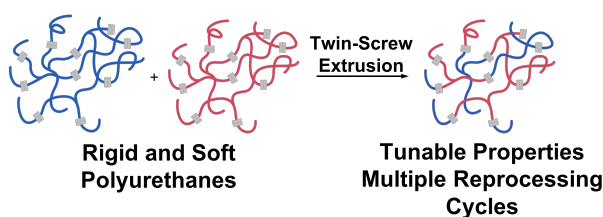# Blending Polyurethane Thermosets
Using Dynamic Urethane Exchange

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Rigid and Soft Polyurethanes + → Twin-Screw Extrusion → Tunable Properties Multiple Reprocessing Cycles

ABSTRACT: Recycling crosslinked polyurethanes (PUs) is accomplished through mechanical or chemical processes that are energy intensive or produce plastics of lesser value. Polymer recycling processes are notably intolerant of polymer mixtures, yet the ability to reprocess and compatibilize two or more crosslinked PUs together will make this process more amenable to mixed waste streams while offering an opportunity to tune the properties of the recycled polymer products. Here we blend a rigid polyester PU and a soft polyether PU using twin-screw extrusion to yield materials with tunable mechanical properties based on the feed composition. Their material properties were compared to compression molded reprocessed blends and to blends where the monomers were mixed prior to synthesis. The extruded materials showed similar mechanical and thermal properties to newly prepared blends and had higher-value mechanical properties compared to the samples reprocessed via compression molding. The morphologies of

the blends were observed using phase imaging via atomic-force microscopy to show that there is less phase separation in the extruded materials compared to compression molded blends. The mechanical properties of these materials were tunable from soft to elastomeric to rigid based on the feed composition and this tunability was demonstrated through four consecutive reprocessing cycles, through which the mechanical properties were steadily varied from rigid to soft by incorporating increasing amounts of soft polyether PU material. This blending method for reprocessing mixed waste compatibilizes different PUs and provides a means to tune the mechanical properties of a PU product, even if starting from waste streams of varying composition. As such, this process represents an intriguing new approach for polymer reprocessing.

Introduction

Polyurethanes (PUs) make up 31% of the commercial crosslinked polymer market value[1] and cover a wide property and application scope, including foams, coatings, and elastomers.[2] PU waste is typically disposed of by landfilling or incineration to recover energy,[3] and their reprocessing or recycling is limited to a small number of commercial processes. PUs have been mechanically downcycled into rebonded foam for carpet underlayers,[4] but this practice has been phased out due to toxicity concerns. Chemical recycling has proven viable in limited cases through glycolytic[5–7] or hydrolytic[8,9] processes to recover polyols, which are used as feedstocks along with new isocyanates to produce polyurethanes with partial recycled content. Chemical recycling of PUs faces complications from undesired side reactions due to impurities and the polyols produced typically lead to products with inferior mechanical properties compared to those based on newly prepared polyols.[10,11] Currently, crosslinked PU materials are not reprocessed into higher or similar-value materials directly, which could in principle produce

materials with 100% recycled content and significant energy savings. Furthermore, the ability to reprocess and compatibilize blends of PU networks using reprocessing methods amenable to industrial processes is attractive to reduce waste buildup and produce PU products without the direct use of isocyanates.[12,13]

Covalent adaptable networks (CANs) have the potential to address the challenge of recycling crosslinked polymers. CANs are polymer networks whose covalent crosslinks undergo degenerate exchange in response to a stimulus, most often heat. These exchanges allow these materials to be reprocessed at elevated temperatures, in contrast to conventional thermosets that are not reprocessable.[14,15] CANs exhibit mechanical properties similar to traditional thermosets at their usage temperatures, yet are amenable to reshaping under conditions when bond exchange accelerates.[16–19] Lewis acid metal catalysts, such as dibutyltin dilaurate (DBTDL) or bismuth (III) neodecanoate, catalyze carbamate exchange in which the urethane crosslinks dissociate to isocyanates and alcohols, which reform carbamate crosslinks as the sample is reprocessed.[20] Most CANs are typically reprocessed using compression molding while some of these materials are amenable to more industrially relevant injection molding and screw extrusion processing.[21,22] Previously, our group used twin-screw extrusion to reprocess model and commercial PU foams into films by post-synthetically introducing DBTDL as a carbamate exchange catalyst.[23] The extruded PUs had no loss of mechanical properties when compared to films synthesized from the same monomers. However, this process converts commercial PU foams to soft, elastomeric films, which are not used for a specific commercial purpose. Additionally, PU foam waste might also be mixed with other PUs rather than being a pure waste stream.[24,25] Reprocessing methods that enable the properties of the product PUs to be tuned to suit particular targets, and that tolerate polymer blends, are necessary for successful mixed waste reprocessing.

While waste streams are typically mixed, blends of waste are typically incompatible due to phase segregation of different polymer structures.[26] Linear polymers are sometimes compatibilized by introducing block copolymers[27–30] or by using reactive interchange to produce block copolymers in situ.[31–34] The compatibilization of CANs might produce miscible blends because the rearranged chemical crosslinks will preclude phase separation.[35–38] However, this concept has not yet been achieved. For example, Zhang and coworkers compression molded two polyester CANs, one rigid and one soft, in the presence of $Zn(OAc)_2$ as a transesterification catalyst.[39] Dynamic mechanical thermal analysis (DMTA) showed that the resulting compression molded materials were phase separated, as evidenced by the observation of two glass-transition temperatures and reduced mechanical properties. Previous work in blending PU by Rabnawaz and co-workers showed that PUs can be mixed and extruded in the presence of excess diols and zinc 2-ethylhexanoate to allow for reprocessability via partial depolymerization.[40] The mechanical properties are inherently altered by this process because the new diols that enable extrusion are incorporated into the structure. The mechanical properties are weakened through the inclusion of excess diols at around 14% composition by weight, where new isocyanate is presumably needed to regain the mechanical properties by cross-linking, although this effect was not demonstrated. Here we blend and compatibilize two PU CANs using twin-screw extrusion in the presence of a carbamate exchange catalyst to produce reprocessed CANs with tunable mechanical properties. Extrusion produced homogenous and fully compatibilized reprocessed blends, as judged by their similar mechanical properties as newly synthesized materials. In reprocessing mixed CAN samples, the effective mixing provided by reprocessing in the extruder was essential, as less effectively mixing compression molded samples showed inferior mechanical properties and distinct polymer domains observed by AFM. The tunability of the

material properties were shown through altering the feed composition of rigid and soft CANs, which provided blended solids with properties ranging from soft to elastomeric to rigid. The tunability of the extruded materials was then demonstrated through multiple reprocessing cycles with the addition of more starting polyurethane film to step down from rigid to soft. These results demonstrate that two or more thermoset networks can be blended to tune their mechanical properties while also compatibilizing otherwise incompatible waste streams.

Experimental Section

Synthesis of polyester (rigid) PU

A vial was charged with poly[trimethylolpropane/di(propylene glycol)-*alt*-adipic acid/phthalic anhydride], polyol (-OH equiv. 2.5, 7.2 g, 36 mmol). The polyol was dried under high vacuum at 90 °C for 16 h prior to network synthesis. Once dried, the polyol was mixed with antioxidant, tris(nonylphenyl) phosphite (364 mg, 2 wt%) and catalyst, dibutyltin dilaurate (341 mg, 1.5 mol% per isocyanate). To this solution, 4,4'-methylenebis(phenyl isocyanate) (4.5 g, 18 mmol), dissolved in DCM (10 mL) was added and the solution was cast into an aluminum mold and placed under reduced pressure at 90 °C for 2 days.

Synthesis of polyether (soft) PU

A vial was charged with poly(ethylene glycol) (400 g/mol, 5.71 g, 14 mmol) and pentaerythritol ethoxylate (15/4 EO/OH, 1.76 g, 2.2 mmol) and dried under high vacuum at 90 °C for 16 h. The polyols were then mixed with antioxidant, tris(nonylphenyl) phosphite (376 mg, 2 wt%) and catalyst, dibutyltin dilaurate (341 mg, 1.5 mol% per isocyanate). To this, 4,4'-methylenebis(phenyl isocayante) (4.5 g, 18 mmol), dissolved in DCM (10 mL), was added and the resulting solution was cast into an aluminum mold and heated at 90 °C for 2 days under reduced pressure.

Compression Molding of Mixed PU Blends

Rigid and soft PU films of a certain composition were ground up with a coffee grinder and mixed. The resulting powder was placed into a rectangular mold and subjected to 160 °C for 1 hour. The resulting film was removed from the mold and placed in a vacuum oven at 90 °C for 2 d to fully cure the materials.

Extrusion of Mixed PU Blends

Rigid and soft PU films of a certain composition were ground up using a coffee grinder and mixed. The twin-screw extruder was heated to 200 °C and put under an N_2 flow and allowed to purge the apparatus. The screws were then rotated at 150 rpm. The mixed PU powder was then fed into the hopper and pushed into the barrel. The resulting rectangular film was cut into films for testing.
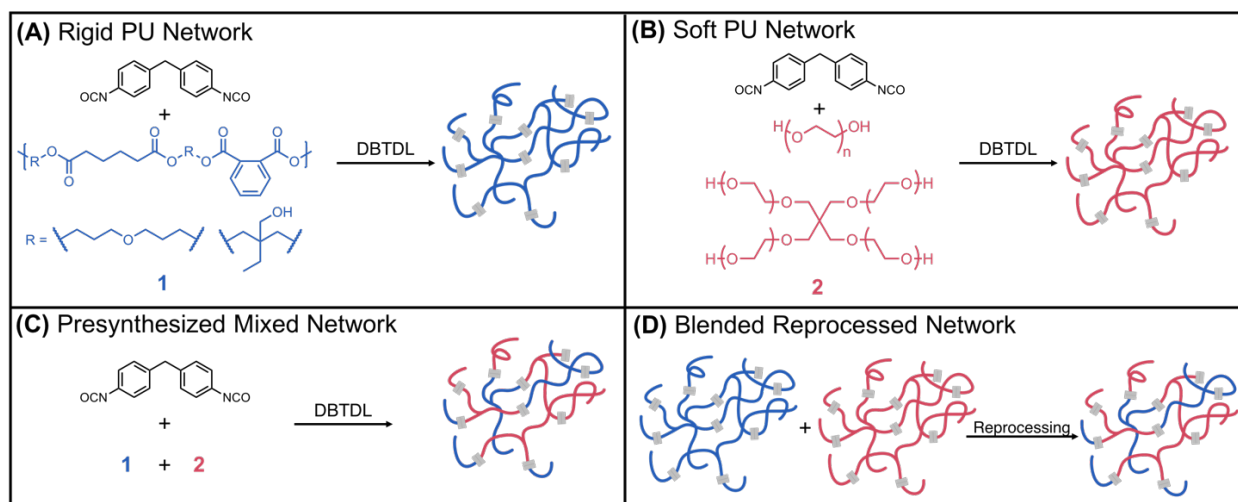

Figure 1. Synthesis of **(A)** rigid polyester polyurethane, **(B)** soft polyether polyurethane, **(C)** as-synthesized mixed polyurethane, and **(D)** blended reprocessed polyurethane networks.

Results and Discussion

PUs with different polyol components were selected as rigid or soft PU networks to evaluate their blending and reprocessing (Figure 1). These PU samples contained 1.5 mol% of DBTDL with respect to their carbamate functional groups to catalyze urethane exchange during reprocessing. Prior to polymerization, both polyols were dried to prevent isocyanate hydrolysis, which leads to urea formation in the network. The polyester PU film had a glass-transition temperature (Tg) of 64.3 °C with a tensile stress of 40 ± 4 MPa, a strain at break of 3.6 ± 0.9 %, and a Young's modulus of 1.6 ± 0.1 GPa (Tables S1-S2). The polyether PU film exhibited a Tg of 10.7 °C, tensile stress of 2.0 ± 0.1 MPa, a strain at break of 430 ± 40 %, and a Young's modulus of 2.0 ± 0.1 MPa.

The polyols were mixed in various ratios and then polymerized to give mixed composition PU networks that had not been reprocessed. The thermal and mechanical properties of these polymer blends were characterized and used to benchmark those of mixed composition samples prepared by reprocessing mixtures of the pure polymer networks (Figure 1C). Dynamic mechanical thermal analysis (DMTA) of these pre-synthesized mixtures shows that the T_g values, as determined by the temperature of maximum of the tan(δ) response, follow a linear trend with composition (Figure 2A, Table S3). Each sample exhibited a similar plateau of the storage modulus at 120 °C, indicating that the pure polymers and synthesized blends all have similar crosslink densities. Tensile plots show that the blends have high strains at break (>200 %), at 75% incorporation of the rigid polyol (Figure 2B). The tensile stress increases with increasing rigid content from 2.1 ± 0.3 MPa for the 25:75 rigid:soft blend to 17.9 ± 0.1 MPa for the 75:25 blend and the strain at break decreases accordingly from 320 ± 10 % to 210 ± 10 % (Table S4). These as-synthesized blends demonstrate how the mechanical properties can be greatly enhanced through blending of the two chemically distinct PU materials. These properties are quantitative

benchmarks for evaluating mixed-composition PU networks obtained by reprocessing mixtures of the two PU homopolymers.
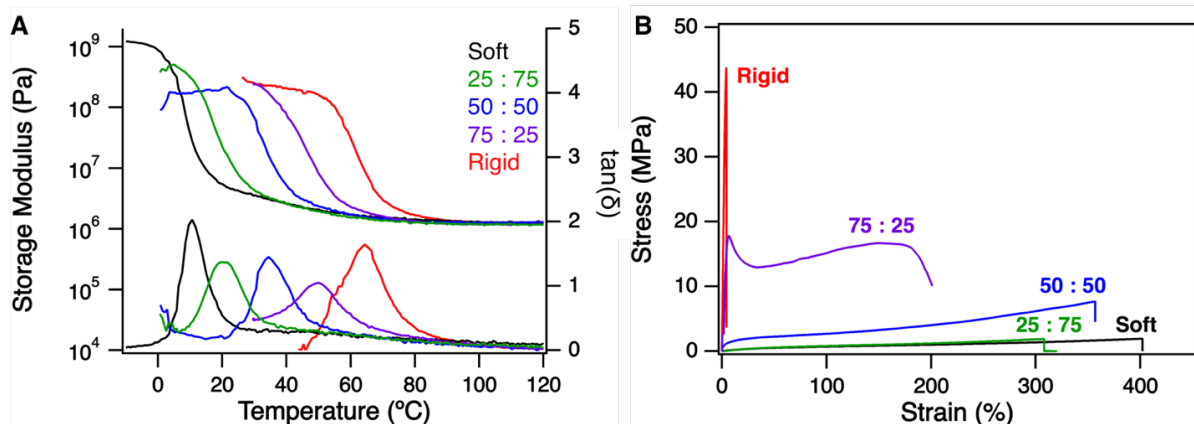

Figure 2. (A) DMTA of the as-synthesized blends, rigid PU, and soft PU showing that the Tg trends linearly with composition and that crosslinking density stays the same for all blends when compared to the starting PUs. **(B)** Tensile plots of the starting PUs and the as-synthesized blends showing the desired mechanical properties of blending these PUs.

Previous work showed that single-component PU film reprocessing was effective using compression molding,[20] but PU foams, with significant air content, required the efficient mixing of extrusion to reprocess into homogenous films of properties comparable to as-synthesized films of similar composition.[23] We hypothesized that twin-screw extrusion would also be beneficial for mixing two PU films efficiently during reprocessing (Figure 1D). Mixtures of the two as-synthesized rigid and soft films were reprocessed using twin-screw extrusion at 200 °C to yield reprocessed blends of varying hard and soft compositions. The screws were co-rotating at 150 rpm under a stream of N2 to prevent oxidation. The extruded blends were first compared to PU blends reprocessed using compression molding, which involved heating the two PU polymers in a rectangular mold for one hour at 160 °C under high pressure. Compression molding at higher temperatures led to bubbling in the samples, which made the samples untestable by tensile

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testing. Following this procedure, the compression molded materials were heated at 90 °C for 2 days in a vacuum oven.

DMTA showed that reprocessing by extrusion gave Tg values and storage moduli similar to newly synthesized blends, whereas compression molding gave inferior properties that implicated inefficient mixing. The compression molded materials seemed homogenous based on the single tan(δ) response by DMTA (Figure S1) yet their plots of storage modulus as a function of temperature showed different Tg values than those for the as-synthesized blends and extruded materials, along with variable crosslinking densities (Figures S2-S4). The Tg values for the more rigid samples were higher than the expected values based upon the extruded blends of the same composition (Table S5), potentially due to the feed composition not matching the composition after compression molding. In contrast, the rubbery plateau of the storage moduli of extruded materials was similar to the as-synthesized networks, indicating that the extruded samples retain most of their crosslink density during reprocessing. DMTA taken at different sections of the extrudate show that the Tg did not vary during the extrusion, indicating that the composition remains constant throughout the extrusion (Figures S5-S7). The crosslinking density of the extruded blends also matches well with the expected based on the storage moduli at 120 °C of the as synthesized rigid and soft PUs. In contrast to compression molding, the DMTA responses for polymer mixtures reprocessed by twin-screw extrusion are similar to polymers synthesized directly from polyol mixtures.
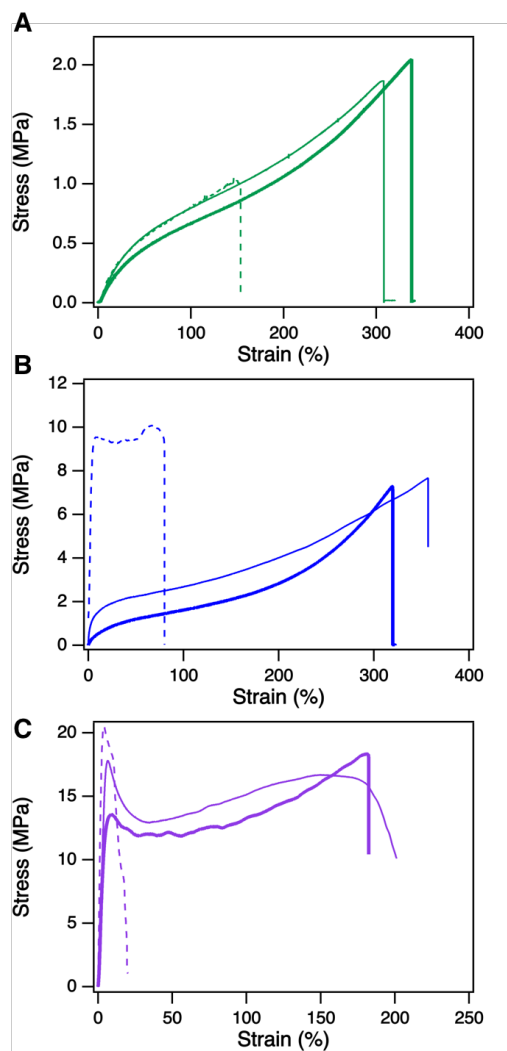
Figure 3. Tensile plots comparing the three methods of PU blending for **(A)** 25:75, **(B)** 50:50, and **(C)** 75:25. Compression molded plots are dashed, as-synthesized are solid, and extruded are bolded.

Reprocessing by extrusion gave materials of similar quality to as-synthesized blends, whereas compression molding produced polymers with inferior mechanical properties (Figure 3). Tensile tests of the extruded materials showed similar stress-strain responses to the as-synthesized blended materials of the same composition, again suggesting efficient reprocessing and mixing

during extrusion. The 25:75 rigid : soft extruded blend, with a T_g of 19.3 °C, had a Young's modulus of 1.1 ± 0.2 MPa, an average strain at break of 310 ± 30 %, and a tensile stress of 1.7 ± 0.4 MPa (Figure 3A, Table S6). The corresponding polymer reprocessed by compression molding had a tensile stress of 0.97 MPa, a strain at break of 153 %, and a Young's modulus of 2 MPa (Table S7). The 50:50 extruded blend, with a T_g of 35.8 °C, had a Young's modulus of 5.3 ± 0.4 MPa, a tensile stress of 7.2 ± 0.2 MPa, and a strain at break of 300 ± 20 % (Figure 3B), which varies drastically from the compression molded 50:50 blend. The compression molded sample had with a T_g of 47.4 °C, tensile stress of 10.1 MPa, strain at break of 79.7 %, and Young's modulus of 260 MPa. The 75:25 extruded blend also had dramatically different mechanical properties from the compression molded blend, in addition to a difference in T_g of 8.3 °C with the extruded blend having a T_g of 48.5 °C and the compression molded blend having a T_g of 56.8 °C. The tensile data shows that the extruded blend had a tensile stress of 16 ± 3 MPa, a strain at break of 170 ± 10 %, and a Young's modulus of 170 ± 40 MPa, in contrast to the compression molded blend which showed 34.4 MPa, 10.4%, and 1300 MPa, respectively (Figure 3C). For all three compositions, the extruded more closely matched the desired mechanical properties found in the as-synthesized blends. Comparison of the tensile data for the three types of PU blending shows that using extrusion as the reprocessing method yields materials with higher quality mechanical properties than compression molding and that the feed composition more closely matches the resulting compositions of the reprocessed materials.
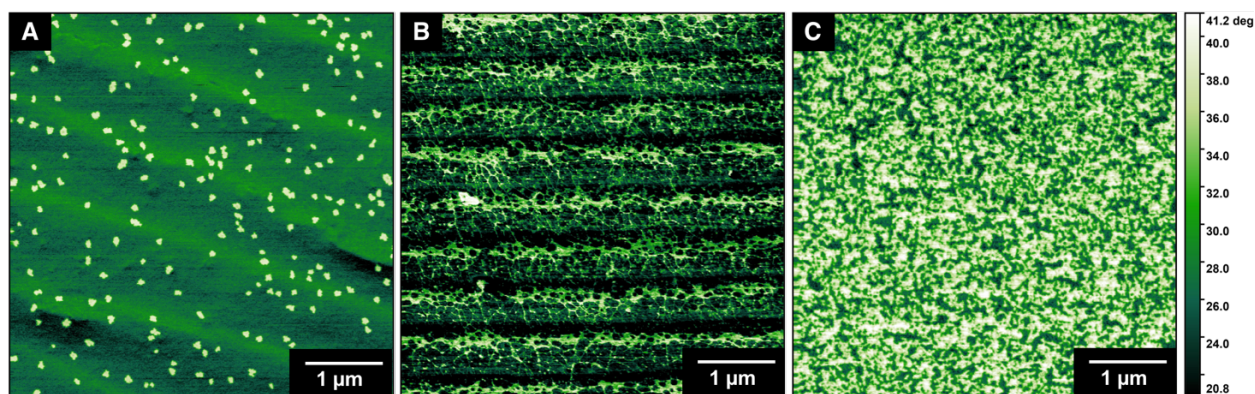
Figure 4. AFM phase imaging of the blended 50:50 PU networks after (A) compression molding, (B) extrusion, and (C) as-synthesized mixtures. Darker areas are more dissipative than lighter areas.

Atomic-force microscopy (AFM) analysis of microtomed cross-sections of the compression molded, extruded, and as-synthesized samples also suggests that extruded samples are more homogenously mixed than compression molded samples (Figure 4). AFM phase imaging shows that the 50:50 compression molded blend has isolated less dissipative domains within a matrix of more dissipative material, suggesting that the compression molded material is phase separated (Figure 4A). Also, the amount of each domain does not match with the expected based on the feed composition, which would correspond to the increased T_g than the expected. AFM phase imaging of the 50:50 extruded blend shows that the extruded material has a different microstructure than the compression molded material (Figure 4B). The extruded material appears better mixed, as it lacks isolated domains. Indeed, the extruded samples approach the uniform images of the as-synthesized blends that appear molecularly mixed (Figure 4C). AFM friction force imaging in contact mode also suggests this microstructure (Figure S8). Overall, AFM phase imaging suggests that the compression molded samples are phase separated and extrusion gives more well-mixed reprocessed samples.

The degree of mixing of the reprocessed compression molded and extruded samples was evaluated chemically by selectively hydrolyzing the polyester polyol, while leaving polyether PU intact. The polyester PU networks were hydrolyzed using hydrochloric acid and water to yield a soluble oil, which was characterized by gel-permeation chromatography (GPC), while the as-synthesized polyether PU did not hydrolyze under these conditions and the resulting material had a gel fraction of 96 %. When the 50:50 blends were subjected to these conditions for 1 d at room temperature, the as-synthesized and extruded blends yielded an oil. In contrast, hydrolysis of the polyester polyol within the compression molded material yielded insoluble particles (Figure S9). GPC analysis of the compression molded byproducts shows evidence for higher molecular weight species compared to the extruded and as-synthesized blends (Figure S10). This finding is also consistent with the compression molded material being more phase separated. GPC of the extruded 50:50 blend suggested, based on the molecular weight of the resulting polyether PU blocks, that this blending method is in between that of compression molding and mixing the polyols pre-synthesis, since the peaks span a large amount of retention times but are lower molecular weight as the compression molded sample.
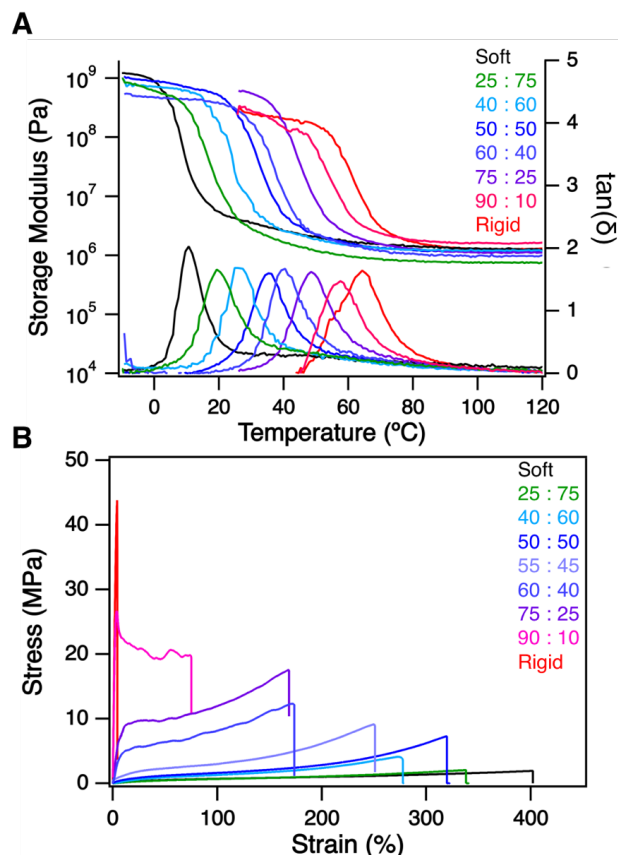
Figure 5. **(A)** DMTA plot showing differing blend composition of the extruded materials and how the T_g trends linearly with the composition. **(B)** Representative tensile data showing the differing mechanical properties for the different blends.

Multiple mixed PUs were reprocessed by extrusion to determine how the composition of the rigid and soft PU feedstocks would influence the T_g and the mechanical properties. Both T_g and the tensile properties of each PU sample were highly tunable based on the rigid:soft composition in samples reprocessed by extrusion (Figure 5). Each of the mixed rigid:soft PUs had gel fractions higher than 80%, indicating that their crosslinks were largely retained throughout the extrusion process (Table S8). DMTA was also consistent with this conclusion, as each sample showed rubbery plateau moduli within 20% of one another, indicating similar crosslink densities. The T_g of each sample followed a linear trend that was proportional to the rigid PU content

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(Figure 5A, Table S9), as determined by plotting the peak of each tan(δ) against weight percent of rigid PU (Figure S11). This simple relationship enables precise tuning of the T_g by varying the PU composition, which may prove valuable for targeting specific target applications for reprocessed PUs or adjusting a future recycling process to ensure consistent properties from variable waste streams. The linear trend of these transition temperatures is similar to the T_g trend seen in miscible thermoplastic polymer blends.[41]

The tensile properties of the reprocessed PU series indicate that these materials can be tuned from rigid to elastomeric to soft polymer networks (Figure 5B, Table S10). The rigid PU blends had compositions ranging from 90:10 to 60:40 with tensile stresses ranging from 33 ± 9 MPa to 13 ± 1 MPa, strains at break between 73 ± 4 % and 170 ± 10 %, and Young's moduli ranging from 1100 ± 30 MPa to 110 ± 30 MPa. Blends with rigid:soft compositions between 55:45 to 50:50 were elastomeric with tensile stresses of 9.4 ± 0.3 MPa and 7.2 ± 0.2 MPa, strains at break of 240 ± 10 % and 300 ± 20 %, and Young's moduli of 12 ± 1 MPa and 5.3 ± 0.4 MPa. Extruded PU blends with rigid contents below 40 wt% were soft crosslinked networks with tensile stresses below 3.8 ± 0.5 MPa, strains at break between 290 ± 20 % and 310 ± 30 %, and Young's moduli below 2.2 ± 0.7 MPa. The mechanical properties of these blends demonstrate how varying the composition over approximately a 5-10 weight percent range can fine-tune the mechanical properties of the sample while retaining its overall mechanical character (*e.g.*, rigid, elastomeric, etc.). These observations provide a high degree of control over the resulting material's properties based on feed composition, which will benefit the overall circularity of PUs reprocessed using this approach.
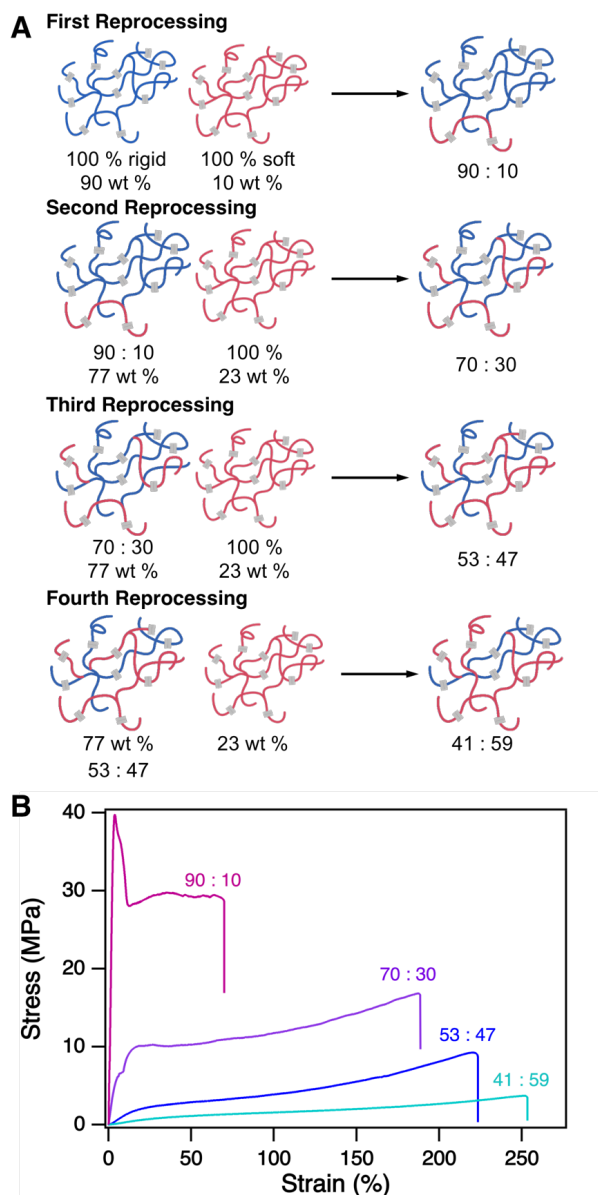
Figure 6. (A) Scheme of the tuning of the composition through multiple extrusion cycles to walk the material from semi-rigid to elastomeric materials. **(B)** Tensile plots for the four reprocessing cycles that show the resulting materials going from semi-rigid to elastomeric in their respective mechanical properties.

To demonstrate the effectiveness and efficiency of twin-screw extrusion as an iterative reprocessing method, the blends were reprocessed multiple times while adding additional newly

synthesized PU to tune the mechanical properties from rigid to soft with each reprocessing step (Figure 6A). The starting blend composition was reprocessed once to yield a 90:10 rigid:soft material. 23 wt % of newly synthesized soft PU was added during the second reprocessing cycle, which provided a film with a resulting composition of 69:31 rigid:soft. This process was repeated twice, each time adding additional newly synthesized soft PUs to yield films with compositions of 53:47 and 41:59 rigid:soft, respectively. Prior to each reprocessing step, we found it important to dry films overnight at 90 °C in a vacuum oven prior to extrusion to remove water absorbed due to the hydrophilicity of the polyols. Films that were not dried rigorously prior to reprocessing showed inferior tensile properties and evidence of urea formation in their infrared spectra (Figure S12). These observations are consistent with a crosslink exchange process in which carbamates transiently dissociate to isocyanates and alcohols at elevated temperatures, which reform new carbamates in the compatibilized materials. The presence of water during this process can decarboxylate isocyanates to amines, which undergo further nucleophilic addition reactions to produce ureas. However, water sensitivity during PU formation is well known in its manufacture[42], and water management is likely to be required in PUs reprocessed using this or related approaches. DMTA of the four iteratively reprocessed polymers shows that the films remain homogenous after each step with the magnitude and breadth of the tan(δ) response mostly unchanged after each reprocessing cycle (Figure S13). The DMTA plots also show that there is no loss in crosslinking density, even after four consecutive extrusions. Furthermore, the T_g for each blend was consistent with the linear composition trend measured for singly reprocessed PUs of different compositions. For each of the four consecutively reprocessed samples, the predicted T_g values were within 2 °C of the values expected based on their rigid:soft composition (Table S11). The tensile properties of the resulting

multiply reprocessed blends were similar to the mechanical properties of blends with similar compositions that were reprocessed only once. The second reprocessing cycle yielded a film composed of 69 weight percent of rigid had a T_g of 43.4 °C, a tensile stress of 17.4 ± 0.9 MPa, a strain at break of 200 ± 30 %, and a Young's modulus of 170 ± 20 MPa (Figures 6B, S12), which matches closely with the mechanical properties of the 75:25 blend. For the third reprocessing cycle, the resulting material had a T_g of 35.5 °C and a composition of 53:47. The mechanical properties for this triply reprocessed material matched the properties of the 55:45 blend with a tensile stress of 9.32 ± 0.08 MPa, a strain at break of 230 ± 10 %, and a Young's modulus of 12 ± 1 MPa. The fourth reprocessing cycle yielded a material with a resulting composition of 41:59 with a T_g of 29.5 °C. The mechanical properties of this extruded film were a tensile stress of 3.5 ± 0.3 MPa, a strain at break of 250 ± 20 %, and a Young's modulus of 2.8 ± 0.3 MPa, which were similar to the 40:60 singly reprocessed blend. All of these multiply reprocessed materials exhibited toughness values that were greater than 90% of the toughness of the singly extruded blends of similar compositions, further indicating the efficiency of this blending method (Table S13). This reprocessing experiment tuning the composition and material properties from rigid to elastomer to soft demonstrates how this reprocessing and blending method again can be predictable and mimics a potential mixed waste feedstock in which already reprocessed materials are mixed with new waste streams.

Conclusion

This work establishes that mixtures of crosslinked PU networks can be reprocessed and simultaneously compatibilized by co-extruding the polymers in the presence of a carbamate exchange catalyst. Use of DBTDL as a carbamate exchange catalyst is being phased out due to the toxicity of tin and future studies into greener alternatives can address these concerns. This

process mixes the polymers and rearranges their covalent bonds efficiently, such that the reprocessed blends have similar thermal and mechanical properties as compared to as-synthesized polymer networks containing mixtures of the two polyol components. Extrusion was superior in this regard compared to reprocessing by compression molding, which produced materials with inferior properties and inhomogenous structures. These findings show great potential for continuous recycling and repurposing PU waste streams to produce polymers of equal or higher value. With further maturation of this method and in combination with statistical methods, unknown mixed PU waste streams might be managed actively to maintain a consistent set of properties in the recycled product. More broadly, this approach might enable specific PU waste streams to be intentionally combined to upcycle these materials into higher value applications.

ASSOCIATED CONTENT

Supporting Information

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

Experimental Section, data tables (Tables S1-S13), DMTA plots, Tensile plots, FT-IR spectra, AFM images, GPC traces (Figures S1-S15) (PDF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

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