STRUCTURE, DYNAMICS AND BARRIER PERFORMANCE RELATIONSHIP IN POLY(PENTAMETHYLENE FURANOATE)

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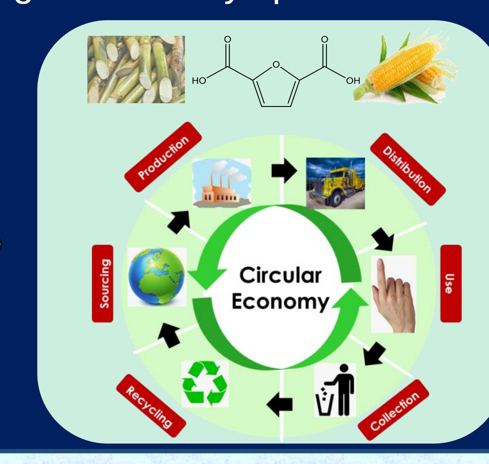
INTRODUCTION

The problem of plastic waste has become particularly urgent in recent years, due to the great volumes involved, which are responsible for a severe environmental impact. Indeed, these massive amounts of waste, after their life cycle, are mainly disposed in landfills[1] or, even worse, in the environment. On the other hand, plastic materials, particularly in sectors like food packaging, cover up almost the half of the total demand, thanks to their low price, lightness, easy production and processability, modulation of properties and durability. In order to reduce the impact of plastics on the environment, the use of bioplastics, i.e. biobased, biodegradable or both biobased and biodegradable materials, should be preferred, as a feasible alternative to common fossil-based ones. In addition, the development of recyclable solutions, characterized by minimum waste production, production and transport efficiency, is constantly growing, as confirmed by the last market data[2]. Also, the European Commission has adopted a Waste Framework Directive (2008/98/EC), aiming to ensure that all plastic packaging would be recyclable by 2030[3]. Moreover, when food is involved, it is necessary a package characterized by good mechanical properties and high barrier performances. For these reasons, the packaging commonly used nowadays is made of multilayers of different materials, which are very difficult to recycle. In addition, recycling is not always possible due to organic matter contamination.

In this complex scenario, polyesters synthesized from 2,5-furan dicarboxylic acid (FDCA) can be considered very interesting candidates, due to their biobased nature together with outstanding mechanical and barrier properties, making them particularly promising recyclable monomaterials for food packaging applications. As a confirmation, FDCA is one of the twelve building blocks identified by the U.S. Department of Energy, that can be produced from renewable sources, like sugars, which can be in turn converted to many high-value bio-based chemicals. Nowadays, only PEF, the alter ego of PET, has been produced on industrial level, although this material is only suitable for the realization of rigid packaging.

In this contribution, poly(pentamethylene furanoate) PPeF was investigated as a new furan-based superpolymer with great potential in the field of flexible food packaging.

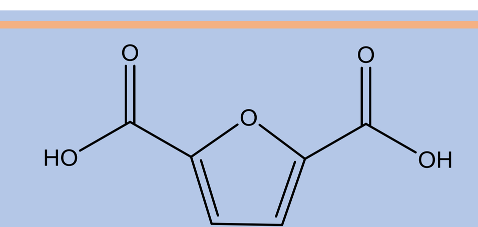


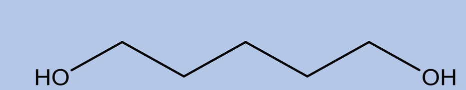
SYNTHESIS

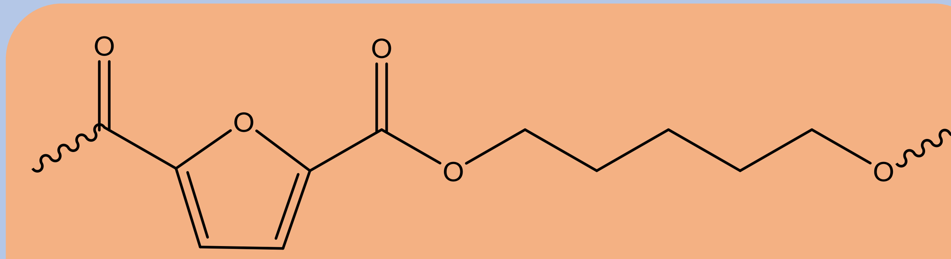
TWO STEP MELT- POLYCONDENSATION

I step T=190°C, N_2 Flux; P atm 100 rpm
II step T 200°C -> 220°C; P_{min} ≈ 0,1 mbar

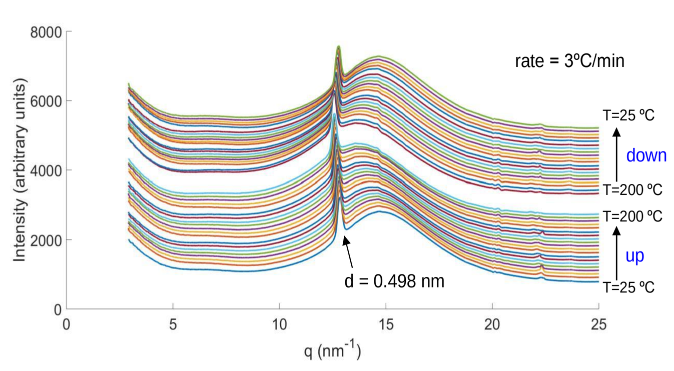
- Catalyst: $Ti(OBu)_4$
- One-pot and solvent free


2,5-furandicarboxylic acid

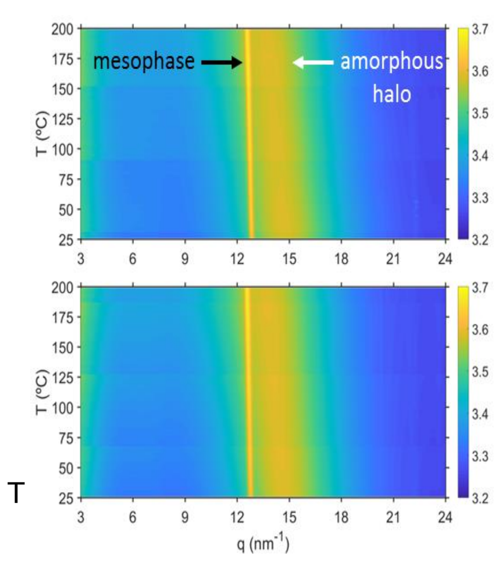

1,5-pentanediol


Poly(pentamethylene furanoate) PPeF

WAXS & SAXS ANALYSES



XRD pattern as a function of q acquired at different temperatures during heating and cooling PPeF film.



Integrated 1D scattered intensity as a function of q and T acquired during heating and cooling PPeF film.

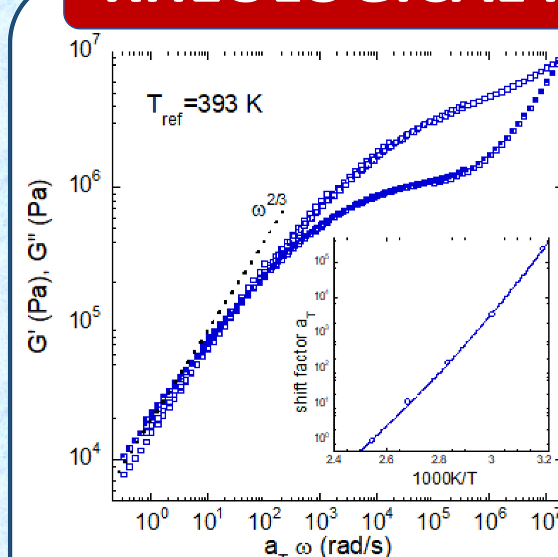
- Very peculiar XRD pattern, not typical of semicrystalline polymers
- Narrow reflection at q= 12.62 nm^{-1}

The peak does not change with temperature

no melting phenomenon

The XRD reflection is compatible with a 1D-ordered structure coming from interchain C-H----O bonds

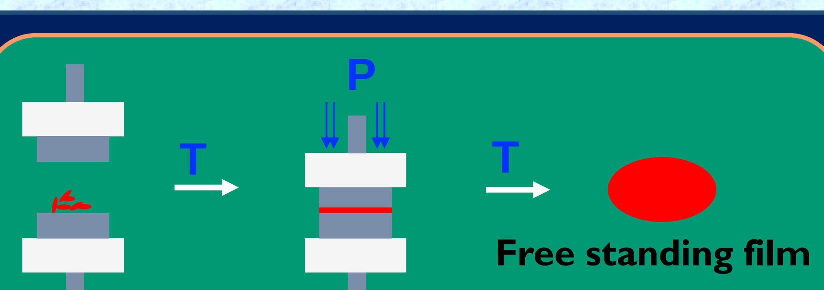
RHEOLOGICAL PROPERTIES



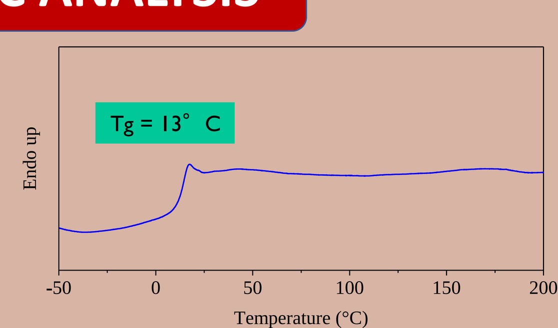
Master curve obtained from the dynamic experiments on PPeF (torsional shear): G' empty and G'' solid symbols. In the inset: the horizontal shift factors and the WLF equation fitting the data.

- Non-conventional behaviour expected for a linear polymer
- Not Newtonian flow even at $T>T_g+100$ K.

exceptional mechanical and gas transport properties at RT



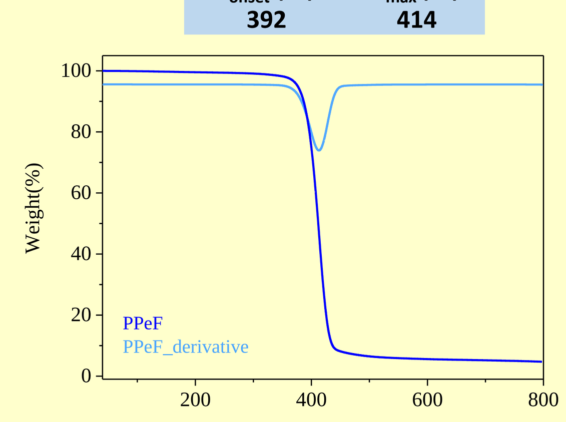
DSC ANALYSIS

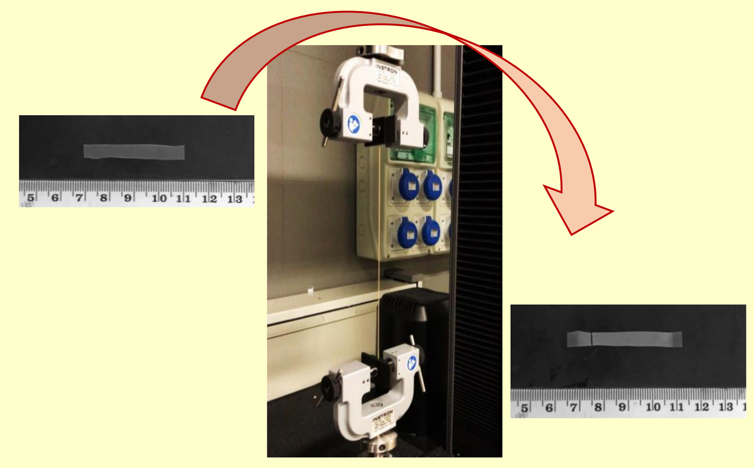


PPeF can be processed into free-standing film even if amorphous and rubbery.

High thermal stability

T_{onset} (°C)	T_{max} (°C)
392	414



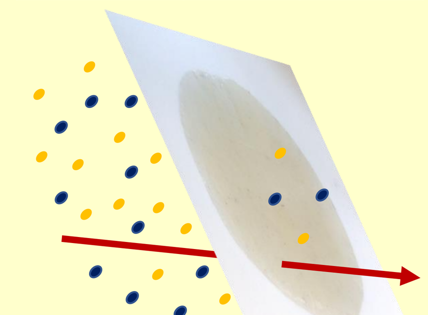


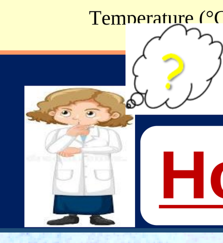
E (MPa)	σ_b (MPa)	ε_b (%)
9±1	6.1±0.5	1050±200

Elastomeric behaviour

Excellent barrier properties

GTR-N_2	GTR-O_2	GTR-CO_2
0.00121	0.00159	0.00144

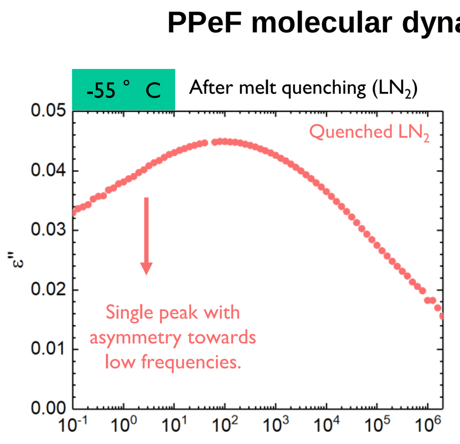


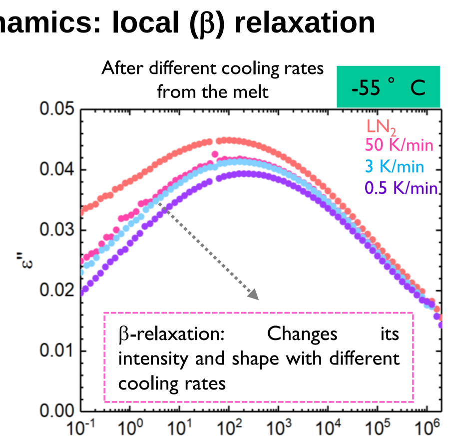


How can we explain these unexpected properties?!?

BROADBANDDIELECTRIC SPECTROSCOPY

PPeF molecular dynamics: local (β) relaxation



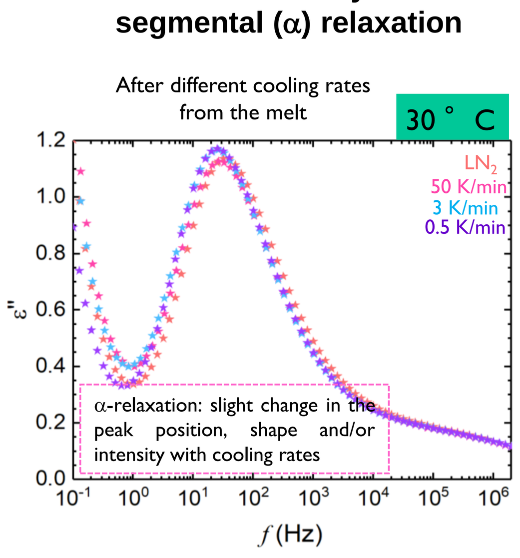


β_2 component, related to furan ring relaxation reduces its intensity → furan-ring flipping is hindered

Segmental relaxation slightly affected by cooling rate: α process is slower, even though PPeF remains amorphous

Both local relaxation (lowering of the β_2 component) and segmental dynamics (slowdown for low cooling rate despite the PPeF amorphous nature) can be explained as due to the formation of C-H ··O interchain bonds involving furan ring subunit.

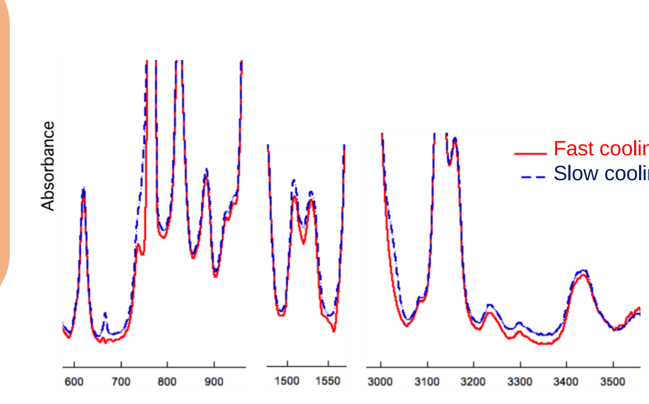
PPeF molecular dynamics: segmental (α) relaxation



IR SPECTROSCOPY

- Small but significant differences
- Absorption at higher frequencies is related to C-H stretching of the furan rings that can be involved in peculiar interactions

This result is compatible with interchain interactions which can be due to C-H----O bonds

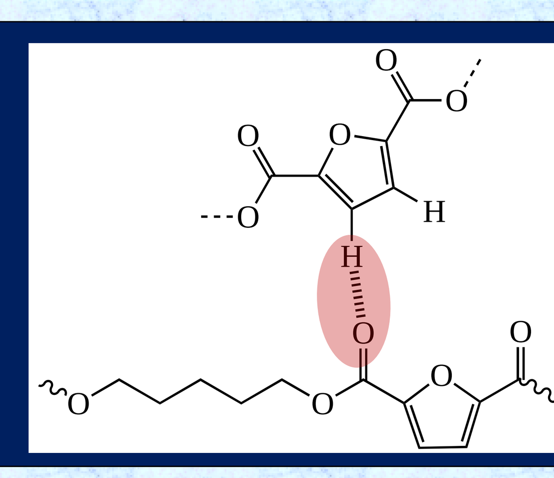


Effect of the cooling protocol on the room temperature infrared absorption of a PPeF film.

CONCLUSIONS

In this study, PPeF was synthesized by two-step melting polycondensation, a one-pot and solvent-free technique, and subjected to a preliminary molecular and thermal characterization. Interestingly, although amorphous and rubbery at room temperature, PPeF could be processed in form of free-standing film. In terms of functional properties, PPeF shows exceptional barrier and mechanical response, making this material a very promising candidate for applications in flexible food packaging. More in details, the mechanical behaviour was typical of elastomers, with low elastic modulus and stress at break together with high elongation at break. An instant shape recovery after breaking could be observed, indicating the presence of net points.

In order to better understand the origin of these peculiar properties, a further study combining calorimetric, diffractometric and spectroscopic techniques was carried out. The results obtained evidenced the formation of a particular microstructure, different from the classical crystalline phase, characterized by partially ordered furan rings and favoured by intermolecular hydrogen bonds.



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