

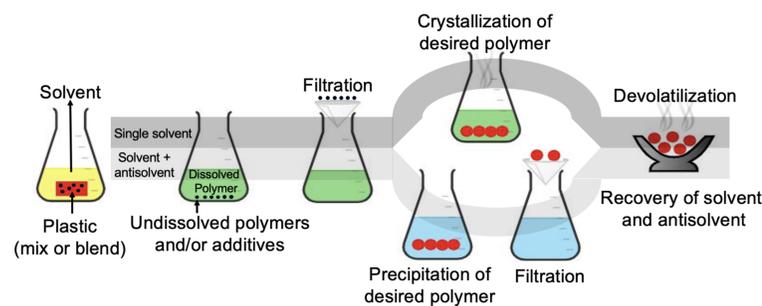
Polyolefin Separation via Dissolution/Precipitation in Novel Solvents for Plastics Recycling

Background and Motivation

- In 2023, global plastics market was 413.8 million tons, projected to reach 579.2 million by 2028.
- Polyolefins such as low density polyethylene (LDPE), high density polyethylene (HDPE), and polypropylene (PP) are the most produced plastics, accounting for 40% of plastic market.
- Plastics recycling rates fell from 9% in 2018 to 5-6% in 2021 due to the growing complexity of plastics, which contain polymers and over 10,000 additives.
- Mechanical recycling cannot fully remove additives and handles rather limited/specific objects.

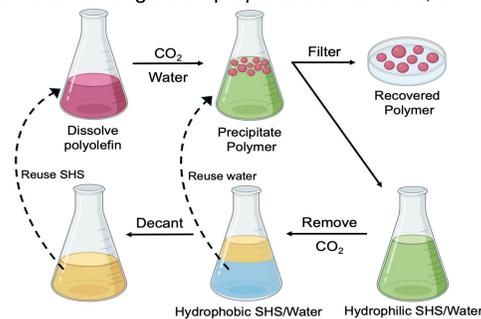
Dissolution-Precipitation Plastics Recycling

- Dissolution-precipitation recycling can yield high-quality polymers similar to virgin materials.
- Dissolution/precipitation removes additives by dissolving the polymer in solvent, filtering undissolved additives, and precipitating the polymer with a nonsolvent.
- Dissolution/precipitation is energy-efficient and produces less CO₂ emissions than pyrolysis.
- However, solvents used in dissolution/precipitation are often hazardous and require antisolvents for polymer precipitation, which adds a lot to the associated costs.



Switchable Solvents for Dissolution-Precipitation

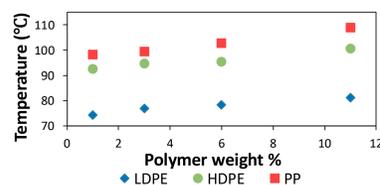
- Switchable hydrophilicity solvents (SHS)** can reversibly switch between a form that is immiscible with water and a form that is miscible with water.
- SHS can change their properties on demand, eliminating need of antisolvents and distillation.



- Primary or secondary amine SHS reacts with CO₂ to form carbamate salt while tertiary amine SHS forms bicarbonate salt which are hydrophilic in nature.
- $2R_2NH + CO_2 \rightleftharpoons R_2NH_2^+ + R_2NCOO^-$
- $NR_3 + CO_2 + H_2O \rightleftharpoons NR_3H^+ + HCO_3^-$

Phase Behavior of Polyolefins in SHS

- Phase behavior of polyolefins in SHS N,N-Dimethylcyclohexylamine (DMCHA), determined via cloud point measurements, indicating phase boundary between semicrystalline polymer and homogeneous solution.



- Interaction parameters (χ), evaluated through Flory-Huggins theory, describe polymer-solvent interactions. Negative χ indicates strong polymer-solvent interactions, positive χ favors polymer-polymer interactions.

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Abstract

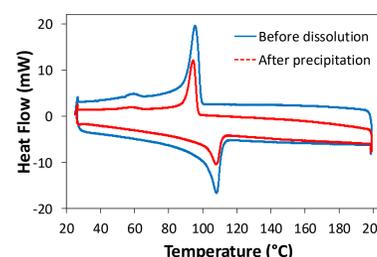
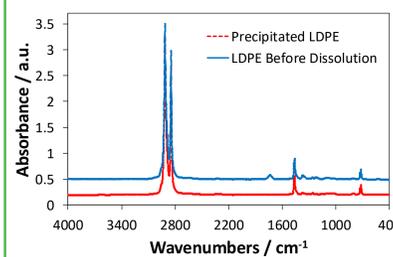
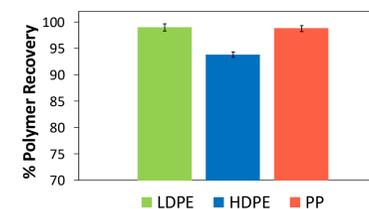
Only a small fraction of the plastics produced are being recycled, with the great majority landfilled or released into the environment. Mechanical recycling is currently used to recycle plastic, however, this method is efficient only for homogeneous and non-contaminated feedstock, and for easily identifiable objects such as bottles made of PET or HDPE. Polyolefins in the plastic waste stream can be processed via pyrolysis, the most common among chemical recycling processes. Pyrolysis, however, decomposes the polymers, resulting in undesirable greenhouse gas (GHG) emissions. Further, pyrolysis is not viewed as recycling when its product, pyrolysis oil, is not converted into new polymers.

Plastics recycling research in our group utilizes physical, solvent-based processes that do not break down the polymer chains. This constitutes true recycling, as the recovered polymer is the same as the starting material. Such molecular recycling processes leave the polymer chains intact, thus maintaining their embodied energy and emitting relatively little GHG. This presentation highlights the application for polyolefin recovery of switchable hydrophilicity solvents (SHS) that can cycle between a form that dissolves the target polymer and a form that does not, hence facilitating closed-loop solvent cycling.

The insights obtained from these studies facilitate the design of solvent systems and processing conditions for the molecular recycling of polyolefins via dissolution-precipitation. Dissolution-precipitation is an energy-efficient and environment-friendly recycling process that can recover specific polymer types from mixtures, blends, or multilayer films, and purify them from additives, without negatively affecting the properties of the original polymers.

Dissolution-Precipitation of Single Polyolefin in SHS

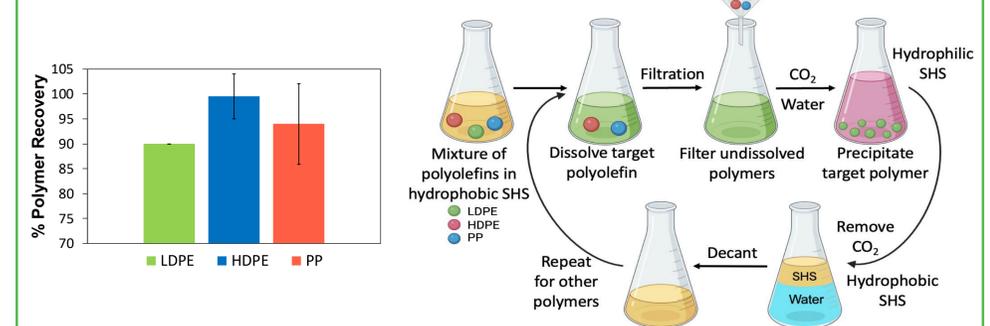
- The bar graph shows % polymer recovery of each polyolefin at precipitation temperature of 0°C in DMCHA.
- Polymer recovery exceeds 90%, demonstrating DMCHA is efficient for polyolefin recycling via the dissolution/precipitation process.



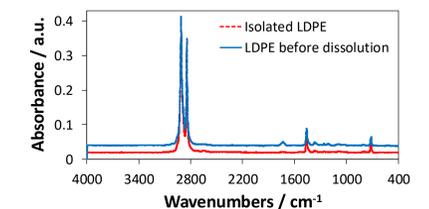
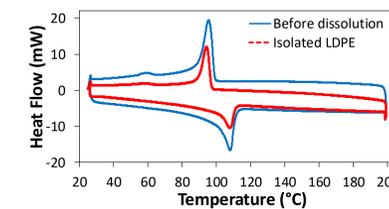
- ATR-FTIR and DSC results show that LDPE's chemistry and thermal properties remain unchanged after dissolution-precipitation in DMCHA.

Recovery of target polymer separated from mixture of polyolefins using SHS

- At the dissolution temperature of the target polymer the other polymers remain undissolved.
- After filtration of undissolved polymers, dissolved polymer is precipitated for recovery.
- This process is repeated to isolate other polymers from the mixture.



- ATR-FTIR and DSC results show that isolated LDPE's chemical and thermal properties remain unchanged after dissolution-precipitation using DMCHA.



Recovery of Switchable Hydrophilicity Solvents

- SHS recovery was achieved by making it hydrophobic again through base-induced deprotonation followed by heating to remove CO₂ from the system.



Conclusions

- The phase behavior of three polyolefins in SHS was obtained and used to rank solvents and evaluating thermodynamic interactions.
- SHS enabled efficient polymer recycling with higher recovery and unchanged chemistry.
- DMCHA separated target polyolefin from the mixture of polyolefins. Due to similar dissolution temperatures, isolated HDPE contained traces of PP and vice versa.
- SHS enabled solvent recovery by switching hydrophilicity, eliminating distillation and reducing material and energy needs.

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