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Chemical-Mechanical Hydrolysis Technique of Modified Thermoplastic Starch for Better Mechanical Performance

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Abstract

The effects of chemical-mechanical hydrolysis on the properties of thermoplastic starch (TPS) were studied. In the presence of citric acid (CATPS) and glycerol (GTPS) along with mechanical hydrolysis, a native starch granule was transformed into a continuous phase as shown by scanning electron microscope (SEM). As shown by thermogravimetric analysis (TGA), the improvement in thermal stability confirmed that the addition of citric acid along with mechanical hydrolysis enhanced the adhesion between glycerol, citric acid and starch. It was proven by Fourier transform infrared (FTIR) spectroscopy, that citric acid form stronger hydrogen bonding than glycerol. Strong hydrogen bond formation induced the improvement in mechanical properties of GTPS. Tensile strength of citric acid modified TPS with 2% citric acid (CATPS) higher than GTPS because citric acid improved the interaction of starch molecule and slippage of starch chain.

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Keywords: Chemical-mechanical hydrolysis; Mechanical properties; Scanning Electron Microscope (SEM); Thermogravimetric Analysis (TGA)

1. Introduction

The research of biodegradable polymer is growing intense as continues growing concern towards the application of green product in worldwide. Extensive studies have been performed on natural polymers such as gluten, zein, lignin, cellulose, chitin and starch[1].

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Among these, starch is recently being used. Starch are widely used as a viable alternative to make biodegradable plastic. It is because starch is cheap, renewable and biodegradable. Furthermore, it easily degrades when exposed to environment and bacterial. Starch usually exists in granular state, which it composes of semi-crystalline polymer structure. Starch can acts like thermoplastic polymer by incorporation of starch granule with plasticizer via aid of heat and shear mechanism[2-5,14]. Thus, it produce thermoplastic starch (TPS), which has properties alike conventional thermoplastic polymer.

Although TPS exhibits thermoplastic-like properties, its lacks in several properties compared with conventional thermoplastics, like mechanical strength and ability to absorb moisture. To mitigate the shortcomings, several modifications are performed. Chemical modification is one of approaches that has been carried out. Starch modification achieved through derivatization, such as etherification, esterification, cross-linking and grafting of starch. These modifications alter starch gelatinization, pasting and retrogradation behavior[3]. Fiber is also used to reinforce TPS. Others approach performed to TPS such as chemical hydrolysis, surface treatment and additives.

Carboxylic acid is usually used to perform chemical modification, where it acts as plasticizer or crosslinker agent in thermoplastic starch processing. Recent carboxylic acid has been used are ascorbic acid, malic acid, citric acid, tartaric acid and others[4,6,13]. Addition of carboxylic acid in TPS increases the hydrogen bonding between starch and glycerol, co-plasticized with carboxylic acid. The measurement of physical properties verified that the strength and flexibility of TPS with carboxylic acid are higher than TPS with polyols[5]. This due -to the existence of carboxyl groups as functional group. Generally, mechanical hydrolysis involves physical process cause substance and water molecule to split into parts. Thus, it increases the free volume and it is possible to cut down polymer chain into small or short length of chain.

The objective of this preliminary research was to study the effect of chemical-mechanical hydrolysis technique onto TPS in order to improve the mechanical properties and thermal stability. The effect of citric acid (CA) content on mechanical performance and thermal performance was also evaluated.

2. Experimental detail

2.1 Materials

Cassava starch (CS) was purchased from Thye Huat Chan Sdn Bhd, CA was purchased from Aldrich Chemical Co. Inc., glycerol (GL) was purchased from HmBG Co. Inc.

2.2 Plasticization

The water content of cassava starch was reduced by drying in an oven at temperature 80 ^{o}C for 30 minutes. TPS was prepared by mixing 65% (w/w) cassava starch with 35% (w/w) glycerol. The mixture was sealed and stored overnight. When citric acid was used, citric acid was firstly dissolved in the additional distilled water. The abbreviations for different samples prepared and their compositions are listed in Table 1. Glycerol-plasticized TPS (GTPS) and citric acid modified TPS (CATPS) were prepared as following -: the mixtures were manually fed in a heated two-roll mill machine at temperature 150 ^{o}C for 10 minutes.

Table 1 . Used symbols and corresponding sample compositions.

Symbols	**Samples (w/w %)**		
	Cassava starch	Glycerol	Citric acid
GTPS	65	35	0
CA1 TPS	65	35	1
CA2 TPS	65	35	2
CA3 TPS	65	35	3
CA4 TPS	65	35	4