

Synthesis and application of modified lignin polyurea binder for manufacturing a controlled release potassium fertilizer

Mingyang Li¹, Gaoyang E¹, Conghui Wang¹, Ruolin Shi¹, Junxi Wang¹, Shuo Wang¹, Yu Wang²,
Yulong Peng³, Qi Chen¹, Zeli Li^{1,*}, Zhiguang Liu^{1,*}

¹ *National Engineering Research Center for Efficient Utilization of Soil and Fertilizer Resources, National Engineering & Technology Research Center for Slow and Controlled Release Fertilizers, College of Resources and Environment, Shandong Agricultural University, Tai'an, Shandong 271018, China*

² *State Key Laboratory of Soil and Sustainable Agriculture, Institute of Soil Science, Chinese Academy of Sciences, Nanjing 210008, China*

³ *Guizhou Provincial Tobacco Company, Zunyi Branch, Zunyi, China*

* Corresponding authors.

E-mail addresses: liuzhiguang8235126@126.com (Z.G.L.), zelili2016@163.com (Z.L.L.).

Figures

Figure S1. The flow chart of the modified polyurea binder controlled-release potassium chloride process.

Figure S2: The thermogravimetric experiment results for polyurea adhesives.

Figure S3: DSC reheating curve of bio-based polyurea binder.

Figure S4: Image of grain roundness of potassium chloride fertilizer.

Figure S5: HN (a) and PGL2:1 (b) potassium chloride laser scould custom view.

Table

Table S1: Synthesis formula of urea grafted lignin.

Table S2: Lignin grafted rate of different lignin and urea ratios.

Table S3: Synthesis formula of lignin-modified polyurea.

Table S4: Different binders and add ratios.

Table S5: The results for the thermogravimetric test of polyurea adhesives.

Table S6: Quantitative classification of radar image.

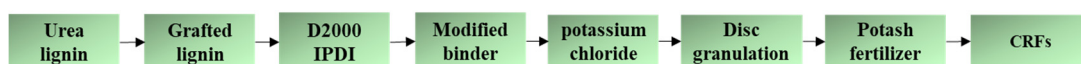


Figure S1. The flow chart of the modified polyurea binder controlled-release potassium chloride process.

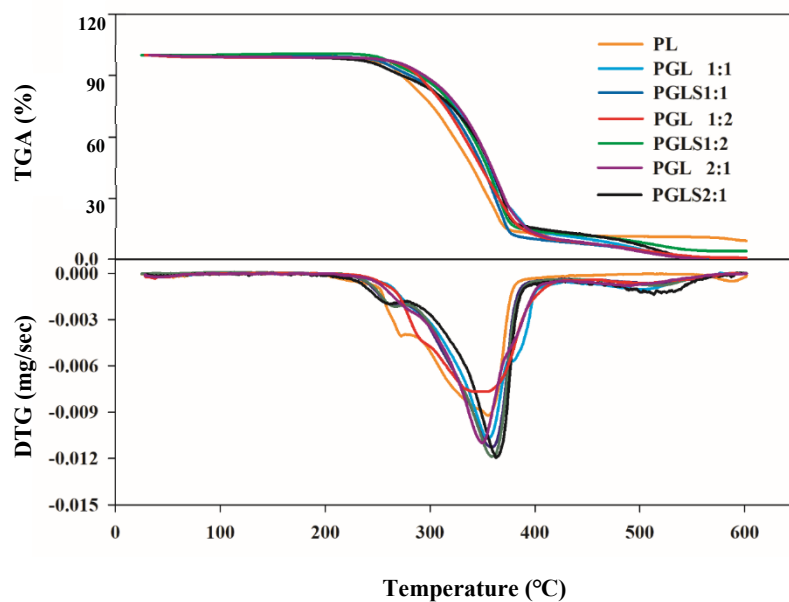


Figure S2. The thermogravimetric experiment results for polyurea adhesives.

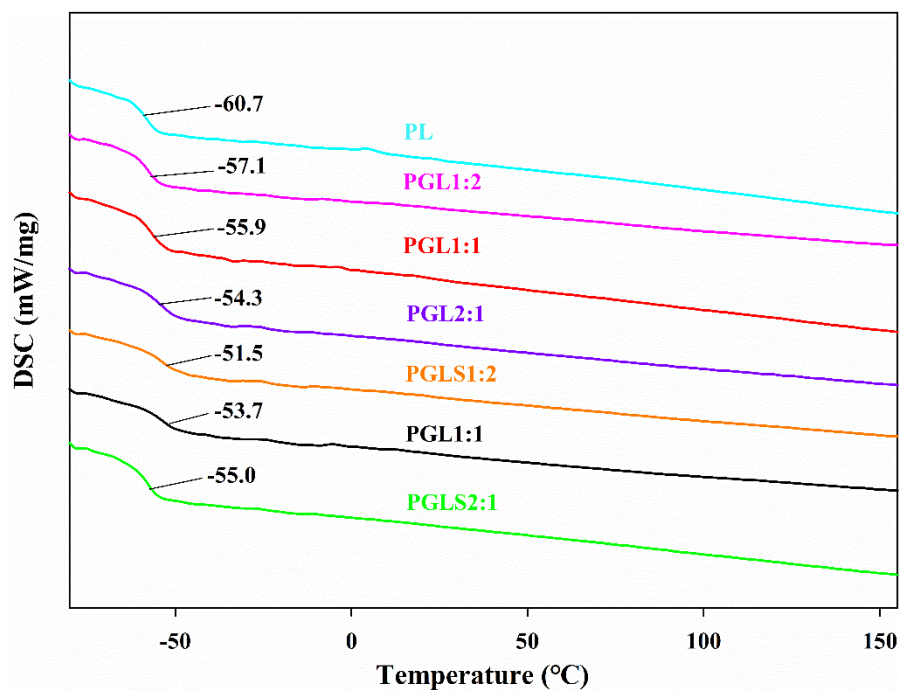


Figure S3. DSC reheating curve of bio-based polyurea binder.

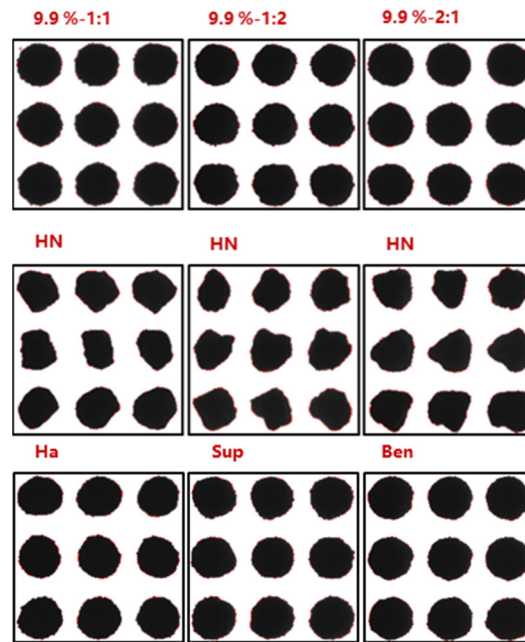


Figure S4. Image of grain roundness of potassium chloride fertilizer.

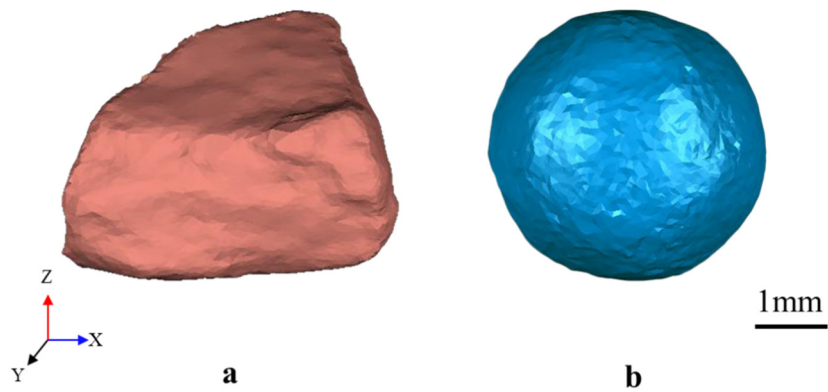


Figure S5. HN (a) and PGL2:1 (b) potassium chloride laser scould custom view.

Table S1. Synthesis formula of urea grafted lignin.^a37% formaldehyde solution; ^{b, c, d}PGL1:1, PGL2:1, PGL1:2 represent polyurea binder containing grafted lignin

Sample	Lignin/g	Urea/g/mol	^a FA/ml/mol	Urea: FA(mol)	Lignin: Urea (mass)
^b PGL1:1	10	10/0.17	1.89/0.02	1:1.4	1:1
^c PGL2:1	10	5/0.08	0.94/0.01	1:1.4	2:1
^d PGL1:2	10	20/0.17	1.89/0.02	1:1.4	1:2

Table S2. Lignin grafted rate of different lignin and urea ratios.

Sample	Lignin/g	Urea/g/mol	FA/ml/mol	Urea : FA(mol)	Lignin : Urea(mass)	Graft ratio/%
PGL2:1	10	5/0.08	10.14/0.12	1:0.7	2:1	62.4
PGL1:1	10	10/0.16	18.92/0.23	1:1.4	1:1	64.5
PGL1:2	10	20/0.32	37.84/0.46	1:2.8	1:2	70.8

Table S3. Synthesis formula of lignin-modified polyurea.

Sample	IPDI/mL	D2000/g	Lignin/g	Urea-grafted Lignin/g	^a S-S/g	DMAC/ml
^b PGL	2.38	9.00	/	1.00	/	13.46
^c PL	2.38	9.00	1.00	/	/	13.46
^d PGLS	2.38	9.00	/	1.00	1.16	13.46

^a disulphide; ^b PGL polyurea binder containing grafted lignin; ^c PL represent polyurea binder containing ungrafted lignin; ^d PGLS represent polyurea binder containing grafted lignin and disulfide, which was used to study the effect of disulfide bond.

Table S4. Different binders and add ratios.

Name of binder	Mass ratio	Symbols
Superphosphate	8%	8-Sup
Water	13%	Water/CK
Humic acid	12%	12-Ha
Bentonite	30%	30-Ben
Bio-based binder	3.3%	3.3-1:1、3.31:2、3.3-2:1
Bio-based binder	6.6%	6.6-1:1、6.6-1:2、6.6-2:1
Bio-based binder	9.9%	9.9-1:1、9.9-1:2、9.9-2:1

Table S5. The results for the thermogravimetric test of polyurea adhesives.

Sample	T _{5%} (°C)	T _{50%} (°C)	T _{max%} (°C)
PL	262.2	334.9	366.3
PGL1:2	274.6	353.1	385.7
PGL1:1	275.6	353.6	387.3
PGL2:1	279.5	354.4	399.3
PGLS1:2	268.5	350.5	371.7
PGLS1:1	261.0	346.2	371.4
PGLS2:1	251.6	353.9	371.2

Table S6. Quantitative classification of radar image.

Property	Range	Unit gradient value
120°C Viscosity	0–8000 (Pa*s)	1000 (Pa*s)
Dry bond strength	0–4 (MPa)	0.5 (MPa)
Elongation at break	0–800 (%)	100 (%)
Tensile strength	0–4 (MPa)	0.5 (MPa)
9.9% Granule intensity	0–80 (N)	10 (N)
Sliding angles C A	0–80 (°)	10 (°)