ACS FALL 2023
August 13 - 17, 2023 | Moscone Center, San Francisco, CA & Hybrid

Upcycling of end-of-life PLA composites using surface-modified cellulose

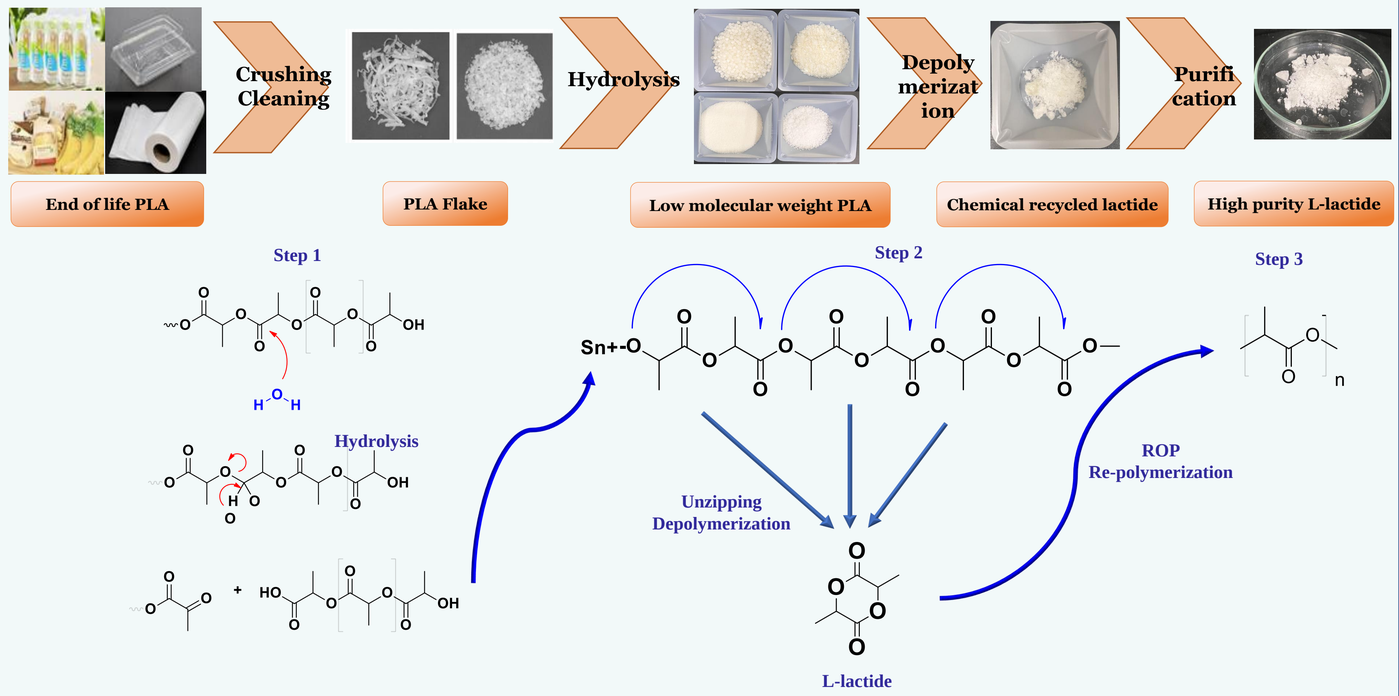
Ju-Hong Lee, Won-Bin Lim, Jin-Gyu Min, Jae-Ryong Lee, Ji-Hong Bae and PilHo Huh*
Department of Polymer Science and Engineering, Pusan National University, Busan 46241, Korea
*** pilho.huh@pusan.ac.kr***

ABSTRACT

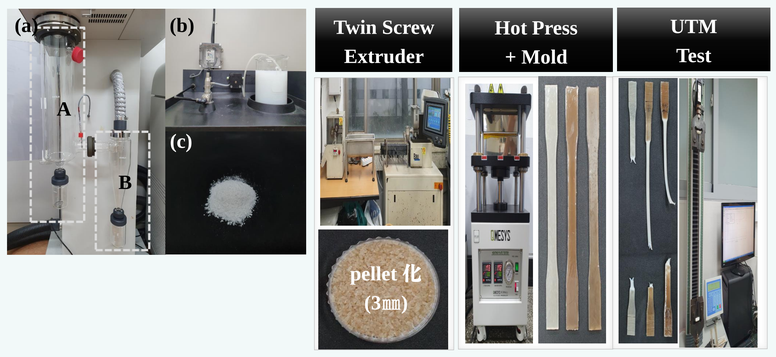
Polylactic acid (PLA) synthesized using high-purity l-lactide produced through chemical recycling was compounded with cellulose nanofibers (CNF) hydrophobized as a silane coupling agent to produce a composite. End of life PLA manufactured through physical processing was decomposed to Mn = 3,000 ~ 5,000 through hydrolysis, and L-lactide having a purity about 98~9% could be produced by back-biting using Sn/Zn-based organometallic and modified zeolite. In this work, we report a repolymerized PLA using the high purity lactide was compounded with CNF and composite of modified CNF/chemically recycled PLA (CNF-re-PLA) exhibited better mechanical properties than universal PLA. The tensile strength and Young's modulus of CNF-re-PLA prepared through extrusion tend to improve as the content of modified CNF increases. In addition, the characteristics according to the hydroxyl group substitution rate of CNF were evaluated using fourier transform infrared spectroscopy and X-ray diffraction. As a result, CNF having a high substitution rate through the silane coupling agent showed good compatibility with PLA and was confirmed through a scanning electron microscope. The obtained CNF-re-PLA composite also exhibits effective performances according to the modification rate and type of CNF. Overall, the CNF-re-PLA upcycling series manufactured using eco-friendly materials will have promising applications in the bio-compatible and plastics industries.

EXPERIMENTAL

<Chemical recycled PLA>



<Compounding PLA with Modified cellulose>



Step 1 Fabrication of surface-modified nanocellulose

Step 2 Compounding with PLA using twin screw extruder

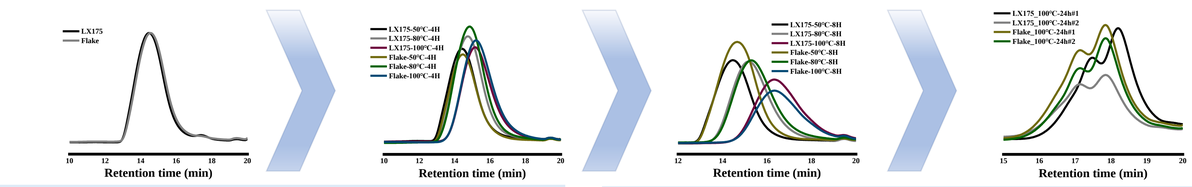
Step 3 Manufacture of dog bone specimens through the press and evaluation of physical properties

OBJECTIVES

1. Carbon and energy savings from recycling end of life PLA
2. Improving the properties of high-purity PLA by chemical recycling
3. Optimization of high purity l-lactide synthesized under depolymerization reaction conditions (catalyst, temperature, etc.)
4. Improving physical properties that are lacking when using recycled PLA by using modified cellulose

RESULTS

Hydrolysis PLA - GPC

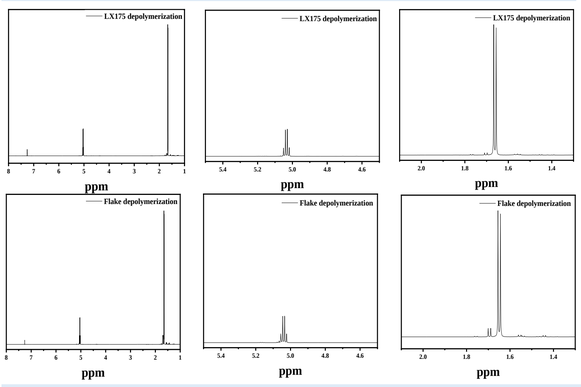


<Hydrolysis PLA molecular weight>

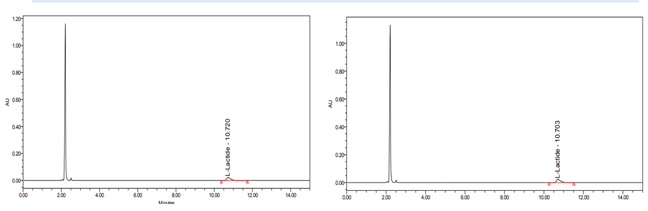
	Time (t)	temperature (℃)	Mn	Mw	PDI
LX175	4	100	36411	59211	1.63
	8	100	12264	21395	1.74
	24	**100**	**3346**	**7050**	**1.83**
Flake	4	100	35282	57853	1.64
	8	100	10421	20351	1.95
	24	**100**	**3497**	**6809**	**1.94**

-. The change in molecular weight according to the hydrolysis time was confirmed.
-. As a result of hydrolysis, PLA with a molecular weight of 60,000 was approximately changed to a molecular weight of 3000

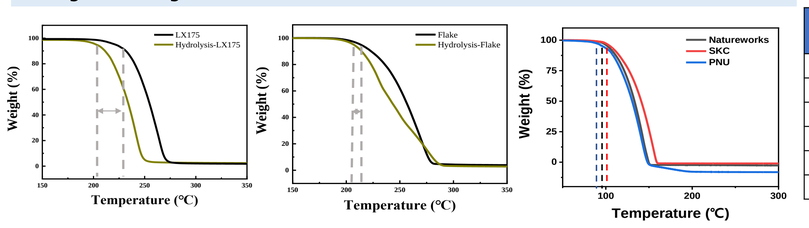
Re-Lactide - NMR



Re-Lactide - HPLC



Hydrolysis PLA and Re-Lactide - TGA

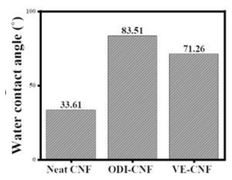


<L-lactide purities >

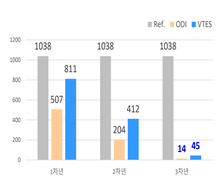
Sn catalyst	Ethanol	Ethanol : Water
#1-1	**97.98**	92.19
#1-2	**98.49**	92.22
#1-3	**98.49**	92.73
#2-1	93.53	95.15
#2-2	93.90	95.57
#2-3	94.19	95.71

-. As a result of structural analysis of lactide produced after depolymerization, it was confirmed that it was the same as L-lactide.
-. According to the optimization of the synthesis ratio, the OH value decreased.
-. After the purification process, HPLC was measured to confirm the purity of lactide, and it showed the highest purity at a constant ratio of water and ethanol.

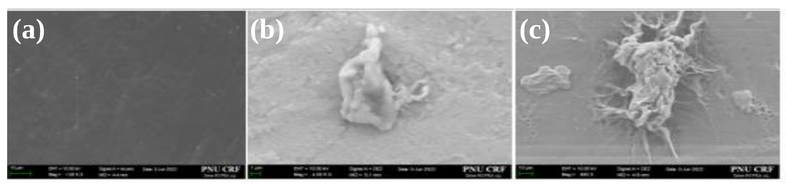
Solvent dispersion & Water CA



OH-value



SEM



-. Water contact angle: modification → 34° → 80° ~ 84°
-. According to the optimization of the synthesis ratio, the OH value decreased.
-. To confirm the composite properties of PLA and modified CNF, the surface of the specimen was observed with SEM, and the images are shown in (a) neat PLA, (b) PLA/ODI-CNF 1wt%, and (c) PLA/VTES-CNF 1wt%

CONCLUSIONS

- ✓ End of life PLA through physical regeneration was hydrolyzed according to process conditions to produce PLA with a molecular weight of 3,000.
- ✓ Depolymerization was performed according to the catalyst type using a low molecular PLA, and a high-purity l-lactide was obtained after a purification process.
- ✓ Upcycling PLA with improved mechanical properties was prepared by combining recycled PLA and modified cellulose.

ACKNOWLEDGEMENT

This work was supported by the Technology Innovation Program (or Industrial Strategic Technology Development Program) (RS-2022-00156186, Development of chemically regenerated lactide high-purity raw material technology and new material level PLA co-polymerization technology) funded By the Ministry of Trade, Industry & Energy(MOTIE, Korea)