Electronic Supplementary Information (ESI)

for

Bio-based green composites with high performance from poly(lactic acid) and surface-modified microcrystalline cellulose

Lin Xiao, Yiyong Mai, Feng He, Longjiang Yu, Limin Zhang, Huiru Tang, Guang Yang*

E-mail: yang_sunny@yahoo.com

The explanations of assignments of solid-state ^{13}C NMR spectrum of g-MC

Solid-state ^{13}C NMR spectra of cellulose and PLA have been well studied (See Ref. 23, Ref. 27 and Ref. 28 in the main text). Here, we focus on the explanations of the assignments of C6, C8, and C9 in g-MC.

As for the C6 in microcrystalline cellulose (MC), usually it shows a single carbon peak at around 65ppm, which is slightly overlapped with the peaks of C2, C3, and C5. After grafting of L-lactic acid oligomers, there are probably double peaks for C6. However, only a very small amount of C6-OH groups is grafted (because the total grafting percentage of L-lactic acid oligomers on C6-OH, C2-OH, and C3-OH groups was calculated to be ca. 3.4%). If there are multiple carbon peaks for grafted and ungrafted C6-OH groups, they will be highly possible to overlap with each other, or cannot be distinguished due to the relatively low resolution of solid state ^{13}C NMR. Thus, it appears that there is only a single shoulder C6 peak in the ^{13}C NMR spectrum (see Ref. 23 in the main text).

In the methyl signal region of 16–21 ppm in ^{13}C NMR spectrum in Fig. 3 in the main text, there are a small carbon peak (20.5 ppm) and a massive peak (17.6 and 16.6 ppm). The small peak (20.5 ppm) is considered to originate from C8 groups in the terminal units of the grafted L-lactic acid oligomers, which have a higher mobility. The massive peak (17.6 and 16.6ppm) is considered to be from C9 groups in the grafted chains, which are located in less mobile regions (See Ref. 29 in the main text).

Spectral deconvolution and integration of the relevant carbon peaks

The spectral deconvolution was performed using the software "DmFit". (See Ref. 32 and Ref. 33 in the main text).

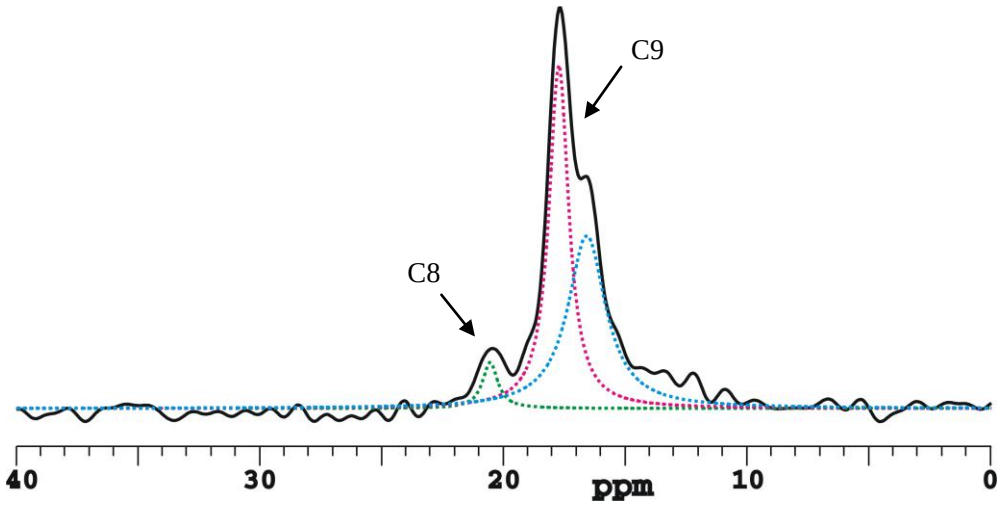

Fig. S1 Deconvolution of ^{13}C-signal of the methyl groups (C8 and C9)

Table S1 The integral area values of the relevant carbon peaks for calculations

Groups	Chemical Shift (ppm)	Integrals
C1	104.6, 105.9	289.3
C8	20.6	29.1[a]
C9	17.7, 16.5	247.4[a]

a: the integral area values were obtained from Fig. S1.

The calculation of the g-MC weight (*m(g-MC)*) based on the obtained grafting percentage (ω) and DP_{avg} of the grafted L-lactic acid oligomers.

$$N(-OH) = \frac{m(MC)}{M(C_6H_{10}O_5)} \times 3$$

$$N(oligomer) = N(-OH) \times \omega$$

$$m(oligomer) = M(C_3H_4O_2) \times DP_{avg} \times N(oligomer)$$

$$m(g-MC) = m(MC) + m(oligomer)$$

In these equations, *N*(-OH) represents the total number of OH groups in MC; *m*(*MC*) means the weight of MC, i.e. 20g in our experiment; *M* ($C_6H_{10}O_5$) denotes the molecular weight of a repeat unit of MC, namely 162. *N* (oligomer) represents the number of the grafted oligomer chains. *m* (oligomer) stands for the weight of the grafted oligomer; *M* ($C_3H_4O_2$) denotes the molecular weight of a repeat unit of the oligomer, i.e. 72; ω = 3.4%; DP_{avg} = 10.

Based on the equations and the given data, *m(g-MC)* is calculated to be ca. 29.1g.