UNIVERSITAT JAUME I · bioPIMA · IMEDMAR · Universidad Católica de Valencia San Vicente Mártir

Marine Degradation of Biodegradable Plastics
A One-Year Field Study in the Mediterranean Sea

Anna Jáuregui[1], Anna Marín[1], Ignacio José Pisa[1], Estefanía Sánchez-Safont[1], J. Tena-Medialdea[2]; J.R. García-March[2], José Gámez-Pérez[1], Luis Cabedo[1]

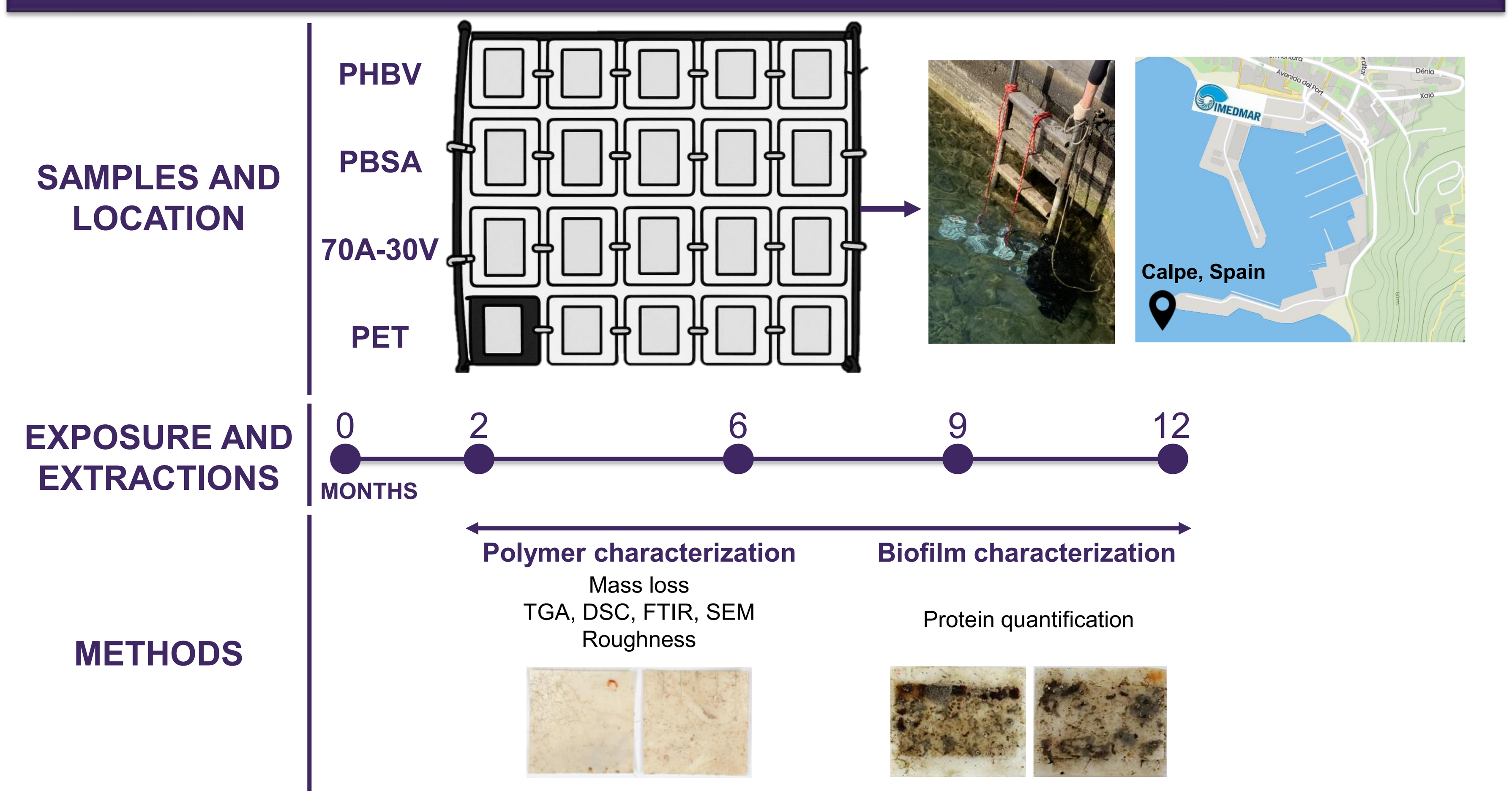
[1]*Polymers and Advanced Materials Group (PIMA), Universitat Jaume I (UJI), Av. de Vicent Sos Baynat s/n, Castellón de la Plana, 12071, Spain*

[2]*IMEDMAR-UCV-Institute of Environment and Marine Science Research, Universidad Católica de Valencia, C. Explanada del Puerto s/n, Calpe, 03710 Alicante, Spain*

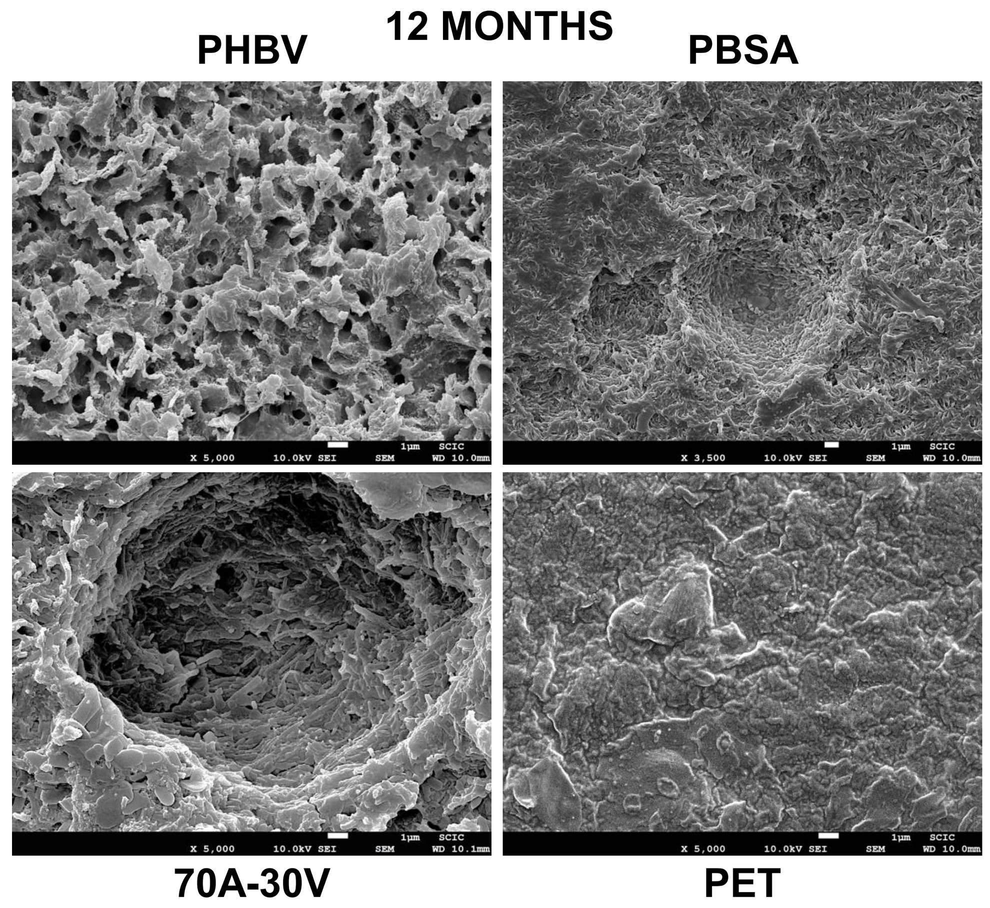
INTRODUCTION & AIM

Plastic pollution is a major threat to marine ecosystems, where millions of tons of waste accumulate each year[1]. Conventional polymers like polyethylene terephthalate (PET) persist for decades, while biodegradable alternatives such as poly(butylene succinate-co-adipate) (PBSA) and poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) offer potential for marine degradation[2]. However, environmental factors such as temperature, salinity, microbial activity, and hydrodynamics strongly influence degradation rates, limiting the relevance of laboratory tests. To bridge this gap, this study assesses the long-term degradation of PBSA, PHBV, a 70% PBSA–30% PHBV blend (70A-30V), and PET under real marine conditions in the Port of Calpe (Spain), providing comparative insight into their environmental performance.

METHODS



SURFACE MORPHOLOGY



Extensive surface deterioration in PHBV, PBSA, and 70A:30V after 12 months inmersion.

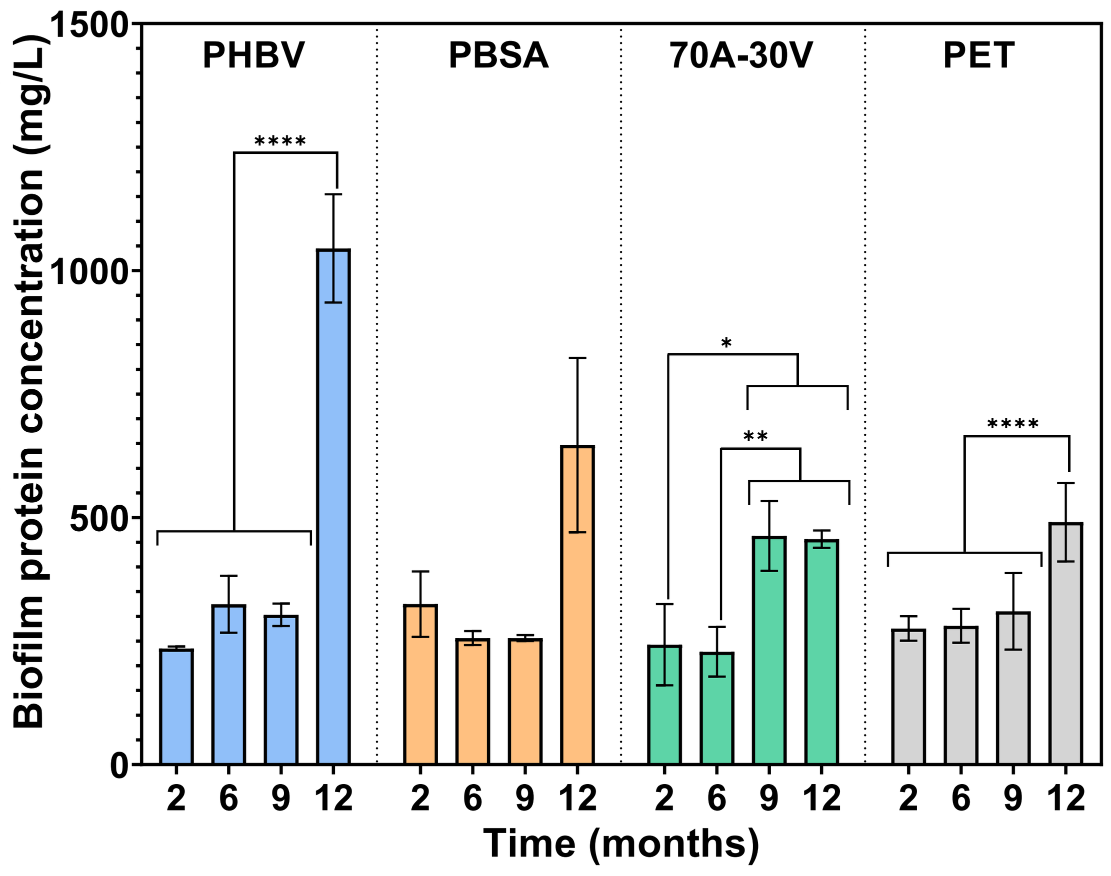
- PHBV surfaces appeared eroded and porous, reflecting extensive enzymatic attack and structural breakdown of the polymer matrix.
- The blend exhibited a heterogeneous, cratered surface, likely resulting from uneven degradation between its two polymeric components.
- PBSA displayed visible holes and surface pitting, typical of degradation in amorphous materials.
- PET maintained a compact, smooth surface, confirming its resistance to microbial attack.

BIOFILM PROTEIN

The amount of extracellular protein associated with the polymer surface increased over time for all materials.

- Microbial colonization and biofilm development causes surface degradation in the biodegradable polymers.
- PET showed a moderate protein increase, likely due to its use as a physical support for microorganisms rather than an assimilable substrate.

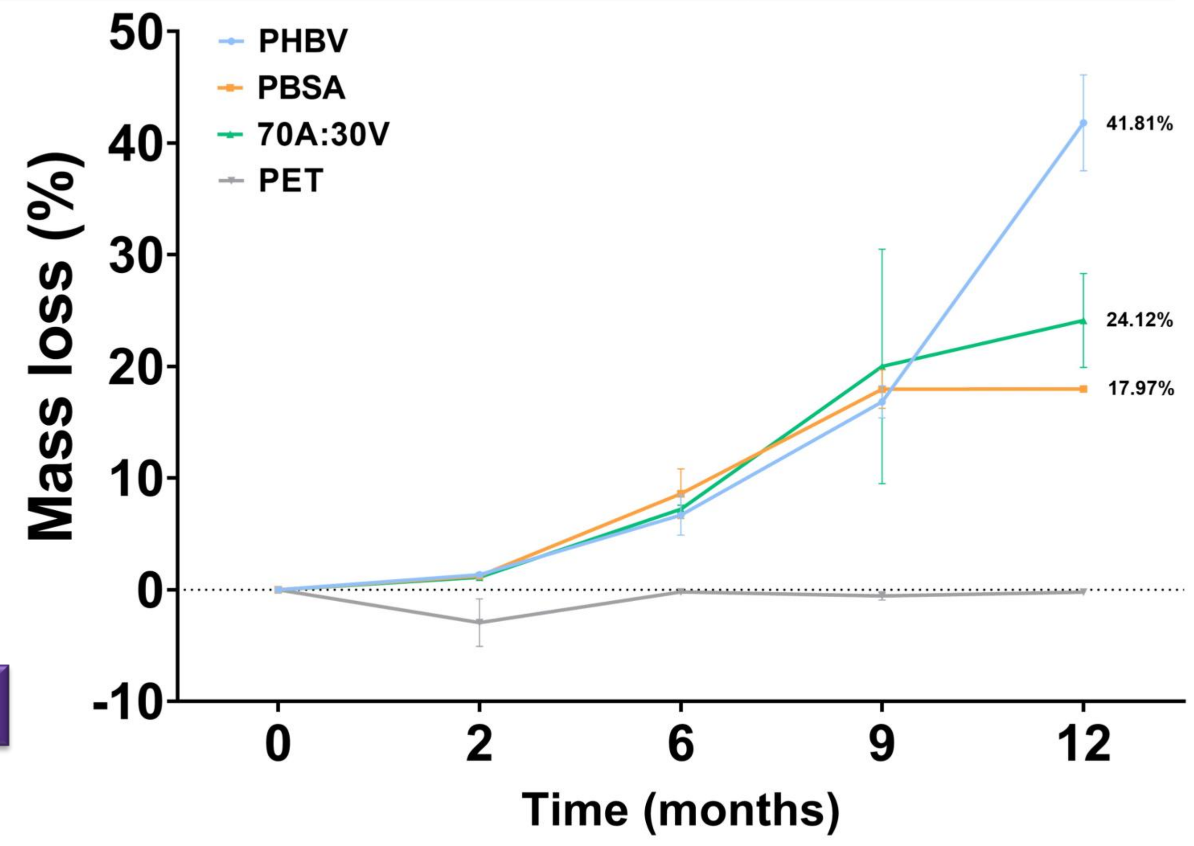
After 12 months, protein content followed the trend: PHBV > PBSA > 70A:30V > PET, matching the overall biodegradation ranking.



RESULTS & DISCUSSION

DISINTEGRATION

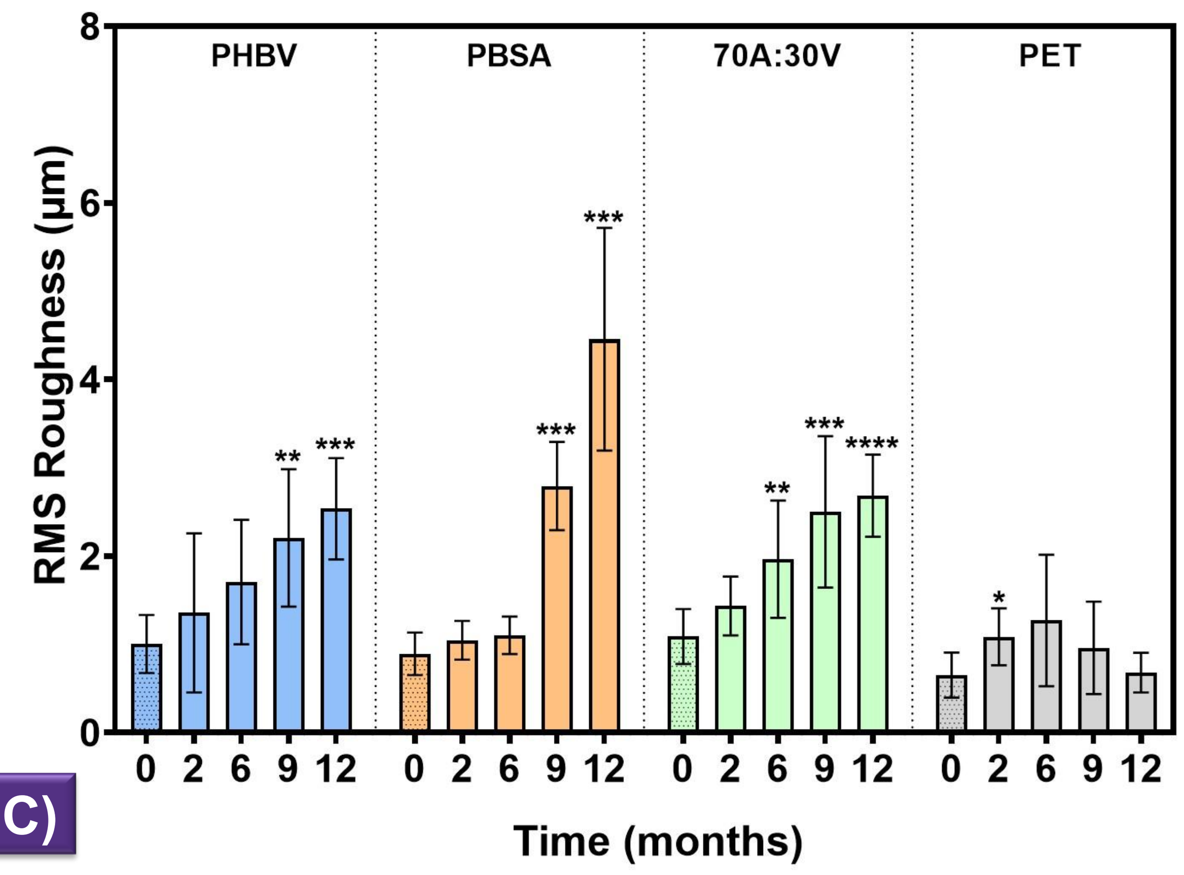
- Biopolymers showed a clear increase in disintegration over time, while PET remained stable.
- PHBV exhibited the most pronounced degradation, followed by 70A-30V and PBSA, confirming different susceptibilities among them.



ROUGHNESS

Increased significantly with time for biopolymers, whereas PET remained almost unchanged.

- The marked increase in PBSA reflects its amorphous nature: microorganisms degrade these regions and produce deeper and more irregular cavities.
- Surface erosion dominates over bulk degradation, with the outermost layers showing the most pronounced structural disruption.

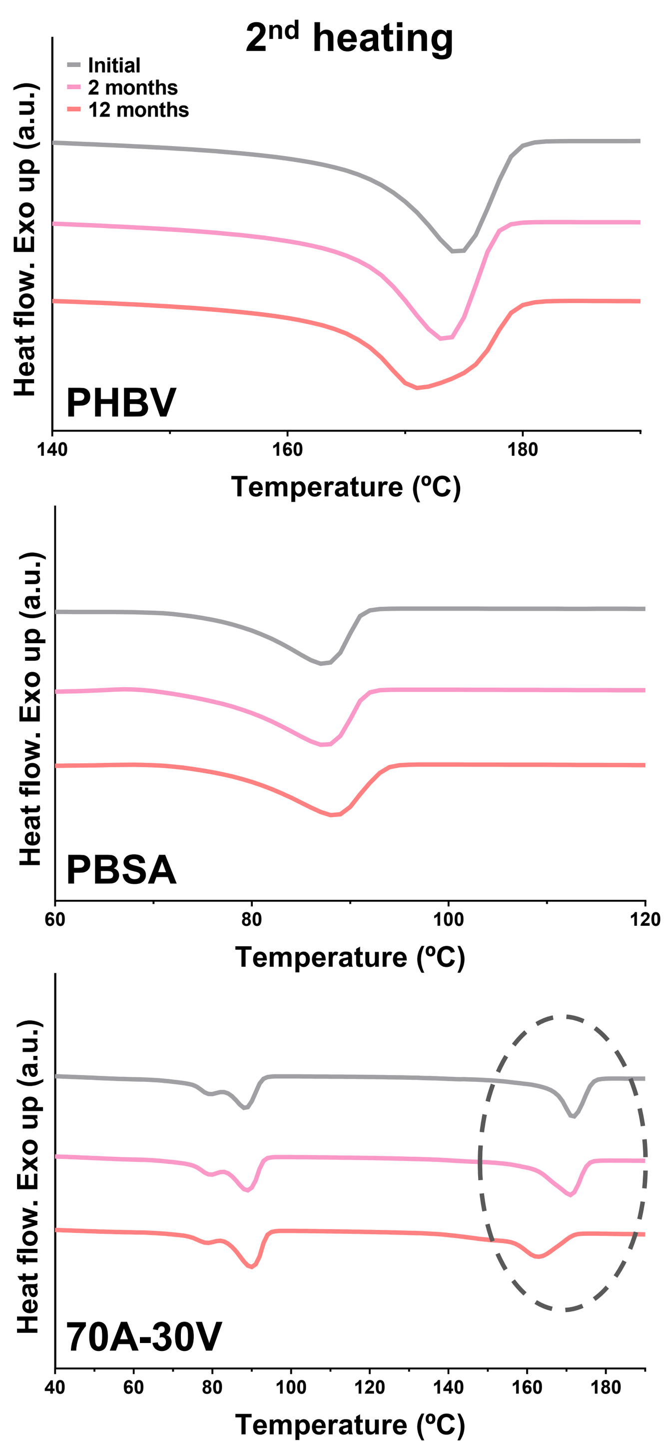


THERMAL BEHAVIOUR (DSC)

The second heating curves of PHBV and the 70A:30V blend displayed progressive shifts and broadening of the melting peaks after 2 and 12 months.

- Presence of imperfect and reorganized crystals, resulting from molecular chain scission and re-crystallization during degradation.
- The blend mimicked the PHBV behavior, suggesting that the PHBV fraction governs its crystalline response.

PBSA, in contrast, showed no relevant change in melting transitions, consistent with its predominantly amorphous structure and slower, surface-limited degradation



CONCLUSIONS

1. **Biodegradable polymers are prone to surface erosion and structural changes over time, unlike PET, which is highly inert.**
2. **Amorphous regions, as in PBSA, are more vulnerable to microbial attack, leading to greater surface roughness and cavity formation.**
3. **Shifts in melting peaks for PHBV and the blend indicate molecular scission and crystal reorganization, while PBSA's minimal thermal change aligns with its surface-limited, amorphous degradation.**
4. **Microbes can colonize all polymers, including PET, though colonization does not necessarily result in visible degradation for highly stable plastics.**

Overall, biodegradable polymers show clear degradation and structural changes over time, whereas PET resists both microbial attack and physical alteration.

ACKNOWLEDGMENTS

This work was supported by TED2021-130211B-C31 and PID2021-128749OB-C32 funded by MCIN/AEI /10.13039/501100011033 and by the European Union NextGeneration EU/PRTR, and by MCIN/AEI/10.13039/501100011033 and ERDEF "A way of making Europe", respectively.

REFERENCES

[1]Jambeck, J.; Geyer, R.; Wilcox, C.; Siegler, T.R.; Perryman, M.; Andrady, A.; Narayan, R.; Law, K.L. Plastic waste inputs from land into the ocean. *Mar. Pollut.* **2015**, *347*, 768–771.

[2]Omura, T., Isobe, N., Miura, T. et al. Microbial decomposition of biodegradable plastics on the deep-sea floor. Nat Commun 15, 568 (2024). https://doi.org/10.1038/s41467-023-44368-8