Supporting Information

A Closed-Loop and Sustainable Approach for the Fabrication of Plastic-Free Oil- and Water-Resistant Paper Products

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Experimental

1. Materials.

Polydimethylsiloxane (PDMS) monoaminopropyl-terminated (M_w = 2000 g/mol, PDMS-2K) was purchased from Gelest, Inc. and used without further purification.   Chitosan (M_w = 50,000-190,000 g/mol) and acetone (99.7%) were purchased from Sigma.   Hexamethylene diisocyanate trimer (HDIT) was purchased from a local Sherwin-Williams store in Detroit Michigan, United States of America. An unbleached Kraft paperboard with a basis weight of 147 g/m^2 (grammage) was selected as a paper substrate for coating.

2. Methods and Characterization

2.1. General procedure for Model Reactions

Model reactions between HDI and ethanolamine (HOEtNH$_2$) and ethanol were performed in order to prove the reaction between amino group (–NH$_2$) and the NCO in an aqueous acidic medium.

Ethanolamine was chosen as a model substrate because of the presence of $-NH_2$ groups like chitosan, while ethanol was applied as the corresponding control. First, $HOEtNH_2$ (1.0 Equvi., 0.42 mL) was dissolved in water at 2wt% to simulate our chitosan solution concentration. Acetic acid was added to achieve pH ~5 was achieved. Then HDI (0.3 mL, 0.5 Equiv. of $HOEtNH_2$) was added. After ~1 min, IR was recorded and an additional 0.3 mL (0.5 Equiv. of $HOEtNH_2$ of HDI) was added. IR was again recorded after an additional 1 min stir, followed by the addition of additional 0.02 mL (0.03 Equiv.) to achieve slight excess of HDI. For ^{1}H NMR analysis, model product was obtained by the extraction of crude reaction mixture with ethyl acetate. The separated model product was vacuum dried before ^{1}H NMR in DMSO-d6.

In another experiment, ethanol and HDI were reacted in the same conditions mentioned above for ethanolamine and HDI. Briefly, ethanol (0.4 mL) solution in water-acetic acid (10 mL).   HDI (0.3 Ml, 0.5 Equiv. of ethanol) was added, and IR was recorded after ~1 and 25 min stirring. As there was no significant change in the NCO peak, therefore, stopped in the experiment.

Synthesis of Model PDMS-NCO: $PDMS-NH_2$ (1 mmol) was dissolved in acetone (~20wt/vol). HDI (1.5 mmol, 20wt% in acetone) was added dropwise into the $PDMS-NH_2$ solution. Once all HDI was added, the mixture was stir for 5 min. Then the crude PDMS-NCO was precipitated from 10 times excess acetonritile, and upon centrifugation, pure PDMS-NCO was obtained.

2.1 Paper coating procedure

First, a stock solution of PDMS-NCO was prepared via a literature method,[34, 35] which is briefly described herein. PDMS-NH$_2$ (26.7 w/v% of PDMS-NH$_2$ in acetone, 133.5 mmol/L) was added dropwise into an HDIT solution (13.3 w/v% HDIT in acetone, 661.7 mmol/L) under stirring. The concentration of the prepared PDMS-NCO stock solution was 20 w/v% PDMS-NCO in acetone. A series of PDMS-NCO solutions with various concentrations (25, 50, 100, 200 and 400% w/v) was prepared by mixing the appropriate volume of PDMS-NCO stock solution with acetone.

Chitosan stock solution was prepared by dissolving 4.0 g of chitosan in 100 mL water in the presence of 2.0% (v/v) acetic acid, and subsequently stirring this solution for 24 h. The concentration of the final chitosan solution was adjusted by adding 3.5 mL of deionized water into 2.5 mL of the chitosan stock solution. Thus, the obtained solution contained 100 mg of chitosan per 6.0 mL of solution, thus having a concentration of 1.67 wt%.

The chitosan-g-PDMS solution was prepared via the dropwise addition of the PDMS-NCO solution into the chitosan solution. Once the addition was completed, the solutions were further stirred for 5 min and the NCO consumption was monitored by ATR-FTIR spectroscopy until the NCO peak had disappeared. The residual acetone was removed from the solution *via* bubbling with air. The obtained water-borne chitosan-g-PDMS solutions containing various amounts of PDMS (12.5, 25.0, 50.0, 100 and 200 mg) along with 100 mg of chitosan (see Table 1). For NMR analysis, the Chitosan-g-PDMS was dried at reduced pressure.

The above chitosan-g-PDMS coating solutions were applied onto one side of an unbleached Kraft linerboard using a K303 Multi Coater (RK PrintCoat Instruments Ltd, UK), and they were subsequently dried in air at room temperature for 24 h. All of the samples were preconditioned at 23 °C and at 50% relative humidity (RH) for 24 h prior to performance analysis.

Table 1 Formulations and corresponding codes used in this article

Abbreviated name	PDMS-NCO (mg)	Chitosan (mg)
U-p[a]	-	-
C-p[b]	-	100
P0.125C-p[c]	12.5	100
P0.25C-p	25	100
P0.5C-p	50	100
P1C-p	100	100
P2C-p	200	100

[a]Unmodified paper (U-p); [b]chitosan-coated (C-p), [c]P0.125C-p (P denotes PDMS, 0.125C denotes the weight of the PDMS with respect to the weight of chitosan, which is expressed as C

2.2 Characterization

2.2.1 Dynamic light scattering (DLS) analysis. DLS characterization was employed to determine the average hydrodynamic diameter of the chitosan-*g*-PDMS micelles. The chitosan-*g*-PDMS coating solutions or chitosan solution (0.5 mL) were added into 50 mL of DI water and subsequently vortexed for ~1 min and then centrifuged at 5000 rpm for 5 min. The solution was subsequently analyzed using a Light Scattering Analytical Instrument (BI-200SM, Brookhaven Instrument, US).

2.2.2 Basis weight and thickness. The basis weights (mass per unit area of paper) of chitosan-*g*-PDMS-coated paper (PC-p), chitosan-coated (C-p) paper, and unmodified paper (U-p) were measured in accordance with the ASTM D646 protocol. Specimens with dimensions of 200 × 200 mm² were weighed with a microbalance. The basis weight was calculated via Eq. 1, and

expressed in grams per square meter (g/m^2, grammage). Measurements were performed in triplicate for each type of paper material. Coating loadings were calculated based on the difference between the coated paper and the unmodified paper. The thickness of each sample was measured using a digital micrometer (Testing Machine Inc., New Castle, DE, USA) at ten different random locations on the same specimen.

$$basis\ weight = \frac{weight\ (g)}{area\ (m^2)} \ \text{(Eq. 1)}$$

2.2.3 Water vapor transmittance rate (WVTR) and water absorption capacity (Cobb60 value). The WVTR values of PC-p, C-p, and U-p were determined using a Permatran-W (Model 3/34, Mocon Inc. MN, USA) system. These measurements were performed at 23 °C and at 50% RH with nitrogen as the carrier gas (flow rate = 12 SCCM). Specimens with dimensions of 20 × 20 mm^2 were masked in aluminum sheets with a 6-mm-diameter opening to fit the sample cell.

Water absorptions of PC-p, C-p, and U-p were determined according to their Cobb values via a TAPPI standard T441 om-09 protocol. A Cobb sizing tester (Büchel BV Inc. Utrecht, Netherlands) was employed to allow 100 mL of DI water to come into contact with a 100-cm^2 specimen for 60 s. The weight of the absorbed water was calculated as the difference in the weight of each specimen before and after the test. The Cobb60 value was expressed as the weight of water absorbed by the specimen in grams per square meter (g/m^2).

2.2.4 Grease-resistance properties. The grease resistance was studied in accordance with a previous study and via a TAPPI T 559 pm-96 standard method.[35] The oil-resistance was quantified and scaled from 1-12 based on their "kit rating" values, where the kit-rating corresponded to the maximum oil resistance.

2.2.5 Contact angle (CA), sliding angle, and surface energy measurements. The CAs of water and castor oil were measured with a 590-U1 Advanced Automated Goniometer (Ramé-Hart Instrument Co., NJ, USA). Droplets with a volume of 5 μL were carefully applied onto the surface of a specimen, and the CAs were then measured and images were taken after 30 s and 5 min. These measurements were performed in triplicate on three random locations of each sample.

Sliding angles were determined by adding a 100 μL droplet of the test liquid onto the surface of each coated paper specimen, which was affixed onto a wood plate. The angle of this wood plate with respect to the horizontal plane was then increased at a constant rate (2 °/s) until the water droplets began to slide. The angle of the wood plate at this point was recorded as the sliding angle of the specimen.

The surface tensions of coated and uncoated paper samples were determined with the use of DROPimage Advanced software (Ramé-Hart Instrument Co., NJ, USA) based on the CAs of water and diiodomethane.

2.2.6 IR analysis. A Shimadzu FT-IR spectrometer IR-Prestige21 (Shimadzu Co., Columbia, MD) equipped with an attenuated-total-reflection accessory (ATR, PIKE Technologies, Madison, WI) was employed to record IR spectra of PC-p, C-p, and U-p. Each spectrum was obtained with an average of 64 scans over a wavenumber range of 4000-600 cm^{-1} with a resolution of 4 cm^{-1}.

2.2.7 Thermogravimetric analysis (TGA). TGA measurements of PC-p, C-p, and U-p samples were performed using a Q-50 thermogravimetric analyzer (TA Instruments, New Castle, DE). Samples (6-10 mg) were heated under a nitrogen atmosphere (flow rate = 40 mL/min) from

23 to 600 °C at a rate of 10 °C/min. Derivative thermogravimetric (DTG) curves were plotted as first derivatives of the corresponding TGA curves.

2.2.8 Scanning electron microscopy (SEM). The surface morphologies of the PC-p, C-p, and U-p samples were observed using a JEOL 6610 SEM (JEOL Ltd., Japan) system. The SEM instrument was operated at an accelerating voltage of 15 kV. Samples were affixed on aluminum stubs with a carbon double-sided tape and they were subsequently coated with a gold layer (15 nm thick) with the use of a sputter coating machine.

2.2.9 NMR characterization

^{1}H NMR analysis was conducted using a 500 MHz NMR spectrometer (Agilent, Santa Clara, CA, USA).

2.3 Recyclability

The recyclability of chitosan-*g*-PDMS-coated paper (PC-p) was studied using a repulping approach. Paper samples (P1C-p) with a weight of 3.0 g were chopped into 2 cm by 2 cm sections and soaked in warm water (~40 °C) for 30 min, and then the soaked paper samples were repulped using a blender. Half of the pulp suspension was made into paper by sequentially pouring this suspension onto the screen of a wood frame to allow filtration to occur, subsequently pressing it with an iron, and then drying the sample at 56 ℃ under vacuum for 1 h. The other half of the pulp was centrifuged and the supernatant was removed after this centrifugation treatment. Freshwater was added again and the sample was then centrifuged and the supernatant was removed again. This step was repeated one more time. The obtained pulp was used to fabricate paper again via the procedure described above. Paper made from the washed and unwashed pulp was analyzed via FT-IR-ATR spectroscopy by monitoring the disappearance of peaks corresponding to PDMS,

which would indicate the presence or absence of the coating. Unmodified-paper (U-p) was recycled in a similar manner as the control samples.

2.4 Mechanical property tests

Bleached Kraft paper samples were coated with chitosan, P0.25C, and P0.5C polymers to study the effect of these coatings on the mechanical properties. Each test was performed in triplicate and in both the cross machine direction (CD) and machine direction (MD).

The tensile strength was studied following a TAPPI standard T 494 protocol using a 5565 Universal Instron testing machine (Instron, MA, USA). A specimen (1" × 11") was loaded on two clamps, where the gap between the clamps was 7.1". The specimen was stretched at a constant rate (0.5 in/min). A plot of the force versus extension was recorded with the use of the Bluehill software package (Instron, MA, USA). Tensile strengths were calculated as the maximum tensile force divided by the width of the specimen.

The ring crush test (RCT) was performed using a TMI crush tester (Model 1210, Instron, MA, USA) following the TAPPI T822 protocol. RCT represents the compression strength of paper board when it stands on its edge, and therefore affects the edgewise compression strength of corrugated board and of a finished container made from this paperboard. Samples were cut into 0.5 inch by 6 inch sections using a standard sample cutter, and carefully slid into a sample holder so that these samples could stand on their edges. Force was applied on the edge of the paperboard, and the amount of force required to crush the sample was then recorded.

The bending stiffness (BS) was studied using a Taber stiffness tester (Model 150-D, Teledyne Taber, NY, USA) following the TAPPI T489 protocol. One end of the specimen (1.5 inches by 2.75 inches) was clamped in the tester, and a force (500 Taber stiffness units) was applied

at the other end to bend the specimen by 15°. The bending stiffness was calculated as the average of left and right readings on the tester.

Internal tearing resistance (ITR) was analyzed following the TAPPI T414 protocol using an ME-1600 Manual Elmendorf-type tearing tester (Oakland Instrument Co, MN, USA). Two piles were loaded for each test and the tearing forces required to tear a single sheet was calculated.
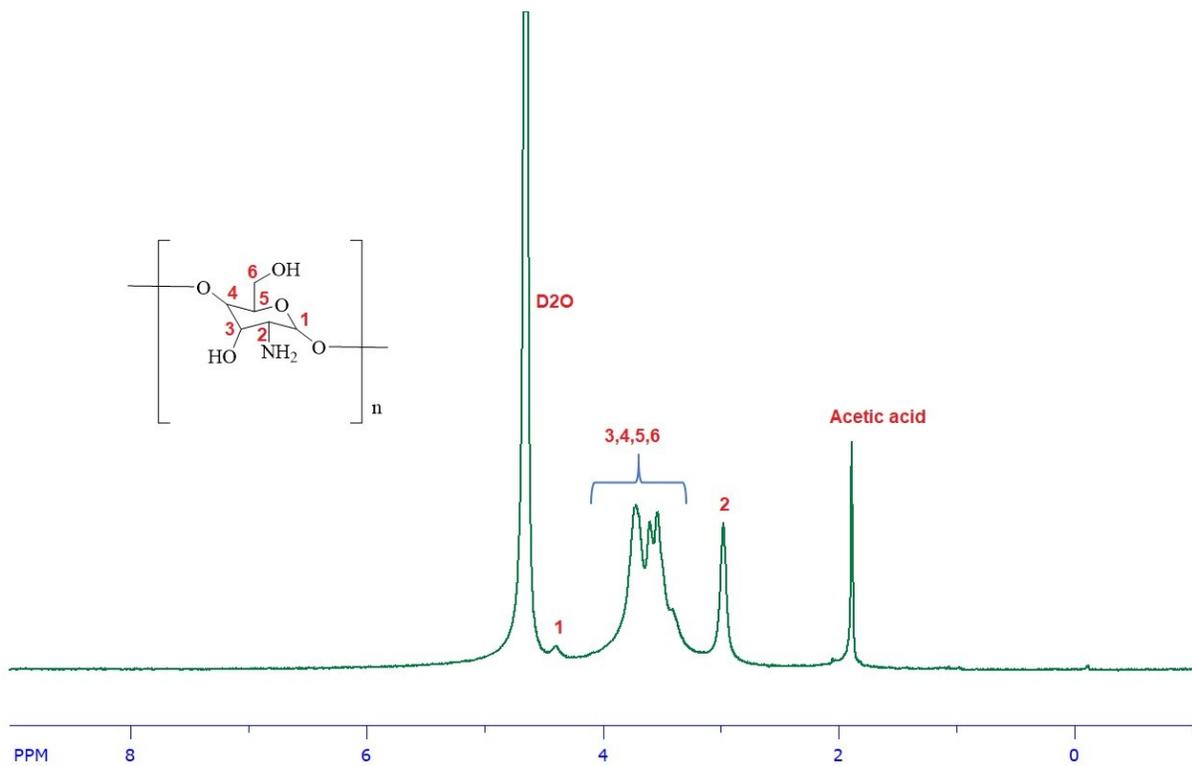
3. Figures

Figure S1: ^{1}H NMR spectra of Chitosan (recorded in D_2O at 2wt% CD_3COOD).
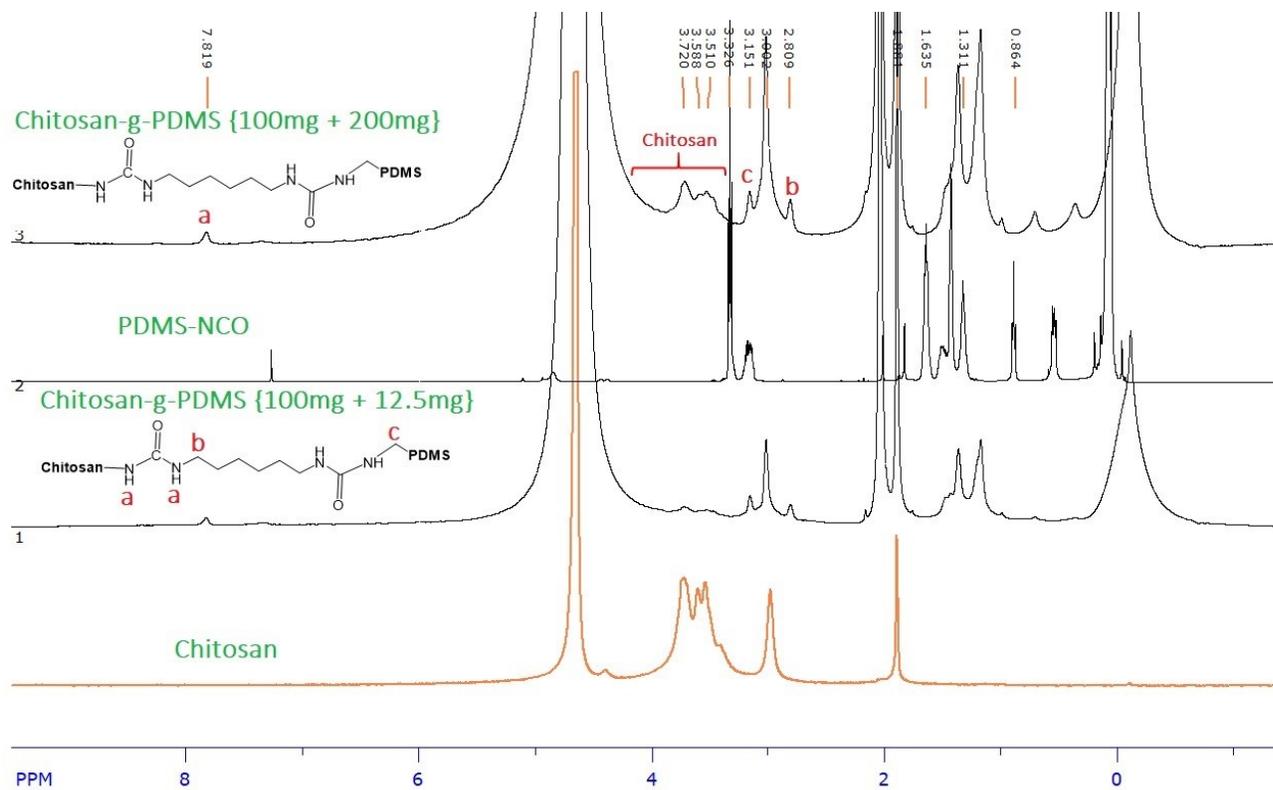
Figure S2: ^{1}H NMR spectra of Chitosan-g-PDMS (after extraction) using D2O with 2wt% CD$_3$COOD.
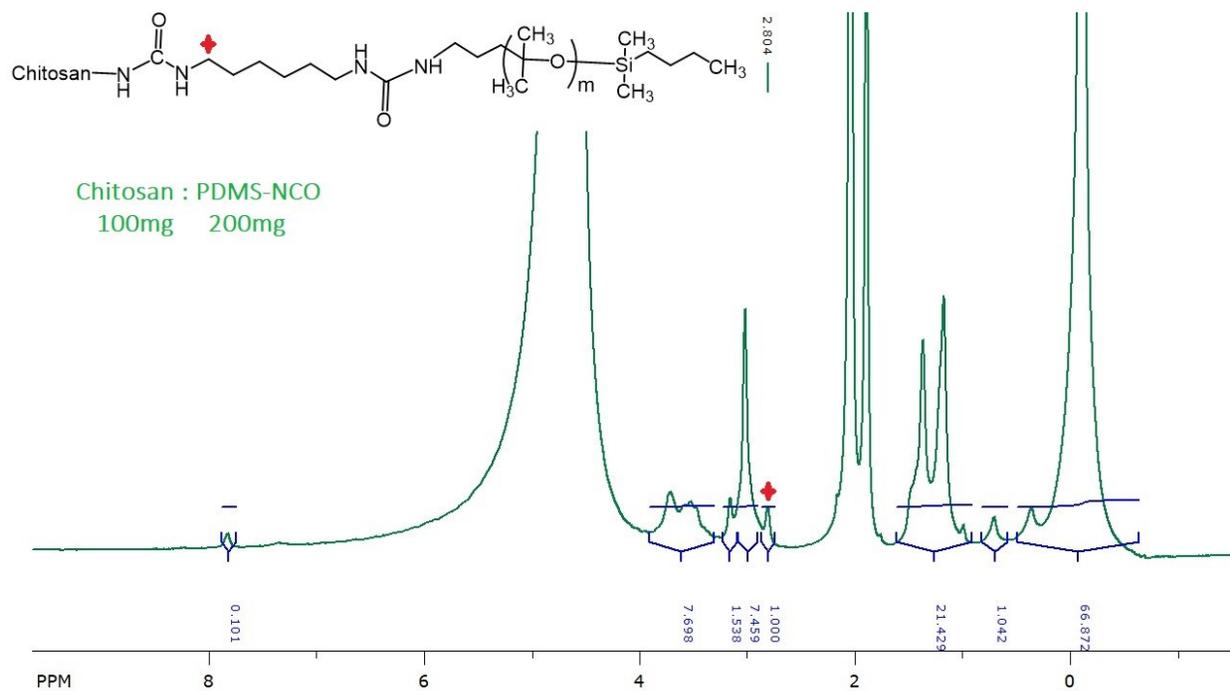
Figure S3: ^{1}H NMR spectra of Chitosan-g-PDMS (after extraction) using D2O with 2wt% CD$_3$COOD.
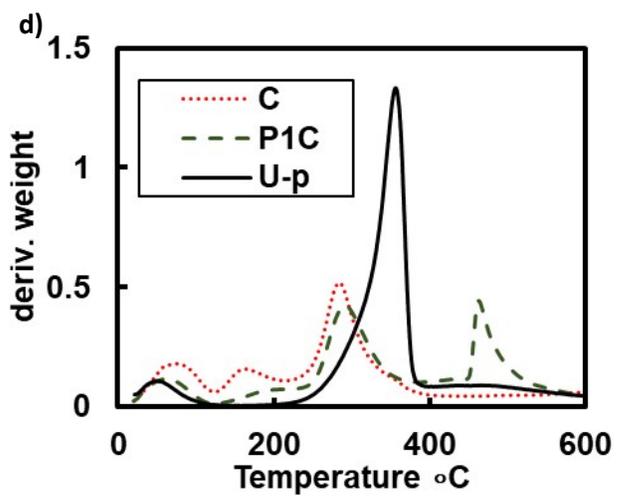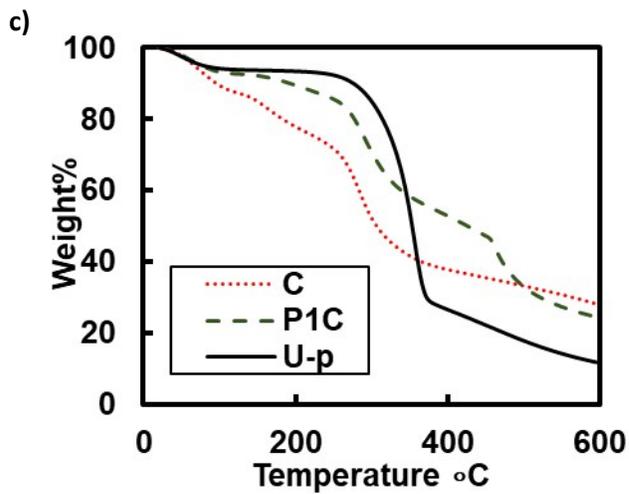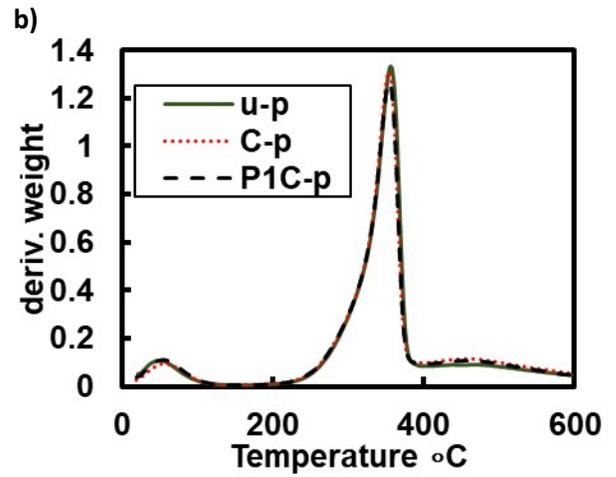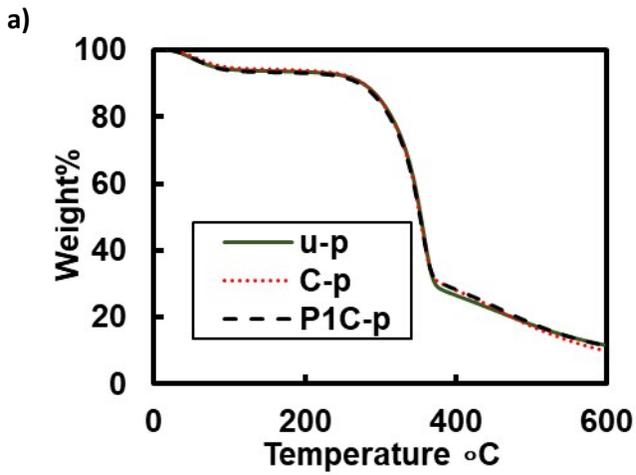
a)

b)

c)

d)

Figure S4. TGA (a) and DTG (b) plots of uncoated paper (U-p) and coated paper (C-p and P1C-p). Also shown are TGA (c) and DTG (d) plots of the chitosan coating (C), P1C coating (P1C), and unmodified paper (U-p)