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Electronic Supplementary Information for:

Chemical Recycling of Poly(ethylene terephthalate): Glycolysis, Oleoyl Chloride Esterification and Vulcanization to yield Durable Composites

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Experimental Details

Synthesis of GPET[1]

Poly(ethylene terephthalate) (PET) chips (20.48 g, 0.11 mol (PET monomer unit)), diethylene glycol (18.45 g, 0.17 mol), and the catalyst, zinc acetate (1.02 g, 5.54 mmol), were put into a 100 mL round-bottom flask equipped with a reflux condenser, a nitrogen inlet and a thermo-couple linked to the heat plate. The reaction mixture was stirred for 10 h at 185 °C. Upon cooling to room temperature, the reaction mixture was extracted by dichloromethane (50 mL) and DI water. The organic layer was collected, and the solvent was removed under reduced pressure. The resultant material, GPET, was slightly viscous at room temperature.

Synthesis of EPET

The preparation of EPET involved the reaction of glycolyzed-PET (GPET) (2.08 g) dissolved in dichloromethane (6.65 g, 0.07 mol), oleoyl chloride (7.37 g, 0.02 mol), sodium bicarbonate (2.06 g, 0.02 mol) and dichloromethane (13.3 g, 0.16 mol). Glycolyzed-PET (GPET) (2.08 g) dissolved in dichloromethane (6.65 g, 0.07 mol) was slowly added to a mixture of oleoyl chloride (7.37 g, 0.02 mol), sodium bicarbonate (2.06 g, 0.02 mol) and dichloromethane (6.65 g, 0.07 mol) while stirring in an ice bath. The reaction mixture was stirred for 24 h at room temperature under an atmosphere of dry N_2 gas. The final reaction mixture was extracted by dichloromethane (10 mL) and DI water. The organic layer was collected and dried at 39 °C under reduced pressure.

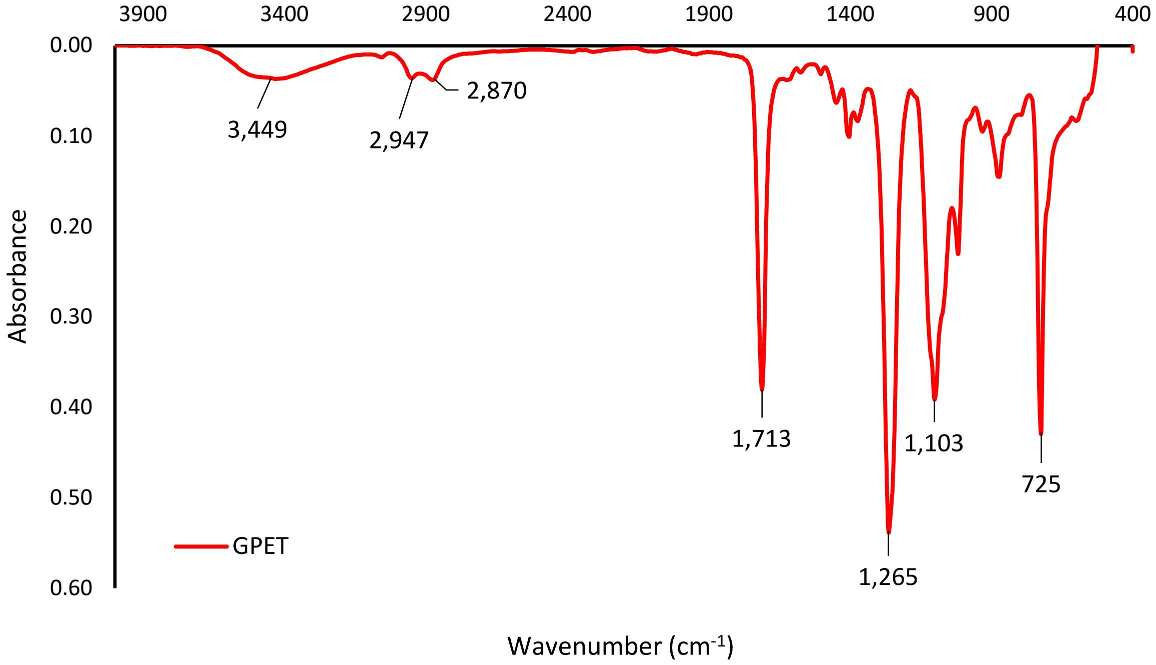


Figure S1. Fourier-transform infrared spectroscopy (FT-IR) traces for GPET.

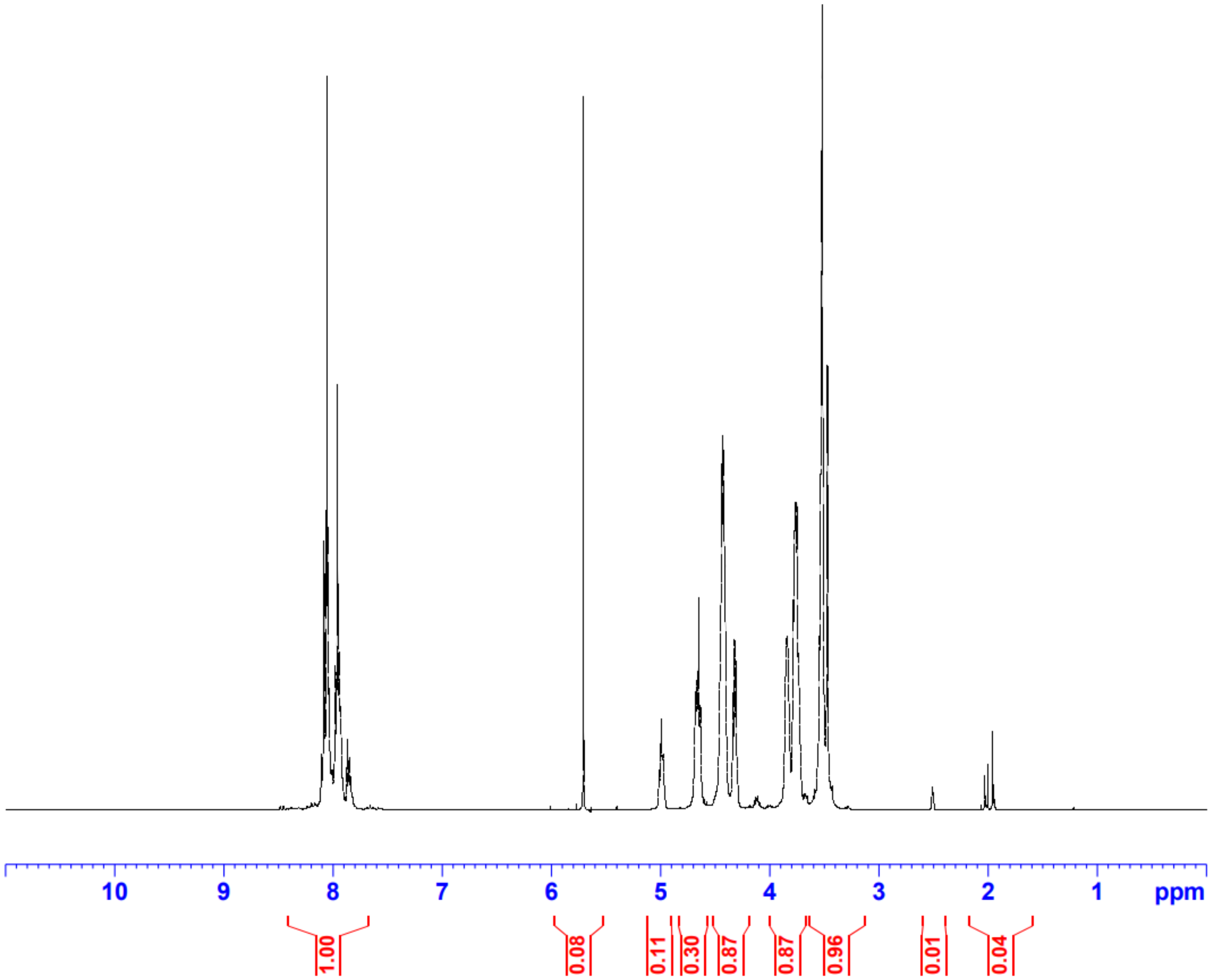


Figure S2. Proton nuclear magnetic resonance (NMR) spectrum of GPET.

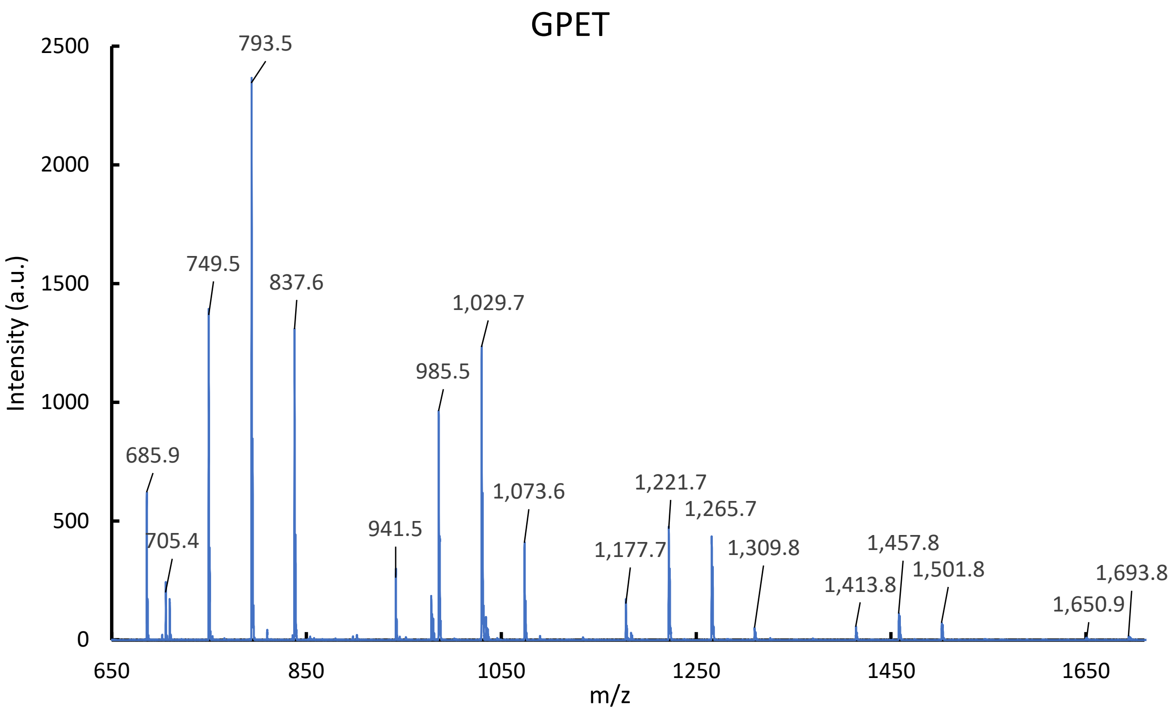
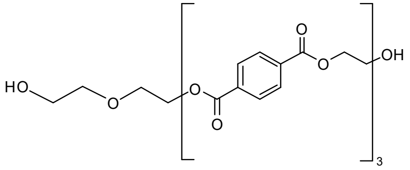
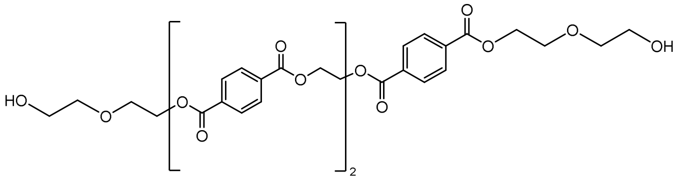
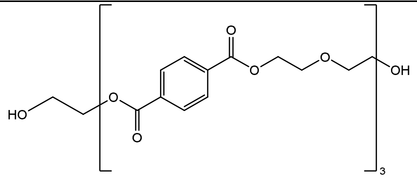
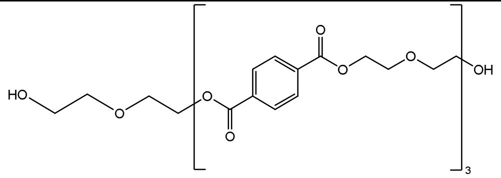
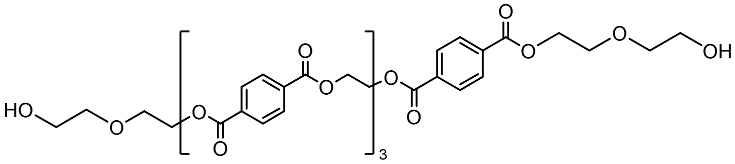
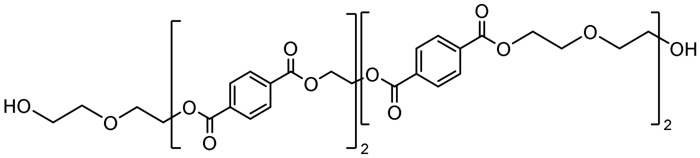
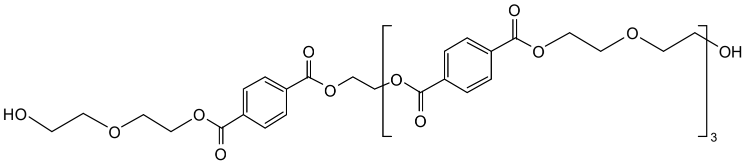


Figure S3. Matrix assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF) spectra in the positive reflectron ion mode for glycolyzed–PET (GPET).

Table S1. Oligomers found in GPET, as determined from MALDI-TOF

Structure	**Theoretical** (*m*/z; cationized species)	**Experimental** (*m*/z; cationized species)
	705.180	705.390
	749.206	749.496
	793.232	793.494
	837.258	837.562
	941.248	941.587
	985.274	985.597
	1029.301	1029.625

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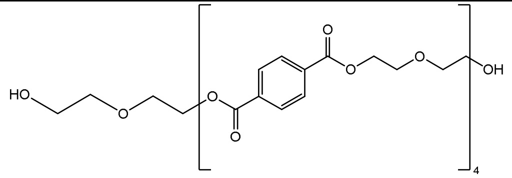
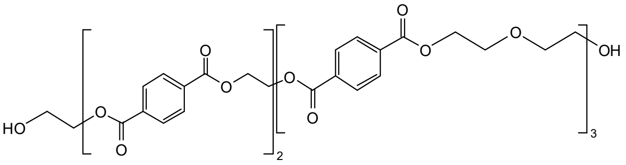
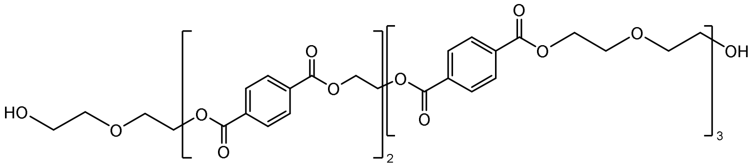
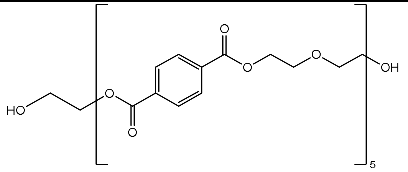
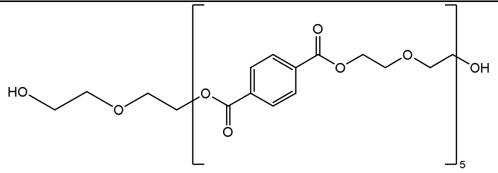
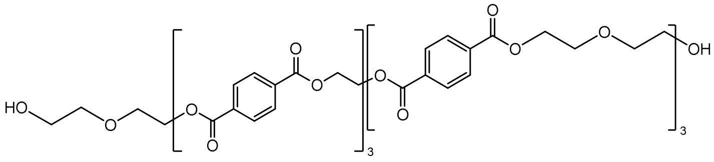
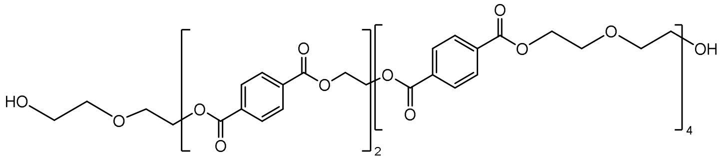
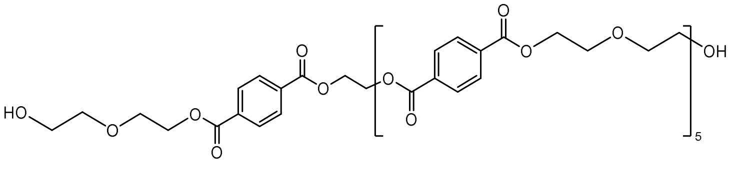
	1073.327	1073.666
	1177.317	1177.703
	1221.343	1221.715
	1265.369	1265.755
	1309.395	1309.787
	1413.385	1413.782
	1457.411	1457.813
	1501.438	1501.825

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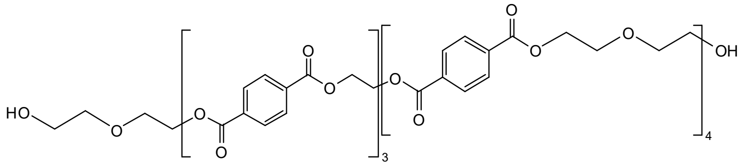
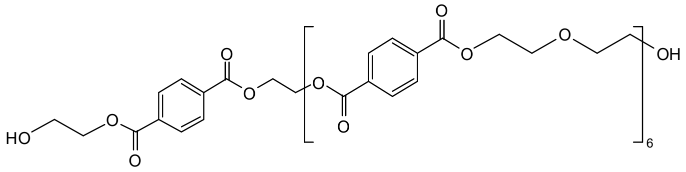
	1649.454	1650.909
	1693.480	1693.808

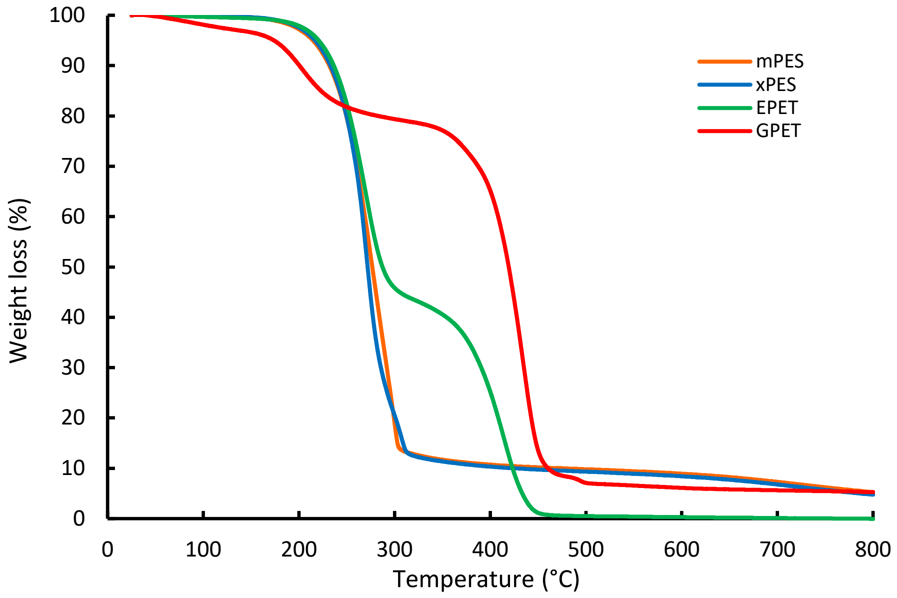


Figure S4. Thermogravimetric analysis (TGA) traces for xPES, mPES, EPET and GPET.

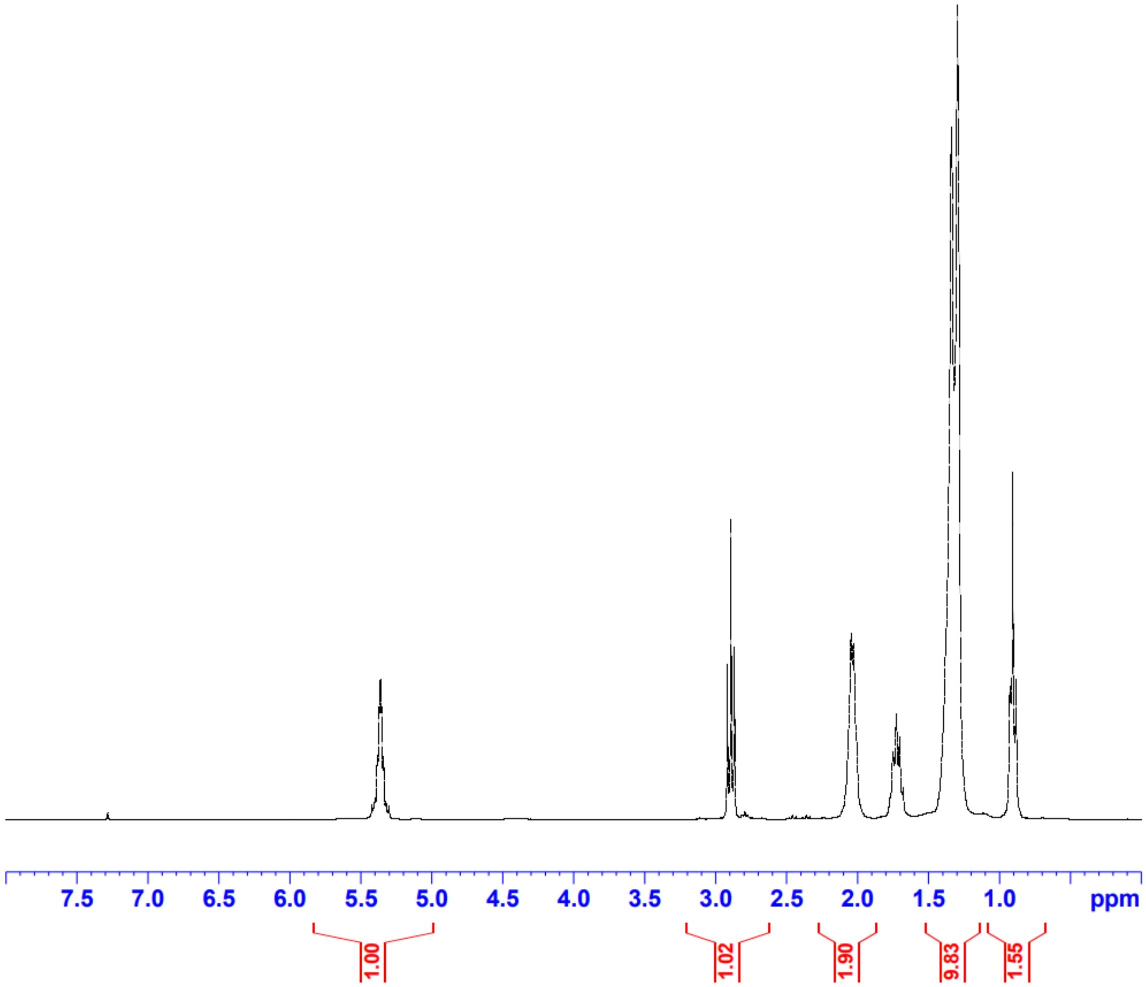


Figure S5. Proton nuclear magnetic resonance (NMR) of oleoyl chloride.

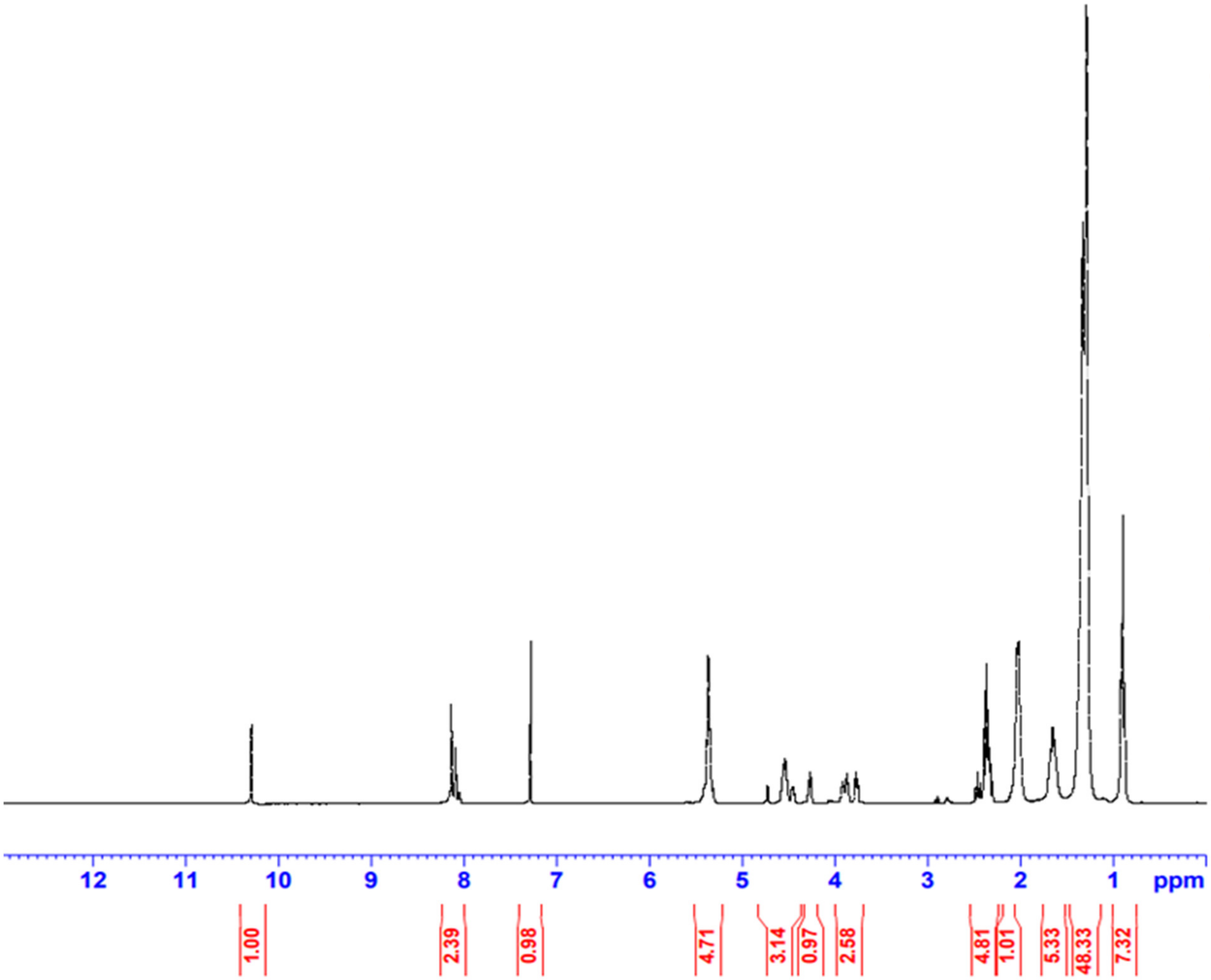


Figure S6. Proton nuclear magnetic resonance (NMR) of EPET using 2,3,4,5,6-pentafluorobenzaldehyde (PFB) as internal standard.

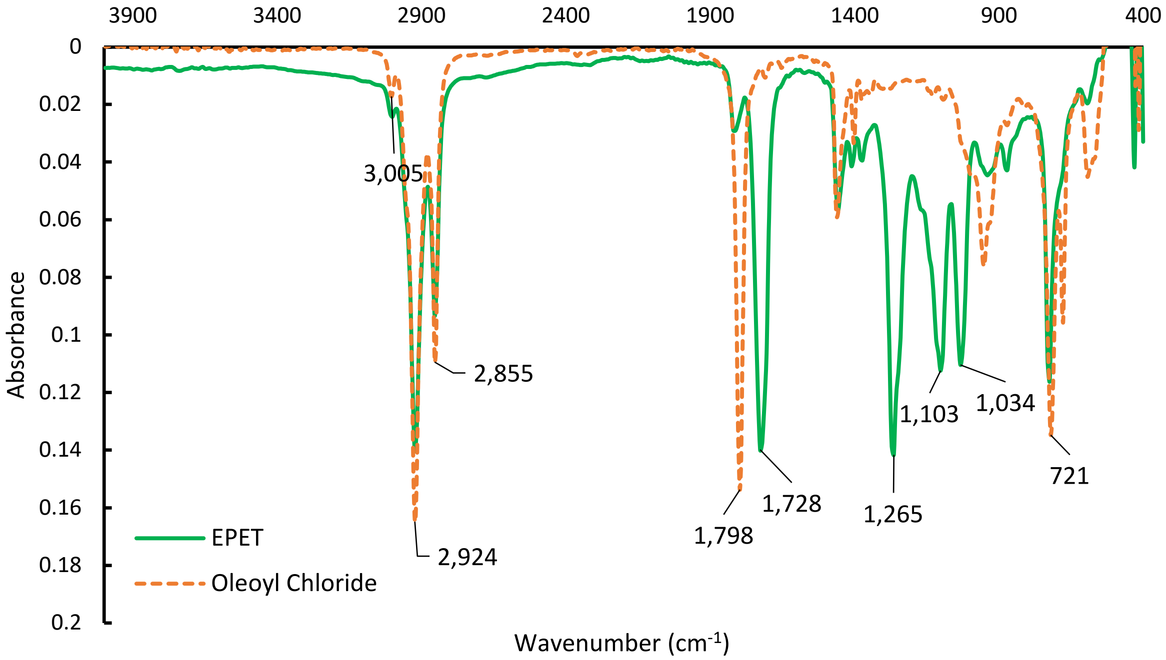


Figure S7. Fourier-transform infrared spectroscopy (FT-IR) traces for oleoyl chloride and esterified PET (EPET).

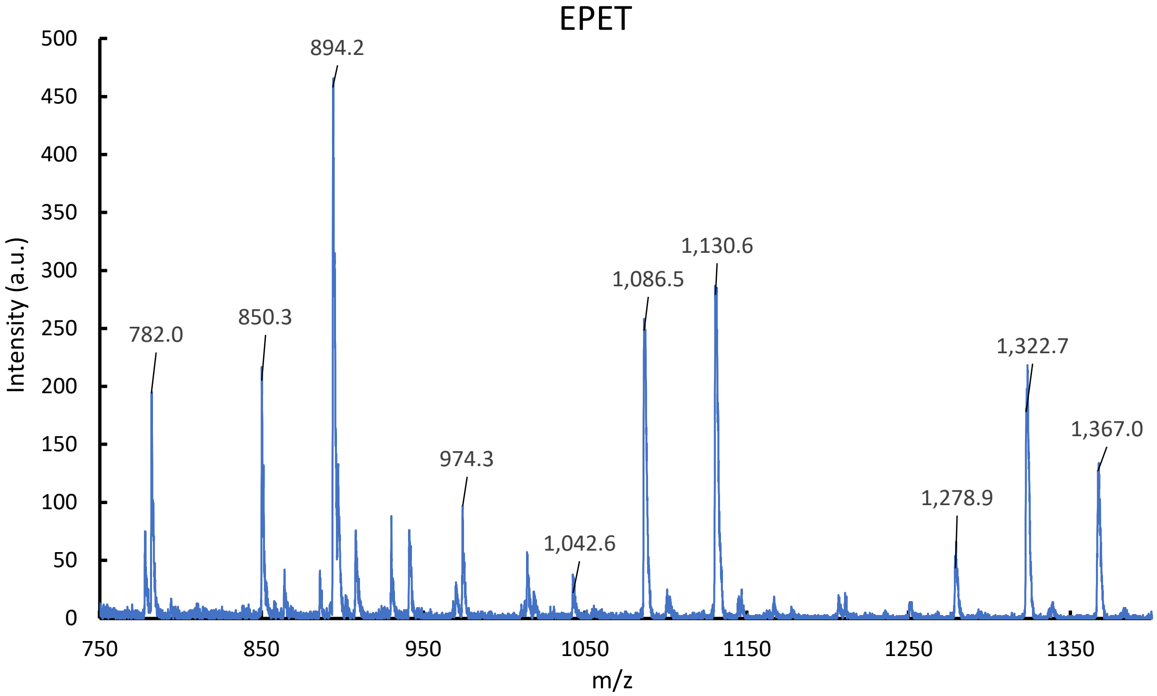
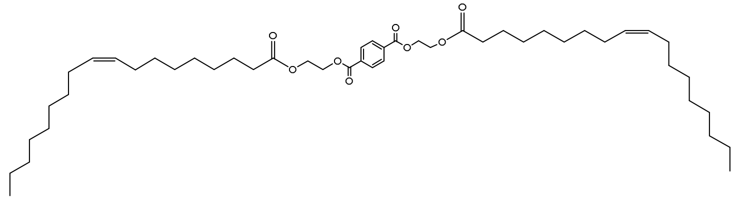
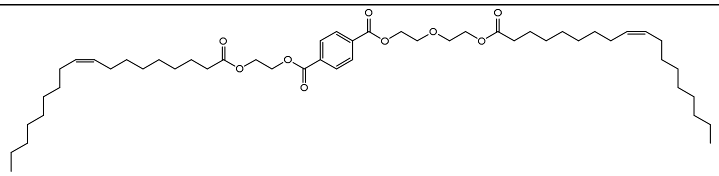
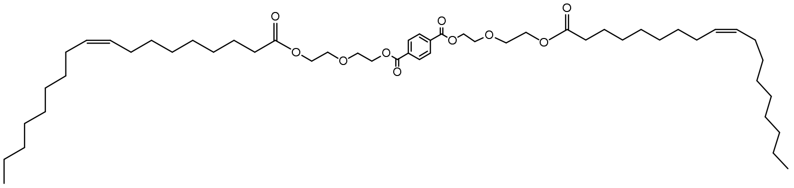
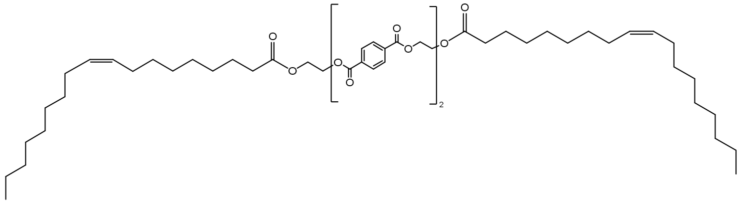
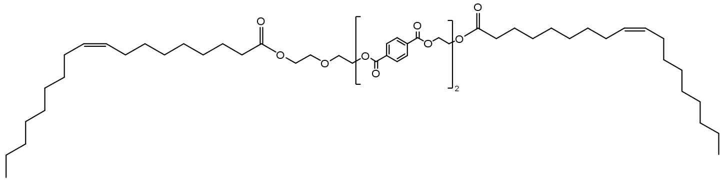
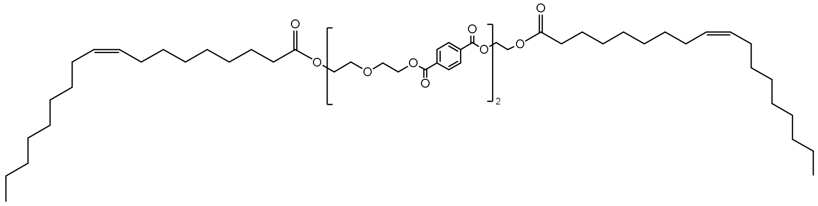


Figure S8. Matrix assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF) spectra in the positive reflectron ion mode for Na-cationized EPET. The oligomers have the general formula **$HOZ(TZ)_nOH$**, where Z represents the glycol units (diethylene glycol or ethylene glycol), and T represents the terephthalate units. The molecular weight (MW) of the oligomers can be quickly estimated as MW= $164n+28m+74x+M_e+23$, where n is the number of terephthalate units, m is the number of ethylene glycol-derived units, x is the number of diethylene glycol-derived units, M_e is the molecular weight of chain ends, and 23 corresponds to the sodium, which cationized the sample in the MALDI technique employed.

Table S2. Oligomers found in EPET, as determined from MALDI-TOF

Structure	**Theoretical** (*m*/z; cationized species)	**Experimental** (*m*/z; cationized species)
	782.102	782.570
	850.244	849.586
	894.197	893.612
	974.318	974.612
	1042.613	1041.628
	1086.556	1085.654

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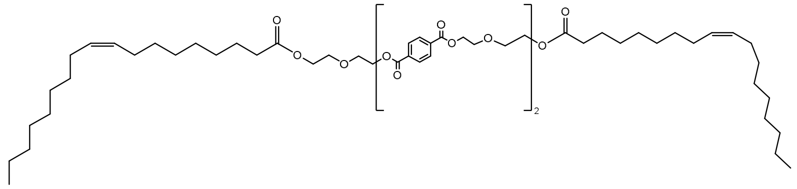
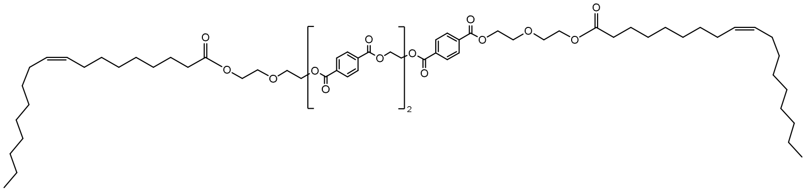
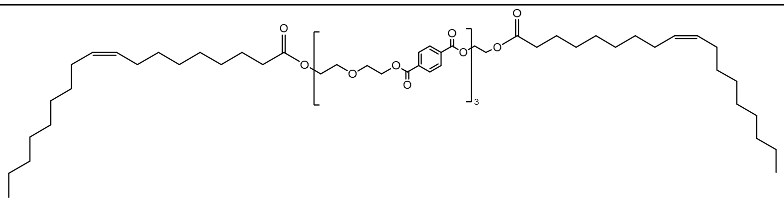
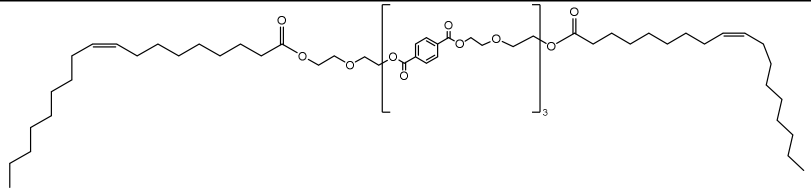
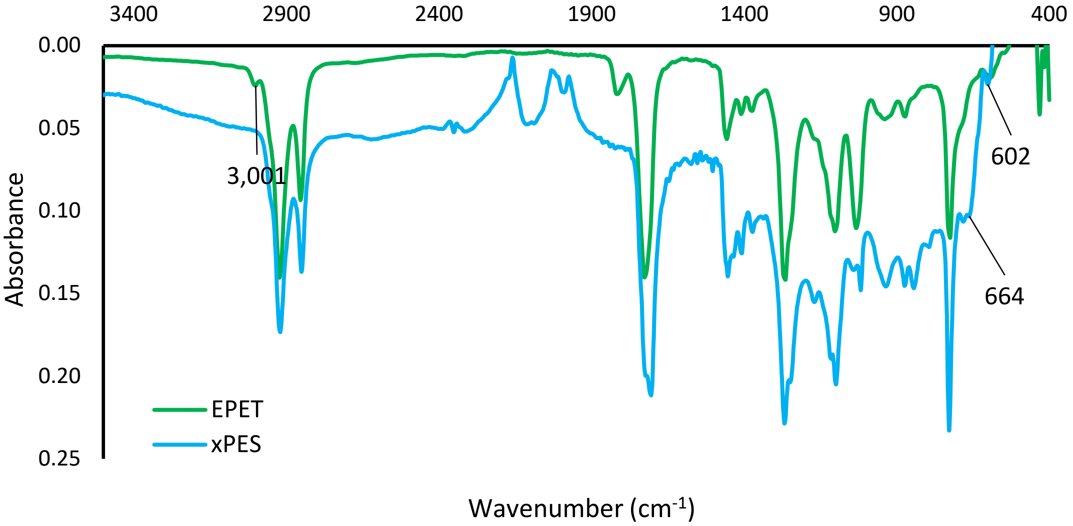
	1130.566	1129.681
	1278.964	1277.697
	1322.811	1321.723
	1367.079	1365.749



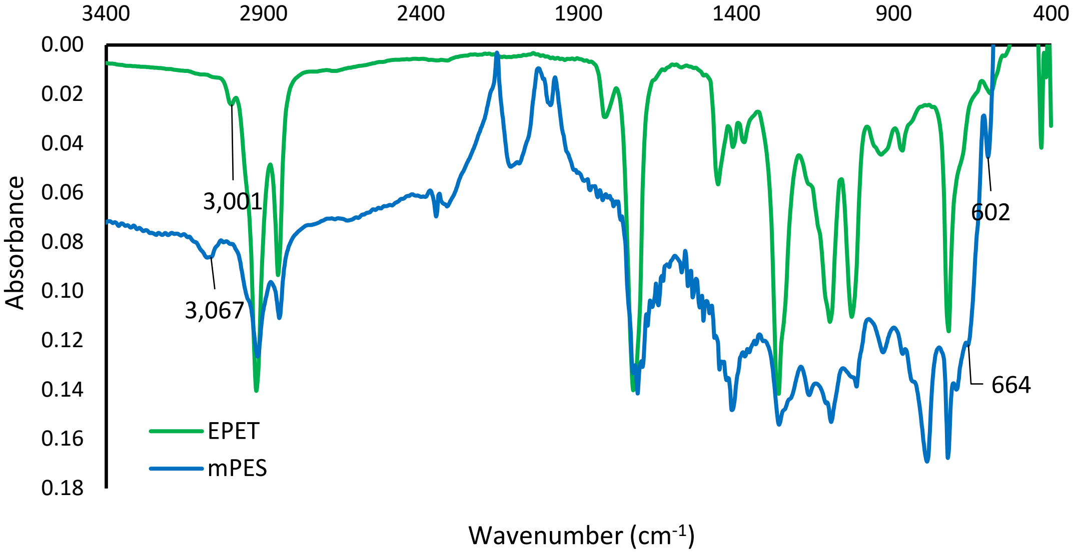


Figure S9. Fourier-transform infrared spectroscopy (FT-IR) traces of EPET compared to those of composites xPES (upper plot) and mPES (lower plot). The feature at 1850–2300 cm^{-1} in the spectrum for the composite is an artifact of the ATR attachment visible only at the lower concentration organic sample (10 wt% organic in the composite compared to 100 % in EPET).

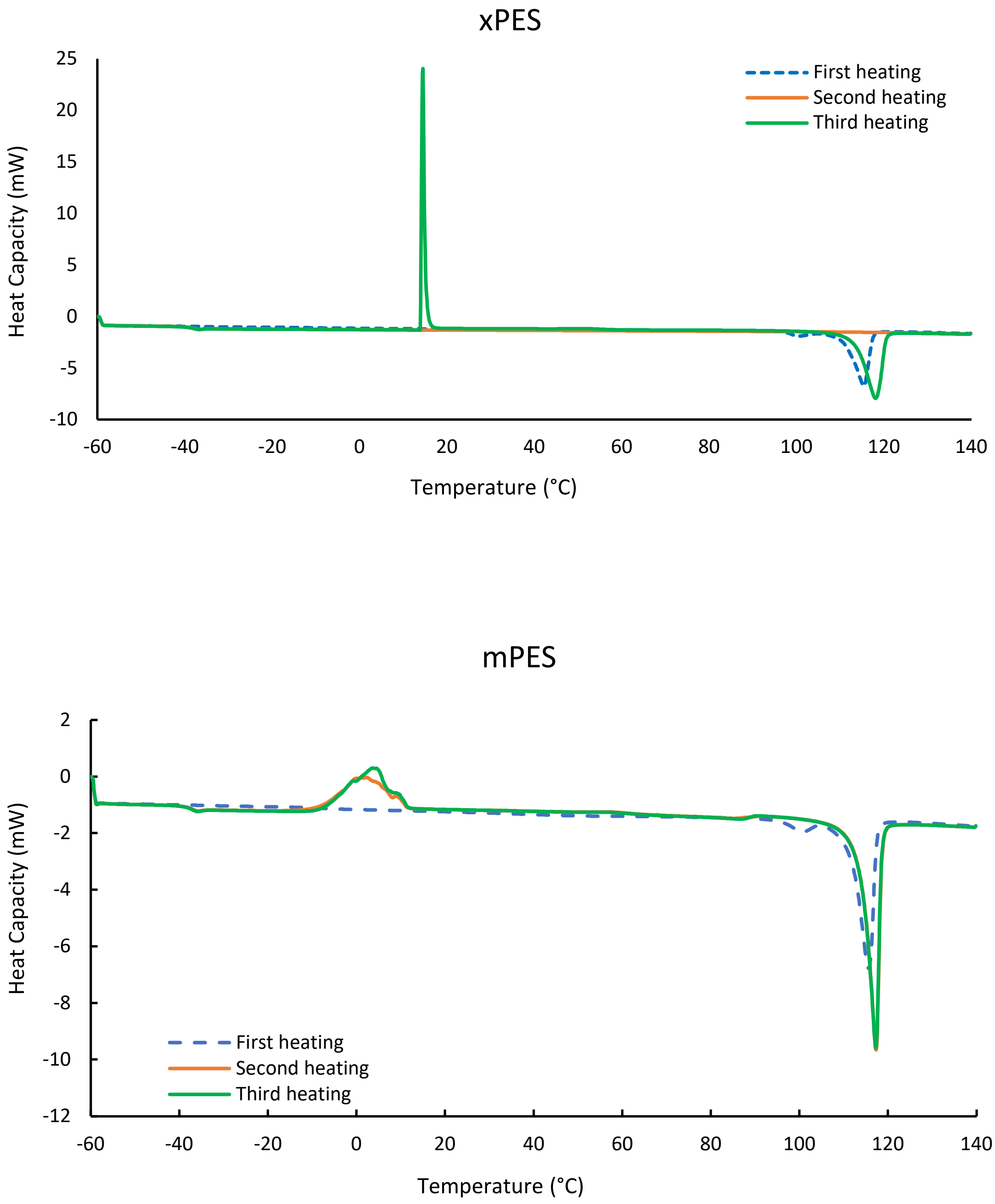


Figure S10. Differential scanning calorimetry (DSC) traces for xPES and mPES. For each compound data for the first heating cycle (blue-dotted line), second heating cycle (orange line), and third heating cycle (green line) were collected.

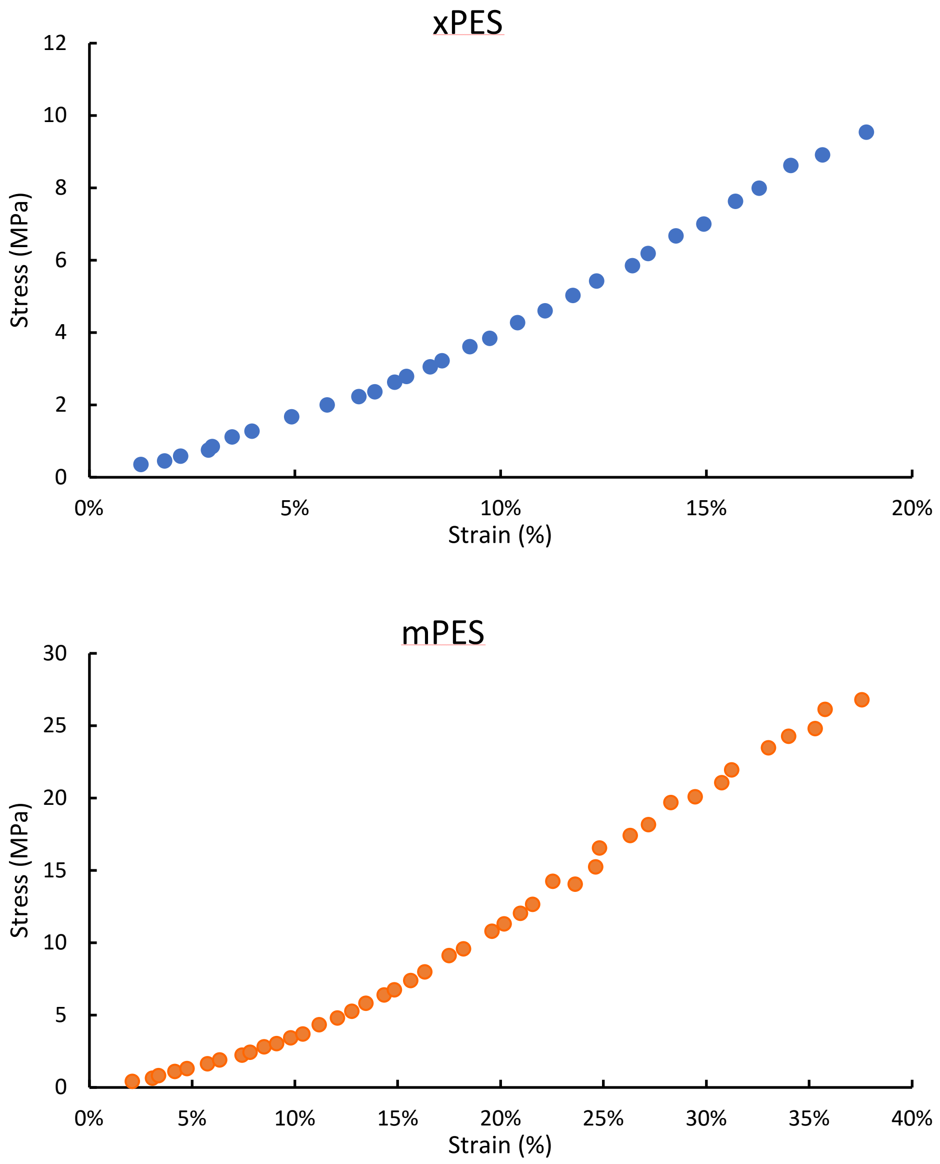


Figure S11. Examples of stress-strain plots for measurements on the compression test cylinders. Data in Table 2 are averages of three independent trials with errors reported as standard deviations.

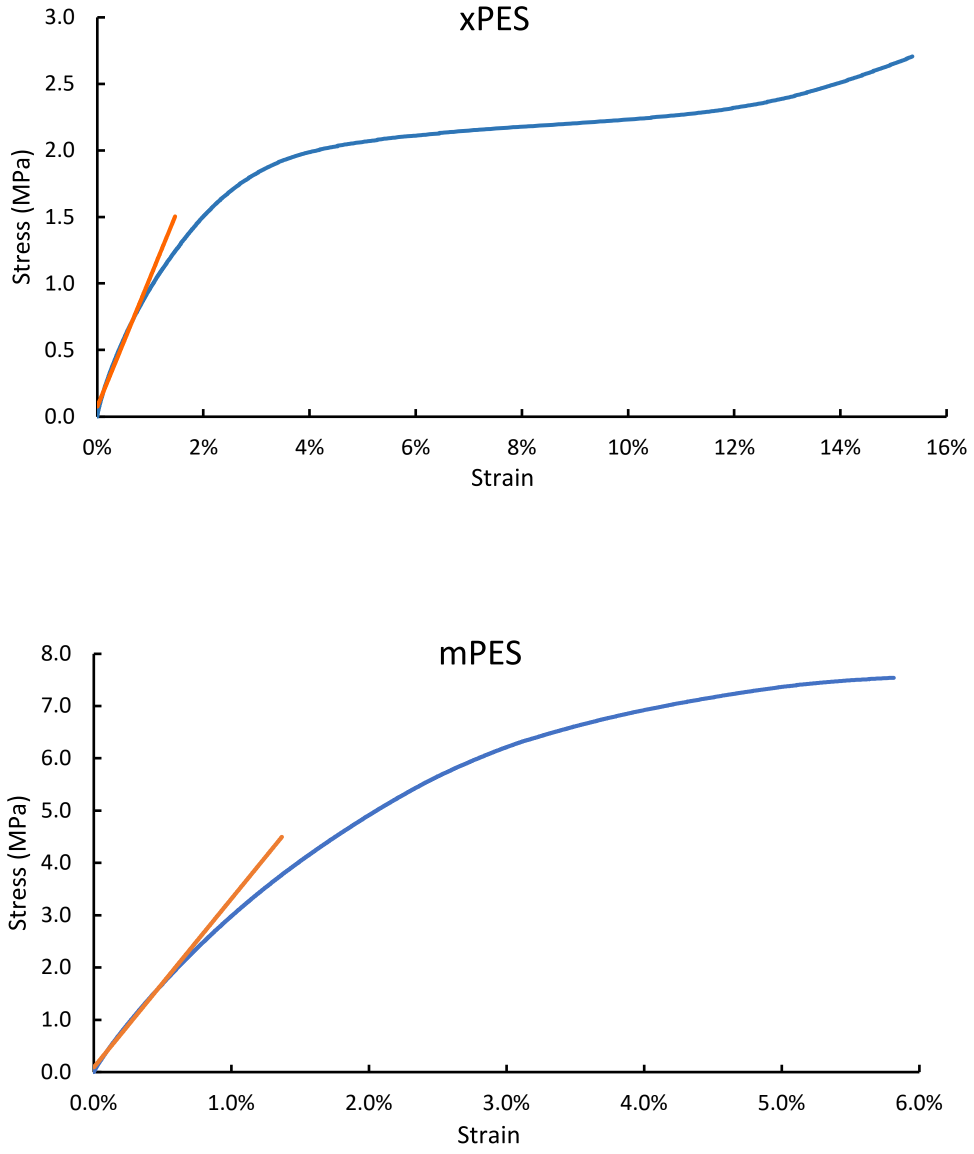


Figure S12. Example stress-strain curves used to determine flexural strength of xPES and mPES from dynamic mechanical analysis (DMA) in single cantilever mode. The orange lines represent the propagations of the linear regions of each stress-strain curve. Data in Table 2 are averages of three independent trials with errors reported as standard deviations.

Table S3. Fractionation studies data using CS_2

Material	Amount weighed (g)	amount remained (g)	% Insoluble	% Soluble
xPES	0.308	0.278	90	10
mPES	0.310	0.249	80	20

The difference in solubilities of the PES materials with CS_2 allowed the direct quantification of free sulfur and polymeric sulfur. Free sulfur is completely soluble in CS_2, and sulfur that was covalently incorporated in the highly crosslinked network is insoluble.

Table S4. Elemental analysis data for PES composites and soluble fractions

xPES Soluble			mPES Soluble		
Element	**Theory**	**Found**	**Element**	**Theory**	**Found**
C	1.00	4.57	C	1.00	1.39
H	0.50	0.45	H	0.50	0.11
S	98.00	93.19	S	98.00	97.89

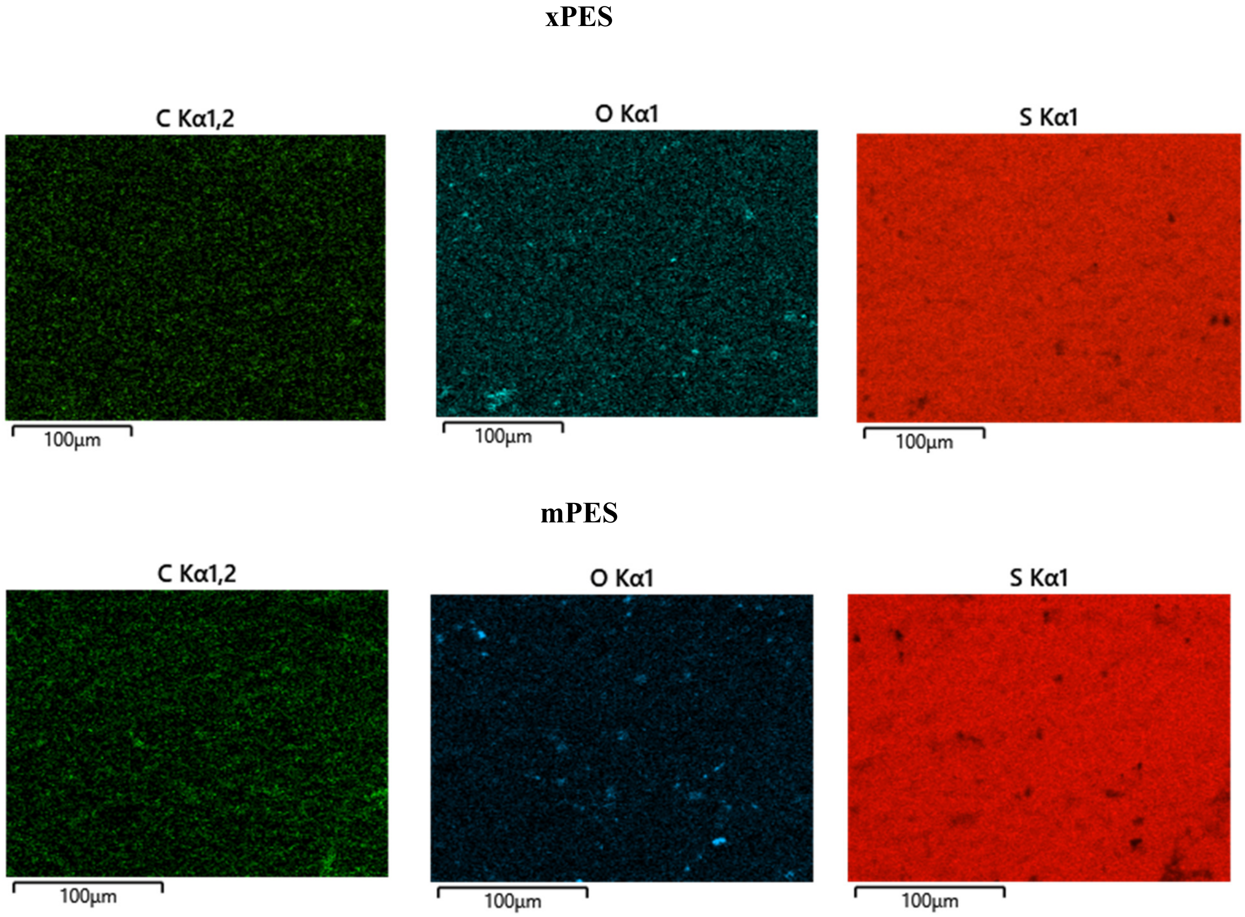


Fig S13. Surface analysis of xPES (top) and mPES (bottom) by EDX revealed a homogeneous distribution of carbon, oxygen and sulfur in the composites.

Equation S1. Sulfur rank calculation (example given for mPES)

$$Sulfur\ rank = \frac{mmol\ incorporatied\ Sulfur}{mmol\ Olefins} = \frac{220}{3.6} = 62$$

Olefin content in EPET was quantified using proton NMR spectroscopy (Fig S6). Specifically, total olefin content was found to be 3.6 mmol olefin/g of EPET from integration of the olefin resonance versus that of the internal standard. Incorporated sulfur was calculated as added sulfur less extractable sulfur (Tables S1 and S2).

Supplemental References

1. H. M. Naguib and X. H. Zhang, *Polym. Test.*, 2018, **69**, 450-455.