



CHAPTER III EXPERIMENTAL

3.1 Materials

3.1.1 Materials Used for the Study on Isotactic Polypropylene/Roselle Fibers

Composites

For the isotactic polypropylene/roselle fibers composites, commercial grades of isotactic polypropylene (i.e. HP500N, CS23, and EP548S) which used in this works were supplied by HMC Polymers Co., Ltd. (Thailand). HP500N was a homopolymer grade with density and melt-flow rate (MFR) values of about $0.90 \text{ g}\cdot\text{cm}^{-3}$ and $12 \text{ dg}\cdot\text{min}^{-1}$, respectively; CS23 was a homopolymer grade with density and MFR values of about $0.90 \text{ g}\cdot\text{cm}^{-3}$ and $25 \text{ dg}\cdot\text{min}^{-1}$, respectively; and EP548S was an impact-modified copolymer grade with density and MFR values of about $0.90 \text{ g}\cdot\text{cm}^{-3}$ and $44 \text{ dg}\cdot\text{min}^{-1}$, respectively. A commercial grade (i.e. Polybond 3200; hereafter PB3200) of maleic anhydride-grafted iPP (MAPP) with the maleic anhydride content of 1.0 wt.%, used as the compatibilizer, was purchased from Crompton Corp. (USA). The density and MFR of PB3200 were $0.91 \text{ g}\cdot\text{cm}^{-3}$ and $115 \text{ dg}\cdot\text{min}^{-1}$, respectively.

Roselle fibers were supplied by Asia Bio-Composites Limited (Thailand). Normally, roselle, after removal of lignin and pectin, is composed of 40 wt.% of bast and 60 wt.% of core materials. In order to investigate the effect of the fiber type on mechanical properties of the as-prepared composites, four types of roselle fibers were prepared and incorporated in iPP: they were 1) bast fibers (BF; the weight ratio of bast/core fibers = 100/0), 2) core fibers (Core; the weight ratio of bast/core fibers = 0/100), 3) whole-stalk fibers (WS; the weight ratio of bast/core fibers = 40/60), and 4) core-added whole-stalk fibers (WC; the weight ratio of bast/core fibers = 20/80). In order to investigate the effect of the size of fibers on mechanical properties of the as-prepared composites, bast fibers of various sizes were prepared by milling the raw bast fibers in a home-made pin mill with different numbers of the mill (i.e. 4 or 6), while both whole-stalk and core fibers of various

sizes were prepared by passing corresponding fibers which were processed in a hammer mill through sieves of varying mesh number (i.e. 20, 30, 40, or 50).

3.1.2 Materials Used for the Study on Poly(vinyl alcohol)/Chitin Whiskers

Nanofiber Nanocomposites

Poly(vinyl alcohol) (PVA) powder ($M_w = 75,000$ Da and degree of hydrolysis (DH) = 98%; Fluka, USA) was first dissolved in warm distilled water (85°C) under slight stirring for 3 hrs to obtain a PVA solution at a fixed concentration of 10 wt.%. α -Chitin whiskers were prepared from chitin flakes derived from shells of *Penaeus merguensis* shrimps [Seafresh Co., Ltd. (Thailand)] were used to prepare the chitin whiskers.

3.1.3 Materials Used for the Study on Poly(vinyl alcohol)/Nylon 4, 6

Nanofiber microcomposites

Nylon 4,6 (density=1.18, Sigma Aldrich, USA) nanofibers were prepared by electrospinning process. Nylon 4,6 was first dissolved in the 98 wt% formic acid (Analytical grade 98/100%, Fisher Scientific, UK) under slight stirring for 7 hrs to obtain a nylon 4,6 solution. And poly(vinyl alcohol) (PVA) powder ($M_w = 72,000$ Da and degree of hydrolysis (DH) \geq 98%; Merck, USA) was dissolved in warm distilled water (85°C) under stirring for 3 hrs to obtain a PVA solution at a fixed concentration of 7.5 wt.%. PVA solution was cooled at room temperature before further use.

3.2 Sample Preparation

3.2.1 Sample Preparation for the Study on the Isotactic Propylene/Roselle

Fibers Composites

The composites were premixed and dried (60 °C, overnight) in tumber mixer for 10 minutes to prepare compounds. The mixed compounds were then fed into a Collin ZK25 self-wiping, co-rotating twin-screw extruder, operating at a screw speed of 100 rpm and with a temperature profile (from the feed zone to the die) of 90, 170, 175, 180, and 185°C, respectively. The composite pellets were dried again at 60 °C, overnight prior to being shape into the specimens for further testing using

an ARBURG Allrounder[®] 270M injection molding machine. The temperature settings (from the feed zone to the nozzle) were 150, 160, 170, 180, and 185°C, respectively. The injection pressure was 1700 bar and the dwelling pressure was 700 bar. Prior to the mechanical tests, all of the test specimens were conditioned in ambient conditions for 7 days.

3.3.2 Sample Preparation for the Study on Poly(vinyl alcohol)/Chitin

Whiskers Nanofiber Nanocomposites

To prepare nanocomposite fiber mats, each of the as-prepared PVA/chitin whiskers mixtures was placed in a 50-ml plastic syringe. A blunt-end stainless-steel gauge 20 needle (i.e. outside diameter = 0.91 mm) was used as the nozzle. The tilt angle of the syringe and the needle was 45° from a horizontal baseline to ascertain a constant presence of a liquid droplet at the tip of the nozzle. The applied potential was fixed at 15 kV over a fixed collection distance between the tip of the nozzle and the screen collector of 15 cm. The collection time was also fixed at 12 hrs. The as-spun fiber mats were kept in room condition for one day prior to further characterization. To prepare nanocomposite films, each of the as-prepared PVA/chitin whiskers mixtures was poured onto a glass petridish by fixing the volume of the mixture at about 15 ml. The sample was let dry in room condition for 3 days prior to further characterization.

3.3.3 Sample Preparation for the Study on Poly(vinyl alcohol)/Nylon 4, 6

Nanofiber microcomposites

Nylon 4,6 solution was placed in a 10-ml plastic syringe. A blunt-end stainless-steel gauge 20 needle (i.e. outside diameter = 0.91 mm) was used as the nozzle. The tilt angle of the syringe and the needle was 20° from a horizontal baseline to ascertain a constant presence of a liquid droplet at the tip of the nozzle. The applied potential was fixed at 17.5 kV over a fixed collection distance between the tip of the nozzle and the collector drum of 12 cm. The thickness of nylon 4,6 as-spun fibers was controlled by fixed the amount of the nylon 4,6 solution 4,6 at 30 ml. The as-spun fiber mats were kept in room condition for one day prior to further characterization.

The composite films were prepared by PVA solution casting on the Nylon 4,6 as-spun fiber mats. The weight fraction of nylon 4,6 as-spun fiber mats in the composites was controlled by the amount of PVA solution which was varied from 3, 4, 5, 6, and 7 ml. The composite films were dried at room temperature 3 days and kept it at room temperature a day before further characterized.

3.3 Characterizations

3.3.1 The Morphology Appearances

JEOL JSM-5200 scanning electron microscope (SEM) was used to observe the morphology of all composites. Each selected specimen was stuck onto an aluminum stub. Prior to observation under SEM, each sample was gold-coated to enhance the conductivity of the surface.

However, for the morphological appearance of the as-prepared α -chitin whiskers, a JEOL JEM-200CX transmission electron microscope (TEM) was used. Samples of the chitin whiskers were prepared from a drop of a dilute chitin whisker suspension which was deposited and let dry on a formvar grid.

3.3.2 The Thermal Properties and Functional Groups Analysis

Thermal degradation behavior of the roselle fibers was characterized using a Perkin–Elmer TGA7 thermal gravimetric analyzer (TGA) over a temperature range of 25–600°C using a heating rate of 10°C min⁻¹ in a nitrogen atmosphere. And a TGA 2950 DuPont thermogravimetric analyzer (TGA) was used to investigate the thermal stability of the samples and to verify the existence of chitin whiskers within the nanocomposite samples. A sample of about 3 to 10 mg was placed in a platinum pan. The scanning range was 30 to 600°C using a heating rate of 10°C·min⁻¹ in nitrogen atmosphere.

A Thermo Nicolet Nexus 671 Fourier-transformed infrared spectroscope (FT-IR) was used to investigate the chemical functionalities of the as-prepared chitin whiskers/PVA fiber mat and film samples. The measurements were carried out at 32 scans and a resolution of 4 cm⁻¹.

3.3.3 The Mechanical Properties

The tensile strength at yield, elongation at yield, and Young's modulus for as-prepared iPP/roselle fiber composites were measured on an Instron 4206 universal testing machine according to ASTM D 638–91 using a 100 kN load cell, a 50 mm.min⁻¹ crosshead speed, and a 50 mm gauge length. Izod impact resistance of these composites was determined on a Swick 5113 impact tester according to ASTM D 256–90b standard test method with the original size of each specimen being about 27 × 62 × 4 mm³, using a 2.7 Joule pendulum and a 124.4° release angle. The flexural strength and flexural modulus of the composites were determined according to ASTM D 790–92, using the three-point loading fixture of the Instron 4206 universal testing machine. All mechanical measurements were carried at room temperature.

A Lloyd LRX universal tester was used to determine the tensile strength, modulus, and elongation at break of the fibers and films samples, according to ASTM D882 standard test method. The dimension of chitin whisker/PVA samples was 10 × 120 mm². The gauge length and the crosshead speed were 50 mm and 20 mm.min⁻¹, respectively. The reported values were averages from 5 measurements.

3.3.4 The Crystal Behavior and Structure

The Rigaku X-ray diffractometer (XRD) system equipped with a RINT 2000 wide angle goniometer and a Cu tube for generating a CuK α 1 radiation was used to study the crystallization behavior and structure. The X-rays of 1.54 Å wave length was generated by a CuK α source. The angle of diffraction was varied from 5 to 45° with the rate of scan is 5°/min and the step of scan is 0.01°.

3.3.5 Surface Area and Porosity

The surface area and porosity of nanofibers were investigated using N₂ adsorption/desorption isotherms which were obtained by Quatachrome Autosorb I using a BET model at -196°C. Samples were first degassed in a vacuum furnace at 100°C, 12 hours. Surface areas were calculated using the BET equation. Pore volumes were determined by the t-plot method of De Boer and pore size distributions were constructed based on Barrett, Joyner and Halenda (BJH) method using the adsorption branch of the nitrogen isotherm.