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Efficient and Robust Dynamic Crosslinking for Compatibilizing Immiscible Mixed Plastics through In Situ Generated Singlet Nitrenes

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Creating a sustainable economy for plastics demands the exploration of new strategies for efficient management of mixed plastic waste. The inherent incompatibility of different plastics poses a major challenge in plastic mechanical recycling, resulting in phase-separated materials with inferior mechanical properties. Here, this study presents a robust and efficient dynamic crosslinking chemistry that effectively compatibilizes mixed plastics. Composed of aromatic sulfonyl azides, the dynamic crosslinker shows high thermal stability and generates singlet nitrene species in situ during solvent-free melt-extrusion, effectively promoting C—H insertion across diverse plastics. This new method demonstrates successful compatibilization of binary polymer blends and model mixed plastics, enhancing mechanical performance and improving phase morphology. It holds promise for managing mixed plastic waste, supporting a more sustainable lifecycle for plastics.

1. Introduction

The inherent incompatibility of polymers presents a fundamental challenge in creating polymer blends[1] and recycling mixed plastic waste.[2] Due to minimal entropic contribution in polymer mixing, the majority of plastics are immiscible unless there are favorable enthalpic interactions between them.[3–5] Such general incompatibility results in phase separation and weak interfacial adhesion within polymer blends, yielding materials with inferior mechanical properties. Conventional compatibilization methods, including nonreactive and reactive approaches, require tailored designs specific to the chemical compositions of the polymers.[6] This customized approach not only hinders the advancement of innovative polymer blends, but also becomes impractical for the compatibilization of mixed plastic waste due to its complex nature. Such waste typically comprises a mixture of polar and nonpolar polymers with ever-changing compositions. Despite the emergence of various innovative recycling and upcycling methods for plastics,[7–17] an effective solution for recycling mixed plastic waste remains elusive.[18] There is a pressing need to devise an efficient method for the general compatibilization of immiscible mixed polymers to enable effective plastic recycling.

Toward this direction, recently Clarke et al.[19] and our lab[20] independently introduced a novel strategy using dynamic covalent crosslinking for the compatibilization of mixed polymers. The creation of dynamic covalent bridges between different polymers enhances their compatibility, and the reversible nature of dynamic covalent crosslinks allows for thermal reprocessability, drawing inspiration from the principles pioneered in covalent adaptable networks[21] and vitrimers.[22] Indeed, recent efforts to exploit dynamic covalent chemistry in phase-separated vitrimers has given rise to tunable mechanical properties based on morphology,[23] as well as high-throughput reprocessing.[24] In the work of Clarke et al.,[19] dynamic crosslinking was achieved through interchain double C—H insertion of carbene intermediates formed from bis(diazirine)-based dynamic crosslinkers, following an earlier design introduced by Lepage et al.[25] In our prior work,[20] dynamic crosslinking was introduced through in situ radical grafting by reactive extrusion. While these innovations mark major strides toward recycling mixed plastic waste, both systems have practical limitations. The radical grafting method involved in our prior study[20] suffers from low efficiency and can cause polymer degradation through β-scission.[26] While the carbene insertion mechanism adopted by Clarke et al.[19] and Lepage et al.[25] addresses issues associated with radical processes, the laborious and costly multistep synthesis of bis(diazirine)-based crosslinkers, combined with processes involving solvent-coating and oven baking, presents practical

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The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/adma.202406203

DOI: 10.1002/adma.202406203

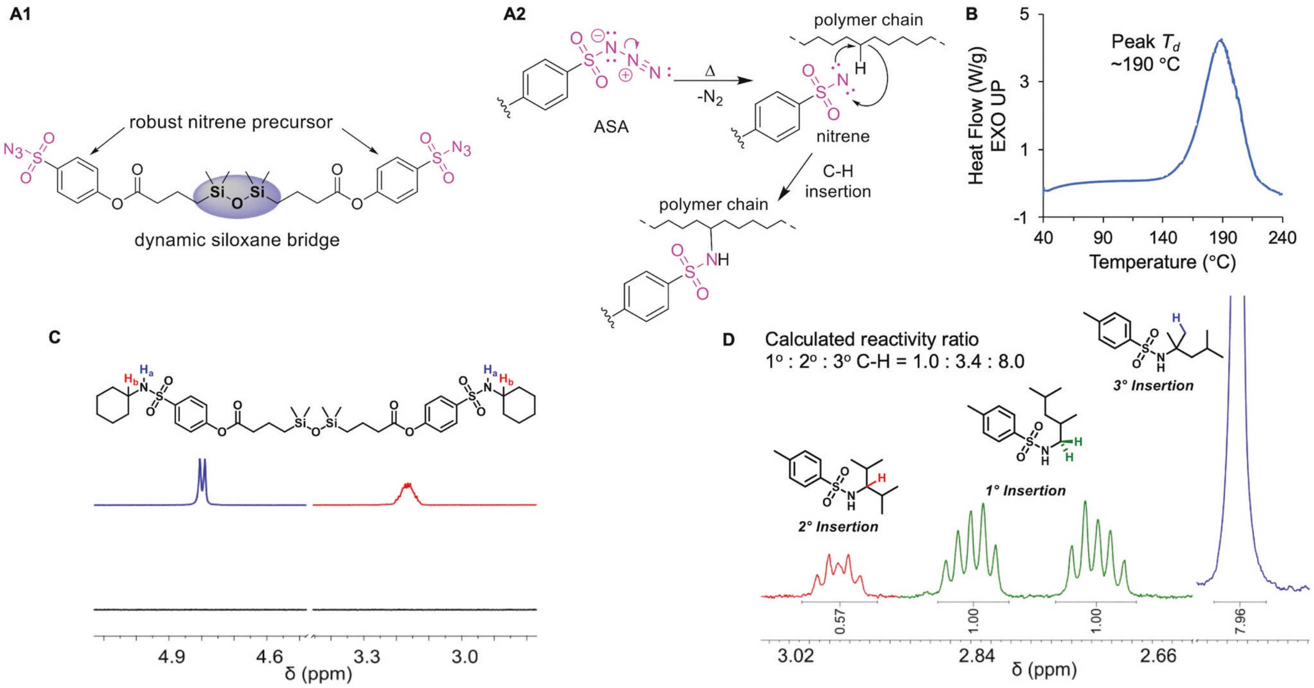

Figure 1. Design of bis-ASA dynamic crosslinker and model studies. A) Design of bis-ASA dynamic crosslinker (A1) and C—H insertion of the singlet nitrene intermediate upon thermal decomposition of the azide (A2). B) DSC thermogram of bis-ASA crosslinker. C) Stacked ^{1}H spectra of the bis-ASA crosslinker in cyclohexane before (black) and after (colored) heating at 180 °C for 3 h. Only key diagnostic peaks are shown in the spectra. D) ^{1}H spectrum of tosyl azide in 2,4-dimethylpentane after heating at 180 °C for 1 h. Only key peaks used for calculating the reactivity ratio are shown. The reactivity ratio for the nitrene insertion to 1°:2°:3° C—H bonds was calculated to be 1.0:3.4:8.0.

challenges. Furthermore, the relatively low temperature for generating reactive carbene species (≈138 °C) limits practical application for many plastics, as most undergo melt-processing at or above 180 °C. A robust, efficient, and temperature-matched dynamic crosslinking chemistry is critically needed for compatibilizing immiscible mixed plastics.

Herein, we report a new dynamic crosslinking chemistry for improving compatibility in immiscible mixed polymers. The new dynamic crosslinker features a central siloxane linkage flanked by two aromatic sulfonyl azides (ASA) on both ends (**Figure** 1A1). ASA motifs have been reported previously for polymer functionalization[27] and crosslinking.[28] Analogous to the diazirine/carbene system, the thermal decomposition of aromatic sulfonyl azides generates highly reactive singlet nitrene species capable of inserting into almost any C—H bond[29] in diverse polymers to induce dynamic crosslinking. Notably, the nitrene system exhibits a distinct advantage over the carbene analog, as ASA decomposes at a significantly higher temperature in creating nitrene species (peak decomposition at ≈190 °C for ASA, Figure 1B, compared to ≈138 °C for diazirine[19,25]), rendering it suitable for the typical melt-processing of numerous commodity plastics. In addition, our new dynamic crosslinker is easily accessible through a two-step synthesis from readily available commercial starting materials. Our selection of the siloxane bridge as the dynamic covalent motif is informed by its demonstrated reversible exchange chemistry at elevated temperatures in the presence of a mild fluoride catalyst, along with its high stability against hydrolysis, oxidation, and thermal conditions as shown in our prior work.[20] By integrating the robust ASA motif with the stable siloxane dynamic covalent bond (Figure 1A1), we create a robust and temperature-matched dynamic crosslinker for compatibilizing immiscible mixed plastics.

2. Results and Discussion

2.1. Small Molecule Model Studies

The symmetric bis-ASA dynamic crosslinker was conveniently synthesized in two steps with good yield (Schemes S1 and S2, Supporting Information). Prior studies indicate that thermally-induced decomposition of sulfonyl azides generates highly reactive singlet nitrene species capable of insertion into both aliphatic and aromatic C—H bonds[29,30] (Figure 1A2), facilitating organic transformation,[31] polymer functionalization,[27] and crosslinking.[28] To ensure our designed bis-ASA is suitable at typical plastic melt-processing temperatures, the thermal decomposition of the synthesized bis-ASA crosslinker was monitored by differential scanning calorimetry (DSC), revealing a peak decomposition at 190 °C (Figure 1B). This is more than 50 °C higher than the peak decomposition temperature of the bis-diazirine crosslinkers reported previously,[19,25] representing a notable advance as most plastics are melt-processed at or above 180 °C industrially. Furthermore, sulfonyl azides thermally decompose to form a long-lived singlet state nitrene capable of direct C—H insertion.[29] This was confirmed by heating the bis-ASA crosslinker in cyclohexane at 180 °C for 3 h(Figure 1C and Scheme S5, Supporting Information). Using cyclohexane as a

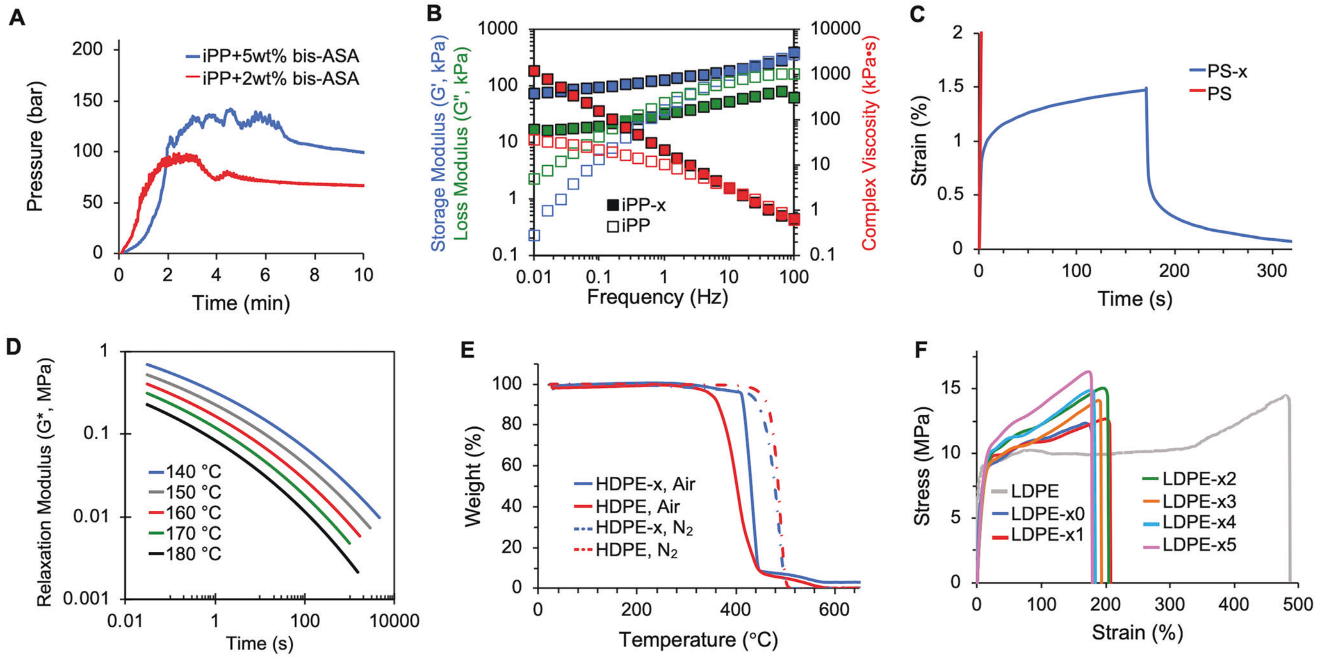

Figure 2. Dynamic crosslinking of pure plastics. A) Pressure evolution during extrusion of iPP-*x* with varying bis-ASA concentrations. B) Rheology data for iPP and iPP-*x* at 200 °C under different shear frequency. C) Creep recovery test of PS and PS-*x* at 190 °C for 180 s under a stress of 500 Pa, followed by recovery for 180 s. D) Stress relaxation of PETg-x at various temperatures with data fitted by the stretched exponential model. E) TGA thermograms of HDPE and HDPE-*x* under atmospheres of nitrogen and air. F) Uniaxial tensile testing of LDPE-*x* over five reprocessing cycles.

model alkane, the bis-ASA(Cy)$_2$ adduct was obtained in yields on par with the analogous carbene reaction for the bis-diazirine crosslinkers heated in cyclohexane at 130 °C.[19,25] To further assess the reactivity of singlet nitrenes toward different type of C—H bonds, another model reaction was conducted by heating an aromatic sulfonyl azide (tosyl azide) in 2,4-dimethylpentane, the smallest symmetrical molecule containing primary, secondary, and tertiary C—H bonds.[29] Thermal decomposition of tosyl azide in 2,4-dimethylpentane at 180 °C for 1 h led to the generation of three regioisomers (Scheme S4, Supporting Information). From ^{1}H NMR (Figure 1D and Figures S3–S11, Supporting Information), the reactivity ratio for the singlet nitrene insertion toward primary, secondary, and tertiary C—H bonds was calculated to be 1:3.4:8.0. The enhanced reactivity of more substituted C—H bonds for nitrene insertion is presumably due to their increased electron density, a result of hyperconjugation.[32] These model studies demonstrates the suitability of the bis-ASA crosslinker toward the demanding processing temperatures of commodity plastics.

2.2. Dynamic Crosslinking of Single Polymers

Next, we proved the general applicability of bis-ASA crosslinker for in situ dynamic crosslinking of a variety of plastics, including both chain-growth (PS, LDPE, HDPE, iPP) and step-growth (PETg) polymers. To show practical relevance and potential scalability, all in situ crosslinking reactions were carried out by simple *solvent-free* melt-extrusion at 180–190 °C using a twin-screw extruder. This is in contrast to the previously reported bis-diazirine polymer crosslinking which typically begins by solvent-coating the crosslinker onto polymers followed by an oven-baking process at 130 °C.[19,25] To achieve optimal crosslinking efficiency, various parameters play a role, with a crucial consideration being the synchronization of reactive species generation with processing time. This is important for radical-based crosslinking in polymer reactive extrusion, where the choice of radical initiators is made by aligning their half-life with the extrusion residence time. We envision that a similar kinetic match is important for the reactive carbene or nitrene species. Based on reported kinetic data,[29,33] the estimated half-lives for generating reactive carbene from diazirine and nitrene from ASA are 7.3 s and 4.55 min at 180 °C, respectively. With a typical reactive extrusion residence time of ≈5–20 min, the nitrene generation kinetics of our bis-ASA crosslinker align seamlessly with standard plastic melt-processing temperatures.

Commodity plastics, including HDPE, LDPE, iPP, PS, and PETg, were individually melt-blended with differing amounts of bis-ASA (1–5 wt%) at 180 °C for 10 min (Table S1, Supporting Information). During reactive extrusion, the bis-ASA crosslinker thermally decomposes, creating a reactive singlet nitrene species in situ, which efficiently inserts into C—H bonds on different polymer chains,[29] leading to dynamic crosslinking. This process is evidenced by the increasing extruder pressure over time, with larger loadings of the bis-ASA crosslinker causing more significant pressure changes (**Figure 2A**). The in situ crosslinking was confirmed by quantifying the gel fraction for all extruded polymers in good solvents under extended heat (Tables S3–S7, Supporting Information), which revealed some differences in the extent of network formation for different polymers. For example, while 5 wt% of bis-ASA yielded a gel fraction of 36% for HDPE, only 2 wt% of bis-ASA is needed to afford 72% gel fraction for iPP. Given that our small molecule model reaction demonstrates increased reactivity of singlet nitrene toward tertiary C—H bonds (Figure 1D), the higher gel fraction observed in iPP is likely due to higher reactivity of the singlet nitrene with the abundant tertiary C—H bonds present in iPP chains. However, the variation in molecular weight between the two polymers may also contribute to differences in gel fraction. To further verify the crosslinking was formed by the bis-ASA dynamic crosslinker, crosslinked HDPE was shown to completely dissolve in xylenes with the addition of excess tetrabutylammonium fluoride (TBAF), indicating that all crosslinks are formed by the siloxane-containing bis-ASA crosslinker in the networks (Figure S15 and Scheme S7, Supporting Information).[20] Moreover, differential scanning calorimetry (DSC) revealed that all samples modified with the bis-ASA crosslinker had reduced degrees of crystallinity; for example, in HDPE the crystallinity decreased from 59% in the control to 48% in the material crosslinked with 5 wt% bis-ASA (Figures S29–S32, Supporting Information). However, the crystallinity of the modified HDPE could be recovered to 58.73% after annealing at 100 °C for 16 h (Figure S30, Supporting Information), suggesting that the exchange of the dynamic crosslinkers upon heating allows for chain rearrangements during the annealing process.

In alignment with the principles of vitrimer design,[20,22,34–39] the dynamic crosslinking of pure plastics through our bis-ASA technology was able to endow the plastics with thermoset performance and thermoplastic recyclability. Indeed, bis-ASA dynamic crosslinking significantly improved the mechanical performance of thermoplastics while maintaining excellent thermal reprocessability. Above the melting transition of a given polymer, the storage modulus of the dynamically crosslinked sample was typically two to three orders of magnitude greater than the control samples at low shearing frequency. However, the dynamically crosslinked plastics exhibited more pronounced shear dependence,[20] allowing the materials to attain low viscosities comparable to those of their linear counterparts at high shearing frequency (Figure 2B and Figures S25–S28, Supporting Information). The crosslinked polymers displayed enhanced creep resistance compared to the linear polymers (Figure 2C and Figures S16–S19, Supporting Information). For example, while linear PS had a low melt strength and flowed easily at 190 °C, the dynamically crosslinked PS (designated as PS-*x*, the same notation is used for other samples) showed substantial creep resistance and excellent creep recovery at this temperature (Figure 2C). The dynamic exchange of the siloxane bridges enables the reconfiguration of network topology, thus allowing the crosslinked network to access flow-state reprocessing at elevated temperatures. This was first demonstrated by stress-relaxation at elevated temperatures (Figure 2D and Figures S20A, S21–S24, Supporting Information). For example, variable temperature stress relaxation of the PETg-*x* revealed an Arrhenius temperature dependence with an apparent activation energy (E_a) of 101.4 kJ mol^{-1} (Figure 2D and Figure S20B, Supporting Information), indicating dynamic exchange for the F$^-$-catalyzed siloxane exchange at high temperature.[20] This suggests that the bis-ASA crosslinked plastics are well-suited for typical melt-processing under high-shear environments. Finally, the thermal stability of the bis-ASA crosslinked materials was compared with their linear controls by thermogravimetric analysis (TGA), which showed negligible differences under an atmosphere of nitrogen, whereas under air, the temperature of half decomposition ($T_{d,1/2}$) increased by 29 °C in the HDPE-*x* relative to its control, revealing an increase in the oxidative stability (Figure 2E and Figures S33–S38, Supporting Information). These data validate the robustness of the bis-ASA crosslinking chemistry.

The stability of both the ASA motif and the siloxane dynamic linkage combined with the fluoride-catalyzed fast siloxane exchange[20] allowed us to reprocess the crosslinked samples repetitively without reducing the mechanical properties (Figure 2F). The strain-at-break for the bis-ASA crosslinked samples is lower than their linear polymer controls, which is expected because crosslinking is known to inhibit elongation. The reduction in extensibility is compensated by the significantly enhaced mechanical strength, highlighting a true advantage of dynamic crosslinking (Figure 2F, Figure S39–S41, Supporting Information). Taking together the data presented so far, we have developed an easily accessible bis-ASA dynamic crosslinker that can efficiently introduce dynamic crosslinks onto various plastics through solvent-free melt-extrusion at industrially relevant temperatures. This offers a robust and scalable dynamic crosslinking chemistry that we will further investigate for compatibilizing immiscible plastics.

2.3. Compatibilization of Binary Polymer Blends

To demonstrate the applicability of bis-ASA crosslinking chemistry for compatibilizing immiscible polymers,[19,20] we melt-blended mixed plastics with bis-ASA crosslinker by solvent-free reactive extrusion at 180 or 190 °C. For initial study, a binary blend of LDPE (nonpolar) and PETg (polar) in a ratio of 60:40 by mass was melt-processed at 180 °C by the aforementioned reactive extrusion method with 3.5 wt% bis-ASA crosslinker (**Figure 3**A, Table S2, Supporting Information). The LDPE/PETg blend was selected for the stark differences in chemical structure and polarity, effectively demonstrating the efficacy of our method. During extrusion processing, there was an increase in extruder pressure for the polymer blend with bis-ASA as compared to its control (Figure 3B), indicating dynamic crosslinking during the extrusion. In addition, upon uniaxial tensile testing, the dynamically crosslinked blend showed 203% improvement in its strain-at-break and 276% improvement in toughness (Figure 3C). During DMTA analysis, the resulting dynamically crosslinked blend exhibited sustained mechanical integrity beyond the glass transition of PETg and the melting temperature of LDPE. This robustness was attributed to the presence of the siloxane dynamic crosslinks, which effectively prevented yielding, in contrast to the control blend (Figure 3D). This leads to enhanced dimensional stability at elevated temperatures, showcasing a significant advantage of the dynamically crosslinked blends. For a nonpolar blend of HDPE and iPP (in a 70:30 ratio by mass) melt-extruded at 190 °C, a similar improvement to the mechanical properties was observed for the dynamically crosslinked system (297% improvement in strain-at-break and 247% in toughness, Figure 3E). Although crosslinking normally diminishes polymer extensibility, the enhanced compatibilization of two immiscible

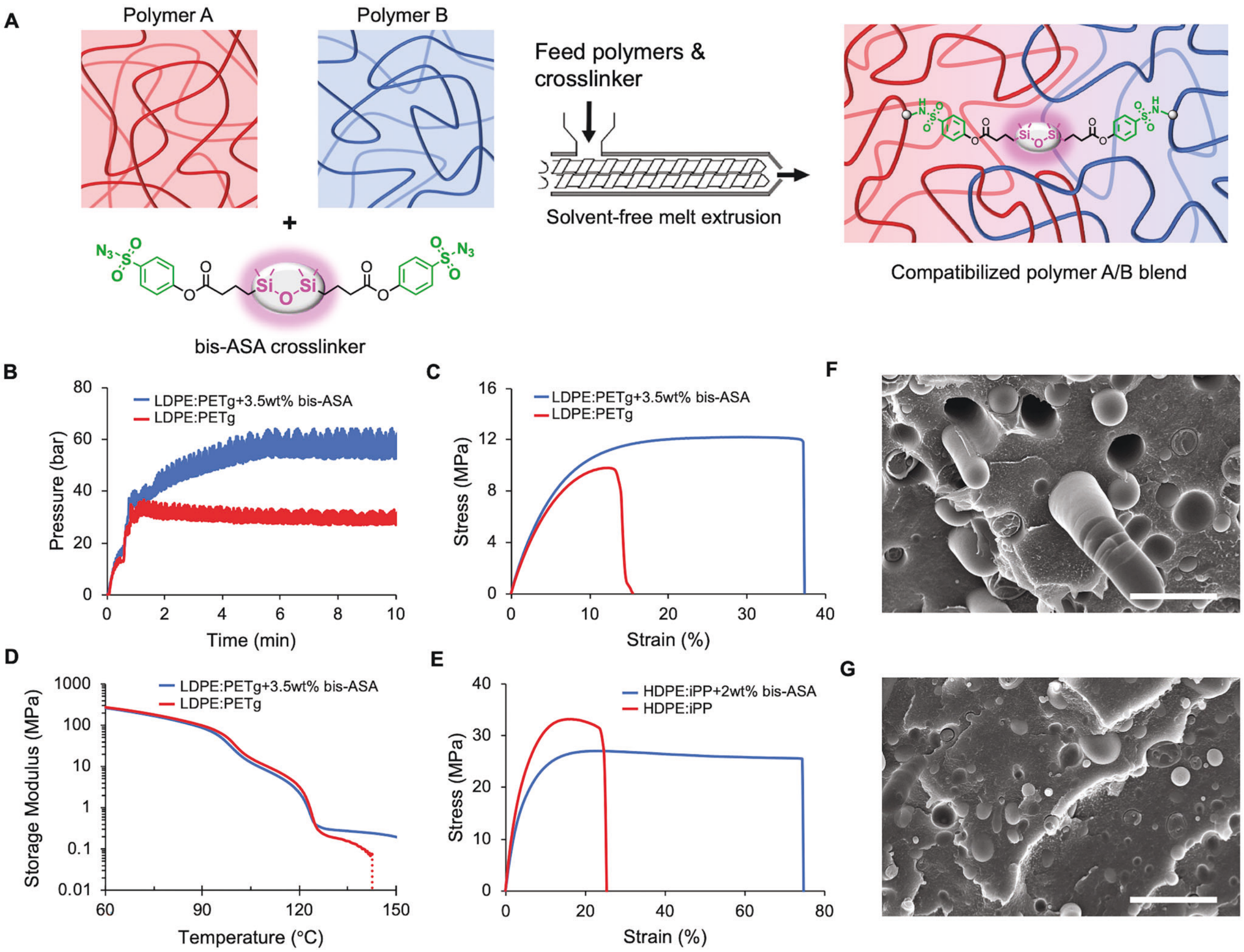

Figure 3. Compatibilization of binary polymer blends through dynamic crosslinking. A) Schematic illustration for compatibilizing two immiscible polymers through dynamic crosslinking via reactive extrusion. B) Pressure evolution during extrusion of LDPE:PETg (60:40) with and without 3.5 wt% bis-ASA. C) Stress–strain curves for binary blends of LDPE:PETg (60:40) made with and without 3.5 wt% bis-ASA. D) DMTA temperature sweeps of a binary blend of LDPE and PETg (60:40) and a sample modified with 3.5 wt% bis-ASA. E) Stress–strain curves for binary blends of HDPE:iPP (70:30) made with or without 2 wt% bis-ASA. F) SEM image of the LDPE:PETg (60:40) control blend and G) its blend made with 3.5 wt% bis-ASA. The scale bar = 10 µm.

polymer phases counteracts this effect, resulting in materials with improved extensibility and toughness. Further quantitation of the soluble fraction in the compatibilized HDPE:iPP sample proved that both HDPE and iPP were dynamically crosslinked during the reactive extrusion process (see Figure S14 and related analysis in the Supporting Information). A recent study reported the in situ generation of triplet state nitrenes for the compatibilization of HDPE/iPP blends.[40] With the diradical character of triplet nitrenes, however, β-scission induced iPP degradation may occur in this system.[26] Scanning electron microscopy (SEM) imaging confirms the improved compatibilization achieved through dynamic crosslinking. The control blend, due to significant differences in chemical structure and polarity between LDPE and PETg, displays extensive phase separation with prominent rod-like structures of PETg dispersed in the LDPE matrix (Figure 3F). In contrast, the LDPE:PETg blend with dynamic crosslinking exhibits enhanced phase mixing, featuring relatively small droplets (Figure 3G).

2.4. Compatibilization of Model Mixed Plastics

The build-up of plastic waste in the environment is a pressing concern,[41,42] often involving complex mixed waste streams containing a variety of polymers. The inherent incompatibility of different plastics prevents direct mechanical recycling of mixed plastic waste.[2,18] To demonstrate the potential applicability of our technology to addressing this critical issue, we collected commodity products made from HDPE (bottle), LDPE (bags), iPP (hanger, straws), PS (disposable plates), and PETg (medical bottles) (**Figure** 4A1), and melt-blended them in a ratio corresponding to their global consumption[41] (Figure 4A2) using solvent-free reactive extrusion in the presence of 1 wt% bis-ASA crosslinker. To showcase the robustness of our technology, these commodity plastics were utilized without any purification, retaining any additives (plasticizers, stabilizers, etc.) present in the samples. The resulting material was analyzed by DMTA, revealing multiple thermal transitions owing to the various glass and

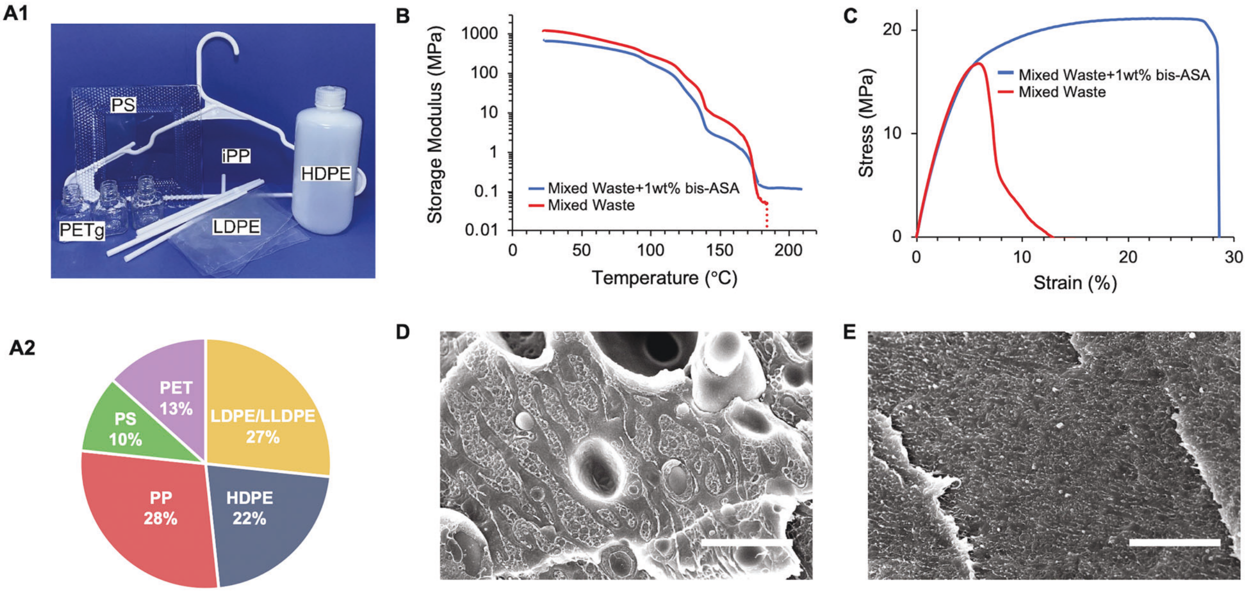

Figure 4. Compatibilization of a simulated mixed plastic waste. A1) Commodity plastic products used to create a simulated mixed plastic waste. The commodity plastic products were used as they are without any purification. A2) The composition of the mixed plastic blends, which is aligned with the relative volume of consumption of these plastic products. B) DMTA temperature sweeps of a mixed plastic waste blend and a sample modified with 1 wt% bis-ASA. The unmodified sample is labeled at the point at which the sample yielded. C) Stress–strain curves for a blend of mixed plastic waste with and without 1 wt% bis-ASA. D) SEM image of the mixed plastic control blend, and E) a compatibilized blend made with 1 wt% bis-ASA. The scale bar = 10 µm.

melting transitions of the constituent polymers (T_g's for PETg and PS at 81 and 105 °C, respectively; and T_m's for LDPE, HDPE, and iPP at 110, 128, and 162 °C, respectively) in the mixed plastic blend, yet the sample modified with 1 wt% bis-ASA crosslinker did not yield after overcoming the highest thermal transition (Figure 4B). Again, the enhanced dimensional stability at elevated temperatures showcases a significant advantage of the dynamically crosslinked blend. Notably, the tensile properties of the dynamically crosslinked mixed plastics demonstrated 214% improvement in its strain-at-break and 500% enhancement in toughness over the control sample, without compromising its tensile strength (Figure 4C). In addition, the model mixed plastics compatibilized with 1 wt% bis-ASA could be subsequently reprocessed over multiple cycles while retaining its mechanical properties (Figure S44, Supporting Information). SEM images show that there exist large phase-separated domains in the control blend (Figure 4D), consistent with the poor mechanical performance of the control. In contrast, the microphase morphology of the dynamically crosslinked blend is much more homogeneous (Figure 4E), confirming enhanced compatibilization by in situ dynamic crosslinking. These results suggest that the bis-ASA dynamic crosslinking chemistry can be directly applied to compatibilize mixed plastic waste using a solvent-free melt-extrusion process, promising a practical solution for the mechanical recycling of mixed plastic waste.

3. Conclusion

We show here a robust and efficient dynamic crosslinking strategy that offers a potential general solution to enhance compatibility for immiscible plastics. Through a dynamic crosslinker incorporating aromatic sulfonyl azides, in situ generation of highly reactive singlet nitrene species facilitate efficient C—H insertion into diverse plastics, forming dynamic crosslinks during *solvent-free* melt-extrusion. The straightforward synthesis of the bis-ASA dynamic crosslinker and the facile extrusion process used for in situ polymer crosslinking suggest that the process could potentially be scalable. Critically, the high decomposition temperature of bis-ASA (≈190 °C) renders them suitable for conventional melt-processing of various commodity plastics. Dynamically crosslinked plastics derived from polar, nonpolar, chain-growth and step-growth polymers demonstrate improved mechanical properties while maintaining reprocessability. Solvent-free reactive extrusion effectively compatibilizes model polymer blends with minimal bis-ASA crosslinker content. Moreover, this approach demonstrates efficacy in compatibilizing model mixed plastics composed of five commodity polymers with distinct characteristics. The resulting polymer blend exhibits significantly enhanced mechanical performance and phase morphology. The bis-ASA technology offers a promising solution to the challenge of mixed plastic waste, promoting the sustainability of plastic lifecycles.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

This work was supported by the U.S. Department of Energy, Basic Energy Science program through Award No. DE-FG02-04ER46162 (measurements) and the U.S. National Science Foundation DMR-1810217 (synthesis), and the facilities and instrumentation at the UC Irvine Materials Research Institute (IMRI) were supported in part by the National Science Foundation through the UC Irvine Materials Research Science and Engineering Center (DMR-2011967). The authors thank Dr. Ali Mohraz at UCI for assistance of data analysis for rheology.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

dynamic covalent crosslinking, mixed plastic recycling, nitrene, polymer compatibilization, sustainable materials

Received: April 30, 2024
Revised: May 16, 2024
Published online: June 16, 2024

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