CHAPTER 4

Hydrogel Synthesis and Properties

Comparison of Initiation Methods

4.1 Initiation Methods

4.1.1 Thermal Initiation

Initially, 1.0-3.0 % mol of EGDM crosslinker per mol of Na-AMPS was added into the 30-50% w/v Na-AMPS solution in distilled water and stirred to give a homogeneous solution. Then 0.1% w/v of potassium persulfate as thermal initiator was added and, as soon as it had dissolved completely, the solution was poured into a vertical mould. The polymerisation reaction was allowed to proceed in an oven at 60°C for 4 hrs [63-67].

4.1.2 Redox Initiation

For redox initiation, the mixing procedure was the same as that described above for thermal initiation except that the initiating system used was 0.5% w/v of each of potassium persulfate as redox initiator and potassium metabisulfite and ferrous sulfate as redox coinitiators. The solution was quickly poured into a vertical mould and the polymerisation reaction allowed to process at room temperature for 24 hrs [68-72].

4.1.3 Photoinitiation

For photopolymerisation, the mixing procedure was again the same as described above, this time with 0.1% w/v of 4,4'-azo-bis(4-cyanopentanoic acid) as photoinitiator. The aqueous solution was poured into a vertical mould and photopolymerisation was carried out at room temperature for 10 mins using a commercially available UV lamp (100-400 nm) [73-77], as shown previously in Figure 3.13.

4.2 Physical Properties

The physical properties of the hydrogel sheets obtained from the 3 methods of initiation are compared in Tables 4.1 and 4.2 and Figures 4.1 – 4.5.

Table 4.1 : Comparison of the physical properties of the Na-AMPS hydrogel sheets (1.0% mol EGDM crosslinker) prepared with different monomer concentrations and using the 3 different methods of initiation.
(Sheet thickness = 1.20 ± 0.20 mm)

Na-AMPS % w/v	**Thermal initiation**	**Redox initiation**	**Photo initiation**
colour	pale yellow colour transparent	pale yellow colour transparent	colourless transparent
30%	loosely coherent weak, tacky	loosely coherent weak, tacky	loosely coherent weak, tacky
40%	coherent sheet, elastic, not smooth	coherent sheet, elastic, smooth	coherent sheet, elastic, smooth
50%	coherent sheet brittle, smooth	coherent sheet brittle, smooth	coherent sheet brittle, smooth

Table 4.2 : Comparison of the physical properties of the 40% Na-AMPS hydrogel sheets with different % crosslinker and using the 3 different methods of initiation.

EGDM % mol monomer	**Thermal initiation**	**Redox initiation**	**Photoinitiation**
1.0 %	coherent sheet, elastic, not smooth	coherent sheet, elastic, smooth	coherent sheet, elastic, smooth
2.0 %	coherent sheet brittle, smooth	coherent sheet brittle, smooth	coherent sheet brittle, smooth
3.0 %	coherent sheet brittle, smooth	coherent sheet brittle, smooth	coherent sheet brittle, smooth

Figure 4.1 : 30% Na-AMPS hydrogel sheet (1.0% mol EGDM) prepared by redox initiation. (Thermal and photoinitiation gave similar results except that, from photoinitiation, the sheets were colourless.)

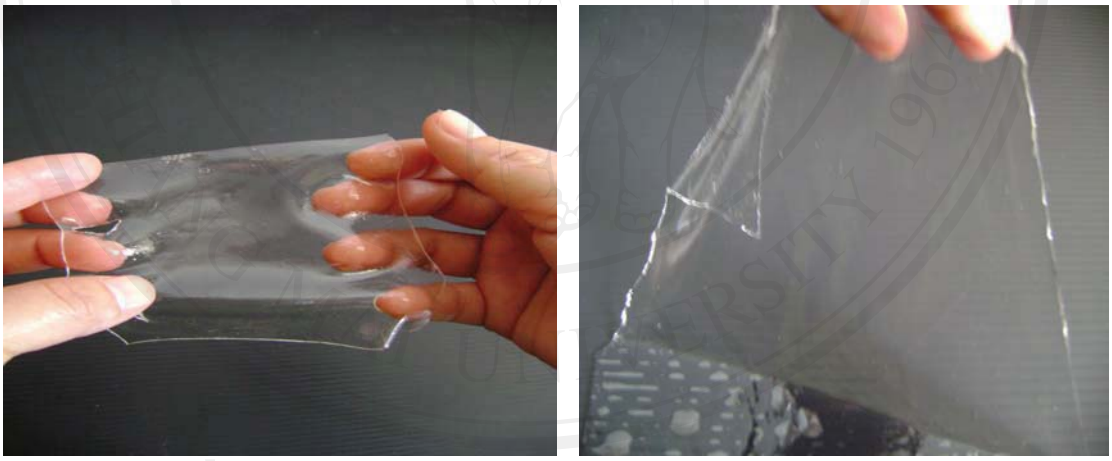


Figure 4.2 : 50% Na-AMPS hydrogel sheet (1.0% mol EGDM) prepared by redox initiation. (Thermal and photoinitiation gave similar results except that, from photoinitiation, the sheets were colourless.)

Figure 4.3 : 40% Na-AMPS hydrogel with 1% mol EGDM using thermal initiation

Figure 4.4 : 40% Na-AMPS hydrogel with 1% mol EGDM using redox initiation

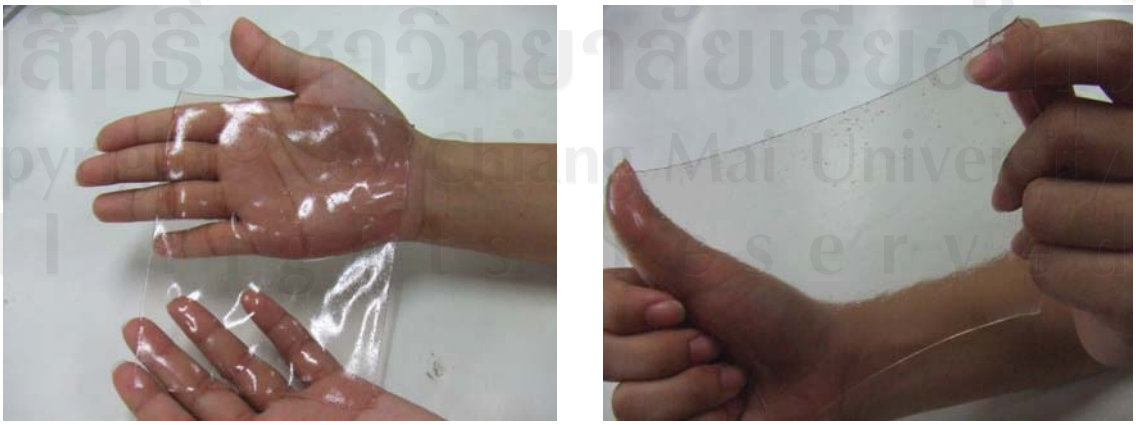


Figure 4.5 : 40% Na-AMPS hydrogel with 1% mol EGDM using photoinitiation

From the physical appearances and properties of the hydrogels, the following conclusions can be drawn:

(1) From the point of view of colour, photoinitiation gave the best results. Using photoinitiation, the hydrogel sheets were colourless whereas those from thermal and redox initiation had a pale yellow discolouration. However, apart from this, all of the sheets were equally transparent.

(2) A monomer concentration, [Na-AMPS], of 40% w/v gave the best mechanical properties in terms of tear strength and elasticity. At the lower concentration of 30% w/v, the hydrogels could only form loosely coherent sheets which was an indication that there was insufficient polymer in the hydrogel network. This meant that the hydrogel sheet had little or no tensile strength. However, too much polymer was also a disadvantage. As the 50% w/v hydrogels showed, they were coherent but significantly weaker than the 40% w/v hydrogels. This demonstrates that, as the polymer content in the hydrogel network increases above a certain level, the polymer-polymer interchain ionic interactions increase as the SO_3 group-solubilizing and plasticizing actions of the water decrese. Since the ionic interactions are effectively physical crosslinkes, the hydrogel starts to lose its elasticity and becomes more brittle.

(3) At the same 40% w/v [Na-AMPS] concentration, an [EGDM] crosslinker concentration of 1.0% mol (relative to [Na-AMPS]) gave the strongest sheet. At the higher [EGDM] concentrations of 2.0 and 3.0 % mol, the hydrogel sheet became progressively less elastic and more brittle. This was undoubtedly due to the increase in the crosslink density making the polymer network less extensible. This serves to illustrate that, while a certain amount of crosslinking is necessary to give the hydrogel sufficient elasticity and tear strength, too much crosslinking can make it less extensible and too brittle.

In summary, it can be concluded that the set of synthesis conditions which gave the best hydrogel properties, both in terms of physical appearance and mechanical properties, was:

Monomer concentration	=	[Na-AMPS]	=	40% w/v
Crosslinker concentration	=	[EGDM]	=	1.0 % mol
Method of initiation	=	photoinitiation		

4.3 Water Absorption Properties [78-82]

For water absorption testing of the hydrogel sheets, the following procedure was adopted:

(1) Since the hydrogel sheets direct from synthesis were already well hydrated, but in a non-equilibrium state, the sheets were allowed to equilibrate in air at room temperature. Equilibrium was considered to have been reached when the decrease in weight due to evaporative water loss ceased and the weight became constant. The hydrogel's remaining water content at equilibrium was its ***equilibrium water content (EWC)*** in air at the prevailing room temperature and relative humidity. For the hydrogel sheets synthesized as described in the previous section 4.1, EWCs in air were typically about 20% by weight and were attained over a period of 20-24 hrs.

(2) After equilibration in air, a 1x1 cm square test piece was cut from the hydrogel sheet and its weight recorded (± 0.0001 g). It was then immersed in distilled water in a circular glass basin at 37±1°C.

(3) At regular time intervals over a period of 30 mins, the hydrogel sample was removed from the distilled water, excess surface water absorbed with soft tissue paper, and the sample quickly weighed (w_h) before being re-immersed in the distilled water for the experiment to continue.

(4) The ***water content (WC)*** of the hydrogel was calculated from the following equation:

$$WC\,(wt\,\%) = \frac{(w_h - w_d)}{w_h} \times 100\,\% \qquad (4.1)$$

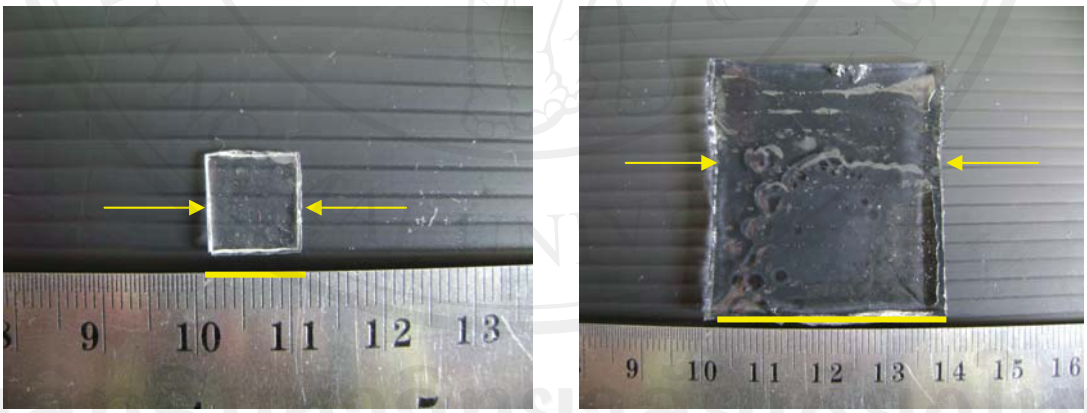
where

w_h = hydrated weight of the hydrogel

w_d = dry weight of the hydrogel

The value of w_d was obtained by drying the hydrogel sample direct from synthesis to constant (dry) weight in a vacuum oven at 60°C for, typically, about 6 hrs.

An illustration of how much the hydrogel sheets swelled due to water absorption is shown in Figure 4.6. The hydrogel sheet in Figure 4.6 shows an approximately 4-fold increase in length and width and a 3-fold increase in thickness.



(a) (b)

Hydrogel sheet before swelling
(1 x 1 x 0.12 cm)
Time t = 0
Water content = 22%

Hydrogel sheet after swelling
(4 x 4 x 0.35 cm)
Time t = 30 mins
Water content = 98%

Figure 4.6 : Hydrogel sheet prepared from 40% w/v Na-AMPS with 1.0% EGDM using photoinitiation (a) before and (b) after immersion for 30 mins in distilled water at 37°C.

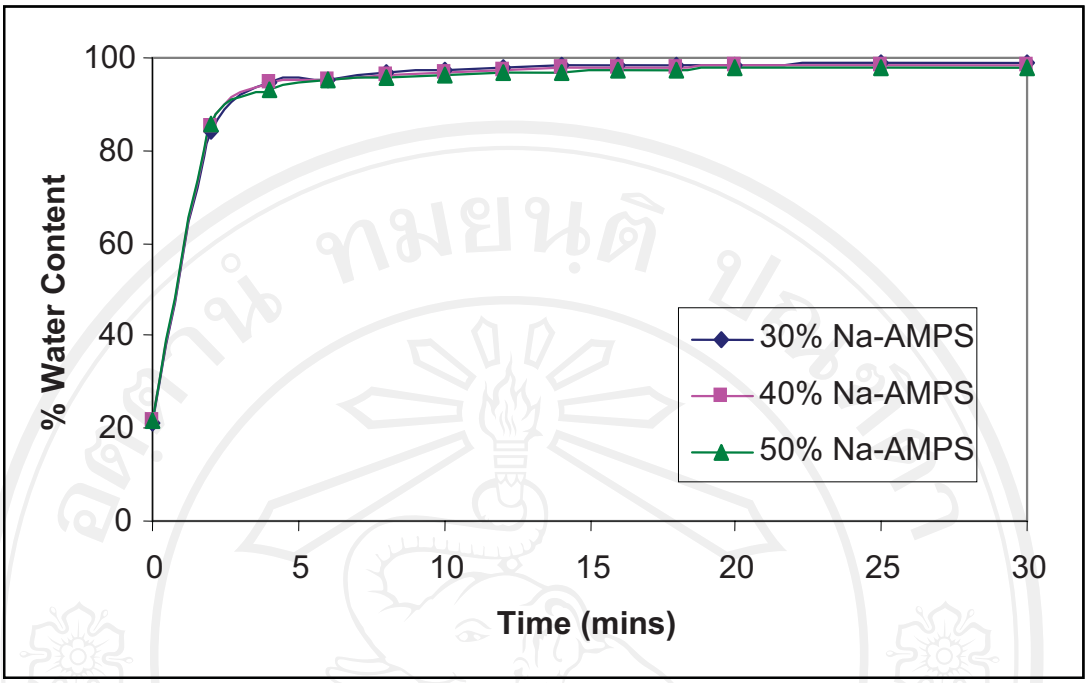


Figure 4.7 : Increase in water content (WC) with time for hydrogel sheets prepared from 30-50% w/v Na-AMPS with 1% mol of EGDM by thermal initiation

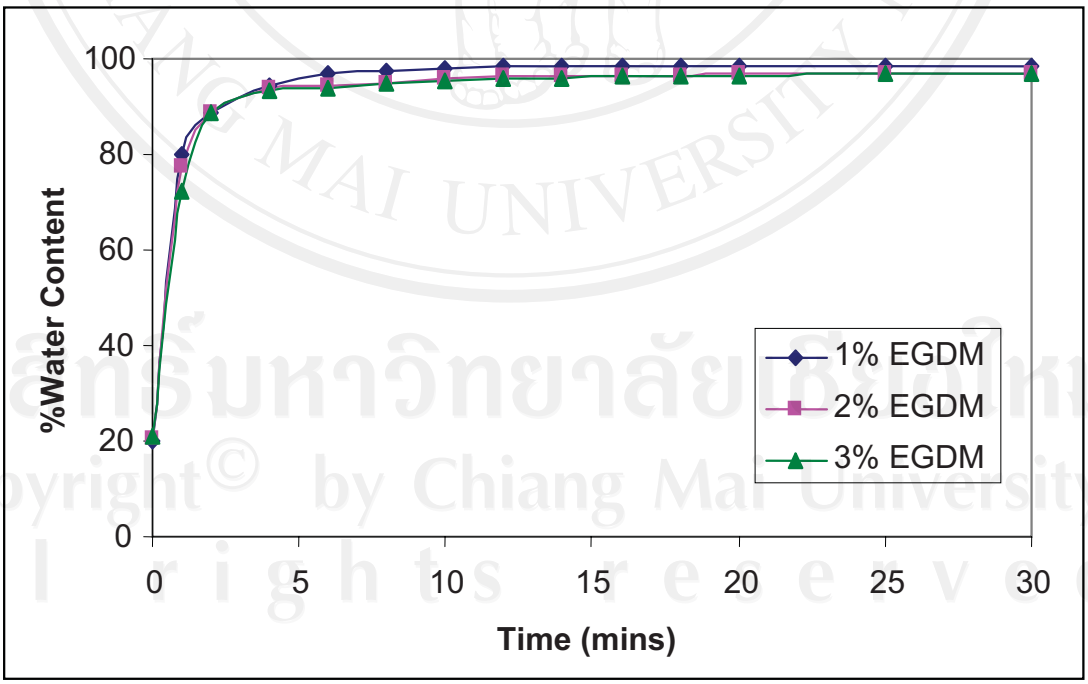


Figure 4.8 : Increase in water content (WC) with time for hydrogel sheets prepared from 40% w/v Na-AMPS with 1-3% mol of EGDM by thermal initiation.

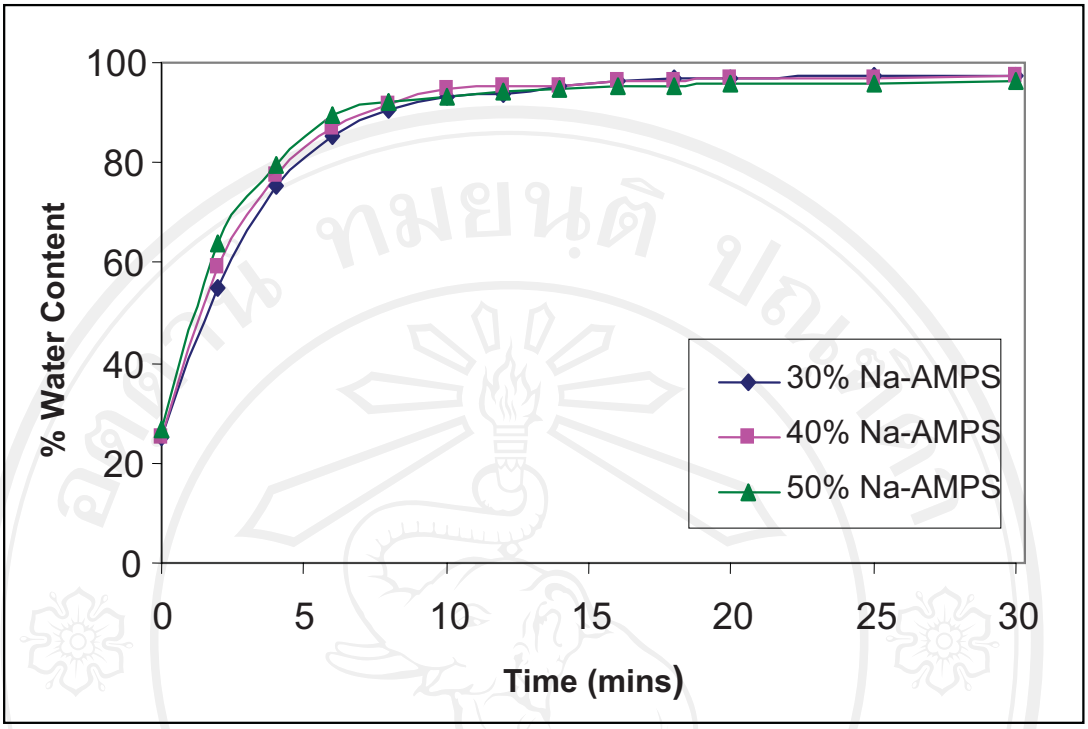


Figure 4.9 : Increase in water content (WC) with time for hydrogel sheets prepared from 30-50% w/v Na-AMPS with 1% mol of EGDM by redox initiation

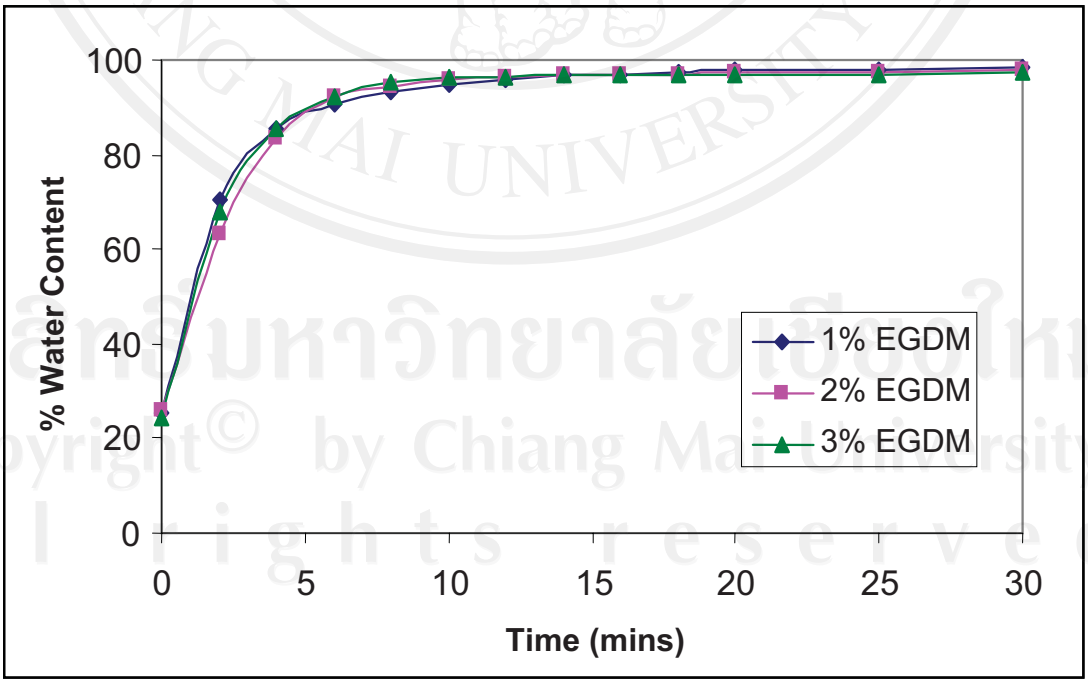


Figure 4.10 : Increase in water content (WC) with time for hydrogel sheets prepared from 40% w/v Na-AMPS with 1-3% mol of EGDM by redox initiation

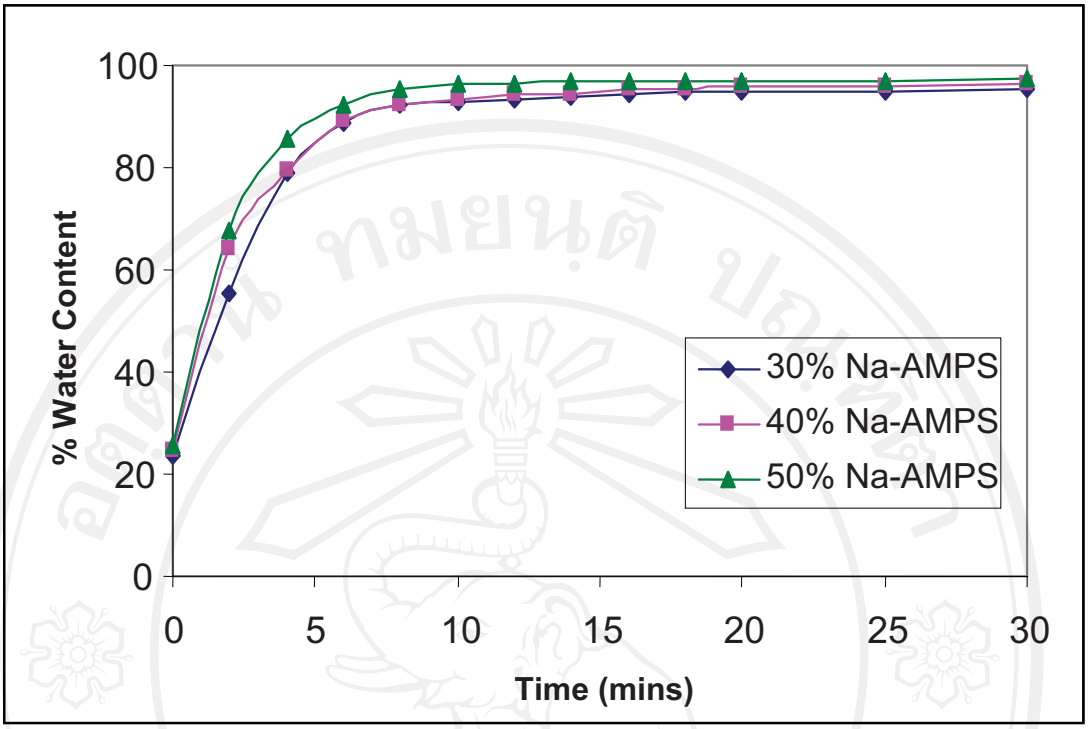


Figure 4.11 : Increase in water content (WC) with time for hydrogel sheets prepared from 30-50% w/v Na-AMPS with 1% mol of EGDM by photoinitiation

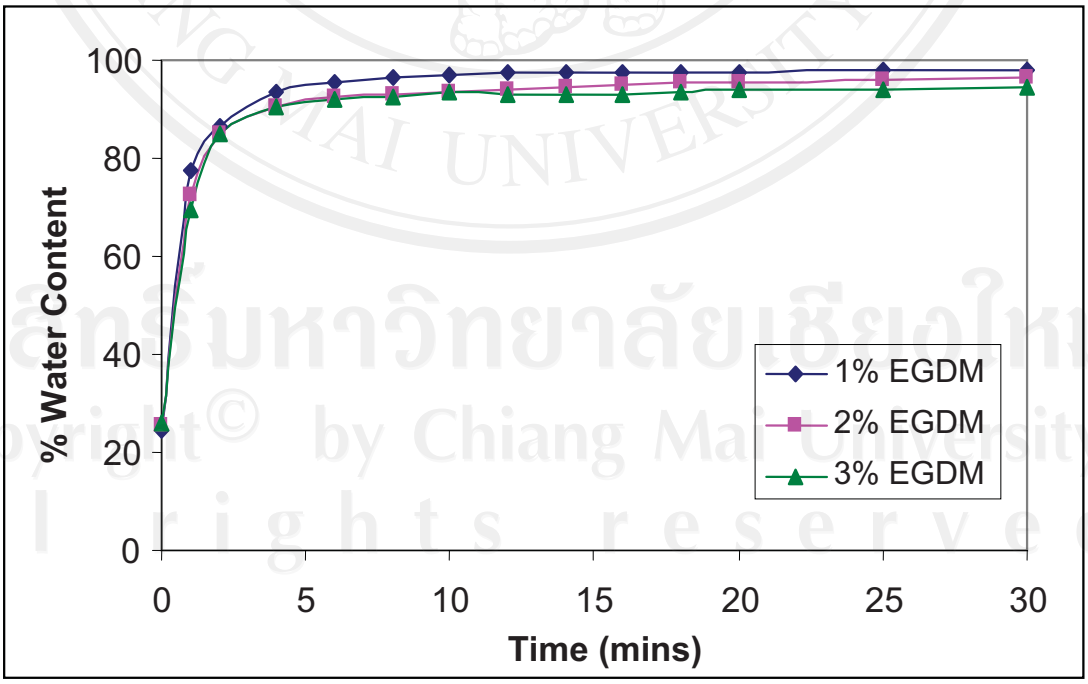


Figure 4.12 : Increase in water content (WC) with time for hydrogel sheets prepared from 40% w/v Na-AMPS with 1-3% mol of EGDM by photoinitiation

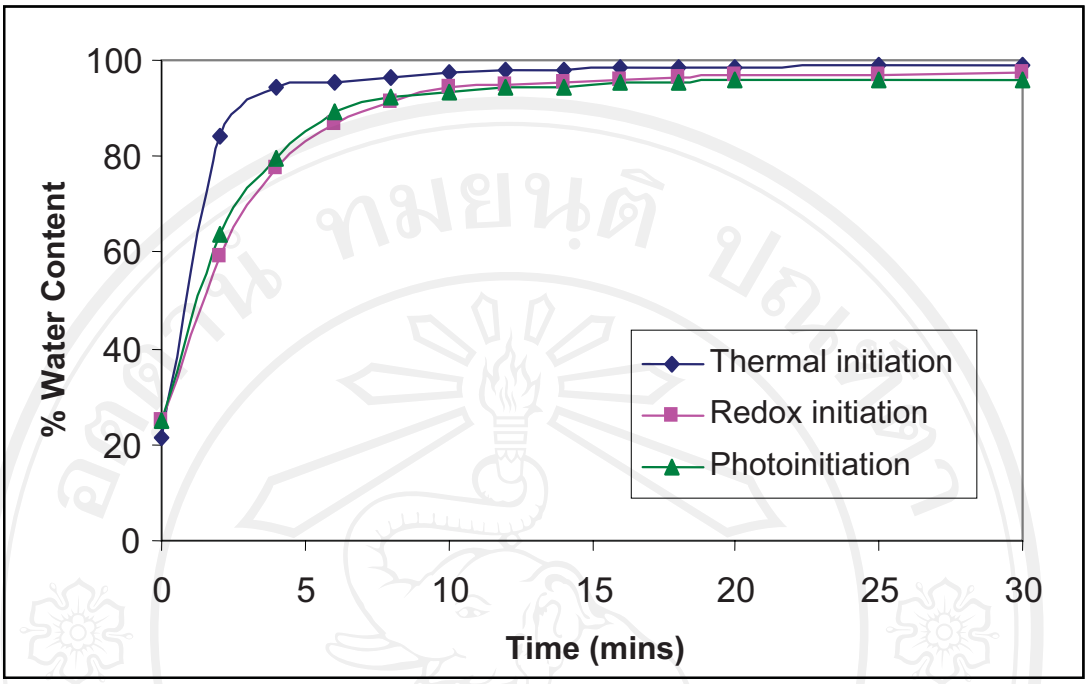


Figure 4.13 : Increase in water content (WC) with time for hydrogel sheets prepared from 40% w/v Na-AMPS with 1% mol of EGDM using the 3 different methods of initiation

The % water content (WC) – time profiles are shown in Figs. 4.7-4.13 and their comparisons enable conclusions to be drawn regarding the effects of :

(a) monomer concentration, [Na-AMPS]
(b) crosslinker concentration, [EGDM]
(c) method of initiation

As shown in Figures 4.7-4.12, neither the [Na-AMPS] nor the [EGDM], within the concentration range studied, had much effect on either the WC-time profile or the final equilibrium water content (EWC). In all cases, the rate of water absorption was very fast leading up to an EWC of 98±1% by weight within 30 mins. These results demonstrate the very strong osmotic power of the sodium sulphonate groups, $Na^{+}SO_3^{-}$, in the poly(Na-AMPS) structure in pulling water into the hydrogel.

The only clear difference in the WC-time profiles is shown in Fig. 4.13 in which the hydrogel from thermal initiation gave a faster initial rate of water absorption than those from redox initiation and photoinitiation. This may have been due to a less uniform hydrogel structure, both in terms of polymer molecular weight and crosslink density, since thermal initiation appeared to be the least controlled method of initiation.

Based on these water absorption profiles and the previous physical property data, it can be concluded that photoinitiation by UV light has given the best overall results. In addition, it can also be said that, in practical terms, photoinitiation has various advantages over thermal or redox initiation such as being easier to control, more easily convertible into a continuous process, and offering the possibility of combining both polymerisation and sterilization into one technological step [83-84]. Therefore, photoinitiation was the method of initiation chosen for the synthesis of all subsequent hydrogels described in this thesis.