Electronic Supplementary Information

Borneol-Grafted Cellulose for Antifungal Adhesion and Fungal Growth Inhibition

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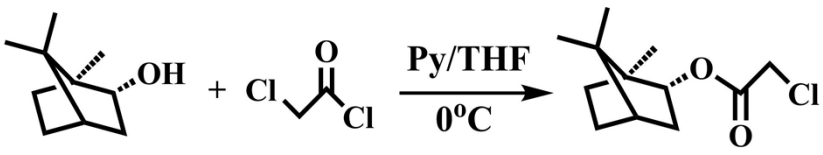
Experimental section

1. Materials

Cellulose (Sigma, powder, dry loss <5%), L-Borneol (J&K, 99%), chloroacetyl chloride (SCR, 99%), and 1-butyl-3-methylimidazolium acetate ([BMIm]Ac, Lanzhou Green-chem ILS, 98.5%) were used as received. Pyridine, tetrahydrofuran (THF) and triethylamine (TEA) were used after a dehydration treatment by molecular sieve.

2. Syntheses and Characterization

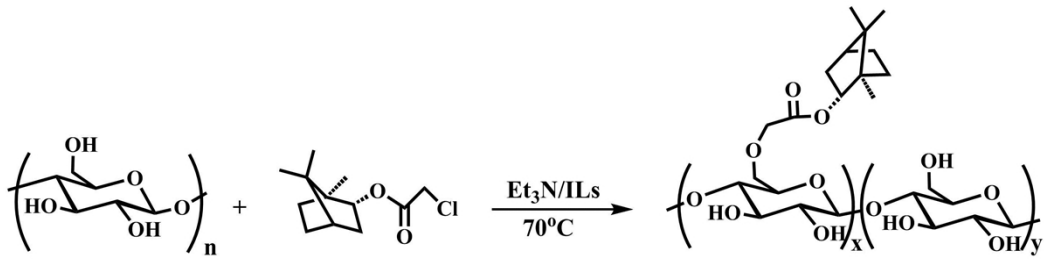
2.1 Syntheses of Chloroacetyl-L-Borneol (CAB)



Scheme S1. Synthesis of the CBA

L-Borneol (1.0 g, 6.47 mmol) and pyridine (0.77 g, 9.71 mmol) were dissolved in 15 mL of THF (solution A). Chloroacetyl chloride (0.7 g, 9.71 mmol) dissolved in 3.3 mL of THF at 0 °C was added dropwise to solution A and maintained at 0 °C for 30 min. The mixture was further stirred for 24 hr at room temperature. After filtration and rotary evaporation, colorless oil was obtained. Subsequently, the oil was dissolved in diethyl ether. The solution was then washed with hydrochloric acid (2 mol/L), saturated sodium bicarbonate and saturated sodium chloride, respectively. The organic layer was then dried with sodium sulfate. After evaporation and dried under vacuum, 1.33 g of CAB was obtained as colorless oil with a yield of 88.85%. The CAB sample was characterized by HPLC-MS (m/z): $[M+H]^+$: 233.2; ^1H NMR (400MHz, DMSO, δ): 0.8–0.9 (s, 9H, CH3), 1.0–2.3 (s, 7H, CH2CH), 4.41 (s, 2H, COCH2), 4.9 (d, 1H, CHOC=O).

2.2 Preparation of BGC



Scheme S2. Synthesis of the BGC

0.70 g of sodium hydroxide was dissolved in 80% ethanol solution. 0.80 g of cellulose was treated with 10 mL as-prepared solution at room temperature for 24 hr. After washed with distilled water and dried under vacuum, the alkali cellulose was obtained as a white solid with a yield of 82%. Then, 0.20 g of alkali cellulose was dissolved in 10 mL of [BMIm]Ac at 90 °C for 2 hr and the solution was adjusted to pH 8 by adding TEA, followed by addition of CBA (0.6 g, 2.6 mmol). The solution was then kept a stirring at 70 °C for 3 days. The product was precipitated from [BMIm]Ac system with diethylether and washed by Soxhlet extraction with 100 mL ethanol for 2 days to remove impurities. Finally, purified BGC was obtained as a white solid with a yield of 93.8%. Based on the EDS analysis (Fig. S1), the grafting rate of borneol could be calculated to be approximately 17% with the help of the ChemBioDraw simulation program (Fig. S2). The internal crystallinity was studied by XRD observation (Fig. S3). When ethanol was used as the solvent for this synthesis, lower borneol-grafting rate BGC (approximately 6.2%) was obtained (Fig. S4), which showed weaker antifungal effect (Fig. S5).

3. Characterization

Fourier transform infrared (FT-IR) spectroscopy was employed. For the measurements, the dried samples were mixed with KBr (about 2 mg sample in 200 mg KBr) and pressed into pellets. The measurement was performed in a Thermo Nicolet Antaris Ⅱ spectrometer. The spectra were recorded using a spectral width ranging from 400 to 4000 cm^{-1}, with a spectral resolution of 4 cm^{-1} and an accumulation of 32 scans. The nuclear magnetic resonance (NMR) spectrum was recorded on a Bruker AVⅢ 400 spectrometer operating at 400 MHz. The test tube was filled up with solid samples, and then the solid-state ^{13}C NMR studies were carried out under ambient conditions. For the small molecules, the normal liquid-state ^{13}C NMR detection was performed with a Bruker Ascend^{TM} 400WB spectrometer operating at 400 MHz with d^6-DMSO used as the solvent. The X-ray photoelectron spectroscopy (XPS) measurements were performed on freeze-dried samples of cellulose before and after CAB modifications with an ESCALAB250 electron spectrometer (ThermoFisher Scientific, USA) and monochromatic Al irradiation at 200 eV for survey and 150 W power at anode. The crystallinity of cellulose before and after borneol grafting was measured by X-ray diffraction (XRD) using Cu Ka (0.15418 nm) radiation. The XRD patterns were recorded on D/Max 2500 VB2+/PC in the range of 2θ=5–90°. Hitachi S-4700 scanning electron microscope (SEM) equipped with energy dispersive X-ray spectroscopy (EDS) analysis system was used to study the chemical composition of the samples.

Supporting data

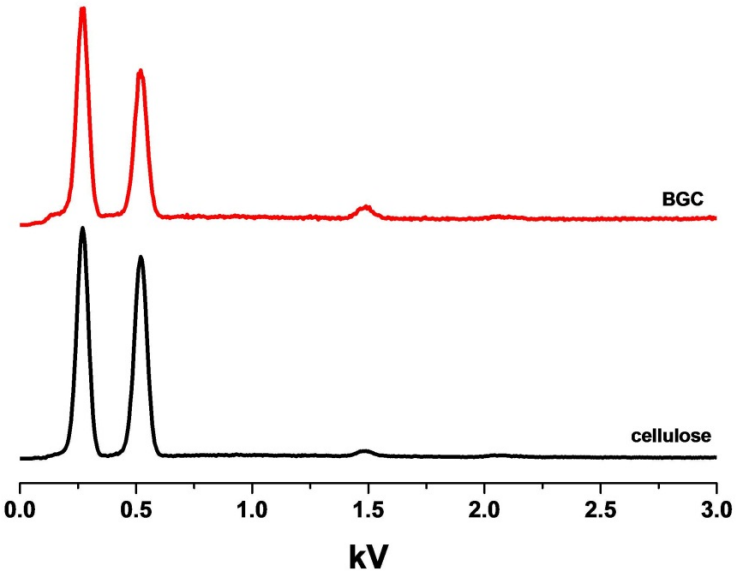


Fig. S1 EDS spectra of BGC (top) and cellulose (bottom). BGC, C: 52.77 wt%, O: 47.23 wt%; cellulose, C: 47.13 wt%, O: 52.87 wt%.

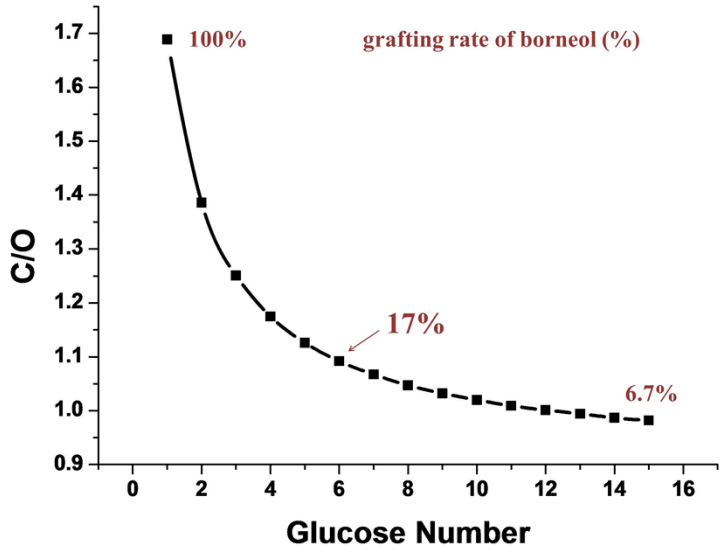


Fig. S2 Standard curve of the C/O ratio with a range of 1-15 glucose units grafted with one CAB molecule, which was plotted with the help of the ChemBioDraw simulation program. The grafting rate of borneol was typically denoted on the plot.

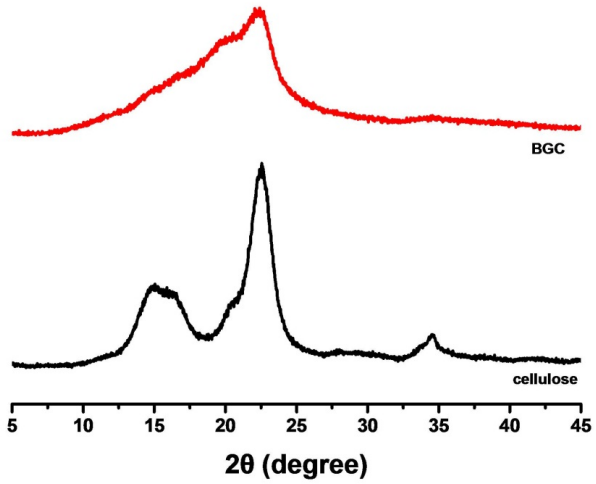


Fig. S3 XRD patterns of BGC (top) and cellulose (bottom).

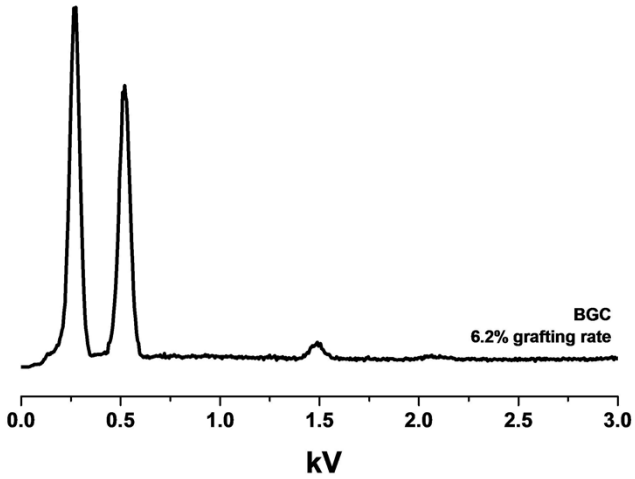


Fig. S4 EDS spectrum of a BGC sample with the grafting rate of approximately 6.2%. BGC, C: 49.33 wt%, O: 50.67 wt%.

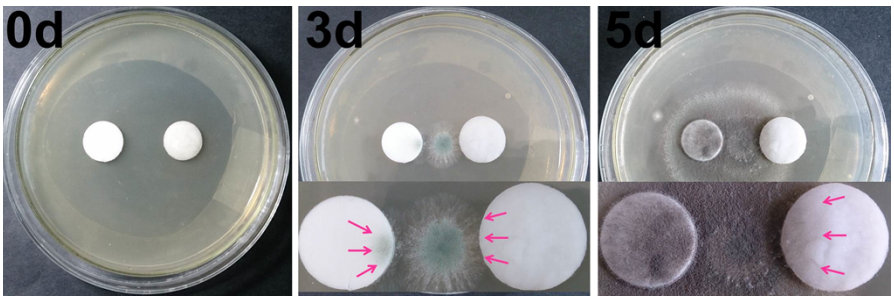


Fig. S5 Effect of antifungal adhesion on cellulose (left) and lower borneol-grafting rate 6.2% BGC (right) pellets. Weaker antifungal effect was demonstrated. Pink arrow: the growth frontier of fungi on the pellets.