Chemical recycling of unsaturated polyester

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Introduction

Unsaturated polyester (UP) is a thermosetting polymer that widely used in naval constructions, offshore applications, water piping, building construction and automotive applications. [1] Recycling thermosets is challenging due to their three-dimensional network structure. [2] However, solvolysis offers a way to convert the UP thermosets into other products like, in this case, Light Mass Unsaturated Polyester (LMUP). This LMUP can be further used to make functional polymers such as aerogel. [3]

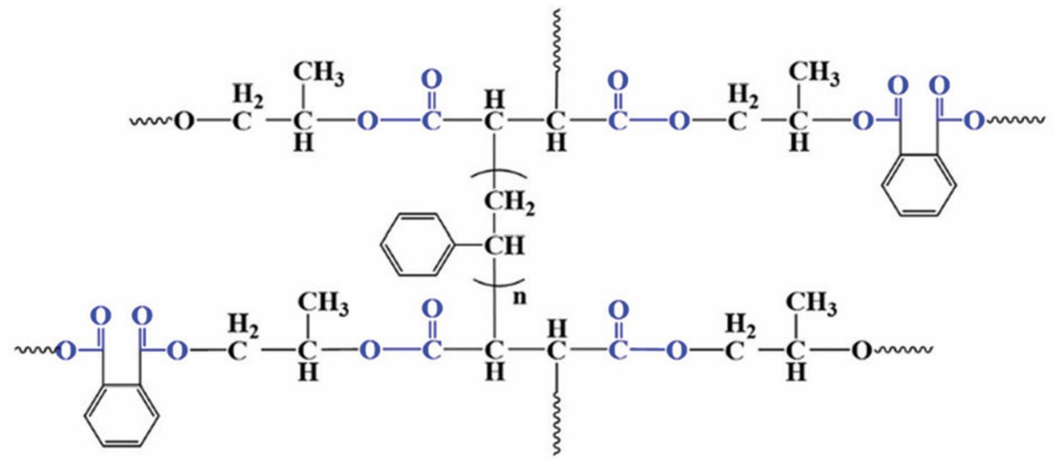

Figure 1: Structure of Unsaturated Polyester cross-linked with styrene [2]

Goal

The goal of this research is to convert the UP thermosets into Light Mass Unsaturated Polyester (LMUP) using solvolysis under mild conditions (80-100 °C, atmospheric pressure).

Method

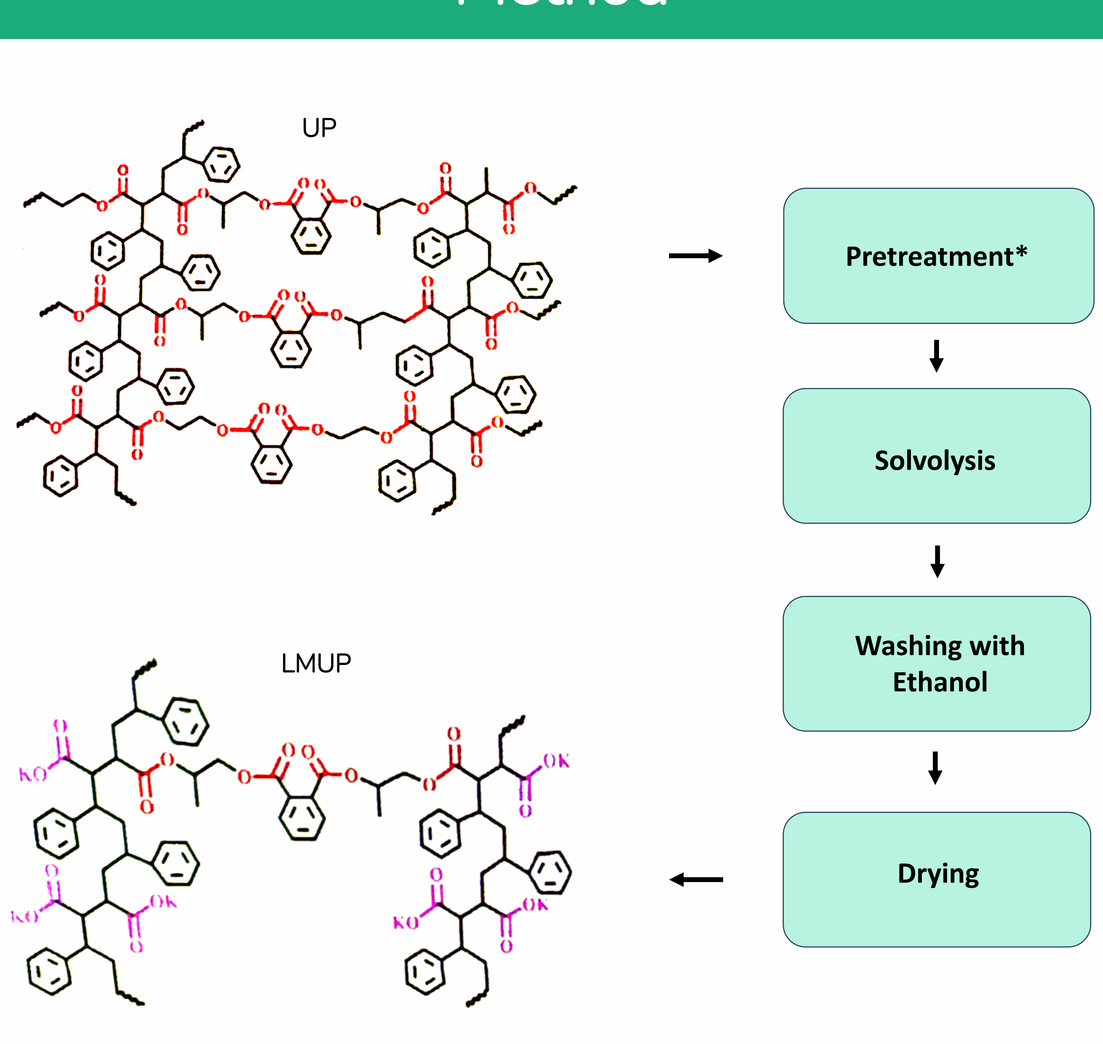

Figure 2: Flowchart of method, showing structure of Unsaturated Polyester and Light Mass Unsaturated Polyester (expected product after solvolysis) [3]

*** Pretreatment methods:** Swelling and Shredding.

Solvolysis conditions:
Solvent: butanol;
catalyst: KOH;
Temperature: 80°C, 100°C;
Time:1 hour, two hours.

Analysis:
- TGA (Thermogravimetric analysis)
- DSC (Differential scanning calorimetry)
- FTIR (Fourier transform infrared)
- GC-MS (Gas chromatography–mass spectrometry)

Results

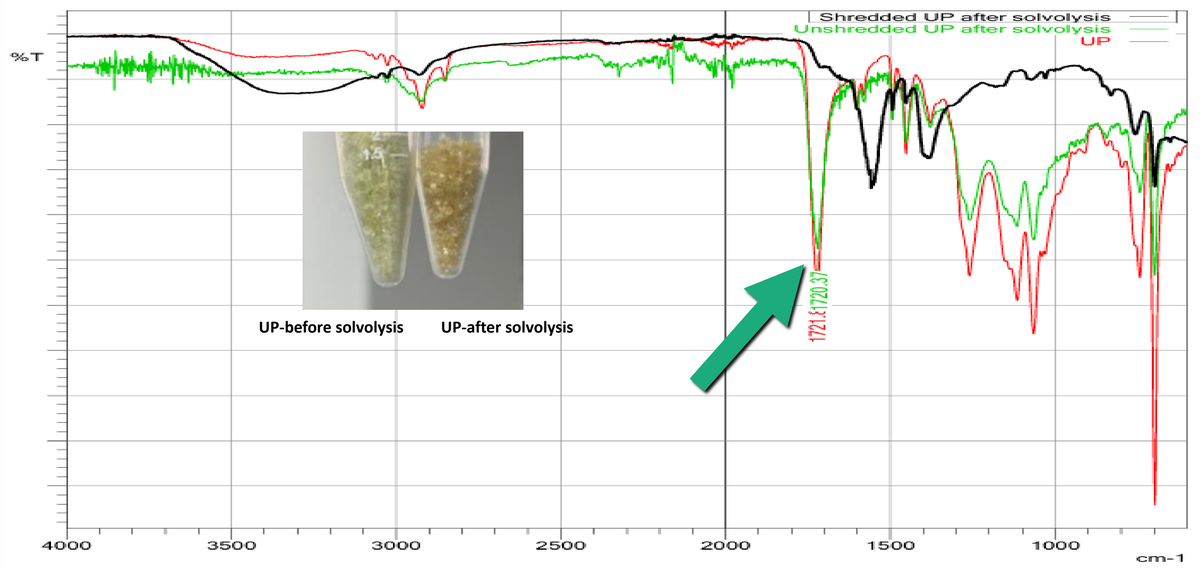

Figure 3: FITR overlay of the samples, Shredded UP after solvolysis, Unshredded UP after solvolysis and UP before solvolysis.

When recycling UP, the ester bond signal at ~1720 cm^{-1} in the FTIR spectrum decreases after solvolysis, indicating bond cleavage, while new peaks at ~1560 cm^{-1} and ~1400 cm^{-1} appear, corresponding to carboxylate groups. Pretreatment like shredding eliminates this ester peak at 1720 cm^{-1} due to increased surface area. Without this pretreatment, solvolysis affects only the surface, leaving the core of the UP intact and resulting in limited ester bond cleavage.

Figure 4: Graph of Residue % after TGA measurement, using a gradient of 20 °C/min to 600 °C

TGA results showed that shredded UP left more residue after solvolysis compared to non-shredded UP under the same conditions, likely due to conversion of -COOK to K_2CO_3.[3] In this case, more residue suggests more reaction taking place during solvolysis. Increasing the solvolysis temperature for the non-shredded sample resulted in more residue compared to the base temperature of 80°C.

Conclusion

Pretreatments such as swelling and shredding can increase the extent of solvolysis of unsaturated polyesters. Increasing temperature and reaction time can both enhance the solvolysis. Future research could focus on alternative solvents to increase the compatibility between the solvent and the unsaturated polyester during the solvolysis process.

References

[1] Dholakiya, B. (2012). Unsaturated polyester resin for specialty applications. In *InTech eBooks*. https://doi.org/10.5772/48479

[2] An, W., Wang, X., Liu, X., Wu, G., Xu, S., & Wang, Y. (2021). Chemical recovery of thermosetting unsaturated polyester resins. *Green Chemistry*, *24*(2), 701–712. https://doi.org/10.1039/d1gc03724b

[3] Qian, Q., Liu, G., Lang, D., Guo, C., Wang, L., & Wu, R. (2022). Recovery of unsaturated polyester resin into oligomer for preparation of oil-water separation aerogel. *Materials Today Sustainability*, *20*, 100254. https://doi.org/10.1016/j.mtsust.2022.100254