CHAPTER IV
RESULTS AND DISCUSSION

4. 1 Thermogravimetric Analysis of Fillers

Thermogravimetric analysis (TGA) was used to investigate the degradation temperature of the fillers. The weight of the tapioca starch, rice husk and burning husk as a function of temperature are shown in Figure 4.1 below.

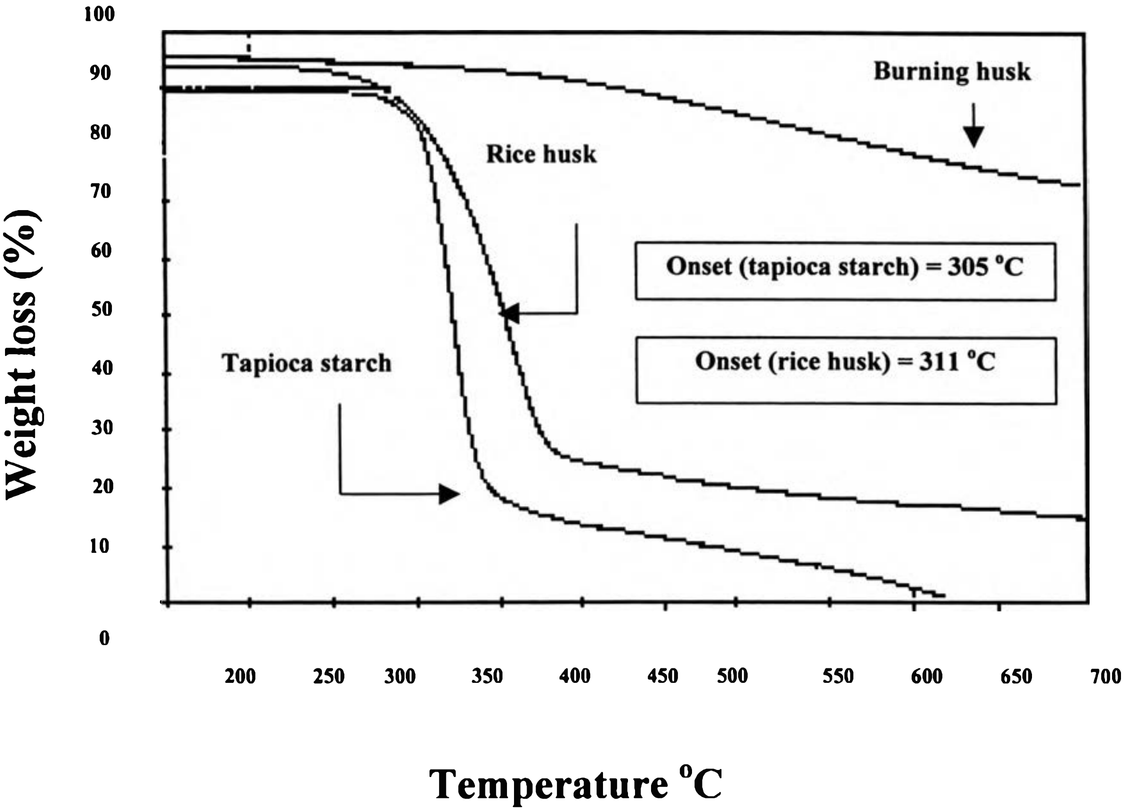


Figure 4.1 TGA thermogram of tapioca starch, rice husk and burning husk.

The weight loss of each filler shows the degradation temperature. By comparing tapioca starch to rice husk, it was found that the degradation temperature of rice husk (T=311 °C) was very close to that of tapioca starch (T=305 °C).

However burning husk did not exhibited degradable property. Therefore, it was possible to use the same processing condition for the blends with the three different types of filler (T=170 °C).

4.2 Filler Density Measurement

Because the mixing process of the polymer blends required the same amount of both fillers and HDPE to control the composition during mixing, the densities of fillers were investigated to find out the optimum weight of fillers for each composition of the blends. The pycnometric technique was applied for the measurement. The densities of the fillers are summarized in Table 4.1.

Table 4.1 Density of fillers.

Type of fillers	Solvent	Density (g/cm^3)
Burning husk	Ethylene glycol	1.83
Rice husk	Ethylene glycol	2.20
Tapioca starch	Ethylene glycol	1.72

4.3 Microstructure Characterization

The mechanical properties of immiscible blends are based mainly on the physical property of the fillers, especially their size and shape. Thus, SEM was applied to study the microscopic structure of fillers and the related microstructure of the blends. The images of fillers are illustrated in Figure 4.2, 4.3 and 4.4.

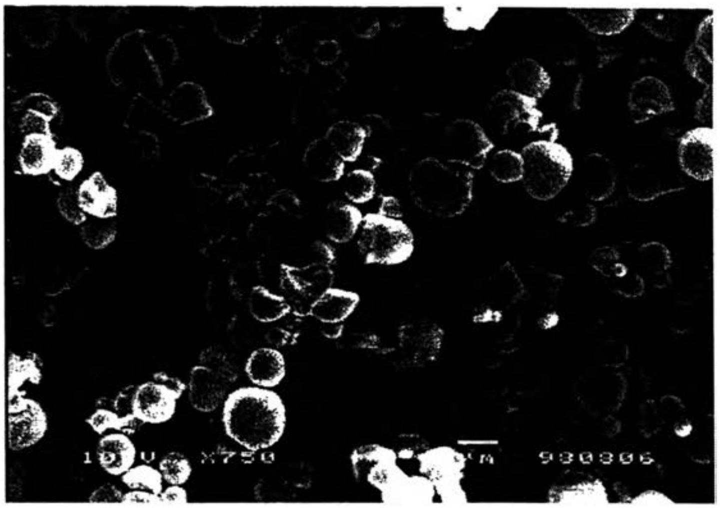


Figure 4.2 SEM micrograph at 750 magnification of tapioca starch particles.

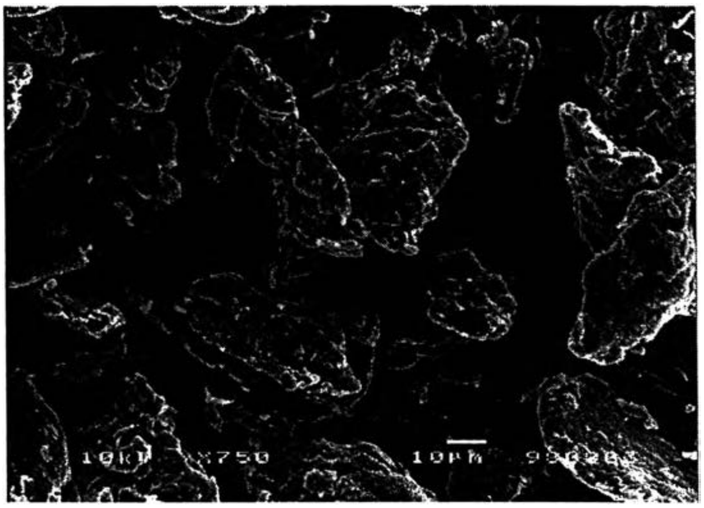


Figure 4.3 SEM micrograph at 750 magnification of rice husk particles.

Figure 4.4 SEM micrograph at 750 magnification of burning husk particles.

From Figure 4.2, tapioca starch is roughly spherical in shape with the size around 8-17 μm. While both of rice husk and burning husk (Figure 4.3 and 4.4, respectively) show as flake particles. The data obtained from scanning electron microscope (SEM) are summarized in Table 4.1.

Table 4.1 Physical properties of fillers.

Fillers	Particle size (micron)	Particle shape
Tapioca starch	8-17	Sphere
Rice husk	38-53, 53-180, 180-425	Flake
Burning husk	38-53, 53-180, 180-425	Flake

The fracture specimens of tapioca starch-filled, rice husk-filled, and burning husk-filled HDPE blends obtained from impact testing procedure were investigated for the filler distribution as well as dispersion in the polymer matrix by SEM.

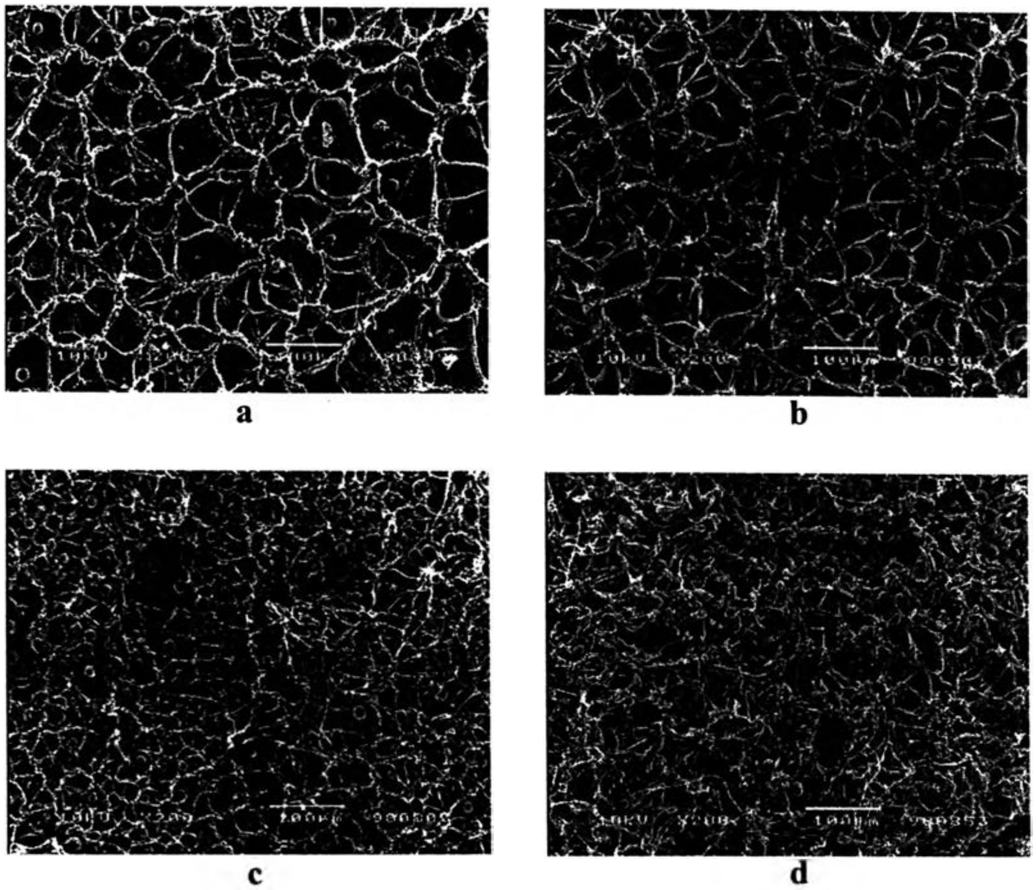


Figure 4.5 SEM micrographs of tapioca starch-filled HDPE at

a) 1% filler content   b) 5% filler content

c) 10% filler content   d) 30% filler content.

Micrographs of fracture surfaces of tapioca starch-filled HDPE blend are presented in Figure 4.5. Tapioca starch particles do not form agglomeration and disperse well in HDPE matrix. At 5% filler content, the fillers are simply trapped inside the HDPE matrix. While at 30% filler content, the high amount of the particles thoroughly penetrates the matrix and induces obstacles to the HDPE packing. In addition, there appears to be little or no adhesion between tapioca starch particles and HDPE.

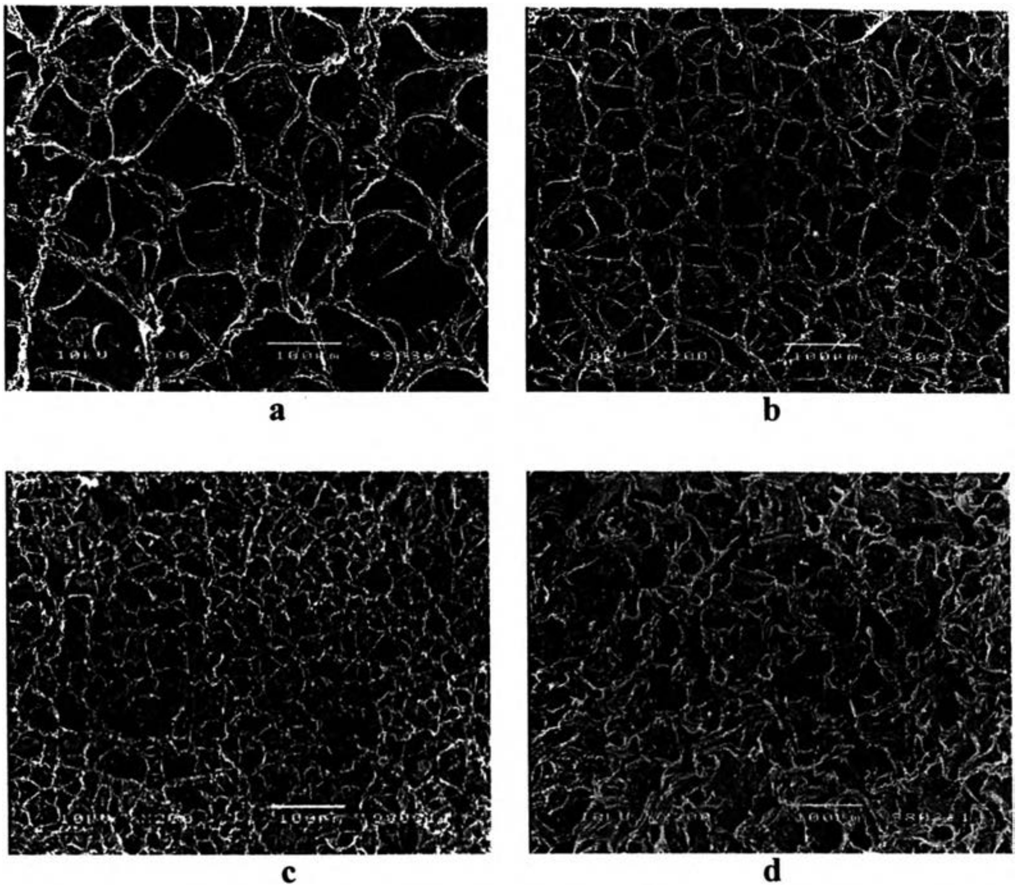


Figure 4.6 SEM micrographs of rice husk-filled HDPE at

a) 1% filler content b) 5% filler content

c) 10% filler content d) 30% filler content.

As shown in Figure 4.6, similar to the blend containing tapioca starch, the agglomeration of rice husk particles are not found from the fracture surfaces of rice husk-filled HDPE blend. The addition of high filler content induces the obstruction of packing of HDPE matrix. Furthermore, SEM micrographs reveal that there is little or no adhesion between rice husk particles and polymer matrix, which is similar to that of tapioca starch-filled HDPE blend.

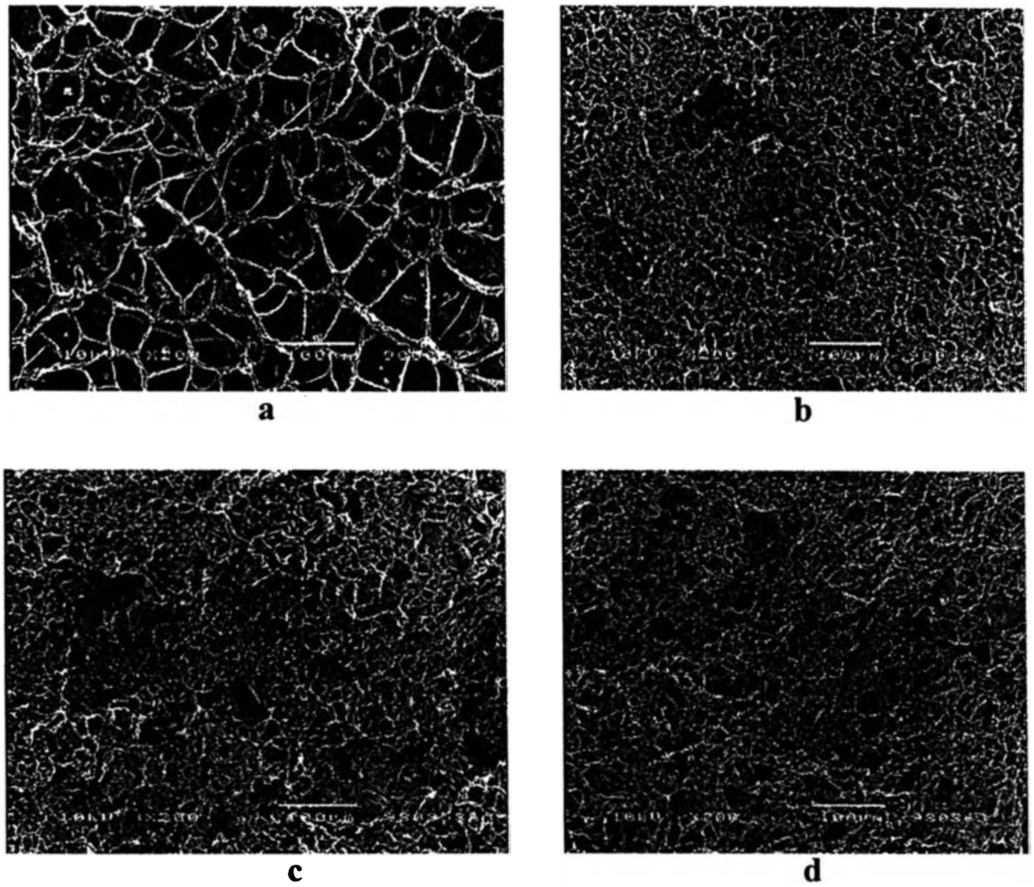


Figure 4.7 SEM micrographs of burning husk-filled HDPE at

a) 1% filler content b) 5% filler content

c) 10% filler content d) 30% filler content.

Burning husk-filled HDPE blend (Figure 4.7) shows the same trends as tapioca starch-filled and rice husk-filled HDPE blends. At 30% filler content, the packing of polymer matrix is interrupted by filler particles same as those of the two previous blends. Again, little or no adhesion between burning husk particles and HDPE matrix is observed by SEM. However burning husk-filled HDPE blend shows the finer texture of fracture surface than those of the two previous blends. This may be due to the hydrophobicity of burning husk is close to that of HDPE matrix.

4.4 Mechanical Properties Testing

It is known that the nature of fillers will effect on the mechanical properties of polymer blends. Therefore, the effect of filler content and size of fillers on the mechanical properties, in terms of tensile properties, flexural properties and impact property, of the polymer blends are studied in this work.

4.4.1 Effect of Filler Content

In order to investigate the effect of filler content, the particle size of rice husk and burning husk was fixed to be 53 μm, while tapioca starch particle was 17 μm. Percent compositions of the fillers were varied and the mechanical properties of the polymer blends were studied.

4.4.1.1 Tensile Properties

Tensile strength and tensile modulus of the polymer blends were studied as a function of filler content. The tensile strengths at yield are plotted versus filler content and the result is shown in Figure 4.8.

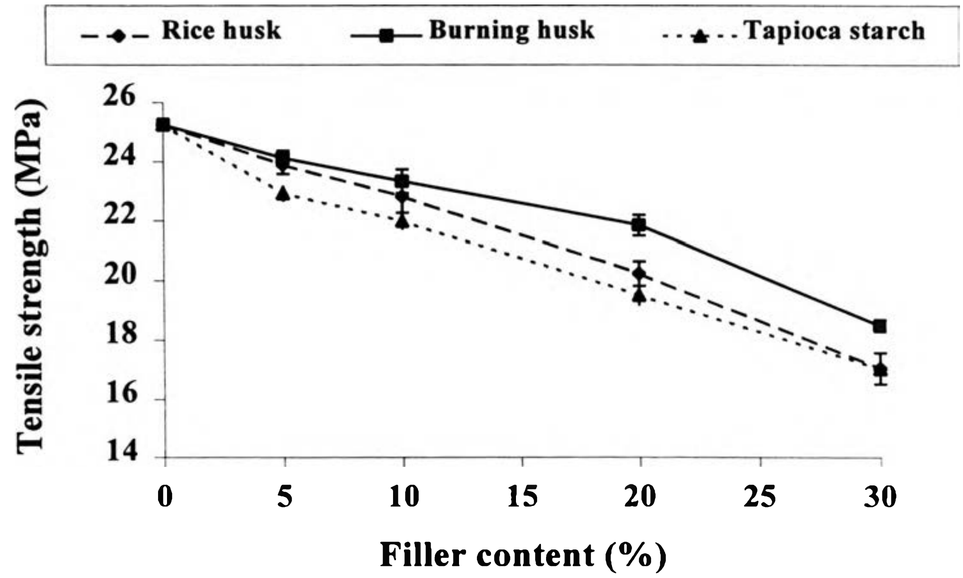


Figure 4.8 Tensile strength at yield of tapioca starch-filled, rice husk-filled and burning husk-filled HDPE blends.

Continuous dropping of tensile strength at yield are observed when the filler content increases. The average tensile strength for the unfilled blends are 25.24 MPa. Decreasing of tensile strength is founded in all cases of the polymer blends. Due to the polymer blends in this work are immiscible blends without a compatibilizer to enhance miscibility of the polymer matrix. Thus, the tensile strength of the blend is mainly depended on the physical properties of each filler. Unfortunately, all of fillers have no functional group capable to react with HDPE matrix. Hence when a stress was applied, the weakest links, consisting of smaller matrix zones, bear the strain and break most readily. The effect of filler content on tensile modulus of the blends is shown in Figure 4.9.

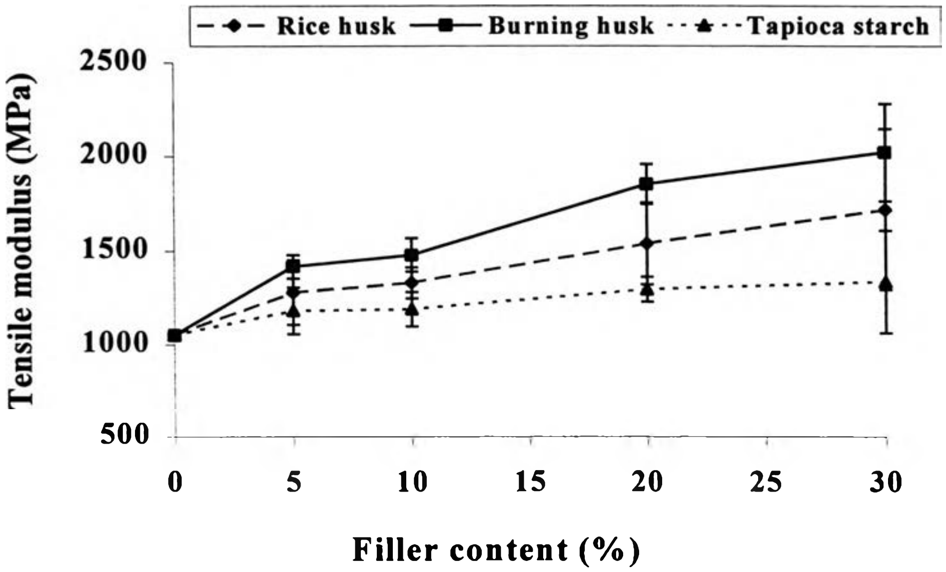


Figure 4.9 Tensile modulus of tapioca starch-filled, rice husk-filled and burning husk-filled HDPE blends.

As shown in Figure 4.9, the tensile modulus of each polymer blend increases as the filler content increases. Addition of the fillers from 0 to 30% results in the increasing of the modulus of tapioca starch-filled HDPE blend from 1052 MPa to 1333 MPa. While the tensile modulus of rice husk-filled HDPE and burning husk-filled HDPE blends at 30% filler content are 1717 and 2021 MPa, respectively. In general, solid fillers will always improve the modulus of composites (Katz, 1974). Especially for blends containing big particles or high filler content, the polymer matrix is restricted in its ability to stretch between packed particles or around filler particles (Katz, 1974). So this causes the increasing in tensile modulus and it is a reason of why tensile modulus values of the blends containing rice husk and burning husk are higher than tapioca starch-filled HDPE blend.

4.4.1.2 Flexural Properties

Flexural properties were investigated as functions of filler content and also types of fillers. Flexural strength was plotted versus filler content for the three types of fillers.

Figure 4.10 illustrates the relation between flexural strength and filler content. For the blends containing tapioca starch and rice husk showed the same trend of slightly decreasing in flexural strength (as compared to pure HDPE) with increasing filler content.

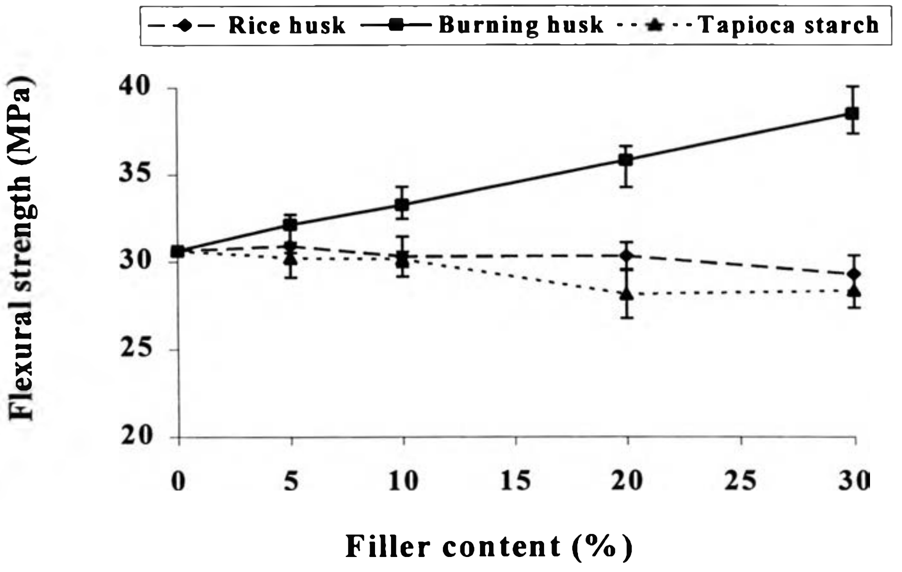
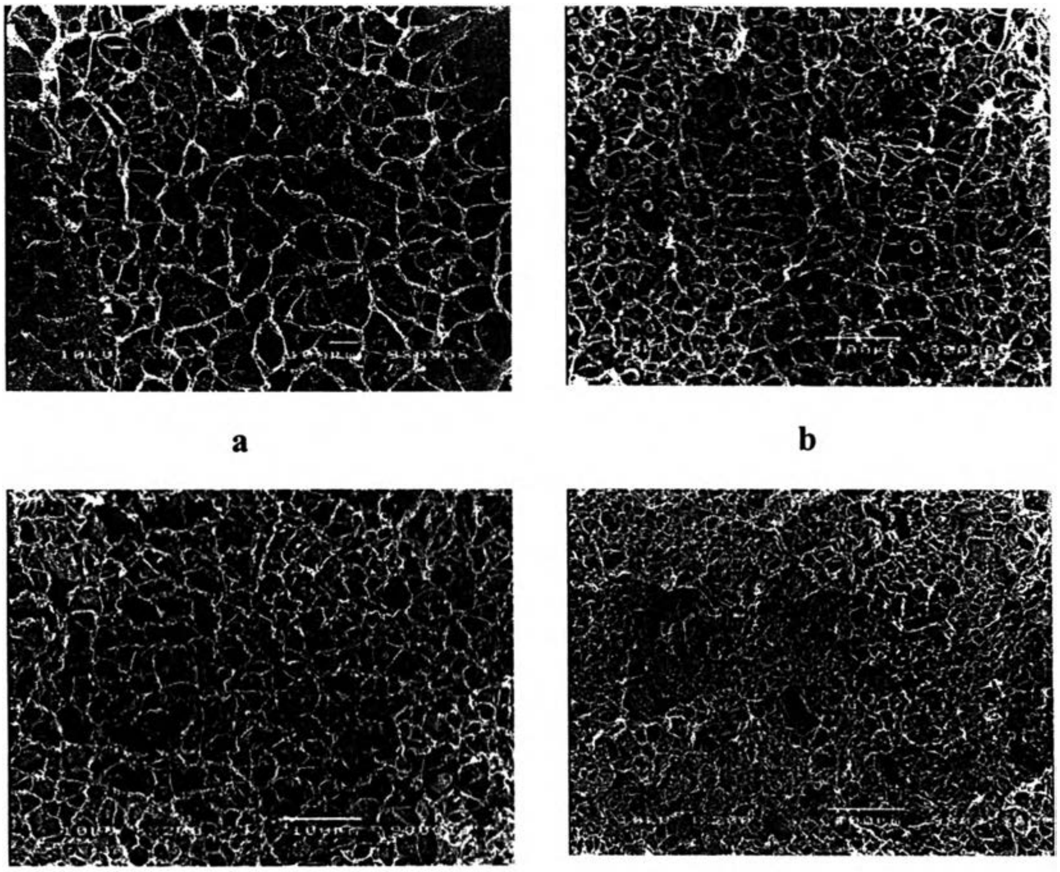


Figure 4.10 Flexural strength of tapioca starch-filled, rice husk-filled and burning husk-filled HDPE blends.

The flexural strength of pure HDPE is 30.62 MPa. While the flexural strength of tapioca starch-filled and rice husk-filled HDPE blends at 30% filler content are 29.31 and 28.46, MPa respectively. The decreasing of flexural strength can be explained in term of poor adhesion between filler particles and polymer matrix. Similar to tensile strength, the failures occur at the fillers/HDPE interface and results in separation of the filler particles from the HDPE matrix.

In contrast, the flexural strength of burning husk-filled HDPE blend increase continuously with increasing filler content (the flexural strength of pure HDPE and burning husk-filled HDPE blend are 30.62 MPa and 38.52 MPa, respectively.). Since burning husk mostly consists of carbon remaining after burning of rice husk at high temperature. So burning husk should have higher hydrophobicity than rice husk or tapioca starch which have hydroxyl groups in their molecules. As a result, burning husk is more compatible to HDPE than rice husk and tapioca starch and burning husk-filled HDPE blend showed the increasing in flexural strength as filler content increased. However, burning husk has no functional group to react with HDPE to form a miscible blend.

In the case of tapioca starch and rice husk, the occurrence of phase separation between filler particles and HDPE matrix can be observed from SEM micrographs as shown in Figure 4.11.



a

b

c

d

Figure 4.11 Fracture surface at 10% filler content of the blends containing a) Pure HDPE b) Tapioca starch c) Rice husk d) Burning husk.

The Pore sizes of fillers in polymer blends was studied by SEM using Semafore program. Comparing the diameters of pore size in HDPE of the blends containing burning husk, rice husk and tapioca starch are mentioned. The average pore size that occurred by burning husk exhibited smaller in diameter than those of rice husk and burning husk. The average diameters, at 10% filler content and 53 micron of particle size, of tapioca starch, rice husk and burning husk are 39, 51 and 23 μm, respectively.

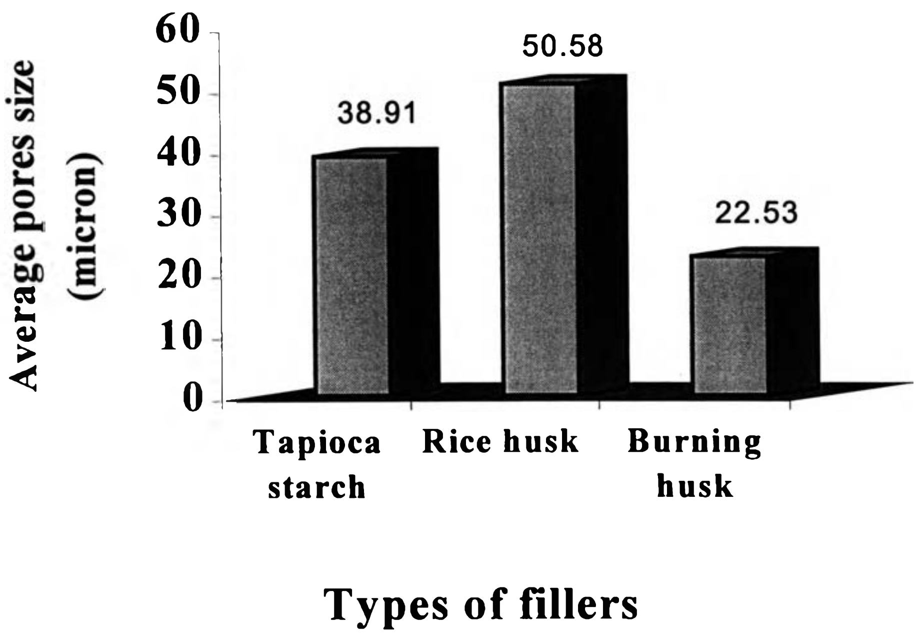


Figure 4.12. Average pore size diameters within the polymer blended with tapioca starch, rice husk and burning husk in the polymer blends.

For flexural modulus, the results from the test can, therefore, give us a good indication of the rigidity or stiffness of the polymer blends. Flexural modulus of the polymer blends are plotted as a function of filler content.

Figure 4.13 illustrates the effect of filler content on three types of polymer blends.

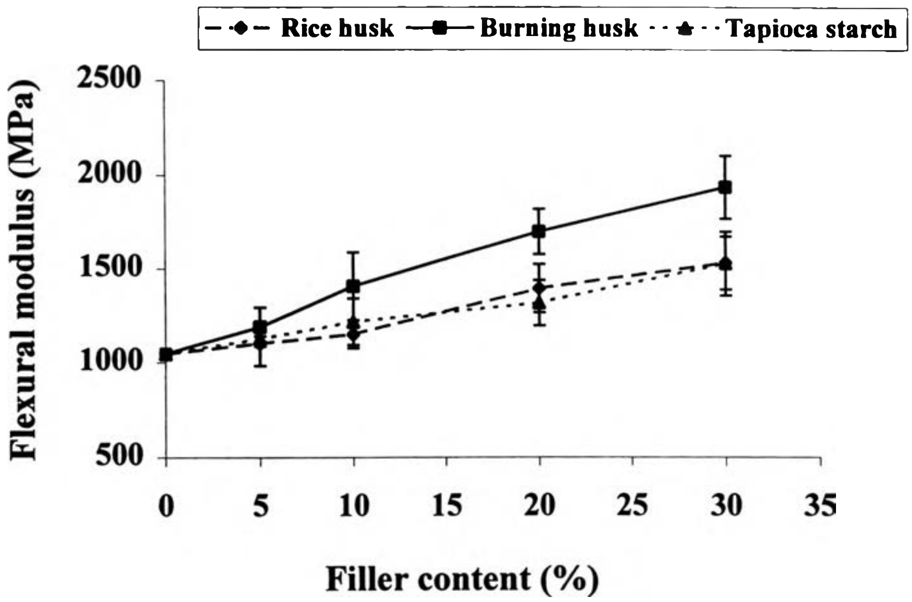


Figure 4.13 Flexural modulus of tapioca starch-filled, rice husk-filled and burning husk-filled HDPE blends.

Similar to the tensile modulus, the flexural modulus of the polymer blends increases as filler content increases. Flexural modulus of burning husk-filled HDPE blend is higher than those of the other two polymer blends. The flexural modulus of burning husk-filled HDPE blend at 30% filler content is 1933 MPa while flexural modulus of tapioca starch-filled and rice husk-filled HDPE blends with the same filler content are 1525 and 1529 MPa, respectively. These results can be explained by stiffening effect (Katz, 1974).

Tapioca starch particle, that is smaller in size than burning husk, can move more freely within the matrix, consequently, the matrix can stretch more easily around them. Therefore tapioca starch-filled HDPE blend shows lower flexural modulus than burning husk-filled HDPE blend.

4.4.1.3 Impact Property

The notched specimens of three types of polymer blends were tested for their impact strength. By varying the amount of fillers, two important regions are observed from the result as shown in Figure 4.14. First region is from 0 to 5% of filler content while the second region is from 10% to 30% of filler content. At the first region, all types of polymer blends show the similar trend of decreasing in impact strength as filler content increases.

The second region shows an increasing of impact strength as the filler content increases in the case of tapioca starch-filled HDPE blend. However impact strength of both rice husk-filled HDPE and burning husk-filled HDPE blends decreases while filler content increases.

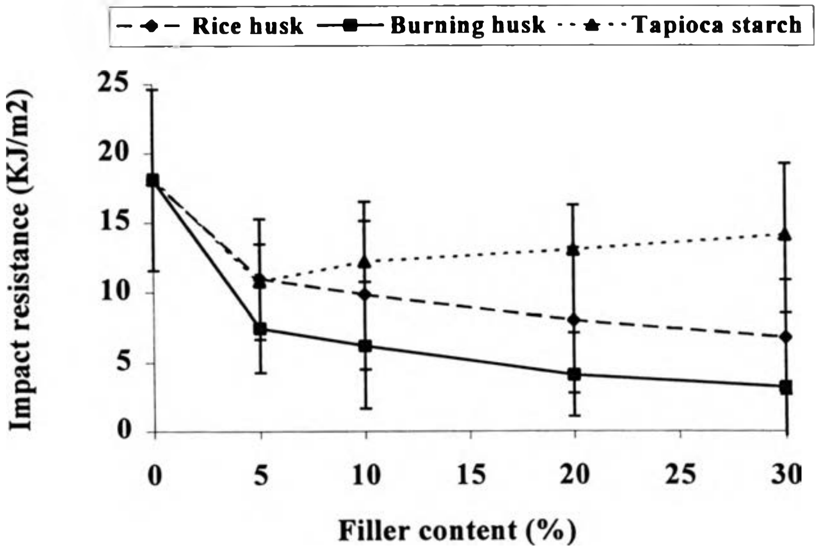


Figure 4.14 Impact strength of tapioca starch-filled, rice husk-filled and burning husk-filled HDPE blends.

The increasing in impact resistance of tapioca starch-filled HDPE blend can be explained by crazing phenomena. Crazes act as load bearing entities that could dissipate energy and thus toughen the blend. At low percent filler content, rigid tapioca starch particles affect the blend to give lower impact strength than pure HDPE. At low starch content, there is a little crazing along the crack propagation path so that it results in decreasing of impact strength of the polymer blend. In contrast, for high filler content, the crack propagation may pass through many particles. The more energy dissipates by the craze, the more improvement in impact strength will be observed.

For the blends containing rice husk and burning husk, they follow the trend of decreasing in impact property with increasing filler content. Especially for burning husk, which is a rigid and brittle material, when it was suffered from impact load, the crack propagation would be easily occurred leading to a decrease in impact strength.

4.4.2 Effect of Particle Size

The size of fillers played an important role in improving the mechanical properties of polymer blends (Maldas *et al.*, 1988). In order to evaluate the effect of particle sizes on the mechanical properties, three different sizes of each filler obtained by passing through three different sizes of sieves, which are 53, 180 and 425μm, were studied.

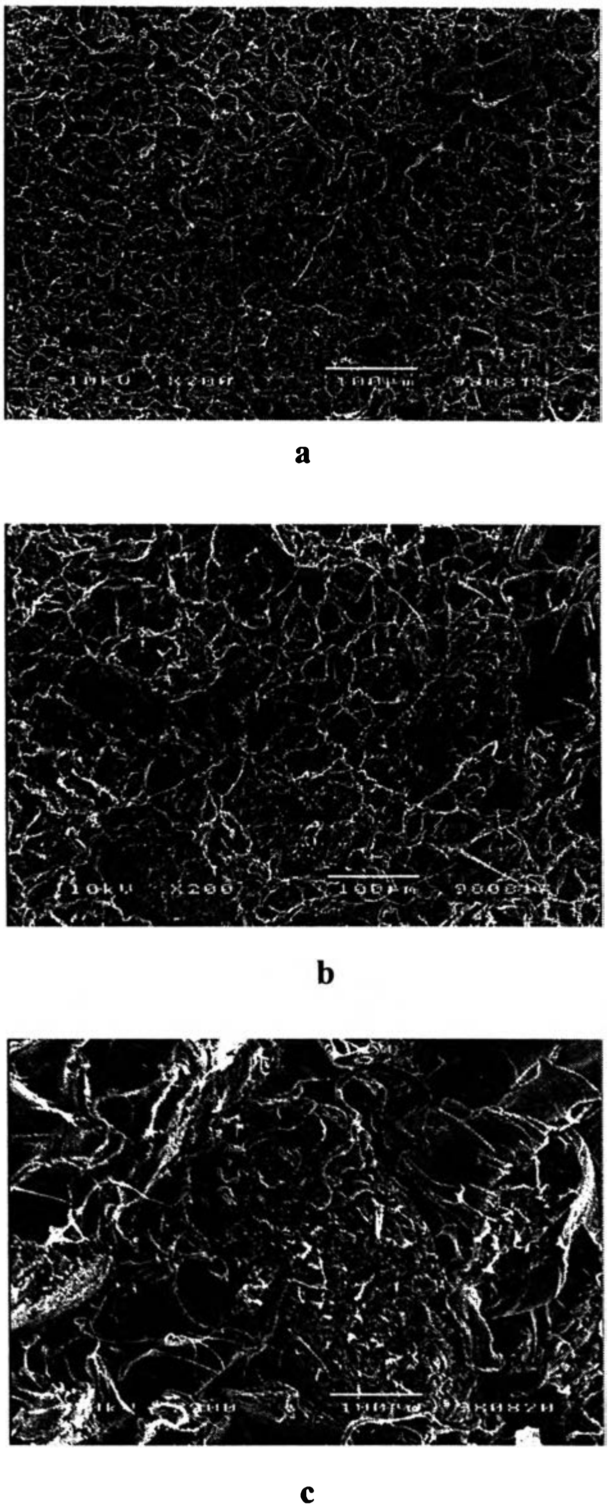


Figure 4.15 SEM micrographs of the polymer blends containing different sizes of rice husk at 10% filler content: a) 53 μm b) 180 μm c) 425 μm.

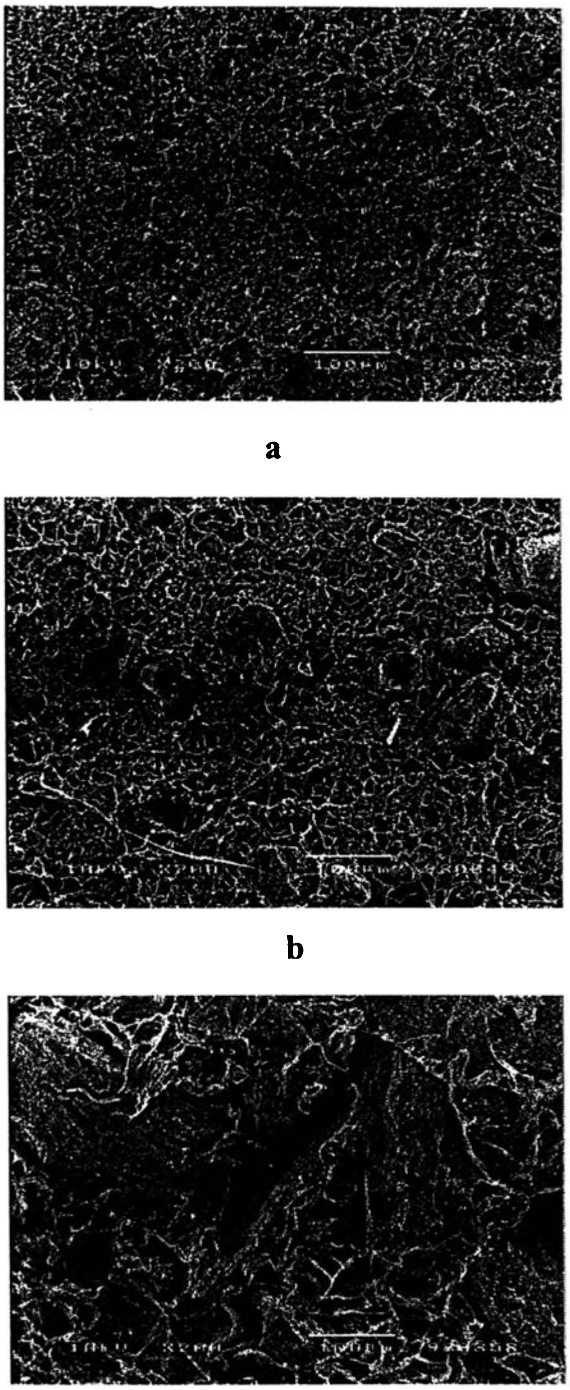


Figure 4.16 SEM micrographs of the polymer blends containing different sizes of burning husk at 10% filler content: a) 53 μm b) 180 μm c) 425 μm.

4.4.2.1 Tensile Property

The effect of particle sizes of rice husk and burning husk on tensile strength at yield is shown in Figure 4.17.

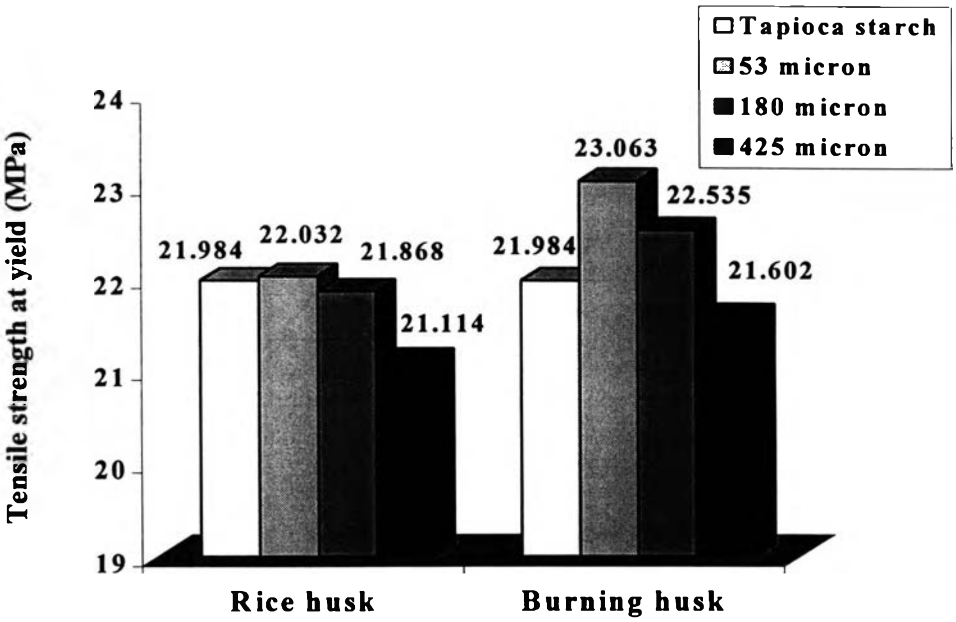


Figure 4.17 Effect of particle sizes on tensile strength of rice husk-filled and burning husk-filled HDPE blends with 10% of filler content as compared to tapioca starch-filled HDPE blend.

The particle size of 53 micron gives slightly higher tensile strength value than that of 180 and 425 μm for both rice husk-filled HDPE and burning husk-filled HDPE blends. The tensile strength of blends containing rice husk of which 53, 180 and 425 μm are 22.94, 22.81 and 22.76 MPa, respectively. While the tensile strength of the blends containing burning husk of which 53, 180 and 425 μm are 25.43, 24.17 and 23.33 MPa, respectively.

4.4.2.2 Flexural Property

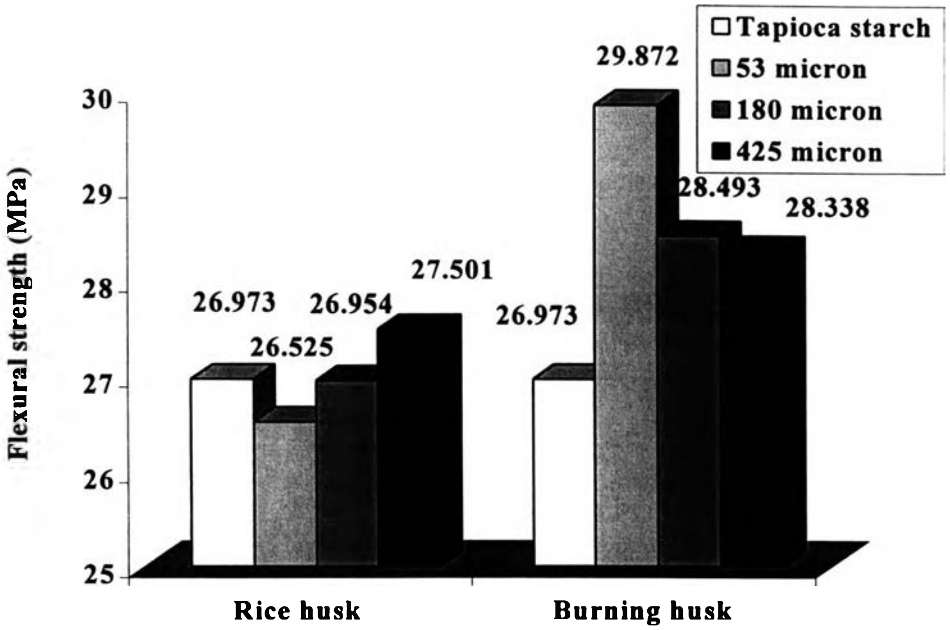


Figure 4.18 Effect of particle sizes on flexural strength of rice husk-filled and burning husk-filled HDPE blends with 10% of filler content as compared to tapioca starch-filled HDPE blend.

The effect of particle sizes on flexural strength of the polymer blends containing 10% filler content is shown in Figure 4.18. Rice husk-filled and burning husk-filled HDPE blends with the particle size of 53 μm have higher flexural strength than those of 180 and 425 μm.

The effect of particle sizes on the decreasing in tensile and flexural properties can be explained that fillers with small particles are more compatible with polymer matrix than the big ones. In other words, smaller particle provides a greater interaction with the polymer matrix. The smaller size of filler offers a larger surface area in the blends than the bigger ones at the same weight fraction (Maldas *et al,* 1988).

4.4.2.3 Impact Property

Impact strength of rice husk-filled and burning husk-filled HDPE blends at 10% filler content as functions of filler sizes and filler content are shown in Figures 4.19 and 4.20, respectively.

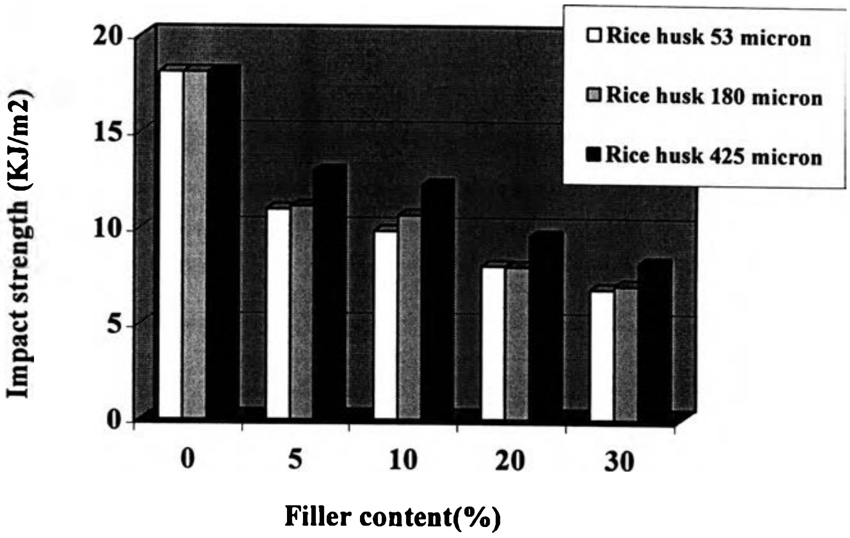


Figure 4.19 Effect of filler content and filler sizes on impact strength of rice husk-filled HDPE blend.

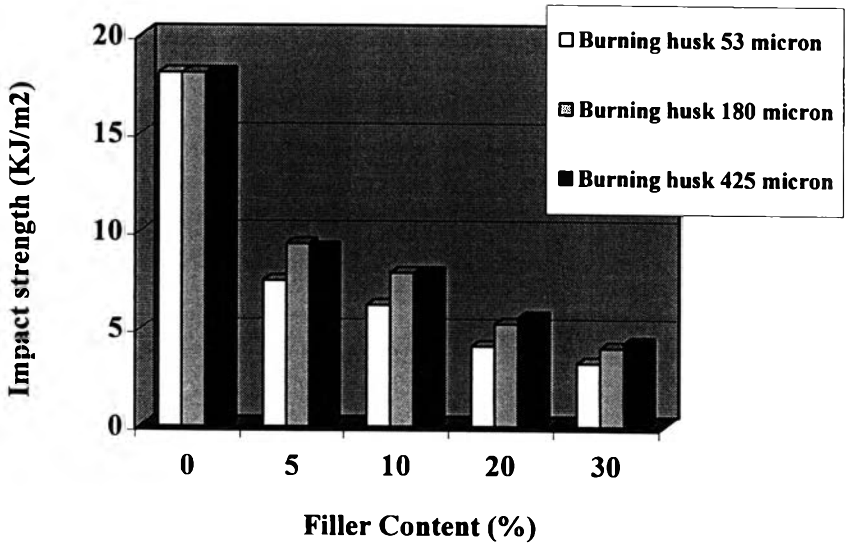


Figure 4.20 Effect of filler content and filler sizes on impact strength of burning husk-filled HDPE blend.

Unlike tensile and flexural properties at a fixed filler content, impact strength decreases as particle sizes of the fillers decrease for both types of the polymer blends. The impact strength of blends containing rice husk of which 53, 180 and 425 μm at 10% filler content are 9.8, 10.6 and 12.2 KJ/m^2, respectively. While the impact strength of burning husk of which 53, 180 and 425 μm at the same filler content are 6.2, 7.9 and 8.1 KJ/m^2, respectively.

It may be occurred from smaller specific surface areas of big particle compared to small particle at the same filler content. Moreover, the big particles show the poor distribution in polymer matrix. Hence there are larger areas of HDPE matrix with containing big particle size fillers that are not damaged by fillers than that of HDPE matrix with small particle size fillers. Figure 4.21 illustrates the cross-sectional area of the blends containing fillers with different sizes.

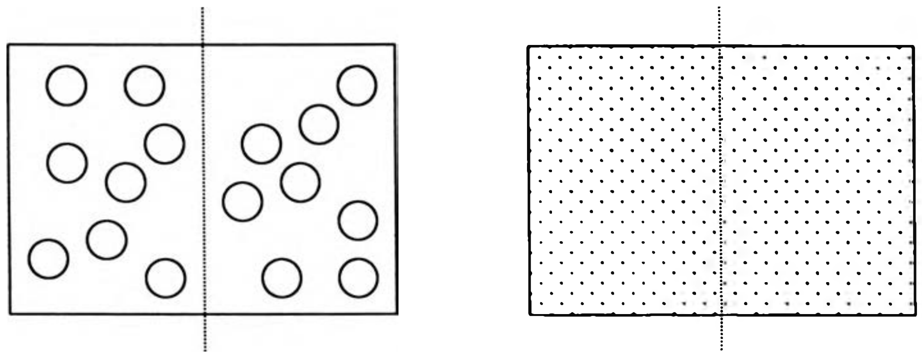


Figure 4.21 Cross-sectional area of the blends containing fillers with difference in diameters.

Thus, when a load applied to the polymer blends, the probability of crack propagation path, which passes through only pure HDPE matrix, is higher than the blends contained smaller particles. As a result, the impact strength increases.

4.5 Water and Moisture Absorption

Water absorption versus time for tapioca starch-filled, rice husk-filled and burning husk-filled HDPE blends are shown in Figures 4.22, 4.23. and 4.24, respectively.

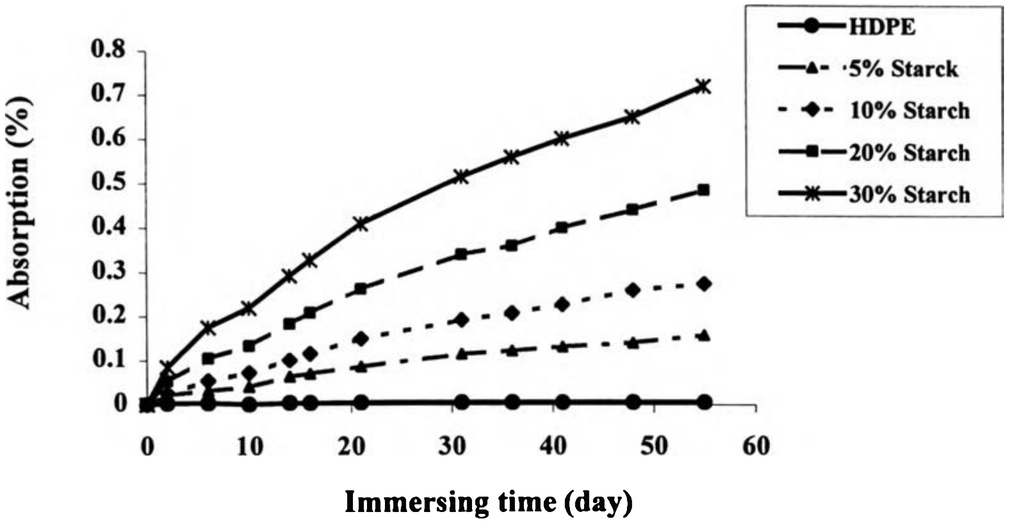


Figure 4.22 Water absorption of tapioca starch-filled HDPE blend at various filler content.

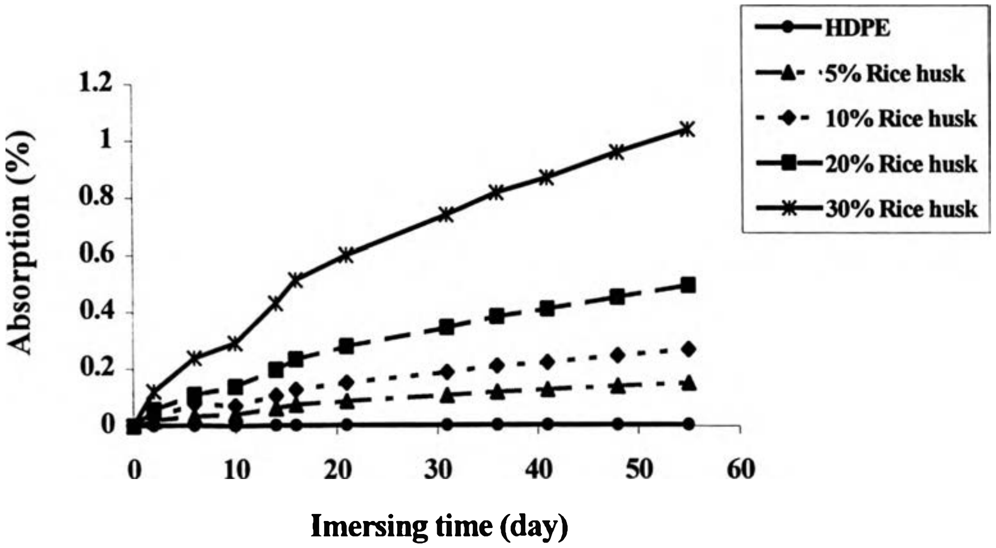


Figure 4.23 Water absorption of rice husk-filled HDPE blend at various rice husk content.

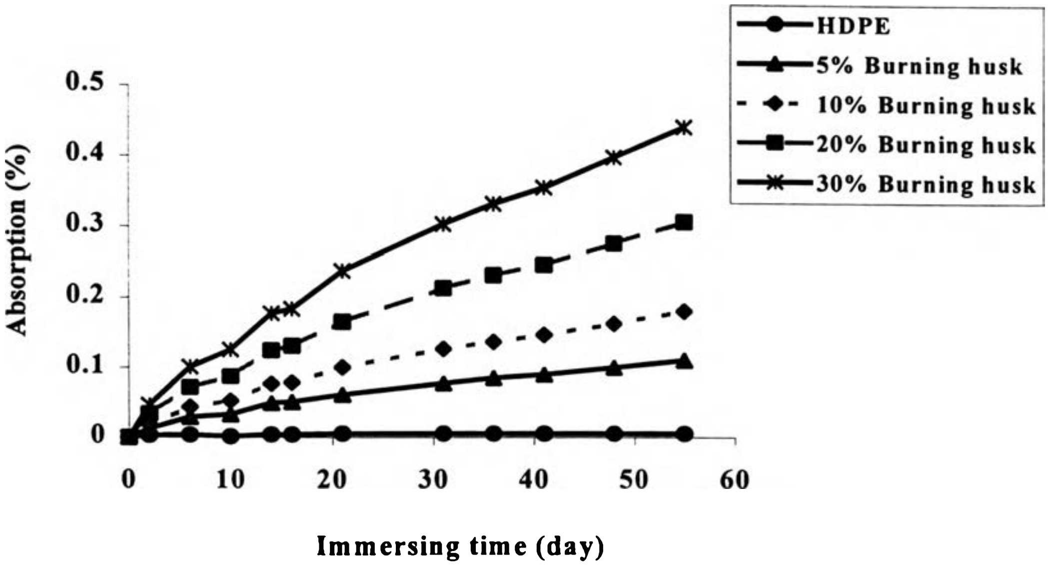


Figure 4.24 Water absorption of burning husk-filled HDPE blend at various burning husk content.

The three types of polymer blends show the similar tendency in water absorption properties that water absorption of the blends increases with increasing filler content and immersing interval. The larger amount of fillers is related to more surface areas contained hydroxyl group, except for burning husk, that can trap more water. Furthermore, the nature of fillers also affects their water absorption property. The result of the effect of types of fillers on water absorption property is shown in Figure 4.25.

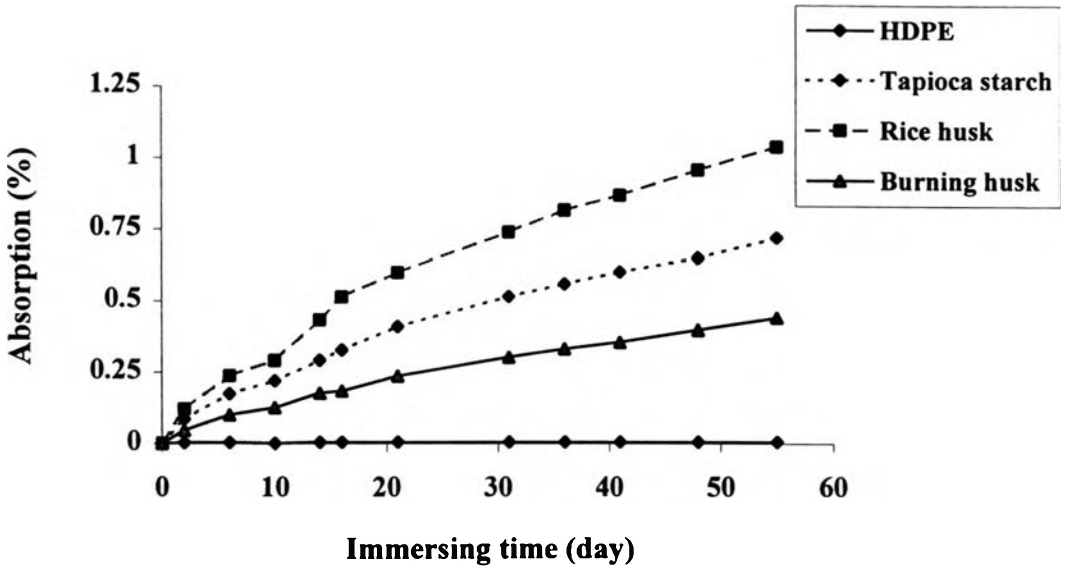


Figure 4.25 Water absorption of tapioca starch-filled, rice husk-filled and burning husk-filled HDPE blends at 30% filler content.

As shown in Figure 4.25, rice husk-filled and tapioca starch-filled HDPE blends absorb more water than burning husk-filled HDPE blend. Owing to its hydrophobic property, burning husk-filled HDPE blend is less sensitive to water than the other two blends. Because rice husk and tapioca starch have hydroxyl group in their molecules that form hydrogen bonding with water, the water uptake of rice husk and tapioca starch are higher than burning husk.