Electronic Supplementary Information

Bio-based solvents for polyolefin dissolution and membrane fabrication: From plastic waste to value-added materials

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Table S1. Densities and viscosities of hydrocarbons used in this work. Density data was obtained from the manufacturers. Viscosities were obtained from the literature.[1, 2]

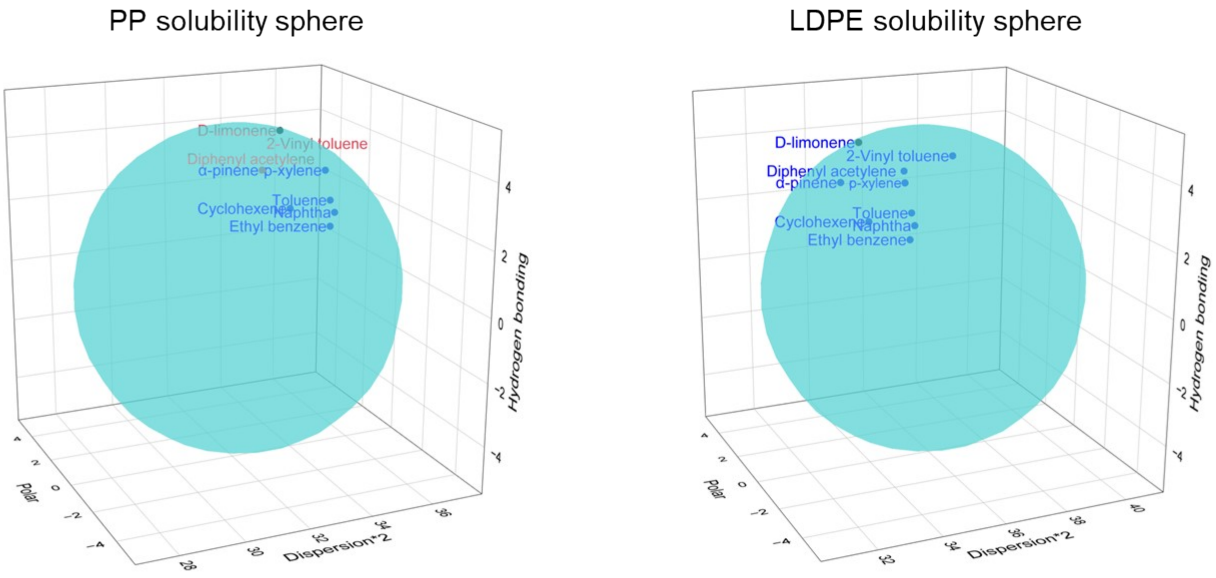
Hydrocarbon	Density (g cm^{-3})	Viscosity (mPa s)
n-hexane	0.659	0.295
Heptane	0.683	0.389
Toluene	0.867	0.554

Table S2. Molecular weights for polymers used in this study obtained by HT-GPC in triple detection mode.

Polymer	Mn (g/mol)	Mw (g/mol)	PDI
Pure LDPE	8,365	189,760	22.7
Pure PP	74,926	289,763	3.9
Waste PP	37,467	206,426	5.5

Table S3. Hansen Solubility Parameters at 25 °C of LDPE, PP, and solvents with HSP values similar to those of *p*-xylene as reference.[3, 4]

Chemical	Source	Pure HSP (MPa$^{1/2}$)			Ra for PP	Ra for LDPE
		δ_d	δ_p	δ_h		
PP	Fossil	16.1	0	0	N/A	N/A
LDPE	Fossil	17.9	0	0	N/A	N/A
D-limonene	Bio	17.2	1.8	4.3	4.7	3.3
α-pinene	Bio	16.9	1.8	3.1	5.2	4.9
p-xylene	Fossil	17.8	1	3.1	3.9	4.1
o-xylene	Fossil	17.8	1	3.1	4.7	3.3
Diphenyl ccetylene	Fossil	18	2	3.2	4.7	3.3
Toluene	Fossil	18	1.4	2	5.4	3.8
Naphtha	Fossil	17.9	0.7	1.8	4.5	2.4
Cyclohexene	Fossil	17.2	1	2	4.1	1.9
2-vinyl toluene	Fossil	18.6	1	3.8	3.1	2.6
Ethyl benzene	Fossil	17.8	0.6	1.4	6.4	4.2



(a)

(b)

Fig. S1. Solvents in the solubility sphere of (a) PP and (b) LDPE. Solvents shown in blue are located inside the sphere, while solvents shown in red are located outside.[3, 4]

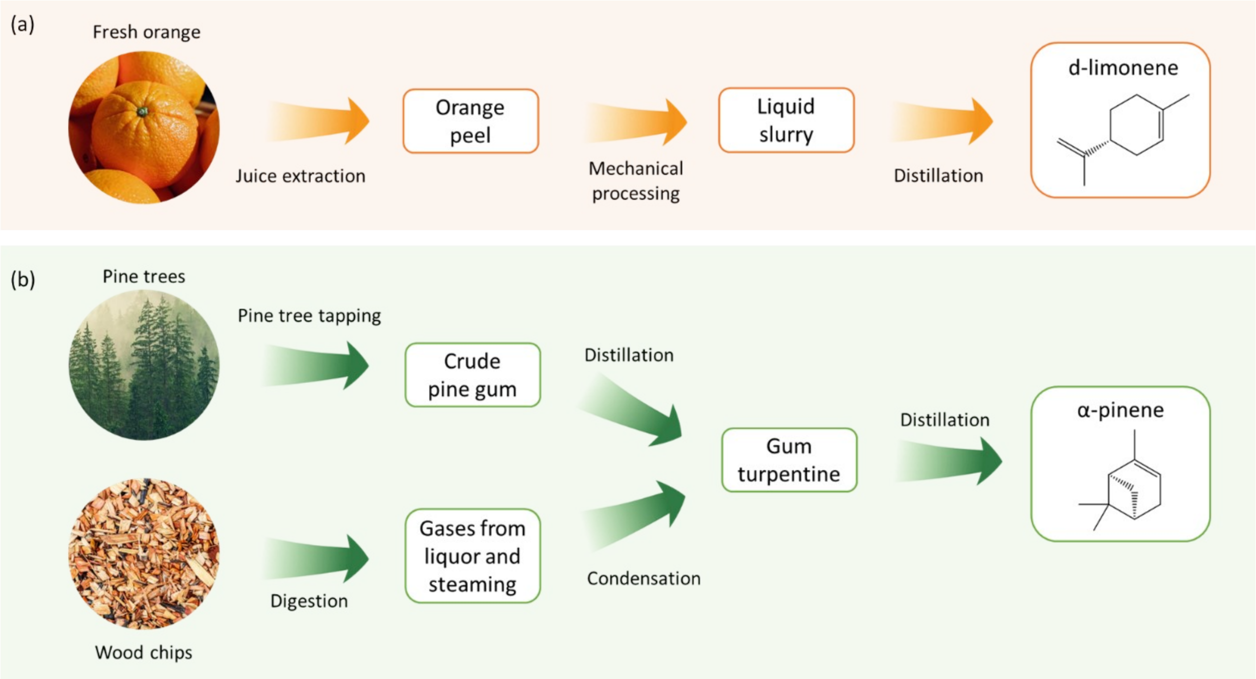


Fig. S2. Schematics of the industrial production processes of (a) d-limonene and (b) α-pinene from biomass. D-limonene is produced as a side-product of the juice industry, where the peels after juice extractions are mechanically processed to obtain molasses and the obtained peel oil can contain up to 95% d-limonene.[5] On the other hand, α-pinene is mainly produced from the pine gum harvested from living pine trees and from the liquor produced during the pulp mill process. α-pinene content in pine gum can be above 90% for some pine tree species,[6] while the liquor from the wood chips digestion contains around 45% of this solvent.[7]

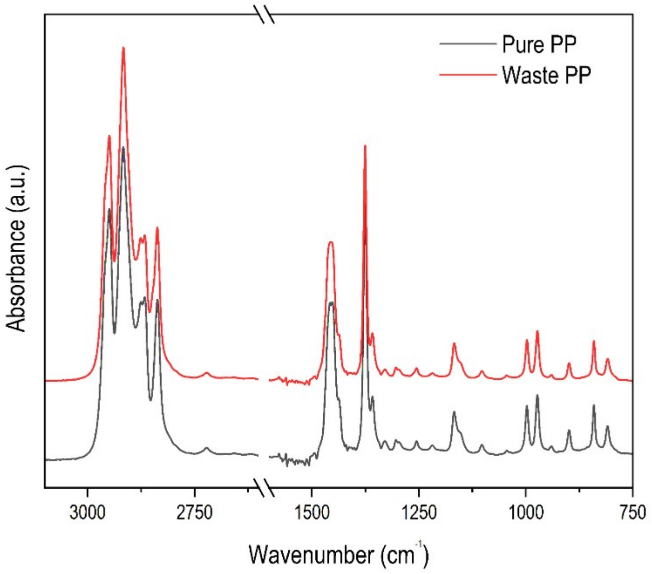


Fig. S3. FTIR spectra of pure PP and waste PP.

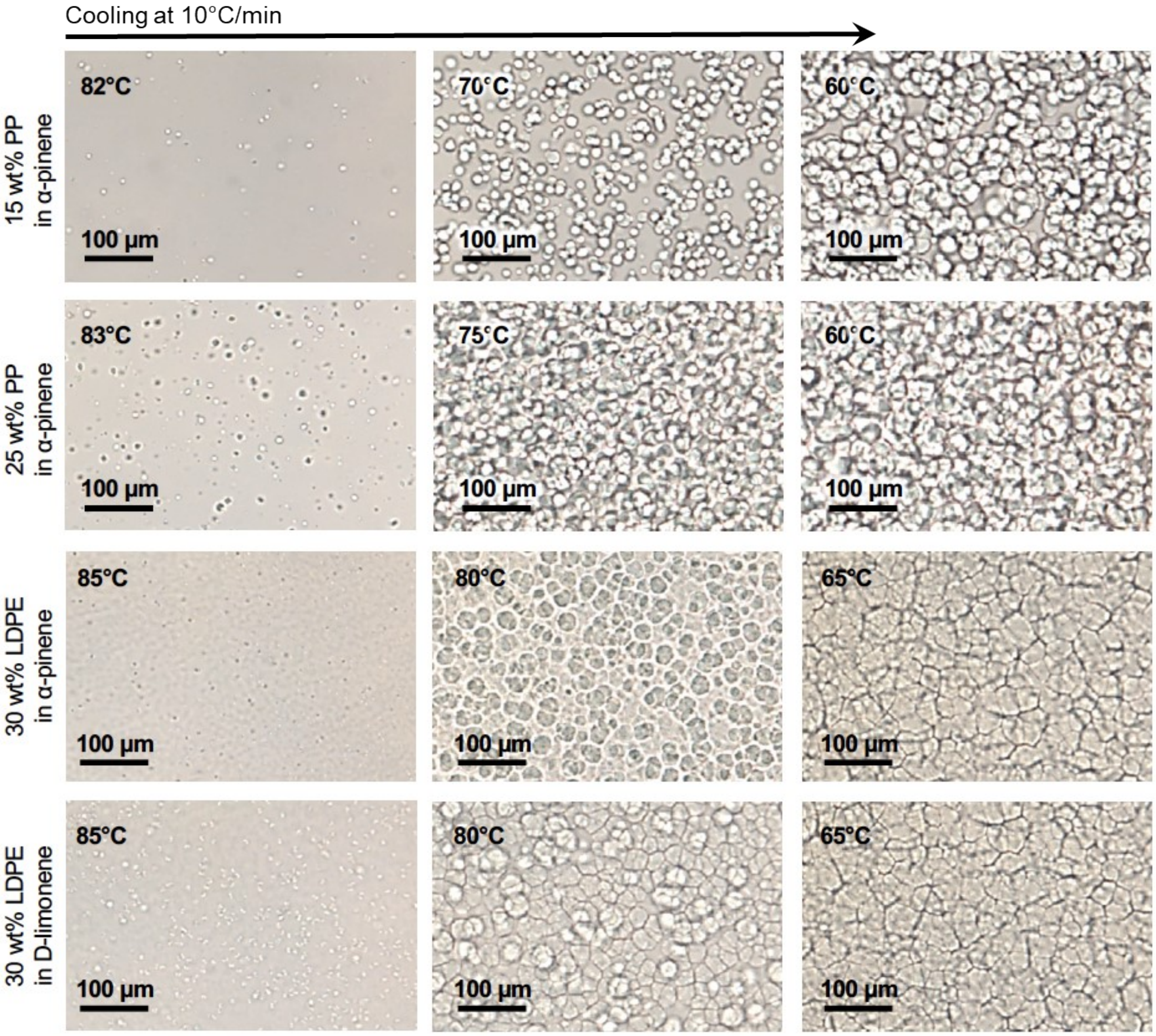


Fig. S4. Optical micrographs of the thermally induced phase separation process of polymer-solvent systems.

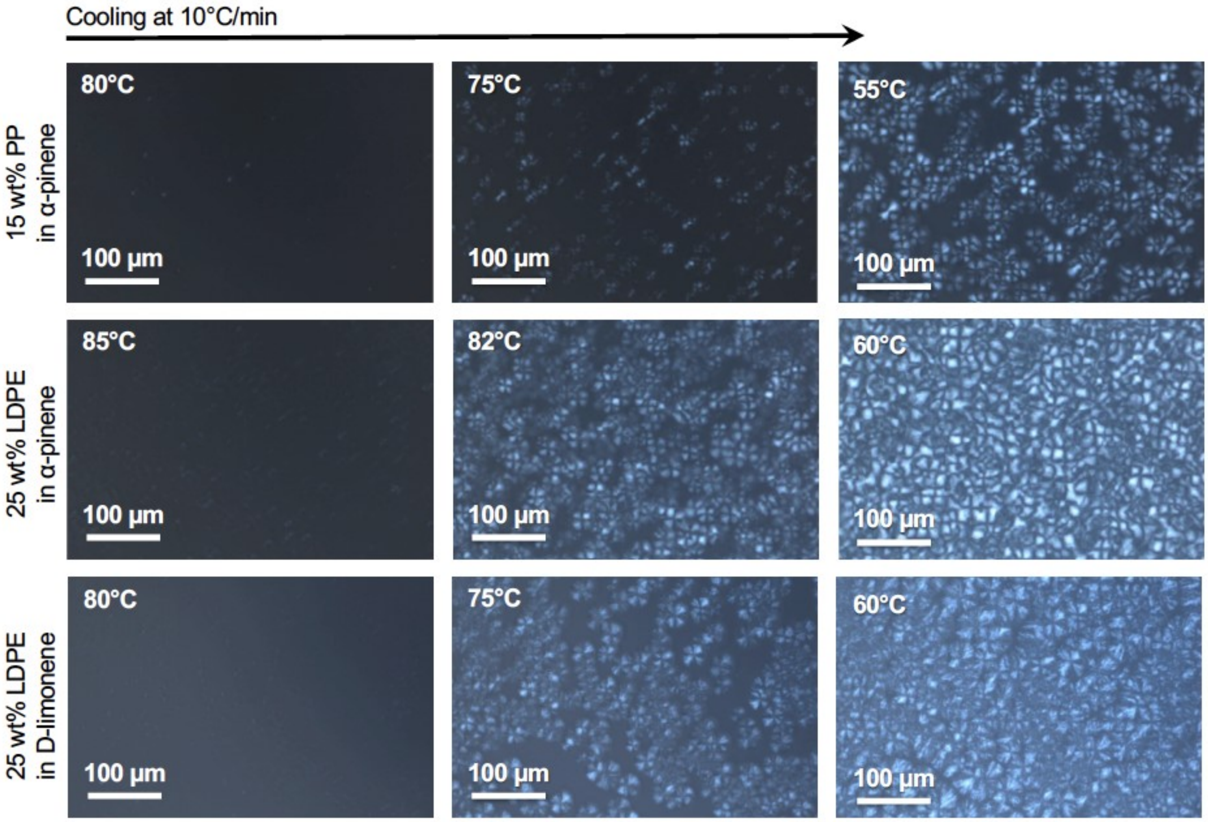


Fig. S5. Micrographs of the phase separation process of PP in α-pinene, LDPE in α-pinene and LDPE in D-limonene under polarized light.

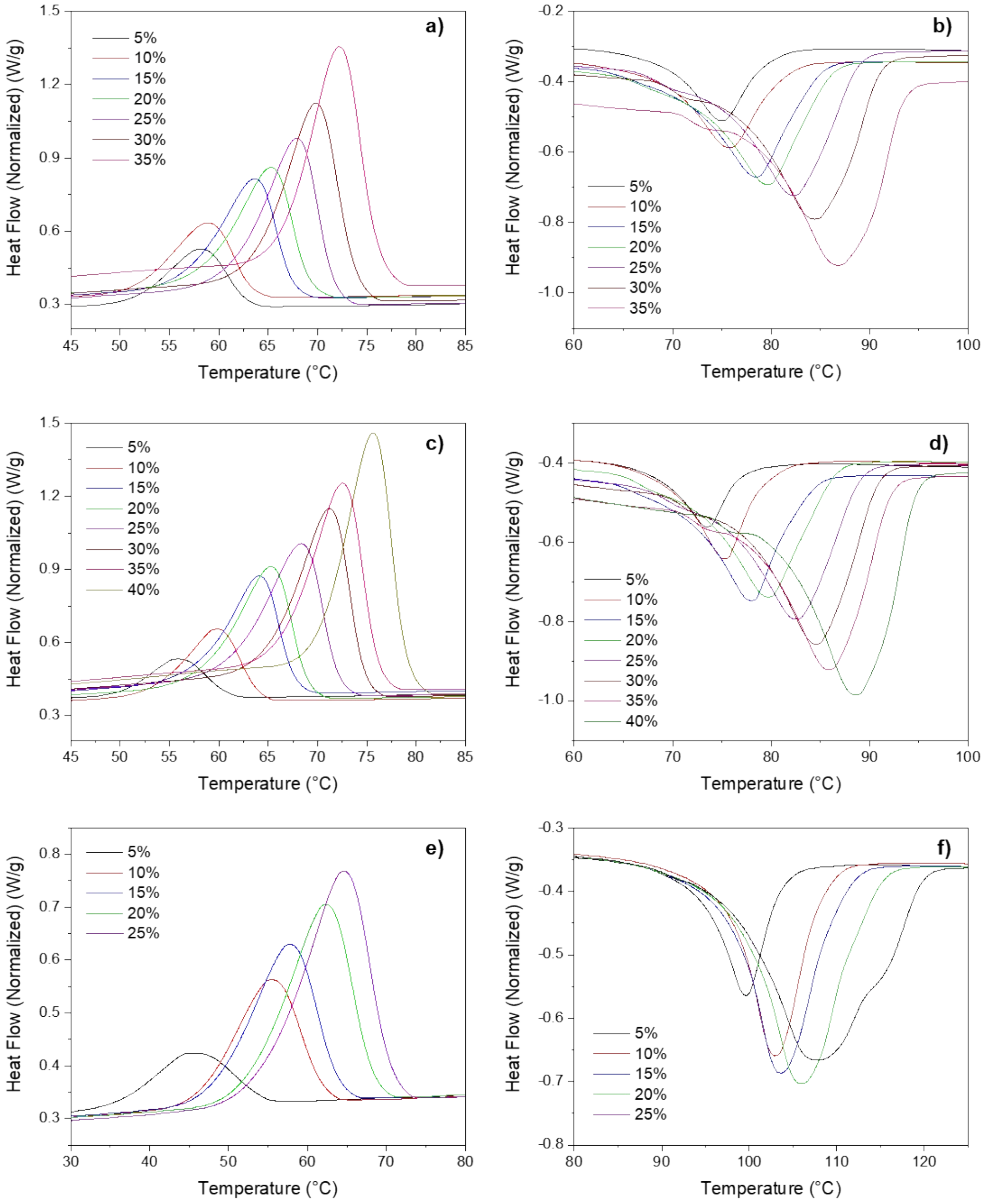


Fig. S6. DSC crystallization and melting curves of (a-b) LDPE in α-pinene, (c-d) LDPE in D-limonene, and (e-f) PP in α-pinene solutions with different polymer contents.

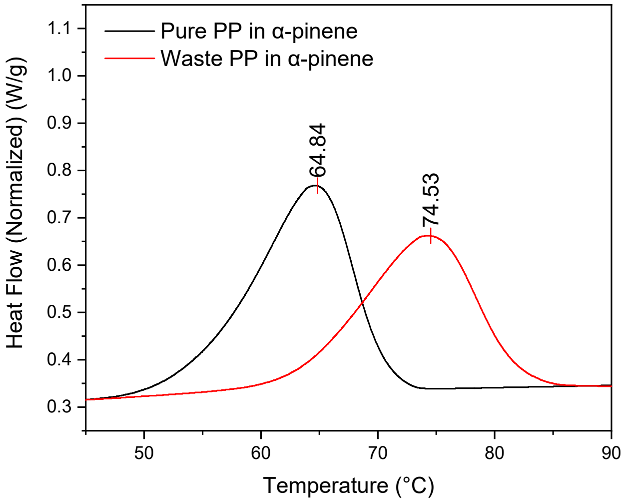
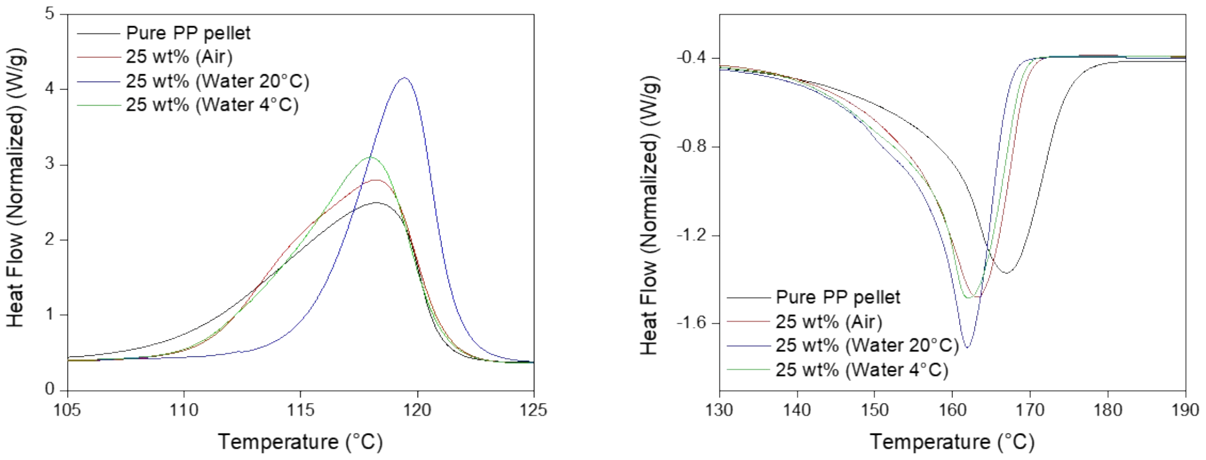


Fig. S7. Crystallization curves of pure PP and waste PP in α-pinene solutions with 25 wt% polymer content.

Table S4. Mechanical properties of pure PP membranes prepared with 15, 20, and 25 wt% polymer content in α-pinene and quenched in air at room temperature, water at 20 °C, and water at 4 °C, and waste PP membranes prepared with 25 and 30 wt% polymer content and quenched in water at 20 °C, and water at 4 °C.

Sample	Young's Modulus (MPa)	Fracture Strain (%)	Tensile Strength (MPa)	Toughness (MPa)
15 wt% pure PP in air	5.0 ± 0.8	10.9 ± 0.8	13 ± 2	109 ± 16
15 wt% pure PP in water at 4 °C	1.9 ± 0.1	29 ± 3.2	5 ± 1	112 ± 30
20 wt% pure PP in air	4.7 ± 0.1	10.2 ± 0.7	12.0 ± 0.3	97 ± 8
20 wt% pure PP in water at 20 °C	0.79 ± 0.02	8 ± 4.4	1.1 ± 0.2	8 ± 6
20 wt% pure PP in water at 4 °C	1.9 ± 0.2	60 ± 9.0	6.0 ± 0.5	313 ± 58
25 wt% pure PP in air	5.0 ± 0.1	17 ± 1.8	14.6 ± 0.1	209 ± 22
25 wt% pure PP in water at 20 °C	0.8 ± 0.2	8 ± 2.5	1.7 ± 0.2	11 ± 4
25 wt% pure PP in water at 4 °C	2.4 ± 0.2	47 ± 3.1	9 ± 1.1	358 ± 19
25 wt% waste PP in water at 20 °C	0.64 ± 0.18	1.90 ± 0.13	0.72 ± 0.09	0.90 ± 0.19
25 wt% waste PP in water at 4 °C	1.78 ± 0.18	3.63 ± 0.07	2.33 ± 0.31	6.22 ± 0.78
25 wt% waste PP in water at 20 °C	1.37 ± 0.19	3.05 ± 0.52	1.37 ± 0.09	3.22 ± 0.70
25 wt% waste PP in water at 4 °C	1.67 ± 0.11	7.96 ± 0.92	2.86 ± 0.03	18.30 ± 2.54



(a) (b)

Fig. S8. Effect of different quenching media on (a) crystallization and (b) melting behavior of pure PP membranes prepared with 25 wt% polymer content.

Table S5. T_c and T_m of pure PP membranes prepared with 15 wt%, 20 wt%, and 25 wt% polymer content in α-pinene and quenched in air at room temperature, in water at 20 °C, and in water at 4 °C.

Sample	**Tc (°C)**	**Tm (°C)**
Pure PP pellet	118.3	166.9
15 wt% in air	117.8	163.2
15 wt% in water at 20 °C	118.3	163.0
15 wt% in water at 4 °C	117.4	162.0
20 wt% in air	117.5	163.9
20 wt% in water at 20 °C	118.5	162.4
20 wt% in water at 4 °C	118.5	162.7
25 wt% in air	118.2	163.2
25 wt% in water at 20 °C	119.5	161.9
25 wt% in water at 4 °C	118.0	162.2

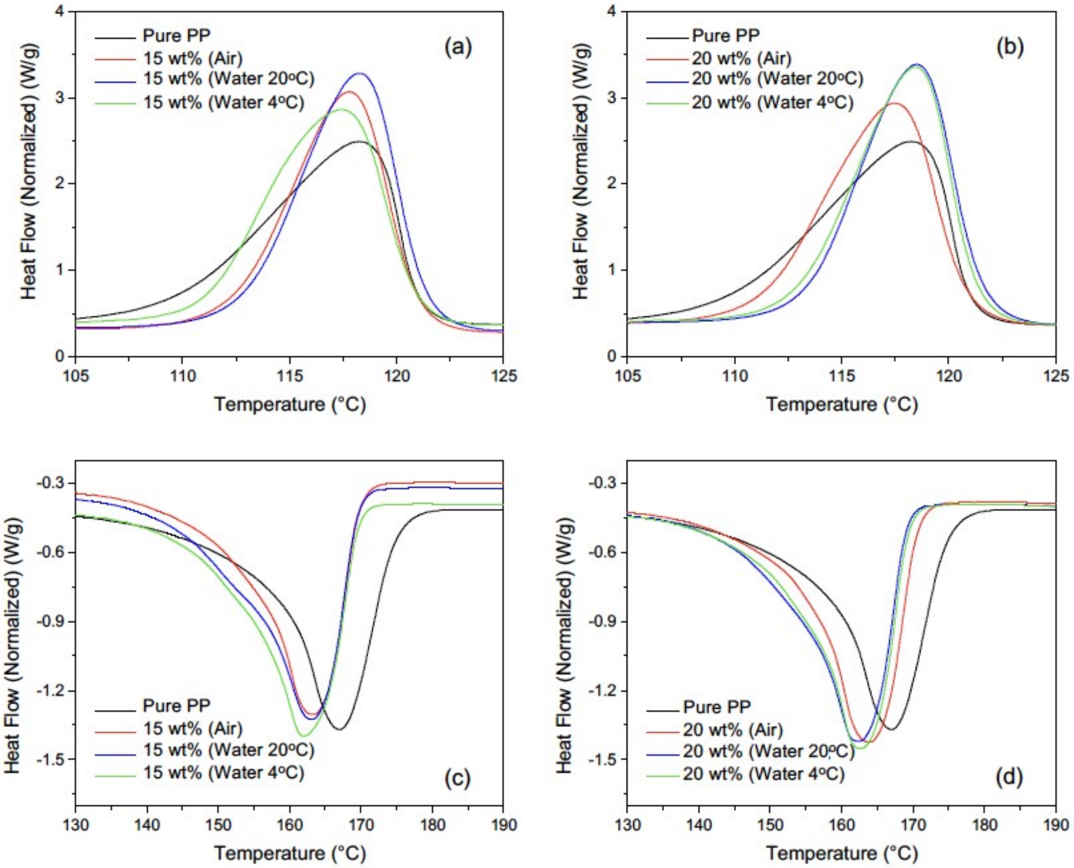


Fig. S9. (a-b) Crystallization and (c-d) melting behavior of pure PP membranes prepared with 15 wt% and 20 wt% polymer content in α-pinene and quenched in air at room temperature, water at 20 °C, and water at 4 °C.

Table S6. Crystallization and melting enthalpy of pure PP membranes prepared with 15 wt%, 20 wt%, and 25 wt% polymer content in α-pinene and quenched in air at room temperature, water at 20 °C, and water at 4 °C.

Sample	Crystallization enthalpy normalized (J/g)	Melting enthalpy normalized (J/g)
Pure PP pellet	96.5	84.9
15 wt% in air	93.2	81.0
15 wt% in water at 20 ℃	96.8	83.9
15 wt% in water at 4 °C	96.7	83.9
20 wt% in air	97.3	81.8
20 wt% in water at 20 °C	96.2	83.9
20 wt% in water at 4 °C	96.2	83.3
25 wt% in air	97.1	82.5
25 wt% in water at 20 °C	97.2	83.8
25 wt% in water at 4 °C	96.8	81.1

Table S7. Pure hydrocarbons permeance, water rejection, and water content in the permeate of tested pure PP and waste PP membranes.

Sample	Permeance			Water-in-toluene water rejection (%)	Permeate water content (ppm)
	Hexane	Heptane	Toluene		
20 wt% pure PPin water at 4°C	0.7 ± 0.1	0.56 ± 0.09	0.48 ± 0.07	94 ± 1	305 ± 10
22.5 wt% pure PP in water at 4°C	0.4 ± 0.2	0.37 ± 0.2	0.3 ± 0.1	95.3 ± 0.3	290 ± 33
22.5 wt% pure PP in water at 20°C	0.6 ± 0.1	0.50 ± 0.1	0.4 ± 0.1	95.7 ± 0.9	259 ± 15
25 wt% pure PP in water at 20°C	0.28 ± 0.05	0.25 ± 0.04	0.22 ± 0.03	95.7 ± 0.4	326 ± 18
25 wt%waste PP in water at 4°C	0.30 ± 0.05	0.29 ± 0.05	0.23 ± 0.03	95.0 ± 0.5	290 ± 25
27.5 wt% waste PP in water at 4°C	0.32 ± 0.03	0.30 ± 0.02	0.24 ± 0.02	94.9 ± 0.2	304 ± 9

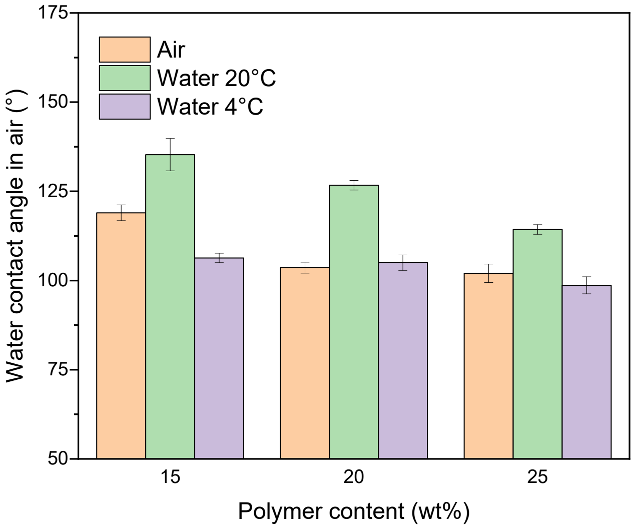
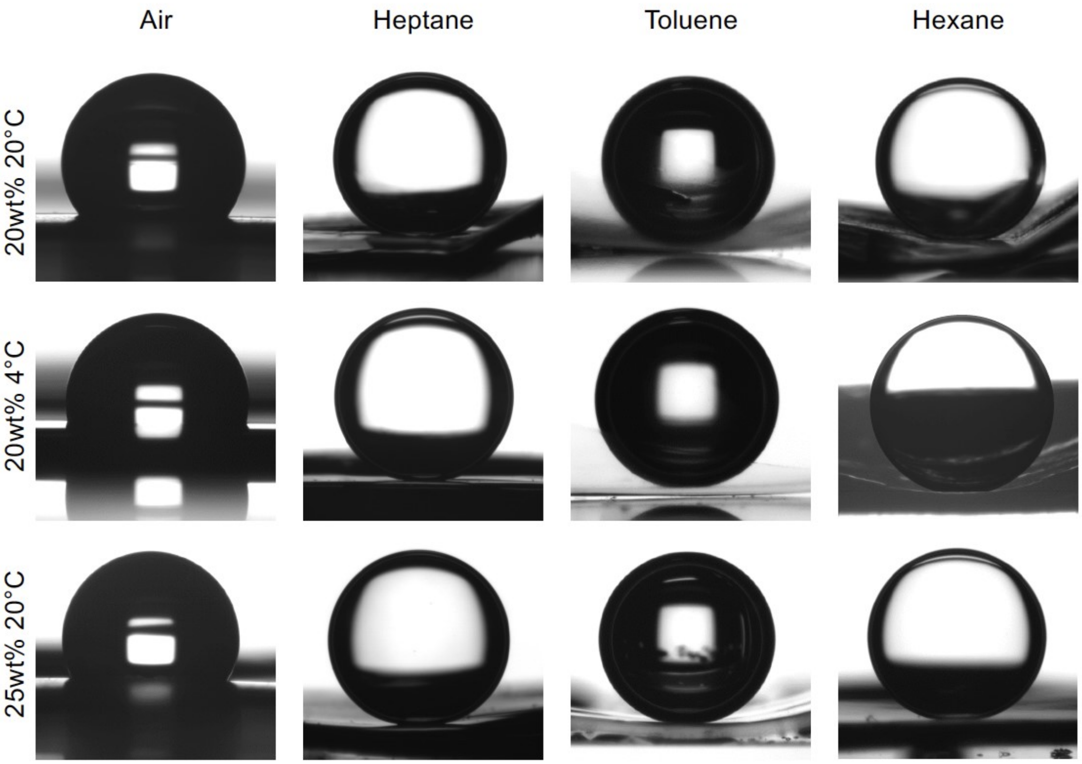
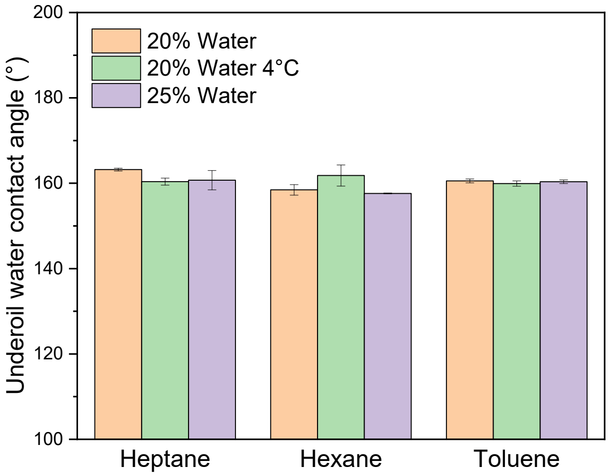


Fig. S10. Water contact angles of films prepared from 15 wt%, 20 wt%, and 25 wt% polymer solutions in different quenching media.

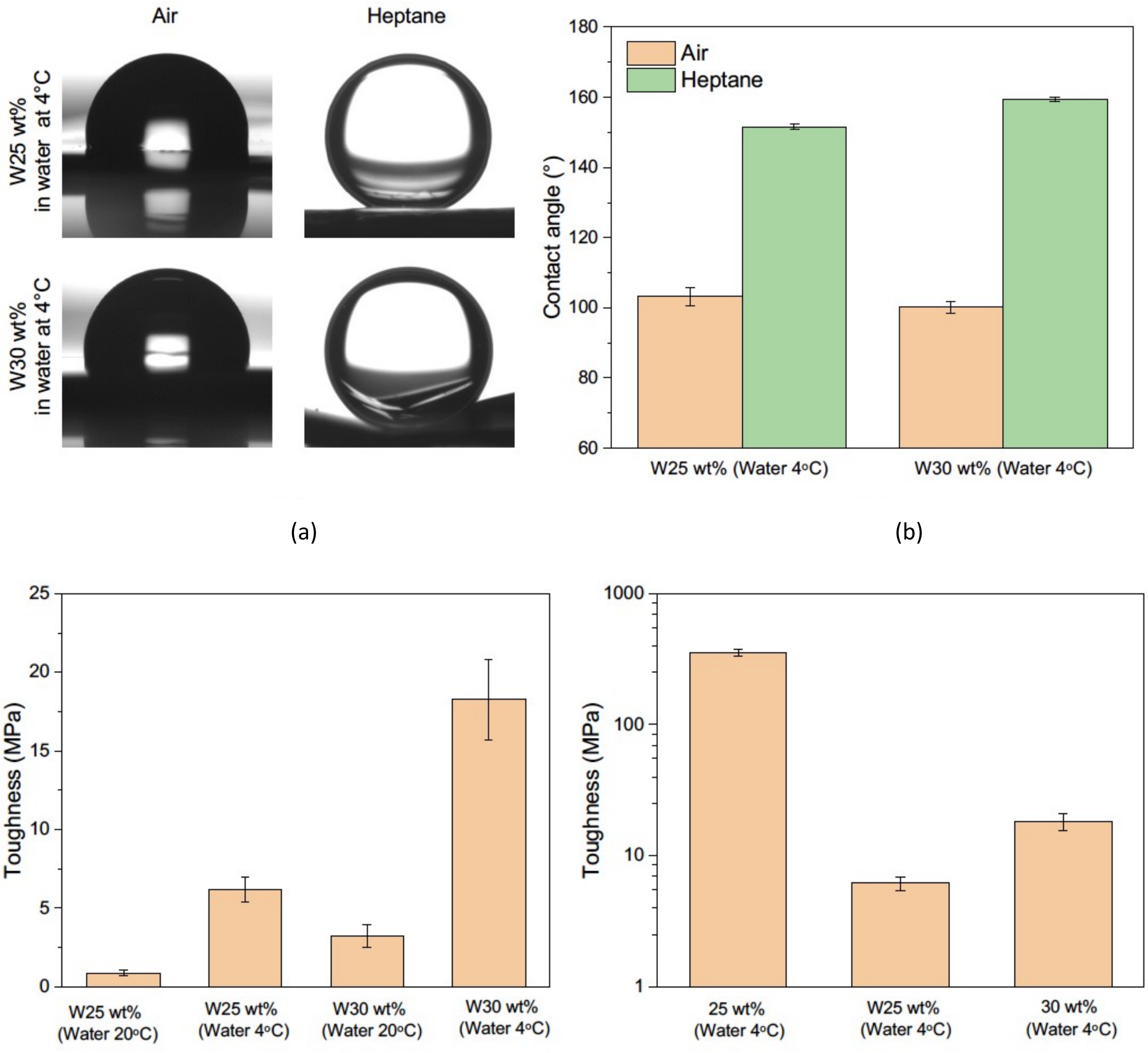


(a)



(b)

Fig. S11. (a) Images of water droplets in air and underoil (heptane, toluene and hexane) for pure PP membranes prepared with 20 wt% and 25 wt% polymer content and different quenching media; (b) corresponding underoil contact angle values.



(a) (b)

(c) (d)

Fig. S12. (a) Water contact angle of waste PP membranes in air and underoil. (b) Toughness of waste PP membranes fabricated with 25 wt% and 30 wt% polymer content and quenched in water at 20 °C and 4 °C. (c-d) Comparison between pure PP membrane (25 wt% PP quenched in water at 4°C) and waste PP membranes quenched in water at 4 °C.

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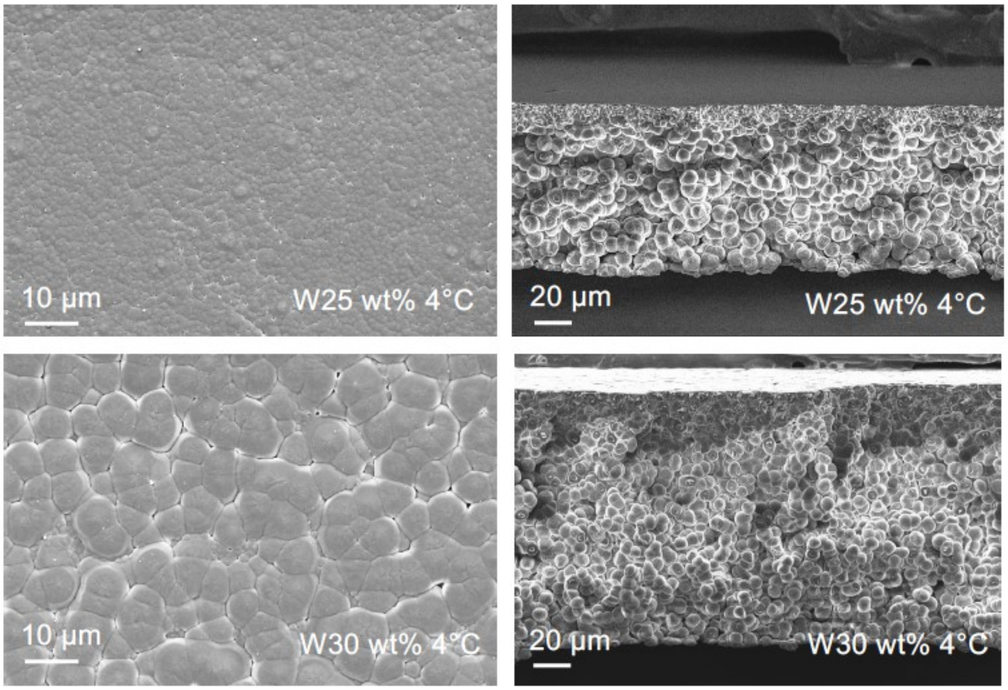

Fig. S13. Surface and cross-sectional SEM micrographs of waste PP membranes prepared with 25 wt% and 30 wt% PP solutions quenched in water at 4 °C.

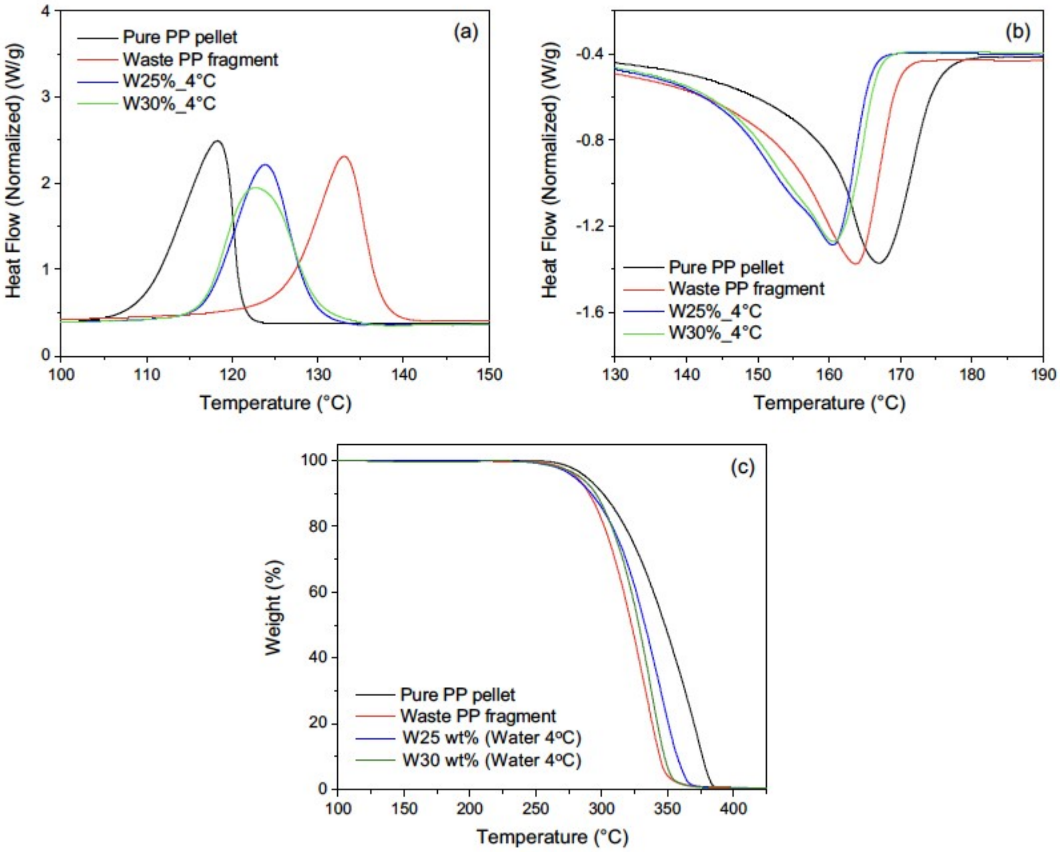

Fig. S14. Thermal properties comparison of waste PP membranes, waste PP source and pure PP pellets. (a) Crystallization. (b) Melting. (c) Thermal decomposition. Waste PP fragments are the waste material before the membrane preparation process.

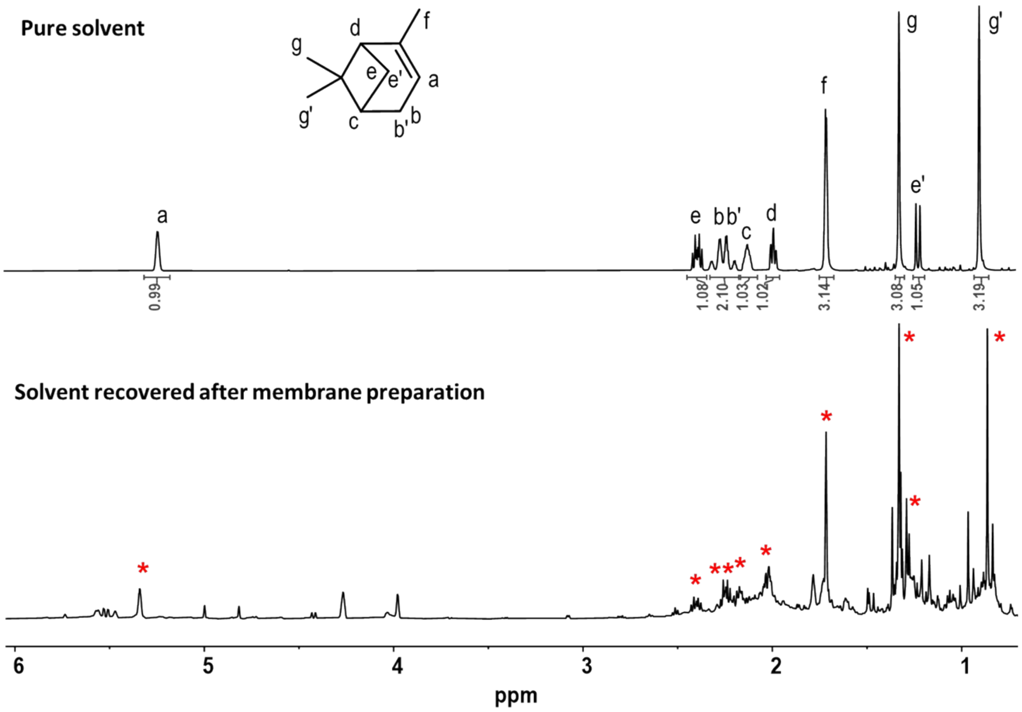

Fig. S15. ^{1}H NMR spectra comparison of the pure solvent (top) and the solvent recovered after the membrane preparation (bottom). The Nuclear Magnetic Resonance (NMR) spectra was obtained in a Bruker Avance-III 400 MHz spectrometer with a Z-axis gradient BBO probe using $CDCl_3$ as solvent.

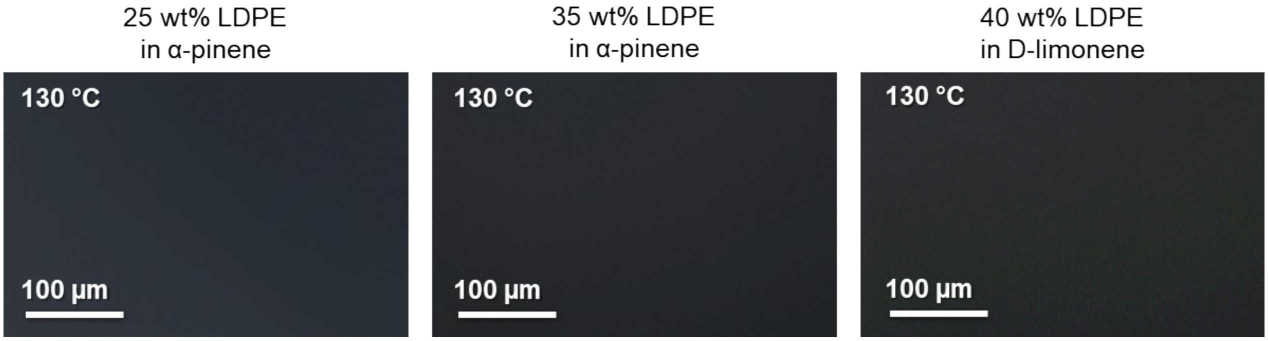

Fig. S16. Optical micrographs of PP in α-pinene, LDPE in α-pinene and LDPE in D-limonene solutions at 130 °C under polarized light.

References

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