Unsaturated Polyester Resin Using Furfural-Derived Monomer

Mikko Aleksi Salonen[a], Andrea Gomez[b], Asmaa M. Ahmed[a], Zainab Al-Maqdasi[b], Juho Antti Sirviö[c], Marja Mikola[d], Juha Ahola[d], Roberts Joffe*[b], Juha P. Heiskanen*[a]

[a] Research Unit of Sustainable Chemistry, University of Oulu, P.O. Box 4300, FI-90014 Oulu, Finland; [b] Department of Engineering Sciences and Mathematics, Luleå University of Technology, Luleå, Sweden; [c] Fibre and Particle Engineering Research Unit, University of Oulu, P.O. Box 4300, FI-90014 Oulu, Finland; [d] Chemical Process Engineering Research Unit, University of Oulu, P.O. Box 4300, 90014 Oulu, Finland

Introduction

From automobiles and marine craft to construction materials, unsaturated polyester resins (UPRs) are widely utilized as binders in different parts of the composite industry.[1] Green alternatives to fossil-based monomers have been studied extensively, but due to high price and low availability, furan-based high-performance monomers derived from sugary biomass have been considered less commercially competitive to be utilized in UPR applications.[2] As the cost of raw materials is starting to decrease and recently made studies with 2,5-furandicarboxylic acid (FDCA) have shown potential, conducting further studies on biobased furans is worthwhile.[3]

In this study, novel unsaturated polyester (UP) prepolymers were synthesized via melt polycondensation using furfural-derived monomer, unsaturated diester monomer, and a mixture of diols. After curing with a reactive diluent, thermal and mechanical properties of the UPRs were studied, demonstrating excellent results with the most optimal UP composition.

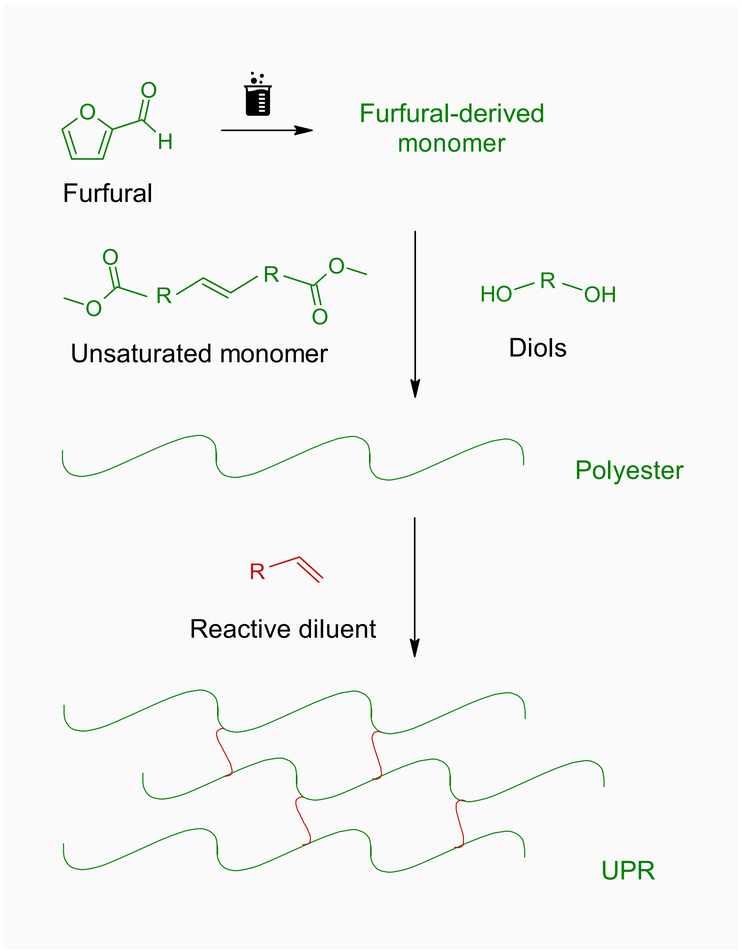

Figure 1. *Resin synthesis from furfural to cured thermoset*

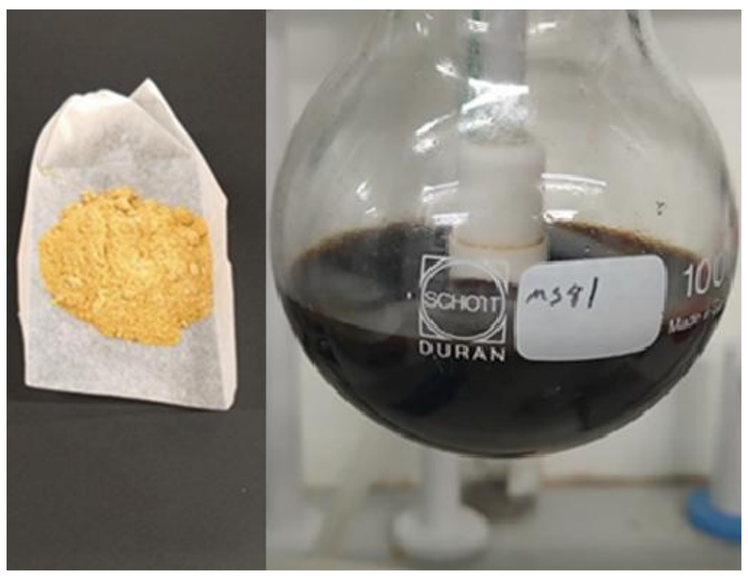

Figure 2. *From bioderived monomer (left) to UPR ready for curing (right)*

Methods

UPR synthesis:

The polyesters in this study were synthesized via catalyzed melt polycondensation. Transition metal catalyst solution, and diol(s) were added into a round-bottom flask and mixed under argon stream. Furfural-derived monomer, unsaturated monomer, and crosslinking inhibitors were added into the reaction flask. The reaction flask was connected to a short-path distillation bridge equipped with a receiving flask, and Ar gas inlet. The polycondensation was performed by heating the mixture under argon atmosphere at 190 °C for 12 h. Then, the temperature was raised to 210 °C and vacuum was gradually applied to 5 mbar until no more excess diol distillate or unreacted sublimated monomer crystals were noticed.

The reaction flask containing polyester was connected to an overhead stirrer and an Ar gas inlet. The UP was warmed at 65–70 °C, then reactive diluent (RD) was mixed with the warmed UP (UP:RD 62:38, w/w) until a homogeneous mixture was formed and no phase separation was observed. At that step, an inhibitor was added to avoid crosslinking during diluting under high temperature and to boost shelf stability.

Figure 3. *Apparatus for polycondensation (left) and dilution (right).*

Curing:

Transition metal accelerator was mixed with UPR at room temperature. Then, peroxide initiator was mixed to the UPR. The UPR was then cast into silicon molds and cured at room temperature for 24 h and thermally post-cured for another 24 h (100 °C for 20 h and at 150 °C for 4 h).

Characterization:

^{1}H NMR, ATR-FTIR, Gel Permeation Chromatography (GPC), dynamic viscosity, gel content, water absorption, Dynamic Mechanical Analysis (DMA), tensile testing, and three-point flexural testing.

Results and Discussion

The polymer structure for the synthesized biobased UPs were based on a commercially available fossil-based resin, which was used as a reference in this study. With the above-described method, it was possible to synthesize UPs with good and uniform quality verified via ^{1}H NMR and ATR-FTIR analyses. Optimization of vacuum distillation step proved to be crucial as insufficient distillation left diol residue, working as a plasticizer, into the polyester system resulting in soft and poor performing UPRs.

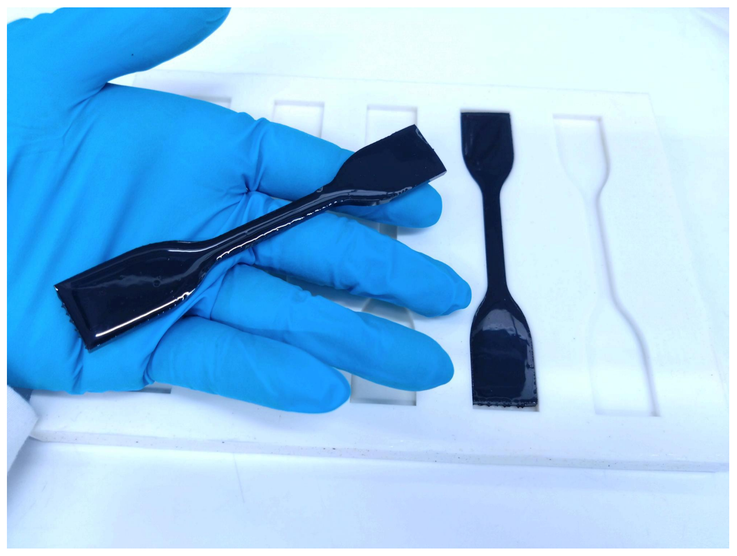

Figure 4. *Cured biobased dogbone samples for tensile testing.*

However, prolonged distillation resulted in UPs with high molar mass and viscosity, which did enhance the mechanical properties of the UPRs, but also made them less applicable for composite molding processes such as vacuum infusion. With optimized diol composition, it was possible to achieve the desired material properties for the UPRs, without excessively increasing the UP molar mass. The crosslinking degrees of the biobased UPRs were comparable to commercial reference, according to gel content studies, determined via Soxhlet extraction in THF.

Considering the thermal properties of the biobased UPRs, the measured glass transition temperatures (T_g) of ca. 100 ° C were comparable with commercial reference, but the calculated crosslinking densities were significantly higher with typical values being $>2 \times 10^3$ mol/m^3 for biobased UPRs compared to commercial reference with crosslinking density of ca. 1.5×10^3 mol/m^3.

Mechanical testing results demonstrated comparable, and partially improved, performance with biobased UPRs compared to the commercial reference. Most notably, the biobased UPR with the most optimal UP composition, had highly improved tensile properties to commercial reference with 76% higher tensile strength and 2.9 times higher elongation at break. Also, the flexural strength of biobased UPR at ca. 110 MPa was comparable with the commercial reference.

Conclusions

In summary, high-quality UPs were synthesized using furfural derived monomer. Cured biobased UPRs were thoroughly tested and their processability, crosslinking degree, and thermal and mechanical properties were compared with commercially available fossil-based analogue. The biobased UPRs performed excellently, demonstrating comparable performance to commercial reference UPR and superior tensile strength. With these promising results, further research will be conducted, studying the compatibility of the UPRs and commonly used fibers, and the recyclability of the UPRs.

Acknowledgements

The research reported in this presentation has been conducted during Interreg Aurora programme funded SUSBICO: Sustainable biocomposites project.

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Interreg Aurora — Co-funded by the European Union

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