Synthesis of lignin nanoparticles using CO_2-responsive amines and film applications

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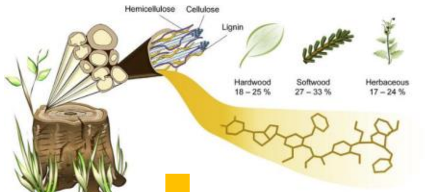
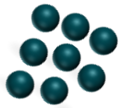
Introduction



Lignin

- Antioxidant
- non-toxic
- Antibacterial
- UV-absorption
- Antiviral
- Biodegradable

Lignin nanoparticles (LNPs)



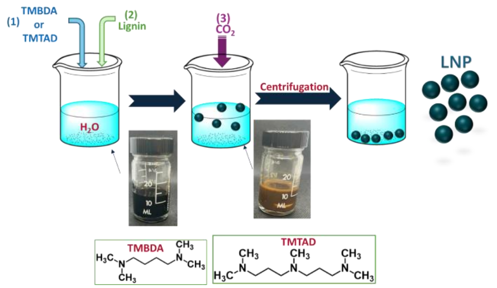
- Tailored morphological structure
  Same properties of lignin
- High surface area
- High surface reactivity
- Enhancing dispersion/dispersion in different environments
- LNPs obtained via solvent exchange, pH-shifting, aerosol evaporation, supercritical fluids, and polymerization

Applications of LNP

CO_2-responsive amines in water

$$B + H_2O \underset{-CO_2}{\overset{+CO_2}{\rightleftharpoons}} [BH^+]\ [HCO_3^-]$$

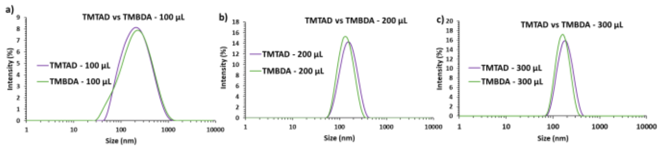
Experimental



Process to obtain LNP from Kraft lignin using TMTAD or TMTAD and CO_2.

Results

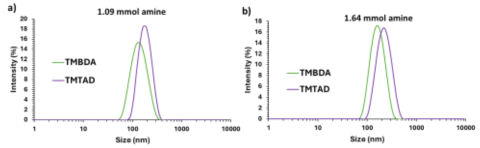
Loading effect



Particle size distributions of LNP using TMBDA or TMTAD at100 µL (a), 200 µL (b) and 300 µL (c).

Water (g)	Lignin (g)	Amine (µL)	TMBDA				TMTAD			
			pH*	pH**	Size (nm)	PDI	pH*	pH**	Size (nm)	PDI
10	0.21	100	10.26	7.58	170	0.28	9.14	6.75	175	0.26
		200	10.76	7.52	127	0.10	9.27	6.85	144	0.11
		300	10.92	7.46	152	0.095	9.67	6.97	170	0.098

Yield effect

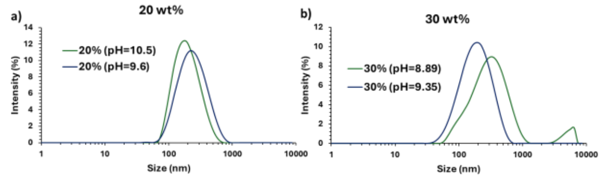


Particle size distributions of LNP using TMBDA or TMTAD at 1.09 mmol (a) and 1.64 mmol (b).

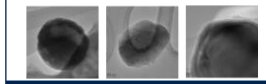
Water (g)	Lignin (g)	mmol amine	TMBDA						TMTAD					
			Amine (µL)	pH*	pH**	Size (nm)	PDI	Yield (%)	Amine (µL)	pH*	pH**	Size (nm)	PDI	Yield (%)
10	0.21	1.09	200	10.76	7.52	127	0.10	84	260	9.74	6.99	173	0.06	94
		1.64	300	10.92	7.46	152	0.095	86	400	10.07	7.06	206	0.08	95

Results

Scale up



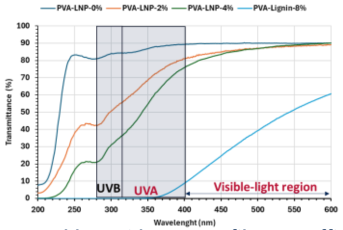
Particle size distribution of LNPs prepared at different pH and lignin concentration, 20 wt% (a) and 30 wt% (b).



TEM images of LNPs obtained with TMTAD (90 µL) and CO2 at 2 wt%.

Applications

PVA-LNP films can be used asUV shielding or antioxidants, by blocking UV light: UVB (280–315 nm) and UVA (315–400 nm). This can find applications in food packaging!.



- At 0%, no UV blocking is observed
- 2 wt% of LNP, UV blocking is improved by almost 60%
- The main improvement is achieved by adding 4%
- At 8% of LNP, UV light is blocked, almost completely
- In the visible region, transparency is sacrificed by adding more LNP
- Light Transmittance is ~90% up to 4% of LNP.

LNP could provide to PVA films an efficient UV block capacity without influencing its visible light transparency

Conclusions

- Kraft lignin was initially dispersed into a basic solution using TMTAD or TMBDA, and then the LNP were precipitated at high yields by sparging with CO_2.
- TMTAD and TMBDA exhibit similar performance with only small differences, with TMBDA giving slightly smaller particle size than TMTAD, while the yield is higher with TMTAD.
- Our current efforts are focused on recovering and re-using the amine to give a process involving minimal or no net consumption of amine.
- This process could increase the use of LNP, leveraging the properties of lignin to enable new bio-based products.
- LNPs can find applications as UV-blocker when dispersed in a polymer matrix for food packaging applications.

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