

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Thermogravimetric Analysis of Starch

The thermogravimetric analysis (TGA) of the tapioca starch gave curve shown in Figure 4.1. In general, weight losses occur when volatiles absorbed by the sample are driven off, and at higher temperature when degradation of the sample occurs with the formation of volatile products. For the analysis of the tapioca starch, the initial weight loss began at approximately 60°C and reached a constant weight plateau after losing 6.9% of its initial weight. This weight loss corresponded to the loss of the water content from the starch. Further weight loss occurred at approximately 308°C. At this temperature the tapioca starch began to degraded.

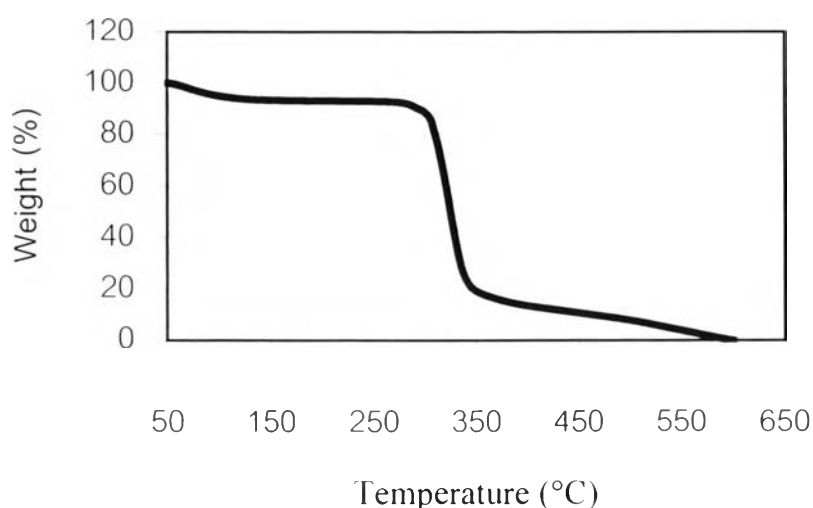


Figure 4.1 TGA thermogram of tapioca starch.

4.2 Starch Density Measurement

Because the mixing process of the polymer blends required the same amount of both tapioca starch and HDPE to control the composition during mixing, the density of tapioca starch was determined. The pycnometric technique was applied for the measurement. The density of tapioca starch was 1.45 g/cm^3 .

4.3 Microstructure Characterization

In polymer blends, it is necessary to study the morphology of the blends since most of its properties, especially the mechanical properties depend on the morphology of the blends. Thus, SEM was applied to study the morphology of the blends.

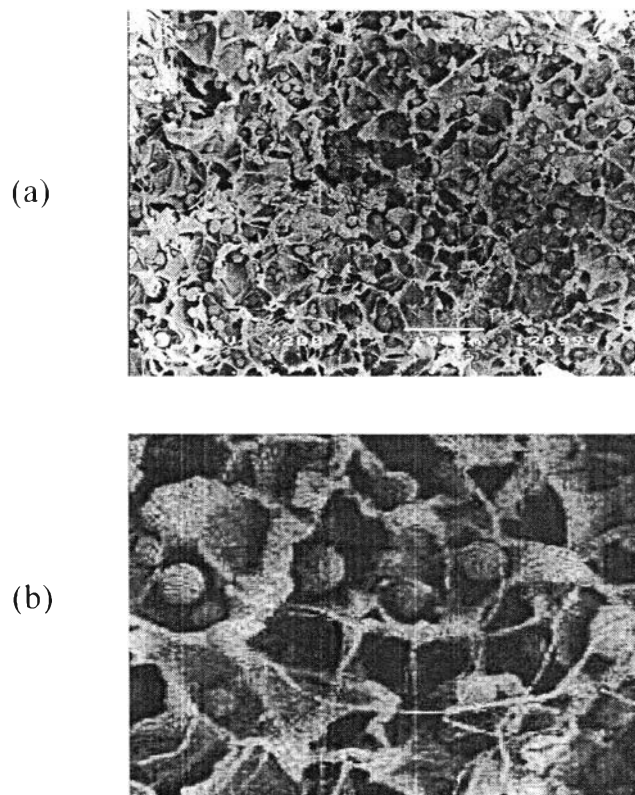


Figure 4.2 SEM micrographs of uncompatibilized blend containing 20 wt% starch at (a) 200 magnification and (b) 500 magnification.

The SEM micrographs of uncompatibilized blends containing 20 wt% starch are shown in Figure 4.2. It can be seen that the starch particles dispersed well in HDPE matrix. However, poor interfacial adhesion between starch particles and HDPE matrix was observed. This is due to the different polar character between starch (hydrophilic) and HDPE (hydrophobic) (Maddever *et al.*, 1987).

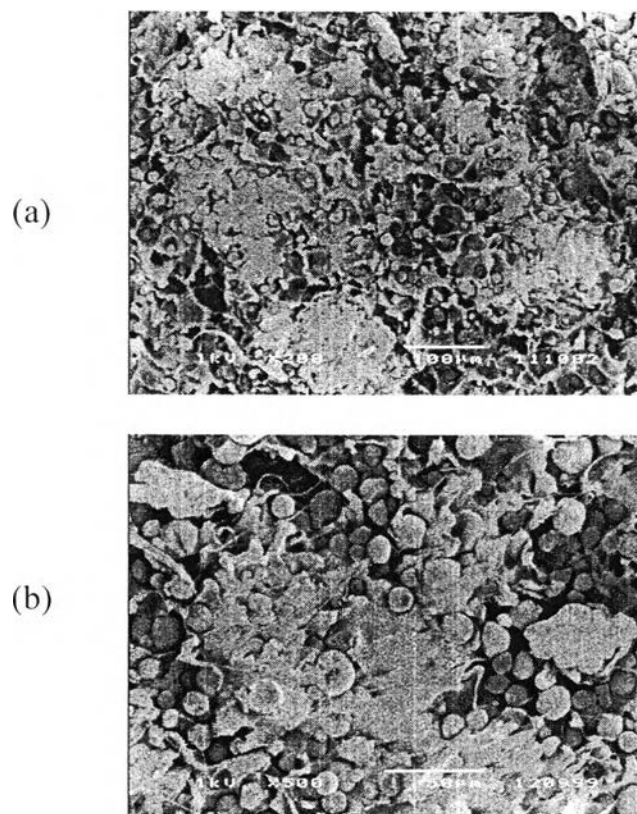


Figure 4.3 SEM micrographs of EAA compatibilized blend containing 20 wt% starch content and 10 wt% EAA based on starch at (a) 200 magnification and (b) 500 magnification.

Figure 4.3 shows SEM micrographs of the blends containing 20 wt% starch and compatibilized with 10 wt% EAA based on starch. It can be seen that when the blends was compatibilized with EAA, it showed the better interfacial adhesion between starch particles and HDPE matrix than the

uncompatibilized blends. The reason is that EAA contains both hydrocarbon part that have good miscibility with HDPE and the carboxylic groups that can form the hydrogen bonds with the hydroxyl groups of starch (Shogren *et al.*, 1992) as shown in Figure 4.4. This structure gives EAA the ability to place itself at the interface of HDPE and starch during blending. The result is the better interfacial adhesion of starch particles and HDPE matrix.

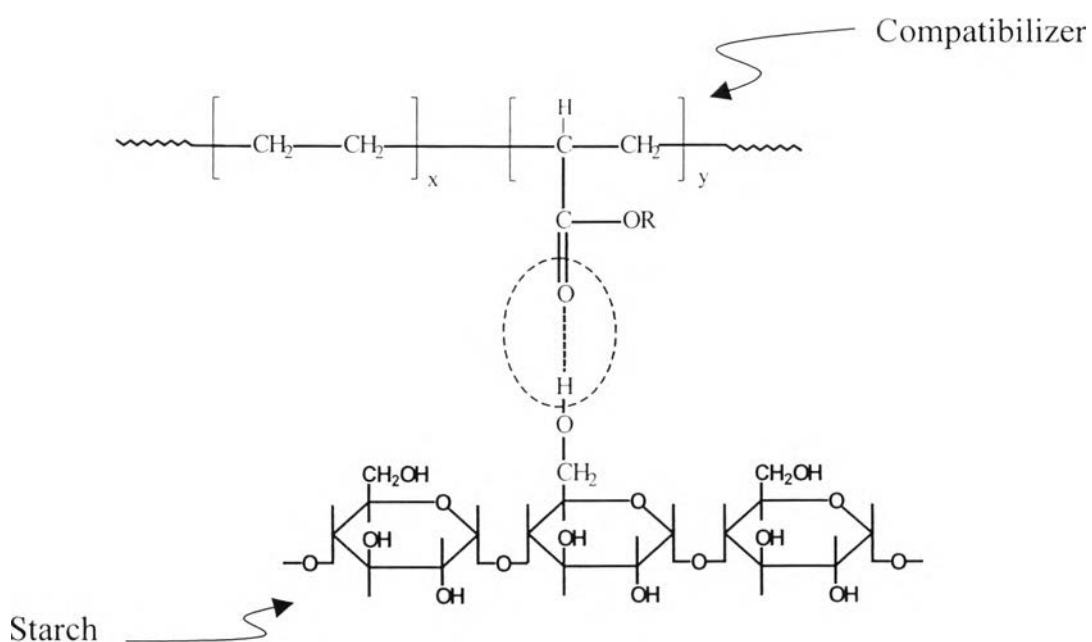


Figure 4.4 Hydrogen bond between starch and compatibilizer.

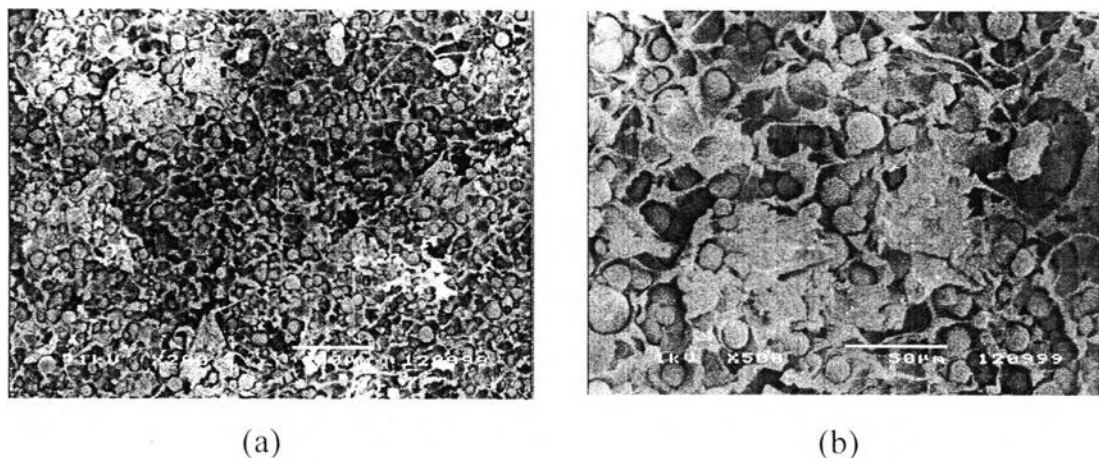


Figure 4.5 SEM micrographs of EVA compatibilized blend containing 20 wt% starch content and 10 wt% EVA based on starch at (a) 200 magnification and (b) 500 magnification.

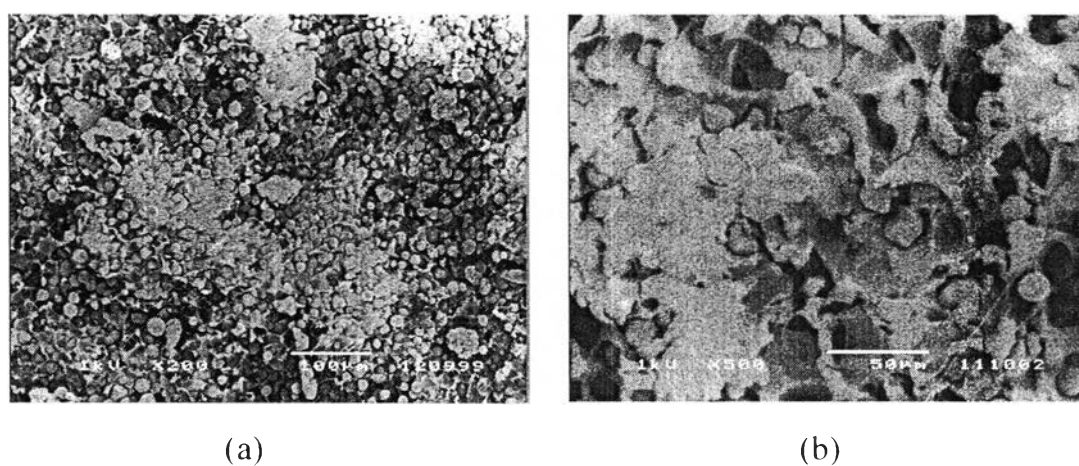


Figure 4.6 SEM micrographs of PE-g-MA compatibilized blend containing 20 wt% starch content and 10 wt% PE-g-MA based on starch at (a) 200 magnification and (b) 500 magnification.

Similar to the EAA compatibilized blends, the EVA and PE-g-MA compatibilized blends had the improvement of interfacial adhesion between

starch particles and HDPE matrix than the uncompatibilized blends as shown in Figure 4.5 and 4.6, respectively.

4.4 Mechanical Properties

The tensile properties, flexural properties, and impact property of the blends were studied in order to investigate the effect of compatibilizers.

4.4.1 Tensile properties

The tensile properties determined as functions of starch and compatibilizer contents were tensile strength, tensile modulus, and elongation at break.

4.4.1.1 Tensile yield strength

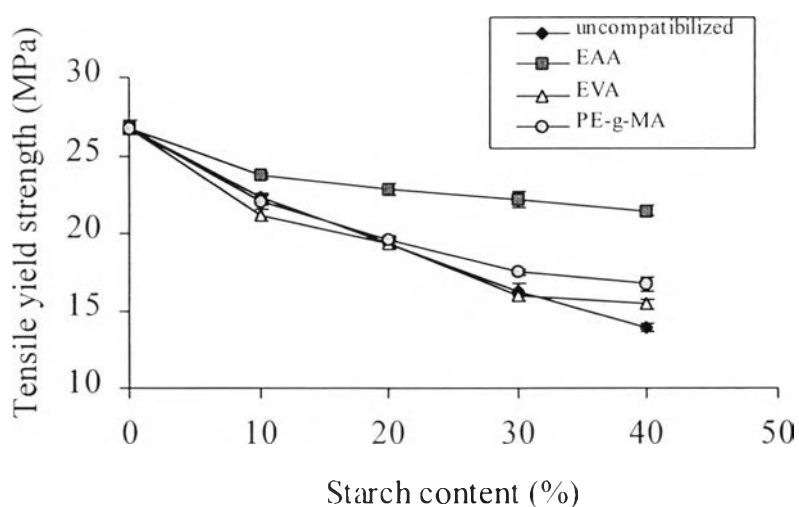


Figure 4.7 Effect of starch content on tensile yield strength of uncompatibilized and compatibilized blends containing 10 wt% compatibilizer based on starch .

Figure 4.7 shows the tensile yield strength of the uncompatibilized and compatibilized blends containing 10 wt% compatibilizer based on starch. In the uncompatibilized blends, there was a continuous decrease in tensile yield strength as the amount of starch increased. This behavior occurs due to the reduction in effective cross-section area caused by starch particles. In addition, there is poor interfacial adhesion between starch particles and HDPE matrix, thus the applied stress can not transfer through rigid starch particles resulting in a decrease in tensile yield strength (Willett, 1994).

In the EAA and PE-g-MA compatibilized blends, the decrease in tensile yield strength was also observed as the amount of starch increased. However, the decrease in tensile yield strength of the EAA and PE-g-MA compatibilized blends was less than that of the corresponding uncompatibilized blends. It was possibly due to the better interfacial adhesion in the compatibilized blends. There are less improvement in tensile yield strength in case of the EVA compatibilized blends. This could be attributed to the lower tensile yield strength of EVA as compared with that of HDPE, EAA, and PE-g-MA (Prinos *et al.*, 1998). The tensile yield strength of HDPE and each compatibilizer are shown in Table 4.1.

Table 4.1 Tensile properties of concerning polymers

Polymer	Tensile strength (MPa)	Tensile modulus (MPa)	Elongation at break (%)
HDPE	26.7	1142	600
EAA	15.2	217	410
EVA	7.1	447	900
PE-g-MA	10.6	577	720

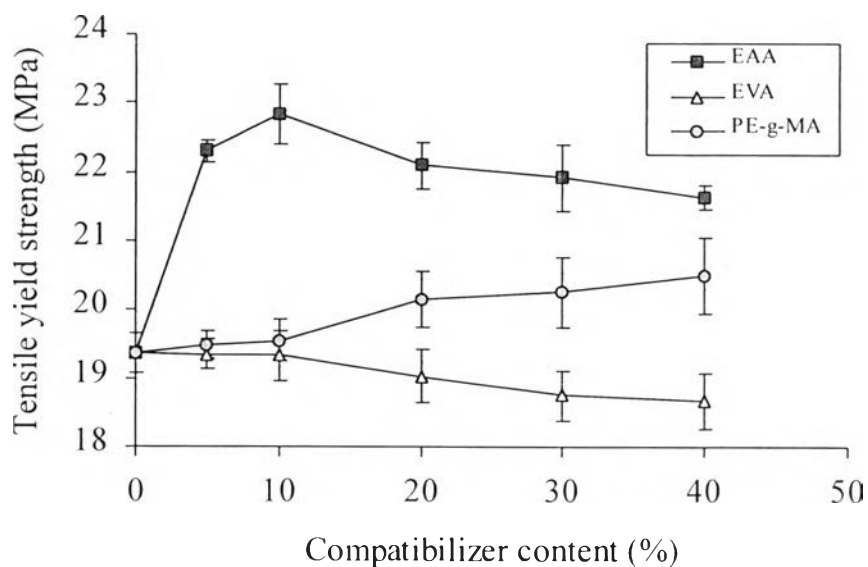


Figure 4.8 Effect of compatibilizer content on tensile yield strength of compatibilized blends containing 20 wt% starch.

The compatibilizer content is one of the important factors for the mechanical properties of the compatibilized blends. The effect of compatibilizer content on tensile yield strength of the compatibilized blends containing 20 wt% starch is shown in Figure 4.8. It was found that tensile yield strength of the EAA compatibilized blends slightly decreased when compatibilizer content was higher than 10 wt% based on starch. Similar to the EAA compatibilized blends, the tensile yield strength of the EVA compatibilized blends slightly decreased with increasing compatibilizer content. In contrast, the tensile yield strength of the PE-g-MA compatibilized blends increased as compatibilizer content increased.

4.4.1.2 Tensile modulus

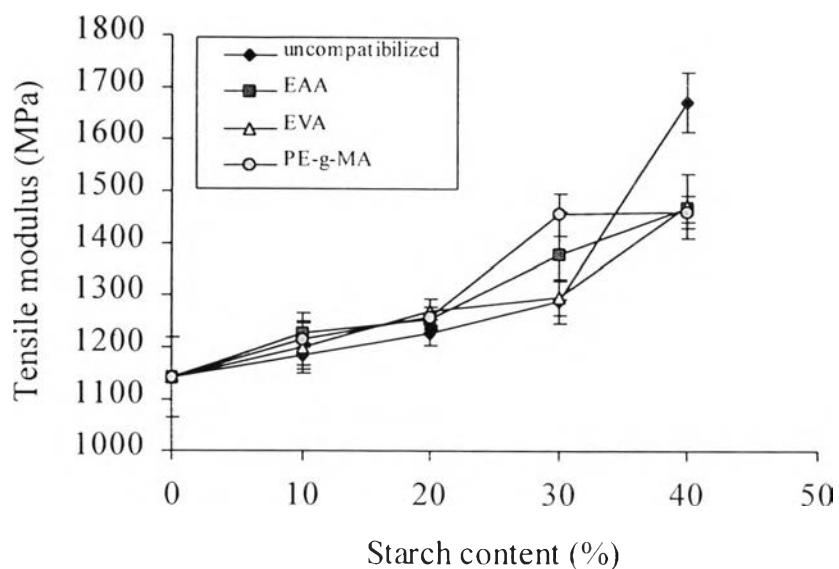


Figure 4.9 Effect of starch content on tensile modulus of uncompatibilized and compatibilized blends containing 10 wt% compatibilizer based on starch.

From Figure 4.9, the increment of tensile modulus in the uncompatibilized blends was observed. This happens because starch is a solid particle, which is generally many times more rigid than HDPE and thus usually increases the modulus of the blends (Katz, 1974).

The compatibilized blends had higher value of tensile modulus than the uncompatibilized blends for the blends containing up to 30 wt% starch. This behavior could be attributed to the better interfacial adhesion between starch particles and HDPE matrix.

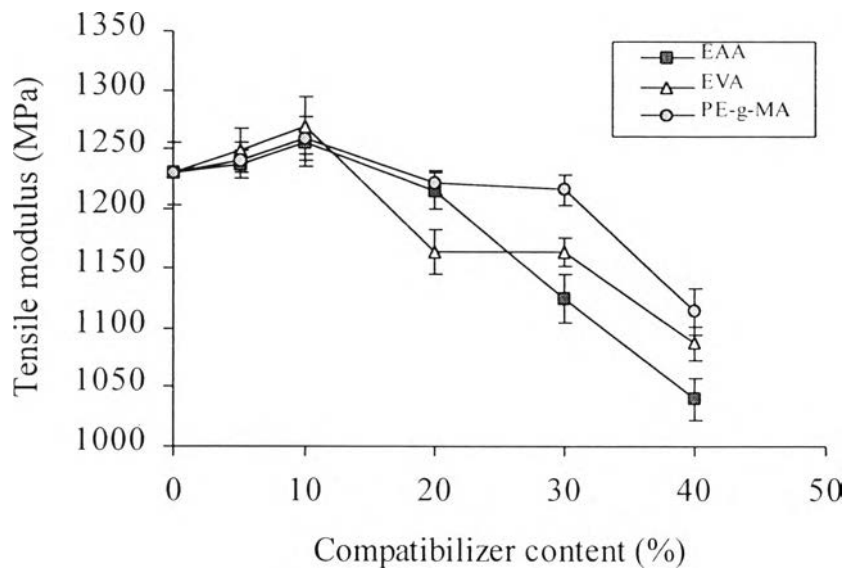


Figure 4.10 Effect of compatibilizer content on tensile modulus of compatibilized blends containing 20 wt% starch.

In Figure 4.10, when the compatibilizer contents were varied from 10 to 40 wt% based on starch, the tensile modulus of the compatibilized blends decreased. This probably due to the lower tensile modulus of the compatibilizers as compared with that of HDPE.

4.4.1.3 Elongation at break

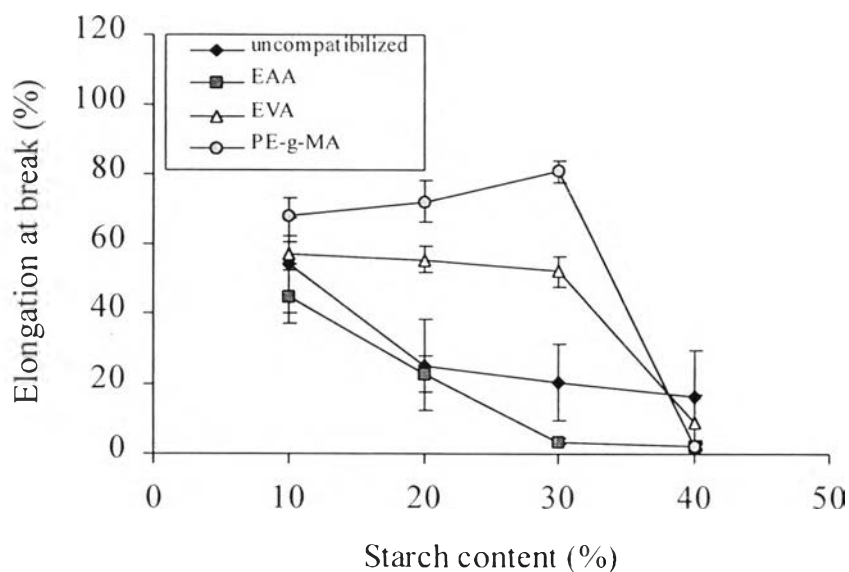


Figure 4.11 Effect of starch content on elongation at break of uncompatibilized and compatibilized blends containing 10 wt% compatibilizer based on starch.

In the uncompatibilized blends, the elongation at break decreased with increasing starch content as shown in Figure 4.11. The decrease in elongation at break arises from the incompatibility of the starch to the polymer matrix. The HDPE matrix confined between two starch particles must undergo a larger strain than a macroscopic strain because the rigid starch particles cannot elongate. Thus, the elongation at break of the uncompatibilized blends decreased with increasing starch content (Bhattacharya *et al.*, 1997).

It was found that the elongation at break of the blends could be improved by using EVA or PE-g-MA as a compatibilizer. This was observed even for the blends containing starch with starch content up to 30 wt%. In

contrast, the elongation at break of the EAA compatibilized blends was lower than that of the uncompatibilized ones.

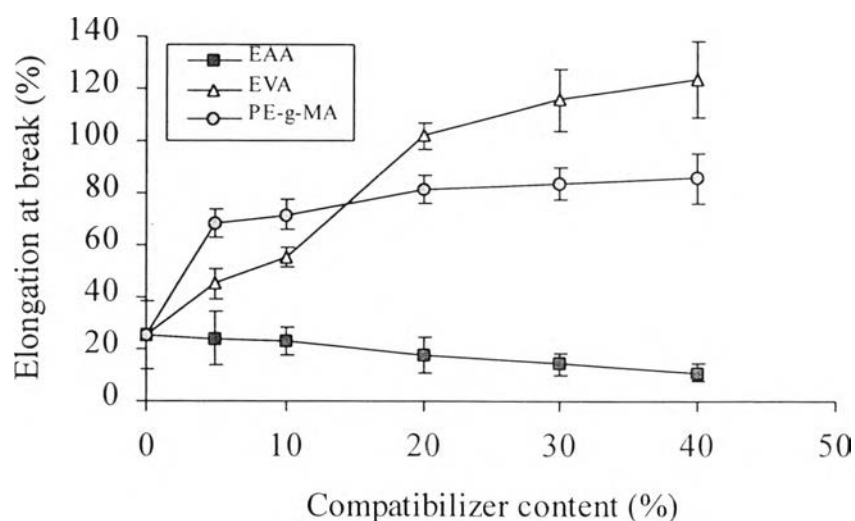


Figure 4.12 Effect of compatibilizer content on elongation at break of compatibilized blends containing 20 wt% starch.

In addition, as the amount of compatibilizer of the blends increased, the elongation at break increased except for the EAA compatibilized blends as shown in Figure 4.12. This negative contribution is due to the lower elongation at break of EAA as compared with that of EVA and PE-g-MA (Prinos *et al.*, 1998).

4.4.2 Flexural properties

The flexural properties determined as functions of starch and compatibilizer contents were flexural yield strength and flexural modulus.

4.4.2.1 Flexural yield strength

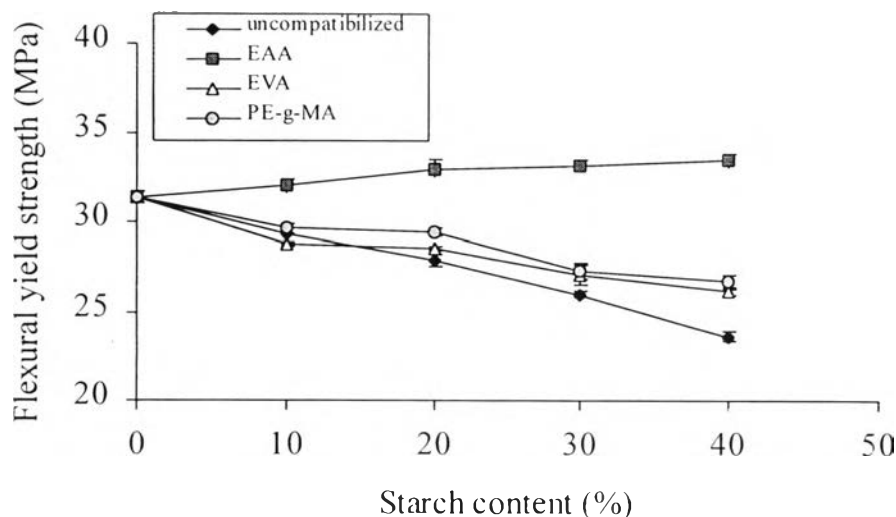


Figure 4.13 Effect of starch content on flexural yield strength of uncompatibilized and compatibilized blends containing 10 wt% compatibilizer based on starch .

Similar to the tensile yield strength, the flexural yield strength of the uncompatibilized blends decreased with an increasing of starch content due to the incompatibility of the blend components. The flexural yield strength could be improved by the addition of the compatibilizer into the blends especially in case of the EAA compatibilized blends.

As clearly shown in Figure 4.13, the effect of compatibilizers on the flexural yield strength of the blends was reflected strongly when EAA was used as a compatibilizer. In case of the EAA compatibilized blends, there was no decrease in flexural yield strength as starch content increased from 0 to 40 wt%. Furthermore, the flexural yield strength of the EAA compatibilized blends was higher than that of pure HDPE.

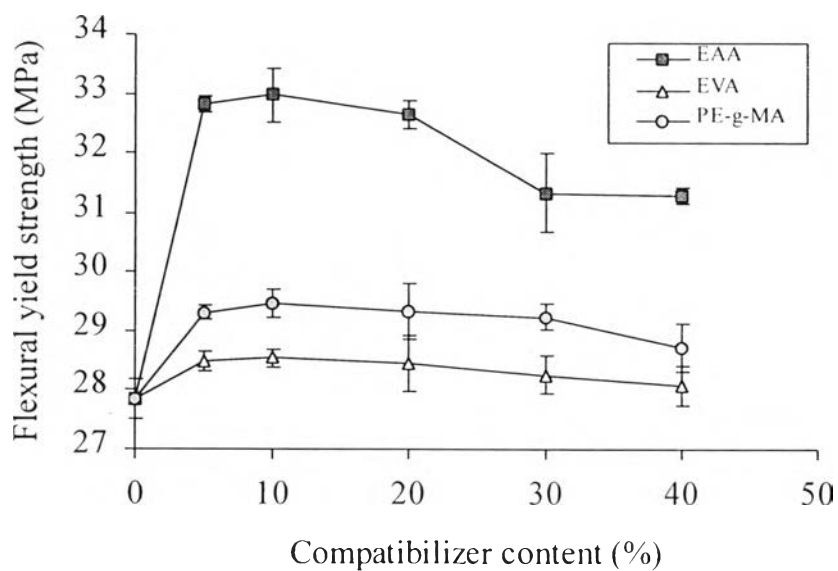


Figure 4.14 Effect of compatibilizer content on flexural yield strength of compatibilized blends containing 20 wt% starch.

In Figure 4.14, it was found that the flexural yield strength slightly decreased when compatibilizer contents in the blends were higher than 10wt% based on starch. However, the values of flexural yield strength for all compatibilized blends were higher than that of the uncompatibilized counterparts.

4.4.2.2 Flexural modulus

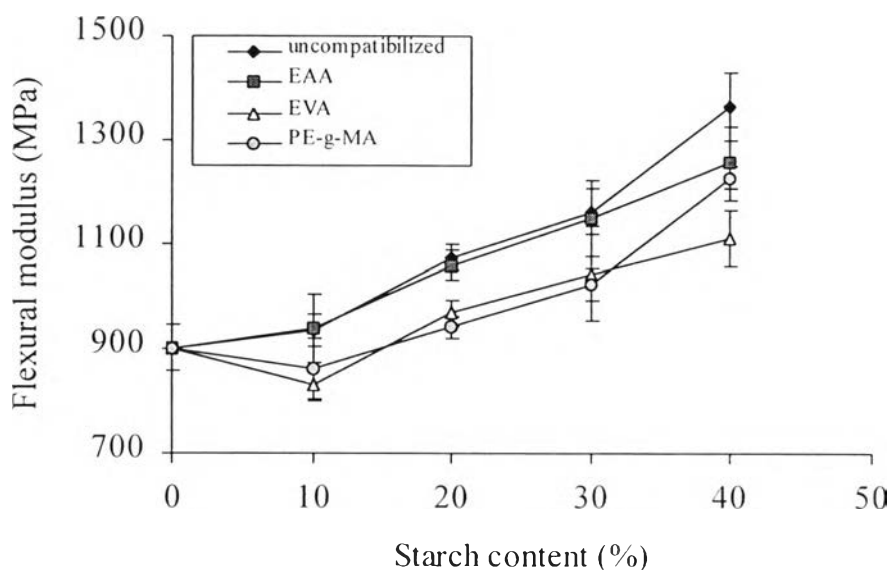


Figure 4.15 Effect of starch content on flexural modulus of uncompatibilized and compatibilized blends containing 10 wt% compatibilizer based on starch.

The effect of starch content on flexural modulus is shown in Figure 4.15. The flexural modulus of the uncompatibilized blends increased with an increasing of starch content. Similar to the increment of tensile modulus in the uncompatibilized blends as a function of starch content, this behavior occurs due to the high rigidity of starch particle as compared with HDPE and therefore the presence of starch particles in the blends could increase the flexural modulus of the blends (Katz, 1974).

The addition of the compatibilizer in the blends could not improve the flexural modulus, on the contrary, the compatibilizer made it worse. This occurs because the compatibilized blends had higher elongation than the uncompatibilized blends, so the compatibilized blends could stretch more easily when it was pressed (Katz, 1974).

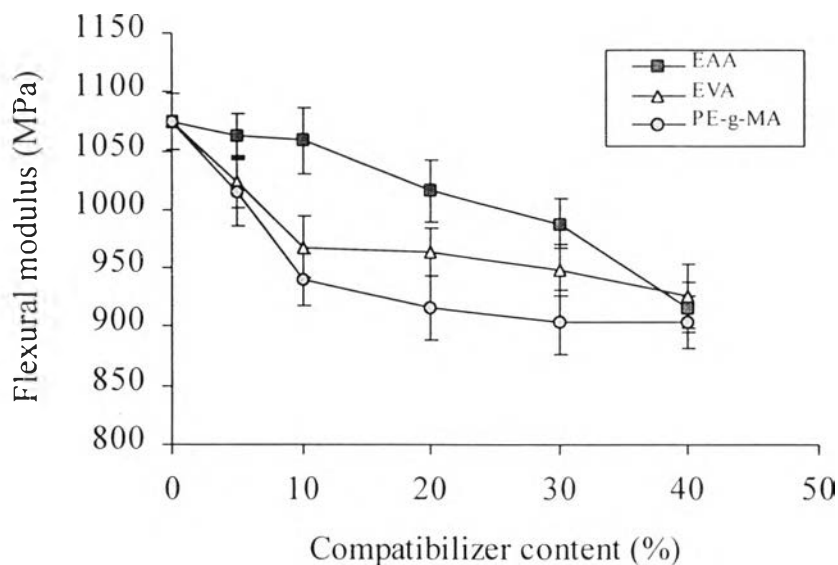


Figure 4.16 Effect of compatibilizer content on flexural modulus of compatibilized blends containing 20 wt% starch.

Moreover, the decreasing of flexural modulus was observed when the amounts of compatibilizers increased as shown in Figure 4.16. This can be concluded that the higher the amount of compatibilizer, the lower the flexural modulus.

4.4.3 Impact property

The impact property determined as functions of starch and compatibilizer contents was impact resistance.

4.4.3.1 *Impact resistance*

The relation between impact resistance and starch content is illustrated in Figure 4.17.

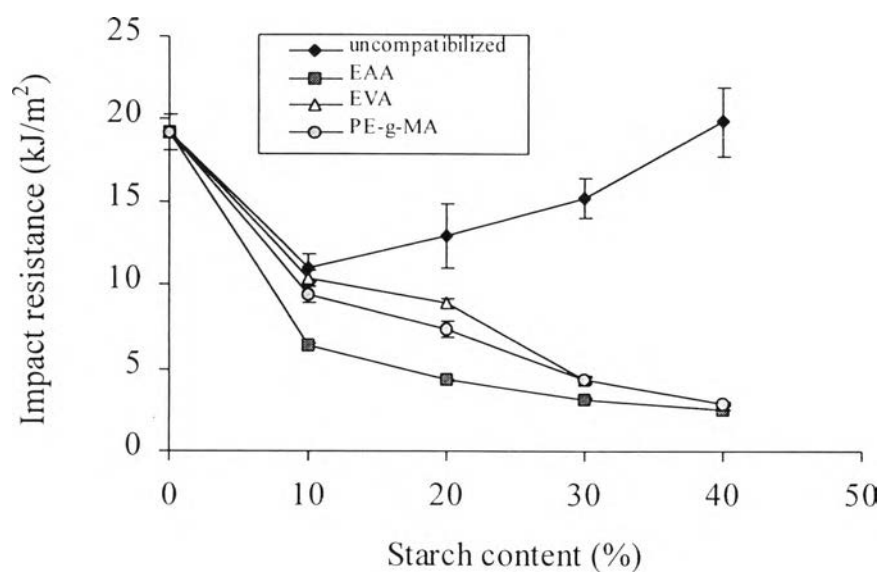


Figure 4.17 Effect of starch content on impact resistance of uncompatibilized and compatibilized blends containing 10 wt% compatibilizer based on starch.

The impact resistance of the uncompatibilized blends decreased as the starch content increased from 0 to 10 wt%. But when the starch content increased from 10 to 40 wt%, the blends showed the increment of impact resistance. This may be explained by crazing phenomena.

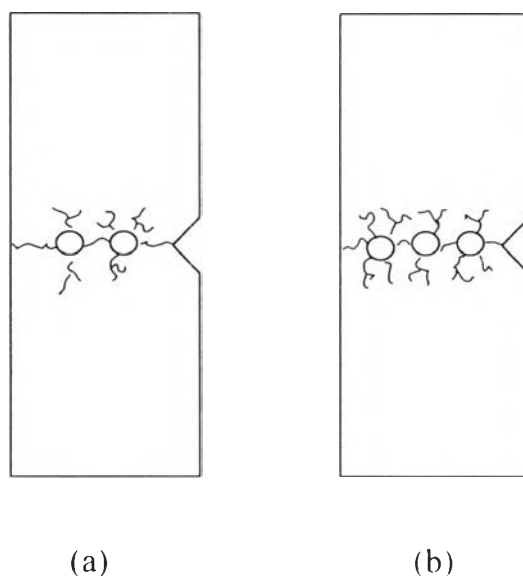


Figure 4.18 Schematic draws of crazing phenomena for the blends containing different amounts of starch: (a) low starch content and (b) high starch content.

As shown in Figure 4.18, crazes acted as load bearing entities that could dissipate energy and thus toughen the blends. At low starch content, there was a little crazing along the crack propagation path so that it resulted in the lower of impact resistance of the polymer blends. In contrast, for high starch content, the crack propagation might pass through many particles. The higher the energy dissipation from the craze, the greater the improvement in impact resistance.

Introducing of the compatibilizers into the blends caused the lower impact resistance. This might be due to the presence of the compatibilizer on the surface of starch particles so the craze could not occur leading to no energy dissipation, and the result is the decreasing of impact resistance.

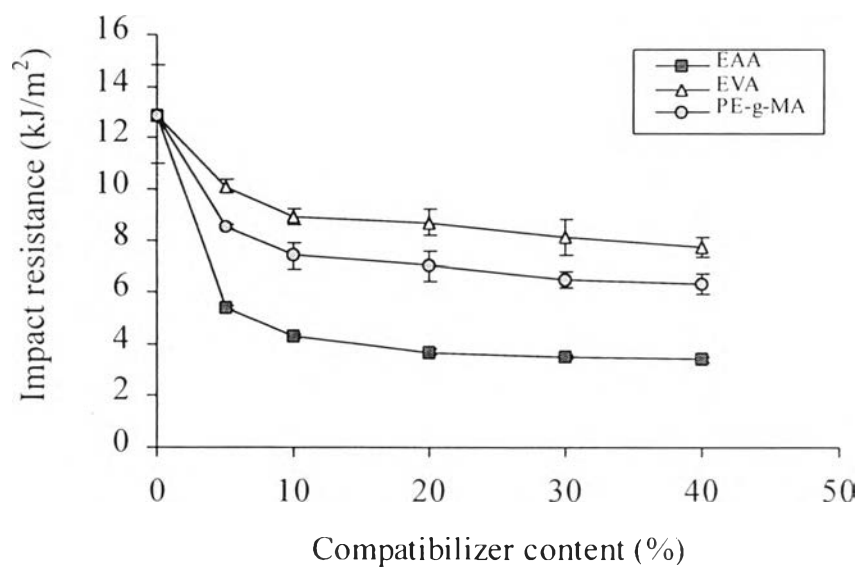


Figure 4.19 Effect of compatibilizer content on impact resistance of compatibilized blends containing 20 wt% starch.

Furthermore, the impact resistance decreased with an increasing of compatibilizer content. These blends showed the same trend of decrement in impact resistance for each compatibilizer as shown in Figure 4.19.

4.5 Water Absorption

Water absorption of the uncompatibilized and compatibilized blends was investigated as functions of immersion time and starch content.

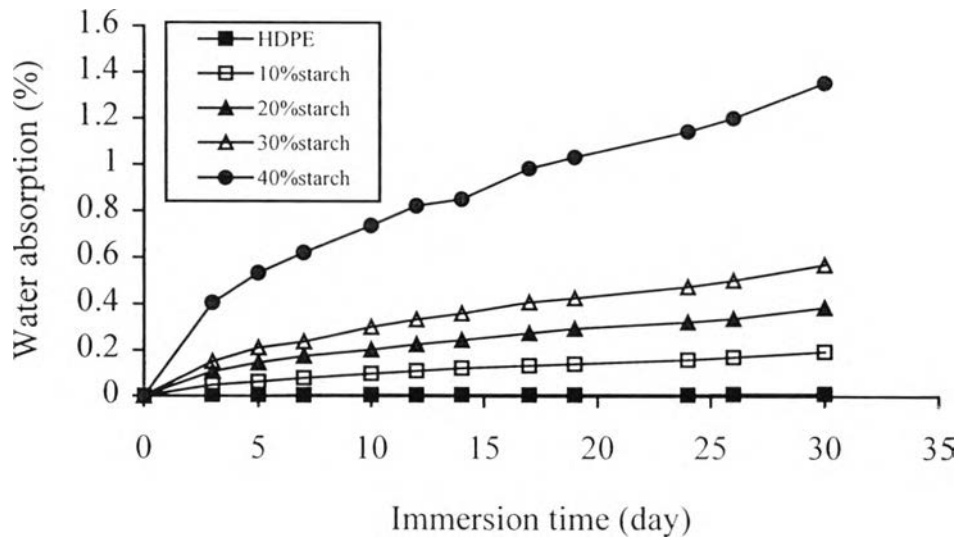


Figure 4.20 Water absorption of HDPE/tapioca starch blends as a function of immersion time at various starch contents.

Figure 4.20 exhibits water absorption of the HDPE/tapioca starch blends. It was found that water absorption of the blends increased with increasing starch content and immersion time. Since starch is a hydrophilic substance, the larger amount of starch results in higher water absorption of the blends.

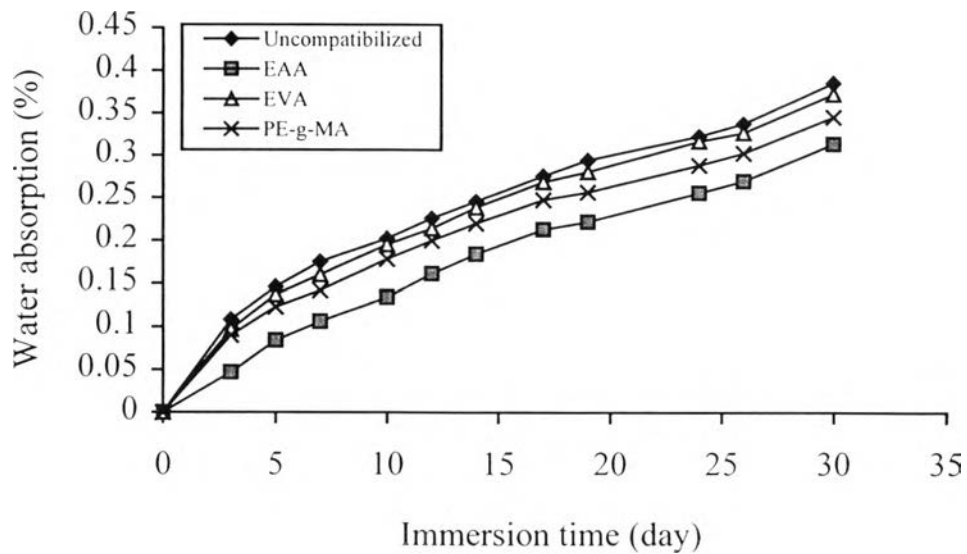


Figure 4.21 Water absorption of HDPE/tapioca starch blends containing 20 wt% starch and 10 wt% compatibilizer based on starch as a function of immersion time.

The slightly decreasing of water absorption of the blends was observed when the compatibilizers were added to the blends as shown in Figure 4.21. It is speculated that the retardation of water absorption was occurred by the covering of compatibilizer on the surface of starch particles (Willett, 1995).

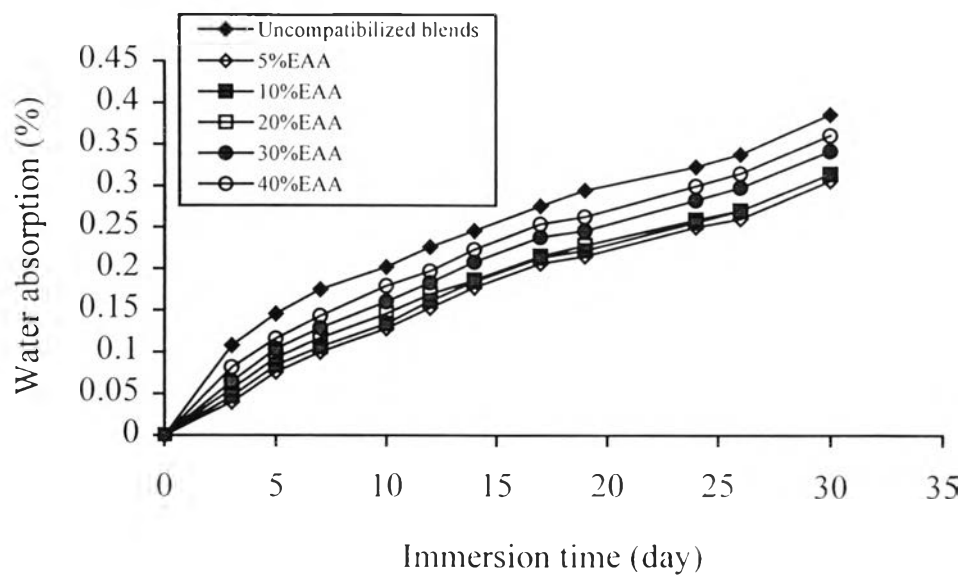


Figure 4.22 Water absorption of EAA compatibilized blends as a function of immersion time at various compatibilizer contents.

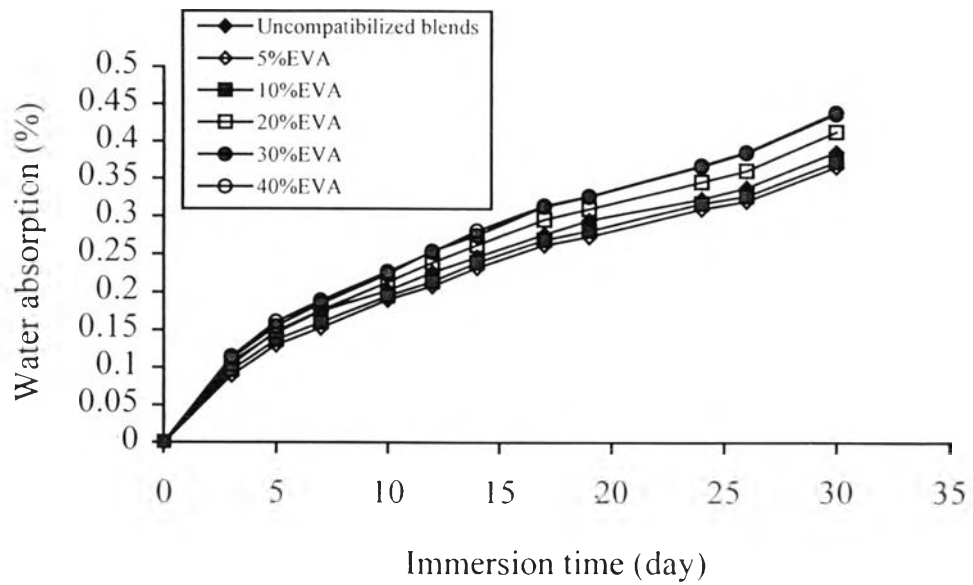


Figure 4.23 Water absorption of EVA compatibilized blends as a function of immersion time at various compatibilizer contents.

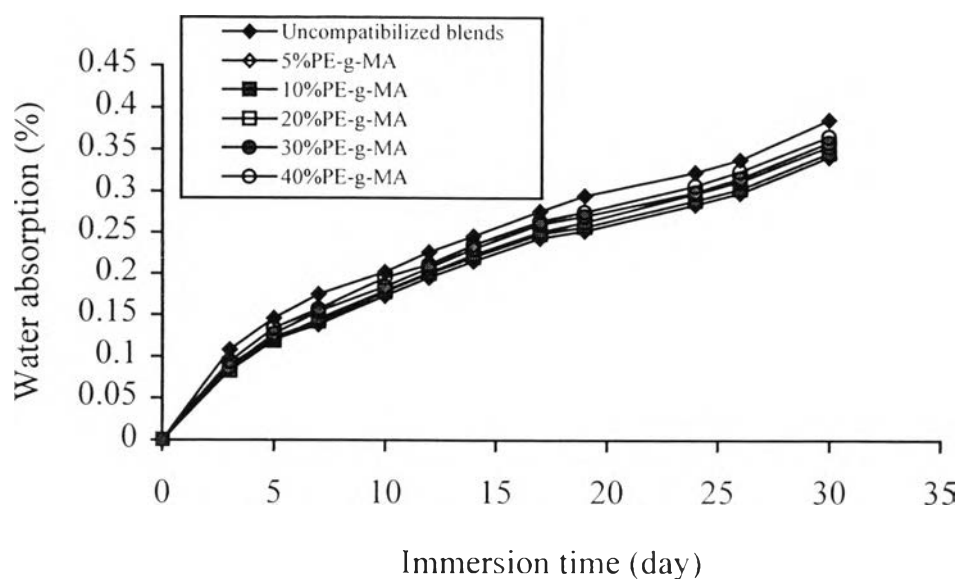


Figure 4.24 Water absorption of PE-g-MA compatibilized blends as a function of immersion time at various compatibilizer contents.

These three types of compatibilized blends showed the similar tendency in water absorption that water absorption of the blends increased with increasing compatibilizer content as shown in Figure 4.22, 4.23, and 4.24. This owing to the higher amount of polar groups in the blends when the compatibilizer content increased. The higher the formation of hydrogen bonds between polar groups of compatibilizer and water, the greater the water absorption property of the blends.