

## Supplementary Information

### **Title: Tunable Enhancement of Polyester Biocomposites Via Extrusion with Fungi-derived Chitin**

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## Materials and Methods

### Materials

All compounds, unless otherwise indicated, were purchased from commercial sources and used as received. The PCL pellets had an average  $M_n$  of 80,000 g/mol according to the supplier (MilliporeSigma, product no. 440744). The commercial Chitin from shrimp shells was purchased from Sigma-Aldrich as a white-to-beige powder (MilliporeSigma, product no. C717). White mushrooms (*Agaricus bisporus*) were purchased from a local shop in Bilbao, Spain. Sodium hydroxide (NaOH,  $\geq 97\%$ ) was purchased from Honeywell Fluka™.

### Methods

*Colloidal ChNFs were isolated* from commercially available *Agaricus bisporus* using a top-down procedure<sup>[1,2]</sup>. 400 g of frozen mushrooms were thawed in 800 mL of distilled water for 30 minutes to remove impurities. The mushrooms were then blended for five minutes at 13,000 rpm using a Stabmixer KOENIG kitchen blender, after which the mixture was heated at 85 °C for 0.5 h under magnetic stirring. After washing by centrifugation at 4,000 rpm for 15 minutes, the material was treated with 1 M NaOH at 65 °C for 3 h. The mixture was then washed by centrifugation and mechanically blended again for 5 minutes. The resulting material was then purified by dialysis using regenerated cellulose dialysis tubing with a molecular weight cut-off (MWCO) of 12–14 kDa (Medicell Membranes Ltd.) for 7 days.

*Room temperature powder X-ray diffraction (XRD)* patterns were obtained with a D8 Discover diffractometer in reflection mode and a Cu K $\alpha$  radiation (45 kV, 40 mA).

*Static water contact angle (WCA)* measurements on the surfaces of the nanocomposites were determined by the sessile drop method using a volume of 10  $\mu$ L. The mean and standard deviation values presented correspond to five measurements.

*Ultraviolet–visible (UV–Vis)* spectroscopy measurements were performed with a Shimadzu UV-1280 spectrophotometer. Total transmittance experiments were conducted in the wavelength range of 190–1100 nm with a sampling interval of 1 nm and 25 accumulations. The opacity of the films is quantified as:

$$\text{Opacity} = \frac{A_{600}}{x \text{ (mm)}} \quad (1)$$

\*where  $A_{600}$  is the absorbance at  $\lambda$  600 nm, and  $x$  is the film thickness [mm]. The results correspond to five measurements.

*The color parameters* of the films were determined using a laboratory colorimeter 8/d (4/8 mm 4 mm, Vetus). The color coordinates  $L^*$  (lightness),  $a^*$  (redness-greenness), and  $b^*$  (yellowness-blueness) were obtained from the reflection spectra of the films. The total color difference ( $\Delta E$ ) was quantified according to<sup>[3]</sup>:

$$\Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \quad (2)$$

\*where  $\Delta L^* = (L^* - L^*_0)$ ;  $\Delta a^* = (a^* - a^*_0)$ ;  $\Delta b^* = (b^* - b^*_0)$ ; and  $L^*_0$ ,  $a^*_0$  and  $b^*_0$  represent the color coordinates of the controls. CIE- $L^*a^*b^*$  coordinates, lightness ( $L^*$ ), hue ( $h^*_{ab}$ ) and chroma ( $C^*_{ab}$ ) were obtained from the reflection spectra [4]. The results correspond to five measurements.

*Fourier transform infrared spectroscopy (FTIR)* was performed using an Agilent Technologies Cary 630 FTIR spectrometer. 64 Scans from 600 to 4000  $\text{cm}^{-1}$  were taken at a resolution of 1  $\text{cm}^{-1}$ . The degree of N-acetylation (DA%) was determined using equation #X for both neat SC and ChNFs by taking the ratio of the Amide I stretch at 1655  $\text{cm}^{-1}$  to the OH stretch at 3450  $\text{cm}^{-1}$ . That ratio was over 1.33 which represents the ratio of this absorbance for a fully acetylated compound.

$$DA\% = \left( \frac{A_{1655}/A_{3450}}{1.33} \right) \times 100 \quad (3)$$

*Hot Pressing* was performed using a Carver Model C laboratory press set to 100°C and the heating plates were set to touch at a force of ~0 lbs to facilitate even melting. After 5 minutes the samples were degassed by rapidly releasing and applying pressure 5-7 times to remove trapped air to ensure a homogenous sample film free of air bubble voids. Then it was pressed at a constant pressure of 2000 lbs for 15 minutes. The temperature was then set to room temperature, and the sample was air cooled under pressure to ensure uniform crystallization kinetics.

*Differential scanning calorimetry (DSC)* thermograms were collected on a Q2000 DSC (TA instruments) equipped with an auto-sampler. Thermograms were obtained in 40  $\mu\text{L}$  aluminum pans from -15 to 90 °C at a heating rate of 5 °C  $\text{min}^{-1}$  for two heating and 1 cooling cycles. Prior to these cycles the sample was heated to the melt and held isothermally for 5 minutes and then quench cooled at 100 °C  $\text{min}^{-1}$  to quench the sample. The crystallization temperature ( $T_c$ ) was determined from the peak in the first cooling cycle, and the melting temperature ( $T_m$ ) was determined from the peak of the second heating cycle. The percentage crystallinity was calculated by integrating the second melting curve and using equation #3:

$$\%X_c = 100 \frac{\Delta H_f}{\Delta H_f^\circ} \quad (4)$$

*Thermal gravimetric analysis (TGA)* thermograms were performed using a Discovery TGA 550 Thermogravimetric analyzer (TA instruments). Thermograms were recorded under an  $\text{N}_2$  atmosphere at a heating rate of 20 °C  $\text{min}^{-1}$  from 25–600 °C for 5-7 mg of sample. To ensure uniformity, sample pucks were punched out from the hot-pressed thin film using a hollow metal punch (diameter = 3 mm) Decomposition temperatures were reported at the 5% weight-loss-temperature ( $T_{d, 5\%}$ ).

*Uniaxial tensile testing* was performed using an Instron 68TM-30 universal mechanical testing instrument fitted with a load cell of 5 kN. Thin films were obtained by hot pressing samples using a Specac® Atlas 15T manual hydraulic press equipped with heated platens (*see hot pressing description for details*). Dog bones were cut from thin films using a Custom ASTM D-638 Type 5 die. Each specimen was clamped into the tensile grips and subjected to an elongation rate of 25  $\text{mm} \cdot \text{min}^{-1}$  until failure. All tensile tests were repeated on  $n \geq 9$  individual specimens (unless otherwise indicated), and an average of the data was taken to find the ultimate tensile stress, strain, and Young's modulus.

*Dynamic mechanical analysis (DMA)* temperature-sweep data were obtained using a TA® instruments DMA 850. Film samples were cut into rectangular samples (length × width × thickness =  $9.5 \pm 1.0$  mm × 6 mm × 0.5 mm), cooled to  $-80$  °C, and held isothermally for *ca.* 5 min. Storage and loss moduli, as well as the loss factor (ratio of  $E''$  and  $E'$ ,  $\tan \delta$ ) were probed as the temperature was ramped from  $-80$  to  $100$  °C and stopped before the sample flowed. Experiments were performed at  $3$  °C·min<sup>-1</sup> ramp rate, 0.1% strain, 1 Hz frequency, and initial static load of 0.01 N.

*Scanning Electron Microscopy (SEM)* data was obtained using an IT-500HR SEM (JEOL, Japan) in Secondary Electron Detector (SED) mode, with an accelerating voltage of 5 kV. The bio-composite images were obtained for the sample with the conditions of 12.5wt%-25rpm-45sec. which were dried overnight in a desiccator, then cryo-fractured. The cryo-fracturing process began by scoring a thin line into the cross sectional of the sample and submerging it in liquid nitrogen for 10 minutes. This ensured the composite was below its  $T_g$  which permitted a clean fracture. The resulting cross-section samples were attached to an adhesive carbon tape on a  $45^\circ / 90^\circ$  SEM Mount, and the surface sample was placed on a pin mount. The neat chitin samples were dispersed in a solution of ethanol and then flash evaporated onto a glass slide. The samples were scraped off onto carbon tape on a flat mount and placed on a pin mount. All samples were sputter-coated with a Pt–Pd layer of 5 nm thickness prior to SEM analysis.

*Gel permeation Chromatography (GPC)* analyses were performed in THF on an Agilent 1260 Infinity II Multi-Detector GPC/SEC System fitted with RI, ultraviolet (UV,  $\lambda = 309$  nm), and viscometer detectors. The polymers were eluted through an Agilent guard column (PLGel 5  $\mu$ M,  $50 \times 7.5$  mm) and two Agilent mixed-C columns (PLGel 5  $\mu$ M,  $300 \times 7.5$  mm) using THF (buffered with 200ppm BHT) as the mobile phase (flow rate =  $1$  mL·min<sup>-1</sup>,  $40$  °C). Number average molecular weight ( $M_n$ ), weight average molecular weight ( $M_w$ ) and dispersity ( $\text{DM} = M_w/M_n$ ) were determined using Agilent GPC/SEC software (vA.02.01) against a 12-point calibration curve ( $M_p = 162 - 6085000$  g·mol<sup>-1</sup>) based on polystyrene standards (Easivial PS-M/H, Agilent).

*Degradation Studies* were performed for a neat PCL sample along with one composite for both SC and ChNFs filler at 5%, 12.5%, and 20%. Each sample puck was 10mm in diameter, punched from the 0.5 mm thick hot-pressed film. The measurements were taken at time points of 1 day, 3 days, 7 days, and every 7 days thereafter for a total of 9 weeks. These studies were done in 3 different solutions (1M HCl, 1M NaOH, and PBS buffer). The samples were placed in 6-dram vials with 20 mL of solution and incubated at  $37$  °C. For obtaining the sample weight at each time point, the pucks were blotted dry prior to weighing with a Kimwipe, and the degradation solution was refreshed between time points.”

*Swelling Studies* were performed to track the initial swelling rate using time points of 0.5, 1, 1.5, 2, 4, 8, 12, 16, 20, and 24 hours. The sample weighing process is the same as described in the “*Degradation studies*” section.

## **Extrusion procedure**

*Twin screw extrusion* experiments were performed using a HAAKE™ MiniLab 3 Micro Compounder with the materials and conditions specified for the DoE and comparison trials. The temperature was held constant at 100 °C for all trials with a 5-min equilibration time after closing the barrel with the instrument specified torquing pattern to ensure the barrel and screws were all at the specified temperature. The PCL pellets and chitin powder were added to the extruder over a 1-min time frame. The piston was then activated to pressurize and push the materials into the screws for mixing. When the piston was fully down, indicating the loading area was cleared of material, a 180-second “pre-mix” period was used to allow for initial loading of the screws and barrel with material. The mixing time was then added in addition to the pre-mix time as it does contribute to the mixing/shear history of the composites. Once the trial was complete, the bypass was switched from circulate to extrude. The extrudate passed through a ribbon die and was collected. The extruder was also opened to collect material that did not extrude. On average, the recovery of material reached ~80% when combining the extruded fraction and unextruded material in the barrel.

## **Design of Experiment (DoE)**

A *three-factor Box Behnken design (BBD)* was employed to evaluate the systematic tunability of three parameters: mixing time, screw speed, and chitin concentration. Each parameter was treated as continuous. This design consisted of 12 edge points and 5 replicated center points, for a total of 17 experimental runs. The 5 central points were important for providing an unbiased estimate of error and for detecting curvature in the response surface. All experiments were randomized to minimize systematic bias. For the analysis, a quadratic response surface model was fitted to the experimental data. The response surface model can be evaluated for each parameter ( $T_{d5\%}$ ,  $T_m$ ,  $T_c$ , Young's modulus, yield strength, ultimate tensile strength, elongation at break, and storage modulus. For this, the Young's modulus was used as a representative example, as the tunability of stiffness was a key takeaway of the work.

**Table S1.** The summary table of fitted coefficients for the quadratic response surface model shows that all three linear factors significantly influence the response.

**Fitted Coefficients**

	Value	Standard Error	95% LCL	95% UCL	t-Value	Prob> t	VIF
Intercept	132.43	3.60367	124.40052	140.45948	36.74862	<0.0001	
Screw speed	-15.00125	3.82227	-23.5178	-6.4847	-3.92469	0.00284	1
Mixing time	-9.53	3.82227	-18.04655	-1.01345	-2.49328	0.03181	1
Chitin_Conc	24.7575	3.82227	16.24095	33.27405	6.47717	<0.0001	1
Mixing time*mixing time	9.325	5.25321	-2.37988	21.02988	1.7751	0.10627	1
Screw speed*mixing time	10.735	5.40551	-1.30923	22.77923	1.98594	0.07513	1
Mixing time*Chitin_Conc	-11.2775	5.40551	-23.32173	0.76673	-2.0863	0.06352	1

Chitin concentration (chitin conc.) exhibited the strongest positive effect ( $\beta = +24.76$ ,  $p < 0.0001$ ), while both screw speed ( $\beta = -15.00$ ,  $p = 0.0028$ ) and mixing time ( $\beta = -9.53$ ,  $p = 0.0318$ ) produced significant negative effects. These results show that increasing chitin concentration increases the response, whereas increasing screw speed or mixing time decreases it. Quadratic curvature in mixing time was positive but not statistically significant ( $\beta = 9.33$ ,  $p = 0.106$ ), suggesting only weak curvature in the design space. Two interaction terms approached significance: screw speed  $\times$  mixing time ( $\beta = 10.74$ ,  $p = 0.075$ ) and mixing time  $\times$  chitin conc. ( $\beta = -11.28$ ,  $p = 0.064$ ), suggesting mild coupling between factors, though not at the 95% confidence level.

**Table S2.** An analysis of variance revealed that all three linear factors significantly influenced the response.

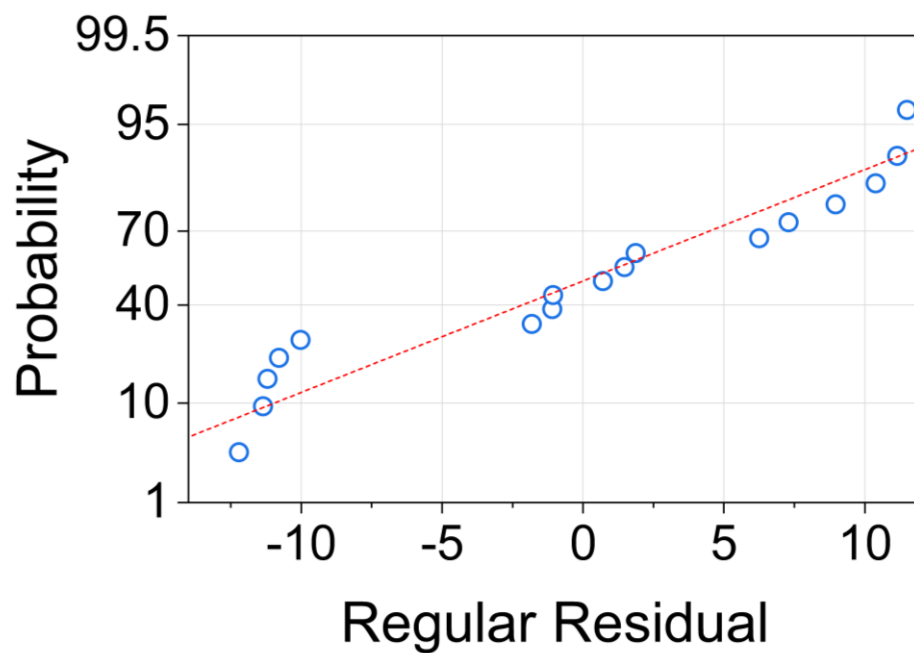
<b>ANOVA</b>					
	<b>DF</b>	<b>Sum of Squares</b>	<b>Mean Square</b>	<b>F Value</b>	<b>Prob&gt;F</b>
Screw speed	1	1800.30001	1800.30001	15.40322	0.00284
Mixing time	1	726.5672	726.5672	6.21645	0.03181
Chitin_Conc	1	4903.47045	4903.47045	41.9537	<0.0001
Mixing time* mixing time	1	368.28265	368.28265	3.151	0.10627
Screw speed* mixing time	1	460.9609	460.9609	3.94394	0.07513
Mixing time* Chitin_Conc	1	508.72803	508.72803	4.35264	0.06352
Error	10	1168.78131	116.87813		
Lack of fit	6	924.07548	154.01258	2.51751	0.19535
Pure Error	4	244.70583	61.17646		
Total	16	9937.09055			

Chitin concentration was the most influential ( $F = 41.95$ ,  $p < 0.0001$ ), contributing the largest share to the model's variance. Screw speed ( $F = 15.40$ ,  $p = 0.00284$ ) and mixing time ( $F = 6.22$ ,  $p = 0.0318$ ) were also significant, showing notable negative linear effects. Quadratic effects of mixing time (mixing time<sup>2</sup>) were not significant ( $F = 3.15$ ,  $p = 0.106$ ), indicating weak evidence of curvature in this range. Two interaction terms were nearly significant: screw speed  $\times$  mixing time ( $F = 3.94$ ,  $p = 0.075$ ) and mixing time  $\times$  chitin concentration ( $F = 4.35$ ,  $p = 0.064$ ), suggesting mild but statistically insignificant factor coupling. The lack-of-fit test was not significant ( $F = 2.52$ ,  $p = 0.195$ ), confirming that the quadratic model fits the data well without needing higher-order terms. Low, consistent error across five replicated center points supports the data's reliability. Overall, the ANOVA indicates the response is mainly driven by strong linear effects, with some interaction effects and minimal curvature.

**Table S3.** Assessment of model fit

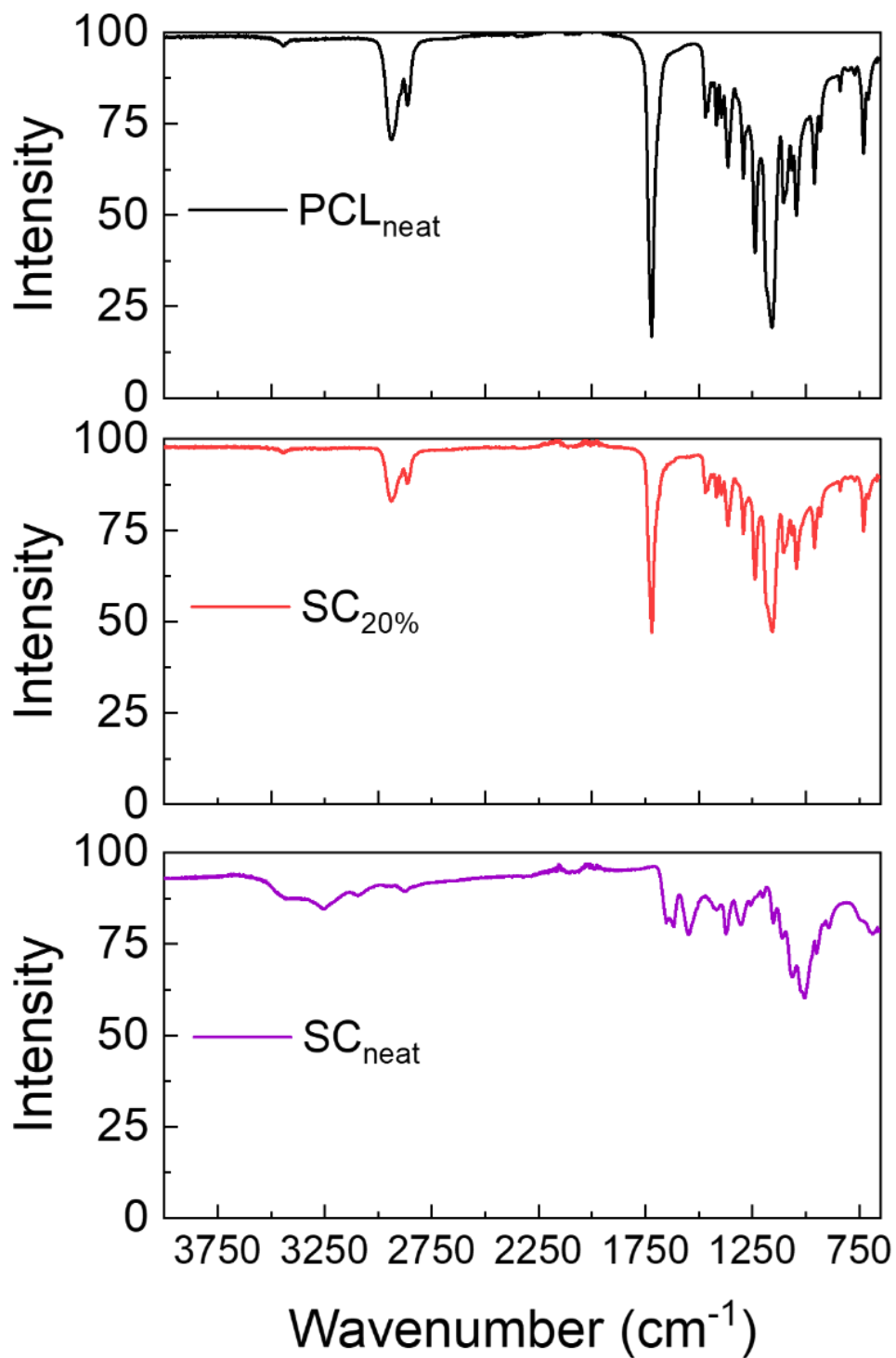
<b>Statistics</b>	
	<b>Modulus</b>
Degrees of Freedom	10
Root-MSE (SD)	10.81102
R-Square	0.88238
Adj. R-Square	0.81181
PRESS	4694.49971
Residual Sum of Squares	1168.78131
Pred. R-Square	0.52758

The quadratic model fit resulted in an  $R^2$  of 0.882, meaning about 88% of the variability in the modulus was explained by the model. The adjusted  $R^2$  (0.812) was also high, indicating that the included terms were suitable considering the model's complexity. The predicted  $R^2$  (0.528) was lower, implying less predictive accuracy for new data, likely due to borderline-significant interaction and quadratic terms. Residuals were small (RSS = 1168.78), with a root-MSE of 10.81, showing good experimental precision. Overall, the model offers a dependable description of the system, with moderate predictive ability.

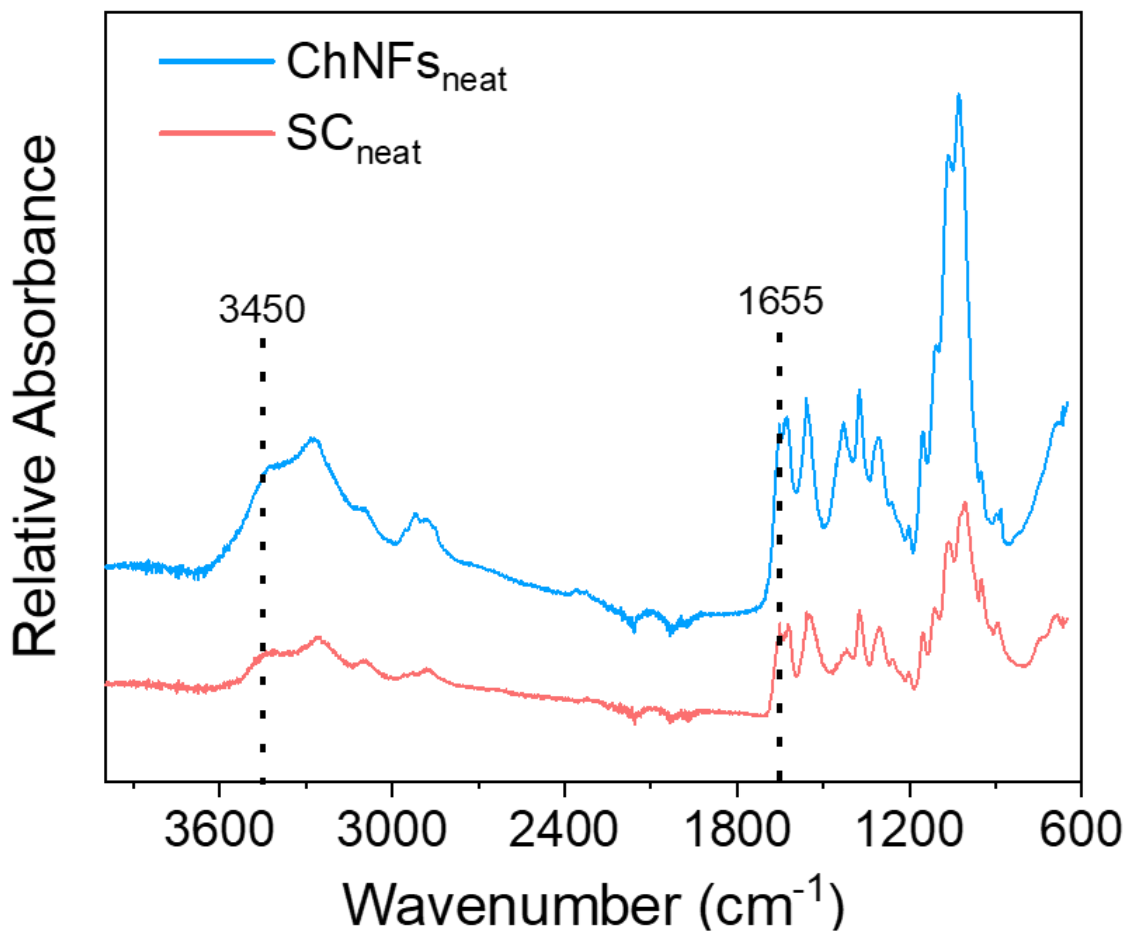


**Figure S1.** The predicted-versus-actual plot shows strong agreement between model predictions and experimental measurements. This can be seen with the points clustering closely around the 45° line, indicating that the fitted model accurately reflects the observed response and exhibits minimal systematic bias.

## FTIR Spectra



**Figure S2.** ATR-FTIR spectra of neat PCL, 20 wt% SC composite, and neat SC to test if it is a viable method to determine incorporation into the matrix.

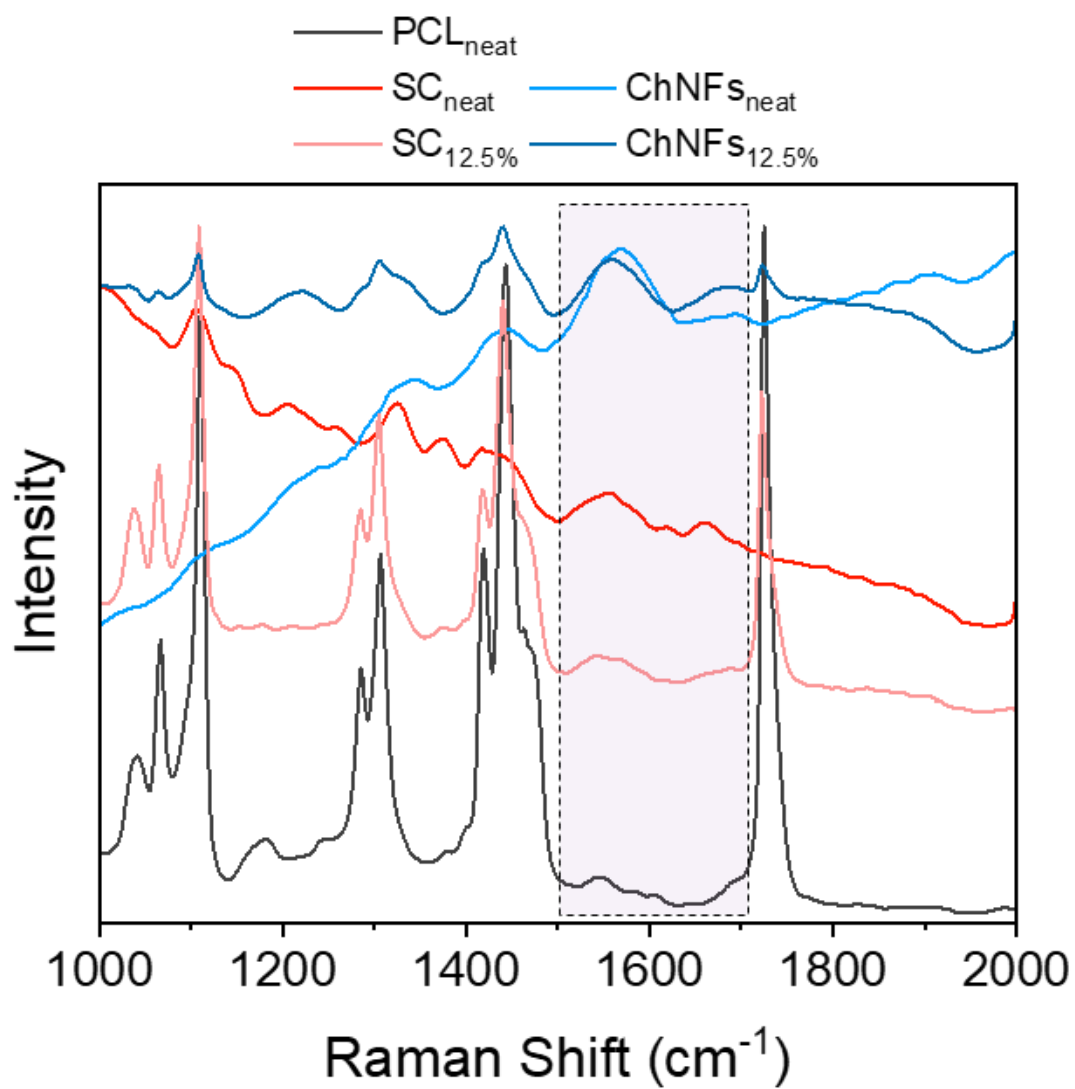


$$DA\% = \left( \frac{A_{1655}}{A_{3450}} \right) \times 100 \quad (3)$$

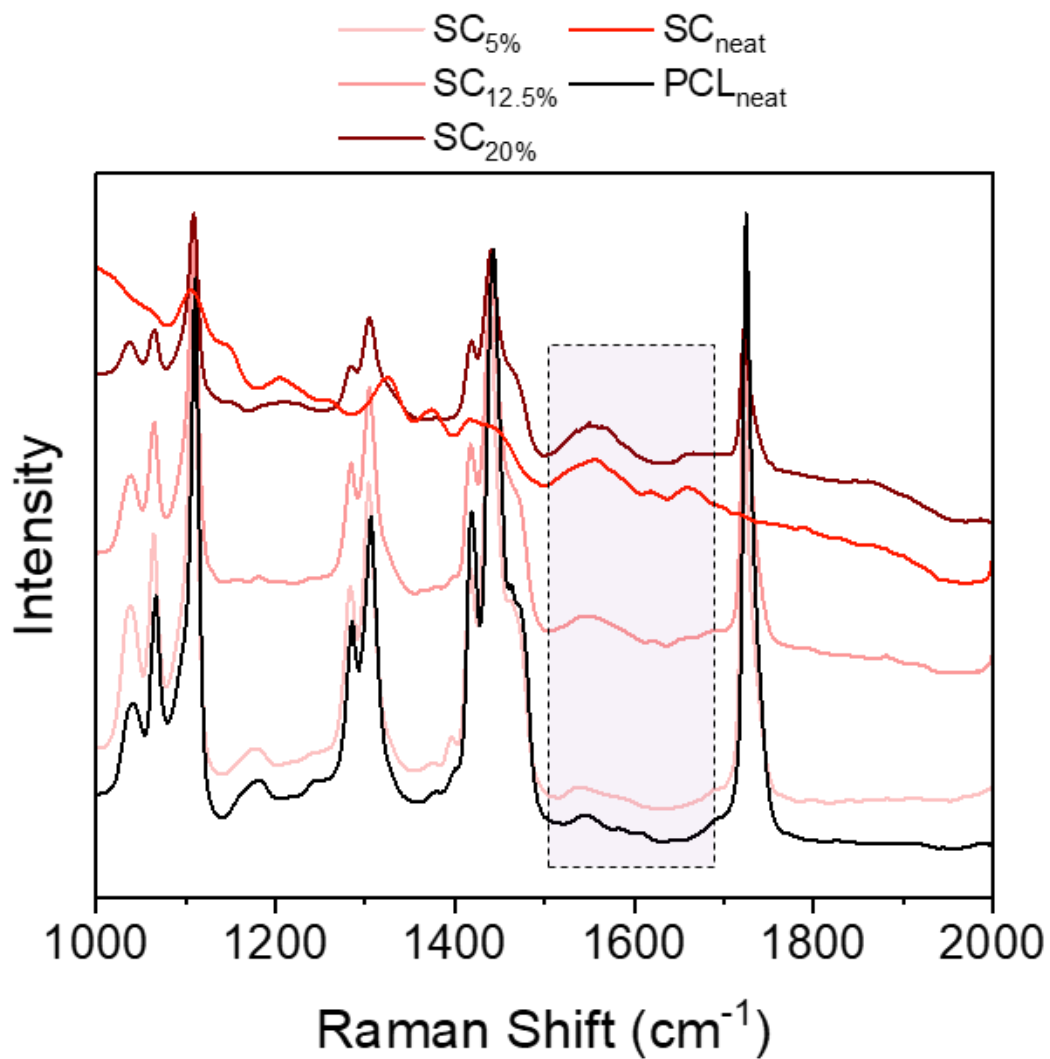
SC = 94.49% DA  
ChNFs = 93.50% DA

**Figure S3.** ATR-FTIR spectra of neat SC and neat ChNFs to calculate the degree of N-acetylation using equation 3.

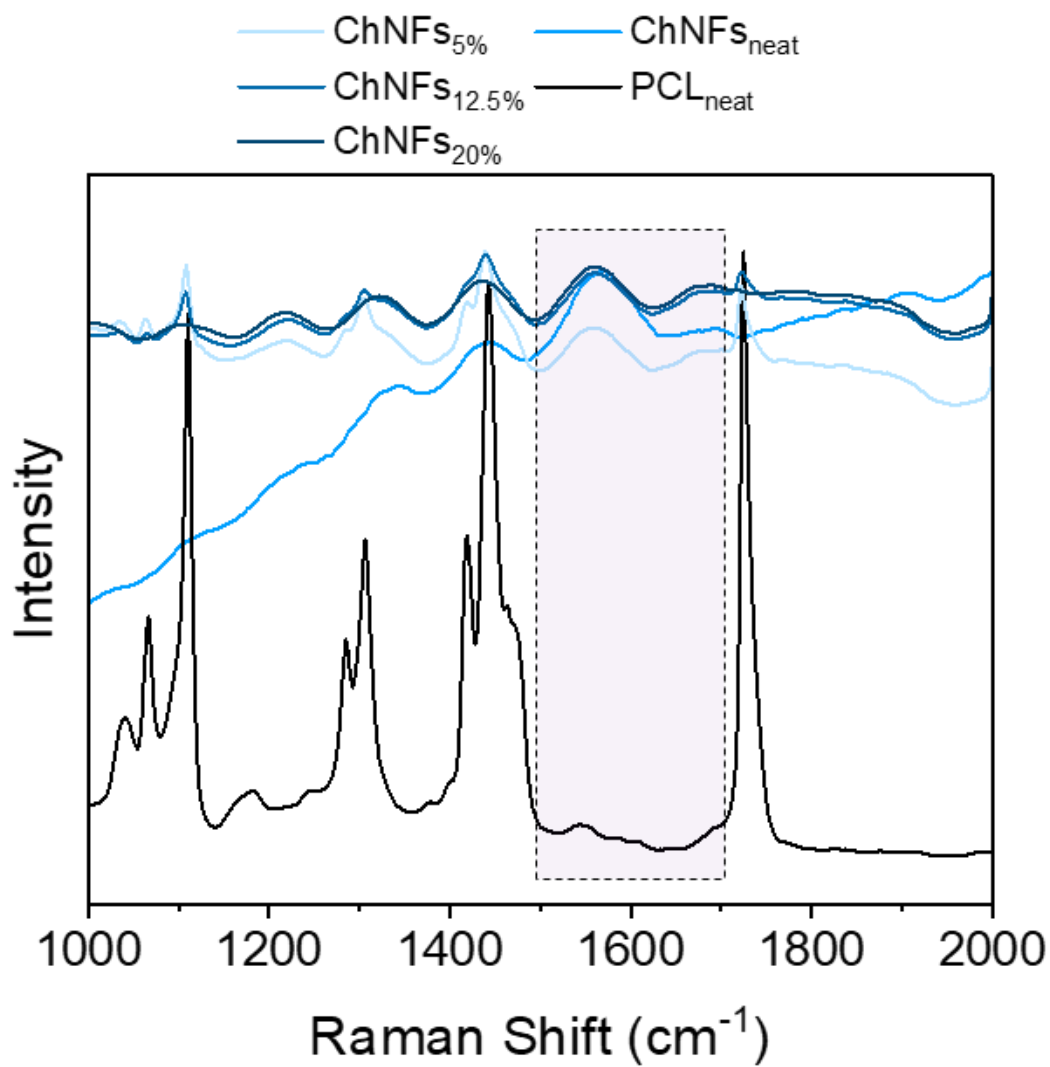
## Raman Microscopy Spectra



**Figure S4.** Raman spectra comparing neat PCL, SC and ChNFs with 12.5% composites of SC and ChNFs.



**Figure S5.** Raman spectra comparing neat PCL and SC to 5%, 12.5% and 20% SC composites.



**Figure S6.** Raman spectra comparing neat PCL and ChNFs to 5%, 12.5% and 20% ChNFs composites.

## DoE Summary Table

**Table S4.** Summary table of the 17 conditions to complete Box Behnken design (BBD) model. SC was used for the DoE as it is the industry standard source for chitin. Additionally, the data from the thermal and mechanical techniques (TGA, tensile, and DMA) are summarized and used to determine the five conditions to compare with the ChNFs biocomposites.

Run Order	Chitin conc. (wt%)	Screw speed (rpm)	Mixing time (sec)	$T_{d5\%}$ (°C)	<sup>a</sup> Young's modulus (MPa)	Yield strength (MPa)	Ultimate tensile strength (MPa)	Elongation at break (%)	<sup>b</sup> Storage modulus (MPa)
0	0.0	112	112	376	91.39	11.15	29.43	1832.72	2873.77
1	5.0	112	45	372	104.46	11.53	27.58	1767.90	2839.72
2	5.0	200	112	362	99.96	10.69	29.54	1835.72	2986.23
3	5.0	112	180	365	108.72	11.36	29.57	1743.92	2954.45
4	12.5	200	45	355	127.02	11.13	23.48	1524.16	2586.72
5	20.0	200	112	321	129.98	10.00	15.92	1191.70	3714.16
6	12.5	112	112	352	138.68	12.42	21.34	1361.86	3713.5
7	12.5	112	112	353	134.30	11.95	23.23	1430.89	3265.14
8	12.5	25	180	346	134.67	12.25	21.41	1356.40	3547.82
9	20.0	25	112	339	160.83	11.43	14.36	924.35	5010.78
10	12.5	200	180	347	128.67	12.20	24.62	1464.77	3912.45
11	5.0	25	112	360	134.17	13.54	31.00	1665.18	3829.59
12	20.0	112	180	327	156.85	11.72	16.71	1123.75	4619.2
13	12.5	112	112	341	141.39	12.54	25.20	1515.12	4292.65
14	12.5	112	112	343	121.24	11.47	21.03	1467.66	3778.57
15	12.5	112	112	351	131.34	13.06	24.45	1420.17	3716.61
16	20.0	112	45	328	197.71	12.53	15.17	874.74	4229.83
17	12.5	25	45	350	175.96	12.60	23.59	1447.44	3060.71

<sup>a</sup>uniaxial tensile testing; <sup>b</sup>DMA

## Chitin Condition Comparison Table

**Table S5.** Comparison conditions for five experiments determined from DoE results.

SC run # from DoE	ChNFs sample #	chitin conc. (wt%)	screw speed (rpm)	mixing time (sec)
<sup>a</sup> 0	<sup>a</sup> 0	<sup>a</sup> 0.0	<sup>a</sup> 112	<sup>a</sup> 112
11	1	5.0	25	112
2	2	5.0	200	112
17	3	12.5	25	45
14	4	12.5	112	112
16	5	20.0	112	45

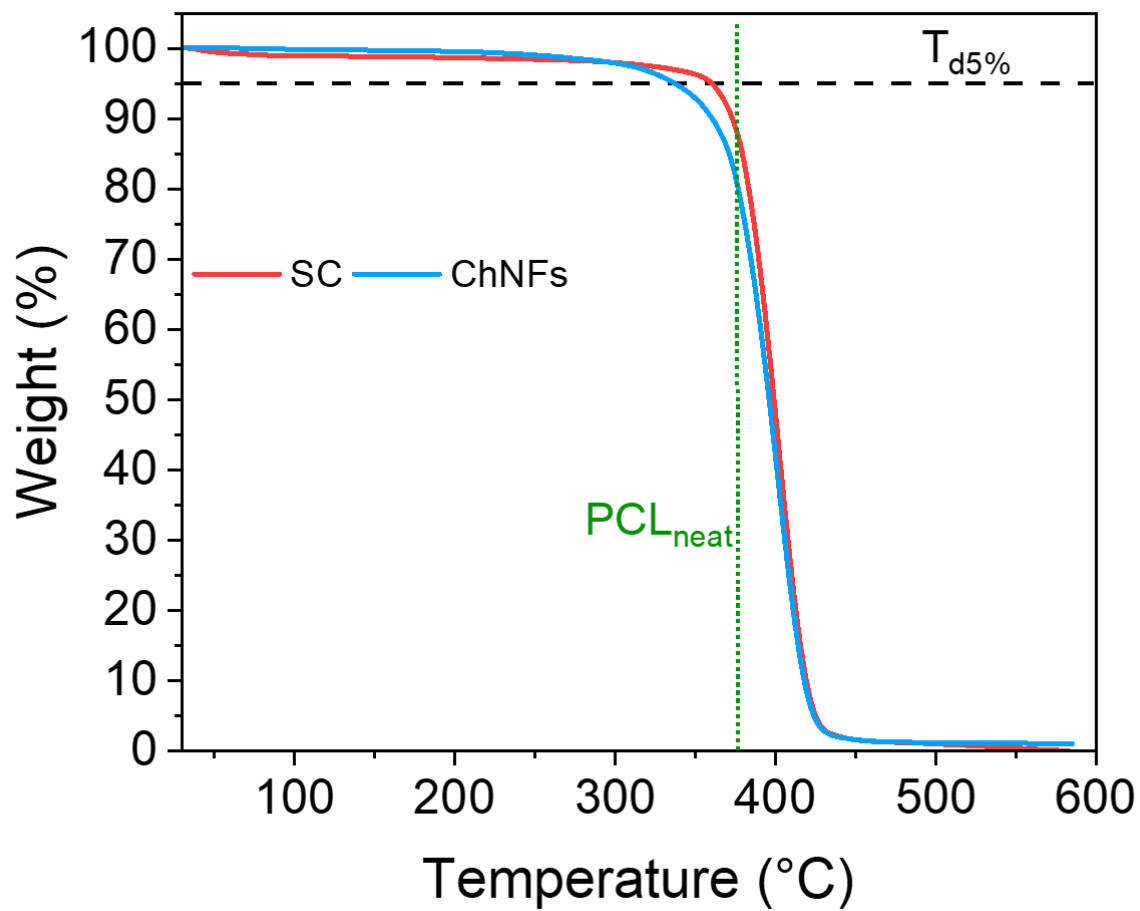
<sup>a</sup>PCL homopolymer (control)

## TGA Data

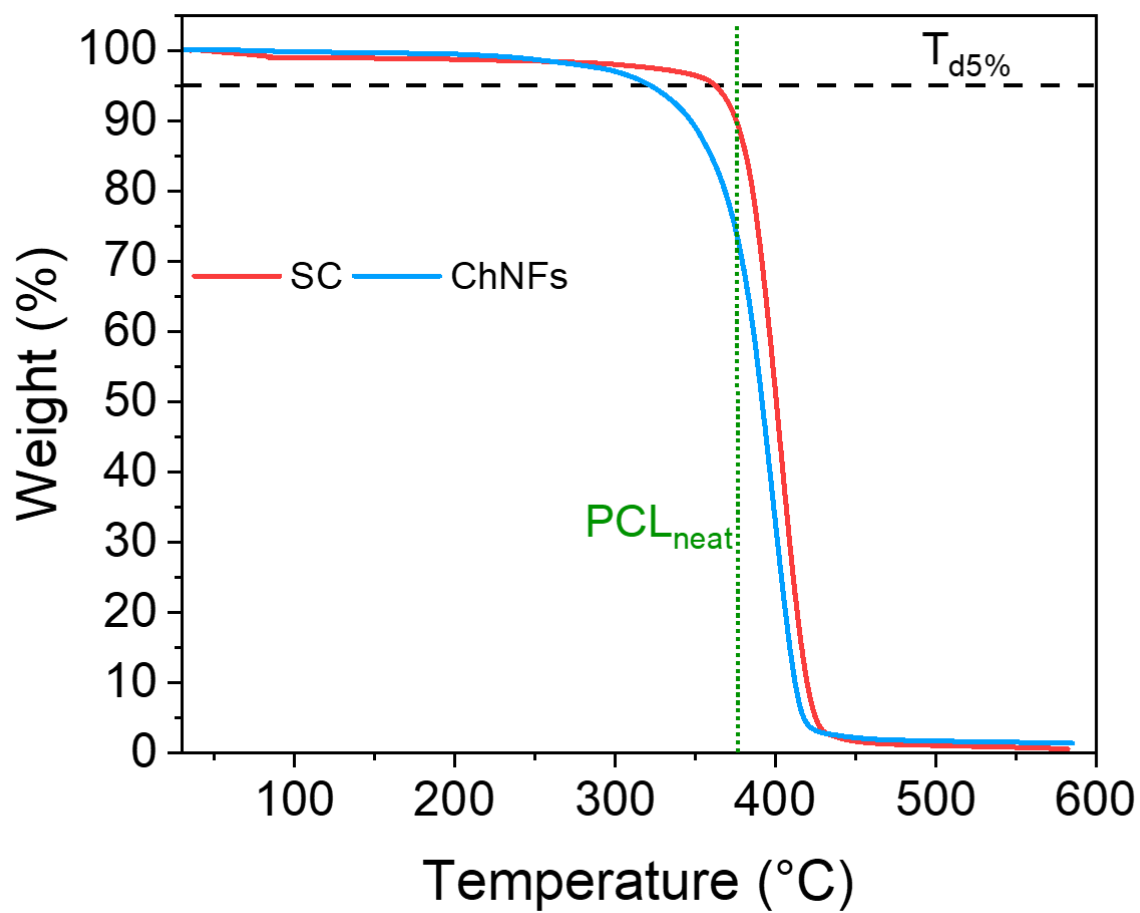
**Table S6.**  $T_{d5\%}$  ( $^{\circ}\text{C}$ ) comparison for each composite.

chitin conc. (wt%)	screw speed (rpm)	mixing time (sec)	PCL <sub>SC</sub>	PCL <sub>ChNFs</sub>
<sup>a</sup> 0.0	<sup>a</sup> 112	<sup>a</sup> 112		<sup>a</sup> 374
5.0	25	112	360	337
5.0	200	112	362	322
12.5	25	45	321	317
12.5	112	112	343	270
20.0	112	45	304	266

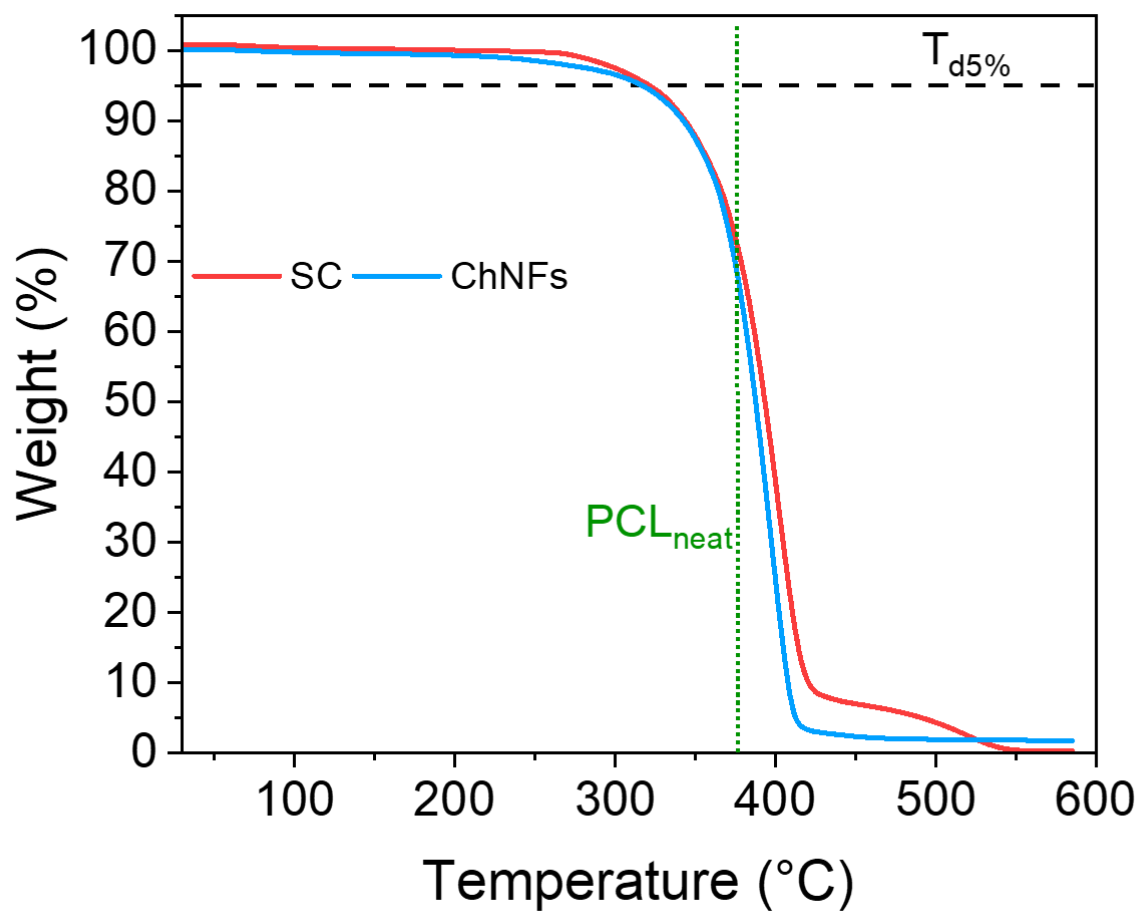
<sup>a</sup>PCL homopolymer (control)



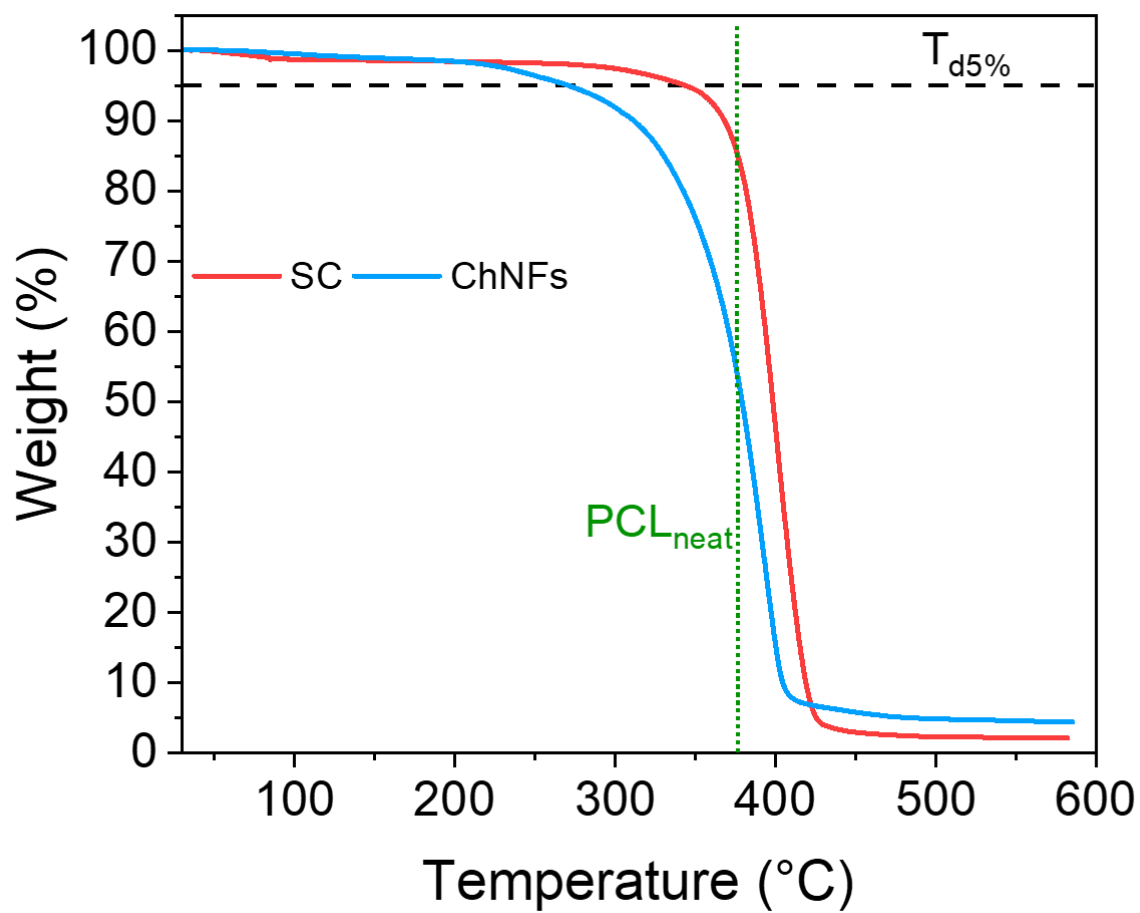
**Figure S7.** TGA of biocomposite comparison processed at 5%-25rpm-112sec.



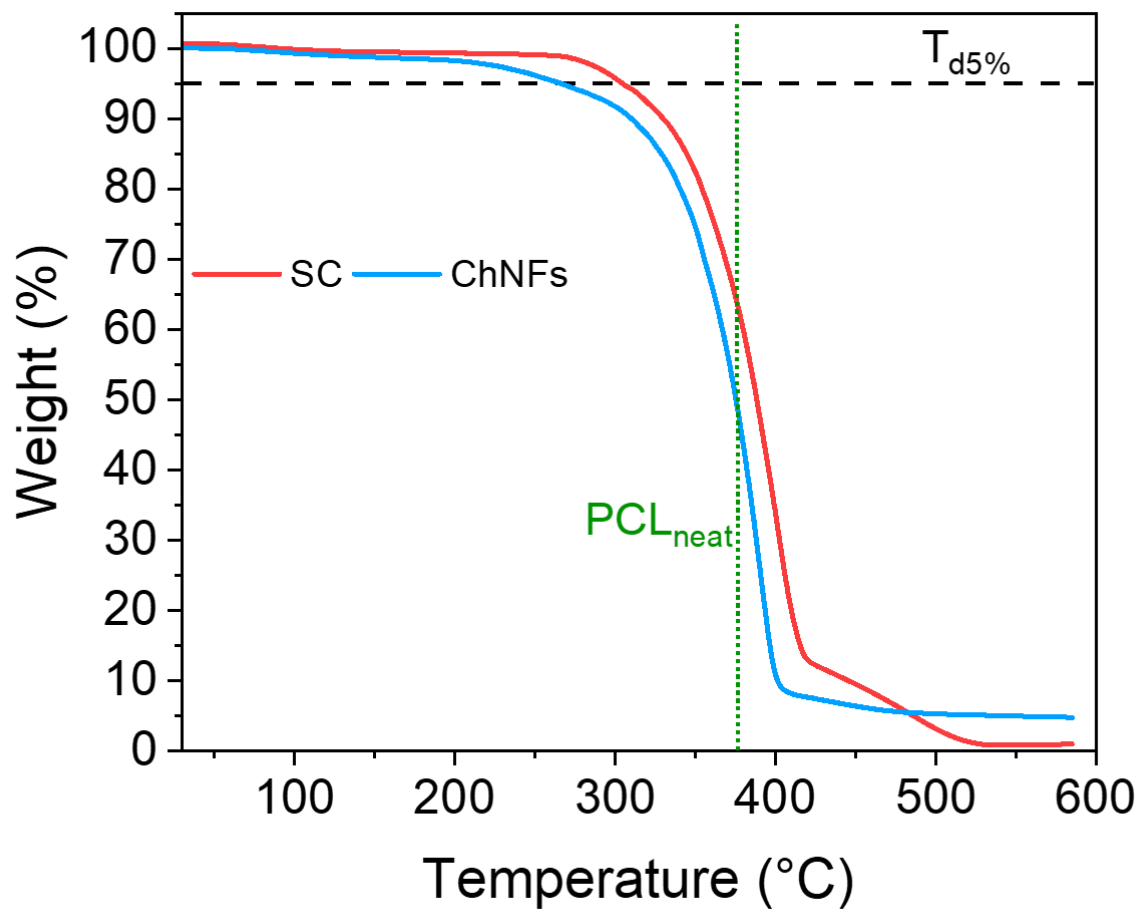
**Figure S8.** TGA of biocomposite comparison processed at 5%-200rpm-112sec.



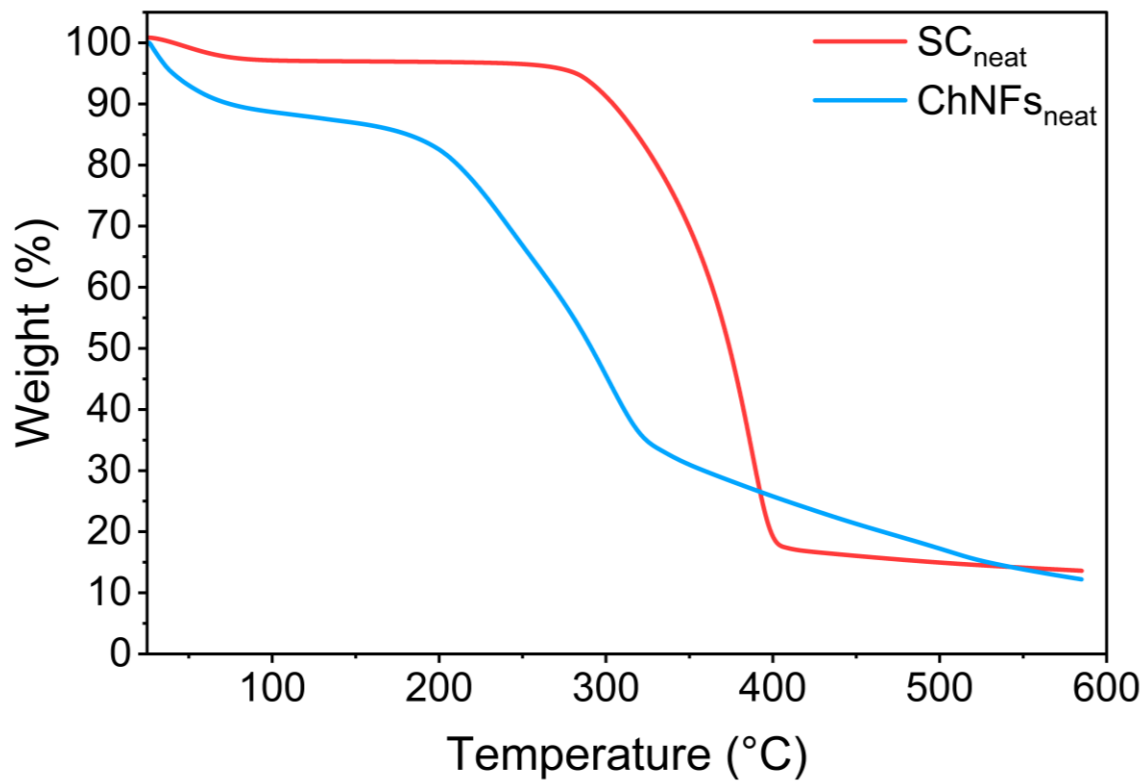
**Figure S9.** TGA of biocomposite comparison processed at 12.5%-25rpm-45sec.



**Figure S10.** TGA of biocomposite comparison processed at 12.5%-112rpm-112sec.



**Figure S11.** TGA of biocomposite comparison processed at 20%-112rpm-45sec.



**Figure S12.** TGA of neat SC and ChNFs samples.

## DSC Data

**Table S7.** Summary table of thermal properties for biocomposites and PCL

chitin conc. (wt%)	screw speed (rpm)	mixing time (sec)	Sample	$T_m$	$T_c$	% crystallinity
<sup>a</sup> 0.0	<sup>a</sup> 112	<sup>a</sup> 112	PCL	56.2	30.9	39.7
5.0	25	112	1-PCL <sub>SC</sub>	56.5	34.1	38.6
			1-PCL <sub>ChNFs</sub>	56.6	34.8	39.0
5.0	200	112	2-PCL <sub>SC</sub>	56.6	34.8	38.3
			2-PCL <sub>ChNFs</sub>	56.7	37.0	37.6
12.5	25	45	3-PCL <sub>SC</sub>	56.7	34.0	36.8
			3-PCL <sub>ChNFs</sub>	57.1	35.5	38.3
12.5	112	112	4-PCL <sub>SC</sub>	56.4	34.5	36.9
			4-PCL <sub>ChNFs</sub>	56.8	35.4	38.3
20.0	112	45	5-PCL <sub>SC</sub>	56.3	34.0	37.1
			5-PCL <sub>ChNFs</sub>	56.9	35.9	36.5

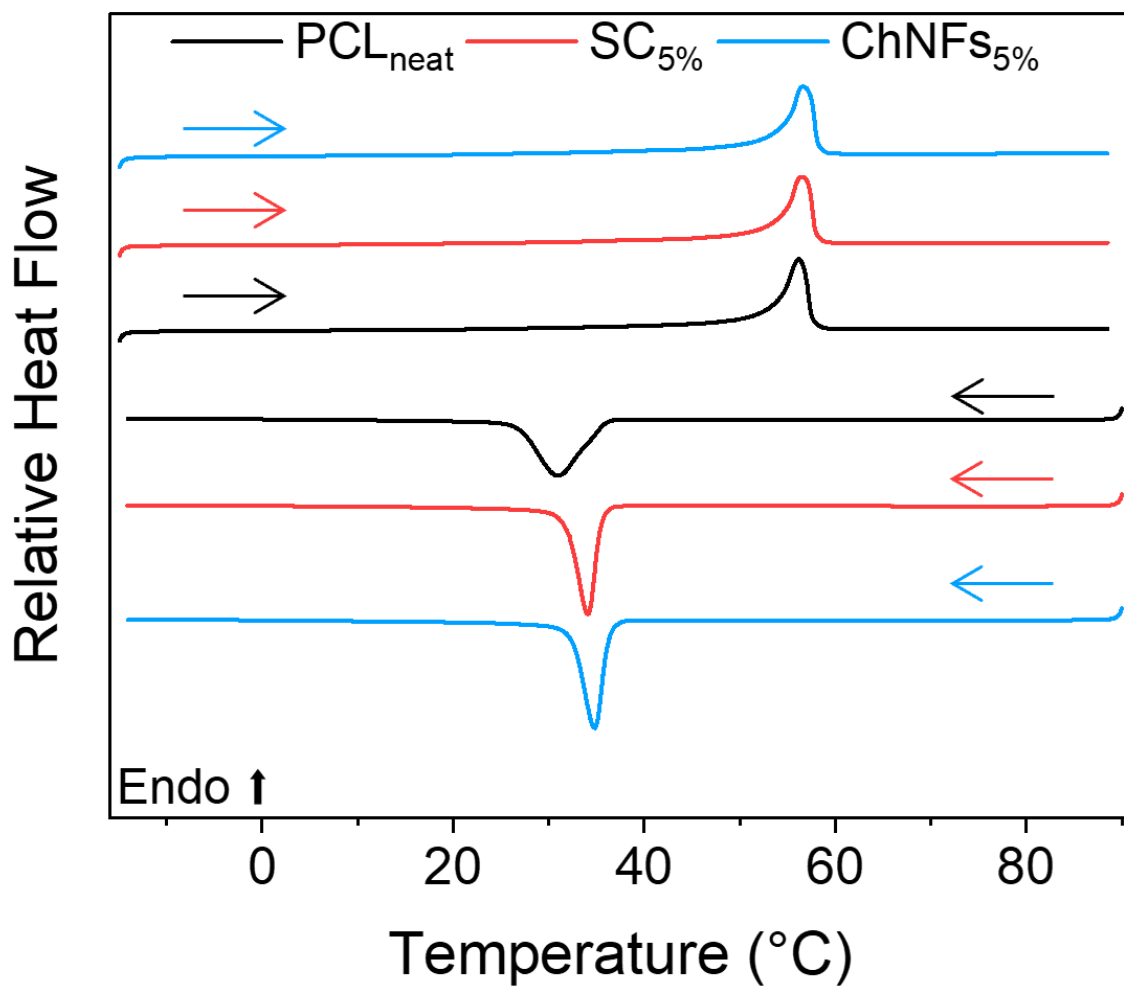


Figure S13. Processing conditions: 5%-25rpm-112sec compared to neat PCL.

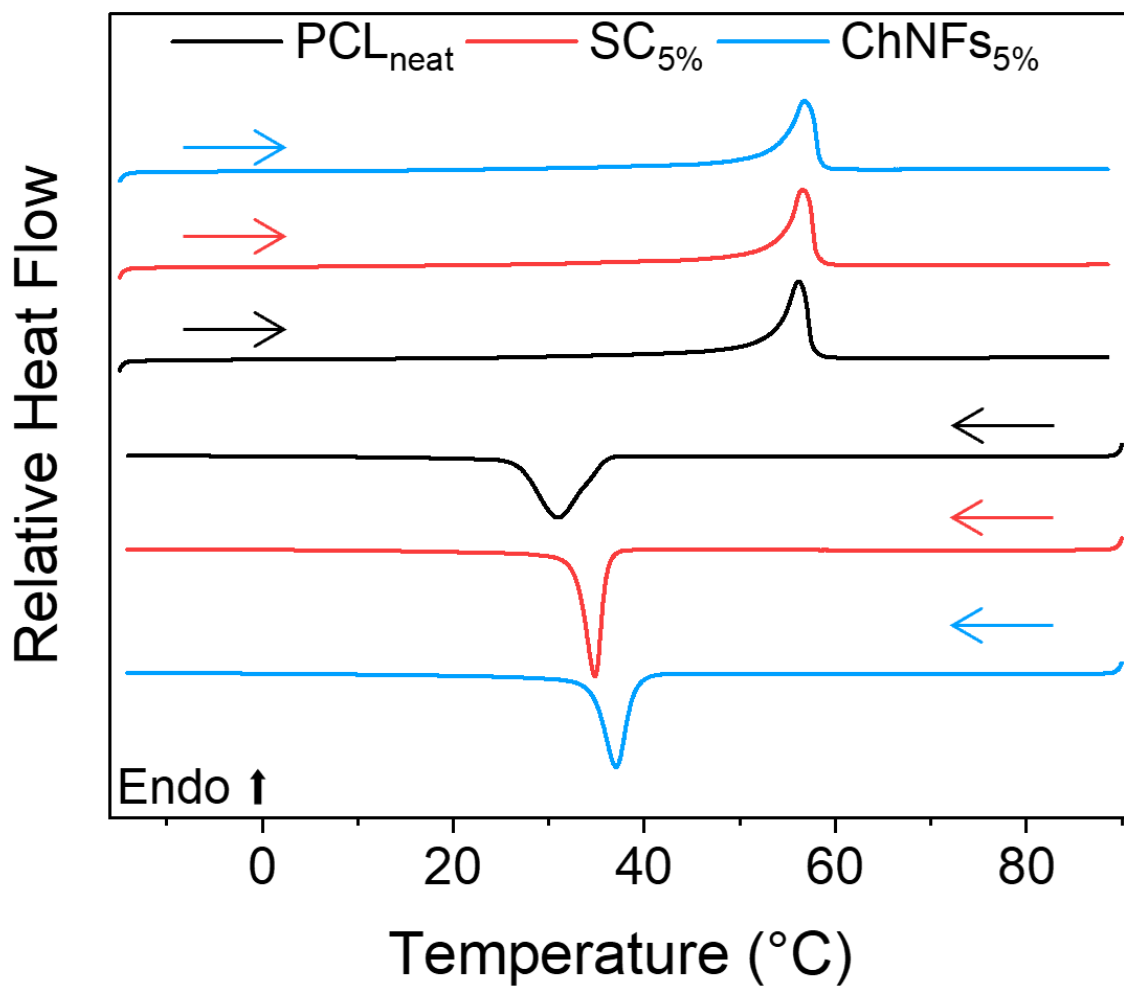
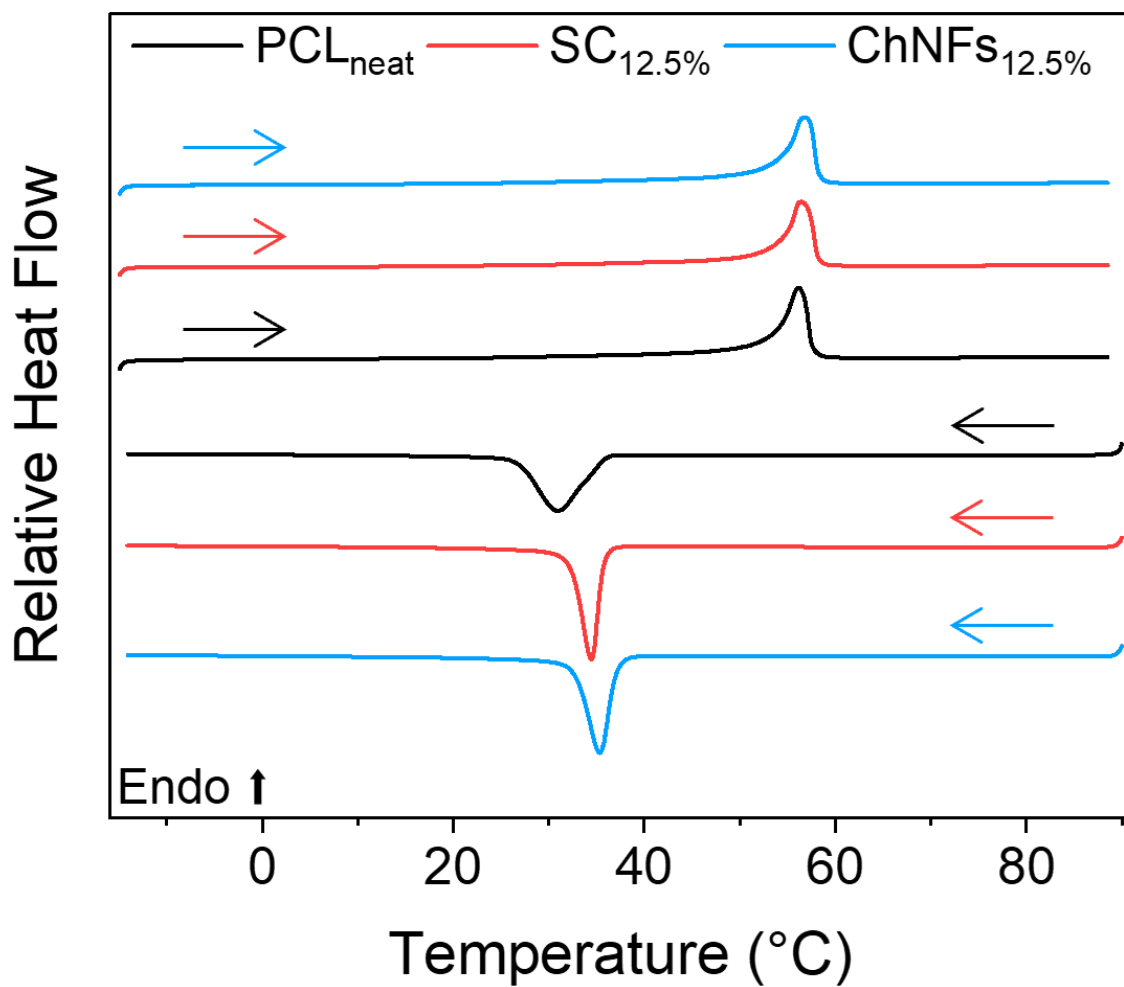


Figure S14. Processing conditions: 5%-200rpm-112sec compared to neat PCL.



**Figure S15.** Processing conditions: 12.5%-112rpm-112sec compared to neat PCL.

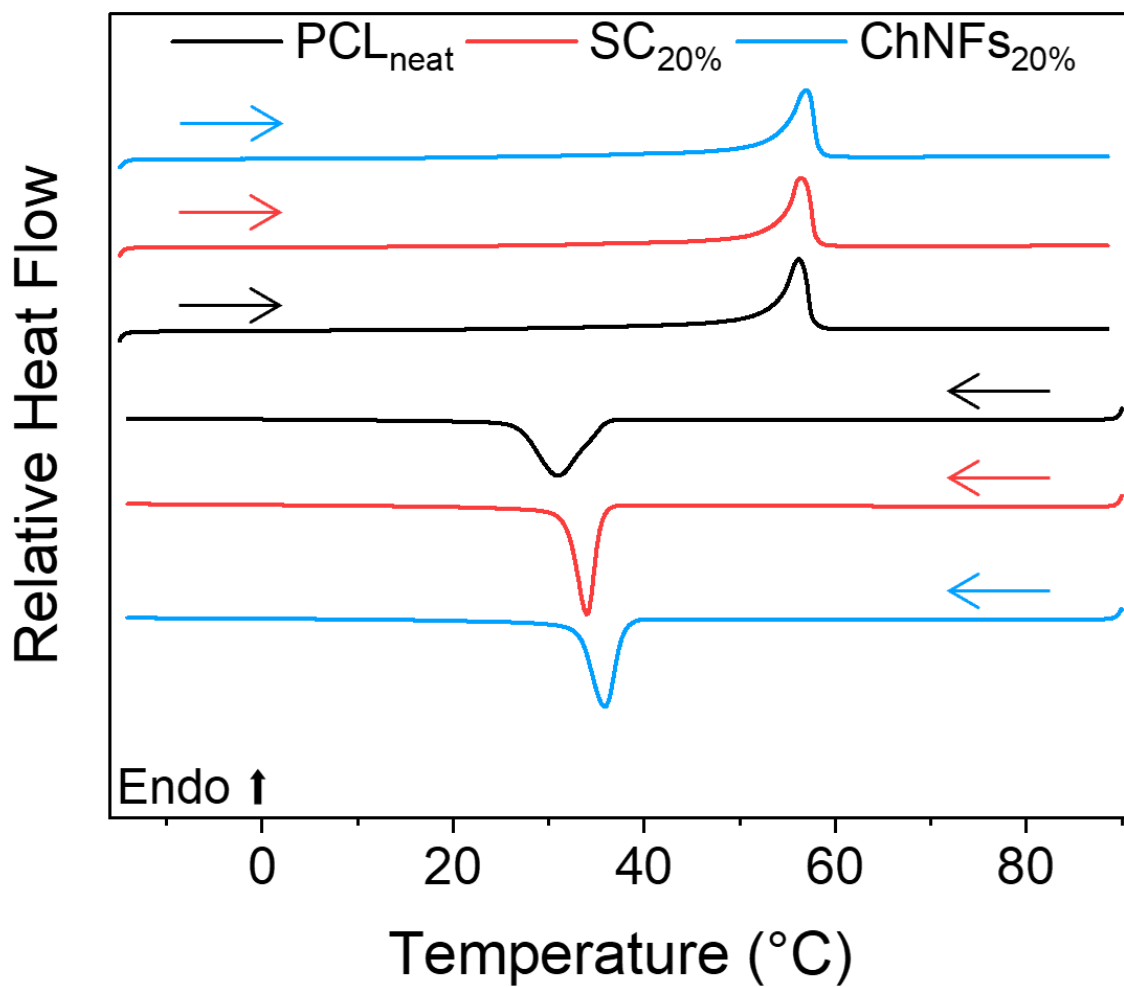
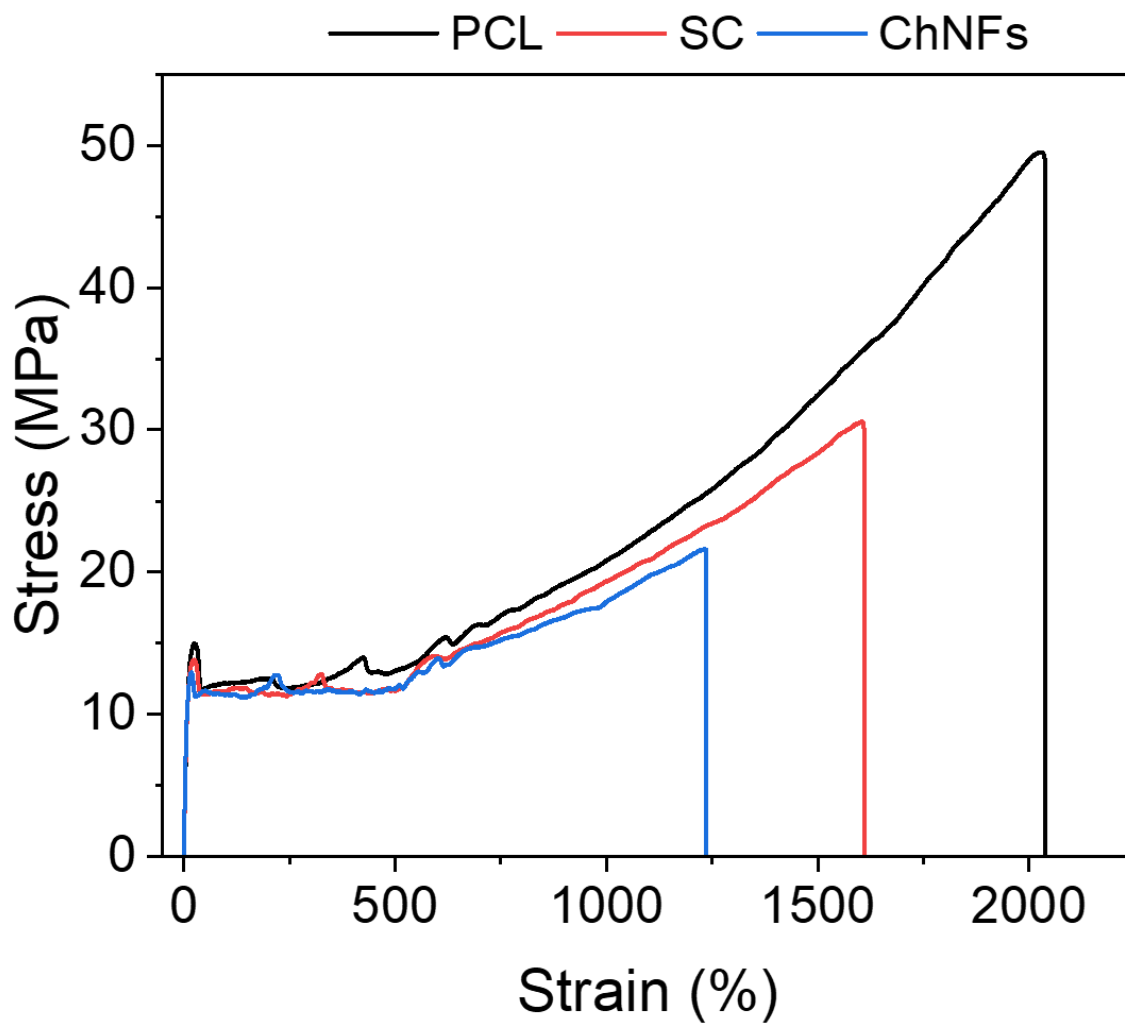
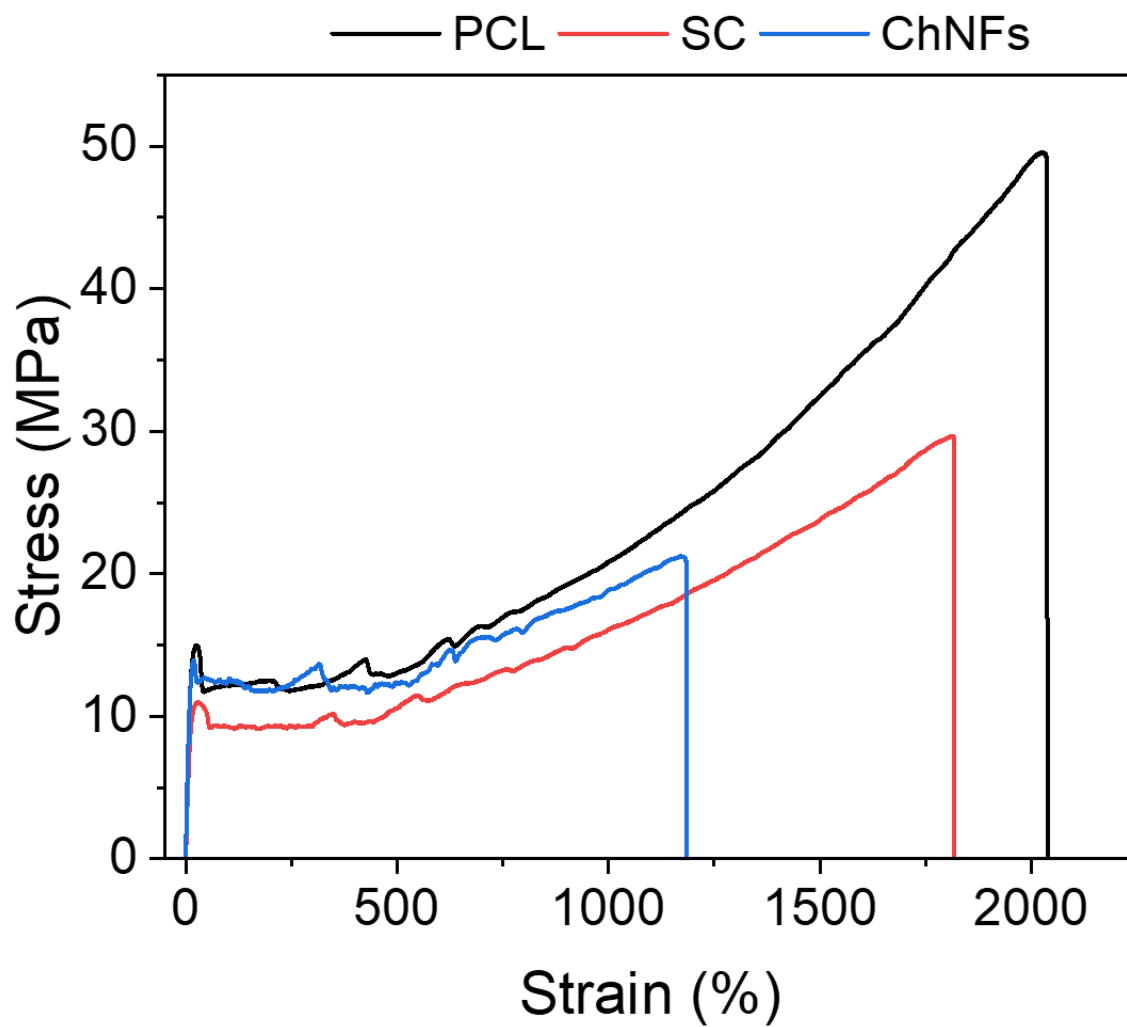


Figure S16. Processing conditions: 20%-112rpm-45sec compared to neat PCL.

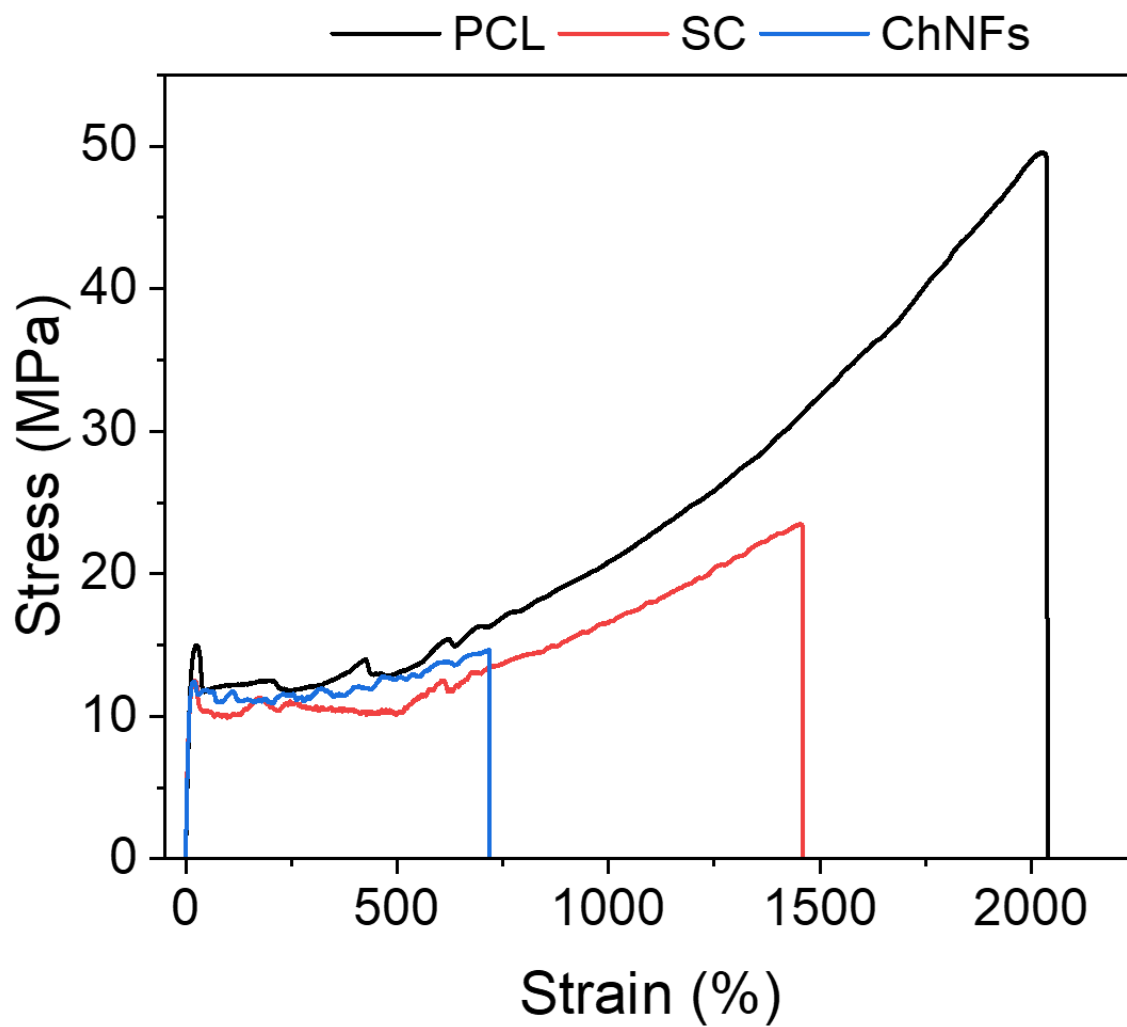
## Tensile Testing



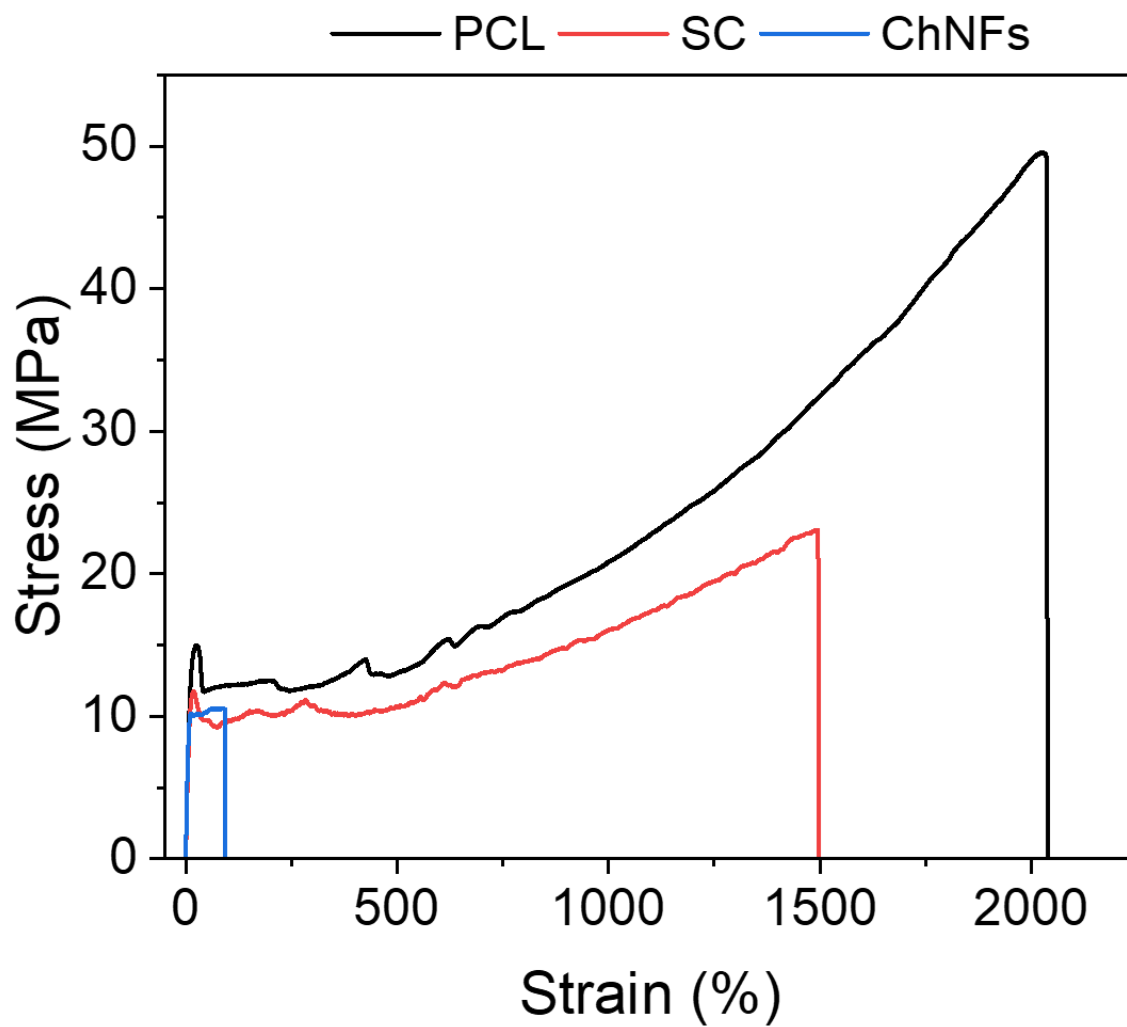
**Figure S17.** Processing conditions: 5%-25rpm-112sec compared to neat PCL. (representative curves)



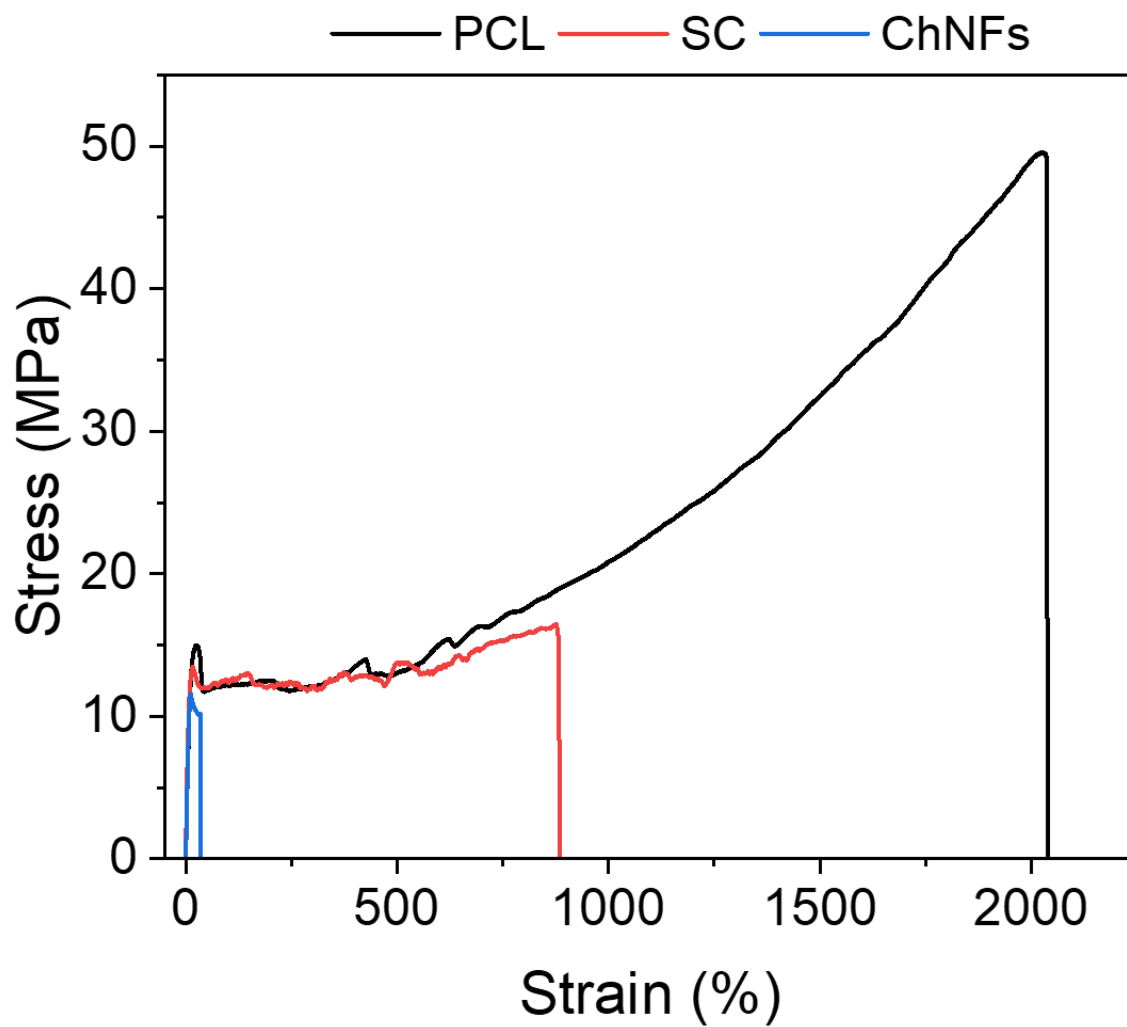
**Figure S18.** Processing conditions: 5%-200rpm-112sec compared to neat PCL. (representative curves)



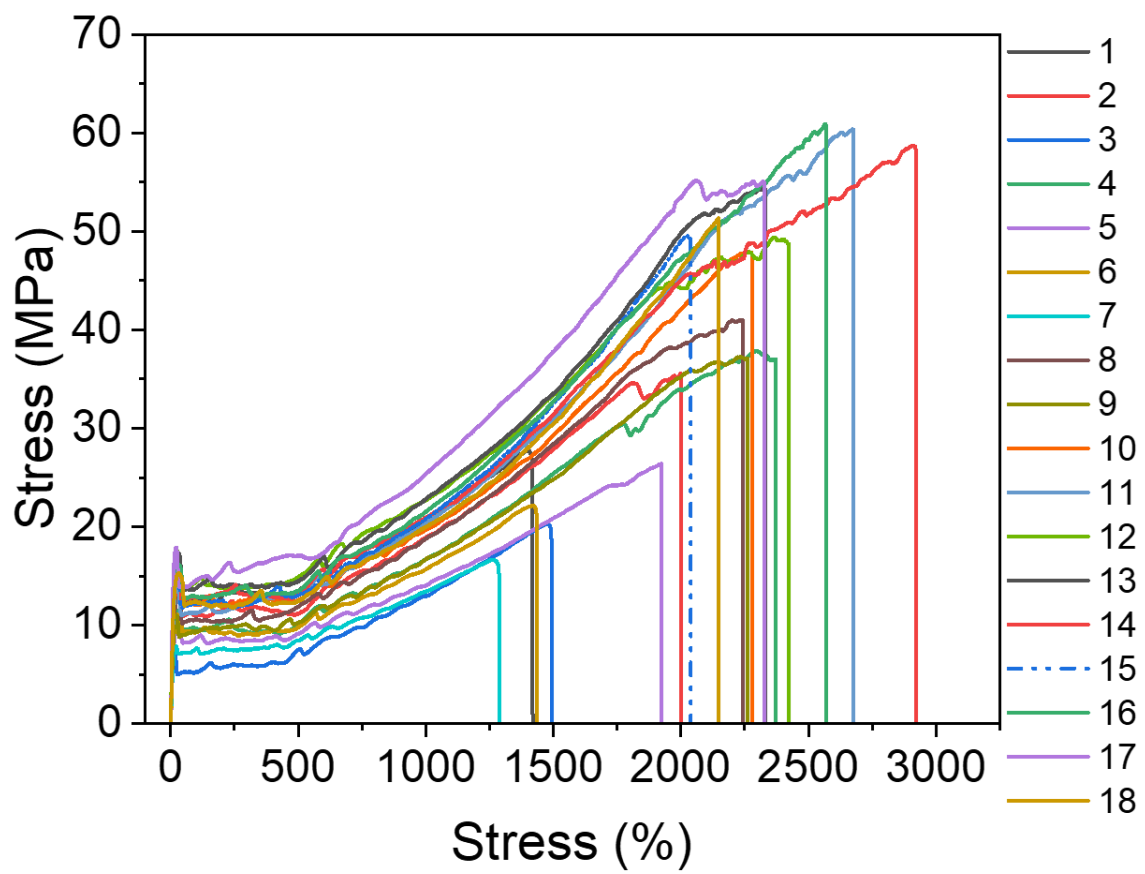
**Figure S19.** Processing conditions: 12.5%-25rpm-45sec compared to neat PCL. (representative curves)



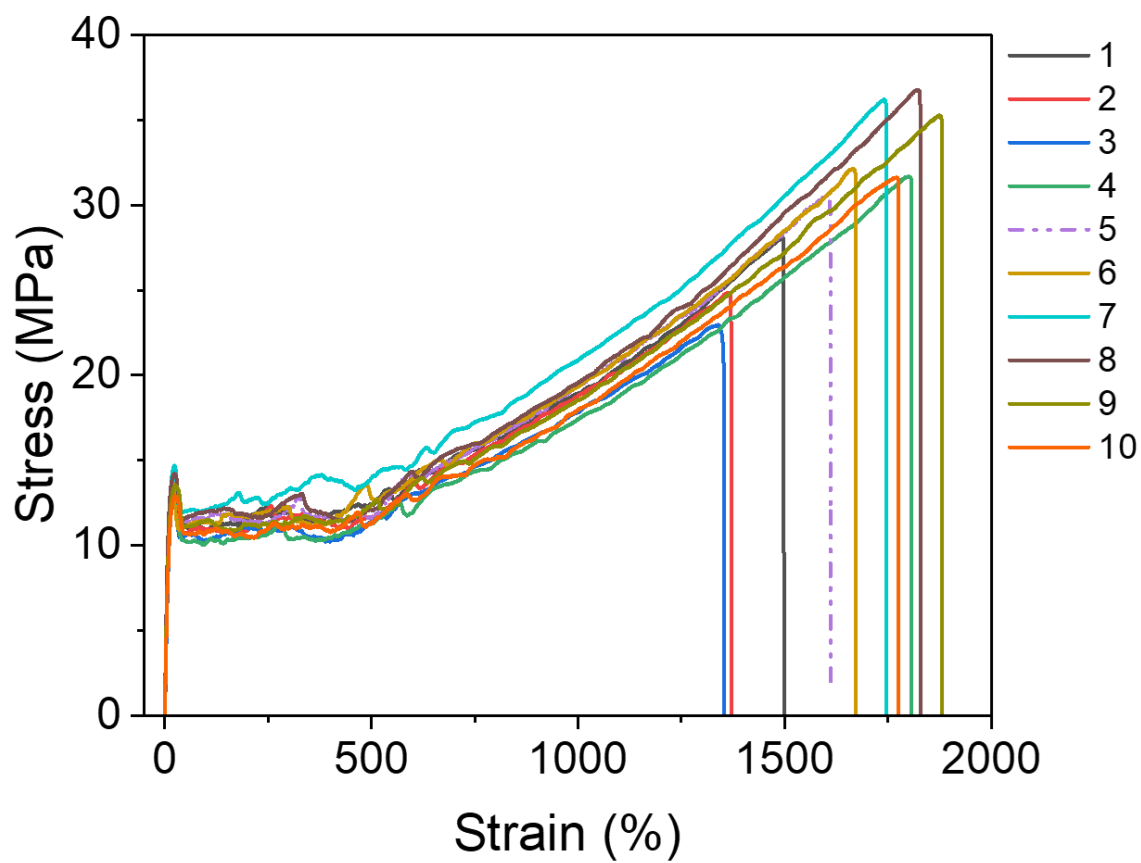
**Figure S20.** Processing conditions: 12.5%-112rpm-112sec compared to neat PCL. (representative curves)



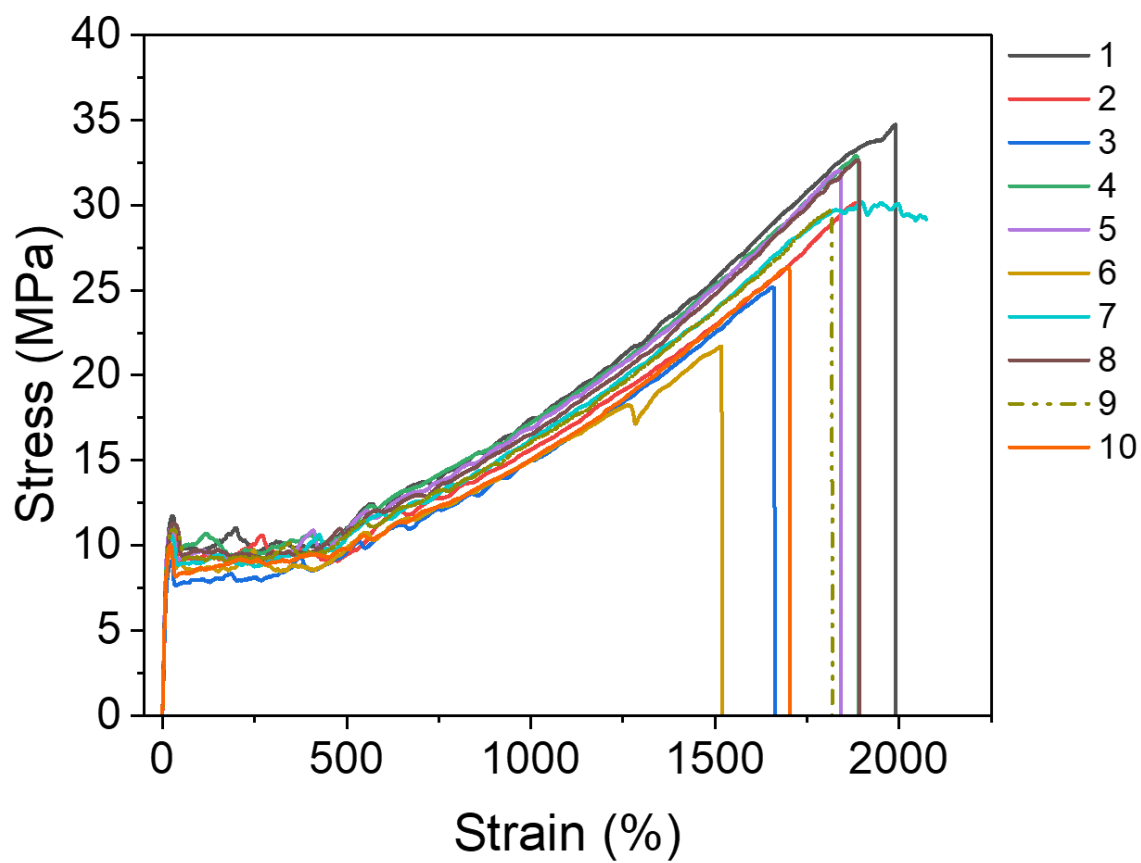
**Figure S21.** Processing conditions: 20%-112rpm-45sec compared to neat PCL. (representative curves)



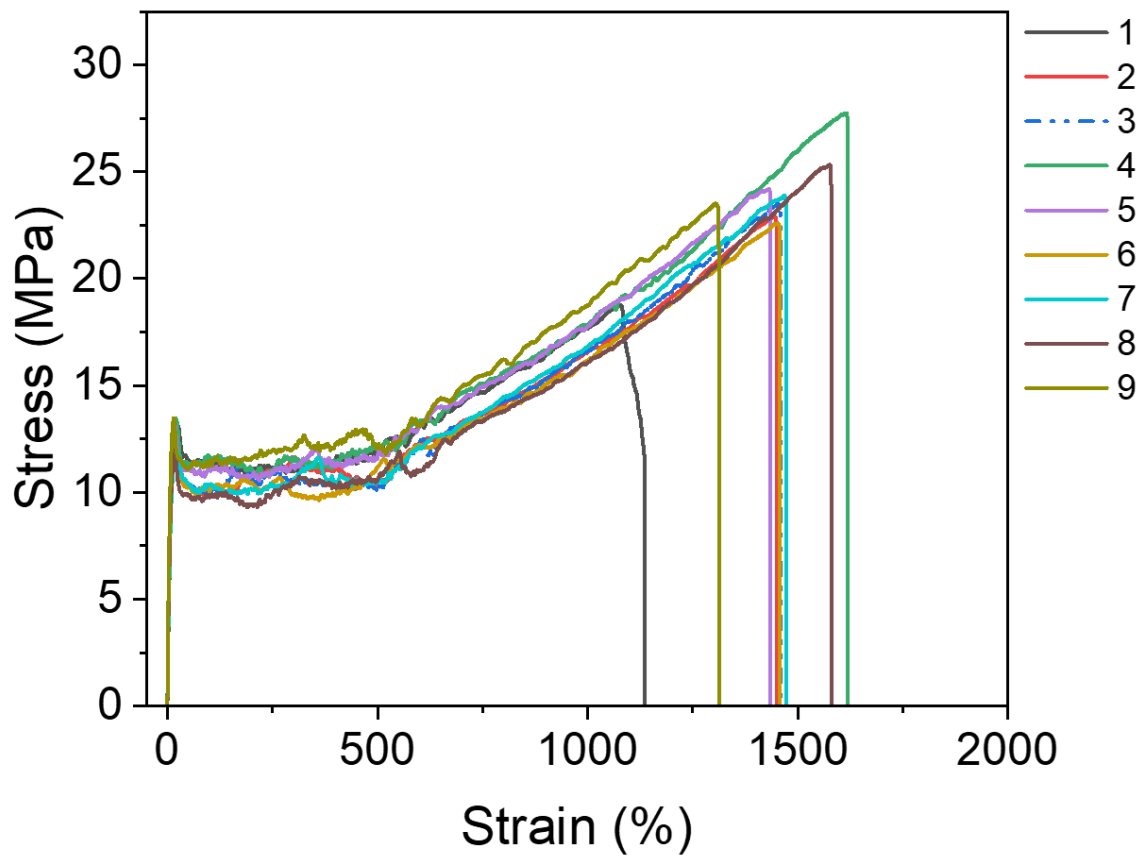
**Figure S22.** Neat PCL n=16 and dotted line is the representative curve.



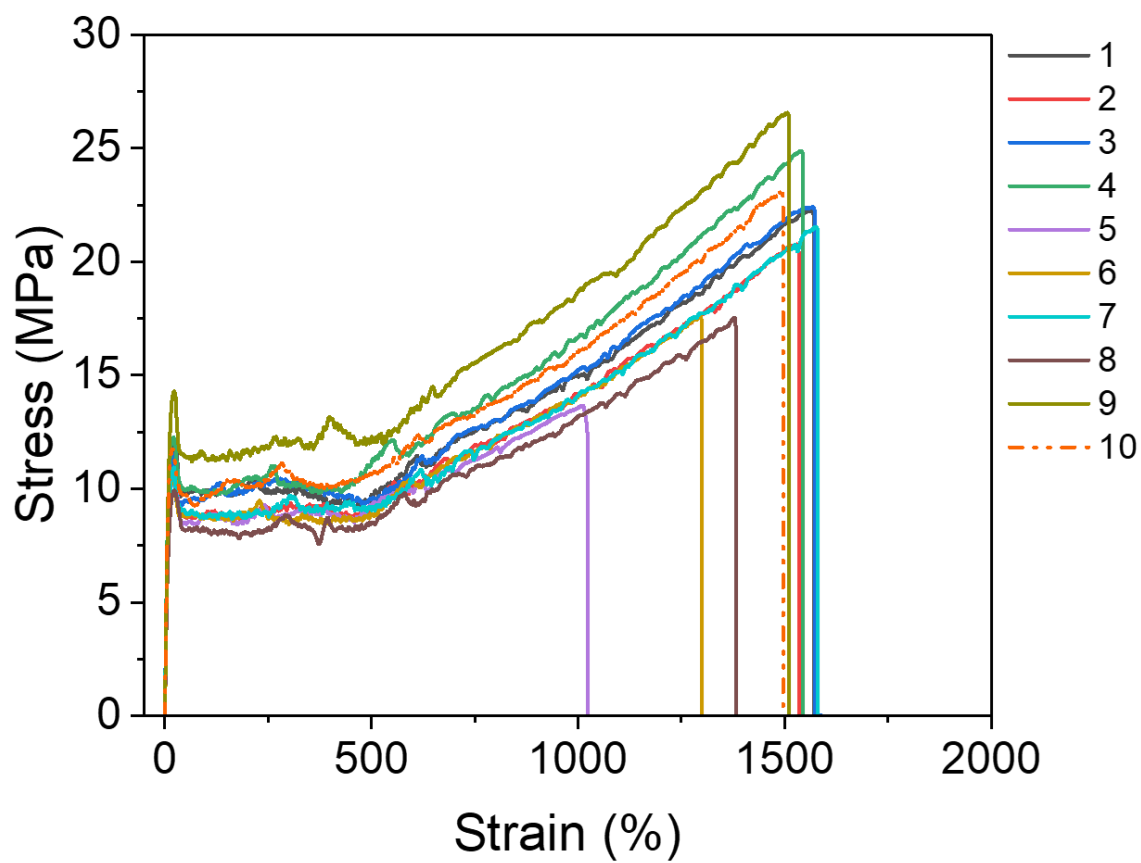
**Figure S23.** SC biocomposite 5%-25rpm-112sec n=10 and dotted line is representative curve.



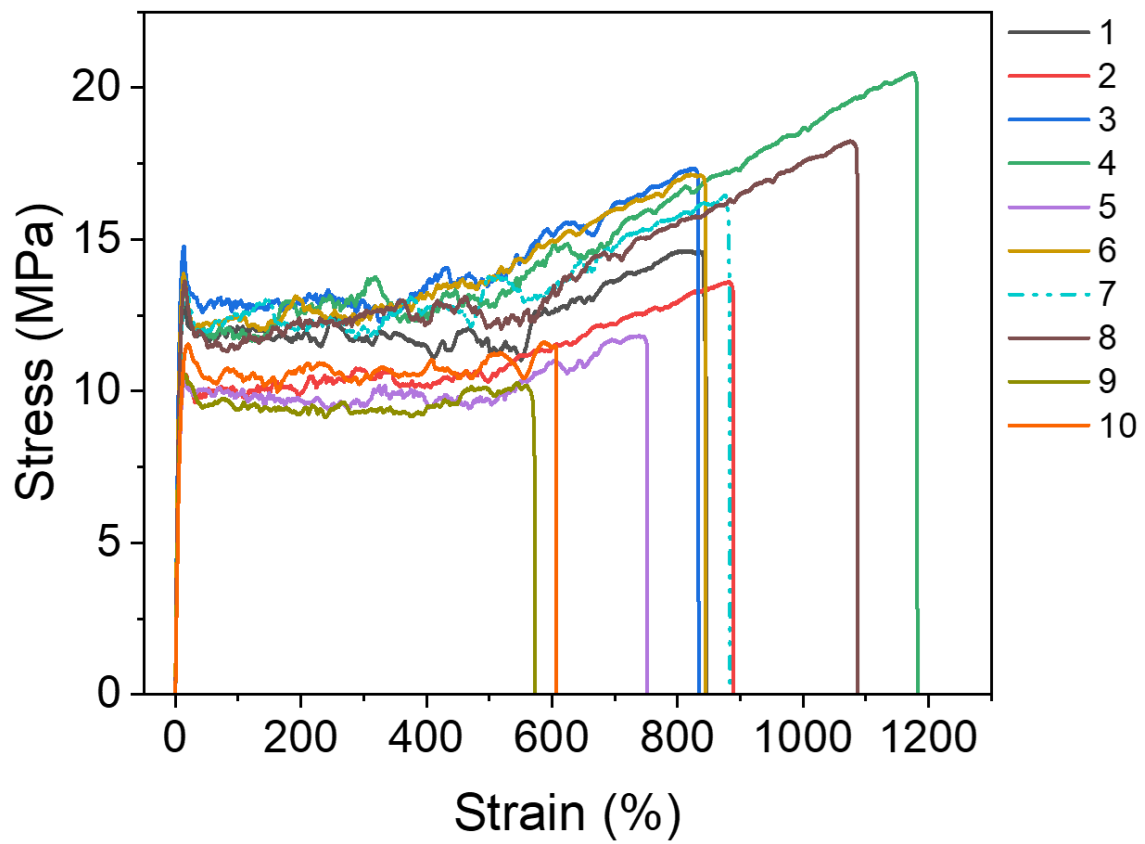
**Figure S24.** SC biocomposite 5%-200rpm-112sec n=10 and dotted line is representative curve.



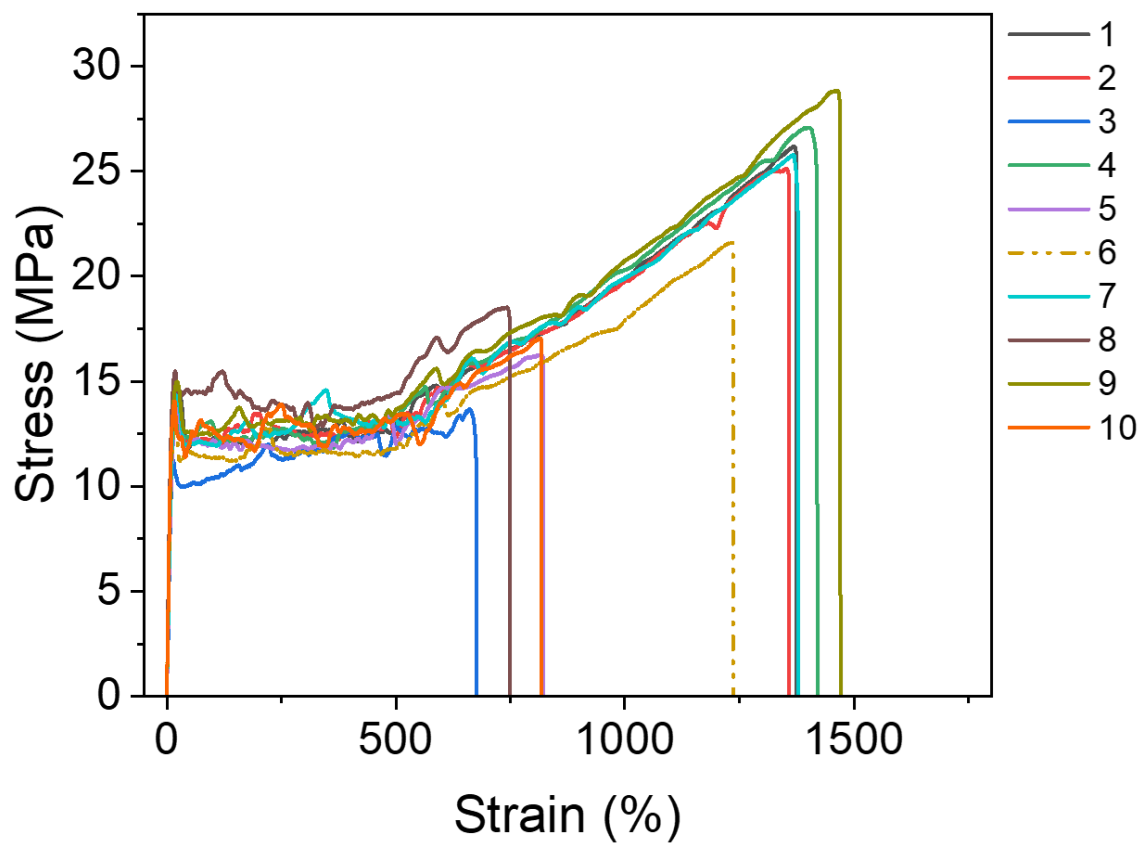
**Figure S25.** SC biocomposite 12.5%-25rpm-45sec n=9 and dotted line is representative curve.



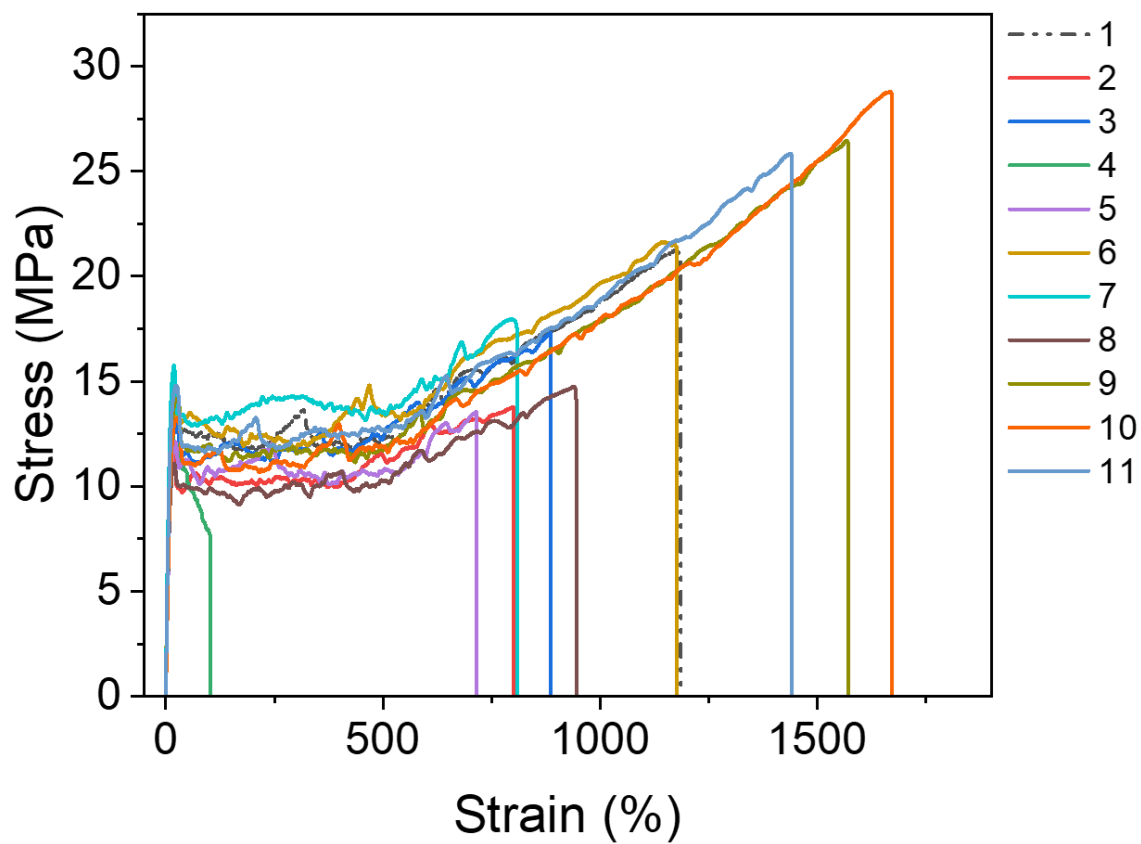
**Figure S26.** SC biocomposite 12.5%-112rpm-112sec n=10 and dotted line is representative curve.



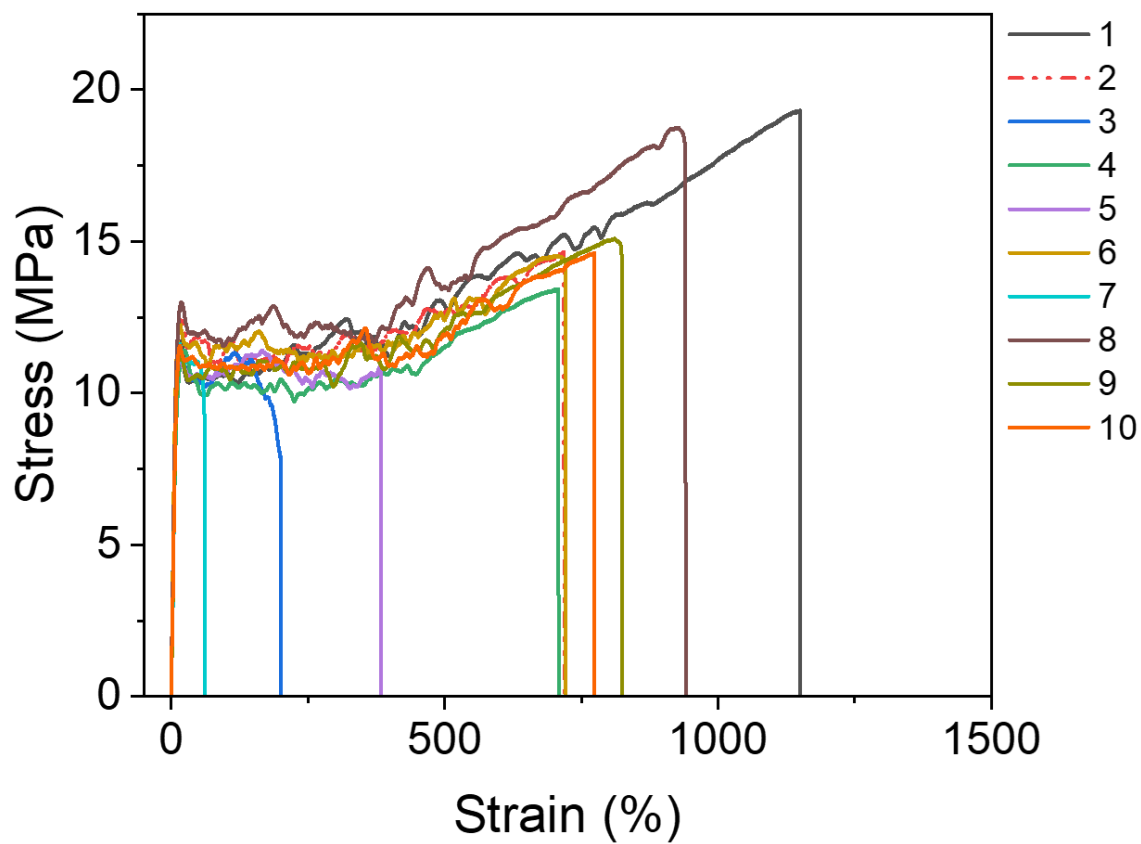
**Figure S27.** SC biocomposite 20%-112rpm-45sec n=10 and dotted line is representative curve.



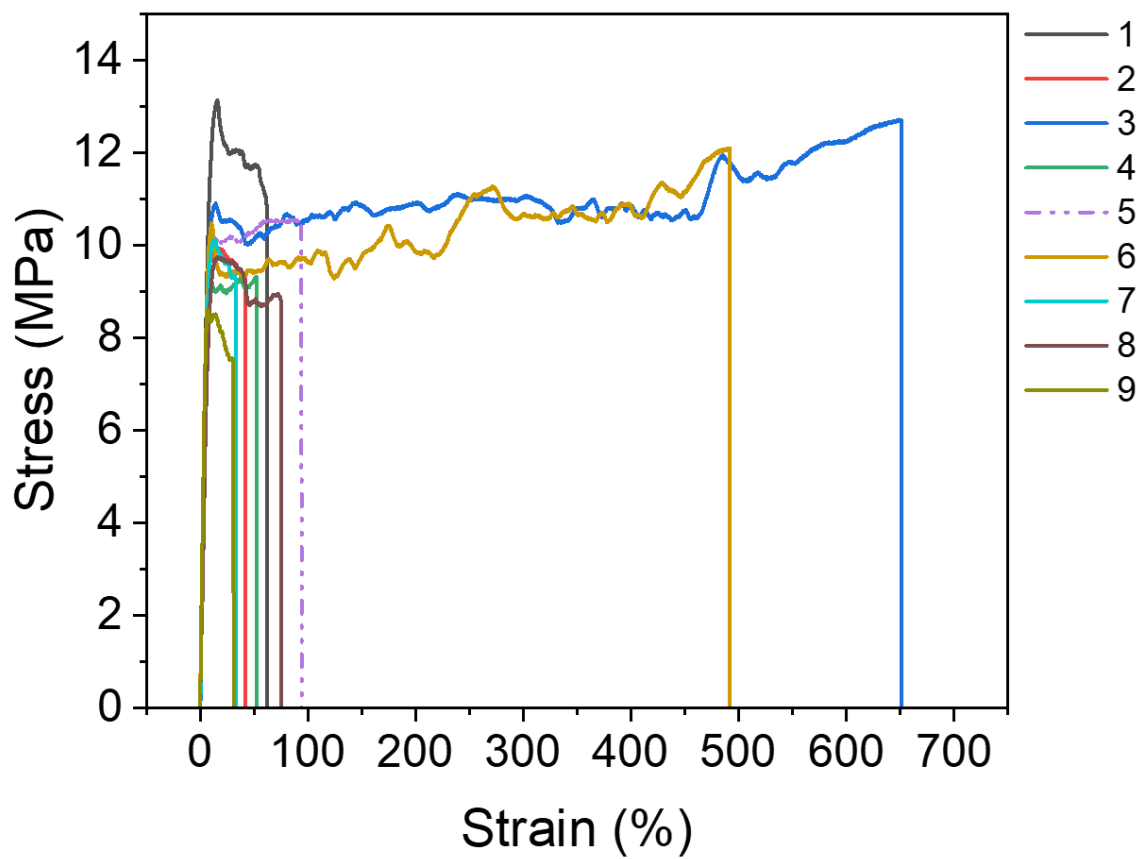
**Figure S28.** ChNFs biocomposite 5%-25rpm-112sec n=10 and dotted line is representative curve.



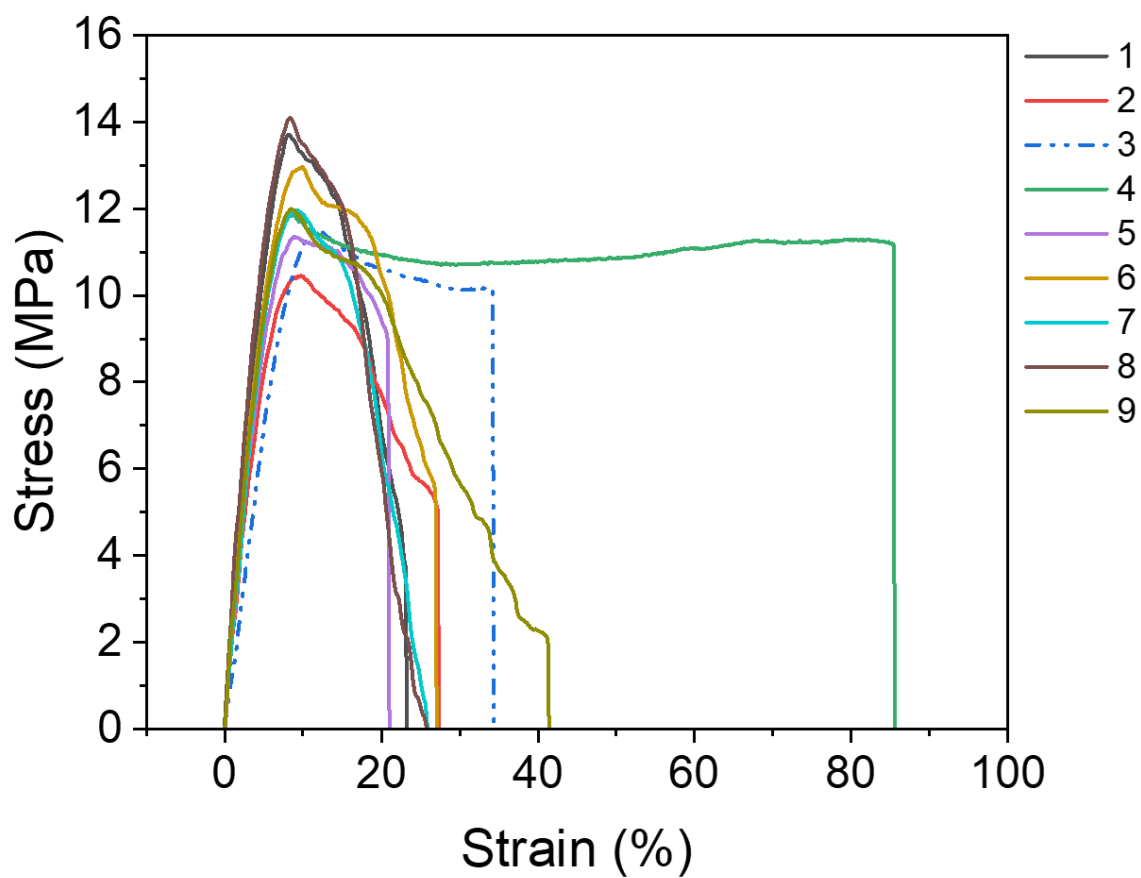
**Figure S29.** ChNFs biocomposite 5%-200rpm-112sec n=11 and dotted line is representative curve.



**Figure S30.** ChNFs biocomposite 12.5%-25rpm-45sec n=10 and dotted line is representative curve.



**Figure S31.** ChNFs biocomposite 12.5%-112rpm-112sec n=9 and dotted line is representative curve.



**Figure S32.** ChNFs biocomposite 20%-112rpm-45sec n=9 and dotted line is representative curve.

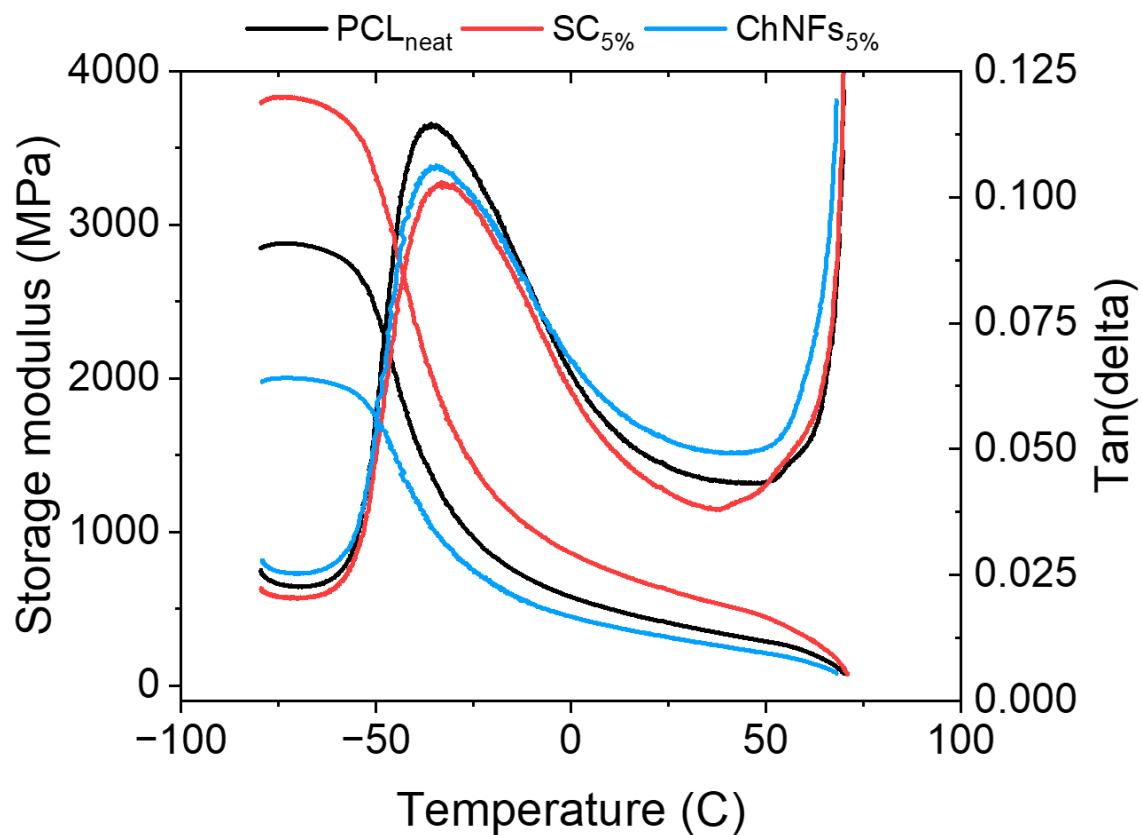
**Table S8.** Statistical analysis of Young’s Modulus through a two-way ANOVA test, looking at the “connecting letters report” ( $p < 0.05$ )

chitin conc. (wt%)	screw speed (rpm)	mixing time (sec)	Sample	Mean	Group
5.0	25	112	1-PCL <sub>SC</sub>	133.8	A
			1-PCL <sub>ChNFs</sub>	160.7	B
5.0	200	112	2-PCL <sub>SC</sub>	99.1	A
			2-PCL <sub>ChNFs</sub>	145.9	B
12.5	25	45	3-PCL <sub>SC</sub>	173.6	A
			3-PCL <sub>ChNFs</sub>	161.1	A
12.5	112	112	4-PCL <sub>SC</sub>	120.3	A
			4-PCL <sub>ChNFs</sub>	175.9	B
20.0	112	45	5-PCL <sub>SC</sub>	192.4	A
			5-PCL <sub>ChNFs</sub>	248.6	B

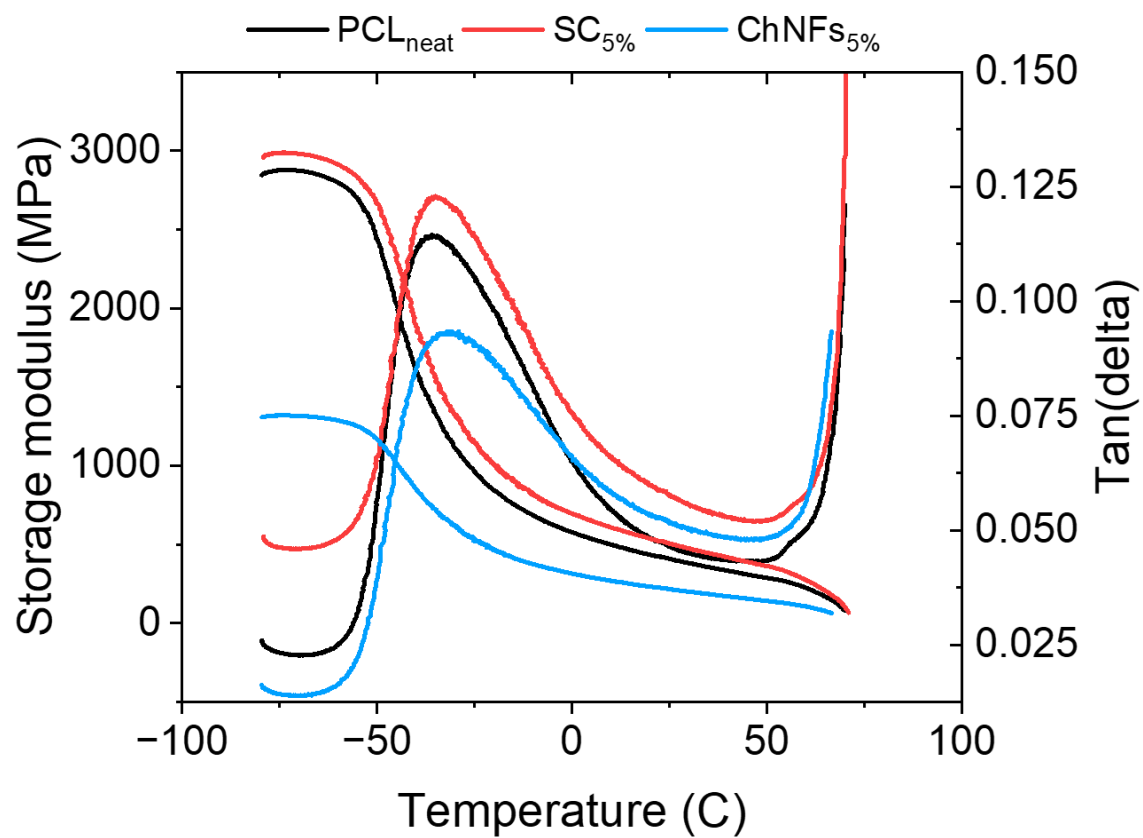
**Table S9.** Statistical analysis of Elongation at break through a two-way ANOVA test, looking at the “connecting letters report” with a confidence interval of 0.05.

chitin conc. (wt%)	screw speed (rpm)	mixing time (sec)	Sample	Mean	Group
5.0	25	112	1-PCL <sub>SC</sub>	1682	A
			1-PCL <sub>ChNFs</sub>	1103	B
5.0	200	112	2-PCL <sub>SC</sub>	1818	A
			2-PCL <sub>ChNFs</sub>	1012	B
12.5	25	45	3-PCL <sub>SC</sub>	1485	A
			3-PCL <sub>ChNFs</sub>	593	B
12.5	112	112	4-PCL <sub>SC</sub>	1455	A
			4-PCL <sub>ChNFs</sub>	184	B
20.0	112	45	5-PCL <sub>SC</sub>	876	A
			5-PCL <sub>ChNFs</sub>	36	B

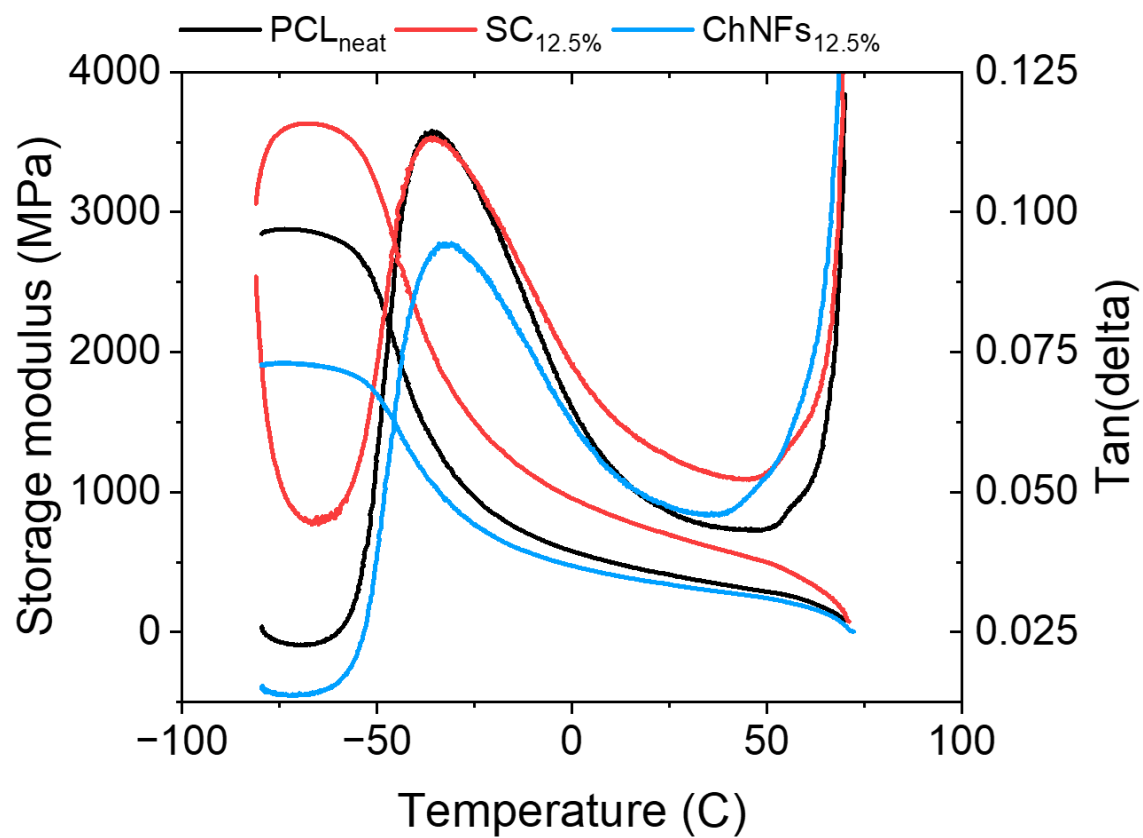
## DMA Data



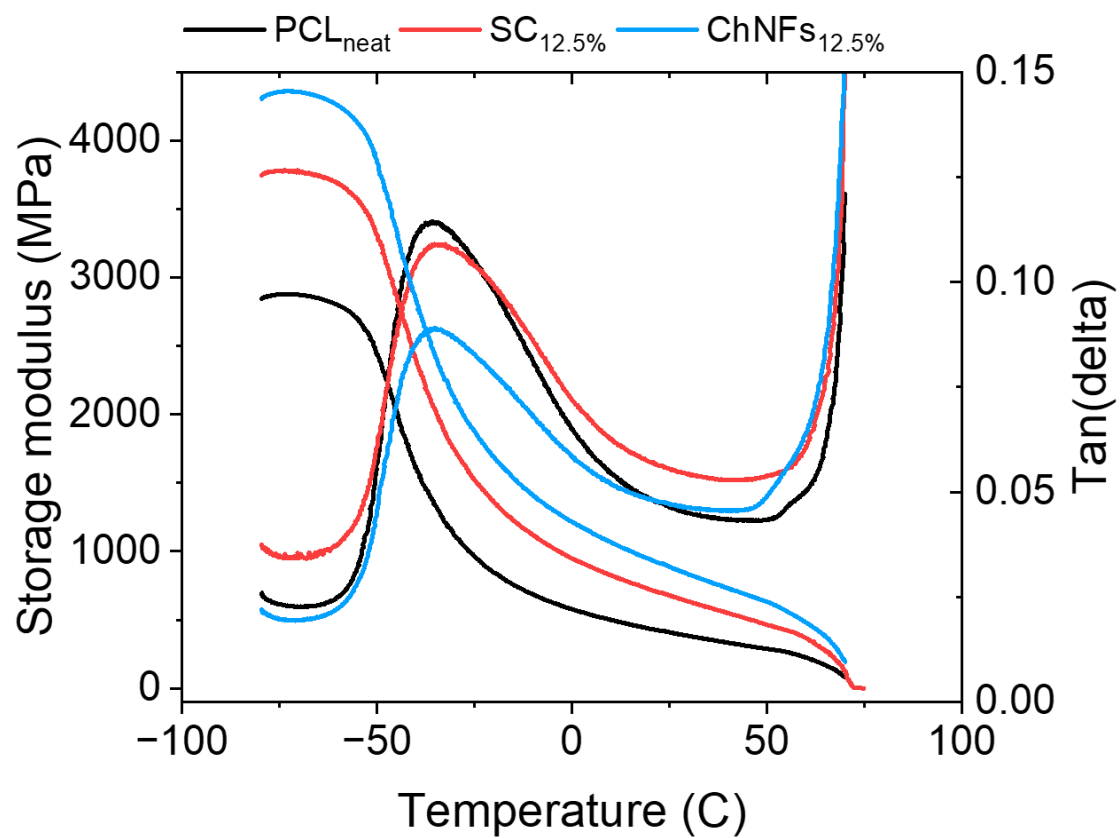
**Figure S33.** Processing conditions: 5%-25rpm-112sec compared to neat PCL.



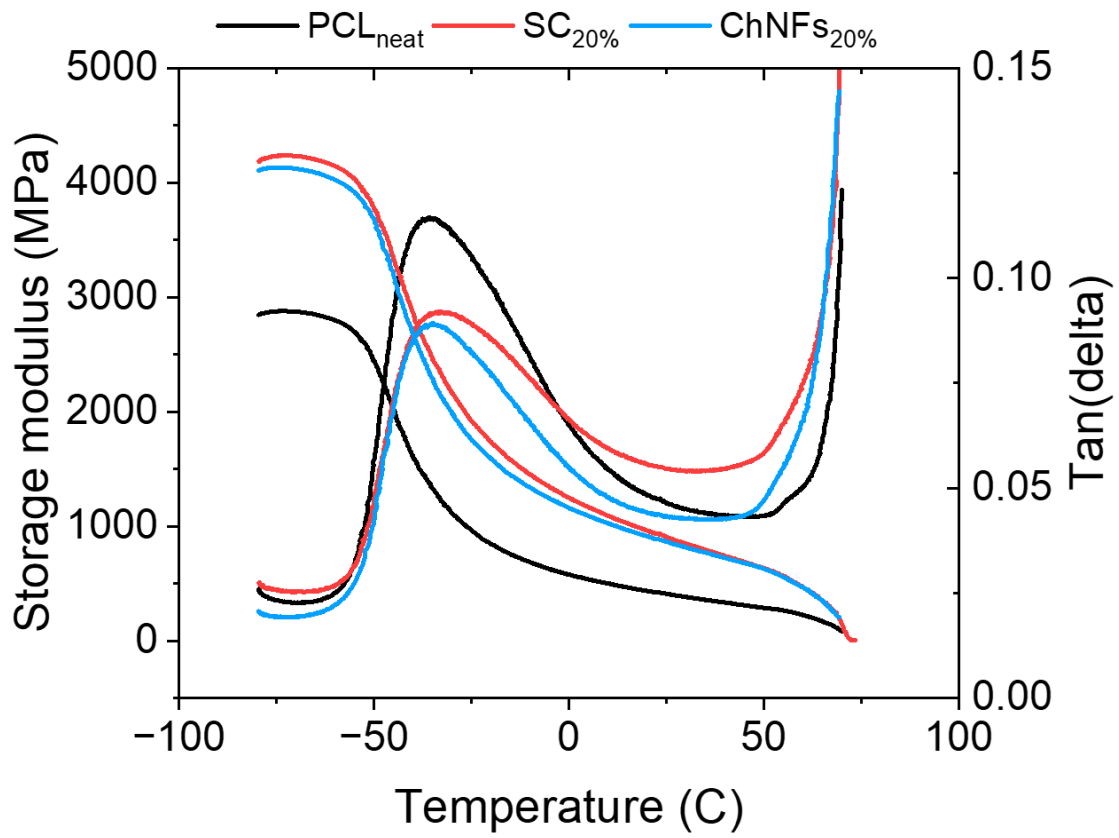
**Figure S34.** Processing conditions: 5%-200rpm-112sec compared to neat PCL.



**Figure S35.** Processing conditions: 12.5%-25rpm-45sec compared to neat PCL.

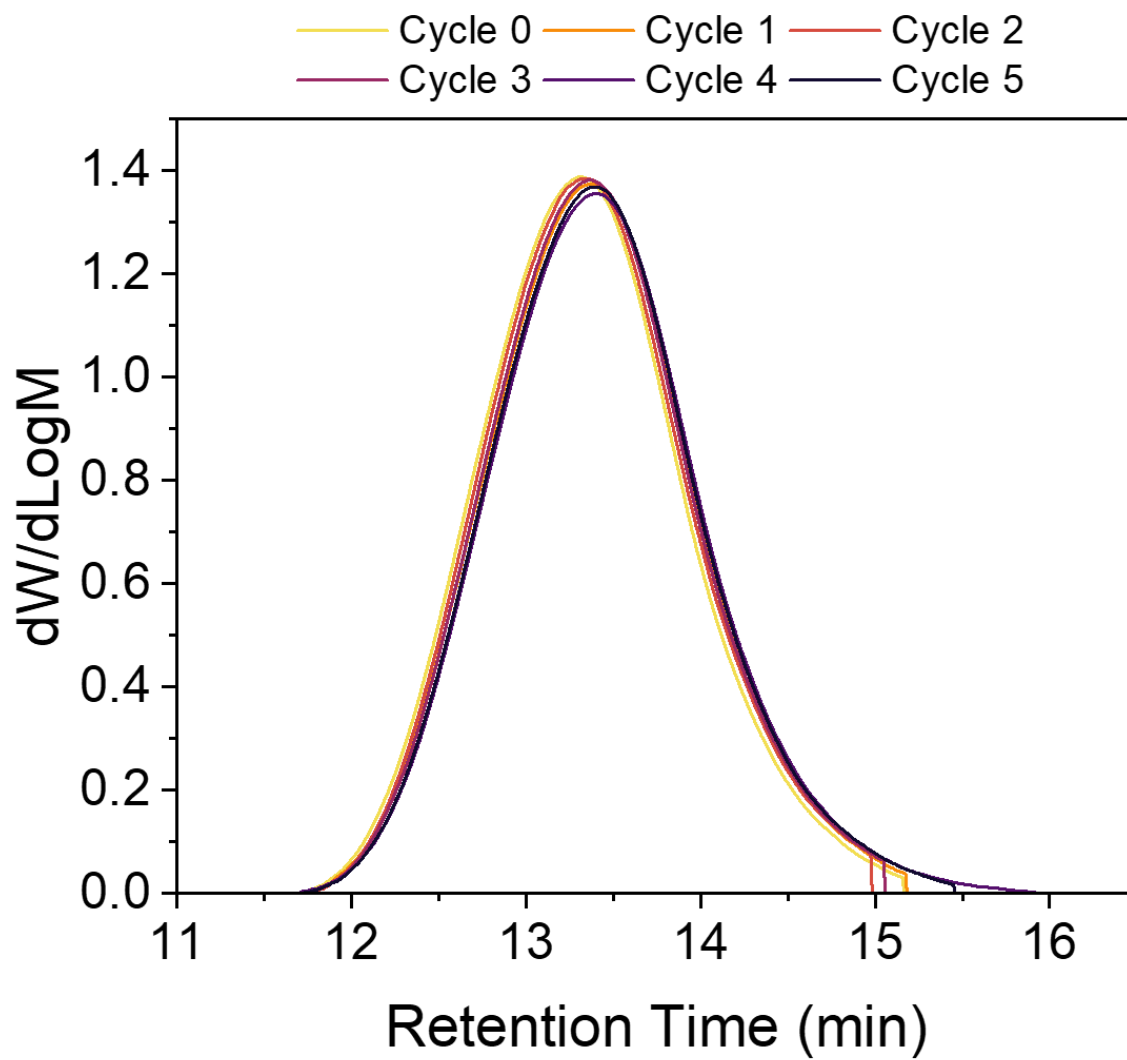


**Figure S36.** Processing conditions: 12.5%-112rpm-112sec compared to neat PCL.



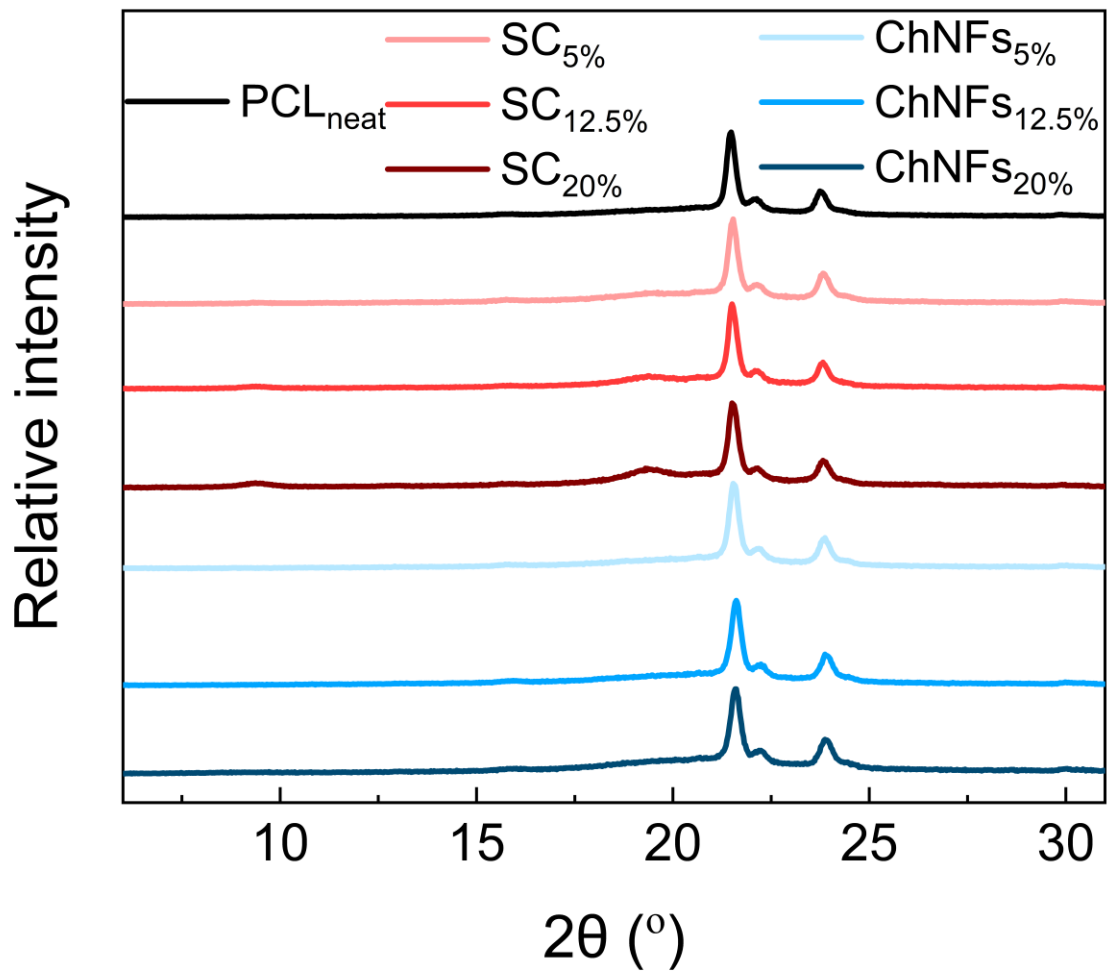
**Figure S37.** Processing conditions: 20%-112rpm-45sec compared to neat PCL.

## GPC Chromatograms

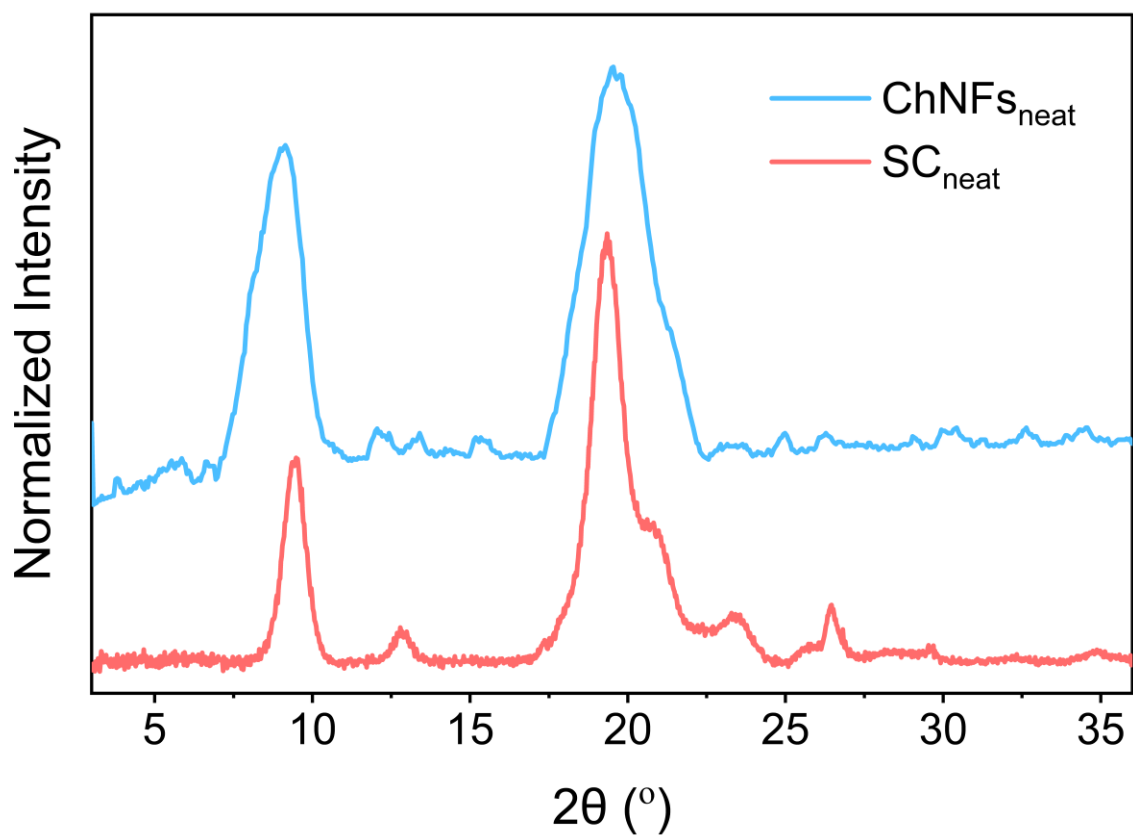


**Figure S38.** GPC chromatograms of neat PCL after multiple extrusion cycles.

## XRD Data

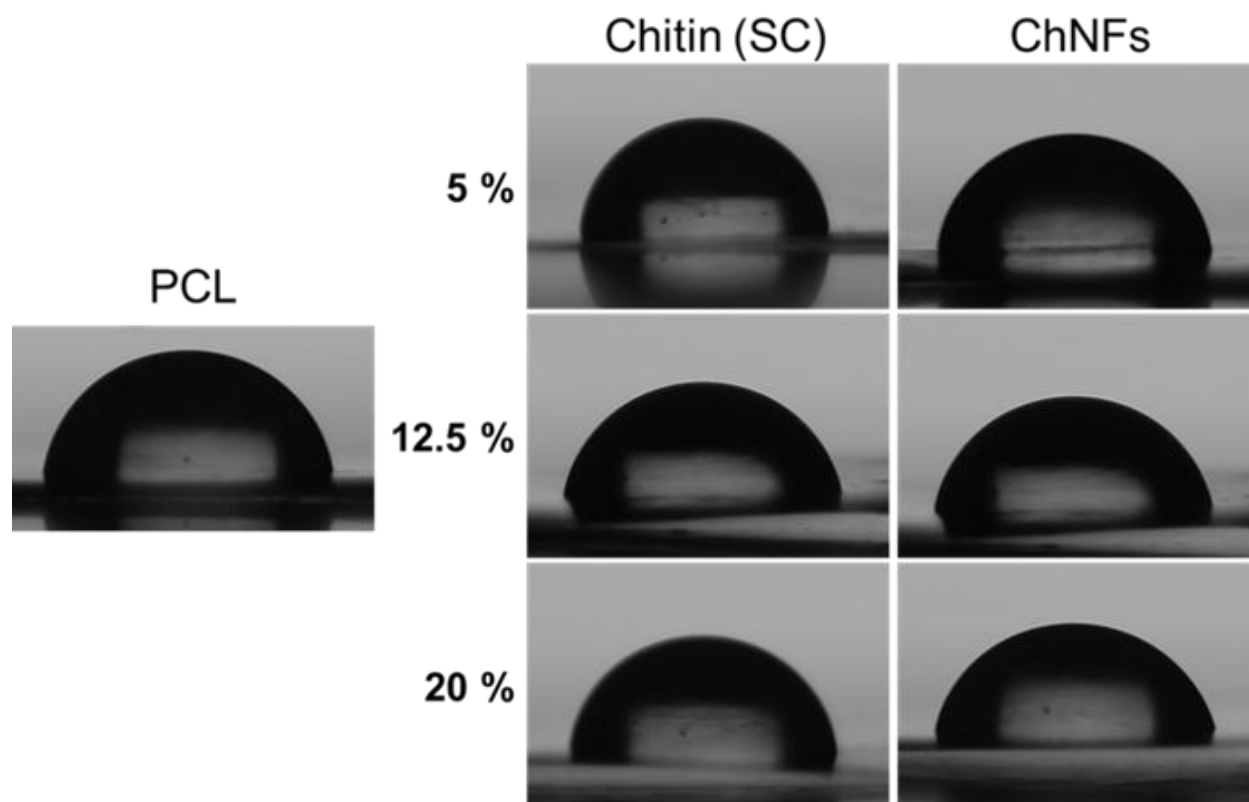


**Figure S39.** XRD patterns of chitin/PCL films.



**Figure S40.** XRD patterns of neat SC and Chitin.

## Contact Angle Data



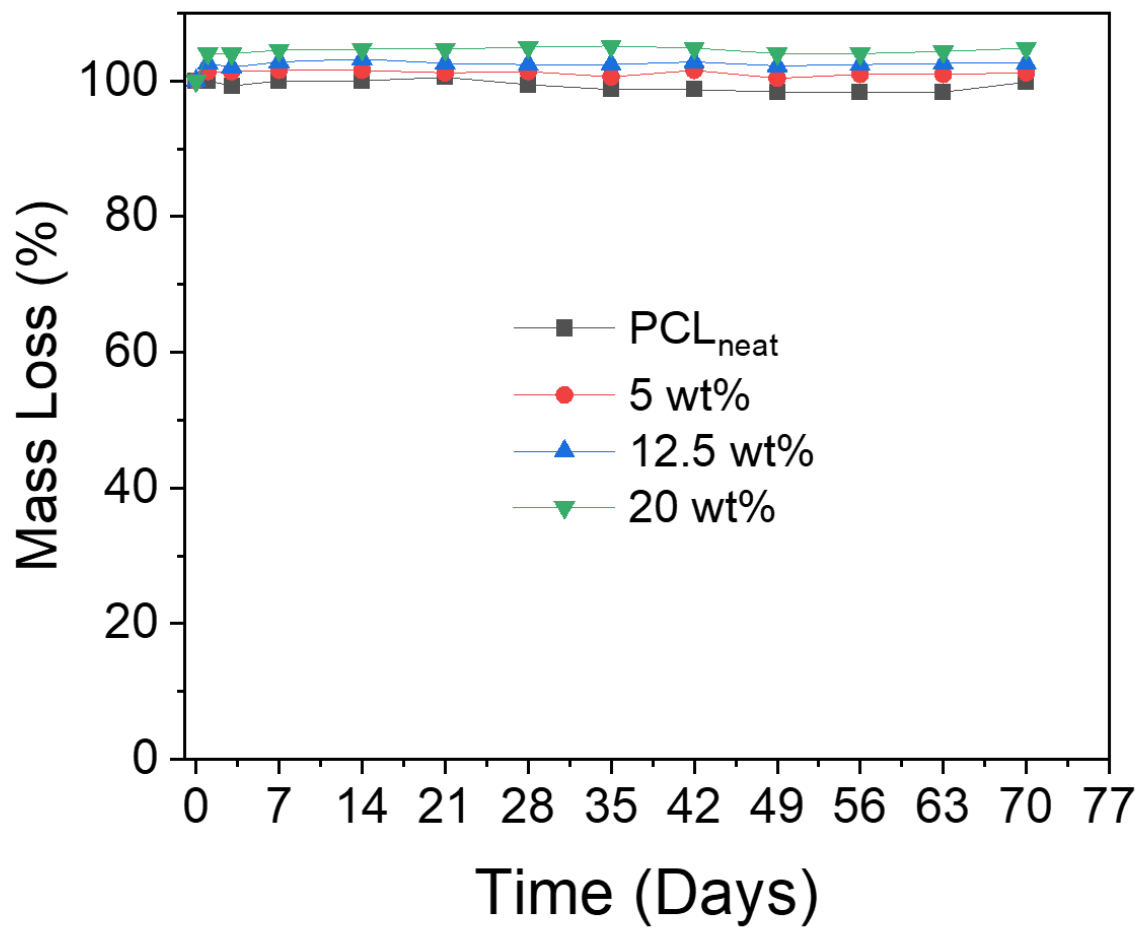
**Figure S41.** Representative optical photographs of a water drop on the surface of chitin/PCL films.

## Optical Properties

**Table S10.** Color properties of PCL/chitin composite films. Lightness difference ( $\Delta L^*$ ), chroma difference ( $\Delta C^*$ ) and color difference ( $\Delta E^*$ ) are reported relative to the neat PCL film.

<b>Sample</b>	<b><math>\Delta L^*</math></b>	<b><math>\Delta C^*</math></b>	<b><math>\Delta E^*</math></b>
Control (PCL)	$0.0 \pm 0.0$	$0.0 \pm 0.0$	$0.0 \pm 0.0$
SC <sub>5%</sub>	$0.8 \pm 0.9$	$-1.3 \pm 0.5$	$3.2 \pm 0.6$
SC <sub>12.5%</sub>	$0.2 \pm 0.6$	$0.0 \pm 1.4$	$1.3 \pm 0.6$
SC <sub>20%</sub>	$-1.4 \pm 1.0$	$3.5 \pm 1.8$	$3.0 \pm 0.9$
ChNFs <sub>5%</sub>	$-10.3 \pm 2.9$	$17.0 \pm 4.7$	$18.9 \pm 2.7$
ChNFs <sub>12.5%</sub>	$-24.9 \pm 9.2$	$23.4 \pm 6.4$	$35.9 \pm 10.8$
ChNFs <sub>20%</sub>	$-38.6 \pm 10.3$	$30.2 \pm 2.4$	$49.4 \pm 8.3$

## Degradation Studies



**Figure S42.** Degradation of SC composite in 1M HCl

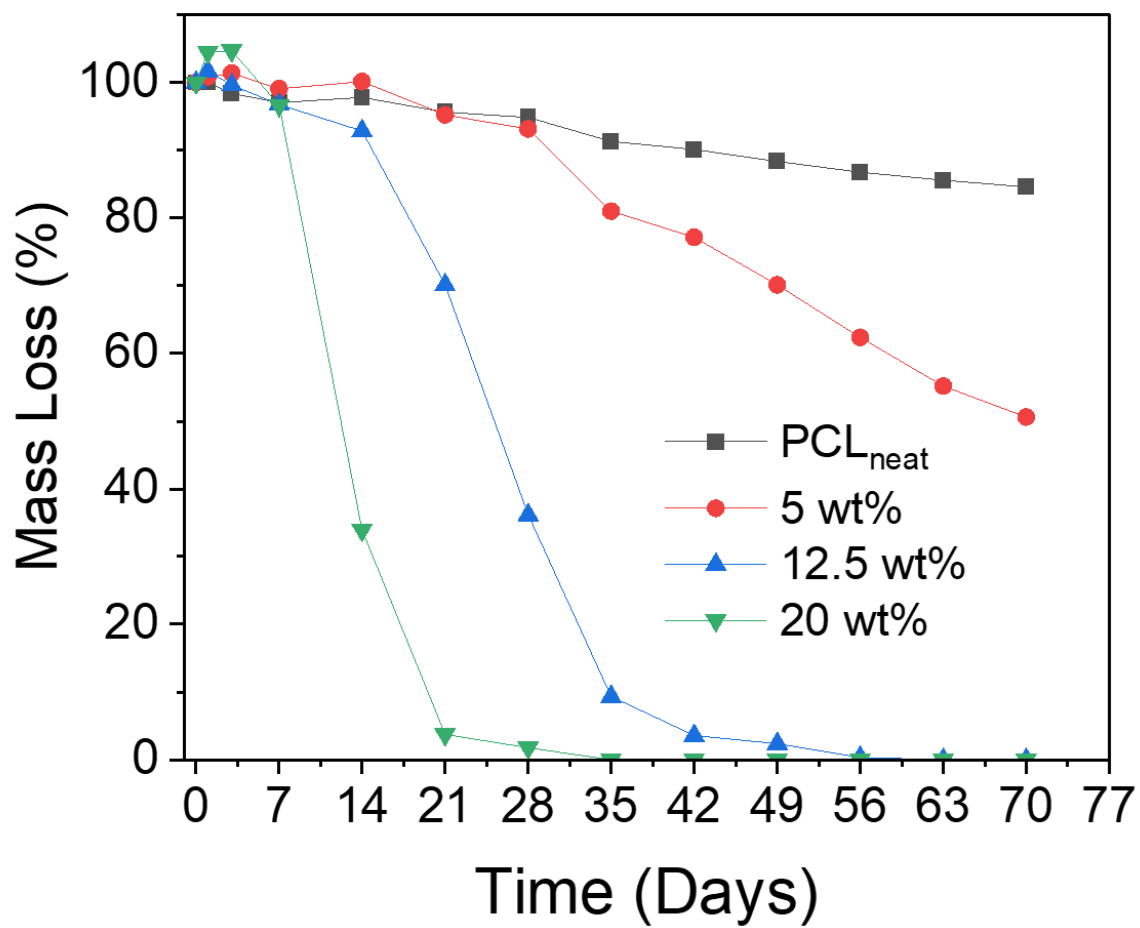
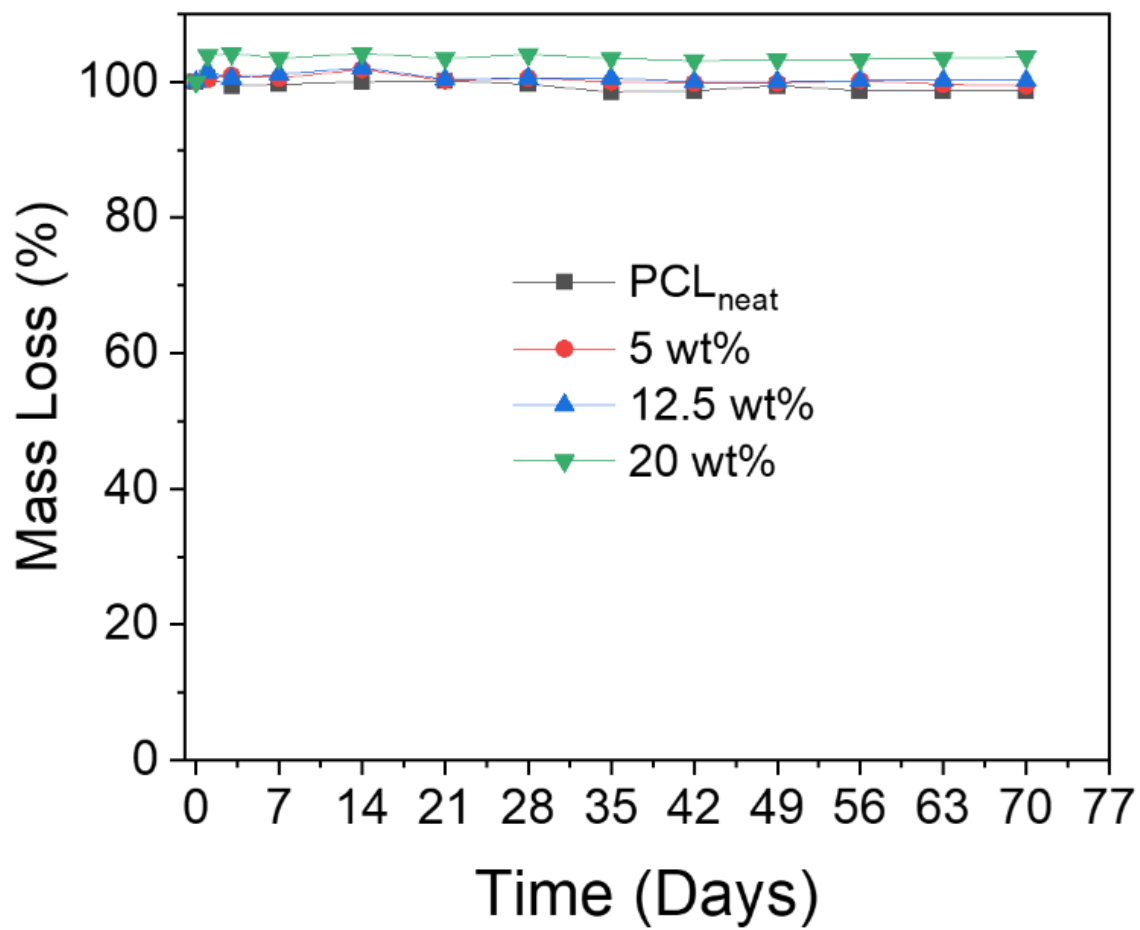
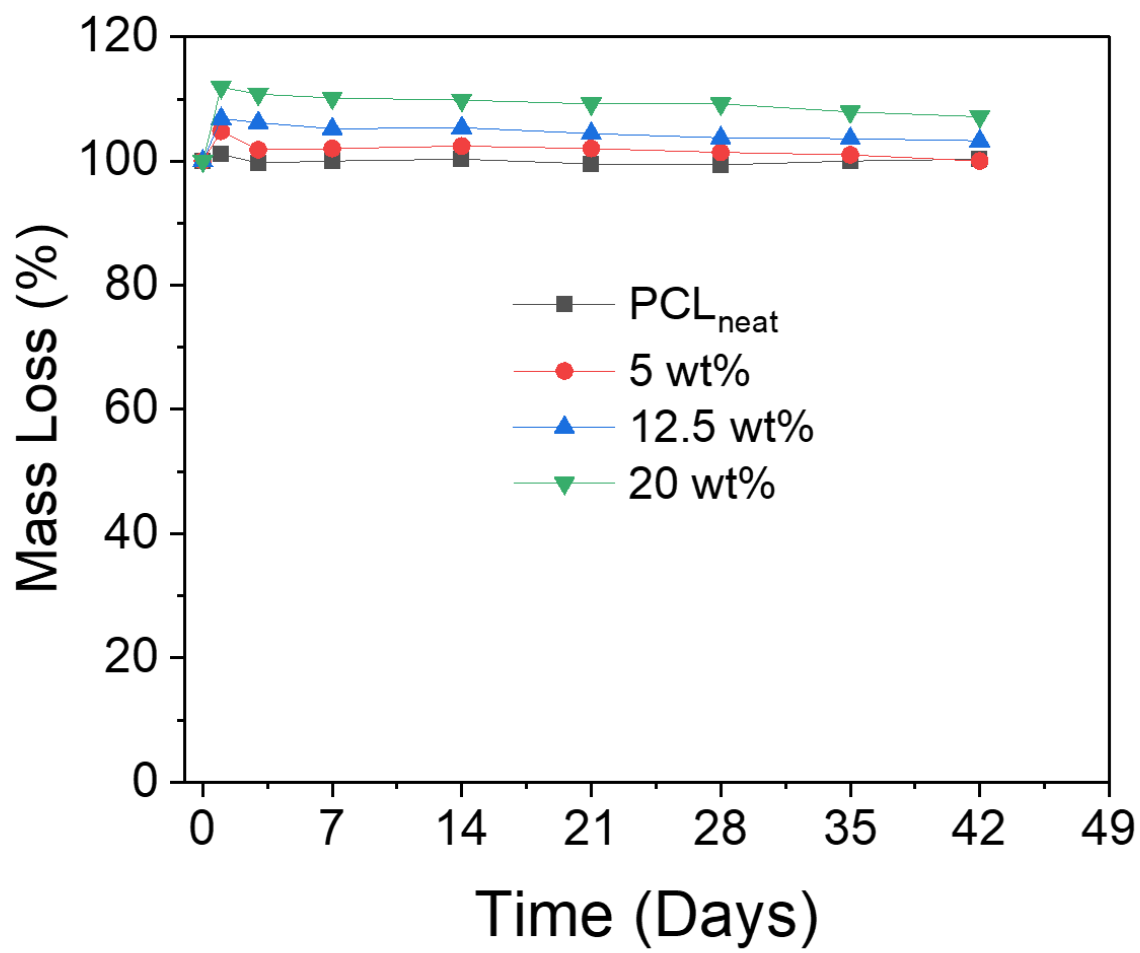


Figure S43. Degradation of SC composite in 1M NaOH



**Figure S44.** Degradation of SC composite in PBS



**Figure S45.** Degradation of ChNFs composite in 1M HCl

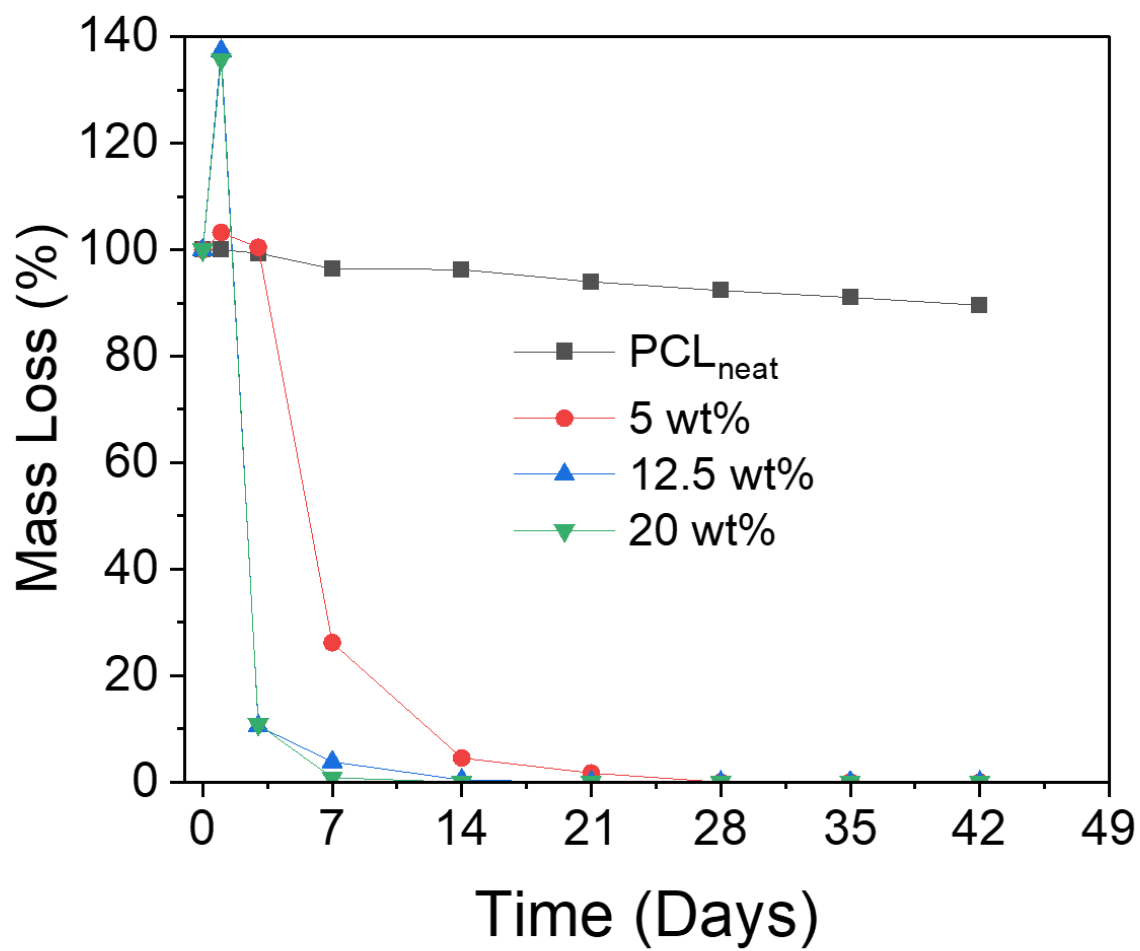


Figure S46. Degradation of ChNFs composite in 1M NaOH

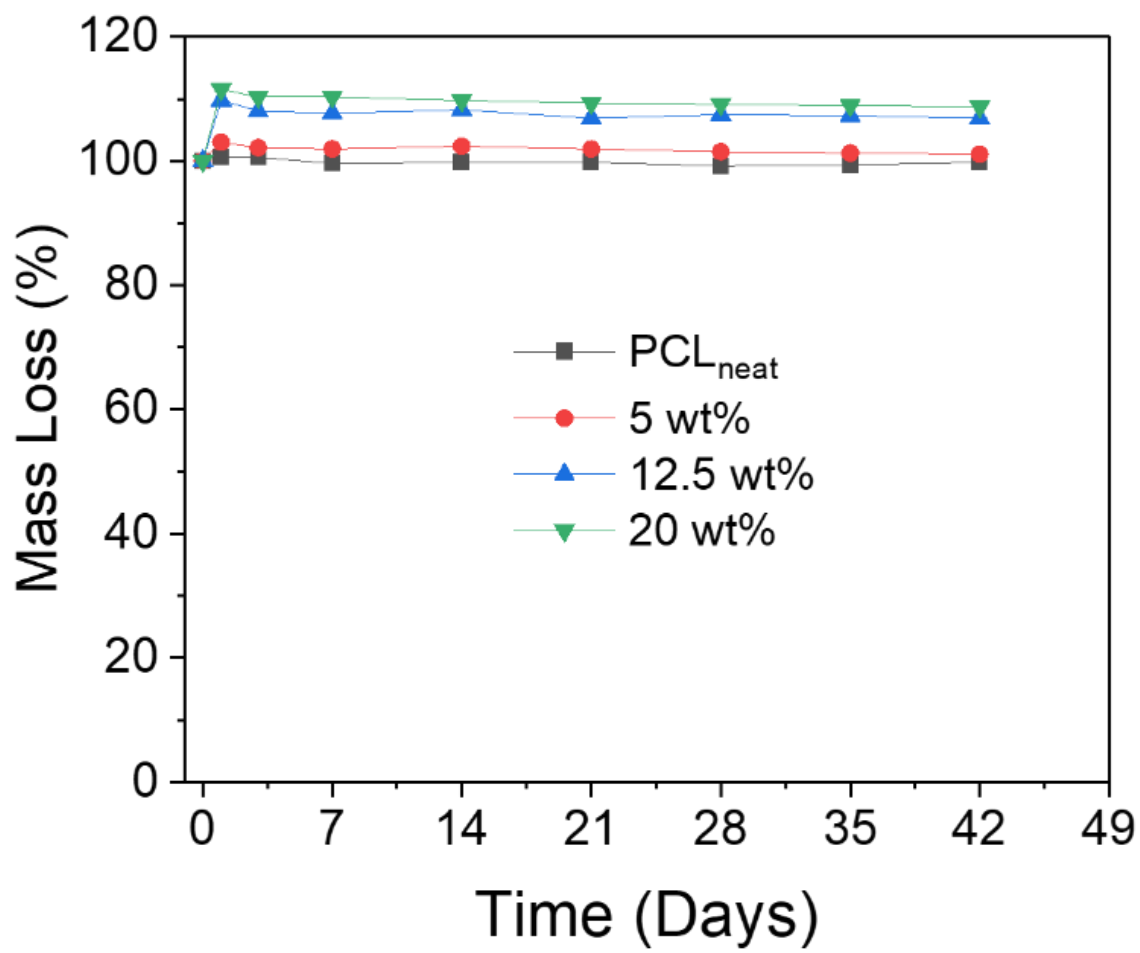
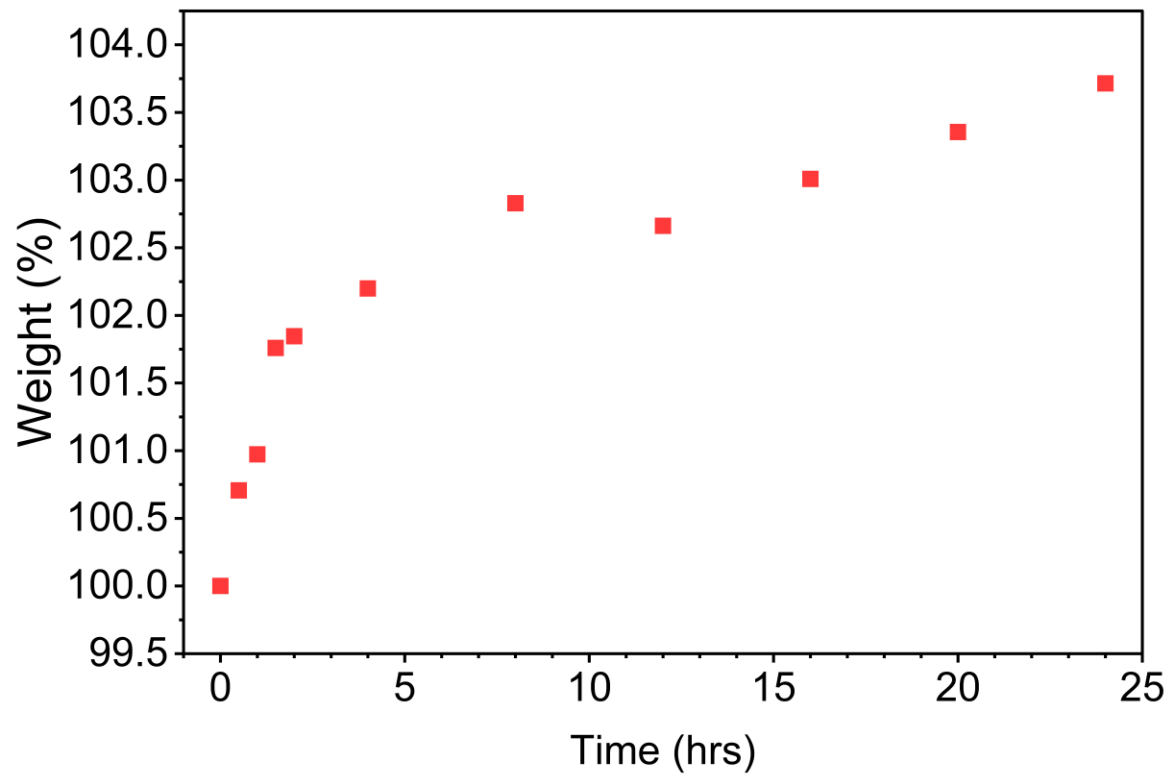
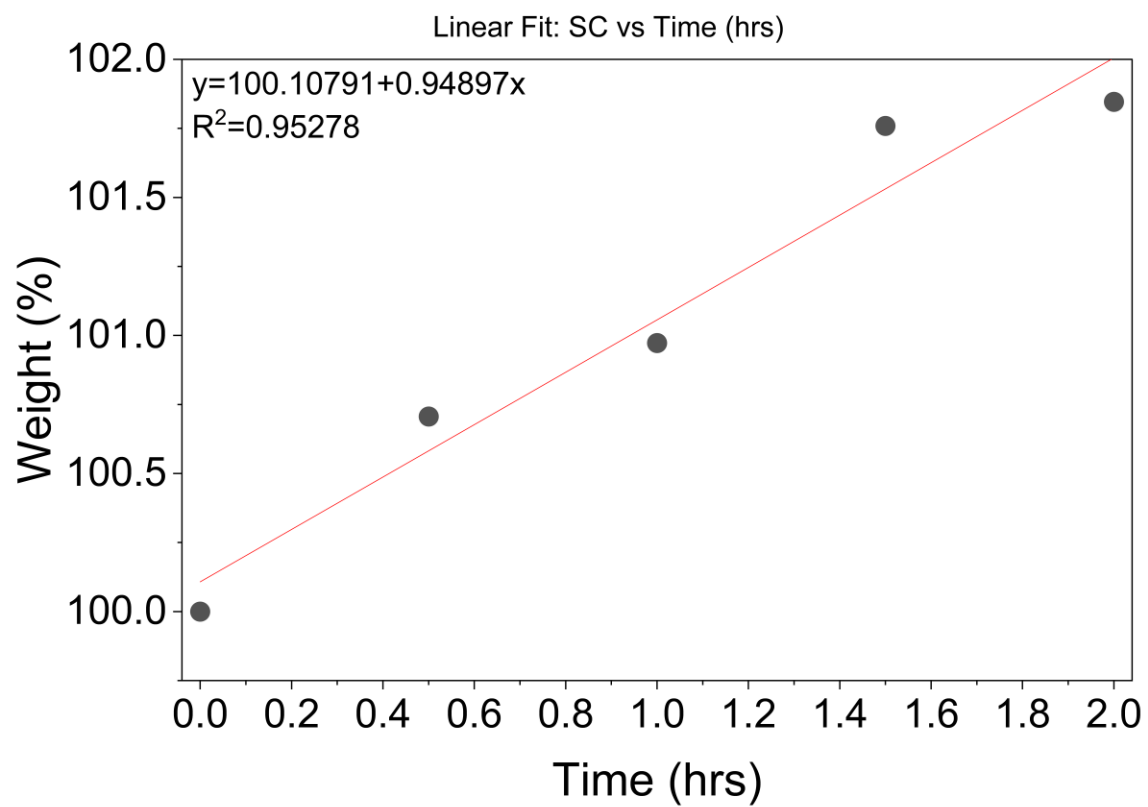


Figure S47. Degradation of ChNFs composite in PBS

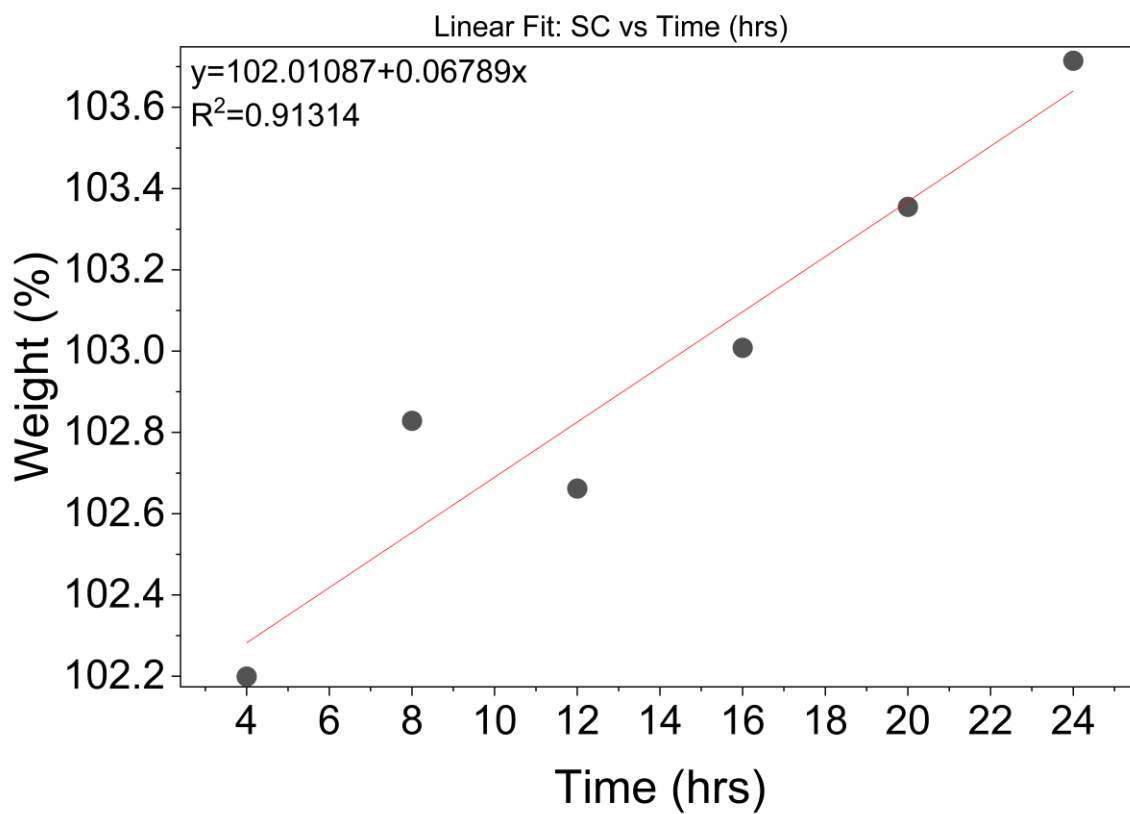
## Swelling Studies



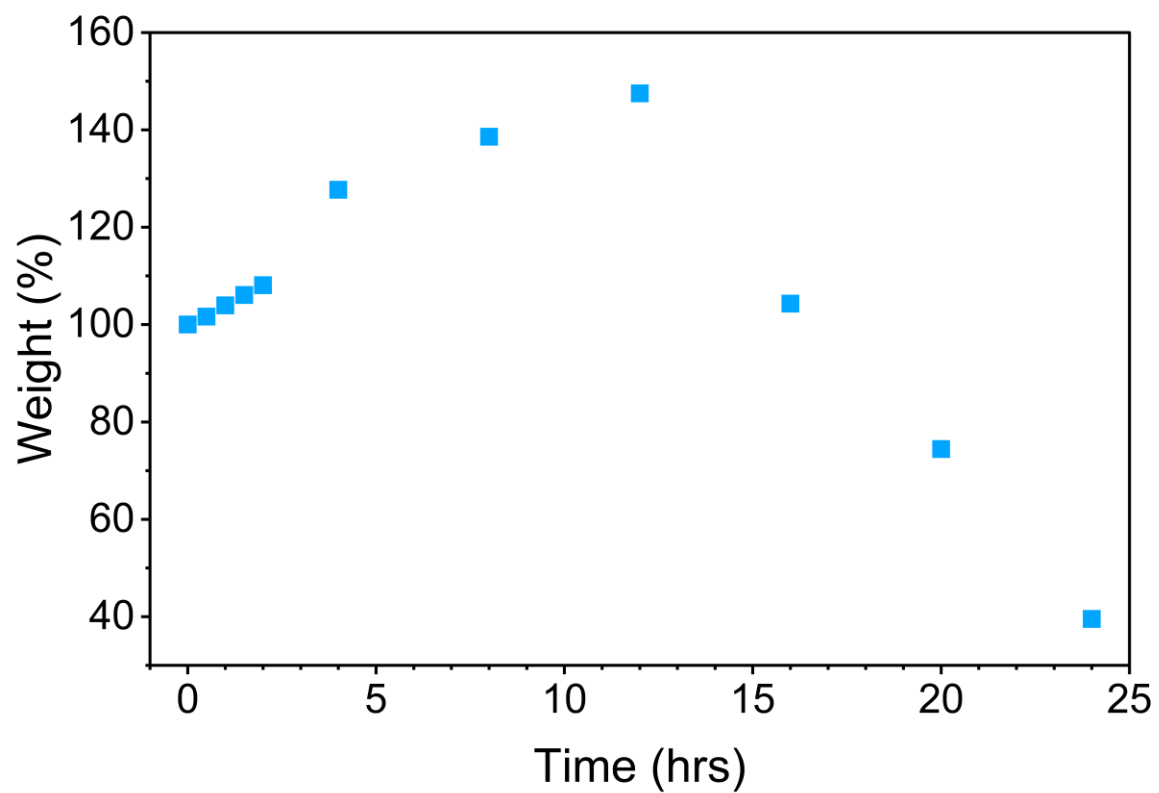
**Figure S48.** 24hr swelling study for SC<sub>12.5%</sub> in 1M NaOH



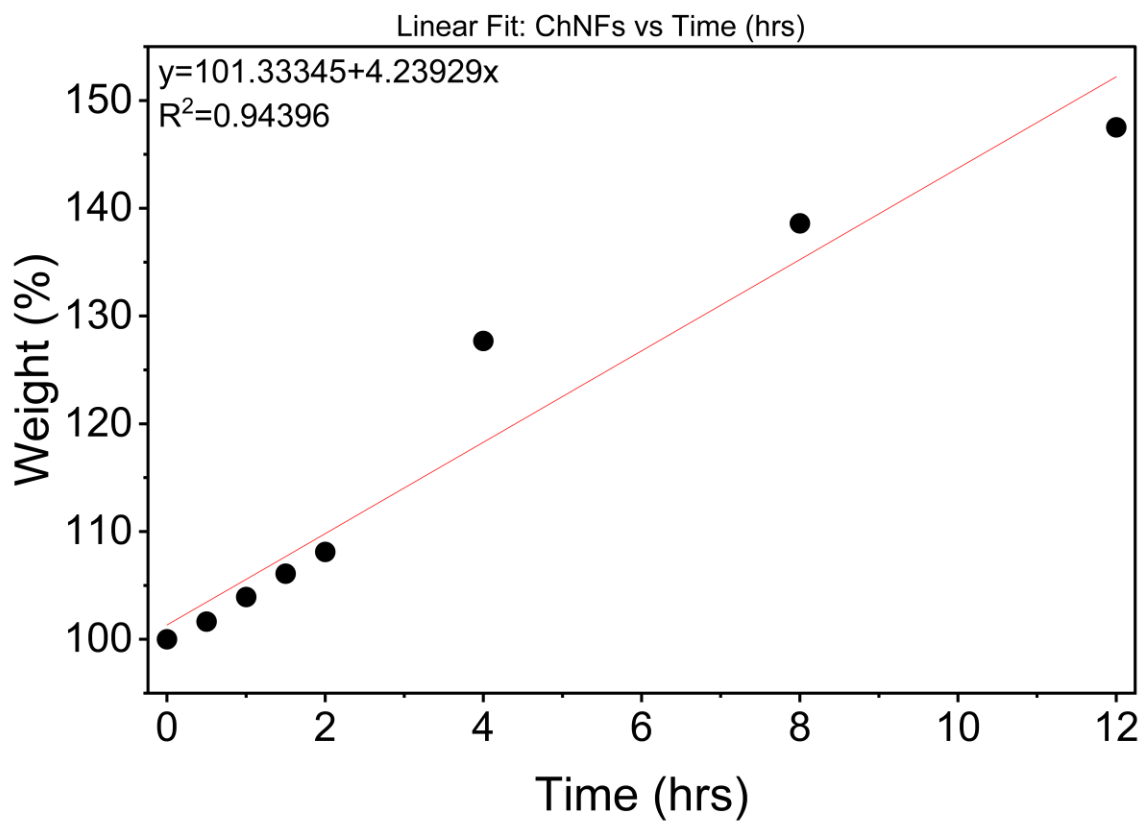
**Figure S49.** 24hr swelling study for SC<sub>12.5%</sub> in 1M NaOH Linear Fit from 0-2 hrs.



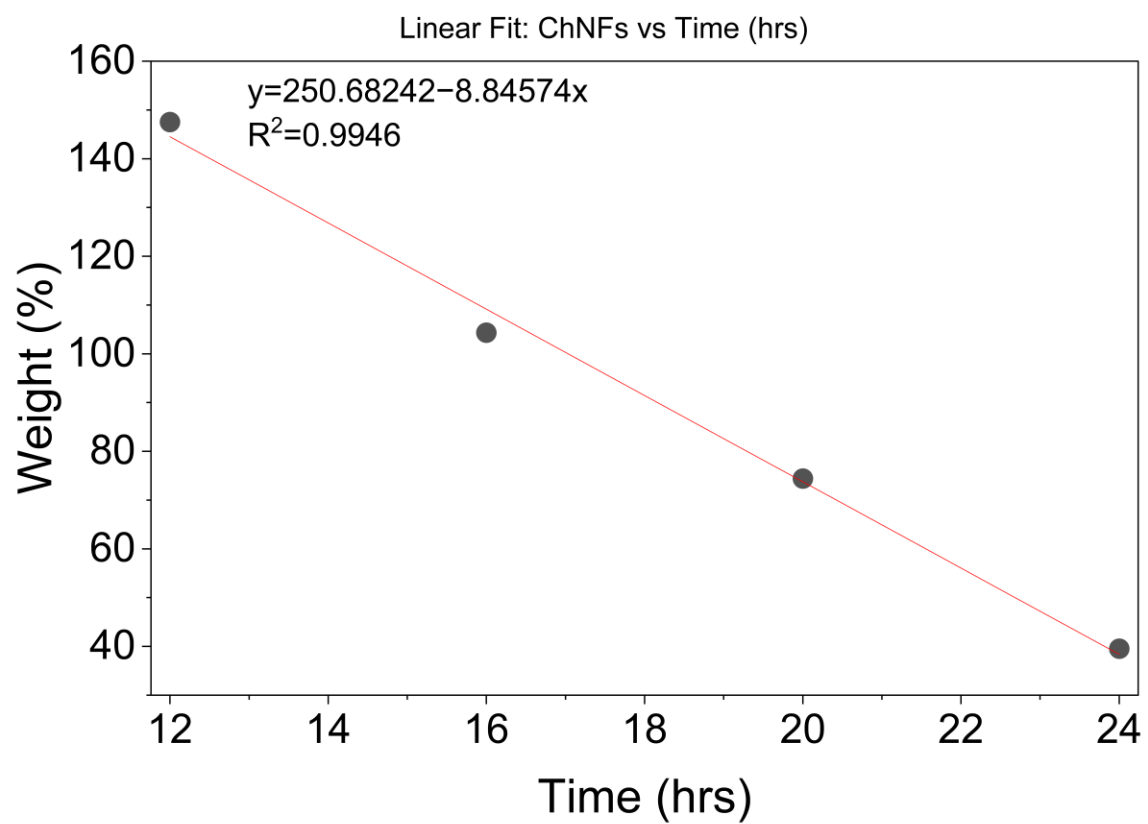
**Figure S50.** 24hr swelling study for SC<sub>12.5</sub> in 1M NaOH Linear Fit from 4-24 hrs.



**Figure S51.** 24hr swelling study for ChNFs<sub>12.5%</sub> in 1M NaOH



**Figure S52.** 24hr swelling study for ChNFs<sub>12.5%</sub> in 1M NaOH Linear Fit from 0-12 hrs.



**Figure S53.** 24hr swelling study for ChNFs<sub>12.5%</sub> in 1M NaOH Linear Fit