Retarding Retrogradation in Polylactide/Thermoplastic Starch Films through Disulfide Chemistry and Biaxial Orientation

Piyawanee Jariyasakoolroj[1], Suttinun Phongtamrug[2], Patakorn Pilasen[3], Wanwisa Limphirat[4], Suwabun Chirachanchai[3]
e-mail: fagipnj@ku.ac.th

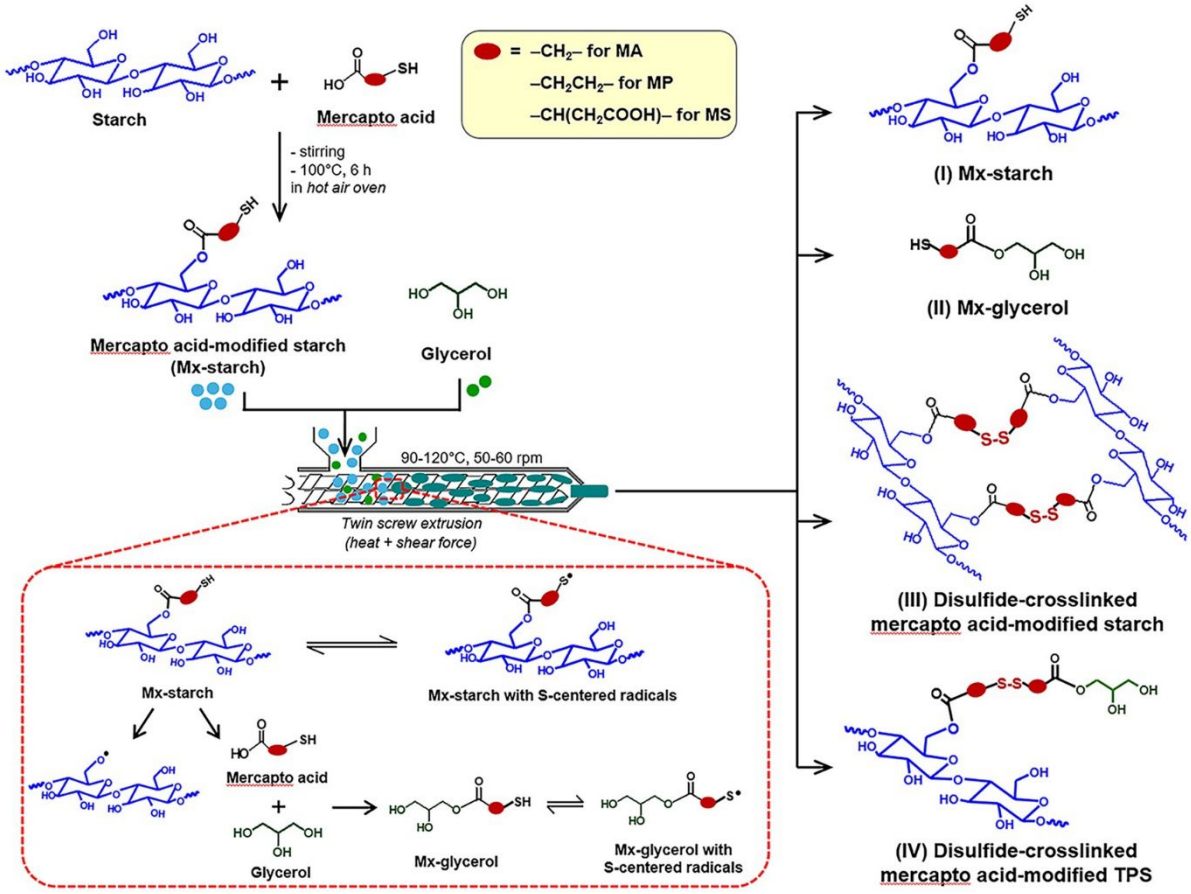
[1]*Department of Packaging and Materials Technology, Faculty of Agro-Industry, Kasetsart University, Thailand*
[2]*Department of Industrial Chemistry, Faculty of Applied Science, King Mongkut's University of Technology North Bangkok, Thailand*
[3]*Center of Excellence in Bioresources to Advanced Materials (B2A-CE), The Petroleum and Petrochemical College, Chulalongkorn University, Thailand*
[4]*Synchrotron Light Research Institute, Thailand*

Abstract

Thermoplastic starch (TPS) is a promising renewable and biodegradable material for sustainable packaging; however, its practical use is restricted by retrogradation, plasticizer migration, moisture sensitivity, and limited compatibility with hydrophobic biodegradable polymers. This study proposes a solvent-free processing strategy to stabilize TPS in polylactide (PLA)-based films by integrating mercapto acid-enabled chemical modification with biaxial orientation. Cassava starch was modified with mercapto acid derivatives and plasticized with glycerol through reactive extrusion to produce crosslinkable modified TPS (Mx-TPS). The Mx-TPS was subsequently melt-blended with PLA and processed into biaxially oriented PLA/Mx-TPS films. During melt processing, thiol groups promoted disulfide linkage formation and partial glycerol immobilization, while biaxial stretching induced PLA crystallization and lamellar alignment. These combined effects restricted starch chain reassociation and suppressed V_H-type starch crystallization during storage. Among the investigated modifiers, mercaptosuccinic acid (MS) provided the most effective stabilization, attributed to enhanced interfacial interactions and reduced molecular mobility. The resulting BO-PLA/MS-TPS films exhibited improved moisture resistance, oxygen barrier performance, water vapor barrier performance, and tensile properties compared with unmodified BO-PLA/TPS films. Oxygen permeability decreased from 1,153.72 to 589.31 cc.mil/m^2.day.atm, while water vapor permeability decreased from 159.21 to 68.90 g.mil/m^2.day.atm. These results demonstrate that combining dynamic disulfide chemistry with orientation-induced crystallization is an effective route to retard TPS retrogradation and improve the long-term performance of biodegradable PLA/TPS films for sustainable packaging applications.

Scheme I

Proposed mechanism of disulfide bond formation in mercapto acid-modified thermoplastic starch (Mx-TPS) during melt extrusion



References 1) P. Jariyasakoolroj, et al., *Polym. Degrad. Stab.* 247, e111962 (2026).

Biography (For Plenary, Keynote, and Invited Speakers)

Name: Piyawanee Jariyasakoolroj

Title: Associate Professor

Affiliation: Department of Packaging and Materials Technology, Faculty of Agro-Industry, Kasetsart University, Bangkok 10900, Thailand

Country: Thailand

Phone: (+66)89-231-9426

E-mail: fagipnj@ku.ac.th

Personal History:
Assoc. Prof. Dr. Piyawanee Jariyasakoolroj is a faculty member in the Department of Packaging and Materials Technology at Kasetsart University, Thailand. She also serves as Assistant Dean for Research and Innovation of the Faculty of Agro-Industry, Kasetsart University, where she contributes to strengthening research strategy and promoting interdisciplinary collaboration. She received her Ph.D. in Polymer Science from the Petroleum and Petrochemical College, Chulalongkorn University. Her academic background and research career focus on polymer science and sustainable packaging materials. Her expertise includes biodegradable polymer blends, reactive compatibilization, microstructure analysis, structure-property relationships, and biaxially oriented film processing. Her research aims to develop high-performance bio-based materials by understanding how molecular structure, processing conditions, and microstructure affect material properties.

Research Keyword (3-5 keywords use commas to separate each word):
Thermoplastic starch, Retrogradation, Disulfide linkage, Biaxial orientation, Biodegradable packaging