日本包装学会 第34回年次大会 学生ベストポスター賞のご紹介

受賞テーマ：
Enhancing the Hydrophobicity of Starch-Based Bioplastics via Internal Blending with Epoxidized Soybean Oil and Citric Acid
（エポキシ化大豆油とクエン酸を用いた内部ブレンドによるデンプン系バイオプラスチックの疎水性向上）

受賞者：
山形大学大学院 **Pansuwan Thanaboon 様**

2025 年８月２８日 懇親会での授賞式 永井会長より表彰

【Pansuwan Thanaboon様の受賞へのお言葉】

During this research, the most difficult challenge I faced was dealing with failed results, which occurred many times. However, I considered these failures as valuable opportunities that allowed me to think carefully, learn from mistakes, and find new ways to overcome the problems. I am deeply grateful to Professor Miyata Ken, who has always supported and guided me, as well as to my laboratory members. Even though there were some language barriers, they still gave me a warm welcome and always tried to support me, which encouraged me to keep moving forward.

My greatest motivation comes from my desire to create sustainable materials for packaging and to add value to agricultural-based resources. Coming from Thailand, a country rich in these raw materials, I strongly hope that my research can contribute not only to my home country but also to protecting the global environment. In the future, I wish for my work to replace petroleum-based packaging with bio-based alternatives, which is my highest goal.

今回の研究において最も困難だったのは、繰り返し失敗する実験結果に直面することでした。しかし、私はその失敗を貴重な学びの機会と捉え、問題をよく考え、改善方法を見つけ出すことで前に進むことができました。常にご指導とご支援をくださった宮田教授に深く感謝するとともに、言語の壁があるにもかかわらず温かく迎え入れ、常に支えてくださった研究室の皆様にも心から感謝申し上げます。
私の最大の原動力は、持続可能な包装材料を開発し、農業由来資源の価値を高めたいという思いです。私は農産資源が豊富なタイの出身であり、この研究が母国だけでなく、地球環境の保護にも貢献できることを強く願っています。将来的には、石油由来の包装材料をバイオベースの代替材料に置き換えることが、私の最大の目標です。


宮田研究室の皆様

山形大学工学部　宮田研究室リンク先
https://pome-oms.yz.yamagata-u.ac.jp/polymorg/laboratory/all/miyata-lab/

【研究内容　文責：日本包装学会　広報委員会】
　タピオカでんぷんにクエン酸とエポキシ化大豆油を用いて架橋し、疎水性（接触角で観察）と緻密な構造（ SEM で観察）を付与し、石油由来プラスティックの代替え素材を開発する研究です。クエン酸のカルボキシ基とエポキシ化大豆油のオキシランのモル比を高くするに従い、基本的に疎水性と密な構造となって行くものの、クエン酸が過剰になりすぎると未反応の親水基またはデンプンの加水分解により、逆に疎水性が低下したという研究で、バイオマスプラスティック開発のための反応と物性の基礎的な研究です。
　末尾の要旨と発表資料を参照してください

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山形大学大学院 ○（学）Pansuwan Thanaboon,（正） 伊藤　浩志 ,（正）宮田 剣

Introduction

The increasing demand for sustainable alternatives to petroleum-based plastics has intensified interest in biodegradable materials derived from renewable resources. Among these, thermoplastic starch (TPS) is particularly attractive due to its abundance, low cost, and biodegradability. However, its high hydrophilicity and poor mechanical stability limit its practical applications. To address these limitations, this study explores an internal blending strategy employing epoxidized soybean oil (ESO) and citric acid (CA) to create a reactive bio-based epoxy system capable of enhancing the hydrophobicity and structural integrity of starch-based bioplastics.

Experimental Setup

Materials

Native tapioca starch with an initial moisture content of 10%wt. was provided by SMS Corporation Co., Ltd., Thailand. Sorbitol (98.0% purity) and CA (98.0+% purity)were purchased from Fujifilm Wako Pure Chemical Co., Ltd., Japan. ESO (~3.9 epoxide group/mole) was purchased from Sanwa Synthetic Chemical Co., Ltd. All the reagents were used as received without any pretreatment.

Preparation of dispersed CA in ESO solution

The molar ratio between carboxylic acid group of CA and oxirane group of ESO were used at 0.2, 0.4, 0.6, 0.8, and 1.0. Initially, CA was dissolved in acetone with 20 wt.% and thereafter heated up to a temperature of 60°C until CA was dissolved. Then, ESO was added to the solution and continue heating to 80°C. The mixture was evaporated acetone to obtain final transparent of dispersed CA in ESO.

Preparation of the starch bioplastic composite

First, starch powder and sorbitol were roughly mixed before being transferred into the torque rheometer (Toyoseiki, Thermo Labo Plastomill 10c100-01). The blending temperature is 120°C, shaft speed at 60 rpm, with duration 3 min. to induce plasticization of starch. Then, dispersed CA in ESO solution was added with the fixed amount at 5 wt.% of solution to starch, and continued blending to 15 min. After that, the obtained blending product was pelletized and thermo-shape forming using compression molding (Toyoseiki, Mini Test Press10) at 120°C with a pressure of 15 MPa for 15 min. The molded composite bioplastic was kept for 2 days at 50-55% relative humidity at room temperature prior to testing.

Results and Discussion

The hydrophobicity of starch-based bioplastic films was assessed by measuring the water contact angle (WCA) over time, as presented in Fig. 1. All samples showed a declining WCA trend, consistent with the water absorption behavior typical of starch-based materials. However, distinct differences were observed in both the initial WCA values and their rate of decline. The sample with a ratio of 0.4 (R0.4) exhibited the highest initial contact angle and the slowest decrease over time, indicating enhanced surface hydrophobicity. This improvement is attributed to the optimal crosslinking between the carboxylic acid and epoxide groups, which effectively reduces the number of hydrophilic hydroxyl groups exposed on the starch surface. In contrast, the sample with the highest ratio (R1.0) showed a faster WCA decline, likely due to an excess of unreacted CA, which introduces additional hydrophilic functional groups into the matrix.

The surface morphology of the fractured films, shown in Fig. 2, provides further insight into the effect of CA/ESO ratios on the internal structure of bioplastics. At lower ratios (e.g., R0.2 and R0.4), the fracture surfaces exhibit rough textures and visible voids, suggesting weak interfacial adhesion and poor dispersion of the ESO-CA oligomer in the starch matrix. As the ratio increases to R0.6, the fractured surface appears more compact and uniform, indicating improved compatibility and the formation of a stronger crosslinked network. This observation correlates well with the enhanced hydrophobicity observed in the WCA results. Interestingly, at higher ratios (R0.8 and R1.0), morphology shows a finer oil phase distribution, which might be expected to improve hydrophobicity. However, the high CA content may lead to partial hydrolysis of starch chains, resulting in increased surface polarity and, consequently, reduced hydrophobic performance.

Conclusion

This study demonstrated that blending CA with ESO and incorporating the mixture into starch-based bioplastics effectively enhances hydrophobicity. By varying the ratio between carboxylic acid and oxirane groups, the water resistance and microstructure of the composite films were significantly affected. An optimal ratio R0.4 resulted in the highest water contact angle and a more compact fracture morphology, indicating improved compatibility and crosslinking within the matrix. In contrast, excessive CA content (R1.0) led to reduced hydrophobicity, likely due to unreacted hydrophilic groups or starch hydrolysis. These findings highlight the importance of tuning the reactive group ratio to achieve a better-performance, bio-based films with enhanced water resistance for potential use in sustainable packaging applications.

References

1. Pansuwan, T., Ito, H. & Miyata, K. Reinforcement of Starch-Based Composite Properties via a Two-Step Blending Process with Citric Acid–Cured Epoxidized Soybean Oil Oligomer. *J Polym Environ* (2025). https://doi.org/10.1007/s10924-025-03613-5

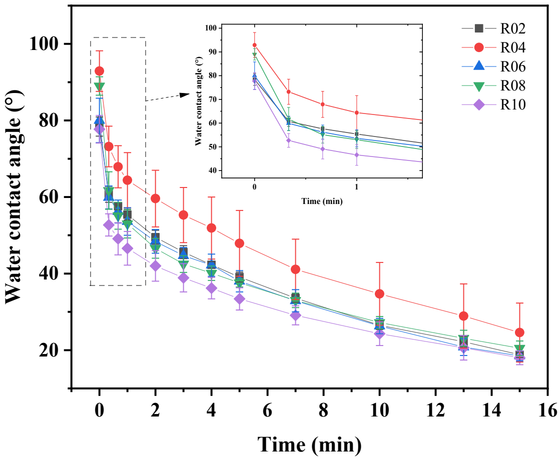

Figure 1. Water contact angle of bioplastic film prepared with varied ratio between carboxylic acid and oxirane group.

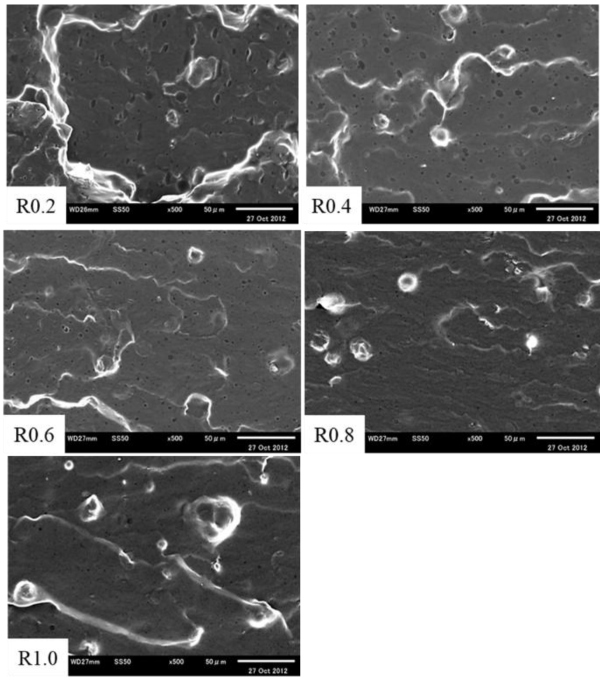

Figure 2. SEM images of tensile fractured surface of bioplastic composite films with different ratio between carboxylic acid and oxirane group.

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山形大学 Yamagata University

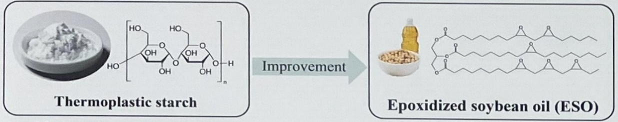
Pansuwan Thanaboon, 伊藤 浩志, 宮田 剣 Graduate School of Organic Materials Science, Yamagata University

Research Purpose

To enhance hydrophobicity of starch bioplastic with natural-based component by internal reactive blending process.

1 Research Background

Blending with additive to enhance hydrophobicity



×High Water Sensitivity

×Low Compatible with Starch

Study Scope

Using internal reactive blending with apply citric acid (CA) as a crosslinker to improve compatibility between starch and ESO.

4 Conclusion

Dispersion of ESO phase in bioplastic matrix

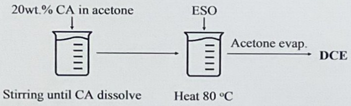
Internal blending process can provide the uniform dispersion of ESO along with balancing of CA content.

Hydrophobicity of bioplastic film

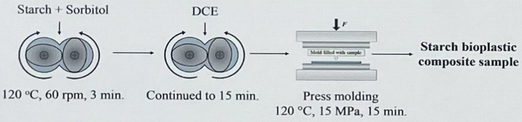
The optimal ratio of carboxylic to oxirane for achieve highest hydrophobicity of starch-based bioplastic was 0.4.

2 Materials and Method

Dispersion of CA in ESO (DCE)



Blending and Molding Process



- Blending machine: Torque rheometer (Toyoseiki, Thermo Labo Plastomill 10c100-01)
- Press machine: Hydraulic press machine (Toyoseiki , Mini Test Press10)

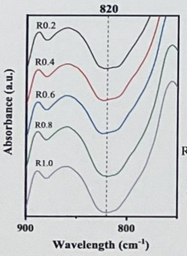
The Bioplastic Composition Table

Sample	wt.% DCE by starch	Mass ratio of DCE		Component content		
		ESO	CA	Starch	Sorbitol	DCE
R0.2	5	1.99	0.11	42	28	2.1
R0.4		1.90	0.20	42	28	2.1
R0.6		1.81	0.29	42	28	2.1
R0.8		1.73	0.37	42	28	2.1
R1.0		1.66	0.44	42	28	2.1

3 Results and Discussion

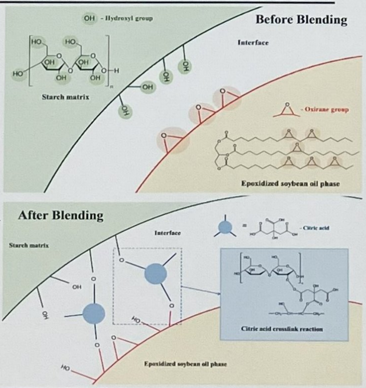
3.1 Characterization of crosslink reaction between starch and ESO

FTIR: IRAffinity-1S (Shimadzu)
- ATR-FTIR: Diamond/KRS-5
- Scan range: 4000-400 cm^{-1}, resolution 2 cm^{-1}
- Sample thickness: 1 mm



IR diagram of bioplastic sample at 820 cm^{-1}, indicated the presence of unreacted oxirane group.

$$R = \frac{\text{Carboxylic group}}{\text{Oxirane group}}$$

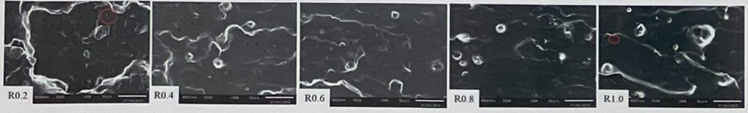


The decreasing of 820 cm^{-1} peak indicated the crosslink reaction on oxirane group, which was reacted by CA.

3.2 Dispersion of ESO phase in bioplastic matrix

Field emission scanning electron microscope (FE-SEM): (JSM-6510 (JEOL))
- Tensile fractured sample coated surface with gold using fine coater JFC-1200 (JEOL)

SEM images of tensile fractured surface of bioplastic with different R.



Large Droplet Size Small

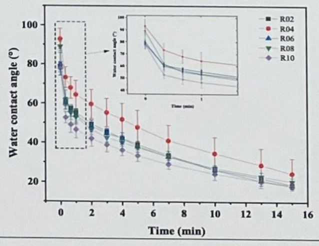
Low Content of CA High

Increasing R (higher CA content) results in a smaller with uniform distribution of the ESO dispersed phase due to a sufficient amount of CA promoting an interphase crosslinking reaction.

3.3 Dynamic water contact angle (WCA)

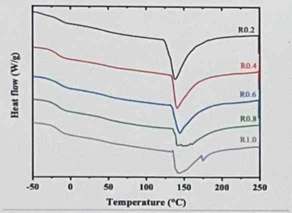
DropMaster DM-501, (Kyowa): Droplet testing volume 3.0 μl. Exposure time: 15 min.

WCA of bioplastic film with different R.



R0.4 sample has a highest WCA, imply the optimal ratio balancing the amount between ESO phase and CA crosslinker for achieve hydrophobic.

3.4 Thermal behavior of bioplastic composite



COOH/OCC ratio	T_g (°C)	T_m (°C)	ΔH_m (J/g)
0.2	-13.6±0.1	142.3±3.7	55.7±13.3
0.4	-16.9±0.5	141.4±1.7	55.1±8.1
0.6	-14.5±0.6	144.8±1.9	47.8±9.8
0.8	-14.9±0.2	144.8±4.1/156.4±3.9	48.1±9.7
1.0	-15.2±0.3	145.8±3.4/178.0±4.7	45.9±4.3

Lowering T_g

▲

Provides a plasticization effect

▲

Increasing R (higher CA)

▼

Exceed amount of CA in starch matrix

▼

Hydrolysis of starch

▼

Broader and separate meting peak

High CA content provide plasticization effect while increasing hydrolysis of starch.

Correspondence to: KEN MIYATA (Tel & Fax: +81-238-26-3069 E-mail: ken@yz.yamagata-u.ac.jp)