S2. Materials and Methods

S.2.2. Methods

S.2.2.1. Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR)

Before the spectral analysis, samples were pulverized into finer homogenates with a porcelain mortar. Approximately 10 mg of the sample was pressured on a diamond ATR plate using a self-leveling sapphire anvil to obtain the FTIR-ATR spectrum of a thin uniform layer of each sample. Two replicate spectra (32 scans/spectrum) of each sample were recorded using different aliquots. Spectra were acquired at a nominal resolution of 4 cm^{-1} and room temperature (24±2°C). Raw spectral data were stored and pre-analyzed using the Agilent Resolutions Pro version 5.3.0 software package (Agilent Technologies, Palo Alto, CA, USA), while further spectral data analysis and processing were carried out using optical spectroscopy software Spectragryph (version 1.2.16.1) and Origin 8.1 (Origin Lab Corporation).

2.2.2. Physicochemical characterization of copper alginate microspheres

S.2.2.2.1. Encapsulation efficiency (EE), loading capacity (LC) and swelling degree (S_w)

(a) The encapsulation efficiency (EE) was calculated from the initial concentration of Cu ions (c_{tot}) and of the content of Cu ions in dry microspheres (c_{load}) by using the method of Xue et al. [1]. Encapsulation efficiency is expressed as a percentage of total Cu (c_{tot}) and is calculated by the equation:

$$EE/\% = (c_{load}/c_{tot}) \times 100, \tag{1}$$

where $c_{load} = c_{tot} - c_f$, and c_f is the concentration of Cu ions in the filtrate.

Encapsulation efficiency determination w**as** performed to obtain information on the yield of copper cations**.** Results on EE (52.71±2.61% (Sample 1), 49.18±3.49% (Sample 2), 45.11±4.28 (Sample 3)) revealed that the increase in Cu ions concentration decreased EE indicating even the lowest Cu concentration was enough for gelling the amount of added alginate.

(b) Copper content or Cu loading capacity (LC) in microspheres prepared at different initial Cu concentrations was determined by dispersing 4 g of dry microspheres in 25 mL of a mixture of 16.80 g (0.2 mol dm^{-3}) NaHCO$_3$ and 17.65 g (0.06 mol dm^{-3}) Na$_3$C$_6$H$_5$O$_7$·2H$_2$O at pH 8. The dispersion was mixed at 400 rpm on a magnetic stirrer (IKA topolino) until all the microspheres were completely dissolved. The resulting solution was filtered through double muslin, and the concentration of Cu ions in the filtrate was determined. The loading capacity is expressed as the amount of Cu in mmol per 1 g of dry microspheres and calculated by the equation:

$$LC = (c_{Cu} \times V/w_c), \qquad\qquad\qquad\qquad (2)$$

where c_{Cu} is the concentration of Cu ions in the sample, V is the volume of the sample, and w_c is the weight of the microspheres.

(c) Samples for swelling degree determination were prepared by dispersion of dry microspheres (0.1 g) in a glass vial containing 10 mL of deionized water and allowed to swell at room temperature for 3 hours. The wet weight of the swollen microspheres was determined by blotting them with filter paper to remove moisture adhering to the surface, immediately followed by weighing [2]. The swelling degree (S_w/%) was calculated using the equation:

$$S_w = \left(\frac{w_t - w_0}{w_0}\right) x\ 100, \qquad\qquad\qquad (3)$$

where w_t is the weight of the swollen microspheres, and w_0 is their initial weight.

3. Results and Discussion

3.1.3. Rheological properties of copper alginate microspheres
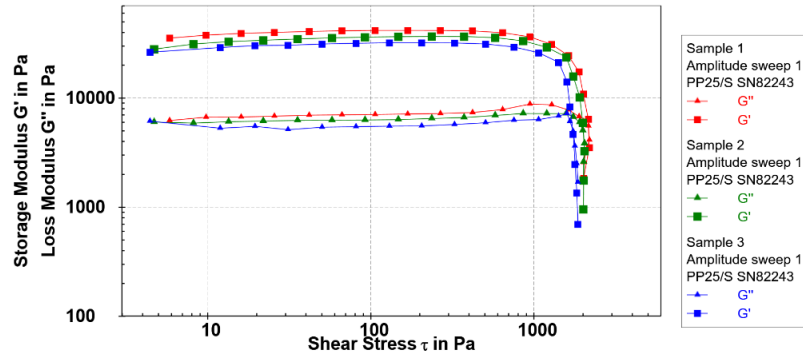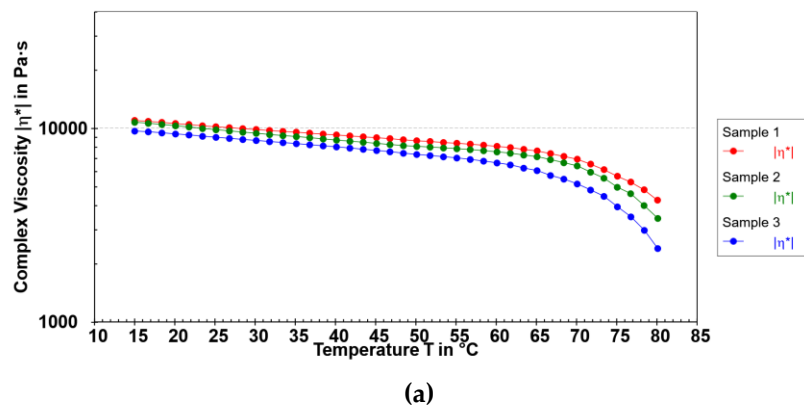
3.1.3.1. Amplitude sweep

Figure S1. Amplitude sweep tests (G′ (■) and G″ (▲) values) of Sample 1 (red), Sample 2 (green), and Sample 3 (blue) were determined at a constant angular frequency of 5 rad/s at 25°C.
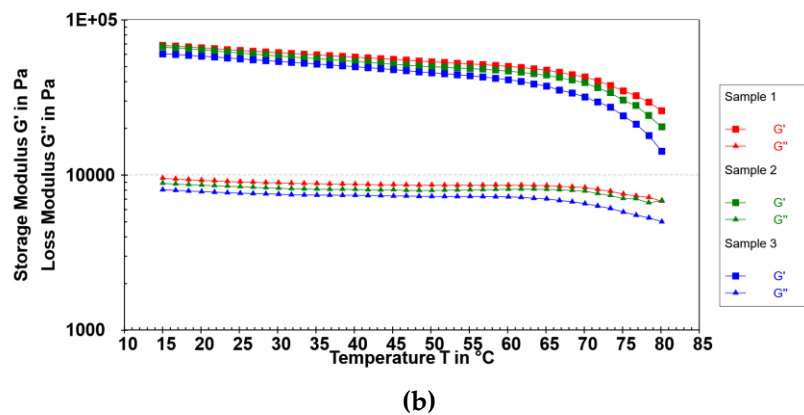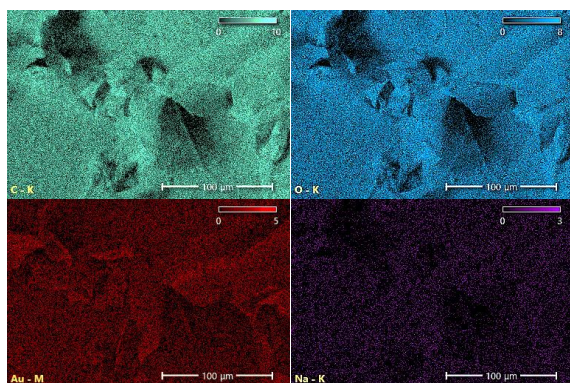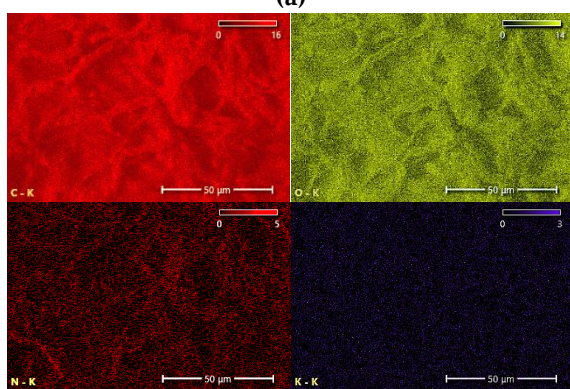
3.1.3.3. Temperature sweep

(a)

(b)

Figure S2. Temperature sweep measurements of Sample 1–3 represented as (a) complex viscosity and (b) storage (G') and loss (G'') modulus dependence determined at a constant strain 0.1% and a frequency of 1 Hz in a temperature range 15–80 °C.

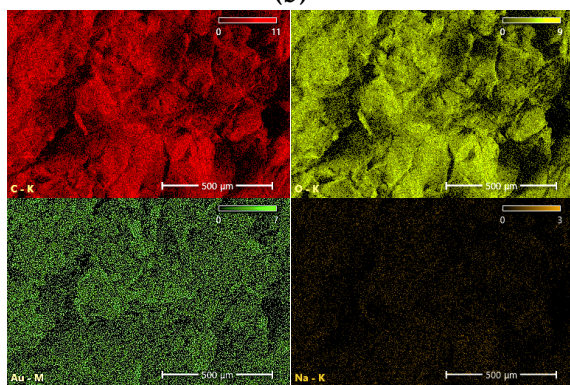3.2.1.2. Morphological properties of *B. cinerea, C. beticola* and *P. ramorum* spores and mycelium

(a)

Element	Atomic %	Atomic % Error
C	41.6	0.2
O	55.4	0.3
Na	0.4	0.0
Al	0.1	0.0
Au	2.5	0.0

(b)

Element	Atomic %	Atomic % Error
N	2.2	0.2
C	46.5	0.2
O	49.6	0.2
Al	0.4	0.0
Si	0.1	0.0
P	0.2	0.0
S	0.4	0.0
K	0.5	0.0
Ca	0.2	0.0

(c)

Element	Atomic %	Atomic % Error
C	41.0	0.2
O	54.7	0.3
Na	0.8	0.0
Au	2.9	0.0
K	0.7	0.0

Figure S3. Energy-dispersive spectroscopy (EDS) element mapping images of mycelium (a) *B. cinerea* (C, O, Au and K distribution) (b) *C. beticola* (C, O, N and K distribution) and (c) *P. ramorum* (C, O, Au and Na distribution) and elemental analysis (expressed in the atomic weight percent) using dispersive X-ray spectroscopy. Bars are indicated.

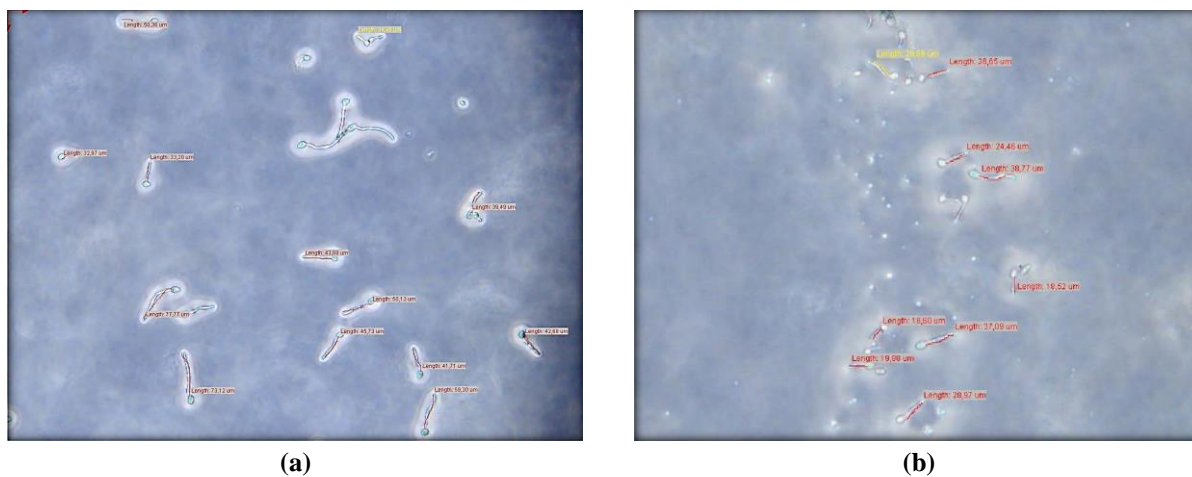3.2.2.1. Antifungal effect of copper alginate microspheres on *B. cinerea*

| (a) | (b) |

Figure S4. Length of *B. cinerea* germ tubes after incubation for 18 hours in (a) control and (b) with ALG/Cu (Sample 3) at 20x magnification.

References

1. Xue, W.M.; Yu, W.T.; Liu, X.D.; He, X.; Wang, W X.; Ma, J. Chemical method of breaking the cell-loaded sodium alginate/chitosan microcapsules. *Chem. J. Chin. Univ.* **2004**, *25*, 1342–1346. http://www.cjcu.jlu.edu.cn/EN/Y2004/V25/I7/1342
2. Mokale, V., Jitendra, N., Yogesh, S.; Gokul, K. Chitosan reinforced alginate controlled release beads of losartan potassium: design, formulation and in vitro evaluation. *J. Pharm. Investig.* **2014,** *44*, 243–252. https://doi.org/10.1007/s40005-014-0122-7