CHAPTER III
RESULTS AND DISCUSSION

3.1 Rheological Studies

Rheology can provide a window into a polymer and also a polymer blend. The rheological properties that were studied in this work were viscous, elastic and viscoelastic behaviors of the starch-HDPE blends.

3.1.1 Viscous Behavior

The viscous understanding of a material is the most crucial factor in blend processing. In this work, the viscosity of blend melts were measured over the shear rate range of 5-7000 1/s. The dependence of melt viscosity on starch content, starch type, and temperature were studied.

3.1.1.1 Effect of Starch Content. Most polymers exhibit shear thinning characteristics. This means that the viscosity of the polymer decreases as shear rate increases.

Figure 3.1 shows that for any given tapioca starch content the blend viscosity is lower at higher shear rate. Hence the blends exhibit shear thinning behavior. As the starch content of the blend is increased, the viscosity also increases for low shear rate conditions. But at high shear rates the viscosity is unchanged for all starch loadings. At the test temperature only HDPE was in the molten state whereas the starch particles remained as unmelted particles. The melting temperature of starch was higher than the test temperature of 180^{o}C. The starch in particle form had the ability to resist the

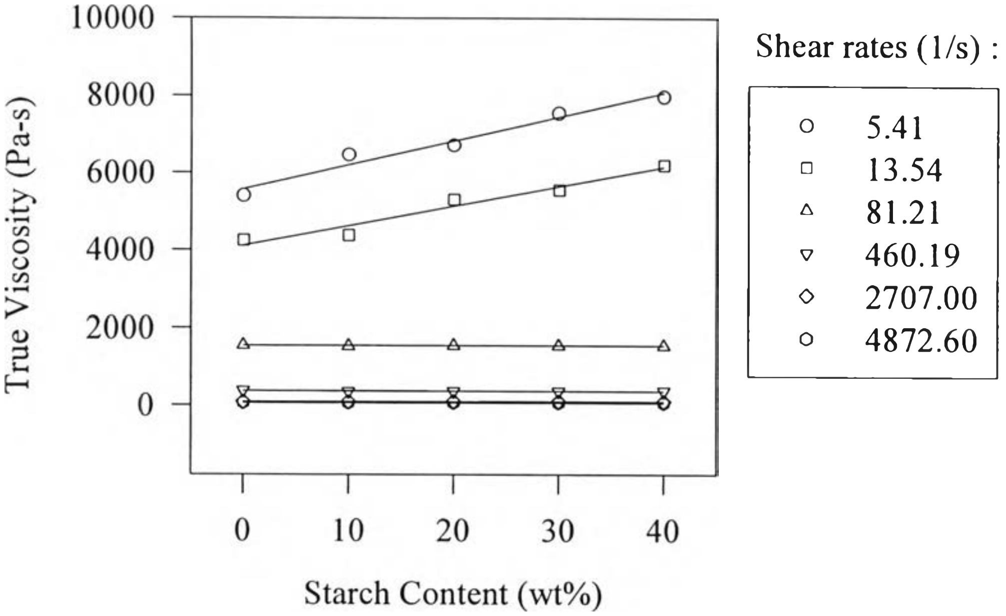


Figure 3.1 Effect of tapioca starch content on viscosity of blends containing 0, 10, 20, 30, and 40 wt % of starch at 180°C at various apparent shear rates.

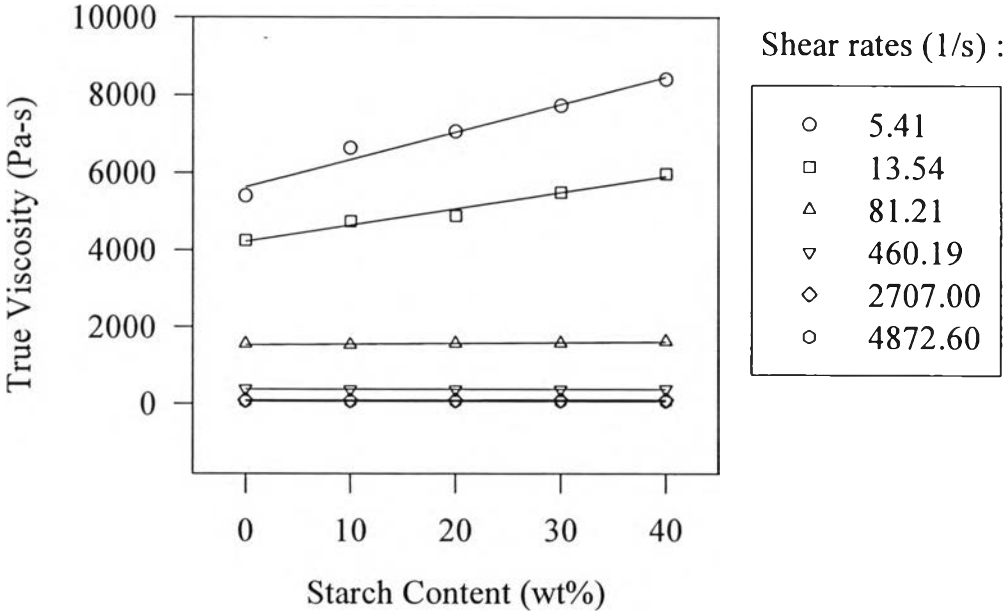


Figure 3.2 Effect of rice starch content on viscosity of blends containing 0, 10, 20, 30, and 40 wt % of starch at 180°C at various apparent shear rates.

flow of HDPE. The effect of starch particles on the resistance to flow depended on the shear rate. It was predominant only at low shear rates resulting in an increase in viscosity with increasing starch content. When the applied shear rates were high, the shear forces allowed the HDPE chains to slide pass each other more easily. The high shear forces overcame the ability of starch particles to resist the flow of polymer melt. Hence the starch particles did not affect the flow of HDPE at high shear rates. Similar results were found for rice starch-HDPE blends as shown in figure 3.2.

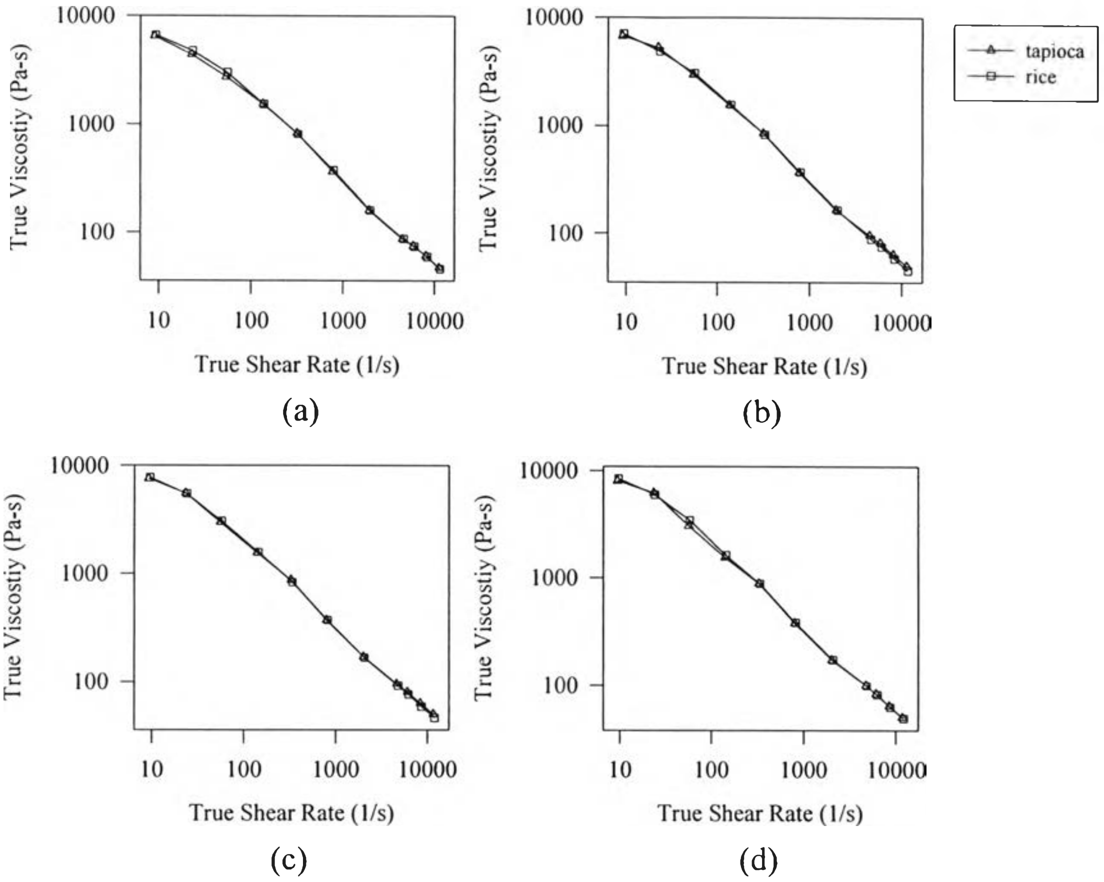
Power law indices were determined, as mentioned in section 2.3.2.1, in the shear rate range of 5-7000 1/s in which the flow curves were rather linear. This implies that the systems obey the power law behavior in this shear rate range. The results are shown in table 3.1.

Table 3.1 Power law index (n) for the starch-HDPE blends at 180^{o}C.

Starch content (wt %)	n	
	Tapioca starch-HDPE blends	Rice starch -HDPE blends
0	0.2910	0.2910
10	0.2714	0.2606
20	0.2687	0.2544
30	0.2572	0.2451
40	0.2522	0.2417

From table 3.1, for both types of starch particles, as the starch contents increased, the power law indices decreased. This meant that the higher the starch content, the more shear thinning behavior of the blends.

3.1.1.2 Effect of Starch Type.



(a) (b) (c) (d)

Figure 3.3 Effect of starch type on viscosity of blends at 180^{o}C : (a) 10 wt % of starch, (b) 20 wt % of starch, (c) 30 wt % of starch, and (d) 40 wt % of starch.

From figure 3.3, at fixed temperature and starch content, the two types of starch particles gave almost the same viscosity for the blended melts. Thus, tapioca starch particles can resist the flow of HDPE in a similar manner to rice starch particles even though the two starch types have different shape, size, and dispersion in the HDPE matrix.

3.1.1.3 Effect of Temperature. This study was performed on HDPE, blends containing 20 wt % of tapioca starch, and blends containing 20 wt % of rice starch. Each sample was tested at on three different temperatures, i.e. 160, 180, and 200°C.

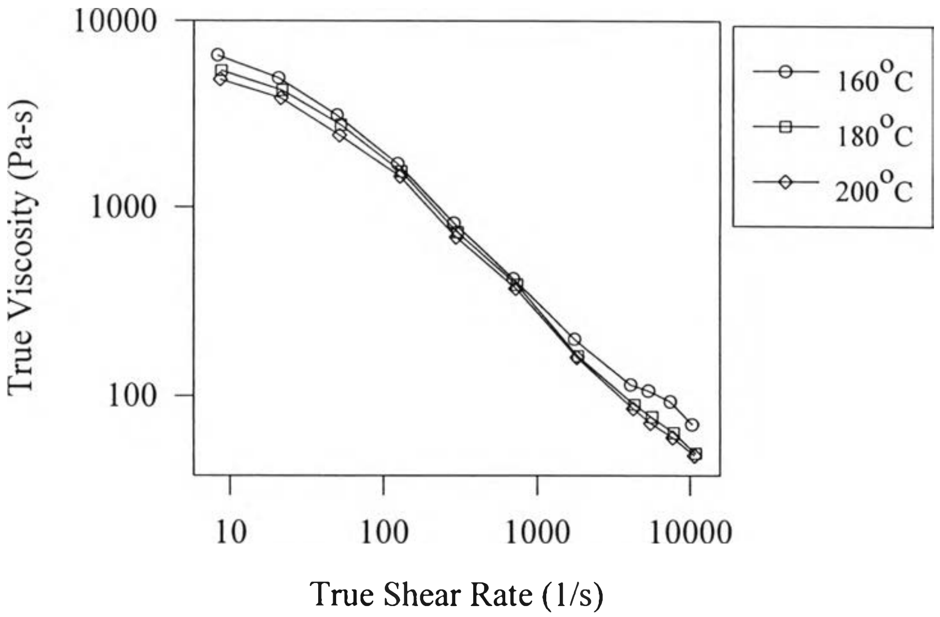


Figure 3.4 Effect of temperature on viscosity of HDPE.

From figure 3.4, the viscosity of the HDPE decreased with increasing temperature. This follows the well-known Arrhenius behavior. Polymer chains have higher energy at elevated temperatures and this allows the material to flow more easily, thus leading to lower viscosity.

The same results were found for blends containing 20 wt % tapioca starch and 20 wt % rice starch as shown in figures 3.5 and 3.6, respectively. The viscosity of the starch-HDPE blends decreased with increasing temperature. As temperature increased, HDPE chains can slide pass each other and also starch particles more easily resulting in a decrease in viscosity. It was observed that for both tapioca and rice starch the particles

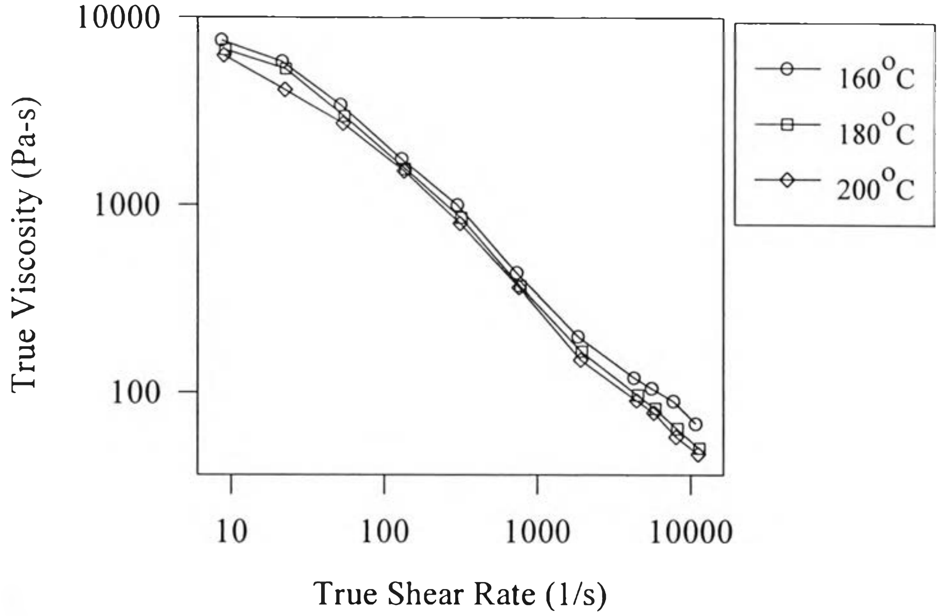


Figure 3.5 Effect of temperature on viscosity of blends containing 20 wt % of tapioca starch.

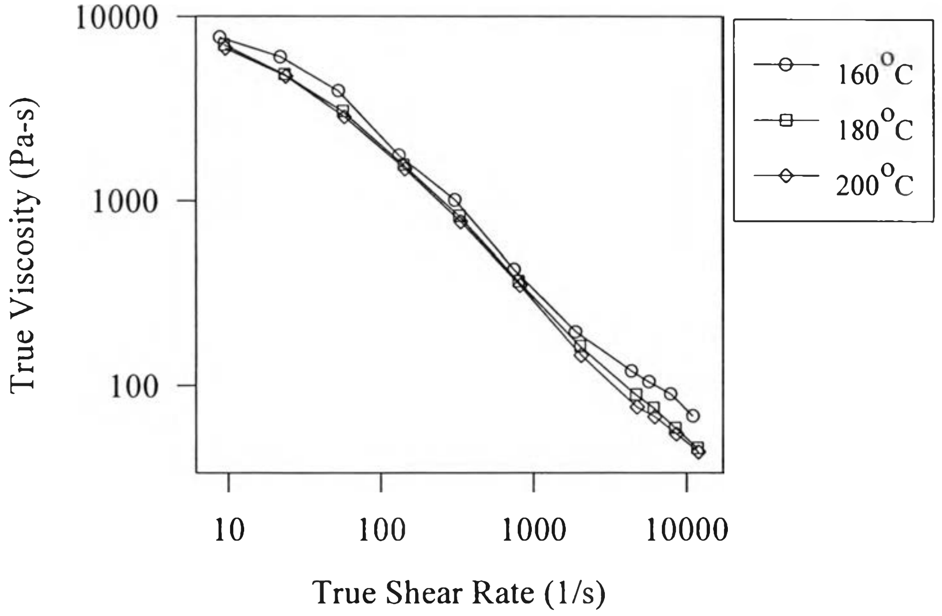


Figure 3.6 Effect of temperature on viscosity of blends containing 20 wt % of rice starch.

started to burn at a test temperature of 200°C. Hence, the processing temperature for starch-HDPE blends should be kept below 200°C.

3.1.2 Elastic Behavior

Rheological data of solid blends from a transient test provides shear stress-strain curves. These curves can be used to predict elasticity, strength, and stiffness of the blends.

3.1.2.1 Effect of Starch Content.

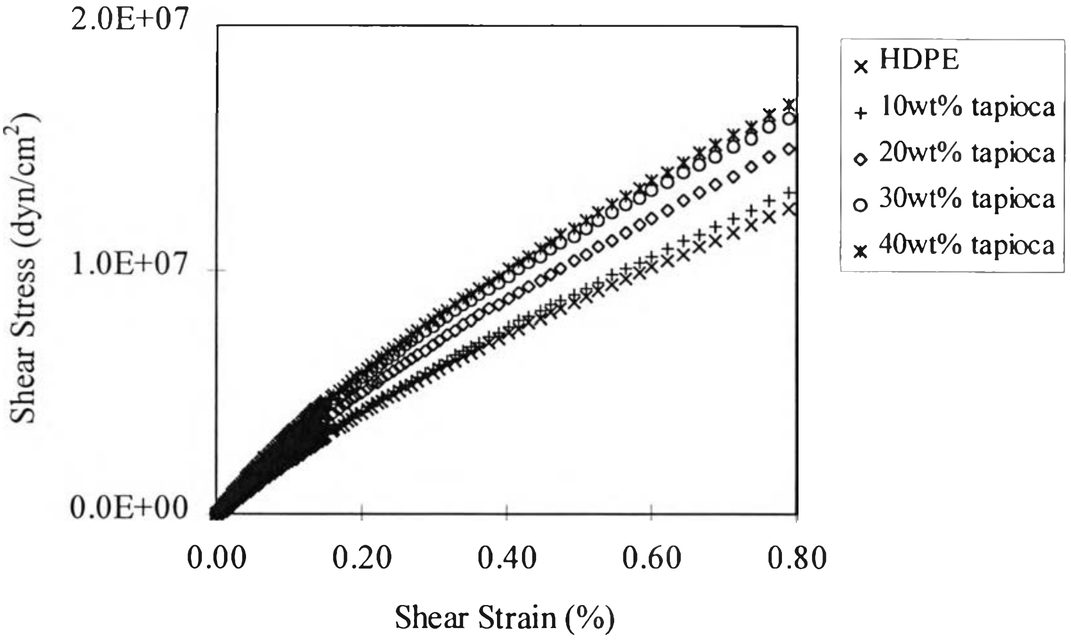


Figure 3.7 Shear stress-strain curves for blends containing different tapioca starch contents analyzed at 30°C.

The shear stress-strain curves of tapioca starch-HDPE blends are shown in figure 3.7. The shear modulus or the stiffness of the blends were measured from the initial slope of the curves. The slope of the curves were steeper at higher starch contents indicating that the blends were stiffer with increasing starch content. This is because tapioca starch particles are stiffer than the HDPE, hence a large increase in modulus was observed as the starch content increased. Shear yield stress and shear yield strain were also obtained from the shear stress-strain curves. The effect of starch content on these two values will be discussed in the next section.

3.1.2.2 Effect of Starch Type.

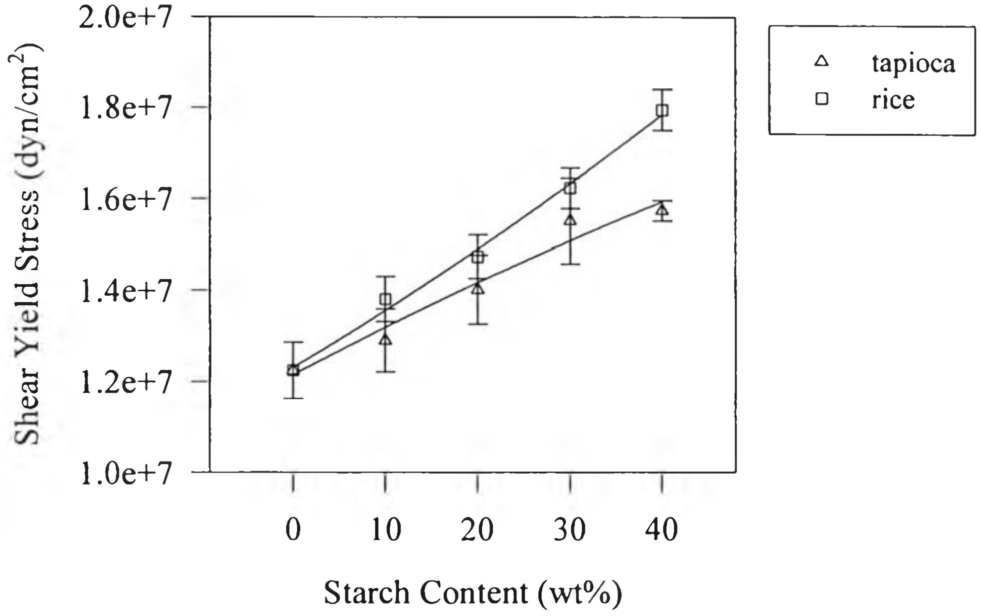


Figure 3.8 Effect of starch type on shear yield stress of blends at 30°C.

Figure 3.8 shows the effect of starch content on the shear yield stress. Yield stress is the minimum stress at which a permanent strain is produced when the stress is removed. With increasing starch content, the blends had higher shear yield stress for both types of starch because starch particles can prevent the deformation of HDPE at starch-size scale. The ability of the blends to resist deformation from the applied stress was higher with increasing amounts of starch. In addition, for the same value of starch contents the blends containing rice starch had higher shear yield stress than the blends containing tapioca starch. The size of rice starch particles was smaller than that of tapioca starch particles. Smaller particle size gives larger surface energy and the higher particle-particle interaction. This caused agglomeration of the starch particles.

Hence rice starch particles were easy to agglomerate. The larger size of rice starch can prevent the deformation of HDPE in larger-size scale leading to the higher shear yield stress of rice starch than tapioca starch.

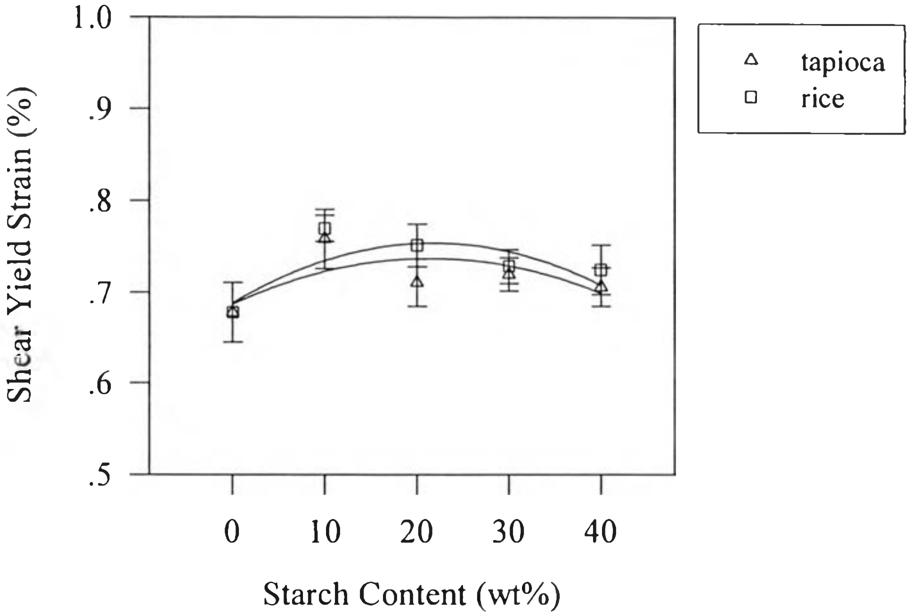


Figure 3.9 Effect of starch type on shear yield strain of blends at 30°C.

For the shear yield strain of the blends, both types of starch showed the same results as shown in figure 3.9. At low starch contents, i.e. below 20 wt %, the shear yield strain tended to increase with increasing starch content. But when starch content was greater than 20 wt %, the shear yield strain tended to decrease with increasing starch content.

Shear modulus data are shown in figure 3.10. With increasing starch content, both types of starch showed an increase in shear modulus. This was due to the stiffening effect of the starch granules. The shear modulus of rice starch-HDPE blends were greater than those of tapioca starch-HDPE blends. This is because the agglomerates of rice starch particles decreased the maximum packing value and therefore increased the modulus.

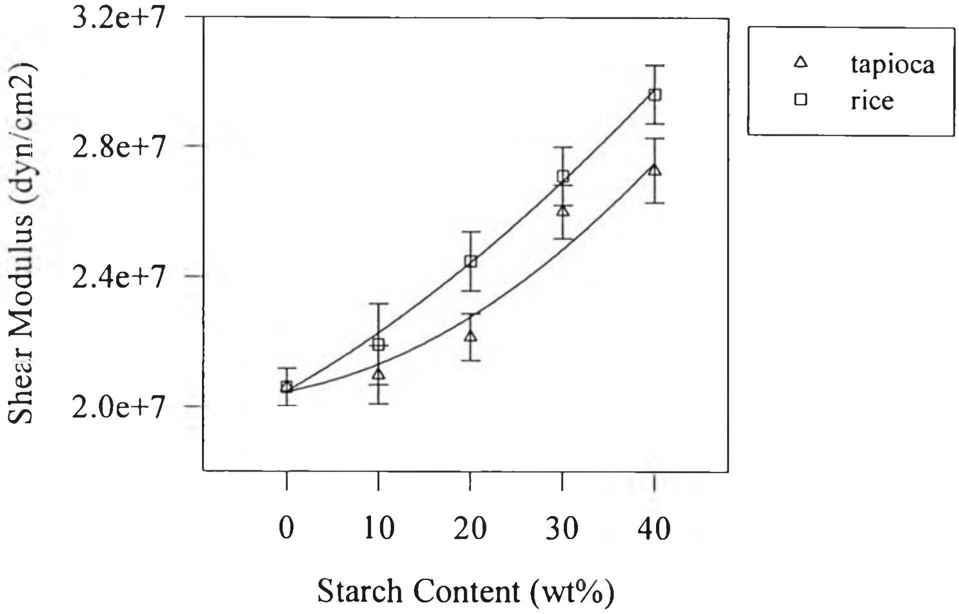


Figure 3.10 Effect of starch type on shear modulus of blends at 30°C.

3.1.3 Viscoelastic Behavior

Rheological data of solid blends from a dynamic test provides viscoelastic properties of the blends. This dynamic test was run in a frequency sweep at 30°C. The frequency ranged from 0.1-100 rad/s. In this work, three parameters of viscoelastic properties were studied. These parameters were storage modulus, loss modulus, and loss tangent.

3.1.3.1 Effect of Starch Content. Storage modulus represents the elastic response of the material, related to the potential energy stored by the material under deformation. The value of the storage modulus signifies the stiffness of the material. Figure 3.11 shows storage modulus measurement results for the tapioca starch- HDPE blends. As the starch content increased, the storage modulus of the blends also increased. Since starch particles are more rigid than HDPE, they can store more deformational energy.

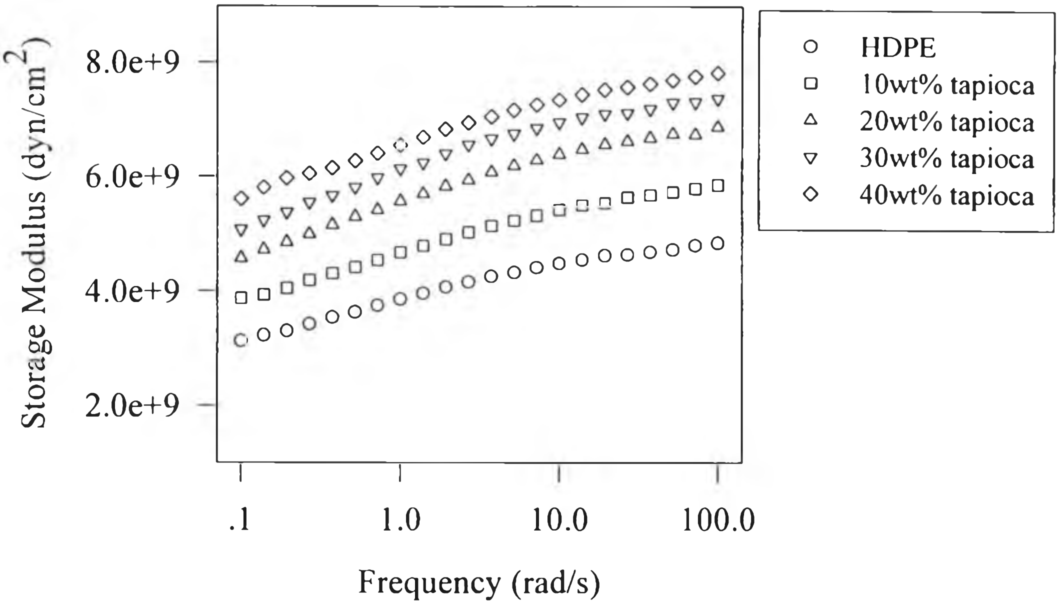


Figure 3.11 Effect of tapioca starch content on storage modulus of blends containing 0, 10, 20, 30, and 40 wt % of starch at 30°C.

Loss modulus is the viscous response of the material. This parameter signifies the dissipation of energy as heat during deformation. Figure 3.12 shows loss modulus for blends containing various amounts of tapioca starch at a range of frequencies. With increasing starch content, the loss modulus increased. The ability to dissipate energy from the blends was probably due to the HDPE matrix rather than the starch particles. But starch particles also contributed to the energy dissipation of HDPE. When starch was blended with HDPE, it was proposed that the crystallization of HDPE was disturbed leading to a decrease in HDPE crystallites which can be further analyzed by Differentail Scanning Calorimeter (DSC), X-ray Diffractometer (XRD), and Transmission Electron Microscope (TEM). Crystallites act as crosslinks by tying segments of many molecules together. As the number of crystallites decrease, less molecules can be tied together. HDPE chains can therefore move easier, leading to more energy was dissipated.

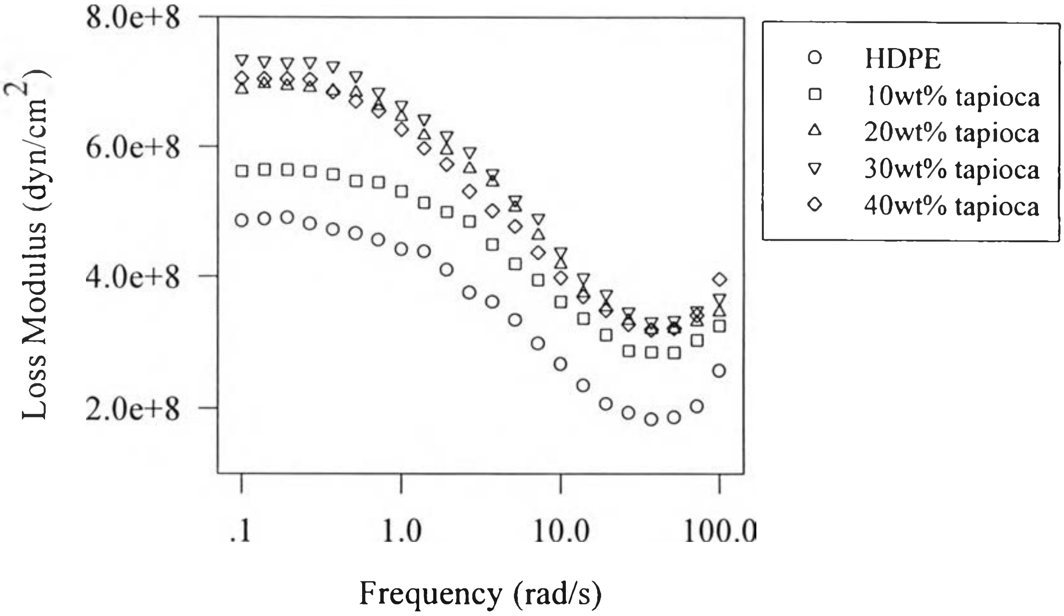


Figure 3.12 Effect of tapioca starch content on loss modulus of blends containing 0, 10, 20, 30, and 40 wt % of starch at 30°C.

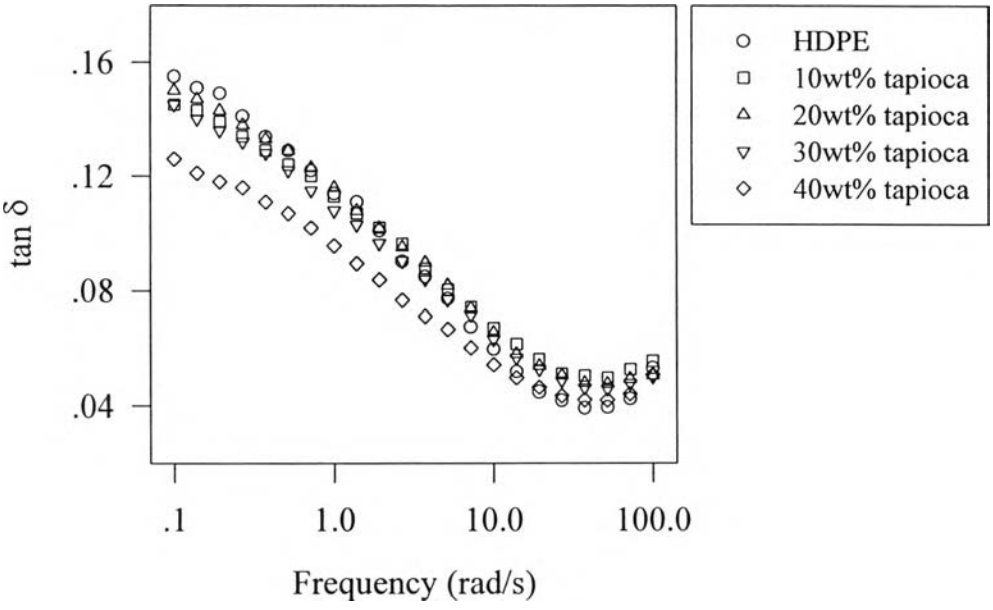


Figure 3.13 Effect of tapioca starch content on loss tangent of blends containing 0, 10, 20, 30, and 40 wt % of starch at 30°C.

Tan δ represents the internal friction or damping and is termed the loss tangent or loss factor. Figure 3.13 shows that the addition of tapioca starch resulted in a lowering of loss tangent for the blends. This is because damping of most rigid particles is very low compared to that of HDPE.

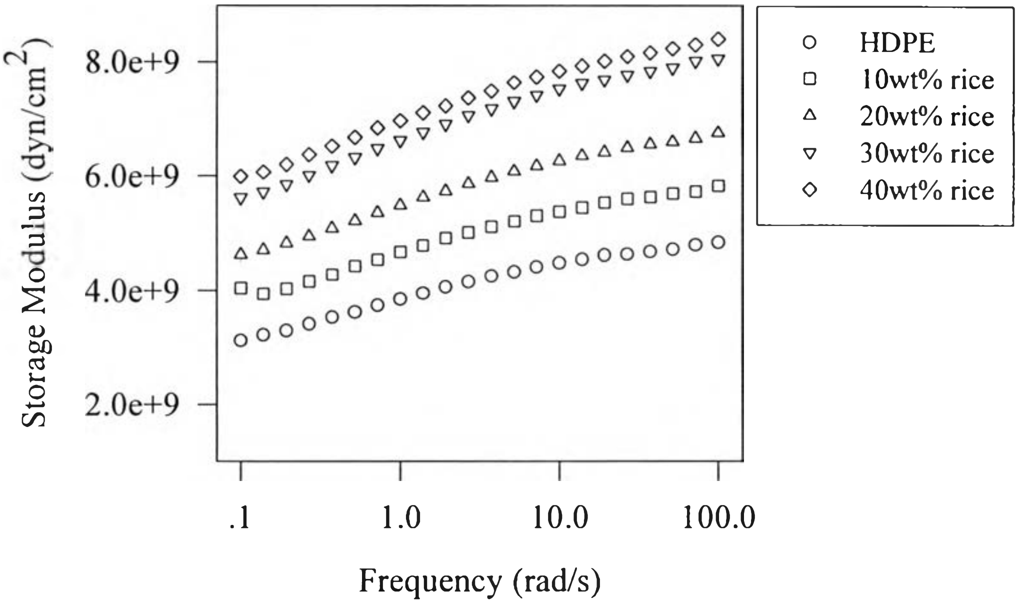


Figure 3.14 Effect of rice starch content on storage modulus of blends containing 0, 10, 20, 30, and 40 wt % of starch at 30°C.

The viscoelastic behavior of the rice starch-HDPE blends showed similar results as for the tapioca starch-HDPE blends, i.e. the storage modulus and loss modulus of the blends increased with increasing rice starch content as shown in figures 3.14 and 3.15, respectively. Similarly, the loss tangent of the blends reduced as the rice starch content increased as shown in figure 3.16.

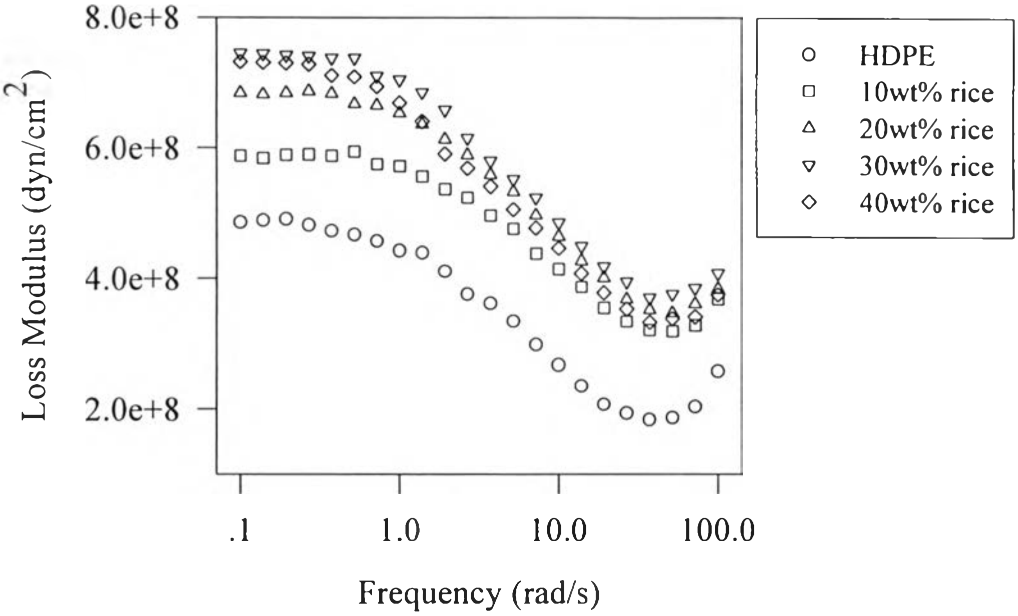


Figure 3.15 Effect of rice starch content on loss modulus of blends containing 0, 10, 20, 30, and 40 wt % of starch at 30°C.

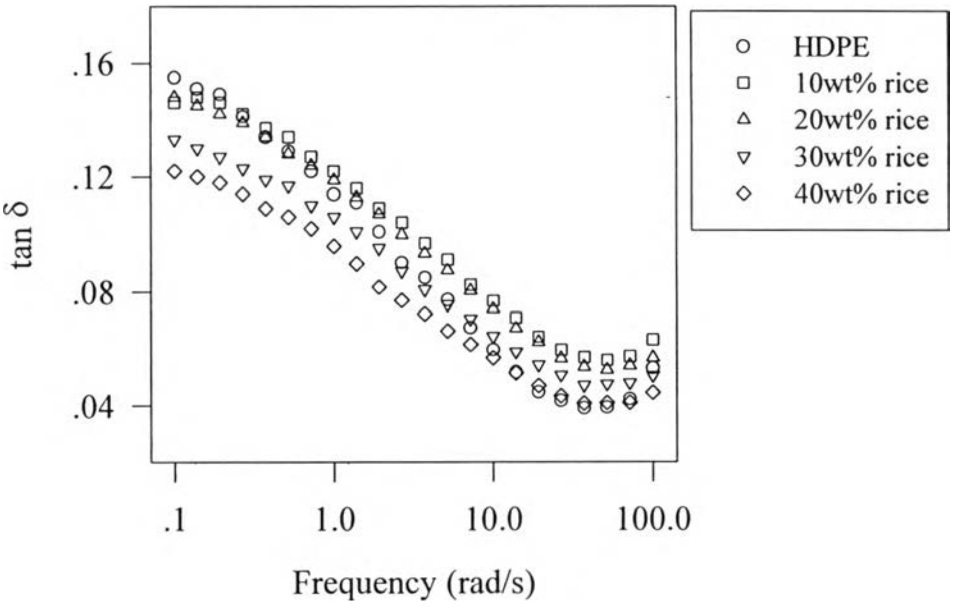
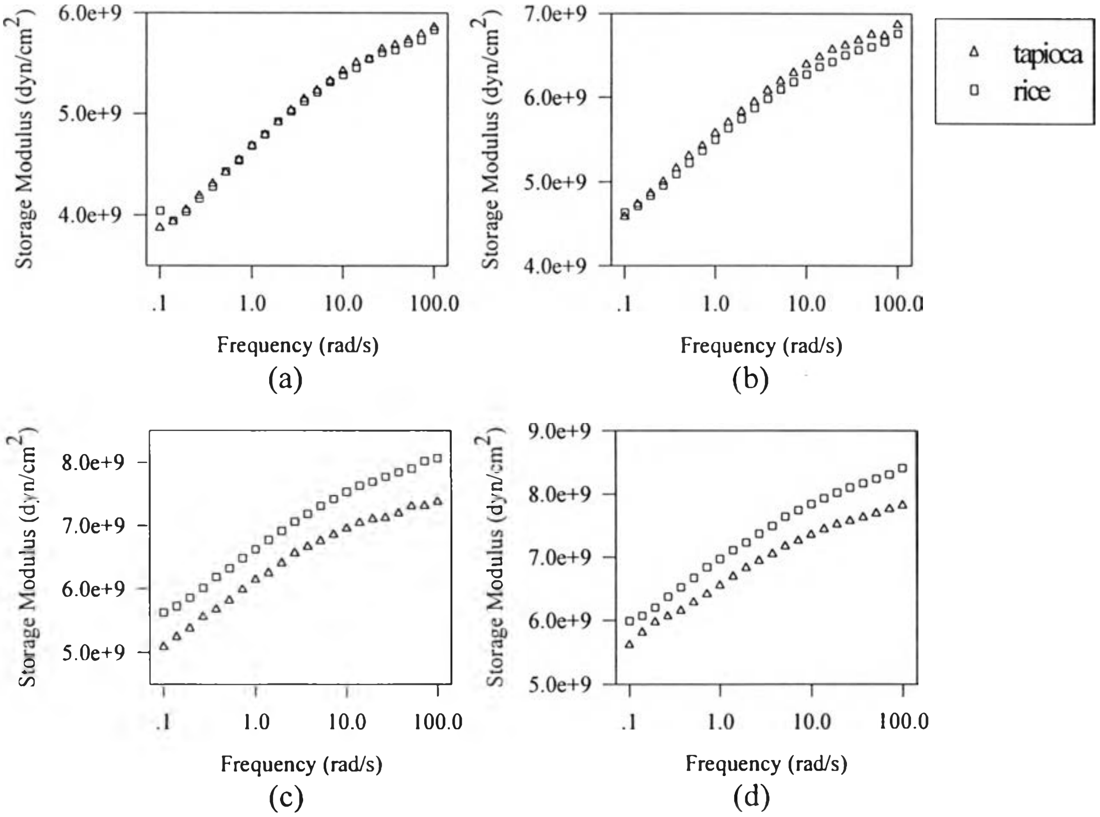


Figure 3.16 Effect of rice starch content on loss tangent of blends containing 0, 10, 20, 30, and 40 wt % of starch at 30°C.

3.1.3.2 Effect of Starch Type. By comparing the storage modulus of blends containing tapioca and rice starches as shown in figure 3.17, it was found that the storage modulus of both types of the blends were the same at 10 wt % of starch. But above 10 wt % starch content the rice starch-HDPE blends had higher values of storage modulus than the tapioca starch-HDPE blends. This may be due to the agglomeration effect of rice starch. Rice agglomerates lower the packing efficiency of particles and have higher ability to store deformatioal energy.



(a) (b)

(c) (d)

Figure 3.17 Effect of starch type on storage modulus of blends at 30°C: (a) 10 wt % of starch, (b) 20 wt % of starch, (c) 30 wt % of starch, and (d) 40 w t% of starch.

Figure 3.18 shows the storage modulus in the glasssy state (G_g) of the blends. Investigations on the material in the glassy state were not only carried out at low-frequency measurements below T_g, but also at high-frequency measurements above T_g. With increasing starch content, the blends had higher G_g. This was due to the higher rigidity of starch particles as compared to HDPE matrix. Comparing between the blends containing tapioca and rice starch, rice starch blends gave higher G_g than tapioca starch blends. Because the agglomarate particles of rice starch were stiffer than primary tapioca particles.

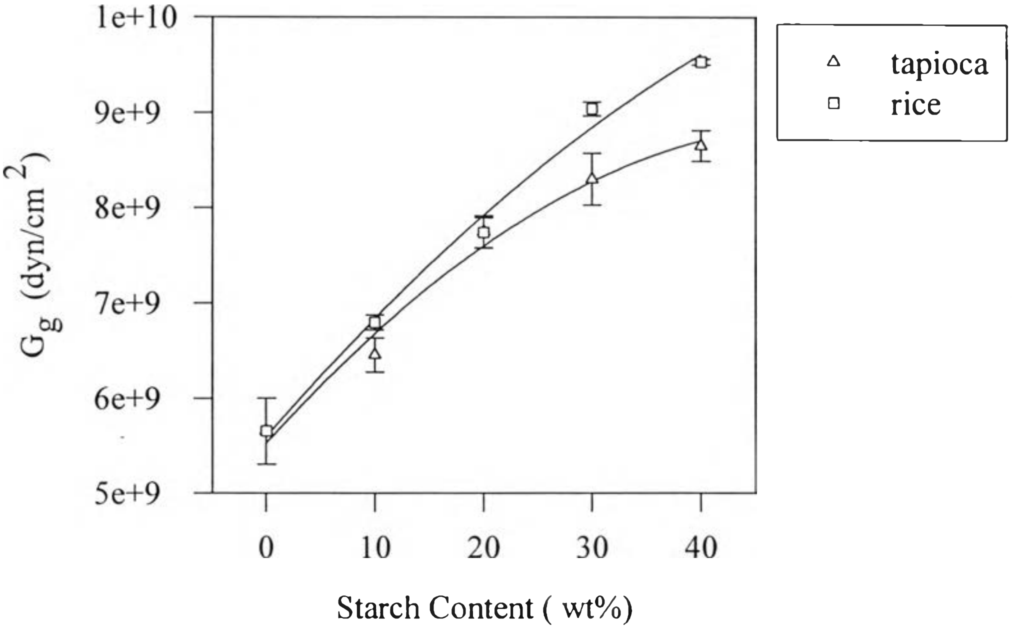


Figure 3.18 Effect of starch type on storage modulus in the glassy state of blends at 30°C.

Figure 3.19 shows the comparison of the loss modulus between tapioca starch-HDPE blends and rice starch-HDPE blends. The loss modulus of tapioca starch-HDPE blends were lower than that of rice starch-HDPE blends at equivalent starch contents. This can also be attributed to the agglomeration of rice starch particles. Agglomeration of starch particles remarkably disturbs the crystallization of HDPE. As the results, it is proposed that the crystallinity of

HDPE in rice starch-HDPE blends is more reduced. Less chains are tied by the crystallites. So they can move more easily resulting in higher loss modulus as compared to tapioca starch-HDPE blends.

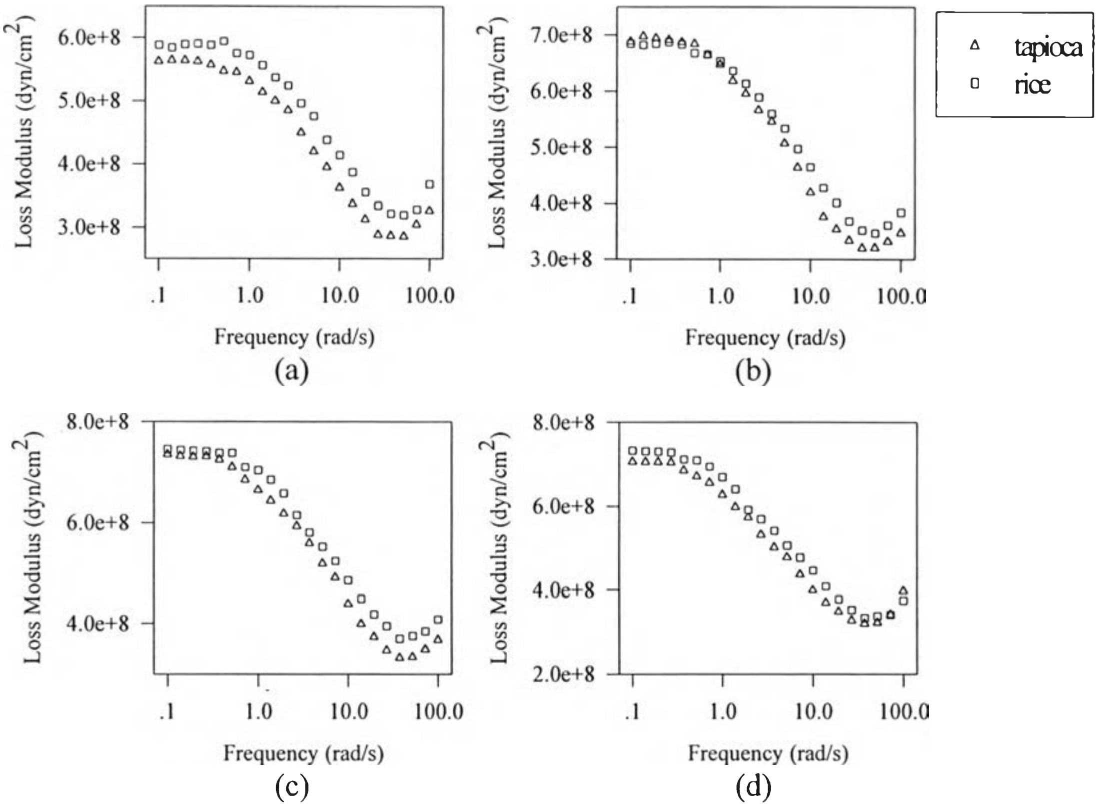


Figure 3.19 Effect of starch type on loss modulus of blends at 30°C: (a) 10 wt % of starch, (b) 20 wt % of starch, (c) 30 wt % of starch, and (d) 40 wt % of starch.

Figure 3.20 shows the effect of different tapioca and rice starch contents on the loss tangent of the blends. The difference in loss tangent between two types of starch was observed at 10 wt % of starch loading. At 20, 30, and 40 wt % of starch in the blends, both starches gave the close values of loss tangent. This was due to the low damping of both starch particles.

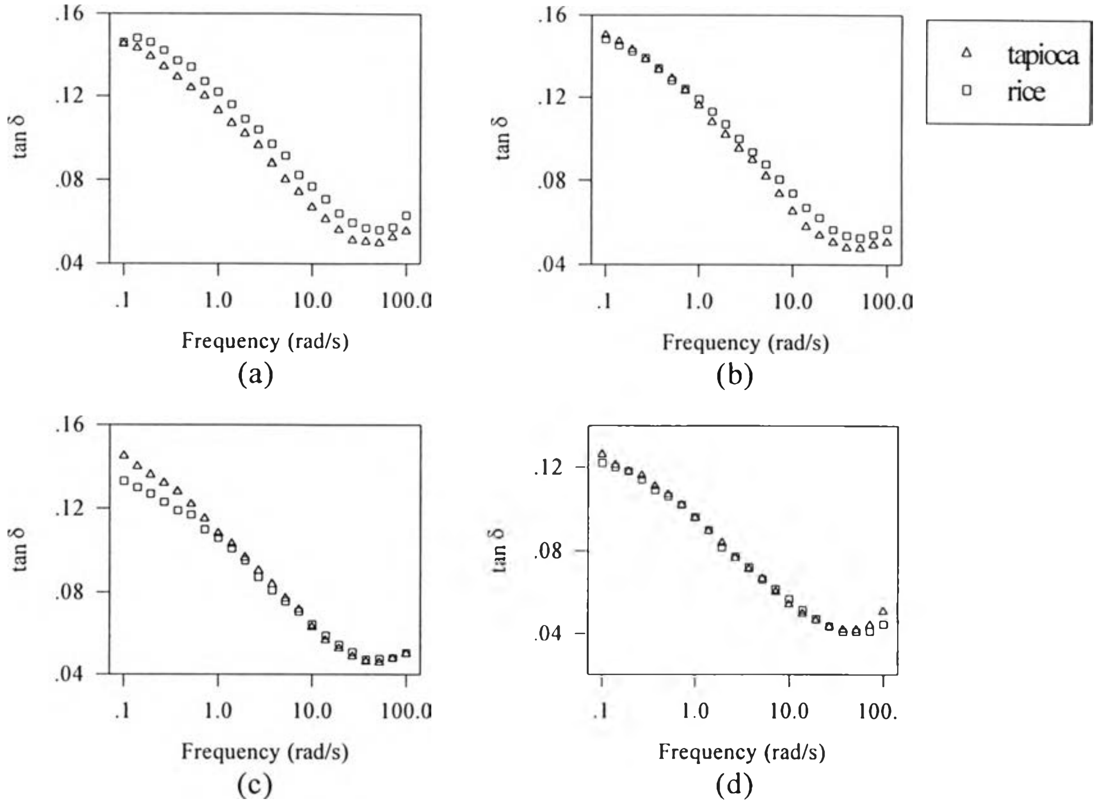


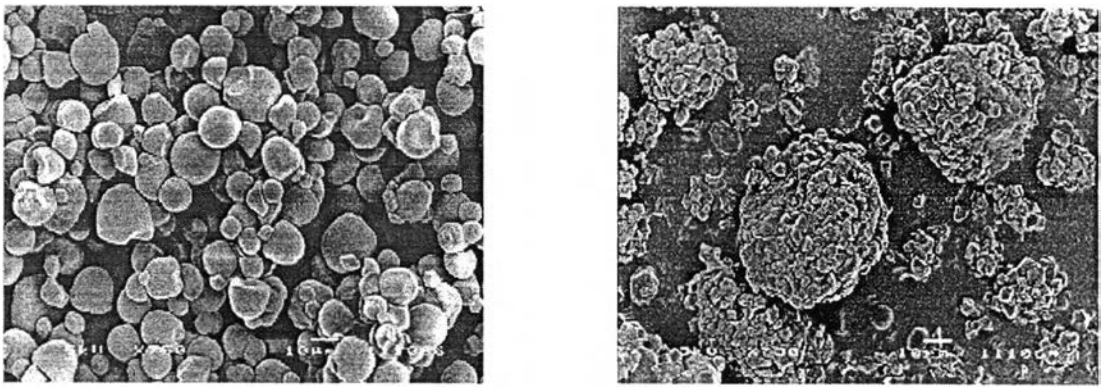
Figure 3.20 Effect of starch type on loss tangent of blends at 30^{o}C : (a) 10 wt % of starch, (b) 20 wt % of starch, (c) 30 wt % of starch, and (d) 40 wt % of starch.

3.2 Microstructure Characterization

Microstructure of the blends were observed from fractured surfaces of specimens. Micrographs can provide useful information about the blends.

3.2.1 Starch

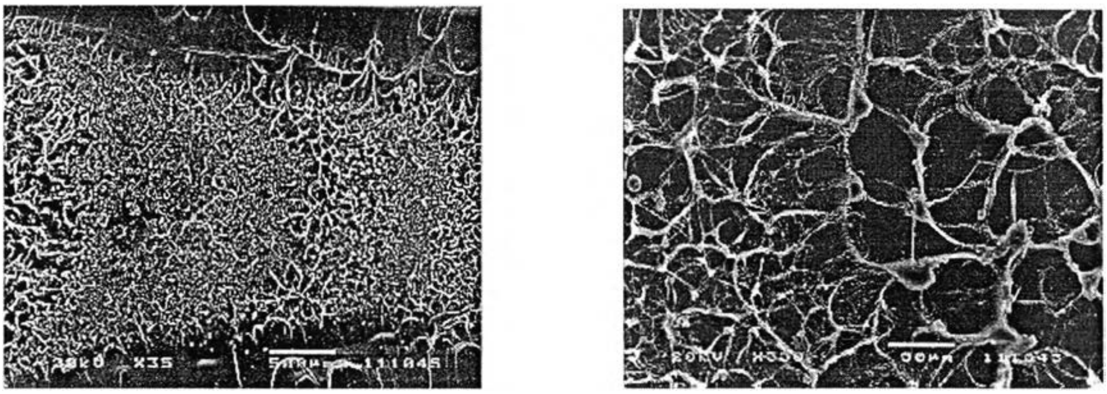
The morphology of tapioca and rice starches are shown in figure 3.21. The shape of tapioca starch particles was spherical with a diameter of about 10-15 μm. The rice starch particles were polygonal in shape, about 3-5 μm in size. Agglomeration of starch particles was observed only in rice starch. This was presumably due to the small size of the rice particles. This will result in a lot of surface energy which can lead to high particle-particle interactions.



(a) (b)

Figure 3.21 Scanning electron micrographs of starches : (a) tapioca starch, and (b) rice starch.

3.2.2 HDPE

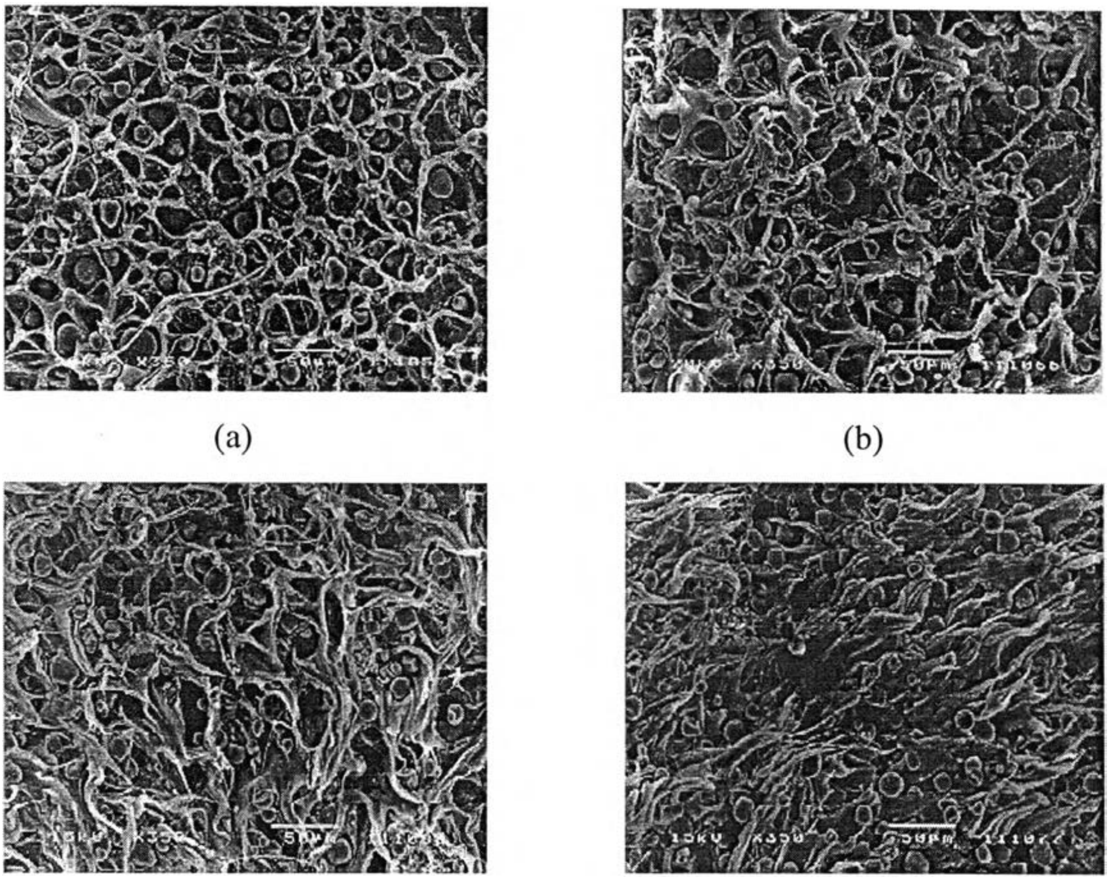


(a) (b)

Figure 3.22 Scanning electron micrographs of fractured surfaces of HDPE : (a) at 35X magnification, and (b) at 1000X magnification.

Micrographs of the fractured surfaces of unblended HDPE are presented in figure 3.22. They were shown to compare with the fractured surfaces of the blends.

3.2.3 Tapioca Starch-based HDPE Blends



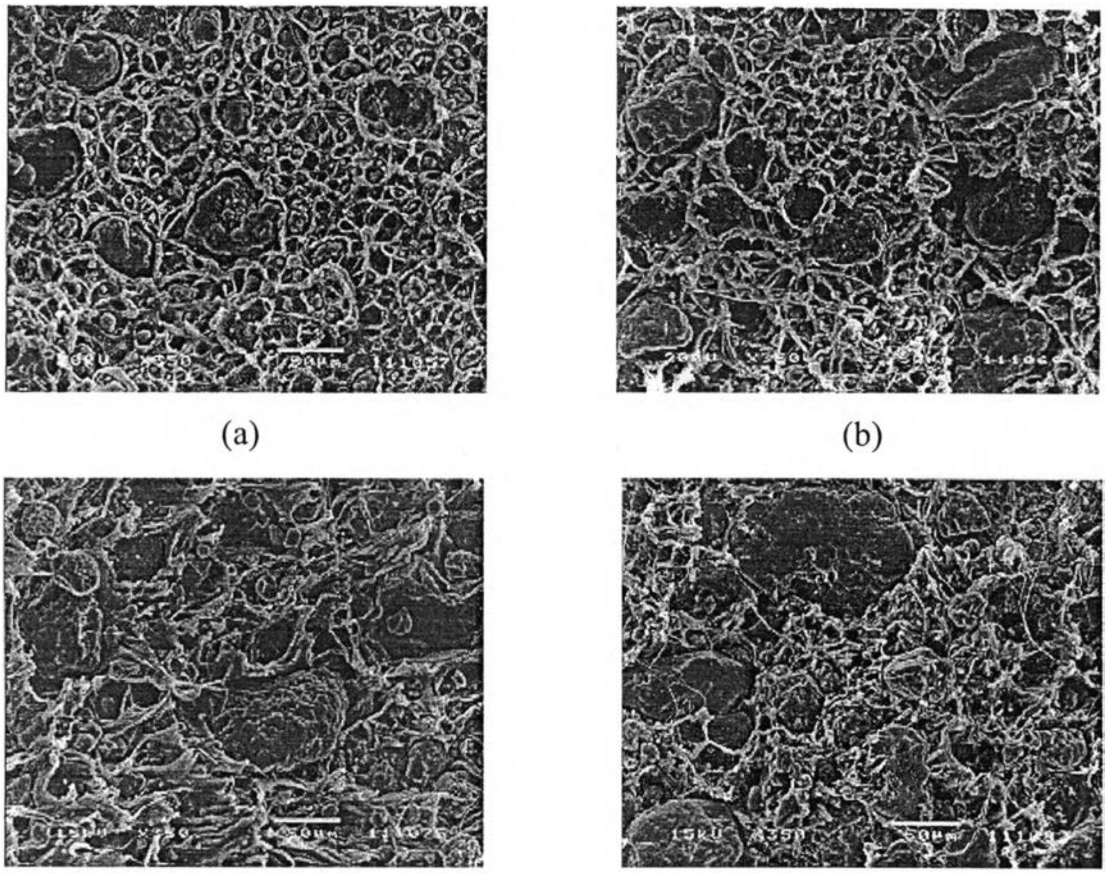
(a) (b)

(c) (d)

Figure 3.23 Scanning electron micrographs of fractured surfaces of tapioca starch-based HDPE blends : (a) 10 wt % of starch, (b) 20 wt % of starch, (c) 30 wt % of starch, and (d) 40 wt % of starch.

Micrographs of fractured surfaces of tapioca starch-HDPE blends are shown in figure 3.23. It was found that tapioca starch particles were simply trapped inside the HDPE matrix ; there was no adhesion between the starch particles and the HDPE matrix. The agglomeration of tapioca starch particles could not be observed. When starch contents were increased from 10 to 40 wt %, the tapioca starch particles were still well distributed in the HDPE matrix.

3.2.4 Rice Starch-based HDPE Blends



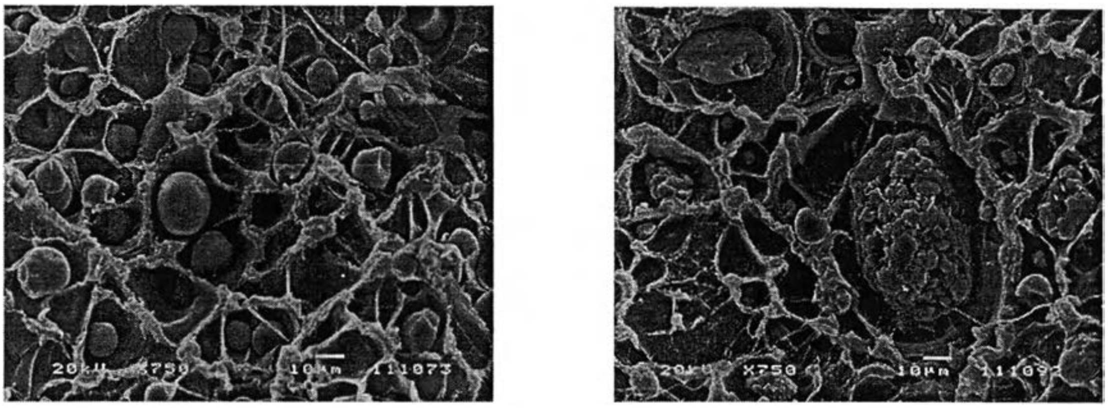
(a) (b)

(c) (d)

Figure 3.24 Scanning Electron micrographs of fractured surfaces of rice starch-based HDPE blends : (a) 10 wt % of starch, (b) 20 wt % of starch, (c) 30 wt % of starch, and (d) 40 wt % of starch.

Figure 3.24 presents the micrographs of fractured surfaces of rice starch-HDPE blends. It showed the poor adhesion between rice starch particles and HDPE matrix. Agglomeration of rice starch particles were observed at every starch content. And the agglomerate size increased with increasing starch content.

3.2.5 Comparison Between Tapioca and Rice Starch-based HDPE Blends



(a) (b)

Figure 3.25 Scanning Electron micrographs of fractured surfaces of blends containing 20 wt % of starch : (a) tapioca starch-based HDPE blend, and (b) rice starch-based HDPE blend.

Figure 3.25 compares the fractured surfaces of tapioca starch-HDPE blend and rice starch-HDPE blends. Both types of starch showed poor adhesion between starch particles and HDPE matrix. In addition, rice starch particles showed agglomeration of starch particles while tapioca starch particles were well distributed in HDPE matrix. The agglomerates of rice starch were larger than primary rice starch and also tapioca starch.