CHAPTER III

EXPERIMENTAL

3.1 Materials

1. Cassava starch (Sinsawat Co., Ltd., Bangkok, Thailand)
2. Natural rubber latex (Rayong Bangkok Rubber, Co., Ltd., Rayong, Thailand)
3. Nonidet P 40 (grade GR, Fluka Supplies, Switzerland)
4. Benzoyl peroxide (grade GR, Fluka Supplies, Switzerland)
5. Acetic acid (grade GR, Merk Supplies, Germany)
6. Calcium carbonate (grade GR, Fluka Supplies, Switzerland)

3.2 Instruments

Major instruments used are listed below.

1. PERKIN ELMER TGA 7 Thermogravimetric Analyzer (Connecticut, USA)
2. PERKIN ELMER DMA 7e Dynamic Mechanical Analyzer (Connecticut, USA)
3. MALVERN Mastersizer S (England)

4. SCIENTIFIC LABORATORY HOTPRESS JST (Lab Tech Engineering Co., Ltd., Bangkok, Thailand)
5. JEOL JSM 6301F Scanning Electron Microscope (Japan)
6. CARL ZIEZZ Polarizing Microscope Model Axioskop-pol (Germany)
7. CARL ZIEZZ Reflected Light Microscope Model Axiotech 100 HD (Germany)
8. INSTRON Universal Testing Machine Model 4502 (USA)
9. Water Bath (Memmert, USA)
10. Vacuum Oven (Sheldon, USA)
11. Precision Balance (Mettler, Switzerland)

3.3 Characterisation of Raw Materials

Starch powder and concentrated natural rubber (NR) latex are the principal raw materials used in the present study. Preparation of starch paste is a prime pre-requisite.

3.3.1 Starch Powder

Starch powder used in this study was purchased from the Sinsawat Co., Ltd. (Bangkok, Thailand). Thermal properties and particle size of the starch were determined.

3.3.1.1 Thermal Property Measuremant

The thermal properties of starch powder were measured by thermogravimetric analysis (TGA, Perkin Elmer, model 7) at a heating rate of 10°C min^{-1}, and temperature between 40 and 850°C under a nitrogen atmosphere. The TGA technique was used to determine the water content and decomposition temperature (T_d) of the starch powder.

3.3.1.2 Particle Size Measurement

The particle size of starch powder was measured using a laser particle size analyser (see Appendix A for detail), Mastersizer S version 2.11 (Malvern) at 25°C. Distilled water was firstly added into the sample chamber and then flushed into the cell to use as background of the measurement. Next, the starch powder was slowly dropped into the sample chamber, with continuous stirring, until the obscuration was in the range of 10-30%.

3.3.2 Natural Rubber (NR) Latex

Concentrated high ammonia NR latex used in this study was purchased from the Rayong Bangkok Rubber Co., Ltd. (Rayong, Thailand). The solid content and particle size of the latex were determined.

3.3.2.1 Total Solid Content (%TSC)

Percentage TSC of a latex is defined as the percentage by weight of the concentrated latex, which is non-volatile at a definite temperature in a vented air oven. The %TSC of concentrated NR latex was determined according to the method described in ASTM D1076-97 and calculated using the following equation [25]:

$$\%TSC = \frac{W}{W_l} \times 100 \qquad (3.1)$$

where, W = the weight of the dry NR sample (g)

W_l = the weight of the NR latex sample (g)

3.3.2.2 Dry Rubber Content (%DRC)

Percentage DRC of a latex is the percentage by weight of the concentrated latex, which is precipitated by adding of 5% acetic acid. The %DRC of concentrated NR latex was also determined using the method described in ASTM D1076-97 [25]:

$$\%DRC = \frac{W_x}{W_l} \times 100 \qquad (3.2)$$

where, W_x = the weight of dry coagulum (g)

W_l = the weight of NR latex sample (g)

3.3.2.3 Particle Size Measurement

The diluted NR latex was determined using Mastersizer S as previously described For detail see appendix A.

3.4 Blending studies

Starch, water, natural rubber latex, non-ionic surfactant, and benzoyl peroxide were mixed according to the composition shown in Tables 3.1-3.4.

All the blend preparations were carried out in the container equipped with a stirrer as shown in Figure 3.1.

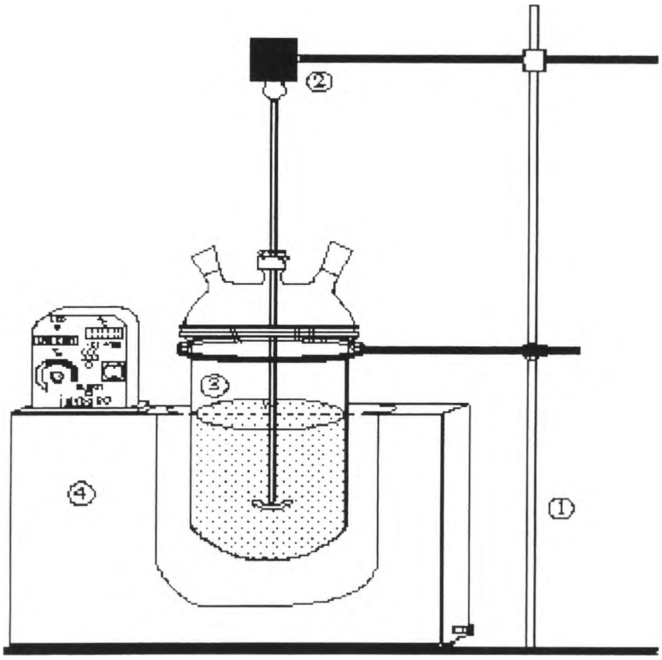

Figure 3.1: Diagram of apparatus used for the blend preparation.

(1) Stand (2) Mechanical stirrer (3) container

(4) Water bath

Non-ionic surfactant (Nonidet P40) was added to natural rubber latex and stirred at room temperature for a few seconds to obtain a stabilized natural rubber latex. Cassava starch, which contains 200% water by weight of starch, is mixed with the natural rubber in the reactor shown in Fig.3.1. The mixture was stirred at 70°C for 15-20 min to obtain a good dispersion of the latex on the gelatinized starch.

3.4.1 Foam from Starch and Water

In Table 3.1, 5 levels of water were formulated to investigate the effect of water content on the cell structure of the starch foam.

Table 3.1 Formulation of starch and water.

Sample	Starch (part)	Water (part per hundred starch)
S/W-1	100	100
S/W-2	100	150
S/W-3	100	200
S/W-4	100	250
S/W-5	100	300

3.4.2 Preparation of NR Dispersed in gelatinized starch

In Table 3.2, 5 various amounts of non-ionic surfactant were formulated to find the suitable amount of non-ionic surfactant, which could stabilize natural rubber latex in the gelatinized starch.

Table 3.2 Effect of the amount of non-ionic surfactant on the blend of starch and NR.

Sample	Starch (part)	Water (part per hundred starch)	NR latex (part per hundred starch)	Nonidet P40 (part per hundred rubber)
S/S-1	100	200	20	0.5
S/S-2	100	200	20	1
S/S-3	100	200	20	1.5
S/S-4	100	200	20	2.0
S/S-5	100	200	20	2.5

3.4.3 Preparation of starch and natural rubber latex blend

The suitable amount of non-ionic surfactant was revealed from the previous experiment and was used to prepare the blends of starch and natural rubber latex at various ratios.

Table 3.3 Formulation of starch and natural rubber latex.

Sample	Starch (part)	Water (part per hundred starch)	NR latex (part per hundred starch)	Nonidet P40 (part per hundred rubber)
S/NR-1	100	200	0	0
S/NR-2	100	200	10	1.5
S/NR-3	100	200	20	1.5
S/NR-4	100	200	30	1.5
S/NR-5	100	200	40	1.5
S/NR-5	100	200	50	1.5

3.4.4 Peroxide curing of natural rubber latex

To increase the strength of the foam from starch and natural rubber latex, benzoyl peroxide was added to the mixture as shown in Table 3.4. Benzoyl peroxide was selected to be a crosslink agent for this system because the half-life time is 1 min at temperature 130°C as see in appendix B. These time and temperature are in the range of time and temperature used to produce the foams.

Table 3.4 Formulation for vary amount of benzoyl peroxide in the mixture.

Sample	Starch (part)	Water (part per hundred starch)	NR latex (part per hundred starch)	Non-ionic surfactant (part per hundred rubber)	Benzoyl peroxide (part per hundred rubber)
S/BP-1	100	200	30	1.5	0
S/BP-2	100	200	30	1.5	2
S/BP-3	100	200	30	1.5	3
S/BP-4	100	200	30	1.5	4
S/BP-5	100	200	30	1.5	5

3.5 Dispersion of natural rubber latex in the gelatinized starch

3.5.1 Polarizing Microscope

Small amounts of the blended materials were directly mounted onto glass microscope slides with cover slips. The dispersion of natural rubber latex in the gelatinized starch was then studied under a polarizing microscope.

3.6 Preparation of the expanded-foam material

The mixture according to Tables 3 1-3.4 was introduced into the mold and compressed by a compression molding machine at 130-180°C. The molding time was 2 min and the pressure used was 110 $kg_f\,cm^{-2}$. Dimensions of the mold were 70 mm long, 60 mm wide, and 1.5 mm deep.

3.7 Morphology of expanded-foam materials

The morphology and cell structure of expanded-foam materials were studied using scanning electron microscope (SEM) and reflected light microscope.

3.7.1 Scanning Electron Microscope (SEM) Measurement.

Expanded-foam samples were cross-sectionally cut and then mounted on an aluminum (SEM) stubs with double-sided adhesive tape and vacuum coated with gold. The morphology of the foams was then examined with a JEOL JSM 6301F Scanning Electron Microscope.

3.7.2 Reflected Light Microscope

Cell structure of expanded-foam samples was studied under a reflected light microscope.

3.8 Mechanical Properties of expanded-foam materials

All foams were kept at room temperature for 1 day after produced, and then subjected to the following mechanical measurement. This can avoided the effect of moisture to the properties of the foams.

3.8.1 Determination of compressive strength

The compressive strength was carried out using an INSTRON universal testing machine model 4502 with a 1 kN static load cell. In each test, three foam specimens were stacked one on top of the other. Three foam specimens were used instead of one to minimize the resistance provided by the solid instron base. The initial height of the three-foam stack varied between 4 and 4.5 mm. By lowering the piston to the foam surface at a rate of 5 mm min^{-1} for a distance of 3 mm. The maximum load at 50% strain was recorded. Compressive strength at 50% strain was calculated as the maximum load/cross sectional area of the probe. Average strength was calculated from five sets of foam specimens.

3.8.2 Dynamic Mechanical Analysis (DMA)

Dynamic mechanical properties and glass transition temperature (T_g) of expanded-foam samples were determined using PERKIN ELMER dynamic mechanical analyzer (DMA 7). The storage modulus (E′), loss modulus (E″) and loss tangent (tan δ) were obtained in a three-point blending measurement system. These properties were measured in a frequency of 1 Hz, and in a temperature range between –80°C and 60°C, the heating rate was 5°C min^{-1}. The testing was performed using about 4 x 10 x 1.5 mm^3 rectangular strips.

One problem with DMA experiments is the possibility of moisture loss during heating and the samples were then broken. Data showed an extra peak at the higher temperature possibly due to this broken phenomenon.

3.9 Effect of calcium carbonate

To study the effect of calcium carbonate addition to the blend of starch and NR, 5-30% of calcium carbanate by weight of the dry starch was added to the blend in the mixing step. No treatment was made for the surface of calcium carbonate. The foams were then tested for compressive strength and dynamic mechanical properties.