SYNTHESIS AND CHARACTERIZATION OF HYPERCROSSLINKED POLYMER: EFFECT OF REACTION TIME

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ABSTRACT

Hypercrosslinked polymers were categorized as one of the new generation of the porous polymers. The interest in hypercrosslinked polymer is growing rapidly due to their unique physical, chemical and potential applications in many fields from drug-delivery to coatings. In this research, non-aqueous dispersion polymerization precursor was used prior to hypercrosslinking reaction in order to obtain hypercrosslinked polymer and it is focus on the effect of reaction time on the morphology of hypercrosslinked polymer. Hypercrosslinked particles were prepared in post-polymerization using the Friedel-Craft reaction that was swollen in anhydrous 1, 2-dichloroethane (DCE). Scanning Electron Microscopy (SEM), Fourier transform infrared spectroscopy (FTIR) and Thermal Gravimetry Analyzer (TGA) were used to characterize the hypercrosslinked particles. The results show that before post-polymerization, the precursor display good quality monodisperse spherical. However, after hypercrosslinking reaction, the quality of final product decrease which is for 12 hours and 24 hours of reaction time, hypercrosslinked particles were agglomerated but for 18 hours of reaction time, the particles can retain their quality similar with quality of precursor. For FTIR analysis, sample of 18 hours, 12 hours and 24 hours showed aliphatic CI streching vibrations at 1290 cm^{-1} ascribed to chloromethyl group derived from VBC residues and for TGA results, samples of 18 hours, 12 hours and 24 have the maximum weight loss with the compositions about 66.11 %, 47.07 % and 39.96 % respectively. Sample of 18 hours has the highest reaction interval compared with the other.

Key words: Hypercrosslinked polymer, hypercrosslinking reaction, Friedel-Craft reaction

ABSTRAK

Polimer persilangan tinggi di kategorikan sebagai salah satu generasi baru untuk polimer berliang. Minat terhadap polimer persilangan sedang berkembang dengan pesat kerana mempunyai polimer ini mwmpunyai keunikan fizikal, kimia dan aplikasikan yang luas dalam pelbagai bidang dari ubat-ubatan hingga salutan. Dalam kajian ini, pelapor pempolimeran digunakan terlebih dahulu sebelum tindak balas persilangan untuk mendapatkan polimer persilangan tinggi. Tambahan pula, kajian ini memberikan fokus kepada kesan suhu ke atas kawasan permukaan dan morfologi polimer persilangan. Polimer persilangan disediakan menggunakan tindak balas Friedel-Craft di mana polimer pelopor membengkak di dalam 1,2-dichloroethane (DCE). Scanning Electron Microscopy (SEM), Fourier transform infrared spectroscopy (FTIR) and Thermal Gravimetry Analyzer (TGA) digunakan untuk mencirikan zarah persilangan. Berdasarkn keputusan, sebelum pelopor pempolimeran menunjukkan morfologi sfera yang baik. Bagaimanapun, selepas tindak balas persilangan kualiti produk menurun iaitu untuk 12 jam dan 24 jam masa bertindak balas, partikel persilangan bergumpal tetapi untuk 18 jam masa tindak balas, partikel kekalkan kualiti morfologi hamper sama dengan pelopor. Manakala, untuk FTIR analisis, sampel 18 jam, 12 jam dan 24 jam menunjukkan alifatik Cl regangan pada 1290 cm^{-1} dinisbatkan kepada kumpulan chloromethyl yang diperolehi daripada sisa VBC dan untuk keputusa TGA, sampel 18 jam, 12 jam dan 24 jam mempunyai maksimum berat yang hilang dengan komposisi masing-masing kira-kira 66.11 %, 44.07 % dan 39.96 %. Sampel untuk 18 jam mempunyai tempoh tindak balas yang paing tinggi berbanding dengan sampel yang lain.

Kata kunci : Polimer persilangan tinggi, tindak balas polimer persilangan, tindak balas Friedel-Craft

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LIST OF ABBREVIATIONS

BET	Brunauer – Ememett – Teller
DCE	1, 2- dichloroethane
FTIR	Fourier Transform Infrared Spectoscopy
SEM	Scanning Electron Microscopy
TGA	Thermal Gravimetry Analayze

1.0 INTRODUCTION

1.1 Hypercrosslinked Polymer

Hypercrosslinked polymers are materials have fine pores. Hypercrosslinked polymers were caused by the unprecedented combination of high sorption capacity towards both polar and non-polar organic compounds and rather easy regeneration (Tsyurupa & Davankov, 2006). They were prepared by extensive crosslinking of linear polystyrene chains in a strongly solvating media. Generally, the basic principle of obtaining hypercrosslinked polymers consists in the formation of a rigid highly solvated three-dimensional network. Owing to the high rigidity and reduced degree of chain entanglement, such “expanded” networks are characterized by loose chain packing, i.e., high free volume, and the unique ability to swell in both good solvents and non-solvents. Typical examples of preparing hypercrosslinked networks include the crosslinking of linear chains of polysulfone and polyarylates, copolymerization of styrene with a large amount of divinylbenzene, self-condensation of *p*-xylylene dichloride. All resulting materials differ substantially from classical polymers of the same chemical nature and comprise a new class of hypercrosslinked polymeric materials. Deformation and relaxation properties of hypercrosslinked polystyrene networks have been studied by thermo mechanical method at a uniaxial compression using individual spherical beads of the polymer (Pastukhov et al., 1999). The networks examined were prepared by post-crosslinking of highly swollen beads of a styrene (0.3 % DVB copolymer) with 0.3–0.75 mole of monochlorodimethyl ether, which results in the introduction of 0.6–1.5 methylene bridges between each two polystyrene phenyl rings (Pastukhov et al., 1999).

The important properties of hypercrosslinked as a hydrolytic stability, pressure resistance and ability to display an almost equal swelling in both polar and non-polar solvent fully justify continuing attempts to prepare mono sized micro beaded material and compare it with common silica-based materials for use as a general HPLC column packing (Davankov et al., 1969). Hypercrosslinked polymers are currently receiving great interest due to their easy preparation, high chemical and thermal stability. These polymers can be considered as promising materials for gas storage and separation, catalysis and heavy ions removal in waste water (Dowbenko and Hart., 1973). For hypercrosslinking particles, various types of important aspects were going to be investigated with a view to study the best operating parameters that may be influenced the quality of the final product (Pastukhov et al., 1999).

1.2 Motivation and statement of problem

Hypercrosslinked polymers are a new generation of permanently porous, polymeric resins with enhanced analyte retention characteristics arising from their high micropore contents and correspondingly high specific surface areas (>1000 m^2 g−1) (Bratkowska et al., 2010). They are able to uptake polar and non-polar solvents. Moreover, they are cheap to produce since the monomers and crosslinked such as divinylbenzene (DVB) are ready to use in the preparation. Their unusual and attractive properties have led to hypercrosslinked materials being chosen as candidates for applications such as iron-exchange resins (Bratkowska et al., 2010), solid-phase extraction (Fontanals et al., 2005) and catalysis (Lyubimov et al., 2009).

In 2004, Vianna-Soares shows that the specific surface area of 2-hydroxyl ethyl methacrylate (HEMA) copolymers are 31 m^2/g while for hyroxylpropyl methacrylate (HPMA) the specific surface area are 142 m^2/g. This surface area is very less for industrial use or any other applications (Vianna-soares et al., 2004). In 2014, Sachin Mane and his co-workers (Mane et al., 2014) show the synthesis of hydroxyl functionalized beaded copolymers from 2-hydroxy ethyl methacrylate by suspension polymerization using two different crosslinking agents; EDMA and DVB, and diluents; 1,1,2,2-tetrachloroethane and 1,2-dichlorobenzene. The maximum surface area obtained with 1,2-dichlorobenzene was 564 m^2/g whereas for 1,1,2,2-tetrachloroethane showned only 399 m^2/g. The variety of the particle size caused an inefficient packing in columns.

Many parameters that involved in hypercrosslinking reaction such as solvent system (Mane et al., 2014), types of catalyst (Lyubimov et al., 2009) were investigated and have been reported. In the best our knowledge, there is lack of research on effect of reaction time on hypercrosslinked polymer. Therefore, in this study, different ranges of time were used to investigate the effect morphology of the hypercrosslinked polymers. Reasonable quality of hypercrosslinked polymers was obtained by manipulating the time of reaction between 12 hours, 18 hours and 24 hours.

1.3 Objectives

The following are the objectives of this research:

- To synthesis hypercrosslinked particles using non-aqueous dispersion polymerization (NAD) precursor.
- To study the effect of reaction time hypercrosslinked polymer.

1.4 Scope of this research

The following are the scope of this research:

Non-aqueous dispersion polymerization (NAD) precursors were used in post-polymerization in order to obtain hypercrosslinked polymers. After that, the precursor was swollen in thermodynamically good solvent and the reaction was carried by using Friedel-Craft reaction chemistry with manipulate the reaction time between 12 hours, 18 hours and 24 hours. Then, hypercrosslinked particles were characterized using equipment such as Scanning Electron Microscopy (SEM), Fourier Transform Infrared Spectroscopy (FTIR) and Thermal Gravimetry Analyzer (TGA) to analysis the final product.

1.5 Organisation of this thesis

The structure of the reminder of the thesis is outlined as follow:

Chapter 1 provides a review of hypercrosslinked polymer, motivation and statement of problems. This chapter also provides the objectives and scope research of hypercrosslinked polymer.

Chapter 2 provides a description of the applications and general design features of hypercrosslinked polymer. A general description on the flow process is presented. This chapter also provides a brief discussion of the advanced experimental techniques available for hypercrosslinked polymer to study effect reaction of time.

Chapter 3 gives a review of the methodology of hypercrosslinked polymer. This chapter also provides the materials, equipments and the characterization that used in this study for hypercrosslinked polymer.

Chapter 4 is devoted to results and discussion for this experiment. This chapter provides the discussion of all the analysis which is Scanning Electron Microscopy (SEM) analysis, Fourier Transform Infrared Spectroscopy (FTIR) analysis and Thermal Gravimetry Analyzer (TGA) analysis.

Chapter 5 provides overall conclusion of this experiment.

2.0 LITERATURE REVIEW

2.1 Overview of Hypercrosslinked Polymer

In the early 1970s, hypercrosslinked polystyrene and sorbents were described in scientific literature (Rogozhin et al., 1969) and substantially come into routine practice by the end of 1990s. Due to the unique physical and chemical properties hypercrosslinked polymers have received attention as well as their potential applications in various fields (Gao & Yan, 2004). Hypercrosslinked polymers have been used in many applications such as sorption (Podlesnyuk et al., 1999), solid supports in catalyst (Sherrington, 2001), enzymes (Marconi, 1984), ion exchanges for cation (Bratkowska et al., 2010) and anion (Fontanals et al., 2008) and other applications. Success in the practical application of hypercrosslinked materials is caused by the unprecedented combination of high sorption capacity towards both polar and non-polar organic compounds and rather easy regeneration (Tsyurupa & Davankov, 2006). The hypercrosslinked polymer can be synthesized by using aqueous dispersion (ADP) polymerization and non-aqueous dispersion (NAD) polymerization particles as precursors prior to hypercrosslinking reaction in order to study about the effect of temperature, solvent system, monomer concentration and amount of catalyst on the specific surface area, pore volume and morphology of the polymeric materials.

Hypercrosslinked formation is different from conventional macroporous system because in the former case microphase separation occurs (Šálek & Horák, 2011). Three-dimensional polystyrene networks are widely used as sorbents and support in industry. The synthesis of such materials can yield three distinct types of network depends on the synthesis conditions. Firstly, it consists of homogeneous networks where the styrene copolymers with divinylbenzene (DVB) or other divinyl monomers are obtained by free radical polymerisation without any micro-phase separation of initial homogeneous system. Secondly, is a group of heterogeneous networks that obtain by copolymerization of styrene with a relatively high amount of DVB in presence a of good solvent. Lastly is the group that consists of heterogeneous networks.

Hypercrosslinked polymers are one of type of microporous polymers which are obtained by extensive post-crosslinking of polymer chains in the presence of good solvent. Many research groups has been probed the porous structure of hypercrosslinked polystyrene. They were also found that polymers of this type can be categorized as a new hypercrosslinked family distinct to conventional macroporous styrene-divinylbenzene (St-DVB) copolymers (Lee and Wi, 2010) due to hypercrosslinked polymers have a rigid three-dimensioned open network. Besides that, it displays extraordinarily high specific surface area (> 1000 m^2/g) and high micropore (> 2 nm) a high micropore contents (about 0.6 mL/g) which arise from the nature of hypercrosslinking process (Tsyurupa & Davankov, 2006).

All hypercrosslinked polystyrene products are materials with very fine pores. Some of the above commercial products additionally display larger transport channels that have been introduced in order to enhance the mass exchange. The latter heterogeneous products are often referred to as bi-porous. Hypercrosslinked adsorbing resins are highly porous materials, but their porosity has little in common with the porosity of traditional macroporous styrene–divinylbenzene sorbents, activated carbons, silica gels, porous glasses and others. There exist many methods to characterize their porous structure. However, only a few of these methods are applicable to the hypercrosslinked sorbents, largely for the reason that the networks of the latter are rather flexible and their porous structure may easily change. Dry hypercrosslinked polystyrenes tend to increase in volume on contacting with any liquid or gas. Besides, the materials are reversibly compressed and expanded on mechanical loading and/or heating. These circumstances strongly complicate and sometimes even render the application of several physical test methods impossible.

Hypercrosslinked sorbents have been applied to the solid-phase extraction (SPE) of several groups of compounds from different samples. Solid-phase extraction has been used in the purification and concentration of several analytes from complex matrices such as environment and biological samples (Fontanals et al., 2005). Traditional SPE sorbents are silica-based, and are normally composed of silica particles which can be modified easily to combine functional groups on their surfaces to enhance SPE selectivity. While silica-based sorbents are quite popular, they do suffer from low recoveries in the extraction of polar compounds and can be very unstable at the pH extremes that are all too often demanded by SPE protocols (Poole, 2003). Carbon-based sorbents such as graphitized carbon blacks or porous graphitic carbon are characterized by high thermal and chemical resistance properties and a superior adsorption capacity. However this enhanced sorption capacity can often result in excessive or irreversible binding of analytes (Masqué et al., 1998). Porous polymeric sorbents combine the most attractive properties of both silica-based and carbon-based materials. The products can be more stable across the entire pH range, while providing good sorption characteristics coupled with facile elution options. The most common polymeric sorbents are copolymers of divinylbenzene (DVB) and styrene, which is combine a hydrophobic structure with a specific surface area of between 500 and 800 m^2/g (Fontanals et al., 2005).

The other properties of polymers are capability to swell in polar and non-polar media and irrespective of the thermodynamic attraction of the medium to the precursor. Furthermore, when in dry state, polymers are extremely low density (Pastukhov et al., 1999). Because of this, many chemical companies such as Dow Chemical and Rohm and Haas were interested in the hypercrosslinked sorbents (R.T Stringfield et al., 1990). A low particle size that combined with a narrow particle size can help to improve the efficiency and packing of these sorbents into SPE cartridges, as well as their performance in use, while a higher specific surface area can enhance their retention properties. Moreover, Davankov-type hypercrosslinked (HXL) resins with a microporous structure and specific surface areas in excess of 1000 m^2/g have been shown to give better retention than the analogous macroporous materials with lower specific surface areas. These hypercrosslinked resins can be chemically modified to introduce functionalities that allow for better selectivity in the SPE process, or groups to increase the polarity of the resins, through either a copolymerization or post-polymerization chemical modification strategy (Cormack et al., 2012).

2.2 Application of hypercrosslinked polymer

2.2.1 Coatings

Hypercrosslinked polymers have been used as the base for various coating resins, such as powder coatings (Johansson et al., 2000), high solid coatings (Ma & Szewczyk, 2002), flame retardant coatings (Zhu & Shi, 2002) and barrier coatings for flexible packaging (Lange et al., 2001). It is depend on their high solubility, low viscosity and abundant functional groups.

2.2.2 Modifiers and Additives

Based on the unique properties of hypercrosslinked polymer, it can be applied as tougheners for thermosets (Mezzenga et al., 2001), curing, crosslinking or adhesive agents (Oh et al., 2001), dye-receptive additives for polyolefins (Burkinshaw et al., 2002), compatilizers (Jannerfeldt et al., 1999), dispersers (Star and Stoddart, 2002), processing aids and rheology modifier or blend components (Hong et al., 1999).

2.2.3 Supramolecular chemistry

Compounds beyond molecules with an order organized by non-covalent interactions are representing supramolecular. The important hypercrosslinked macromolecules in the supramolecular area self-assembly films and layer, core-shell amphiphiles, self-association objects, macroscopic molecular self-assembly, liquid-crystalline materials and host-guest encapsulation (Gao & Yan, 2004).

2.2.4 Other applications

Other application of hypercrosslinked polymer is for gas and solution separation. Hypercrosslinked polyimides were used as gas separation (Fang et al., 2001).

3 MATERIALS AND METHODS

3.1 Chemicals

The reagents that were used in the hypercrosslinked reaction are anhydrous 1,2-dichloroethane (DCE) (99.8 % grade), methanol (99.7 % grade) and iron (III) chloride (97 % grade). They were supplied by Sigma-Aldrich and were used as received.

3.2 Equipments

The hypercrosslinked polymers are performed in a three-necked, round-bottomed flask fitter with a condenser, overhead stirrer and two-blade PTEE-type stirrer. The reaction vessel was heated up using heating block at 80 °C.

3.3 Methodology

The non-aqueous dispersion (NAD) precursor (1.5 g) was added into a round-bottomed flask which is contains anhydrous 1,2-dichloroethane (DCE) (40 mL). Then, left it to swell fully under the nitrogen for 1 hour. After that, iron (III) chloride ($FeCl_3$) (in a 1:1 molar ratio of CH_2Cl: $FeCl_3$) is suspended in DCE (40 mL) were added. The mixture was heated up rapidly to 80 °C. The reaction was continued for 18 hours with continuous stirring over the entire reaction. The hypercrosslinked particles were filtered using vacuum filtration on a 0.22 µm nylon membrane filter. They were washed with MeOH and several times with aqueous HNO_3 (pH 2). Then, they were extracted overnight with acetone in a Soxhlex Extractor and dried *vacuo* (60 mbar) at 40 °C (Šálek & Horák, 2011).

3.4 Apparatus set up

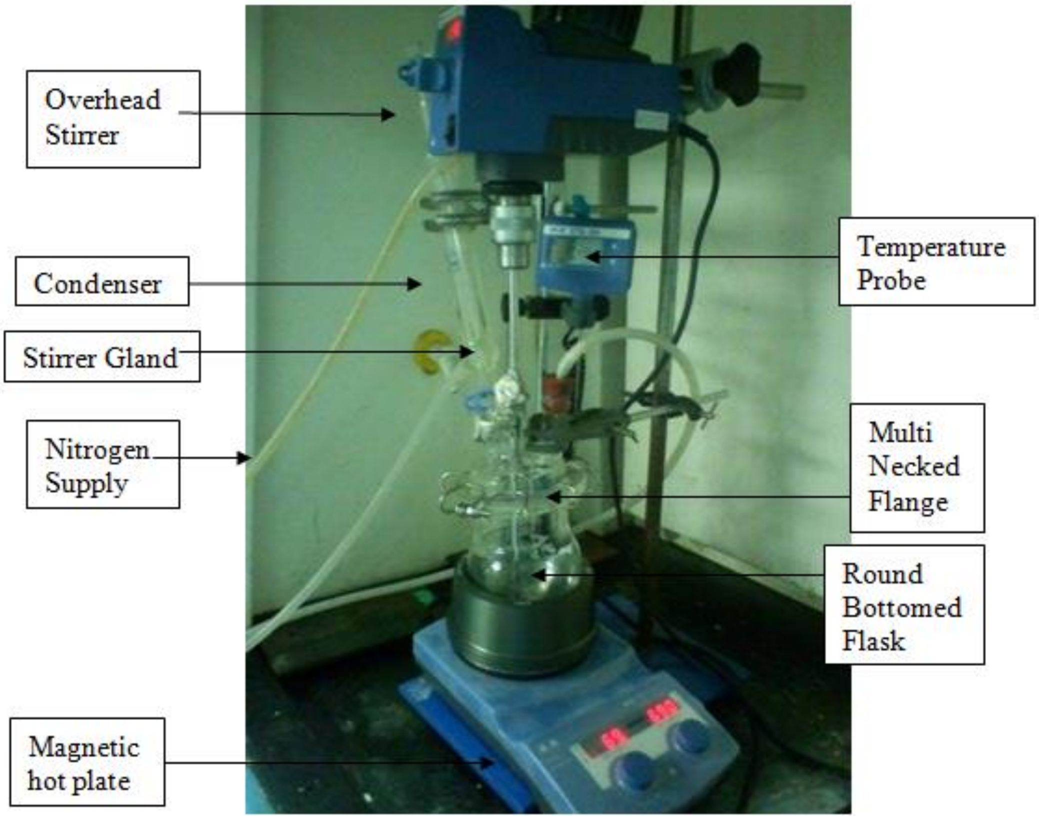

Figure 3-1: Apparatus set up for the experiment

Figure 3-1 shows the apparatus is set up to run an experiment. All reactions are performed under a nitrogen atmosphere. The nitrogen circuit included a flask with silica, to absorb any moisture present in the system. A multi-necked flange is placed on top of a round-bottomed reaction vessel and a metal clasp is used to secure the system. An overhead, four-bladed Teflon stirrer is used to agitate the system. The position of the stirrer is highlighted in order to ensure the system is agitated gently and efficiently. The position of the stirrer should not touch the bottomed of the reaction vessel to avoid the abrasion of the particle. If the stirrer is set too high, the agitation will result inefficient.

Figure 3-2: 0.22 µm nylon membrane is used to filter the hypercrosslinked particles

Figure 3-2 shows 0.22 µm nylon membrane is used to filter the hypercrosslinked particles.

3.5 Characterization of hypercrosslinked particles

3.5.1 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR analysis was carried out in order to identify the functional groups in the hypercrosslinked particles. FTIR relies on the fact that the most molecules absorb light in the infra-red region of the electromagnetic spectrum. This absorption corresponds specifically to the bonds present in the molecule. The frequency ranges are measured as wave numbers typically over the range 4000 – 600 cm^{-1}.

The background emission spectrum of the IR source is first recorded, followed by the emission spectrum of the IR source with the sample in place. The ratio of the sample spectrum to the background spectrum is directly related to the sample's absorption spectrum. The resultant absorption spectrum from the bond natural vibration frequencies indicates the presence of various chemical bonds and functional groups present in the sample. FTIR is particularly useful for identification of organic molecular groups and compounds due to the range of functional groups, side chains and crosslinks involved, all of which will have characteristic vibrational frequencies in the infra-red range. Below are the picture of the analyzer.

Figure 3-3 : Fourier Transform Infrared Spectroscopy

3.5.2 Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) was used for identify the morphological features and surface characteristic of the samples. In a scanning electron microscope, the specimen is exposed to a narrow electron beam from an electron gun, which rapidly moves over or scans the surface of the specimen. This causes the release of a shower of secondary electrons and other types of radiations from the specimen surface. The intensity of these secondary electrons depends upon the shape and the chemical composition of the irradiated object. These electrons are collected by a detector, which generates electronic signals. These signals are scanned in the manner of a television system to produce an image on a cathode ray tube (CRT).

The image is recorded by capturing it from the CRT. Modern variants have facility to record the photograph by digital camera. This microscope is used to observe the surface structure of microscopic objects. Below are the picture of the analyzer.

Figure 3-4 : Scanning Electron Microscopy

3.5.3 Thermal Gravimetry Analyzer (TGA)

Thermal Gravimetry Analyzer (TGA) was used to know the temperature where the sample is decomposed. Samples were weighed approximately 5 mg. Before start of each experiment, the systems was purged with N_2 gas at 100 mL/min for about 30 min (at 50 ºC) to remove entrapped gases. The samples were heated with constant heating rate at 10 ºC/min. The initial temperature was set at 30 ºC and final temperature was set at 900 ºC. Air cool for 50 min, and data sampling interval set at 0.50 s/pt. The weight loss and maximum conversion temperature were discussed. Below are the picture of the analyzer.

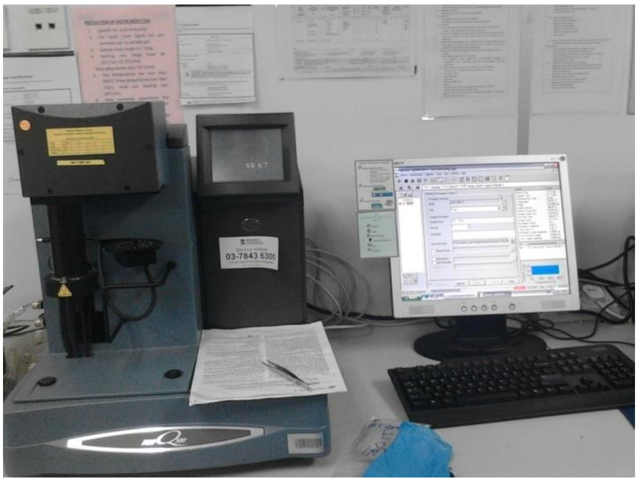

Figure 3-5 : Thermal Gravimetry Analyzer

4 RESULT AND DISCUSSION

4.1 Overview

Initial solution of monomer with dichloroethane was transparent and a white color. When the catalyst dissolved in dichloroethane was mixed, reaction initiated and the solution rapidly turned to dark violet. Viscosity of mixed solution was increased with reaction time and phase of mixture was converted from liquid to a gel-like state. After the cleaning step, final product was formed to brownish powder. Result for the Scanning Electron Micrography analysis, Fourier Transform Infrared Spectroscopy analysis (FTIR) and Thermogravimetric analysis were tabulated and discussed.

4.2 The Morphological of Hypercrosslinked Particles

SEM images of the precursor and hypercrosslinked samples were scanned at 5000× magnification as shown in Figure1. Figure 1 (a) and (b) showed a uniform spherical nature of copolymer precursor beads while in Figure 1 (c) and (d) showed that there was agglomeration of hypercrosslinked polymer beads. Apart from the agglomeration of polymer beads, there still some beads that formed from the reaction as shown in Figures 1(c) and (d) below. The differences in structure of the beads were certainly related to differences time of reaction of hypercrosslinked particles. The quality of particles decreases when the temperatures increase. This happen most probably because of some precursor dissolved in the solvent due to most probably very light crosslinker presence in the precursor and resulting they cannot retain their shape after hypercrosslinking reaction. As can be seen in the Figure 1 (b-d), the dissolved precursor also contaminate the surface of hypercrosslinked polymer where the surface of hypercrosslinked polymer quit rough compare to surface of precursor (Figure 1 (a)).

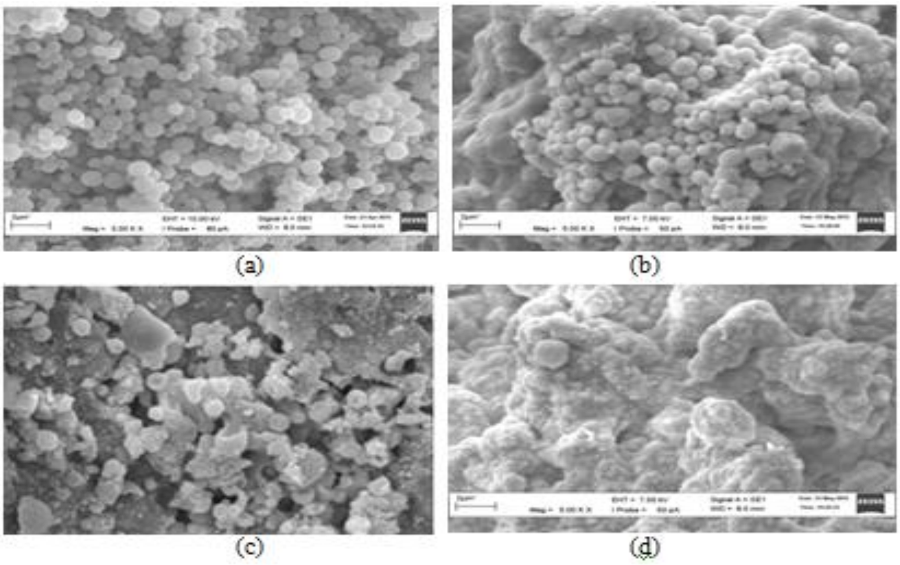

Figure 4-1 : SEM images of precursor and it hypercrosslinked derivative (a) Precursor, (b) hypercrosslinked polymer at 12 hours, (c) hypercrosslinked polymer at 18 hours and (d) hypercrosslinked polymer at 24 hours at 5000x magnifications

4.3 Functional Groups in the Hypercrosslinked Particles

FTIR spectrum analysis is very helpful for distinguish of functional groups that represents in copolymers. The FTIR spectrum of 18 hours, 12 hours and 24 hours reaction of time were done under ambient conditions in the wave range of 4000 to 400 cm^{-}1. The FTIR spectra of these samples were presented in Figure 4-2 below. Based on the graph, FTIR spectrum elucidate absorption peaks for CI for 12 hours, 18 hours and 24 hours were at 1290.85 cm^{-1}, 1291.07 cm^{-1} and 1291.17 cm^{-1}, respectively ascribed to chlorometyl group derived from VBC residues. Next, peaks near1445.89 cm^{-1}, 1449.17 cm^{-1} and 1416.19 cm^{-1} are attributed to methyl C-H asymmetrical bending vibrations that arising from benzene group.

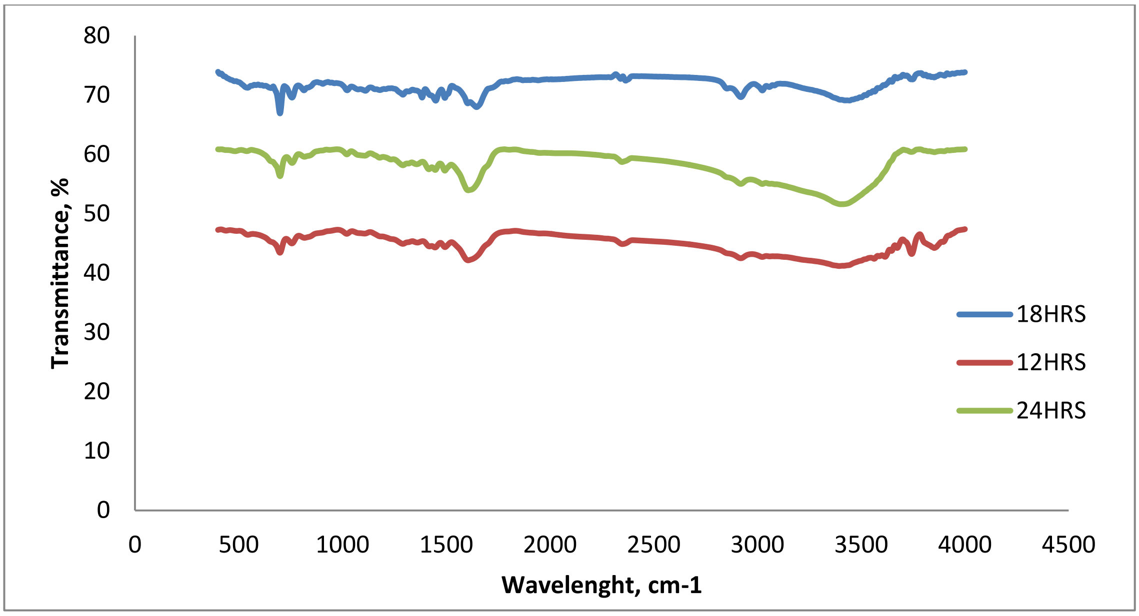

Figure 4-2 : FTIR spectrum of 12 hours, 18 hours, 24 hours for hypercrosslinked particles

Figure 4-3 showed FTIR spectrum for precursor that has 75% of styrene and 25% of VBC. The FTIR spectrum of 18 hours, 12 hours and 24 hours reaction of time were done under ambient conditions in the wave range of 4000 to 400 cm^{-}1. The FTIR spectra of these samples were presented in Figure 4-3 below. Based on the graph, FTIR spectrum elucidate absorption peaks for CI for 12 hours, 18 hours and 24 hours were at 1240.85 cm^{-1}, 1280.25 cm^{-1} and 1281.07 cm^{-1}, respectively ascribed to chlorometyl group derived from VBC residues. Next, peaks near for 12 hours, 18 hours and 24 hours reaction of time at 1425.17 cm^{-1}, 1445.25 cm^{-1} and 1443.15 cm^{-1} are attributed to methyl C-H asymmetrical bending vibrations that arising from benzene group.

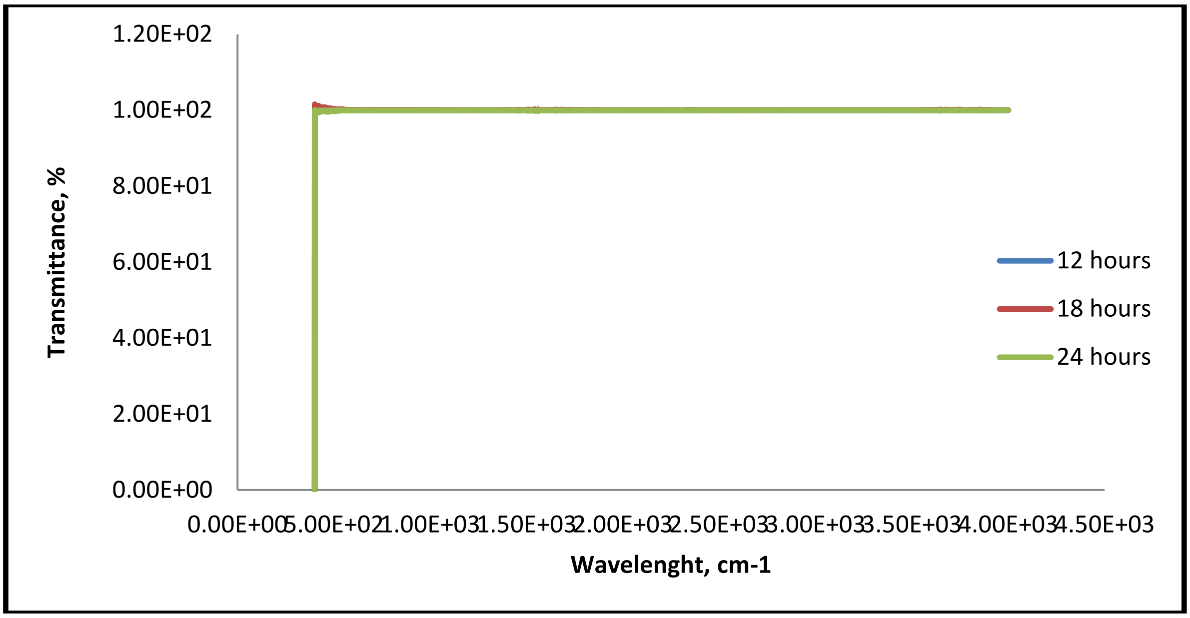

Figure 4-3: FTIR spectrum of 12 hours, 18 hours and 24 hours of hypercrosslinked particles of 75% styrene: 25% vbc

4.4 Decomposition of Hypercrosslinked Particles.

Based on the Figure 4-4, the TG curve shows that it is multistage decomposition. Derivative thermogravimetric curve (DTG) represents rate of mass change (dm/dt) as a function of temperature while the peak point of the derivative curve indicates the point of the greatest rate change on the weight loss at maximum reaction rate occurs (Shinde & Singarvelu, 2014). Figure 3and 4 showed TGA profile of weight and derivative weight for precursor, 18 hours, 12 hours and 24 hours of hypercrosslinked particles at heating rate 10 ºC/min respectively. In the first stage temperature up to 100 ºC, all the samples lost their mass in the range between 1-10% as evaporation of moisture content. High volatile matter is burned approximately in the temperature between 200 ºC to 300 ºC. Meanwhile, medium volatile matter is burned in the range of 200 ºC to 700 ºC. The difference between final temperature point and initial temperature point shows reaction interval. Within this range, tested sample lost its most of the weight.