

CHAPTER III

EXPERIMENTAL

3.1 Raw materials and chemicals

3.1.1 Ethylene vinyl acetate copolymers (EVA)

The ethylene vinyl acetate copolymer that was used in this experiment was 28% of vinyl acetate contents called MV1055 was obtained in powder form from Thai Petrochemical Industry Co., Ltd. Its specifications were shown in Table 3.1.

Table 3.1 The specifications of EVA (MV1055).

| Properties | Value |
|--|-------------|
| Melt flow index 190/216, g/10min | 7-9 |
| Density, g/cm ³ | 0.951-0.955 |
| Vinyl acetate content, % | 26-30 |
| Variation | < 30 |
| Tensile strength at yield, N/mm ² | > 15 |
| Tensile strength at break, N/mm ² | > 13 |
| Elongation at break, % | > 700 |
| Bulk density, g/cm ³ | 0.50-0.54 |
| Hardness shore D | 23-27 |
| Dielectric constant | 2.3 |
| Dielectric strength, KV/mm | 35 |
| Melt viscosity, Cps at 150 ^o C | >100,000 |

3.1.2 Rosin esters

Rosin esters as tackifiers were studied and reported in 1997 by H. H. Shin and G. R. Hamed. Rosin esters had better compatibility with EVA than the C5-C9 resins. The bond strength of tackified EVA to adherence depends not only on compatibility, but also on viscoelastic properties and the glassy C5-C9 rich-domains acted as reinforcing filler, resulting in a higher storage modulus. A higher T-peel strength, resulting in a higher storage modulus meaning that rosin esters and C5-C9 resins could also be used to hot melt adhesives. In this experiment, rosin ester was supplied by Komo Chemicals Co., Ltd. The commercial name KOMOTAC™ KF464S was a granular form, light color, low order modified gum rosin pentaerythriol ester with high melt viscosity. Its specifications were shown in Table 3.2.

Table 3.2 The specifications of rosin ester (KOMOTAC™, KF464S).

| Properties | Value |
|-----------------------------------|-------------|
| 1. Softening point, R&B, °C | 108-115 |
| 2. Color, Gardner (solid) | 3-5 |
| 3. Acid number, mgKOH/g, max | 20 |
| 4. Specific gravity, 20 °C | 1.08 |
| 5. Melt viscosity, Cps. at 150 °C | 2,800-3,000 |
| 6. Ash (as weight), %, max | 0.1 |
| 7. Flash point, °C | 260 |
| 8. Molecular weight | 1,350 |

3.1.3 The functional group modified starches

Modified starch was supplied from Tapioca Development Corporation Company Limited. The hydroxyl group was modified to acetyl group as in EVA, therefore, it had better compatibility with EVA and rosin which resulting in a higher T-peel strength. The modified starch's specifications are shown in Table 3.3.

Table 3.3 The specifications of acetyl group modified starch.

| Properties | Value |
|---|-------|
| 1. Moisture content, % | 11.80 |
| 2. pH (10% solution) | 7.04 |
| 3. Brookfield viscosity, Cps.(RVT 20 rpm) at 45% solution, 90 ^o C | 768.0 |
| 4. Degree of substitution(acetyl group) | 0.049 |

3.1.4 Polyethylene waxes

The wax component was presented to reduce viscosity mean that application temperatures were raised to get an adhesive to flow, and this may result in unwanted thermal degradation. Wax also acted as an extender and a wetting agent and in some compositions as a set time improver. For many applications, it was necessary to employ a relatively expensive synthetic wax to achieve a desired combination of properties. In this experiment, the polyethylene wax called PE300 was used and obtained from Thai Petrochemical Industry Public Company Limited. Its specifications were shown in Table 3.4.

Table 3.4 The specifications of polyethylene wax.

| Property | Method | Value |
|-----------------------------|-------------|-------------|
| Color appearance | - | Pale- white |
| Viscosity at 140 °C, Cps | ASTM D-445 | 301-500 |
| Contamination, No | TPI method | < No.3 |
| Drop melting point, °C | ASTM D-127 | 115-120 |
| Density at 25 °C | TPI method | 0.9-0.93 |
| Acid number, mgKOH/g | ASTM D-1386 | <0.03 |
| Penetration hardness, 0.1mm | ASTM D-1321 | 3-5 |
| Average particle size | TPI method | |
| - Flake form, mm | | <15 |
| - Powder form, micron | | <700 |
| Yellow index, - | TPI Method | <10 |

Table 3.4 (Continued)

| Property | Method | Value |
|---------------------|------------|-------|
| Volatile content, % | TPI method | <5 |
| Ash content, % | TPI method | <0.5 |

3.1.5 Antioxidants

Antioxidant was used for the reduction of thermal degradation of hot melt adhesives during process. In this experiment, BHT was used and it was obtained from Yoshitomi Fine Chemical Co., Ltd.

3.2 Raw materials premixing

1. Hand premixing all of compositions including EVA powder, modified starch, polyethylene wax, rosin ester and antioxidant were done by increasing the content of modified starch from 10 20 30 40 and 50 % whereas polyethylene wax from 10 to 20% before fed into the mixer and extruder.
2. Preheated the extruder about 1.5 – 2 hours at suitable barrel temperature, cleaned extruder screw and barrel with EVA.
3. The premixed raw materials were introduced directly to the feeding zone of mixer and extruder with continuous feeder.

3.3 Blending preparation

Blends were prepared in a batch mixer and in extruder. The batch mixer was equipped with roller blades (C. W. Brabender Instruments Inc., South Hackensack, NJ) and connected to a variable speed motor through a torque meter. EVA, modified starch, rosin ester and polyethylene wax were dried in a vacuum oven at 90^oC overnight. All compositions of hot melt adhesive were mixed and introduced into the mixer that preheated to 180^oC. To produce hot melt adhesives, the experiments contained amount of starch in the blend was 0, 20, 40, 50% by weight and only hot melt adhesive that contained 20% of starch was compared between modified starch and native

starch. For each formulation, the mixer speed was set at 50 revolutions per minute (RPM) and mixing time was 15 minutes. During the blending process, the torque and melt temperature were recorded continuously and stored in a microcomputer (IBM PC / AT). The mixer was quickly dismantled and the material was removed with the help of a spatula.

The laboratory scale extruder that used for the blends was co-rotating twin screws extruder (Leistritz ZSE35GL, Germany). The screw diameter was 35 mm., length to diameter ratio was 20:1 as shown in Figure 3.1. The extruder was divided into ten zones of electrical heating device with cooling air. The barrel temperature was set from zone no. 2 to 10 of heating zones at 90 120 125 135 145 145 150 150 and 150 °C (zone no.1 was always closed). The temperature was measured by thermocouple with temperature controller. The materials were extruded through 4 x 2.5 mm. of capillary dies and cooled down by cooling air, the physical properties were determined.

For this set of experiments, the moisture content of the starch was 10% to enhance processability. Only 10 20 30 40 and 50 % modified starch were made in extruder. At higher starch content (>60%), the pressures and torque were limited by the manufacture safety limitation. The minimum residence time for all cases was approximately 45 seconds.

Starches often had limited compatibility with rubber and to processing under heat. As this work, it was not successful that two times processed for starch blending with EVA in extruder. When blend of EVA/starch was done again with rosin and wax to produce of EVA- based hot melt adhesives, starch was thermal degraded during heating process. Hence, all of components were premixed together before fed into feeding zone of the extruder. All of hot melt adhesive formulations were shown in Table 3.5.

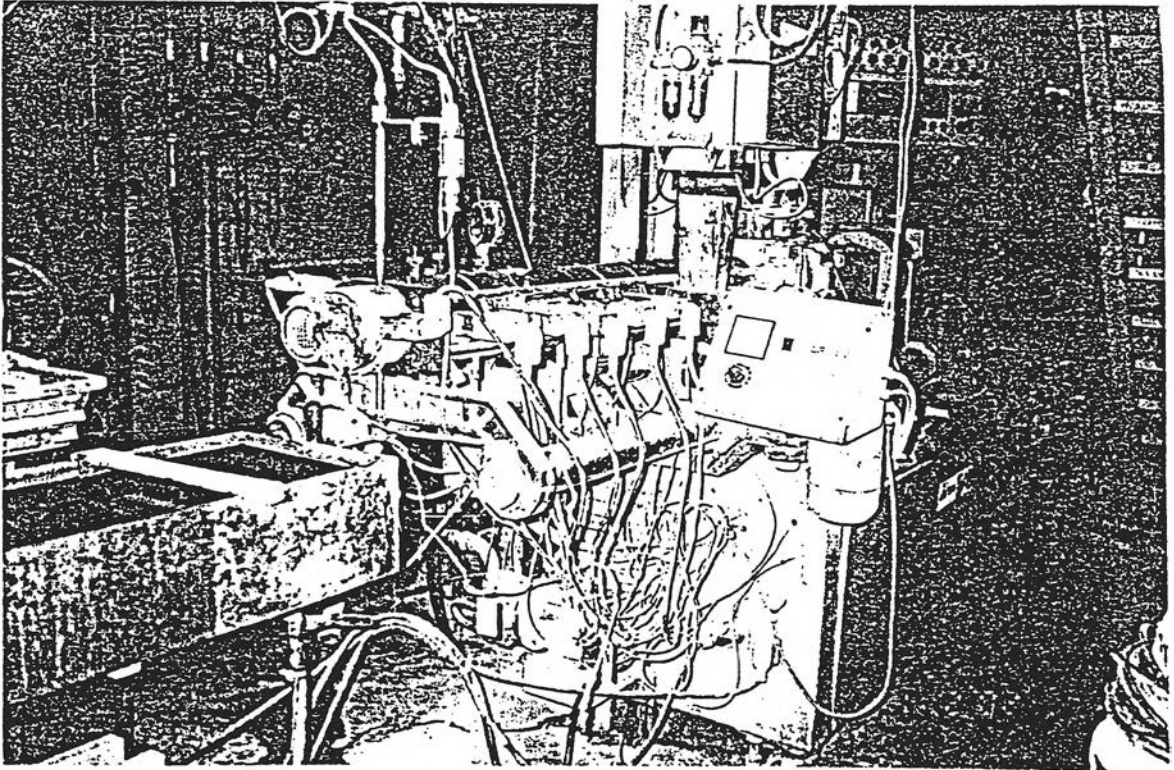
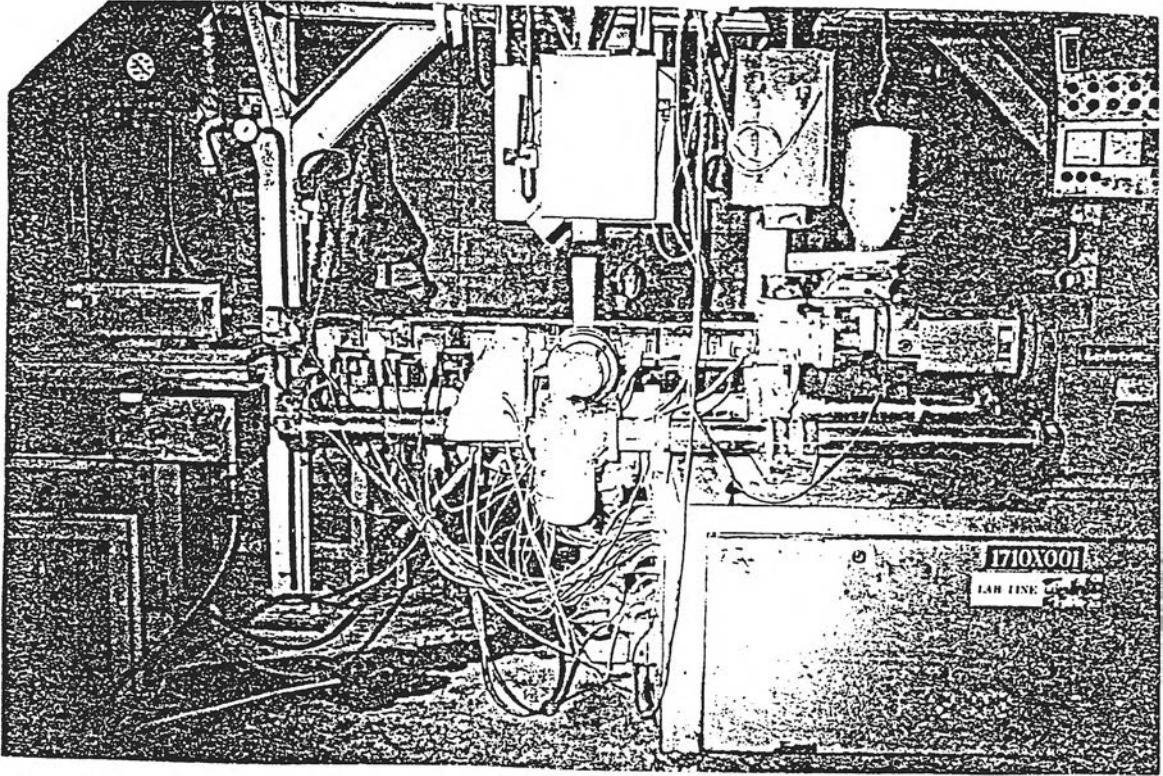


Figure 3.1. The Leistritz ZSE 35 GL twin screw co-rotating extruder with accessories to conversion of mixed raw materials to finished products

The technical data of co-rotating twin screw extruder are as following;

| | |
|--|--------------------|
| Brand name..... | Leistritz, Germany |
| Model..... | ZSE 35 GL |
| Screw diameter..... | 34 mm |
| Center distance of screw..... | 30 mm |
| Flight depth..... | 4 mm |
| Number of heating zones..... | 9 |
| Heating bands without air cooling..... | 1 |
| Heating bands with air cooling..... | 8 |
| Heating/cooling unit..... | 0 |
| Total heating power..... | 12.6 kW |
| Permissible pressure during continuous Operation..... | 250 bar |
| Feeding area..... | Water cooling |
| Permissible pressure for temporary Over loads..... | 350 bar |
| Max. permissible temperature..... | 400 °C |
| Drive speed..... | 10.5 kW |
| Motor speed..... | 2200 rpm |
| Ratio of motor speed..... | 1 : 50 |
| Reduction gear..... | i = 1.3 |
| | Conversion from |
| | Low to high speed |
| Permissible torque, co-rotating per screw shaft..... | 123 Nm |
| Screw Speed, Co-Rotating..... | 8 - 390 rpm |
| B 10 Rating of Bearing..... | 20.000 Bh |

Table 3.5. The EVA/modified starch blends–based hot melt adhesive compositions

| Hot melt sample code | Hot melt composition | | | | |
|-------------------------|----------------------|----------------------|------------|-------------|-----------|
| | EVA % | Modified starch % | Rosin % | PE wax % | AO phr |
| HMA(EVA) | 40 | 0 | 45 | 15 | 0.25 |
| HMA10/1 | 60 | 10 | 20 | 10 | 0.25 |
| HMA10/2 | 50 | 10 | 30 | 10 | 0.25 |
| HMA10/3 | 40 | 10 | 40 | 10 | 0.25 |
| HMA10/4 | 30 | 10 | 50 | 10 | 0.25 |
| HMA10/5 | 50 | 10 | 20 | 20 | 0.25 |
| HMA10/6 | 40 | 10 | 30 | 20 | 0.25 |
| HMA10/7 | 30 | 10 | 40 | 20 | 0.25 |
| HMA10/8 | 20 | 10 | 50 | 20 | 0.25 |
| HMA20/1 | 50 | 20 | 20 | 10 | 0.25 |
| HMA20/2 | 40 | 20 | 30 | 10 | 0.25 |
| HMA20/3 | 30 | 20 | 40 | 10 | 0.25 |
| HMA20/4 | 20 | 20 | 50 | 10 | 0.25 |
| HMA20/5 | 40 | 20 | 20 | 20 | 0.25 |
| HMA20/6 | 30 | 20 | 30 | 20 | 0.25 |
| HMA20/7 | 20 | 20 | 40 | 20 | 0.25 |
| HMA30/1 | 40 | 30 | 20 | 10 | 0.25 |
| HMA30/2 | 30 | 30 | 30 | 10 | 0.25 |
| HMA30/3 | 20 | 30 | 40 | 10 | 0.25 |
| HMA30/4 | 30 | 30 | 20 | 20 | 0.25 |
| HMA30/5 | 20 | 30 | 30 | 20 | 0.25 |
| HMA30/6 | 10 | 30 | 40 | 20 | 0.25 |
| HMA40/1 | 40 | 40 | 10 | 10 | 0.25 |
| HMA40/2 | 25 | 40 | 15 | 20 | 0.25 |
| HMA40/3 | 20 | 40 | 20 | 10 | 0.25 |
| HMA40/4 | 10 | 40 | 20 | 30 | 0.25 |

Table 3.5. (Continued)

| Hot melt sample code | Hot melt adhesive composition | | | | |
|-------------------------|-------------------------------|----------------------|------------|-------------|-----------|
| | EVA % | Modified starch % | Rosin % | PE wax % | AO Phr |
| HMA40/5 | 20 | 40 | 30 | 10 | 0.25 |
| HMA40/6 | 15 | 40 | 30 | 15 | 0.25 |
| HMA40/7 | 35 | 40 | 10 | 15 | 0.25 |
| HMA50/1 | 30 | 50 | 10 | 10 | 0.25 |
| HMA50/2 | 20 | 50 | 20 | 10 | 0.25 |
| HMA50/3 | 10 | 50 | 20 | 20 | 0.25 |
| HMA10/5 | 50 | 10 | 20 | 20 | 0.25 |

3.4 Molding

Products of hot melt adhesives were molded for tensile testing by compression molding machine. The platens of the press were heated to 180°C. The mold cavity was filled with the material, covered with the top plate, and placed between the two platens of the press. After 5 min, the platens were slowly pressed together until the force was 10 tons. Pressure was applied for a period of 10 min, after which the platens were cooled to 50°C, the pressure relaxed, and the mold removed from the press.

3.5 Tensile strength

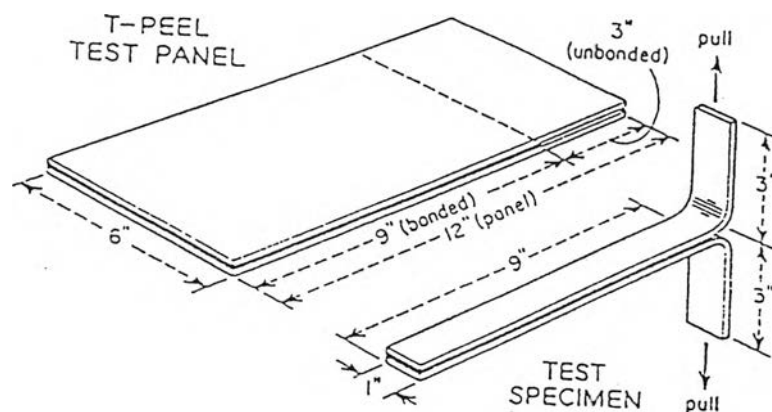
For each composition of hot melt adhesives, the sample was molded using a standard dog bone shaped mold as per the specifications of ASTM D-638 standard test method. The cross-head speed was 3 mm/min and stress was the measured force per unit cross – sectional area of the sample. Percentage of elongation is the ratio of the change in the gauge length at any time to the original gauge length of the sample. The gauge length at any time was calculated from the time elapsed since the start of the test and the cross – head speed. Tensile strength was determined from the initial linear portion of the stress – strain curve. Samples were conditioned at room

3.6 T-peel strength

The T-peel strength was measured according to ASTM D-1876 standard test method. Most of hot melt adhesives were dried in a vacuum oven at 90°C overnight before testing. Laminated test panels (see Figure 3.2) were consisted of two packaging paper boxes and bonded together with the hot melt adhesives. The prepared test panels were cut at 152 mm (6 in.) wide by 305 mm (12 in.) long and bonded only over approximately 241 mm (9 in.) of their length. The test panels of these same dimensions were cut from larger fully lamination panels. The specimens were treated for 7 days at a relative humidity of $50 \pm 2\%$ at $23 \pm 1^\circ\text{C}$ and then clamped the bent, unbonded ends of the test specimen in the test grip of an Instron Universal testing machine. Applied the load at a constant head speed of 254 mm (10 in.)/min. and determined the peel resistance over at least a 127 mm (5 in.) length of the bond line after the initial peak. Peel energy was determined from the peel force by the following equation:

$$G = 2F / b$$

Where G was the peeling energy (N/mm); F was the average force required peeling a specimen apart (N); and b was the width of the test specimen (mm).



Metric equivalents

| | | | | | |
|-----|----|----|-----|-----|-----|
| in. | 1 | 3 | 6 | 9 | 12 |
| mm. | 25 | 76 | 152 | 229 | 305 |

Figure 3.2 Test panel and test specimen for T-peel strength

3.7 Viscosity

The viscosity was determined according to ASTM D-3236 standard test method. The samples with only 10-30% of starch content in hot melt adhesives were investigated.

3.8 Differential Scanning Calorimetry (DSC)

Sample size of about 10 mg, was used to measure the glass transition temperature of EVA, rosin ester, polyethylene wax and product of EVA/modified starch blends – based hot melt adhesives. Temperature was increased from room temperature to 100°C at 10°C/min. Then, samples were quenched to room temperature and rerun from -50 to 150°C at 10°C/min. under nitrogen atmosphere.

3.9 Scanning Electron Microscope (SEM)

The fractured samples obtained after tensile testing were cut at about 2-3 mm. below the fracture surface and stuck to aluminum stubs. The samples were then coated with an Au/Pd alloy by vapor deposition and observed under a Hitachi 80 electron microscope.

3.10 Biodegradation testing

The degradation could be seen with visual observation after inoculation. The hot melt adhesive samples of HMA(EVA), HMA20/3 and HMA40/3 were placed in sterile petri dishes containing solidified nutrient salt agar. A mixed fungus spore solution was prepared and filled into in sterile petri dishes. The covered petri dishes were sealed with a paraffin film. The only carbon source for the growth of the fungi was from the samples.