

A Preliminary Study on the Preparation of Environmentally Friendly Materials from Modified Glutinous Starch

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ABSTRACT

Modified glutinous starch was prepared from the reaction between glutinous starch and maleic anhydride using sodium hydroxide as a catalyst and water as a solvent at 50°C. The modification conditions with respect to the amounts of maleic anhydride were 5%, 15%, 25%, 35%, 50%, 65%, 75% and 85% and to the reaction times were 30, 60, 90 and 120 minutes. After the reaction finished, the obtained products were neutralized by adding hydrochloric acid solution and the chemical structures of the modified glutinous starches were determined by FT-IR spectroscopy. The sheet samples were prepared from modified starches by casting and their characteristics including drying time, moisture absorption ability and tensile properties were investigated. It was found that both the amount of maleic anhydride and the reaction time affected the characteristics of the obtained sheets. Suitable modification conditions which result in the sheet sample exhibiting better overall characteristics than those prepared with other conditions was at 35% of maleic anhydride and a reaction time of 30 minutes.

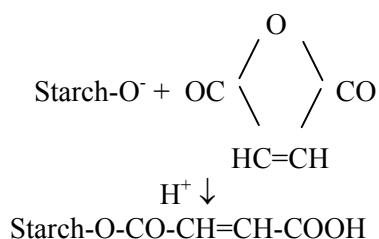
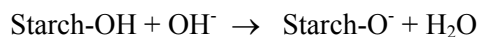
Keywords: glutinous starch, modification, biodegradable

INTRODUCTION

Studies on the preparation of environmentally friendly materials, especially biodegradable materials have rapidly increased. These materials are expected to substitute materials having difficulty in destruction, such as polystyrene, polypropylene, poly(ethylene terephthalate), etc. When some types of these polymers are burnt, they can release dangerous gases to the atmosphere while the burial method cannot destroy them because they are not biodegradable. Therefore, biodegradable materials based on natural polymers, such as starch, have been developed to replace commonly used synthetic polymers (Thiebaud, *et al.* 1997; Kiatkamjornwong, *et al.* 1997; Kiatkamjornwong, *et al.* 1999; Thakore, *et al.* 2001; Kiatkamjornwong, *et al.* 2001; Narayan, *et al.* 1999; McCarthy, *et al.* 1999; Wurzburg, *et al.* 1986; and Pimpan, *et al.* 2001).

Generally, blending or copolymerizing natural polymers with synthetic polymers are

common methods used to prepare biodegradable materials (Thiebaud, *et al.* 1997; Kiatkamjornwong, *et al.* 1997; Kiatkamjornwong, *et al.* 1999; Thakore, *et al.* 2001; and Kiatkamjornwong, *et al.* 2001). However, the obtained products are partially biodegradable (Narayan, *et al.* 1999; and McCarthy, *et al.* 1999). Therefore, the preparation of fully biodegradable materials from chemically modified natural polymers is alternatively studied. One successful modification method for starch was to use acid chlorides or anhydrides as modifying agents in aprotic solvents, such as DMSO, and catalysts, such as pyridine (Narayan, *et al.* 1999; and Wurzburg, *et al.* 1986). Although this method is effective, the chemicals are expensive and dangerous. Therefore, other safer methods for modifying starch based on aqueous processing have been developed (McCarthy, *et al.* 1999; Wurzburg, *et al.* 1986; and Pimpan, *et al.* 2001). One method whose reactions are given below is to use maleic anhydride as a modifying agent, sodium hydroxide as a catalyst and water as a solvent (Pimpan, *et al.* 2001).



Previous studies have found that this method can be used to prepare modified cassava starch with ease and safety. Furthermore, the obtained modified cassava starch can be cast into sheet form. These sheets can be dried by water evaporation which is also does not pollout to the environment (Pimpan, *et al.* 2001). The obtained sheets are fully biodegradable. They are insoluble in typical solvents, such as chloroform or in acidic solution, at both room and elevated temperatures while they are soluble in hot basic solution (Pimpan, *et al.* 2001).

For this research, the main objective is to study the possibility to use other types of starch to prepare environmentally friendly materials using the above method (Pimpan, *et al.* 2001). Glutinous starch was selected for this study since this starch is one type of starch which is mostly produced in Thailand, but it is rarely used in biodegradable material development.

MATERIALS AND METHODS

Materials

Glutinous starch, a commercial grade was used. Maleic anhydride (MA) and sodium hydroxide (NaOH) were purchased from Fluka. Hydrochloric acid (HCl) was purchased from Aldrich. All materials were used as obtained without further purification.

Methods

1. Modification of Glutinous Starch (Pimpan, *et al.* 2001).

Glutinous starch was dried in a vacuum oven at 80°C overnight and left to cool down in a desiccator. The dried starch was slowly added into a beaker containing aq. NaOH solution and the mixture was stirred at 50°C until it was homogeneous. MA was then slowly added to the mixture and then stirred at 50°C for a period of desired reaction time. After that, the obtained product was neutralized by aq. HCl solution.

The amounts of MA used were 5 %, 15 %, 25%, 35%, 50%, 65%, 75% and 85% of MA acidic groups in molar proportions to hydroxyl groups of the starch.

The amount of NaOH used depended on the amount of MA. For each formula, the ratio of NaOH:MA was 2.2:1 in molar proportions.

The reaction times used were 30, 60, 90 and 120 minutes.

2. Characterization of Modified Glutinous Starch

One portion was taken from each modified starch mixture and poured into a beaker containing ethanol. The precipitate was recovered, washed with ethanol and dried in a vacuum oven. Then it was characterized using a FT-IR Spectrometer Nicolet-Impact 400 model.

3. Preparation of Sheet Samples from Modified Starch by Casting and Determination of Drying Time

The modified starch mixtures obtained from method #1 were poured into molds. The samples were left to dry in a normal atmosphere (at room temperature and 60% relative humidity). The drying time was determined from the moment that the mixtures were poured into molds to the moment that the sheet samples completely dried.

4. Investigation of Tensile Properties of Sheet Samples

Tensile properties of the samples were determined based on ASTM D 638-91 (ASTM, 1991) using a Universal Tensile Testing Machine with a load cell of 10 kN, a strain rate of 5 inch/min at a temperature of 23±2°C and a relative humidity of 50±5 %.

5. Determination of Moisture Absorption of Sheet Samples

The samples with a size of 1 x 1 x 0.3 cm were dried in desiccators until their weights became constant (W_0). These samples were then placed in a normal atmosphere (60% relative humidity) for 24 hours. After that, the samples were weighed (W_1). % moisture absorption, (%M), can be calculated from the following equation:

$$\%M = [(W_1 - W_0) / W_0] \times 100$$

RESULTS AND DISCUSSION

The FT-IR spectroscopic results shown in Figures 1 and 2 suggest that the amount of MA has a significant effect on the chemical structures of the modified glutinous starches. It can be seen that as the amount of MA increases, single broad peaks at a wavenumber range of 3200-3600 cm^{-1} which correspond to OH stretching actually split. This

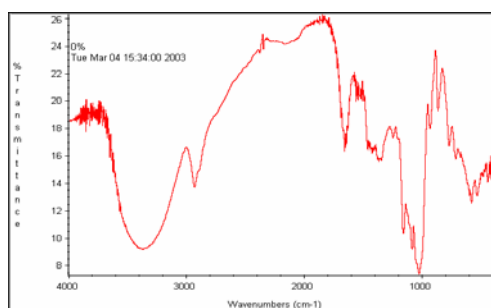
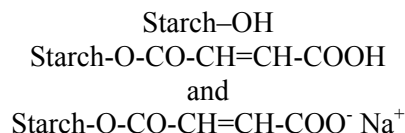


Figure 1 FT-IR Spectrum of Unmodified Glutinous Starch

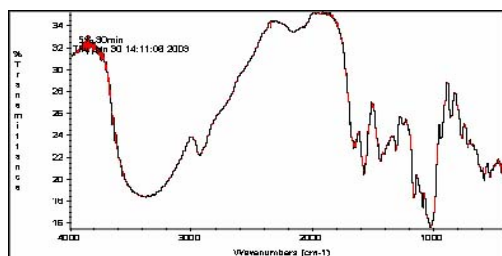
indicates the existence of different types of OH stretching which are from OH groups and COOH groups. All modified starches show peaks at a

wave number range of 1400–1600 cm^{-1} which correspond to $-\text{COO}-$ of ester groups, COOH groups and $\text{COO}^- \text{Na}^+$. The intensities of these peaks increase with increasing amount of MA. The peaks at the wavenumber of around 870 cm^{-1} of the modified starches indicate the presence of a carbon-carbon double bond (C=C). These results confirm that the chemical structures of modified glutinous starch consist of the following structures:

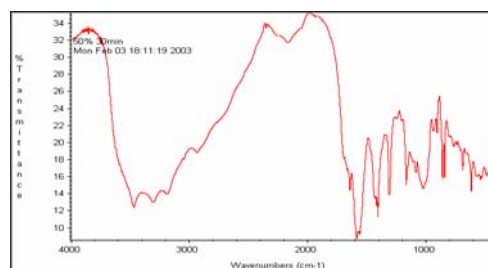


The last structure is a result of uncompleted neutralization of the starch-sodium salt by aq. hydrochloric acid solution. This observation was also found in a previous study with cassava starch (Pimpan, *et al.* 2001).

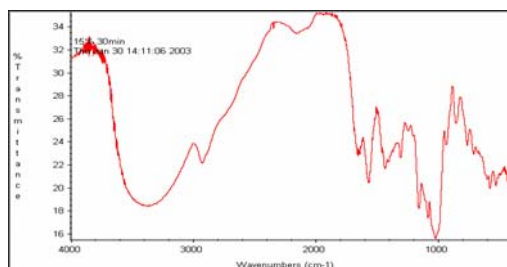
The FT-IR spectra of the modified glutinous starches prepared with different amounts of MA for other reaction times (60, 90 and 120 minutes) also exhibited the same behaviors.



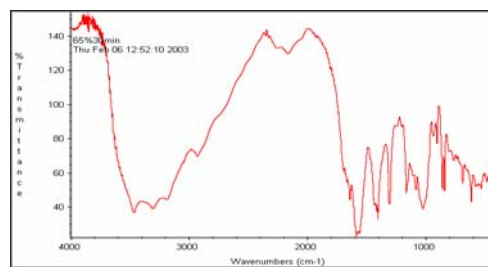
MA 5%



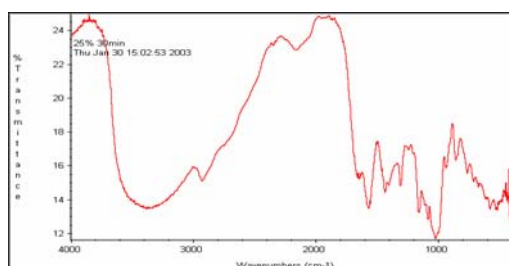
MA 50%



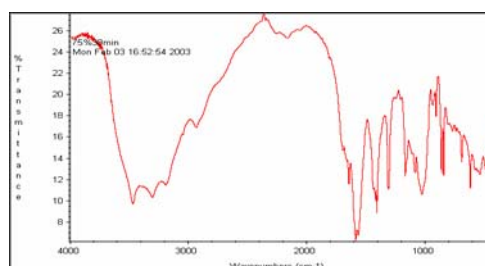
MA 15%



MA 65%



MA 25%



MA 75%

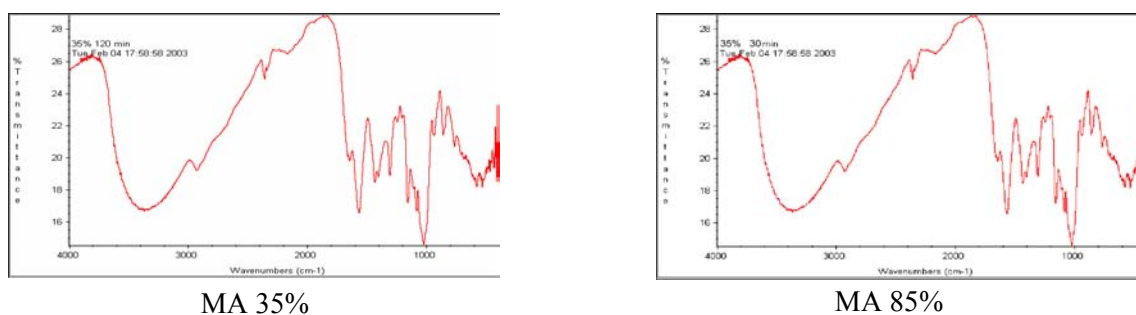


Figure 2 FT-IR Spectra of Modified Glutinous Starches Prepared with Different Amounts of MA and Reaction Time of 30 Minutes

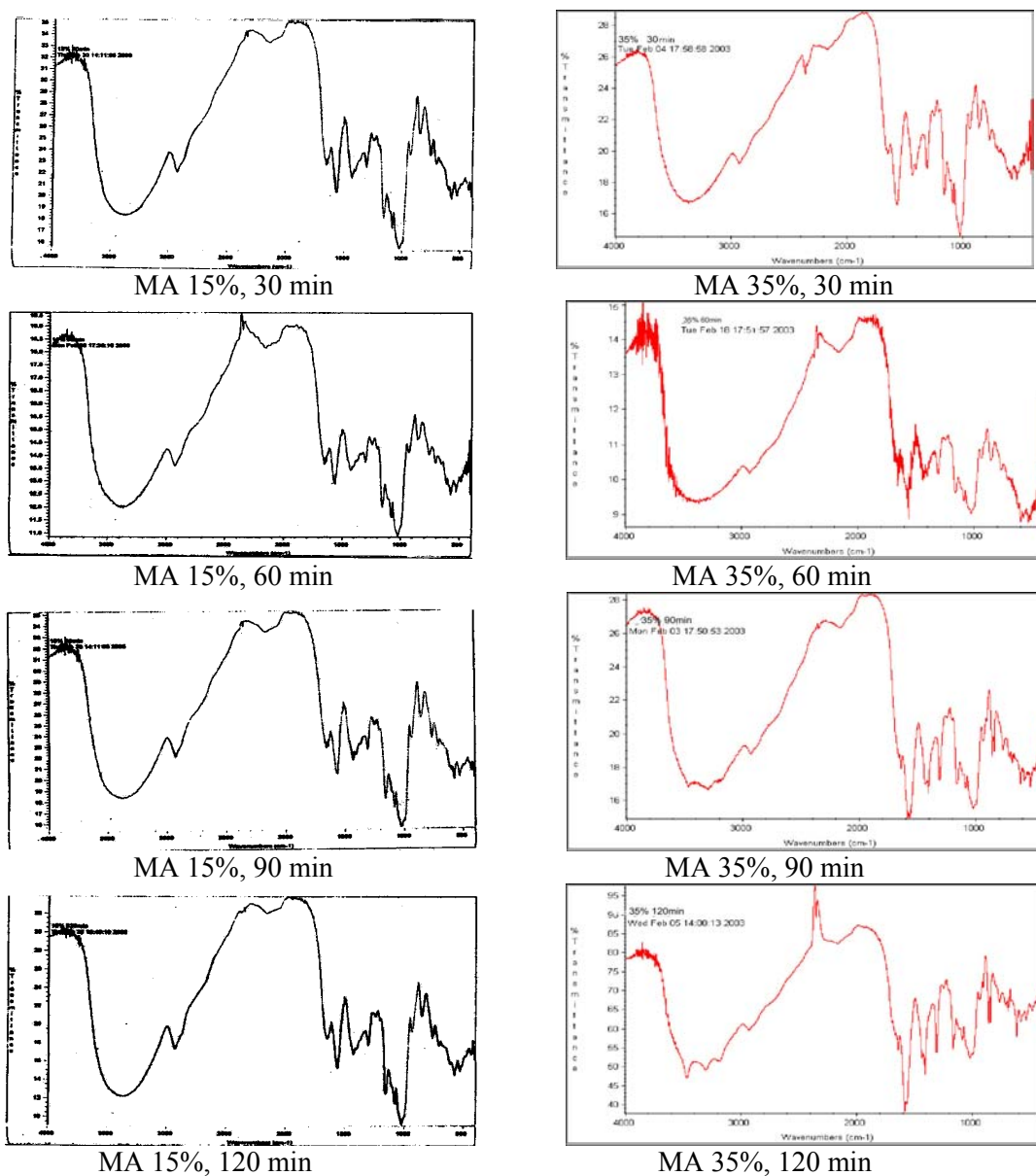


Figure 3 FT-IR Spectra of Modified Glutinous Starches Prepared with 15% and 35% of MA and Different Reaction Times.

The effect of the reaction time on the chemical structures using FT-IR spectra of modified starches was found that at lower amounts of MA, such as those prepared with 15% of MA, the FT-IR spectra of modified starches prepared using different reaction times are similar as shown in Figure 3. On the other hands, for those prepared at higher amounts of MA, such as those prepared with 35% of MA, it can be seen that as the reaction time increases, the peaks corresponding to COOH groups and ester groups are clearly seen as shown in Figure 3. These results suggest that longer reaction times may be required when a higher amount of MA is used.

Figures 4 and 5 show that the drying time is longer and % moisture absorption is higher for the sheet samples prepared with a higher amount of maleic anhydride when using the same reaction time. The greater the amount of maleic anhydride, the more the chemical structures of glutinous starch were modified as previously shown in Figure 1. As a result, looser packing and less hydrogen bonding indicated more free hydroxyl groups were obtained. Therefore, it is easier for water molecules to penetrate between starch molecules and create hydrogen bonds with free hydroxyl groups on starch molecules. On the other hand, there are slight differences in both drying time and % moisture absorption for the samples prepared with the same amount of MA but using different reaction times.

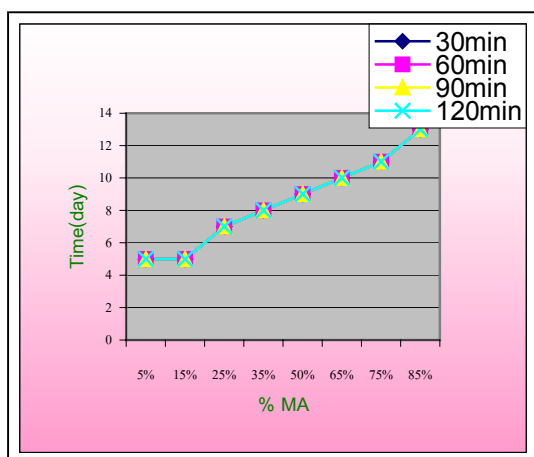


Figure 4 Drying Time of Sheet Samples Prepared from Modified Glutinous Starches.

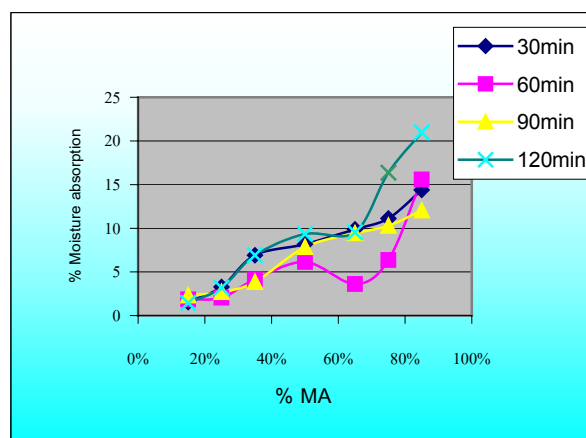


Figure 5 % Moisture Absorption of Sheet Samples Prepared from Modified Glutinous Starches.

When considering the tensile strength of the sheet samples, it is clearly seen from Figure 6 that for most cases, at the same reaction time, the sample prepared with 35% of MA gives the highest tensile strength of 5.18 MPa. This may be because as the amount of MA is less than 35%, the samples still

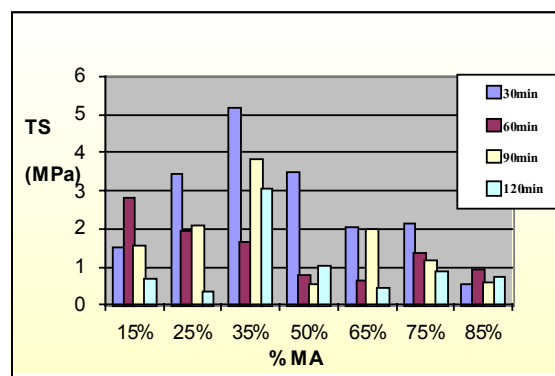


Figure 6 Tensile Strength (TS) of Sheet Samples Prepared from Modified Glutinous Starches.

have one main characteristic of unmodified starch which is brittleness. This characteristic is due to the fact that starch molecules are tightly bound by hydrogen bonds between their hydroxyl groups. As a result, it is difficult for starch molecules to move without cracking when the load is applied. Therefore, as the amount of MA less than 35%, a lower tensile strength was observed. On the other hand, as the amount of MA reached higher than 35%, hydrogen bonds which are the main

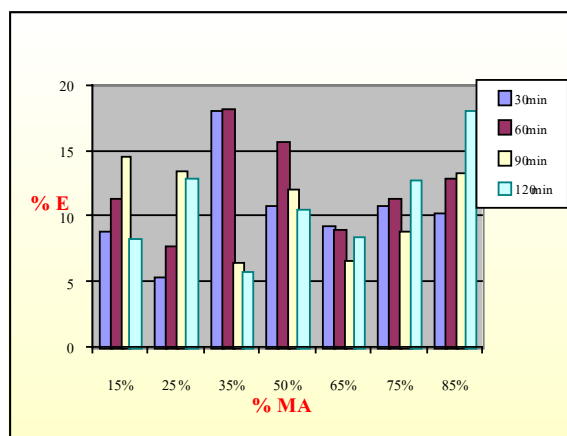


Figure 7 % Elongation (%E) of Sheet Samples Prepared from Modified Glutinous Starches.

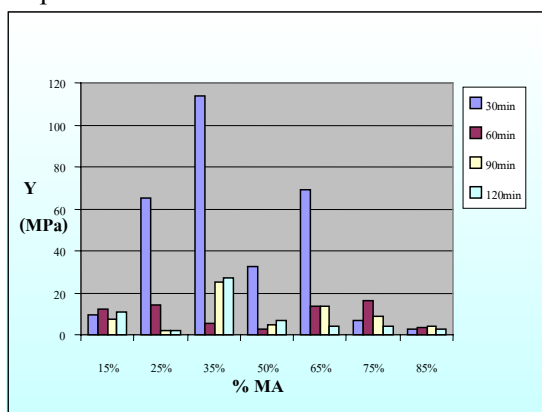


Figure 8 Modulus of Elasticity (Y) of Sheet Samples Prepared from Modified Glutinous Starches.

intermolecular forces between starch molecules were excessively decreased due to their structural irregularity caused by the presence of maleic anhydride segments. Consequently, a lower tensile strength was observed. Furthermore, it can be seen from Figure 6 that at the same amount of MA, the samples prepared using a reaction time of 30 minutes exhibits the highest tensile strength. This suggests that a reaction time of 30 minutes may be possibly enough for starch modification. At the longer reaction time, the starch molecules may encounter degradation caused by excessive exposure to the modification environment, such as heat, pH, etc. Therefore, lower tensile strength was observed. These results indicate that at 35% MA and a reaction time of 30 minutes, the sample has the highest tensile strength. These modification conditions also yield a sample with high % elongation (17.91 %) and highest modulus of elasticity (114.18 MPa) when

compared to those prepared with other modification conditions, as shown in Figures 7 and 8, respectively.

CONCLUSION

Glutinous starch can be modified by using maleic anhydride as a modifier, sodium hydroxide as a catalyst and water as a solvent at 50°C. The sheet samples can be formed from the modified starches by casting. The investigation of a few characteristics of both modified starches and their sheet samples indicated that the amount of maleic anhydride and the reaction time used in starch modification affected those characteristics. It was found that when 35% maleic anhydride and a reaction time of 30 minutes were employed, the sheet samples exhibited better overall characteristics than those prepared with other modification conditions. This study suggests that modified glutinous starch can be used to prepare environmentally friendly materials.

ACKNOWLEDGEMENTS

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