

CHAPTER III

RESULTS AND DISCUSSION

3.1 Pretreatment of starch

The thermogravimetric analysis (TGA) of the rice starch and the tapioca starch gave curves shown in Figures 3.1 and 3.2, respectively. In general, weight losses occur when volatiles absorbed by the sample are driven off, and at higher temperatures when degradation of the sample occurs with the formation of volatile products. For the analysis of the rice starch, the initial weight loss began at approximately 60°C and reached a constant weight plateau after losing 9.6% of its initial weight. This weight loss corresponded to the loss of the water content from the starch. Further weight loss occurred at approximately 270°C. At this temperature the rice starch began to degrade.

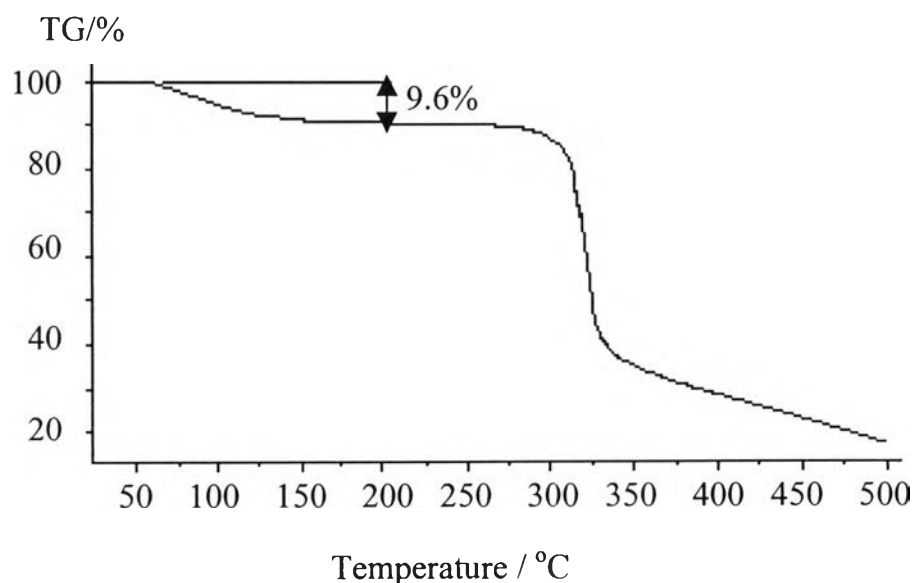


Figure 3.1 TGA of rice starch.

The analysis of the tapioca starch gave a similar curve to that of the rice starch. The water content of the tapioca starch was found to be 7.5% which was slightly lower than that of the rice starch. The degradation temperature of the tapioca starch was also approximately 270°C.

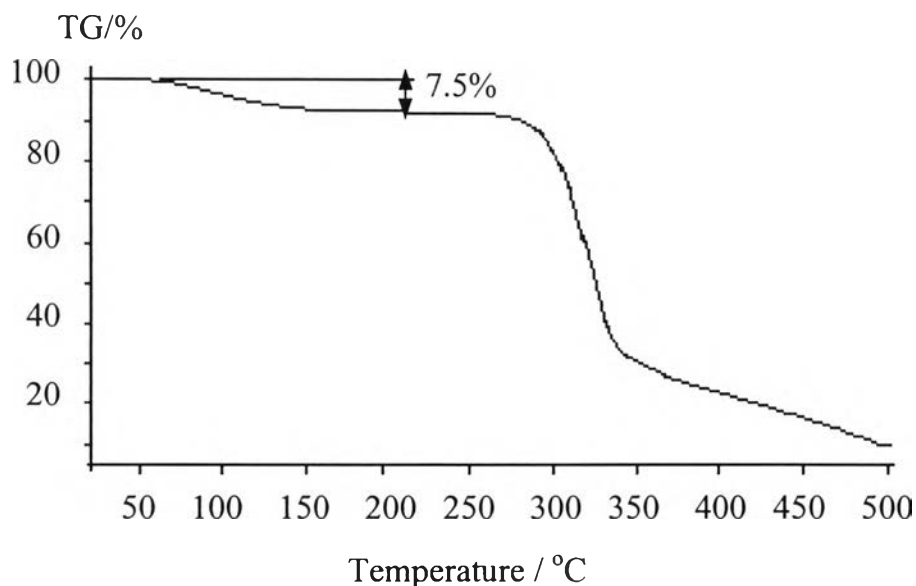


Figure 3.2 TGA of tapioca starch.

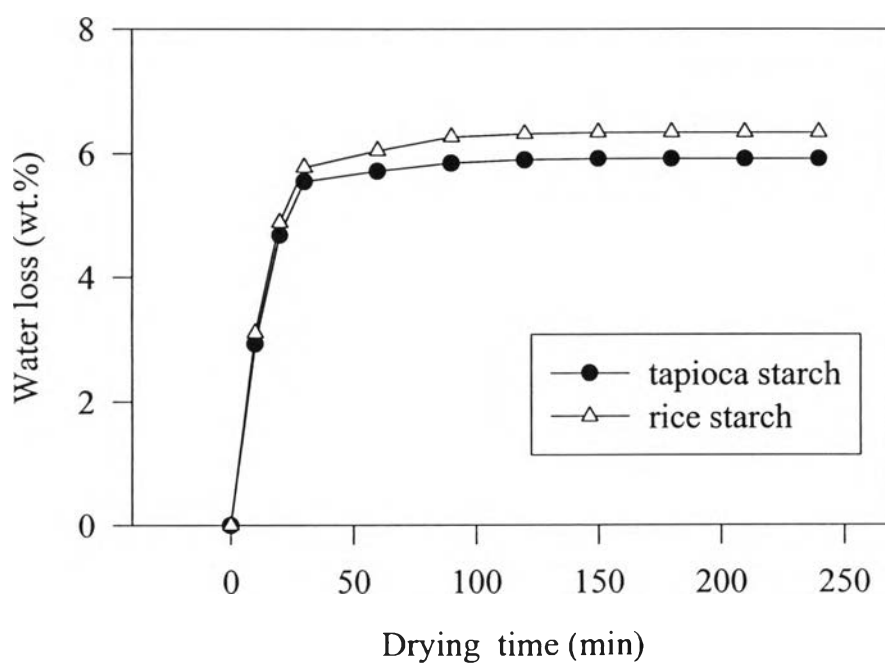


Figure 3.3 Drying curves of rice and tapioca starch.

Figure 3.3 shows the weight loss (%) due to water removal of the rice starch and the tapioca starch heated at 100°C in a hot-air oven. The curves show that it took approximately 150 minutes for both starches to reach a constant weight plateau.

These results helped in the determination of suitable drying conditions for the starches. The starches were dried by heating at 100°C in the hot-air oven for 2.5 hours prior to use. Calcium oxide (CaO) was added as a desiccant in order to prevent moisture reabsorption during processing.

3.2 Starch density measurement

The densities of the rice starch and the tapioca starch were determined by the pycnometric technique. The values are shown in Table 3.1.

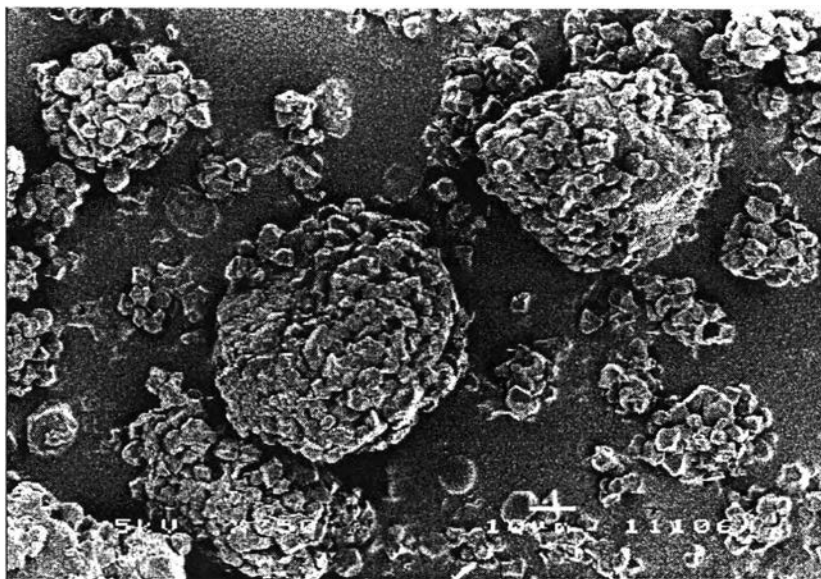
Table 3.1 Density of starches

| Type of starch | Density (g/cm ³) |
|----------------|------------------------------|
| Rice | 1.50 |
| Tapioca | 1.42 |

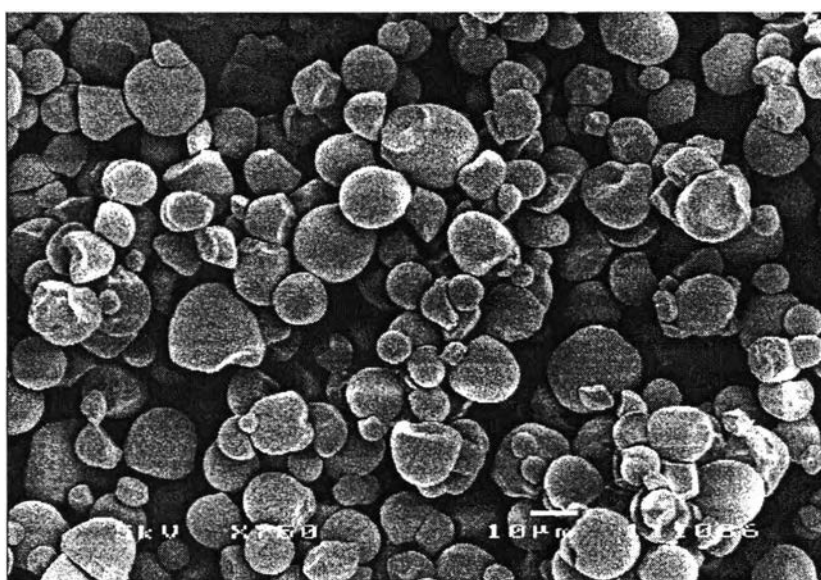
3.3 Processability of starch-based HDPE blends – mixing process

Figure 3.4 shows the electron micrographs of the rice starch and the tapioca starch at 750X magnification. Tapioca starch particles were spherical in shape while rice starch particles formed clusters. A closer look at a cluster (Figure 3.5) revealed that the individual rice starch particles were polygonal in shape and smaller than the tapioca starch particles. Rice starch particles

formed agglomerates due to their high surface energies which lead to high particle-to-particle interaction.



Rice starch



Tapioca starch

Figure 3.4 Scanning electron micrographs of rice starch and tapioca starch.

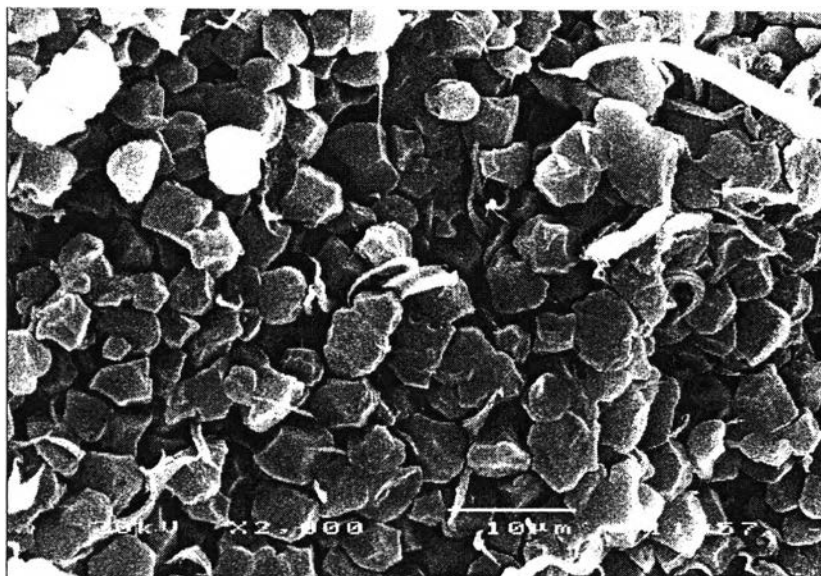


Figure 3.5 Scanning electron micrograph of rice starch at 2000X magnification.

In an attempt to break down the rice starch agglomerates a range of mixer-head rotational speeds was used. The effect of different rotor speeds on the mixing of starch-based HDPE blends was studied.

Figures 3.6 and 3.7 show the torque and stock temperature of the rice starch-based and tapioca starch-based HDPE blends, respectively. Screw speeds of 30, 40, 50, 60, 75, and 90 rpm were used. The starch content was fixed at 20% by weight and a circulating oil temperature of 160°C used.

The stock temperature of both rice and tapioca blends increased with increasing screw speed. The stock temperature in the measurements was defined as the final temperature of the melt in the rheomixer after stabilization of the mixing process. It was observed that the stock temperature often exceeded the set temperature of the circulating oil. This increase in temperature was the result of internal friction, (which generated heat) created during the mixing process.

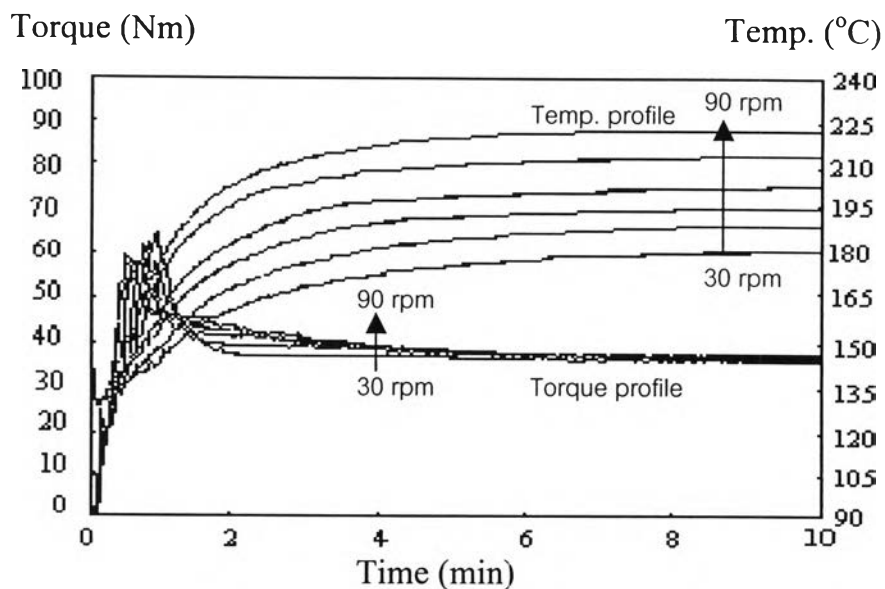


Figure 3.6 Torque and stock temperature of rice starch-based HDPE blends measured at screw speed of 30, 40, 50, 75, and 90 rpm.

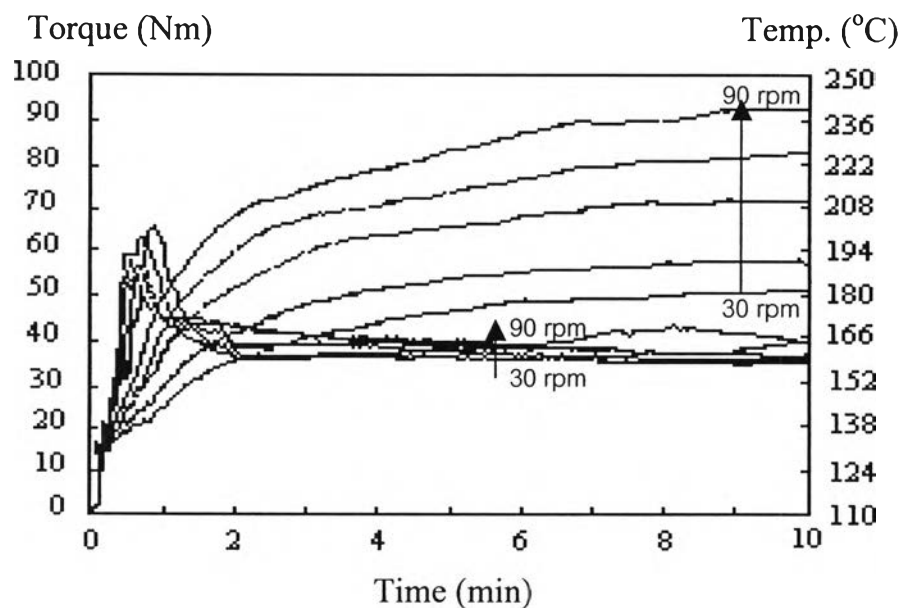


Figure 3.7 Torque and stock temperature of tapioca starch-based HDPE blends measured at screw speed of 30, 40, 50, 75, and 90 rpm.

For the torque measurements, all of the screw speeds used resulted in one common torque value for both blend types. Slower screw speed, however, resulted in faster torque stabilization, i.e. the mixing time was shortened when using slower screw speeds. The torque stabilized after approximately six minutes for both starch-based blends, suggesting that good mixing had occurred within this time period. A noticeable disruption in the torque profile, and its corresponding temperature profile, of the tapioca starch-based HPDE blend at a screw speed of 90 rpm resulted from the degradation of the thermomechanical shear-sensitive starch.

The effects of starch content on torque during mixing were studied. HDPE was masticated in the mixer-measuring head for three minutes to obtain a stable torque before the starch was added. Figures 3.8 and 3.9 show the torque of the rice starch-based and the tapioca starch-based HDPE blends, respectively, measured at 0, 10, 20, 30, and 40% starch contents. The circulating oil temperature of 160°C and a screw speed of 50 rpm were used.

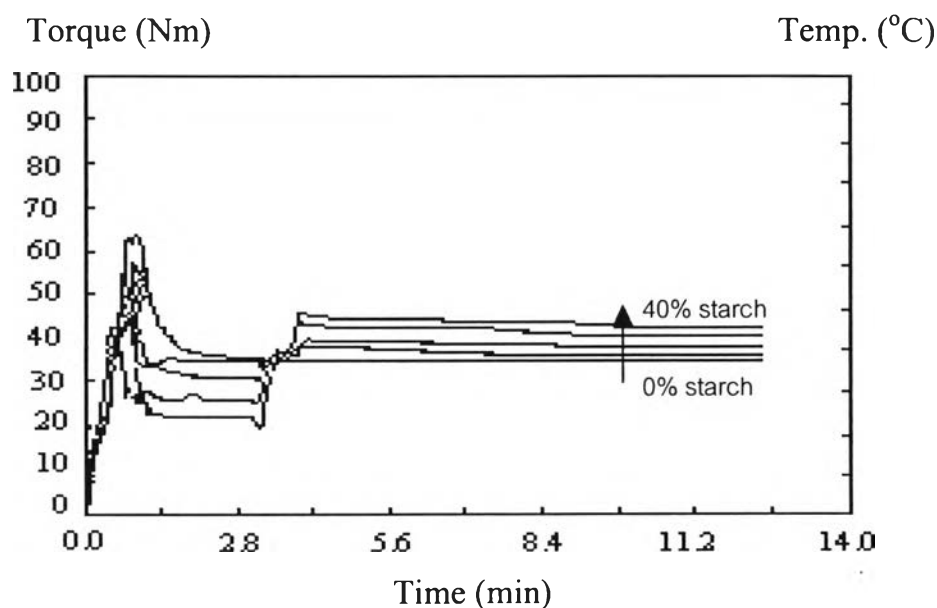


Figure 3.8 Torque of rice starch-based HDPE blends measured at 0, 10, 20, 30, and 40% starch content.

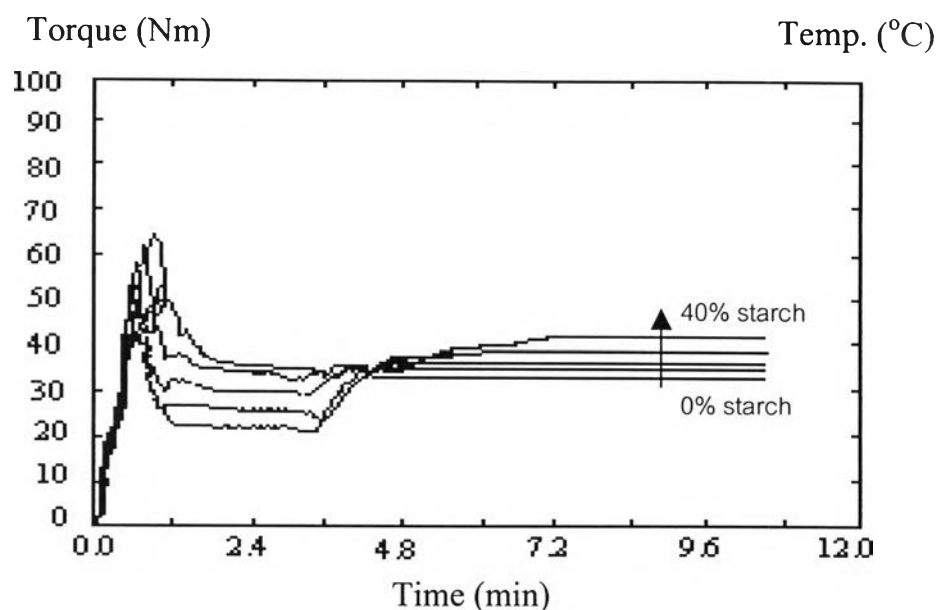


Figure 3.9 Torque of tapioca starch-based HDPE blends measured at 0, 10, 20, 30, and 40% starch content.

As Figures 3.8 and 3.9 show, the torque of both blend systems increased after the addition of starch. Furthermore, the final torque increased with increasing starch content of the blends. This phenomenon can be explained by the higher stiffness that the starch possesses compared to that of HDPE. The mixing time required for stabilizing the torque also increased with increasing starch contents of the blends. A slight decrease in the final torque for the rice starch-based HDPE blends was attributed the break down of the rice starch agglomerates.

A comparison of torque measurements of the rice and tapioca starch blends is shown in Figure 3.10. At similar levels of starch loading, the blends containing rice starch gave higher torque readings. This phenomenon can be explained by the existence of agglomerates in the rice starch-based blends. Agglomerates or flocculated particles provide higher modulus than would finely dispersed particles of equal volume, and thus higher torque value,

because the portion of the polymer matrix that is present in the agglomerates is less able to react to stress and strain than the continuous phase polymer.

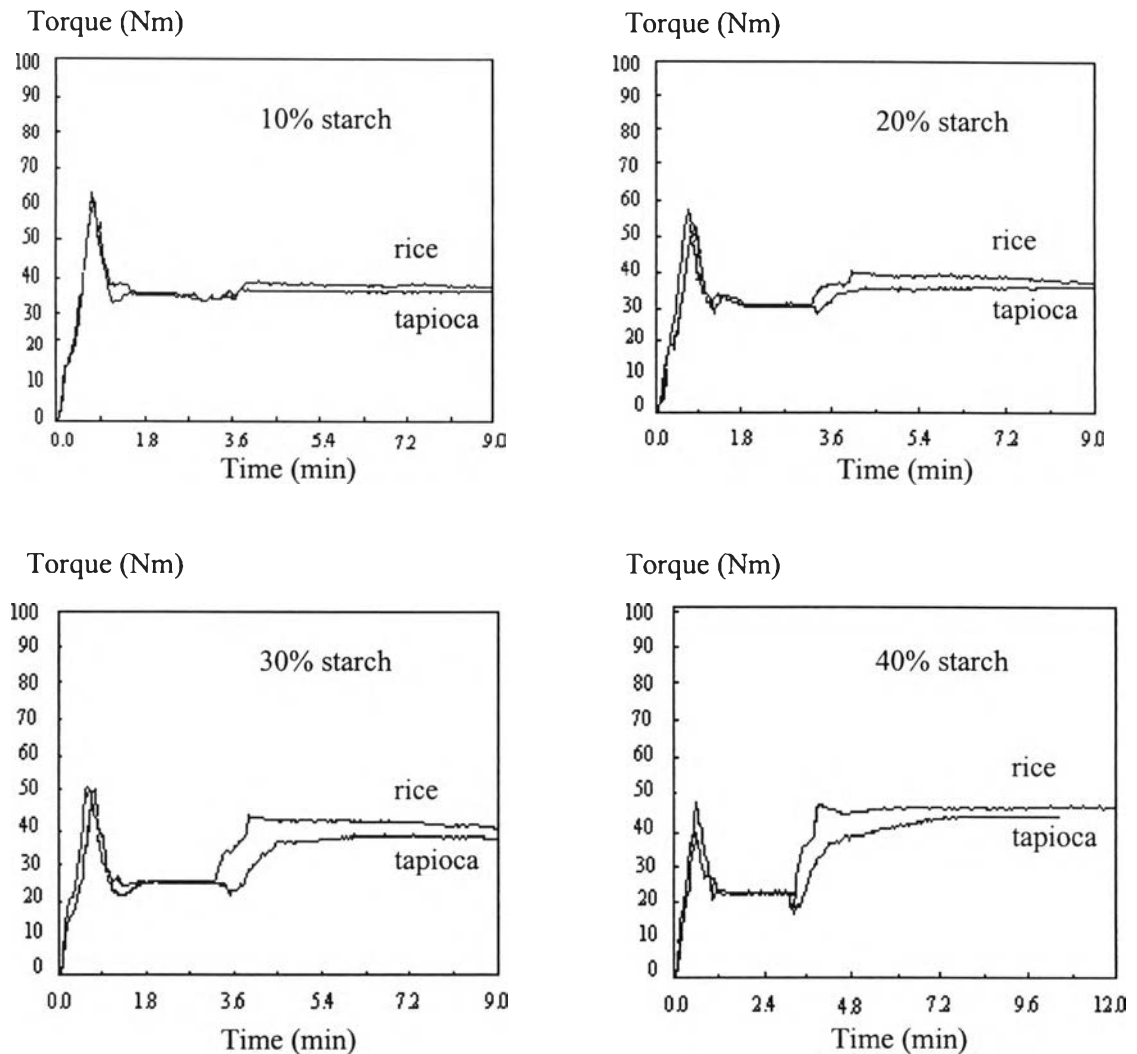


Figure 3.10 Torque of rice starch and tapioca starch-based HDPE blends measured at 0, 10, 20, 30, and 40% starch content.

Distribution and dispersion of the starch particles in the HDPE matrix were studied as a function of mixing time. Figure 3.11 and 3.12 show the morphologies of the rice starch-based and tapioca starch-based HDPE blends after 1, 3, 5, and 7 minutes of mixing in a Brabender rheomixer.

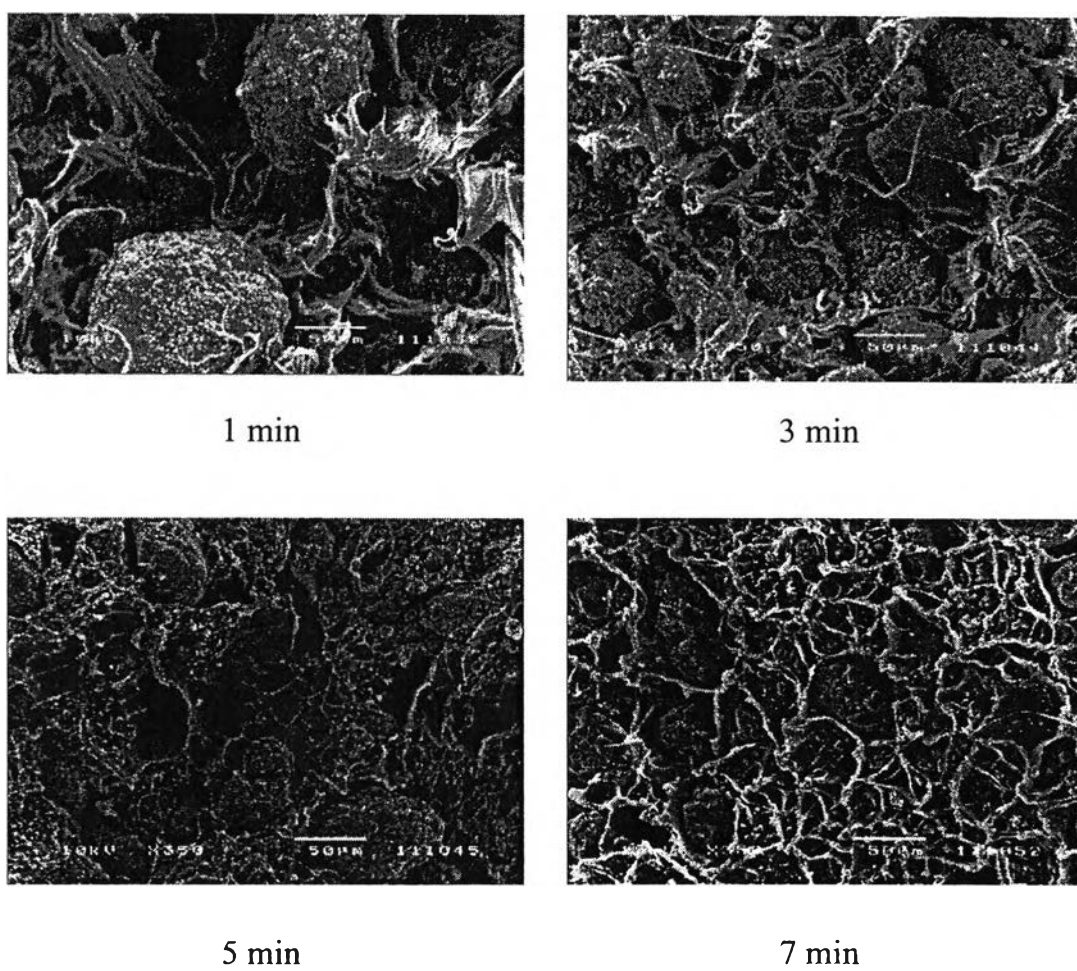


Figure 3.11 Scanning electron micrographs of the fractured surface of rice starch-based HDPE blends at various mixing times.

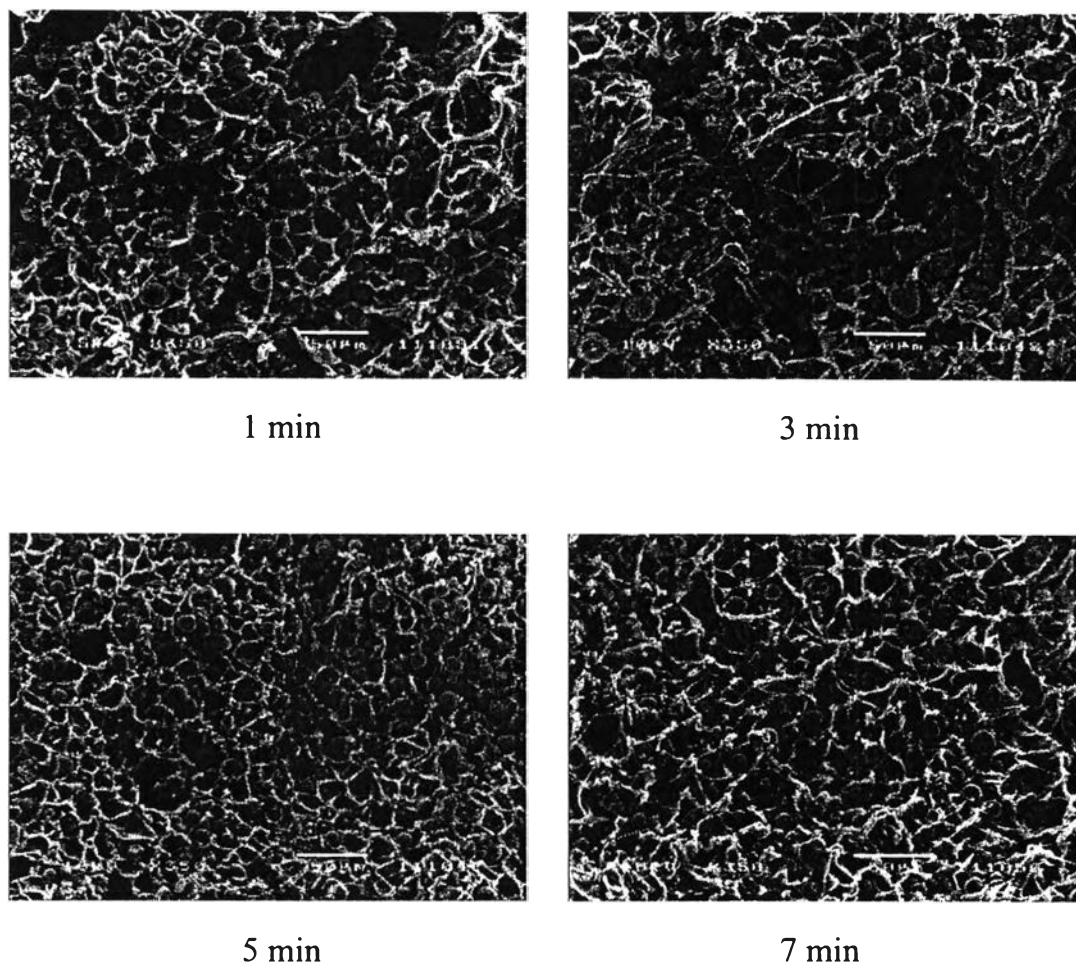


Figure 3.12 Scanning electron micrographs of the fractured surface of tapioca starch-based HDPE blends at various mixing times.

For both types of blends, poor interfacial adhesion between the starch particles and the HDPE matrix could be observed. In the tapioca starch-based blends, the starch particles were uniformly dispersed and distributed throughout. In the rice starch-based blends however, agglomerates of the rice starch were present, resulting in the non-uniform distribution of rice starch particles. The distribution and dispersion of the rice starch particles improved with increasing time. After 1 minute of mixing, large agglomerates could be found in the HDPE matrix. After 3 minutes of mixing, the agglomerates

decreased in size significantly. Scanning electron micrographs of the rice starch-based blends after 5 and 7 minutes of mixing were very similar suggesting that mixing had reached a steady state after about 5 minutes.

A Semafore program was used to analyze the size of the rice starch agglomerates and their number fraction. These results are shown in Figure 3.13.

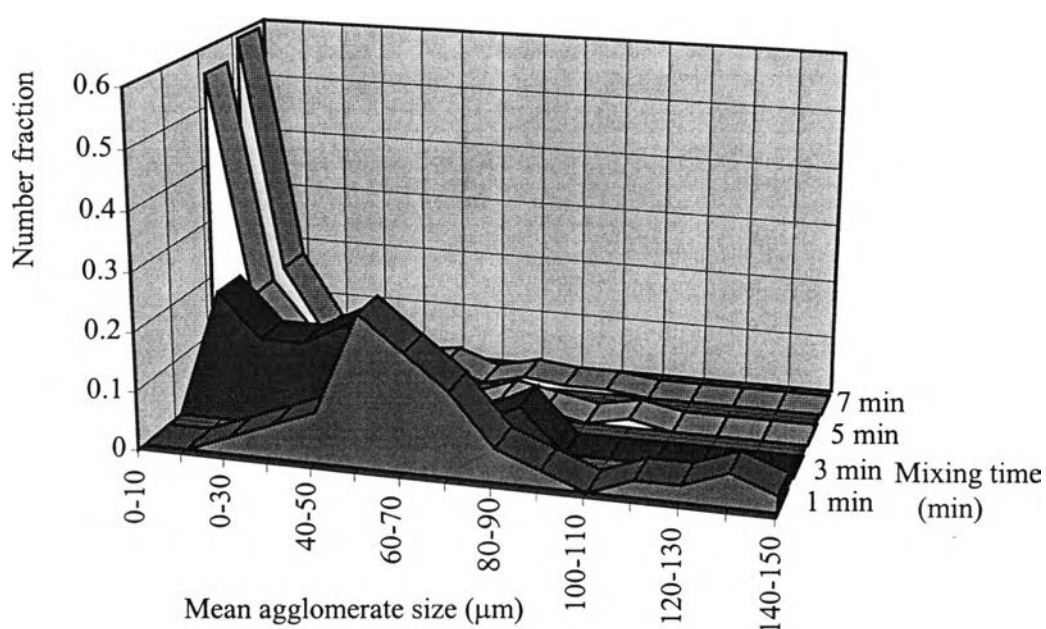


Figure 3.13 Size distribution of rice starch.

Figure 3.13 shows the size fraction distribution of the rice starch agglomerates at 20% starch loading, at different mixing times. The mean agglomerate size decreased with increasing mixing time. It is expected that the large agglomerates found in the HDPE matrix when shorter mixing times were used would cause a decrease in tensile strength, elongation, and tear resistance of the films due to larger voids that these larger agglomerates would cause. Therefore sufficient mixing time must be allowed in order to obtain better dispersion within the blends. From Figure 3.13 it can be seen that 5 minutes of mixing is sufficient.

3.4 Mechanical properties of starch-based HDPE blown film

Starch-based blown films with a nominal thickness of 85 μm were prepared using the Betol single screw blown film extruder. Specimens were cut from these films and the mechanical properties tested.

3.4.1 Tear resistance

Tear resistance of the rice starch-based HDPE blown film is shown in Figure 3.14.

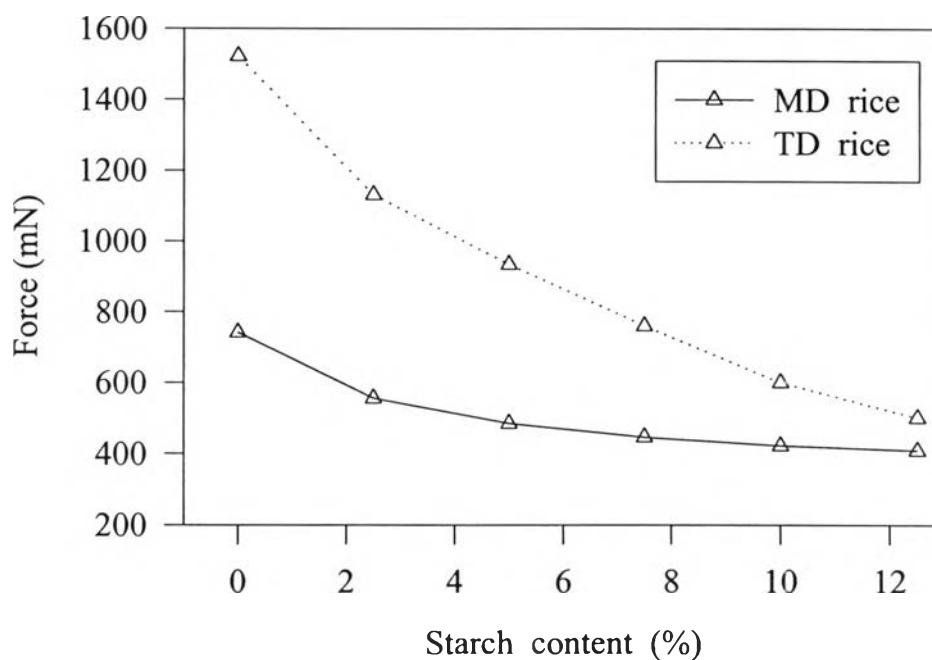
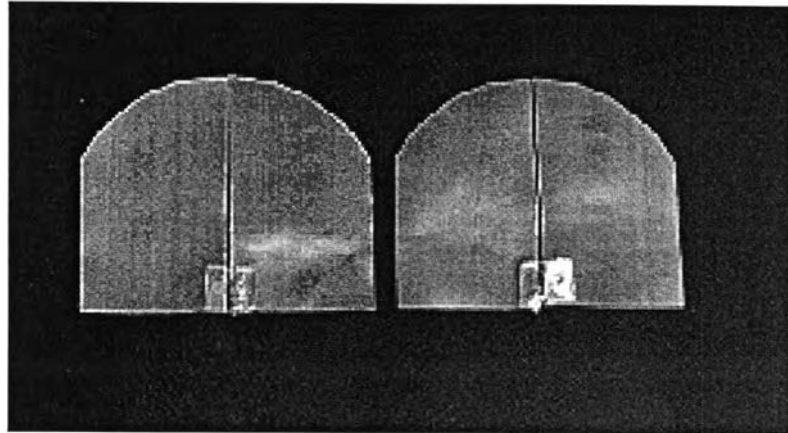
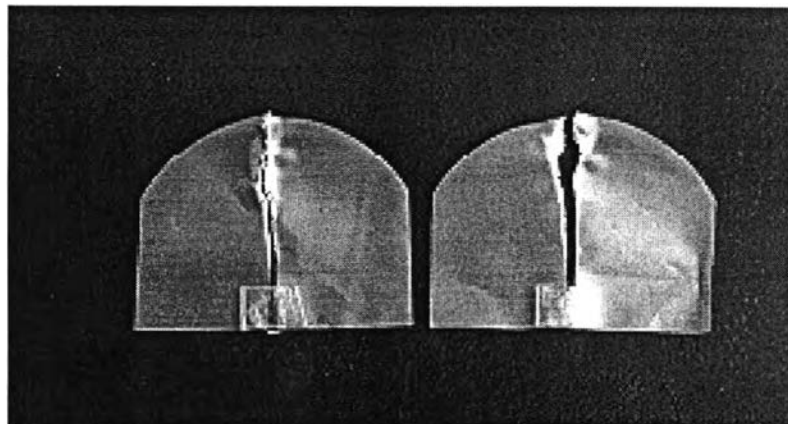


Figure 3.14 Tear resistance of the rice starch-based HDPE blown film

Tear resistance of the films decreased with increasing starch content in both the machine direction (MD) and the transverse direction (TD). The rice starch agglomerates acted as weak points in the film and the propagation of tearing of the film was thus made easier. The tear resistance in the TD was higher than in the MD suggesting that the preferential orientation is parallel to the MD. Figure 3.15 shows photographs of the torn specimens.



a.) machine direction (MD)



b.) transverse direction (TD)

Figure 3.15 Torn specimens in a.) machine direction (MD)
b.) transverse direction (TD).

In the MD tearing, the torn edges were smooth. There was not much resistance to tear propagation. On the other hand, the torn edges in the TD tearing were jagged and rough because tearing must propagate across the highly orientated HDPE chains in the MD of the film.

The tear resistance of the tapioca starch-based HDPE blown film is shown in Figure 3.16.

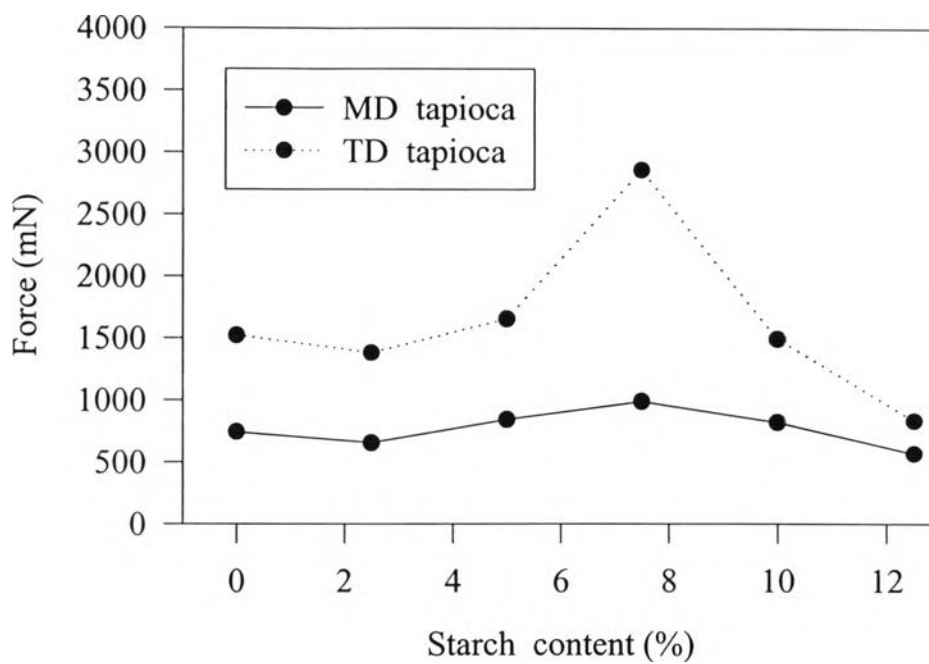


Figure 3.16 Tear resistance of the tapioca starch-based HDPE blown film.

Unlike the rice starch where tearing can propagate through the weakly held agglomerates, the tapioca starch particles are rigid and are thought to cause the crazing phenomena to occur. Tough, rigid polymers can be further toughened by the addition of rigid particles [Nielsen, (1974)]. Crazes act as load bearing entities which can dissipate energy and thus toughen the film.

In both directions of tearing there existed a maximum value of tear strength corresponding to a starch loading of 7.5%. This can be explained in terms of the tear resistance before and after the peak value.

For the first part of the curve, leading up to the maximum tear strength, there was an initial decrease followed by an increase in tear

resistance. The strengthening effect is resulted from craze formation. The initial decrease can be explained schematically in Figure 3.17.

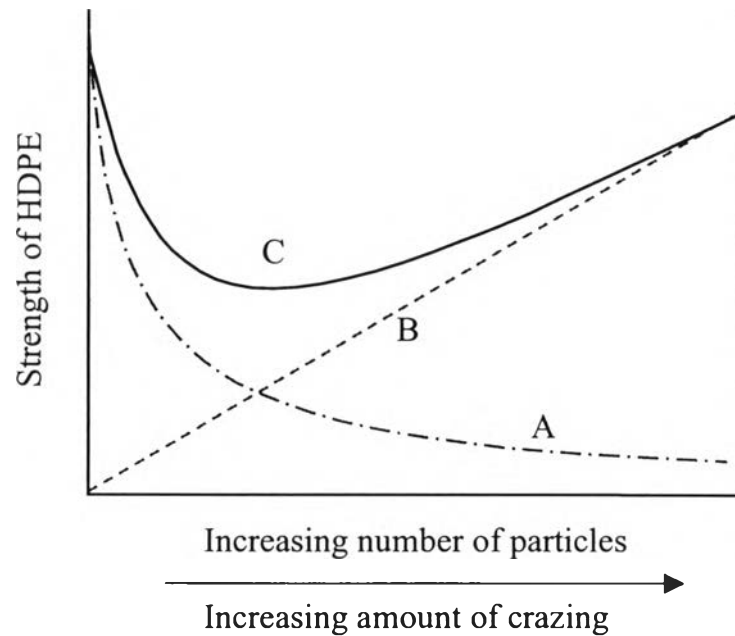


Figure 3.17 Tear resistance HDPE blown film.

Figure 3.17 shows the effect of starch content and crazing on the tear resistance of tapioca starch-based HDPE blown film. Curve A is the effect due only to the amount of the tapioca starch particles present (no crazing). There is a decrease in tear strength as more starch is added. Curve B is the effect due only to the amount of crazing which takes place. The tear strength increases with increasing extent of crazing. Curve C represents the combined effect of starch content and extent of crazing is the curve C where there is an initial decrease in tear resistance followed by an increase as the crazing effect becomes dominant.

For the second part of the curve, the tear resistance decreases with increasing starch content. This weakening effect is thought to result from a type of craze overlap phenomena. A proposed model is shown in Figure 3.18.

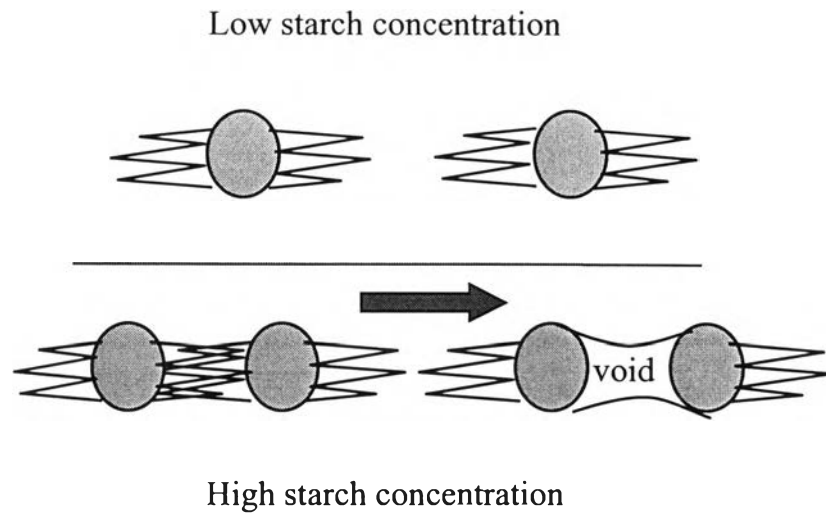


Figure 3.18 Crazing at low and high starch concentration.

At low starch concentrations, the crazes strengthen the blend. But at high starch concentrations, where the starch particles become closely packed, craze overlapping occurs. This results in a decrease in the actual amount of crazes since two crazes that overlap account effectively for just one actual craze. Furthermore, as craze cracks occur and propagate they will join up and form one giant void which will constitute a weak point resulting in a weakening effect. For these reasons, the tear resistance decreases at higher starch concentrations.

The tear resistance in the TD was higher than the tear resistance in the MD. This was also due to the higher orientation of the films in the MD.

A comparison of the tear resistance of rice starch-based and tapioca starch-based HDPE blown film is shown in Figure 3.19. The film containing tapioca starch provided higher tear resistance. This was because the tear can propagate through the rice starch agglomerates relatively easily; there are no agglomerates present in tapioca starch.

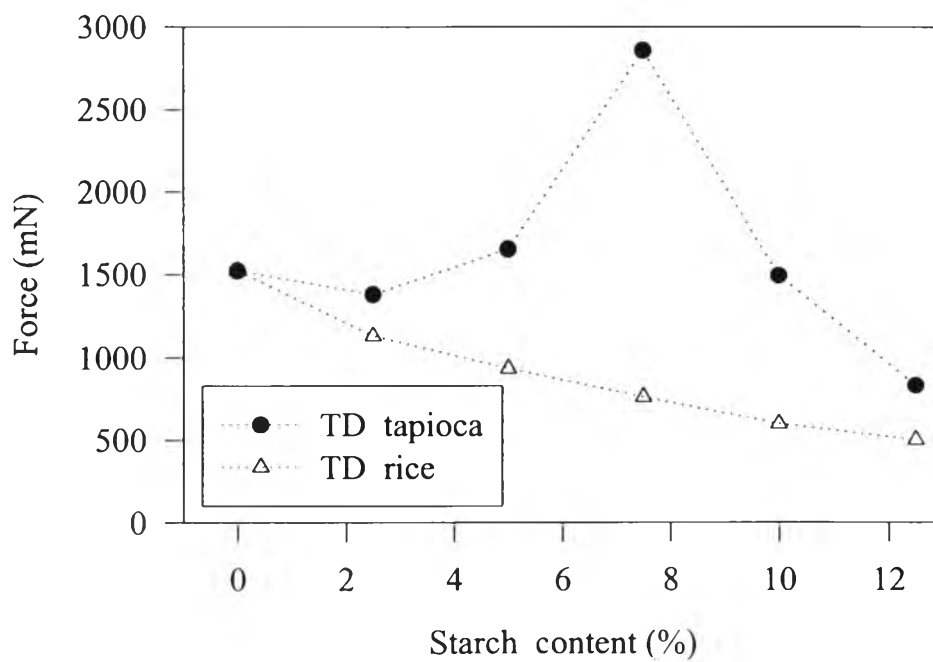
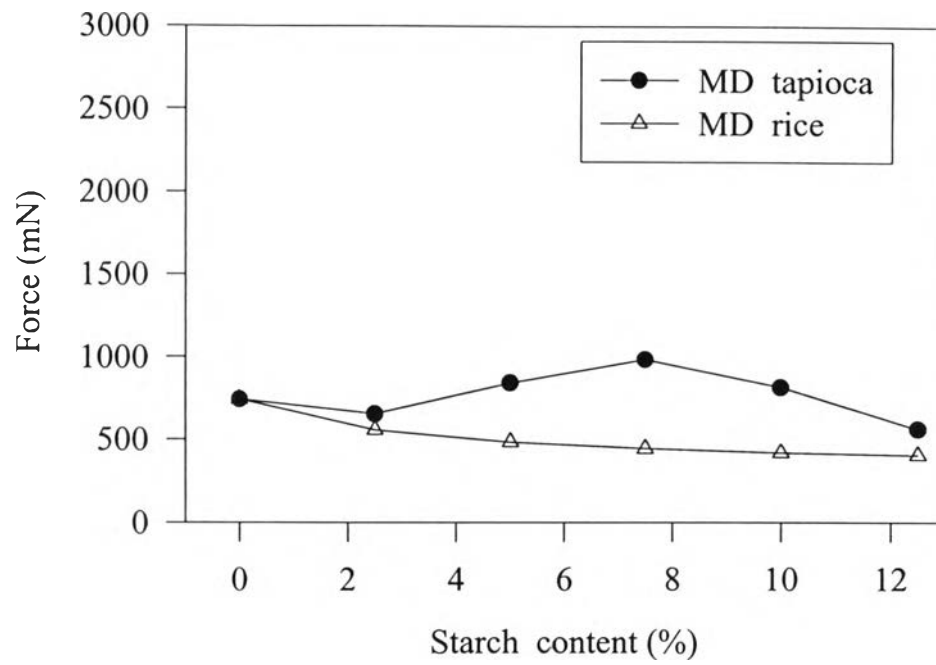


Figure 3.19 Tear resistance of rice and tapioca starch-based HDPE blown film.

3.4.2 Tensile properties testing

The tensile strength at yield of the rice starch-based and tapioca starch-based HDPE blown film are shown in Figs. 3.20 and 3.21, respectively.

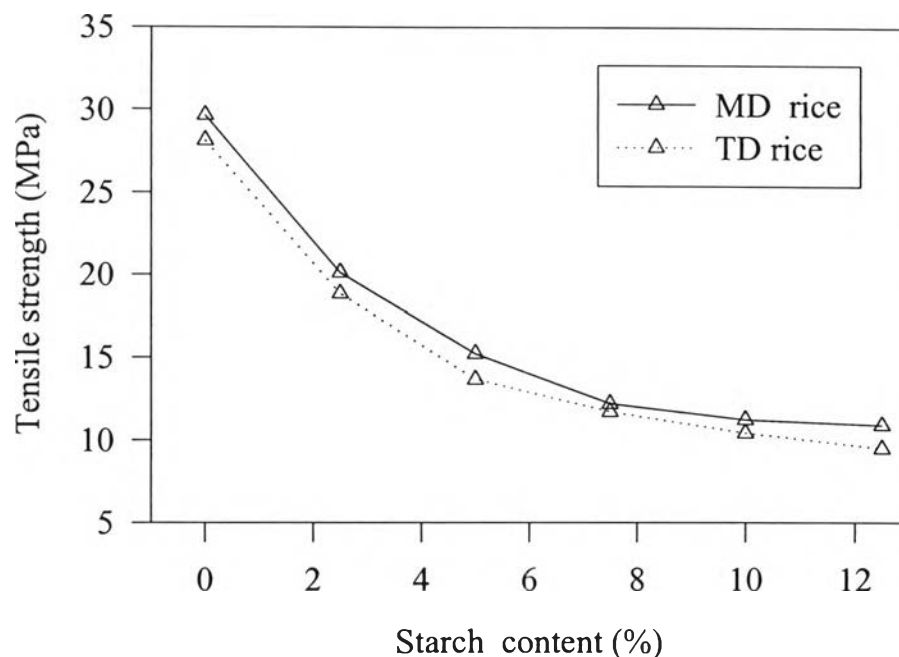


Figure 3.20 Tensile strength at yield of rice starch-based HDPE blown film.

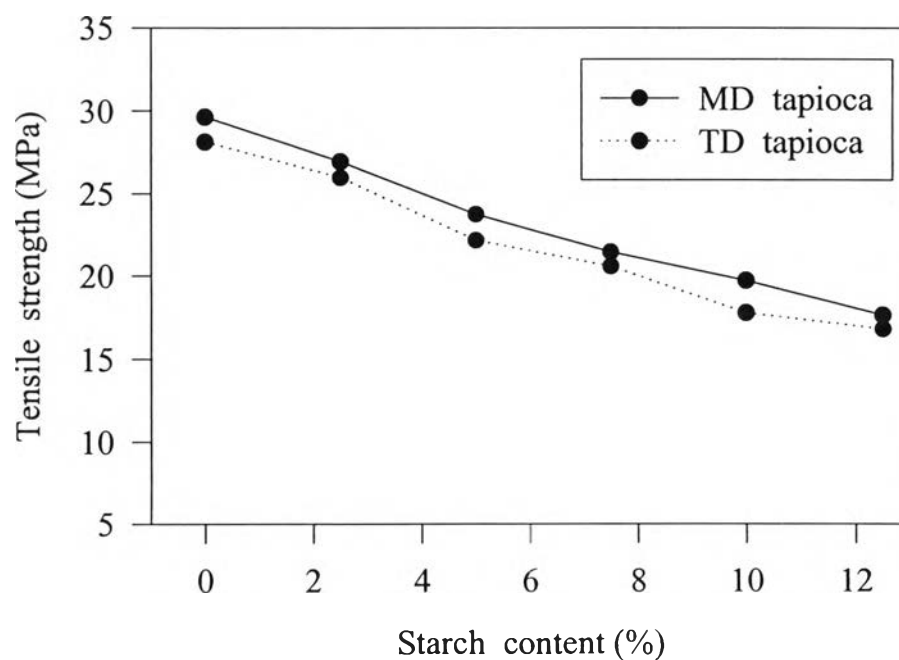


Figure 3.21 Tensile strength at yield of tapioca starch-based HDPE blown film.

The tensile strength of both types of blends decreased with increasing starch content. This was the result of a reduction in the effective cross-sectional area of the specimen to bear the applied load. The poor adhesion between the starch particles and the HDPE matrix resulted in higher actual stresses in the HDPE matrix for a given applied load. If perfect adhesion between filler and matrix were present the load would be transferred to the starch filler and no reduction in the effective cross-sectional area would result.

The tensile strength of the film in the MD was higher than the TD. This was again thought to be due to the higher orientation in the MD thus making the film stronger in this direction.

Figure 3.22 shows the comparison of the tensile strength of the film containing the two starches.

The tensile strength of the tapioca starch-based HDPE blown film was higher than that of the rice starch-based HDPE blown film at similar starch contents. This can be explained by the differences in the starch particle sizes. Although rice starch particles are smaller than tapioca starch particles, they form agglomerates and each agglomerate possesses the properties of one big particle. The effect of the differences in particle sizes is illustrated in Figure 3.23

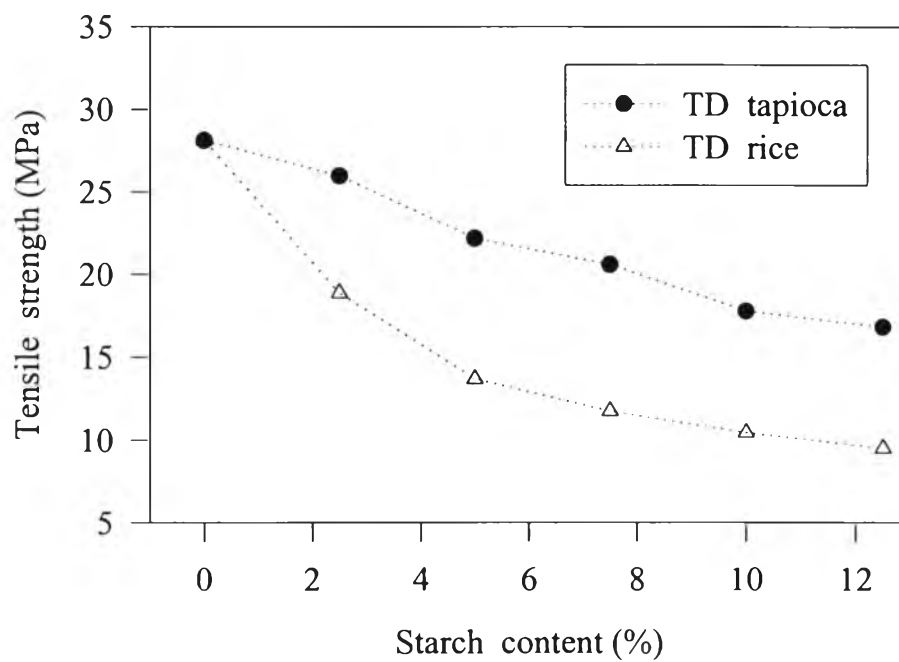
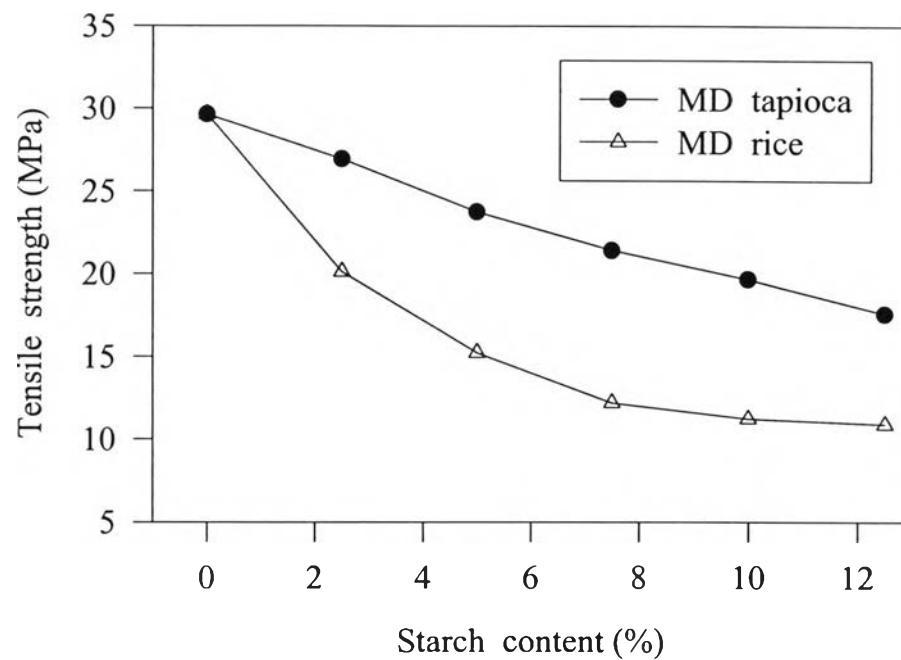


Figure 3.22 Tensile strength at yield of rice and tapioca starch-based HDPE blown film.

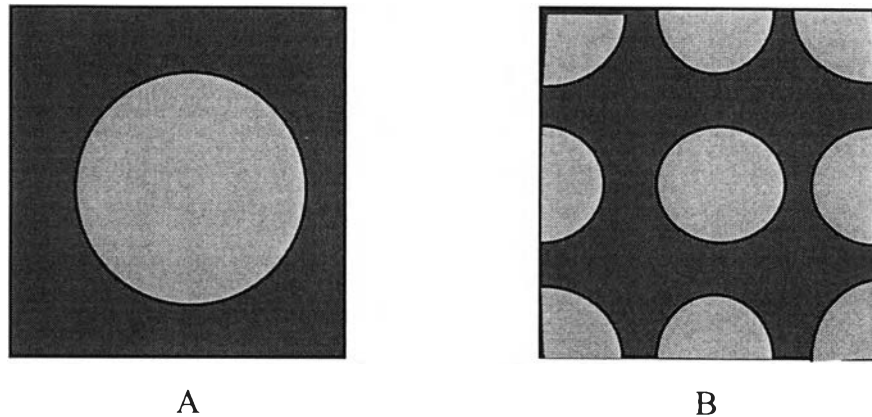


Figure 3.23 Cross-sectional area of a composite containing filler with diameters A.) $1D$ and B.) $0.5D$.

Figure 3.23 shows differences due to particle size – at one diameter and at one-half diameter. This illustrates that when a stress is applied perpendicular to the plane of the page, the strain is borne by a larger individual cross section of matrix with one particle, whereas, when the particle size is halved, there are four matrix zones between particles to bear the load. Stress is thus less uniformly distributed in A where the matrix must stretch around the entire surface of one particle. It is also apparent that the cross section becomes more homogeneous as the particle size decreases. Taken to the extreme, very small particles will provide a material giving the most uniform or homogeneous cross section and therefore the most uniform distribution of stress.

Furthermore, due to the poor adhesion (weak interfacial bonding) between the starch particles and the HDPE matrix, almost immediate separation of the matrix from the particles will occur when a stress is applied, resulting in the formation of minute voids. For a given critical strain and equal interfacial bonding, the immobility and the greater surface area of a large particle will cause larger voids than would occur with an equal volume of

smaller particles. Larger voids caused by larger particles act as higher stress concentration points which cause the matrix to yield at a lower stresses.

Non-uniform distribution of stress and large voids caused by large particles are all weakening effects.

The tensile elongation at yield of the rice starch-based and tapioca starch-based HDPE blown film are shown in Figures 3.24 and 3.25, respectively.

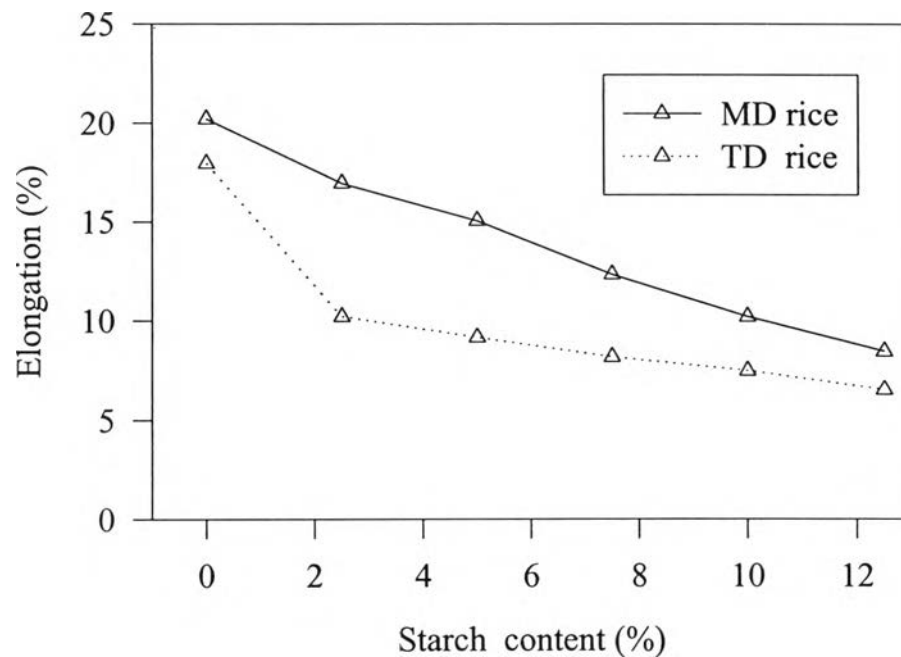


Figure 3.24 Elongation at yield of rice starch-based HDPE blown film.

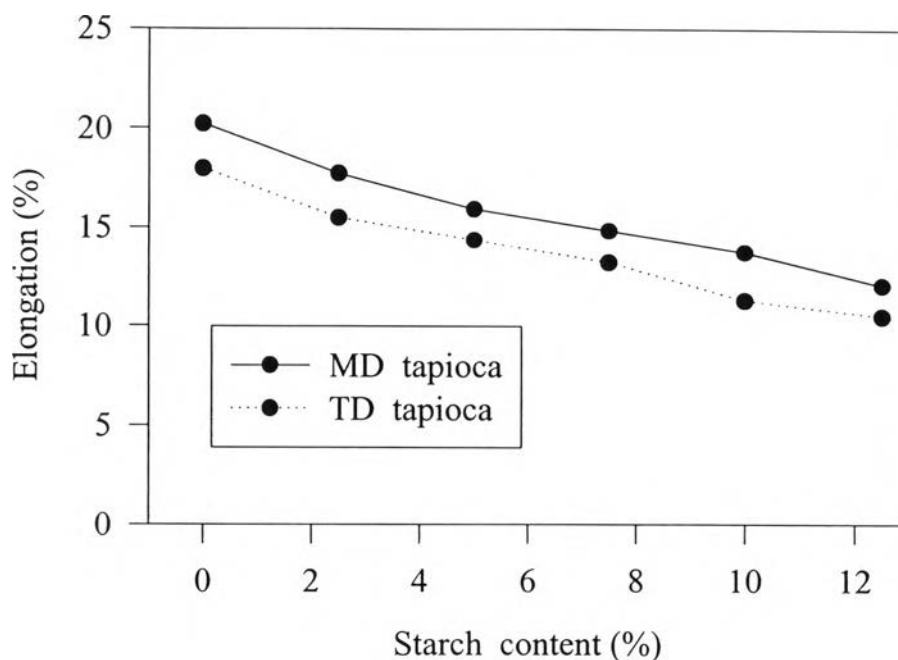


Figure 3.25 Elongation at yield of tapioca starch-based HDPE blown film.

The elongation at yield of both the rice starch-based and the tapioca starch-based HDPE blown film decreased with increasing starch content. This can be explained by the rigidity of starch particles. Starch is a rigid, very high-modulus material which undergoes virtually no elongation. Starch has been estimated to have the modulus of about 15 GPa [Willett, (1994)]. Therefore most of the elongation of a starch/HDPE blend will come from the stretching of the polymer matrix alone. With increasing starch content, the HDPE matrix will be correspondingly reduced, thus leading to a reduction in % elongation at yield. In addition, the weak interfacial bonding between the starch particles and the HDPE matrix will cause almost immediate separation of the matrix from the particles, and cavitation will begin at low elongation. Voids are stress concentrators.

Figure 3.26 shows the comparison of the elongation at yield of the film containing the two starches.

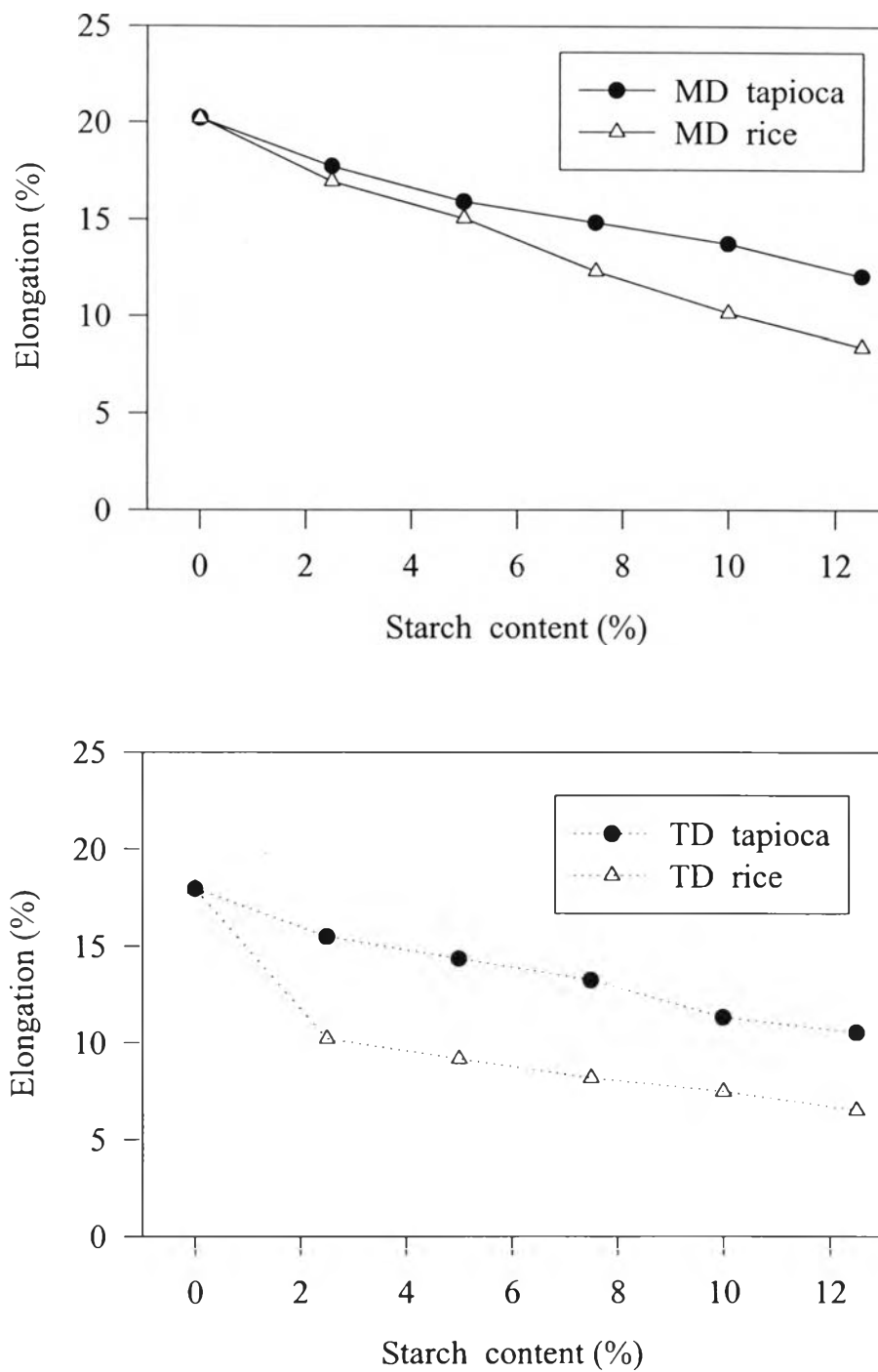


Figure 3.26 Elongation at yield of rice and tapioca starch-based HDPE blown film.

The elongation at yield of the tapioca starch-based HDPE blown film was higher than that of the rice starch-based HDPE blown film. This, again, may be explained by the differences in size of the starch particles. The polymer matrix is restricted in its ability to stretch around large filler particles (agglomerates), and dewetting or debonding of the particles causes cavitation, which appears as stress whitening. Smaller particles can move more freely with the matrix, and, consequently, the matrix can stretch more easily around them. And again, the weak interfacial bonding between the starch particles and the HDPE matrix results in formation of voids which cause the matrix to yield more quickly.

3.5 Water and moisture absorption of starch-based HDPE blown film

The plots of water absorption versus time for rice starch-based and the tapioca starch-based HDPE blown films are shown in Figure 3.27 and 3.28. The water absorption increased with increasing starch content. Films containing higher starch content also took longer times for equilibrium to be established. No significant water absorption was observed for films containing no starch.

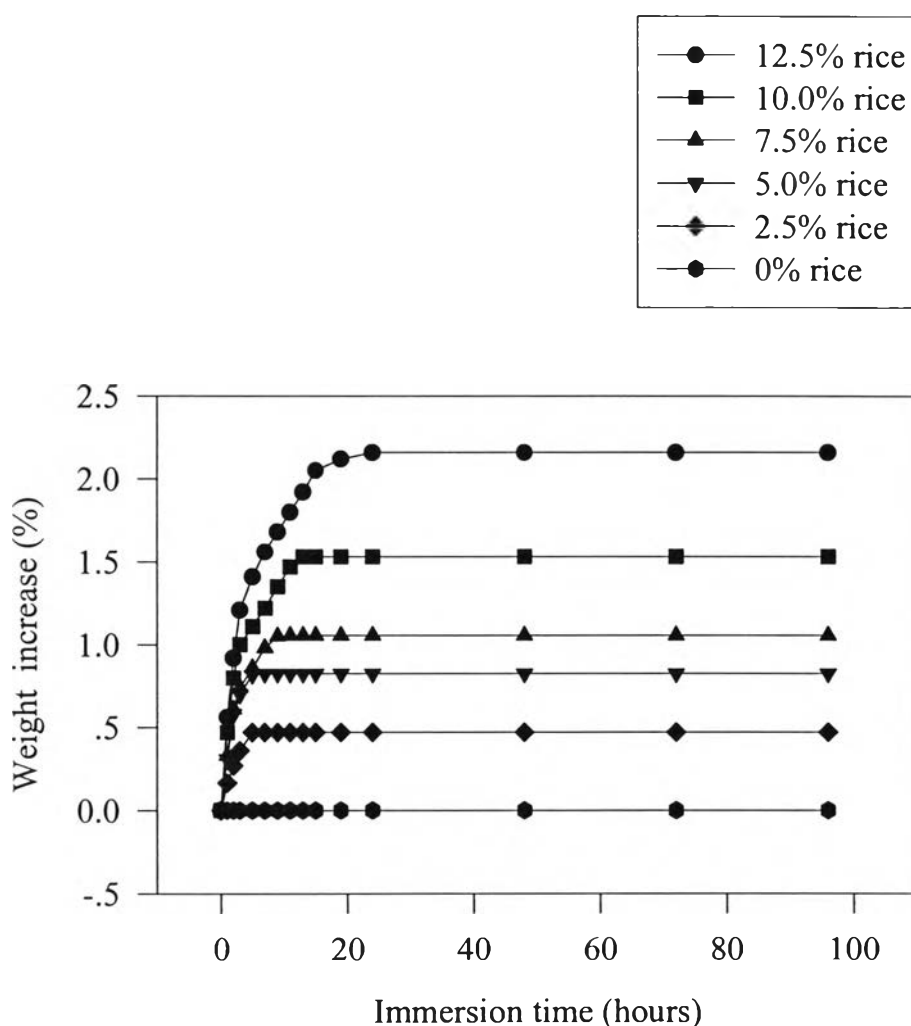


Figure 3.27 Water absorption of rice starch-based HDPE blown film.

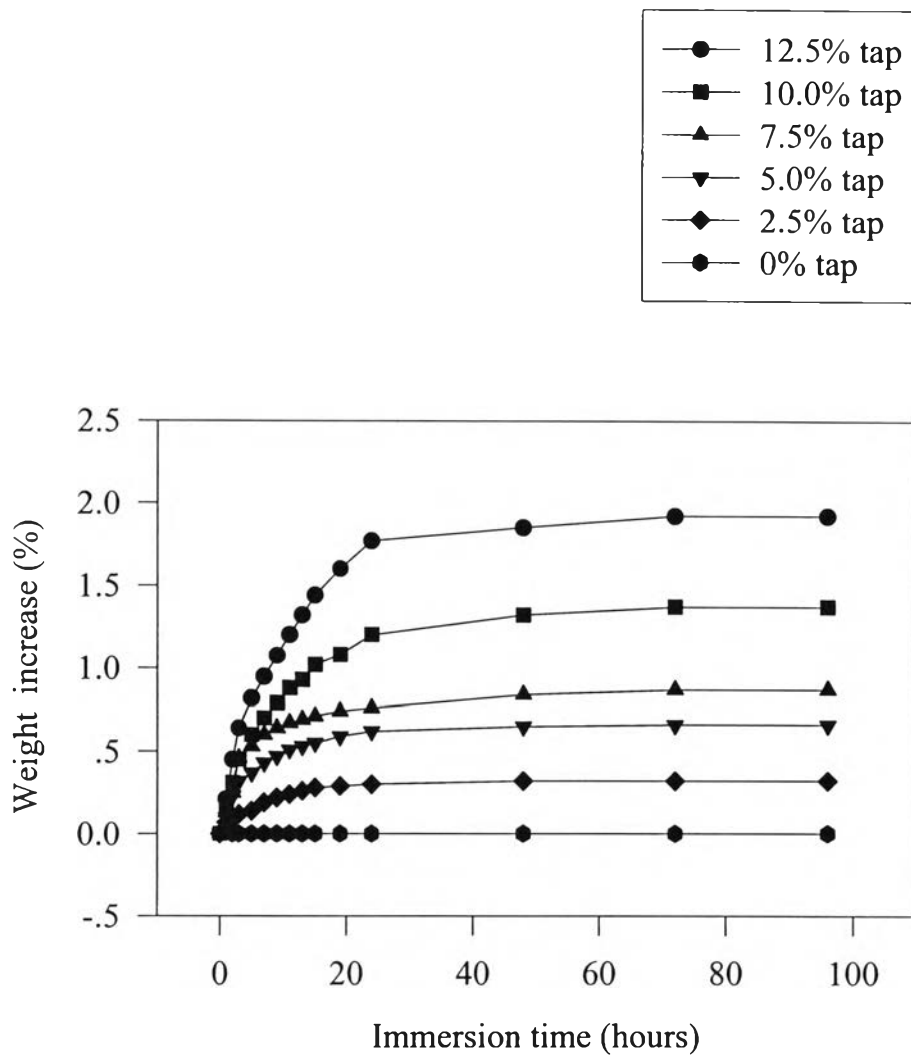


Figure 3.28 Water absorption of tapioca starch-based HDPE blown film.

Figure 3.29 compares the water absorption of the film containing both types of starches at 10% starch loading. The film containing rice starch absorbed more water than the film containing tapioca starch. Further more, the film containing rice starch took less time to become saturated with water. It can be concluded that the rice starch has higher water affinity than the tapioca starch.

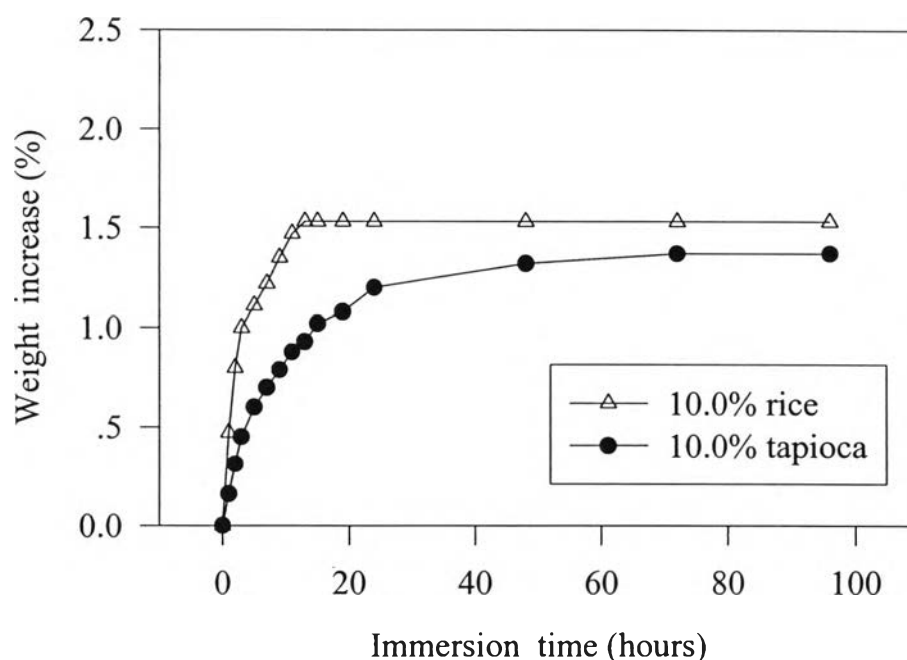


Figure 3.29 Water absorption of rice starch-based and tapioca starch-based HDPE blown film at 10% starch content

The tensile strength of rice starch-based and tapioca starch-based HDPE blown film before and after the water treatment are shown in Figures 3.30 and 3.31. A decrease in tensile strength was observed for film after being treated with water. This decrease could have resulted from the presence of larger voids caused by the swelling of the starch particles.

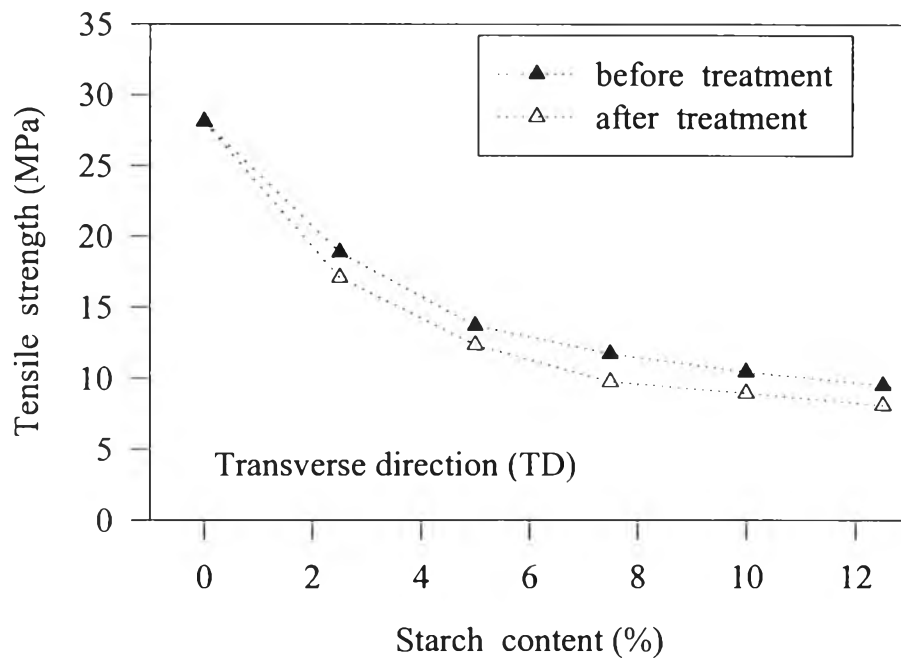
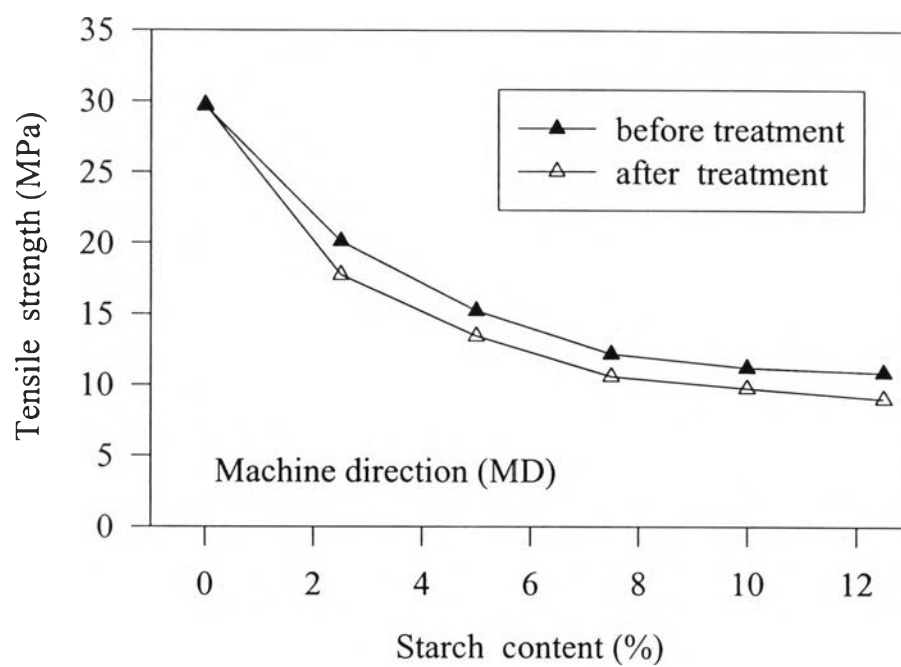


Figure 3.30 Tensile strength of rice starch-based HDPE blown film before and after water absorption treatment.

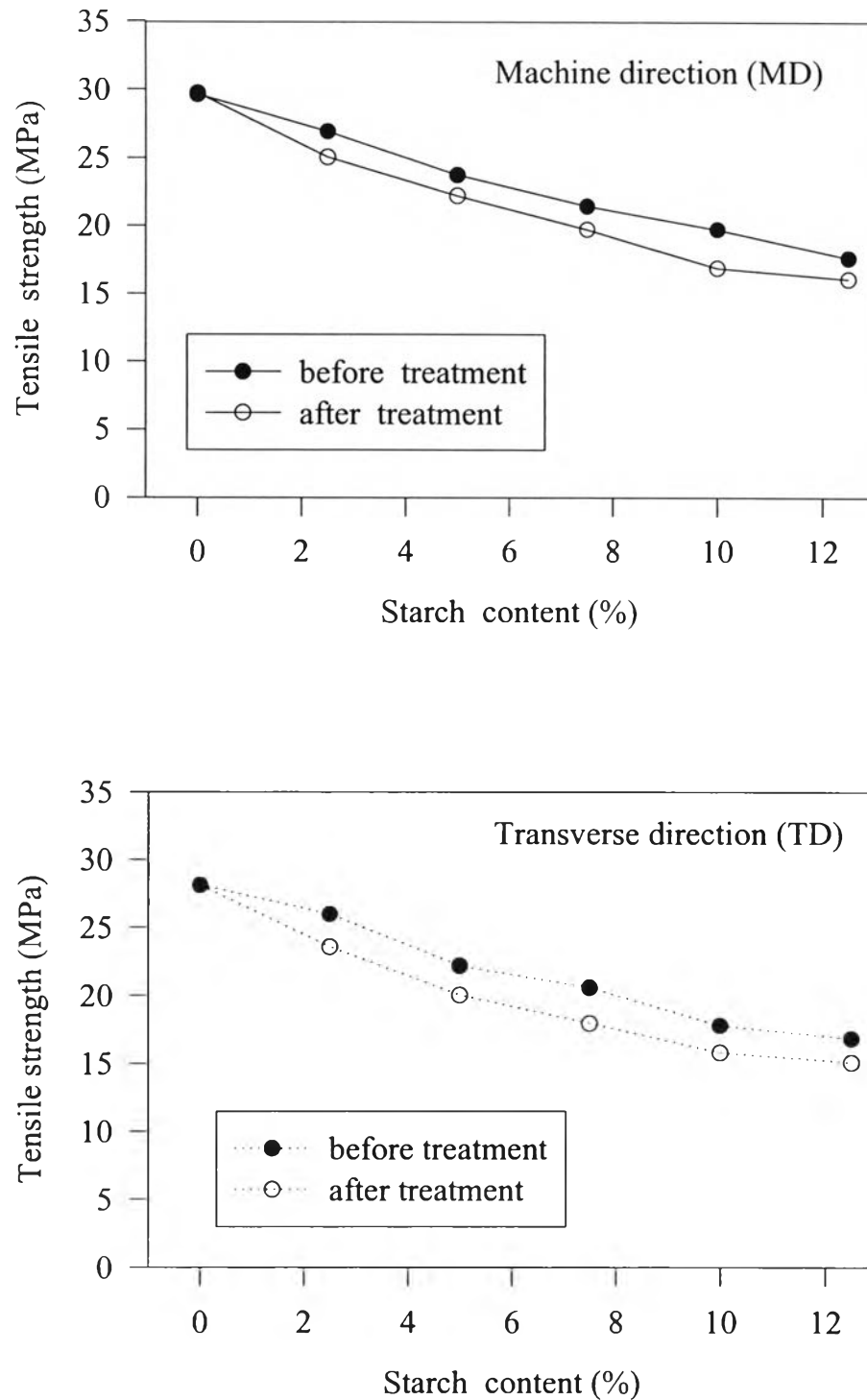


Figure 3.31 Tensile strength of tapioca starch-based HDPE blown film before and after water absorption treatment.

Table 3.2 shows the moisture absorption of the rice starch-based and the tapioca starch-based HDPE blown film in 70% relative humidity after 28 days of exposure. The amount of moisture absorbed increased with increasing starch content. Films containing rice starch absorbed more moisture than films containing tapioca starch. This result confirms that blends with rice starch were more hydrophilic, which would lead to a reduction in dimensional stability of the blends (more swelling).

Table 3.2 Moisture absorption (%) of rice starch-based and tapioca starch-based HDPE blown film in 70% relative humidity

| Starch content (%) in blends with HDPE | Moisture absorption (%) of rice starch | Moisture absorption (%) of tapioca starch |
|--|--|---|
| 0 | 0 | 0 |
| 2.5 | 0.209 | 0.130 |
| 5.0 | 0.259 | 0.163 |
| 7.5 | 0.351 | 0.309 |
| 10.0 | 0.634 | 0.489 |
| 12.5 | 0.748 | 0.714 |