Unravelling mechanisms behind biomass-clay interactions using comprehensive multiphase nuclear magnetic resonance (NMR) spectroscopy

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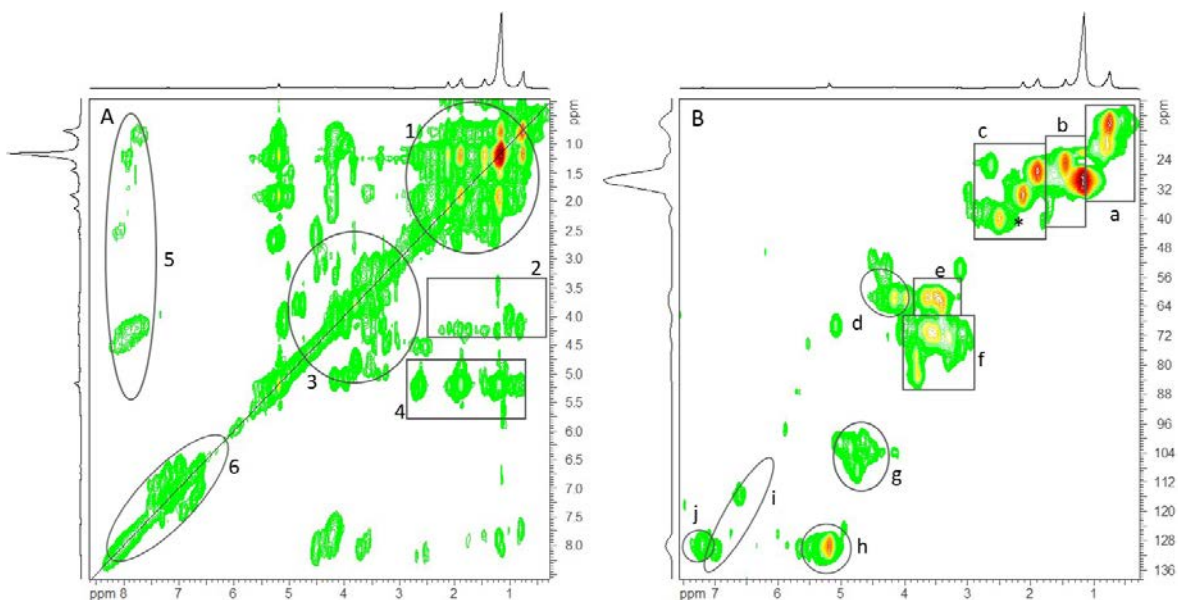
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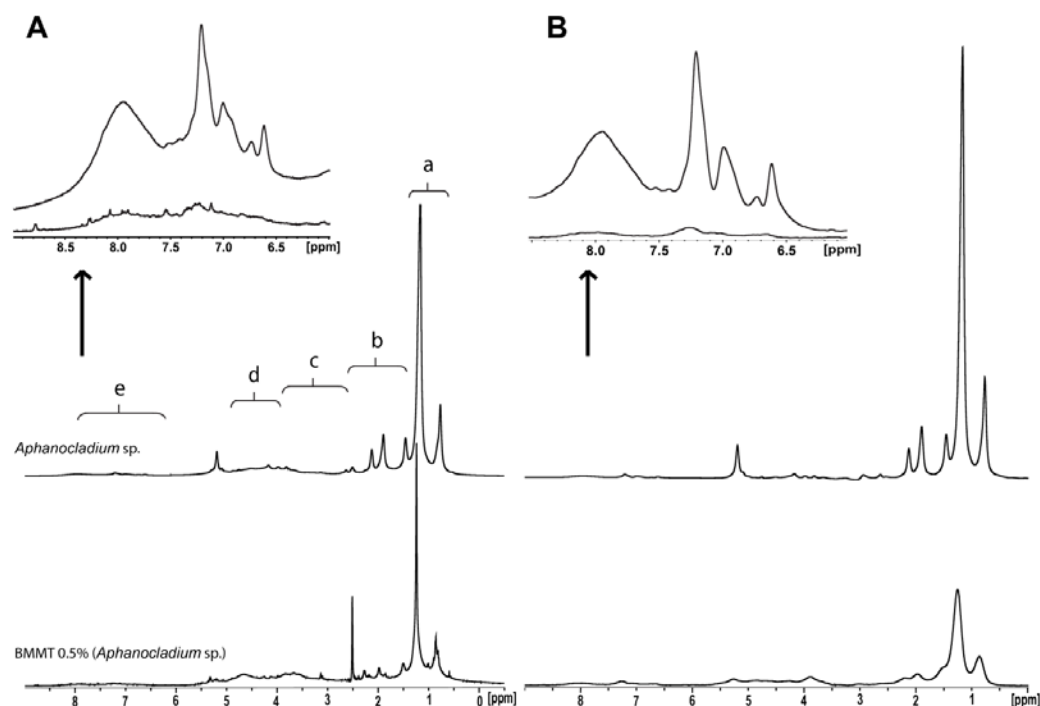André J. Simpson. E-mail: andre.simpson@utoronto.ca

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Figure S1. (A): ^{1}H–^{1}H TOCSY NMR spectrum at 500 MHz of *Apha* biomass: (1) Aliphatic chains; (2) correlation between α-H and peptide side chains in amino acids, peptides and proteins; (3) signals from carbohydrates; (4) correlation of unsaturation to aliphatic chains from lipids; (5) correlation between amides to α-H and side chains from proteins/peptides; (6) signals from aromatic compounds. (B): ^{1}H-^{13}C HSQC NMR spectrum of *Apha* biomass: (a) CH$_3$ from lipids and/or peptides; (b) CH$_2$ in lipids; (c) C-H bonds in various aliphatic structures including fatty acids and amino acids; (d) α-H/C in peptides; (e) CH$_2$ in carbohydrates; (f) C-H bonds in carbohydrates; (g) anomeric H (carbohydrates); and (h) C=C from double bonds in aliphatic chains; (i) Tyrosine; (j) Phenylalanine. *DMSO= dimethyl sulfoxide.
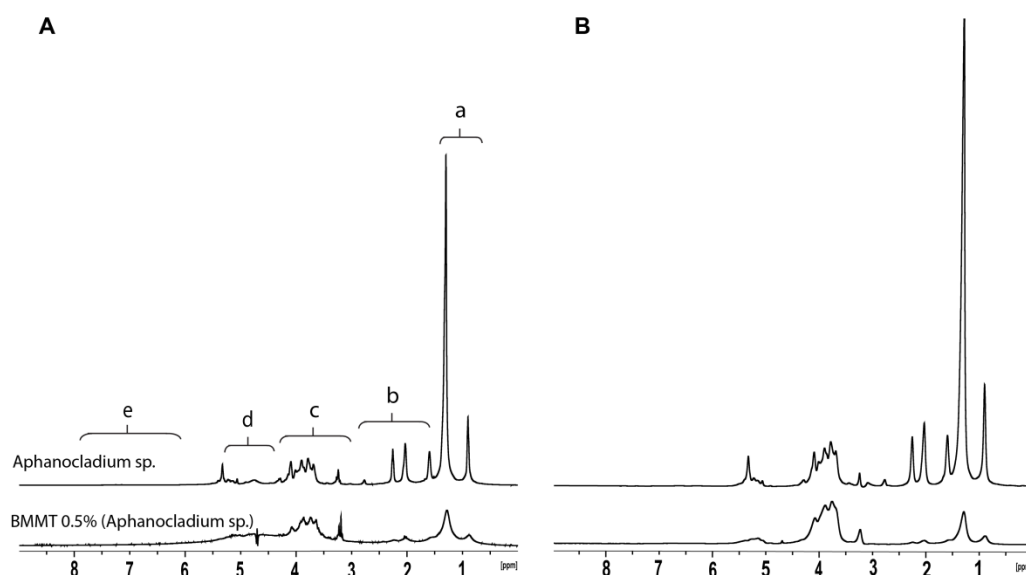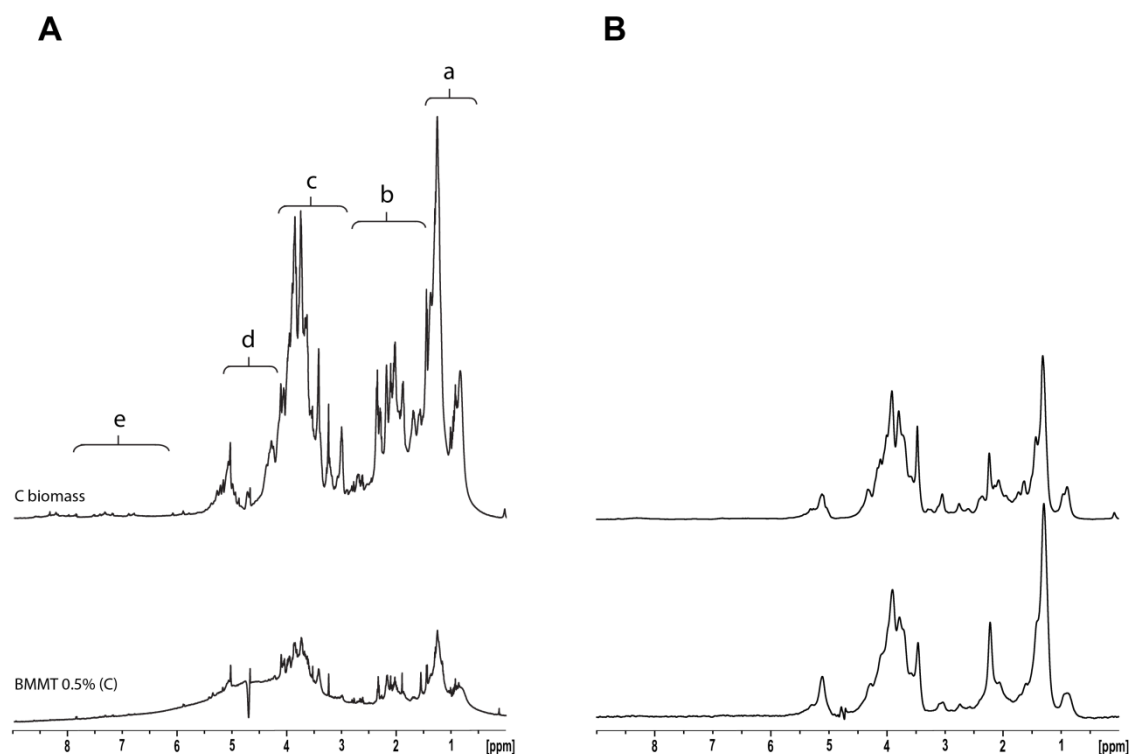
Figure S2. (A), ^{1}H CMP-MAS NMR spectra of BMMT (*Apha*) at different loading of biomass in D_2O. (B), ^{1}H CMP-MAS NMR spectra of BMMT (*Apha*) at different loading of biomass in D_2O using a diffusion edited experiment. Assignments are as follows: (a) terminal methyl and methylene groups between 0.6-1.3 ppm; (b) signals due to *O-* and *N-*substituted aliphatic structures in the 1.3-2.9 ppm region; (c) signals due to *O*-alkyl structures mainly from carbohydrates in the 2.9-4.1 ppm region; (d) overlapping weak resonances in the 4.1-5.4 ppm region generally attributed to a number of moieties including α-H from peptides, anomeric H in carbohydrates and double bonds; and (e) signals from the aromatic structures, in the 6.2-7.8 ppm region.
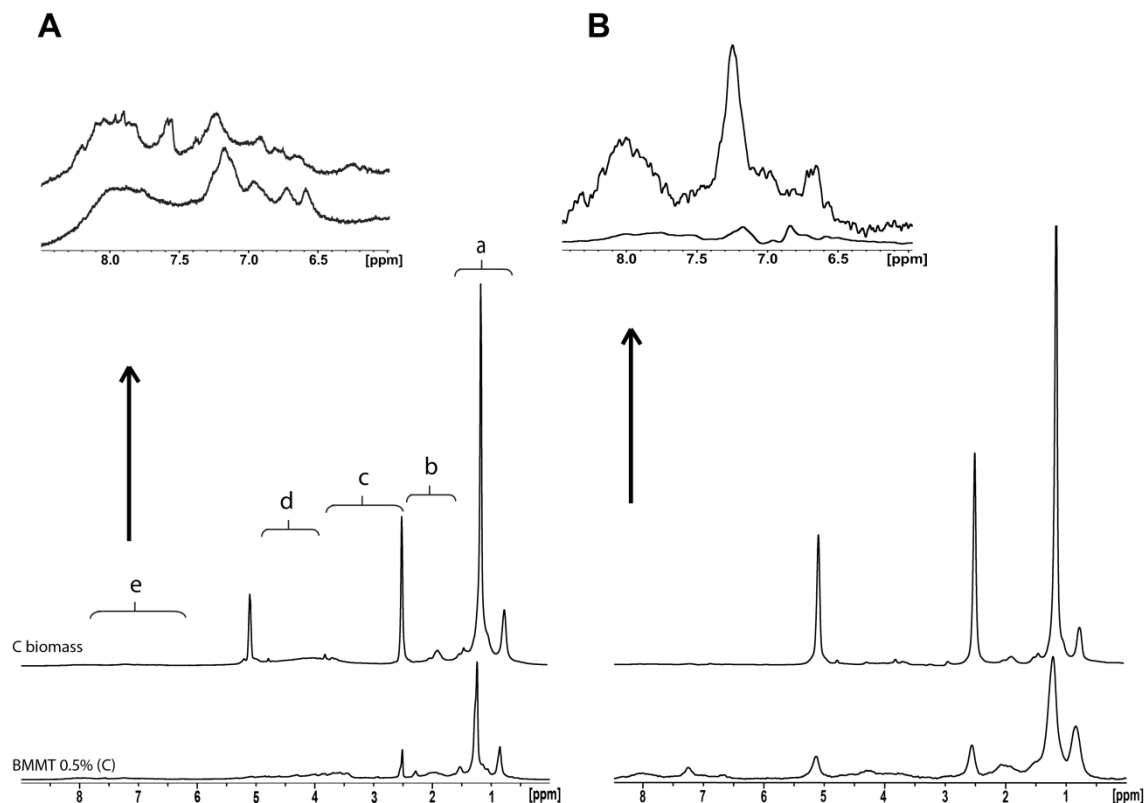
Figure S3. (A), ^{1}H CMP-MAS NMR spectra of BMMT (*Apha*) at different loading of biomass in DMSO-d$_6$. (B), ^{1}H CMP-MAS NMR spectra of BMMT (*Apha*) at different loading of biomass in DMSO-d$_6$ using diffusion edited experiment. Arrow indicates a detail of the proteins region (9-6 ppm). Assignments are as follows: (a) terminal methyl and methylene groups between 0.6-1.3 ppm; (b) signals due to *O*- and *N*- substituted aliphatic structures in the 1.3-2.9 ppm region; (c) signals due to *O*-alkyl structures mainly from carbohydrates in the 2.9-4.1 ppm region; (d) overlapping weak resonances in the 4.1-5.4 ppm region generally attributed to a number of moieties including α-H from peptides, anomeric H in carbohydrates and double bonds; and (e) signals from the aromatic structures, in the 6.2-7.8 ppm region.
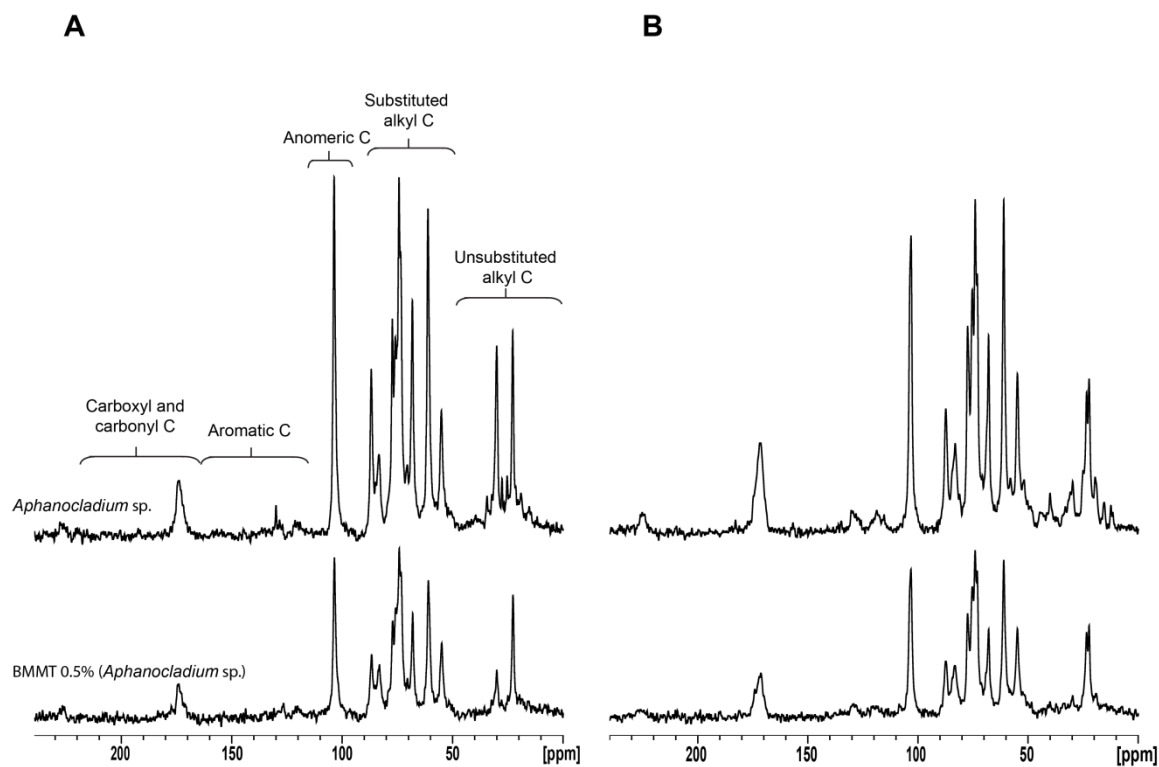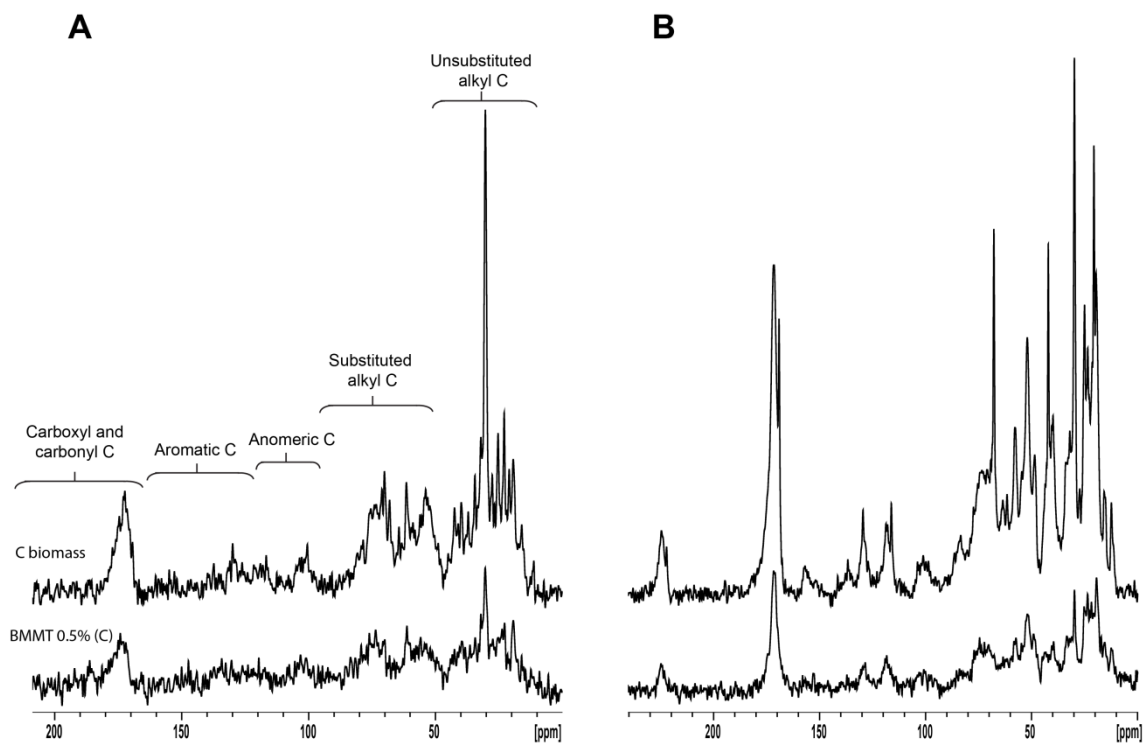
Figure S4. ^{13}C CP-MAS NMR spectra of BMMT (*Apha*) at different loading of biomass in (A), D$_2$O and (B), DMSO-d$_6$.

Figure S5. (A), ^{1}H CMP-MAS NMR spectra of BMMT (C) at different loading of biomass in D_2O. (B), ^{1}H CMP-MAS NMR spectra of BMMT (C) at different loading of biomass in D_2O using a diffusion edited experiment. Assignments are as follows: (a) terminal methyl and methylene groups between 0.6-1.3 ppm; (b) signals due to *O*- and *N*- substituted aliphatic structures in the 1.3-2.9 ppm region; (c) signals due to *O*-alkyl structures mainly from carbohydrates in the 2.9-4.1 ppm region; (d) overlapping weak resonances in the 4.1-5.4 ppm region generally attributed to a number of moieties including α-H from peptides, anomeric H in carbohydrates and double bonds; and (e) signals from the aromatic structures, in the 6.2-7.8 ppm region.
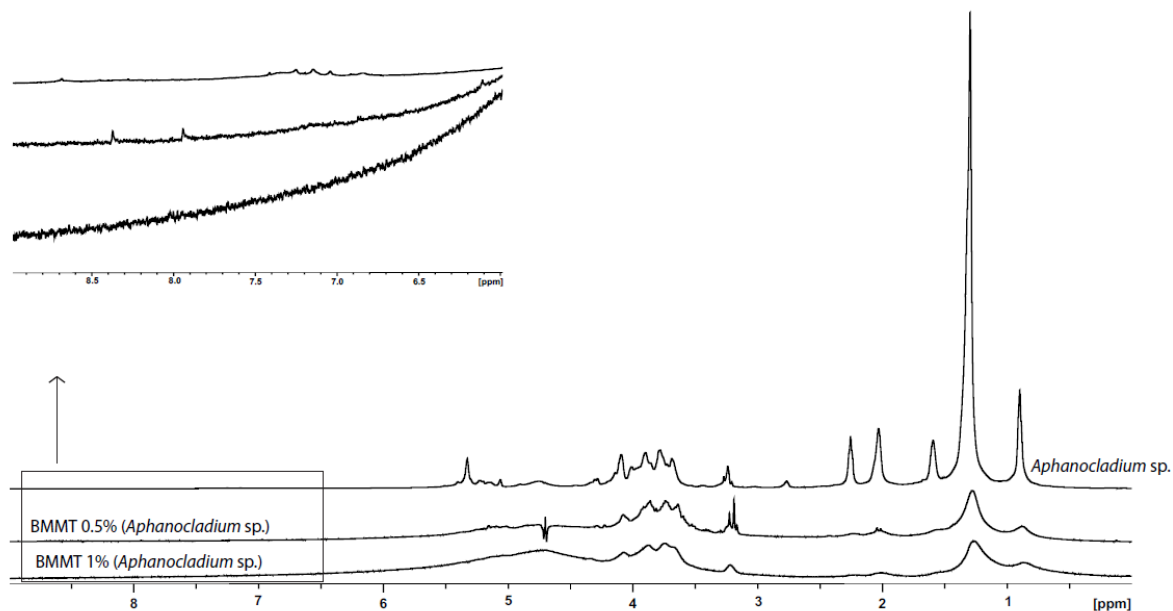
Figure S6. (A), ^{1}H CMP-MAS NMR spectra of BMMT (C) at different loading of biomass in DMSO-d_6. (B), ^{1}H CMP-MAS NMR spectra of BMMT (C) at different loading of biomass in DMSO-d_6 using diffusion edited experiment. The arrows indicate a detail of the proteins region (9-6 ppm). Assignments are as follows: (a) terminal methyl and methylene groups between 0.6-1.3 ppm; (b) signals due to *O*- and *N*- substituted aliphatic structures in the 1.3-2.9 ppm region; (c) signals due to *O*-alkyl structures mainly from carbohydrates in the 2.9-4.1 ppm region; (d) overlapping weak resonances in the 4.1-5.4 ppm region generally attributed to a number of moieties including α-H from peptides, anomeric H in carbohydrates and double bonds; and (e) signals from the aromatic structures, in the 6.2-7.8 ppm region.

Figure S7. ^{13}C CP-MAS NMR spectra of BMMT (C) at different loading of biomass in (A), D_2O and (B), DMSO-d_6.

Figure S8. ^{1}H CMP-MAS NMR spectra of BMMT (*Apha*) at different loading of biomass in D_2O. Assignments are as follows: terminal methyl and methylene groups between 0.6-1.3 ppm; signals due to *O*- and *N*- substituted aliphatic structures in the 1.3-2.9 ppm region; signals due to *O*-alkyl structures mainly from carbohydrates in the 2.9-4.1 ppm region; overlapping weak resonances in the 4.1-5.4 ppm region generally attributed to a number of moieties including α-H from peptides, anomeric H in carbohydrates and double bonds; and (box and arrow) signals from the aromatic structures, in the 6.2-8.5 ppm region.

Figure S9. Scanning electron micrograph of MMT.