A lysine-derived Flame Retardant for Improved Flame Retardancy, Crystallinity, and Aqueous-phase Degradation of Polylactide

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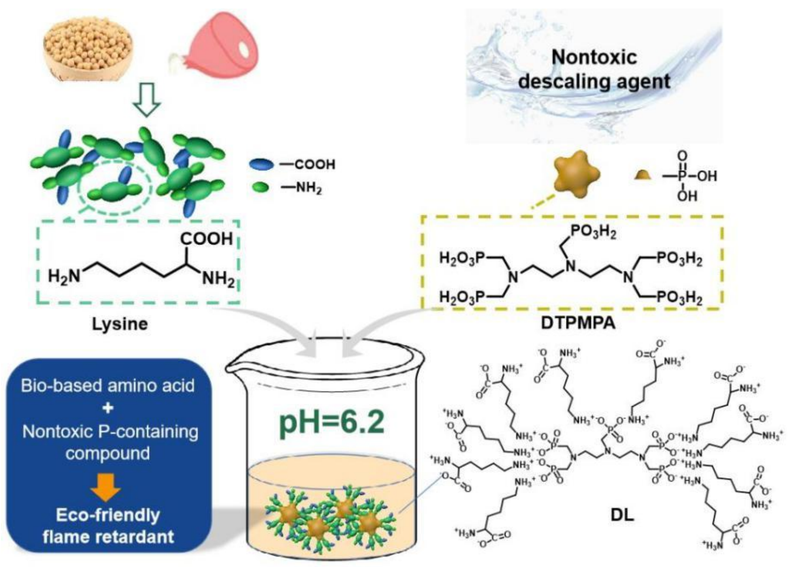
Introduction

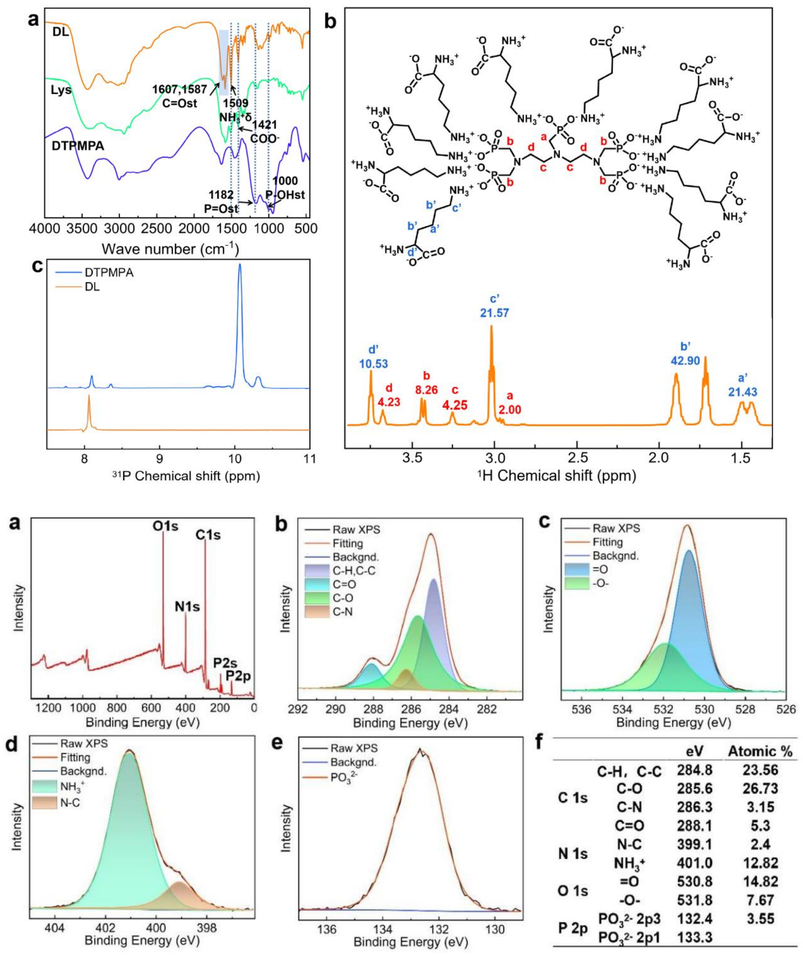
- Polylactide (PLA) as one of the excellent representative bioplastics had attracted attention worldwide.
- High flammability and poor crystallization behavior of PLA limit its further application.
- The aqueous degradation rate of the pure PLA has been reported extremely low in natural environment (e.g. in water or soil).

Methods and Materials



Characterization of DL

- FTIR : Peak intensity of NH_3^+ ↑
- ^1H NMR, XPS : actual molar ratio of DTPMPA to Lys is around 1:10
- ^{31}P NMR : 10.06 → 8.10 ppm



		eV	Atomic %
C 1s	C-H, C-C	284.8	23.56
	C-O	285.6	26.73
	C-N	286.3	3.15
	C=O	288.1	5.3
N 1s	N-C	399.1	2.4
	NH_3^+	401.0	12.82
O 1s	=O	530.8	14.82
	-O-	531.8	7.67
P 2p	PO_3^{2-} 2p3	132.4	3.55
	PO_3^{2-} 2p1	133.3	

Flame retardancy

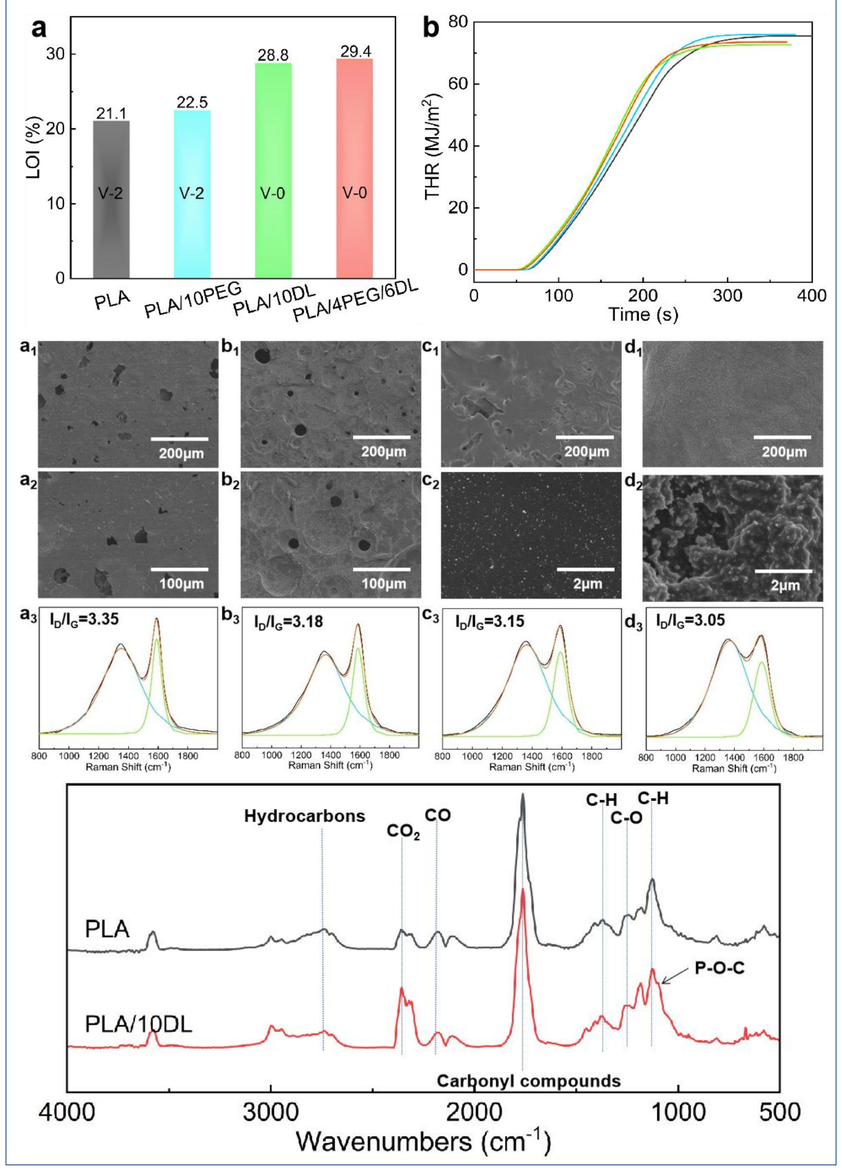
- UL94 V-0 LOI :29.4%
- THR : 76.2 MJ/m² → 73.6 MJ/m²

Condensed mechanism

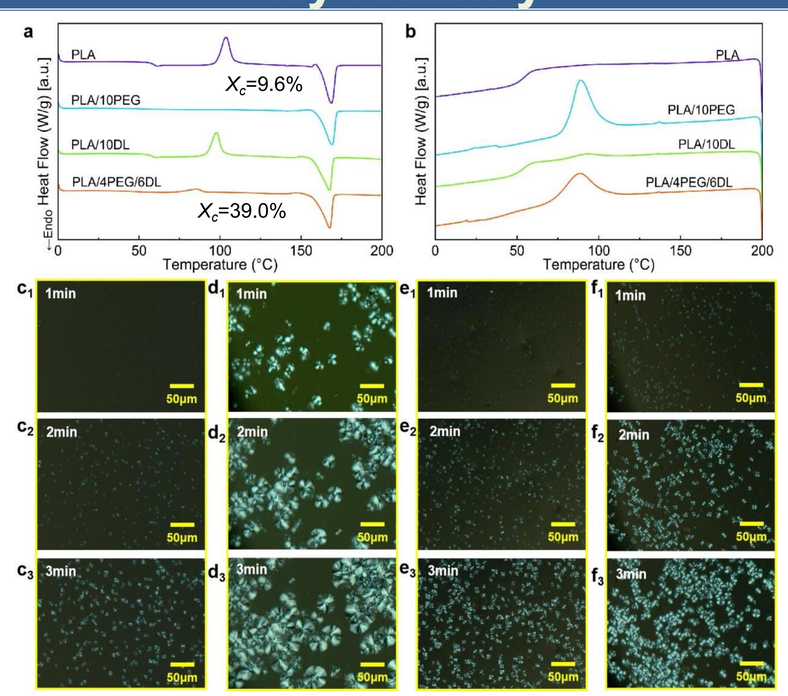
- The quantity and the quality of char were both ameliorated.
- I_D/I_G : 3.35 → 3.15

Gas phase mechanism

- A new absorption peak at 1100 cm^{-1} of P-O-C.

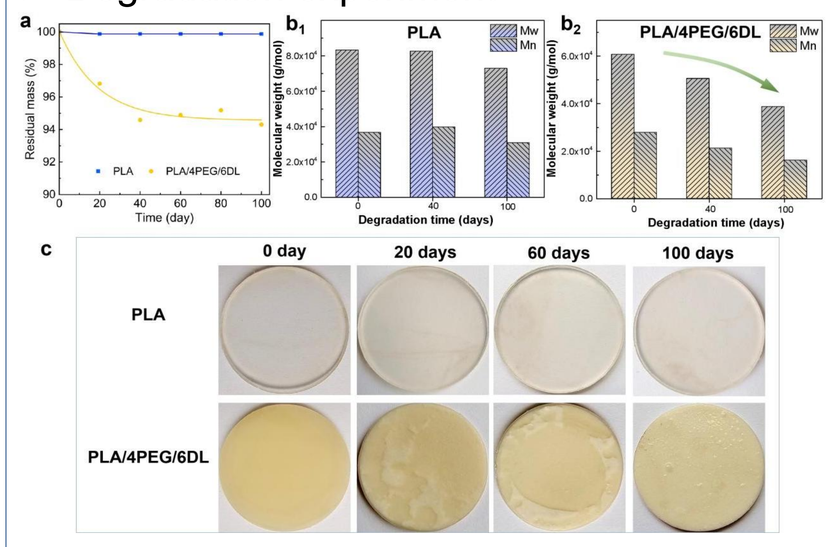


Crystallinity



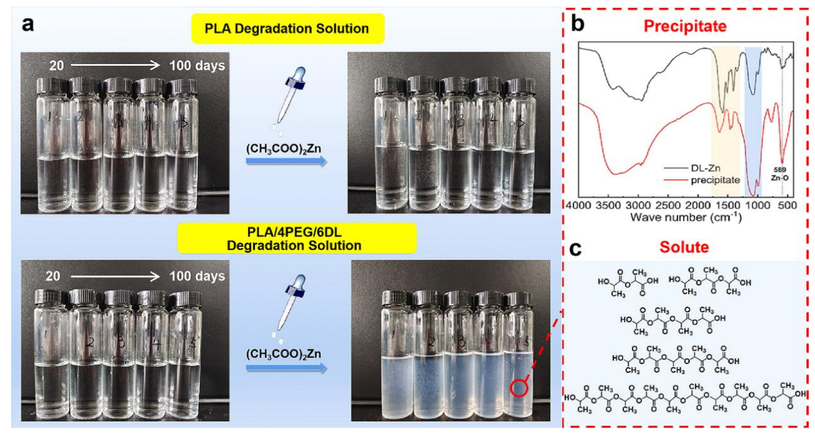
Hydrolytic degradation

- Degradation experiment

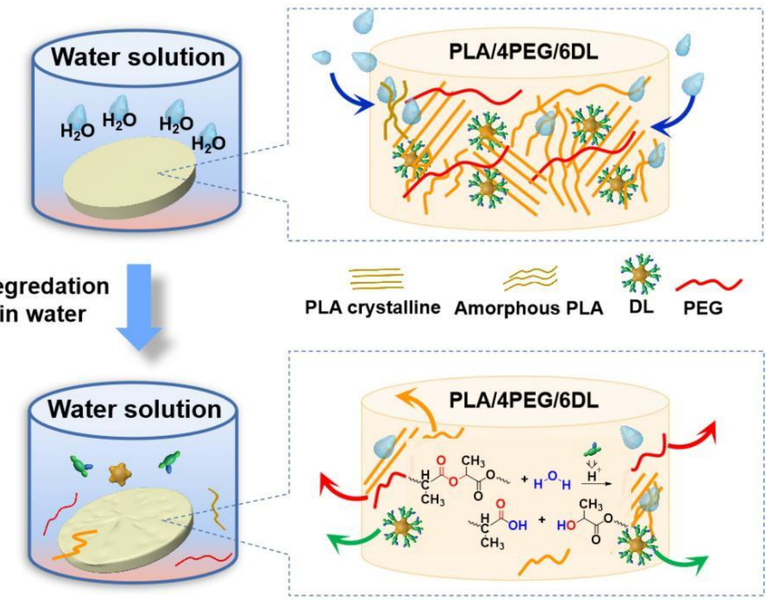


The M_n and M_w of PLA/4PEG/6DL decreased significantly

- Characterization of hydrolysate
  - The phosphates of DL has the ability to chelate with zinc ions.
  - The water-soluble oligomers such as dimers, trimers, tetramer and etc.



- Hydrolysis mechanism



- PEG and DL partially dissolved into water.
- The phosphoric acid group and -COOH of DL catalyze the ester cleavage.
- The carboxylic acid of oligomers providing an autocatalytic effect for degradation.

Conclusions

- The preparation process was carried out in aqueous phase, fully matches the concept of environmental protection.
- PLA/4PEG/6DL reached UL94 V-0 level with the high LOI value of 29.4%.
- Both of PEG and DL can promote crystallinity of PLA as manifested by the high degree of crystallinity PLA/4PEG/6DL of 39.0%.
- The introduction of DL and PEG into PLA accelerated the degradation of PLA matrix in purified water at ambient temperatures, inducing the decrease of Mn by 42% at 100 days.