CHAPTER II

METHODOLOGY

2.1 Materials

Polypropylene (PP) extrusion grade 1102 H obtained from Thai Petrochemical Industry Co., Ltd. was used as a matrix. Melt flow index is 1.8 g/min. The molecular weight is 17 $x10^4$.

Maleic anhydride modified polypropylene (MAPP) grade 3002 supplied by Uniroyal Co., Ltd. was used as an adhesive agent The melt flow index is 9.03 dg/min and the maleic content is 0.62 %.

Kunipia F supplied by Kunimine Industry was a Na^+ type montmorillonite, with a cation exchange capacity 119 mequiv / 100g.

3-aminopropyl dimethylethoxysilane was supplied by United Chemical Technology and used as silane coupling agent. Its structure is shown in fig. 2.1.

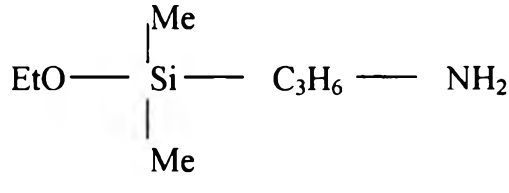

Figure 2.1 Chemical structure of aminopropyl dimethylethoxysilane.

2.2 Experimental Procedures

2.2.1 Nanocomposite Preparation

2.2.1.1 The grafting of aminosilane to the silicate clay.

Silane coupling agent 3-aminopropyl dimethylethoxysilane 2% was stirred in the mixture of 95 % ethanol and 5 % water for 1 hr. to hydrolyze the silane coupling agent. The coupling agent was applied to the silicate clay by putting the silane solution and clay powder together in an Erlenmeyer flask and stirred at room temperature. Then the treated clay was dried in a hot air oven at 50 °C. The modified clay was characterized by an XRD from sample having different stirring times (10, 30, 60, 90, 120 min.) drying times (12, 24, 48, 72 hr.) and silane concentration (2, 5, 16, 25, 30, 40 wt %) for finding appropriate grafting conditions.

2.2.1.2 The grafting of MAPP with modified silicate clay

The modified silicate clay was dispersed in dimethylacetamide (DMAC) at 90 °C and stirred for 3 hr. MAPP was dissolved in hot xylene at 125 °C for about 20 min. The grafting of MAPP with the modified silicate clay occurred in the solution reaction by mixing the dispersed clay solution and the dissolved MAPP solution, producing a reaction at 125 °C for 30 and 60 min. Then the modified clay was precipitated with tetra hydrofuran (THF) and dried at 50 °C for 24 hr. This material becomes a nanofiller. The characterizations of the grafting reaction and level of filler dispersion were carried out using XRD, TEM, DSC and DRIFT techniques.

To ensure that our product were nanofillers, the prepared nanofillers in the present form were ready for the characterization by XRD and

DSC. For the DRIFT model experiment, we used a 25 % silane concentration solution with the silicate clay in order to identify the coupling of the reaction. The samples were analyzed against a KBr powder reference.

For the TEM characterization, the sample film was soaked into 2 % (w/v) solution of $RuCl_3$. $3H_2O$ in sodium hypochlorite for 3 hr before sectioning [Montezinos, 1985].

2.2.1.3 Nanocomposite Preparation

Nanofiller and PP were roll milled onto a Lab Tech LRM 110 two roll mill. The PP composites were milled at 170 °C. The matrix was put on the mill for about 5 minutes before the addition of nanofiller and then processed for about 15 min. The material was removed from the mill and ground by a granulator.

The granules of the nanocomposites were pressed on a Wabash V50H hot press. The composites were pressed at 200 °C. Each sample was heated between the press plaques for 10 mins. Then the sample were cooled to room temperature. The entire cooling process took about 10 min. The plaques were machined for the required dimension for each testing.

2.2.2 Mechanical Properties Testing

The prepared nanocomposites were tested on the tensile, flexural and impact properties. We studied the effect of filler content, the effect of clay content and the effect of silane concentration.

2.2.2.1 The effect of filler content.

The nanocomposites were tested on the effect of the filler content. By fixing 10 wt. % and 60 wt. % for the clay content in the nanofiller, we then varied the filler content to study its effect.

2.2.2.2 The effect of clay content

The effect of clay content of the nanocomposite was studied . By fixing 10 wt % and 30 wt % of the filler content, we then varied clay content to study its effect.

2.2.2.3 The effect of silane coupling agents

To study the effect of silane concentration, we fixed the amount of clay content at 10 wt % and 60 wt % and fixed the filler content at 10 wt %. We then varied wt % silane concentration.

2.2.2.4 The effect of filler content on the resistance to the slow crack growth.

The nanocomposites were tested on the resistance to slow crack growth by studying the effect of filler content with respect to the pure PP. The details of the testing procedure will be discussed in the next section.

2.3 Mechanical Properties Testing Techniques

2.3.1 Tensile Testing

The tensile properties were studied using the Instron Universal Testing Machine model 4206 in the extension mode. The tensile strength and tensile modulus were determined according to ASTM D638-91. The testing temperature was 26 °C. The specimen were machined into dogbone shapes following the ASTM 638-91 type I for specimen dimensions, the width of narrow section was 13 mm and the gage length was 50 mm. All tests were performed at a crosshead speed of 50 mm/min with a 1 kN load cell.

The tensile strength is the maximum tensile stress sustained by a specimen during a tension test. Tensile modulus is defined as the stress divided by the strain.

2.3.2 Flexural Testing

The flexural properties were studied using the Instron universal testing machine using a three - point bending. The flexural strength and flexural modulus were determined according to ASTM D790 - 92 type I. A three point loading system utilizing center loading on a simply supported beam. The specimens were machined into 12.75 x127.5 mm. The testing temperature was 26 °C. All tests were performed at a crosshead speed of 13 mm/min with 1 kN load cell.

Flexural strength is equal to the maximum stress at the outer part at the moment of breaking. Flexural modulus, in common with tensile modulus, was obtained by the tangent modulus which is defined as the stress divided by the strain.

2.3.3 Impact Testing

Izod impact testing was done at 26 °C with a notch specimen according to the specification of ASTM D256 - 92. The specimen was held as a vertical centilever beam and was broken by a single swing of the pendulum with the line of initial contact at a fixed distance from the specimen clamp. By using Izod type, Zwick, the impact pendulum was a 2.7 joule pendulum. The specimens were machined from the composite plaques and cut into 12.75 x 63.5 mm and a 2.5 mm notch was carved into them by a notching machine. Impact strength is the property of the material to resist failure when subjected to a rapidly increasing applied force. It is expressed as the impact energy

Impact strength is the property of the material to resist failure when subjected to a rapidly increasing applied force. It is expressed as the impact energy which is the energy absorbed by the object during fracture at a very high testing rate.

2.3.4 Slow Crack Growth Testing (SCG)

Our test followed Brown's procedure [1992]. A single edge notched test specimen was exposed to a constant load at a controlled temperature. The crack opening displacement was measured with a microscope.

Specimen geometry

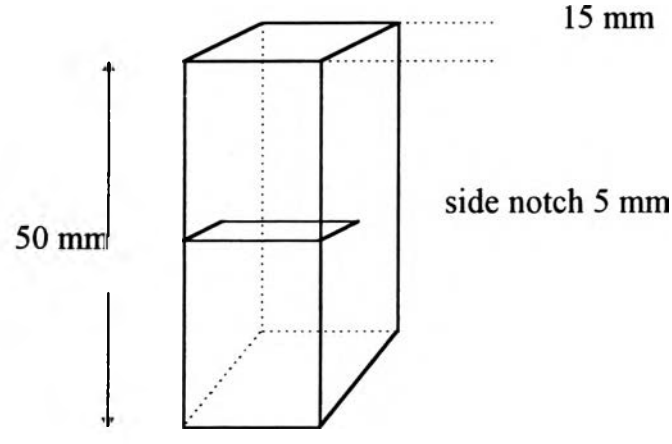

Figure 2.2 The sketches of specimen dimensions.

Figure 2.2 shows a sketch of the specimen taken from a compression molded resin. The specimens for the SCG test were 15 x 2 mm in cross section. The notch was introduced by pressing a fresh razor blade into the specimen. A fresh razor blade should not be used for more than about four specimens. Each specimen had a 5 mm notch. The notch length was 2 mm.

aligned and centered with respect to the longitudinal axis of the specimen. The constant load tensile test was conducted under 9 MPa stress at 60 °C. The temperature was carefully controlled within ± 1. It is not recommended that polyolefins should be tested above 80°C because significant morphological changes can occur during the test. The rate of slow crack growth is monitored through a Zoom stereo microscope with a 13.4 x magnification by measuring the crack opening displacement versus time.

Figure 2.3 shows our homemade SCG apparatus.

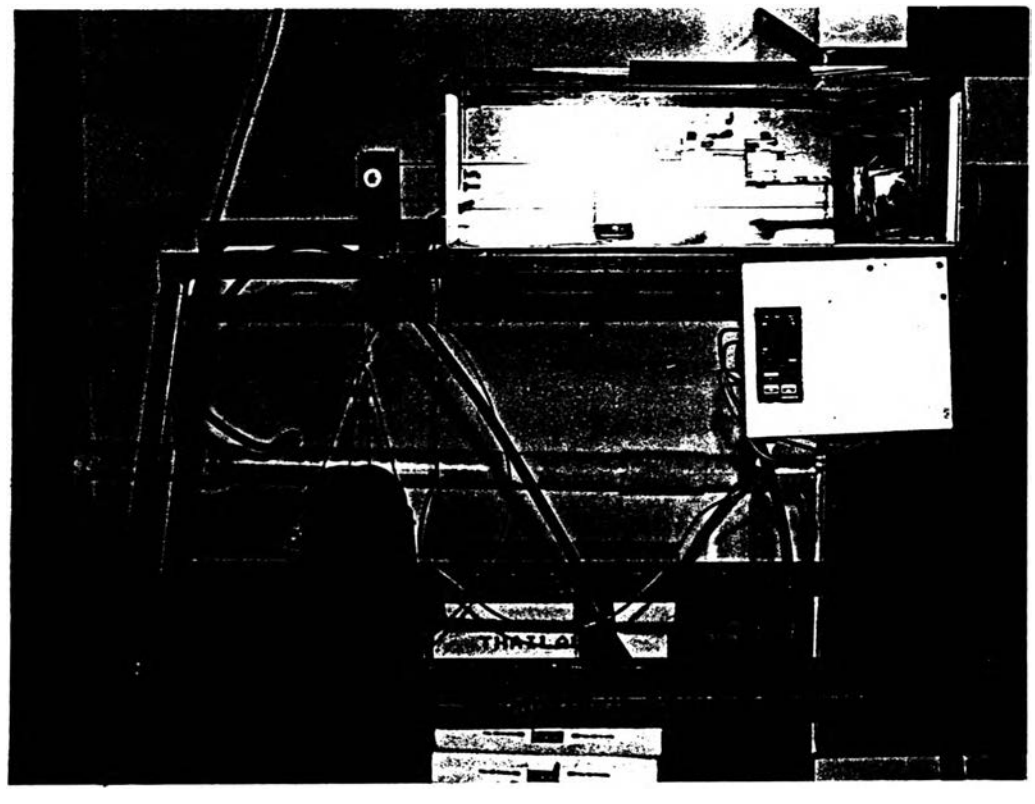

Figure 2.3 Test fixture and specimen configuration for the constant load tensile test.

2.4 Characterization Techniques

2.4.1 X - Ray Diffraction Spectroscopy (XRD)

X - ray diffraction measurements by monitoring the intensity vs. the diffraction angle of 2 θ from 2 ° to 30 ° on a Philips PW3710 X - ray diffratometer. The diffractometer was equipped with a CuK_{α} radiation source operated at 40 kv and 30 mA. The scanning speed and the step size used were 1°/min. Si was used as a calibration standard.

2.4.2 Diffuse Reflectance Infrared Spectroscopy (DRIFT)

Diffuse reflectance (DRIFT) spectra were taken using a Bio - rod FTIR. The sample were analyzed against a KBr powder reference. DRIFT spectra were taken at resolution of 2 cm^{-1} with 16 coadded scans. All DRIFT spectra are plotted according to the Kubelka - Munk function

2.4.3 Differential Scanning Calorimetry (DSC)

The samples for DSC analyses were sealed hermetically in the aluminum sample pans and the DSC curves were recorded under N_2 (50 ml/min) on a Netzch differential scanning calorimetry at a heating rate of 10 K/min.

2.4.4 Transmission Electron Microscopy (TEM)

Transmission electron micrograph was obtained with JEOL JEM - 200 cx using acceleration voltage of 100 kv. The stain on the sample was prepared by dissolving 2 % (w/v) solution of $RuCl_3.3H_2O$ in sodium hypochlorite for 3 hours[Montezinos, 1985].