Πανεπιστήμιο Ιωαννίνων

ΙΝΣΤΙΤΟΥΤΟ
ΕΠΙΣΤΗΜΗΣ ΥΛΙΚΩΝ
ΚΑΙ ΥΠΟΛΟΓΙΣΜΩΝ

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Instrumentation

Shimadzu DSC-60

Shimadzu GPC

TGA/DTA STA 449C (Netzch-Gerätebau, GmbH, Germany)
TMA (Netzch-Gerätebau, GmbH, Germany)
Glassware

Interests

Πανεπιστήμιο Ιωαννίνων

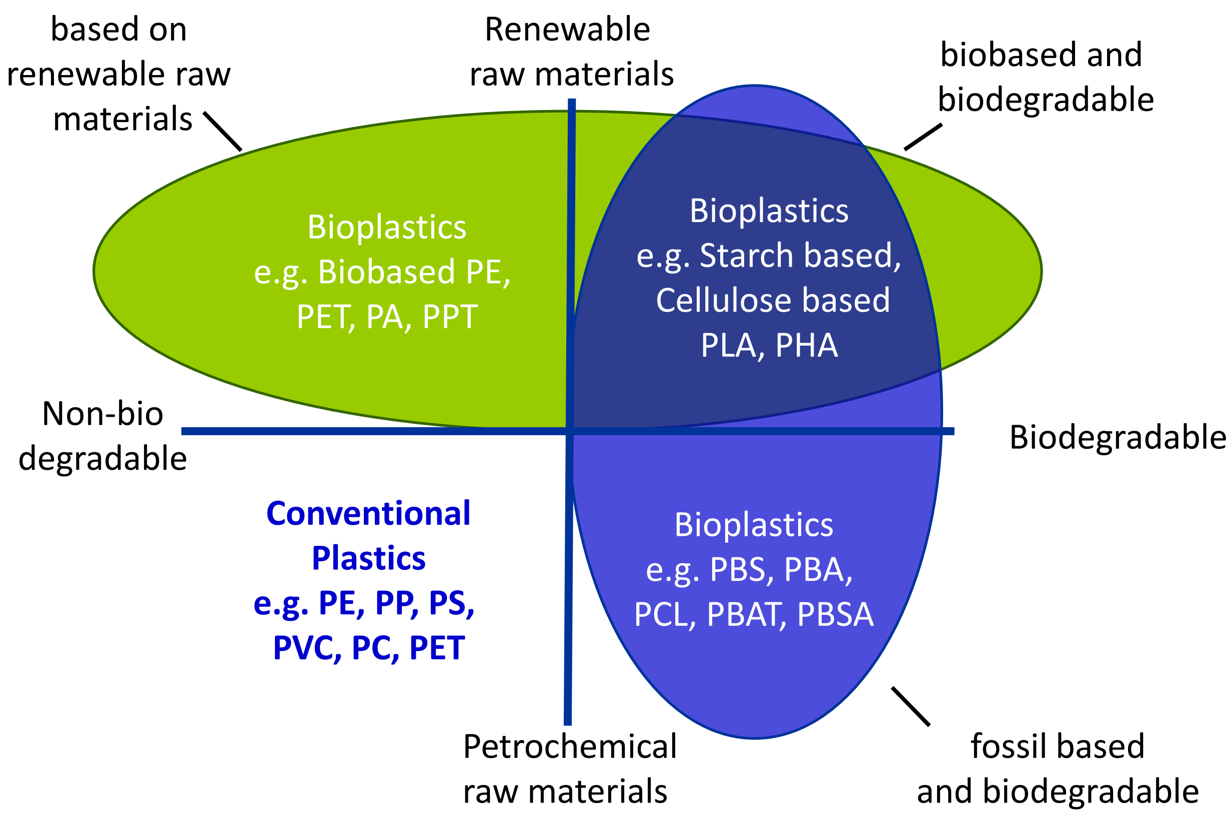
ΙΝΣΤΙΤΟΥΤΟ ΕΠΙΣΤΗΜΗΣ ΥΛΙΚΩΝ ΚΑΙ ΥΠΟΛΟΓΙΣΜΩΝ

Sustainable Industrial Chemistry

Production Process-Structure-Properties Relationship in Polymeric Materials

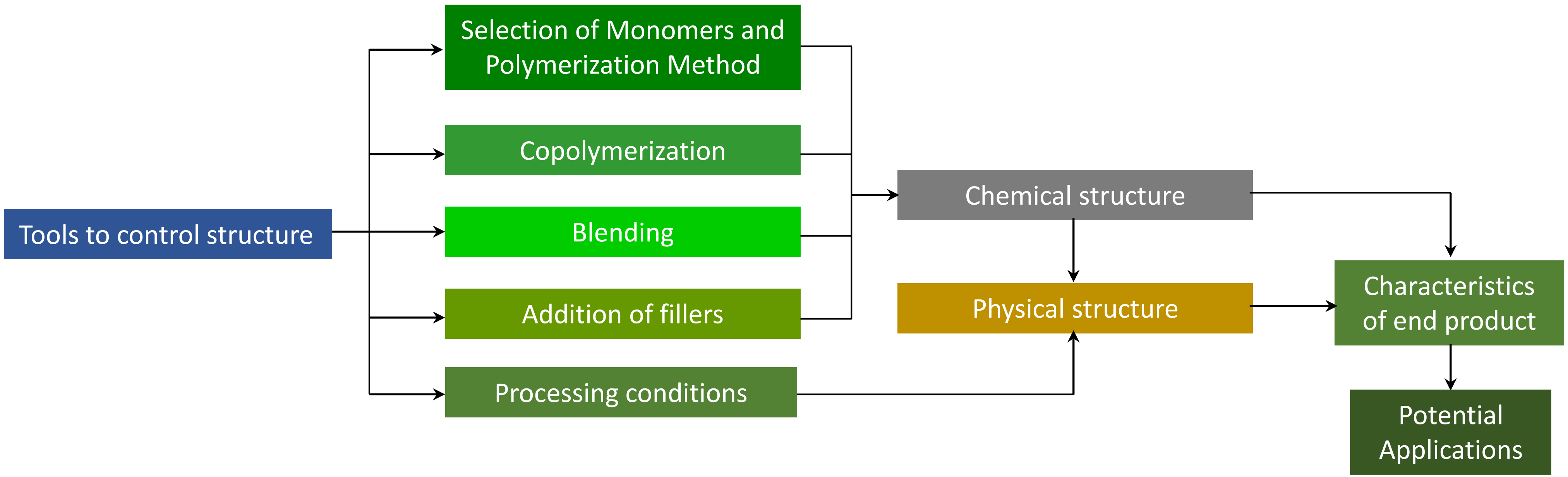
- Sustainable Polymers from Renewable Resources
- Biodegradable Polymers
- Copolymers and Blends
- Polymer composites and nanocomposites
- Applications of Polymers in Drug Delivery Systems

Polymers


based on renewable raw materials
Renewable raw materials
biobased and biodegradable
Bioplastics
e.g. Biobased PE, PET, PA, PPT
Bioplastics
e.g. Starch based, Cellulose based PLA, PHA
Non-bio degradable
Biodegradable
Conventional Plastics
e.g. PE, PP, PS, PVC, PC, PET
Bioplastics
e.g. PBS, PBA, PCL, PBAT, PBSA
Petrochemical raw materials
fossil based and biodegradable

Tailor made polymeric materials

Tailoring properties



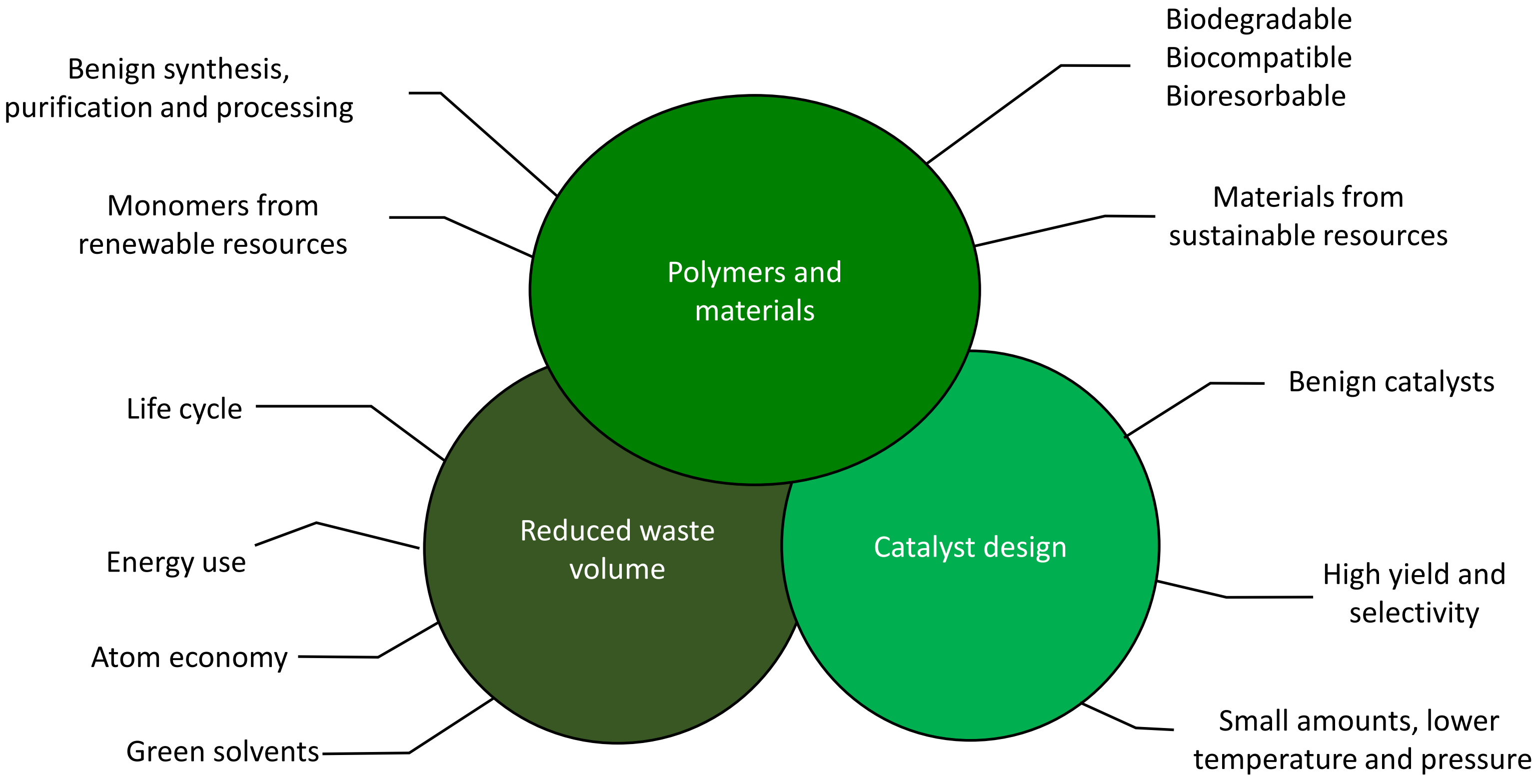
Thinking Green: Sustainable Polymers from Renewable Resources, George Z. Papageorgiou, Polymers 2018, 10, 952; doi:10.3390/polym10090952

Tuning the Properties of Furandicarboxylic Acid-Based Polyesters with Copolymerization: A Review, Z. Terzopoulou, L. Papadopoulos, A. Zamboulis, D.G. Papageorgiou, G.Z. Papageorgiou, D.N. Bikiaris, Polymers 2020, 12, 1209; doi:10.3390/polym12061209

Sustainable Polymeric Materials

Πανεπιστήμιο Ιωαννίνων

ΙΝΣΤΙΤΟΥΤΟ ΕΠΙΣΤΗΜΗΣ ΥΛΙΚΩΝ ΚΑΙ ΥΠΟΛΟΓΙΣΜΩΝ



Polymers from Renewable Resources

Πανεπιστήμιο Ιωαννίνων

ΙΝΣΤΙΤΟΥΤΟ ΕΠΙΣΤΗΜΗΣ ΥΛΙΚΩΝ ΚΑΙ ΥΠΟΛΟΓΙΣΜΩΝ

I. Modification of natural polymers

Natural polymers (e.g. starch, cellulose) → **Bio-based plastics** (e.g. cellulose acetate)

II. 2-Step biomass conversion (Biorefinery concept)

Biomass (lignocellulose, starch, sucrose) — chemical catalysis / bio-chemical catalysis → **'Novel' monomers** (e.g. lactide, FDCA); **'Drop-in' monomers** (e.g. ethylene, terephthalic acid) → **Bio-based plastics**
novel: PLA, PBS, PEF, PHA, ...
drop-in: bio-PE, bio-PET, ...

III. Direct production in plants or by microorganisms

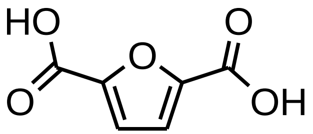
CO_2 + H_2O —photo-synthesis or microorganisms→ **Bio-based plastics** (e.g. PHA)

H. Storz, K.-D. Vorlop · Landbauforsch · *Appl Agric Forestry Res* · 4 2013 (63)321-332

2,5-Furandicarboxylic acid: The biobased alternative to TPA

Πανεπιστήμιο Ιωαννίνων

ΙΝΣΤΙΤΟΥΤΟ
ΕΠΙΣΤΗΜΗΣ ΥΛΙΚΩΝ
ΚΑΙ ΥΠΟΛΟΓΙΣΜΩΝ

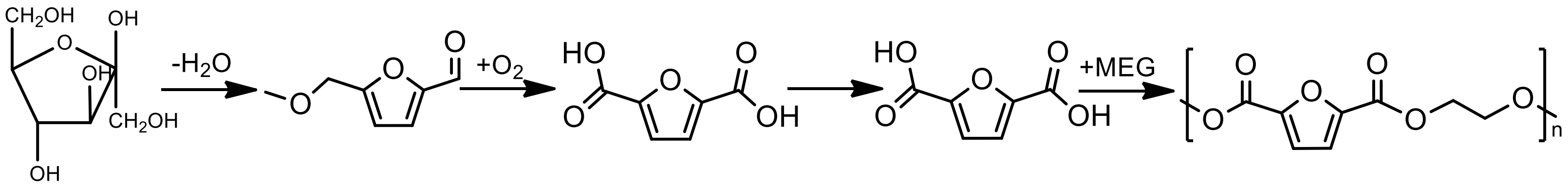


2,5-Furandicarboxylic acid (FDCA)

Avantium, BP

Poly(ethylene furanoate) (PEF)
is the biobased alternative to PET

Sugar Dehydration ⇨ Oxidation ⇨ Purification ⇨ Polymerization ⇨ Processing ⇨ PEF

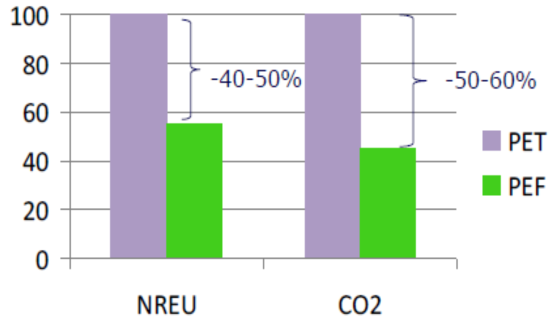


Carbohydrate -Fructose | 5-Methoxy-Methyl-Furfural | 2,5-Furandicarboxylic acid | 2,5-Furandicarboxylic acid | Poly(ethylene furanoate)

Atom economy

Significant reduction in NREU and CO_2

NREU: Non Renewable Energy Use



Source: Avantium Chemicals B.V.

Poly(ethylene 2,5-furandicarboxylate) (PEF)

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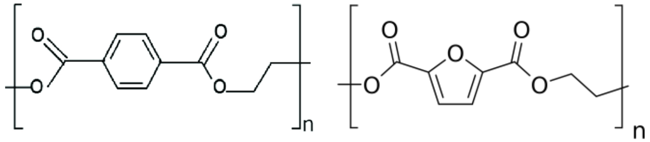
PEF is a 100% bio-based 100% recyclable polymer, alternative to PET

PEF has superior properties compared to PET



Property	PET	PEF
Density of amorphous polymer	1.335 g/cm^3	1.428 g/cm^3
Density of crystalline polymer	1.453 g/cm^3	1.565 g/cm^3
O_2 permeability	0.114 barrer	0.0107 barrer (11X barrier)
CO_2 permeability	0.46 barrer	0.026 barrer (19X barrier)
T_g	~79°C	~88°C
T_m	250-270°C	210-230°C
E-modulus	2.1-2.2 GPa	3.1-3.3 GPa
Yield strength	50-60 MPa	90-100 MPa
Quiescent Crystallization time	2-3 min	20-30 min

P(barrer)=10^{-10}cm^3(STP)·cm/(cm^2·s·cmHg)

Source: Avantium Chemicals B.V. and S. Burgess (PhD project Georgia Tech, funded by The Coca-Cola Company)

Polymerization Reaction Engineering

Πανεπιστήμιο Ιωαννίνων

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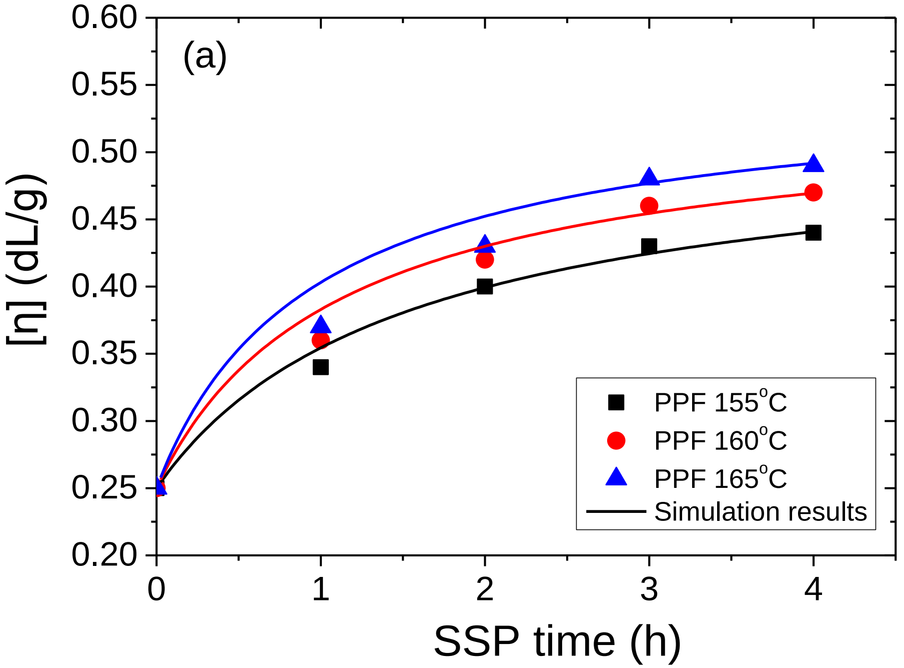
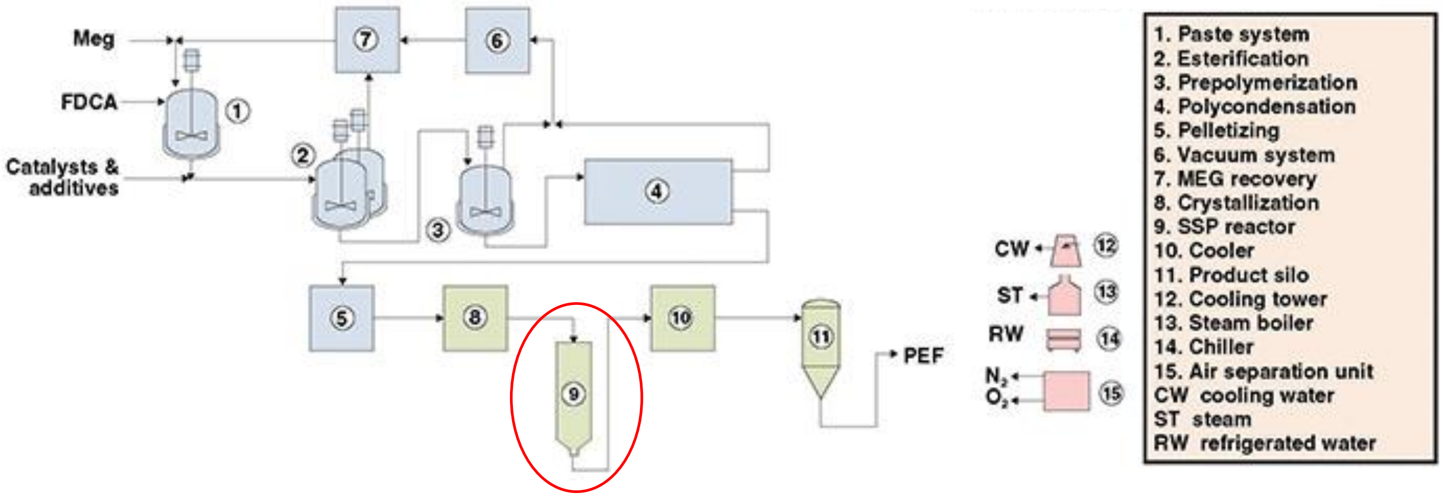
Modelling Solid State Polymerization





https://dalinyebo.com/fdca-to-pef-polyethylene-furanoate_a-production-cost-analysis/2/

Effect of catalyst type on molecular weight increase and coloration of poly(ethylene furanoate) biobased polyester during melt polycondensation, Z. Terzopoulou, E. Karakatsianopoulou, N. Kasmi, V. Tsanaktsis, N. Nikolaidis, M. Kostoglou, G.Z. Papageorgiou, D.A. Lambropoulou, D.N. Bikiaris, Polym. Chem., 2017, 8, 6895–6908

Polymerization of Poly(Ethylene Furanoate) Biobased Polyester, III: Extended Study on Effect of Catalyst Type on Molecular Weight Increase, Y. Chebbi, N. Kasmi , M. Majdoub, G.Z. Papageorgiou, D.S. Achilias, D.N. Bikiaris, Polymers 2019, 11, 438; doi:10.3390/polym11030438

Thermal and Enzymatic Degradation

Πανεπιστήμιο Ιωαννίνων

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TGA
Pyrolyzer/GC-MS
Enzymatic degradation tests in lab
Soil burial test

Effect of catalyst type on recyclability and decomposition mechanism of poly(ethylene furanoate) biobased polyester, Z. Terzopoulou, E. Karakatsianopoulou, N. Kasmi, M. Majdoub, G.Z. Papageorgiou, D.N. Bikiaris, Journal of Analytical and Applied Pyrolysis 126 (2017) 357–370

Thermal degradation kinetics and decomposition mechanism of polyesters based on 2,5-furandicarboxylic acid and low molecular weight aliphatic diols, Vasilios Tsanaktsis, Evangelia Vouvoudi, George Z. Papageorgiou, Dimitrios G., Papageorgiou Konstantinos Chrissafis, Dimitrios N. Bikiaris, Journal of Analytical and Applied Pyrolysis 112 (2015) 369–378

Crystallization and melting of poly(alkylene 2,5-furandicarboxylates)

Πανεπιστήμιο Ιωαννίνων

ΙΝΣΤΙΤΟΥΤΟ ΕΠΙΣΤΗΜΗΣ ΥΛΙΚΩΝ ΚΑΙ ΥΠΟΛΟΓΙΣΜΩΝ

Differential Scanning Calorimetry

Conventional DSC

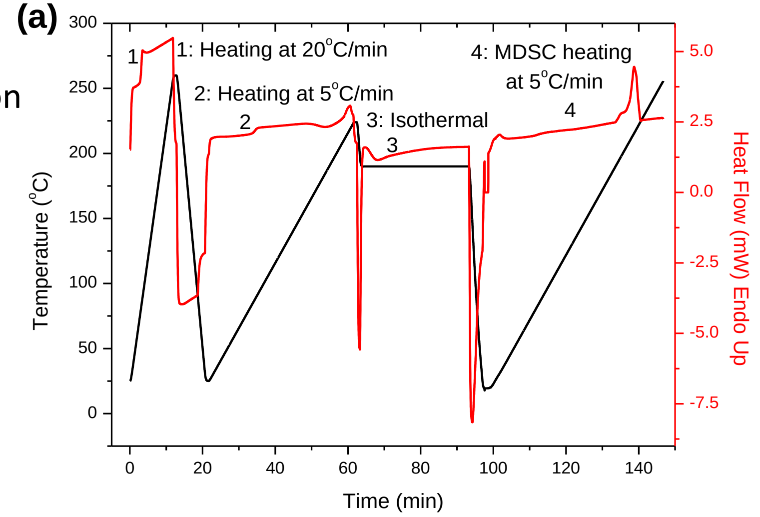
Step-Scan DSC

Modulated Temperature DSC

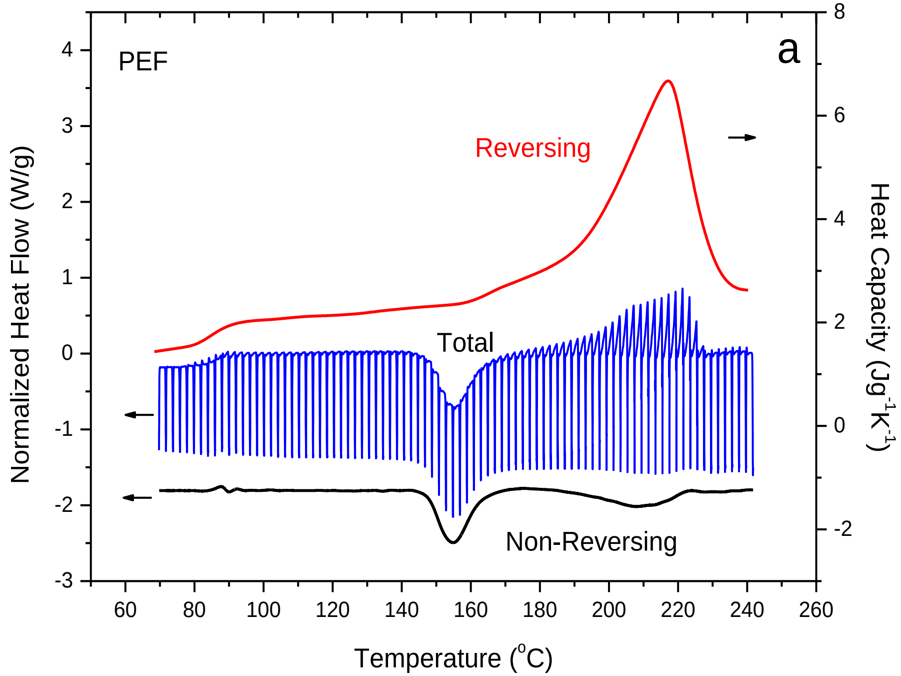
Hyper DSC

Fast Scanning Calorimetry FSC

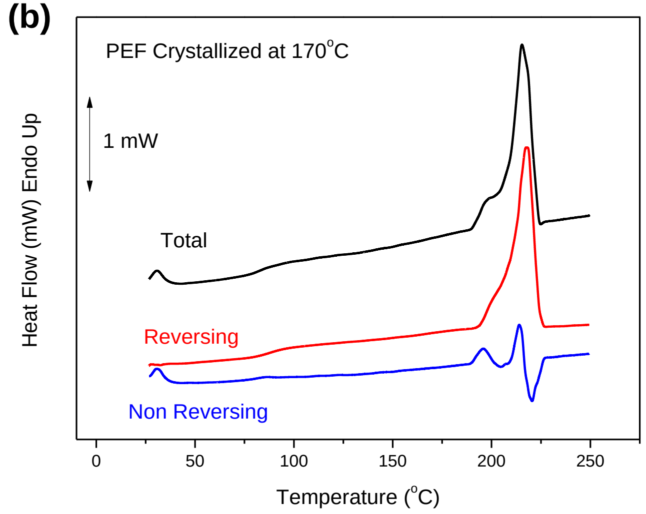
Self-nucleated crystallization



Step Scan DSC (SSDSC)



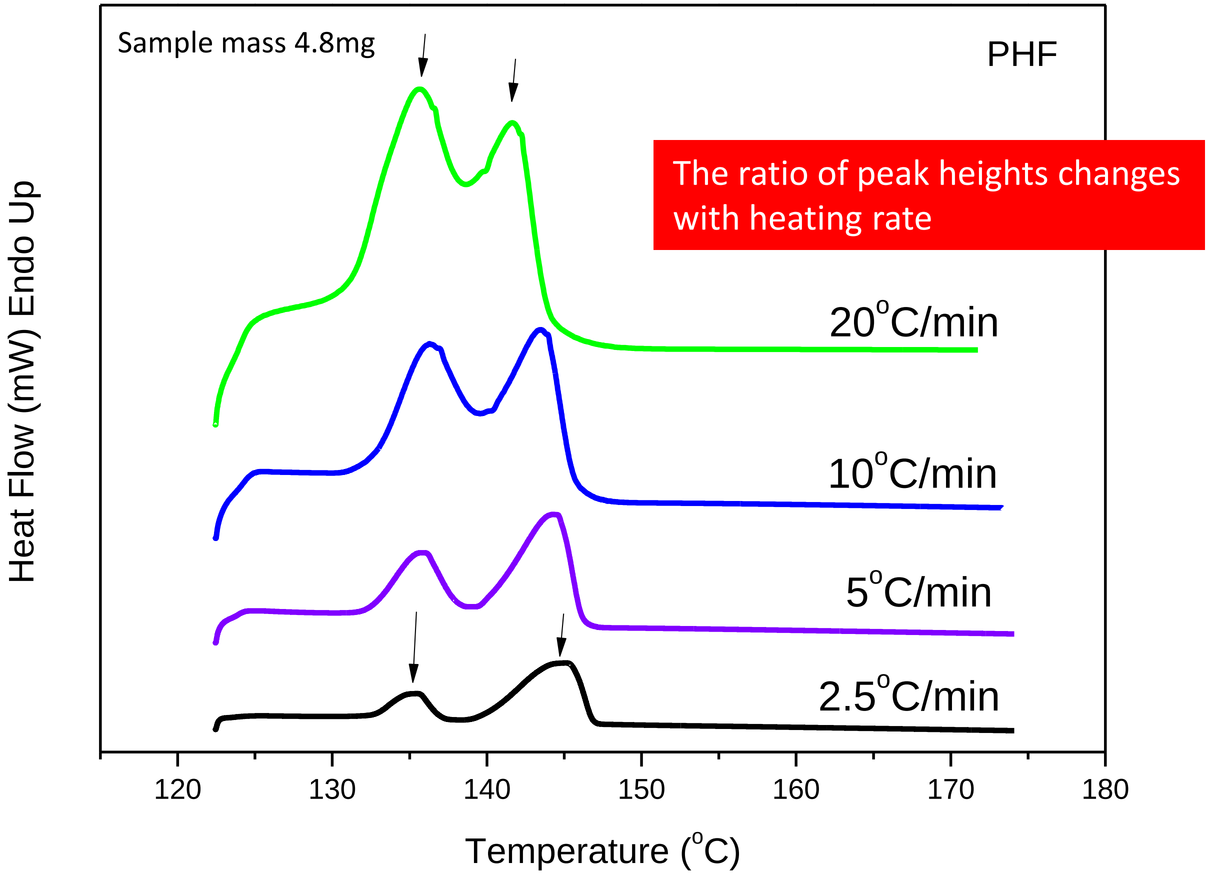
MDSC



Crystallization and melting of poly(alkylene 2,5-furandicarboxylates)

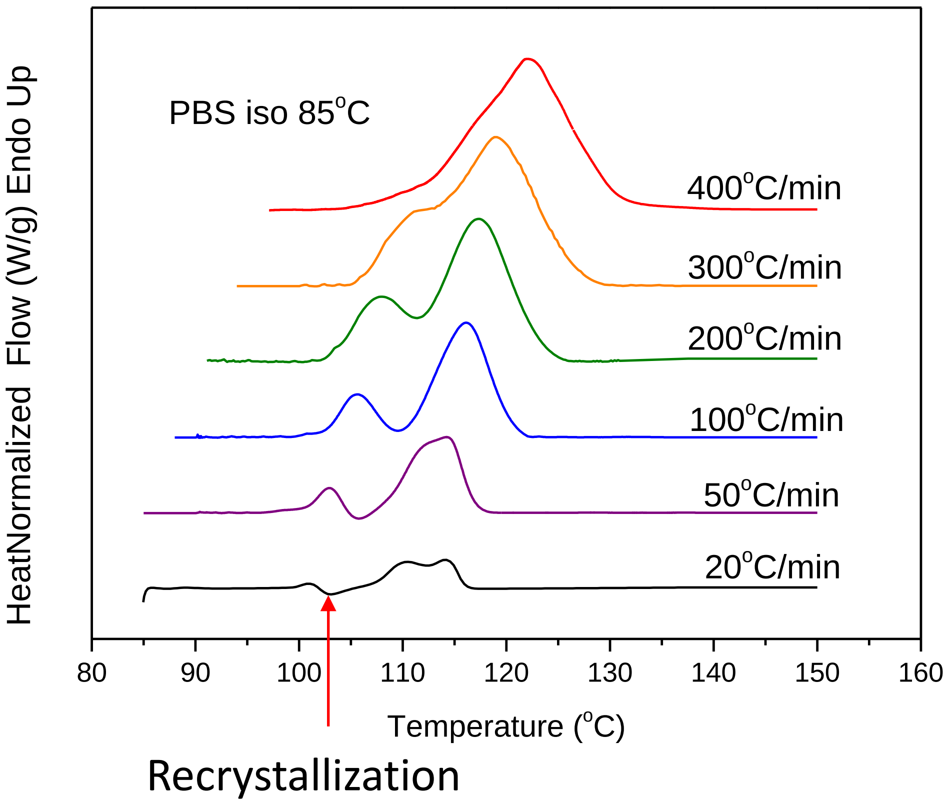
Recrystallization/reorganization takes place during a slow heating scan

Poly(hexamethylene 2,5-furandicaboxyalate) (PHF)



Hyper DSC

Low mass sample (0.23 mg) wrapped in aluminum foil



G.Z. Papageorgiou et al. European Polymer Journal 67 (2015), 383-396

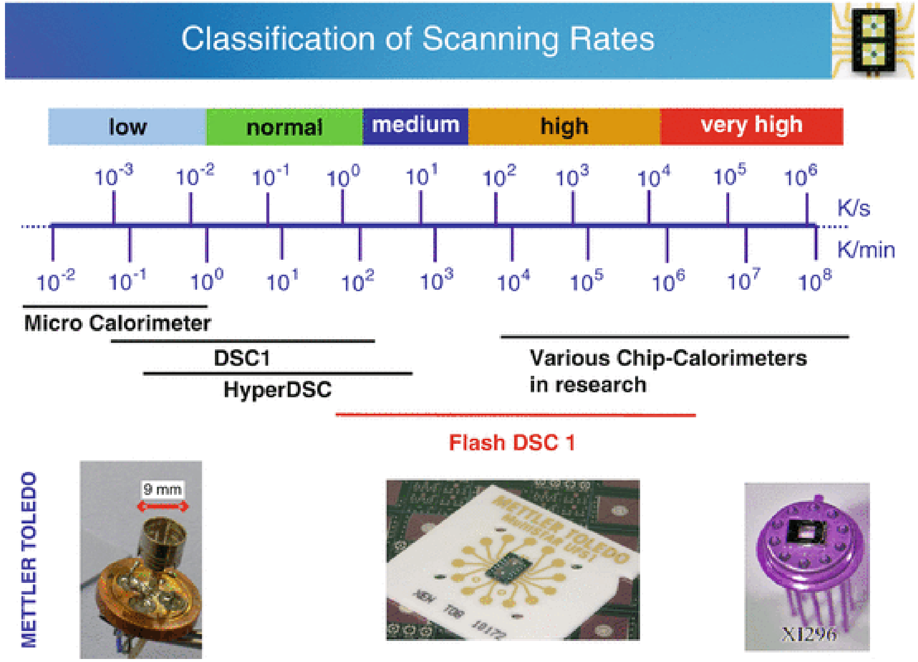
Crystallization and melting of poly(alkylene 2,5-furandicarboxylates)

Πανεπιστήμιο Ιωαννίνων

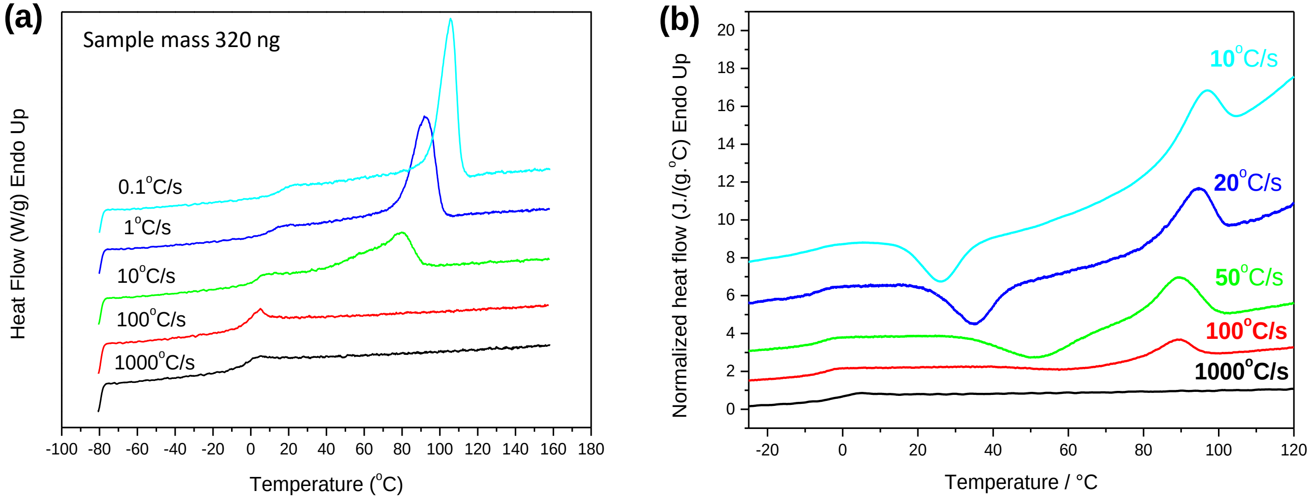
ΙΝΣΤΙΤΟΥΤΟ ΕΠΙΣΤΗΜΗΣ ΥΛΙΚΩΝ ΚΑΙ ΥΠΟΛΟΓΙΣΜΩΝ

Fast Scanning Calorimetry (FSC)

Simulates industrial processes (heating/cooling rates)
Fast crystallizing polymers can be obtained in the amorphous state
Prevents reorganization upon heating



Fast Crystallization and Melting Behavior of a Long-Spaced Aliphatic Furandicarboxylate Biobased Polyester, Poly(dodecylene 2,5-furanoate), D.G. Papageorgiou, N. Guigo, V. Tsanaktsis, S. Exarhopoulos, D.N. Bikiaris, N. Sbirrazzuoli,G.Z. Papageorgiou, Ind. Eng. Chem. Res. 2016, 55, 5315−5326



a) FSC heating curves at 1000 °C/s (60,000 °C/min) of samples previously cooled from the melt at different cooling rates ranging from 0.1 to 1000 °C/s (6-60,000 °C/min).
b) FSC heating curves at different rates ranging from 10 to 1000 °C/s (60-60,000 °C/min) of samples previously cooled from the melt at 1000 °C/s.

Competitive Crystallization of a Propylene/Ethylene Random Copolymer Filled with a β-Nucleating Agent and Multi-Walled Carbon Nanotubes. Conventional and Ultrafast DSC Study, D. G. Papageorgiou, G.Z. Papageorgiou, E. Zhuravlev, D. Bikiaris, C. Schick, K. Chrissafis, J. Phys. Chem. B 2013, 117, 14875−14884

https://link.springer.com/chapter/10.1007/978-3-319-31329-0_7

Crystallization and melting of poly(alkylene 2,5-furandicarboxylates)

Πανεπιστήμιο Ιωαννίνων

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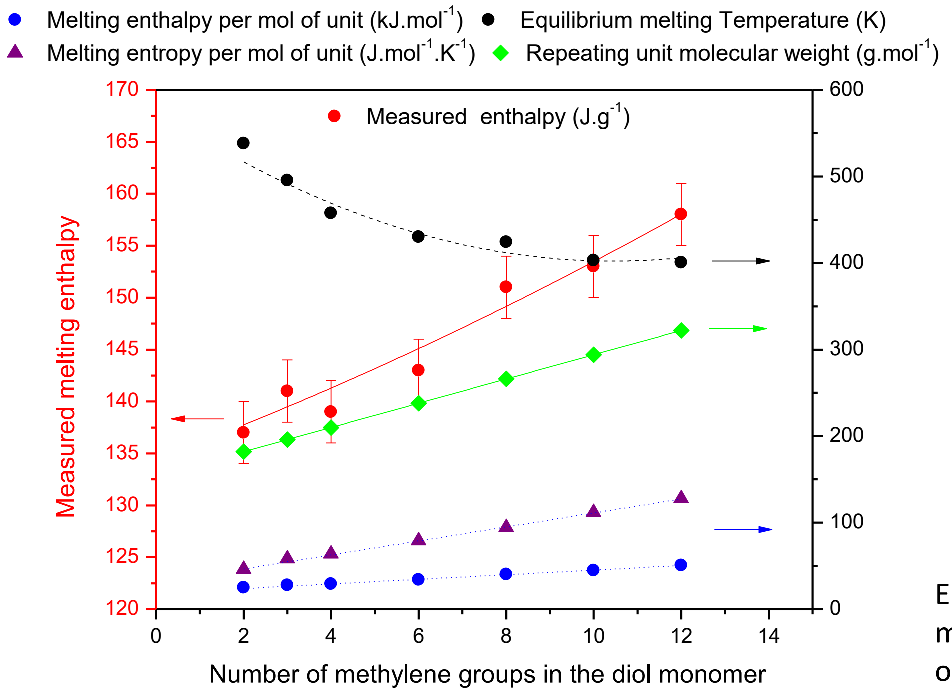


Xc= % degree of crystallinity= $100(\Delta H_m - \Delta H=)/\Delta H_m^o$

Enthalpy and entropy of melting of pure crystalline poly(alkylene furanoates), equilibrium melting temperature and molecular weight of the repeating unit as a function of the number of methylene groups in the corresponding diol monomer for poly(alkylene furanoates).

Production of bio-based 2,5-furan dicarboxylate polyesters: Recent progress and critical aspects in their synthesis and thermal properties, G.Z. Papageorgiou, D.G. Papageorgiou, Z. Terzopoulou, D.N. Bikiaris, European Polymer Journal 83 (2016) 202–229.

Synthesis of poly(ethylene furandicarboxylate) polyester using monomers derived from renewable resources: thermal behavior comparison with PET and PEN, G.Z. Papageorgiou, V. Tsanaktsis. D.N. Bikiaris, Phys. Chem. Chem. Phys., 2014, 16, 7946—7958.

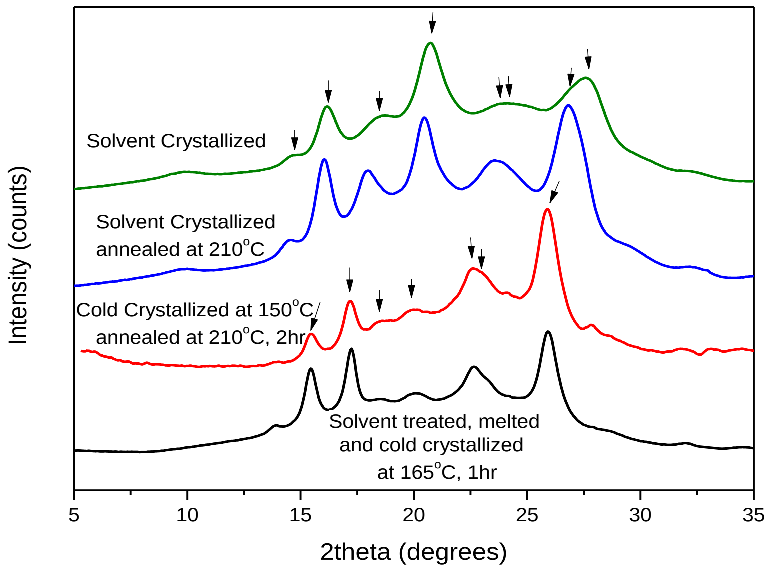
Evaluation of polyesters from renewable resources as alternatives to the current fossil-based polymers. Phase transitions of poly(butylene 2,5-furan-dicarboxylate), G.Z. Papageorgiou, V. Tsanaktsis, D.G. Papageorgiou, S. Exarhopoulos, Maria Papageorgiou, D.N. Bikiaris, Polymer 55 (2014) 3846-3858.

Polymorphism of poly(ethylene 2,5-furandicarboxylate)

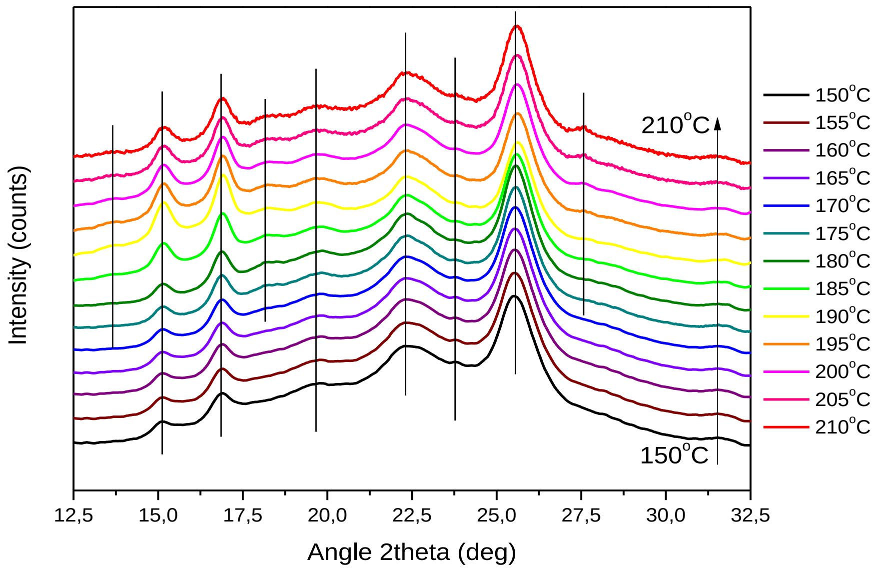
Πανεπιστήμιο Ιωαννίνων

ΙΝΣΤΙΤΟΥΤΟ ΕΠΙΣΤΗΜΗΣ ΥΛΙΚΩΝ ΚΑΙ ΥΠΟΛΟΓΙΣΜΩΝ

Crystallization from solution leads to a new polymorph, different to that observed in crystallization from the melt or the glass



Comparison between WAXD patterns of solvent crystallized and cold-crystallized PEF samples

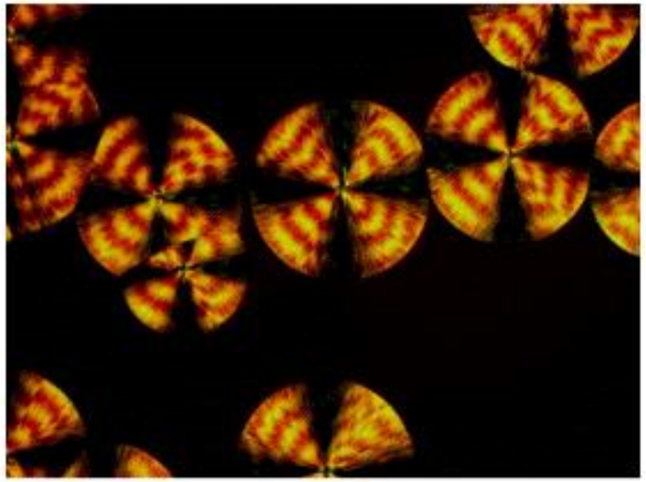


WAXD patterns of PEF samples melt-crystallized at different temperatures.

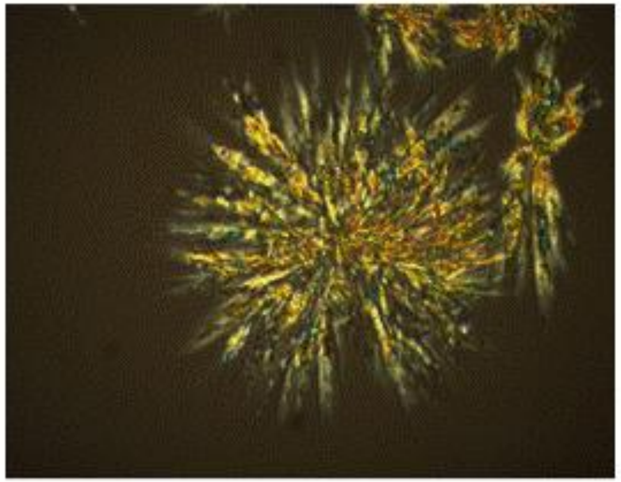
Crystallization and Polymorphism of Poly(ethylene furanoate), V. Tsanaktsis, D.G. Papageorgiou, S. Exarhopoulos, D.N. Bikiaris, G.Z. Papageorgiou, Cryst. Growth Des. 2015, 15, 11, 5505–5512

Polymorphism in polymers and pharmaceutics

Polarized Light Microscopy



Poly(propylene terephthalate-co-succinate) 95/5 (PPTS) crystallized at 195^oC. Formation of β-PBN crystals.



Poly(butylene 2,5-naphthalene dicarboxylate-co-adipate) 95/5 (PBNA) crystallized at 210^oC. Formation of β-PBN crystals.

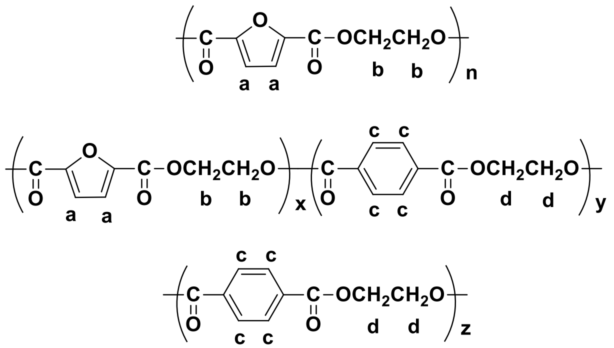
Biobased copolymers of FDCA

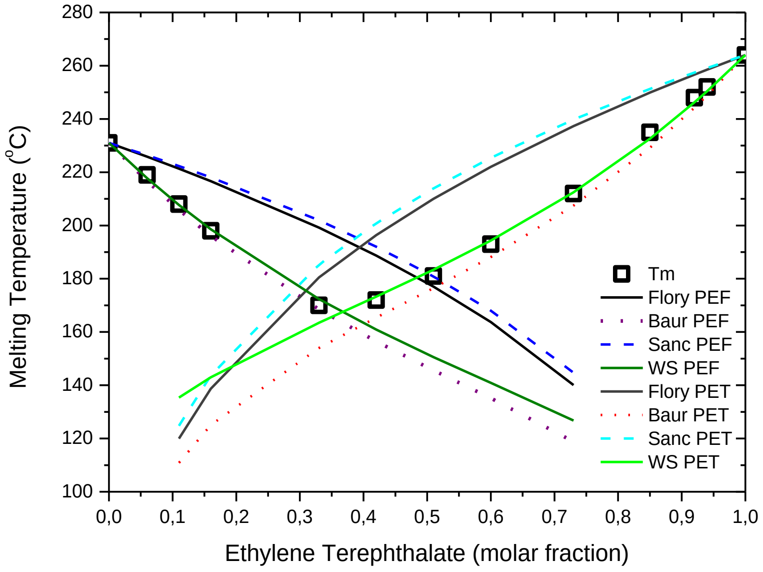
Πανεπιστήμιο Ιωαννίνων

ΙΝΣΤΙΤΟΥΤΟ ΕΠΙΣΤΗΜΗΣ ΥΛΙΚΩΝ ΚΑΙ ΥΠΟΛΟΓΙΣΜΩΝ

Various types of furan-based copolymers were synthesized and their thermal properties and the cocrystallization behavior were studied, including Poly(ethylene furanoate-co-terephthalate)s, and biodegradable poly(ethylene furanoate-co-ethylene succinate).

Poly(ethylene furanoate-co-terephthalate)s





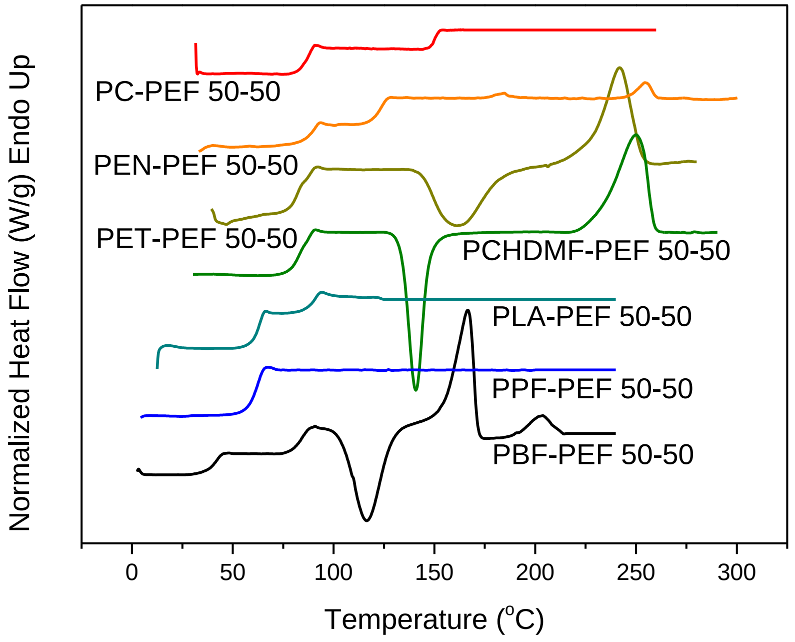
Theoretical melting temperatures and experimental values.

Biobased poly(ethylene furanoate-co-ethylene succinate) copolyesters: solid state structure, melting point depression and biodegradability, Zoe Terzopoulou, Vasilios Tsanaktsis, Dimitrios N. Bikiaris, S. Exarhopoulos, D.G. Papageorgiou, G.Z. Papageorgiou, RSC Adv., 2016, 6, 84003–84015
Synthesis, Characterization, and Mechanical Properties of new fully biobased poly(1,10-decylene-co-isosorbide 2,5-furandicarboxylate) copolyesters from renewable resources with enhanced biodegradability,Y. Chebbi, N. Kasmi, M. Majdoub, P. Cerruti, G. Scarinzi, M. Malinconico, G.Z. Papageorgiou, D.N. Bikiaris, ACS Sustainable Chem. Eng. 2019, 7, 5501−5514, DOI: 10.1021/acssuschemeng.8b06796

Blends of FDCA polyesters

Πανεπιστήμιο Ιωαννίνων

ΙΝΣΤΙΤΟΥΤΟ ΕΠΙΣΤΗΜΗΣ ΥΛΙΚΩΝ ΚΑΙ ΥΠΟΛΟΓΙΣΜΩΝ



Green polymeric materials: On the dynamic homogeneity and miscibility of furan-based polyester blends, N. Poulopoulou, A. Pipertzis, N. Kasmi, D.N. Bikiaris, D.G. Papageorgiou, G. Floudas, G.Z. Papageorgiou, Polymer 174 (2019) 187–199

Sustainable Plastics from Biomass: Blends of Polyesters Based on 2,5-Furandicarboxylic Acid, N. Poulopoulou, D. Smyrnioti, G.N. Nikolaidis, I. Tsitsimaka, E. Christodoulou, D.N. Bikiaris, M.-A. Charitopoulou, D.S. Achilias, M. Kapnisti, G.Z. Papageorgiou, Polymers 2020, 12, 225; doi:10.3390/polym12010225

Blends of FDCA polyesters

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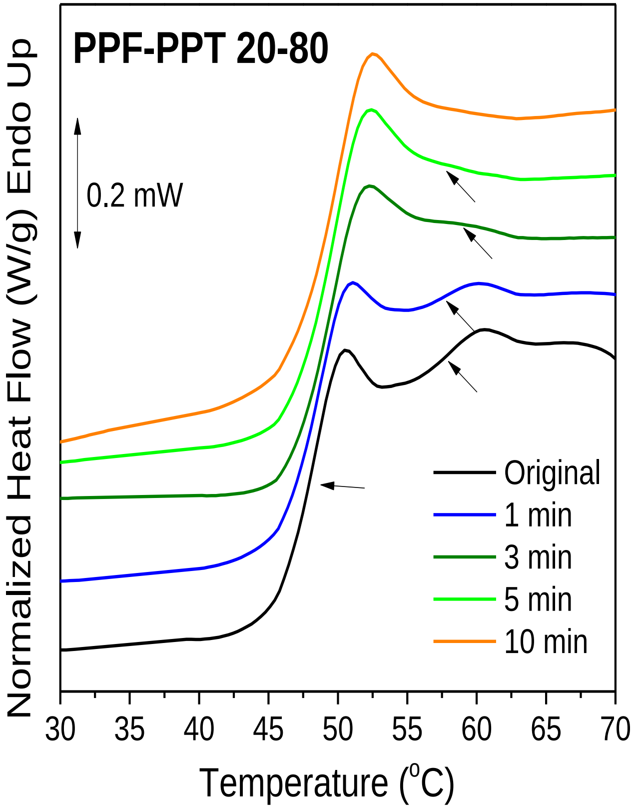
ΙΝΣΤΙΤΟΥΤΟ ΕΠΙΣΤΗΜΗΣ ΥΛΙΚΩΝ ΚΑΙ ΥΠΟΛΟΓΙΣΜΩΝ

Simulating real processes

Reactive blending



Effect of the time of reactive blending on the DSC thermograms of the PPF-PPT 20-80 sample.

Exploring Next-Generation Engineering Bioplastics: Poly(alkylene furanoate)/Poly(alkylene terephthalate) (PAF/PAT) Blends, N. Poulopoulou, N. Kasmi, M. Siampani, Z.N. Terzopoulou, D.N. Bikiaris, D.S. Achilias , D.G. Papageorgiou, G.Z. Papageorgiou, Polymers 2019, 11, 556; doi:10.3390/polym11030556

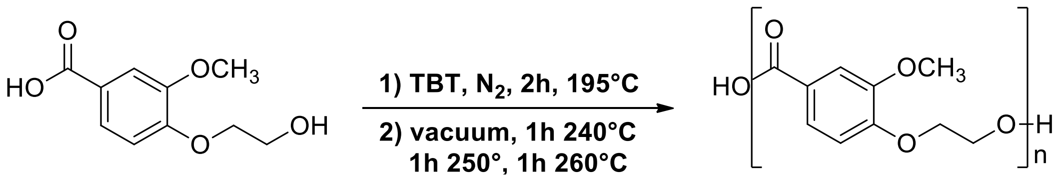
Polymers of Vanillic Acid

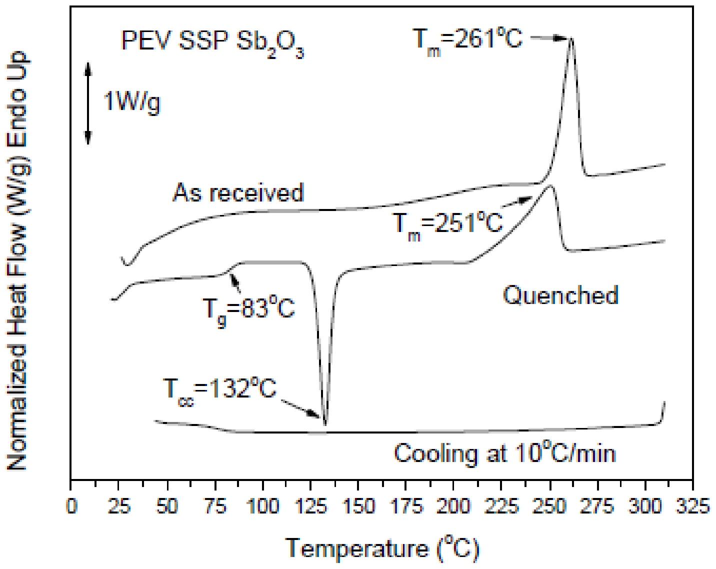
Πανεπιστήμιο Ιωαννίνων

ΙΝΣΤΙΤΟΥΤΟ
ΕΠΙΣΤΗΜΗΣ ΥΛΙΚΩΝ
ΚΑΙ ΥΠΟΛΟΓΙΣΜΩΝ

Lignin ⇨ Vanillic Acid ⇨ Polymers

Synthesis, Thermal Properties and Decomposition Mechanism of Poly(Ethylene Vanillate) Polyester, A. Zamboulis, L, Papadopoulos, Z. Terzopoulou, D.N. Bikiaris, D. Patsiaoura, K. Chrissafis, M. Gazzano, N. Lotti G.Z. Papageorgiou, Polymers 2019, 11, 1672; doi:10.3390/polym11101672



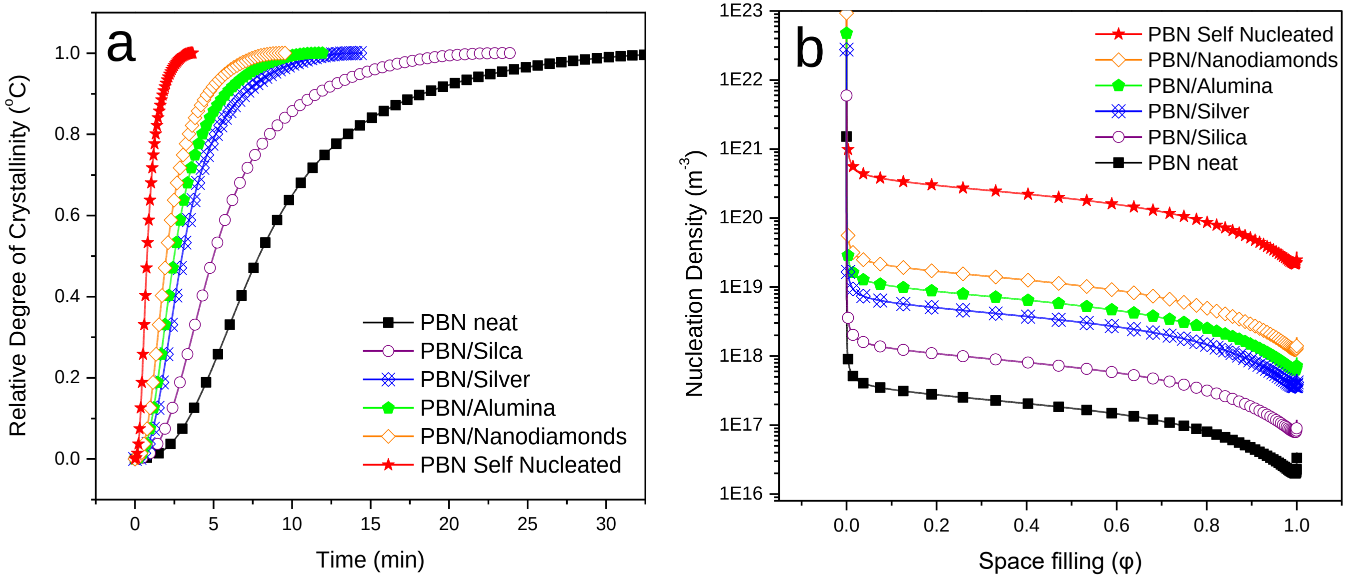


Polymer matrix nanocomposites

Πανεπιστήμιο Ιωαννίνων

ΙΝΣΤΙΤΟΥΤΟ ΕΠΙΣΤΗΜΗΣ ΥΛΙΚΩΝ ΚΑΙ ΥΠΟΛΟΓΙΣΜΩΝ

Synthesis and controlled crystallization of in situ prepared poly(butylene-2,6-naphthalate) nanocomposites D, G. Papageorgiou, D.N. Bikiaris, G.Z. Papageorgiou, CrystEngComm, 2018, 20, 3590–3600, DOI: 10.1039/c8ce00260f

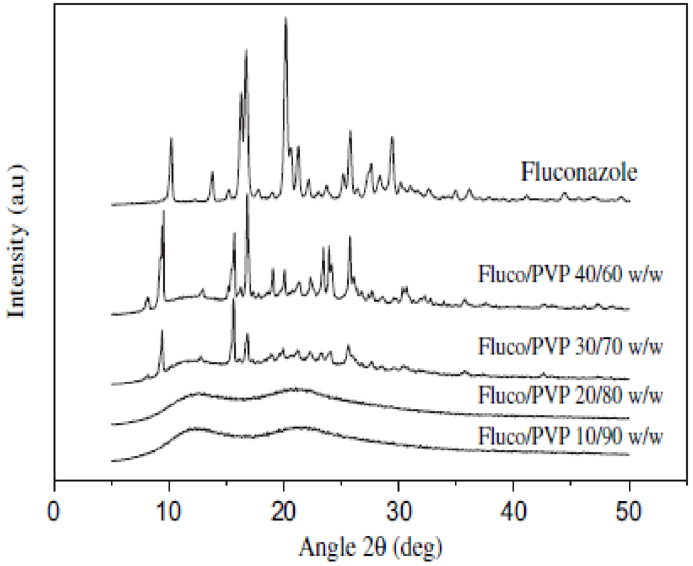


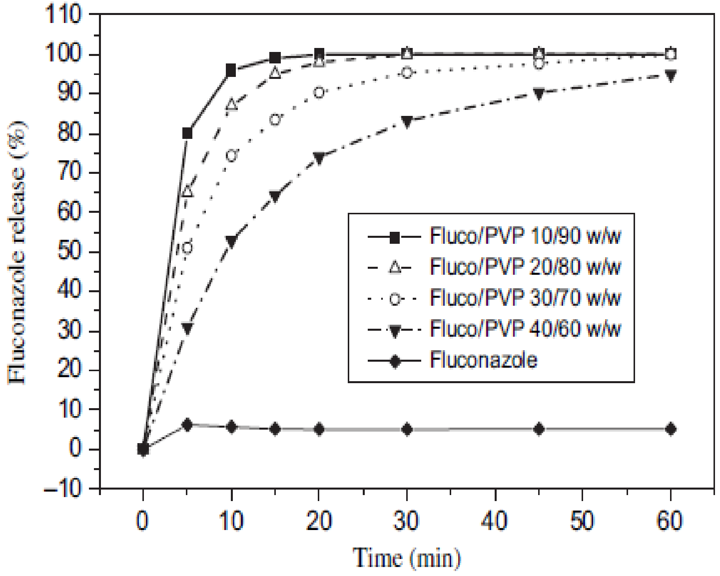
a) Evolution of the relative degree of crystallinity with time during isothermal crystallization of PBN and the nanocomposites at 220 °C and b) nucleation density as a function of the space filling for the nanocomposites and the neat PBN on quiescent and PBN on crystallization after self-nucleation.

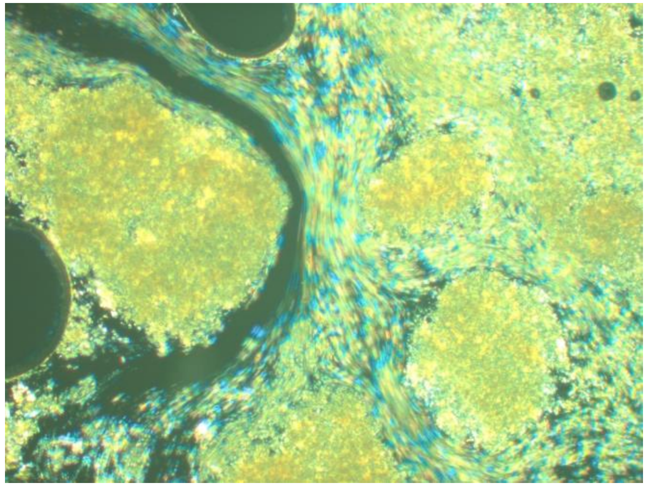
Thermal and structural response of in situ prepared biobased poly(ethylene 2,5-furan dicarboxylate) nanocomposites, Nadia Lotti, Andrea Munari, Matteo Gigli, Massimo Gazzano, Vasilios Tsanaktsis, Dimitrios N. Bikiaris, George Z. Papageorgiou, Polymer 103 (2016) 288-298, Πανεπιστήμιο Ιωαννίνων

ΙΝΣΤΙΤΟΥΤΟ ΕΠΙΣΤΗΜΗΣ ΥΛΙΚΩΝ ΚΑΙ ΥΠΟΛΟΓΙΣΜΩΝ

Tailoring the Release Rates of Fluconazole Using Solid Dispersions in Polymer Blends, G.Z. Papageorgiou, D. Bikiaris, F.I. Kanaze, E. Karavas, A. Stergiou, E. Georgarakis, Drug Development and Industrial Pharmacy, 34:336–346, 2008







PLM: Nimo/PEG 50/50 solid dispersion at 70^{o}C

Effect of Physical State and Particle Size Distribution on Dissolution Enhancement of Nimodipine/PEG Solid Dispersions Prepared by Melt Mixing and Solvent Evaporation, G.Z. Papageorgiou, D. Bikiaris, E. Karavas, S. Politis, A. Docoslis, Y. Park, A. Stergiou, Emmanouel Georgarakis, The AAPS Journal 2006; 8 (4) Article 71 (http://www.aapsj.org).

New Biodegradable Poly(l-lactide)-Block-Poly(propylene adipate) Copolymer Microparticles for Long-Acting Injectables of Naltrexone Drug, S. Nanaki, A. Viziridou, A. Zamboulis, M. Kostoglou, G.Z. Papageorgiou, D.N. Bikiaris, Polymers 2020, 12, 852; doi:10.3390/polym12040852