Dodecylated lignin-*g*-PLA for effective toughening of PLA

Wei Ren, Xiaoyong Pan, Guan Wang, Weiren Cheng and Ye Liu*

*Institute of Materials Research & Engineering, A*STAR 2 Fusionopolis Way, #08-03, Innovis, Singapore 138634. E-mail: ye-liu@imre.a-star.edu.sg*

Supporting information:

1. Alkylated carboxylic OH percentage (%) and total alkylated OH percentage (%) of lignin:

   3.33 mmol/g of phenolic OH of alkaline lignin was conjugated with dodecane:
   $W_{dodecane}$ = 3.33 x 169/1000 = 0.56 (g) (where 169 is the molecular weight of $-C_{12}H_{25}$)

   Assuming x mmol/g of carboxylic OH and no aliphatic OH were alkylated:

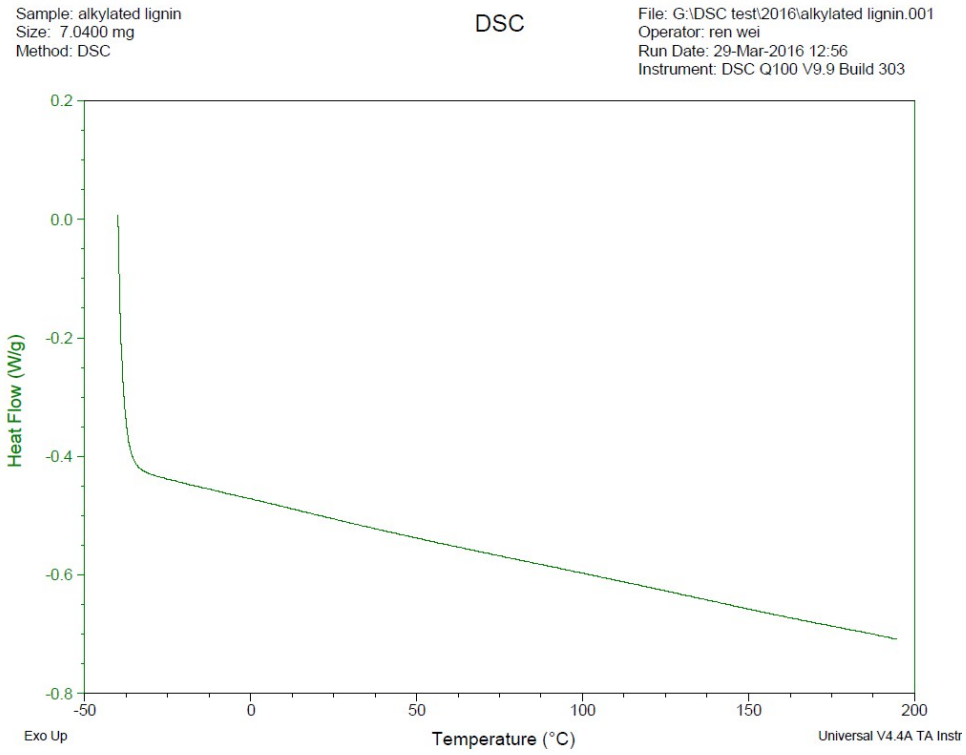
$$\frac{0.93 - x}{x \times \frac{169}{1000} + 0.56 + 1} = 0.14$$

   Therefore: x = 0.70 mmol/g.

   alkylated carboxylic OH% = 0.70/0.93 x 100% = 77%.

   total alkylated OH%:
   (0.70+ 3.3)/6.92 x 100% = 58%.

2. Figure S1. DSC thermogram of dodecylated lignin:



3. Lignin% (w/w) in lignin/PLA blends:

   Lignin% (w/w) in dodecylated lignin was determined by analysis of ^{31}P NMR of alkylated lignin:
   Lignin% = 1/(0.58 x 169/1000 + 1) x 100% = 59.5%

   Lignin%(w/w) in lignin/PLA blend = 0.595/(1+1.47 (total OH mmol/g in dodecylated lignin) x Mn of PLA grafted chain/1000) x100% (assuming all the OH were grafted with PLA)
   With M_n(PLA chain) being determined from ^1H NMR of lignin-*g*-PLA, total OH mmol/g in dodecylated lignin being determined from ^{31}P NMR of dodycylated liginin.

4. Figure S2. GPC profiles of dodecylated lignin-g-PLA sample 1 in Table 2 using ELS and UV detector, respectively.

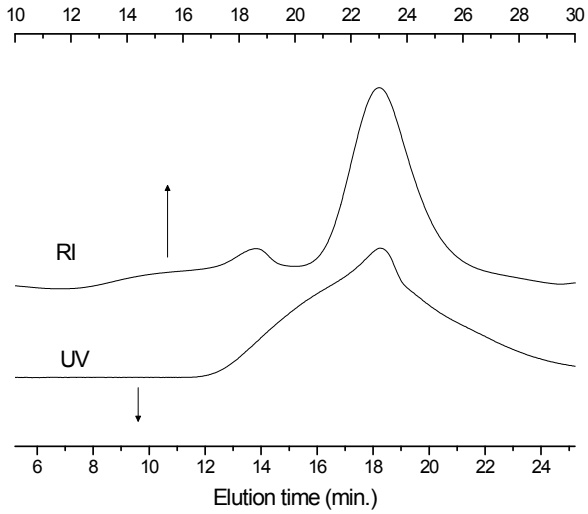
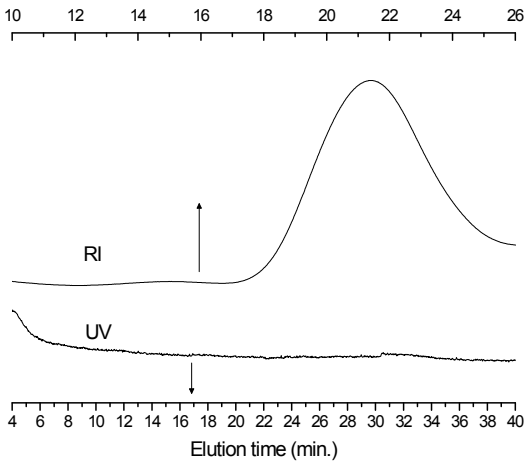
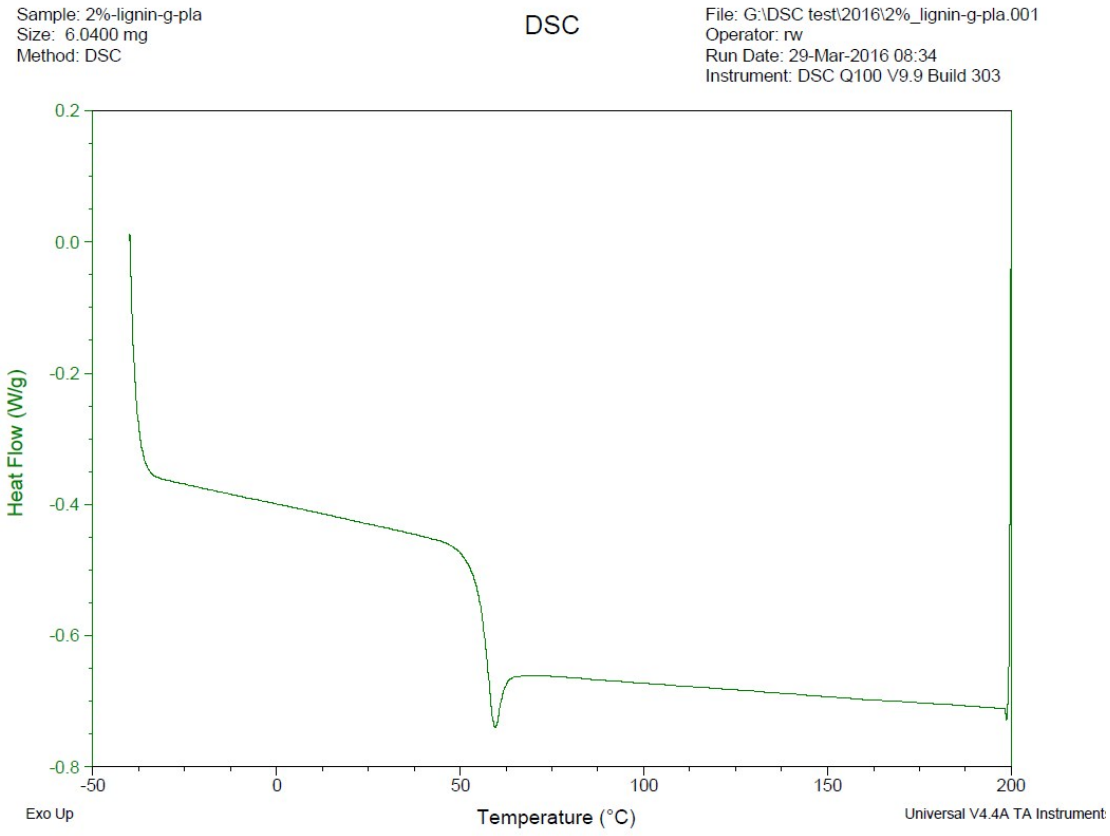


Figure S3: GPC profiles of PLA using ELS and UV detector, respectively



5. Figure S4. Photos of lignin/PLA blend samples 7 to 10 in Table 3 (from left to right) and 5% alkali lignin-*g*-PLA/PLA blend.

6. Figure S5. Typical DSC thermogram of selectively dodecylated lignin-g-PLA (sample 1 in Table 2):



7. Figure S6. TGA thermograms of PLA and lignin/PLA blend samples 7 to 10 in Table 3.