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Authors: Kosuke Yokoyama; Zhibin NM Guan, Prof.

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A Vitrimer Acts as a Compatibilizer for Polyethylene and Polypropylene Blends

Kosuke Yokoyama[a] and Zhibin Guan* [a][b][c]

[a] K. Yokoyama, Prof. Z. Guan, Department of Chemistry, University of California, Irvine, Irvine, California 92697, United States
[b] Prof. Z. Guan, Department of Materials Science and Engineering, Irvine, California 92697, United States
[c] Prof. Z. Guan, Department of Chemical and Biomolecular Engineering, Irvine, California 92697, United States
E-mail: zguan@uci.edu

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Abstract: Polymer compatibilization plays a critical role in achieving polymer blends with favorable mechanical properties and enabling efficient recycling of mixed plastic wastes. Nonetheless, traditional compatibilization methods often require tailored designs based on the specific chemical compositions of the blends. In this study, we propose a new approach for compatibilizing polymer blends using a dynamically crosslinked polymer network, known as vitrimers. By adding a relatively small amount (1-5 w/w%) of a vitrimer made of siloxane-crosslinked high-density polyethylene (HDPE), we successfully compatibilized unmodified HDPE and isotactic polypropylene (iPP). The vitrimer-compatibilized blend exhibited enhanced elongation at break (120%) and smaller iPP domain sizes (0.4 μm) compared to the control blend (22% elongation at break, 0.9 μm iPP droplet size). Moreover, the vitrimer-compatibilized blend showed significantly improved microphase stability during annealing at 180 °C. This straightforward method may hold potential for applications across different polymer blend systems.

Polymer blending is a highly desirable approach for improving plastic performance and creating novel materials without the need of inventing new polymers.[1] Nonetheless, the inherent immiscibility of many polymers presents a significant obstacle in the creation of polymer blends.[2–4] This immiscibility leads to phase separation and weak interfacial adhesion, ultimately yielding materials with inferior mechanical properties.[4] To surmount this challenge, various methods have been reported for compatibilizing immiscible polymers with the aim of improving the overall performance of polymer blends.[2,3,5–14]

The conventional methods of compatibilization can be broadly categorized into nonreactive and reactive compatibilization. Nonreactive compatibilization involves incorporating pre-made compatibilizers, such as designed block copolymers,[5–7,15,16] graft copolymers,[8–10,14] and random copolymers,[17] into polymer blends. These compatibilizers are capable of partitioning into the interfaces of both polymer phases, thereby reducing interfacial energy and enhancing polymer mixing. On the other hand, reactive compatibilization involves *in situ* chemical reactions between functional groups present in the component polymers.[11–13] These reactions promote grafting or cross-linking reactions with the polymers in the blends, effectively connecting the interfaces between phase-separated domains and improving the mechanical properties of the blends. Although these methods have proven successful in laboratory research and industrial production, they both have significant limitations. Nonreactive additives require custom-made compatibilizers tailored to each specific blend combination. Reactive compatibilization, on the other hand, relies on component polymers possessing complementary functional groups that can efficiently react during the blending process. Both approaches require tailored designs based on the specific chemical compositions of the blends. Consequently, this not only restricts the development of new polymer blends but also poses a fundamental challenge for the mechanical recycling of mixed plastics waste. Such mixed plastics typically exhibit incompatibility and phase separation for melt blending, resulting in materials with notably inferior properties.[18] The intricate nature of mixed plastic waste, coupled with its constantly changing compositions, adds an additional layer of challenge to the conventional compatibilization methods, rendering them increasingly difficult, if not impossible.

The development of covalent adaptable networks (CANs)[19,20] and vitrimers[21–26] presents new possibilities for addressing the persistent challenge of polymer compatibilization. We[27] and others[28,29] have recently shown the effectiveness of introducing dynamic covalent crosslinkers between immiscible polymers to achieve blend compatibilization. In our previous work,[27] we introduced a highly robust and versatile dynamic covalent chemistry, namely fluoride-catalyzed dynamic siloxane exchange, for the preparation of high-performance vitrimers from commodity thermoplastics. Furthermore, we demonstrated that the dynamic siloxane exchange between different polymers during melt blending led to self-compatibilization and remarkable enhancements in the mechanical properties of a PMMA/HDPE blend.[27] Nevertheless, there is no previous study demonstrating the use of a vitrimer to compatibilize a polymer blend comprising multiple unmodified polymers.

In the current study, we propose a simple approach by adding a pre-made vitrimer as a compatibilizer for *unmodified* polymers. Our key hypothesis is illustrated in Figure 1. Briefly, a small quantity of a vitrimer (green) is added as a compatibilizer to a mixture of immiscible polymers (red and blue in Figure 1a). Through heat, high shear forces, and rapid exchange of dynamic crosslinks during melt blending, the immiscible polymer chains and the vitrimer are compelled to intermix with each other, facilitating the distribution of the vitrimer across different polymer

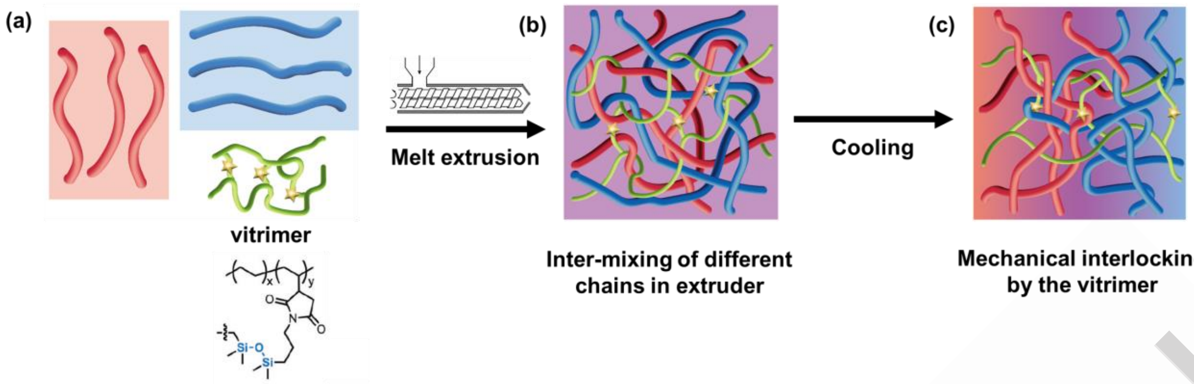

Figure 1. Schematic illustration of compatibilization by a vitrimer. (a) Components of the blend before blending, red and blue chains represent two immiscible polymers and green network represents a vitrimer with dynamic crosslinker shown as stars. (b) During melt blending the polymer chains are inter-mixed. (c) Upon cooling following the blending process, the dynamic covalent exchange within the vitrimer is arrested, creating mechanical interlocks that effectively inhibit subsequent phase separation of the two polymers.

phases (Figure 1b). As the blend exits the extruder and undergoes rapid cooling, we propose that dynamic covalent exchange within the vitrimer is arrested during the microphase separation of the two polymers, leading to the creation of semi-interpenetrating covalent networks. These networks entrap the immiscible polymer chains, effectively impeding any subsequent phase separation (Figure 1c). Different from traditional compatibilization methods, *this approach does not require specific chemical information with the polymers involved, thus making it potentially applicable to different polymer blends.*

We have selected polyethylene (PE) and isotactic polypropylene (iPP) as our initial examples to demonstrate our concept. PE and iPP are the two most widely produced plastics globally, with annual sales exceeding ~$200 billion. Approximately 116 million metric tons of PE and 68 million metric tons of PP are manufactured each year, accounting for a major fraction of the global plastics market.[30] While they receive extensive use in various applications, these high-volume plastics have also created significant environmental challenges due to their chemical stability and the difficulties involved in separating them during recycling processes. Currently, less than 1% of iPP and around 7% of PE are recycled, leading to the majority of these plastics ending up in landfills or natural environment.[31] While various methods, including both reactive[11–13] and nonreactive approaches,[5–10,14–16] have been reported for compatibilizing polyolefin blends, there remains an urgent need to develop a straightforward and efficient method for compatibilizing PE/iPP blends. Such methods are not only crucial for creating new polyolefin blends but also vital for recycling mixed plastic waste that is dominated by polyolefins.

To demonstrate the concept, following our previously reported protocol,[27] we first synthesized a high-density polyethylene vitrimer (HDPE-v) containing 5 wt% siloxane crosslinker and 16 mol% fluoride catalyst relative to the crosslinker through reactive extrusion of commercially available high-density polyethylene (HDPE). Next, HDPE/iPP (70/30 w/w) blends were prepared on a twin-screw extruder at 200 °C with 200 rpm shearing rate for 20 minutes with and without the addition of HDPE-v as a compatibilizer. For all vitrimer-compatibilized blends, the amount of added HDPE-v will be counted toward the total HDPE weight fraction. The resulting blends were molded at 180 °C for 5 minutes. Representative transmission electron microscopy (TEM) images of the control blend (HDPE/iPP = 70/30) and vitrimer-compatibilized blend (HDPE/HDPE-v/iPP = 65/5/30) are shown in Figure 2. Both the control and vitrimer-compatibilized blends show phase separated morphology, with the darker continuous phase for HDPE while the brighter droplet domains as dispersed iPP (Figure 2a and 2d).[32] The average droplet sizes were calculated from area size detected using imageJ by assuming all droplets as circles. The average diameter of iPP domains for vitrimer-compatibilized blend is 0.4 μm, which is less than half of the value for the control blend (0.9 μm). The distribution of iPP domain size for the vitrimer-compatibilized blend is significantly narrower than the control blend (Figure 2b and 2e). The shapes of iPP droplets in the vitrimer-compatibilized blend are also less elongated compared to the neat blend (Figure 2a and 2d). The TEM results were corroborated by scanning electron microscopy (SEM) images of cryo-fractured blend surfaces (Figure 2c and 2f), which showed significantly larger domain sizes in the control blend. These findings indicate that the aadition of HDPE-v is effective in enhancing the compatibilization of the HDPE/iPP blend. The observed phase morphologies align with similar HDPE/iPP blends that have been compatibilized using other types of compatibilizers such as multiblock copolymers[5–7,15,16] and graft copolymers.[8–10,14] These results support our hypothesis that the added HDPE-v can reduce interfacial tension between the two polymer phases and compatibilize the blend (Figure 1). Considering the structural similarity between HDPE-v and unmodified HDPE, it is anticipated that HDPE-v should mix well with unmodified HDPE during processing. Furthermore, since some PE and PP exhibit upper critical solution temperature (UCST) phase behavior,[33] it is expected that HDPE-v/HDPE should mix with iPP to some extent at the high processing temperature and shearing during blending. The rapid dynamic exchange of the siloxane crosslinkers, facilitated by fluoride catalysts at elevated temperatures,[27] should allow the penetration of HDPE-v into both HDPE and iPP phases, leading to the formation of dynamic interpenetrating

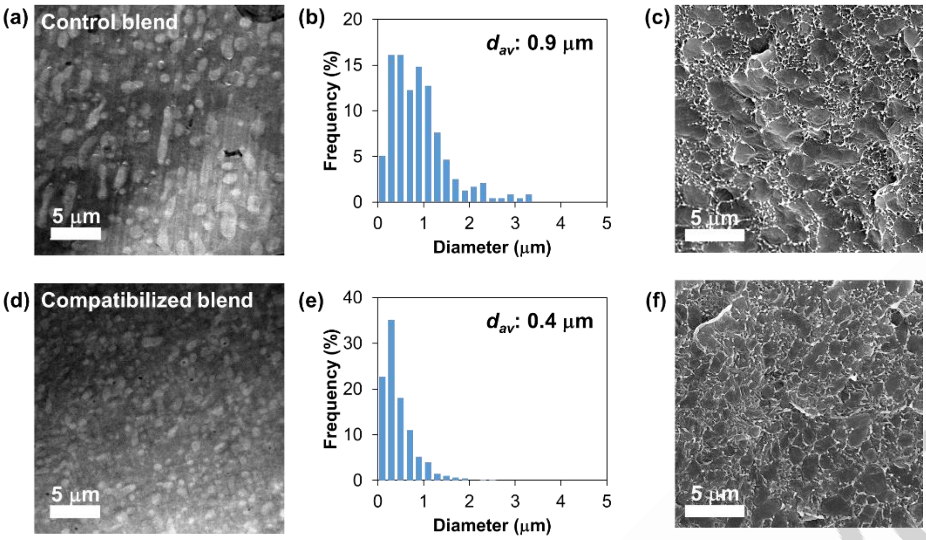

Figure 2. Microphase analyses of the blends by TEM and SEM. TEM images and corresponding size distribution of iPP droplets for the control HDPE/iPP 70/30 blend (a,b) and the vitrimer-compatibilized HDPE/HDPE-v/iPP 65/5/30 blend (d,e). The d_{av} values in the size distribution figures are the number-average diameters of the more than 200 individual droplets. SEM images of cryo-fractured surface for the control and compatibilized blends (c,f).

networks during cooling. In the control blend, the iPP droplets often display elongated shapes, likely resulting from the coalescence of dispersed droplets under shear stress during extrusion.[34] In contrast, the vitrimer-compatibilized blend shows a reduced presence of elongated droplets, indicating improved interfacial stabilization achieved by the vitrimer.

To investigate the impact of compatibilization on the mechanical properties, we conducted tensile tests on HDPE/iPP blends containing varying amounts of HDPE-v (Figure 3, and Figure S2). While individual HDPE and iPP are very ductile materials, the control HDPE/iPP blend exhibits a highly brittle behavior (with a maximum elongation of ~ 22%), in agreement with previous studies.[5,6,9] In contrast, upon adding 1 and 2 wt% HDPE-v, the elongation at break significantly improves to approximately 51% and 120%, respectively. The effect levels off with further increase of HDPE-v amount (Figure 3b). The tensile data correlates with the microphase morphologies observed through TEM imaging (Figure S3), indicating that the addition of 1-2 wt% of HDPE-v initially causes a significant reduction in iPP domain size, with this effect stabilizing thereafter. Notably, other mechanical properties, such as Young's modulus, strain, and stress at yield, remain relatively constant across all blends (Table S1). Similarly, the thermal transitions, thermal mechanical properties, and thermal degradation properties exhibit similar behavior for the blends with and without 5 wt% HDPE-v vitrimer (Figure S4-S5, S8, and Table S3). The enhancement in tensile properties of the HDPE/iPP blend with the addition of a relatively small amount of HDPE-v (2 wt%) can be attributed to several factors, including improved interfacial adhesion, reduced droplet size, and more efficient stress transfer between the phases. These findings from the tensile tests align with the morphological results observed in the TEM and SEM images (Figure 2) and provide further evidence supporting our hypothesis that a vitrimer can effectively serve as a compatibilizer for polymer blends. While it is challenging to experimentally elucidate the exact molecular mechanism behind the compatibilization effects, our proposed mechanical interlocking mechanism appears reasonable, especially considering that the added vitrimer does not exhibit any chemical reactivity toward either of the polymers in the blend.

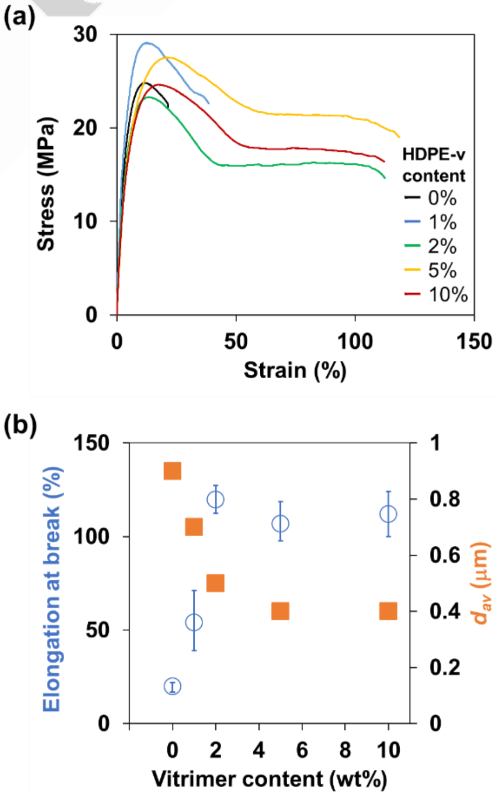

Figure 3. (a) Representative stress-strain curves of HDPE/iPP blends with varying HDPE-v content. (b) Tensile elongation at break and average diameter of iPP droplets of HDPE/iPP blends as a function of HDPE-v content.

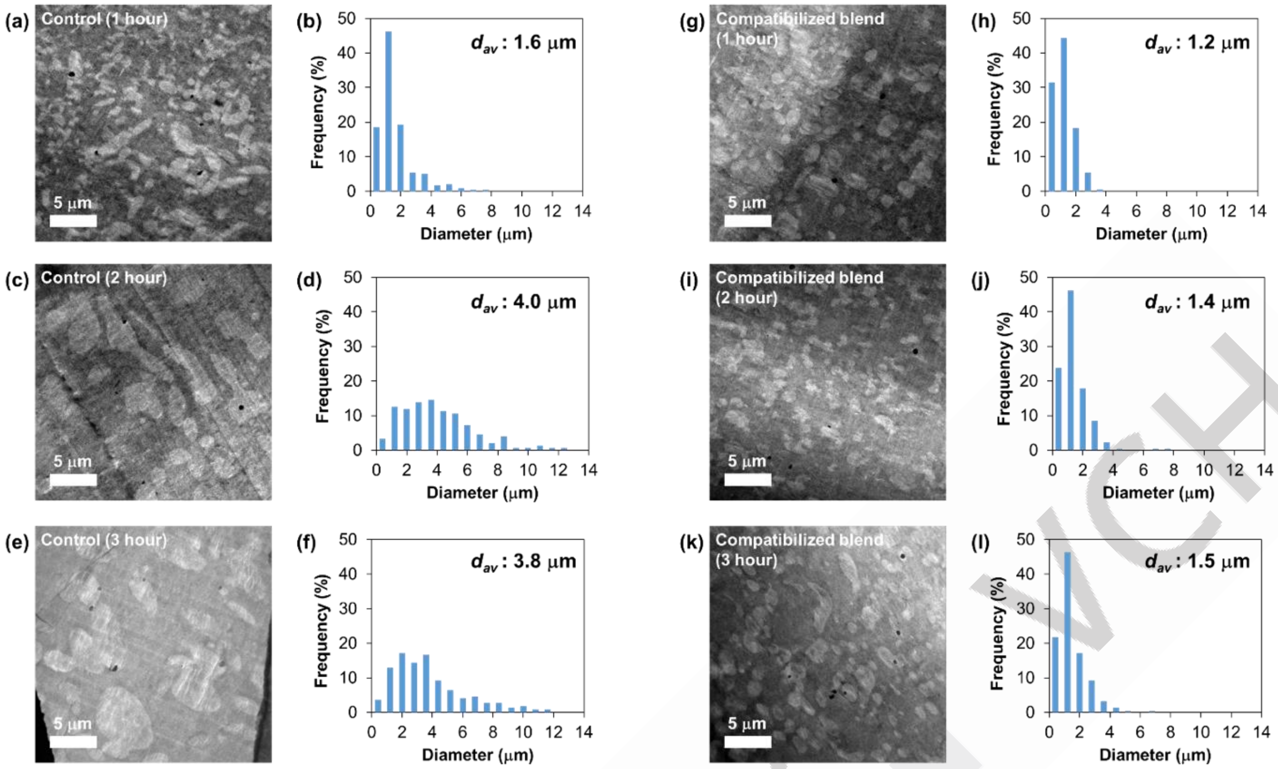

Figure 4. TEM images and size distributions of iPP droplets for HDPE/iPP = 70/30 control blend annealed for (a,b) 1 hour, (c,d) 2 hours, (e,f) 3 hours, and HDPE/HDPE-v/iPP = 65/5/30 annealed for (g,h) 1 hour, (i,j) 2 hours, (k,l) 3 hours.

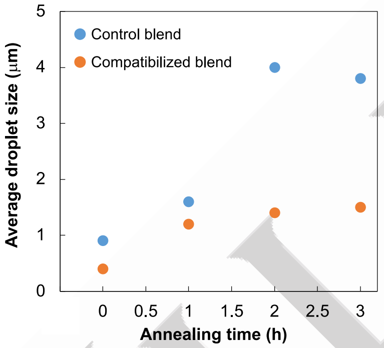

Figure 5. Average iPP domain size measured from TEM images as a function of annealing time at 180 ºC for both the control and vitrimer-compatibilized blend.

Uncompatibilized immscible polymer blends face a significant challenge where a freshly prepared blend will undergo phase separating over time until it reaches thermodynamic equilibrium. As a result, the mechanical properties of such polymer blends will deteriorate over time. Compatibilization should reduce the interfacial tension and stabilize the phase morphology of polymer blends. To investigate such effects in our system, we monitored the time-dependent phase morphologies by annealing the samples at 180 °C. As shown in Figure 4 and Table S2, the phase morphology for the control blend exhibits relatively large changes with time, with the iPP droplets continuously coalescing during annealing. The average diameter for the droplets increases from 0.9 to 4.0 µm after annealing for 2 hours and then levels off. For the HDPE-v compatibilized blend, during the first hour of annealing, the very small droplets of the initial blend (Figure 2d) coalesce to form larger droplets (Figure 4g). After 1 hour, no appreciable further coalesce was observed. The growth of iPP droplet size during annealing is significantly slowed down for the vitrimer-compatibilized blend (Figure 5) and the final iPP droplet sizes are also much smaller for the compatibilized blend (Figure 4k,l) than the control blend (Figure 4e,f). These results further support our hypothesis that the vitrimer compatibilizer can reduce the interfacial tension and stabilize the phase morphology.

In summary, we report a novel polymer compatibilization approach utilizing vitrimers. Through the addition of a small quantity of HDPE-v, unmodified HDPE and iPP were effectively compatibilized as supported by TEM/SEM imaging data and tensile testing. The vitrimer-compatibilized blend exhibited significantly smaller iPP droplet size and a narrower size distribution compared to the control blend. Moreover, the addition of HDPE-v notably improved the mechanical properties of the blend, increasing the elongation at break from 22% in the control to 120% in the compatibilized blend. Additionally, the vitrimer-compatibilized blend demonstrated enhanced phase stability during annealing at 180 °C. These findings suggest that the vitrimer can effectively reduce interfacial tension and enhance compatibility for the polymer blend. In future studies, we will investigate the detailed mechanisms underlying these observed compatibilization effects of vitrimers. As this method does not rely on specific chemical attribute about the polymer blend, we speculate there is potential for its application in other polymer blend systems.

Acknowledgements

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Keywords: polymer blends, vitrimer, compatibilization, dynamic covalent chemistry, polyolefins

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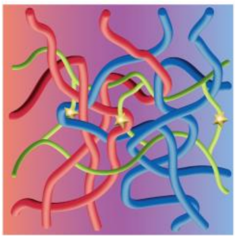
Mechanical interlocking for polymer compatibilization



A vitrimer can compatibilize a polymer blend. By adding a relatively small amount of a vitrimer made of siloxane-crosslinked high-density polyethylene (HDPE), we successfully compatibilized unmodified HDPE and isotactic polypropylene (iPP). The vitrimer-compatibilized blend exhibited enhanced elongation at break (130%) and smaller iPP domain sizes (0.4 µm) compared to the control blend (22% elongation at break, 0.9 µm iPP droplet size).