**Supplementary Materials**

Self-assembled CNF/rGO/Tannin composite: Study of the Physicochemical and Wound Healing Properties

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**1. Materials and Methods**

*1.1 Materials*

Graphite powder (flakes; mesh 325) was purchased from Asbury Online (Asbury Carbons, New Jersey, USA). Dopamine hydrochloride (𝐷𝐴 − 𝐻𝐶𝑙, ≥ 98.0%) was purchased from Sigma-Aldrich Company (St. Louis, MO). The other chemicals and solvents, such as tris(hydroxymethyl)aminomethane (buffer Tris), sulfuric acid (H2SO4, 98%), phosphoric acid (H2PO3, 85%), oxygenated water (H2O2, 60 vol), silver nitrate (AgNO3, 0.1 N), potassium permanganate powder (KMnO4, 99.9%) and hydrochloric acid (HCl, 37% v/v), were purchased from Merck (Darmstadt, Germany). These chemicals were used as received, without further purification. Milli-Q® water and distilled water were used throughout the study. Cellulases Quimizime B was provided by CHT group (Santiago, Chile).

*1.2. Material characterization*

*X-ray diffraction (XRD).* The X-ray diffraction (XRD) was used to determine the oxidation degree of GO and the crystallinity of rGO/NCF and rGO/CNF/TA composites. The measurements were carried out on the X-ray diffractometer (Bruke Axs, D4 Endeavor, USA) with reference target: Cu Kα radiation (λ=1,541841 Å; 2,2 kW), voltage: 40 kV, and current: 20mA. The samples were measured from 2 to 50° during 141 s with steps of 0.02°.

*Fourier Transform Infrared Spectroscopy (FTIR).* The FTIR was used to investigate the chemical nature of interaction of rGO/NCF and rGO/CNF/TA composites. The spectra were recorded in the Perkin Elmer UATR Two FTIR Spectrometer. The wavenumber range analyzed was 4000-500 cm-1 and a total of 40 accumulated scans were acquired.

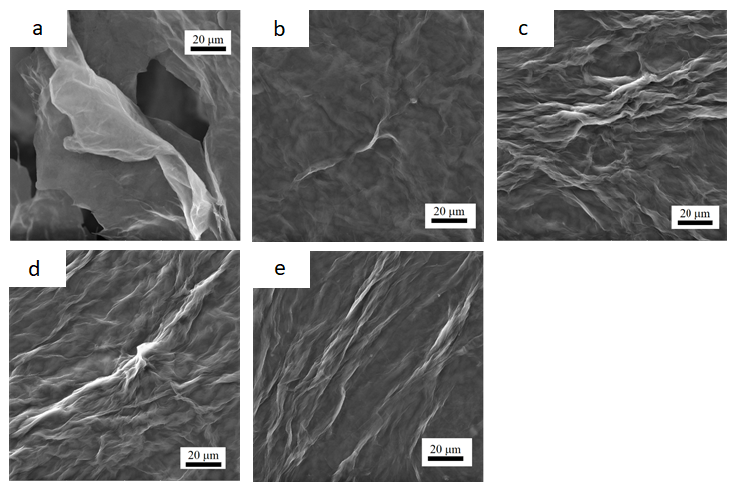
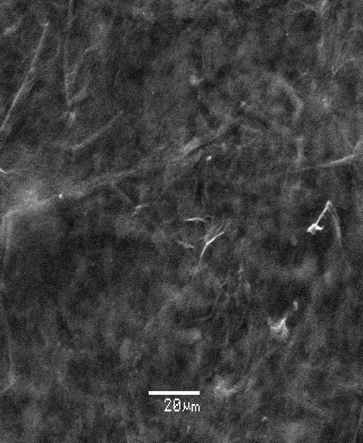
*Raman analysis.* The Raman was used to identify the spectra features and structural properties of GO and rGO/NCF and rGO/CNF/TA composites. The data were acquired by high-resolution confocal (LabRamHR Evolution Horiba Jobin Yvon microscope, Japan) at 633 nm of wavenumber in the excitation laser line, a power of 13.3 mW and 1.96 eV. The laser spot was focused on the samples using an optic Objective Olympus 100x VIS and a NUV camera (B/S UV 50/50 + Lens F125 D25). The measurements were carried out in quadruplicate at room temperature, and with a laser intensity constant to avoid damaging on the samples. In addition, for the calculation of either the intensity and the area of the D and G bands were applied a Lorentzian function in the spectral region 1000-1800 cm-1.

*X-ray photoelectron spectroscopy (XPS).* XPS technique was used to quantitatively identify the surface chemistry of rGO/NCF and rGO/CNF/TA composites, also the raw components NCF, TA and rGO were analyzed. The measurements were carried out in a Surface Analysis Station 1 (STAIB model RQ300/2, USA) at ultravacuum conditions (< 10-9 bar) equipped with a hemispherical electron analyzer (SPEC PHOIBOS 100, Germany). The photoelectrons were excited with non-monochromatic radiation Mg Kα (1486.6 eV) and analyzed with a constant energy step of 1 eV. The X-ray source was used with a strength of 300 W.

*Thermogravimetric analysis (TGA).* TGA technique was used to evaluate the thermal stability of gelatin, GO and rGO/NCF and rGO/CNF/TA composites. The measurements were carried out in a Cahn-Versatherm thermogravimetric analyzer with sensitivity of 0.1 μg, heating rate of 10°C/min under nitrogen atmosphere (100 mL/min) and a temperature range from 30°C to 800°C.

*Scanning electron microscopy (SEM).* The SEM analysis was used to investigate the micromorphology of rGO/NCF and rGO/CNF/TA composites. SEM images were recorded using a JEOL JSM-6380LV, Japan model microscope at 10 kV. The aerogels were coated using a gold sputter coater and their surfaces were observed at different resolutions. In addition, the SEM images were processed using ImageJ® software to determinate the average pore sizes.

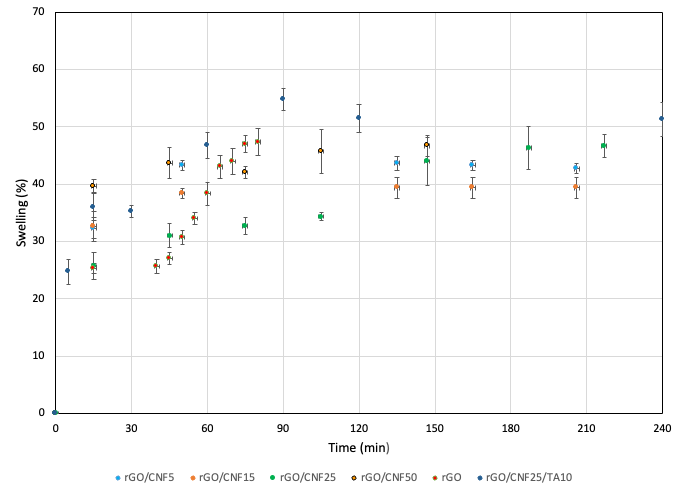
*Surface charge measurements*. The surface charge was determined through ζ-potential measurements using the Dynamic Light Scattering principle (SZ-100 Nano particle analyzer, Horiba Scientific, Japan). The measurements were carried out for the GO and gelatin-GO aerogels. Samples 1.0 cm3 in volume were dissolved in Milli-Q® water pH 6.5, shaken and sonicated for 20 min to achieve homogeneity. Finally, the samples were measured in triplicate.



f

20 μm

**Figure S1.** SEM images a) GO, b) rGO/CNF5, c) rGO/CNF15, d) rGO/CNF25, e) rGO/CNF50 f) rGO/CNF25/TA.



**Figure S2.** Swelling behavior of neat materials and composite samples on PBS fluid on time.

**Table S1.** Phenol composition and content of the *Pinus Radiata* bark extract

|  |  |
| --- | --- |
| Compounds | Content (mg per gram of extract) |
| (-)-Catechin | 13.8 |
| Taxifolin | 13.9 |
| p-Hydroxybenzoic acid | 7.6 |
| Homovanillic acid a | 6.7 |
| Quercetin | 4.3 |
| Proanthocyanidin *B-2* | 3.3 |
| (+)-Epicatechin | 2.8 |
| Dihydroxybenzoic acid b | 2.7 |
| Dihydroxybenzoic acid b | 1.8 |
| Syringic acid a | 1.1 |
| 3,4-dihydroxyphenyl acetic acid | 0.9 |
| Dihydroxybenzoic acid b | 0.2 |
| Epigallocatechin | n.d. |

n.d.: not detected, a: tentatively identified compounds, b: not recognized isomers.

**Table S2.** Average molecular weight number (Mn) of pine extracts at different percentages of sample development, determinate by GPC.

|  |  |
| --- | --- |
| % sample development | Mn |
| 10 | 438 |
| 25 | 749 |
| 50 | 1355 |
| 100 | 63277 |
|  |  |