

# Compatibilization of polyolefin blends through acid–base interactions

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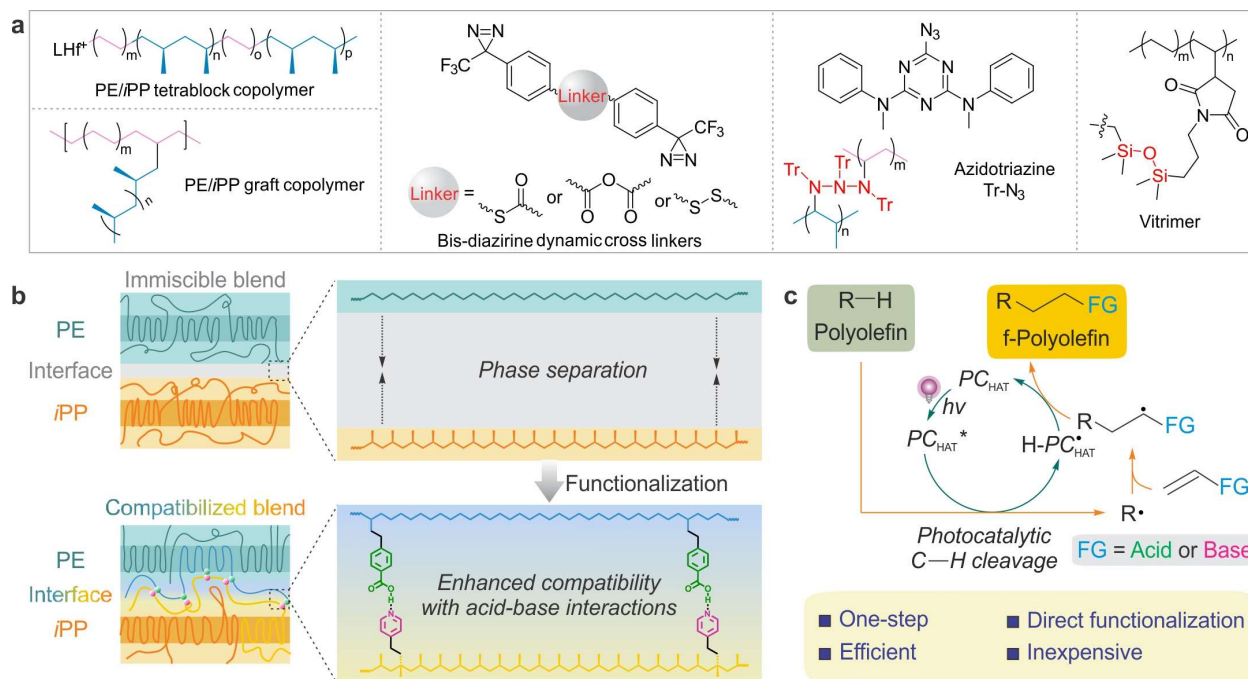
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**Abstract:** Polyolefins are ubiquitous in consumer products but are notoriously difficult to recycle due to the inherent incompatibility of their common varieties. Existing approaches to addressing this challenge either require complex syntheses or compromise the properties of the parent materials. Here, a new method to compatibilize mixed polyolefins is developed. With a single-step photocatalysis, acid or base functionality can be readily installed onto polyolefins. The combination of acid- and base-modified polyolefins functions as compatibilizers. Incorporating them into polyolefin blends results in excellent mechanical strength, with up to an 82-fold increase in ductility. Importantly, compatibilization can be readily achieved on post-consumer polyolefin mixtures. Furthermore, direct functionalization and compatibilization of polyolefin blends is achieved. This strategy promises to transform polyolefin recycling and will likely find broad applications.

**Main Text:** Polyethylene (PE) and isotactic polypropylene (*i*PP) combined account for approximately half of all plastic synthesized thanks to their excellent mechanical properties and ease of production.<sup>1</sup> They feature similar optical properties and densities and therefore are difficult to separate.<sup>2</sup> Once mixed, as is often the case in post-consumer plastic waste, PE and *i*PP result in brittle materials with poor mechanical properties because they are inherently immiscible,

presenting one of the most significant challenges in plastic recycling.<sup>3,4</sup> Recognizing this issue, numerous strategies have been proposed to compatibilize polyolefin blends with the addition of compatibilizers (**Fig. 1a**). One approach involved using block or graft copolymers.<sup>5–9</sup> While effective, the cost of these tailor-made copolymers would need to be further reduced for large-scale implementations. Alternatively, dynamic crosslinkers have been explored as reactive compatibilizers and shown promise.<sup>10–12</sup> While encouraging, these strategies face significant limitations. Chief among the concerns is the need for complicated catalysts, as well as the intricate and multi-step reactions necessary for compatibilizer preparation. Furthermore, with the exception of the copolymer-based approach, these strategies compromise ductility of the resulting polymer blend that are characteristic of their parent polyolefin components.



**Fig. 1. Design of acid-base compatibilizers for PE and iPP compatibilization.** (a) Examples of previously reported compatibilizers for PE/iPP compatibilization. (b) Schematic illustration of PE/iPP immiscible blend and compatibilized blend via acid-base interactions. (c) Scheme of HAT-initiated polyolefin functionalization with acid and base units. PC = photocatalyst; FG = functional group.

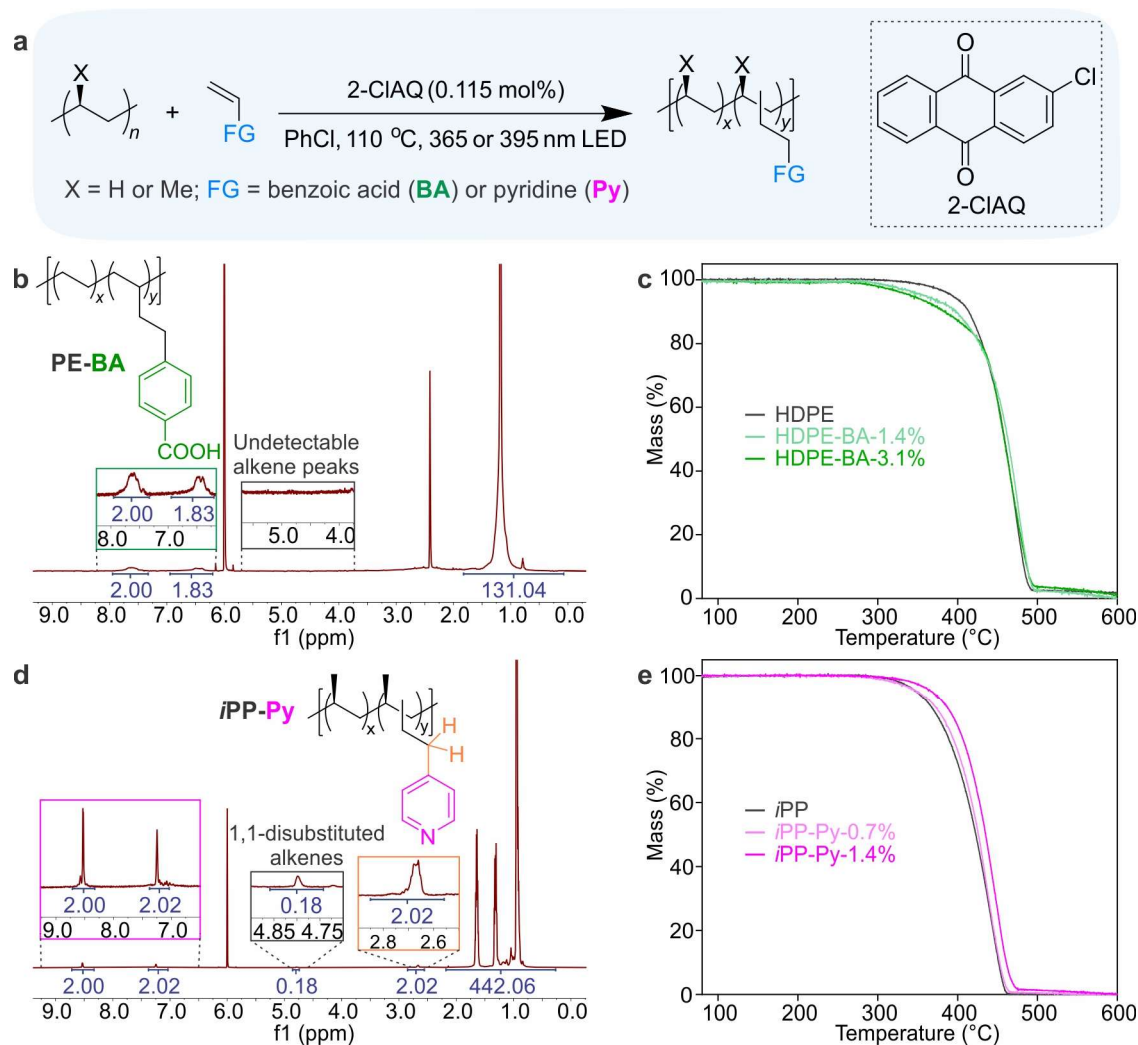
It was within this context that our attention was drawn to the possibility of compatibilizing polyolefins with noncovalent interactions, such as those forming between acid and base functional groups. Similar concepts have been introduced as “ionic compatibilizers,” which utilized strong acid and base pairs to compatibilize synthetic polystyrene and polydimethylsiloxane as a model demonstration.<sup>13,14</sup> Therefore, addressing the practical issue of compatibilizing mixed polyolefin waste with similar interactions is highly appealing and promising. Uniquely, here acid–base compatibilizers (ABCs) are synthesized through direct polyolefin modification, with acid or base units *randomly* installed onto polyolefin backbones via facile hydrogen atom transfer (HAT)-initiated C–H activation, followed by Michael-type radical addition reactions (**Fig. 1c**). When mixed with polyolefin blends, the polyolefins modified with acid and base functional groups form close pairs through acid–base interactions and act as compatibilizers. We further hypothesize that the PE and *i*PP segments of ABCs co-crystallize with their respective non-functionalized components and thereby exhibit cohesive interactions with their counterparts at the interface through acid/base interactions; as a result, the interfacial tension and domain sizes are minimized, generating compatibilized blends (**Fig. 1b**). As a proof-of-concept, we show that an 82-fold increase in elongation at break ( $\epsilon_b$ ) can be achieved with the addition of 10wt% of ABCs that are modestly functionalized (1.4% installation of acid onto high-density PE (HDPE) and 1.4% installation of base onto *i*PP). Importantly, the strategy is demonstrated to be readily applicable to polyolefin blends, including post-consumer plastic mixtures, by directly functionalizing mixed polymers using the same photochemistry, achieving a high degree of compatibilization. All chemicals involved in the synthesis are commercially available and of low-cost, and the functionalization is a one-step reaction with high atom efficiency (**Fig. 1c**), promising prospect of ready large-scale implementations.

## Reaction development

A natural approach to post-polymerization functionalization of polyolefins is to activate the C–H bonds. A major challenge of this approach is the inert nature of aliphatic hydrocarbons.<sup>15</sup> While organic peroxide initiators have been shown effective in generating radicals at high temperatures for the grafting of maleic anhydride groups, this process often leads to undesired side reactions, including  $\beta$ -scission, chain transfer, and cross-linking reactions that significantly degrade the thermal and mechanical properties of the resulting materials.<sup>16</sup> Researchers are, therefore, inspired to solve the issue by borrowing recent advances in C–H functionalization of small molecules and applying them to polymers.<sup>17–24</sup> The direct introduction of acid or base functional groups to polyolefins, however, remains a challenge. This is because reactive acid/base species tend to poison or degrade catalysts involved. Recognizing the promises by acid/base functionalized polyolefins in compatibilizing their mixed blends, we are motivated to solve the challenges of directly grafting acid/base functional groups onto polyolefins. To this end, a key inspiration comes from recent successes in HAT catalysis by photocatalysts, which are highly specific in activating C–H bonds in polyolefins without inducing significant side reactions and can be compatible with acid/base species.<sup>25</sup> In choosing a prototypical photocatalyst to work with, we prioritize candidates which will not leave a residue in the resulting polymer that would compromise its mechanical properties, aside from reactivity and availability. Based on these considerations, 2-chloroanthraquinone (2-ClAQ), a small molecule HAT photocatalyst, was selected as a prototypical catalyst for polyolefin activation.<sup>26</sup> Upon illumination, photoexcited 2-ClAQ species feature highly electrophilic oxygen centers, which abstract H atoms from electron-rich polyolefins. The resulting nucleophilic carbon-centered polyolefin radicals then react with the Michael acceptors—olefins connected to electron-withdrawing functional groups—via conjugated

addition. The functionalized polyolefins are produced by hydrogen back-donation, simultaneously regenerating 2-ClAQ (Fig. 1c).

## Preparation and characterization of functionalized polyolefins

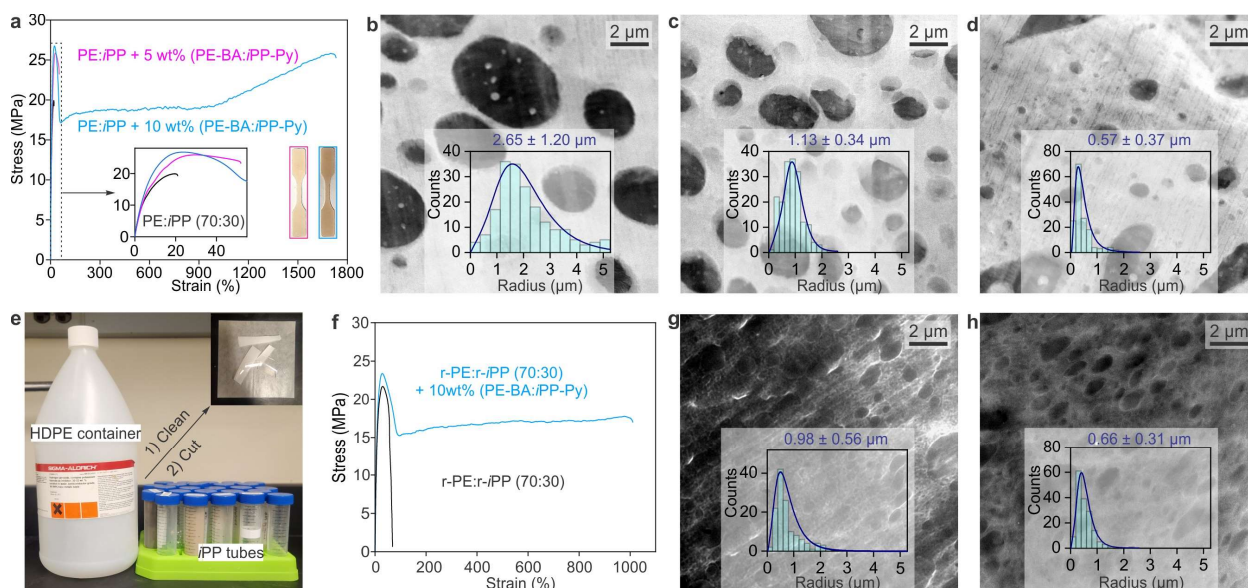


**Fig. 2. Synthesis of PE-BA and iPP-Py and their characterization.** (a) Synthetic scheme of functionalized polyolefins with 2-ClAQ. (b) Representative  $^1\text{H}$  NMR spectrum of HDPE-BA. The peak at ca. 2.41 ppm corresponds to dimethyl sulfoxide, which was added to facilitate the dissolution of the polymer. (c) TGA traces of HDPE and HDPE-BA with varying degrees of functionalization. (d) Representative  $^1\text{H}$  NMR spectrum of iPP-Py. (e) TGA traces of iPP and iPP-Py with varying degrees of functionalization.

Given their availability and feasibility as acceptors for Michael-type radical addition reactions, 4-vinylbenzoic acid (v-BA) and 4-vinylpyridine (v-Py) were chosen for the functionalization reactions. A typical reaction involved 0.115 mol% of 2-ClAQ, 10 mol% of v-BA (or 20 mol% v-Py, with all mol% compared to the repeat unit of polyolefins), and PE or *i*PP in PhCl with 365 nm or 395 nm light irradiation at 110 °C (**Fig. 2a**). The successful functionalization and degree of functionality were determined by proton nuclear magnetic resonance (<sup>1</sup>H NMR) spectra. With varying reaction times, a functionality degree ranging from 0.3 mol% to 5.8 mol% was obtained (Supplementary Table 1). In the cases of PE-BA, the signals of alkenes were neglectable, indicating that the β-scission side reactions were minimum under the reaction conditions (**Fig. 2b**). This observation is also supported by the slightly reduced number-average molecular weight ( $M_n$ ) determined by high-temperature size-exclusion chromatography (HT SEC) analysis (Supplementary Fig. 2). Although *i*PP has a propensity for β-scission under radical-mediated conditions, only a small amount of degradation products was detected (< 0.2 mol%), benefiting from the high reactivity of the acceptors (**Fig. 2d**). The  $M_n$  of *i*PP-Py decreased with increasing functionality degree (Supplementary Fig. 2). Thermogravimetric analysis (TGA) indicated that the functionalized polyolefins maintained high thermal stability compared to their virgin counterparts (**Fig. 2c and e**). The differential scanning calorimetry (DSC) measurements showed that the introduction of a small portion of functional groups had little impact on the melting temperatures and crystallization temperatures (Supplementary Fig. 3 and 4). Additionally, the semicrystalline structures and features of HDPE and *i*PP remained intact after modification with BA and Py, as shown in their wide-angle X-ray scattering (WAXS) profiles (Supplementary Fig. 5 and 6). All characterization results demonstrated the newly achieved polymers exhibited thermal and physical properties similar to their parent ones.



## Compatibilization of HDPE/*i*PP blends with functionalized polyolefins



**Fig. 3. Compatibilization tests of HDPE/*i*PP blends with functionalized polyolefins as ABCs. (a)** Representative uniaxial tensile elongation experiments of blends of 70/30 HDPE/*i*PP with varying HDPE-BA/*i*PP-Py content. **(b–d)** Representative HAADF-STEM images of blends of 70/30 HDPE/*i*PP with varying HDPE-BA/*i*PP-Py content. **(e)** Photograph of a post-consumer HDPE container (r-PE) and *i*PP tubes (r-*i*PP) for compatibilization of real-world mixed plastics. **(f)** Representative uniaxial tensile elongation experiments of blends of 70/30 rPE/r*i*PP without (black) and with 10 wt% (blue) HDPE-BA/*i*PP-Py. **(g and h)** Representative HAADF-STEM images of 70/30 rPE/r*i*PP without **(g)** and with **(h)** 10 wt% HDPE-BA/*i*PP-Py. Insets in **b–d, g and h** are histograms of the size distribution of *i*PP grains (see details for domain statistics of TEM images in Supplementary Information and Supplementary Fig. 1).

The key to acid- and base-functionalized polymers performing as compatibilizers is the interactions between the acid and base functional groups. Due to the relatively small difference in  $pK_a$  values for BA and Py ( $\Delta pK_a \approx 1.77$ ), an un-ionized H-bonding interaction was anticipated and confirmed by Fourier-transform infrared spectroscopy (FTIR) analysis.<sup>27</sup> A uniform mixture of HDPE-BA and *i*PP-Py with the same molar amount of BA and Py functional groups as ABCs was prepared through dissolution and reprecipitation, whose FTIR spectrum was compared with

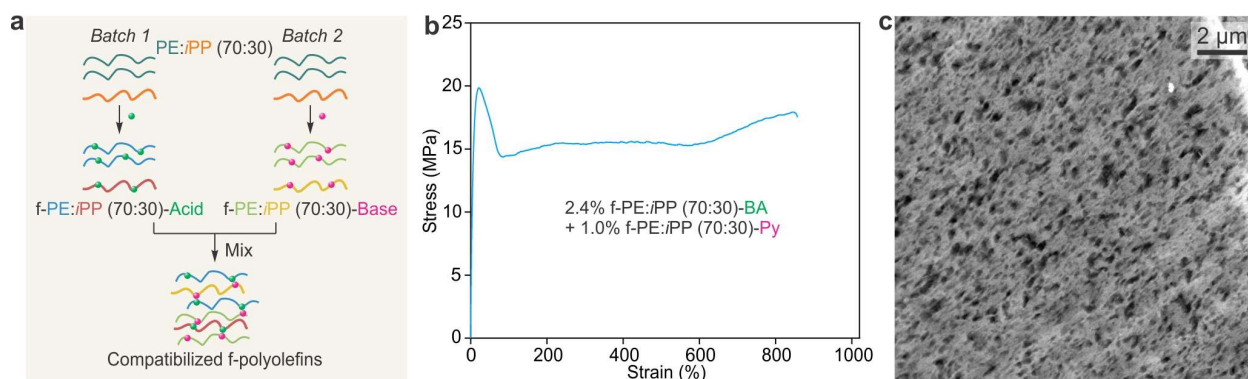
those of the individual components. The C=O stretch in the mixture shifted from 1693  $\text{cm}^{-1}$  to 1699  $\text{cm}^{-1}$ , indicating the un-ionized H bond formation between BA and Py moieties (Supplementary Fig. 7). The interaction observed with a small portion of acid and base in the polymers supported their functionality in compatibilizing HDPE/*i*PP blends. To test this hypothesis, a specific amount of ABCs (a mixture of 1.4%-HDPE-BA and 1.4%-*i*PP-Py) was added to a polyolefin blend containing 70 wt% HDPE and 30 wt% *i*PP, with this mixture representing typical polyolefin municipal waste. Due to phase separation and fragile interfaces in the blend of PE and *i*PP, the PE/*i*PP blend lost the original ductility of the individual components, exhibiting poor mechanical properties ( $\epsilon_b = 21\%$ ) (**Fig. 3a** and Supplementary Fig. 8). With the addition of 5 wt% of ABCs, the mechanical properties of the blend moderately improved, with an  $\epsilon_b$  of 52% measured. Strikingly, when the amount of ABCs increased to 10 wt%, a remarkable 82-fold enhancement in ductility ( $\epsilon_b = 1730\%$ ) was achieved (**Fig. 3a**). The effective compatibilization of polyolefin blends with the addition of ABC was further illustrated by the reduction of *i*PP grain size, as observed in the high-angle annular dark-field scanning transmission spectroscopy (HAADF-STEM) images (**Fig. 3b–d**). The average radii of *i*PP grains were reduced from 2.65  $\mu\text{m}$  to 1.13  $\mu\text{m}$  with 5 wt% ABC and to 0.57  $\mu\text{m}$  with 10 wt% ABCs (see the supplementary materials for the probability density function used to calculate the 3-dimensional domain sizes).

Moreover, the acid-base compatibilization can be readily applied to real-world mixed plastic waste (**Fig. 3e–h**). Commonly used chemical containers made of HDPE (hereafter denoted as r-PE, where r represents recycled) and centrifuge tubes made of *i*PP (denoted as r-*i*PP) were cleaned, cut into pieces, and used for mechanical tests without further treatments. The blend of r-PE and r-*i*PP (70:30) exhibited an  $\epsilon_b$  of 60%. The average grain size of r-*i*PP was *ca.* 0.98  $\mu\text{m}$  (**Fig. 3g**). With the addition of 10 wt% ABCs, the tensile properties significantly improved, showing a 17-fold increase in  $\epsilon_b$  (1011% versus 60%) (**Fig. 3f**). The average radius of *i*PP droplets was also further



reduced (**Fig. 3g** and **3h**), strongly supporting the improved compatibilization in post-consumer polyolefin blends. The reduced domain sizes and stress transfer between phases were evidenced by scanning electron microscopy (SEM) images of the fractured blend surfaces for both pure and post-consumer polyolefin blends (Supplementary Fig. 9 and 10). Taken together, we demonstrated that the introduction of 10 wt% ABCs, synthesized through post-polymerization functionalization, restores ductility to the polyolefin blends, promising the reuse of recycled polyolefins.

### Direct functionalization of HDPE/*i*PP blends and compatibilization



**Fig. 4. Compatibilization of HDPE and *i*PP via direct functionalization of their blends and *in situ* generated acid-base interactions.** (a) Schematic illustration. Representative uniaxial tensile elongation experiment (b) and representative HAADF-STEM image (c) of blend of f-PE:*i*PP (70:30)-BA and f-PE:*i*PP (70:30)-Py.

With encouraging results demonstrated by using individually functionalized PE and *i*PP as ABCs, we next took the scheme one step further and aimed to directly functionalize HDPE/*i*PP blends. This approach would allow for the direct utilization of mixed polyolefin waste without the need to separately synthesize compatibilizers. Instead of pursuing selective functionalization, we propose that introducing respective acid and base groups to two separate batches of polyolefin blends will result in acid-base interactions between components once they are blended, achieving compatibilization of the otherwise immiscible materials (**Fig. 4a**). Given that the HAT-initiated

modification strategy can introduce acid or base units onto both PE and *i*PP chains, we anticipate that such reactions will occur on both components when a blend is employed. To test this hypothesis, we prepared BA- and Py-functionalized HDPE:*i*PP blends. Since the functional groups on HDPE and *i*PP are indistinguishable in <sup>1</sup>H NMR spectra, we calculated average functional degrees to demonstrate the amounts of BA and Py functional groups in the blends. Similar to the preparation of ABCs, two blends respectively functionalized with BA and Py were mixed with the same molar amount of functional groups. An  $\epsilon_b$  of 857% was detected, representing a 41-fold enhancement compared to the HDPE/*i*PP blend (**Fig. 4b**). The *i*PP domain sizes observed in the compatibilized blends were significantly reduced in comparison to neat HDPE/*i*PP blends (**Fig. 3b and 4c**), which was corroborated by the SEM images of the fractured blend surfaces (Supplementary Fig. 11), demonstrating the effectiveness of this strategy. The reactions were effectively applied to the post-consumer polyolefin blends without requiring further treatment or purification, aside from minimum washing to remove contaminants (Supplementary Table 1). This result demonstrates the practical applicability of the current methods for direct utilization in processing real-world plastic waste.

## Conclusions

Overall, we have demonstrated the effective compatibilization of HDPE and *i*PP using ABCs through a straightforward and cost-effective strategy. This strategy involves directly functionalizing polyolefins by installing acid and base units onto the polyolefin molecular chains via photocatalytic HAT-initiated Michael-type radical addition reactions. By incorporating 10 wt% of ABCs with a functionality degree of approximately 1 mol%, the HDPE/*i*PP blend exhibited significantly improved mechanical properties, with of an  $\epsilon_b$  of 1730%, representing an 82-fold enhancement in ductility compared to the untreated blends. Additionally, we demonstrated successful compatibilization in post-consumer plastic blends. Furthermore, PE/*i*PP blends,

including those from post-consumer sources, can undergo modification under the same reaction conditions, yielding materials with excellent ductility when the resulting acid- and base-modified blends are combined. The compatibilization strategy reported here offers a practical, low-cost solution for reusing mixed plastics, demonstrating both superior compatibilization and proven practicality.

## References

1. Geyer, R., Jambeck, J. R. & Law, K. L. Production, use, and fate of all plastics ever made. *Sci. Adv.* **3**, e1700782 (2017).
2. Schyns, Z. O. G. & Shaver, M. P. Mechanical recycling of packaging plastics: a review. *Macromol. Rapid Commun.* **42**, 2000415 (2021).
3. Teh, J. W., Rudin, A. & Keung, J. C. A review of polyethylene–polypropylene blends and their compatibilization. *Adv. Polym. Technol.* **13**, 1–23 (1994).
4. Koning, C., Van Duin, M., Pagnoulle, C. & Jerome, R. Strategies for compatibilization of polymer blends. *Prog. Polym. Sci.* **23**, 707–757 (1998).
5. Eagan, J. M. *et al.* Combining polyethylene and polypropylene: Enhanced performance with PE/*i*PP multiblock polymers. *Science* **355**, 814–816 (2017).
6. Klimovica, K. *et al.* Compatibilization of *i*PP/HDPE blends with PE-*g*-*i*PP graft copolymers. *ACS Macro Lett.* **9**, 1161–1166 (2020).
7. Shen, L. *et al.* Threading-the-Needle: Compatibilization of HDPE/*i*PP blends with butadiene-derived polyolefin block copolymers. *Proc. Natl. Acad. Sci.* **120**, e2301352120 (2023).
8. López-Barrón, C. R. & Tsou, A. H. Strain hardening of polyethylene/polypropylene blends via interfacial reinforcement with poly(ethylene-*cb*-propylene) comb block copolymers. *Macromolecules* **50**, 2986–2995 (2017).

- 232 9. Lin, T.-W. *et al.* Advances in nonreactive polymer compatibilizers for commodity polyolefin  
233 blends. *Chem. Rev.* **124**, 9609–9632 (2024).
- 234 10. Clarke, R. W. *et al.* Dynamic crosslinking compatibilizes immiscible mixed plastics. *Nature*  
235 **616**, 731–739 (2023).
- 236 11. Vialon, T. *et al.* Upcycling polyolefin blends into high-performance materials by exploiting  
237 azidotriazine chemistry using reactive extrusion. *J. Am. Chem. Soc.* **146**, 2673–2684 (2024).
- 238 12. Yokoyama, K. & Guan, Z. A vitrimer acts as a compatibilizer for polyethylene and  
239 polypropylene blends. *Angew. Chem. Int. Ed.* **63**, e202317264 (2024).
- 240 13. Fredrickson, G. H. *et al.* Ionic compatibilization of polymers. *ACS Polym. Au* **2**, 299–312  
241 (2022).
- 242 14. Xie, S. *et al.* Compatibilization of polymer blends by ionic bonding. *Macromolecules* **56**,  
243 3617–3630 (2023).
- 244 15. Boasen, N. K. & Hillmyer, M. A. Post-polymerization functionalization of polyolefins. *Chem.*  
245 *Soc. Rev.* **34**, 267–275 (2005).
- 246 16. Gloor, P. E., Tang, Y., Kostanska, A. E. & Hamielec, A. E. Chemical modification of  
247 polyolefins by free radical mechanisms: a modelling and experimental study of simultaneous  
248 random scission, branching and crosslinking. *Polymer* **35**, 1012–1030 (1994).
- 249 17. Fazekas, T. J. *et al.* Diversification of aliphatic C–H bonds in small molecules and  
250 polyolefins through radical chain transfer. *Science* **375**, 545–550 (2022).
- 251 18. Williamson, J. B., Lewis, S. E., Johnson III, R. R., Manning, I. M. & Leibfarth, F. A. C–H  
252 functionalization of commodity polymers. *Angew. Chem. Int. Ed.* **58**, 8654–8668 (2019).
- 253 19. Plummer, C. M., Li, L. & Chen, Y. The post-modification of polyolefins with emerging  
254 synthetic methods. *Polym. Chem.* **11**, 6862–6872 (2020).

20. Williamson, J. B. *et al.* Chemo- and regioselective functionalization of isotactic polypropylene: a mechanistic and structure–property Study. *J. Am. Chem. Soc.* **141**, 12815–12823 (2019).
21. Chen, L. *et al.* Selective, catalytic oxidations of C–H bonds in polyethylenes produce functional materials with enhanced adhesion. *Chem* **7**, 137–145 (2021).
22. Jasinska-Walc, L., Bouyahyi, M. & Duchateau, R. Potential of functionalized polyolefins in a sustainable polymer economy: synthetic strategies and applications. *Acc. Chem. Res.* **55**, 1985–1996 (2022).
23. Plummer, C. M. *et al.* A direct functionalization of polyolefins for blend compatibilization by an insertion of 1,1-bis(phenylsulfonyl)ethylene (BPSE). *Polym. Chem.* **10**, 3325–3333 (2019).
24. Ciccio, N. R. *et al.* Diverse functional polyethylenes by catalytic amination. *Science* **381**, 1433–1440 (2023).
25. Capaldo, L., Ravelli, D. & Fagnoni, M. Direct photocatalyzed hydrogen atom transfer (HAT) for aliphatic C–H bonds elaboration. *Chem. Rev.* **122**, 1875–1924 (2022).
26. Kamijo, S. *et al.* Alkylation of nonacidic C(sp<sup>3</sup>)–H bonds by photoinduced catalytic Michael-type radical addition. *Org. Lett.* **18**, 4912–4915 (2016).
27. Johnson, S. L. & Rumon, K. A. Infrared spectra of solid 1:1 pyridine-benzoic acid complexes; the nature of the hydrogen bond as a function of the acid-base levels in the complex. *J. Phys. Chem.* **69**, 74–86 (1965).

## Data availability

All data are available in the main text or the Supplementary Information.

## **Supplementary information**

Materials and Methods, Supplementary Figures 1–11 and Supplementary Table 1.

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## **Author contributions**

Y.Y., J.A.B., M.Z., J.N., and D.W. conceived the project. Y.Y., J.H., J.L., J.S., M.-C.W., T.G., and J.W. conducted the experiments. Y.Y., J.H., J.L., J.S., J.A.B., M.Z., J.N., and D.W. analysed the data. Y.Y. designed the figures. Y.Y. wrote the original draft; M.Z., J.N., J.L., J.H., and D.W. reviewed and edited the manuscript. D.W. M.Z., and J.N. supervised the project. All authors discussed the results and contributed to the final manuscript.

## **Competing interests**

Authors declare that they have no competing interests.

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