Chapter 2

Experimentals

2.1 Chemicals

Cassava starch was obtained from Thai Wah Co. LTD. It was produced from tapioca cultivated in summer. Its specifications are given in Table 2.1.

Table 2.1 Specification of cassava starch

Moisture (%)	12.80
Ash (%)	0.07
SO_2 (ppm)	32.57
pH	5.80
Viscosity at 66-77°C (27 g dry) (BU)	780

Acrylonitrile (98.0% pure) was obtained from Siam Resin & Chemical Co. LTD. It was purified by fractional distillation at atmospheric pressure through a 14-inch Vigreux column and stored in the refrigerator under nitrogen. Methanol, of commercial grade from BDH, was also purified by fractional distillation at atmospheric pressure. Other chemicals, of analytical grade, listed in Table 2.2, were used without further purification.

Table 2.2   Chemicals

Chemicals	Company
Calcium chloride ($CaCl_2$)	May & Baker
N,N-dimethylformamide (DMF)	Carlo Erba
Magnesium chloride decahydrate ($MgCl_2 \cdot 10\ H_2O$)	Fluka
Manganese sulfate monohydrate ($MnSO_4 \cdot H_2O$)	BDH
Potassium hydroxide (KOH)	Carlo Erba
Potassium permanganate ($KMnO_4$)	Merck
Sodium chloride (NaCl)	Carlo Erba
Sulphuric acid (H_2SO_4)	Merck
Tetrasodium pyrophosphate deca-hydrate ($Na_4P_2O_7 \cdot 10\ H_2O$)	BDH

2.2   Procedure

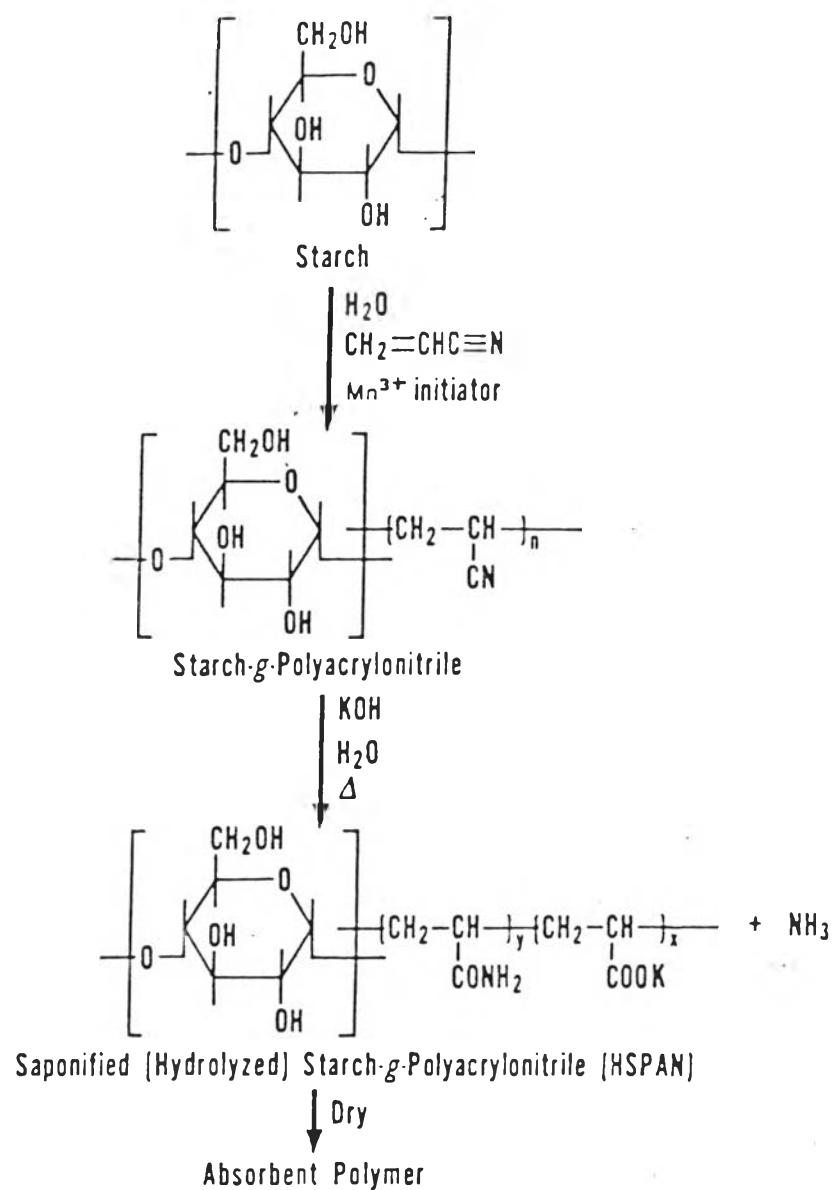Cassava starch-g-PAN was synthesized according to the reaction scheme shown in Figure 2.1.

Figure 2.1   Preparation of saponification starch-g-PAN
absorbent polymer

2.2.1 Graft copolymerization

2.2.1.1 Preparation of initiator solution [22].

(a) Preparation of $MnSO_4$ solution.

1.6226 g (0.0096 mole) of $MnSO_4.H_2O$ was dissolved in 100 ml of distilled water.

(b) Preparation of $KMnO_4$ solution.

0.3794 g (0.0017 mole) of $KMnO_4$ was dissolved in 100 ml of distilled water.

(c) Preparation of $Na_4P_2O_7$ solution.

13.38 g (0.03 mole) of $Na_4P_2O_7.10H_2O$ was dissolved in 250 ml of distilled water.

(d) Preparation of initiator solution.

25 ml of $KMnO_4$ solution was required to oxidize 25 ml of $MnSO_4$ solution. For a concentration of 1 mmole/L of Mn^{3+} to be used in the reaction vessel, 50 ml of a solution of Mn^{3+} ions was added to 250 ml $Na_4P_2O_7$ solution.

2.2.1.2 Preparation of acidified water [22].

25 ml H_2SO_4 (95-97% pure) was poured into a 500-ml volumetric flask and distilled water was added up to the mark.

2.2.1.3 Gelatinization

Into a 500-ml 5-necked round bottom reaction flask, 10 g of cassava starch were mixed with 185 ml of distilled water. The system was heated for one hour at 65°C (or 80°C) under N_2 atmosphere to form a slurry.

2.2.1.4 Grafting reaction

The gelatinized starch was then cooled to 35°C, and according to the experiments, an increasing amount of acrylonitrile was added. The starch(g)/AN(ml) ratios used were 10:2.5, 10:5.0, 10:7.5, 10:10.0, 10:12.5, 10:15.0, 10:17.5, 10:20.0, 10:25.0, and 10:30.0.

To each of these mixtures was added 50 ml of freshly prepared initiator solution of Mn^{3+} (1 mmole/L), and 50 ml of acidified water (85.8 mmole/L of H_2SO_4). The mixture was stirred under nitrogen atmosphere for 3 hrs at 35°C. The reaction product was then precipitated with methanol, filtered and washed with methanol again before being dried for 30 hours at 65°C.

2.2.2 Homopolymer extraction by N,N-dimethylformamide (DMF).

In a 500-ml Erlenmeyer flask, 5 g of the dried starch-g-PAN sample, ground into a powder form, was stirred in 250 ml of DMF for 24 hr at room temperature.

The extracted product was filtered, washed with methanol, and dried again for 30 hours at 65°C. 100 ml of the clear extract was then precipitated in an excess of methanol, filtered and washed again with methanol. The precipitate was dried for 3 hours at 65°C and weighed to determine the amount of homopolymer.

2.2.3 Copolymer characterization

2.2.3.1 Determination of % add-on

In order to determine the % add-on, which is the amount of AN grafted onto starch, it was necessary to cleave PAN from the starch matrix.

In a 250-ml Erlenmeyer flask mounted with a condenser, 1.50 g DMF-extracted polymer was stirred in 150 ml of 1 M H_2SO_4, and refluxed for 90 min. The water insoluble copolymer was isolated by filtration, washed with water and methanol and then dried. The weight percent of PAN in the graft copolymer (% add-on) was calculated from the weight of the graft copolymer after the removal of starch by acid hydrolysis [27].

2.2.3.2 Determination of the viscosity average molecular weight ($\overline{M}_v$).

The intrinsic viscosity of the grafted PAN obtained by acid hydrolysis was determined in DMF

solution   using a Cannon-Fenske viscometer No 100.   The
molecular   weight was   calculated using the   following
equation [23]:

$$[\eta] = 3.92 \times 10^{-4} \overline{M}_v^{0.75}$$

2.2.4 Saponification

A   suspension   of   10   g   DMF-extracted
starch-g-PAN in   200 ml of 8.5% KOH solution (10 g   of   KOH
(85%   pure) in   100 ml distilled water) was heated to 100 °C
with   an oil bath.   The mixture was stirred with a   magnetic
stirrer,   and   the saponification reaction was   carried   out
for 2 hrs.   It   was then allowed to cool to room temperature
and   precipitated with methanol.   The product was   isolated
by filtration and washed thoroughly with methanol until pH 7
was reached, and then dried in the oven at 65 °C for 30   hrs.
The material was ground into a powder form.

Saponification of starch-g-PAN can be carried
out   either   in KOH or NaOH solution, but   since   sodium   is
toxic to some plant species, we used KOH to obtain the   salt
[29].

2.2.5 Infrared analysis.

In   order   to follow the   different   reaction
steps   leading   to   the saponified starch-g-PAN,   an   IR
spectrophotometer Shimadzu model IR 440 was used   for   this

purpose. A KBr pellet was used for all IR analysis. The %
weight of sample was 5 % (prepared by grinding 5 mg of
sample with 100 mg of KBr).

2.2.6   Determination of water absorption value in
deionized water

         To determine the water absorbency, 0.1000 g
of powder sample was allowed to soak for 30 min. in 100 ml
of deionized water. The swollen polymer was then separated
by filtration through a weighed wet filter paper Whatman
no.41 [15]. The polymer on the filter was allowed to drain
for 20 min and then weighed to determine the weight of the
water-swollen gel. Corrections were made for the water
retention of the filter paper. The water absorption value
was calculated in g/g units as follows [30]:

$$\text{Water absorption value} = \frac{\text{Wet weight} - \text{Dry weight}}{\text{Dry weight}}$$

2.2.7   Determination of water absorption in NaCl,
CaCl$_2$, and MgCl$_2$ solutions

         This procedure was identical to the
determination of the water absorption value, but instead of
using deionized water, salt solutions of 0.5%, 1% and 2%
w/v were used. The water absorption in each solution was
expressed in gram of water per gram of dry sample as

defined above.

2.2.8   Determination of water retention in sand with
saponified starch-g-PAN

Sand was mixed with dried polymer at a concentration of 0%, 0.5%, 1%, 1.5% and 2% w/w. 20 g of the amended sand was placed in a 200-ml container having small holes at the bottom. 100 ml deionized water was then poured over it. The sand was allowed to drain for 20 min and then weighed to determine the weight of the wet sand. The water absorption of sand was calculated in grams per 100 grams of mixed sand as follows:

$$\text{Water retention in sand (\%)} = \frac{\text{Wet weight} - \text{Dry weight}}{\text{Dry weight}} \times 100$$

2.2.9   Reproducibility

All experimental data were determined three times. The data given in subsequent Tables represented the average value.