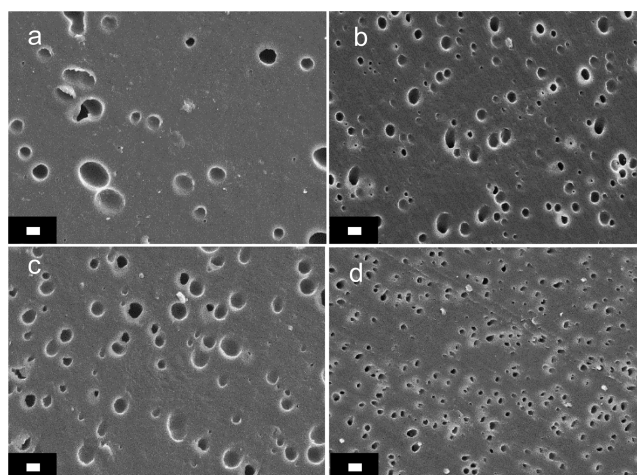


Figure 1. Representative SEM images of blends with 1 μm scale bars: (a) PE/PLA (90/10); (b) PE/HO-PE-OH/PLA (60/30/10); (c) PE/PLA/HO-PE-OH/ SnCl_2 (60/30/10/0.4); (d) PE/PLA/HO-PE-OH/ SnOct_2 (60/30/10/0.8).

Table 2. Droplet Sizes of Blends

blend (weight fraction of component)	droplet size (μm , $\langle d_n \rangle \pm \text{S.D.}$)	number of droplets sized
HDPE/PLA (90/10)	0.77 ± 0.20	189
HDPE/HO-PE-OH/PLA (60/30/10)	0.44 ± 0.07	861
HDPE/HO-PE-OH/PLA/ SnCl_2 (60/30/10/0.4)	0.53 ± 0.30	412
HDPE/HO-PE-OH/PLA/ SnOct_2 (60/30/10/0.8)	0.26 ± 0.04	1514

molecule model reactions and literature showing it is an effective catalyst for esterification and ester exchange.^{37–39} In contrast, SnOct_2 was effective at reducing droplet size further than HO-PE-OH alone.

Adhesion was measured to verify reaction at the interface of HO-PE-OH and PLA. Trilayer samples were laminated for 1 h at 180 $^\circ\text{C}$ (HDPE/HO-PE-OH/PLA) and tested for peel strength (see Supporting Information for details). Samples without HO-PE-OH showed no adhesion, delaminating before removal from the mold. HO-PE-OH samples displayed lower adhesion than reported for most reactive systems^{14,40,41} but appreciably higher than most nonreactive laminates⁴² and even some reactive ones.⁴³ When 0.01 M catalyst is blended into the HO-PE-OH compatibilizing layer before lamination, adhesion values increase further. Adhesion shows that reaction occurs with or without catalyst and that the droplet size decrease seen in SEM is from reaction, not from catalyst acting as surfactant.

Transmission electron microscopy with energy dispersive X-ray spectroscopy (TEM EDS) was used to determine SnOct_2 catalyst localization in the blends (FEI Tecnai T12, 120 kV). This technique is used to give elemental information as a function of position.^{44,45} Blends were cryo-microtomed to 50 nm sections and transferred to a Formvar-coated copper grid for imaging (Ted Pella). Figures 2a and 3a show representative PLA droplets (light) in the HDPE matrix (dark). The dark inclusions in the PLA droplet are presumably HDPE. The contrast gradients in the HDPE are attributed to thickness or crystallinity variations.

EDS spectra were obtained inside droplets, in the nearby matrix, and on the interface for several drops. The minimum spot size is approximately 50 nm. Spectra were analyzed for

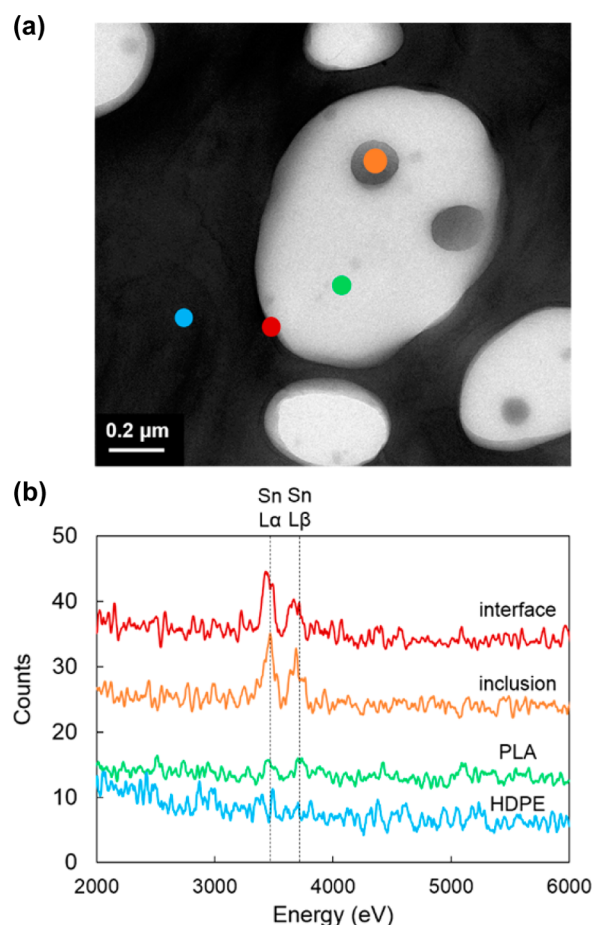


Figure 2. Representative TEM image of HDPE/PLA/HO-PE-OH/SnOct₂ blend (a), with estimated EDS spot size (from left-to-right, HDPE, interface, PLA, and inclusion). EDS spectra (b) with expected tin peaks, shifted vertically.

expected Sn L α and L β transitions around 3500 eV. The SnOct₂ blend interface (or inclusion interface) spots consistently showed Sn peaks, whereas the matrix, droplet, and SnCl₂ blend interface spots did not (Figures 2b and 3b). To our knowledge, this represents the first direct evidence of interfacial localization of catalyst in reactive compatibilization.

Localization demonstrates why SnOct₂ is more effective than SnCl₂ at reducing droplet size in reactive blends and can be explained in part through solubility parameters. The catalyst solubility parameter should lie between those of the homopolymers for interfacial localization. In this case, SnCl₂ ($\delta = 42.3 \text{ MPa}^{1/2}$) has a higher solubility parameter than PE ($\delta = 17 \text{ MPa}^{1/2}$) or PLA ($\delta = 20.5 \text{ MPa}^{1/2}$; all values at 25 °C)^{46,47} leading to catalyst aggregation. In contrast, δ is estimated to be 20.0 MPa^{1/2} for SnOct₂,⁴⁸ between that of PE and PLA and localizes on the interface. It is apparent that catalyst localization can be roughly predicted by solubility parameters and is important in reactive blending.

In summary, interface localized catalysts are a promising method of improving conversion in reactive compatibilization. Catalysts that segregate preferentially to the interface can be added in submonolayer quantities to obtain large improvements in adhesion and dispersion. This work examined the effect of two tin catalysts on the reactive compatibilization of telechelic hydroxyl functional polyethylene and PLA. There is a weak reaction, even without catalysts, and improved dispersion

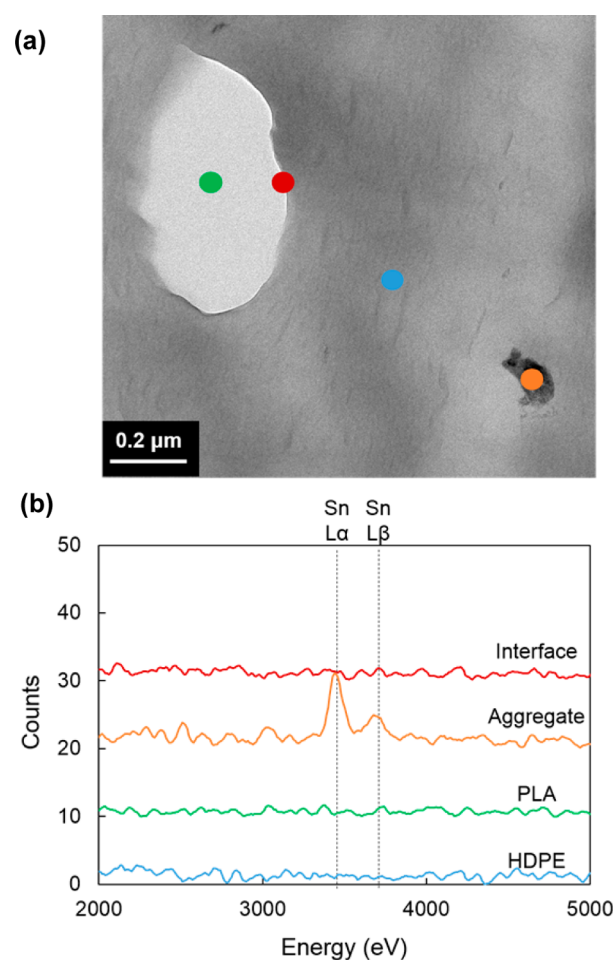


Figure 3. Representative TEM image of HDPE/PLA/HO-PE-OH/SnCl₂ blend (a), with estimated EDS spot size (from left-to-right, PLA, interface, HDPE, and aggregate). EDS spectra (b) with expected tin peaks, shifted vertically.

and adhesion compared to HDPE/PLA materials. SnOct₂ was more effective as a catalyst in blend compatibilization than SnCl₂, which is attributed to its interfacial localization, as confirmed directly by TEM with EDS.

■ ASSOCIATED CONTENT

📄 Supporting Information

Experimental details, including synthesis and characterization of HO-PE-OH, rheology, thermal properties, and catalyst activity studies using small molecules. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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