Dihydroxy polyethylene additives for compatibilization and mechanical recycling of polyethylene terephthalate/polyethylene mixed plastic waste

*Aristotle J. Zervoudakis[†], Caitlin S. Sample[‡], Xiayu Peng[†], Davis Lake[†], Marc A. Hillmyer[‡], Christopher J. Ellison[†]**

[†]Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, MN 55455, United States
[‡]Department of Chemistry, University of Minnesota, Minneapolis, MN 55455, United States
*To whom correspondence should be addressed: cellison@umn.edu

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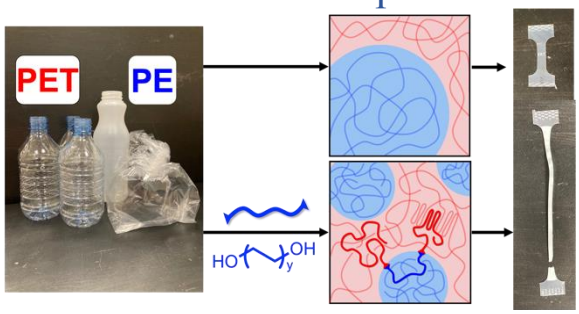

Abstract

Polymer blend compatibilization is an attractive solution for mechanical recycling of mixed plastic waste because it can result in tough blends. In this work, hydroxy-telechelic polyethylene (HOPEOH) reactive additives were used to compatibilize blends of polyethylene terephthalate (PET) and linear low-density polyethylene (LLDPE). HOPEOH additives were synthesized with molar masses of 1–20 kg/mol by ring-opening metathesis polymerization of cyclooctene followed by catalytic hydrogenation. Melt-compounded blends containing 0.5 wt% HOPEOH displayed reduced dispersed phase LLDPE particle sizes with ductilities comparable to virgin PET and almost seven times greater than neat blends, regardless of additive molar mass. In contrast, analogous blends containing monohydroxy PE additives of comparable molar masses did not result in compatibilization even at 2 wt% loading. The results strongly suggest that both hydroxy ends of HOPEOH undergo transesterification reactions during melt mixing with PET to form predominantly PET-PE-PET triblock copolymers at the interface of the dispersed and matrix

phases. We hypothesize that the triblock copolymer compatibilizers localized at the interface form trapped entanglements of the PE mid-blocks with nearby LLDPE homopolymer chains by a hook-and-clasp mechanism. Finally, HOPEOH compounds were able to efficiently compatibilize blends derived solely from post-consumer PET and PE bottles and film suggesting their industrial applicability.

Main Discussion

Mechanical recycling is the dominant plastics recycling technology in many countries today.[1] One major challenge is that physical sorting before mechanical recycling is imperfect, and because most polymers are incompatible, plastic waste mixtures form macrophase-separated blends upon melt reprocessing.[2] Such blends are usually brittle compared to their pure components due to narrow and mechanically weak interfaces,[3,4] making them undesirable for most applications. In addition, some products like multilayer films are impossible to sort because their components are strongly adhered with adhesive layers. New methods for compatibilizing polymer blends to impart more desirable properties are needed to address these challenges.[3–7] A common pathway to compatibilization involves melt (re)processing blends with interfacially localizing additives, such as block copolymers (BCP). To produce mechanically tough blends, sufficient BCP must localize at the interface between blend components, and the individual blocks must mechanically anchor in each phase. Co-crystallization or molecular entanglements between the blocks and blend components can serve as anchoring mechanisms, allowing efficient stress transfer between domains.

This work develops an *in-situ* reactive compatibilization approach for mechanical recycling of polyethylene terephthalate (PET) and polyethylene (PE) blends that comprise almost 60% of total plastic waste in the US[8] and are often used together in multilayer film products like meat packaging.[9] Recent work has shown that this system can be compatibilized using premade linear multiblock copolymers (MBCPs) at low MBCP content (ca. 0.5 wt%);[3] while these MBCPs are efficient, their synthesis is practically challenging. Therefore, compatibilizers formed *in-situ* during melt blending would be an attractive alternative. Related previous compatibilization research of polyester/PE blends has shown that anhydride or epoxy graft-functionalized PE materials can be effective, albeit at relatively high loadings (5

wt% or more) of functionalized polymer[10–12] or with the addition of catalyst.[13] Other studies using telechelic-functionalized PEs have shown some success as well, but relied on high loadings of the functionalized PE (up to 30 wt%)[14] or required protecting groups.[15] Herein, we demonstrate that reactive hydroxy-telechelic polyethylene (HOPEOH) additives can compatibilize PET/linear low-density polyethylene (LLDPE) blends at low loadings (~0.5 wt%), without addition of catalysts or protecting groups.

Full details for all materials and methods can be found in Supplemental S1. Linear, hydroxy-telechelic HOPEOH additives with number average molar masses, M_n, = 1, 4, 13, and 20 kg/mol and molar mass dispersities, $Đ$, ranging from 1.4–1.5 were synthesized by ring-opening metathesis polymerization of cyclooctene followed by catalytic hydrogenation, as previously reported.[16] Monohydroxy, lightly branched polyethylene additives (PEOH) with M_n = 3 and 17 kg/mol and $Đ$ = 1.02 and 1.01, respectively, were synthesized through anionic polymerization of 1,3-butadiene followed by addition of a single unit of ethylene oxide, and catalytic hydrogenation. Both additive types are miscible and able to co-crystallize with the LLDPE homopolymer used in this study (Supplemental S2).[17,18]

HOPEOH or PEOH was used as an additive in melt compounding blends of virgin PET and LLDPE or postconsumer PET and LLDPE or high-density polyethylene (HDPE). The base blend composition was 80/20 PET/PE, and the HOPEOH or PEOH additive loading is reported as weight percent of the blend (e.g., 8 g PET pellets, 2 g LLDPE pellets, and 0.05 g HOPEOH would be reported as 0.5 wt% HOPEOH). The 80/20 PET/PE blend composition was chosen because it results in brittle neat blends which allows straightforward diagnosis of compatibilizer effectiveness. After melt-mixing in a microcompounder at 270 °C for 5 minutes, all blends were subsequently compression molded into films at 280 °C and quenched resulting in crystallinity of around 14 and 17% for PE and PET, respectively (Supplemental S3). Specimens were cut from these films for testing.

Representative stress–strain data for PET homopolymer and PET/LLDPE blends are shown in Figure 1a. The neat PET and LLDPE homopolymer components are ductile and tough thermoplastics with average strains at break (ε_b) of 320 and 860%, respectively (Table 1). PET/PE 80/20 neat blends exhibit an intermediary modulus and yield stress to the neat components, but are brittle achieving an ε_b of 40%.

Brittle behavior in neat blends is expected as thermodynamic immiscibility results in sharp ~1 nm thick[3] domain interfaces that are mechanically weak. Figure 1 and Table 1 show that addition of ~0.5 wt% of HOPEOH to PET/PE blends greatly improved ductility with ε_b values comparable to neat PET, a signature of effectively compatibilized blends. The fact that 1 kg/mol HOPEOH was effective is surprising given that the bulk molar mass between entanglements for PE, M_e, is ~0.8 kg/mol;[19] we note that entanglements influence bulk melt viscosity and mechanical properties when molar mass is greater than the critical entanglement molar mass (M_c), ~2–3 times M_e.[19] At lower loadings (Figure 1b and Supplemental S4), ε_b eventually decreases below that of neat PET at some HOPEOH molar masses, and ε_b uncertainty values increase indicating nonuniformly compatibilized blends.

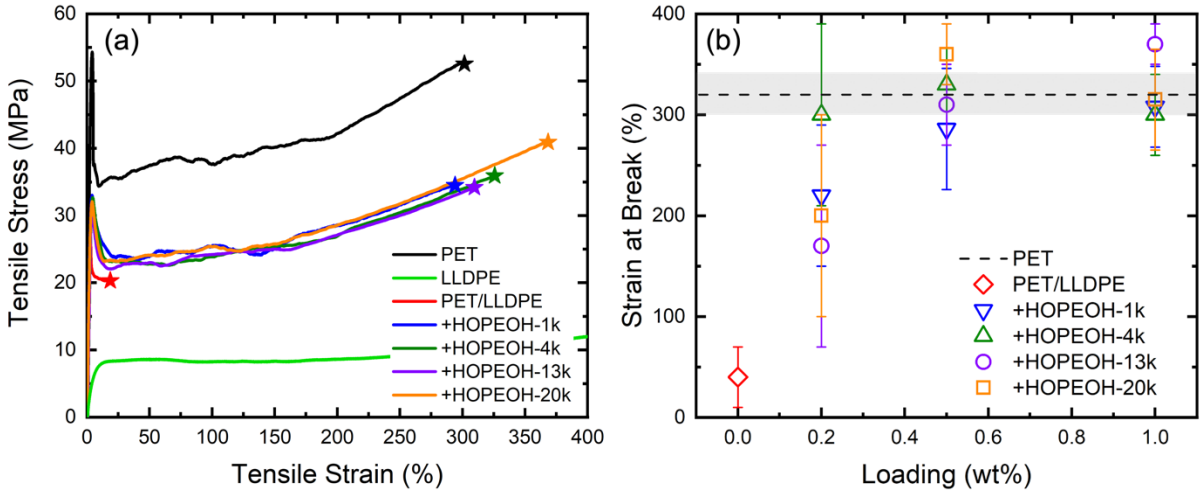

Figure 1. (a) Representative tensile stress-strain data for PET and LLDPE homopolymers and PET/PE blends with and without 0.5 wt% additive. Fracture points are notated with ★. Note: LLDPE samples have a ε_b of 860% and only a portion of the data is shown here for clarity. (b) Strain at break values for PET homopolymer (average value given as a dashed line with uncertainty indicated by the shaded region) and different blends. Error bars represent the standard deviation of all samples tested for a given sample type.

Table 1: Mechanical properties of neat homopolymers and blends (+/- values represent the standard deviation of all samples tested for a given sample type)

Sample Name	*Modulus (GPa)*	*Yield Stress (MPa)*	*Strain at Break (%)*
PET Homopolymer	1.62 ± 0.38	53.6 ± 0.7	320 ± 20

LLDPE Homopolymer	0.18 ± 0.03	8.8 ± 0.1	860 ± 70
PET/LLDPE (80/20)	1.24 ± 0.05	27.6 ± 1.5	40 ± 30
+0.5 wt% HOPEOH-1k	1.33 ± 0.05	33.2 ± 0.6	280 ± 60
+0.5 wt% HOPEOH-4k	1.42 ± 0.06	34.6 ± 3.5	330 ± 60
+0.5 wt% HOPEOH-13k	1.42 ± 0.16	31.7 ± 1.8	310 ± 40
+0.5 wt% HOPEOH-20k	1.38 ± 0.04	32.0 ± 0.5	360 ± 30

The blend morphologies were characterized by scanning electron microscopy (SEM) to assess dispersed phase particle sizes at three stages of the process: (i) following melt-mixing ("as-mixed"), (ii) after compression molding into films ("annealed"), and (iii) after tensile testing ("tested"). Representative micrographs are shown in Figure 2. Dispersed LLDPE particle sizes in both the as-mixed and annealed specimens are larger for the neat blends (Figure 2a,b) than compatibilized blends (Figure 2d,e). Moreover, voids between the LLDPE particles and PET matrix caused during cryofracturing are apparent in neat, uncompatibilized blends (Figure 2a,b), indicating poor interfacial adhesion. Poor interfacial adhesion is even more apparent in tested samples (Figure 2c), where the PET matrix pulls away from LLDPE particles with little particle deformation. Conversely, tested compatibilized blends (Figure 2f) show commensurate deformation of LLDPE particles with the PET matrix, indicating successful stress transfer across the interface consistent with effective compatibilization. Tested samples containing additives of different molar masses at the same additive concentration all showed signs of successful stress transfer between phases (Supplemental S5).

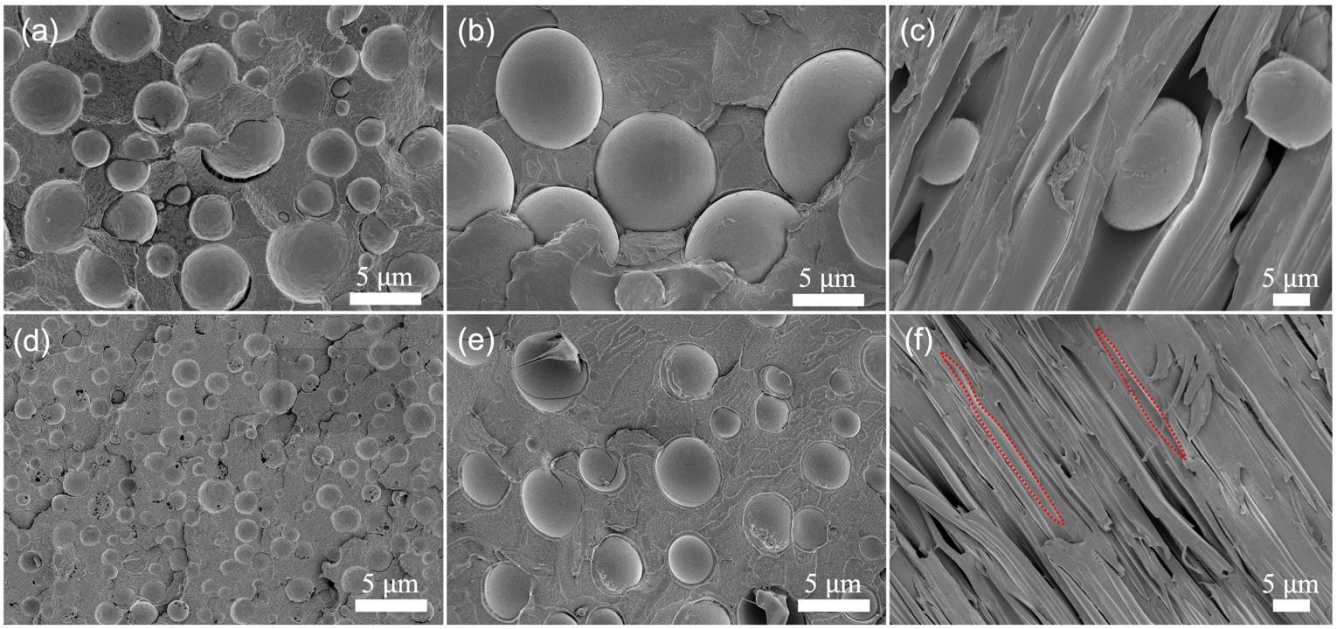

Figure 2. SEM images of uncompatibilized (top) and compatibilized (+0.5 wt% HOPEOH-4k) (bottom) blends after mixing (a, d), annealing into films (b, e), and testing (c, f). Deformed LLDPE particles outlined in red in (f).

The effect of HOPEOH additives on average dispersed phase particle diameter (d) was quantified for the "as mixed" (Figure 3a) and "annealed" (Figure 3b) samples using atomic force microscopy (AFM) after cryomicrotoming. Only neat blends and blends containing HOPEOH-1k and -4k are presented here (blends containing HOPEOH-13k and -20k displayed similar results - see Supplemental S6). In as-mixed samples, the addition of 0.5 wt% HOPEOH-1k ($d = 1.0 \pm 0.2\mu m$) significantly reduced average particle diameter compared to neat blends ($d = 3.4 \pm 1.1\mu m$). After annealing, the neat blend particle size almost doubles with the distribution broadening significantly ($d = 6.4 \pm 3.8\mu m$), while the compatibilized blend particle sizes increased less with a more uniform particle size distribution (e.g., HOPEOH-1k at 0.5 wt%, $d = 1.8 \pm 0.6\mu m$). Both the reduction in average particle size and suppression of coarsening upon annealing (i.e., stabilization) are indications of compatibilizer localization at domain interfaces. Similar effects have been reported for pre-made MBCPs.[3,4,6,20–22] These similarities suggest that HOPEOH additives likely undergo transesterification reactions with PET to form interfacially active compatibilizers that enable compatibilization at comparable loadings but lower additive molar masses compared to premade compatibilizer analogs. While addition of catalyst is not required, we acknowledge residual transesterification catalyst in commercial PET samples may promote incorporation of HOPEOH. We have

confirmed near identical compatibilization results for two different commercial PET samples (Supplemental S7), suggesting the compatibilization success is general.

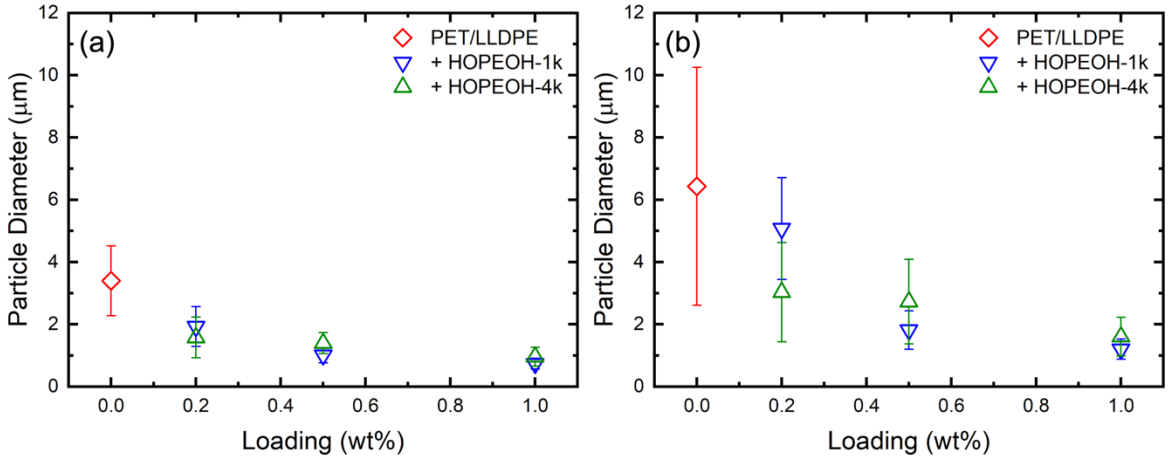

Figure 3. Measured particle diameters for (a) as-mixed and (b) statically annealed blends. Values reported are the average of at least 40 particles measured using ImageJ, with error bars representing the standard deviation of all measurements for each sample type.

We hypothesize that both hydroxy end groups of the HOPEOH additives undergo transesterification reactions during melt mixing with the PET homopolymer to form PET-PE-PET triblock copolymers. Formation of MBCPs with more than three blocks or PE-PET-PE triblock copolymers is unlikely due to the large stoichiometric excess of PET chains. Following from previous discussion, the hypothesized PET-PE-PET triblock copolymers must be mechanically anchored in both domains adjoining the interface for effective compatibilization. On the PET side, the average PET end block molar mass after transesterification should be approximately half that of the neat commercial homopolymer that possesses a nominal molar mass of ~30,000 g/mol. As a result, the PET end block molar mass is expected to be significantly larger than that required for that block to span the amorphous interfacial zone (~3,000 g/mol)[3] indicating it can co-crystallize with the PET matrix. In addition, the same PET end blocks are ~10 x M_e (~1,450 g/mol)[23] on average, suggesting the PET chain ends are also highly entangled with PET homopolymer. Given these two possible mechanisms for the PET end blocks to promote stress transfer, it is unlikely they are significant mechanical weak points in the blends prepared here.

On the PE side, compatibilization was observed with PE additives possessing a molar mass significantly less than that required to span the amorphous interfacial width (~4,200 g/mol)[3] and nearly as small as M_e, indicating sufficient length to co-crystallize or participate in bulk-like entanglements is not a key requirement. Instead, we hypothesize that reaction of both HOPEOH end groups and the formation of a PE loop in the triblock architecture may be critical for compatibilizer performance here. To test this hypothesis, we compared the performance of HOPEOH additives against monohydroxy analogs (PEOH) with similar molar masses. PEOH additives most likely form diblock copolymer compatibilizers through transesterification of their single hydroxy end with PET homopolymer, which is available in stoichiometric excess. Naturally, the proposed diblock copolymers lack the ability to form PE loops near domain interfaces, unlike the aforementioned PET-PE-PET triblock copolymers.

Comparative blends containing monohydroxy PEOH additives at 1 wt% loading were prepared. Generally, dispersed phase sizes decreased with PEOH-3k ($d_{as\text{-}mixed}$ = 1.7 $\pm$ 0.6 μm, $d_{annealed}$ = 3.0 $\pm$ 1.3 μm) or PEOH-17k ($d_{as\text{-}mixed}$ = 2.8 $\pm$ 0.8 μm, $d_{annealed}$ = 5.2 $\pm$ 2.3 μm) additives compared to neat blends ($d_{as\text{-}mixed}$ = 3.4 $\pm$ 1.1μm, $d_{annelaed}$ = 6.4 ± 3.8μm). Similar particle sizes ($d_{as\text{-}mixed}$ = 1.7 $\pm$ 0.6 μm, $d_{annealed}$ = 5.0 $\pm$ 2.2 μm) were observed for higher loadings of PEOH-17k at 2 wt%. These data support that an interfacially active copolymer was formed from the monohydroxy additive during melt mixing.

Representative tensile stress-strain data for PEOH- and HOPEOH-containing blends at comparable molar mass and total hydroxy group concentration (i.e., HOPEOH loading at half that of PEOH) are shown in Figure 4a (mechanical properties for all PEOH-containing blends are in Supporting Information S8). Blends containing 1 wt% PEOH additive are brittle (ε_b = 21$\pm$ 22 % and 48 $\pm$ 48 % for PEOH-3k and -17k, respectively) compared to HOPEOH-containing counterparts (ε_b = 330 $\pm$ 60 % and 310 $\pm$ 40 % for HOPEOH-4k and -13k, respectively). Increasing the loading of PEOH-17k to 2 wt% (comparable hydroxy concentration to HOPEOH-13k at 1 wt%) does lead to an increase in ε_b albeit with greater variability (ε_b = 161 $\pm$ 85 %) than in the dihydroxy-containing materials (ε_b = 370 ± 20), indicating non-uniform compatibilization. Cross-sectional SEM images of tensile tested PEOH-containing blends (Figure 4 b,c) show poor interfacial adhesion at the PET/LLDPE interface, as evidenced by separation of the matrix from the particles, consistent with the poor bulk mechanical properties.

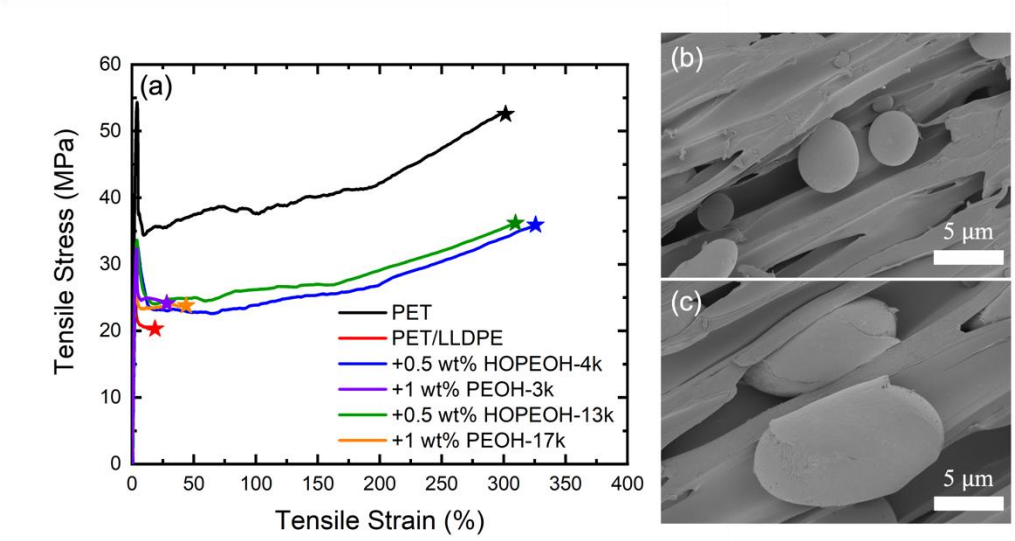

Figure 4. (a) Representative tensile stress-strain data for PET homopolymer and blends of PET/LLDPE, without additive or with either PEOH or HOPEOH additive. Fracture point notated with ★. SEM of tensile tested samples for (b) PEOH-3k and (c) PEOH-17k.

Clearly, monohydroxy additives are not as effective at compatibilization as dihydroxy additives. For the PEOH-3k blends, we hypothesize that the formed PE block is not long enough to appreciably entangle with the PE homopolymer phase.[24,25] The M_e for PE is ~0.8 kg/mol,[19] so it is likely that the PEOH-3k-derived block can disengage from the interface by chain pullout. On the other hand, the PEOH-17k-derived block is well above M_c, and is also long enough to span the amorphous interface between domains to potentially undergo co-crystallization with the bulk PE homopolymer.[3] Even with these two possible anchoring mechanisms (entanglement and co-crystallization) that could promote stress transfer across the interface, mechanically inferior blends result compared to HOPEOH analogs. Although the exact reason is not presently clear, it is possible that the interfacial coverage of PEOH-17k-derived BCP compatibilizers is low. This hypothesis is supported in SEM images of tested samples from this blend that show both deformed and undeformed dispersed phase particles indicating low and inconsistent surface coverage (Supplemental S9). The monohydroxy additive results strongly suggest that dihydroxy analogs are forming triblock compatibilizers by reaction of both chain ends which are more effective compatibilizers; the finer dispersion[26,27] and enhanced mechanical properties[28,29] of blends containing triblock copolymers compared to diblock copolymers is consistent with previous work.

It is remarkable that HOPEOH additives ranging from 1-20 kg/mol are effective reactive compatibilizers at only 0.5 wt%. This range of molar masses includes two additives (HOPEOH-1k and 4k) that do not produce PE mid-blocks of sufficient chain length to reach through the amorphous interface to co-crystallize or significantly exceed M_c. In contrast, the other two additives (HOPEOH-13k and 20k) form mid-blocks that could participate in both co-crystallization and bulk entanglements. Considered together, these results strongly suggest that co-crystallization and significantly exceeding the bulk M_c are not essential requirements for interfacial adhesion with the midblock in the formed triblocks, defying conventional wisdom that one or both are required.[3,4,6] One possible explanation is that the PE middle block can form loops near domain interfaces through reaction of both chain ends, entrapping PE homopolymer chains inside the loops and anchoring them with the triblock to provide interfacial adhesion. This is a significantly different mechanism than that for an un-looped end block, the performance of which will have a molar mass dependence similar to diblock copolymers.[30,31]

We hypothesize the following steps are important for entrapping homopolymer chains with looping midblocks (also shown in Figure 5): 1.) localization of the HOPEOH additive near the PET/PE domain interface, possibly promoted by the intrinsic interfacial affinity of the additive with hydroxy ends (PET-phillic) and aliphatic main chain (LLDPE-phillic), 2.) reaction of the first chain end through a transesterification reaction with PET homopolymer (the "hook") which constrains the second chain end near the domain interface and many PET esters, and 3.) reaction of the second hydroxy chain end with a second PET ester (the "clasp") which entraps some PE homopolymer chains in a newly formed loop. It is important to appreciate that entanglements formed with an interfacially anchored loop are fundamentally different from the dynamic entanglements formed by bulk homopolymer chains, so invoking the concept of bulk M_c in describing the molecular origins of adhesion for looped chain entanglements is not appropriate. Moreover, it is possible to estimate the number of PE homopolymer chains that become entangled/entrapped in the formed loops due to the "hook and clasp" mechanism (Supplemental S10). Briefly, the number of entrapped PE homopolymer chains can be found by dividing the approximate cross-sectional area of a HOPEOH chain tethered to the interface by the end-on cross-sectional area of a free PE homopolymer chain. We estimate that the triblock formed by the HOPEOH-1k additive can entrap up

to 28 PE homopolymer chains compared to 562 chains for HOPEOH-20k. We hypothesize that this mechanism of entrapping homopolymer chains can firmly anchor the formed triblock compatibilizer in the LLDPE dispersed phase as interfacial failure would require significant disentanglement or chain scission of many entrapped homopolymer PE chains.

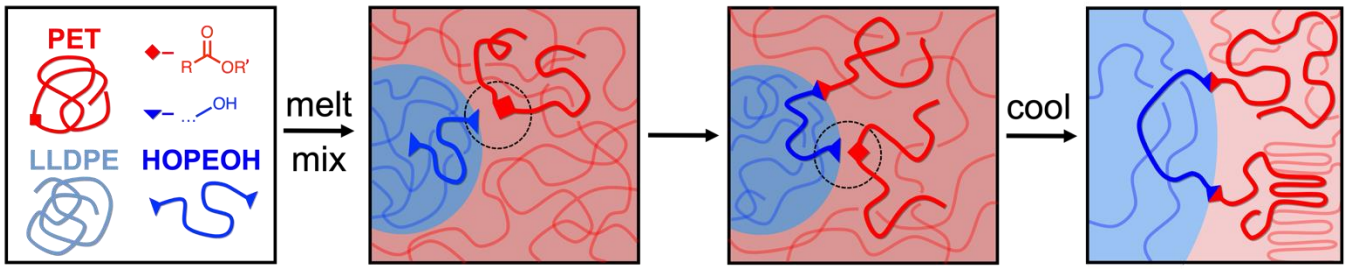

Figure 5. Schematic representation of the "hook and clasp" compatibilization mechanism. From left to right: 1) Graphical representations of the materials used. Note that PET homopolymer chains contain many ester groups, but only one is shown for clarity. 2) During melt mixing, HOPEOH preferentially localizes at the PE/PET interface where one chain end can undergo a transesterification reaction with PET homopolymer ("hook"). 3) The opposite chain end of a tethered HOPEOH reacts with another PET ester ("clasp") to complete the loop. 4) Upon cooling, PE homopolymer chains become entrapped by the resultant loop and anchor the loop in the PE homopolymer phase while PET chain ends can undergo co-crystallization or bulk entanglements with the PET homopolymer.

To highlight that these additives are viable for use in a mechanical recycling process using post-consumer feedstock, we prepared blends using PET from plastic water bottles (rPET) and two different PE sources in gusset bags (rLLDPE) and a milk jug (rHDPE). Composition and mechanical data for the neat materials and blends can be found in Supplemental S11. As with blends prepared using virgin materials, the addition of 0.5 wt% of HOPEOH-13k significantly increased ε_b for both rPET/rLLDPE and rPET/rHDPE blends compared to the brittle neat analogs. It is promising that the efficiency of these additives is maintained across different kinds of PE, as it is difficult to sort different types of PE during the recycling process. Moreover, dihydroxy polyolefin additives have shown promise in blends containing PET and isotactic polypropylene (Supplemental S12), suggesting the broader applicability of our findings to other important systems.

In summary, we have demonstrated that hydroxy-telechelic polyethylene additives are potent compatibilizers for PET/LLDPE blends that are effective at loadings of ~0.5 wt%. Moreover, blend properties were similar for HOPEOH additive molar masses from 1 to 20 kg/mol. The ability of these additives to efficiently anchor on the PE side of the interface was attributed to the ability to form loops that entrap homopolymer chains, which was supported by comparisons to analogous monofunctional additives. Finally, these simple difunctional additives were also successful in compatibilizing blends of post-consumer PET/LLDPE or HDPE suggesting their utility for mechanical recycling.

Supporting Information

Materials and methods information; Miscibility and co-crystallization of PE additives with homopolymer; Crystallinity of pressed and tested specimens; Representative mechanical properties; SEM images and particle size data for blend samples; Compatibilization using different PET grades; Estimation of number of entrapped homopolymer chains; Properties of neat post-consumer materials and blends; Dihydroxy additive data for PET/iPP; Effect of pressing procedure on neat blends

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