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ELECTROSPINNING OF NEAT AND ALUMINIUM-DOPED RESORCINOL/FORMALDEHYDE GEL

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เส้นใยคาร์บอนและอนุภาคทรงกลมคาร์บอนที่มีโครงสร้างรูพรุนแบบเมโซ สามารถเตรียมได้จากวิธีโซลเจลผนวกกับการปั่นเส้นใยด้วยไฟฟ้าสถิต โดยคาร์บอนที่มีโครงสร้างรูพรุนแบบเมโซสามารถควบคุมขนาดรูพรุนได้โดยผ่านปฏิกิริยาไพโรไลซิสของ เรโซซินัล/ฟอร์มัลดีไฮด์ (อาร์เอฟ) เจล โดยอาร์เอฟเจล นั้นเตรียมได้จากปฏิกิริยาโซล-เจล คอนเดนเซชันจากเรโซซินัล และฟอร์มัลดีไฮด์ โดยมีโซเดียมคาร์บอเนต เป็นตัวเร่งปฏิกิริยา จากการทดลองพบว่า รูปร่างและการกระจายตัวของเส้นใยอาร์เอฟและอนุภาคอาร์เอฟ สามารถควบคุมได้จากสภาวะการบ่ม, ระยะเวลาในการบ่ม, ปัจจัยในการเตรียมอาร์เอฟเจล และตัวแปรในกระบวนการปั่นเส้นใย ผลิตภัณฑ์จากการปั่นเส้นใยด้วยไฟฟ้าสถิตเมื่อใช้การเตรียมอาร์เอฟเจลที่แตกต่างกัน แต่ทำการบ่มในสภาวะแวดล้อมที่มีความชื้นสัมพัทธ์ 8 เปอร์เซ็นต์ จะเป็นเส้นใยที่มีขนาดในระดับไมครอน โดยมีขนาดเส้นผ่านศูนย์กลางเฉลี่ยของเส้นใยอยู่ในช่วง 1-5 ไมโครเมตร เมื่อนำอาร์เอฟเจลบ่มในสภาวะแวดล้อมที่มีความชื้นสัมพัทธ์สูง (ความชื้นสัมพัทธ์ 45, 75 และ 100 เปอร์เซ็นต์)มาเป็นเส้นใย ผลิตภัณฑ์ที่ได้ส่วนมากเป็นอนุภาคทรงกลมอยู่บนแผ่นรองรับ ทั้งนี้ได้มีการศึกษาถึงการเติมสารตั้งต้นอะลูมิเนียม เช่น อะลูมิเนียมอะซิติลอะซิโตเนตลงในอาร์เอฟเจล การปั่นเส้นใยด้วยไฟฟ้าสถิตเช่นเดียวกัน

ภาควิชา ....วิศวกรรมเคมี.......ลายมือชื่อนิสิต.......พนิตนาฏ อุบลเลิศ.......
สาขาวิชา..........วิศวกรรมเคมี.......ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์หลัก....................
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PANITNART UBOLLERS: ELECTROSPINNING OF NEAT AND ALUMINIUM-DOPE RESORCINOL/FORMALDEHYDE GEL. ADVISOR: ASST. PROF. VARONG PAVARAJARN, Ph.D., CO-ADVISOR: PROF. PITT SUPAPHOL, Ph.D., 102 pp.

Mesoporous structure of carbon fibers and carbon nanospheres were successfully prepared from combination of sol-gel method and electrospinning techniques. Mesoporous carbon with controllable pore size can be formed via the pyrolysis of resorcinol/formaldehyde (RF) gel. The RF gel was prepared by the sol-gel polycondensation of resorcinol (R) and formaldehyde (F) with sodium carbonate (C) as basic catalyst. Morphology and size distribution of RF fibers and RF particles can be controlled by aging condition, aging time of RF gel, preparation condition for RF gel and the processing parameters. Products from electrospinning of RF gel prepared by different condition and aged in 8% RH environment are micro-fibers with the average fiber diameter in the range of 1-5 μm. For the RF-gel aged under high humidity (e.g. 45%, 75% and 100% RH), the products were found to be mostly spherical particles deposited on the collector. Addition of aluminium precursor, i.e., aluminium acetylacetonate into the RF gel followed by electrospinning of the gel were also investigated.

Department : Chemecal Engineering
Field of Study : Chemecal Engineering
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Student's Signature พนิตนาฏ อุบลเลิศ
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Finally, I would like to dedicate this thesis to my parents and my families, who have always been the source of her support and encouragement.

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CHAPTER I

INTRODUCTION

Synthesis of carbon fibers have a received a considerable attention in recent years because of their enormous potential in a wide range applications wide range applications, from sports equipment to the aerospace industry [1]. Carbon fibers have very large surface area to volume ratio, flexibility in surface functionalities, superior mechanical performance are receiving increasing attention in characteristics that make the polymer nanofibers have many importance applications such as nanocomposites, rechargeable batteries, advance catalyst support, super capacitors, drug delivery and filtration. Fiber properties such as tensile strength, modulus (modulus between 100-450Gpa), porosity, and surface functionality depends on the type of precursor, the processing conditions, etc [2].

Electrospinning technique is a relatively simple and versatile method for fabricating nanofibers. In typical electrospinning process, a droplet of solution held by its surface tension at the end of a capillary tube is subjected to an electric field. Charge is induced on the liquid surface by electric field. As the intensity of the electric field is increased, the hemisphereical surface of the solution at the tip of the capillary tube elongates to form a conical shape know as the Taylor cone. When the electric field reaches a critical value at which the repulsive electric force overcomes the surface tension force, a charged jet of the solution is ejected from the tip of the Taylor cone. Since this jet is charged, its trajectory can be controlled by the electric field. As the jet travels in air, the solvent evaporates, leaving a charged fiber behind which lays itself randomly on a collecting metal screen. Thus, continuous fibers are laid to from a non-woven fabric [3]. In the continuous-feeding mode, the number of fibers can be formed within short period of time as short as a few seconds. Those fibers are often collected on the surface of a conductor to form non-woven mats that have high surface areas and relatively small pore sizes. For the past several decades, more than 20 different types of organic polymers have been successfully as ultrathin fibers using the electrospinning technique, with typical examples including various engineering plastics, biopolymer, and electronically conductive polymer [3].

In this work, the sol-gel method is combined with electrospinning technique to produce carbon fiber and spherical carbon particles. Resorcinol/formaldehyde (RF) gel was incorporated to the precursors to create porosity of the obtained carbon fibers and spherical carbon particles. RF gel can be prepared by the sol-gel polycondensation of resorcinol (R) and formaldehyde (F) with sodium carbonate (C) as basic catalyst [4], [5]. Resorcinol/formaldehyde gel is a special type of highly cross-linked aromatic polymers with high pore volume and large specific surface area. Due to the unique function of the RF-derived carbon cryogels, which is relating to their excellent pore characteristics, we aimed to employ RF-gel to control pore size of carbon fibers and spherical carbon particles. The carbon gels derived from RF gel are used in variety of applications including electrode materials in rechargeable batteries, advanced catalyst supports, chromatographic packing, adsorbents for gas separation, etc [6-8]. There are several reports to form carbon micro-spheres by disperst in RF sol in organic solvent by pyrolysis in inert atmosphere. To the best of our knowledge, it is the first report on synthesis of carbon fibers by electrospinning method.

Aim of this study is to understand the influence of various effects of various processing parameters, such as applied electrical field strength, working distance, applied voltage, as well as the preparation condition for RF gel, such as composition and aging time, on the size, size distribution, morphology, surface area and pore volume of carbon fibers and carbon nanospheres prepared by electrospinning followed by pyrolysis. Addition of aluminium precursor, i.e., aluminium acetylacetonate into the RF-gel by electrospinning method was investigated. This research intends to investigate the production of carbon fibers and carbon nano-spheres to produce mesoporous structure while RF gel was in the gelation process and investigated in more detail of their physical and chemical properties.

Objectives of the research:

1. To synthesize mesoporous structure of carbon fibers and carbon nanospheres from RF gel by electrospinning technique.
2. To investigate size, size distribution, morphology, as well as physical and chemical properties of fibers and nanospheres of RF gel by changing the processing parameters and preparation condition for RF gel and to investigate the formation and morphology of RF fibers and RF nanospheres aged in different relative humidity.
3. To investigate rheological behavior of the spinning solution.
4. To investigate product obtained from doping aluminium into RF gel and fabricated by electrospinning technique.

The present study is arranged as follows:

Chapter I is the introduction of this work

Chapter II described the basic theory about carbon fibers, sol-gel process and resorcinol/formaldehyde (RF) gel, electrospinning process. Furthermore, literature survey of the previous works related to this research is also presented in this chapter.

Chapter III shows materials, the experimental equipments, the preparation of RF fiber and RF particles by the elctrospinning process and characterization equipment.

Chapter IV describes the results and discussion of the research.

In the last chapter, the overall conclusions of this research and future work are given.

CHAPTER II

THEORY AND LITERATURE SURVEY

2.1 Physical Properties of Carbon Fibers

Carbon fibers are importanct industrially and have wide range applications, from sports equipment to the aerospace industry [1]. Carbon fibers have very large surface area to volume ratio, Carbon fibers are important industrially and have wide range applications, from sports equipment flexibility in surface functionalities, superior mechanical performance are some of the characteristics that make the polymer nanofibers optimal candidates for many importance applications such as composites, protective clothing, advance catalyst support, drug delivery and filtration. Fiber properties such as tensile strength, modulus (modulus between 100-450Gpa), porosity, and surface functionality depends on the type of precursor, the processing conditions, etc [2].

2.2 Resorcinol-Formaldehyde (RF) Gel

2.2.1 Sol-gel processing

The sol-gel process involves the formation of sol followed by gelation. Sol is a stable suspension of colloidal solid particles within liquid. For sol to exist, the solid particles, denser than the surrounding liquid, must be small enough for the forces responsible of dispersion to be greater than that of gravity. Particles in the colloidal sol must have size comprised between 2 nm to 0.2 μm. On the other hand, gel is a porous three-dimensionally interconnected solid network that expands in a stable fashion throughout liquid medium and is only limited by the size of the container [9]. When a catalyst is added to create the appropriate condition for interparticle condensation, the viscosity of the solution can increase very rapidly as the semi-solid state is reached. At gel point, the solid in the wet gel phase can define a high surface area network of pores that confine the liquid within the structure.

By applying the sol-gel process, it is possible to fabricate advanced materials in a wide variety of forms, e.g. ultra-fine or spherical shaped powders, thin film coatings, ceramic fibers, microporous inorganic membranes, monolithic ceramics and porous aerogel materials as shown in Figure 2.2.

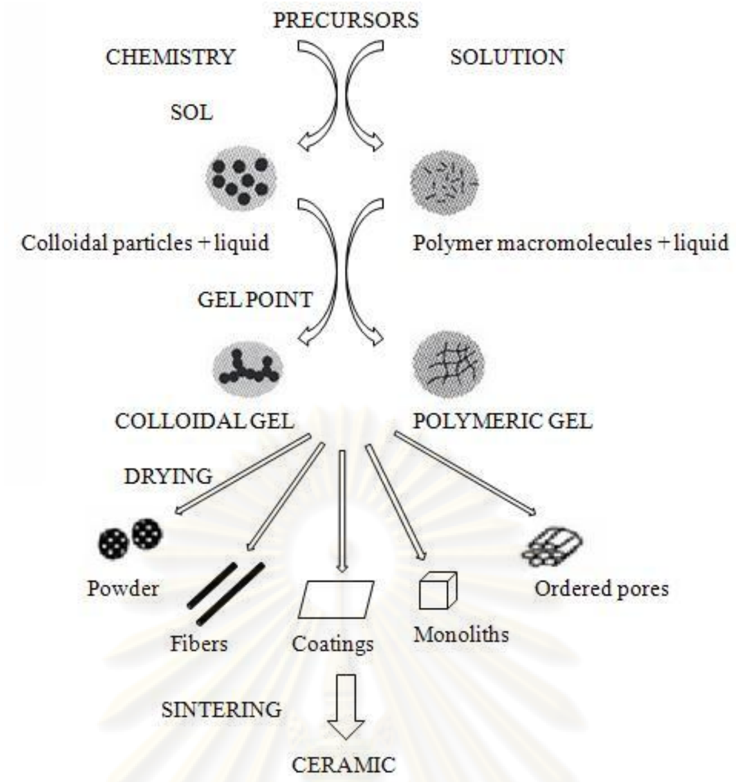


Figure 2.2: Simplified chart of sol-gel process.

The precursor in the sol-gel preparation can either be metal salt/alkoxide dissolved in appropriate solvent or stable colloidal suspension of preformed sols. Metal alkoxides have been the most extensively used because they are commercially available in high purity and their solution chemical has been well documented. At its simplest level, sol-gel chemistry with metal alkoxide can be described in term of two classes of reaction:

$$\begin{aligned} \text{Hydrolysis:}\quad & \text{M-O-R} + H_2O \longrightarrow \text{M-OH} + \text{R-OH} \\ \text{Water condensation:}\quad & \text{M-OH} + \text{HO-M} \longrightarrow \text{M-O-M} + H_2O \\ \text{Alcohol condensation:}\quad & \text{M-O-R} + \text{HO-M} \longrightarrow \text{M-O-M} + \text{R-OH} \end{aligned}$$

where M and R are metal atom and alkyl group, respectively.

Because hydrolysis and condensation are both nucleophilic displacement reactions, the reactivity of metal alkoxides depends on the positive charge of partially charged metal atom and its coordination number.

For sol-gel parameters, gelation time is defined as the time that the solution undergoes rapid rise in viscosity which is corresponding to the transition from viscous fluid to elastic gel. At the gel point, the solid phase forms a continuous structure that reflects the formation and branching of particles under specific growth condition. This particular phase is important because it is the genesis of structural evolution that takes place in all subsequent processing steps [10].

2.2.2 Formation of RF gel

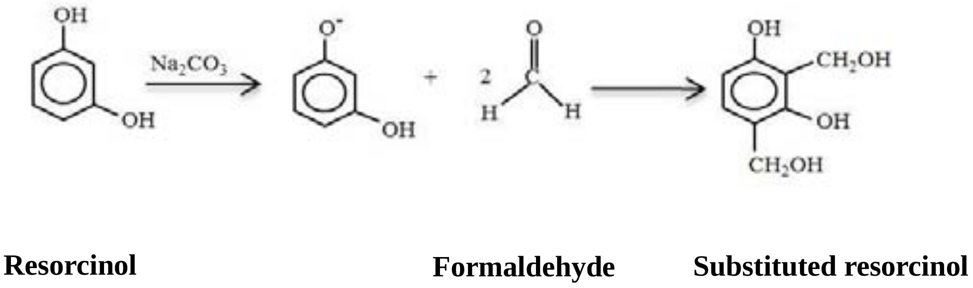
The first resorcinol-formaldehyde gel was produced by Pekala via the sol-gel polycondensation of resorcinol (R) and formaldehyde (F) with sodium carbonate (C) as basic catalyst [4]. The intermediates formed during the reactions further react to for a cross-linked polymer network.

The two major reactions include:

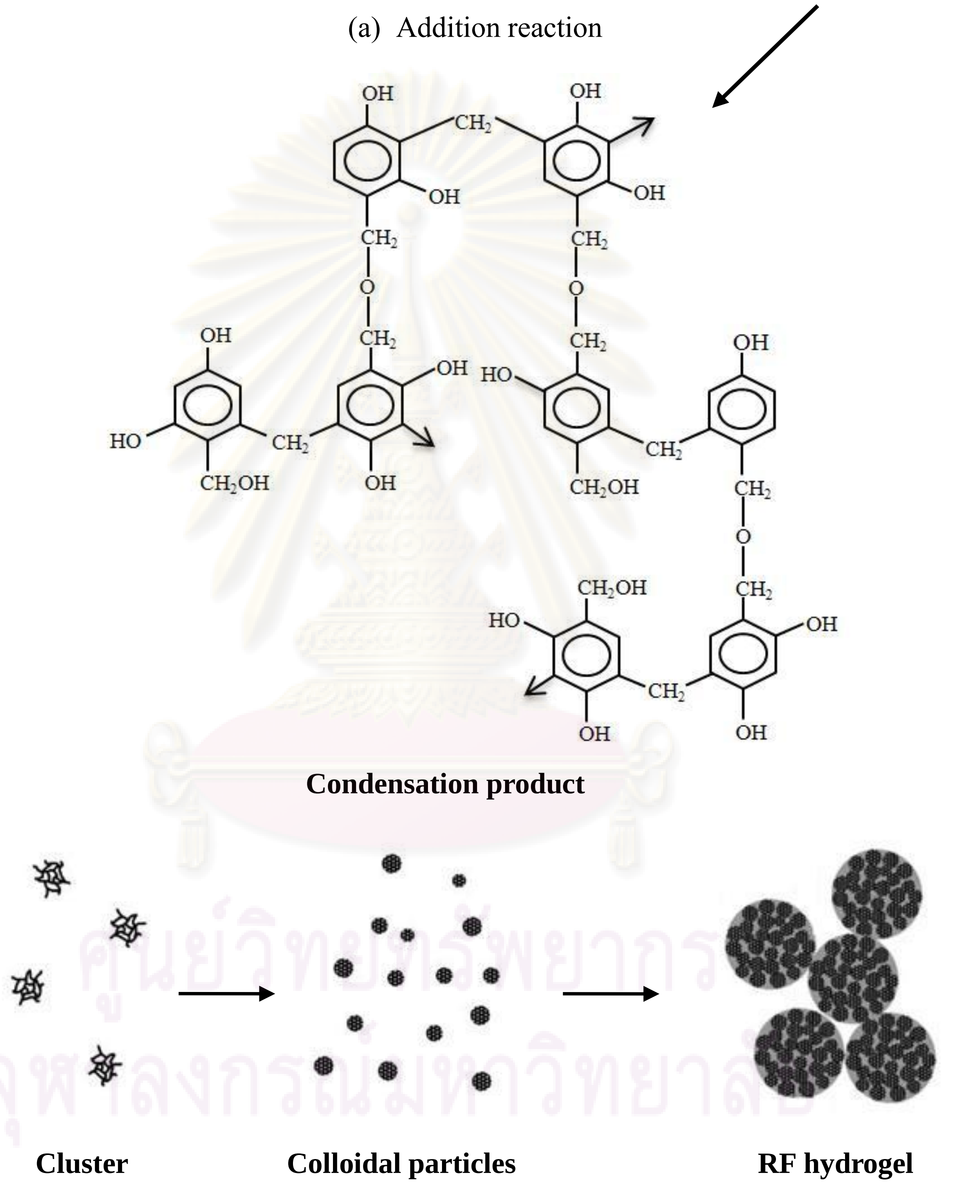
(a) The formation of hydroxymethyl (-CH_2OH) derivatives of resorcinol.

(b) The condensation of hydroxymethyl derivatives to form methylene (-CH_2-) and methylene ether (-CH_2OCH_2-) bridged compounds [11].

The catalyst initially promotes the generation of resorcinol anions. These anions are subsequently transformed into substituted resorcinol, which forms RF clusters through polycondensation. Then the RF clusters react with each other and grow into colloidal particles, which finally form a RF hydrogel [12]. The schemetic diagram of the sol-gel polycondensation of RF-gel is shown in Figure 2.3.



(a) Addition reaction



(b) Condensation reaction

Figure 2.3: Schematic diagram of the sol-gel polycondensation of RF solution
(a) addition reaction, (b) condensation reaction [12].

The carbon gels derived from RF gel are used in variety of applications including electrode materials in rechargeable batteries, advanced catalyst supports, chromatographic packing, adsorbents for gas separation, etc. Morphology of these carbon gel particles is one of the most important factors in considering their potential for a specific application [13].

2.2.3 Effects of various parameters on properties of RF gel

Various parameters in RF-gel preparation great have effect on properties of the synthesized RF-gel. Effect of amount of catalyst (R/C ratio) is the dominant factor that controls surface area, total pore volume, and mechanical properties of RF aerogels. As the R/C ratio is increased, mesoporosity of the aerogels is developed [14]. Saliger and coworkers (1997) described that the amount of catalyst controled size of particles constituting the gel network. In the case of R/C = 1500, aerogels with micron-sized particles could be obtained. The gel had a few sites for the substitution reaction and less condensation sites which leaded to formation of bigger particles. High catalyst concentration (R/C = 1000) allowed the product to build up as big particles with mesopores [15]. In 2009, Mirzaeian and coworkers studied the control of porosity at nano scale in resorcinol-formaldehyde derived carbon aerogels. The nitrogen adsorption-desorption measurements showed that the porous structure and mesoporosity of the aerogels was increased with increasing R/C ratio. Carbon aerogels were obtained by carbonization of RF aerogels. The sample synthesized with R/C = 100 was microporous. In the sample prepared with R/C = 200, micropores and mesopores were found. Samples with R/C = 500 and 600 contained mesopores with larger diameter in the structure. Therefore, the R/C ratio is the principal parameter that controls the size of interconnected particles which consequently affect the scale and size of pores in the gel structure [16].

In 2004, Shaheen and coworkers reported the preparation and properties of resorcinol-formaldehyde organic and carbon gels. By decreasing R/F ratio, it resulted in product with smaller particle and pore sizes, and increased surface area of the particles [17]. The influence of dilution ratio (R/W) on the morphology of particles in xerogel was described by Chandra and coworkers. It was found that, average size of the RF-derived carbon particles (d_{av}) decreased from about 28 μm to almost 1 μm when the dilution ratio was increased from 0.0037 to 3.7. The increased amount of water decreases the effective catalyst concentration in the sol, and hence the rate of the polymerization reaction between the monomer slows down. Therefore, the sol takes more time to form a cross-linked polymer (gel), resulting in the deformation of the particle from spherical to elongated irregular shapes and resulting in large diameter droplets of the particle [18].

The apparent viscosity of the RF gel increased with elapsed time in the gelation process [19]. The sol-gel RF transition was a gradual transition from a viscoelastic liquid to a viscoelastic solid [20]. Horikawa and coworkers (2004) showed that the apparent viscosity of RF sol had a significant effect on size of the RF-derived carbon aerogel particles. The low apparent viscosity of the RF sol resulted in smaller particle diameters, while the high apparent viscosity of RF sol produced larger particle diameters. Thus they could control the size of the RF carbon aerogel particles for their applications by changing the RF sol apparent viscosity [7].

2.3 Electrospinning Technique

2.3.1 Mechanism of electrospinning process

Electrospinning process involves polymer science, applied physics, fluid mechanics, electrical engineering, mechanical engineering, chemical engineering, material engineering and rheology. Electrospinning is a process that creates nanofibers through an electrically charged jet of polymer solution or polymer melt. The electrospinning process in its simplest form consists of the tip to hold the polymer solution, two electrodes and a DC voltage supply in the kV range. The polymer drop from the tip is drawn into a fiber after applying the high voltage. The jet is electrically charged and the charge causes the fibers to bend in such a way that every time the polymer fiber looped, its diameter is reduced. The fiber is collected as a web of fibers on the surface of a grounded target [21]. A schematic drawing of the electrospinning process is shown in Figure 2.4.

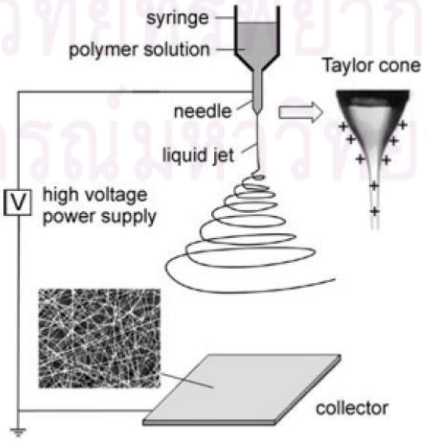


Figure 2.4: Schematic representation the electrospinning process.

The electrospinning process produces fibers with diameter in the range of one or two orders of magnitude smaller than that of conventional textile fibers. The small diameter provides large surface area-to-mass ratio, in the range from 10 m^2/g (when the diameter is around 500 nm) to 1000 m^2/g (when the fiber diameter is around 50 nm). The equipment required for electrospinning is simple and only a small amount of polymer sample is needed to produce nanofibers.

Important features of electrospinning should comply with following guideline:

(a) Suitable solvent should be available for dissolving the polymer.

(b) The vapor pressure of the solvent should be suitable so that it evaporates quickly enough for the fiber to maintain its integrity when it reaches the target but not too quickly to allow the fiber to harden before it reaches the nanometer range.

(c) The viscosity and surface tension of the solvent must neither be too large to prevent the jet from forming nor be too small to allow the polymer solution to drain freely from the tip.

(d) The power supply should be adequate to overcome the viscosity and surface tension of the polymer solution to form and sustain the jet from the tip.

(e) The gap between the pipette and grounded surface should not be too small to create sparks between the electrodes but should be large enough for the solvent to evaporate in time for the fibers to form [22].

The literatures relating to electrostatic spray contain many helpful insights into the electrospinning process. In 1882, Lord Rayreigh studied the stabilities that occur in electrically charged liquid droplets. He showed, over 100 years ago, that when the electrostatic force overcame the surface tension, a liquid jet was created [23]. In 1935, Zelene considered the role of surface instability in electrical discharges from droplets. He published a series of papers around 1935 on discharged from charged droplets falling in electric fields, and showed that, when the discharge began, the theoretical relations for surface instability were satisfied [24]. In 1952, Vonnegut and Neubauer produced uniform stream of highly charged droplets with diameter of around 0.1 mm, by applying potential of 5 to 10 kV to liquid flowing from capillary tubes. Their experiment proved that monodispersed aerosols with a particle radius of a micron or less could be formed from the pendent droplets at the end of the pipette. The diameter of the droplet was sensitive to the applied potential [25]. In 1962, Wachtel and coworkers prepared emulsion particles using an electrostatic method to make monodispersed emulsion of oil in water. The diameter of the emulsion particles was in the range from 0.5 to 1.6 microns [26]. In the 1960’s, Taylor studied the disintegration of water droplets in an electrical field. His theoretical papers demonstrated that a conical interface, with a semi-angle close to 49.3°, was the limiting stable shape [27].

Many researchers have made further contributions to understanding the electrospinning process and characterizing the electrospun nanofibers in recent years. For example Doshi and Reneker prepared electrospun nanofibers from water soluble poly(ethylene oxide), with diameters of 0.05 to 5 microns. They described the electrospinning process, the processing conditions, fiber morphology and some possible uses of electrospun fibers [28].

2.3.2 Effects of electrospinning parameters

The properties of fibers obtained from this process depend on two types of parameters. The first set of parameters are system parameters including molecular weight, molecular weight distribution, architecture of the polymer (e.g. branched or linear chain), and solution properties (viscosity, conductivity and surface tension). The second one are processing parameters including electrical field strength, flow rate, solution concentration, distance between the capillary and the collector, and ambient parameters (temperature and humidity) [29].

Many parameters, including the electric field, solution viscosity and working distance, could affect the fiber morphology. The electric field has an influence in the stretching and accerelation of the jet. At a higher voltage, it has been found that there is a greater tendency for beads formation. The shape of the beads changes from spindle-like to spherical-like with increasing voltage. The increases in the beads density due to increased voltage may be the result of increased instability of the jet as the Taylor cone recedes into the syringe needle [30]. Varying the distance between the tip and the collector has a direct influence in both the flight time and the electric field strength. Decreasing the distance has the same effect as increasing the voltage supplied, which causes an increase in the field strength. When the field strength is too high, the increased instability of the jet may encourage beads formation [31]. Increasing the distance results in a decrease in the average fiber diameter, because the longer distance give rise to the longer flight time for the solution to be stretch before depositing on the collector [32].

Viscosity of the solution has a profound effect on electrospinning and the resultant fiber morphology. Generally, the viscosity of the solution is related to extent of chains entanglement of molecules within the solution. When the viscosity of the solution is too low, electrospraying may occur and particles are formed instead of fibers. At low viscosity where generally the condensation product chain entanglement is lower, there is a increased possibility that beaded fibers would be obtained instead of smooth fibers. Therefore, factors that affect the viscosity of the solution will also affect the electrospinning process and resultant fibers [22]. For the solution with relatively low viscosity when the viscosity is gradually increased, the shape of the beads from is gradually changed spherical to spindle-like until a smooth fiber was finally obtained [33],[34].

CHAPTER III

EXPERIMENTAL

This chapter describes the experimental procedures for RF and RF/alumina preparation. It is divided into four parts: materials used, electrospinning apparatus, experimental procedures and samples characterizations.

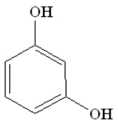
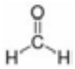
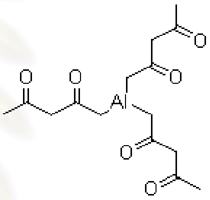
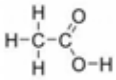
3.1 Materials

List of chemicals employed in this work and their structures are listed in Table 3.1 and 3.2, respectively.

Table 3.1 List of chemical agents used in the research.

Chemical agents	Using for	Manfacturer / Grade
Resorcinol ($C_6H_4(OH)_2$)	Synthesis of Resorcinol-Formaldehyde (RF) solution	Fluka, 99%
Formaldehyde (HCOH)	Synthesis of Resorcinol-Formaldehyde (RF) solution	Ajax Fine Chemical, 37% w/v; stabilized by 11-14 wt% methanol
Sodium carbonate(Na_2CO_3)	Synthesis of Resorcinol-Formaldehyde (RF) solution	Ajax Fine Chemical, 99%
Distilled water (H_2O)	Synthesis of Resorcinol-Formaldehyde (RF) solution	
Aluminum acetylacetonate ($C_{15}H_{21}AlO_6$)	Synthesis of Alumina / Resorcinol-Formaldehyde (RF) gel	Fluka, 95%
Acetic acid (CH_3COOH)	Synthesis of Alumina / Resorcinol-Formaldehyde (RF) gel	QReC , 97%

Table 3.2 Chemical structure of compounds used in this research.

Chemical name	Designation	Chemical structure
Resorcinol	R	
Formaldehyde	F	
Sodium carbonate	C	
Aluminum acetylacetonate	A	
Acetic acid	Ac	

3.2 Electrospinning Apparatus

The schematic of the electrospinning apparatus used in this work is shown in Figure 3.1. The components of the apparatus and their functions are described as follows.

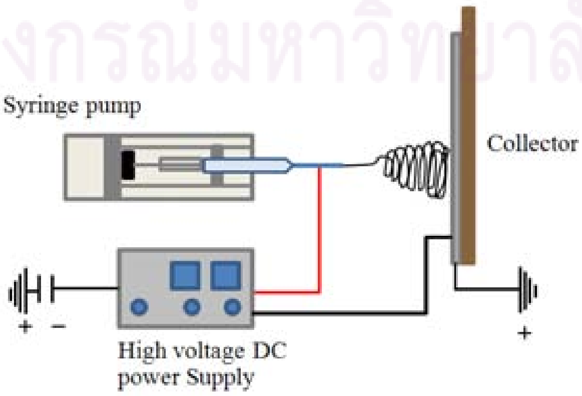


Figure 3.1: Schematic of an electrospinning setup.

The system is consisting of:

- A high-voltage power supply (Protek, DF 1730SB3A, U.S.A) was used to generate either positive or negative DC voltage up to 30 kV, with very low electrical current of 166 microamperes.
- A 5 ml syringe was used as a container for electrospinng solution. The syringe is made of a plastic and set in horizontal orientation.
- A syringe pump (kdScientific, U.S.A) mounted with a syringe to control the flow rate of the spinning solution to be 0.8 ml/h.
- A stainless steel needle (gauge No.21 and the inner diameter of 0.514 mm) was used as a nozzle. The tip of the needle was cut into a flat shape and the length of the needle was 1 cm. The needle is connected to the negative electrode of the DC supply.
- Aluminum foil was used as a ground collector.

3.3 Experimental Procedures

3.3.1 Preparation of RF gel

RF-gel were synthesized by polycondensation of resorcinol (R) and formaldehyde (F) according to the method proposed by Pekala et al [4]. Measured quantities of resorcinol and distilled water (W) were added into a beaker and mixed properly for about 15 min with the help of a magnetic stirrer. Sodium carbonate (C) was dissolved in distilled water in separate beaker. The two solutions were then mixed and stirred continuously for 15 min. Then added formaldehyde into the mixer and stirred continuously for 15 min. The ratio of C/W was kept constant at 10 mol/m^3. The molar ratio of R/F, R/W and R/C were varied in this study in the range of 0.1-2.0, 0.03-2.0, and 50-2000, respectively.

3.3.2 Preparation of aluminium-doped RF gel

In the preparation of aluminium-doped RF-gel, aluminium acetylacetonate (A) was used as a precursor for aluminium. RF-gel was firstly prepared according to the method described earlier. The RF-gel was aged for predetermined period of time before being added with a mixture containing F and A in the molar ratio A/F of 1.1, using A/R molar ratio in the range of 0.167-0.236 and F and A mixed properly for about 45 min with the help of a magnetic stirrer. The mixture was stirred for 15 min. In this study, the aging period was varied to investigate the extent of the reaction between Al-precursor to the RF-gel.

3.3.3 Freeze drying of the RF- products

The RF products were pre-frozen by a liquid N_2 for 24 h to freeze the solvent inside the pores, then moved the RF products to a vacuum freeze-drying chamber and dried at -54°C for 2 days.

3.3.4 Pyrolysis of the RF –products

After drying, the RF products were put into a ceramic boat, placed in a horizontal tubular flow reactor and heated up to 250°C under constant flow of nitrogen gas. The flow rate of nitrogen was maintained at 40 ml/min. The heating rate was fixed at 10°C/min. After being held at 250°C for 2 h, the temperature was raised to 750°C using the same heating rate and held at 750°C for 4 h.

3.4 Sample Characterizations

3.4.1 Scanning electron microscopy (SEM)

Morphology of the obtained products was studied using scanning electron microscope (SEM) model JSM-6400 at Scientific and Technological Research Equipment Centre Foundation, Chulalongkorn University. Size of the products was then measured from the micrographs, using image processing software (JEOL Semafore 5.0).

3.4.2 Viscosity measurement

Viscosity of the electrospinning solution was measured using a Brookfield Programmable DV II+ viscometer at the Center of Excellence on Particle Technology, Chulalongkorn University. Using small sample adaptor, spindle No.27, fixed stirring speeds at 40 rpm and sample volume 10 ml.

3.4.3 Fourier transform infared spectroscopy (FT-IR)

Function groups of spinning solution were identified by using Fourier transform infrared spectrophotometer (FT-IR) Model Spectrum One (Perkin Elmer). Infrared spectra were recorded between wavenumber of 600 and 2000 cm^{-1}.

3.4.4 Surface area measurement

The surface area, pore volume and pore size were measured by an ASAP 2420 adsorption analyzer (Micromeritics) using nitrogen as the adsorbate at the Center of Excellence on Particle Technology, Chulalongkorn University. The operating conditions are as follows:

Sample weight	~ 0.1-0.2 g.
Degas temperature	200 ^{o}C
Vacuum pressure	< 10 mmHg

CHAPTER IV

RESULTS AND DISCUSSION

In this chapter, RF-particles and RF-fibers fabricated by combined electrospinning technique and sol-gel method were investigated in detail. And study the influence of various effects of various processing parameters and the preparation condition for RF gel on the size, size distribution and morphology of RF-product. Carbon fibers and carbon particles prepared by electrospinning and have been obtained by pyrolyzing RF product in an inert atmosphere. Addition of aluminium precursor, i.e., aluminium acetylacetonate into the RF-gel by electrospinning method was investigated.

4.1 Effect of Preparation Conditions and Aging Time for RF Gel on the Product

4.1.1 Effect of RF aging time on morphology of RF-particles

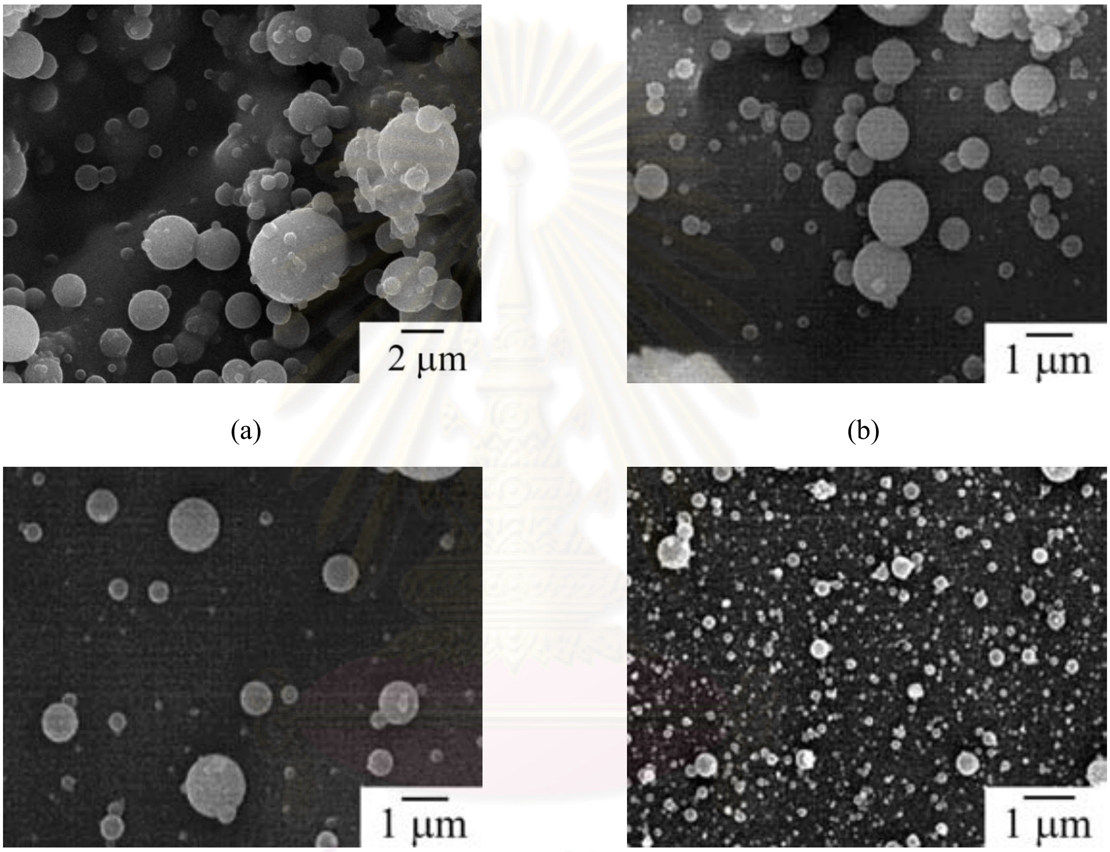
RF solution was prepared by sol–gel polycondensation according to reported procedures in literature [6], using resorcinol and formaldehyde as raw materials and Na_2CO_3 as catalyst. In the initial period, the sol-gel process slowly converts RF solution into nanoparticles suspended in liquid or sol. Then, the colloidal nanoparticles are linked together in three dimensional to form liquid-filled solid network or gel. The mechanism for the sol-gel process was shown in Figure 4.1.

(a) (b) (c)

Figure 4.1: Progress of the reaction of RF solution: (a) solution (b) colloid and (c) gel.

Aging time is one of the factors that directly influence viscosity of RF gel, which is a critical factor for electrospinning. In this part, morphology of products spun from RF gel that was aged for different period of time was investigated. Figure 4.2 shows SEM images of the resulting products from electrospinning of RF gel that had been aged for 24, 26, 27 and

27.5 h, respectively. The gel was prepared by using R/F, R/C and R/W molar ratios of 0.50, 86.64 and 0.15 respectively. The electrical potential applied was 1.5 kV/cm, the volumetric flow rate of the gel was fixed at 0.8 ml/h, using a syringe pump. Most of the obtained products appear to be agglomerated spherical particles that are deposited on the collector. According to the SEM images, size of the particles decreases with increasing in aging time of RF gel.



(a) (b)

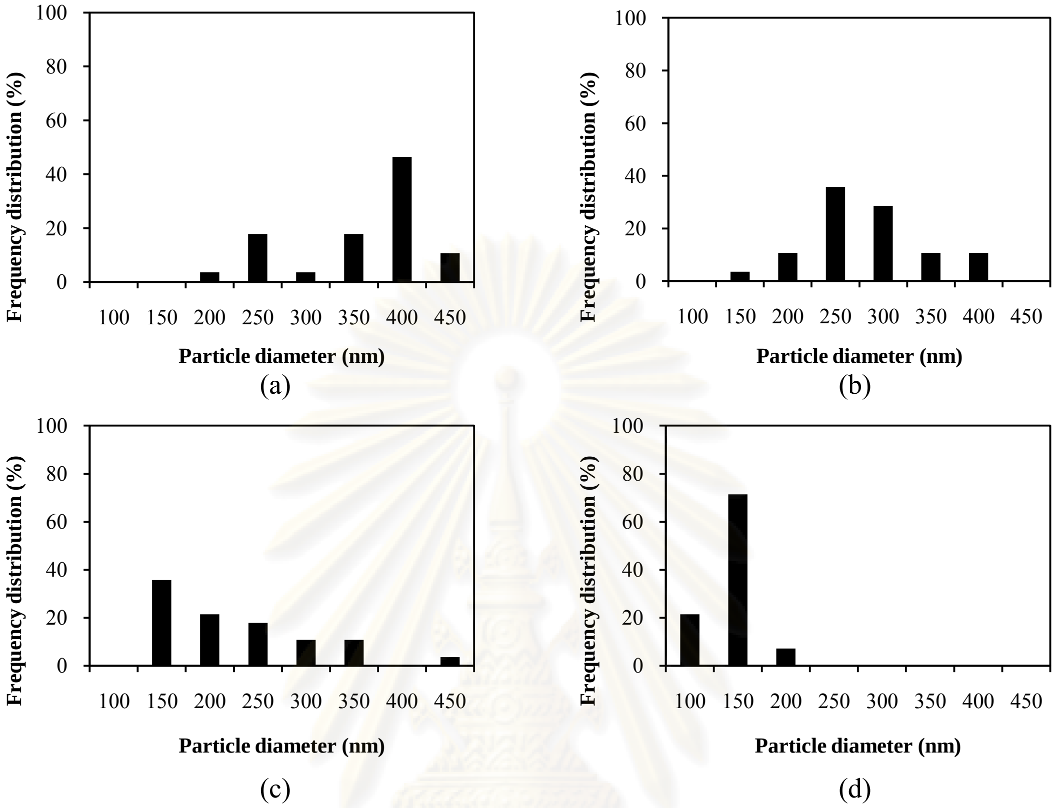
(c) (d)

Figure 4.2: SEM images of products obtained from electrospinning of RF gel that had been aged for 24 h (a), 26 h (b), 27 h (c) and 27.5 h (d).

The initial RF solution is colorless, but after aging time of 24 h, the solution turns into yellow and orange, respectively. Finally, at the aging time of 27.5 h, the mixture becomes highly viscous which indicates gel formation, and color changes to dark red. The RF solutions aged in a period of time were significantly different in both physical and chemical properties.

The size distributions of the electrospun particles are presented in Figure 4.3. Diameters of 100 randomly selected particles from SEM imaged were measured by SemAfore

4.0 program. The average diameters of RF-particles obtained from RF gel that had been aged for 24, 26, 27 and 27.5 h are 336.9, 258.6, 201.4 and 123.2 nm, respectively.



(a) (b) (c) (d)

Figure 4.3: Particle size distribution of products obtained from electrospinning of RF gel that had been aged for 24 h (a), 26 h (b), 27 h (c) and 27.5 h (d).

For the RF gel aged for 24 h, the viscosity was too low that it was unsuitable for electrospinning. At a low viscosity, high amount of solvent molecules and a few chain entanglements would cause surface tension to be a dominant influence along the electrospinning jet resulting in the droplets to form large particles [35]. When the aging time of RF gel is increased, the apparent viscosity and the conductivity of spinning solution are increased (as shown in Figure 4.4). The conductivity of the RF gel has increased due to water, which is by-product from the condensation reaction. The conductivity of the RF gel affects the stretching of RF gel, causing the repulsion of the charges at the surface of the spinning droplet. For the RF gel aged for 27.5 h has high viscosity and conductivity, charges are accumulated on the surface of the gel before being ejected. As the RF gel is being stretched, there will be a greater viscoelestic force acting against the Coulombic forces of the charges [36]. When the repulsive electrical forces overcome the surface tension, the jet splits into several mini-jets, which subsequently disintegrate into small droplets. Therefore, the products from RF-gel aged for 27.5 h are very small particles. For the RF gel aged for more than 27.5 h, the viscosity of the RF gel was too high that making it very difficult to pump through the needle. Moreover, the solution may plug at the tip of the needle before electrospinning could be initiated.

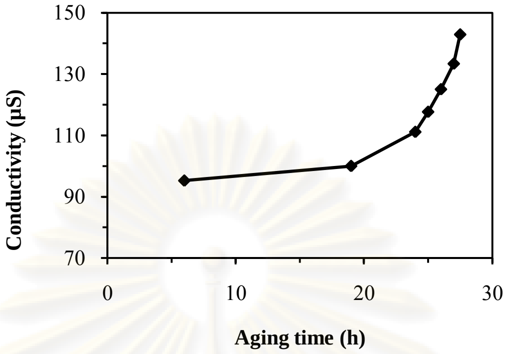


Figure 4.4: Relationship between the conductivity and aging time of RF solution.

It is more clearly represented by a graph in Figure 4.5, which shows the average diameter of the particles obtained as a function of viscosity of the gel. The error bars in the Figure represent standard deviation of the data. The apparent viscosity of the RF-gel increased with elapsed time in the gelation process. According to the measurement of the viscosity, it was found that RF gel exhibited non-Newtonian behavior, i.e., its viscosity depended upon the force exerted to the gel [37], probably due to the gelation transition from a viscoelastic liquid to a viscoelastic solid [38]. Suitable solution viscosity for the electrospinning was in the range of 1000-5000 cP.

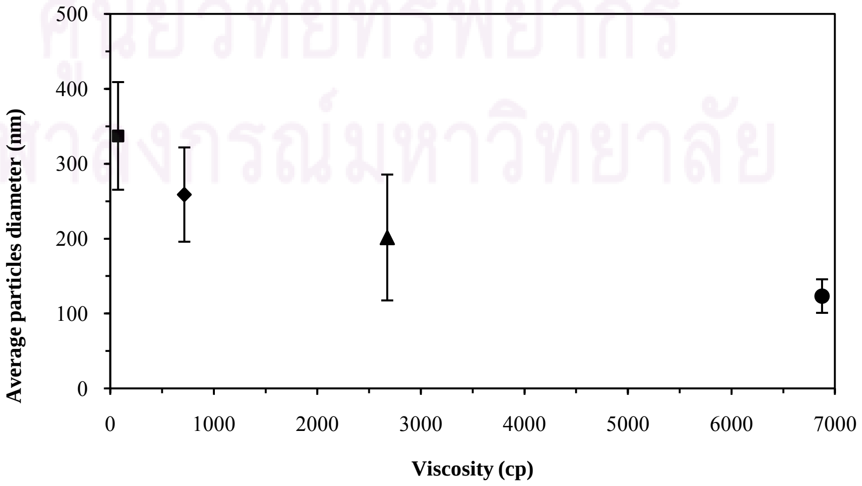
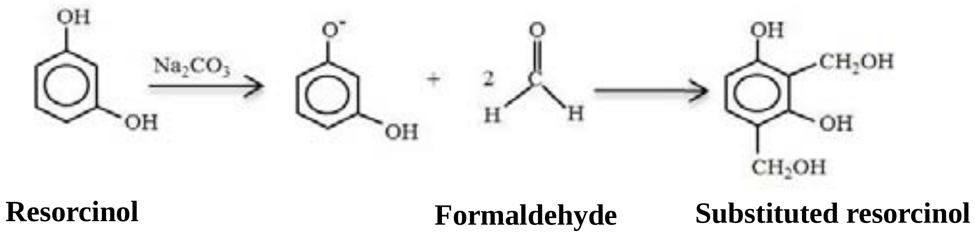
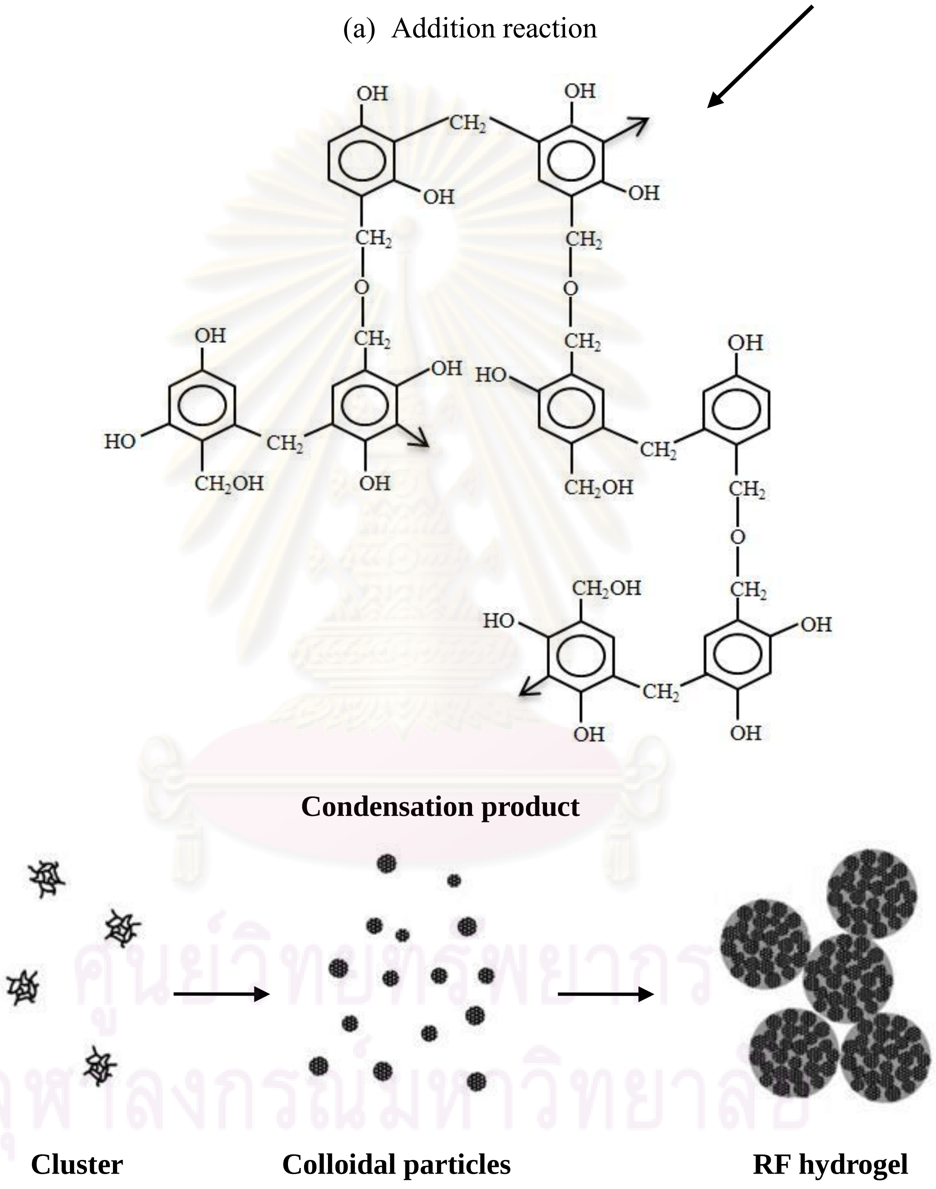


Figure 4.5: Average diameter of the obtained particles as a function of gel viscosity. The RF gel was aged for 24 h (■), 26 h (◆), 27 h (▲) and 27.5 h (●).

Figure 4.6 shows the structural image of RF-gel networking. Resorcinol reacts with formaldehyde under alkaline conditions to form mixtures of addition and condensation compounds which could react to form a crosslinked network. The principal reactions involve include (1) addition reaction of resorcinol and formaldehyde lead to the formation of methylol groups (CH_2OH) at 2, 6 (ortho) and 4 (para) position of phenolic, (2) the condensation of the hydroxymethyl derivatives ($-CH_2OH$) is able to form covalent bridges between the resorcinol rings and in the form of methylene ($-CH_2-$) and methylene ether ($-CH_2OCH_2-$) bridged compounds. The condensation product is transformed into RF cluster, Then RF clusters react with each other and grow into colloidal particles, which finally form a RF hydrogel [6, 39].



(a) Addition reaction



(b) Condensation reaction

Figure 4.6: Schematic diagram of the sol-gel polycondensation of RF solution [40].

In figure 4.7 compares FTIR spectra of RF gel aged for various periods of time. The assignment of characteristic absorption bands was done according to the values reported in literatures [6, 14, 41, 42]. The bands at wavenumber of 1619 cm^{-1} corresponding to C=C aromatic ring stretching vibration, at 1299, 1228 and 1170 cm^{-1} corresponding to C-C-O asymmetric stretch vibrations, and at 1475 cm^{-1} for CH_2- scissor vibration were observed. It should be noted that the CH_2- bonding is a result from a cross-linking bridge formed from the condensation of hydroxymethyl derivatives. Furthermore, absorption bands corresponding to methylene ether (CH_2-O-CH_2) were also detected at wavenumber of 1220 and 1092 cm^{-1}. The CH_2-O-CH_2 bridge was a cross-linking bond formed between aromatic rings due to polycondensation of resorcinol by formaldehyde. Table 4.1 summarizes identifications of the bands that have been proposed to associate with functional groups of the RF solution. Furthermore, Fourier self-deconvolution (FSD) method was used to determine integrated intensities of the absorption bands. This procedure requires input data such as the form of the apodization function, band width and enhancement [8].

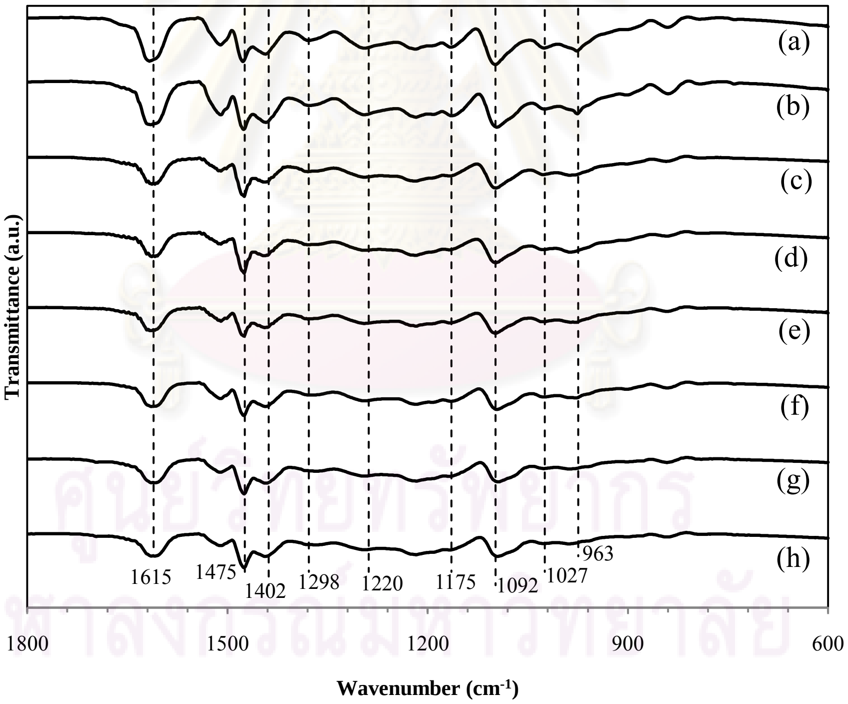


Figure 4.7: FTIR spectra of RF gel aged for 5 h (a), 10 h (b), 15 (c), 20 h (d), 24 h (e), 26 h (f), 27 h (g) and 27.5 h (h).

Table 4.1 Assignments of FTIR absorption bands of RF gel.

IR bands [cm^{-1}]	Function groups
1615	C=C aromatic ring [43]
1475	-CH$_2$- methylene bridge [6]
1402	OH in plane [43]
1298	C-O stretching [43]
1220	C-O-C stretching vibrations of methylene ether bridges between resorcinol molecules [6]
1175	CH aromatic, in plane [43]
1092	C-O-C stretching vibrations of methylene ether bridges between resorcinol molecules [6]
1027	Aliphatic hydroxyl [43]
963	2,4-substituted benzene ring [43]

The increase in viscosity of the RF solution with increasing aging time is conformed to the increase in methylene and methylene ether bridges formed (shown in Figure 4.8), due to highly cross-linking of cluster to form RF gel. At 24 h, signal ratio of methylene bridge increased rapidly could seen from viscosity of the solution, that means RF solution was highly cross-linked of cluster to form RF gel. It should be noted that the results shown in Figure 4.8 are taken in form of the ratio between the integrated signal from the interested band and that of the aromatic rings, which are used as reference for all cases. The use of such ratio eliminates the effect of sample size taken in the FTIR measurement.

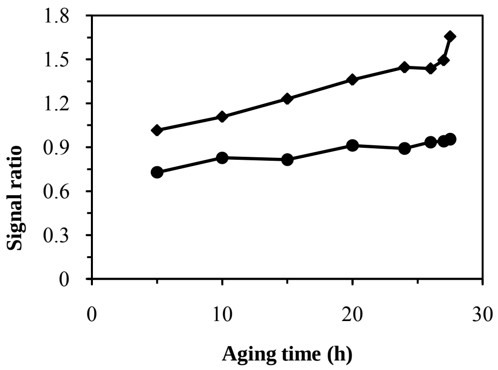
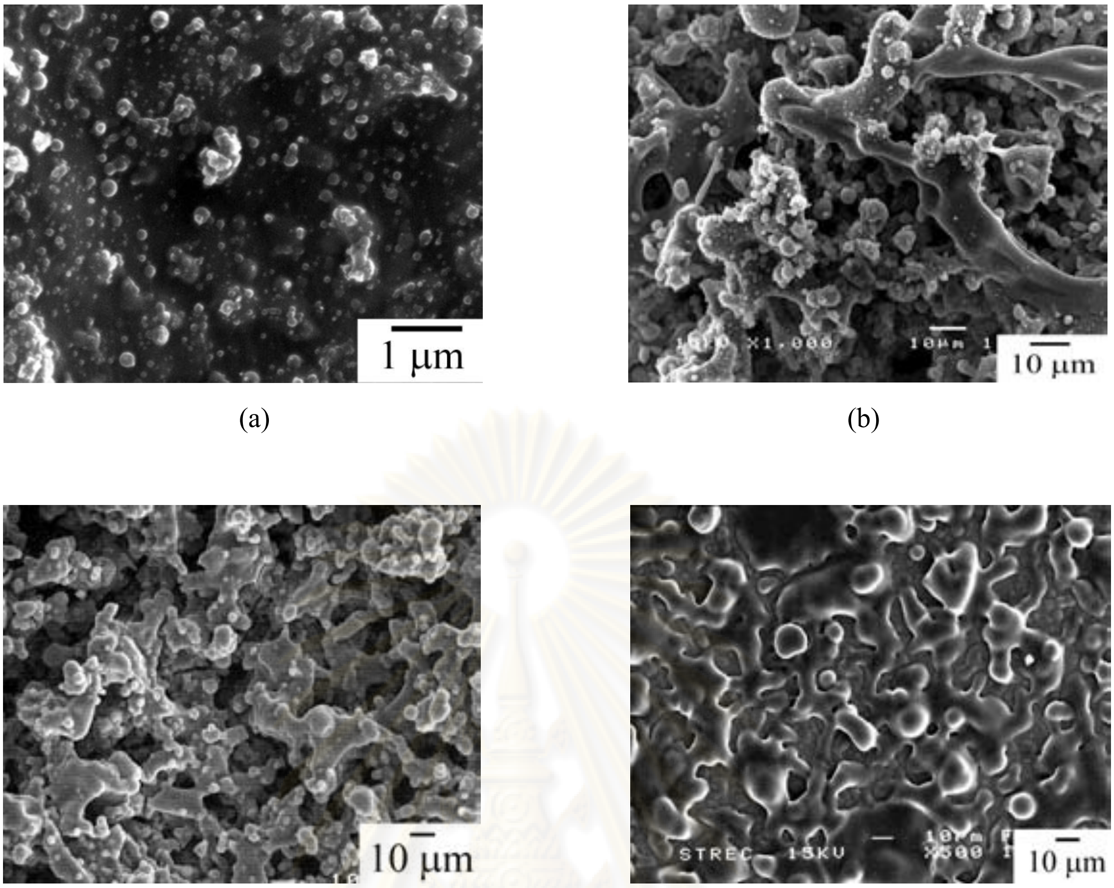


Figure 4.8: Relationship between FTIR signals corresponding to methylene bridge (◆) and methylene ether bridge (●), with respect to that of aromatic rings, and aging time of RF solution.

4.1.2 Effect of resorcinol/formaldehyde molar ratio

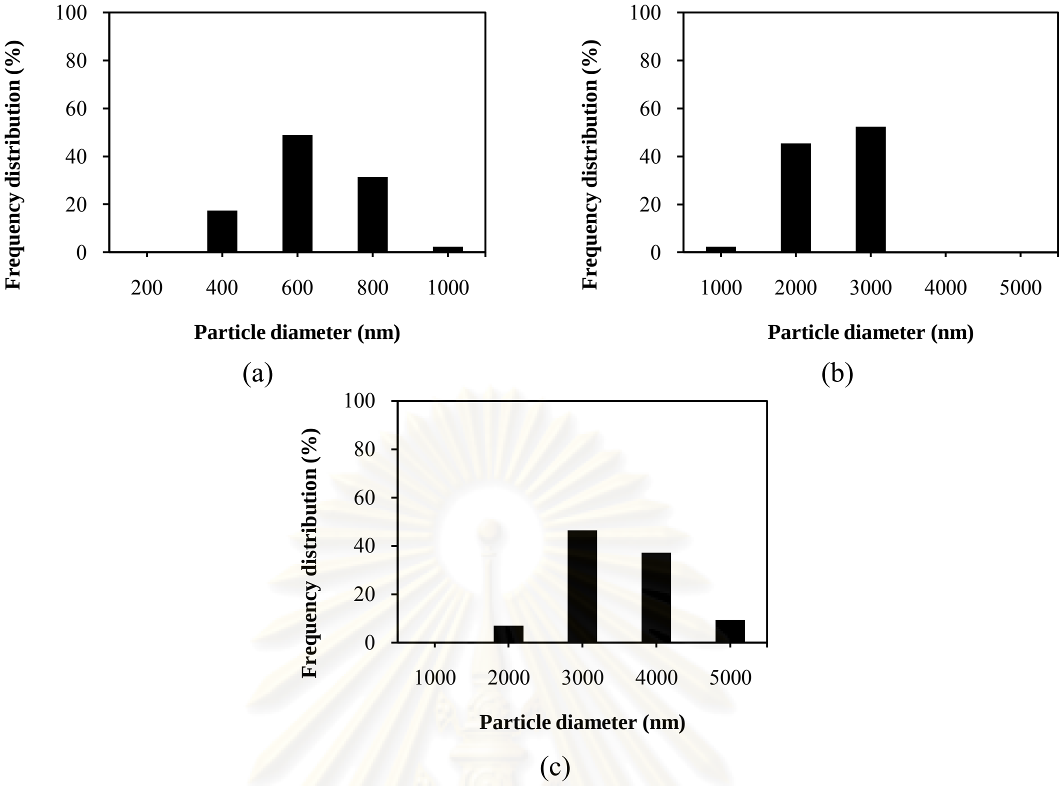
In this section, the effect of R/F molar ratio is investigated. All samples were prepared using R/C and R/W molar ratio of 86.64 and 0.15, respectively. Figure 4.9 compares SEM images of electrospinning products, using RF gel prepared with R/F molar ratio of 0.1, 1.0, 1.5 and 2.0, respectively. As the polycondensation reaction proceeds, when the gel is prepared under the condition of low R/F ratio, color of the gel is light. On the other hand, dark red gel is obtained at high R/F ratio. According to this Figure, as the R/F molar ratio is increased, the average diameter of the particles is increased. The frequency distributions for the size of the electrospun RF particles are presented in Figure 4.10. The average diameter of the RF particles prepared using R/F ratio of 0.1, 1.0 and 1.5 is found to be 540.7 nm, 1.96 μm and 2.97 μm, respectively.



(a) (b)

(c) (d)

Figure 4.9: SEM images of collected particles electrospun from RF gel that was prepared by: (a) R/F molar ratio of 0.1 and being aged for 198 h, (b) R/F molar ratio of 1.0 and being aged for 33 h, (c) R/F molar ratio of 1.5 and being aged for 232 h and (d) R/F molar ratio of 2.0 and being aged for 366 h.



(a)

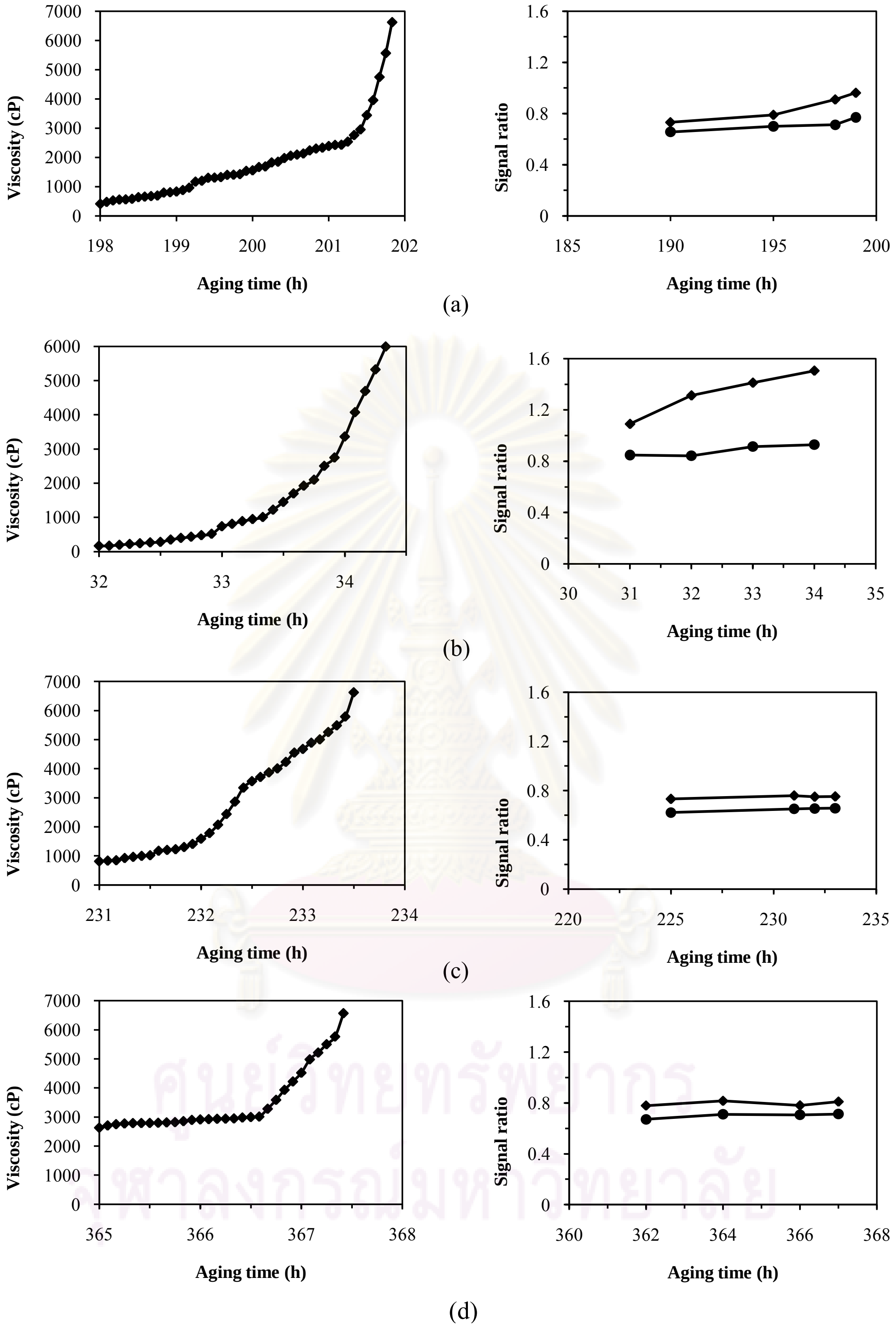
(b)

(c)

Figure 4.10: Size distribution of the particles obtained from electrospinning of RF gel prepared by using different R/F molar ratio: R/F molar ratio of 0.1 (a), R/F molar ratio of 1.0 (b) and R/F molar ratio of 1.5(c).

The sample of RF gel with R/F ratio of 0.1 is an agglomeration of small spherical particles. For R/F ratio of 1.0 and 1.5, the particles are heavily agglomerated and merged together to form porous structure. In the extreme case using the R/F ratio of 2.0, the products merge together into a film. The binding of particles suggests that the evaporation of solvent from the particles in this case was rather slow. The size distribution of the particles is also very broad.

Different from R/F molar ratio to prepared RF gel that making RF aging times for 4 samples is not equal. According to stoichiometry, 2 mol of formaldehyde is required for the complete three dimensional cross-linking of 1 mol of resorcinol. Cross-linking of the RF network is limit due to excess amount of resorcinol (R/F ratio 1.5 and 2.0) and formaldehyde (R/F ratio is 0.1). As confirm by the investigated signal from the interested band and that of the aromatic rings which increases slightly with increases in aging time, as shown in Figure 4.11.



(a)

(b)

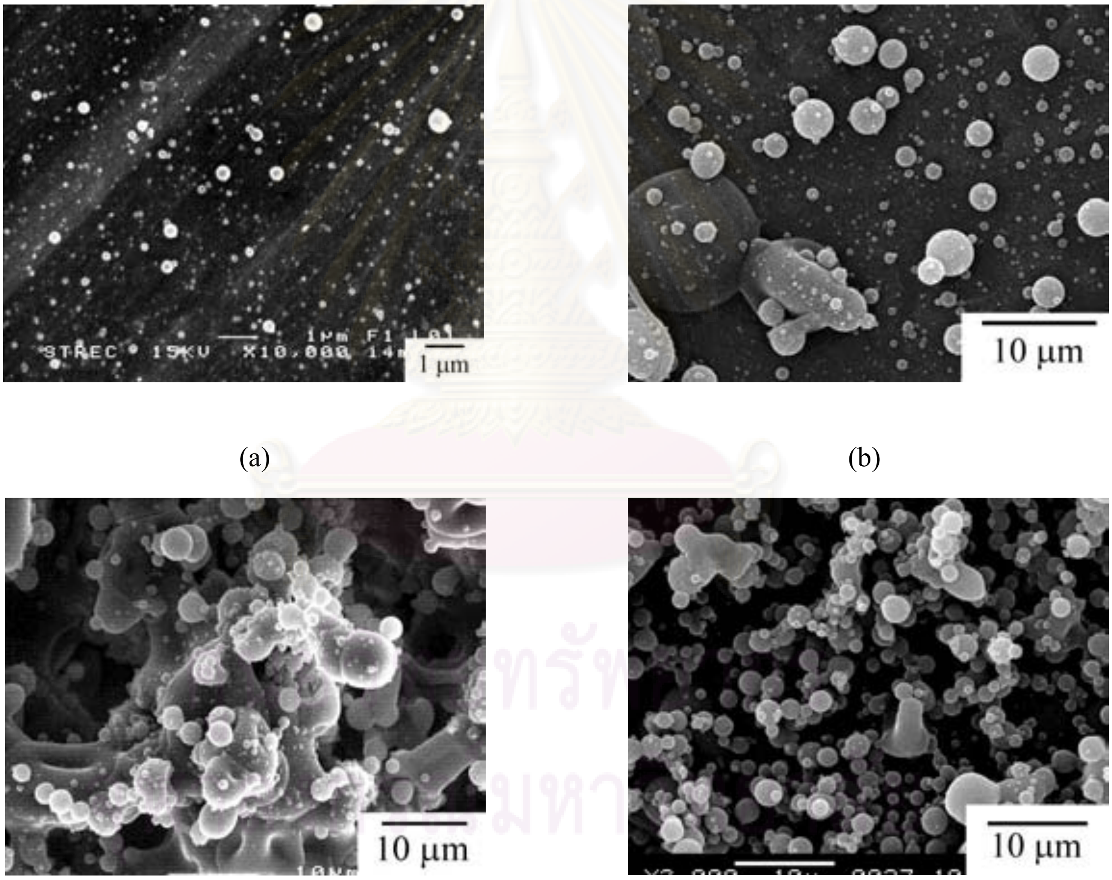
(c)

(d)

Figure 4.11: Apparent viscosity of RF gel and FTIR signal ratios of methylene bridge (◆) and methylene ether bridge (●) with respect to aromatic rings, as a function of aging time for RF solution. The RF gel was prepared using R/F molar ratio of: 0.1 (a), 1.0 (b), 1.5 (c) and 2.0 (d).

4.1.3 Effect of resorcinol/catalyst molar ratio

Catalyst, i.e., sodium carbonate, is another factor affecting cross-linking of the RF gel network. The catalyst instigates the formation of resorcinol anions, which are more reactive to formaldehyde than resorcinol molecules [44]. Subsequently, RF clusters could be formed via polycondensation process. Further cross-linking resulted in the formation of RF gel. The lower the catalyst content used the longer aging time would be required to achieve optimum viscosity for electrospinning. All samples were prepared using R/F and R/W molar ratio of 0.5 and 0.15, respectively. SEM images of the obtained products prepared using various R/C ratio are shown in Figure 4.12.

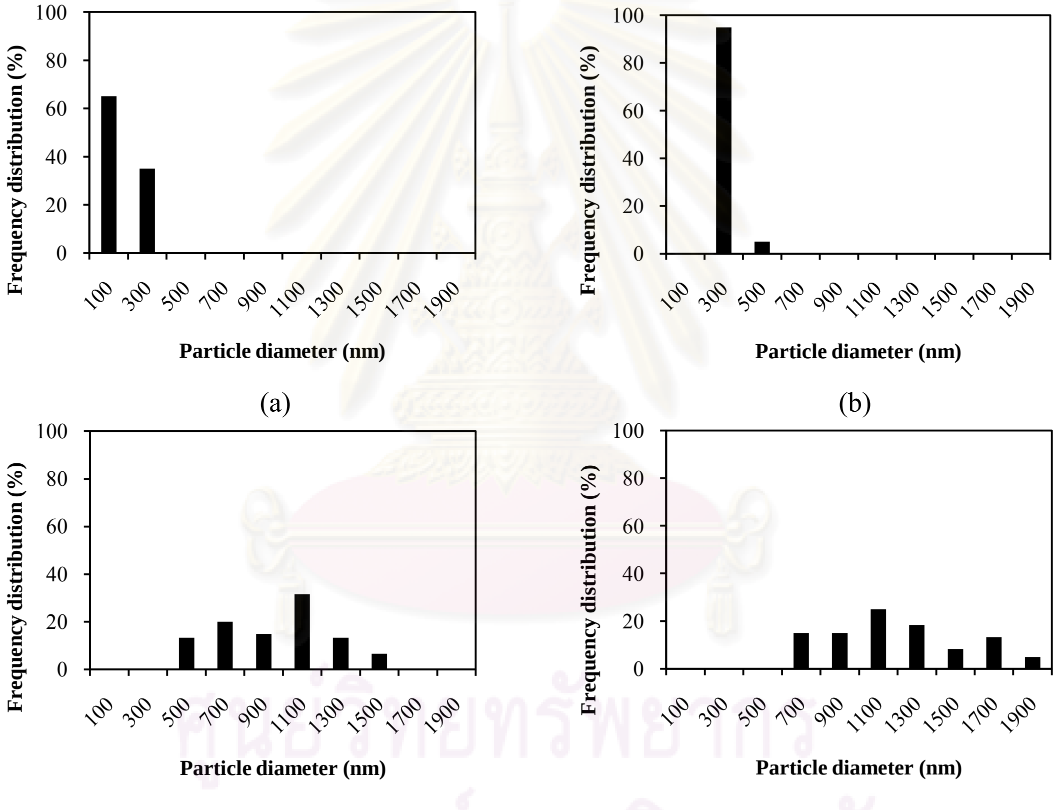


(a) (b)

(c) (d)

Figure 4.12: SEM images of collected particles electrospun from RF gel that was prepared by: (a) using R/C ratio of 50 and being aged for 6 h, (b) using R/C ratio of 600 and being aged for 28 h, (c) using R/C ratio of 1000 and being aged for 33h and (d) using R/C ratio of 2000 and being aged for 36 h.

Most of the particles deposited on the collector appeared to be spherical particles. The average diameter, as well as particle size distribution, depended upon the R/C ratio, as shown in Figure 4.13. The increase in the R/C ratio, result in an increasing average diameter. The average size of the particles prepared using R/C ratio of 50, 600, 1000 and 2000 was found to be 96.3, 191.0, 865.7 and 1103.9 nm, respectively. A dispersed particle was obtained with R/C ratio of 50, whereas an increase in R/C ratio produces poly-dispersed particles. Low R/C ratios results in small particles that are interconnected with large necks. In contrast, high R/C ratios results in large particles that are connected by narrow necks in a string of pearls fashion [39].



(a) (b) (c) (d)

Figure 4.13: Size distribution of the particles obtained from electrospinning of RF gel prepared by using different R/C molar ratio: R/C molar ratio of 50 (a), R/C molar ratio of 600 (b), R/C molar ratio of 1000 (c) and R/C molar ratio of 1.5 (d).

The decreases of the gelation time with high catalyst concentration due to the higher reactivity toward hydrolysis and condensation of the RF gel. As seen Figure 4.14, the gelation time increases with increasing R/C ratio. In the other words, the gelation process could occur more rapidly with low R/C ratio. From this figure, the catalyst concentration are insignificant effect on signal ratio of methylene and methylene ether bridges.

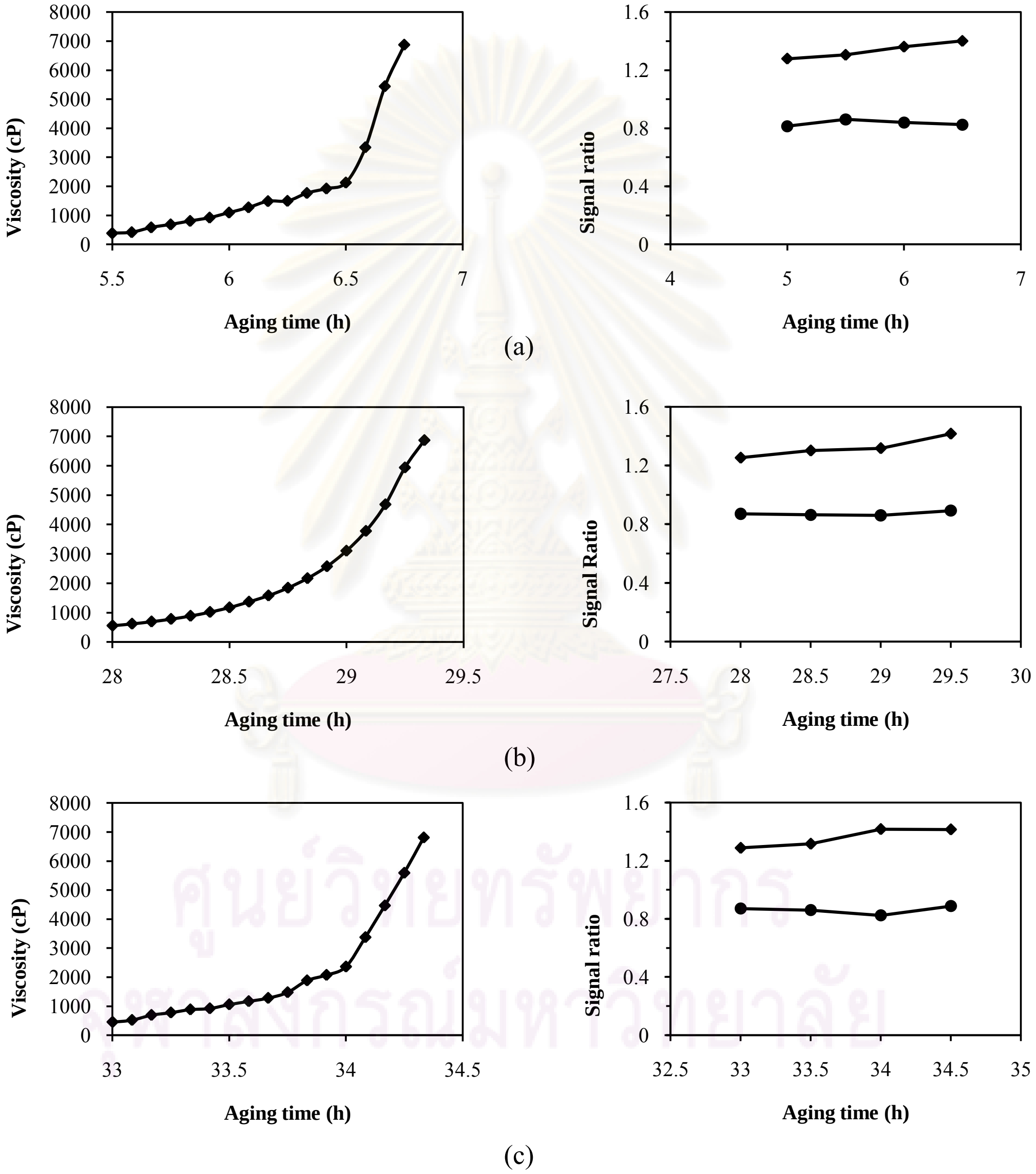
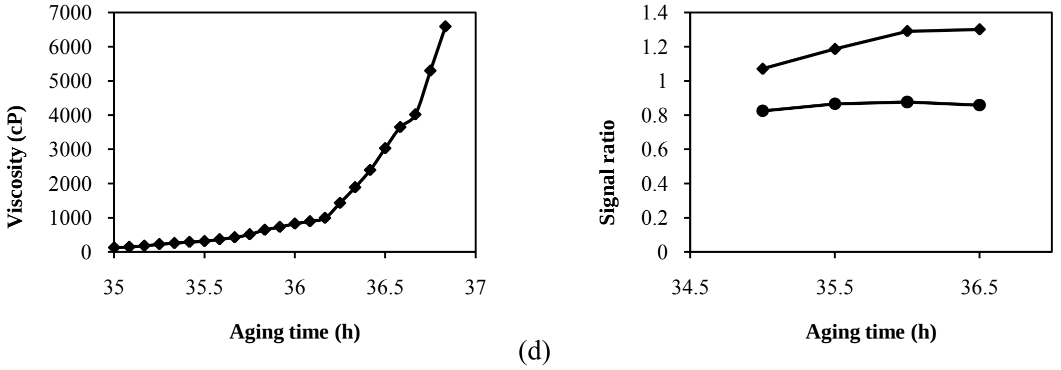


Figure 4.14: Apparent viscosity of RF gel and FTIR signal ratios of methylene bridge (◆) and methylene ether bridge (●) with respect to aromatic rings, as a function of aging time for RF solution. The RF gel was prepared using R/C molar ratio of: 50 (a), 600 (b), 1000 (c) and 2000 (d).



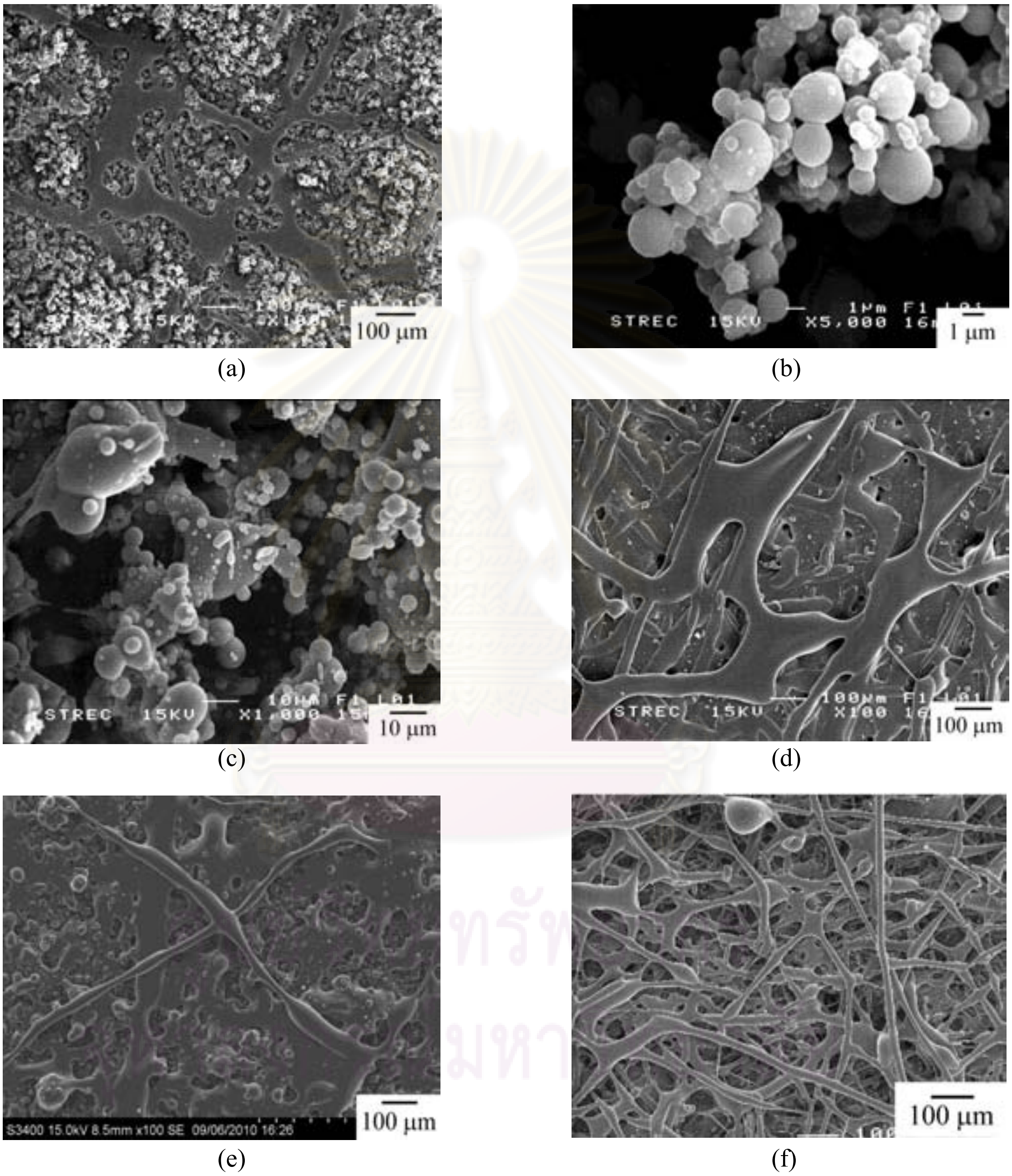
(d)

Figure 4.14: (continued)

4.1.4 Effect of resorcinol/water molar ratio

Another variable affecting the polycondensation process of RF gel is the dilution ratio, represented by R/W ratio. This factor influences size of RF clusters, which indirectly affect viscosity of the gel. In order to investigate this effect, samples were prepared using R/F and R/C ratios of 0.5 and 86.64. The value of R/W ratio was varied from 0.03, 0.45, 0.75, 1.00, 1.30, 1.50 and 2.00 respectively.

Figure 4.15-16 show SEM images of the obtained products. The results show that certain condition can result in the formation of fibers. At the R/W ratio 0.03, the RF solution could not form into gel because the solution has excess amount of water, so that the solution could not be spun. At the R/W ratio of 0.45, most of the products are agglomeration of non-uniform spherical particles (see Figure 4.15a). For the RF gel with the R/W ratio of 0.75 and being aged for 26 h, product is agglomerated spherical particles (see Figure 4.15b) with average diameter of 1.07 μm. Prolonging aging time to 27 h, the particles are mixed between spherical and elongated particles, yet they are heavily agglomerated as shown in Figure 4.15c. Finally for the same gel aged for 28h, fibers are obtained (Figure 4.15d). When the R/W ratio of the RF gel is increased further to 1.0 and 1.3, the gel is spinnable after 27h of aging time. Shape of the products obtained resembles microfibers. However, the product from RF gel with the R/W ratio of 1.0 appears to be merged together (Figure 4.15e). When the R/W ratio to is increased to 1.5, ether droplets or microfibers can be obtained, depending on the aging time of the gel. For the gel aged for 26 h, spherical droplets with average diameter of 2.8 μm (see figure 4.16a) were collected. Prolonged aging time results in the formation of microfibers (figure 4.16b). As the R/W ratio is further increased to 2.0, the products deposited on the collector are fibers, regardless of the aging time. However, the product spun from the gel aged for 25 h are heavily merged together into a film. Figure 4.17 compares frequency distribution for diameters of the RF-products that were obtained in the form of fibers. It can be seen that the decreasing in water content (i.e., high R/W ratio) generally causes the average diameter of the fibers to increase. Moreover, the average diameter of fibers is increased as the aging time of RF gel is prolonged. The R/W ratio of 1.5 is form to mostly produce microfibers.

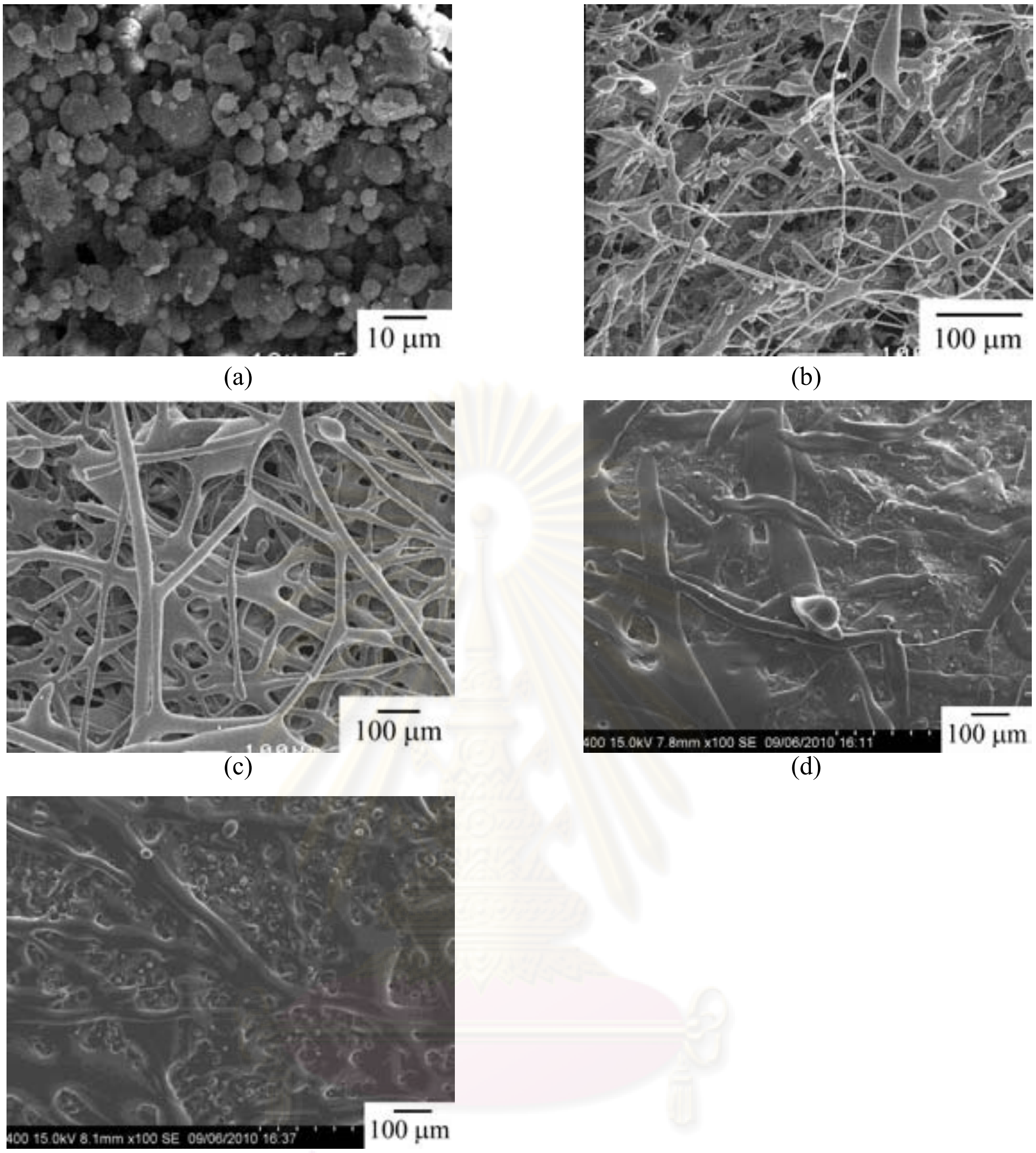


(a) (b)

(c) (d)

(e) (f)

Figure 4.15: SEM images of collected particles electrospun from RF gel that was prepared by: (a) using R/W ratio of 0.45 and being aged for 28 h, (b) using R/W ratio of 0.75 and being aged for 26 h, (c) using R/W ratio of 0.75 and being aged for 27 h, (d) using R/W ratio of 0.75 and being aged for 28 h, (e) using R/W ratio of 1.00 and being aged for 27 h, (f) using R/W ratio of 1.30 and being aged for 27h.



(a) (b) (c) (d) (e)

Figure 4.16: SEM images of collected particles electrospun from RF gel that was prepared by: (a) using R/W ratio of 1.50 and being aged for 26 h, (b) using R/W ratio of 1.50 and being aged for 27 h, (c) using R/W ratio of 1.50 and being aged for 28 h, (d) using R/W ratio of 2.0 and being aged for 24 h, (e) using R/W ratio of 2.0 and being aged for 25 h.

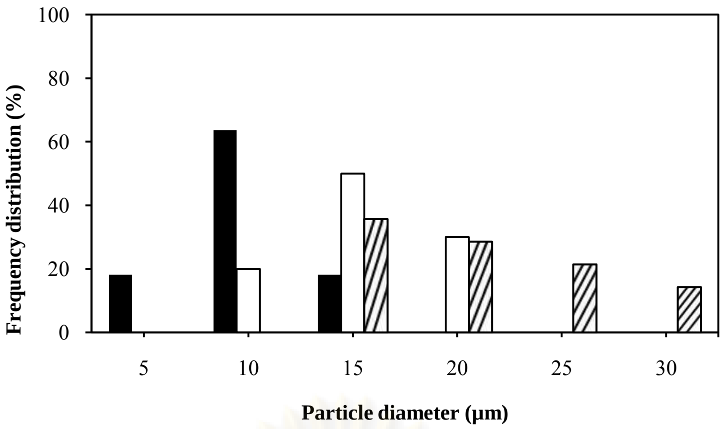
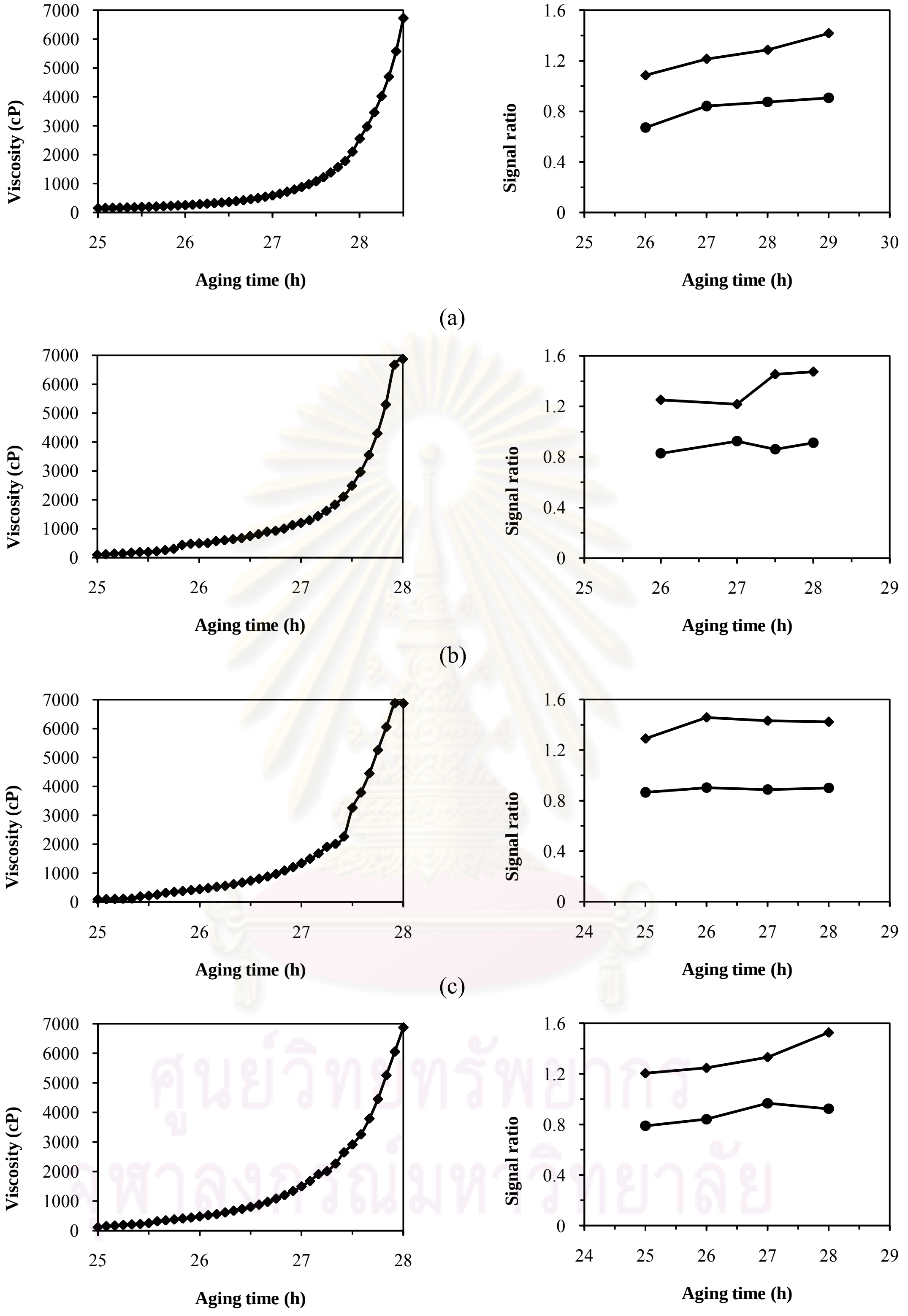


Figure 4.17: Shows frequency distribution of fiber diameters of RF gel prepared by using different R/W ratios and aged of RF gel: R/W ratio of 1.3 and being aged for 27h (■), R/W ratio of 1.5 and being aged for 27h (▣), R/W ratio of 1.5 and being aged for 28h (□).

RF gel could be spun in the form of fibers only when water content is low so that the RF clusters can form into continuous particulate gels. This is supported by the result shown in Figure 4.18 that the signals for methylene and methylene ether bridges increase significantly when water content is decreased. Low amount of water also minimizes breakage of the jet of solution ejected from the nozzle, which consequently yield products in a form of continuous fibers.



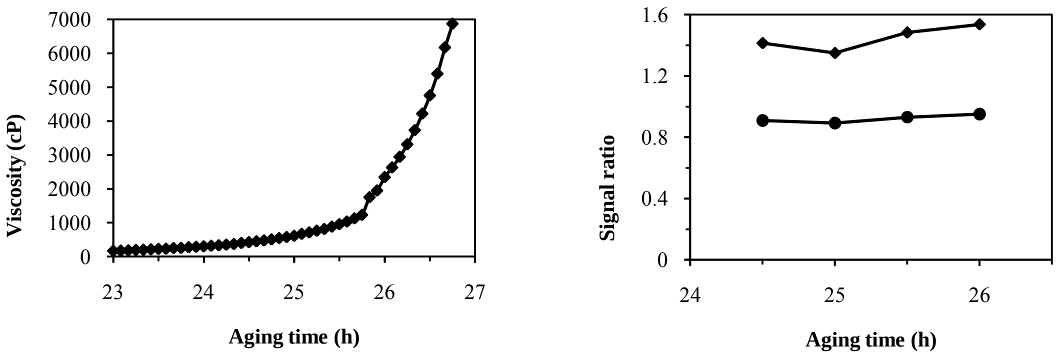
(a)

(b)

(c)

(d)

Figure 4.18: Apparent viscosity of RF gel FTIR signal ratios of methylene bridge (◆) and methylene ether bridge (●) with respect to aromatic rings, as function of aging time for RF solution. The RF gel was prepared using R/W molar ratio of: 0.45 (a), 0.75 (b), 1.0 (c),1.5 (d) and 2.0 (e).



(e)

Figure 4.18: (continued)

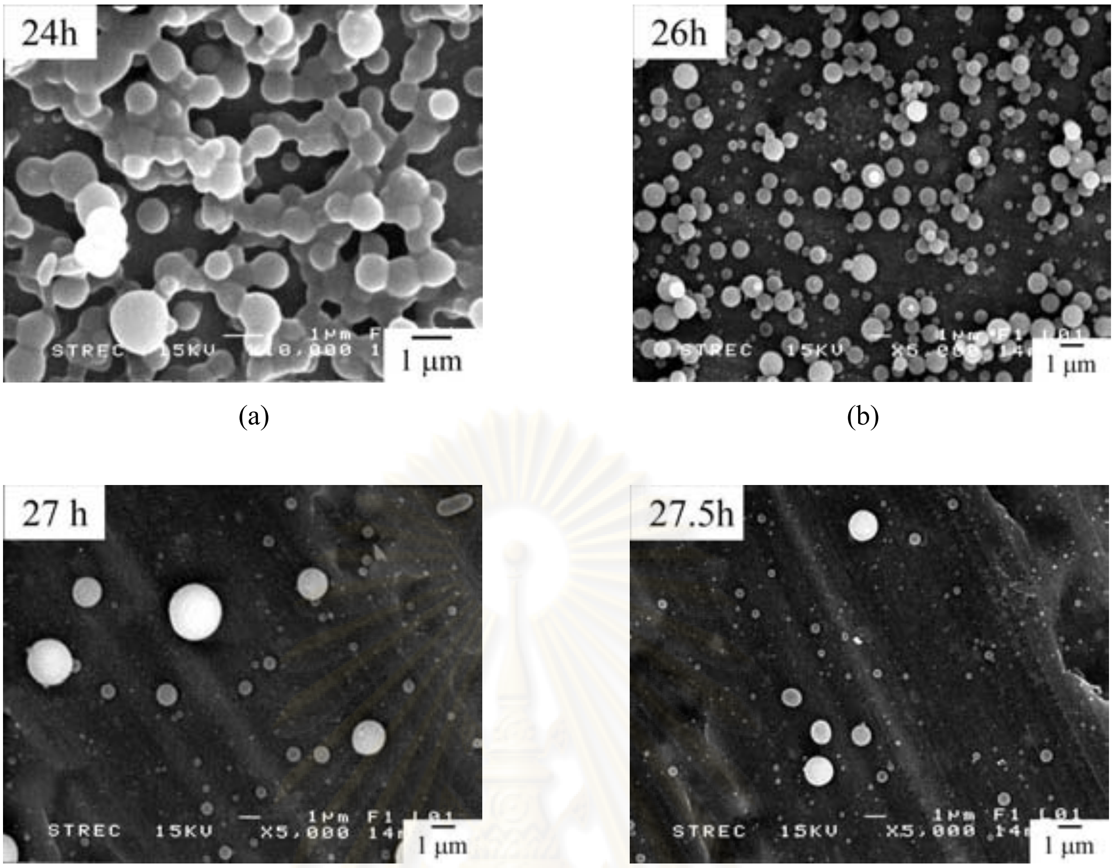
4.2 Effect of Electrospinning Conditions on RF-Products

4.2.1 Effect of applied electric field strength on size and morphology of product

A crucial element in the electrospinning is the strength of applied electric field. In this section, the electric potential was applied in the range of 1.0 to 2.0 kV/cm with increment of 0.5 kV/cm. The volumetric flow rate of the gel was fixed at 0.8 ml/h, using a syringe pump, and the RF gel was prepared by using R/F, R/C and R/W molar ratios of 0.50, 86.64 and 0.15 respectively, for all experiments in this part.

Figure 4.19 shows SEM images of products fabricated by using the field strength of 1 kV/cm. For the RF gel aged for 24 h, although the product resembles spherical particles, the particles are merging together. For the RF gel aged for 26, 27 and 27.5 h, the obtained products appear to be nearly mono-dispersed spherical particles. Average diameter of the particles decreases with prolonged aging time of the RF gel, as shown in Figure 4.20. The same trend is formed when the electric potential is increased to 1.5 and 2 kV/cm (see Figure 4.21-4.24), the particles tend to agglomerate and merge together to form porous structure, when the aging time is not long enough. And Figure 4.25 compares the average diameter of the obtained particles produced by using different electric field strength.

Increasing electric field strength results in an increase in both the electrostatic force, which is responsible for the transport of the charged jet from injection orifice to the collective target, and the Coulombic repulsion force, which is responsible for ejected jet segment. The increase in electrostatic force gives rise to the increase in mass throughput of the liquid jet from the nozzle, while the increased Coulombic repulsion force results in the increase in the average diameter of the particles. When electric field strength becomes too high, the spinning jet becomes unstable, and the average diameter of the particles was found to decrease with increasing electric field strength [45].



(a) (b)

(c) (d)

Figure 4.19: SEM images of products obtained from electrospinning of RF gel by using electric field strength of 1 kV/cm. The RF gel had been aged for 24 h (a), 26 h (b), 27 h (c) and 27.5 h (d).

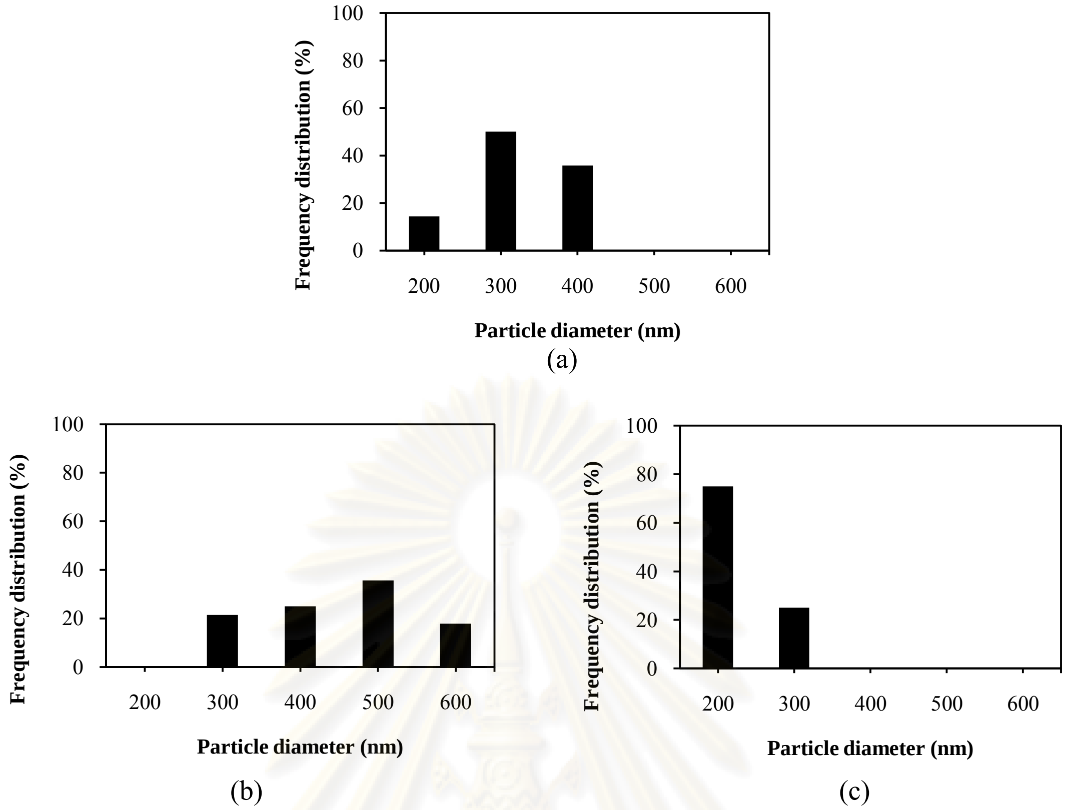
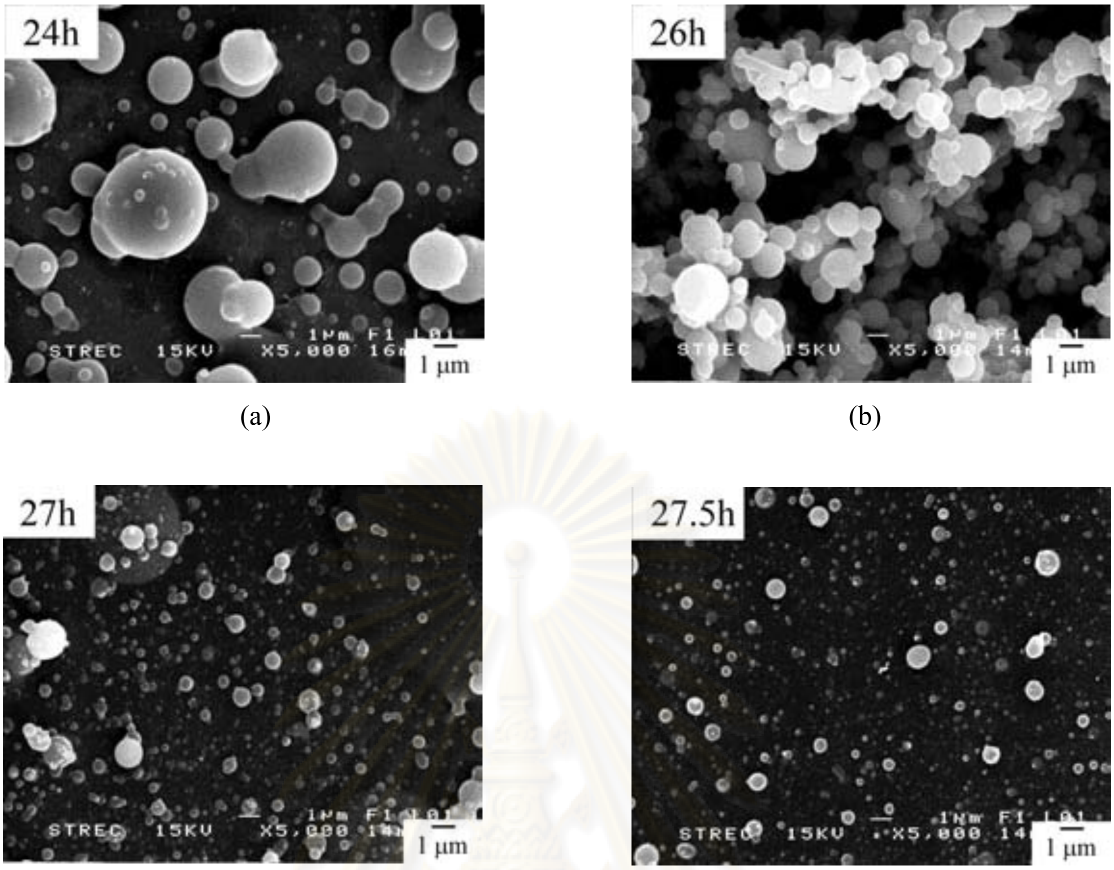


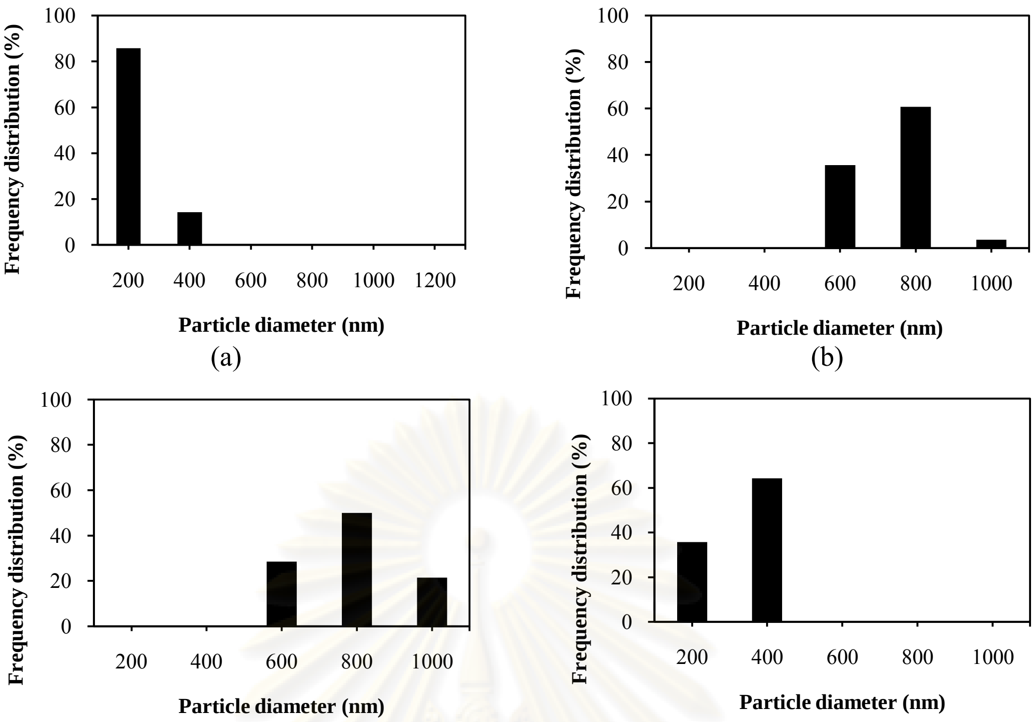
Figure 4.20: Frequency distribution of products obtained from electrospinning of RF gel by using electric field strength of 1 kV/cm. The RF gel had been aged for 26 h (a), 27 h (b) and 27.5 h (c).



(a) (b)

(c) (d)

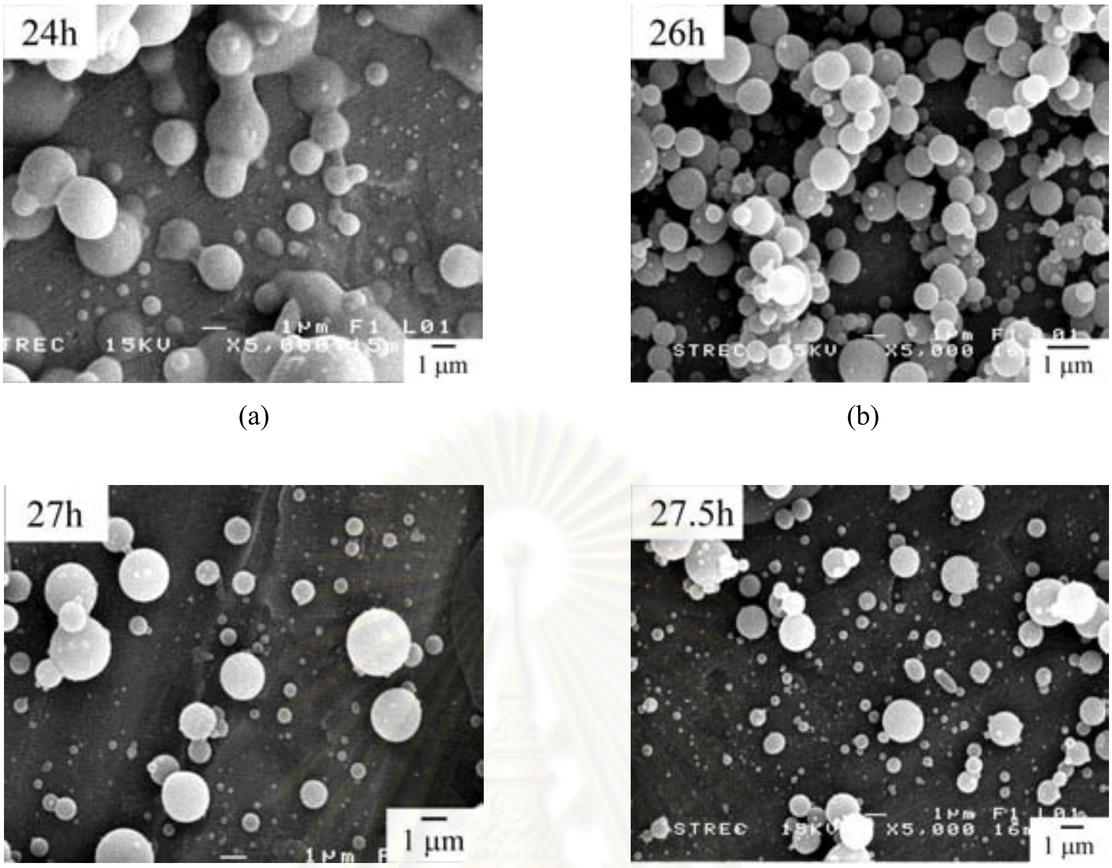
Figure 4.21: SEM images of products obtained from electrospinning of RF gel by using electric field strength of 1.5 kV/cm. The RF gel had been aged for 24 h (a), 26 h (b), 27 h (c) and 27.5 h (d).



(a) (b)

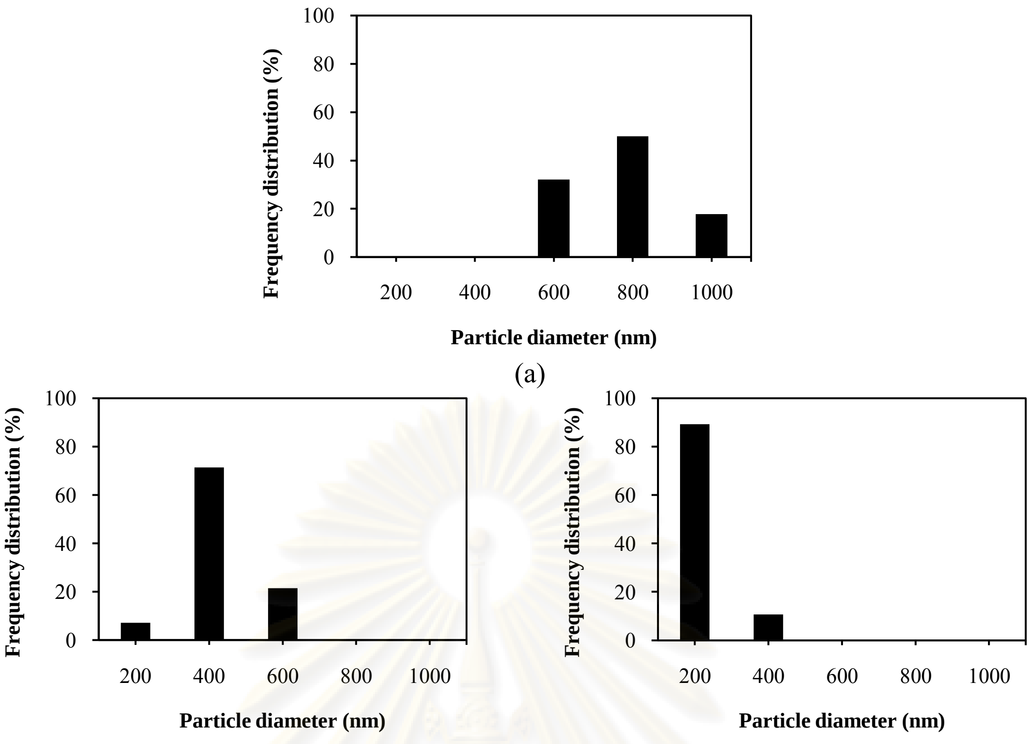
(c) (d)

Figure 4.22: Frequency distribution of products obtained from electrospinning of RF gel by using electric field strength of 1.5 kV/cm. The RF gel had been aged for 24 h (a), 26 h (b), 27 h (c) and 27.5 h (d).



(a) (b) (c) (d)

Figure 4.23: SEM images of products obtained from electrospinning of RF gel by using electric field strength of 2.0 kV/cm. The RF gel had been aged for 24 h (a), 26 h (b), 27 h (c) and 27.5 h (d).



(a)

(b)

(c)

Figure 4.24: Frequency distribution of products obtained from electrospinning of RF gel by using electric field strength of 2.0 kV/cm. The RF gel had been aged for 26 h (a), 27 h (b) and 27.5 h (c).

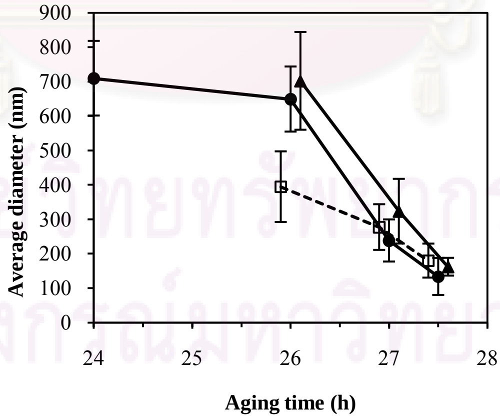


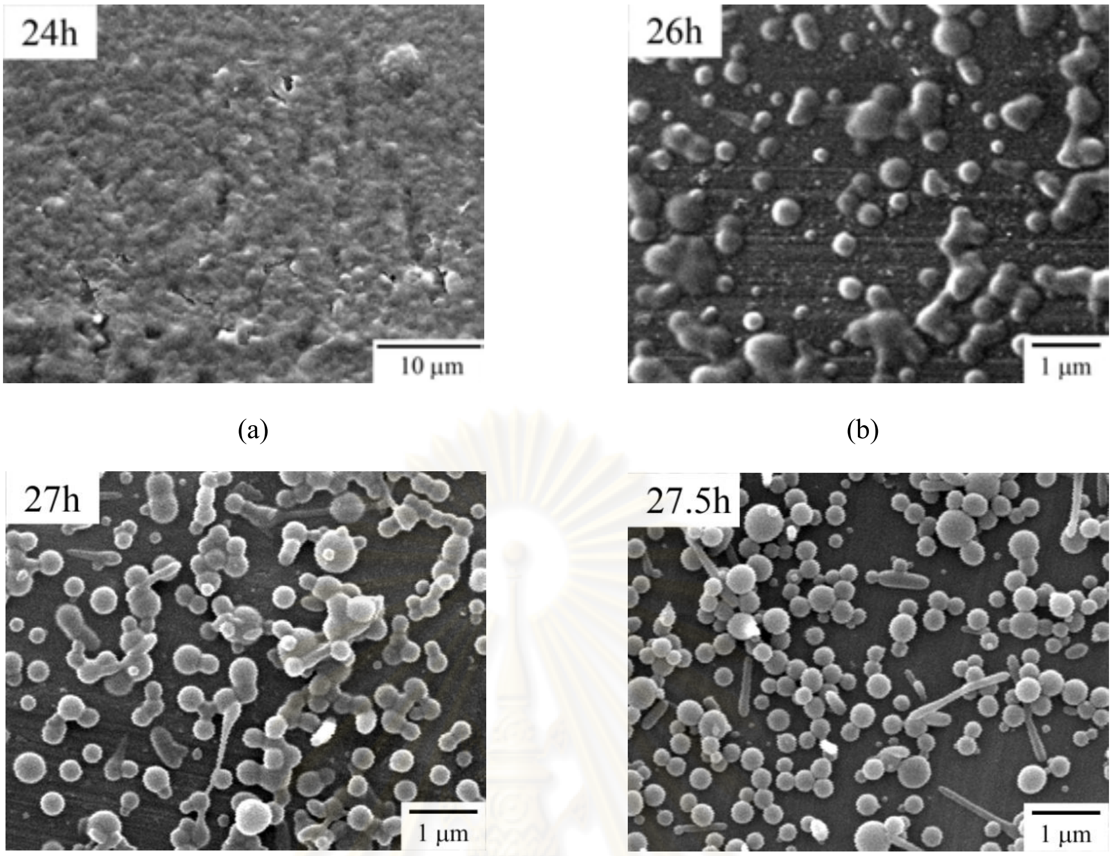
Figure 4.25: Average diameter of products obtained from electrospinning of RF gel by using different electric field strength, i.e, 1.0 (□), 1.5 (●) and 2.0 kV/cm (▲), as a function of aging time of the RF gel. Noted that the aging time investigated are 24, 26, 27 and 27.5 h. The data points are intentionally shifted for the clarity of the plot.

4.2.2 Effect of applied voltage on size and morphology of product

The applied electric potential is another key factor determining the morphology and diameter of the electrospun particles. In this work, RF particles were produced by using applied voltage of 7, 10 and 18 kV, respectively. The distance between the tip and the collector was kept at 10 cm. SEM images of the resulting products from electrospinning of RF gel by using different applied voltage are shown in Figure 4.26-28.

Product obtained by using voltage of 7 kV and 10 kV (e.g., RF gel aged for 26 h and 27 h) are elongated particle. At 7 kV and 10 kV, when the aging time of RF gel is increased, the average diameter of the particles obtained decreases. As the applied voltage is increased, the average diameter is increased. The frequency distributions of the average diameter of the particles fabricated by different condition are shown in Figure 4.29, and summarized in Figure 4.30. When low potential is applied in a solution of low viscosity (RF gel had been aged for 24 h), the reduced acceleration of the jet and the weaker electric field would cause surface tension to be a dominant influence along the electrospinning jet result in the droplets to form a merging of particles into a film.

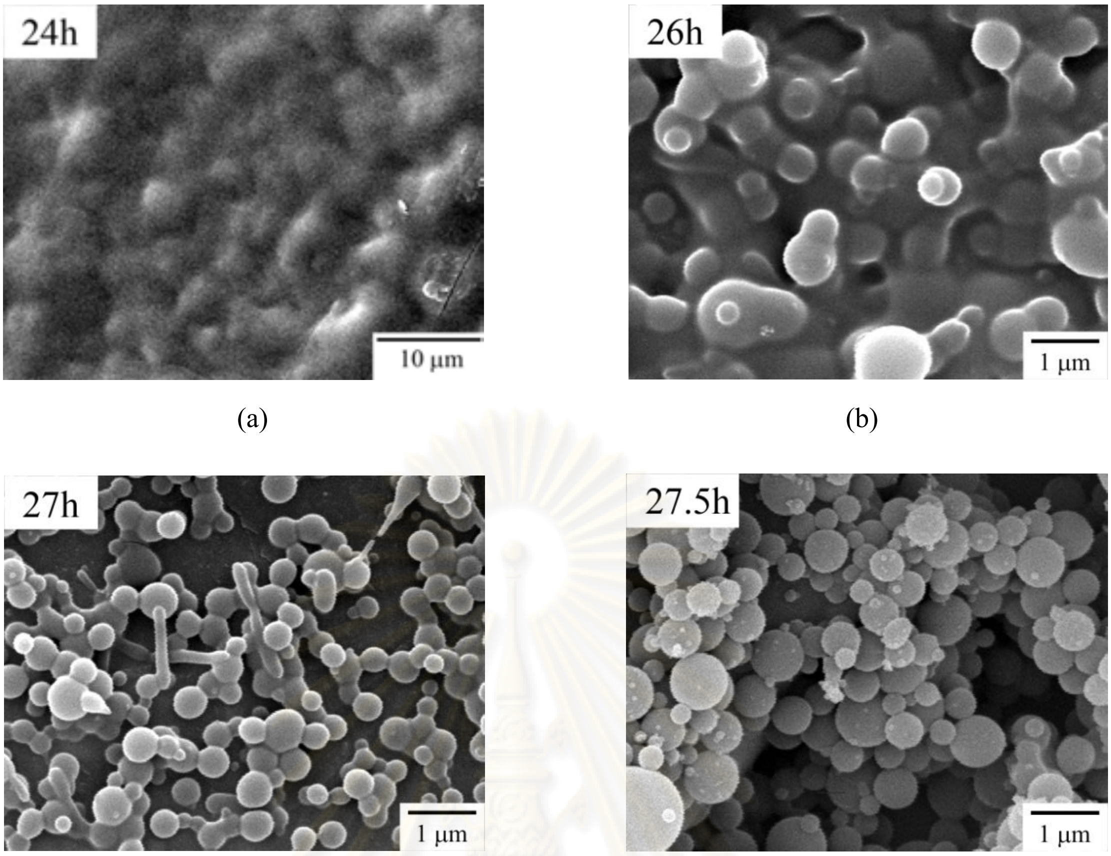
The high voltage will induce the necessary charges on the solution and together with the external electric field, will initiate the electrospinning process when the electrostatic force in the solution overcomes the surface tension of the solution [22]. However, the applied voltage of 18 kV is too high in this case. The grater amount of charges causes the jet to accelerate faster and large volume of solution will be drawn from the tip of the nozzle to the collector such that the deposition of the RF gel onto the collector is faster than the evaporation of the solvent. This results in a merging of particles into a film.



(a) (b)

(c) (d)

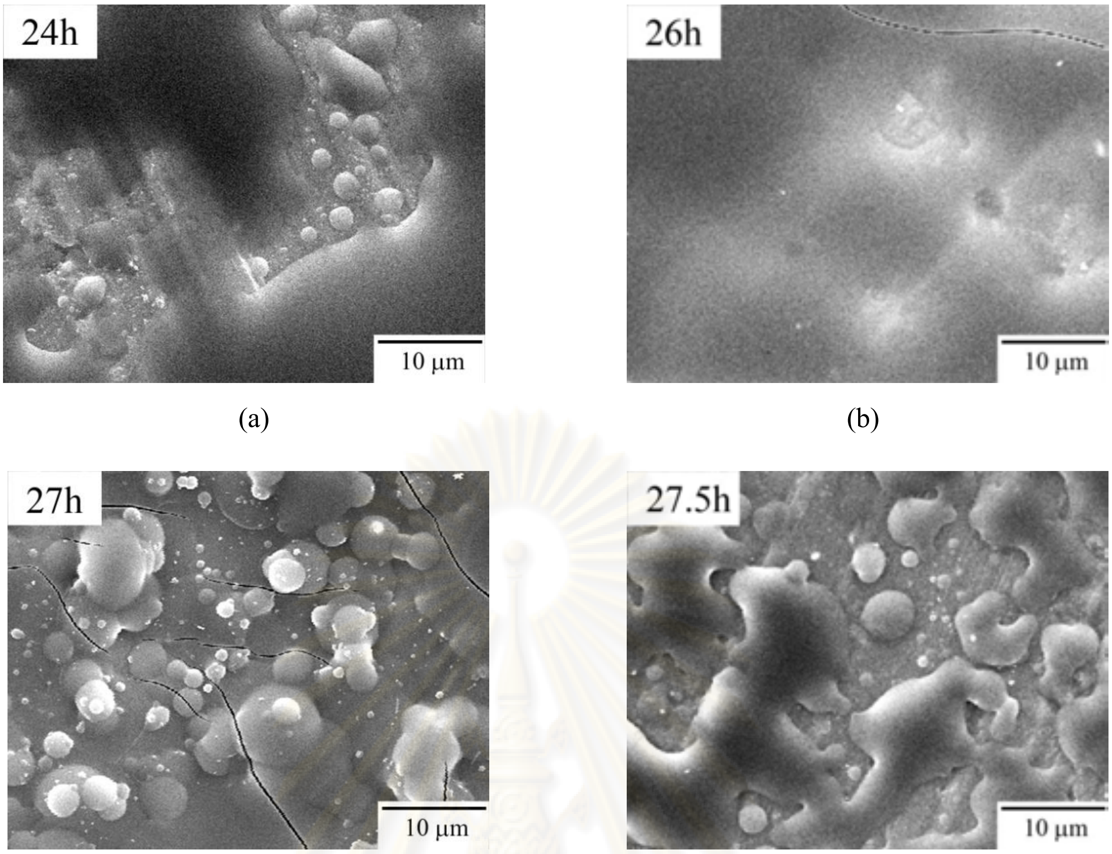
Figure 4.26: SEM images of products obtained from electrospinning of RF gel by using applied voltage of 7 kV. The RF gel that had been aged for 24 h (a), 26 h (b), 27 h (c) and 27.5 h (d).



(a) (b)

(c) (d)

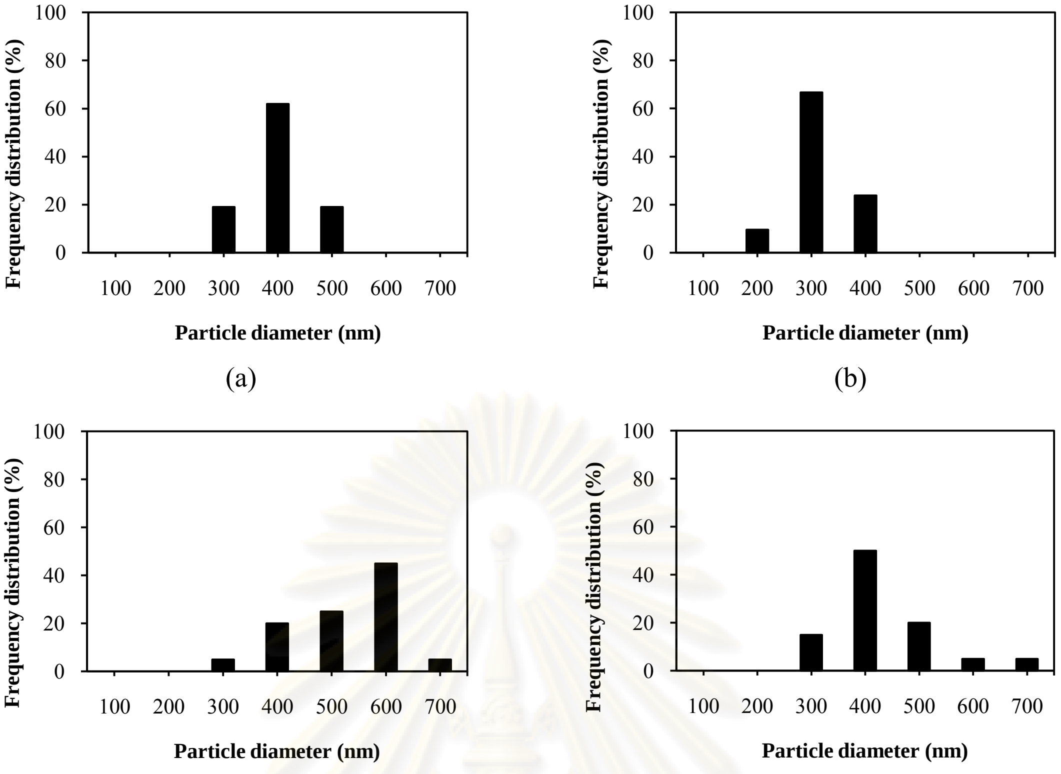
Figure 4.27: SEM images of products obtained from electrospinning of RF gel by using applied voltage of 10 kV. The RF gel that had been aged for 24 h (a), 26 h (b), 27 h (c) and 27.5 h (d).



(a) (b)

(c) (d)

Figure 4.28: SEM images of products obtained from electrospinning of RF gel by using applied voltage of 18 kV. The RF gel that had been aged for 24 h (a), 26 h (b), 27 h (c) and 27.5 h (d).



(a) (b)

(c) (d)

Figure 4.29: Frequency distribution of products obtained from electrospinning of RF gel by using different applied voltage and aging time: using 7kV for the gel aged for 27 h (a), using 7kV for the gel aged for 27.5 h (b), using 10kV for the gel aged for 27 h (c) and using 10kV for the gel aged for 27.5 h (d).

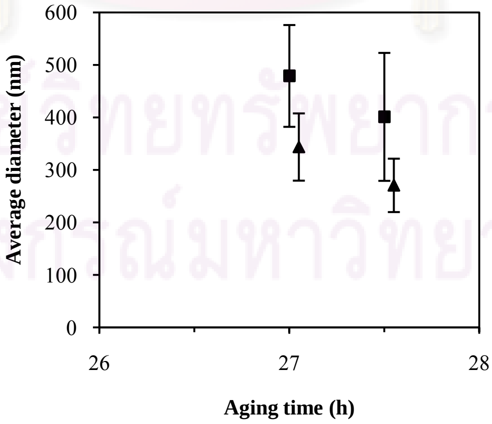
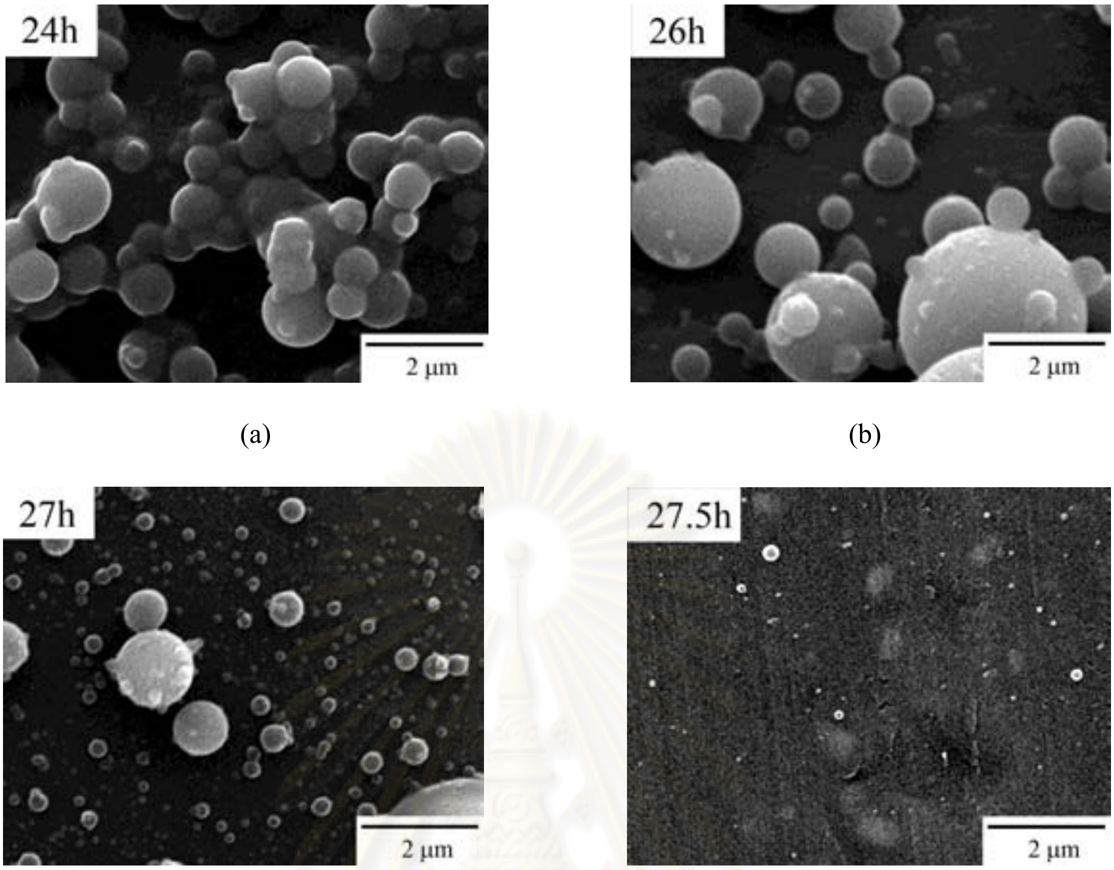


Figure 4.30: Average diameter of products obtained from electrospinning of RF gel by using different applied voltage, i.e., 7(▲) and 10 kV (■), as a function of aging time of RF gel. Noted that the aging time investigated are 27 and 27.5 h. The data points are intentionally shifted for the clarity of the plot.

4.2.3 Effect of distance between tip and collector on size and morphology of product

Varying the distance between the tip and the collector will have a direct influence in both the flight time and the electric field strength. In this research, the working distance in the range of 5 to 20 cm. The applied voltage was kept at 15 kV. According to Figure 4.31, when the working distance is set at 5 cm, the jet of the RF gel ejected from the nozzle will have a shorter distance to travel before being collected that make the RF particle may not have enough time for solvents to evaporate when it collect on the collector, so it results in large particle. On the other hand when the working distance is increased to 15 and 20 cm (shown in Figure 4.33, 4.35) under the same applied potential, the electrical field strength is decreased so that majority of the solution drops down instead of being ejected toward the collector. This is the main reason for the small amount of product collected. And we found that viscosity of RF gel is significant factor for electrospinning.

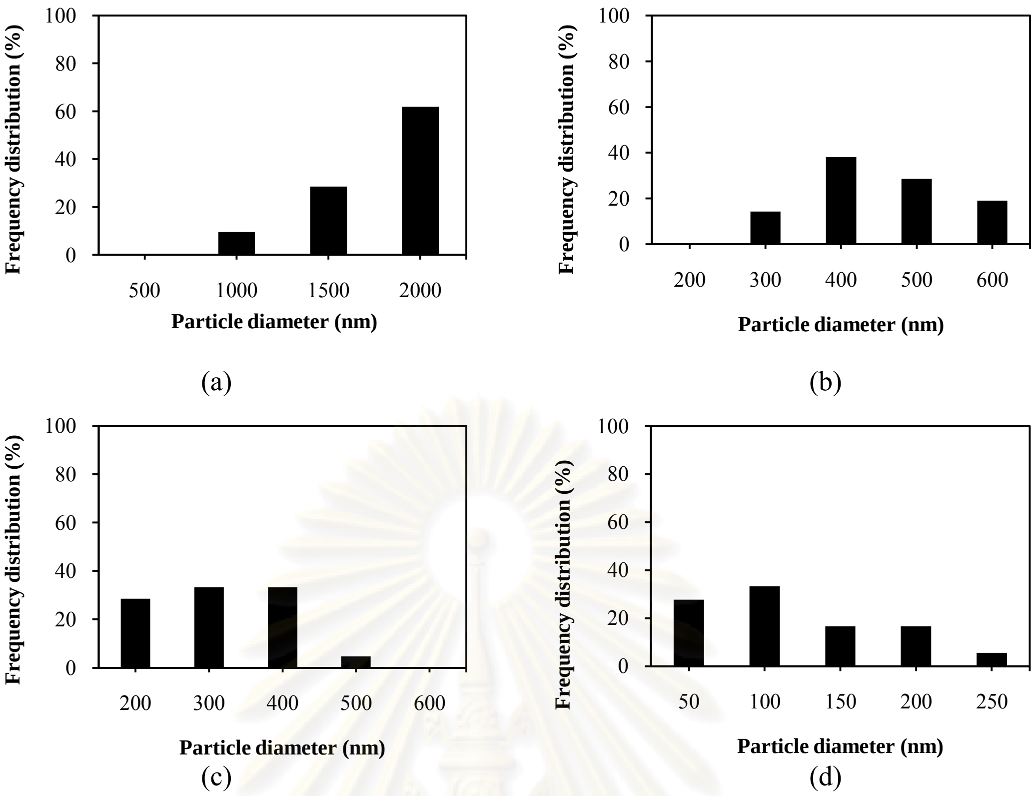
The relationships between the diameter of the as-spun particles and the distance between tip and collector are shown in Figure 4.37. As the general trend, when the aging time of RF gel is increased, the average diameter of the obtained product decreases. The working distance is found to significantly affect the product only at short aging time. For the RF gel aged for 27.5 h, the working distance shows insignificant effect on the average diameter of the particles.



(a) (b)

(c) (d)

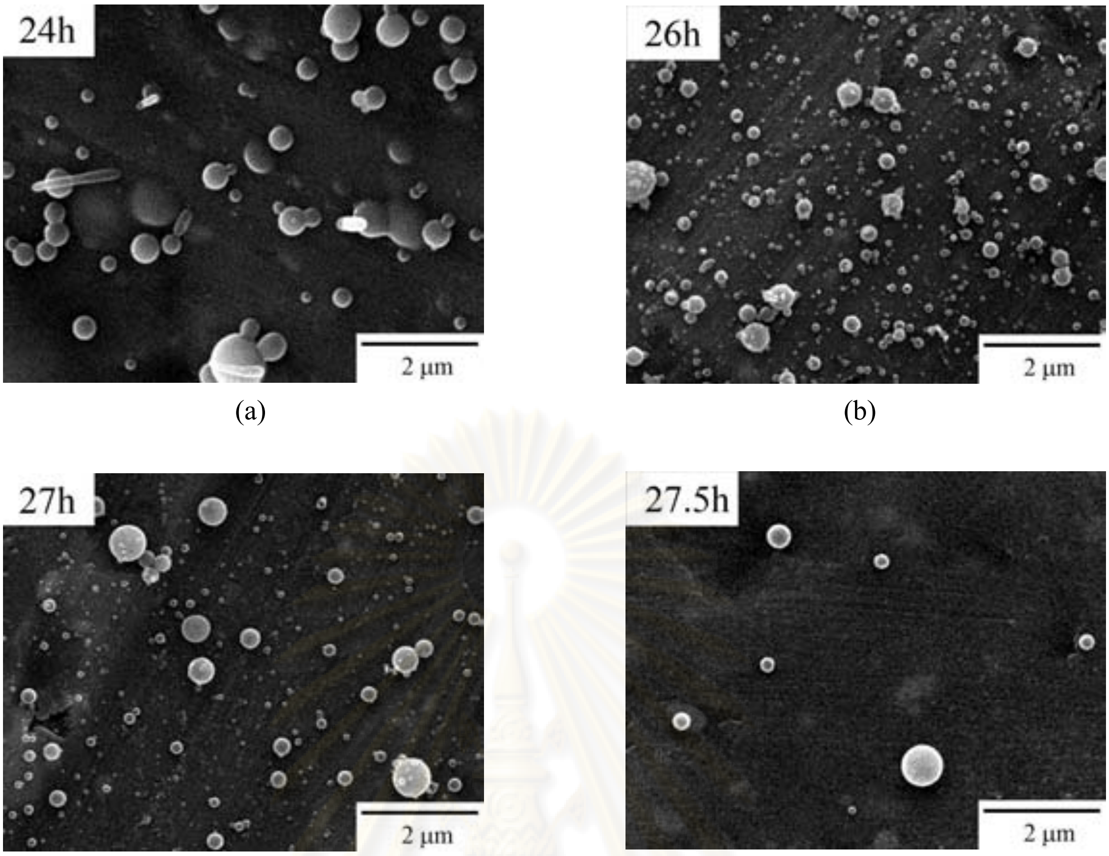
Figure 4.31: SEM images of products obtained from electrospinning of RF gel by using working distance of 5 cm. The RF gel that had been aged for 24 h (a), 26 h (b), 27 h (c) and 27.5 h (d).



(a) (b)

(c) (d)

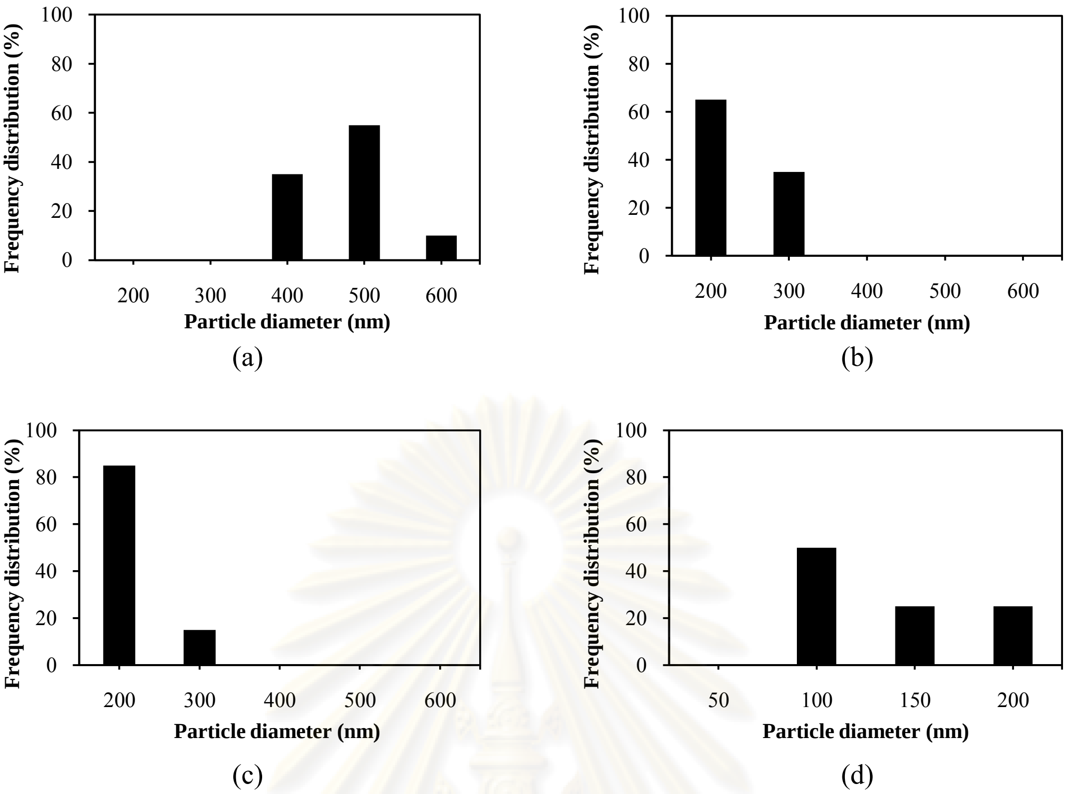
Figure 4.32: Frequency distribution of products obtained from electrospinning of RF gel by using tip-to-collector of distance between at 5 cm and being aged for 24 h (a), being aged for 26 h (b), being aged for 27 h (c) and being aged for 27.5 h (d).



(a) (b)

(c) (d)

Figure 4.33: SEM images of products obtained from electrospinning of RF gel by using working distance of 15 cm. The RF gel that had been aged for 24 h (a), 26 h (b), 27 h (c) and 27.5 h (d).



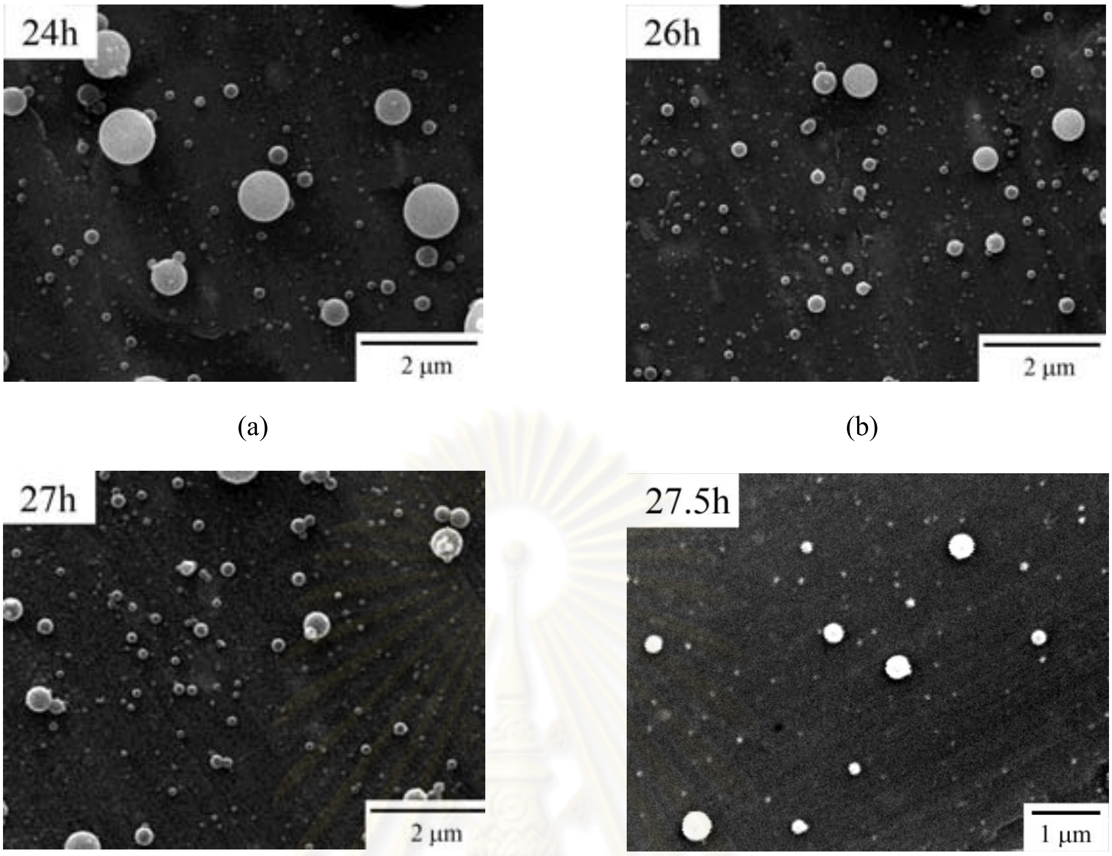
(a)

(b)

(c)

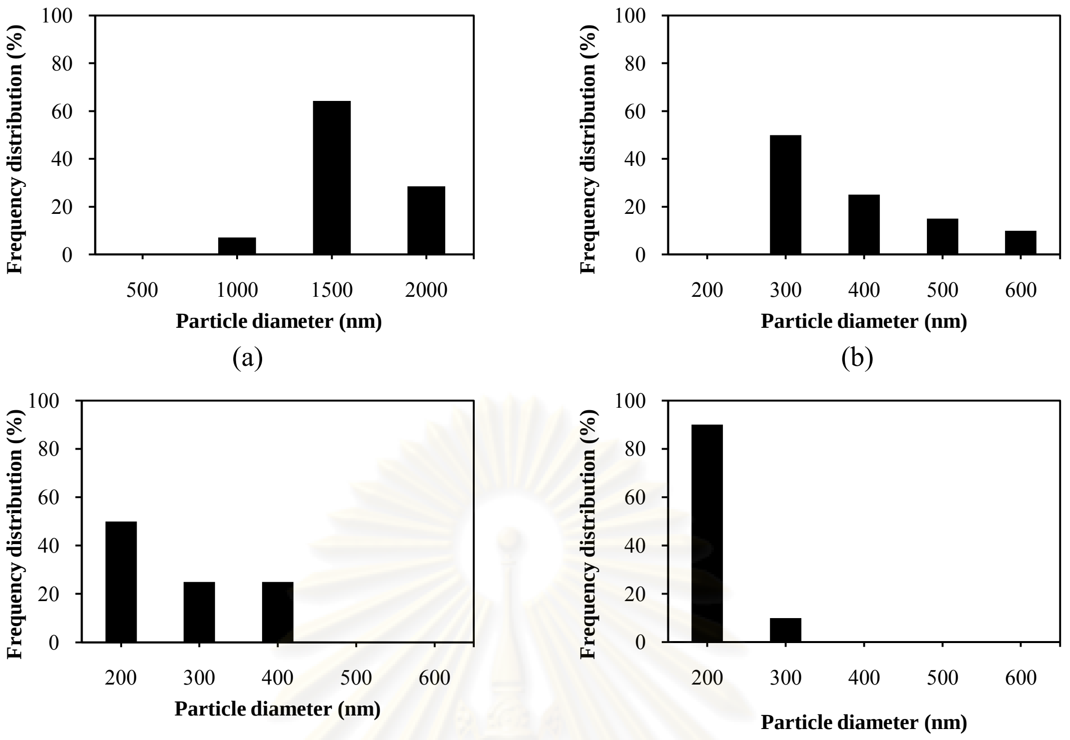
(d)

Figure 4.34: Frequency distribution of products obtained from electrospinning of RF gel by using tip-to-collector of distance between at 15 cm and being aged for 24 h (a), being aged for 26 h (b), being aged for 27 h (c) and being aged for 27.5 h (d).



(a) (b) (c) (d)

Figure 4.35: SEM images of products obtained from electrospinning of RF gel by using working distance of 20 cm. The RF gel that had been aged for 24 h (a), 26 h (b), 27 h (c) and 27.5 h (d).



(a) (b) (c) (d)

Figure 4.36: Frequency distribution of products obtained from electrospinning of RF gel by using tip-to-collector of distance between at 20 cm and being aged for 24 h (a), being aged for 26 h (b), being aged for 27 h (c) and being aged for 27.5 h (d).

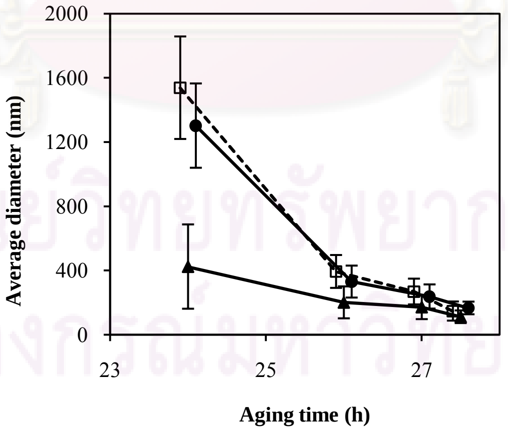


Figure 4.37: The relationships between the diameter of the as-spun particles the distance between tip and collector: 5cm (●), 15cm (▲) and 20cm (■).Noted that the aging time investigated are 24, 26, 27 and 27.5 h. The data points are intentionally shifted for the clarity of the plot.

4.3 Effect of Aging Conditions on RF-Particles

Different humidity in the aging atmosphere has effect on the formation and morphology of particles. In this experiment, pure water, saturated solution of sodium chloride and silica-gel were used to control the relative humidity of the aging system to be 100%, 75% and 8% at 25°C, respectively. For the electrospinning, the electric potential was applied at 15 kV and working distance was fixed at 10 cm. The volumetric flow rate of the gel was fixed at 0.8 ml/h, using a syringe pump, for all experiments in this part. The RF gel was prepared by using R/F, R/C and R/W molar ratios of 0.50, 86.64 and 0.15 respectively.

Morphology of the particles electrospun from RF gel that had been aged under 100% RH and 75% RH is the same as morphology of the particles aged under ambient condition, as seen in Figure 4.38. The mono-dispersed particles are obtained from the RF gel aged for prolonged aging time. The frequency distributions of the obtained products are shown in Figure 4.39. It is formed that the average diameter of the particles decreases when the RF gel is aged in atmosphere with higher the relative humidity. In the mean time, prolong aging time of the RF gel results in decreased average diameter of the obtained product, as shown in Figure 4.40.

The particles fabricated from the RF gel aged under 100% RH is bigger than that aged under 75% RH. Due to the RF gel aged under 100% RH has less evaporated than that gel aged under 75% RH when the electrospinning jet reaches the collector. Large particles (i.e., aged RF gel 29 and 30 h) due to RF gel have few chains entanglement (low viscosity as show in Figure 4.41) that make surface tension of the RF gel has a dominant influence along the electrospinning jet [22].

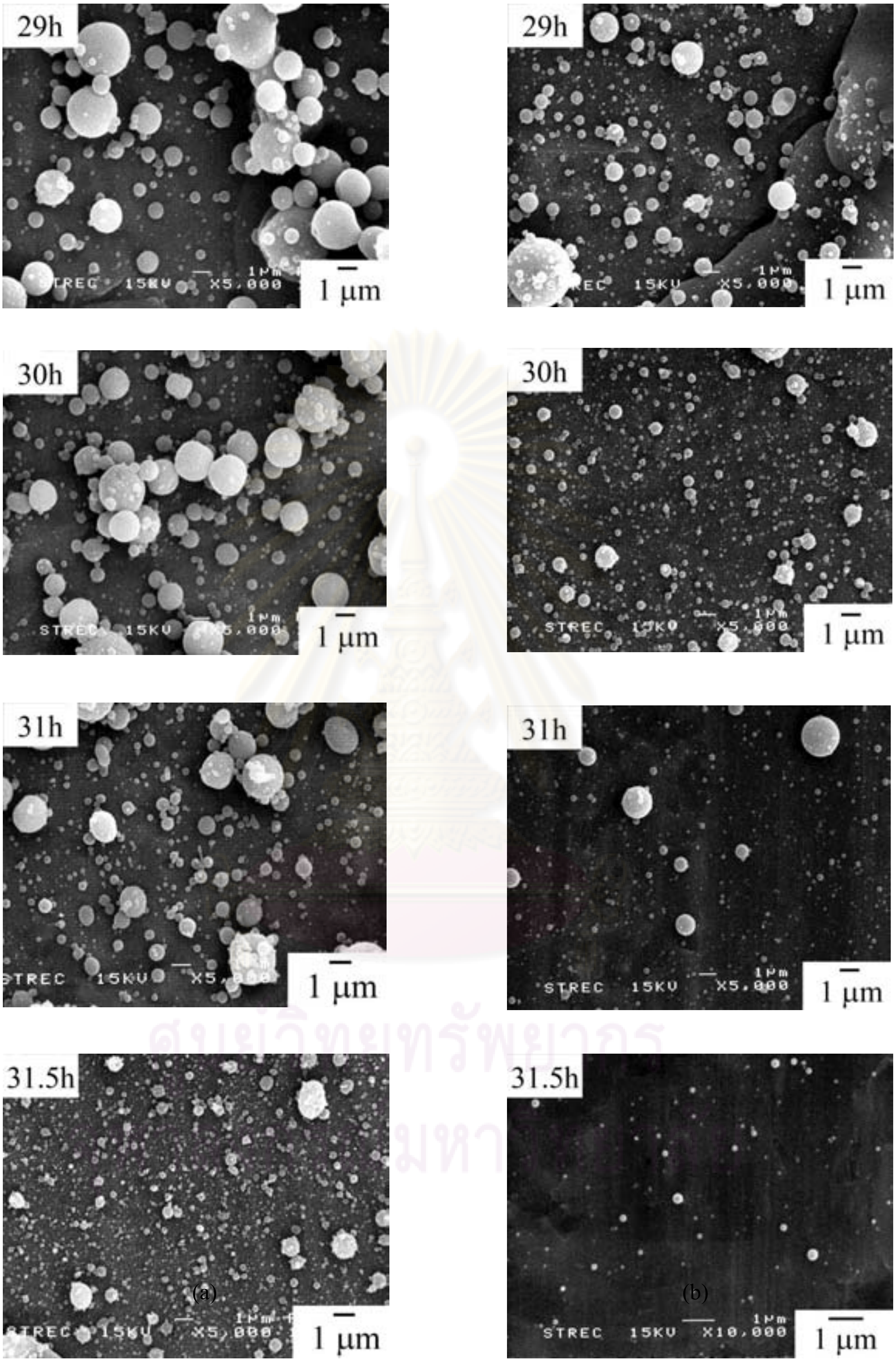
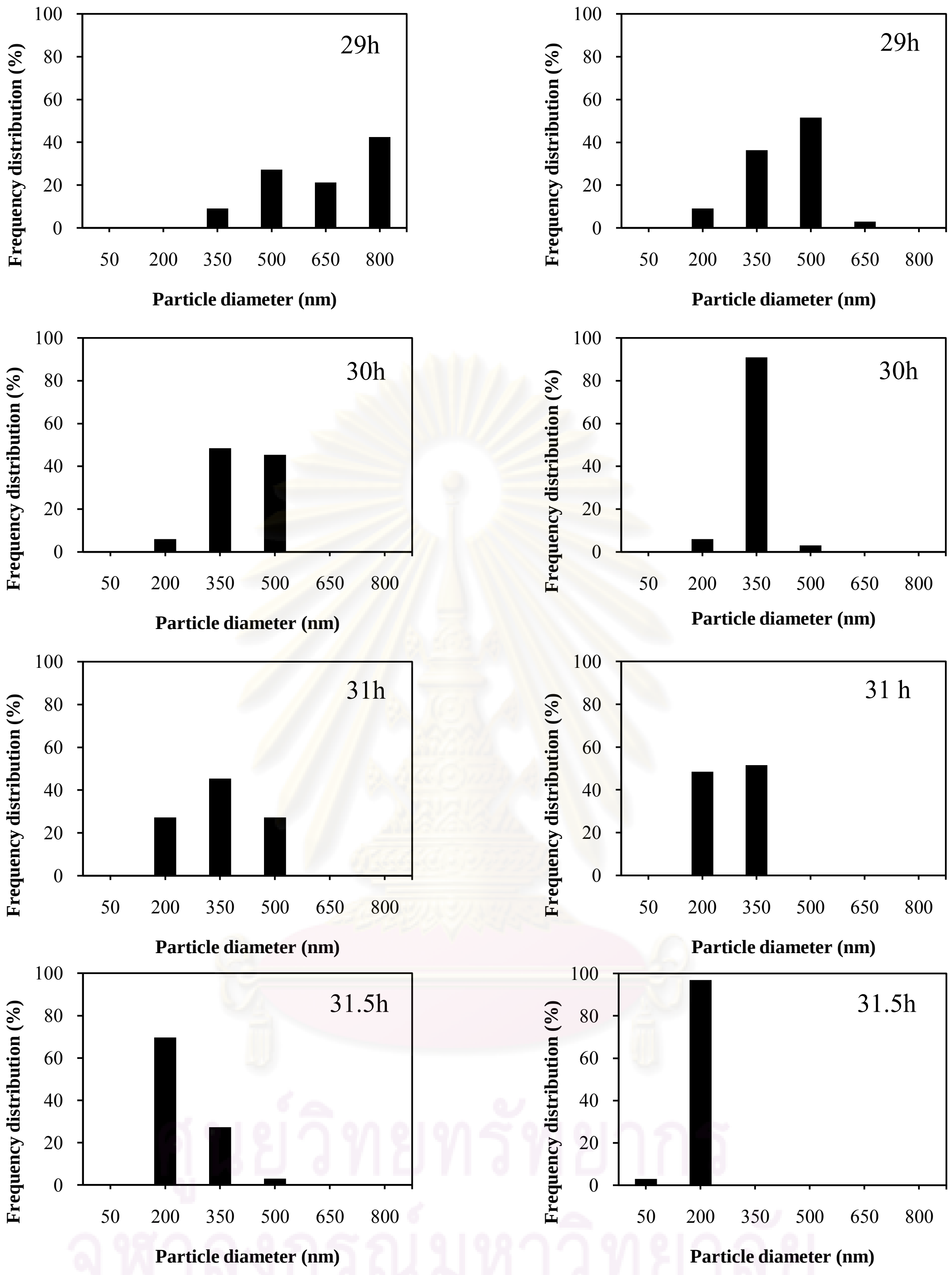


Figure 4.38: SEM images of products obtained from electrospinning of RF gel aged under the atmosphere of: 100% RH (a) and 75% RH (b) for various period of time.



(a) (b)

Figure 4.39: The frequency distributions of obtained products from electrospinning of RF gel aged under the atmosphere of 100% RH (a) and 75% RH (b), for various period of time.

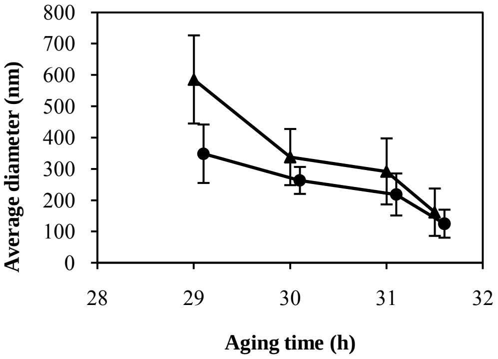


Figure 4.40: Average diameter of products obtained from electrospinning of RF gel aged under the atmosphere of 100% RH (▲) and 75% RH (●), as a function of aging time. Noted that the aging time investigated are 24, 26, 27 and 27.5 h. The data points are intentionally shifted for the clarity of the plot.

As shown in Figure 4.41, the signals of methylene and methylene ether bridges with respect to that of aromatic rings of RF gel aged under 75% RH is higher than those observed from RF gel aged under 100% RH. Since of the atmosphere with relative humidity of 100% is saturated, water which is a by-product from the condensation reaction could not evaporate from the gel. As the aging time is prolonged, signals of methylene and methylene ether bridges increase, which indicate higher cross-link. Figure 4.42 compares the viscosity of the RF gel aged under different atmosphere and confirms that the high cross-linking of the RF gel takes place faster if the gel is aged in the atmosphere with lower relative humidity.

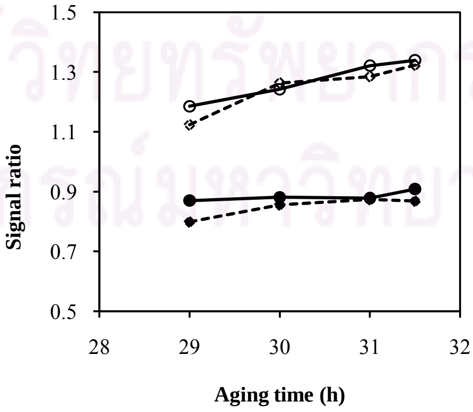


Figure 4.41: Relationship of FTIR signals of methylene bridge (solid points) and methylene ether bridge (blank points) comparing to that of aromatic rings in RF gel aged in 100% (---) and 75% ( )relative humidity, w~~ith~~ respect to aging time.

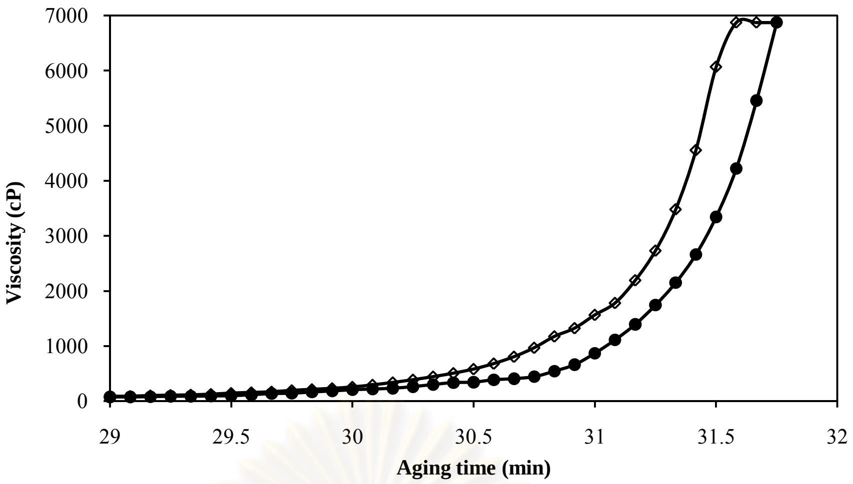


Figure 4.42: Apparent viscosity of RF gel aged under 100% RH (●) and 75% RH (◇).

In previous sections, the RF gel can not spun to obtain the fiber because the molecular chains entanglement are low and high amount of solvent.

When the relative humidity of the aging system is adjusted to be 8%, it highly affects morphology of the spun RF gel. Figure 4.43 shows the morphology of the product from electrospinning of RF gel aged for 26 and 26.5 h are formed into micro-fibers. Micro-fibers are formed because water which is by-product from the condensation reaction was evaporated from the RF gel. It should be noted that silica-gel absorbs moisture continuously from the atmosphere to keep low humidity. The continuous removal of water from the gel increases rate of the RF condensation, which increases molecular chain entanglement. This is also confirmed by the increase in methylene and methylene ether bridges from Figure 4.44. The average fiber diameter increases from 2.83 to 4.67 µm when the aging time of RF gel is increased. This is probably due to the greater resistance of the RF gel to be stretched by the charges on the jet. At the aging time is prolonged, the apparent viscosity of the RF gel is increases, as seen in Figure 4.45.

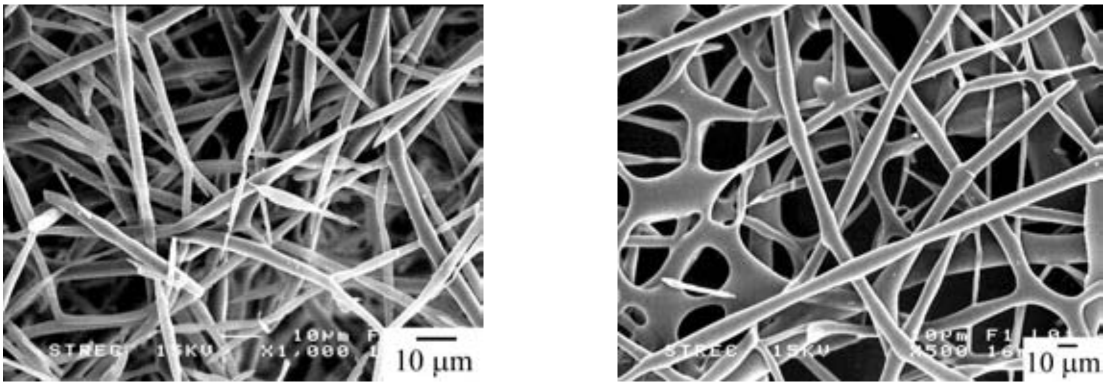
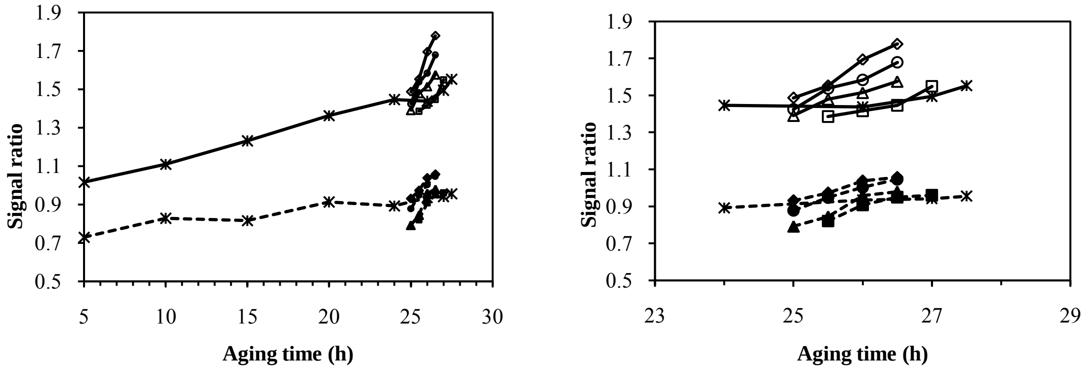


Figure 4.43: SEM images of products obtained from electrospinning of RF gel aged under the atmosphere of 8% RH for 26 h (a) and 26.5 h (b).

The RF gel has been firstly aged in several of time in ambient atmosphere before being aged in 8% RH atmosphere have affect on rate of the RF condensation and molecular chain entanglement. As seen in Figure 4.44, the RF gel has been firstly aged for 10 and 15 h in ambient atmosphere have slow rate of the RF condensation and less amount of molecular chain entanglement (as seen in signals ratio). And in the second step (being aged in 8% RH atmosphere), the RF gel has been firstly aged for 10 h have rate of the RF condensation faster than the RF gel has been firstly aged for 15 h and chain entanglement are much more than the RF gel has been firstly aged for 15 h, as seen in signals ratio of the RF gel aged for the total period of 25-26.5 h. The RF gel has been firstly aged for 20 h in ambient atmosphere have high cross-link network (Figure 4.44). So in the second step, rate of RF condensation are slow that make chain entanglement increases a little. It should be note that, the gel formation and the obtained product are different.



(a) (b)

Figure 4.44: Relationship of FTIR signals ratio of methylene and methylene ether bridge (blank points) comparing to that of aromatic rings in RF gel aged in 2-step fashion, i.e. in ambient and in 8% RH atmosphere respectively, with respect to the total aging time of the RF gel. The aging time in the first step is varied from 0h (◆), 10 h (●), 15 h (▲) and 20 h (■). And (✱) FTIR signals ratio of RF gel in ambient atmosphere (a) and the relationship of FTIR and aging time at 24 - 27.5 h are plot for the clarity (b).

An increasing in the RF gel has been firstly aged in several of time in ambient atmosphere before being aged in 8% RH atmosphere, the gelation process and apparent viscosity are decreases, as seen in Figure 4.45. And suitable solution viscosity for the electrospining was in the range of 1300-4000 cP.

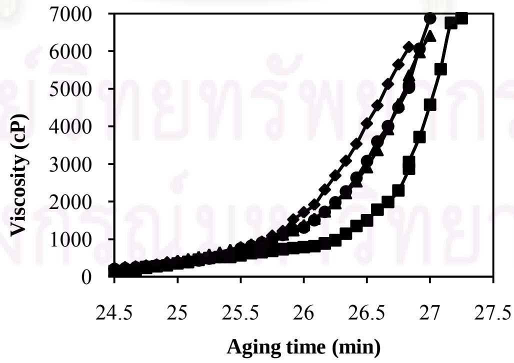
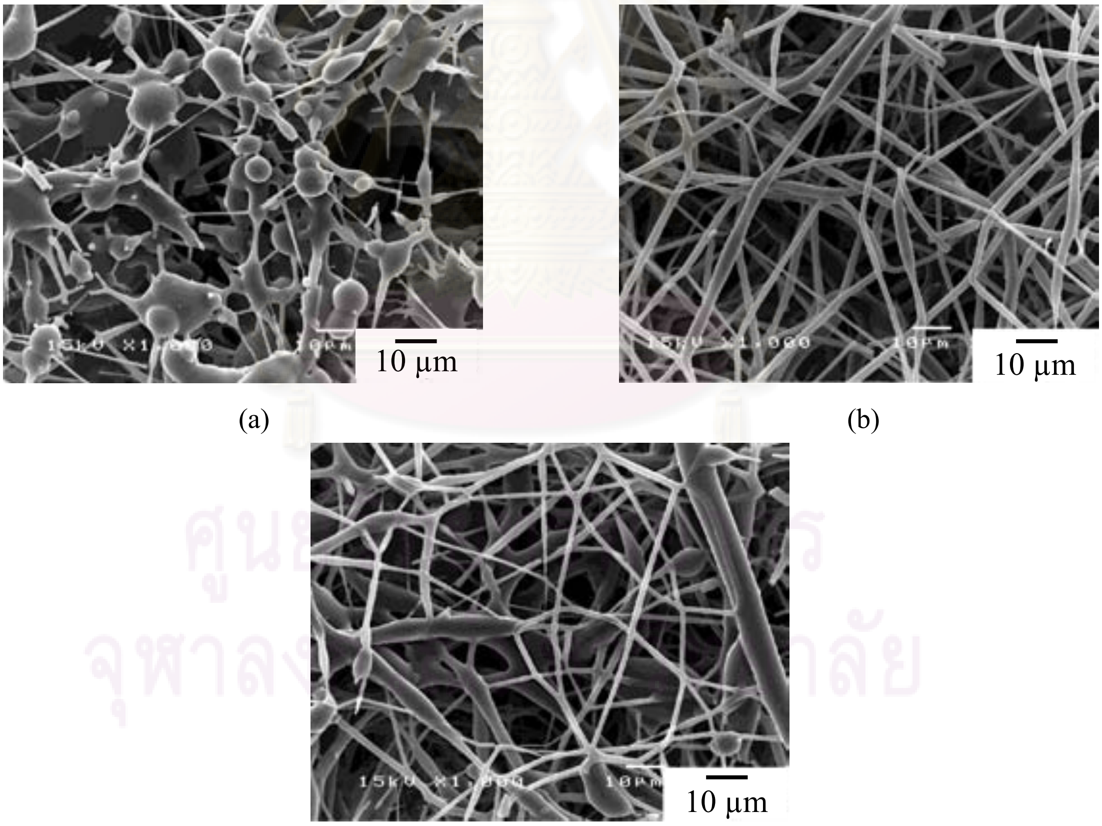


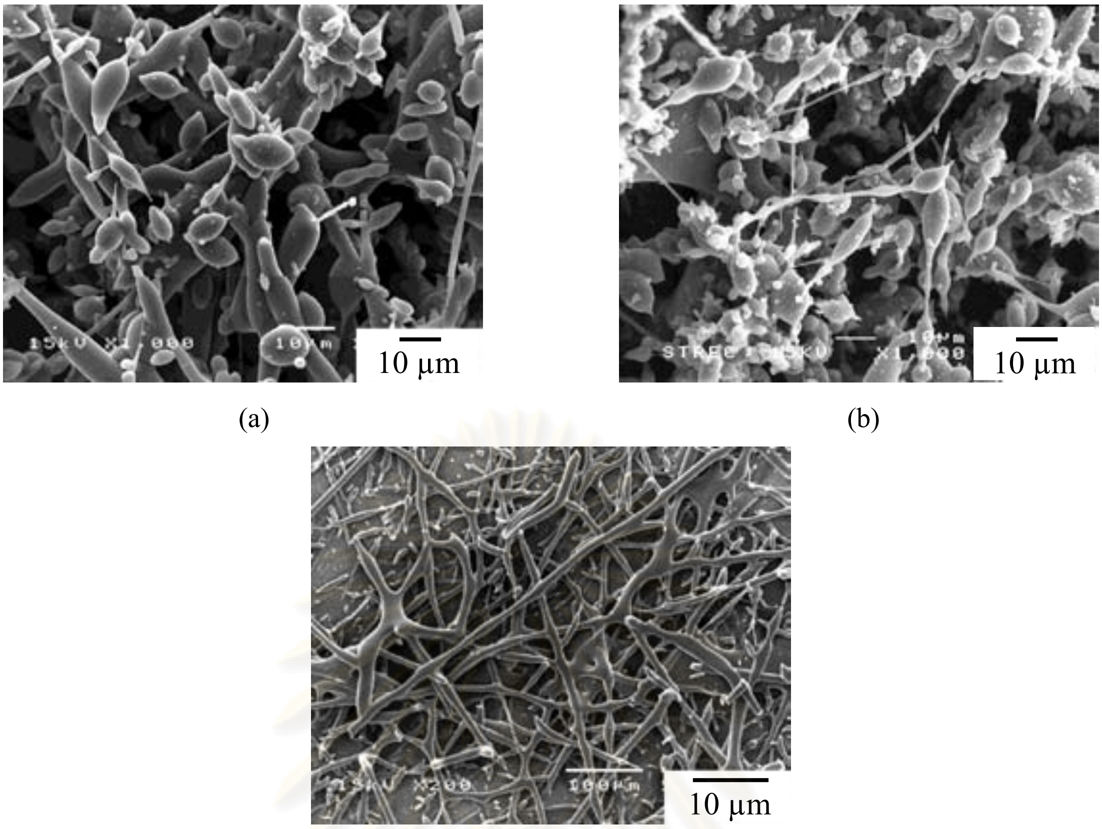
Figure 4.45: Apparent viscosity of RF gel aged in 2-step fashion, i.e. in ambient and in 8% RH atmosphere respectively, with respect to the total aging time of the RF gel. The aging time in the first step is varied from 0h (◆), 10 h (●), 15 h (▲) and 20h (■).

Figure 4.46 shows the electrospinning product from RF gel that has been firstly aged for 10 h in ambient atmosphere before being aged in 8% RH atmosphere environment. At the aging time in 8% RH is increased, the morphology of the product changes from beads on the strings to well-formed micro-fibers and the average fibers diameter increase from 2.03 to 2.16 μm. When the time for the first step of aging is changed to 15 h, the products from the gel aged for the total period of 26 h and 26.5 h are elongated particles. Non-uniform fibers are finally obtained when the total aging time is prolonged to 27 h, as seen in figure 4.47. Finally, for the RF gel aged for 20 h in ambient atmosphere before further aging in 8% RH, the obtained products are spherical droplets mixed with elongated particles, as show in Figure 4.48. In general, as the cross-linking of the RF network increases, the fraction of beads in the product decreases. This is due to the increased degree of chain entanglement, which is necessary to form continuous fibers. The increased bridging with the increase in aging time of RF gel is confirmed by FTIR signals summarized in Figure 4.44.



(a) (b) (c)

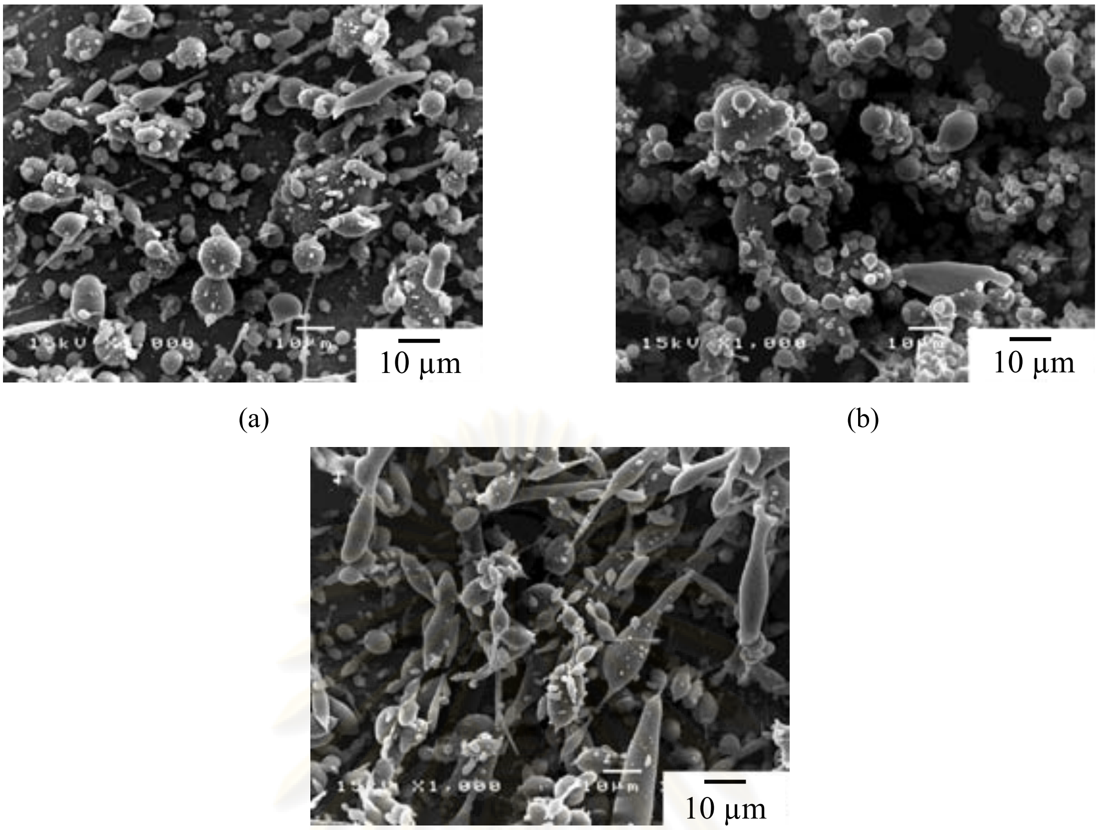
Figure 4.46: SEM images of products obtained from electrospinning of RF gel aged in 2 steps. The first step is 10 h aging in ambient atmosphere, while the second step is aging in 8% RH. The total time of aging is 25.5 h (a), 26 h (b), and 26 h (c).



(a) (b)

(c)

Figure 4.47: SEM images of products obtained from electrospinning of RF gel aged in 2 steps. The first step is 15 h aging in ambient atmosphere, while the second step is aging in 8% RH. The total time of aging is 25.5 h (a), 26 h (b), and 26 h (c).



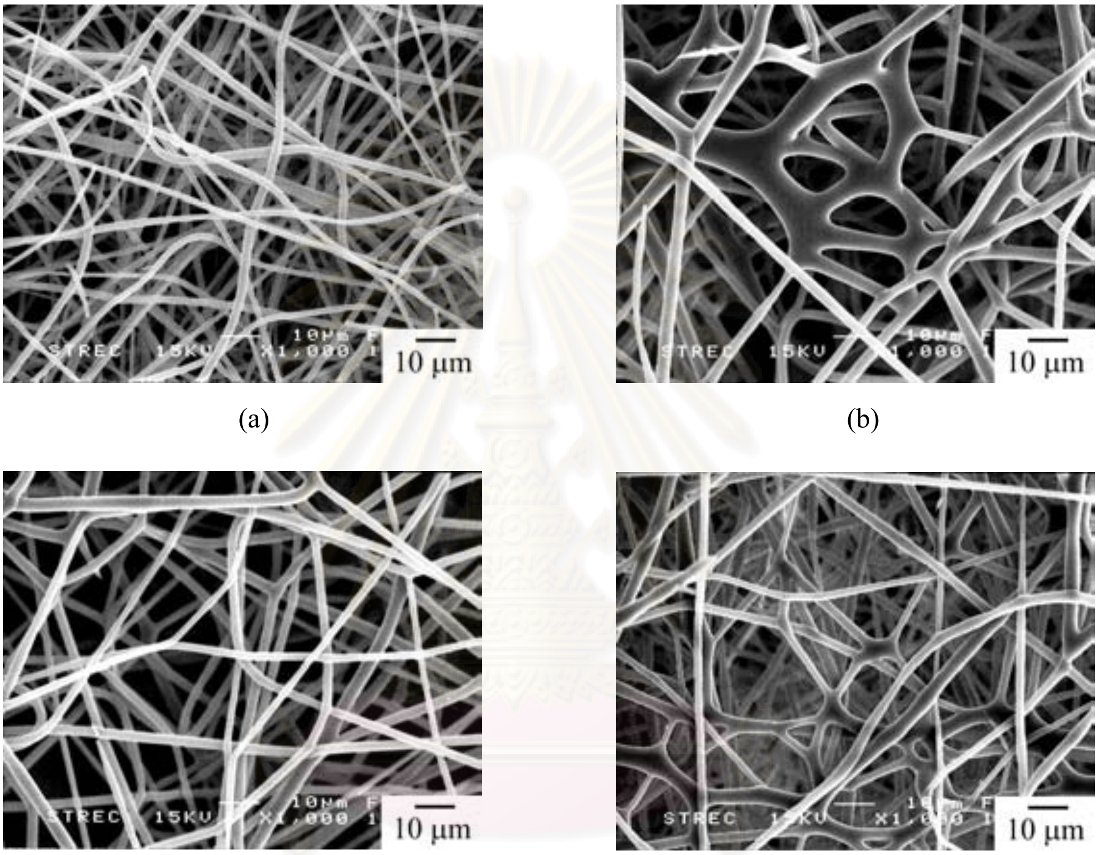
(a) (b)

(c)

Figure 4.48: SEM images of products obtained from electrospinning of RF gel aged in 2 steps. The first step is 10 h aging in ambient atmosphere, while the second step is aging in 8% RH. The total time of aging is 25.5 h (a), 26 h (b), and 26 h (c).

As shown in Figure 4.49, products from electrospinning of RF gel that is formed by using various values of R/F, R/C and R/W molar ratio and aged in the aging chamber 8% RH are all well-formed micro-fibers. Micro-fibers are formed because the chain entanglement of the RF gel in every condition is greater than that of RF gel aged under ambient condition. Figure 4.50 compares frequency distribution of fiber diameters of RF products prepared by using R/F ratio of 1.0 (R/C ratio of 86.64 and R/W ratio 0.15) and R/C ratio of 2000 (R/F ratio of 0.5 and R/W ratio of 0.15). In both case, the average fiber diameter increases with the increase in aging time of RF gel. For the R/F ratio of 1.0, the average fiber diameter increased from 1.75 to 2.64 µm, whereas for the R/C ratio of 2000, the average fiber diameter increases from 2.10 to 2.61 µm. The

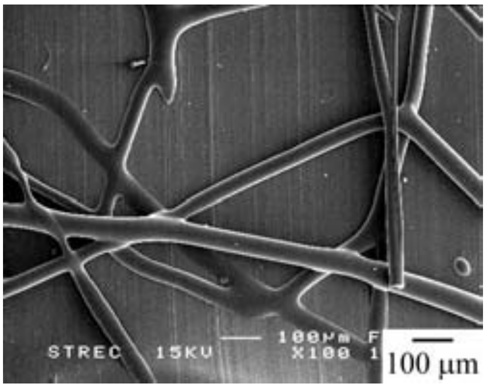
R/W molar ratio of 1.5 have less amount of water, when the RF gel being aged in 8% RH atmosphere environment , rate of RF condensation and molecular chain entanglement are increases extremely (as seen in signals ratio in Figure 4.51) and take the gelation time decreases (as seen in Figure 4.51). From the high chain entanglement, and due to the greater resistance of the RF gel to be stretched by the charges on the jet [46], it make diameter of fiber bigger than R/W ratio 1.5 aged in ambient condition (Figure 4.49). The average fiber diameter is 40.03 μm. The apparent viscosity of RF gel was shown in Figure 4.51. Suitable solution viscosity for the electrospining to produce micro-fibers was in the range of 1200-4000 cP.



(a) (b)

(c) (d)

Figure 4.49: SEM images of products obtained from electrospinning of RF gel aged under the atmosphere of 8% RH. The RF gel was prepared using different conditions: (a) R/F molar ratio of 1.0 aging time of 24 h, (b) R/F molar ratio of 1.0 aging time of 24.5 h, (c) R/C molar ratio of 2000 aging time of 30.5 h, (d) R/C molar ratio of 2000 aging time of 31 h, (e) R/W molar ratio of 1.5 aging time of 19 h.



(e)

Figure 4.49: (continued)

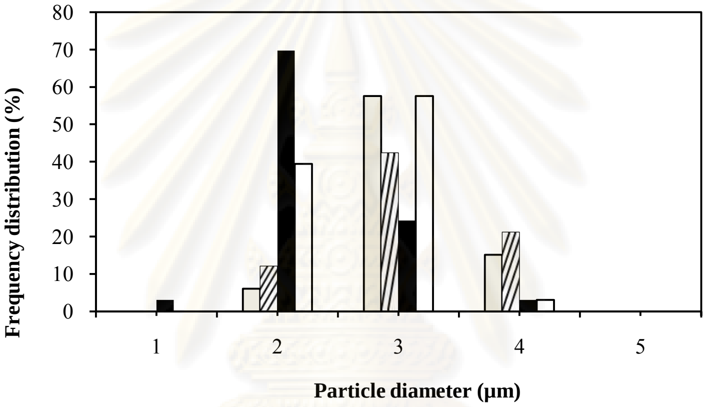


Figure 4.50: Frequency distributions of fiber diameters of the product electrospun from RF gel aged in the aging under the atmosphere of 8% RH. The RF gel was prepared using different conditions: (■) R/F molar ratio of 1.0 aging time of 24 h, (▣) R/F molar ratio of 1.0 aging time of 24.5 h, (□) R/C molar ratio of 2000 aging time of 30.5 h and (▣) R/C molar ratio of 2000 aging time of 31 h.

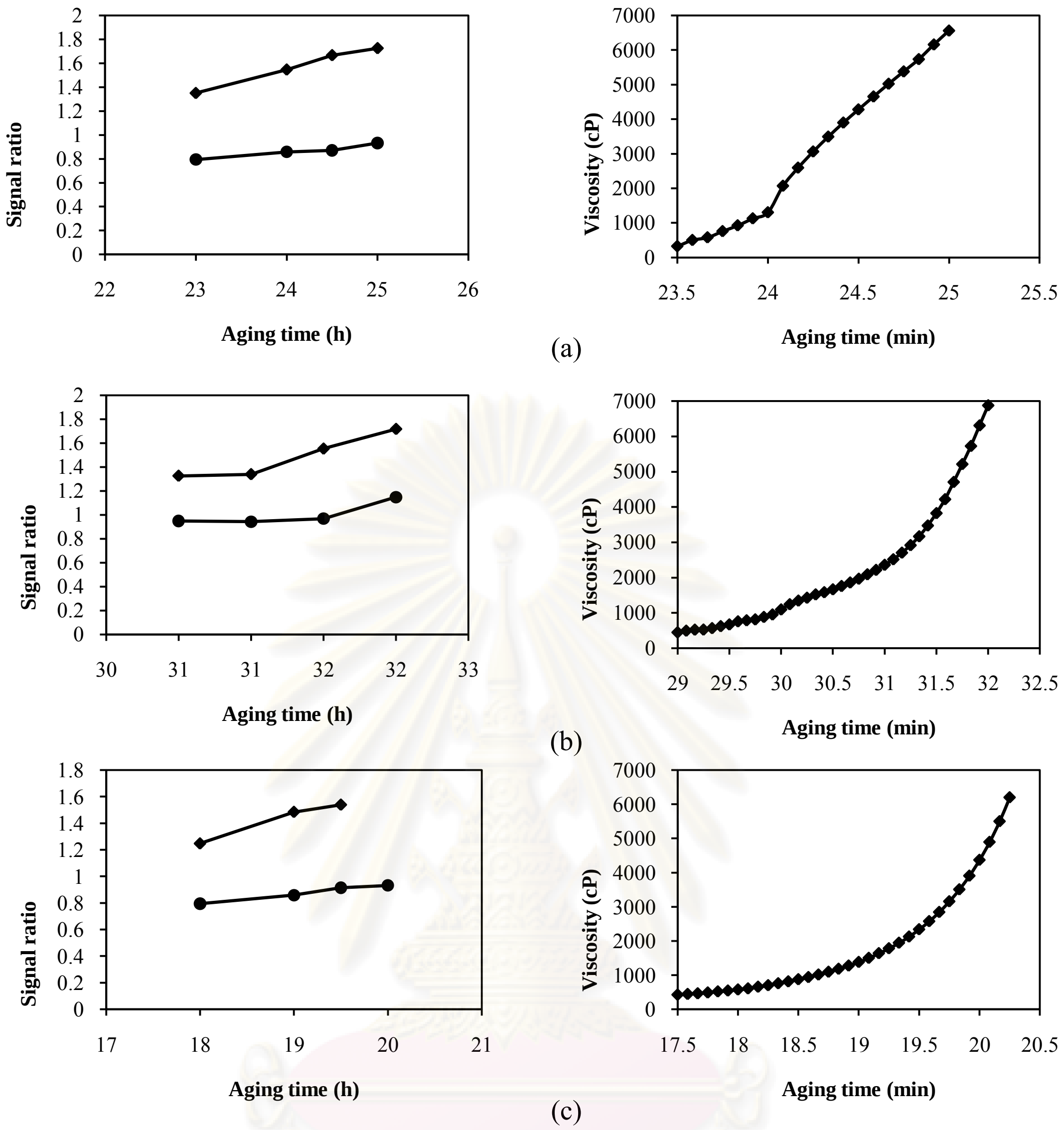


Figure 4.51: Apparent viscosity of RF gel and relationship of FTIR signals of methylene (◆) and methylene ether bridge (●) comparing to that of aromatic rings in RF gel aged in 8% RH, with respect to aging time. The RF gel was prepared using different condition: R/F ratio of 1.0 (a), R/C ratio of 2000 (b) and R/W ratio of 1.5 (c).

4.4 Pyrolysis of the RF-Products

The products obtained from electrospinning of RF gel were subjected to freeze drying. After drying, the RF product were pyrolyzed to form carbon particles and to form carbon fibers. For this section RF gel was prepared using various values of R/F, R/C and R/W as listed in Table 4.2. Adsorption and desorption isotherms of N_2 on adsorption the RF products are shown in Figure 4.52.

Table 4.2 Preparation conditions for RF gel to be pyrolysis.

Sample	R/F	R/C	R/W	Aging condition	Aging time (h)	Morphology
A1	0.5	86.64	0.15	Ambient	26	Not-spun
A2	0.5	86.64	0.15	Ambient	26	spherical
A3	0.5	86.64	1.5	Ambient	27	fiber
B1	0.5	86.64	0.15	8% RH	26	fiber
B2	0.5	2000	0.15	8% RH	30.5	fiber
B3	1	86.64	0.15	8% RH	24	fiber

Table 4.3 shows the change of S_{BET} (BET surface area, m^2g^{-1}) and V_{mes} mesopore volume, cm^3g^{-1}) of the carbon particles and carbon fibers prepared with various values of R/F, R/C, R/W and aging conditions. Sample B1 and B2, S_{BET} and V_{mes} are much more than S_{mic} (surface area of micropores, m^2g^{-1}) and V_{mic} (micropore volume, cm^3g^{-1}) so that carbon particles and carbon fibers are mesoporous structure (as seen in table 4.3). Other sample has microporous structure mix with mesoporous structure.

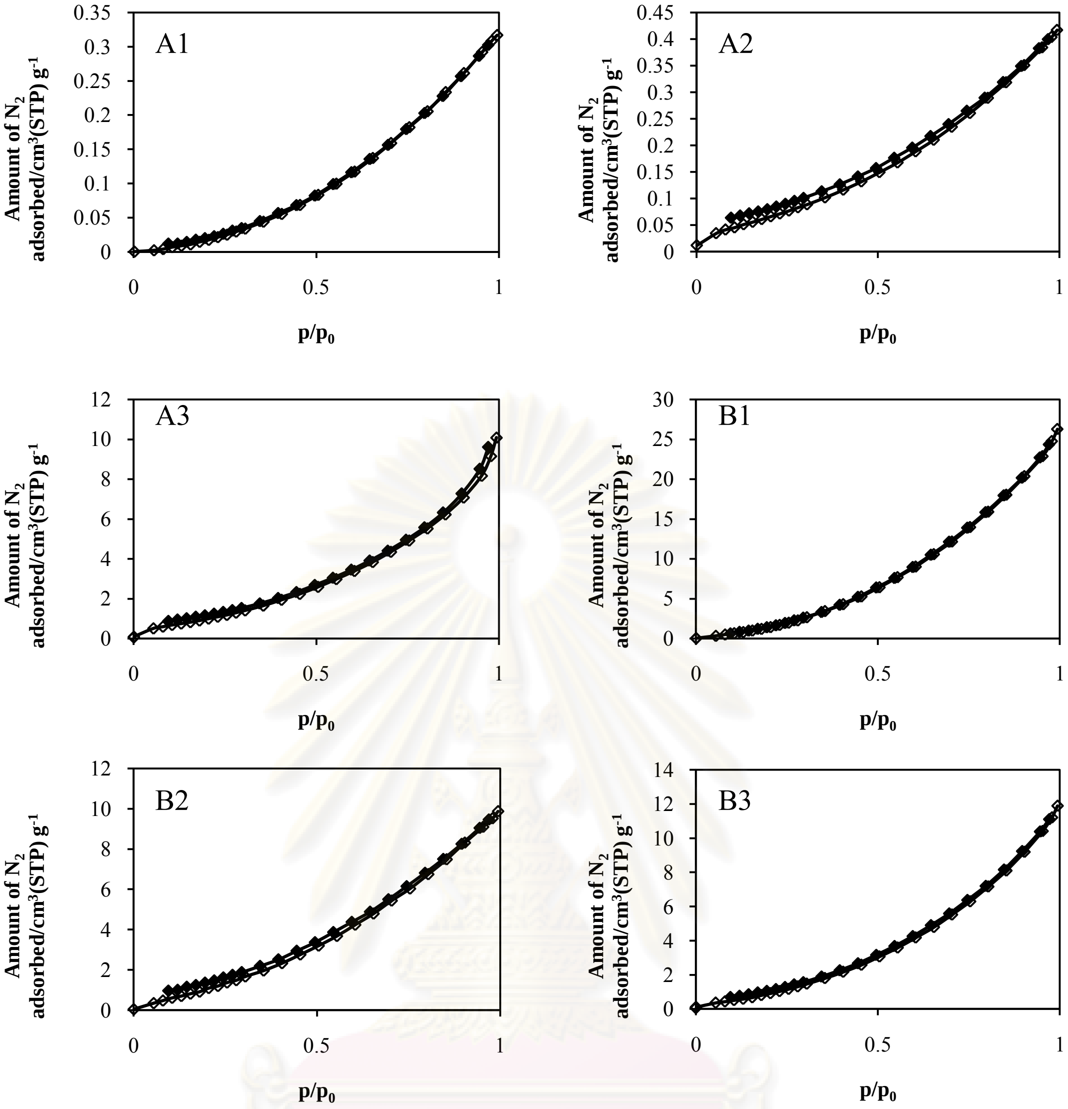


Figure 4.52: Adsorption isotherm and desorption isotherms of carbon particles and carbon fibers: adsorption (◇), desorption (◆).

Table 4.3 Physical properties of carbon particles and carbon fibers.

Sample	S_{BET} (m^2 g^{-1})	S_{mic} (m^2 g^{-1})	V_{meso} (cm^3 g^{-1})	V_{mic} (cm^3 g^{-1})
A1	0.362	0.352	6.905×10^{-4}	9.649×10^{-5}
A2	0.686	0.352	5.969×10^{-4}	3.423×10^{-5}
A3	6.504	8.580	1.718×10^{-2}	9.649×10^{-5}
B1	39.63	25.76	4.907×10^{-2}	1.191×10^{-3}
B2	9.401	8.893	1.756×10^{-2}	1.524×10^{-3}
B3	10.49	11.34	2.135×10^{-2}	2.735×10^{-4}

S_{BET} and V_{mes} of the product that was not spun (A1) is much smaller than the obtained product from electrospinning. Figure 4.53 confirms that during the process of electrospinning, the solvent in the RF gel was evaporated. Since evaporation of the solvent from sample A1 and A2 are less (as seen in Figure 4.54), the pores of the RF gel are filled with water. During the process of freezing prior to freeze drying, the volume of the water increases to some extent. Hence, there is a danger that the pore of RF gel are destroyed when the gels are frozen [47]. The surface area of the fiber product (A3) was found to be higher than that of the spherical particles (A2). This is suggested to be a result from high extent of cross-linking network within the gel that allows the formation of fiber, which also prevents collapses of pores during the pyrolysis.

Table 4.4 Sample weight loss from freeze drying and pyrolysis of the obtained product.

Sample	%weight loss from freeze drying	%weight loss from pyrolysis
A1	48.26	31.38
A2	7.56	47.24
A3	14.87	48.66
B1	25.49	69.28
B2	18.90	50.67
B3	20.34	57.77

The product aged under 8% RH (B1, B2 and B3) has higher surface area than the product aged under ambient condition because the product aged under 8% RH has high cross-linked structure so that more of the remaining of hydrogen, oxide and some part of carbon can be removed from the product than that from the oneaged under ambient condition. Sample B1 has the highest weight loss by pyrolysis that increases the pore volume of fiber and results in the highest surface area.

Sample B1 has higher surface area than sample B2, because the condition with low catalyst (B2) yields large colloidal RF gel that are interconnected with narrow necks in a "string of pearls" that results in low amount of volume of pore [48]. Sample B1 has higher surface area than sample B3 because sample B3 contains low cross-linking network and the remaining resorcinol induces the collapse of pore structure. The solvent in the RF gel evaporates continuously and it is confirmed that the solvent in the RF gel also evaporates during the process of electrospinning (as seen in Figure 4.53).

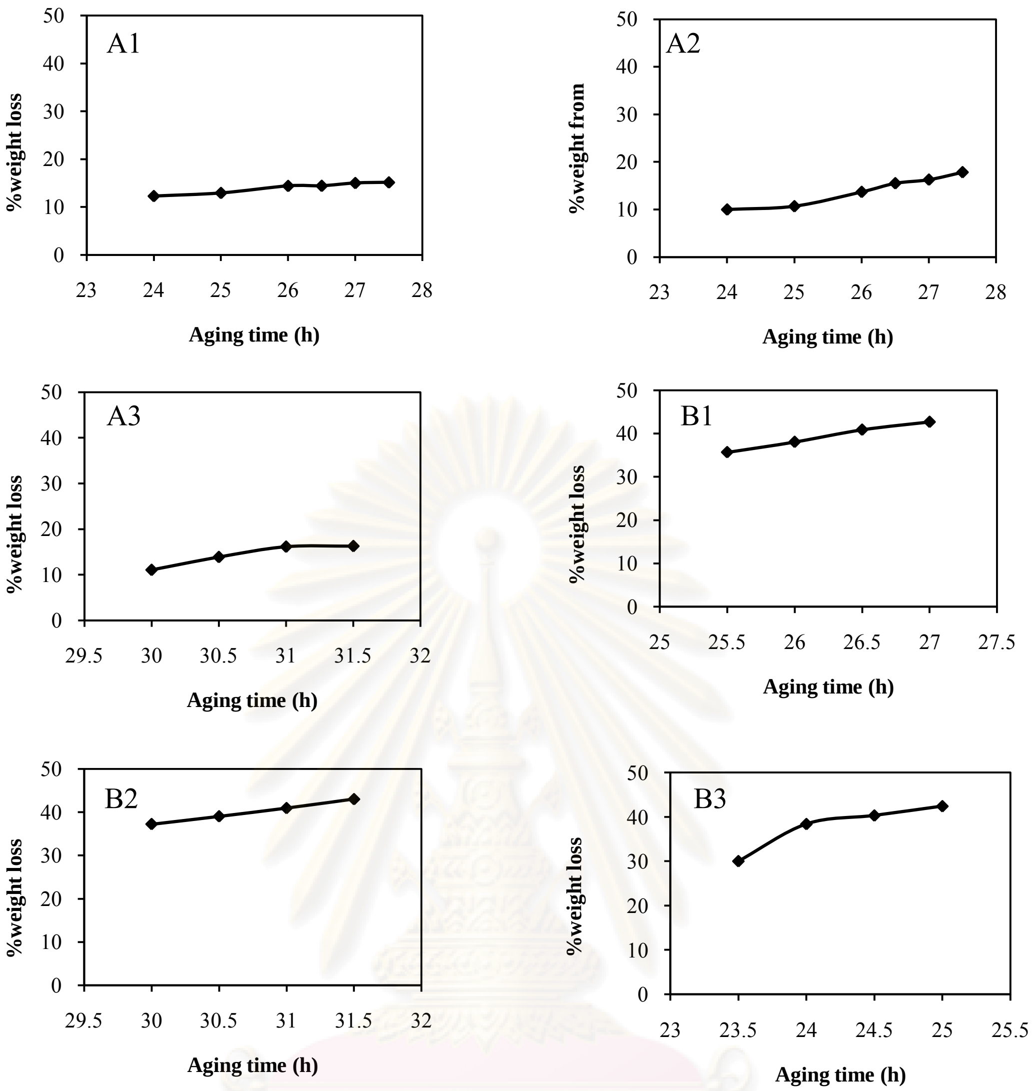
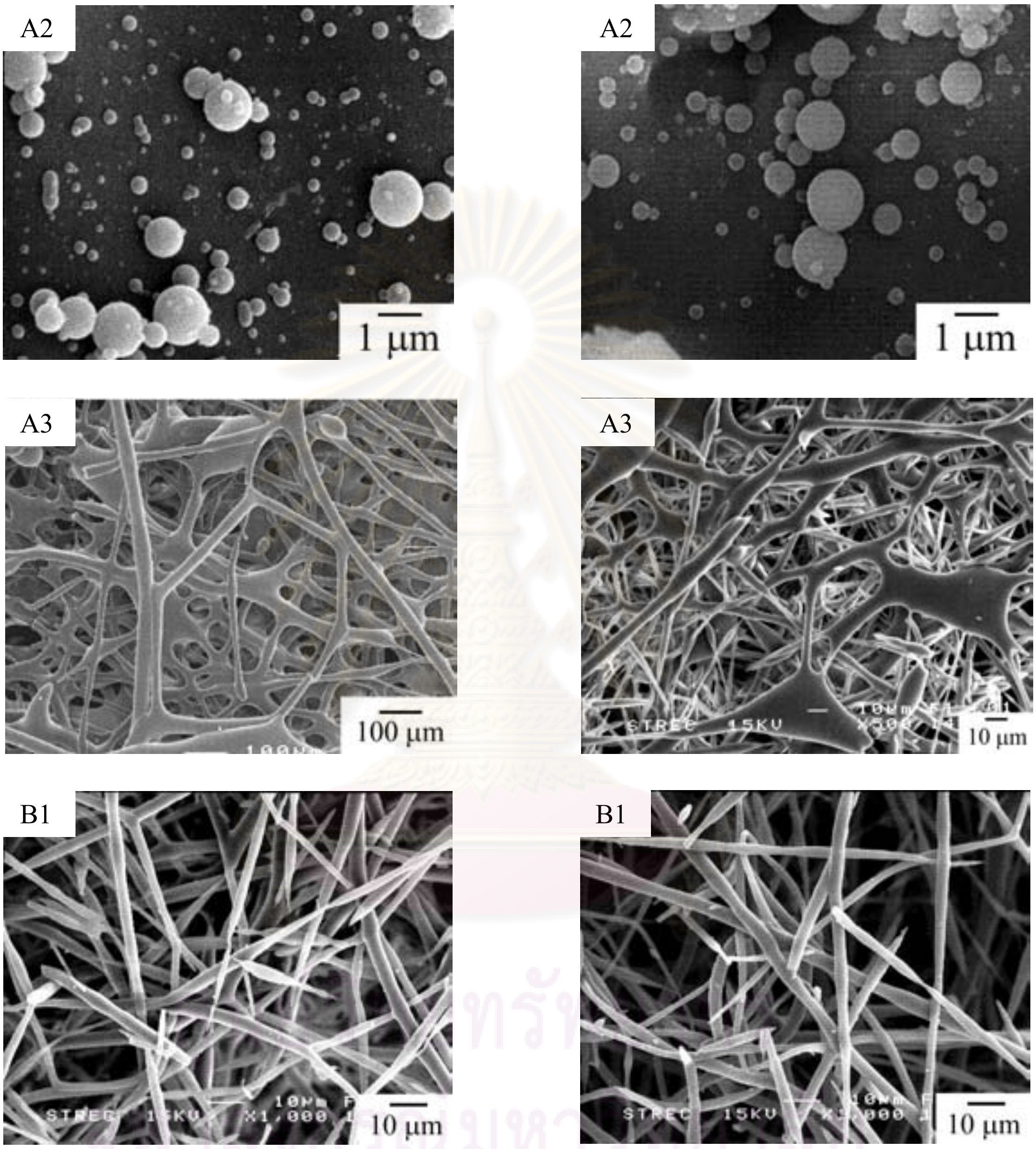


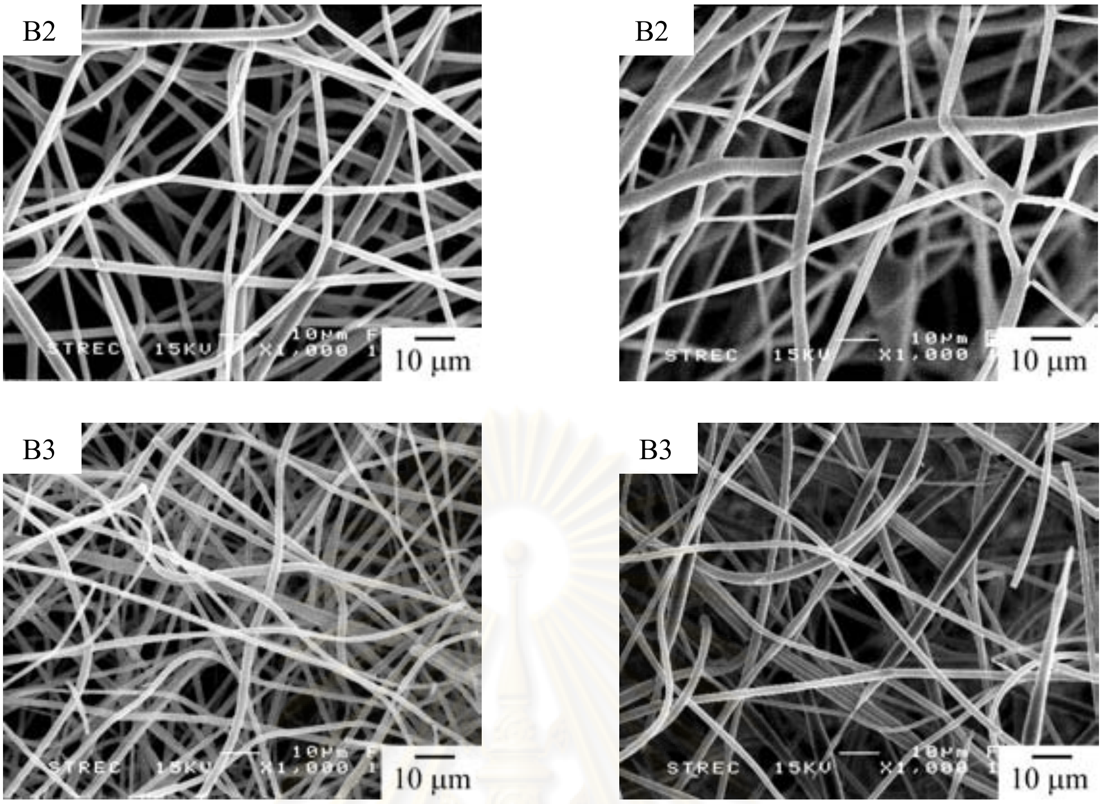
Figure 4.53: Percentage of weight loss during evaporation of solvent during aging under ambient atmosphere and under 8% RH.

Morphology of carbon particles and carbon fibers are not different from morphology of RF particles before pyrolyzed, as seen in Figure 4.54.



(a) (b)

Figure 4.54: SEM images of morphology of carbon particles and carbon fibers: before pyrolysis (a) and after pyrolysis (b).



(a) (b)

Figure 4.54: (continued)

4.5 Addition of Aluminium Precursor into RF Gel.

In this section, the effect of the addition of aluminium precursor was investigated. RF gels were prepared using R/F, R/W, R/C and C/W ratio of 0.5, 0.15, 86.64 and 10.0, respectively. The gels were aged for predetermined period of time before being added with aluminium precursor.

When aluminium acetylacetonate, which is used as a precursor for aluminium, is added into RF gel, interaction occurs, as witnessed from the rapid increase in viscosity and the change in color of the mixture. It is suggested that aluminium acetylacetonate formed bonds with the RF network that could accelerate the cross-linking process. The aluminium-doped gel was immediately electrospinning afterward. The products are shown in Figure 4.55. It can be seen that majority of the products merge together into either large structure or a film. The results suggest that water was trapped and the evaporation of water was too low such that the products deposited on the collection had a chance to merge together [22]. The obtained product could not be calcined to form alumina, because the period in which the gel was electrospinable was very short. The amount of sample obtained was very small.

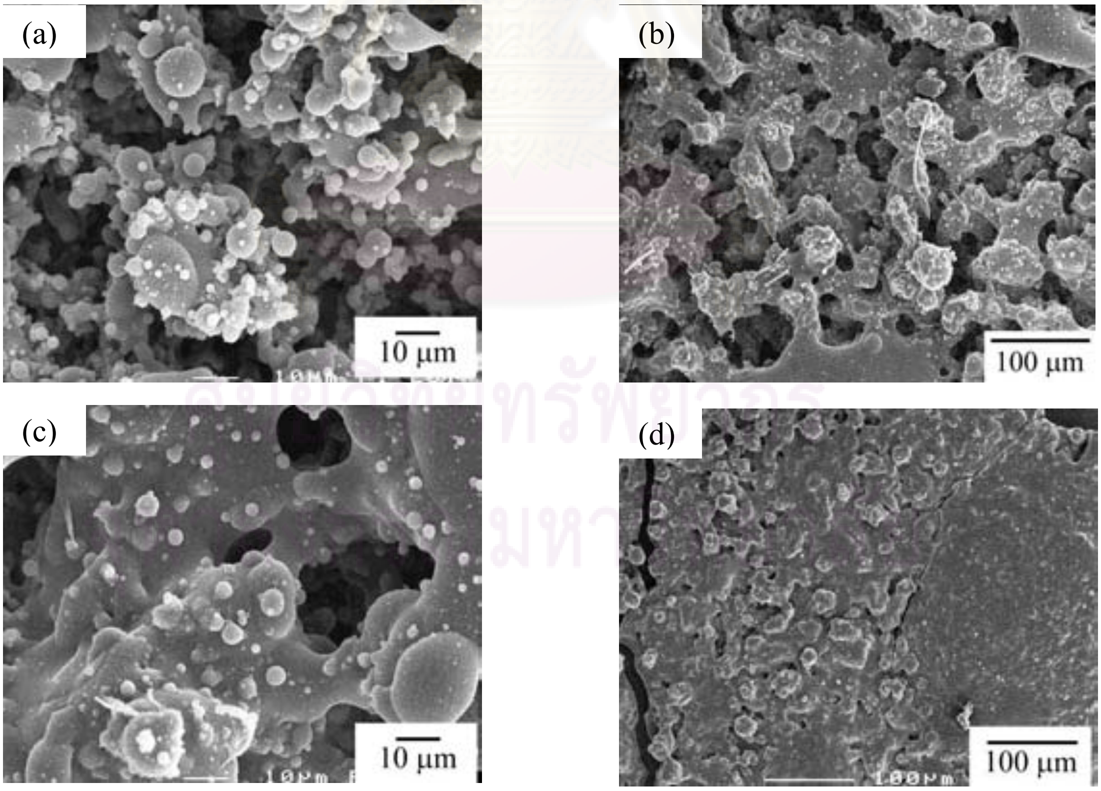


Figure 4.55: SEM images of collected particles electrosprayed from RF gel that was prepared and aged for 19 (a), 21 h (b), 22 h (c) and 24 h (d) before being added with aluminium acetylacetonate.

Upon the addition of aluminium precursor into the RF-gel, however, the mixture became highly viscous and rapidly turned into a solid, as shown in Figure 4.56, in which the blank markers indicate the gel before the addition of aluminium precursor and the solid markers represent viscosity of the gel after the addition. This behavior suggests that the aluminium precursor aided the condensation as well as the cross-linking process of the sol. Suitable viscosity of aluminium-doped RF gel solution for the electrospining is in the range of 600-1200 cP.

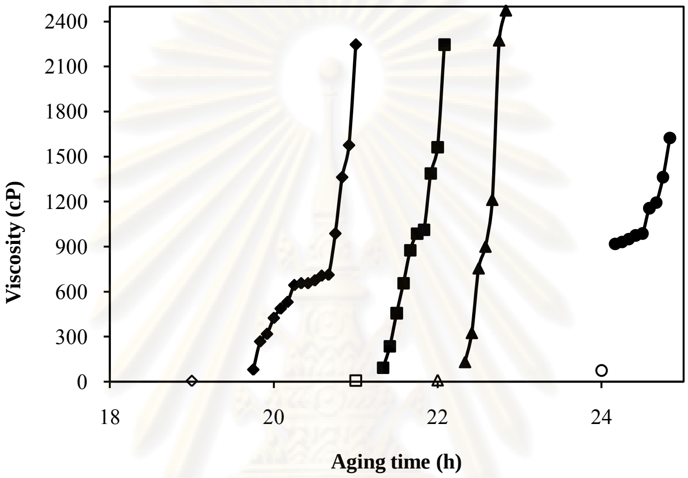


Figure 4.56: Apparent viscosity of RF gel that was prepared and aged for 19 h (◇), 21 h (□), 24 h (△) and 27 h (○) before being added with aluminium acetylacetonate. The solid markers represent the gel after the addition.

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

1. The conclusions of the present research are the following:
2. RF gel can be used as a precursor for synthesis of mesoporous structures of carbon fibers and carbon nanospheres by electrospinning techniques.
3. Morphology and size distribution of RF fibers and RF particles can be controlled by controlling aging time of RF gel and preparation condition for RF gel.
4. Changing in the processing parameters, such as applied electric field strength, applied voltage and distance between tip and collector has effect on the size and morphology of RF particles.
5. Fiber are formed when the RF gel has high cross-link network and the RF gel has suitable viscosity.

5.2 Recommendations for the Future Studies

In this study effects of various processing parameters, such as applied electrical field strength, working distance, applied voltage, as well as the preparation condition for RF gel, such as composition, aging time and addition of aluminium precursor, i.e., aluminium acetylacetonate into the RF-gel by electrospinning method were investigated. Some recommendations for future work are listed as follows:

1. Effect of the other metal alkoxide precursors in spinning solution on physical and chemical properties of the RF gel fibers should be investigated.
2. Although it is found that carbon micro-fiber were form under aging RF in 8%-relative humidity (RH), the effects of various processing parameters to reduce the averaged diameter of carbon fiber should be investigated.
3. Physical properties, i.e., tensile strength, modulus of carbon fibers should be investigated.
4. Effect of humidity of the electrospinning environment should be investigated.
5. Doping of-aluminium into the RF gel should be done together with a means to retard condensation process before taken it to be spun.

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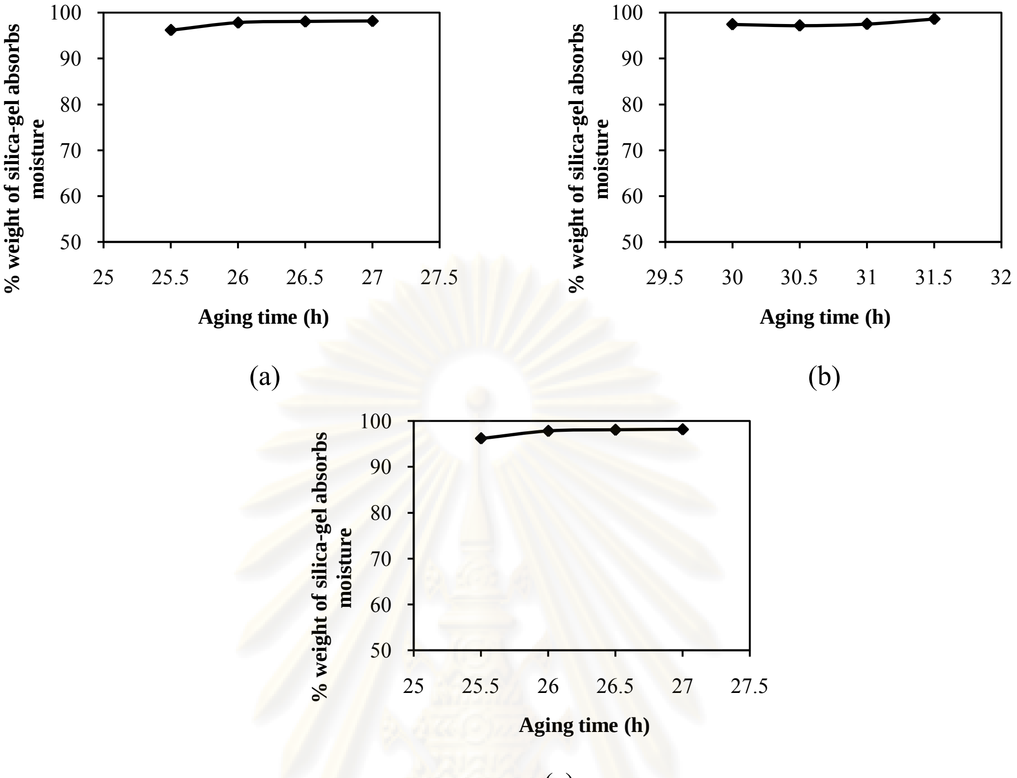
APPENDIX

EFFECT OF SILICA-GEL TO MOISTURE CONTENT



(a) (b)

(c)

Figure A.1: Percentage of weight of silica-gel absorbing moisture from RF gel aged under the atmosphere of 8% RH. The RF gel was prepared using different conditions: (a) R/F ratio 0.5, (b) R/C ratio 2000 and (c) R/F ratio 1.0.

VITA

Miss Panitnart Ubollers was born on October 1st, 1985 in Mahasarakham Province, Thailand. She received the Bachelor's Degree of Engineering with major in Chemical Engineering from Thammasat University, Bangkok, Thailand in March 2009. She entered the master of Engineering in Chemical Engineering at Chulalongkorn University, Bangkok, Thailand in May 2011.

LIST OF PUBLICATIONS

1. Panitnart Ubollers , Pitt Supaphol and Varong Pavarajarn. "Electrospraying of Neat and Aluminium-Doped Resorcinol/Formaldehyde Gel". The 17th Regional Symposium on Chemical Engineering, Bangkok, Thailand, November 22-23, 2010, p.241.

2. Panitnart Ubollers , Pitt Supaphol and Varong Pavarajarn. "Fabrication of Fibers of Resorcinol/Formaldehyde Gel by Electrospinning toward the Formation of Mesoporous Carbon Fibers". The 7th Asian aerosol conference, Xi-an, China, August 17-20, 2011.