Summary of selected publications:

Development of Sustainable Bioplastics

NEJIB KASMI
1. Development of next-generation sustainable Furanoate Bioplastics

2. Different studies on biobased poly(ethylene furanoate) (PEF)

3. Furanoate Polyurethanes and other sustainable materials

4. Furan-based Polyester Blends
1. Development of next-generation sustainable Furanoate Bioplastics
Fully biobased poly(1,4-cyclohexanedicarboxylate-co-isosorbide 2,5-furandicarboxylate) (PCIsFs):

- Controlled crystallization rates
- Enhanced thermal properties were achieved by isosorbide insertion.
- Excellent thermal stability up to 360 °C
- An obvious structure-thermal properties relationship in PCIsFs was found:

 Isosorbide molar ratio $T_g$ and $T_c, T_m$

- 219.7°C $< T_m < 257.2$°C
- 161°C $< T_c < 204$°C
- 76.8°C $< T_g < 103.5$°C

Development of next-generation Furanoate Bioplastics

Development of next-generation Furanoate Bioplastics


- Synthesis of highly heat-resistant poly(hexamethylene-co-isosorbide-2,5-furandicarboxylates) copolyesters
- Great resistance to heat up to 360 °C ($T_{d,5\%}$)
- Very wide $T_g$ range: $10^\circ C < T_g < 135^\circ C$
- Wholly amorphous materials (except for extremely low contents in isosorbide)

PHIsF have the potential to serve as promising fully biobased amorphous materials for practical applications that demand high $T_g$ values.

N. Kasmi,* Z. Terzopoulou, D.N. Bikiaris, Y. Habibi. Tuning thermal properties and biodegradability of poly(isosorbide azelate) by compositional control through copolymerization with 2,5-furandicarboxylic acid, Submitted to ACS Sustain. Chem. Eng. 2021
2. Different studies on biobased poly(ethylene furanoate) (PEF)
Effect of catalyst type on molecular weight increase of PEF during SSP

- Three different catalysts:
  - tetrabutyl titanate (TBT)
  - titanium(IV) isopropoxide (TIS)
  - dibutyltin(IV) oxide (DBTO)

- Solid-state polymerization (SSP) was conducted at different reaction times (1, 2, 3.5, and 5 h) and temperatures 190, 200, and 205°C, under vacuum.

  - SSP time and temperature
  - IV and MW
Extended study on **Effect of catalyst type on molecular weight increase** of PEF during SSP

- Five different catalysts:
  - antimony acetate (III) (Sb Ac)
  - zirconium (IV) isopropoxide isopropanal (Zr Is Ip)
  - antimony (III) oxide (Sb Ox)
  - zirconium (IV) 2,4-pentanedionate (Zr Pe)
  - germanium (IV) oxide (Ge Ox)

- **Zr Is Ip** catalyst shows the best catalytic characteristics
- **Ge Ox** catalyst resulted in the highest activation energies, thus leading to lower molecular weight PEF

An Efficient and Facile Method to Synthesize, through SSP, High Molecular Weight PEF Polyester Appropriate for Food Packaging Applications

- This work is the first study which investigated the feasibility of SSP after remelting process to synthesize high molecular weight PEF, which could be applicable in food packaging applications.

- Remelting process resulted in a higher increase of the polymerization rate

- Very high molecular weight PEF

Effect of additives on the thermal and thermo-oxidative stability of PEF biobased polyester

- PEF stabilizers have been studied for the first time.
- Phenolic antioxidant (Irganox 1098) and two phosphorus-containing thermal stabilizers have been evaluated.

It was found that:

- All the stabilizers;
  - slightly improved the thermal stability of PEF in inert and oxidative atmosphere
  - increased the oxidation induction time
  - slightly reduced the % crystallinity.

- Triphenyl phosphate was the most efficient stabilizer.

The stabilizers can successfully decelerate the thermal degradation and physical aging of PEF in very small quantities, with the P-containing ones PA and mainly TPP being the most effective.

Effect of catalyst type on molecular weight increase and coloration of PEF biobased polyester during melt polycondensation

- tetrabutyl titanate (TBT)
- titanium(IV) isopropoxide (TIS)
- tin(II)2-ethylhexanoate (TEH)
- dibutyltin(IV) oxide (DBTO)

It was found that:

✓ The catalysts used affected both the transesterification and melt polycondensation reactions during synthesis of PEF.

✓ Titanate catalysts TBT and mainly TIS were found to be the most effective ones (MW), compared with tin catalysts like TEH and DBTO, which have the lowest reactivity.

✓ Titanate catalysts lead to the highest coloration.

✓ Polycondensation time affected the colouration, colour intensity was increased progressively by increasing polycondensation time.

This is due to the decomposition of by-products.

Effect of catalyst type on recyclability and decomposition mechanism of PEF biobased polyester

- Tetrabutyl titanate (TBT)
- Titanium(IV) isopropoxide (TIS)
- Tin(II)2-ethylhexanoate (TEH)
- Dibutyltin(IV) oxide (DBTO)

It was found that:

✓ IV values continuously decrease by increasing remelting cycles, while -COOH end group numbers have the opposite trend.

✓ With titanate catalysts accelerating PEF decomposition at a higher extent than tin catalysts.

✓ The molecular weight decrease causes a substantial increase in the degree of crystallinity of the remelted samples, while the thermal stability is decreased.

✓ The decomposition of polyesters synthesized with titanium catalysts (TBT and TIS) takes place mainly via heterolytic routes (β-hydrogen scission).

# In the samples with TEH and DBTO, homolytic scission is more extensive.

➢ Thermal Degradation mechanism study (Pyrolysis-GC/MS):

Identification of pyrolysis products producing mainly vinyl and carboxyl end groups
An in-depth kinetic study of the polymerization of high-purity FDCA with ethylene glycol (EG) with two different catalysts and at three different temperatures.

**Antimony Acetate** $\text{Sb(CH}_3\text{COO)}_3$

**Antimony Oxide** $\text{Sb}_2\text{O}_3$

**PDCA**

**Polyethylene Furanoate (PEF)**

**Characterizations of PEF Polyester**
- Conversion at 160 °C during esterification step:
  - $\text{Sb}_2\text{O}_3$ catalyst is more active than $\text{Sb(CH}_3\text{COO)}_3$
- Polycondensation stage:
  - $\text{Sb}_2\text{O}_3$ catalyst exhibited the best activity

3. Furanoate Polyurethanes and other sustainable materials
Solvent-free synthesis of monomers is one among the most promising ways to develop greener polymers. It was described as one of the “grand challenges” facing chemists.

A truly efficient, practical, and more greener solvent-free synthetic route was successfully applied to prepare for the first time three novel 100% renewable resources-based diols derived from vanillic acid.

New Monomers
- Excellent thermal stability
- High melting points (121 °C - 142 °C)

Polyesters
- High thermal stability (314°C < T_d,5 % < 373 ºC)
- A very wide glass transition temperatures (-2.8 ºC – 69 ºC)

Synthesis and characterization of new fully biobased polyesters with tunable branched architectures

Development of next-generation Furanoate Bioplastics

Different studies on biobased poly(ethylene furanoate) (PEF)

Furanoate Polyurethanes and other sustainable materials

Furan-based Polyester Blends

Summary of selected publications (Development of Sustainable Bioplastics) – Nejib Kasmi

High-performance eco-friendly materials with broad application domains

Intermediate substrates for:
- Chain extension
- Crosslinking
- Co-polymerization

6 Branched polyesters
bearing Carboxyl end groups

- Good thermal stability with $168 \degree C < T_{d,5\%} < 236 \degree C$
- Wide $T_g$ range: $-57 \degree C < T_g < -18 \degree C$
- Wholly amorphous materials

6 Branched polyesters
bearing Hydroxyl end groups

- Good resistance to heat with $180 \degree C < T_{d,5\%} < 268 \degree C$
- Very wide $T_g$ range: $-37 \degree C < T_g < 19 \degree C$
- Wholly amorphous materials

N. Kasmi, C. Pinel, D. Da Silva Perez, R. Didden, Y. Habibi. Synthesis and characterization of fully biobased polyesters with tunable branched architectures, Polymer Chemistry 2021, 12, 991-1001 (LINK)
A green strategy for the synthesis of fully biobased isocyanate-free polyester-urethanes (NIPHEUs) was developed.

- These materials were synthesized by step-growth polymerization combining sugar-derived dimethyl-2,5-furan dicarboxylate with polyhydroxylurethanes adducts bearing four hydroxyl groups (HU-tetraols).

Furanoate Isocyanate-free polyester-urethanes

✓ Satisfactory thermal stability (170°C < T_d,5% < 220°C)
✓ High melting temperatures (93°C < T_m < 110°C)

• The resulting networks exhibited striking thermal behavior upon repetitive heating cycles.
✓ This is related to a thermal-induced bond exchange probably driven by transcarbamoylation reaction.

Such interesting vitrimer-like behavior for this new type of NIPHEUs is unique.

Pave the way toward the design of a new range of functional green materials.
An in-depth study on the thermal behaviour of Poly(1,4-cyclohexane dimethylene 2,5-furandicarboxylate)

Biomass

renewable feedstock-based
PCHDMF thermoplastic

petroleum-based resources analogues

Development of next-generation Furanoate Bioplastics

Different studies on biobased poly(ethylene furanoate) (PEF)

Furanoate Polyurethanes and other sustainable materials

Furan-based Polyester Blends

Poly(1,4-cyclohexanedimethylene 2,6-naphthalate) polyester with high melting point: Effect of different synthesis methods on molecular weight and properties

N. Kasmi, Z. Terzopoulou, G.Z. Papageorgiou, D.N. Bikiaris*. Poly(1,4-cyclohexanedimethylene 2,6-naphthalate) polyester with high melting point: effect of different synthesis methods on molecular weight and properties, EXPRESS Polym. Lett. 2018, 12, 227-237 (LINK)
4. Furan-based Polyester Blends
Three different series of novel fully biobased furan-based polyester blends were prepared for the first time:

- **PEF-PPF 50-50** (dynamic homogeneity and miscibility)
- **PBF-PPF 50-50** (partial miscibility)
- **PEF-PBF 50-50** (partial immiscibility)

- The blends are dynamically homogeneous when the backbones differ by a single methylene unit.
- Reactive blending promotes thermodynamic miscibility of the furanoate-based homopolymers.
- After reactive blending, a copolymer was formed, making the blend dynamically homogeneous.
Evaluation whether poly(alkylene furanoate)s can successfully form blends with poly(alkylene terephthalate)s.

✓ Three different types of blends with different compositions:

- Poly(ethylene furanoate)/poly(ethylene terephthalate) (PEF/PET)
- Poly(propylene furanoate)/poly(propylene terephthalate) (PPF/PPT)
- Poly(1,4-cyclohexenedimethylene furanoate)/poly(1,4-cyclohexane terephthalate) (PCHDMF/PCHDMT)

It was found that:

- PEF/PET and PPF/PPT blends 

- Heating at $T > T_m$

- (PEF) and (PPT) random copolyesters

- Immiscibility and compatibility of the individual components of the blends

Thank you