

CHAPTER III

EXPERIMENT

In the study of glass fiber reinforced PVC/SAN composites, the effects of glass fiber and coupling agents on the mechanical properties of PVC/SAN were studied. The problem of compatibility between glass fiber and polymer blend can be overcome by improving with the traditional coupling agents. The agents, used in this polymer blend, were organofunctional silanes.

3.1 Raw Materials and Reagents

3.1.1 Poly(vinyl chloride)

Commercial grade chemicals were used in this study. A suspension polymerized homopolymer PVC having intermediate molecular weight or a K-value of 61 was used. It was supplied by Thai Plastic and Chemical Public Co. Ltd. (TPC). Typical data of SG 610 are shown in Table 3.1

Table 3.1 Typical data of SG 610

Properties	Test method	unit	Value
K-value	DIN 53726		61
Apparent bulk density	ISO 60	g/ml	0.53
Volatile matters	ISO 1269	%	<0.3
Sieve analysis	ASTM D 1921-63		
- Retained on 60 mesh		%	0
- Retained on 270 mesh		%	>98
Ash as sulfates	ISO 1270	%	<0.1
Impurities and foreign matter	ISO/R 1265	point	<5

3.1.2 Styrene–Acrylonitrile Copolymer (SAN)

The SAN used in this study was transparent resin : PORENE AS 330 PC, general purpose grade and molding temperature at 50-85°C. It was supplied by Thai Petrochemical Industry Public Co. Ltd. Typical data of PORENE AS 330 PC are shown in Table 3.2.

Table 3.2 Typical data of PORENE AS 330 PC

Properties	Test Method	Unit	Value
MFI	ASTM D 1238	g/10 min	3.3
Izod notched Impact strength	ASTM D 256	kg-cm/cm	2.6
Tensile strength	ASTM D 638	kg/cm ²	780
Flexural strength	ASTM D 790	kg/cm ²	1300
Flexural modulus	ASTM D 790	kg/cm ²	3.8
Rockwell hardness	ASTM D 785	M-scale	96
Heat distortion temperature	ASTM D 648	°C	86

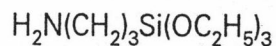
3.1.3 Glass Fiber

“E” glass fiber used in this study was chopped strand. Length of glass fiber was 6 mm. Fiber diameter was 15 μ m. It was supplied by Asia Glass Industry Co, Ltd.

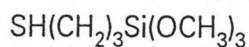
3.1.4 Coupling Agents: Organofunctional Silanes

Two types of organofunctional silanes were used as:

a) γ - amino propyl triethoxy silane (A-1100);



b) γ - mercapto propyl trimethoxy silane (A-189);



Both organofunctional silanes were supplied by O.S.I. SPECIALTY Co., Ltd. These coupling agents are clear liquid. The physical properties of silanes A-1100 and A-189

are shown in Table 3.3

Table 3.3 Typical Physical Properties of Silane A-189 and A-1100

Properties	A-189	A-1100
Molecular Weight, g/mole	196.4	221.4
Physical Form	Clear liquid	Clear liquid
Color	Light straw	Light straw
Specific Gravity, 25/25°C	1.057	0.946
Refractive Index, nD 25°C	1.440	1.420
Boiling Point, °C	212	217
Flash Point, Tag closed cup, °C	88	96

3.1.5 Reagents

- 1) Methyl alcohol, commercial grade.
- 2) Ethyl alcohol, commercial grade.
- 3) Glacial acetic acid, AR grade.
- 4) Butyltin mercaptide, Thermolite 395 Stabilizer (T-395).
- 5) Stearic acid as lubricant.
- 6) Tribasic leadsulfate as stabilizer.

3.2 Apparatus and Equipment

1. Two roll mill: LRM 110, Labtech. Engineering Co., Ltd.

2. Compression molding: LP 20, Labtech. Engineering Co., Ltd.
3. Universal testing machine: Instron Model 5583, 500 KN.
4. Wilson Rockwell hardness tester: series 500
5. Scanning electron microscope: JSM T-220A JEOL Co., Ltd.
6. Heat distortion temperature machine: Shimadzu HDT
7. Differential scanning calorimetry: DSC 200 NETZSCH Thermal Analysis.
8. Electric furnace
9. Drying oven
10. Circular saw cutting machine: Hitachi 6"

3.3 Experimental Procedures

3.3.1 Dry blending of PVC

The composition of PVC compound is shown in Table 3.4.

Table 3.4 Formulation of PVC compound (phr)

PVC resin	100
Lubricant	1.5
Stabilizer	3.5

The compound as dry blended by manual, using the following sequence: stirring 100 times clockwise and then 100 times counterclockwise.

3.3.2 Treatment of Organofunctional Silane on Glass Fiber

To improve the adhesion at the matrix-fiber interface in composites, the glass fiber chopped strand were treated with silane coupling agents. A mercaptosilane, gamma-mercapto propyl trimethoxy silane (A-189), and an aminosilane, gamma-amino propyl triethoxy silane (A-1100) were the two coupling agents used. The glass fiber treatment involved the dilution of the coupling agents in a solvent and the spray on the fibers.

1) The glass fibers were burnt in an electric furnace at 550 °C for 5 hours and cooled down in a dessicator for moisture prevention.

2) A 95% ethanol - 5% water solution, adjusted to a pH of 4.5 with acetic acid, was used as solvent for the mercaptosilane coupling agent. And then this agent was added to 250 ml. of the solvent with stirring to yield 0.5, 1.0, 1.5, and 2.0% by weight for the final concentration.

3) A 95% methanol - 5% water solution, adjusted to a pH of 4.5 with acetic acid, was used as solvent for the aminosilane coupling agent. And then this agent was added to 250 ml. of the solvent with stirring to yield 0.5, 1.0, and 1.5% by weight for the final concentration.

4) Each solution was sprayed onto 250 g of glass fiber that stirred throughly with glass rod until all the solution was gone.

5) Each type of treated glass fiber was dried in a hot oven at the optimum drying condition from Section 3.3.2.1.

3.3.2.1 Determination of drying condition in treating glass fiber with both silane coupling agents

The vital thing in treating glass fiber is the drying condition used. The experiment was performed as follows:



1. All procedures in Section 3.3.2 were performed, but only 0.5% for the final concentration of both silane coupling agents were prepared.

2. To find the optimum condition, the drying time and temperature were varied as follows;

- 24 hours at room temperature
- 7 minutes at 110 °C
- 7 minutes at 130 °C
- 7 minutes at 150 °C
- 7 minutes at 170 °C.

3. The next procedures in Section 3.3.3 and 3.3.4 were performed by an arrangement of PVC:SAN:treated glass fiber ratio of 60:40:10, respectively.

3.3.3 Preparation of the Composites

In this study, three different composites were defined as follows:

1. The composites were composed of untreated glass fiber and PVC/SAN blend.

2. The composites were composed of treated glass fiber with mercaptosilane coupling agent (A-189) at the suitable drying condition and PVC/SAN blend.

3. The composites were composed of treated glass fiber with aminosilane coupling agent (A-1100) at the suitable drying condition and PVC/SAN blend.

All the PVC/SAN composites were formulated as shown in Table 3.5.

3.3.4 Compounding

Small portion of PVC/SAN was preheated on the two roll mill at 180°C for 5 min. The polymer was blended quickly to form thin film, then the whole quantity of polymer was added to the desired formulation. The glass fiber was introduced into

Table 3.5 Formulation of Glass Fiber Reinforced of PVC/SAN Composites (phr).

Composite	PVC resin	SAN resin	Glass fiber	A-1100	A-189	T-395	Stabilizer	lubricant
B60/40	60	40	0	0	0	0	2.1	0.9
B70/30	70	30	0	0	0	0	2.45	1.05
B80/20	80	20	0	0	0	0	2.8	1.2
B60/40-G10	60	40	10	0	0	0	2.1	0.9
B60/40-G20	60	40	20	0	0	0	2.1	0.9
B60/40-G30	60	40	30	0	0	0	2.1	0.9
B70/30-G10	70	30	10	0	0	0	2.45	1.05
B70/30-G20	70	30	20	0	0	0	2.45	1.05
B70/30-G30	70	30	30	0	0	0	2.45	1.05
B80/20-G10	80	20	10	0	0	0	2.8	1.2
B80/20-G20	80	20	20	0	0	0	2.8	1.2
B80/20-G30	80	20	30	0	0	0	2.8	1.2
B60/40-G10/A0.5	60	40	10	0.05	0	0	2.1	0.9
B60/40-G20/A0.5	60	40	20	0.1	0	0	2.1	0.9
B60/40-G30/A0.5	60	40	30	0.15	0	0	2.1	0.9
B60/40-G10/A1.0	60	40	10	0.1	0	0	2.1	0.9
B60/40-G20/A1.0	60	40	20	0.2	0	0	2.1	0.9
B60/40-G30/A1.0	60	40	30	0.3	0	0	2.1	0.9
B60/40-G10/A1.5	60	40	10	0.15	0	0	2.1	0.9
B60/40-G20/A1.5	60	40	20	0.3	0	0	2.1	0.9
B60/40-G30/A1.5	60	40	30	0.45	0	0	2.1	0.9
B70/30-G10/A0.5	70	30	10	0.05	0	0	2.45	1.05
B70/30-G20/A0.5	70	30	20	0.1	0	0	2.45	1.05
B70/30-G30/A0.5	70	30	30	0.15	0	0	2.45	1.05
B70/30-G10/A1.0	70	30	10	0.1	0	0	2.45	1.05

Table 3.5 (continued)

Composite	PVC resin	SAN resin	Glass fiber	A-1100	A-189	T-395	Stabilizer	lubricant
B60/40-G30/M2.0	60	40	30	0	0.6	0.03	2.1	0.9
B70/30-G10/M0.5	70	30	10	0	0.05	0.035	2.45	1.05
B70/30-G20/M0.5	70	30	20	0	0.1	0.035	2.45	1.05
B70/30-G30/M0.5	70	30	30	0	0.15	0.035	2.45	1.05
B70/30-G10/M1.0	70	30	10	0	0.1	0.035	2.45	1.05
B70/30-G20/M1.0	70	30	20	0	0.2	0.035	2.45	1.05
B70/30-G30/M1.0	70	30	30	0	0.3	0.035	2.45	1.05
B70/30-G10/M1.5	70	30	10	0	0.15	0.035	2.45	1.05
B70/30-G20/M1.5	70	30	20	0	0.3	0.035	2.45	1.05
B70/30-G30/M1.5	70	30	30	0	0.45	0.035	2.45	1.05
B70/30-G10/M2.0	70	30	10	0	0.2	0.035	2.45	1.05
B70/30-G20/M2.0	70	30	20	0	0.4	0.035	2.45	1.05
B70/30-G30/M2.0	70	30	30	0	0.6	0.035	2.45	1.05
B80/20-G10/M0.5	80	20	10	0	0.05	0.04	2.8	1.2
B80/20-G20/M0.5	80	20	20	0	0.1	0.04	2.8	1.2
B80/20-G30/M0.5	80	20	30	0	0.15	0.04	2.8	1.2
B80/20-G10/M1.0	80	20	10	0	0.1	0.04	2.8	1.2
B80/20-G20/M1.0	80	20	20	0	0.2	0.04	2.8	1.2
B80/20-G30/M1.0	80	20	30	0	0.3	0.04	2.8	1.2
B80/20-G10/M1.5	80	20	10	0	0.15	0.04	2.8	1.2
B80/20-G20/M1.5	80	20	20	0	0.3	0.04	2.8	1.2
B80/20-G30/M1.5	80	20	30	0	0.45	0.04	2.8	1.2
B80/20-G10/M2.0	80	20	10	0	0.2	0.04	2.8	1.2
B80/20-G20/M2.0	80	20	20	0	0.4	0.04	2.8	1.2
B80/20-G30/M2.0	80	20	30	0	0.6	0.04	2.8	1.2

polymer blends and homogenized for 10 min at 180°C. During the mixing period, a brass knife and a wood-scraper were necessary for a manual mixing so as to increase good homogeneity in all directions. Finally, the sheet was removed from the two roll mill.

3.3.5 Molding

The milled sheet was cut into strips in the mill direction and placed into a preheated mold. The mold was placed in a hot press at 175°C and preheated for 10 min. The molding time was 3 min and the pressure used was 1000 psi. After hot pressing, the mold was transferred to a water cooled press under the same pressure for 10 min. The sheets was cut to the standard specimens according to the ASTM test method

3.4 Mechanical Testing

Mechanical properties of the composites were measured by the following ASTM test methods:

ASTM D638 M-93: Standard test method for tensile properties of plastic materials
(metric unit)

The test specimen dimension is presented in Figure 3.1.

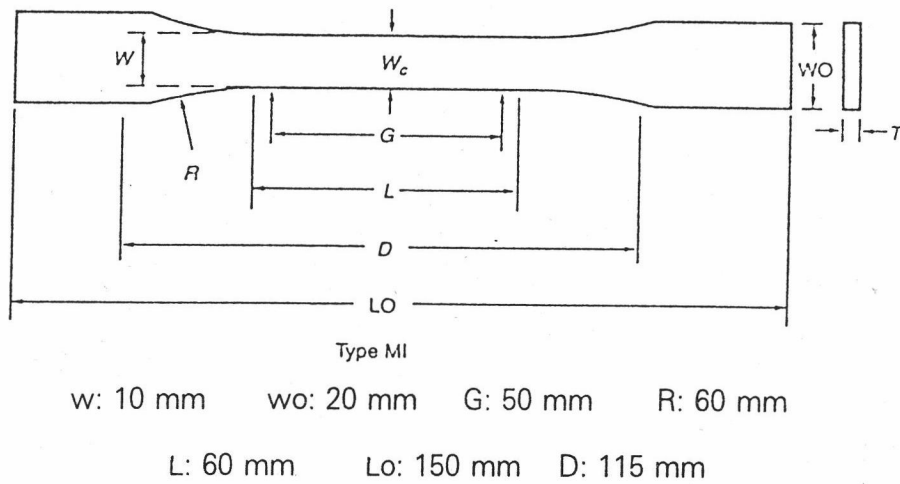


Figure 3.1 Schematic dimension of tensile test specimen (type M-1)

The tensile testing conditions were as follows:

temperature:	25°C
Relative humidity:	50%
Speed of testing:	4 mm/min
Distance between grips:	115 mm
Gage length:	50 mm

ASTM D 790M-93: Standard test methods for flexural properties of unreinforced and reinforced plastic (metric)

1. The specimens, having 25 mm in width, 60 mm in length, and approximately 3 mm in thickness were cut by the circular saw cutting machine and the rim was trimmed with a cutter.

2. For a 3-point bending flexural testing, the length of the support span depends upon the thickness. In this case 48 mm span length was used in order to have a support span-to-thickness ratio of 16:1. A test specimen was loaded via a diameter of crosshead loading nose by using the rate of crosshead motion at 1.2 mm/min. The flexural testing conditions were as follows:

Temperature:	25°C
Relative humidity:	50%
Rate of cross-head:	1.2 mm/min

ASTM D785-93: Standard test method for rockwell hardness of plastic

The standard test specimen had a minimum thickness of 6 mm. The surface of the specimen was flat and parallel over an enough area to permit the presser foot to contact the specimen.

In this experiment, the M scale for this specimen was chosen. The conditions in testing were shown as follows:

Temperature:	25°C
Relative humidity:	50%

ASTM D-648-82: Standard test method for deflection temperature of plastics under flexural load.

The specimens, having 127 mm in length, 13 mm in width and 3 mm in thickness were cut by the circular saw cutting machine. At least two test specimens having smooth flat surfaces free from saw cuts, excessive sink marks, or flash were used.

The conditions in testing were shown as follows:

Temperature:	25°C
Relative humidity:	50%
Loading:	264 psi

3.5 Fiber and void content determination

ASTM D2584-68: Test method for ignition loss of cured reinforced resins.

1. The specimens were cut along the deflect line of the dumbbell test with the circular saw cutting machine and the rim was trimmed with a cutter. The specimens have a dimension of 10 mm in width and 25 mm in length.

2. The specimens were weighed and placed in a crucible and then heated with a bunsen burner until the contents were ignited.

3. When the burning ceased and remained only ash and carbon, the crucible and residue were heated in a furnace at 550°C until all carbonaceous material had disappeared.

4. The crucible was cooled at room temperature in a desiccator and the weight was determined.

5. The ignition loss of the specimens in weight percent was calculated by the following equation:

$$\text{Ignition loss, weight \%} = [(W_1 - W_2) / W_1] \times 100$$

where

W_1 = weight of specimens (g)

W_2 = weight of residue (g)

ASTM D2734-91: Void content of reinforced plastics

1. The specimens were cut by the circular saw cutting machine to a dimensions of 10 mm in width and 25 mm in length.

2. The density of the specimens was determined by dividing the weight by the volume; expressed as grams per cubic centimeter.

3. The resin content and the glass fiber content were determined by following ASTM D2584-68.

4. The void content was calculated by the following equation:

$$V = 100 - M_d [(r / d_r) + (g / d_g)]$$

where

V = void content (% volume)

M_d = measured density

r = resin (%weight)

g = glass (%weight)

d_r = density of resin

d_g = density of glass

3.6 Microstructure of the Fracture Surface of the Composites

3.6.1 Preparation of specimens

1. The fracture surfaces of tensile testing specimens were dipped in liquid nitrogen.

2. The dipped specimen was broken with pincers.

3. The new fracture surface was held on stub with nail-varnish.

4. The samples were coated with gold before an observation with SEM.

5. The microstructure of specimens were studied with JEOL T-220A scanning electron microscope, operated at 15 KV.

3.7 Differential Scanning Calorimetry of the Composites

All types of composites were investigated with DSC 200 at a heating rate of 20°C/min. Each sample was first heated from room temperature to 200°C. Then a second run was made where the onset, the mid-point, and the end-point of the heat capacity change in the glass transition region were recorded.