Supporting information

Sustainable fabrication and application of bio-based membranes: combining a polyhydroxyalkanoate (PHA) as biopolymer and Cyrene[™] as green solvent.

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Figure S1. DSC thermogram of the PHBHV Enmat Y1000P.

The crystallinity ratio (\Box_c) of the polymer was calculated based on the melting enthalpy measured at the first cycle ($\Delta H_m = 89,99 \text{ J/g}$). The following equation was used :

 $\Box_{\rm c} (\%) = (\Delta H_{\rm m} / \Delta H^0_{\rm PHB}) \ge 100$

With $\Delta H^0_{PHB} = 146 \text{ J/g}$, the melting enthalpy of the polymer 100% crystalline.





Figure S2. Schematic overview of the laboratory scale pervaporation set up.



Figure S3. SEM images of the PHBHV based membranes prepared with different polymer and additive (PEG200) concentrations (evaporation of 1.5 min). Top surface, with magnification, on the left and cross section, with magnification, on the right.



Figure S4. Swelling degree of the three selected PHBHV based membranes into different solvent solutions



Figure S5. TGA thermograms of the three selected PV membranes.



Figure S6. pH monitoring of sea water and lipase solution incubated with M-5 and M-1.5-PEG 200 membranes over 105 days, at 25°C.



Figure S7. SEM surface images of the membranes before and after the degradation tests into the Lipase solution or sea water-based solution.

 Table S1. Hansen solubility parameters of the polymer, additives, and solvents. Also include the kinetic diameters of the solvents [1,2].

		Kinetic diameter (nm)	$\delta_t (MPa^{1/2})$
Polymer	PHBHV (2.3 mol% HV)	/	20.6
Solvents to separate	MeOH	0.40	29.6
	MTBE	0.62	16.2

Additives	PEG200	/	24.3
	EBO	/	18.6

Table S2. Apparent pervaporation activation energies (Ei) (KJ.mol-1) for MeOH and MTBE partial fluxes and total flux for all investigated membranes.

	E _i MeOH (KJ.mol ⁻¹)	E _i MTBE (KJ.mol ⁻¹)	E _i MeOH/MTBE 14.3/85.7 (w/w) (KJ.mol ⁻¹)
M-5	23.0	70.6	35.7
M-5-5PEG200	15.8	60.8	36.3
M-5-5EBO	22.6	21.4	21.8

References

- S. Zereshki, A. Figoli, S.S. Madaeni, S. Simone, M. Esmailinezhad, E. Drioli, Pervaporation separation of MeOH/MTBE mixtures with modified PEEK membrane: Effect of operating conditions, J. Memb. Sci. 371 (2011) 1–9. https://doi.org/10.1016/j.memsci.2010.11.068.
- [2] P. Tomietto, Contribution des polyhydroxyalcanoates (PHA) dans l'élaboration de matériaux membranaires pour des séparations en phase liquide, University of Rennes 1, 2020.