Copolymers Prepared by Exchange Reactions Enhance the Properties of Miscible Polymer Blends

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Abstract

Although many polymers are not miscible or chemically incompatible, some form miscible blends, which feature tunable properties relative to those of their constituent polymers. Here we introduce an approach to enhance the mechanical properties of miscible blends of a thermoplastic polyurethane and a sustainable polyester, polycaprolactone, by introducing a copolymer of the two corresponding monomers. Rather than polymerizing the copolymers from new monomers, they were generated by a solvent-free, ester/urethane bond exchange process conducted during the coextrusion of polyurethane and polycaprolactone. Urethane/ester exchange was confirmed by quantitative ^{13}C NMR spectroscopy, along with well-defined size exclusion chromatograms for the copolymers. Extrusion time and temperature affected the extent of exchange, with shorter residence time and lower temperatures giving limited bond exchange and blockier copolymers. In contrast, longer extrusion times and higher temperatures provided more extensive exchange and approximately random copolymers. Mixtures of the polyurethane and polyester homopolymers with 10 wt% copolymer demonstrated improved tensile stress and strain relative to coextruded mixtures of TPU and PE, because of the enhanced crystallization of the miscible homopolymer blend facilitated by the added copolymer compatibilizer. This approach represents a simple and general strategy for obtaining copolymers from homopolymers rather than using specialized polymerization techniques, allowing for products from mixed polymer waste to be used as compatibilizers or otherwise enhance the properties of the original homopolymer mixtures.

Introduction

The properties of miscible polymer blends can be tuned by varying the relative amounts of the constituent polymers.[1,2] Polymers are miscible when they are structurally similar or otherwise have low interfacial energy differences.[3–6] For example, mixtures of polystyrene and poly(phenylene oxide) combine the heat resistance, hydrolytic stability, and electrical resistance of poly(phenylene oxide) with the high dimensional stability and processability of polystyrene.[7] For mixtures of incompatible polymers, small amounts of added multiblock copolymers can serve as compatibilizers. Effective multiblock copolymer compatibilizers can dramatically enhance the otherwise poor properties of these homopolymer mixtures and therefore are of interest for enabling or enhancing the recycling of mixed commodity plastics.[8,9] In a notable example by Bates, Coates, LaPointe, and coworkers, mixtures of polyethylene (PE) and isotactic polypropylene (*i*PP) showed higher toughness and strains at break when compatibilized with as little as 5 wt% of a multiblock PE-*i*PP copolymer.[10–12] In contrast to their ability to compatibilize immiscible polymers, the effects of adding multiblock copolymers to miscible polymer blends have not been explored. We hypothesized that multiblock polymers might improve the properties of miscible blends by increasing cohesive interactions or improving the organization of the polymer chains. Here we demonstrate that adding multiblock copolymers to miscible polyurethane/polyester blends enhance their mechanical properties, in this case by increasing the crystallinity of the polyester component of the blend.

As interest in block copolymer compatibilizers or property enhancers increases, simple and effective methods to access multiblock copolymers are desirable because their direct polymerization is often not straightforward.[13] Often, multiblock copolymers are prepared using alternating, controlled polymerizations of two monomers,[14] which provide the highest degree of structural control but require specialized conditions and catalysts capable of enchaining both monomers and alternating between them.[15–17] To prepare the copolymers studied here, we introduce a simple and solvent-free approach by co-extruding polyurethane and polyester homopolymers in the presence of dibutyltin dilaurate (DBTDL),[18,19] which catalyzes both urethane exchange and transesterification reactions (Figure 1A). Urethane exchange results from the dissociation of carbamates to the respective isocyanates and alcohols, these alcohols can either reform carbamates through reacting with an isocyanate or can react with the ester through transesterification. This process was performed by co-extruding the polyester and polyurethane homopolymers in the presence of DBTDL at elevated temperatures. The resulting copolymers are soluble in organic solvents, which enables structural characterization by solution NMR. This feature also gives direct insight into catalyst activity as a function of the extrusion conditions. By varying the extent of carbamate and ester exchange, the copolymer microstructure evolves from blocky at low degrees of bond exchange to that of a random copolymer at high degrees of bond exchange. After their synthesis, small amounts of these copolymers were added to mixtures of the homopolymers and improved the mechanical properties of the blends by increasing their crystallinity (Figure 1B). We envision that this approach might someday be used to derive high-value property enhancers or compatibilizers from mixed plastic waste streams and enable their recycling.

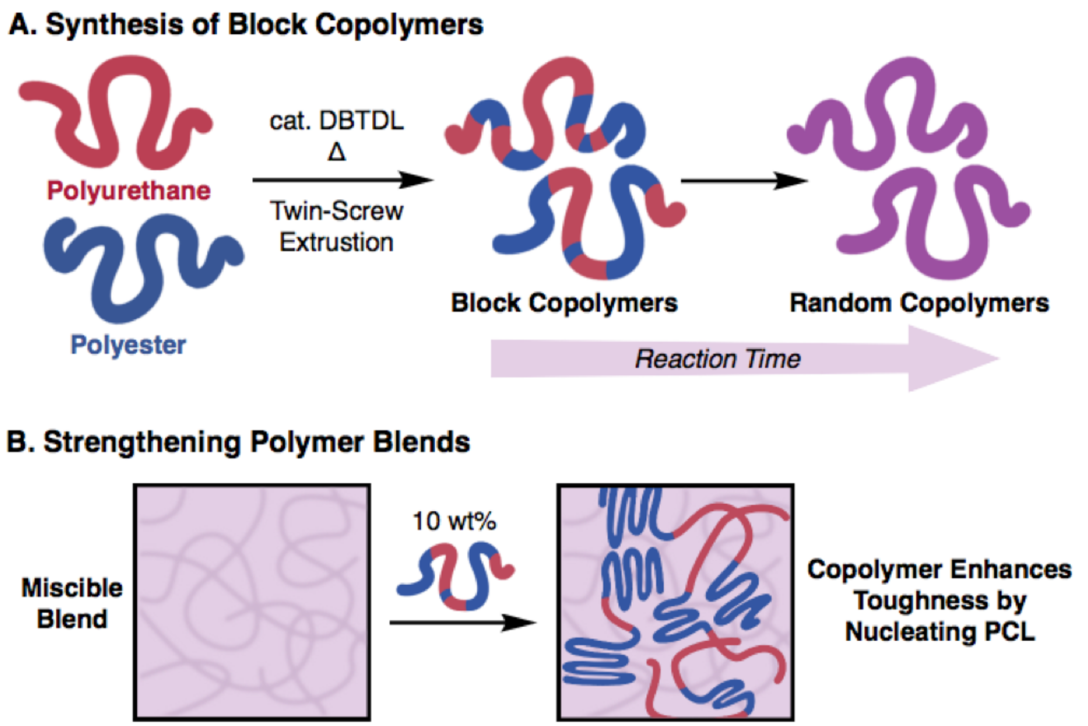


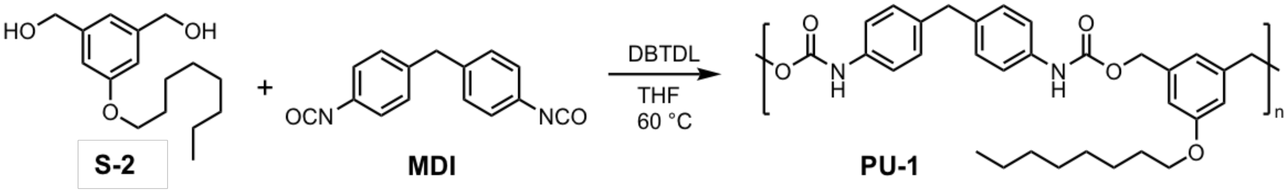
Figure 1. (**A)** Copolymer synthesis via bond exchange between a PU and PE using a twin screw extruder with varying residence times during extrusion resulting in blocky structures at low extrusion times to more random-like copolymers at longer processing times. **(B)** Incorporation of the copolymer that results in higher degrees of crystallinity in a miscible PCL/TPU blend through the block copolymer nucleating PCL.

Results and Discussion

Synthesis and Characterization of Linear Polyurethane.

We selected linear polycaprolactone (PCL, M_n = 80 kDa) as the polyester in this study due to its commercial availability and moderate melting point of 60 °C. We designed **PU-1**, which contains an aromatic backbone, so as to distinguish its carbamates within a ^{13}C NMR spectrum from the aliphatic carbamates formed upon exchange with PCL. A Williamson ether synthesis using **S-1** and 1-bromooctane provided ether (**S-2**) in good yield.[20] **S-2** was reduced to the corresponding diol **S-2** using $LiAlH_4$. **PU-1** was synthesized via step-growth polymerization of diol **S-2** and methylene diphenyl diisocyanate (MDI), a commonly used PU monomer. This polymerization was catalyzed by dibutyltin dilaurate (DBTDL), which catalyzes both the formation of urethanes as well as the thermal reversion of urethanes back into alcohols and isocyanates.[21] The mechanism for which DBTDL activates the carbonyl for the reversion of polyurethanes makes this catalyst a good candidate to also catalyze the transesterification in polyesters. After polymerizing in THF at 60 °C for 24 h, **PU-1** was precipitated into MeOH and isolated as a white powder.

Scheme 1. Synthesis of thermoplastic polyurethane **PU-1**.



The SEC chromatogram of DMF-soluble **PU-1** showed a monomodal distribution with a moderate *Đ* of 1.33. Multiangle static light scattering (MALS) analysis suggested an M_n of 22.1 kDa. Subsequent polymerizations yielded polymers with similar values of *Đ* and M_n (Figure S1). A 1:1 ratio of $CDCl_3$ and DMSO-d_6 was used for NMR analysis because this mixture dissolved both **PU-1** and PCL. The ^1H NMR spectrum of **PU-1** exhibited the anticipated signals, including a broad singlet at 9.53 ppm, corresponding to the hydrogen bonded to the urethane nitrogen. Quantitative ^{13}C NMR spectroscopy was performed with added $Cr(acac)_3$ as a paramagnetic relaxation agent, indicated that the carbonyl signal of **PU-1** resonated at 153.3 ppm, which was well resolved from PCL's carbonyl resonance at 172.6 ppm. The solubility of both polymers and well-resolved carbonyl resonances were key observations to enable quantitative analysis of copolymers generated from bond exchange during their coextrusion.

Synthesis of Copolymers via Twin Screw Extrusion

The extent of bond exchange between polycaprolactone and **PU-1** in the extruded copolymers was characterized by quantitative ^{13}C NMR spectroscopy, from which the average degree of polymerization (DP_n) of the PU and PCL segments was calculated. Equal masses of PCL and **PU-**

1 were combined along with DBTDL (0, 0.5, or 1 wt%) in a solution of DCM, which corresponded to a 2.3:1 molar ratio of ester to carbamate functional groups in the polymer mixtures. Following evaporation of the solvent, the mixture was loaded into a twin screw extruder, which was heated to 200 °C with the screws rotating at 150 rpm. The polymers moved through the extruder with specific residence time of 2 minutes. SEC analysis of the extruded polymer showed a monomodal peak with a calculated M_n of 16.7 kDa and a $Đ$ of 1.72 (Figure S2). No peaks in the chromatogram corresponded to the starting PCL or **PU-1** samples, suggesting that they reacted to form copolymers. This finding is consistent with differential scanning calorimetry (DSC) measurements, which showed that the resulting copolymers had one T_g around -13 °C which is between those of PCL (-60 °C) and **PU-1** (56 °C) (Figure S3). ^{13}C NMR spectroscopy of the copolymer showed the original carbamate and ester carbonyl resonances at 172.6 and 153.3 ppm, as well as new peaks corresponding to new ester and urethane carbonyl carbons at 172.5 and 153.7, respectively (Figures 2, S4). The new urethane carbonyl resonance at 153.7 ppm corresponds to the carbamate formed between the aliphatic alcohol derived from PCL and an isocyanate formed from carbamate reversion of **PU-1**. The new ester carbonyl resonance at 172.5 ppm corresponds to the ester formed from the **PU-1** alcohol and a carboxylic acid of polycaprolactone.

By integrating these resonances in quantitative ^{13}C NMR spectra, the amount of exchange in the extruded product was determined, which gives insight into the catalyst activity under the extrusion conditions and the microstructure of the resulting copolymers. If the two polymers are fully consumed and undergo exhaustive exchange, a random copolymer will be formed. If exchange is less prevalent, multiblock microstructures are formed. For the conditions of low residence time (2 min), catalyst loading of 0.5 wt%, and an extrusion temperature of 200 °C, the percentage of carbamates resulting from exchange was 25% (Table 1, Copolymer **1**). Given the initial molar ratio of 2.3:1 ester:carbamate groups, if all of the urethanes underwent exchange with the esters, a maximum of 43% of the esters can be transformed. Based on the ratios of residual and exchanged carbonyl signals in the ^{13}C NMR spectrum, the average molecular weight of the PCL and **PU-1** blocks are 1100 and 1000 Da, respectively (Table S1). These values correspond to an average DP_n of 9.33 units for the PCL blocks and 1.96 units for the **PU-1** portions. Given the short average block length of the **PU-1** segments, this polymer is best considered an approximately random copolymer. In contrast, a copolymer extruded under the same conditions in the absence of DBTDL exhibited significantly reduced levels (9%) of exchanged urethane in its ^{13}C NMR spectrum. As a result, these copolymers have longer average block lengths, with a DP_n of 33.9 units for PCL and 6.8 units for **PU-1**. The difference in block lengths of the exchange products demonstrates the role of DBTDL to catalyze transesterification and transcarbamoylation during extrusion.

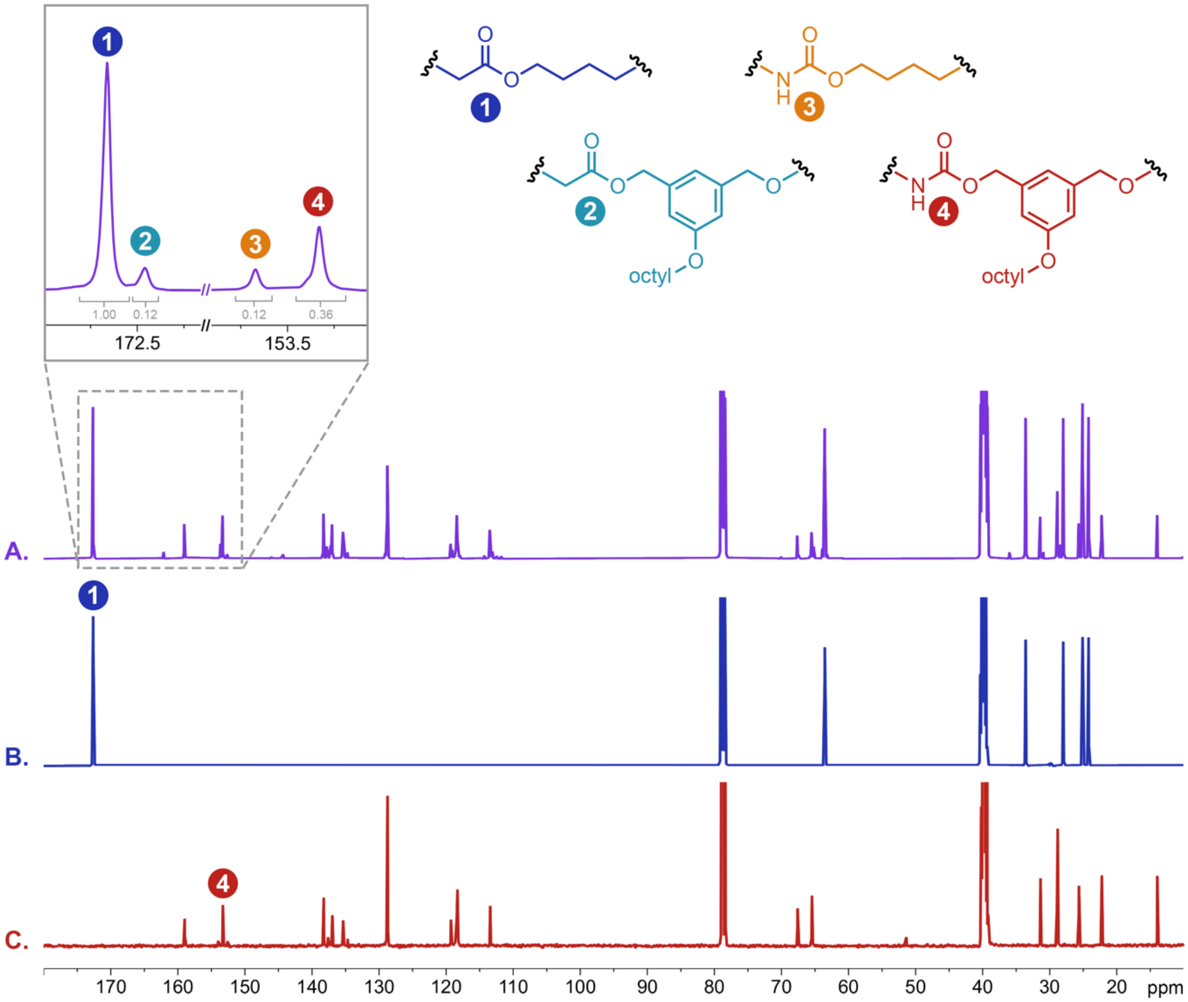


Figure 2. Quantitative ^{13}C NMR spectra of **(A)** a copolymer synthesized via extrusion of PCL and **PU-1** at 200 °C with low residence time (Table 1, Entry 1), with an inset showing the carbonyl region, **(B)** PCL, and **(C) PU-1**. The carbonyl carbon signals have been labeled to show that two new carbonyl signals were seen after extrusion due to dynamic exchange.

Table 1. Copolymers of PCL and **PU-1** formed via dynamic exchange using a twin screw extruder. All experiments were performed at 150 rpm. [a]Time that the sample spent in extruder. [b]Calculated from the carbonyl signals in the quantitative ^{13}C NMR spectra.

Copolymer Sample	Temperature (°C)	Residence time (min)[a]	DBTDL amount (wt %)	New urethane carbonyl (%)[b]	Average M_n of PU-1 Block (Da)
1	200	2	0.5	25	1000
2	200	2	1	21	1500
3	200	2	0	9	3600
4	200	10	0.5	58	400
5	200	20	0.5	66	400

6	200	30	0.5	71	400
7	120	2	0.5	0	N/A
8	150	2	0.5	6	5500
9	180	2	0.5	10	2900
10	220	2	0.5	66	400

Lowering the extrusion temperature also yielded copolymers with less exchange between PCL and **PU-1**. No urethane exchange was detected by ^{13}C NMR spectroscopy when the temperature of the reaction was decreased to 120 °C in the presence of 0.5 wt% DBTDL and a extrusion time of 2 minutes. Raising the extrusion temperature to 150 and 180 °C resulted in modest exchange, with 6 and 10% new urethane detected, respectively. These copolymers had longer average block segments than the copolymers extruded at 200 °C. As anticipated, heating the system to 220 °C showed a significant increase in exchange, with 66% of all urethanes having undergone exchange. Overall, varying the temperature during extrusion yielded copolymers with tunable extent of exchange and average block lengths, with higher temperatures resulting in more exchange and a more random copolymer and lower temperatures resulting in less exchange and block copolymers.

We next varied the residence time during extrusion and found that the average block lengths for the PCL and PU segments decreased with increasing residence time (Table 1). As the average block lengths decrease, the more extensively exchanged samples have structures approaching being random copolymers. While holding the catalyst loading and temperature constant, we coextruded the PU-1 and PCL homopolymers at 200 °C with 0.5 wt% of catalyst for 10, 20, and 30 min, resulting in copolymers **4**, **5**, and **6** respectively. Copolymer **4** showed an increase in exchanged carbamates of 58% at 10 min residence time, as compared to 25% for copolymer **1** at 2 min residence time. Subsequent increases in residence times resulted in more modest increases in exchange, with 20 minute (copolymer **5**) and 30 minute (copolymer **6**) residence times, which provided 66 and 71% of exchanged carbamates, respectively. The SEC traces for copolymers **4** and **5** showed similar molecular weights of 17.1 and 17.9 kDa, respectively, and peak shapes, indicating that side reactions that would influence the average chain length are not operative (Figure S1). However, for copolymer **6**, the M_n of the copolymer decreased to 5.9 kDa, suggesting that chain scission occurs at this extended extrusion time. The increased exchange that arises from longer reaction times gives copolymers that have near random structures, as the average DP_n of the **PU-1** segments approaches 1. Such samples have very short urethane segments or even isolated carbamate groups distributed along the PCL backbone. These results demonstrate the formation of copolymers with tunable microstructures, ranging from block to random copolymers, based on reaction time, resulting from dynamic exchange of two homopolymers.

Properties of PCL/PU-1 Polymer Blends

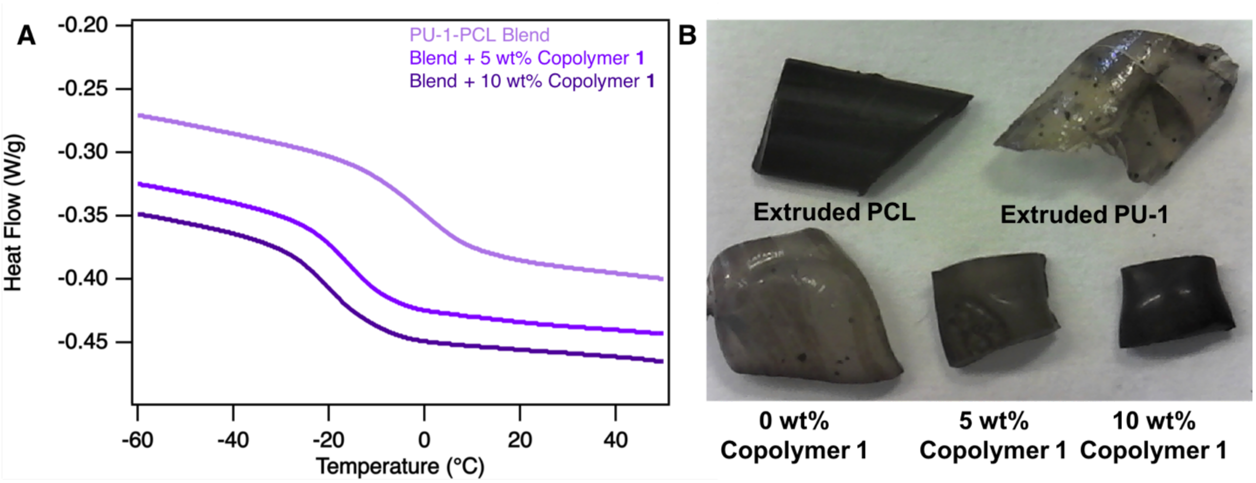


Figure 3. (A) DSC heat ramps of the three blends with varying copolymer **1** incorporation showing a single distinct T_g suggesting that these two homopolymers are miscible. **(B)** Optical images of the stained extruded blends and starting polymers. These images indicate increased staining with increased copolymer **1** incorporation in the blends.

When copolymer **1** was incorporated into blends of PCL and **PU-1**, the crystallinity of the polymer blend increased in a dose-dependent fashion. PCL and **PU-1** (50:50 wt%) were co-extruded with varying amounts of copolymer **1** (0, 5, or 10 wt%). To minimize urethane/ester exchange during the coextrusion of PCL, **PU-1**, and their copolymers, the extrusion was performed at 120 °C with no additional exchange catalyst. SEC analysis confirmed that no additional exchange occurred during this extrusion, as the two peaks corresponding to the starting homopolymers were observed. These chromatograms were unchanged both in the presence and absence of added copolymers (Figure S5). DSC of this blend revealed a single T_g at –0.28 °C, which is between those of the starting PCL (-60 °C) and **PU-1** (56 °C), and close to that of the copolymer (Figure 3A). The homopolymer blends incorporating either 5 or 10 wt% of the PCL/**PU-1** copolymer **1** also exhibited similar T_g values. These findings suggest that the homopolymers are miscible under these processing conditions, even in the absence of added copolymer. Transmission electron microscopy (TEM) of the cross-sections of these blends with and without the copolymer incorporated also indicates that these blends are miscible, since only one phase is present even after staining the films with RuO_4 to enhance their contrast (Figures S6, S7). However, the degree of staining increased throughout the materials with increasing copolymer content (Figure 3B). The film containing no copolymer turned slightly gray after 11 min of exposure to a solution of RuO_4 and the films with 5 and 10 wt% of copolymer **1** incorporation were darker, going from dark gray for the 5 wt% sample to black for the 10 wt% sample under the same exposure to the RuO_4 solution. We also observed that extruded PCL, which is relatively crystalline, stains to a greater degree than extruded **PU-1**, which is amorphous. This difference has been noted for staining semi-crystalline polymers.[22,23] Therefore, the increased staining of the blends led us to further investigate if the copolymer imparts higher crystallinity to the homopolymer blends.

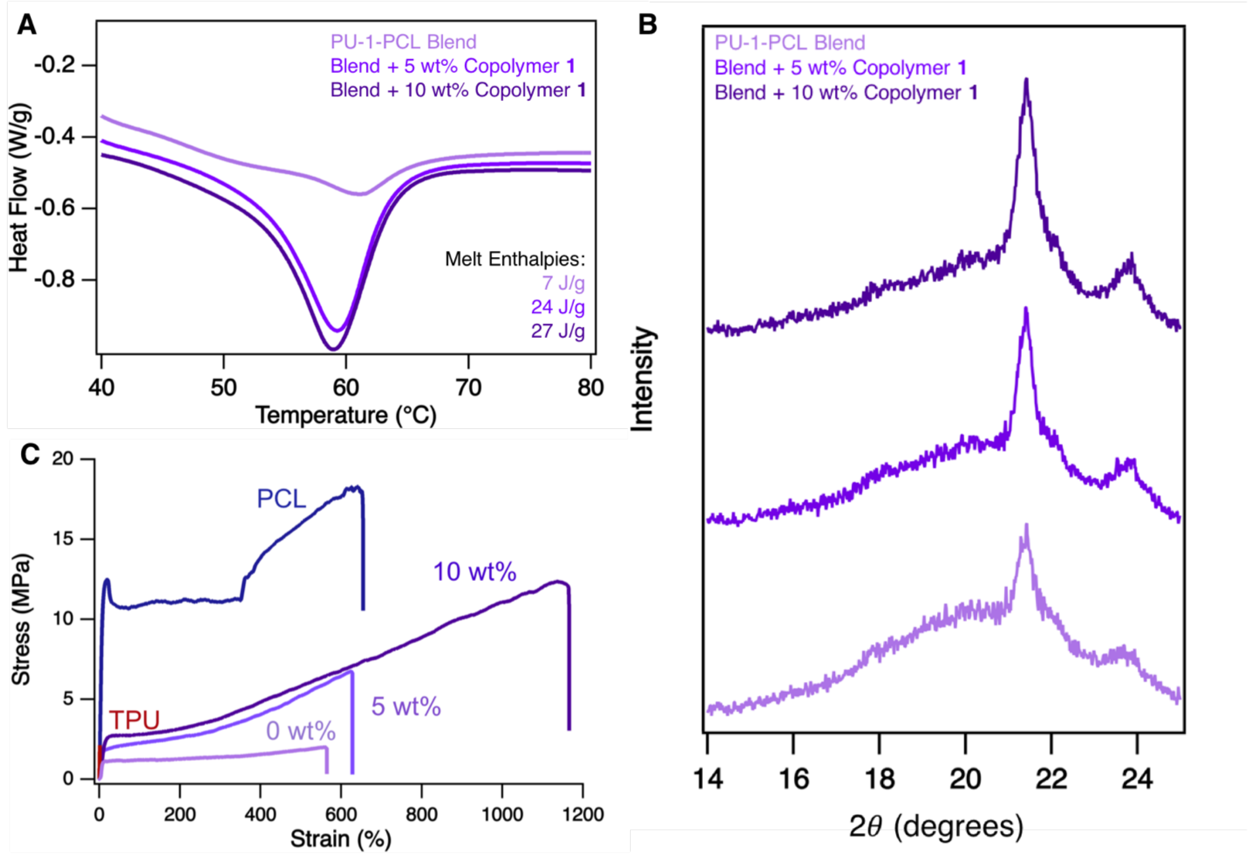


Figure 4. (A) Endotherms during the initial DSC heat ramp for 0, 5, and 10 wt% added copolymer. **(B)** XRD analysis of the same blends. The peak at ca. 21.8 degrees is associated with crystalline PCL, which is enhanced with increased copolymer incorporation. **(C)** Stress-strain curves of PCL and TPU (**PU-1**), as well as PCL/TPU blends with varying amounts of added copolymers (0, 5, and 10 wt%).

Analysis of the miscible blends with different amounts of copolymer **1** revealed that increased amounts of added copolymer resulted in blends with greater crystallinity after extrusion. DSC analysis of these extruded blends corroborated this effect of added copolymer (Figure 4A). On the initial heat ramp during the DSC procedure, endotherms resulting from the melting of crystallites were found starting at 55 °C for all compositions. However, the magnitude of the enthalpy differs with the three blends, suggesting different degrees of crystallinity, which is consistent with the staining behavior. The enthalpy for the melting transition for the 0 wt% blend was 7 J/g, compared to an enthalpy of 24 J/g for the 5 wt% blend and 27 J/g for the 10 wt% blend, supporting that the blends containing copolymer **1** are more crystalline. X-ray diffraction (XRD) analysis further confirmed that the blends with more copolymer are more crystalline, based on the more intense diffraction pattern that corresponds to the PCL crystalline regimes (Figure 4C). The extruded PCL and extruded blends contained peaks at 21.4 and 23.6 degrees which correspond to the (110) and (200) Bragg diffraction peaks for PCL,[24] while the extruded **PU-1** is amorphous (Figure S8). The blend without any copolymer showed a lower intensity diffraction compared to the blends containing copolymer as well as a larger broad amorphous feature. These analyses demonstrated that the extruded blends containing copolymer are more crystalline through better nucleation of the PCL regimes in the blend.

The enhanced crystallinity from the copolymer incorporation in the **PU-1**/PCL blends resulted in higher quality elastomeric materials with better mechanical properties (Figure 4D, Table S2). Without added copolymer, the 50:50 blend had undesirable tensile properties as compared to the starting films of PCL and **PU-1**. This **PU-1**/PCL blend (with 0 wt% added copolymer) had a tensile stress of 1.6 ± 0.4 MPa, strain at break of 500 ± 100 %, and a Young's modulus of 30 ± 10 MPa. Films that contained 5 wt% of copolymer **1** had enhanced mechanical properties with a tensile stress 8 ± 1 MPa, a strain at break of 670 ± 50 %, and a Young's modulus of 21 ± 6 MPa. Adding 10 wt% of copolymer **1** yielded samples with still higher strains at break (1000 ± 200 %), tensile stresses (14 ± 3 MPa), and Young's moduli (40 ± 10 MPa). The addition of the copolymer **1** increases the toughness from 600 ± 200 J/m^3 in the absence of copolymer to 2300 ± 900 J/m^3 for the 5 wt% blend, and 7000 ± 2000 J/m^3 with 10 wt% blend. Incorporating the PE-PU copolymer into blends of PE and PU thermoplastics enhances the mechanical toughness of these blends. Tensile testing showed the enhancement of the mechanical properties in the blends containing copolymer from the crystallinity through better nucleation of the PCL chains during extrusion.

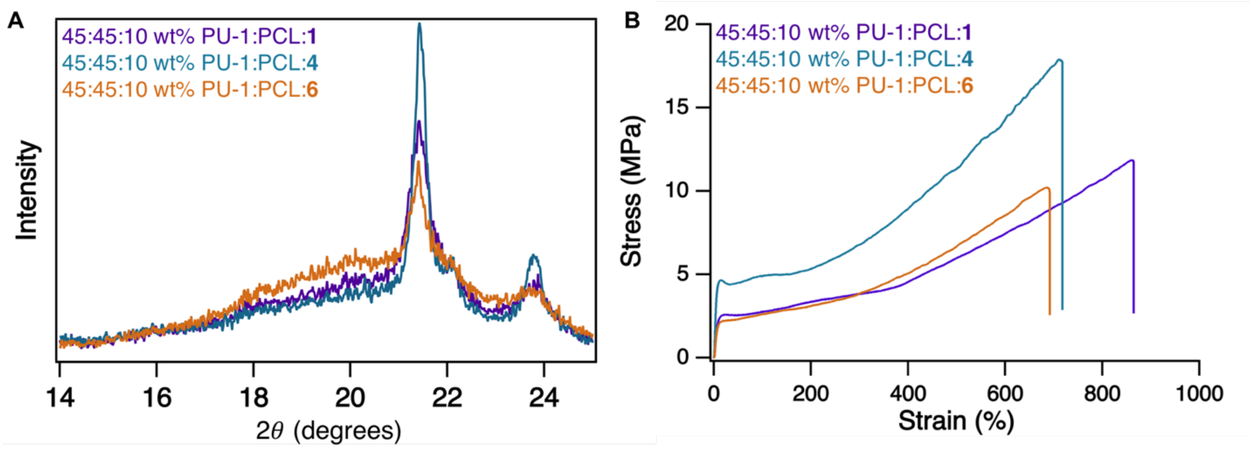


Figure 5. (A) XRD analysis of **PU-1**:PCL blends with added copolymers (10 wt%) of with variable levels of urethane/ester exchange. **(B)** Stress-strain curves of these blends, indicating that the mechanical properties of the blends are dependent upon the length of the copolymer microstructure as well as molecular weight of the copolymers.

The copolymers showed differences in crystallinity and mechanical properties when incorporated into **PU-1**:PCL blends. Copolymers with more random structures resulted in enhanced crystallinity and higher toughness, but copolymers extruded for extended periods showed inferior properties, perhaps because of their reduced molecular weight (Figure 5). 10 wt% each of **1**, **4**, or **6** were incorporated into an identical 50:50 blend of **PU-1** and PCL. XRD analysis of the blends containing each copolymer demonstrated the change in crystallinity with differing copolymers (Figure 5A). The blend containing **4** was the most crystalline with the highest intensity peaks of any of the blends. We hypothesize that the random structure of the copolymer allows the material to nucleate PCL crystallites more efficiently than the blockier copolymer with the shorter residence time. The blend containing **6** had the least amount of crystallinity with the least intense peaks as a result of the lowered molecular weight of the copolymer after these longer residence times. The crystallinity differences between the three 10wt% blends were also evident from the magnitude of the initial melting endotherms by DSC (Figure S9). Incorporation of copolymer **4** increased the tensile stress from 14 ± 3 MPa for the copolymer **1** blend to 18 ± 2 MPa (Figure 5B, Table S3). However, the tensile strain at break decreased to 700 ± 100 % while the Young's modulus increased to 90 ± 20 MPa. The tensile properties of the blend copolymer **6** were reduced compared to the blend containing **4** and the blend containing **1**. The addition of copolymers with near-random structure demonstrated that the randomness of the copolymer enhanced the mechanical toughness of the blend due to increased crystallinity. However, if the copolymer has a low molecular weight, the property enhancement from the copolymer may not be observed.

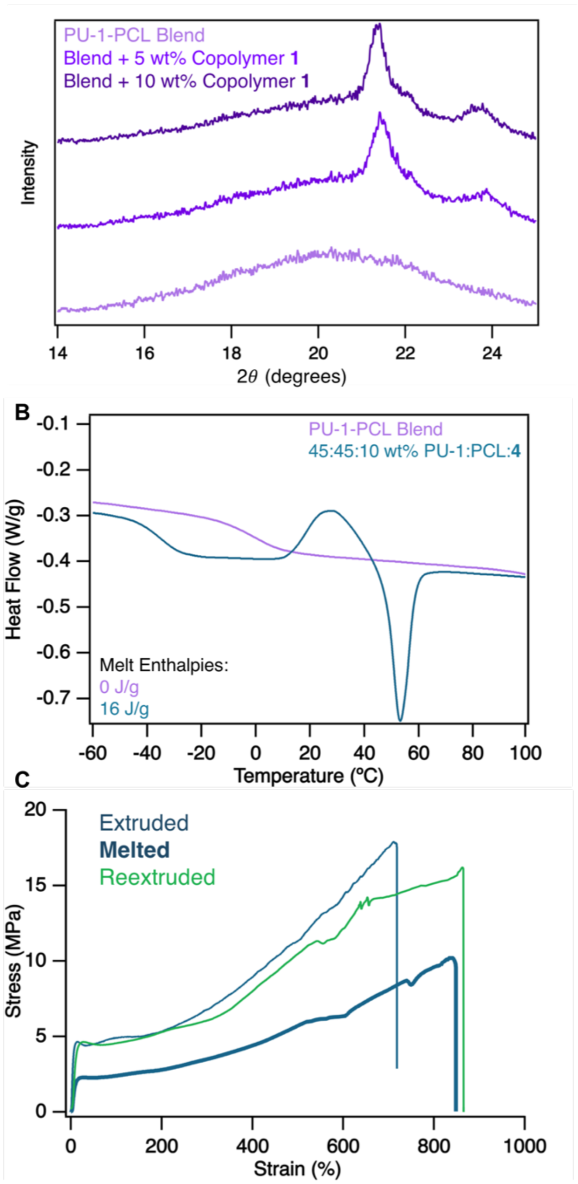


Figure 6. **(A)** XRD analysis of blends with different amounts of copolymer **1** after heating showing that the copolymer containing blends are still crystalline after heating. **(B)** DSC heat ramp of blend without copolymer and the blend with containing 10 wt% of copolymer **4** which contains a cold crystallization exotherm that is not present in the DSC trace without the copolymer. **(C)** Tensile testing of the blend with 10 wt% of copolymer **4** showing the effect of extrusion on the mechanical properties of the blend and that the mechanical properties are regained after melting of the extruded materials followed by reextrusion of the blend.

When the blends were heated past the melting temperature, the blends containing the copolymers retained some crystallinity due to a cold crystallization transition that allows for partial retention of the mechanical properties (Figure 6). DSC of the blends demonstrated an endothermic melting transition but not an exothermic crystallization transition during the return cooling cycle. However, XRD of the DSC samples after the heating showed that the samples containing copolymer **1** (5 and 10 wt%) remained semi-crystalline while the blend lacking copolymer was not crystalline (Figure 6A). The XRD spectrum for the blend without copolymer contained only a broad amorphous feature with no peaks. The blends with 5 and 10 wt% of copolymer **1** both contained peaks at similar 2θ positions as PCL and the original extruded blends. The partial crystallinity in the heat-treated blends containing copolymer despite no crystallization temperature in the DSC arises from the ability of those blends to undergo cold crystallization at elevated temperatures above the T_g (Figure 6B), which has been shown previously for blends containing PCL.[25] This feature was seen in the second heat ramp of the DSC trace with an onset temperature of 9.5 °C, resulting in crystallization and subsequent melting that is not seen in the trace for the blend without added copolymer. Cold crystallization occurs when the polymer chains are able to move at temperatures above the T_g, resulting in nucleation and crystallization of the polymer chains. It is believed that the copolymer allows for enhanced motion of the chains at these elevated temperatures leading to this transition and reformation of the crystallites. However, the enthalpy of melting after this cold crystallization event was 16 J/g for the blend containing copolymer **4**, which is significantly less than the 45 J/g melting enthalpy seen during the initial heating of the extruded blend via DSC (Table S4). Tensile testing comparing the originally extruded blend containing the blend containing **4** to the heat-treated blend, which was melted by heating to 120 °C and shaped into a tensile sample, showed that the crystallization via cold crystallization process occurs to a lesser extent than that which occurs during coextrusion (Figure 6C). The tensile stress of the heat-treated sample was reduced to 10.2 MPa and the strain at break was 838 %. Nevertheless, these properties were still superior to those of the homopolymer blend without copolymer. Overall, copolymer incorporation not only imparts better mechanical properties and crystallinity on the blends but allows them to cold crystallize at elevated temperatures, which enables partial retention of their crystallinity after heating.

The ability of the PCL/**PU-1** copolymers to enhance the crystallinity of the homopolymer blends during the extrusion was further confirmed by performing multiple melting and extrusion cycles. The extruded 50:50 blend of the two homopolymers and copolymer **4** (10 wt%) was melted at 120 °C and then reextruded. The tensile properties of the blend were largely recovered after reextruding the blend under the same conditions as those used in their original mixing. DSC also shows that the crystallinity can be mostly recovered by reextrusion with the melting enthalpy in the initial heating ramp being 29 J/g compared to 45 J/g of the originally extruded blend (Figure S10). XRD also shows this trend in crystallinity through the different processing steps with the crystallinity decreasing after heat treatment then increasing after reextrusion (Figure S11). The cycling of melting and extruding also shows the effect of the mechanical processing of extrusion has on the enhancement of the overall crystallinity of the blend, which is why extruded samples have higher degrees of crystallinity and higher toughnesses than the melted samples. Overall, blends containing the copolymers are able to recover the mechanical properties that were partially lost after heat-treatment through reextrusion under the same conditions as the initial processing of the blends.

Conclusions

These findings demonstrate that copolymers synthesized from two homopolymers can enhance the properties of miscible homopolymer blends, which may enable such blends to be used more extensively. Miscible polymer blends are both desirable for their tunable properties and potentially more sustainable if they can replace difficult-to-recycle multilayer plastics. We also introduce a new strategy to obtain these copolymer property enhancers that avoids the need to develop specialized conditions that needed to enchain two or more monomers with different functional groups and reactivities. The exchange processes demonstrated here can in principle be applied to any polymer mixtures whose bonds can undergo catalyzed exchange processes, and the reaction occurs during extrusion in the absence of solvent, which bodes well for its scalability. Finally, this approach is also of interest for evaluating catalysts and reprocessing conditions for reprocessing thermosets as covalent adaptable networks[26–28] via extrusion, because the reactivity of linear polymers is more easily characterized via in-solution spectroscopy.

ASSOCIATED CONTENT

Supporting Information

Supporting Information is available free of charge at https://pubs.acs.org/doi/XX.XXXX/jacs.XXXXXXX.

Experimental Section, data tables (Tables S1-S5), NMR spectra, DSC traces, and SEC spectra (Figures S1-S26) (PDF)

Conflicts of interest. The authors declare no conflicts of interest.

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