Evaluating brittleness and fragmentation of conventional polymers and biopolymers upon photoaging

Astrid Delorme[1*], Luna Valero[1], Florence Delor-Jestin[1], Haroutioun Askanian[1]

[1] Université Clermont Auvergne, CNRS, Clermont Auvergne INP, ICCF, 63000, Clermont-Ferrand, France

[*]astrid.delorme@sigma-clermont.fr

SEALIVE (**S**trategies of circular **E**conomy and **A**dvanced bio-based solutions to keep our **L**ands and seas al**IVE** from plastics contamination) is a H2020 **innovation project**, which vision is to **reduce plastic waste** and contamination on land and in seas by boosting the use of biomaterials and contributing to the circular economy with cohesive **bio-plastic strategies**.

Demonstrators: New bio-plastic solutions will be up-scaled and their performance will be demonstrated by 8 end-applications (fig. 1) in 6 regions spanning across Europe and South America. The strategically selected demonstrators have high potential for pollution reduction on soils and water media. To guarantee their adoption, SEALIVE innovations and strategies will be supported by policy measures, proposals for new harmonized biodegradability standards and training on the use and benefits of the solutions.

WP7 - Pre-normative studies and standardisation of biodegradable solutions

Background: As part of WP7, polymer degradation is investigated in several real service-life and end-of-life conditions, through the respective demonstrator products. This will allow us to assess the life cycle of polymers and to eventually develop international biodegradation and ecotoxicity standards for bioplastics. Particularly, urgent concerns of polymers' end-of-life are focused on the potential hazards and risks associated with microplastics. A prevailing source of microplastics is the fragmentation of macro plastics or product wear, however studies on the rates of fragmentation of polymers under various conditions are to date limited [1, 2].

Method: High Density Polytethylene, HDPE, (Versalis) of thickness 50 µm, and an emerging biopolymer film, polylactic acid, PLA, (Total Corbion PLA L175) of thickness 150 µm were aged in an accelerated photoaging chamber (fig.2). Here, we investigate the interrelation between the photoaging and brittleness of the polymers.

Fig. 2: SEPAP 12/24 device, Atlas Corp. λ >300nm, 4Hg lamps, T=60°C

Mechanical properties: Tensile testing of HDPE aged films (fig. 3a) show that after 100 h of aging the polymer undergoes a drastic transition from ductile to brittle behaviour. For PLA, a rather large drop in the elongation break is observed after only 25 h of aging in the SEPAP chamber (fig. 3b).

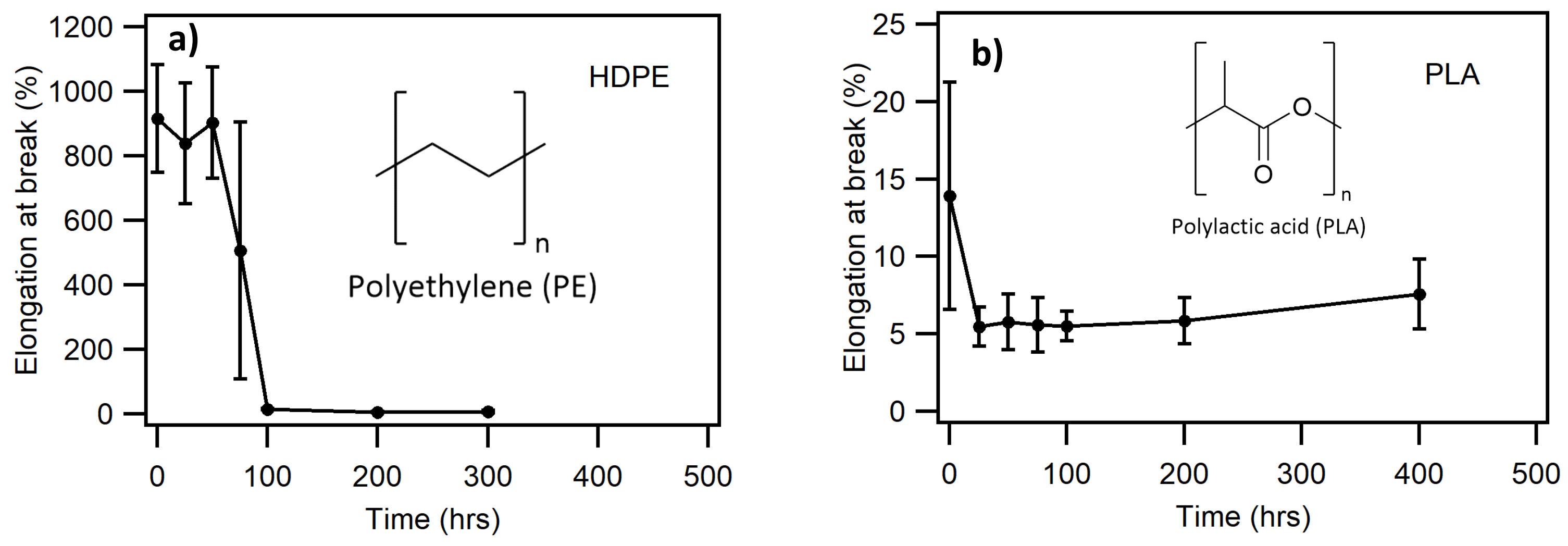


Fig. 3: Elongation at break measured in machine direction at a testing speed of 30 mm/min of unaged and aged a) HDPE films and b) PLA films.

Degradation by-products: From Attenuated Total Reflectance (ATR) infrared spectroscopy a broad peak at 1712 cm^{-1} in the carbonyl region appeared after 500 hours of photoaging for the HDPE films (fig. 4a). This peak corresponds to different carbonyl groups formed during degradation. For the PLA films the evolution of carbonyl degradation products is difficult to detect due to the presence of the ester group in the polymer backbone (fig. 4b), however a broadening in the carbonyl peak is observed in Fourier-Transform Infrared spectroscopy (FTIR) analyses.

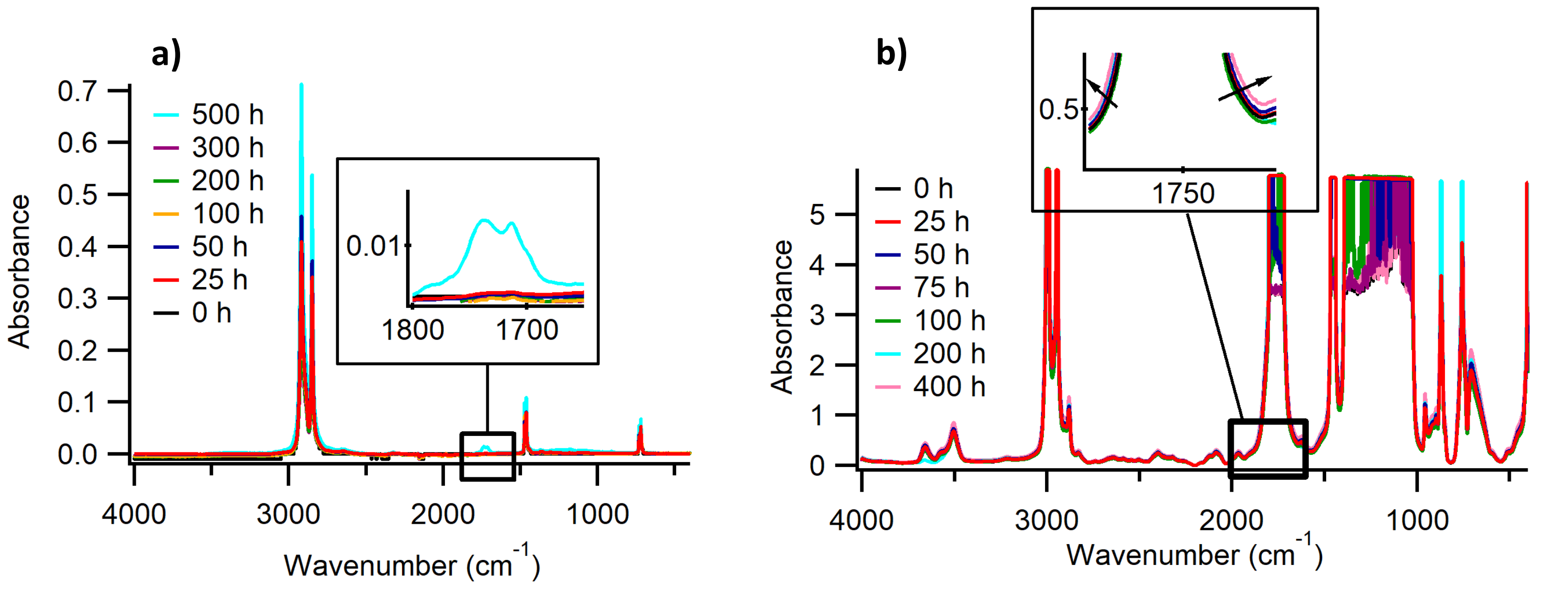
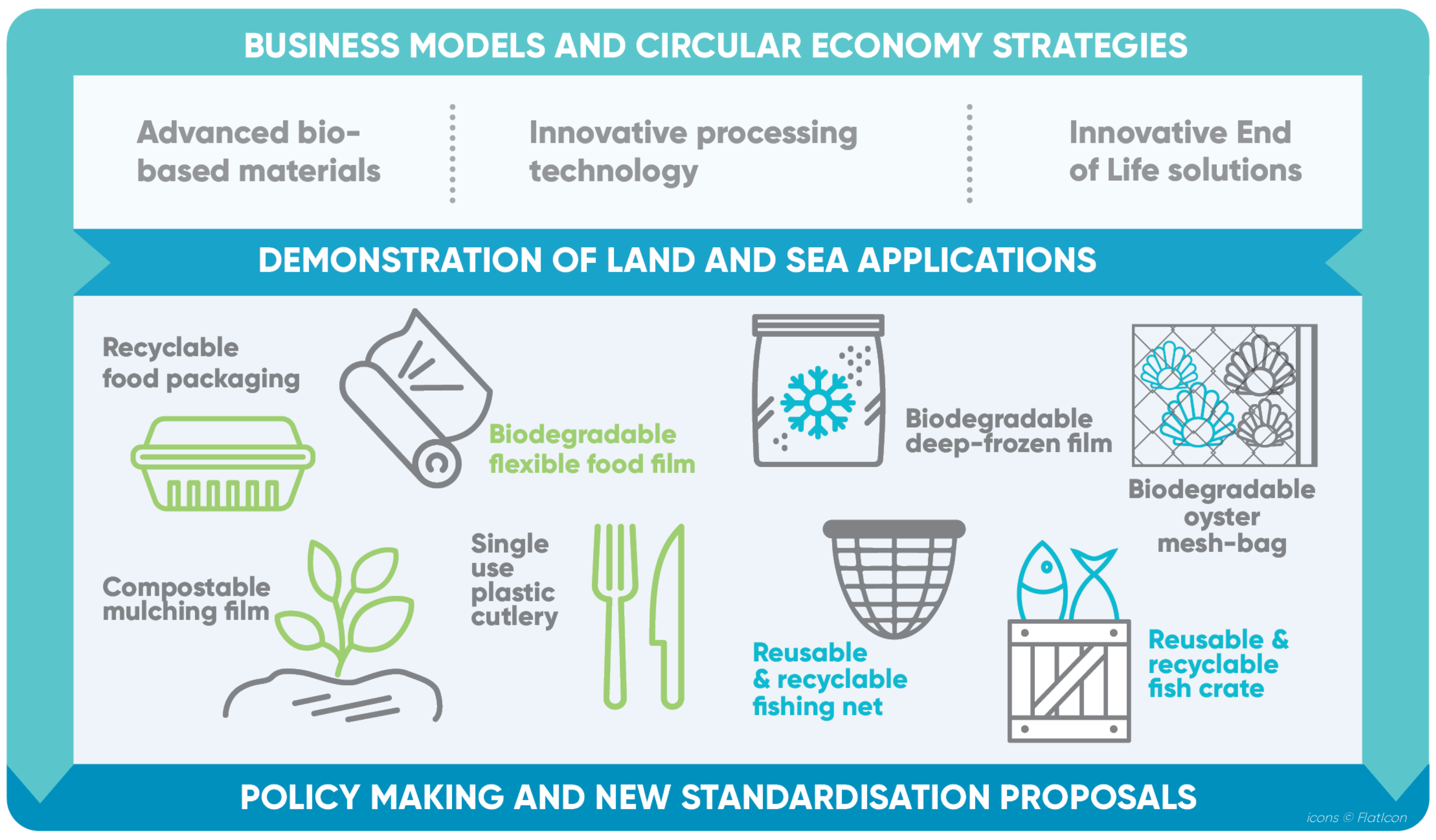


Fig. 4: Infrared spectra of polymer films after various exposure times in the SEPAP chamber of a) HDPE films and b) PLA films. All the spectra have been baseline corrected.



BUSINESS MODELS AND CIRCULAR ECONOMY STRATEGIES

Advanced bio-based materials

Innovative processing technology

Innovative End of Life solutions

DEMONSTRATION OF LAND AND SEA APPLICATIONS

Recyclable food packaging

Biodegradable flexible food film

Biodegradable deep-frozen film

Biodegradable oyster mesh-bag

Compostable mulching film

Single use plastic cutlery

Reusable & recyclable fishing net

Reusable & recyclable fish crate

POLICY MAKING AND NEW STANDARDISATION PROPOSALS

icons © Flaticon

Fig. 1: The 8-end applications that serve as demonstrators in order to test the performance of the biobased and biodegradable plastic solutions developed within SEALIVE.

Viscoelastic behaviour: For HDPE (fig. 5a) there is an initial increase in viscosity (η) up until 100 h which is then followed by a decrease in viscosity. For PLA there is a drop in viscosity after only 25 h of aging (fig. 5b). A decrease in elongation at break is usually explained as a result of chain scissions and as observed in fig. 3 and fig. 5 there is a good correspondence between the drastic drop in elongation at break with the drop in viscosity (dominating chain scission events within polymer materials) of the PLA and HDPE films studied here [3, 4].

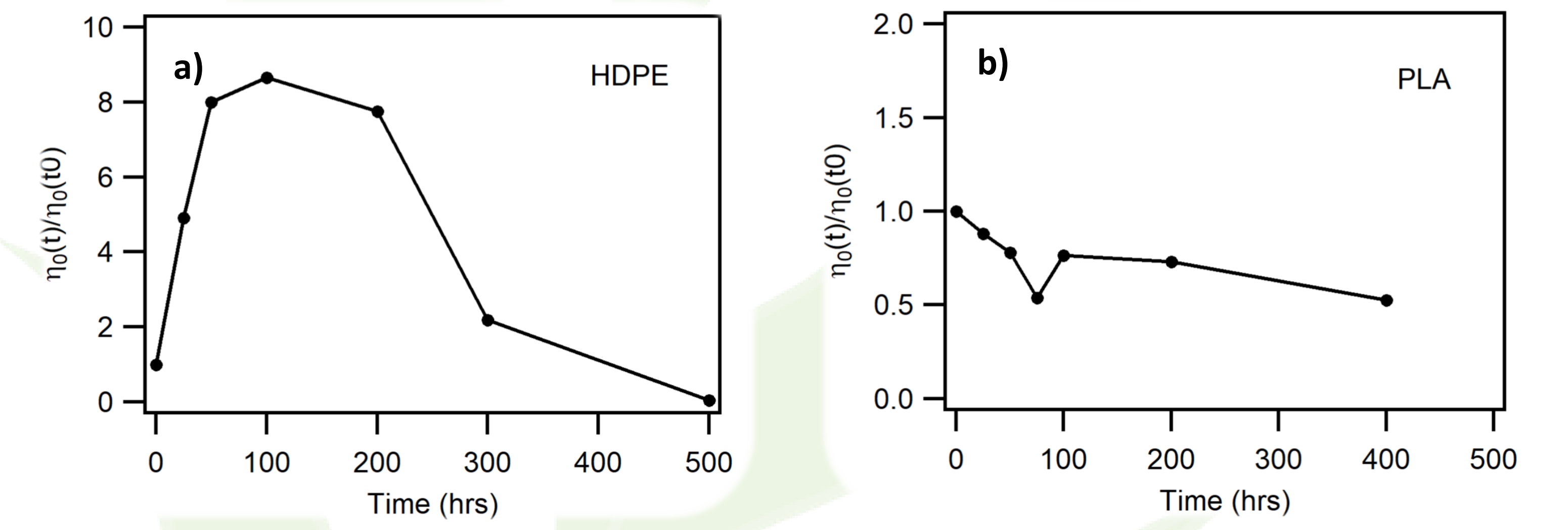


Fig. 5: Differences in viscosity of a) HDPE films and b) PLA films as a function of exposure time in the accelerated photoaging chamber.

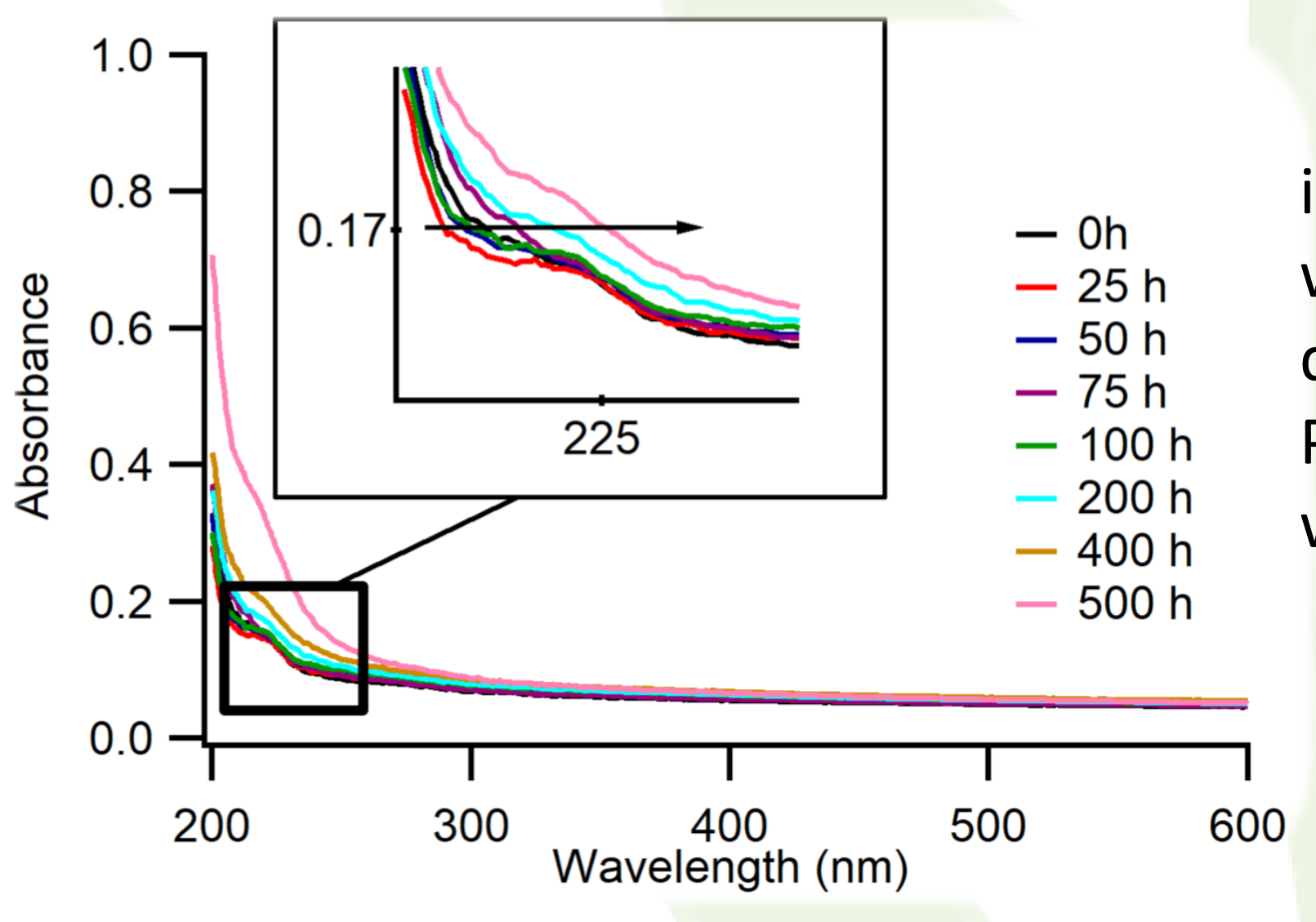


Fig. 6: UV-Vis spectra of aged HDPE films.

UV-Vis absorbance: For the HDPE films there is a shift in absorption of UV light towards longer wavelength (fig. 6), which is likely to be a result of carbonyl and/or conjugated degradation by-products formed as the film is aged. For the PLA films, no significant changes in the UV-Vis absorbance were observed.

Thermal properties: The degree of crystallinity, X_c, decreases after only 50 hours of aging for HDPE films (fig. 7), which is likely to be a result of the chain cross-linking mechanism, also observed in fig. 5. The degree of crystallization of PLA increases upon aging, which is likely to be a result of chemicrystallization due to chain scissions occurring.

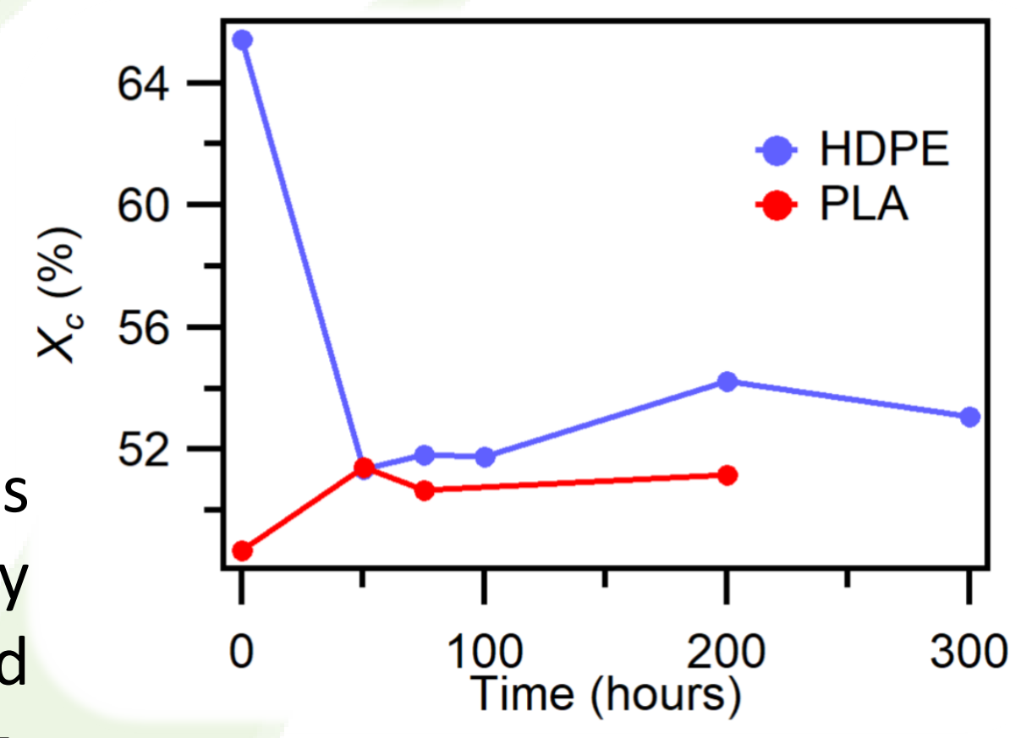


Fig. 7: Degree of crystallization (X_c) of aged HDPE films (blue line) and PLA films (red line).

Concluclusion

- Clear changes in the mechanical properties were observed after 100 h of photoaging for HDPE films and after 25 h of photoaging for PLA.
- Initial degradation evolutions on molecular level were depicted for both PLA and HDPE very clearly by melt rheology.

Future work

- Photoaging-fragmentation study will be extended to other biodegradable and biobased polymers.
- Analytical tools will be extended and adapted for the different polymers investigated.
- Study the aging of polymers under wet conditions and cycles of wet-dry conditions, as well as aging-biodegradation relationship.

References
[1] A. A. Koelmans, N. H. Mohamed Nor, E. Hermsen, M. Kooi, S. M. Mintenig, J. De France. *Water Res.*, 2019, 155, 410-422.
[2] M. Kooi, A. A. Koelmans. *Environ. Sci. Technol.*, 2019, 6, 551–557.
[3] S. Commereuc, H. Askanian, V. Verney, A. Celli. *Macromol. Symp*. 2010, 296, 378–387.
[4] S. Commereuc, H. Askanian, V. Verney, A. Celli, P. Marchese, C. Berti. *Polym. Degrad. Stab*. 2013, 98, 1321–1328.

Find out more:
www.sealive.eu
@EU_SEALIVE

Project Manager:
Marian Garcia Fernandez
ITENE
Email: marian.garcia@itene.com

Project Coordinator:
Miriam Gallur
ITENE
Email: miriam.gallur@itene.com

Communications & Press
Annette Wilson
Intrigo
Email: annette@intrigo.eu

This project has received funding from the European Union's Horizon 2020 Research and Innovation programme under grant agreement No 862910 (SEALIVE). This output reflects only the author's view and the European Union cannot be held responsible for any use that may be made of the information contained therein.