

Supplementary Materials

Table S1. Chemical analysis of untreated hemp fibres. All results are reported as wt%. Ash analysis was performed gravimetrically on an oven-dried sample (104°C overnight) by combustion in a muffle furnace at 525°C for one hour. Extractives contents was determined gravimetrically by Soxhlet extraction using dichloromethane (45 minutes boiling time, then 45 minutes rinsing time). Extracted samples were air dried and then placed in an oven at 55°C overnight prior to lignin and carbohydrate analysis. Acid-insoluble lignin was measured following a modified method based on the TAPPI Standard Method T 222 om-88, and acid-soluble lignin using a modified method based on TAPPI Useful Method UM 250. Carbohydrates were identified and quantified according to a modified wood sugar analysis by anion chromatography as described by Pettersen et. al. (*J. Wood Chem. Technol.* **1991**, 11, 495). The samples were digested using 72% sulphuric acid in a water bath at 30°C for one hour. They were then diluted to ca. 3 % sulphuric acid (total sample volume 87 ml) and autoclaved for one hour at 121°C at 15 psi. Once autoclaved, they were allowed to cool before being vacuum filtered onto pre-oven dried and weight GFA paper for acid insoluble (Klason) lignin quantification. The filtrate was kept at 4°C for acid-soluble lignin and carbohydrate analysis. Acid-soluble lignin was measured by taking the absorbance reading at 205 nm on a UVvis spectrophotometer. Samples filtrates were diluted twenty times prior to reading the absorbance. Carbohydrate analysis was performed by diluting the filtrate, adding an internal standard, filtering through a 0.45 µm nylon filter and running on a Dionex ICS600 instrument with a PA1 column and eluent generation at 2 mM KOH. All analyses were performed in duplicate.

Ash	Extractives	Lignin		Neutral carbohydrates as anhydrosugars				
		Acid-insoluble	Acid-soluble	Arabinosyl	Galactosyl	Glucosyl	Xylosyl	Mannosyl
1.73	0.49	4.49	0.97	0.73	2.21	70.27	2.51	4.71
1.73	0.50	4.79	0.97	0.77	2.56	67.75	2.10	4.18

Table S2. DSC heat-cool-heat programmes for starting materials, emulsions and composites.

DSC steps	Waxes and Vacuum-dried	Composites
	Emulsions	
Cooling Ramp 1 (10°C/min)	25 to -50°C	25 to -60°C
Isothermal	5 minutes at -50°C	5 minutes at -60°C
Heating Ramp 1 (10°C/min)	-50 to 110°C	-60 to 180°C
Isothermal	5 minutes at 110°C	5 minutes at 180°C
Cooling Ramp 2 (10°C/min)	110 to -50°C	180 to -60°C
Isothermal	5 minutes at -50°C	5 minutes at -60°C
Heating Ramp 2 (10°C/min)	-50 to 110°C	-60 to 180°C

Table S3. Degradation transitions, with corresponding temperature and weight loss percentage under nitrogen atmosphere for the dried emulsions. Experimental uncertainties are represented as one standard deviation (n = 3).

		First transition	Second transition	Third transition	Combined mass loss
CPW-T20	Onset (°C)	260.5 ± 4.9	369.5 ± 5.9	406.0 ± 7.3	
	End of transition (°C)	319.4 ± 3.8	400.4 ± 4.9	424.1 ± 5.2	
	Weight loss (%)	37.5 ± 2.6	35.0 ± 2.6	14.6 ± 1.7	87.1 ± 2.3
CPW-Sp	Onset (°C)	260.1 ± 8.2	363.3 ± 8.1	415.3 ± 3.2	
	End of transition (°C)	319.0 ± 5.6	391.5 ± 6.9	448.2 ± 2.7	
	Weight loss (%)	35.9 ± 2.8	29.7 ± 3.0	15.6 ± 1.2	81.2 ± 2.3
RPW-T20	Onset (°C)	265.9 ± 1.3	375.0 ± 1.9	424.7 ± 1.0	
	End of transition (°C)	316.9 ± 1.5	413.2 ± 1.3	436.3 ± 2.0	
	Weight loss (%)	26.0 ± 0.4	53.5 ± 0.6	8.4 ± 0.4	87.9 ± 0.5
RPW-Sp	Onset (°C)	272.9 ± 2.6	375.4 ± 6.4	421.8 ± 6.4	
	End of transition (°C)	323.7 ± 9.1	406.7 ± 7.6	449.7 ± 5.0	
	Weight loss (%)	22.0 ± 1.9	45.3 ± 5.9	15.6 ± 3.0	82.9 ± 3.6
BW-T20	Onset (°C)	263.6 ± 5.3	370.2 ± 5.5	412.2 ± 4.8	
	End of transition (°C)	316.3 ± 6.5	403.7 ± 5.7	438.0 ± 4.8	
	Weight loss (%)	23.1 ± 4.2	45.5 ± 2.1	25.2 ± 4.0	93.8 ± 3.4
BW-Sp	Onset (°C)	258.3 ± 3.7	362.6 ± 3.5	407.3 ± 4.5	
	End of transition (°C)	307.4 ± 4.3	395.5 ± 5.1	430.7 ± 7.7	
	Weight loss (%)	24.1 ± 3.9	43.5 ± 1.3	19.8 ± 4.3	87.4 ± 3.2

Table S4. Thermal transitions for the composite materials obtained by DSC (first heat ramp and cooling ramp). Experimental uncertainties are represented as one standard deviation (n = 3).

	1st heat ramp				Cool ramp	
	Tg (°C)	Enthalpy (J/g)	Crystallinity (%)	Max peak (°C)	Enthalpy (J/g)	Max peak (°C)
bPBS	-31.4 ± 0.7	62.6 ± 1.0	31.3 ± 0.5	116.6 ± 1.2	66.3 ± 0.8	88.0 ± 0.2
bPBS-Hf- Control	-32.4 ± 0.3	61.0 ± 1.6	33.9 ± 0.9	116.3 ± 0.7	58.2 ± 1.6	79.7 ± 0.2
bPBS-Hf- CPW-T20	-32.9 ± 0.5	58.2 ± 0.6	32.3 ± 0.4	115.5 ± 0.4	58.3 ± 0.5	79.3 ± 0.1
bPBS-Hf- CPW-Sp	-31.8 ± 0.2	56.8 ± 0.2	31.5 ± 0.1	116.2 ± 0.4	58.1 ± 0.7	79.3 ± 0.1
bPBS-Hf- RPW-T20	-32.7 ± 0.1	59.4 ± 1.2	33.0 ± 0.7	116.9 ± 1.5	58.4 ± 1.1	79.5 ± 0.1
bPBS-Hf- RPW-Sp	-32.4 ± 0.9	60.0 ± 1.1	33.4 ± 0.6	116.2 ± 1.3	59.5 ± 0.2	79.1 ± 0.1
bPBS-Hf- BW-T20	-32.1 ± 0.6	59.9 ± 0.9	33.3 ± 0.5	116.6 ± 1.1	59.1 ± 0.5	79.9 ± 0.1
bPBS-Hf- BW-Sp	-32.6 ± 0.4	59.5 ± 1.1	33.1 ± 0.6	115.7 ± 0.9	58.6 ± 0.4	80.2 ± 0.1

Table S5. Comparison of outcomes of the current study with earlier reports on similar materials systems (polymer composites reinforced with coated hemp fibres). PBS: Poly(butylene succinate); PHB: Poly(hydroxy butyrate); PLA: Poly(lactic acid); LDPE: Low density polyethylene; PBSA: Poly(butylene succinate-co-adipate).

Filler type	Coating material	Coating loading	Polymer matrix type	Filler fraction in composite	Composite property	Relative effect of fibre addition	Relative effect of fibre coating	Reference
Hemp fibre	Crude and refined pine waxes, beeswax	2 wt% - 3 wt%	PBS	10 wt%	Tensile strength	-15 %	< 1 %	This work
					Young's modulus	+71 %	-3 % to +2 %	
					Strain at break	-95 %	-3 % to +5 %	
					Flexural strength	+31 %	-3 % to -1 %	
					Flexural modulus	+74 %	-5 % to +2 %	
					Impact resistance	-36 %	0 % to +5 %	
					Absorbed energy	-35 %	-1 % to +3 %	
Hemp fibre	PHB, PLA	Not determined	Epoxy resin	9 wt%	Tensile strength	Not recorded	+18 % to +29 %	<i>J. Comp. Mater.</i> 2022 , 56, 929
					Tensile modulus	Not recorded	+9 % to +17 %	
					Impact strength	Not recorded	+40 % to +48 %	
Hemp fibre	Wood distillate	Approx. 10 wt%	Epoxy resin	Approx. 30 wt%	Tensile strength	-6 % to -35%	Not recorded	<i>Ind. Crops. Prod.</i> 2018 , 111, 422
					Tensile modulus	+53 % to +76 %	Not recorded	
					Flexural strength	-52 % to -63%	Not recorded	
					Flexural modulus	-18 % to 0%	Not recorded	
					Tensile strength	Not recorded	-12 % to -9%	
Hemp fibre	(3-glycidylloxypropyl) trimethoxysilane	Not determined	Epoxy resin	40.8 – 42.9 wt%	Tensile modulus	Not recorded	+4 % to +10 %	<i>Comp. Part B</i> 2018 , 133, 210
					Flexural strength	Not recorded	-4 % to +5 %	
					Flexural modulus	Not recorded	0 % to +5 %	
					Stress at break	+20 % to +40%	Up to -40 %	
Hemp fibre	Paraffin wax	10 wt%, 15 wt%	LDPE	15 wt%, 20 wt%, 25 wt%	Young's modulus	+100 % to +230 %	Ca. +100 %	<i>Mater. Today Proc.</i> 2023 , in press
					Elongation at break	Up to -80 %	Up to -70 %	
					Young's modulus	-11 % to +4 wt%	-17.2 % to +2.5 %	
Rice and wheat bran	Beeswax	4 wt%, 8 wt%	PLA/PBSA blend	5 wt%, 10 wt%	Stress at break	-20 % to +5 %	-5.4 % to +6.4 %	<i>Polymers</i> 2022 , 14, 3389
					Elongation at break	-98 % to -94 %	-20.9 % to +8.3 %	
					Impact Strength	-59 % to -46 %	-5.0 % to +12.0 %	

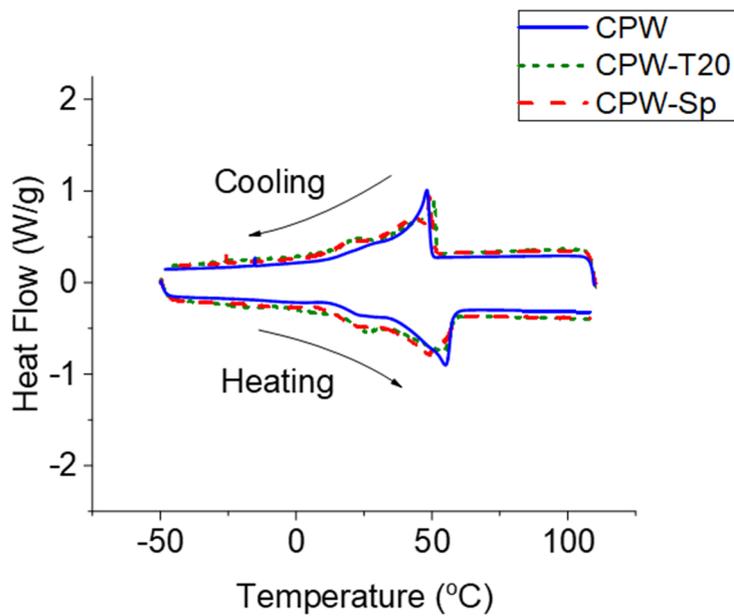


Figure S1. DSC thermograms of CPW and its emulsions with T20 and Sp (cooling run and second heating run; exo up).

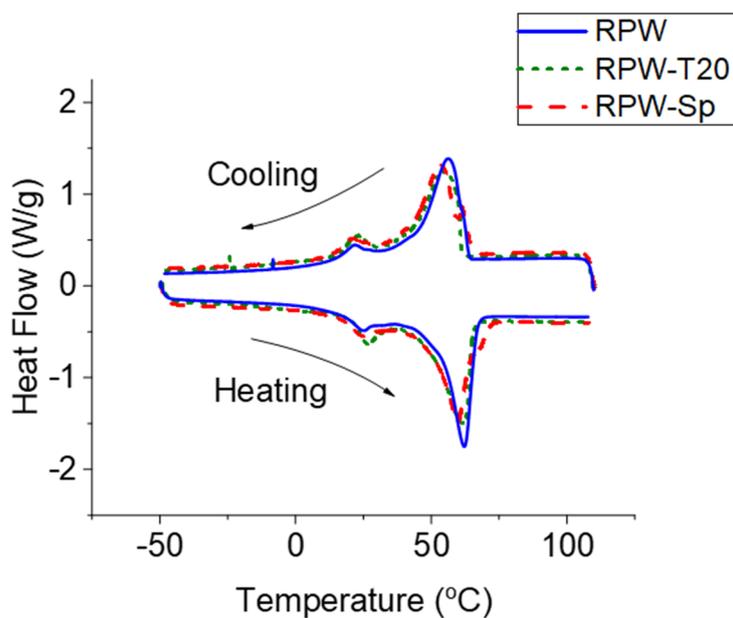


Figure S2. DSC thermograms of RPW and its emulsions with T20 and Sp (plotted on same scale as Fig. S1 for direct comparison with CPW) (cooling run and second heating run; exo up).

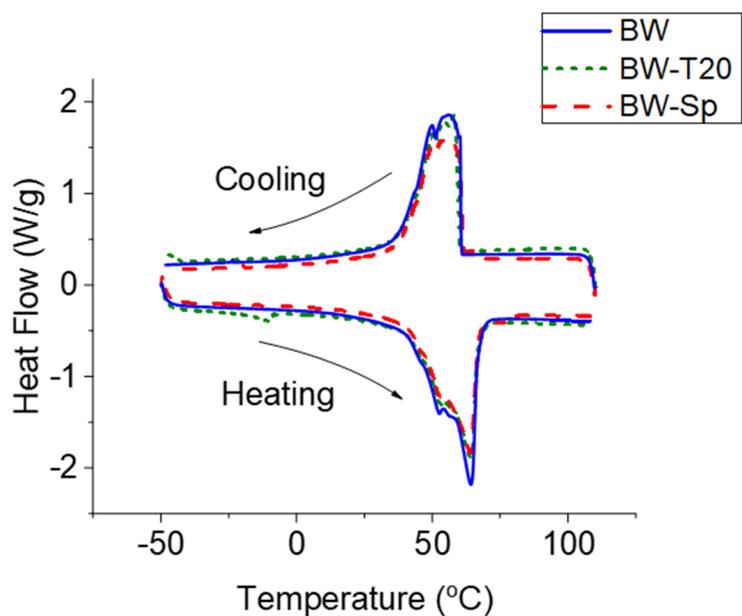


Figure S3. DSC thermograms of BW and its emulsions with T20 and Sp (plotted on same scale as Fig. S1 for direct comparison with CPW) (cooling run and second heating run; exo up).

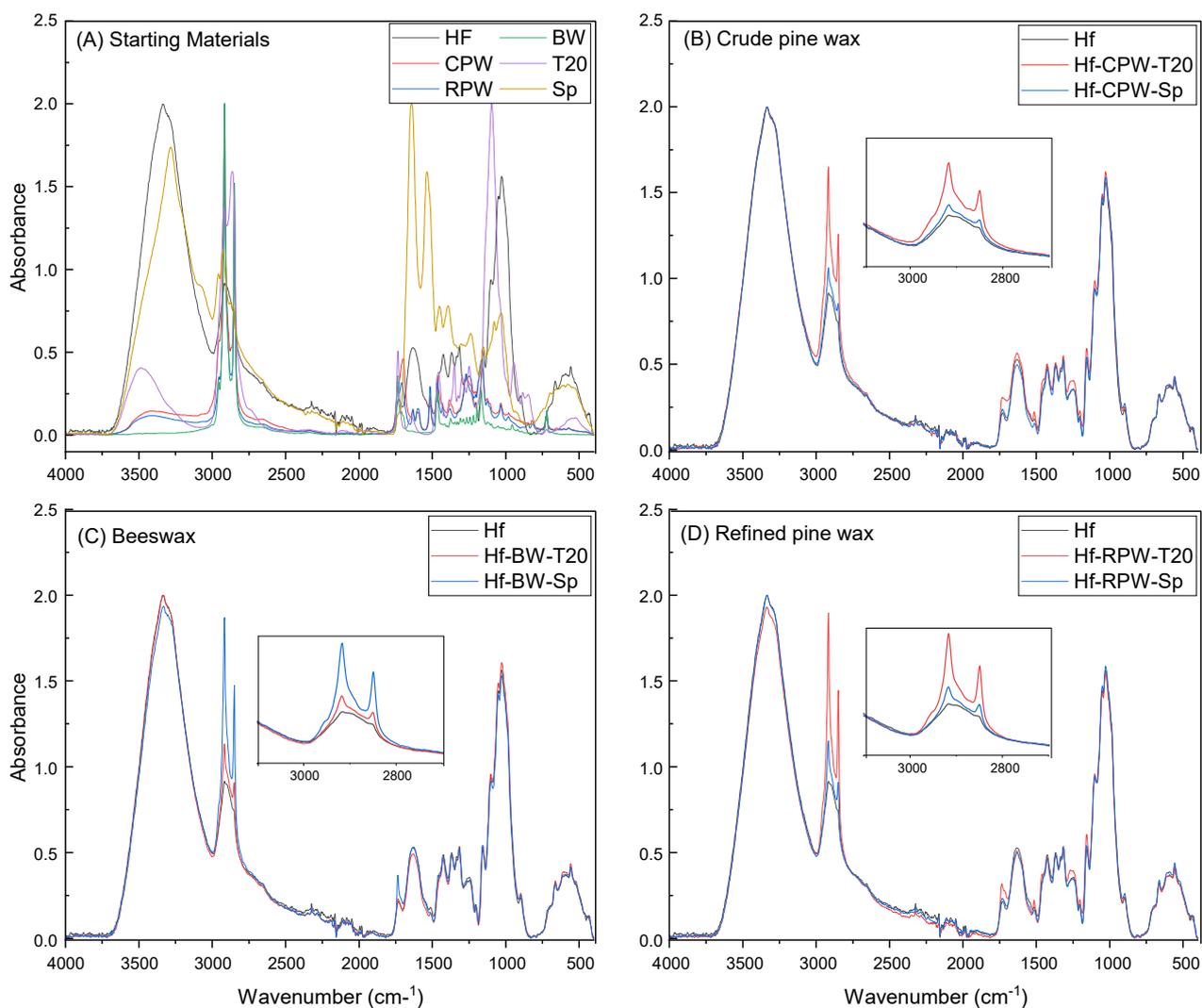


Figure S4. FTIR spectra of (A) starting materials, (B) CPW formulations, (C) BW formulations, and (D) RPW formulations. Insets highlight the spectral region of the CH stretching vibrations.

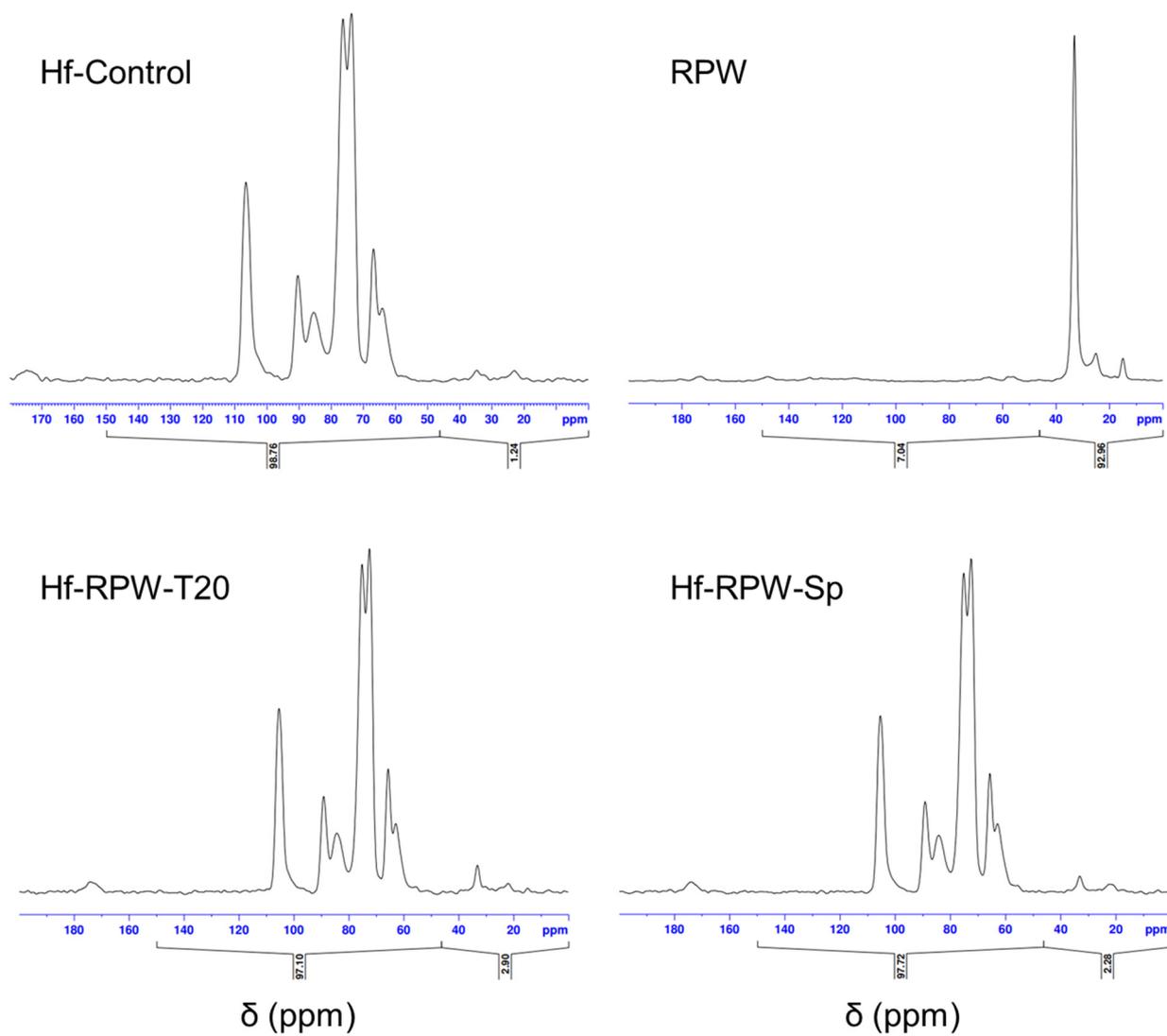


Figure S5. Exemplar ^{13}C CP/MAS NMR spectra of untreated Hf, RPW, and Hf coated with either RPW-T20 or RPW-Sp emulsions.

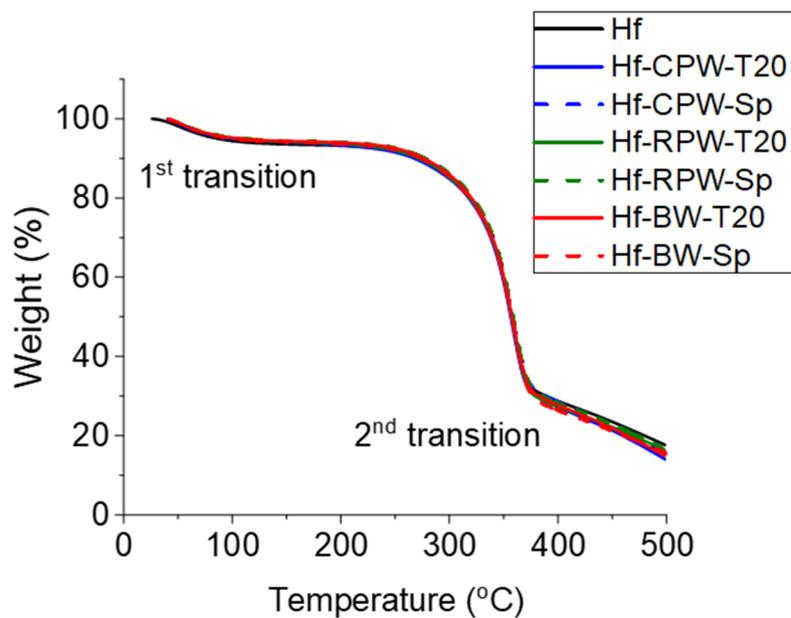


Figure S6. Thermal degradation behaviour (determined by TGA) of Hf fibres coated with different wax formulations, and uncoated control.

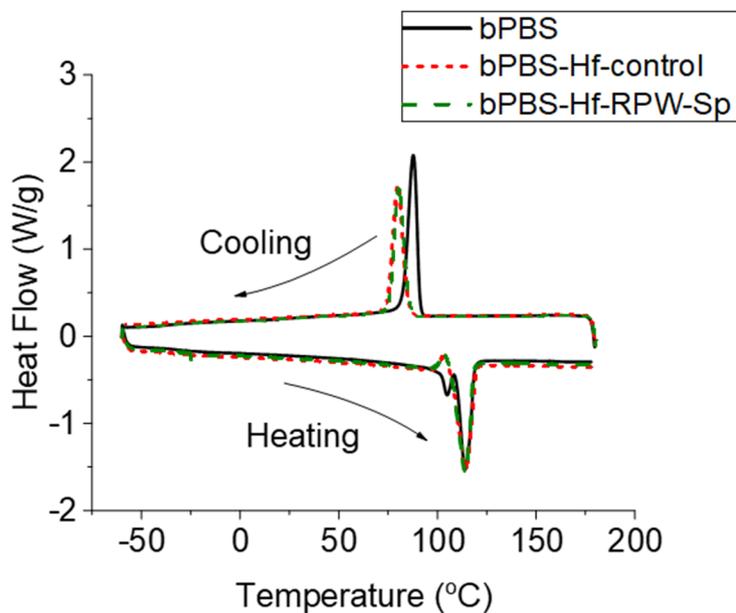


Figure S7. DSC thermograms of bPBS and its composites with untreated Hf and Hf coated with RPW-Sp emulsion (cooling run and second heating run; exo up).

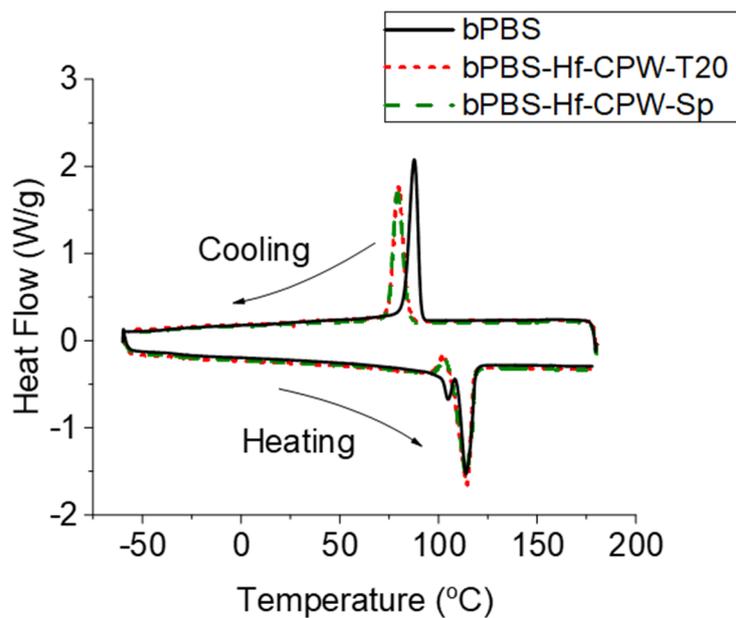


Figure S8. DSC thermograms of bPBS and its composites with untreated Hf and Hf coated with CPW-T20 and CPW-Sp emulsions (cooling run and second heating run; exo up).

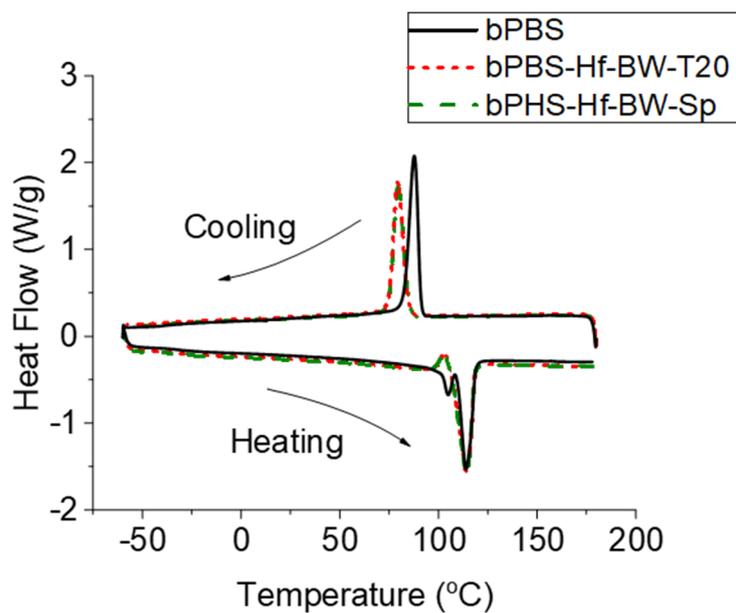


Figure S9. DSC thermograms of bPBS and its composites with untreated Hf and Hf coated with BW-T20 and CPW-Sp emulsions (cooling run and second heating run; exo up).

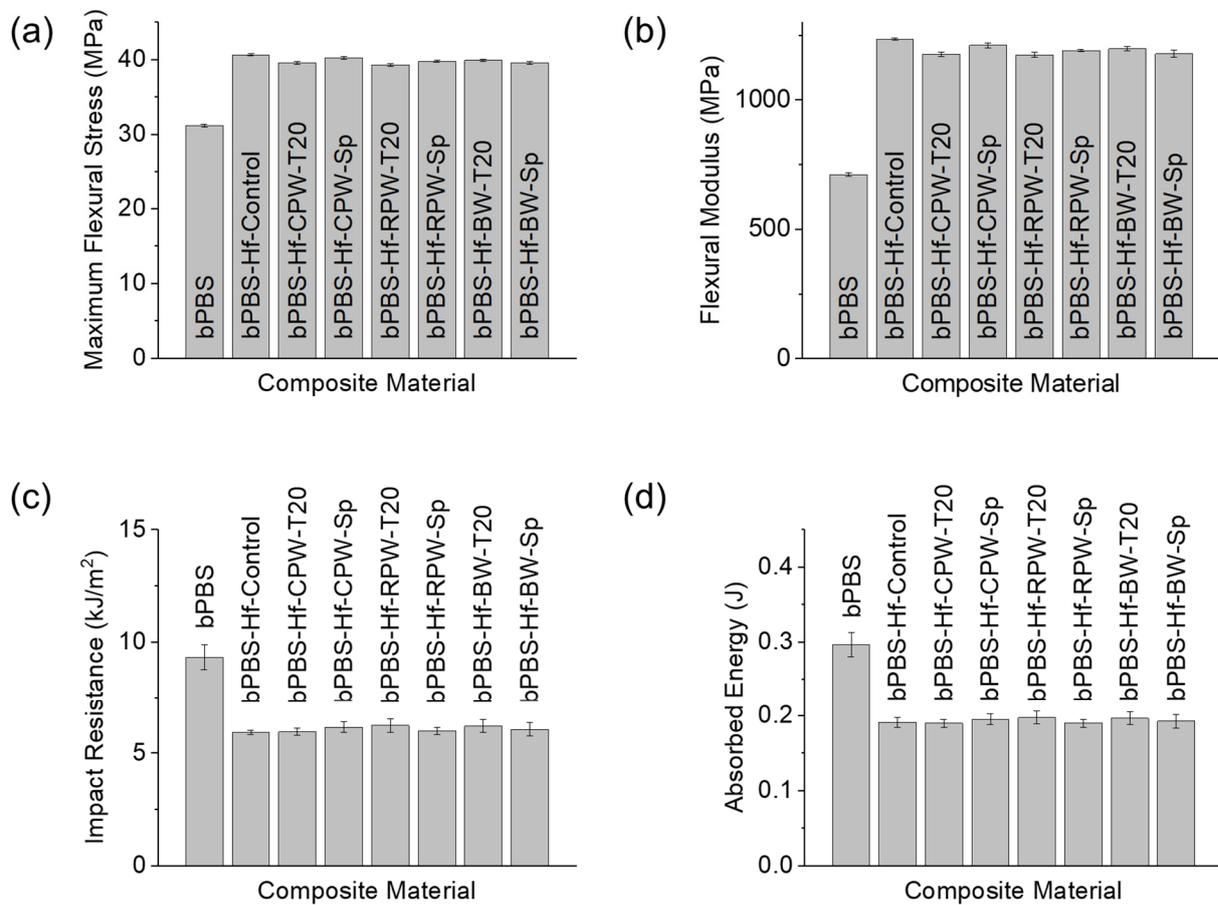


Figure S10. Mechanical performance comparison of bPBS and its composites with coated and uncoated Hf (flexural and impact testing). **(a)** Maximum flexural stress, **(b)** Flexural modulus, **(c)** Impact resistance, **(d)** Absorbed energy during impact testing. Error bars represent the standard deviation.