

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Characterization of Chitin

Shrimp shells consist of three major components which are (1) chitin, (2) calcium carbonate and (3) protein. Since the chitin does not dissolve in common solvents, calcium carbonate and protein can be removed by solvent extraction and chitin will be obtained as the remaining portion.

In this research, chitin was prepared from shells of *Penaeus merguensis* shrimp by demineralization with hydrochloric acid solution and deproteinization with aqueous sodium hydroxide solution in order to remove the calcium carbonate and the protein, respectively. The yield obtained during chitin production is shown in Table 4.1. Chitin was obtained as a white flaky material.

Table 4.1 Yield of chitin production from shrimp shells.

Material	Yield*, %
Shrimp shell	100
Product after demineralization	53
Product after deproteinization (chitin)	31

*dry weight basis

The FTIR spectrum of chitin is shown in Figure 4.1 and the absorption frequencies of characteristic bands of chitin are summarized in Table 4.2.

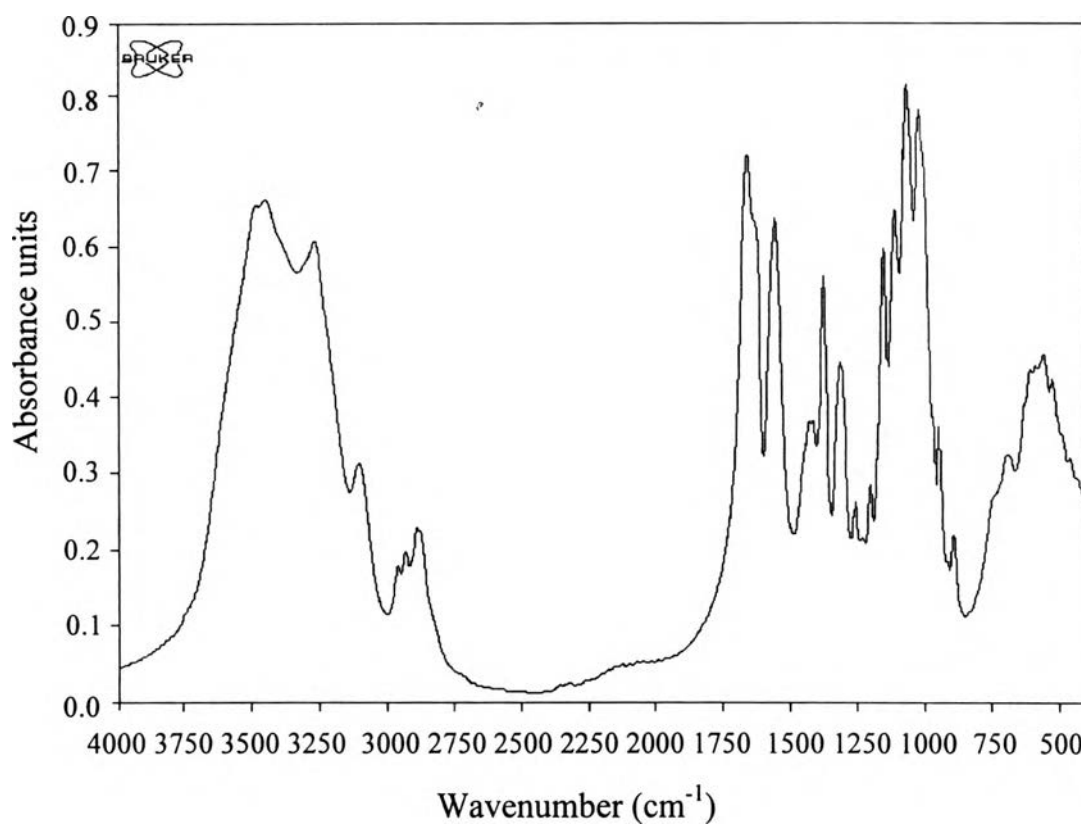


Figure 4.1 FTIR spectrum of chitin.

Table 4.2 Absorption frequencies of characteristic bands of chitin.

Frequency (cm ⁻¹)	Assignment and remarks	Reference(s)
1659 and 1621	C=O stretching	Muzzarelli, 1977;
1556	NH deformation in CONH plane	Kurita <i>et al.</i> , 1993;
1310	CN bond and CH ₂ wagging	Kim <i>et al.</i> , 1996
3258 and 3100	C ₂ amide group	Waiprib, 1991
1076 and 1029	C-O stretching vibration	Kim <i>et al.</i> , 1994

Chitin has some extent of amino groups rather than acetamide groups at C₂ position of N-acetyl glucosamine repeating units. The degree of deacetylation of chitin depends on the nature of chitin resources and the conditions used during deproteinization. The chitin used in this study was inevitably subjected to N-deacetylation during deproteinization process under alkaline condition and heating. According to the method of Sannan *et al.*, 1978, the degree of deacetylation of chitin can be calculated from FTIR to obtain the value of 9.3%.

4.2 Physical Properties of Fillers

Some physical properties of chitin and rice starch are summarized in Table 4.3.

Table 4.3 Physical properties of chitin and rice starch.

Property	Chitin	Rice starch
Density (g/cm ³)	1.65	1.49
Particle size (μm)	38-53	2-5
Particle shape	flake	polygonal

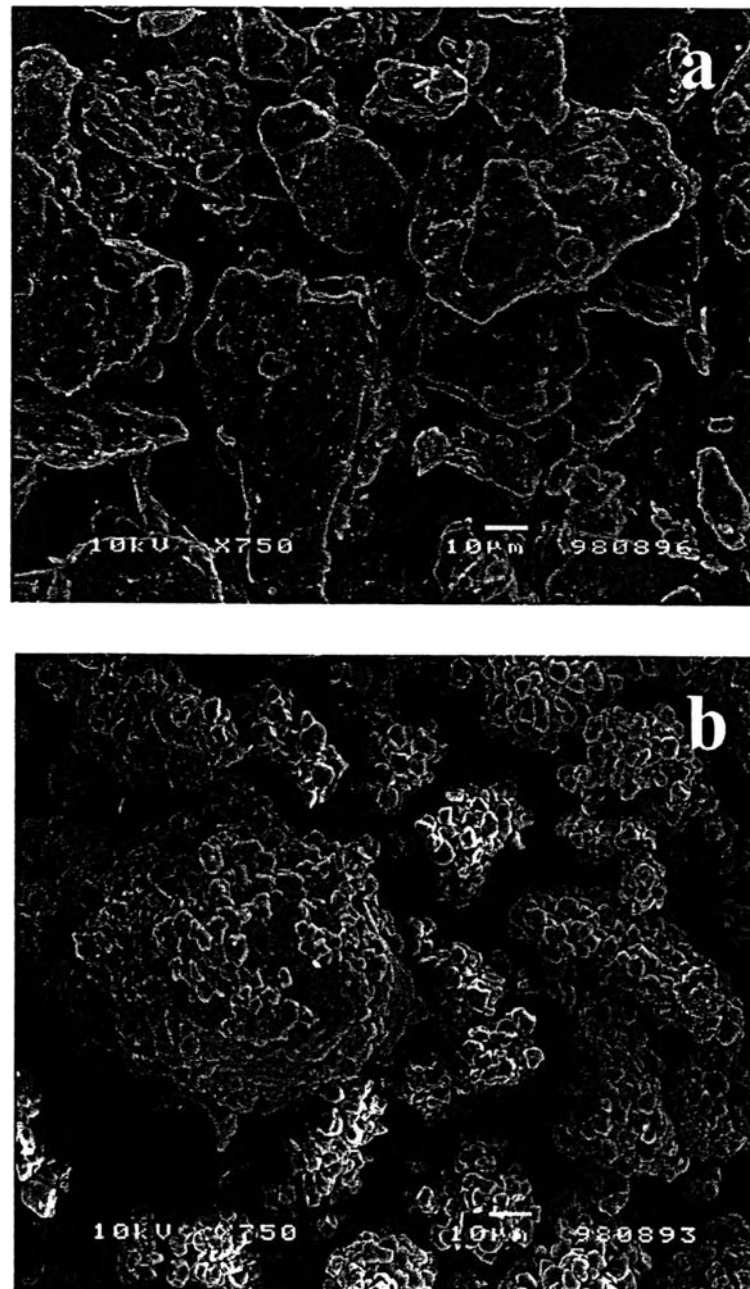


Figure 4.2 Scanning electron micrographs of a) chitin and b) rice starch.

Figure 4.2 shows scanning electron micrographs of chitin and rice starch at 750x magnification. The shape of chitin particles is in flake form while that of rice starch particles is polygonal and the size of rice starch

particles is much smaller than that of chitin flakes. Moreover, the particles of rice starch form agglomerates.

Thermogravimetric analysis (TGA) of chitin and rice starch is shown in Figure 4.3. The initial weight loss of chitin corresponds to the loss of water content of 4.24% and further observable weight loss begins at approximately 199°C where chitin begins to degrade (Kim *et al.*, 1994). A similar result is obtained for rice starch. The water content of rice starch is 5.09% and degradation temperature is approximately at 190°C (Suranakapan, 1998).

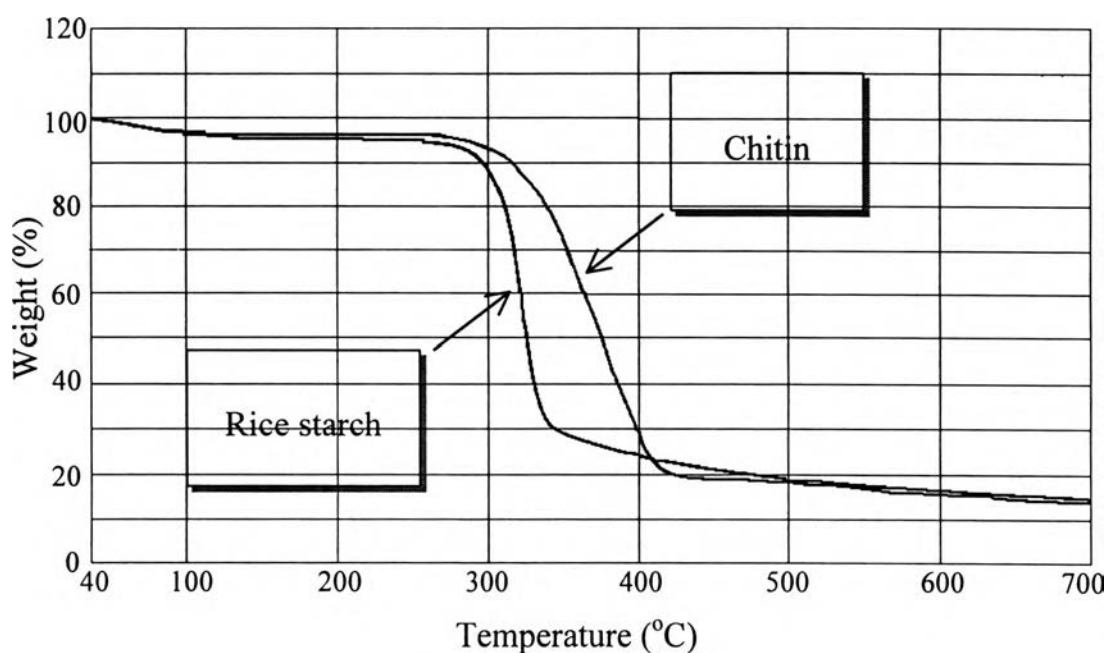


Figure 4.3 TGA thermograms of chitin and rice starch.

4.3 Tensile Properties

The tensile yield strength, strain at yield, and tensile modulus were studied in order to compare the effect of two fillers, chitin and rice starch, on tensile properties of the blends.

4.3.1 Tensile Yield Strength

The tensile yield strength of chitin-filled and rice starch-filled HDPE blends are shown in Figure 4.4. It shows that tensile yield strength decreases from 25.6 MPa in the unfilled HDPE to 20-21 MPa for blends with 30% filler. This behavior probably occurs due to the reduction in effective cross-section area caused by filler particles. In addition, there is little or no adhesion between the HDPE matrix and filler particles, thus the applied stress can not transfer through rigid filler particles and results in a decrease in tensile yield strength (Winlett, 1994).

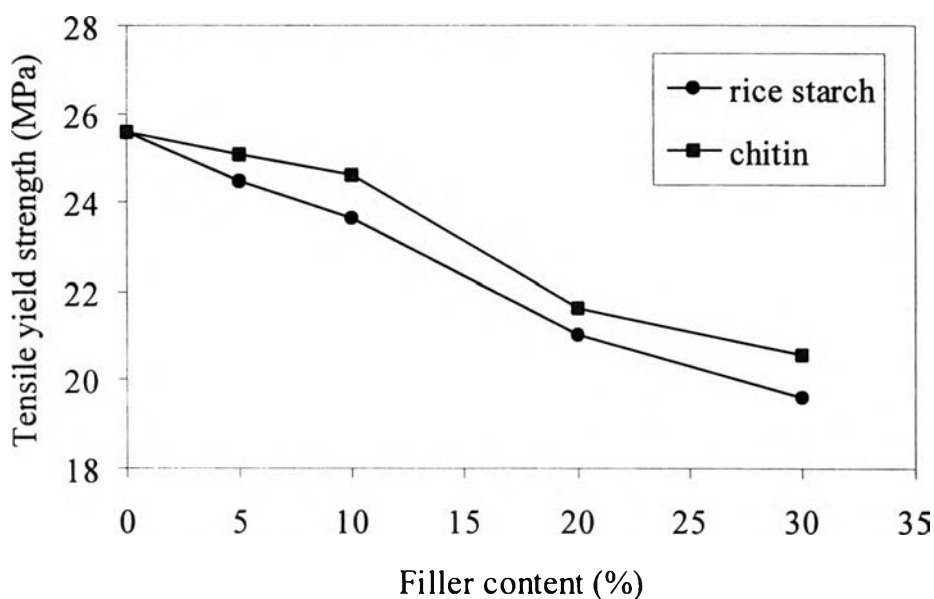


Figure 4.4 Tensile yield strength of chitin-filled and rice starch-filled HDPE blends.

Large particles are generally known to cause greater stress concentrations in the matrix than smaller ones, and this results in lower tensile yield strength (Mlecnik and La Mantia, 1997). From SEM micrographs (Figure 4.5), the starch agglomerated size is found to be bigger than chitin particle size. The large agglomerated size and a lot of facets and irregular

angles between faces of starch particles prevents uniform strain pattern and causes the lower strain yield strength of rice starch-filled HDPE blends than that of chitin-filled HDPE blends (Katz and Milewski, 1974; Tavman, 1996).

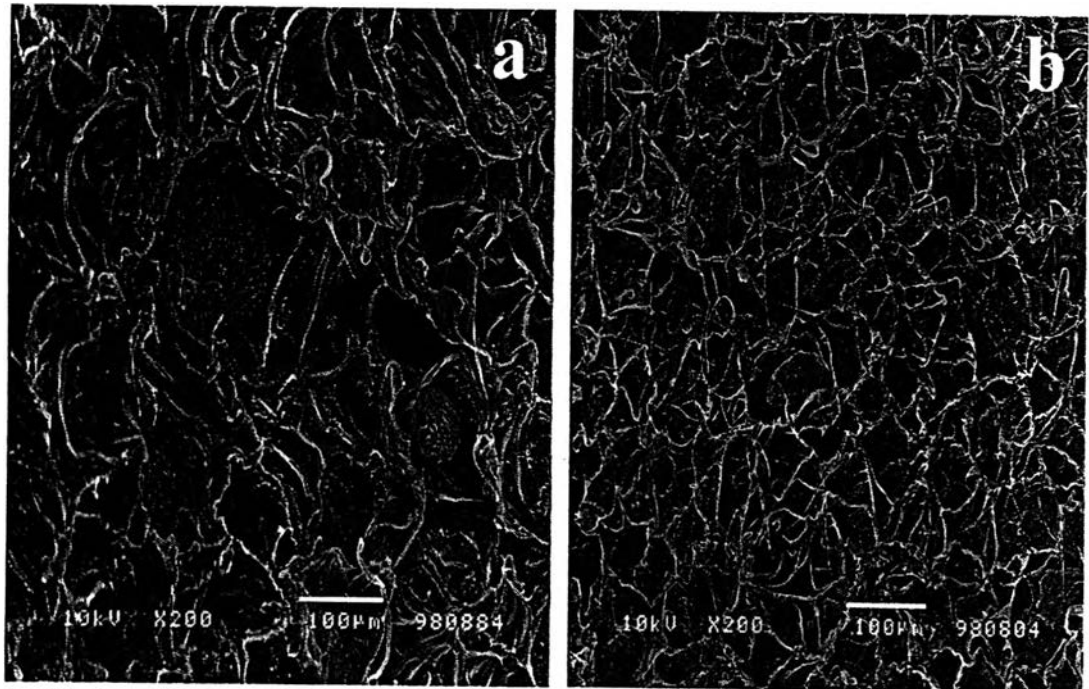


Figure 4.5 SEM micrographs of a) 10% rice starch-filled and b) 10% chitin-filled HDPE blends.

4.3.2 Strain at Yield

Similar to tensile yield strength, the strain at yield of both blends decreases as the filler content increases, as shown in Figure 4.6. The strain at yield is 9.3% for the unfilled blends, and decreases to approximately 5-6% for the 30% filled blends. This behavior may be due to the incompatibility of the fillers to the polymer matrix. The HDPE matrix confined between two filler particles must undergo a larger strain than a macroscopic strain because the rigid filler particles can not elongate (Bhattacharya *et al.*, 1995; Mlecnik and La Mantia, 1997). Thus the strain at yield of the blends decreases with increasing filler.

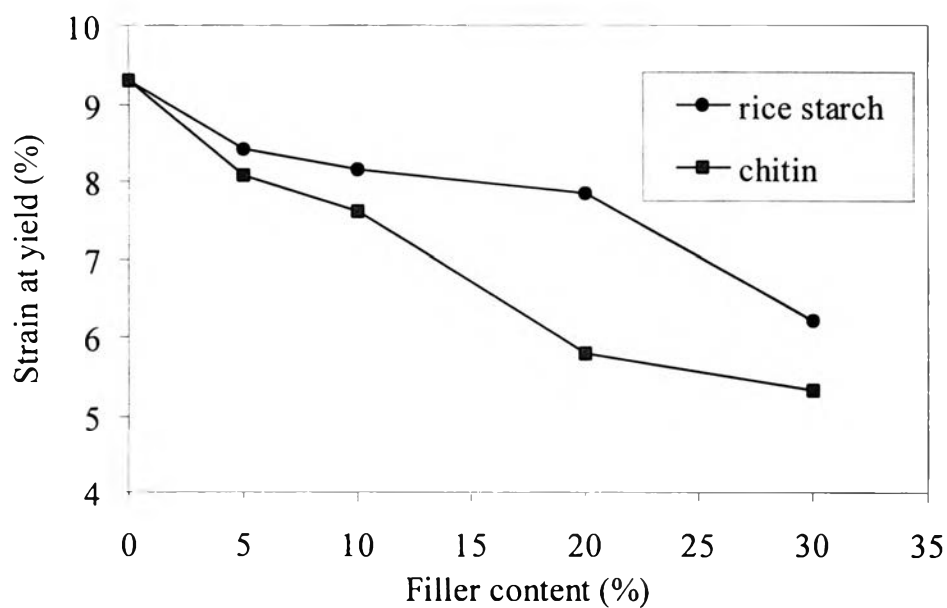


Figure 4.6 Strain at yield of chitin-filled and rice starch-filled HDPE blends.

4.3.3 Tensile Modulus

The effect of filler content on tensile modulus is shown in Figure 4.7.

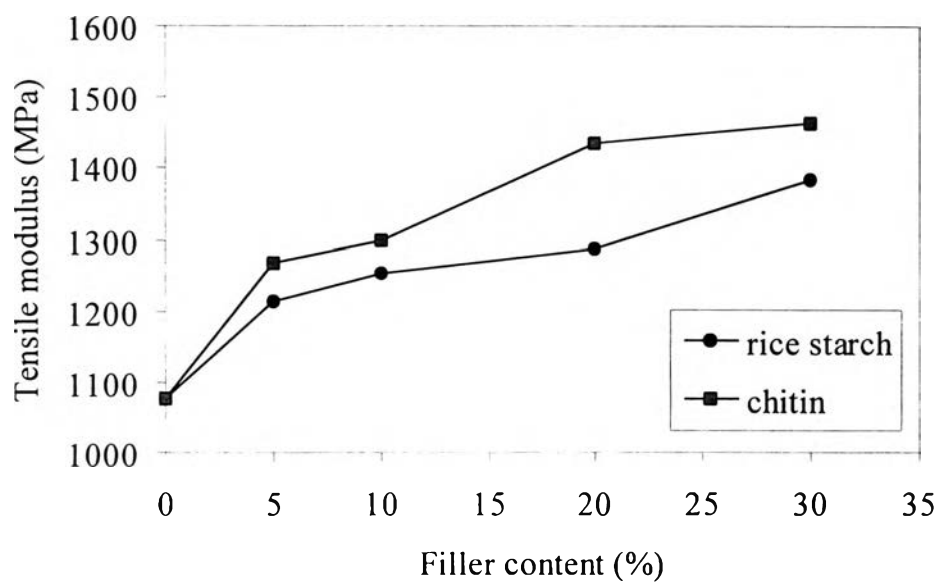


Figure 4.7 Tensile moduli of chitin-filled and rice starch-filled HDPE blends.

Solid fillers are generally many times more rigid than polymers and thus usually increase the moduli of the blends (Katz and Milewski, 1974). From Figure 4.7, the moduli increases as the filler content increases because the filler particles are stiffer than HDPE matrix (Winlett, 1994; Kim *et al.*, 1995a).

4.4 Flexural Properties

The flexural yield strength and flexural modulus of chitin-filled and rice starch-filled HDPE blends were investigated as a function of filler content.

4.4.1 Flexural Yield Strength

Figure 4.8 shows flexural yield strength of chitin-filled and rice starch-filled HDPE blends. The blends containing chitin and those containing rice starch show the same trend of decreasing in flexural yield strength as the filler content increases.

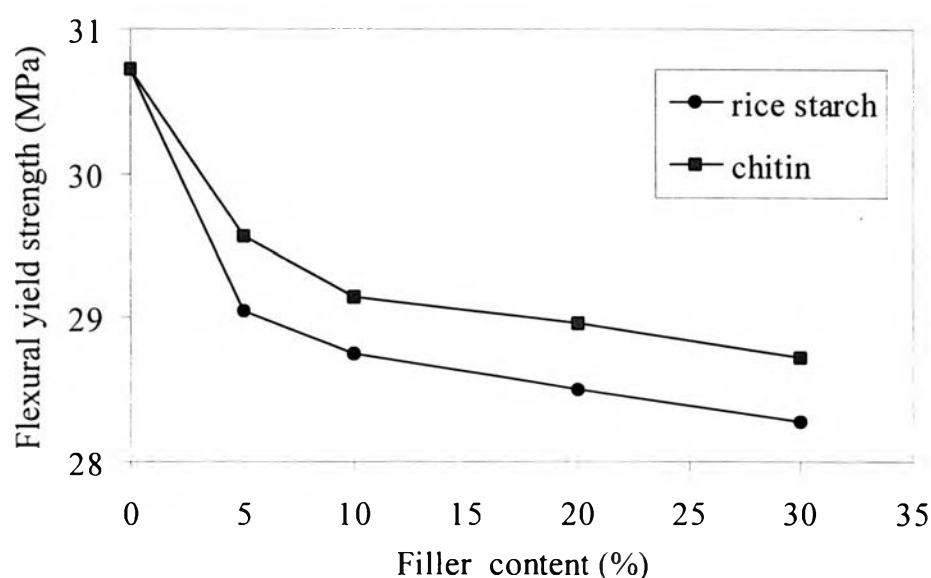


Figure 4.8 Flexural yield strength of chitin-filled and rice starch-filled HDPE blends.

4.4.2 Flexural Modulus

Figure 4.9 shows the effect of filler content on flexural moduli of chitin-filled and rice starch-filled HDPE blends. The flexural moduli increases from approximately 1100 MPa with no filler to approximately 1500 MPa at 30% filler. For intermediate concentrations, the chitin is more efficient than rice starch in improving the stiffness.

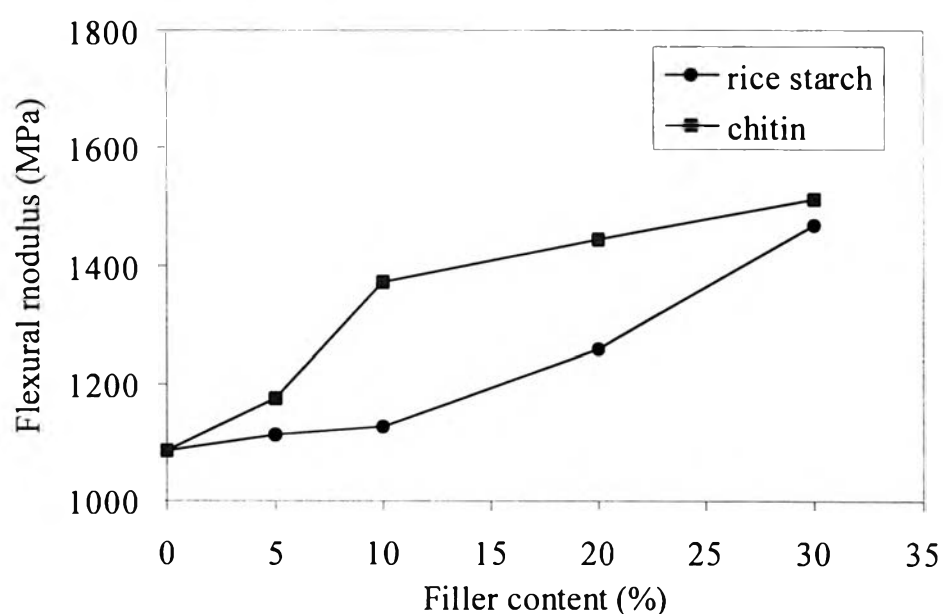


Figure 4.9 Flexural moduli of chitin-filled and rice starch-filled HDPE blends.

4.5 Impact Strength

The relation of impact resistance and filler content on chitin-filled and rice starch-filled HDPE blends is shown in Figure 4.10. The decrease in impact strength of both blends is evidently related to the brittleness of the filler particles and the limited adhesion between the matrix and the fillers. Moreover, impact strength of rice starch-filled HDPE blends are slightly higher than that of chitin-filled HDPE blends. This may be due to the more uniform dispersion of the rice starch acting as a more effective toughening agent for the blends (Bartczak *et al.*, 1999).

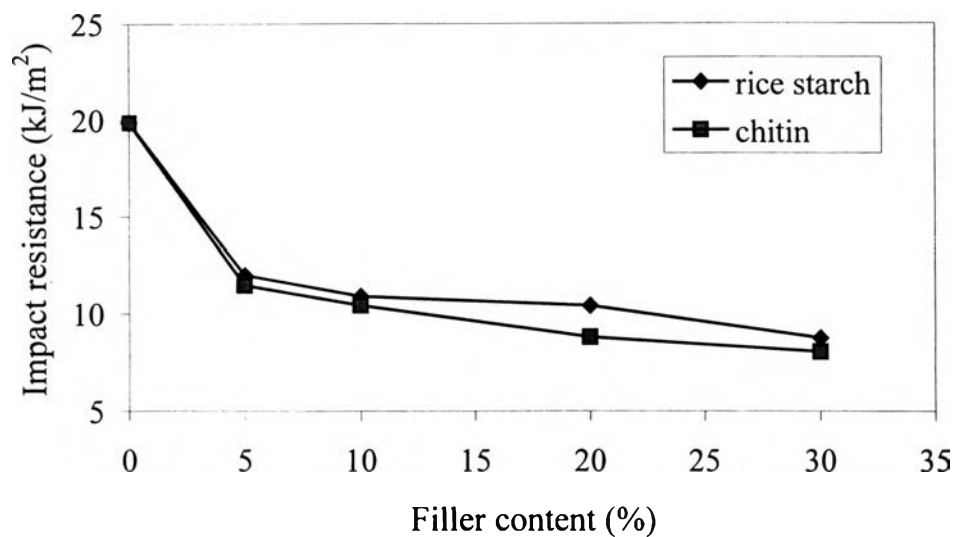


Figure 4.10 Impact resistance of chitin-filled and rice starch-filled HDPE blends.

4.6 Hardness

The Shore D hardness of the chitin-filled and rice starch-filled HDPE blends are shown in Figure 4.11. The results indicate that chitin-filled HDPE blends show no significant change in hardness while the rice starch-filled HDPE blends show a small decrease in Shore D hardness with increasing starch content.

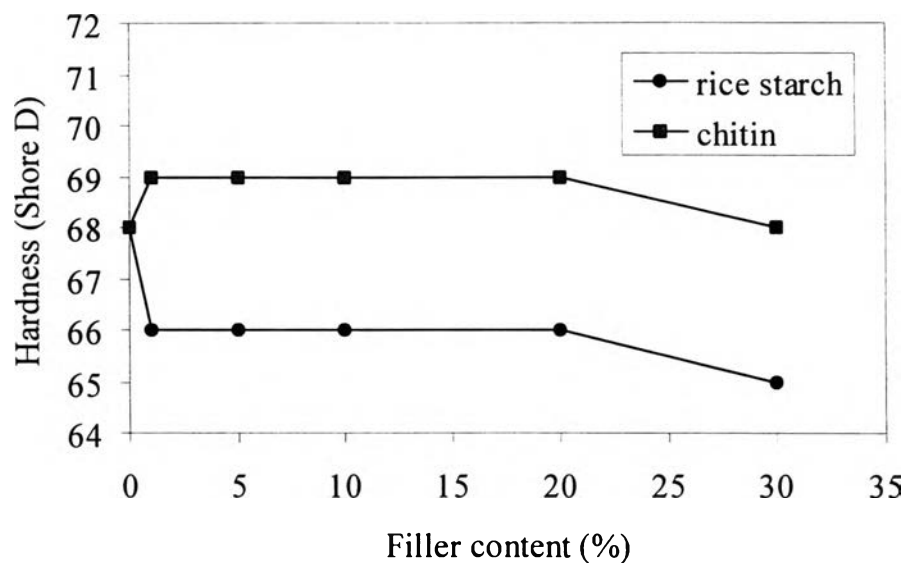


Figure 4.11 Shore D hardness of chitin-filled and rice starch-filled HDPE blends.

4.7 Microstructure

The microstructure of the chitin-filled and rice starch-filled HDPE blends was studied by using scanning electron microscope (SEM). In chitin-filled HDPE blends (Figure 4.12), chitin is regularly dispersed in the HDPE matrix with little or no interfacial adhesion to the polymer matrix. The morphology of rice starch-filled HDPE blends (Figure 4.13) is similar, with little or no interfacial adhesion observed. Moreover, rice starch forms agglomerated particles within the HDPE matrix. The agglomerate size increases with increasing starch content in the blends. This suggests that the decrease in mechanical properties of the blends containing rice starch over those containing chitin may be due to this agglomeration.

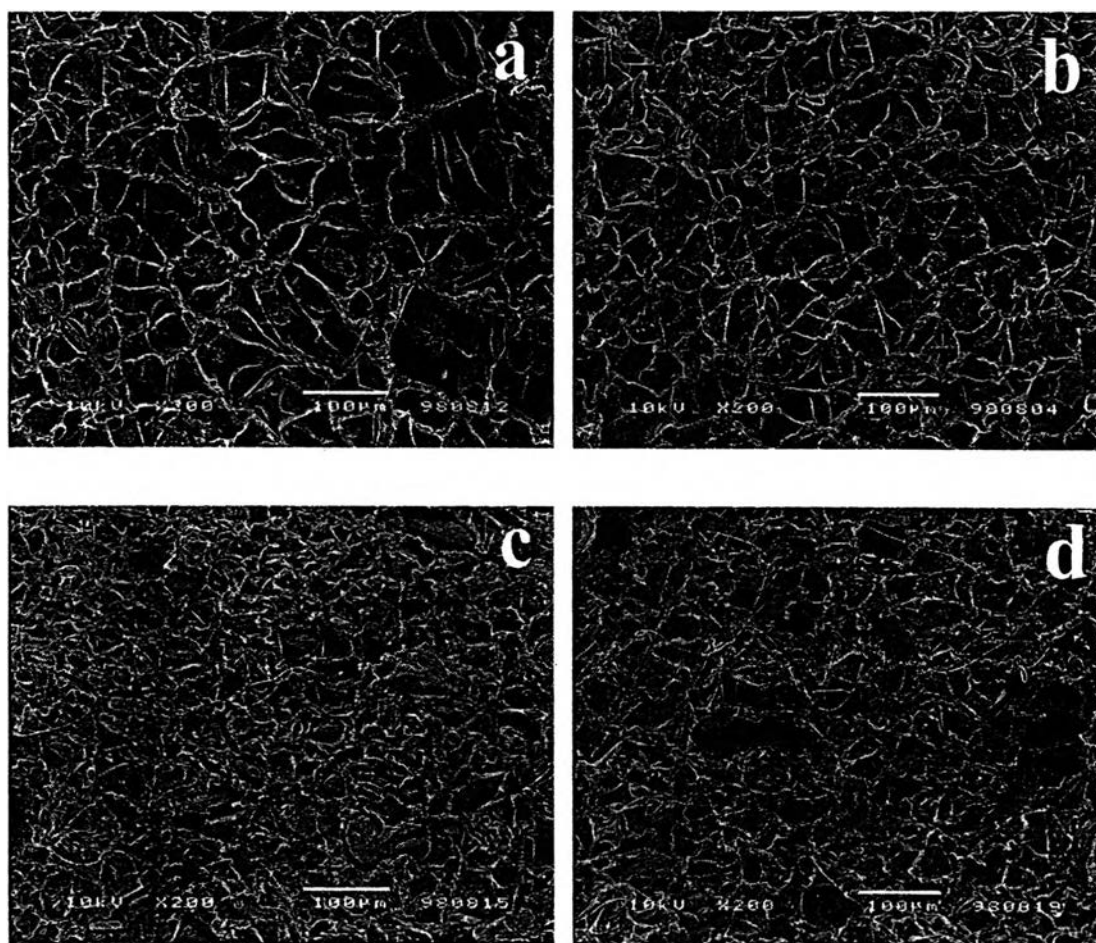


Figure 4.12 SEM micrographs of chitin-filled HDPE blends a) 5% chitin, b) 10% chitin, c) 20% chitin, and d) 30% chitin.

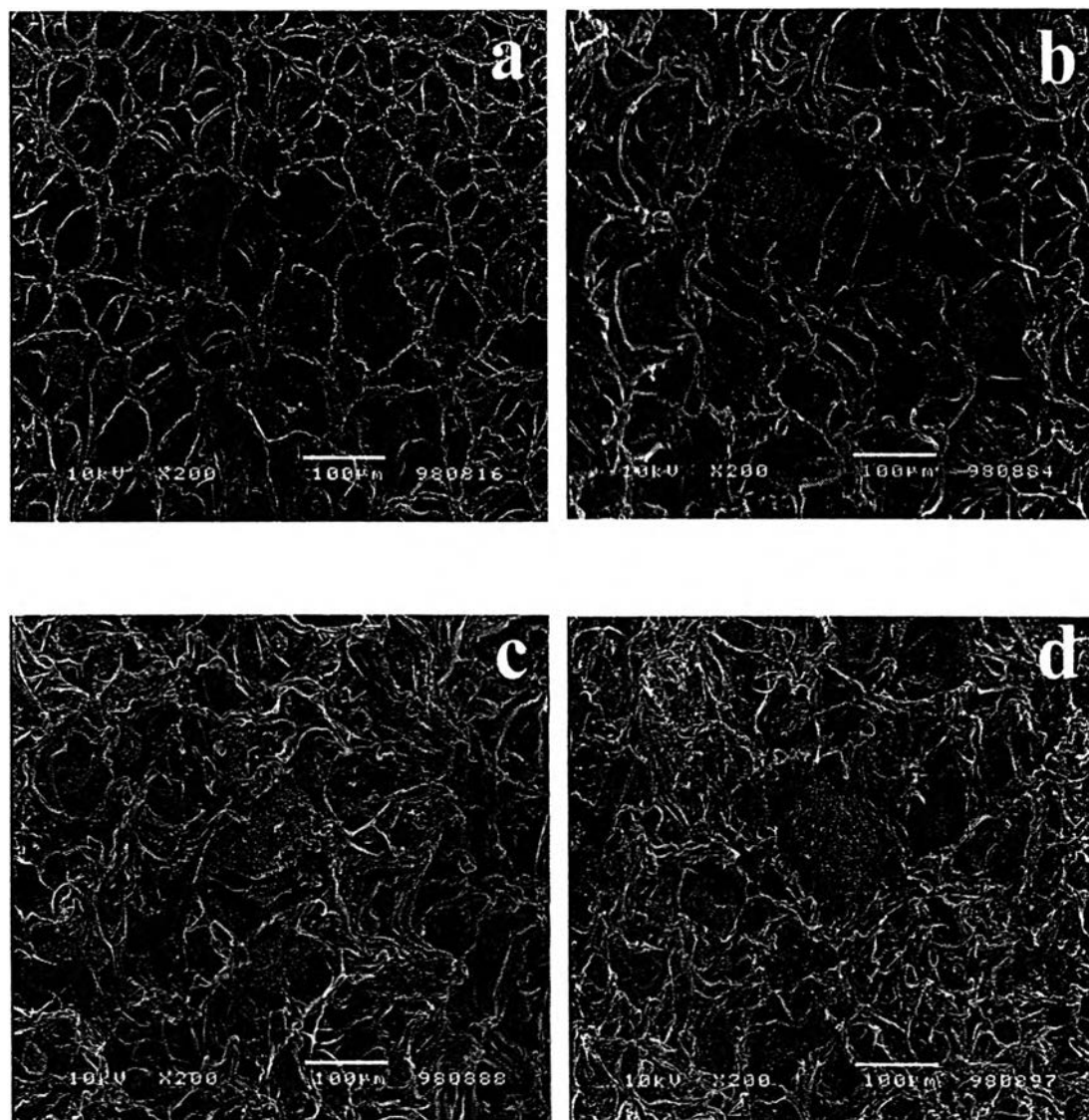


Figure 4.13 SEM micrographs of rice starch-filled HDPE blends a) 5% rice starch, b) 10% rice starch, c) 20% rice starch, and d) 30% rice starch.

4.8 Water Absorption

The water absorption of the chitin-filled and rice starch-filled HDPE blends as a function of immersion time is shown in Figure 4.14.

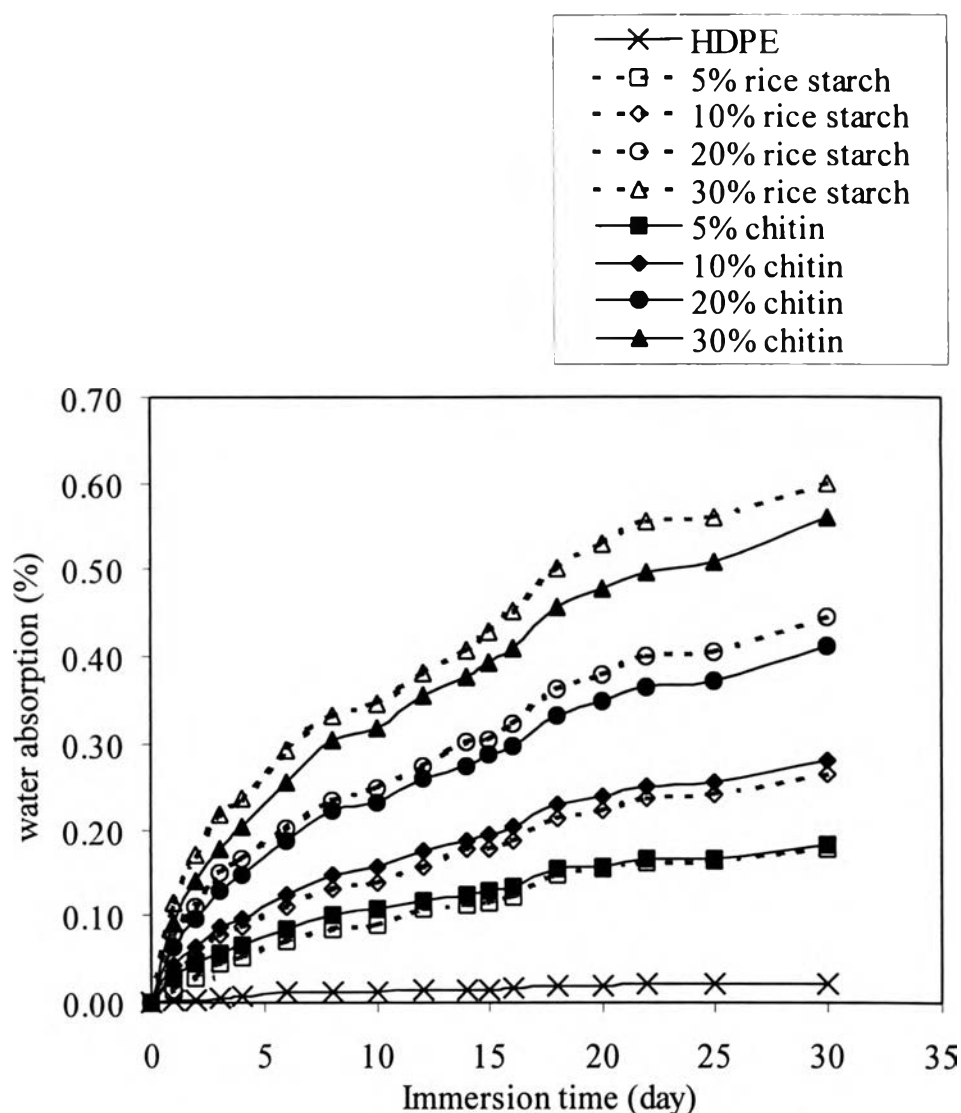


Figure 4.14 Water absorption of chitin-filled and rice starch-filled HDPE blends.

The water absorption of chitin-filled and rice starch-filled HDPE blends increases with increasing filler content due to the hygroscopic property of both fillers (Sannan *et al.*, 1978; Thiebaud *et al.*, 1997). At high content of filler, rice starch-filled HDPE blends absorb more amount of water than chitin-filled HDPE blends. It is speculated that rice starch has more surface area, hence more interaction with water and leads to higher water absorption by rice starch-filled HDPE blends.