

## CHAPTER 4

### RESULTS AND DISCUSSION

Mostly starch-based biodegradable plastic had been developed by using corn starch in both native and modified forms. No report on the usage of tapioca starch being made as biodegradable plastics had been found, except the work done by Miss Thanida (1995). However, her work had focussed on biodegradation and photo-oxidation of starch-filled polyethylene. As shown in Table 1.2, tapioca starch is different from corn starch in term of chemical compositions. The significant difference between these two types of starch is the content of amylose and amylopectin. In this research, the mechanical properties, i.e., tensile strength and elongation at break, of LDPE/tapioca starch blends had been measured according to ASTM D638 using dumbbell shaped specimens prepared by injection molding. All results are the average value of each experiment.

#### **4.1 Straight blending of LDPE with tapioca starch**

The blends of LDPE and tapioca starch without additive were prepared with five different compositions. All of the blends were white, slightly white in color. Table 4.1 exhibits tensile strength and elongation at break of each blend.

Table 4.1 The effect of starch on mechanical properties of LDPE/tapioca starch blends .

Sample Code	Tensile Strength (MPa)	Elongation at Break ( %)
P/T00	9.41 (0.03)	120.0 (3.22)
P/T05	9.23 (0.02)	101.5 (0.26)
P/T10	9.24 (0.03)	91.0 (2.01)
P/T15	8.63 (0.09)	86.8 (0.59)
P/T20	8.40 (0.03)	80.5 (0.57)

Standard deviation indicated in the parentheses

LDPE had an average tensile strength of 9.41 MPa and percent elongation at break of 120 . A 5% tapioca starch incorporation caused a dramatic reduction of both tensile strength and elongation at break to 9.23 MPa. and 101.5%, respectively . The higher starch content was the lower tensile strength and elongation at break of LDPE/tapioca starch blends were observed.

Reduction in tensile strength and elongation at break of LDPE blended with other type of starch have also been reported by several researchers ( Griffin, 1977, Lim et. al, 1992). These could be explained that the covalent linkage between polyethylene and starch was not likely formed during processing . Polyethylene is hydrophobic while starch is hydrophilic . They are thus not compatible . The presence of starch granules in the polymer matrix are just the dispersion only. More starch incorporated would enhance the discontinuity of the blends. Furthermore starch can easily absorb moisture from atmosphere which causes air bubble within polymer matrix after processing and then cooling. The air bubble will decrease both tensile strength and elongation at break even more. Consequently, the appropriate compatibilizer, shall

be added into the blends to enhance compatibility of two substances. Similar results had been reported by several other worker ( Jane et al., 1994, Onteniente et al., 1996 ).

#### 4.2 The failure of some compatibilizers .

Several substances were used as compatibilizer . Stenhouse P. J. (1991) prepared the mixture of glycerol and corn starch in 1 : 1 ratio by extrusion and then prepared the blown films . Therefore glycerol was attempted to used as the compatibilizer of blending between LDPE and tapioca starch . It was found that glycerol was not suitable in this case, since glycerol has low boiling point . When the mixture of starch and glycerol contacted to the roll of two-roll mill, the mixture was separated into pieces with white smoke during the mixing . Probably by extrusion, glycerol may be able to use for LDPE/tapioca starch blend .

Another compatibilizer, poly (ethylene-co-acrylic acid) (EAA), also attempted to be use in biodegradable compounds. Swanson C. L. (1993) compounded carbohydrate with EAA and LDPE . Again corn starch and EAA were extrusion-compounded and blown into flexible and water-resistance film by Otey et al (1987) . EAA was PRIMACORE 5981 form Dow Chemical Co. It contained about 20% acrylic acid and had a melt index of 300, a weight - average molecular weight of 18,000 in pellet forms. This grade was not available in Thailand. However, another grade PRIMACORE 1410 , that normally used as adhesive layer or sealant layer and skin film, was tried. 1%w/w of EAA was compounded into mixture of LDPE/tapioca starch on two-roll mill. The compound were cut into small chips and then prepared the dumbbell specimens by compression molding instead of injection molding owing to acidity of EAA. It was found that the compound was tie to the metal plate. The dumbbell specimen was not able to prepared and indicated that Primacore 1410 was not suitable to this application.

### 4.3 Mechanical properties of LDPE /tapioca starch blends with compatibilizer

Lubricant is one substance that functions as compatibilizer. Jane. J. L. et al. (1993) found that the lubricants such as glycerol monostearate and polyethylene glycol stearate could improve the physical properties of degradable plastics which made from starch and protein. The best results were obtained at 1% concentration; further increase of the lubricant decrease the physical strength.

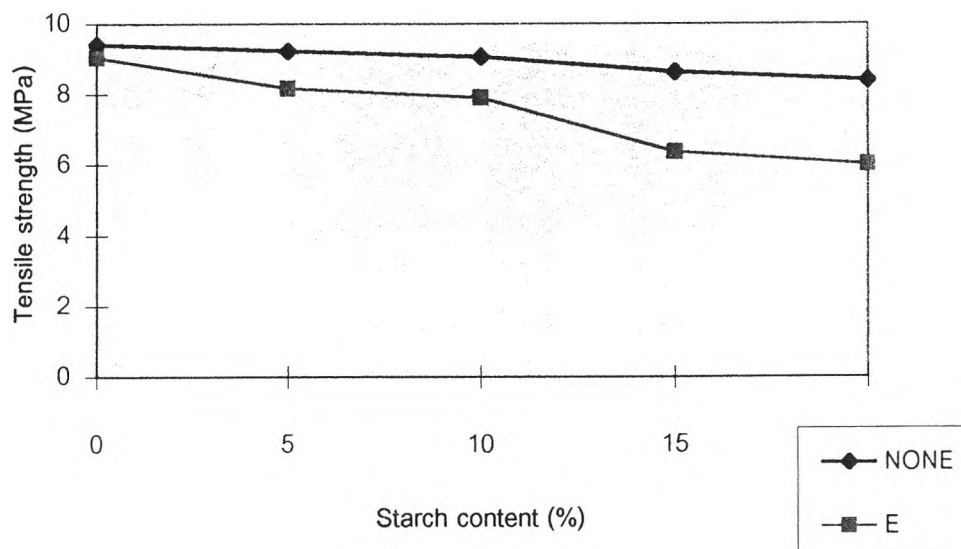
Three types of lubricant, epolene, glycerol monostearate and zinc stearate, were chosen to added into LDPE/tapioca starch blends. The amount of compatibilizer was limited at 1% by weight of LDPE/tapioca starch blend. Epolene is the trade name of low molecular weight oxidized polyethylene which applied from Eastman Co. Ltd. It was wax-like which normally used as coupling agent of polyolefins. Glycerol monostearate, in flake form, is fatty acid ester of glycerol. Zinc stearate, in powder form, is metallic soap.

Table 4.2 Mechanical properties of LDPE/ tapioca starch blends in the presence of epolene.

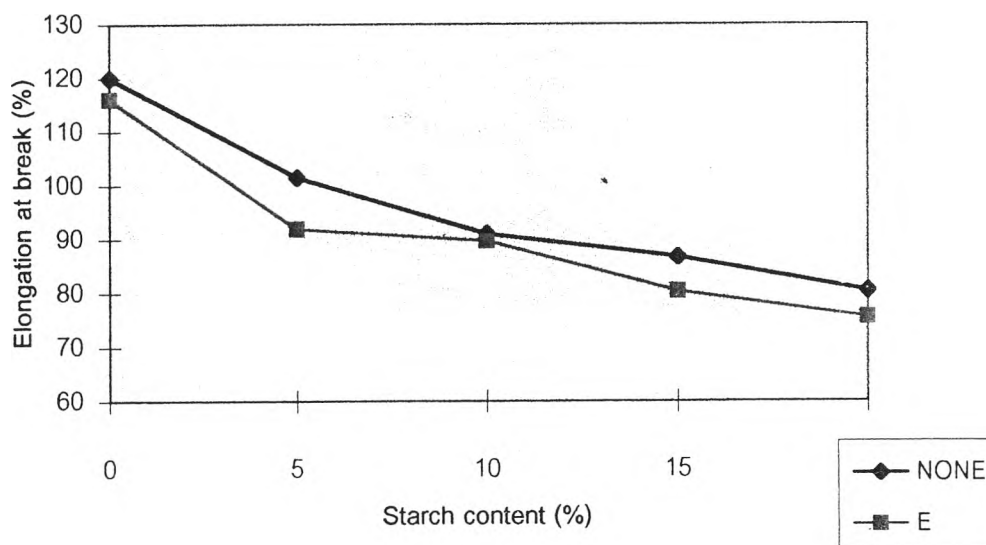
Sample Code	Tensile Strength (MPa)	Elongation at Break (%)
P/T00-E	9.04 (0.11)	116.1 (1.60)
P/T05-E	8.17 (0.39)	91.9 (0.94)
P/T10-E	7.91 (0.06)	89.7 (0.32)
P/T15-E	6.38 (0.26)	80.4 (1.56)
P/T20-E	6.02 (0.13)	75.6 (1.38)

Standard deviation indicated in the parentheses.

Table 4.2 exhibits the resulting mechanical properties of LDPE/tapioca starch blends with epolene. All data were plotted and compared with LDPE/tapioca blends without epolene that presented in Figure 4.1 . Surprisingly, all of the blends have worse tensile strength and elongation at break than the corresponding blends without epolene. Even LDPE with no starch, the addition of epolene led to lower tensile strength and elongation at break of LDPE .



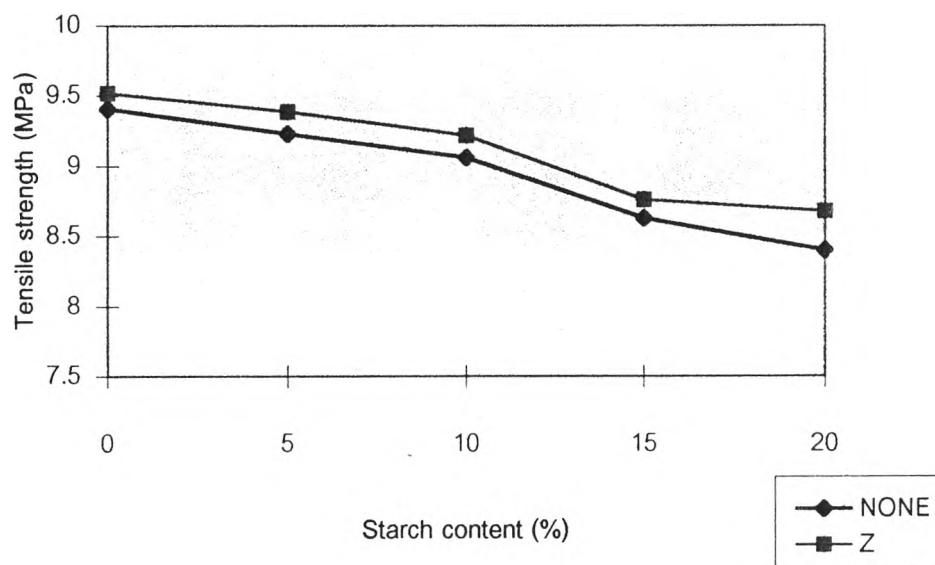
(a)



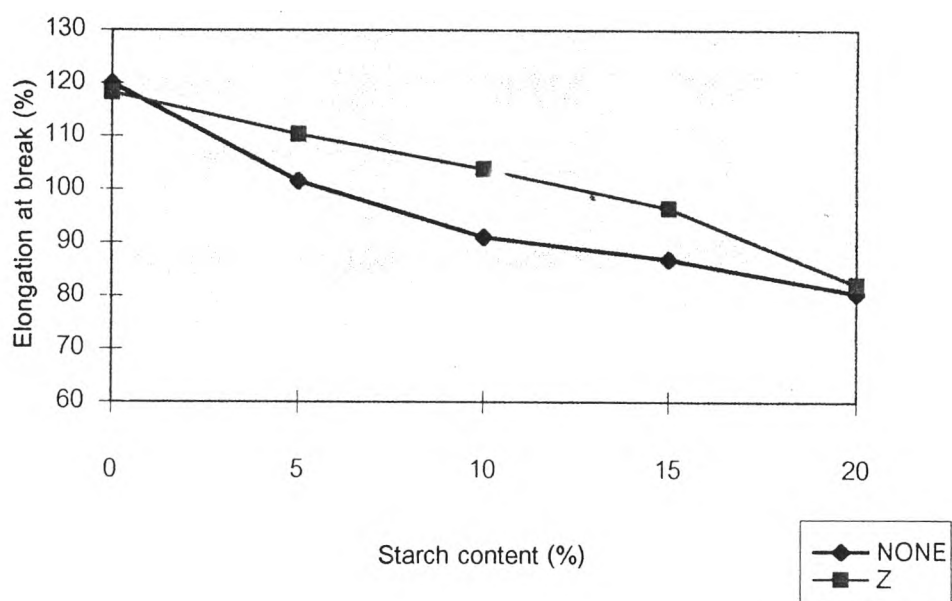
(b)

Figure 4.1 (a) Tensile strength (b) Elongation at break of LDPE/tapioca starch blends with and without epolene.





(a)

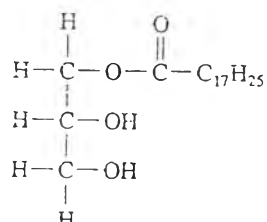


(b)

Figure 4.2 (a) Tensile strength (b) Elongation at break of LDPE/tapioca starch blends with and without zinc stearate.



The other compatibilizer, glycerol monostearate, has been selected for this study. It is the fatty acid ester. The chemical structure illustrates below :

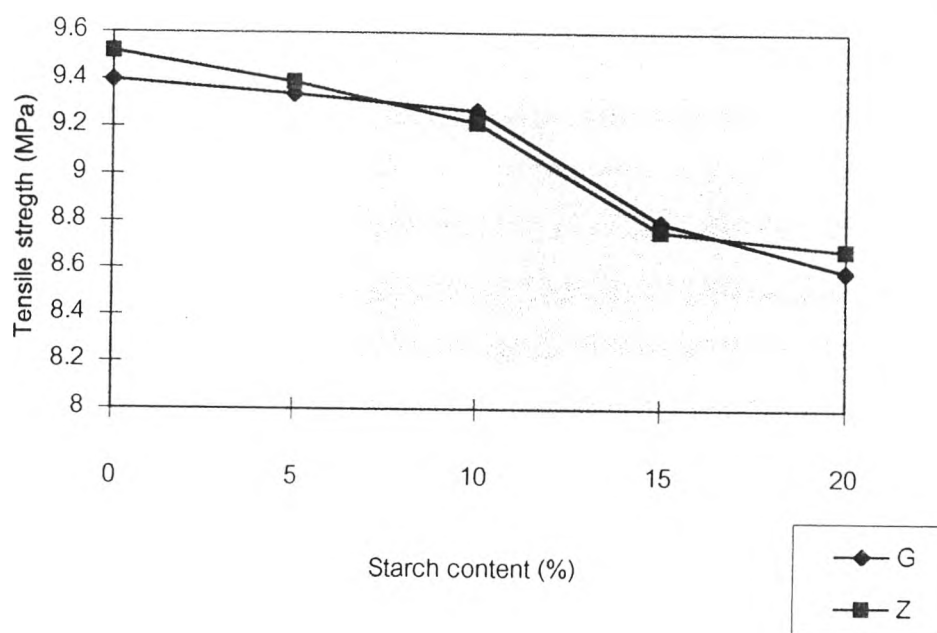


It shows both hydrophobic domains, stearate segment, and hydrophilic domains, glycerol segment, in the structure . Considerable its structure compared with zinc stearate, glycerol monostearate presents more polarity, effected of hydroxyl groups, than zinc stearate . Therefore, by adding glycerol monostearate in the blends would have more an effective compatilbility than zinc stearate . Indeed, the resulting in Table 4.4 and Figure 4.3 obviously shows that the tensile strength and elongation at break of LDPE/tapioca starch blends with glycerol monostearate were higher than the blends with zinc stearate in most proportion .

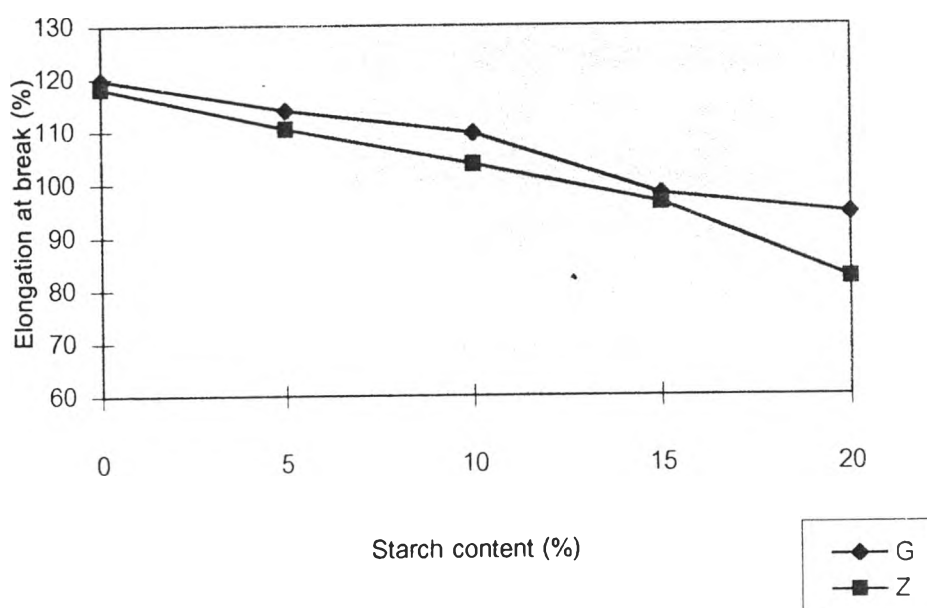
Table 4.4 Mechanical properties of LDPE /tapioca starch blends in the presence of glycerol monostearate .

Sample Code	Tensile Strength (MPa)		Elongation at Break (%)	
P/T00-G	9.40	(0.01)	119.8	(0.94)
P/T05-G	9.34	(0.02)	113.9	(0.99)
P/T10-G	9.27	(0.03)	109.6	(1.14)
P/T15-G	8.80	(0.09)	98.1	(0.88)
P/T20-G	8.59	(0.11)	94.4	(1.15)

Standard deviation indicated in the parentheses.



(a)



(b)

Figure 4.3 (a) Tensile strength (b) Elongation at break of LDPE/tapioca starch blends with glycerol monostearate or zinc stearate

Table 4.2, 4.3 and 4.4 list the tensile strength and elongation at break of LDPE/tapioca starch blend with compatibilizer . Both tensile strength and elongation at break of blends are plotted in Figure 4.1, 4.2 and 4.3 as a function of starch content and types of compatibilizer . Mechanical properties of specimens differed among each compatibility. The blends containing glycerol monostearate appeared white color and shown slightly greater tensile strength and elongation at break than did that containing zinc stearate and epolene. When the content of tapioca starch were increased, tensile strength and elongation of the blends exhibit and inverse relation to starch content. However LDPE/tapioca starch blends with glycerol monostearate or zinc stearate exhibited the better tensile strength and elongation than without compatibilizer. In contrast, blends with epolene inhibited tensile strength and elongation at break .

#### 4.4 Reproducibility of blend.

LDPE/tapioca starch blends with glycerol monostearate were prepared in two replications for every composition in order to assure the reproducibility of the blend. The mechanical properties of both blends were compared as shown below :

Sample Code	Tensile Strength (MPa)		Elongation at Break (%)	
	Rep.1	Rep.2	Rep.1	Rep.2
P/T05G	9.18	9.19	113.9	114.1
P/T10G	9.08	9.08	109.6	109.9
P/T15G	8.80	8.84	96.6	98.2
P/T20G	8.59	8.60	94.4	95.5

Rep.1 and Rep.2 = replication 1 and replication 2 respectively

It can be seen that both blends at every composition shown about the same value. Therefore, it can be assumed that all the results are acceptable.

#### 4.5 Comparison of the mechanical properties of LDPE/tapioca starch blends with LDPE/ corn starch blends .

Normally, the major starch which used in starch-filled polyethylene researches was corn starch as referred in the previous chapter. It is possible or not to use tapioca starch replace to corn starch. So that it is necessary to prepare LDPE/corn starch blends and compare with LDPE/tapioca blends. The blend of LDPE and starch need to have compatibilizer, glycerol monostearate and zinc stearate were used for this purpose .

Table 4.5 Mechanical Properties of LDPE/corn starch blends .

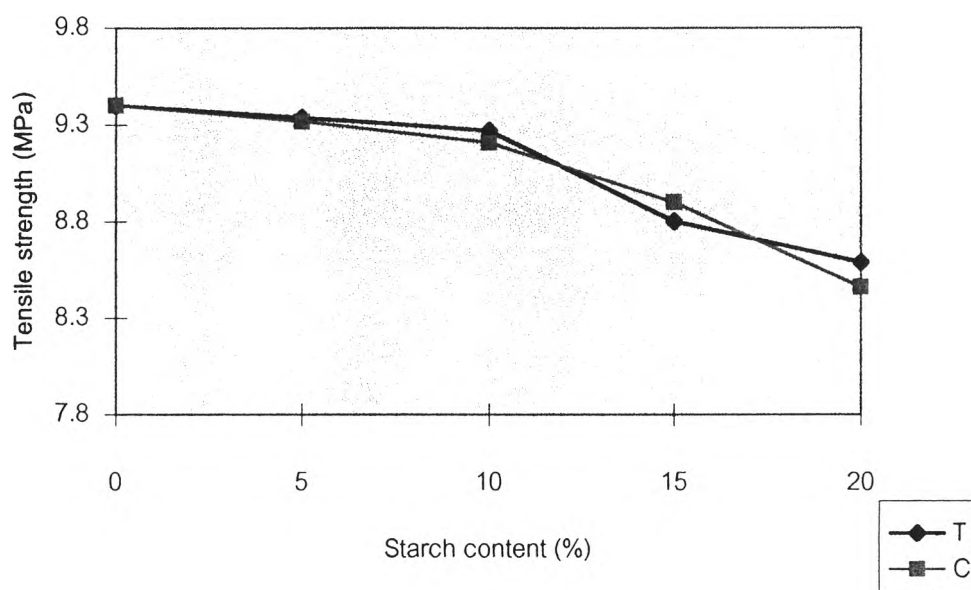
Sample Code	Tensile Strength (MPa)		Elongation at Break (%)	
P/C00-G	9.40	(0.04)	118.9	(1.57)
P/C05-G	9.32	(0.04)	97.9	(0.93)
P/C10G	9.21	(0.03)	92.6	(3.22)
P/C15-G	8.88	(0.08)	89.5	(0.88)
P/C20-G	8.46	(0.06)	84.9	(1.60)
P/C00-Z	9.21	(0.09)	120.0	(1.45)
P/C05-Z	9.16	(3.90)	98.0	(0.06)
P/C10-Z	8.70	(0.06)	90.8	(1.92)
P/C15-Z	8.13	(0.09)	83.1	(1.44)
P/C20-Z	7.80	(0.02)	77.0	(0.53)

Standard deviation indicated in the parentheses.

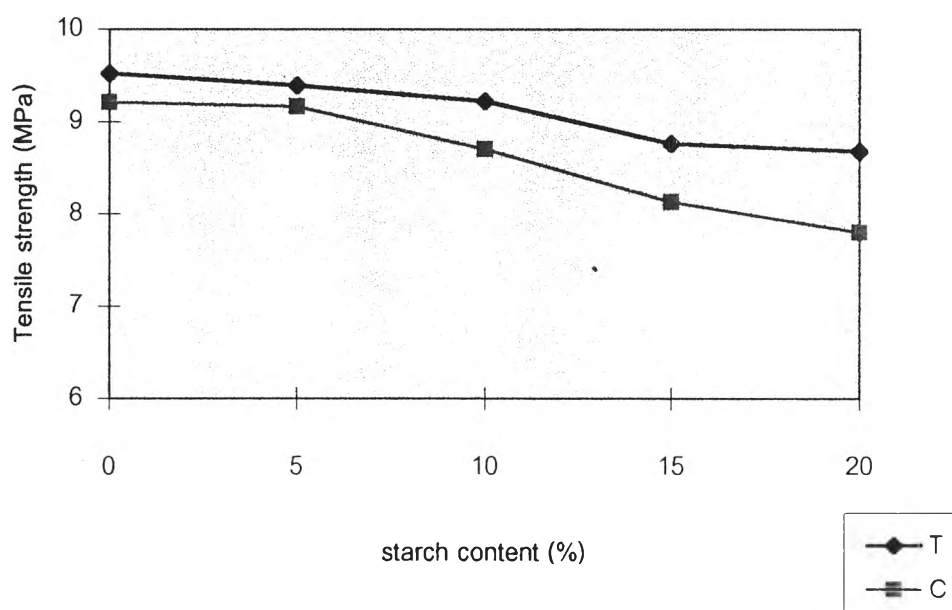
Table 4.5 list the tensile strength and elongation of LDPE/corn starch blends, compounded with glycerol monostearate and zinc stearate. The resulting were compared with LDPE/tapioca starch blends presented in Figure 4.4 and 4.5. Most blends of LDPE/tapioca starch are higher tensile strength and elongation at break than LDPE/corn starch blends except the blends with glycerol monostearate are lower .

Considerable of both starch, there are different among tapioca starch and corn starch in term of shape, size, and chemical composition. Corn starch granule are medium size and round or polygonal in shape, tapioca starch granule are round or truncated at one end to form kettledrum shape, see in Figure 4.6. The average diameter of corn starch and tapioca starch used in this experiment, determined by particle size analyzer Marvern Co. model master seizer S, are 14.88 and 13.21  $\mu\text{m}$  respectively, see in appendix A. The higher mechanical strength resulting of LDPE/tapioca starch blends owing to tapioca starch granule is smaller in diameter than corn starch which according to Lim et al. (1992) investigation . They concluded that using small-particle starch exhibited greater mechanical strength and elongation at break. In fact, smaller particle can occupy in more area. For the blends of LDPE/corn starch with glycerol mono stearate, on the other hand, had higher tensile strength but lower elongation at break. Whistler et al.(1980) described that the presence of lipid in common cereal starches has profound effect on the physical properties of the starches. The lipid exist as an amylose-lipid complex in the starch granules . The linear amylose forms helical clathrates with polar fatty substance. The resulting of LDPE/corn starch with glycerol monostearate may be effect from this phenomena. Because glycerol monostearate is fatty acid ester that possible to form complex with amylose fraction in corn starch granules in the presence of water, from moisture content of raw materials, at high temperature.

Lipid-amylose complex exhibited crystalline characteristic that are insoluble but dissociation . This behavior indicated the strength of complexion bonding that more strength but low elasticity. For all mention reasons described the resulting of LDPE/corn starch blends with glycerol monostearate resulting.

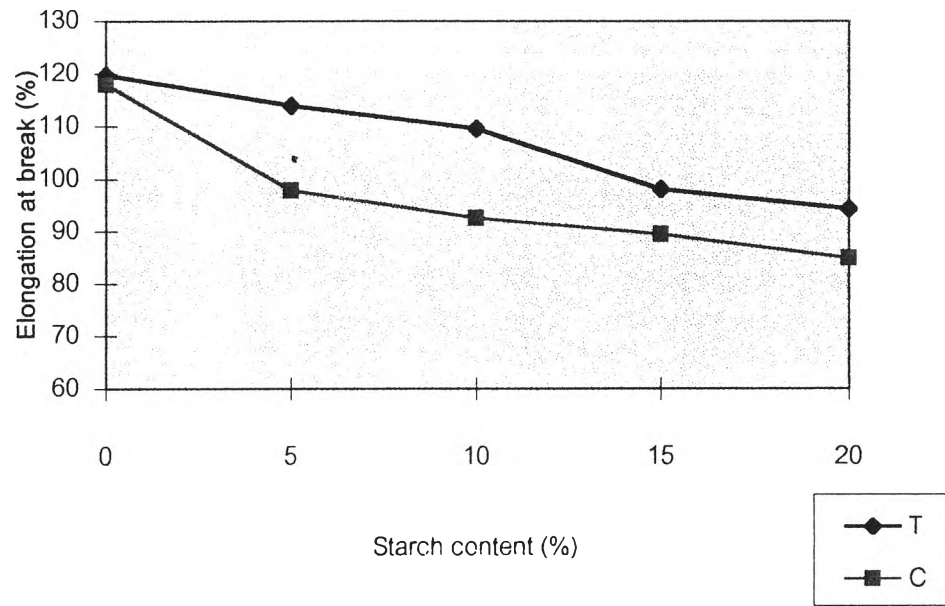


( a )

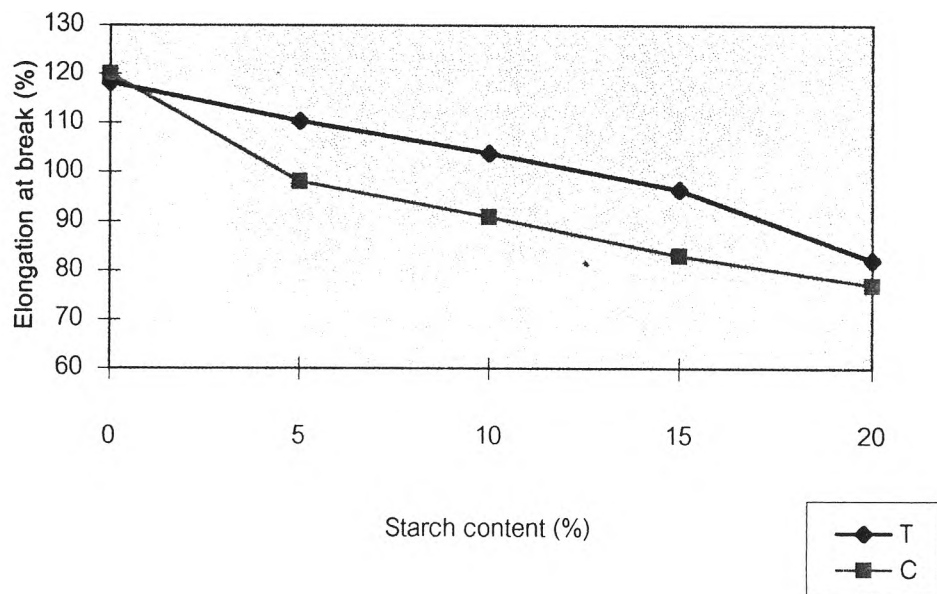


( b )

Figure 4.4 Tensile strength of LDPE/tapioca starch blends and LDPE/corn starch blends with (a) glycerol monostearate and (b) zinc stearate .



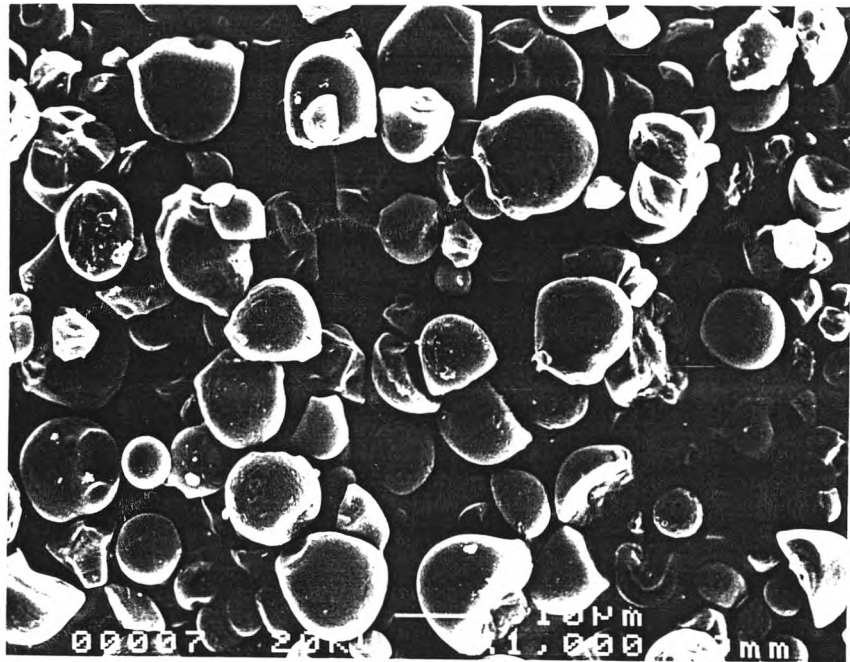
( a )



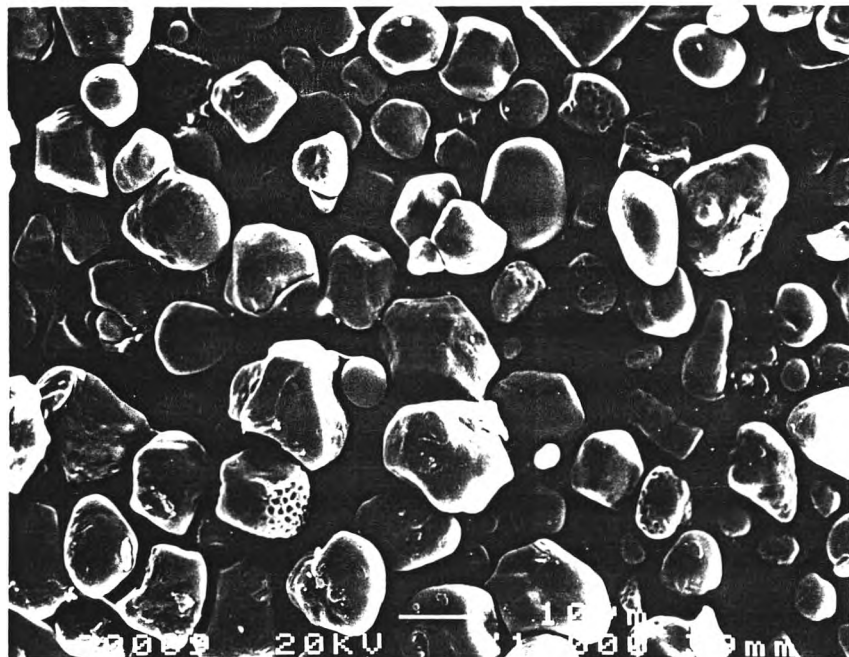
( b )

Figure 4.5 Elongation at break of LDPE/tapioca starch blends and LDPE/corn starch blends with (a) glycerol monostearate ( b ) zinc stearate .





( a )



( b )

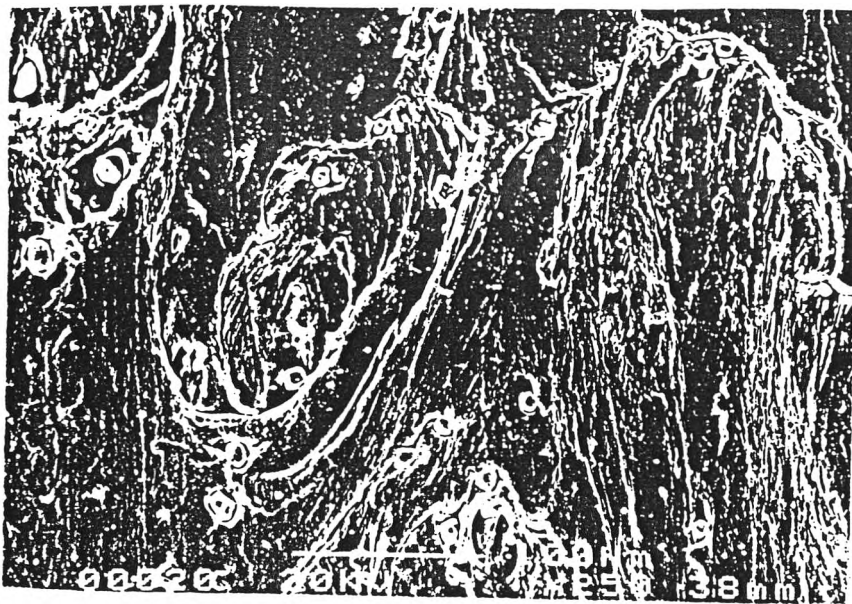
Figure 4.6 Scanning electron microscopy ( SEM ) of  
( a ) tapioca starch granules ( b ) corn starch granules  
Scale bars represent 10  $\mu\text{m}$  .

#### **4.6 Dispersion of the starch granules and compatibilizer in the blends .**

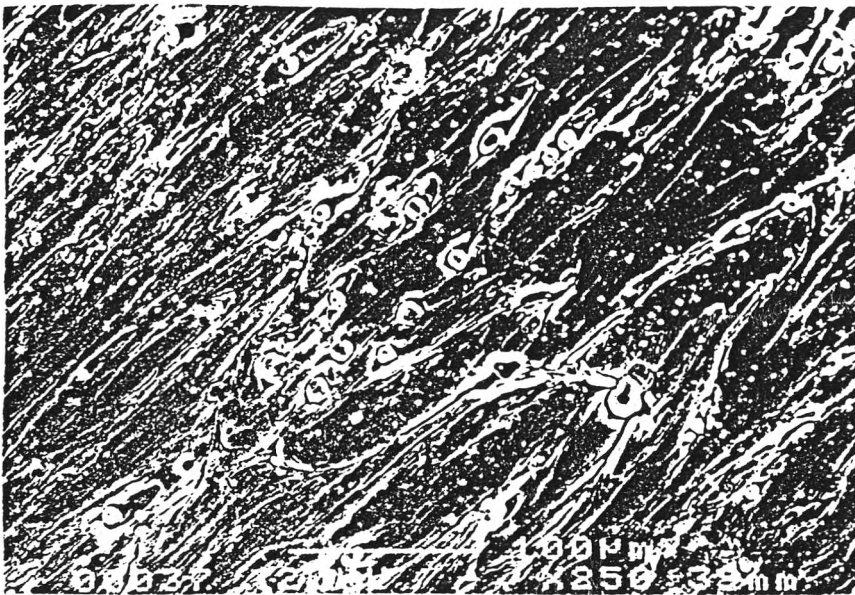
Electron microscopy was next performed to obtain information on LDPE/tapioca starch blends. Figure 4.7 shown the dispersion of starch granules on the LDPE matrix. It can be seen that the dispersion of tapioca starch on LDPE matrix are same as corn starch and similar to dispersion of corn starch into commercially biodegradable plastics. Scanning electron microscope (SEM) indicated that small tufts can be visible on the blends. Starch was dispersed in polymer matrix and caused to occur tiny hole on specimens surface. The dispersibility depend on the compatibilizer efficiency . The size of starch granule and moisture content effected to dispersion on LDPE matrix .

#### **4.7 Film Blowing .**

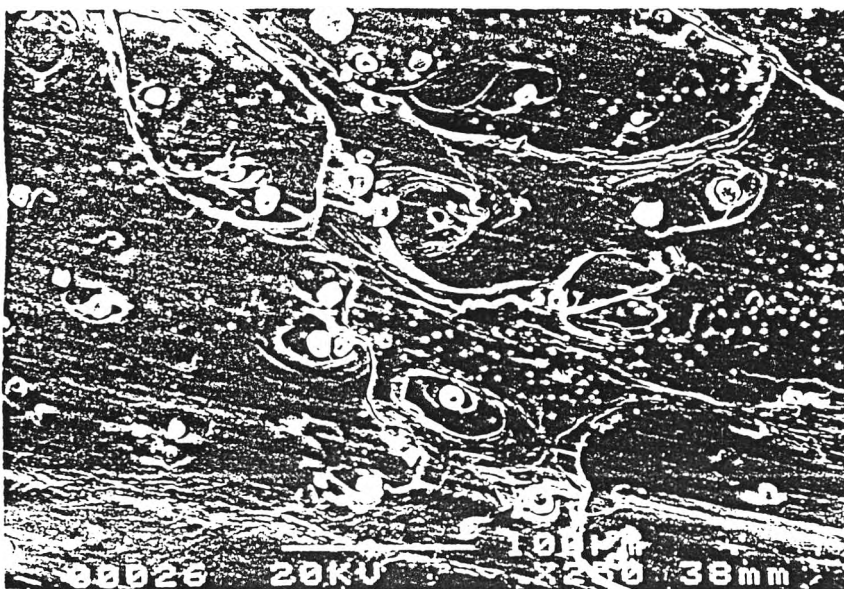
5% by weight starch content of LDPE/tapioca starch blends with conpatibilizer were attempted to blow into films, see in Figure 4.8 and 4.9. Pure LDPE is easy to blow into film while LDPE/tapioca starch films tended to possess air bubble and the blown extrusion became difficult to control . It can be seen the air bubble on no compatibilizer LDPE/tapioca starch films. LDPE/tapioca starch containing glycerol monostearate or zinc stearate shown the good appearance films. Blend of LDPE/tapioca starch with zinc stearate can be blown into thinner film than blend with glycerol monostearate. Otherwise SEM shown that film with zinc stearate had smoother surface than other. However another ratios were attempted to blow into film but it could not because of many air bubble was produced which caused by the moisture content in starch granules and blend.



(a) Commercially biodegradable plastic resin (containing approximately 15% corn starch)



(b) P/T15Z



(c) P/C15Z

Figure 4.7 Dispersion of starch granules in polymer matrix, revealed by SEM

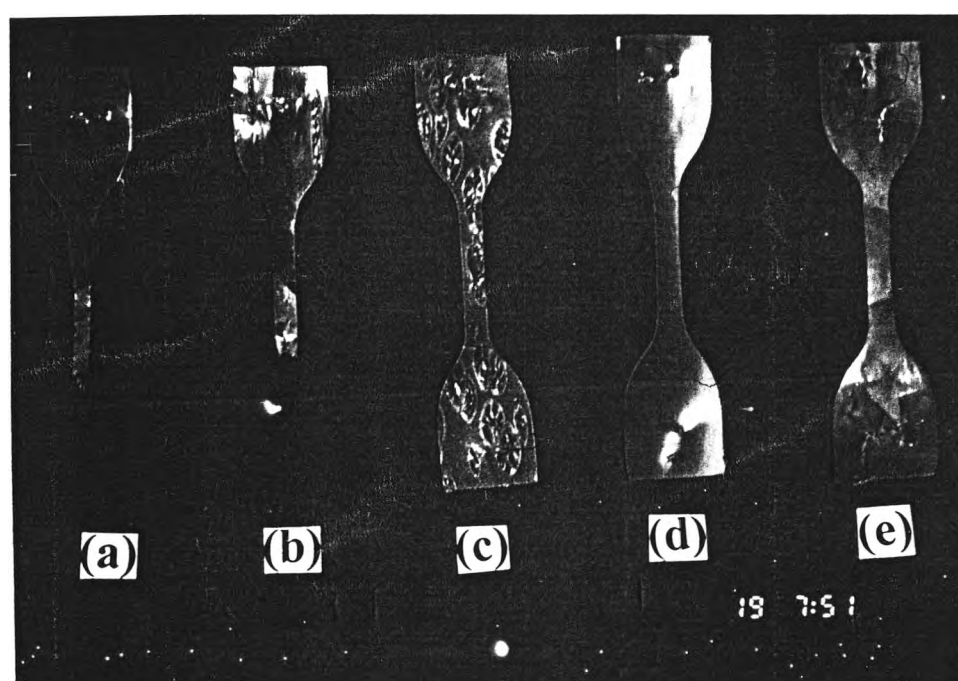
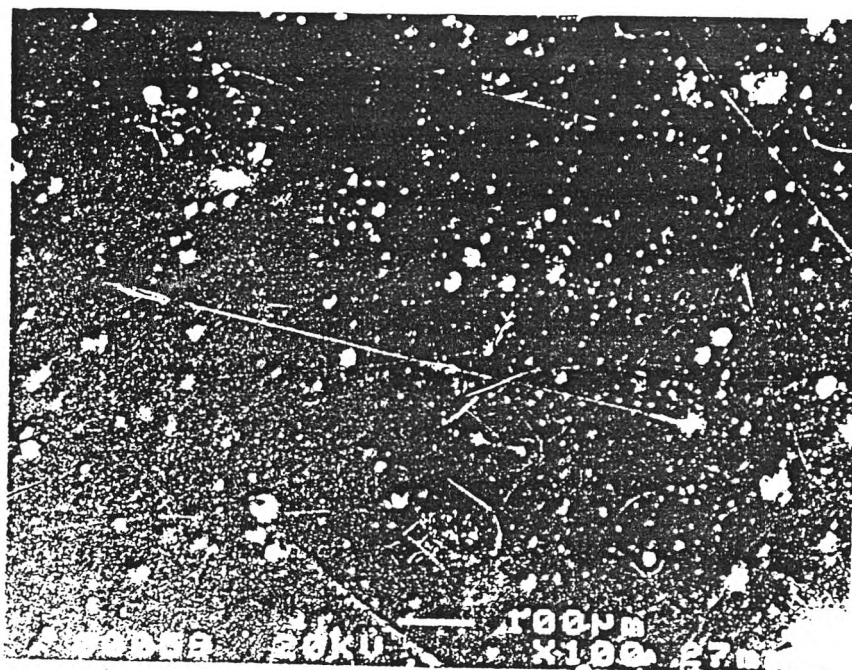
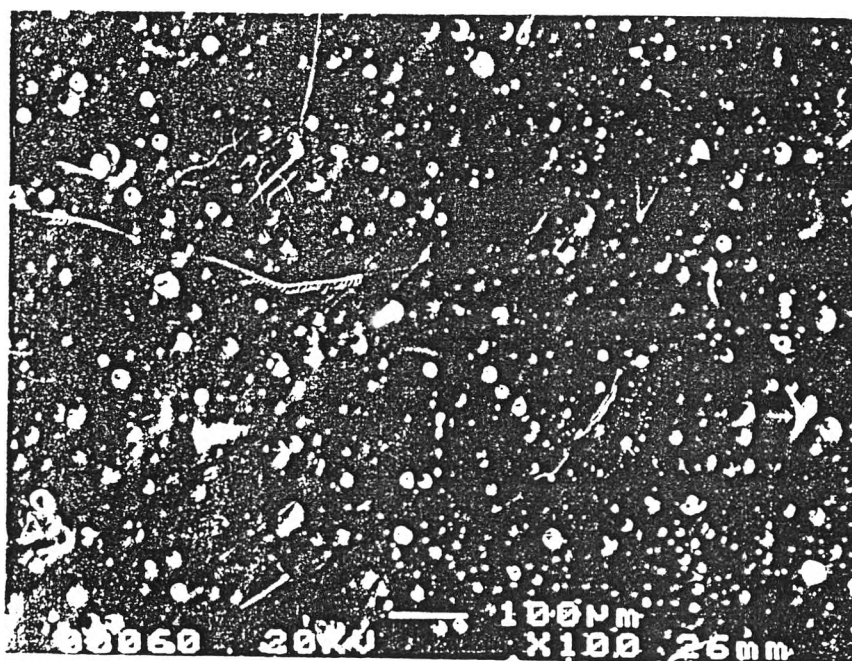


Figure 4.8 Blown films (a) LDPE (b) P/T05 (c) P/T05E  
(d) P/T05G (e) P/T05Z



(a)



(b)

Figure 4.9 SEM of blown films (a) P/T05Z (b) P/T05G