

CHAPTER IV

RESULTS AND DISCUSSION

4. The results of research

The experimental results were divided into two parts: part one was the study of the effect of processing parameters on ethylene vinyl acetate copolymer and starch blends and part two was the study of the physical properties of ethylene vinyl acetate copolymer and starch blends as biodegradable hot melt adhesives.

4.1 Effect of process parameters on EVA/modified starch blends as biodegradable hot melt adhesives

In its natural state, starch existed in a granular form. The size and shape of the starch granules was varied dependent on their origin. Native tapioca starch consisted of polygonal or round granules ranging from 5 to 35 μm in diameter.^[23] Starch behaves like a thermoplastic only under high shear and high moisture (>10%) conditions. At lower moisture content (<10%), the starch granules can be melted when subjected to high shear and temperature, but can be also led to the partial degradation of starch macromolecules, resulting in the lowering of molecular weight. When the native starch, at low moisture content, was blended with a functionalized synthetic polymer in a batch mixer, the resulting blend contains a mixture of molten polymer, molten starch, unmolten or partially melted starch granules and a small amount of graft copolymer of starch and polymer. The small concentration of graft copolymers formed during the blending can be significantly improved the properties of the blend. The extent of starch melting and degradation depended on the blending conditions.

The experimental results of the effect of the process parameters on EVA/modified starch blends as biodegradable hot melt adhesives were investigated by studying influences of the following independent variables: screw speed, melt temperature, torque and back melt pressure on tensile strength, tensile modulus and percentage elongation of blends. The results of the experiment from several process parameters and those of properties obtained for EVA/modified

starch blends were summarized in Table 4.1. The influence of each variable mentioned above was shown in Figures 4.1, 4.2, 4.3, respectively.

Table 4.1 Range of properties obtained for EVA/modified starch blends–based hot melt adhesives

<i>Composition</i>	<i>Tensile strength (Mpa)</i>	<i>Percentage elongation (%x10)</i>	<i>Tensile Modulus (MPax10)</i>
HMA(EVA)	6.2	21	2.3
HMA20/3(M. starch)	6.32	18.2	11
HMA20/3(N. starch)	6.52	11.2	12.2
HMA40/5	6.8	2.2	13.5
HMA50/3	7.0	1.4	15.3

Remark;

- *M. starch = the modified starch, N. starch = the native starch.*

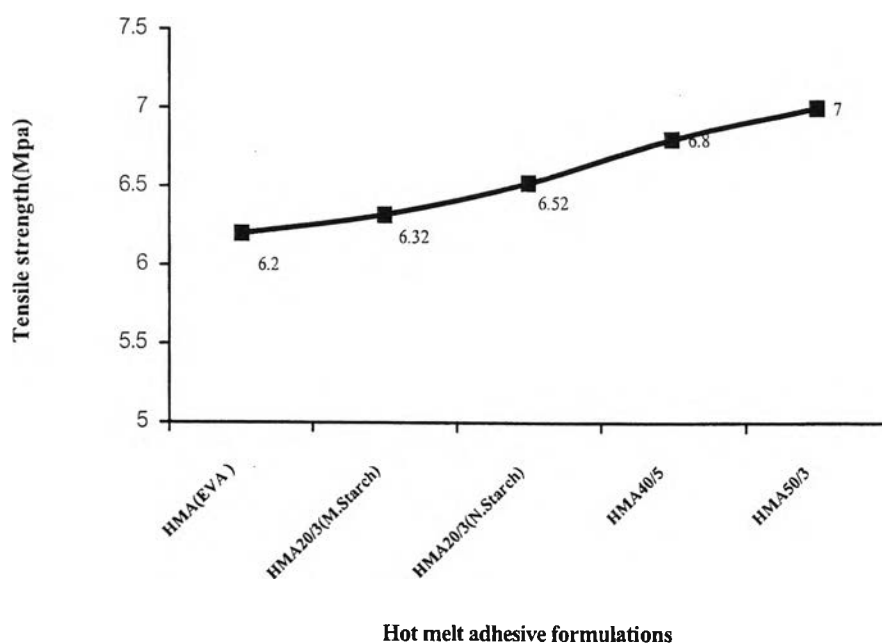


Figure 4.1 Effect of tensile strength obtained for EVA/modified starch blends–based hot melt adhesives

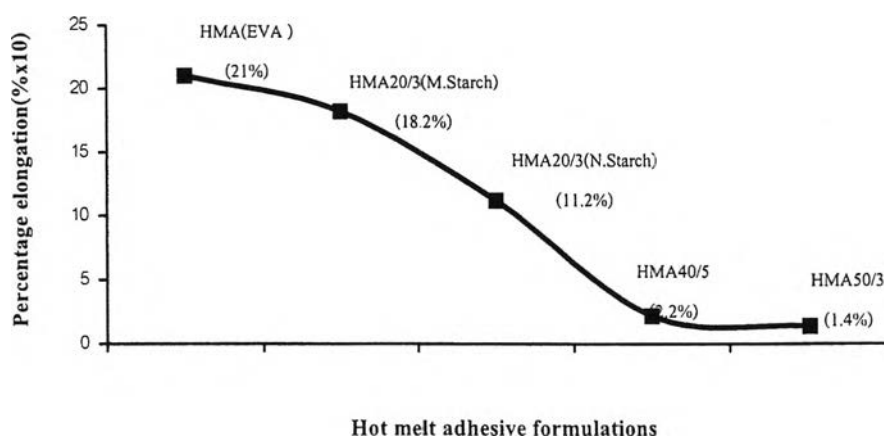


Figure 4.2 Effect of percentage elongation obtained for EVA/modified starch blends–based hot melt adhesives.

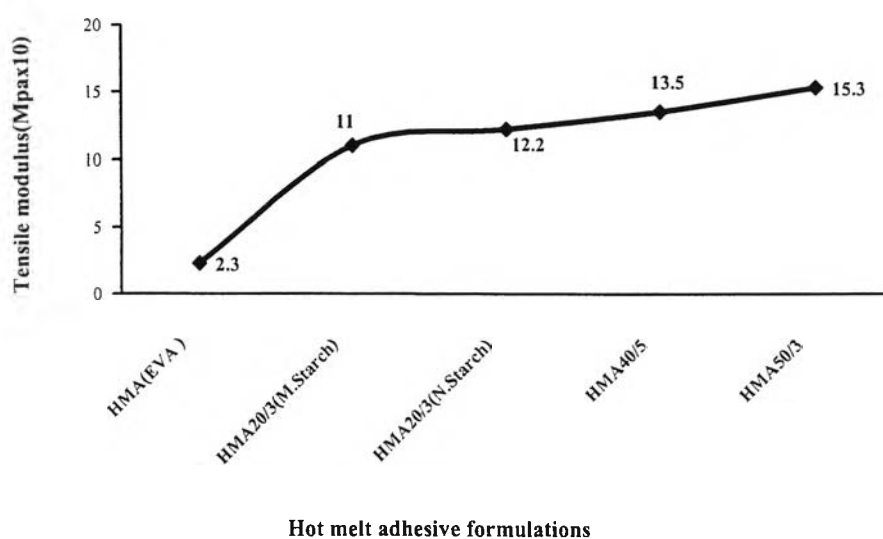


Figure 4.3 Effect of tensile modulus obtained for EVA/modified starch blends–based hot melt adhesives

A number of extrusion parameters were known to affect the properties of the end product. These include screw speed, torque, melt temperature, residence time and back melt pressure. In addition, for shear-sensitive materials such as starch, gate and nozzle or die

dimension also became important. A screening experiment was designed to study the effect of these variables using a two-level (high and low) value for each variable. The high and low end of screw speed were selected to evaluate the effect at the extreme processing condition variable from a 35 mm. screw diameter twin screws extruder. The barrel temperature was selected based on visual acceptance of the product because starch was a heat-sensitive material. Too high temperature led to a product that displayed decomposition. The color of product was brown, while at too low temperature, the unmelted material was left and led to a product with surface roughness. The barrel temperature was kept constant for each type of blend.

From Table 4.1, the corresponding values for the pure synthetic polymers hot melt adhesive, HMA (EVA) were also given. When starch was added, there was a dramatic reduction in the elongation at failure of these materials. It should be noted that these blends did not have any plasticizers, and the water content in the blend was approximately 10%. The addition of plasticizers had in general led to the increase of elongation. From Table 4.2 the properties of EVA/modified starch blends-based hot melt adhesive contained 20% of modified starch (HMA20/3) with several processing parameters were summarized.

Table 4.2 Effect of processing parameters on EVA/modified starch blends-based hot melt adhesive contained 20% of modified starch.

Properties/Conditions	Tensile strength (Mpa)	Percentage elongation (%)	Tensile modulus (Mpa)
Melt temperature	NS	S ↑	S ↓
Screw speed	NS	NS	S ↑
Back pressure	NS	NS	NS

Level of significance for statistical analysis was chosen at 5 %

S = statistically significant, NS = not statistically significant.

↑ *Indicates an increase with increase in independent variables,*

↓ *Indicates an decrease with increase in independent variables,*

The melt temperature affected the elongation and tensile modulus, but did not effect the tensile strength. A higher melt temperature gave a higher elongation, but lower in tensile modulus. The screw speed affected the tensile modulus but did not affect any other the properties. When HMA (EVA) was blended with the 20% of modified starch and extruded, the tensile strength was 10-20% increased, but the elongation at failure was a second that of corresponding EVA-based hot melt adhesive.

4.1.1 Mixing torque and melt temperature from Brabender's batch mixer.

The results of torque versus time and melt temperature versus time for EVA/modified starch blends-based hot melt adhesives containing 20 and 40% of modified starch contents from the batch mixer were shown in Figure 4.4 and 4.5. A reference blend with EVA/native starch-based hot melt adhesive and native starch was made at 20% and 40% contents. Typically, during blending in a batch mixer, as the polymer was introduced into the mixer, the temperature first was decreased and then increased rapidly to the set temperature of the mixer (see appendix A). During this time, the polymer started to melt forms a viscous mass and then, torque started to increase. As the temperature was increased due to the external heating, the polymer was completely melted. This was led to the decrease in torque that then either remains unchanged for the remainder of the experiment, due to reaction and / or degradation of polymer. Data collected for mixer speed of 50 rpm was applied for the following discussion.

During 2-4 min, the material was not homogeneous and still played under the process of melting and dispersing; hence, the later part of the data was considered for comparison. Torque was increased with the increasing in amount of starch in the hot melt adhesives. It could be explained that the increasing contribution of starch, which had a much higher viscosity. At the end of 15 min run, the torque for the EVA/modified starch-based hot melt adhesives containing 20% modified starch was about 1.25 Nm, while for a blends containing 40% modified starch was about 1.3 Nm. For EVA/native starch blends-based hot melt adhesives containing 20% and 40% of native starch, they were 0.5 Nm and 1.2 Nm, respectively. The hot melt adhesives containing 20% of modified starch, exhibited higher torque (1.25 Nm) compared to the hot melt adhesives containing native starch (0.5 Nm) with the same percentage of starch. This could be attributed to the increase in the viscosity of EVA/modified starch blends due to the interaction and / or the association between modified starch and EVA molecules.

A substantially higher torque of 0.6 Nm for the blend without any starch was increased to about 1.2 Nm when 20% of modified starch content was added. At 40% of modified starch was added, the observed torque was 1.5 Nm and the blend appeared extremely dry and powdery. As mentioned earlier, starch was melted and flowed only under high shear. At 80% of EVA content (20% of modified starch) - based hot melt adhesive, the viscosity of the EVA melt probably had enough torque to melt the modified starch and the molten starch further increased the torque. The comparison of non starch hot melt adhesives and the hot melt adhesives containing 20% of native starch, with increasing native starch content, the shear stress was considerably reduced probably due to slippage (evident from the reduced torque) that prevented the modified starch from melting. Thus, the higher torque for the blend made from modified starch compared to native starch, did not conclusively prove that a reaction was generated, but at least indicated some interaction with the modified starch did occur.

The melt temperature of the mixer was set at 150°C, the viscous heating increased the melt temperature above the set temperature. Figures 4.5 showed the increasing in the melt temperature with time for various hot melt adhesives. The increasing of starch content in the blend were increased the melt temperature in the blends. The melt temperature was depended on the viscosity and the heat of reaction. The viscosity was increased with increasing in the melt temperature. The hot melt adhesives containing 20% of starch content were displayed lower melt temperature (148°C) due to lower viscosity. For the hot melt adhesives containing 40% of starch content the temperature was reached 151°C (see appendix A). Furthermore, the actual torque for the hot melt adhesives containing modified starch would be higher than the hot melt adhesives containing native starch at the same given temperature.

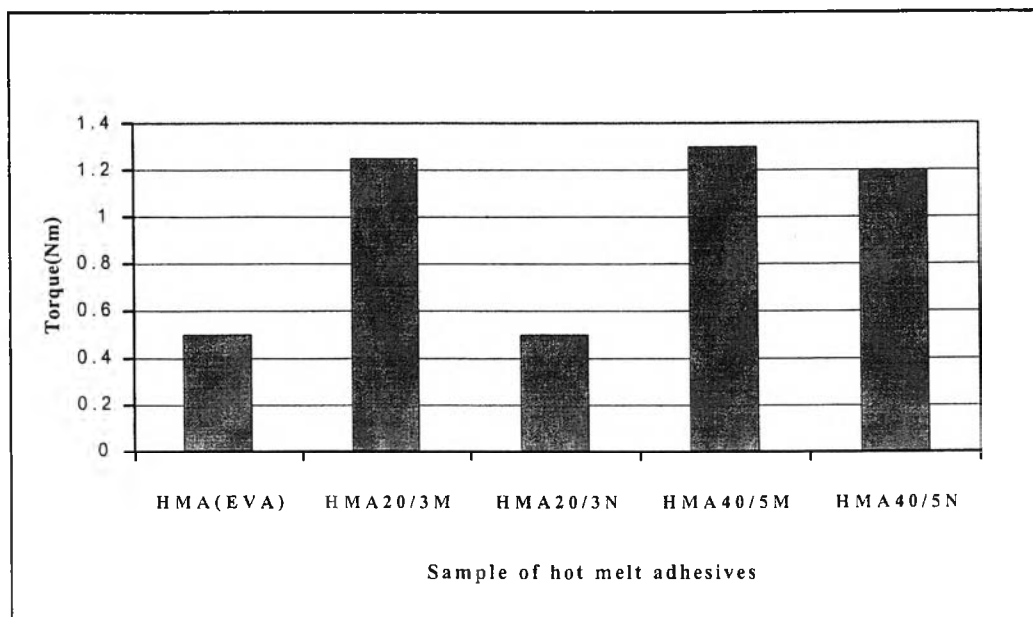


Figure 4.4 Torque versus time for EVA/modified starch and EVA/native starch blends – based hot melt adhesives in batch mixer.

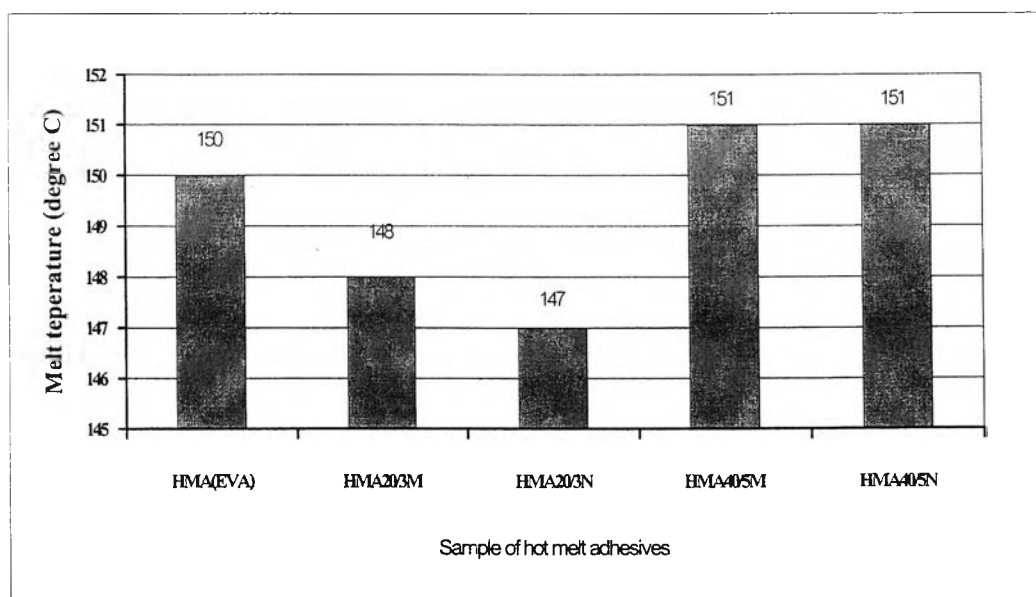


Figure 4.5 Melt temperature versus time for EVA/modified starch and EVA/native starch blends-based hot melt adhesives in batch mixer.

4.2 Physical properties of EVA/modified starch-based hot melt adhesives

Attempts to prepare the EVA/modified starch-based hot melt adhesives from the EVA/modified starch blends were not successful. This failure could be due to many repetitive extrusions that will make starch decomposed from excessive thermal degradation, resulting in a burnt material and color changed to dark yellow and rough in surface. The EVA/modified starch blends-based hot melt adhesives should be prepared by premixed all of dried raw materials together and then extruded with suitable process conditions.

4.2.1 Effect of percentage of modified starch on T-peel strength of hot melt adhesives

The T-peel strength of hot melt adhesives was depended on many factors: compatibility between based polymers and tackifiers, type and content of tackifiers^[7] and if wax was used in the composition, the weak boundary layer of wax and the increasing of rubbery response in the stick–slip region from wax would be considered.^[8] For this experiment, the T-peel strength with respected to percentage of modified starch was summarized in Table 4.3 and was shown in Figure 4.6 and Figure 4.7. The T-peel strength was decreased with the increasing in starch content in the blends (see Figure 4.6). The reason could be explained that the compatibility of the blends containing modified starch was decreased but still had higher than the blends containing native starch blends. These results indicated that some interaction was generated between EVA/modified starch blends, which was discussed before in the section of mixing torque and temperature. The T-peel strength of 10% of modified starch blends–based hot melt adhesives was 7–8 N/mm whereas 20% of modified starch blends was 4-6 N/mm. However, the T-peel strength could not be lower than that normally be applied for packaging application which kept the T-peel strength between 4–12 N/mm.^[6] So, the EVA/modified starch blends–based hot melt adhesive at 20% of modified starch was chosen for this work. The blends containing 30% of modified starch were limited due to T-peel strength and rough in surface. It could be explained that a large fraction of starch had still unmelted and the compositions were appeared more like a highly filled system.

Table 4.3 The T-peel strength of all formulations of EVA/modified starch blends-based hot melt adhesives.

Hot melt	T- peel strength (N/mm)			
	Test#1	Test#2	Test#3	Avg
HMA(EVA)	8.440	8.524	9.484	8.816
HMA10/1	6.159	6.669	6.896	6.575
HMA10/2	6.620	6.596	6.980	6.732
HMA10/3	6.732	6.753	6.820	6.768
HMA10/4	6.885	6.971	6.642	6.833
HMA10/5	6.787	6.759	6.655	6.734
HMA10/6	6.838	7.023	7.259	7.040
HMA10/7	6.883	6.998	6.955	6.945
HMA20/1	4.513	4.065	4.752	4.443
HMA20/2	4.623	4.698	4.888	4.736
HMA20/3 (M)	5.563	5.123	6.356	5.681
HMA20/3 (N)	2.335	2.562	2.928	2.608
HMA20/4	4.112	4.688	4.098	4.299
HMA20/5	4.596	4.280	5.060	4.645
HMA20/6	5.121	5.650	5.327	5.366
HMA20/7	4.865	4.236	4.865	4.655
HMA30/2	2.518	2.349	2.473	2.447
HMA30/3	2.259	2.349	2.630	2.413
HMA30/5	2.899	3.006	2.079	2.661
HMA30/6	2.529	2.574	2.666	2.590
HMA40/1	2.800	2.900	2.800	2.833
HMA40/3	1.990	1.826	1.226	1.681
HMA40/4	1.665	1.349	1.394	1.469
HMA50/1	0.698	0.158	1.349	0.735
HMA50/2	1.888	1.529	1.529	1.649
HMA50/3	1.529	1.349	1.259	1.379

In order to evaluate the differences in the magnitudes of T-peel strength between the native and acetyl modified group of starch blends, the experiments could be conducted with native starch, modified starch and their blends with 20% starch as in HMA20/3 formulation. When the same mass of both starch and other components were contained in the blends, the T-peel strength was 2.608 N/mm for native starch and 5.681 N/mm for modified starch. This 3.07 N/mm difference for the same starch content and other components could be indicated that some possible physical and/or chemical interactions were occurred between EVA and acetyl group of the modified starch.

4.2.2 Effect of EVA/rosin ester blends on viscoelastic properties

Rosin ester and EVA were also not completely compatible when the concentration was above 50% of rosin ester,^[8] but they were compatible at 40% rosin ester or less. For homogeneous blends (20 - 40% of rosin ester), the values of storage modulus (E') were higher than those of EVA. When the temperature lower than their glass transition temperature, the E' value of EVA/rosin ester blends containing 20-40% of rosin ester was became lower than that of EVA. For the blends containing 50% or more of rosin ester, heterogeneous blends, the cross over temperature was located at the higher than the glass transition temperature, corresponding to the rosin-rich phase. These finding suggested that when the temperature was higher than specific temperature (either the T_g of homogeneous blends or heterogeneous blends), tackifier acted as a plasticizer, diminishing EVA entanglements, thereby a lower storage modulus. As temperature was failed below this critical temperature, the tackifier acted as reinforcing filler, a higher storage modulus, thus higher T-peel strength. For this experiment, the DSC thermograms of EVA, rosin ester, polyethylene wax and EVA/Modified starch blends-based hot melt adhesive were shown in Appendix B. They revealed that the glass transition temperature of EVA was -18 to -20°C whereas the T_g of polyethylene wax was -120°C and T_g of rosin ester was 73°C. From the thermograms, some of samples showed unclear in T_g and relatively complicated T_m due to intrinsic nature and/or compositions of the sample, which were blended with starch. However, the thermograms of hot melt adhesives showed nearly the same pattern as T_m of polyethylene wax was 120°C separation from T_m of EVA at 70°C. However, the T_m of EVA was very closed to T_g of rosin ester which was difficult to interpret.

4.2.3 Effect of rosin ester on T-peel strength of EVA/modified starch blends–based hot melt adhesives

Figures 4.8, 4.9 and 4.10 illustrated the effect of rosin ester on T-peel strength of hot melt adhesives. The results indicated that the T-peel strength increased with increasing content of rosin ester in the blends and then decreased when 50% of rosin ester was contained in the blends. It could be explained that the phase separation was occurred between EVA and rosin ester that was reported by H. H. Shin, 1997^[8] and the effect of modified starch in the blends. From the results, it could be concluded that the rosin ester content should not more than 40% by weight.

4.2.4 Effect of polyethylene wax on T-peel strength of EVA/modified starch blends–based hot melt adhesives

The influence of wax on the viscoelasticity and peel adhesion of EVA-based hot melt adhesives was evaluated and reported by H. H. Shin.^[7] Wax did not affect the glass transition temperature of a homogeneous EVA/rosin ester blend. However, for a heterogeneous EVA/rosin ester blend, wax addition increasing the EVA-rich phase portion that gave higher rubbery response. The T-peel fracture energies of EVA/tackifier/wax blends bonded to adherent were controlled by two factors: (1) a weak boundary layer of wax, which had a deleterious effect on bonding, and (2) on the other hand, an increased rubbery response in the stick-slip region, which tended to strengthen joints.

In this experiment, the 10-20% of polyethylene wax was applied in order to reduce cost and melt viscosity. For the blends, which contained 10 and 30% of modified starch, the T-peel strength increased with the increasing of polyethylene wax (10 to 20%) as shown in Figures 4.8 and 4.10.



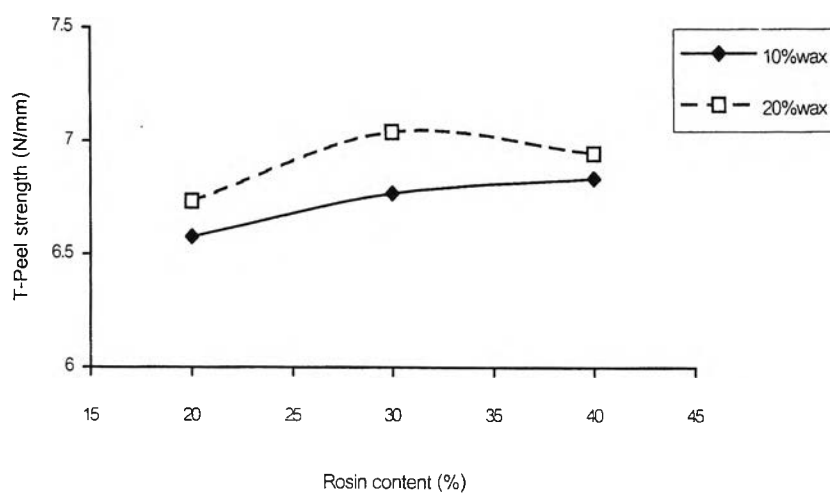


Figure 4.8 Effect of rosin ester on T- peel strength at 10% modified starch

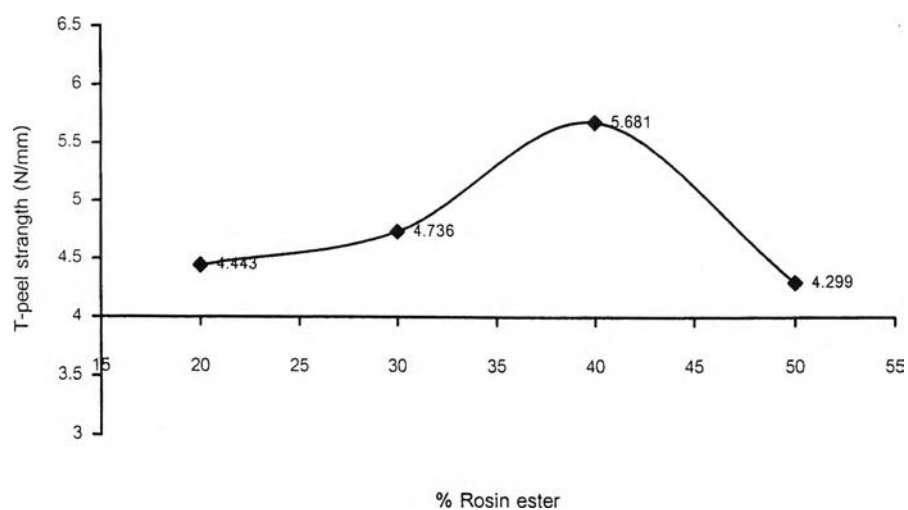


Figure 4.9 Effect of rosin ester on T-peel strength 20% modified starch 10 %polyethylene wax

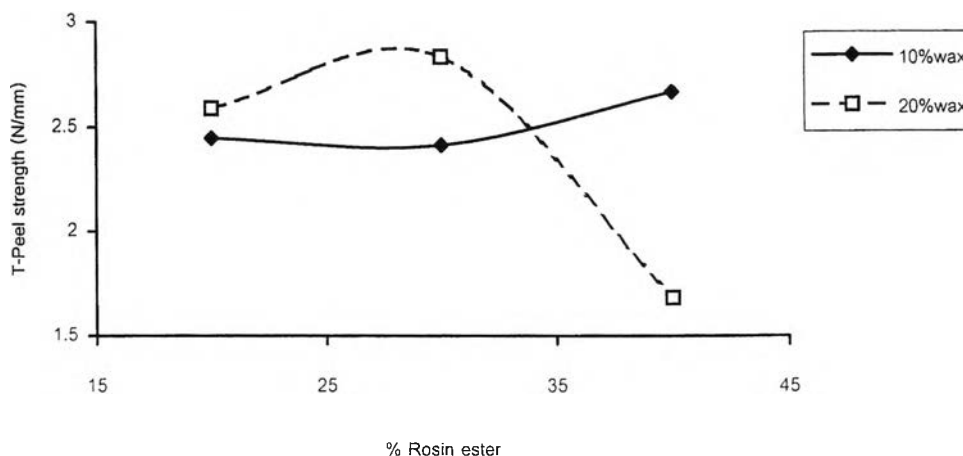


Figure 4.10 Effect of rosin ester on T-peel strength at 30% modified starch/EVA blends – based hot melt adhesives.

4.2.5 Viscosity of EVA/modified starch–based hot melt adhesives

The viscosity of each composition and the highest T-peel strength product at 20% of modified starch were shown in Table 4.4. The highest viscosity was EVA (>100,000 Cps at 150^o C). The viscosity of sample that gave the highest T-peel strength product (HMA20/3) was 46,870 Cps at 150^o C. The commercial EVA–based hot melt adhesives for packaging application had viscosity about 15,000 to 80,000 Cps at 150^o C depended on type of work. The two samples of the commercial EVA-based hot melt adhesives had viscosity at 17,400 and 33,050 Cps at 150^o C. The effects of modified starch on viscosity of EVA/modified starch blends–based hot melt adhesives were shown in Figure 4.11.

Table 4.4 The viscosity of raw materials and hot melt adhesives at several modified starch contents.

Materials	Viscosity	Unit
EVA (MV1055)	>100,000	Cps @ 150°C
Modified starch	768	Cps @ 45% Solution @ 90°C
Rosin ester (KOMOTAC, KF464S)	2,800	Cps @150 °C
Polyethylene wax (PE300)	500-700	Cps @150°C
HMA (EVA)	102,400	Cps @150°C
HMA 10/3	94,800	Cps @150°C
HMA 20/3	46,870	Cps @150°C
HMA 30/3	28,670	Cps @150°C
Commercial hot melt adhesive-based EVA (Sample A)	33,050	Cps @150°C
Commercial hot melt adhesive-based EVA (Sample B)	17,400	Cps @150°C

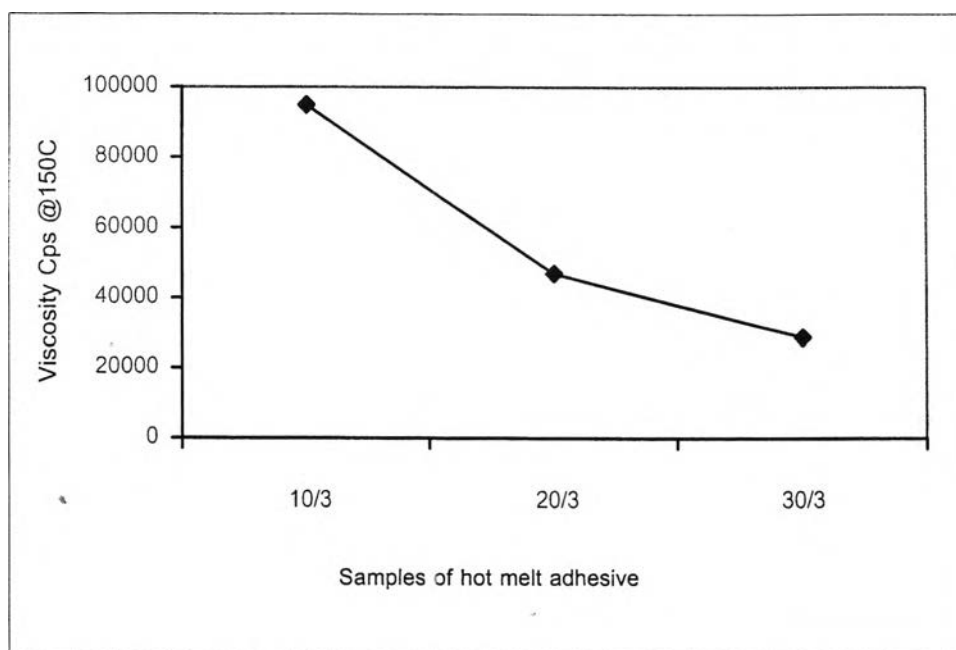


Figure 4.11 The effect of modified starch on viscosity of EVA/modified starch blends-based hot melt adhesives

The effect of modified starch on viscosity at various compositions was shown in Figure 4.11. The results indicated that the viscosity decreased with increasing starch content. It could be due to the low viscosity of starch compared with EVA. Furthermore, it was lower viscosity of EVA/modified starch-based hot melt adhesives compared to the corresponding EVA-based hot melt adhesives.

4.2.6 Scanning Electron Microscopy (SEM)

The SEM micrographs of hot melt adhesive were shown in Figures C1-C25. The islands (lighter, droplet or white spots) and sea (slightly gray area) had seen for each composition.

Sample preparations

Because of their different in objectives, the samples were prepared to SEM studying by two methods. The first method used the sputtering technique for 100 seconds coated on samples 1-3. The second method, the samples were fractured in liquid nitrogen and also were coated with gold in the same way.

Table 4.5 The details of each sample for SEM analysis.

Sample	Composition		
	Modified starch %	Rosin ester %	Polyethylene wax %
1.(HMA10/2)	10	30	10
2.(HMA10/3)	10	40	10
3.(HMA10/4)	10	50	10
4.(HMA10/6)	10	30	20
5.(HMA20/2)	20	30	10
6.(HMA20/3)	20	40	10
7.(HMA20/4)	20	50	10
8.(HMA20/5)	20	20	20
9.(HMA20/6)	20	30	20
10.(HMA40/3)	40	20	10

Table 4.6 The objective to each sample for SEM analysis.

Samples	Objective
1-3	To compare the effect of variation of rosin ester at 10% modified starch
1,4	To compare the effect of variation of polyethylene wax at 10% modified starch
5-7	To compare the effect of variation of rosin ester at 20% modified starch
5,9	To compare the effect of variation of polyethylene wax at 20% modified starch
2,6	To compare the effect of variation of modified starch
10	To study morphology

SEM micrographs of EVA (MV1055) were shown in Figures C1 and C2 (see appendix C). with different degree of magnification. The particles had irregular shape with 100-600 μm in size.

Figures C3 and C4 were SEM micrographs of rosin ester and polyethylene wax (PE300), respectively. They illustrated that the surfaces were covered with a little flake.

Figures C5-C10 were SEM micrographs of HMA 10/2, 10/3 and 10/4. Each sample consisted of 10% of modified starch but changed the amount of rosin ester at 30, 40 and 50%, respectively. As shown in Figures C5, C7 and C9, higher content of rosin ester made modified starch granules more compatible with their matrix. The starch granules of HMA 10/4 (Figure 4.20) were closed to their matrix.

Figures C11 and C12 were SEM micrographs of HMA10/6. This sample was compared to HMA10/2 (Figures C5 and C6) for studying the effect of percentage variation of wax. It could be seen clearly that morphology of 20% polyethylene wax was more compatible than 10% polyethylene wax.

Figures C13 – C18 were SEM micrographs of HMA20/2, 20/3 and 20/4. All modified starches of each sample showed that the granules had good compatibility.

To study the effect of percentage variation of polyethylene wax in the sample of starch at 20% and rosin ester 30% content, HMA20/2 was compared to HMA20/6. Morphology of both (Figures C13- C14) was not different by observation under SEM.

The effect of the variation of modified starch could be approached by comparing HMA10/3 with HMA20/3. As shown in SEM micrographs, Figures C7 and C8, more modified starch granules content in matrix was seen in HMA20/3 than in HMA10/3 (Figures C15 and C16).

For HMA40/3, SEM micrographs showed that all granules had good compatibility with their matrix (Figure C24).

4.2.7 Biodegradation testing

All samples of hot melt adhesive were facilitated the growth of fungi. The fungus growth could be seen with visual observations after 4-7 days. Fungus kept growing rapidly with time. The rate of fungus growth increased with the amount of starch in the hot melt adhesives. Starch that includes in the hot melt adhesives, being a natural polymer, could be readily used as a carbon

source by the fungus. On the other hand, a synthetic polymer-based hot melt adhesive did not serve as an efficient carbon source. Therefore, in the blends, starch component was degraded and used up by the fungi, leaving EVA-based hot melt adhesive largely unaffected. As the starch content was increased, the starch becomes a continuous phase in the blends and could be accessed by the organisms. Furthermore, during extrusion process, starch played under word that called “cooking” due to high shear and led to greater amounts of gelatization and degradation compared to the other simple mixing. Thus, the gelatization and thermal degradation was further supported the faster fungus growth. At very low starch contents, the starch might be encapsulated in the synthetic polymer thereby made it difficult for the organisms to access and use it as carbon source. In such a case the fungus growth would be slow. The control sample, made from pure EVA-based hot melt adhesive did not show any fungus growth.