Functionalization and Repurposing of Polypropylene to a Thermoset Polyurethane

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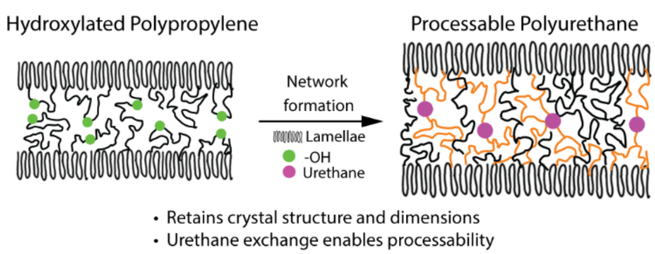
ABSTRACT: Developing effective recycling pathways for polyolefin waste, enabling a move to a circular economy, is an imperative that must be met. Post-use modification has shown promising results in upcycling polyolefins, removing the limitation of inertness, and improving the final physical properties of the recycled material while extending its useful lifetime**.** Grafting of maleic anhydride groups to polypropylene is an established industrial process that enhances its reactivity and provides a convenient route to further functionalization and upcycling. In this work, maleic anhydride grafted polypropylene (PPgMAH) was hydroxylated, and subsequently cured with a diisocyanate to form a thermoset polyurethane (PU). The crystal structure (unit cell and lamellar structure) of the polypropylene (PP) was preserved in the PU. At room temperature, the PU showed high modulus due to the crystallization behavior of the PP; upon increasing the temperature above the melting temperature, the modulus decreased to a rubbery plateau, consistent with formation of a network. The resulting PU showed higher glass transition temperature and lower degree of crystallinity than its PP predecessor due to the crosslinked nature of the polymer. The mechanical integrity of the PU was maintained through several reprocessing cycles due to the melt processability enabled by the presence of a urethane exchange catalyst. This functionalization and upcycling route thus offers a promising alternative to repurposing PP waste, in which the creation of melt-processable thermoset polymers expands applications for the materials.

Table of Contents Graphic:



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The global production of plastic is growing at a rapid pace. Since the 1950s, a total of 8.3 billion metric tons have been produced, for which 6.3 billion metric tons have become plastic waste. At this rate, it is estimated that the global accumulation of plastic waste will reach 12 billion metric tons by 2050.[1,2] Consequently, the versatility and convenience of plastics have also created a threat to the environment.[3] Polyolefins (POs) represent the largest contribution to plastic production: in the U.S., around 65% of all plastics produced are polyethylenes and polypropylenes, and around 4% of that produced is recycled.[4,5] Therefore, more efficient methods of recycling POs are needed to move towards a circular economy.

Mechanical recycling is the predominant method of recycling POs, in which PO-rich streams are melt extruded. A major limitation of this practice is the downgrading of properties, due to many factors, such as chain degradation due to the high-temperature processing and presence of mechanical stresses, as well as presence of contaminants, which can be other polymers and additives which are combined in a sub-optimal way in waste streams.[6] Another possibility is chemical recycling, such as pyrolysis, which reduces the polymer to smaller molecules through thermal decomposition in the absence of oxygen. This process yields light olefins and liquid oils that can be used for fuels, yet is energy-intensive due to the stable C-C single bonds that comprise POs. Additionally, the process can be sensitive to the PO waste composition and purity.[7–9] An alternative solution to overcome these challenges is to first chemically functionalize POs in order to overcome their inertness, and then subsequently upcycle them to value-added goods.[10] In particular, we are interested in upcycling waste POs to durable materials with long product lifetimes, which may divert their future waste from landfills and incineration.

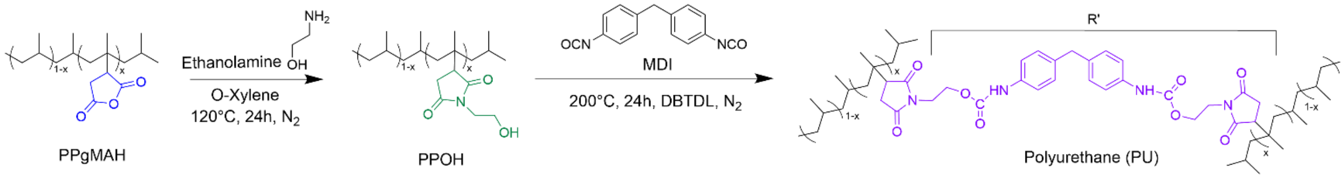
Post-polymerization modification (or functionalization) of POs is a topic of much recent interest to expand the range of properties that can be accessed. The concept is to graft various functional groups to the PO chain to increase the polarity and reactivity of the polymer, thus increasing their versatility.[11] Several PO functionalization strategies have been introduced. One example is the catalytic grafting of hydroxyl groups to polyethylene (PE), which can be further converted to caprolactam groups useful for creating a compatibilizer for polymer blends.[12] PE films were also functionalized using a cold plasma treatment and this enhanced barrier properties for permeation of CO_2, O_2 and N_2.[13] In addition, a common practice in PO functionalization is to add maleic anhydride (MAH) groups to the chain.[14] The MAH group is highly reactive and can be used to add other functional groups such as amines,[15,16] this offers the possibility to upcycle the PO to value-added products.[17–19]

The functionalization of POs with hydroxyl groups provides new opportunities in the development of polyurethanes (PUs). PUs are synthesized by the polycondensation of hydroxyl (-OH) and isocyanate (-NCO) moieties to form urethane linkages. PUs are versatile polymers with tunable properties based on the type of polyol or isocyanate used, ratio of hard and soft segments, as well as the polyol crystallinity, segment flexibility, chain entanglement, inter-chain forces, and crosslinking density.[20,21] As POs are flexible polymers with low T_g, there is an opportunity to incorporate the PO into the soft segment of the PU to achieve unique properties. Jiang et al. have demonstrated this concept, through functionalizing polypropylene (PP) with terminal hydroxyl groups through pyrolysis, and then producing thermoplastic PUs through a copolymerization of the end-functionalized PP with 4,4'-methylenebis(cyclohexyl isocyanate) and polytetrahydrofuran.[22] Nevertheless, the upcycling of PP to thermoset PUs has not yet been explored. Thermoset PUs, known for their long-lasting properties, are frequently used in foams, elastomers, and film production.[23–25] This provides the opportunity to upcycle the PP to durable, value-added products with long lifetimes.

In this work, a strategy is presented for converting PP waste to thermoset PUs. Grafting of MAH to PP is a well-established industrial process.[26–28] Maleic anhydride-grafted polypropylene (PPgMAH) was obtained from industrial sources, functionalized with hydroxyl groups and used as the polyol for thermoset PU synthesis. Maleic anhydride-grafted polypropylene (PPgMAH) was hydroxylated to form hydroxylated PP (PPOH) through a substitution reaction with ethanolamine in o-xylene.[29] Then, the PPOH was fully dissolved in o-xylene at 130°C and reacted with methylene diphenyl diisocyanate (MDI) (1:1 NCO:OH ratio) in the presence of catalyst (dibutyltin dilaurate, DBTDL) in *o*-xylene to form the PU network. The mixture remained homogeneous throughout the curing process. The PU was further cured at 200 °C (over the melting temperature of PP) to ensure full conversion of the functional groups (Scheme 1). The roles of crystallization of the PP and the formation of a crosslinked network in governing the resulting PU properties was explored, and the impact of incorporation of the PP in the PU network on thermal and mechanical properties was quantified. The use of a urethane exchange catalyst in the PU synthesis enabled the creation of processable PU thermosets.

The hydroxylation of PPgMAH to PPOH through a reaction with ethanolamine was confirmed and quantified with proton nuclear magnetic resonance (^{1}H NMR) (Figures S1a,b). The characteristic peaks for the PP backbone were observed from 0.90–1.67 ppm.[30–32] After hydroxylation, the appearance of characteristic peaks (CH_2-CH_2) at 3.70 and 3.77 ppm confirmed the addition of the ethanolamine to the maleic anhydride ring.[29,33] The relative peaks areas of protons associated with ethanolamine (g and h) and methylene (CH_2) groups from the PP backbone (c) were used to quantify the level of hydroxylation (eqns. S1-S3). The number of hydroxyl groups per chain (f_{OH}) was calculated to be 15 ± 1, which is an OH value of 6.9 ± 0.5 mgKOH/g, and also represents a mole fraction of hydroxylated repeat units (x in Scheme 1) of 0.0051 ± 0.0003. The PP functionalization and conversion to PU was confirmed with Fourier-transform infrared (FTIR) spectroscopy (Figure S1c). PPgMAH showed characteristic anhydride peaks at 1864-1860 cm^{-1} (C=O asymmetric stretching) and 1786-1784 cm^{-1} (C=O symmetric stretching). In PPOH, a new absorption band was observed at 3460 cm^{-1} corresponding to the hydroxyl group (OH, stretching). Following hydroxylation to form PPOH, the anhydride peaks shifted to 1714 and 1783 cm^{-1} due to conversion to the succinimide group.[33,34] The PU showed three characteristic peaks that correspond to the urethane linkage, the aromatic amine (N-H) stretching at 3450 cm^{-1}, the carbamate group (N-

C=O-O-) stretching at 1600 cm^{-1}, and the alkenyl (C=C) stretching at 1560 cm^{-1}.[35–37] There was no evidence of products of side reactions observed in the FTIR spectra that may occur between the PPOH and MDI at high temperatures (Figure S1c). The molecular weight increased as PPgMAH was converted to PPOH (Figure S2, Table S1).



Scheme 1. Synthesis of a thermoset PU by hydroxylation of PPgMAH and polycondensation of the -NCO and -OH functional groups to form a thermoset network.

In order to form a network with a diisocyanate, the PPOH must contain more than two hydroxyl groups per chain. In this study, f_{OH} = 15 ± 1, which is significantly greater than this threshold value. Thus, we anticipated the possibility of creating a thermoset PU. To confirm network formation, dynamic mechanical analysis (DMA) was performed in tensile mode (Figure 1). The room temperature modulus was high, consistent with the presence of crystallinity in the polymer, as the material was above the T_g of PP. Upon heating, the modulus dropped drastically and ultimately reached a rubbery plateau, consistent with the formation of a network. Producing a PU network from a PP-based polyol has not been previously reported. From the rubbery plateau modulus, the crosslink density for the PU was calculated (using eqn. S6) to be 0.0127 ± 0.002 mmol/cm^3 (rubbery plateau modulus at 200 °C was 0.15 ± 0.02 MPa, corresponding to a molecular weight between crosslinks of 75 ± 14 kg/mol). While the sample was quite rigid and stiff at room temperature (image inset in Figure 1 at 30 °C), the high temperature behavior was consistent with an elastomer (image inset in Figure 1 at 210 °C). The gel fraction of the PU (42 ± 3 %) was consistent with previous work in which crosslinked PP was prepared with a similar crosslink density to that in our study.[17,38]

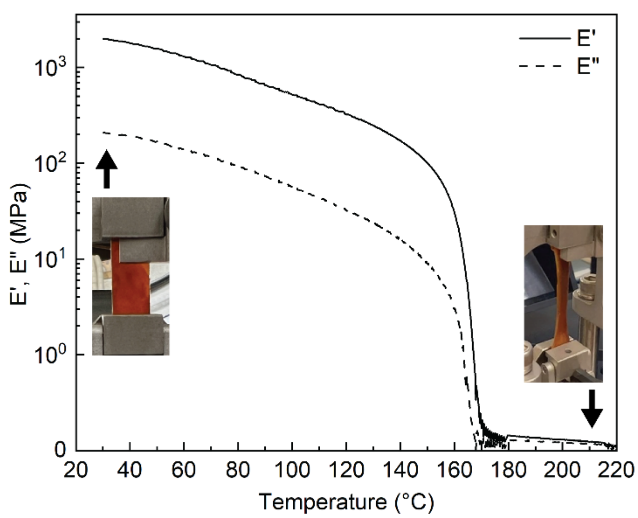


Figure 1. Storage modulus (E') and loss modulus (E") vs. temperature obtained for the PU showing higher modulus at lower temperatures (due to presence of crystallization) and formation of a rubbery plateau at high temperature (above the melting temperature of the PPOH). Insets shows images of the samples mounted in the tensile apparatus at 30°C and 210°C under tension.

The PU exhibited a high modulus at room temperature, indicating the crystal structure might have been preserved during the network formation. The thermal properties of the polymers were therefore directly examined with differential scanning calorimetry (DSC, Table 1, Figure S3). The degree of crystallinity (X_c), glass transition temperature (T_g) and final melting temperature ($T_{m,f}$) of PPgMAH and PPOH were indistinguishable within the error on the measurement. Upon formation of a PU network, the crystallinity decreased and T_g (associated with PP) increased. Furthermore, a new T_g was observed, corresponding to the network, at 50 ± 1 °C. The network formation hindered the chain order, decreasing the crystallinity, and constrained the chain mobility, thereby increasing the T_g.[17,39–41] The crystal morphology was explored with wide-angle and small-angle X-ray scattering (WAXS and SAXS) to determine if the unit cell and lamellar structure were disrupted by the presence of the crosslinked network (Figure 2a,b). Surprisingly, PP retained the α-form of the unit cell in the PU network corresponding to planes (110), (040), (130), (111), (131/041).[42,43] No changes were observed in the long period nor the lamellar thickness upon hydroxylation and conversion to PU (Figure 2c). While the absolute values of crystallinity determined from WAXS and DSC differed, due to the different cooling rates used in each method, both showed that incorporating PP into the PU network decreased the crystallinity. The hindering of chain order caused a decrease in crystallinity and an increase in the interlamellar spacing, as the crosslinks concentrated in the amorphous layer.[38,44]

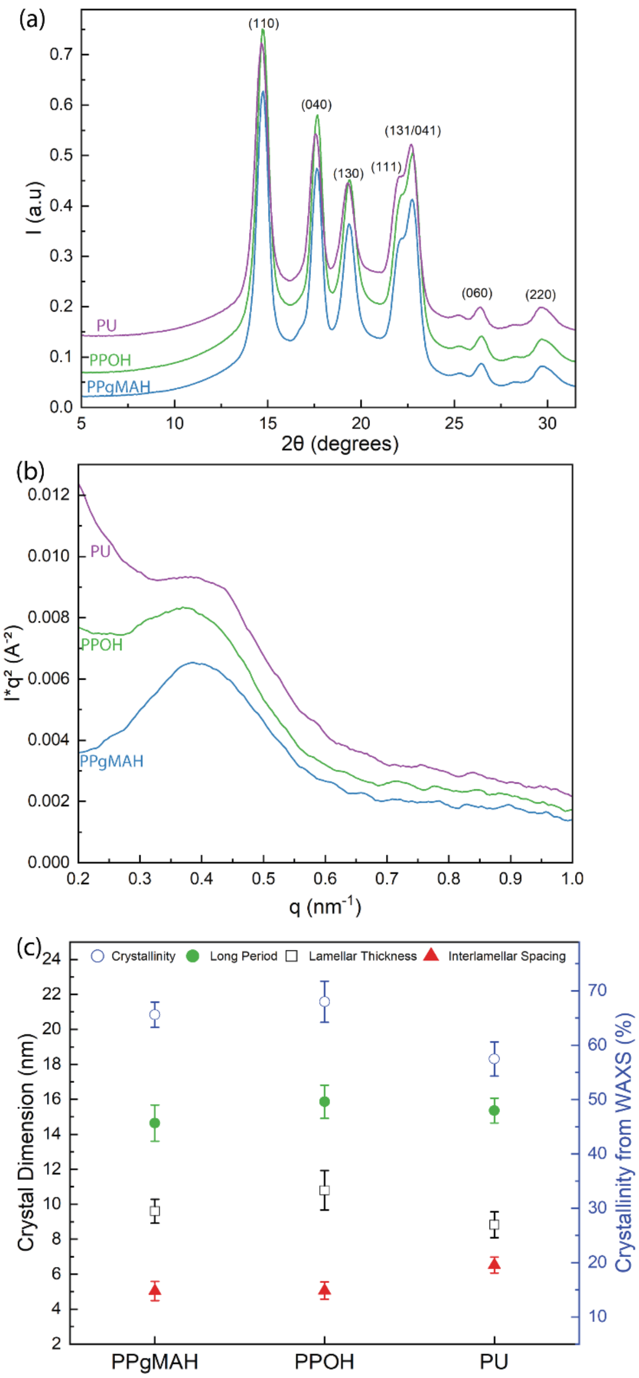


Figure 2. (a) WAXS data and (b) Lorentz-corrected SAXS data obtained for PPgMAH (blue), PPOH (green), and PU (purple) after isothermal crystallization at 115°C. (c) Crystallinity (blue ○), long period (green ●), lamellar thickness (black □), and interlamellar thickness (red ▲).

Mechanical properties were explored with tensile testing (Figures 3 and S4, Table S2). The tensile strength, modulus, and strain at break remained unchanged as PPgMAH was hydroxylated to PPOH (Figure 4), therefore the functionalization did not impact the tensile properties. Upon conversion to a PU, the modulus increased, while the tensile strength and strain at break decreased. Though the PP crystal structure was preserved in the PU network, the presence of crosslinks enhanced the rigidity and brittleness of the PU, increasing the modulus and reducing the strain at break. PUs created from polyester polyols are closely related to our system, due to the semi-crystalline nature of the polyol. Common ranges for the mechanical properties reported for polyester-based PUs are 3-60 MPa, 2-33 MPa, and 300-800% for tensile strength, modulus, and elongation at break, respectively.[45] The tensile strength of the PP-based PU (15 ± 5 MPa) was in the range reported for polyester-based PUs. Potentially due to the preserved crystallinity of the PP in the PU, the modulus of the PP-based PU (4.3 ± 0.2 GPa) was higher compared to the polyester PUs, with the tradeoff of a decrease in the strain at break (0.5 ± 0.2% for the PP-based PU). When comparing to polyether-based PUs, which are not derived from a semi-crystalline polyol, and have a typical range of mechanical properties of 0.80-70 MPa, 4.5-43.80 MPa, and 480-2000% for modulus, tensile strength, and strain at break, respectively, the PP-based PUs still exhibited a higher modulus and reduced strain at break.[46]

Table 1. Thermal properties of PPgMAH, PPOH and PU.[1]

Polymer	X_c, DSC (%)	$T_{m,f}$ (°C)	PP T_g (°C)
PPgMAH	48 ± 1	174 ± 2	-5 ± 2
PPOH	50 ± 1	173 ± 1	-5 ± 1
PU	46 ± 1	173 ± 2	1 ± 1

[1] Degree of crystallinity (X_c), final melting temperature ($T_{m,f}$), and PP glass transition temperature (T_g) were determined from DSC (shown in Figure S3).

The use of a urethane exchange catalyst (DBTDL)[47–51] allowed for melt processing of the PU using compression molding, and all of the measurements presented in this manuscript were obtained on melt-processed specimens. The ability to melt process the sample also enhances its recyclability, as it could potentially be reprocessed into something new at the end of the product lifetime, and therefore the development of catalysts (including those that are green alternatives for DBTDL) for urethane exchange is an active area of research.[47,48,51,52] To test the ability of the PU to be reprocessed, the tensile specimens were cut into small pieces, and then compression molded into new test specimens. After each cycle, the specimens underwent tensile testing. The tensile properties generally remained consistent over 4 reprocessing cycles, and reprocessing did not diminish the properties (Figure 4). A statistical analysis of this data is presented in the *Supporting Information* (Figure S5, Tables S3-S6) to ensure that any observed variations did not represent statistically significant differences after four reprocessing cycles.

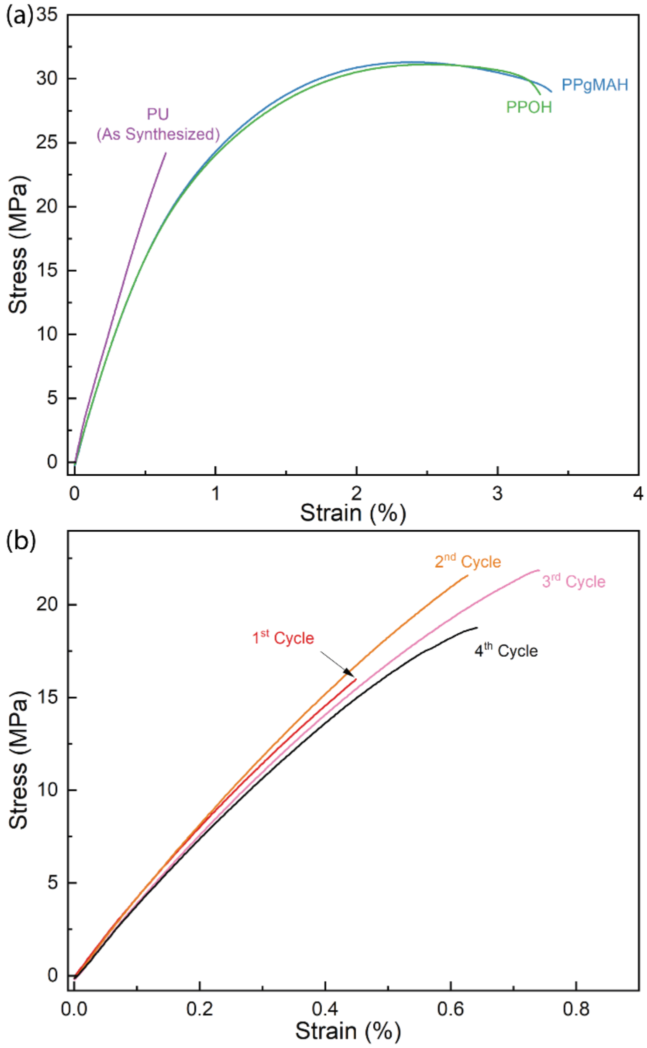


Figure 3. (a) Representative tensile stress vs strain curves for PPgMAH (blue), PPOH (green), and PU (as-synthesized) (purple). (b) Representative stress-strain curves for the PU after multiple reprocessing cycles. In each cycle, the test specimens were cut into small pieces and compression molded into new test specimens, and then tensile testing data was subsequently obtained. The full set of tensile testing data is shown in Figure S4 and Table S2).

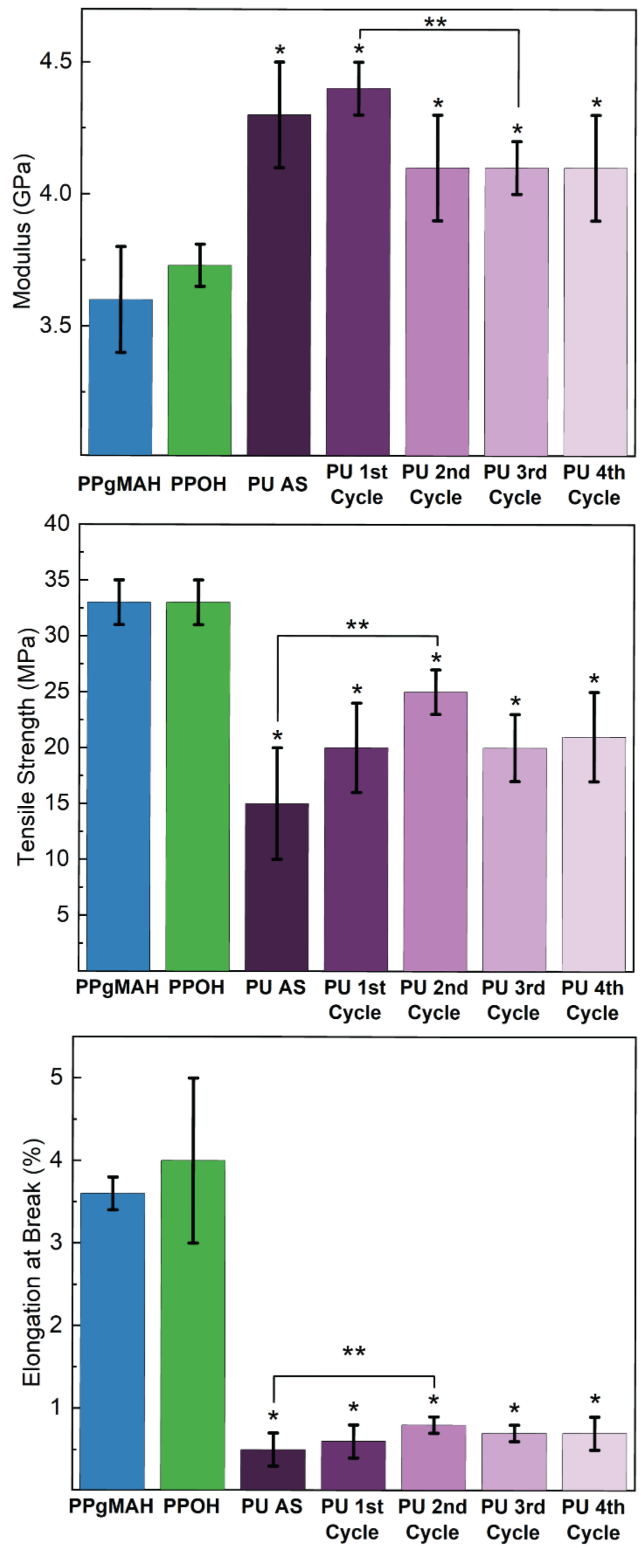


Figure 4. Mechanical properties obtained for PPgMAH, PPOH, and PU (as synthesized, AS) and the reprocessed PU up to four processing cycles. Values shown and error bars represent the mean and standard deviation for measurements obtained on five specimens. The asterisk (*) indicates the values obtained for the PU (AS and reprocessed) are significantly different compared to that of PPgMAH and PPOH. The double asterisk (**) indicates a statistically significant difference between two measurements with a probability value (p-value) < 0.05.

In conclusion, the increasing production of plastics, specifically POs, has led to critical concerns surrounding the accumulation of waste. The exploration of alternative approaches, such as upcycling, offers promising solutions towards a more sustainable future. This work presents a pathway to upcycle PP through the formation of a processable thermoset PU. This strategy employs MAH-grafting of PP, an established industrial process, in which the MAH groups are further functionalized with OH groups, forming a polyol for thermoset PU synthesis. A crosslinked PU network was formed, demonstrated by the rubbery plateau observed in the modulus above the melting temperature of the PP. The PU showed a high room temperature modulus due to preservation of the PP crystallinity in the PU network, which still adopted the traditional PP α-form crystal structure, with similar lamellar thickness compared to the starting PP. The crosslinked nature of the PU provided an increase in modulus with a decrease in strain at break and tensile strength compared to the PP precursor. The PU modulus was greater than that observed in traditional polyester or polyether PUs, with a trade-off in diminished tensile strength and elongation at break. The use of a urethane exchange catalyst enabled the melt-processability of the PU over several reprocessing cycles without loss of properties.

ASSOCIATED CONTENT

The supporting information is available at:

Experimental methods, 1H NMR and FT-IR data for PPgMAH. PPOH, and PU (Figure S1), gel permeation chromatography data for PPgMAH and PPOH (Figure S2, Table S1), raw thermographs for all the polymers (Figure S3), stress vs. strain curves for all the polymers,reprocessing cycles, and photos of PU tensile bars after test (Figure S4), summary of mechanical properties (Table S2), and statistical analysis for the reprocessing cycles (Figure S5, Tables S3-S6).

The data underlying this study are openly available in the Texas Data Repository at https://doi.org/10.18738/T8/BRHKVZ.

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REFERENCES

(1) Geyer, R.; Jambeck, J. R.; Law, K. L. Production, Use, and Fate of All Plastics Ever Made. *Sci. Adv.* **2017**, *3* (7), e1700782. https://doi.org/10.1126/sciadv.1700782.

(2) Zhou, A.; Zhang, Y.; Xie, S.; Chen, Y.; Li, X.; Wang, J.; Zou, J. Microplastics and Their Potential Effects on the Aquaculture Systems: A Critical Review. *Rev. Aquac.* **2021**, *13* (1), 719–733. https://doi.org/10.1111/raq.12496.

(3) North, E. J.; Halden, R. U. Plastics and Environmental Health: The Road Ahead. *Rev. Environ. Health* **2013**, *28* (1), 1–8. https://doi.org/10.1515/reveh-2012-0030.

(4) Vogt, B. D.; Stokes, K. K.; Kumar, S. K. Why Is Recycling of Postconsumer Plastics so Challenging? *ACS Appl. Polym. Mater.* **2021**, *3* (9), 4325–4346. https://doi.org/10.1021/acsapm.1c00648.

(5) US EPA, O. *Plastics: Material-Specific Data*. https://www.epa.gov/facts-and-figures-about-materials-waste-and-recycling/plastics-material-specific-data (accessed 2022-05-05).

(6) Schyns, Z. O. G.; Shaver, M. P. Mechanical Recycling of Packaging Plastics: A Review. *Macromol. Rapid Commun.* **2021**, *42* (3), 2000415. https://doi.org/10.1002/marc.202000415.

(7) Jubinville, D.; Esmizadeh, E.; Saikrishnan, S.; Tzoganakis, C.; Mekonnen, T. A Comprehensive Review of Global Production and Recycling Methods of Polyolefin (PO) Based Products and Their Post-Recycling Applications. *Sustain. Mater. Technol.* **2020**, *25*, e00188. https://doi.org/10.1016/j.susmat.2020.e00188.

(8) Miandad, R.; Rehan, M.; Nizami, A.-S.; El-Fetouh Barakat, M. A.; Ismail, I. M. The Energy and Value-Added Products from Pyrolysis of Waste Plastics. In *Recycling of Solid Waste for Biofuels and Bio-chemicals*; Karthikeyan, O. P., Heimann, K., Muthu, S. S., Eds.; Environmental Footprints and Eco-design of Products and Processes; Springer: Singapore, 2016; pp 333–355. https://doi.org/10.1007/978-981-10-0150-5_12.

(9) Karayannidis, G. P.; Achilias, D. S. Chemical Recycling of Poly(Ethylene Terephthalate). *Macromol. Mater. Eng.* **2007**, *292* (2), 128–146. https://doi.org/10.1002/mame.200600341.

(10) Tan, T.; Wang, W.; Zhang, K.; Zhan, Z.; Deng, W.; Zhang, Q.; Wang, Y. Upcycling Plastic Wastes into Value-Added Products by Heterogeneous Catalysis. *ChemSusChem* **2022**, *15* (14), e202200522. https://doi.org/10.1002/cssc.202200522.

(11) Menendez Rodriguez, G.; Díaz-Requejo, M. M.; Pérez, P. J. Metal-Catalyzed Postpolymerization Strategies for Polar Group Incorporation into Polyolefins Containing

C–C, C═C, and Aromatic Rings. *Macromolecules* **2021**, *54* (11), 4971–4985. https://doi.org/10.1021/acs.macromol.1c00374.
(12) Bunescu, A.; Lee, S.; Li, Q.; Hartwig, J. F. Catalytic Hydroxylation of Polyethylenes. *ACS Cent. Sci.* **2017**, *3* (8), 895–903. https://doi.org/10.1021/acscentsci.7b00255.
(13) A. Rossi; L. Incarnato; V. Tagliaferri; D. Acierno. Modification of Barrier Properties of Polymeric Films of LDPE and HDPE by Cold Plasma Treatment. *J. Polym. Eng.* **1995**, *14* (2–3), 191–197. https://doi.org/10.1515/POLYENG.1995.14.2-3.191.
(14) *Effect of maleic anhydride-grafted polypropylene on the flow orientation of short glass fiber in molten polypropylene and on tensile properties of composites - Uematsu - 2018 - Advances in Polymer Technology - Wiley Online Library*. https://onlinelibrary.wiley.com/doi/abs/10.1002/adv.21834 (accessed 2022-05-12).
(15) *POLYOLEFIN COMPOSITIONS AND ARTICLES PREPARED THEREFROM AND METHODS OF MAKING THE SAME - Patent 2294102*. https://data.epo.org/publication-server/rest/v1.1/patents/EP2294102NWB1/document.html (accessed 2024-07-15).
(16) Chuang, P.-L.; Nien, Y.-H. Synthesis and Characterization of Maleic Anhydride Grafted SEBS Modified with Ethanolamine, 2-Amino-2-Methyl-1-Propanol or Glycerine. *J. Polym. Res.* **2019**, *26* (3), 66. https://doi.org/10.1007/s10965-019-1723-7.
(17) Kar, G. P.; Saed, M. O.; Terentjev, E. M. Scalable Upcycling of Thermoplastic Polyolefins into Vitrimers through Transesterification. *J. Mater. Chem. A* **2020**, *8* (45), 24137–24147. https://doi.org/10.1039/D0TA07339C.
(18) Muljana, H.; Arends, S.; Remerie, K.; Boven, G.; Picchioni, F.; Bose, R. K. Cross-Linking of Polypropylene via the Diels–Alder Reaction. *Polymers* **2022**, *14* (6), 1176. https://doi.org/10.3390/polym14061176.
(19) Létoffé, A.; Hoppe, S.; Lainé, R.; Canilho, N.; Pasc, A.; Rouxel, D.; Jiménez Riobóo, R. J.; Hupont, S.; Royaud, I.; Ponçot, M. Resilience Improvement of an Isotactic Polypropylene-*g*-Maleic Anhydride by Crosslinking Using Polyether Triamine Agents. *Polymer* **2019**, *179*, 121655. https://doi.org/10.1016/j.polymer.2019.121655.
(20) Wang, H.; Zhang, L.; Peh, K. W. E.; Yu, Q.; Lu, Y.; Hua, W.; Men, Y. Effect of Phase Separation and Crystallization on Enthalpy Relaxation in Thermoplastic Polyurethane. *Macromolecules* **2022**, *55* (19), 8566–8576. https://doi.org/10.1021/acs.macromol.2c01504.
(21) Long, T. R.; Elder, R. M.; Bain, E. D.; Masser, K. A.; Sirk, T. W.; Yu, J. H.; Knorr, D. B.; Lenhart, J. L. Influence of Molecular Weight between Crosslinks on the Mechanical Properties of Polymers Formed via Ring-Opening Metathesis. *Soft Matter* **2018**, *14* (17), 3344–3360. https://doi.org/10.1039/C7SM02407J.
(22) Jiang, H.; Ye, L.; Wang, Y.; Ma, L.; Cui, D.; Tang, T. Synthesis and Characterization of Polypropylene-Based Polyurethanes. *Macromolecules* **2020**, *53* (9), 3349–3357. https://doi.org/10.1021/acs.macromol.0c00159.
(23) Qian, Y.; Lindsay, C. I.; Macosko, C.; Stein, A. Synthesis and Properties of Vermiculite-Reinforced Polyurethane Nanocomposites. *ACS Appl. Mater. Interfaces* **2011**, *3* (9), 3709–3717. https://doi.org/10.1021/am2008954.
(24) Xie, F.; Deng, H.; Zhang, W.; Shi, H.; Wang, X.; Zhang, C. Scalable Production of Self-Toughening Plant Oil-Based Polyurethane Elastomers with Multistimuli-Responsive Functionalities. *ACS Appl. Mater. Interfaces* **2022**, *14* (44), 50090–50100. https://doi.org/10.1021/acsami.2c12535.
(25) Elizalde, F.; Aguirresarobe, R. H.; Gonzalez, A.; Sardon, H. Dynamic Polyurethane Thermosets: Tuning Associative/Dissociative Behavior by Catalyst Selection. *Polym. Chem.* **2020**, *11* (33), 5386–5396. https://doi.org/10.1039/D0PY00842G.
(26) Lu, B.; Chung, T. C. Synthesis of Maleic Anhydride Grafted Polyethylene and Polypropylene, with Controlled Molecular Structures. *J. Polym. Sci. Part Polym. Chem.* **2000**, *38* (8), 1337–1343. https://doi.org/10.1002/(SICI)1099-0518(20000415)38:8<1337::AID-POLA18>3.0.CO;2-8.
(27) Krause-Sammartino, L. E.; Lucas, J. C.; Reboredo, M. M.; Aranguren, M. I. Maleic Anhydride Grafting of Polypropylene: Peroxide and Solvent Effects. *Plast. Rubber Compos.* **2006**, *35* (3), 117–123. https://doi.org/10.1179/174328906X103132.
(28) Shi, D.; Yang, J.; Yao, Z.; Wang, Y.; Huang, H.; Jing, W.; Yin, J.; Costa, G. Functionalization of Isotactic Polypropylene with Maleic Anhydride by Reactive Extrusion: Mechanism of Melt Grafting. *Polymer* **2001**, *42* (13), 5549–5557. https://doi.org/10.1016/S0032-3861(01)00069-6.
(29) Abbasian, M.; Ghaeminia, H.; Jaymand, M. A Facile and Efficient Strategy for the Functionalization of Multiple-Walled Carbon Nanotubes Using Well-Defined Polypropylene-Grafted Polystyrene. *Appl. Phys. A* **2018**, *124* (8), 522. https://doi.org/10.1007/s00339-018-1943-4.
(30) Miyauchi, K.; Saito, K. High-Sensitivity Determination of Graft Ratio of Maleic Anhydride-Grafted Polyolefin by Anhydride Methylation in Supercritical Methanol Followed by 1H NMR Spectroscopy. *Polymer* **2011**, *52* (16), 3519–3521. https://doi.org/10.1016/j.polymer.2011.05.050.
(31) Busico, V.; Cipullo, R. Microstructure of Polypropylene. *Prog. Polym. Sci.* **2001**, *26* (3), 443–533. https://doi.org/10.1016/S0079-6700(00)00046-0.
(32) Monaco, G.; Zambelli, A. Simple Trends in NMR Spectra of Vinyl Polymers: The 1H NMR Spectrum of Poly(Propylene). *Macromol. Chem. Phys.* **2005**, *206* (2), 203–209. https://doi.org/10.1002/macp.200400375.
(33) Abbasian, M.; Shahparian, M.; Bonab, S. E. S. Chemical Modification of Polypropylene by Nitroxide-Mediated Radical Graft Polymerization of Styrene. *Iran. Polym. J.* **2013**, *22* (3), 209–218. https://doi.org/10.1007/s13726-012-0120-4.
(34) Yang, L.; Zhang, F.; Endo, T.; Hirotsu, T. Microstructure of Maleic Anhydride Grafted Polyethylene by High-Resolution Solution-State NMR and FTIR Spectroscopy. *Macromolecules* **2003**, *36* (13), 4709–4718. https://doi.org/10.1021/ma020527r.

(35) Dias, R. C. M.; Góes, A. M.; Serakides, R.; Ayres, E.; Oréfice, R. L. Porous Biodegradable Polyurethane Nanocomposites: Preparation, Characterization, and Biocompatibility Tests. *Mater. Res.* **2010**, *13*, 211–218. https://doi.org/10.1590/S1516-14392010000200015.
(36) Wong, C. S.; Badri, K. H. Chemical Analyses of Palm Kernel Oil-Based Polyurethane Prepolymer. *Mater. Sci. Appl.* **2012**, *3* (2), 78–86. https://doi.org/10.4236/msa.2012.32012.
(37) Chandra, S.; Karak, N. Environmentally Friendly Polyurethane Dispersion Derived from Dimer Acid and Citric Acid. *ACS Sustain. Chem. Eng.* **2018**, *6* (12), 16412–16423. https://doi.org/10.1021/acssuschemeng.8b03474.
(38) Saed, M. O.; Lin, X.; Terentjev, E. M. Dynamic Semicrystalline Networks of Polypropylene with Thiol-Anhydride Exchangeable Crosslinks. *ACS Appl. Mater. Interfaces* **2021**, *13* (35), 42044–42051. https://doi.org/10.1021/acsami.1c12099.
(39) Shefer, A.; Gottlieb, M. *Effect of crosslinks on the glass transition temperature of end-linked elastomers*. ACS Publications. https://doi.org/10.1021/ma00041a028.
(40) Xiao, Y.; Liu, P.; Wang, W.-J.; Li, B.-G. Dynamically Cross-Linked Polyolefin Elastomers with Highly Improved Mechanical and Thermal Performance. *Macromolecules* **2021**, *54* (22), 10381–10387. https://doi.org/10.1021/acs.macromol.1c01249.
(41) Paajanen, A.; Vaari, J.; Verho, T. Crystallization of Cross-Linked Polyethylene by Molecular Dynamics Simulation. *Polymer* **2019**, *171*, 80–86. https://doi.org/10.1016/j.polymer.2019.03.040.
(42) Nishino, T.; Matsumoto, T.; Nakamae, K. Surface Structure of Isotactic Polypropylene by X-Ray Diffraction. *Polym. Eng. Sci.* **2000**, *40* (2), 336–343. https://doi.org/10.1002/pen.11167.
(43) Lu, Y.; Chen, R.; Zhao, J.; Jiang, Z.; Men, Y. Stretching Temperature Dependency of Fibrillation Process in Isotactic Polypropylene. *J. Phys. Chem. B* **2017**, *121* (28), 6969–6978. https://doi.org/10.1021/acs.jpcb.7b05071.
(44) Sadri, M.; Patil, S.; Perkins, J.; Gunter, Z.; Cheng, S.; Qiang, Z. Polymeric Dynamic Crosslinker for Upcycling of Fragile Low-Molecular-Weight Polypropylene. *ACS Appl. Polym. Mater.* **2023**, *5* (6), 4056–4068. https://doi.org/10.1021/acsapm.3c00289.
(45) Touchet, T. J.; Cosgriff-Hernandez, E. M. 1 - Hierarchal Structure–Property Relationships of Segmented Polyurethanes. In *Advances in Polyurethane Biomaterials*; Cooper, S. L., Guan, J., Eds.; Woodhead Publishing, 2016; pp 3–22. https://doi.org/10.1016/B978-0-08-100614-6.00001-9.
(46) Yilgör, I.; Yilgör, E.; Wilkes, G. L. Critical Parameters in Designing Segmented Polyurethanes and Their Effect on Morphology and Properties: A Comprehensive Review. *Polymer* **2015**, *58*, A1–A36. https://doi.org/10.1016/j.polymer.2014.12.014.
(47) Tao, Y.; Liang, X.; Zhang, J.; Lei, I. M.; Liu, J. Polyurethane Vitrimers: Chemistry, Properties and Applications. *J. Polym. Sci. n/a* (n/a). https://doi.org/10.1002/pol.20220625.
(48) Sheppard, D. T.; Jin, K.; Hamachi, L. S.; Dean, W.; Fortman, D. J.; Ellison, C. J.; Dichtel, W. R. Reprocessing Postconsumer Polyurethane Foam Using Carbamate Exchange Catalysis and Twin-Screw Extrusion. *ACS Cent. Sci.* **2020**, *6* (6), 921–927. https://doi.org/10.1021/acscentsci.0c00083.
(49) Imbernon, L.; Norvez, S.; Leibler, L. Stress Relaxation and Self-Adhesion of Rubbers with Exchangeable Links. *Macromolecules* **2016**, *49* (6), 2172–2178. https://doi.org/10.1021/acs.macromol.5b02751.
(50) Zhao, G.; Zhou, Y.; Wang, J.; Wu, Z.; Wang, H.; Chen, H. Self-Healing of Polarizing Films via the Synergy between Gold Nanorods and Vitrimer. *Adv. Mater.* **2019**, *31* (18), 1900363. https://doi.org/10.1002/adma.201900363.
(51) Bakkali-Hassani, C.; Berne, D.; Ladmiral, V.; Caillol, S. Transcarbamoylation in Polyurethanes: Underestimated Exchange Reactions? *Macromolecules* **2022**, *55* (18), 7974–7991. https://doi.org/10.1021/acs.macromol.2c01184.
(52) *Reprocessing Cross-Linked Polyurethanes by Catalyzing Carbamate Exchange | Macromolecules*. https://pubs.acs.org/doi/10.1021/acs.macromol.9b01134 (accessed 2024-06-07).