STUDY ON OPTIMUM CONDITION OF EMPTY FRUIT BUNCH (EFB) BASED SUPERABSORBENT POLYMER COMPOSITE

SITI AISYAH SHAMSHUN BAHARIN

Thesis submitted in fulfillment of the requirements
for the award of the degree of
Bachelor of Chemical Engineering

Faculty of Chemical Engineering & Natural Resources
UNIVERSITY MALAYSIA PAHANG

FEBRUARY 2013

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ABSTRACT

This research presents an upgrade of superabsorbent polymer composite (SPC) towards water absorbency by adding a fibre using empty fruit bunch (EFB). The scope of this study was to determine the optimum condition of EFB based SPC when the filler, crosslinker and initiator amount being varied and also the effect of water absorbency towards different pH solution. The technique used was solution polymerization. The SPC were characterized by Fourier Transform Infrared Spectroscopy (FTIR), Field Emission Scanning Electron Microscopy (FESEM) and Thermo Gravimetric Analysis (TGA). Optimum water absorbency were achieved at 119.64 g/g at 25wt%, 129.005 g/g at 20wt% and 144.778 g/g at 5wt% for the initator, crosslinker and empty fruit bunch amount, respectively. Optimum condition of water absorbency was found to be in alkaline solution which is at pH 8 for initiator content, pH 10 for crosslinker concentration and pH 8 for filler content.

KAJIAN TERHADAP KONDISI OPTIMAL SERABUT TANDAN KOSONG TERHADAP POLIMER KOMPOSIT PENYERAP LAMPAU

ABSTRAK

Kajian ini membentangkan tentang pembaharuan dalam polimer komposit penyerap lampau (SPC) terhadap penyerapan air dengan mengunakan serat serabut tandan kosong (EFB) dari kelapa sawit. Tujuan kajian ini adalah untuk mendapatkan kondisi optimal serabut tandan kosong terhadap polimer komposi penyerap lampau apabila pengisi, pemaut silang dan pemula diubah-ubah dan juga kesan terhadap penyerapan air dalam kondisi larutan pH yang berbeza. Teknik yang digunakan adalah kaedah pempolimeran larutan. Polimer komposit penyerap lampau telah dicirikan dengan menggunakan spektroskopi jelmaan Fourier infra-merah (FTIR), Field Emission Scanning Electron Microscopy (FESEM) dan Analisa Thermogravimetric (TGA). Kondisi optimal telah dihasilkan pada 119.64g/g pada 25% berat, 129.005 g/g pada 20% berat dan 144.778 g/g pada 5% berat masing-masing untuk pemula, pemaut silang dan pengisi. Kondisi optimal untuk penyerapan air telah didapati berada dalam larutan alkali iaitu pada pH 8 untuk pemula, pH 10 untuk pemaut silang dan pH 8 untuk pengisi.

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LIST OF ABBREVIATIONS

AA	Acrylic Acid
AM	Acrylic Amide
APS	Ammonium Persulphate
EFB	Empty Fruit Bunch
FESEM	Field Emission Scanning Electron Microscopy
FTIR	Fourier Transform Infrared Spectroscopy
KPS	Potassium Persulphate
MBA	N,N-methylene-bis-acrylamide
SPC	Superabsorbent Polymer Composite
TGA	Thermogravimetric Analysis

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF THE STUDY

Superabsorbent polymer composites (SPC) are organic material with lightly cross-linked three-dimensional structure possessing very high swelling capacity in aqueous medium (Yao et al., 2012). It is a modified or advanced type of hydrogel which have similar characteristics with hydrogels, only that superabsorbent materials have a high potential to absorb water or other fluid and swell 1000 times than of their dried weight (Laftah et al., 2011). The uses of non-hygienic uses of SPC is commonly used in industries such as agricultural applications, pharmacy and medicine, separation or water treatment, fibers and textiles, water-swelling rubbers, electrical applications and civil structures while for hygienic uses include fire-extinguishing gels, re-freshening systems, sludge or coal dewatering, enzyme or catalyst support, packaging and artificial snow (Zohuriaan-Mehr et al., 2010).

The synthesis of the first water-absorbent polymer goes back to 1938 and in 1950s, the first generation of hydrogels appeared. In 1970s the first commercial SPC was produced and the hydrolyzed product was developed up until 1978 when the commercial production of SPC began in Japan for uses in feminine napkins (Zohuriaan-Mehr and Kabiri, 2008). For more than three decades, improvement towards the uses of SPC has been made rapidly with the production of SPC for personal care products (baby diapers and feminine incontinence products) accounts for about 80% of the overall hydrogel production.

In these recent years, producing biodegradable polymers have attracted interest of many researchers globally. Extensive attention has been directed towards SAPs being prepared through graft copolymerization of monomers onto the chain of such natural fibres to render the SPCs to be biodegradable, and hence producing environmentally friendly SPC, which may offer advantages for many applications (Hashim and Jamaludin, 2011). Various experiments have been conducted in order to produce an eco-friendly polymer for example cross-linked starches or polyvinyl alcohol with SPC (Zhao et al., 2005), grafting of sepiolite nanocomposite with poly(acrylic acid-co-acrylamide) (Zhang et al., 2005), SPC based on flax yarn waste (Yao et al., 2012) and graft-copolymerization of wheat straw (Li et al., 2011).

Therefore, this research of incorporating a biodegradable filler; empty fruit bunch (EFB) with SPC will help to upgrade the limitation biodegradability of SPC and help to create a greener environment.

1.2 PROBLEM STATEMENT

Synthetic polymer based SPCs are poor in degradability especially for application in agriculture and horticulture properties which can create significant problems to the environment. This imperfection can be reduced with the incorporation of fibre with SPC in order to render it to be biodegradable, environmental friendly and also reduce its toxicity and cost. EFB is chosen as the fibre because it is an abundance waste of oil palm which means that it is easily to be found, a renewable resource that decomposes relatively quickly into the environment which not only a good contribution to the health of the soil but also economical friendly because it is cheap in costs. Thus an EFB based SPC has the ability to biodegrade and compost safely into the environment and the polymer can be used in a larger scope of application.

1.3 OBJECTIVES

The objectives of this research are:

a) To determine the optimum condition of EFB based SPC by determine:
    i. Effect of amount of empty fruit bunch towards water absorbency
    ii. Effect of amount of crosslinker towards water absorbency
    iii. Effects of amount of initiator used towards water absorbency
b) To determine effect of water absorbency towards different pH solution

1.4 SCOPE OF STUDY

The scopes of this study were to incorporate the fibre that is oil palm empty fruit bunch (OPEFB) with the SPC. Two types of monomers used were acrylic acid (AA) and acrylamide (AM) while the initiator used to initiate radical reaction was Ammonium persulphate (APS). Cross-linking agent that acted as linkers between polymer chains used in this research was N,N-methylene-bis-acrylamide (MBA). 3-necked flask equipped with a mechanical stirrer, condenser, thermometer, nitrogen line and hot plate were used in synthesizing the SPC. Polymerization technique used for this synthesis is solution polymerization. Tea-bag method was used for water absorbency determination in different pH solutions.

1.5 SIGNIFICANT OF STUDY

Advancement in its features and uses has been made for superabsorbent materials being able to be exploited in a variety, broader field since the findings and commercialization of hydrogel materials decades ago. Almost all types of fields nowadays have applied superabsorbent materials, depending on its particular uses such as construction, electrical industries, pharmaceuticals and biomedical fields. Therefore, this research will be a great contribution not only to the health and hygienic industries but also to the other areas mentioned. This research will add to the current status of SPC materials and its application where the biodegradability of SPC will be improved, cost being reduced and creating an eco-friendly polymer through which more research conducted by scientists can be done to develop more products and create new frontiers. In addition, countries that are the major oil palm cultivating countries like Latin America countries, Indonesia and India can benefit from this research where EFB based SPC can be rapidly exported to other countries due to the high demands in the industries and as a result increasing the economy rate of these developing countries.

CHAPTER 2

LITERATURE REVIEW

2.1 SUPERABSORBENT POLYMER COMPOSITES (SPC)

Superabsorbent polymer composite (SPC) material is a modified or advanced type of hydrogel which have similar characteristics with hydrogels, only that superabsorbent materials have a high potential to absorb water or other fluid and swell 1000 times than of their dried weight. (Laftah et al. 2011).

Superabsorbent polymer composite possess an excellent characteristics of being able to absorb a large amount of water even under pressure and the absorbed water are hardly removable (Raju and Raju, 2003). Tthat makes it a polymer composite that catches the interest of scientists to always upgrade it in terms of its absorbency and swelling rate to be benefited in various application in industries. Meanwhile, Hashim and Jamaluddin (2011) defines superabsorbent polymers as “three-dimensional networks of flexible polymer chains that carry dissociated and ionic functional groups which characterized by hydrophilicity."

SPC can be divided into two main classes that are synthetic and natural superabsorbent polymer (Zohuriaan-Mehr and Kabiri, 2008) while Laftah et al. (2011) classified polymer hydrogels into three classes which are semi-synthesized polymer, natural macromolecules and synthesized polymers based on material resources point of view. There are various techniques to synthesize and prepare superabsorbent materials but among the most and commonly used techniques are solution polymerization, suspension polymerization and polymerization by irradiation (Laftah et al., 2011). Zohuriaan-Mehr and Kabiri (2008) classified the techniques of polymerization into solution polymerization and inverse-suspension polymerization.

Some of the characteristics of SPC that scientists are upgrading in order to have an effective and quality SPC are their absorbency, gel strengths and absorption rate (Raju et al., 2004). Hashim et al. (2011) emphasizes that the desired features of SPC are high swelling capacity, high swelling rate and high absorbency under load (AUL). Furthermore, water absorbency of SPC is usually highly influenced by its composition, molecular weight, degree of cross-linking, the molecular conformation of the polymer and also by the properties of liquids to be absorbed. Superabsorbing materials have the ability to absorb deionized water as high as 1000- 100 000% (10-1000 g/g) while the common hydrogels (non-superabsorbing materials) have only the absorption capacity not more than 100% (1 g/g) (Zohuriaan-Mehr and Kabiri, 2008).

Figure 2.1 shows the different structure of the hydrogel formed in various conditions.

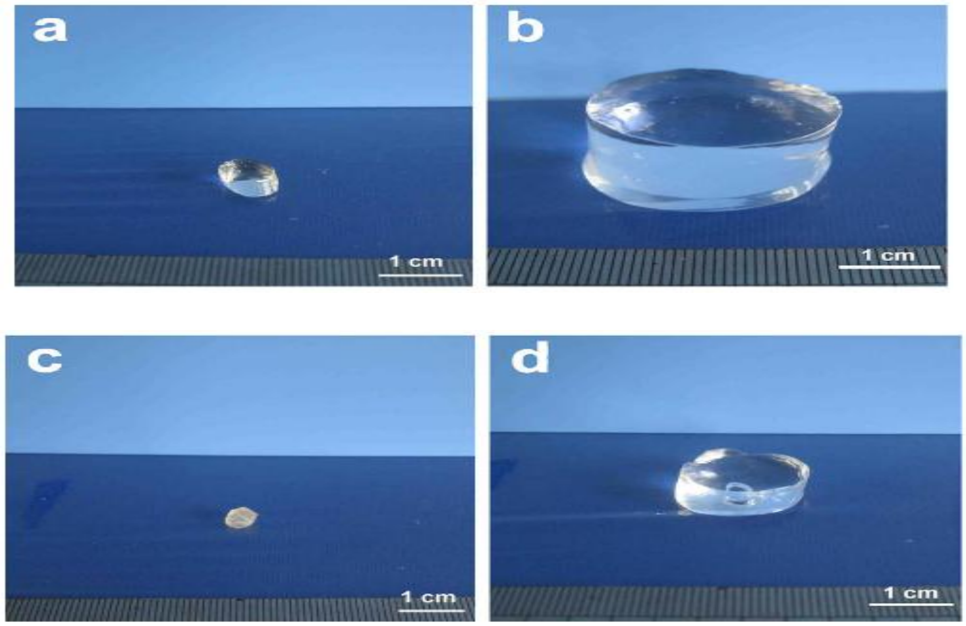

Figure 2.1 a) original hydrogel, b) swollen hydrogel, c) dried hydrogel and d) hydrogel after swelling in NaCl solution for a week

(Source: Zhang et al., 2010)

2.2 EMPTY FRUIT BUNCH (EFB)

Oil palm empty fruit bunch (EFB) is a natural fiber is a lignocellulosic waste from palm oil mills (Rahman et al, 2006) that has many uses in todays' industries and also seen as one of the potential renewable energy for the long run. According to a study by Amin et al. (2007), palm oil industry in Malaysia is among the biggest contributer to the country's economic growth.

Empty fruit bunch proves to be a good raw material for biocomposites due to its content of having cellulose content of oil palm fiber in the range of 43%-65% and lignin content in the range of 13-25% (Shinoj et al., 2011). Hence, this makes EFB suitable to be incorporated with polymer matrices; not only with SPC but other polymers such as natural rubber, polypropylene, polyvinyl chloride, epoxy, polyester to form a biocomposite product. Biocomposites are defined as the materials made by combining natural fiber and petroleum derived non-biodegradable polymer or biodegradable polymer. This is highly beneficial to the environment because SPC is a non-biodegradable material. Not only that, but the composites are found to be more hydrophilic which increases the water absorbency of the SPC when oil palm fiber is incorporated (Shinoj et al., 2011).

Moreover, the suitability of EFB for composite application is due to its high cellulose content, high toughness values and with the presence of hydroxyl group makes the fibre hydrophilic thus this cause low interfacial adhesion with hydrophobic polymer matrices during composite fabrication. EFB as a fibre may also contribute to the mechanical properties of the material such as in a research of a hybrid composite synthesized using oil palm EFB and glass fibre as reinforcing agents in polypropylene matrix showed that composites with oil-extracted EFB produced significantly higher flexural, tensile strength and toughness than those without unextracted EFB (Rozman et al., 2001). EFB acts as an excellent filler for a non-biodegradable polymer due to high potential to increase in the mechanical properties and water absorbency.

In the oil extraction of EFB, the treatment of the filler was carried out by refluxing the EFB fibres in a solvent mixture of toluene, acetone and ethanol with a particular volume for 3 hours and finally the extracted EFB were dried in an oven at 150C for 5 hours (Rozman et al., 2001).

Physical characteristic of the fibrous elements are shown in Table 2.1. With regards to its physical properties when compared with a Canadian trembling aspen, EFB fibers have similar length cell diameter but much thicker cell wall and as a result, higher coarseness and rigidity index.

Table 2.1 Fiber properties of Empty Fruit Bunch and Aspen Fiber

Property	EFB fiber	Aspen fiber
Length-weighted fiber length, mm	0.99	0.96
Fiber diamenter (D), µm	19.1	20.8
Cell-wall thickness (T), µm	3.38	1.93
Fiber coarseness, mg/m	1.37	1.01
Fines (<0.2mm), % (arithmetic mean)	27.6	18.1
Rigidity index, $(T/D)^3 \times 10^{-4}$	55.43	7.99

(Source: Law et al., 2007)

Even with the many advantages of a SPC, it has its limitation in uses such as its non-biodegradability and the toxicity that might cause long term environmental problems. Therefore, by adding filler to the polymer, it will create a more biodegradable and hence producing an environmentally friendly SPC which offer a larger scope of uses and applications. Besides that, the addition of fibre with the SPC is to increase its absorbency capacity (AC) and swelling rate because fiber contributes to increase the network of the cross linkers thus acting as cross linker agent itself which will affect the AC of the SPC. Figure 2.2 shows the chemical reaction in synthesizing a SPC.

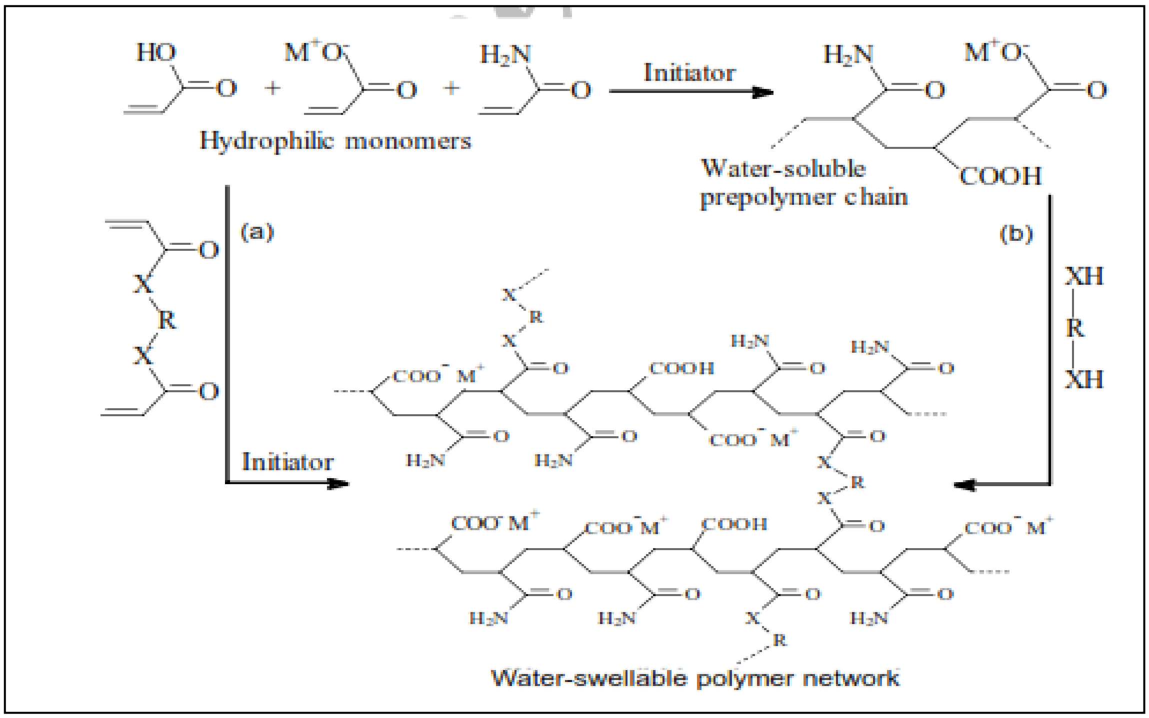

Figure 2.2 Chemical structures of the reactants and general pathways to prepare an acrylic SPC network

(Source: Zohuriaan-Mehr & Kabiri, 2008)

2.3 MONOMER (AA-AM)

Different monomer ratio used to produce a superabsorbent polymer composite (SPC) will create different swelling behavior and absorbency rate. Study by Raju et al. (2004) reveals that the experimental results of SPC's shows good absorbency in two solutions, water and NaCl solution when acrylamide, calcium acrylate and sodium methacrylate were used as monomers via aqueuos solution polymerization. Ammonium persulfate (APS) was used as initiator and N, N-methylene-bis-acrylamide (MBA) as the cross linking agent.

Monomer ratios or ionic units give a huge difference to the swelling capacity of superabsorbent polymer composites. It was found that swelling increases with the increase in ionic units in the backbone chain (Mohan et al., 2004). Figure 2.3 illustrates the behavior of effect monomer ratio towards water absorbency. From the findings, it was found that when the monomer in the feed was 0.1mole/L, the water absorbency (Q) was 110 while when the monomer in the feed was 0.22, the water absorbency increases to 500. This was supported by Wang and Li (2005) whom observes that the water absorbency increases when the monomer ratio parameter was varied from 0.2 to 1.0 and maximum condition was obtained at 0.51.

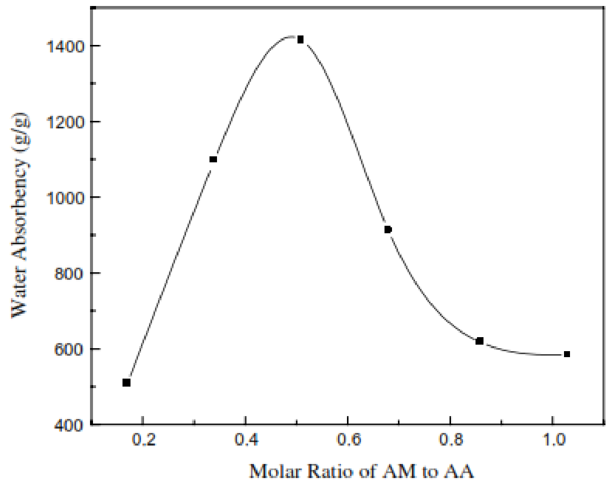

Figure 2.3 Effect of monomer ratio towards water absorbency

(Source Wang and Li, 2005)

According to Laftah et al. (2011), absorbency capacity and swelling rate increase when the monomers with hydrophilic groups such as –OH, CONH-, -SO_3H is used in contrast with monomers with hydrophobic groups which will hinders the absorption of water easily.

2.4 INITIATOR

Ammonium persulphate (APS) is the commonly used initiator either in solution polymerization or inverse-suspension method of polymerization besides potassium persulphate (Zohuriaan-Mehr and Kabiri, 2008). Study by Laftah et al. (2011) found that as the initiator content increases, absorbency capacity decreases. The indirectly proportional formula is due to the structure that takes place during polymerization where when the content of initiator is low, it will create a low polymerization rate. Hence, creating a larger network of SPC and aiding the fluid molecules to enter the network. This will eventually give rise to the absorbency rate.

Wang and Li (2005) reveals that the water absorbency increases as ammonium persulphate (APS) content rises from 0.2% to 1.0% and decreases with further increase in the content of APS. This shows that the amount of initiator used is directly proportional to the water absorbency until an optimum condition is achieved. Afterwards, the water absorbency will decrease with respect to the APS content.

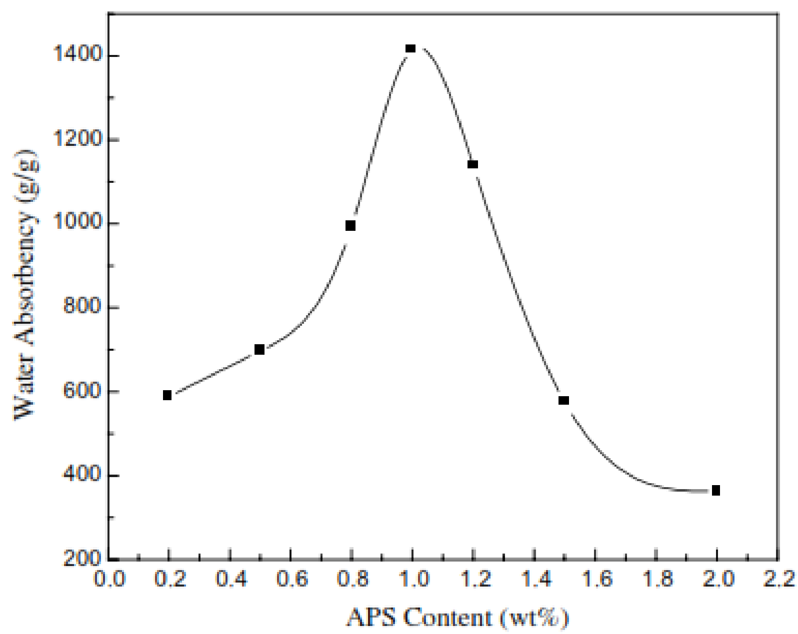

Figure 2.4 Effect of initiator content towards water absorbency

(Source: Wang and Li, 2005)

In addition, Zhang et al. (2012) experimented the effect of initiator content of superabsorbent nanocomposites towards water absorbency found that the maximum swelling was obtained at initiator concentration of 0.3 wt% when potassium persulphate

(KPS) was used as the initiator. However, APS is more commonly used as initiator when solution polymerization technique is conducted.

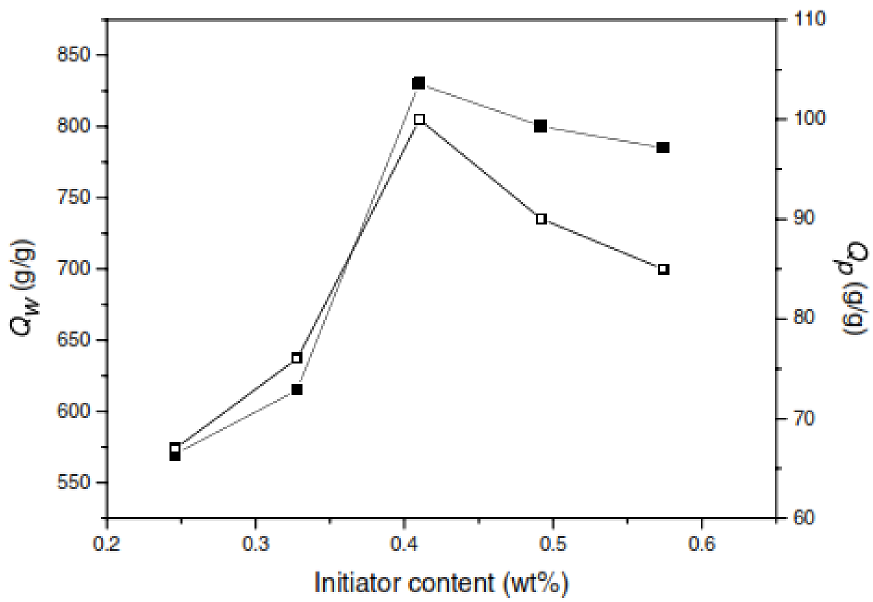

Figure 2.5 Influence of the initiator content on the water absorption capacity

(Source: Zhang et al., 2005)

2.5 CROSS-LINKING AGENT

Cross linkers play a major role in producing the desired feature of the SPC as it gives effect on the absorption and mechanical properties. The cross linker agents give changes to the SPC in terms of its concentration used. The higher the cross-linkers concentration, the lower will be the absorbency rate. This is due to the network does not allow water to easily enter it due to the high concentration of the cross-linkers (Laftah et al., 2011). This is proven by Wu et al. (2003) in their research that it can be obviously