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.

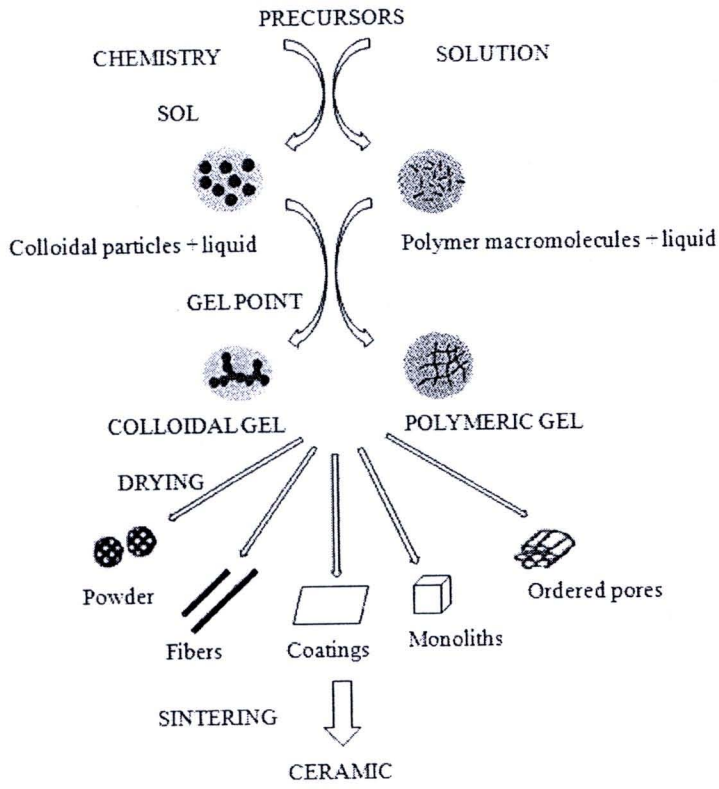

Figure 2.2: Simplified chart of sol-gel process.

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:

$$\text{Hydrolysis: } \text{M-O-R} + \text{H}_2\text{O} \longrightarrow \text{M-OH} + \text{R-OH}$$

$$\text{Water condensation: } \text{M-OH} + \text{HO-M} \longrightarrow \text{M-O-M} + \text{H}_2\text{O}$$

$$\text{Alcohol condensation: } \text{M-O-R} + \text{HO-M} \longrightarrow \text{M-O-M} + \text{R-OH}$$

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.

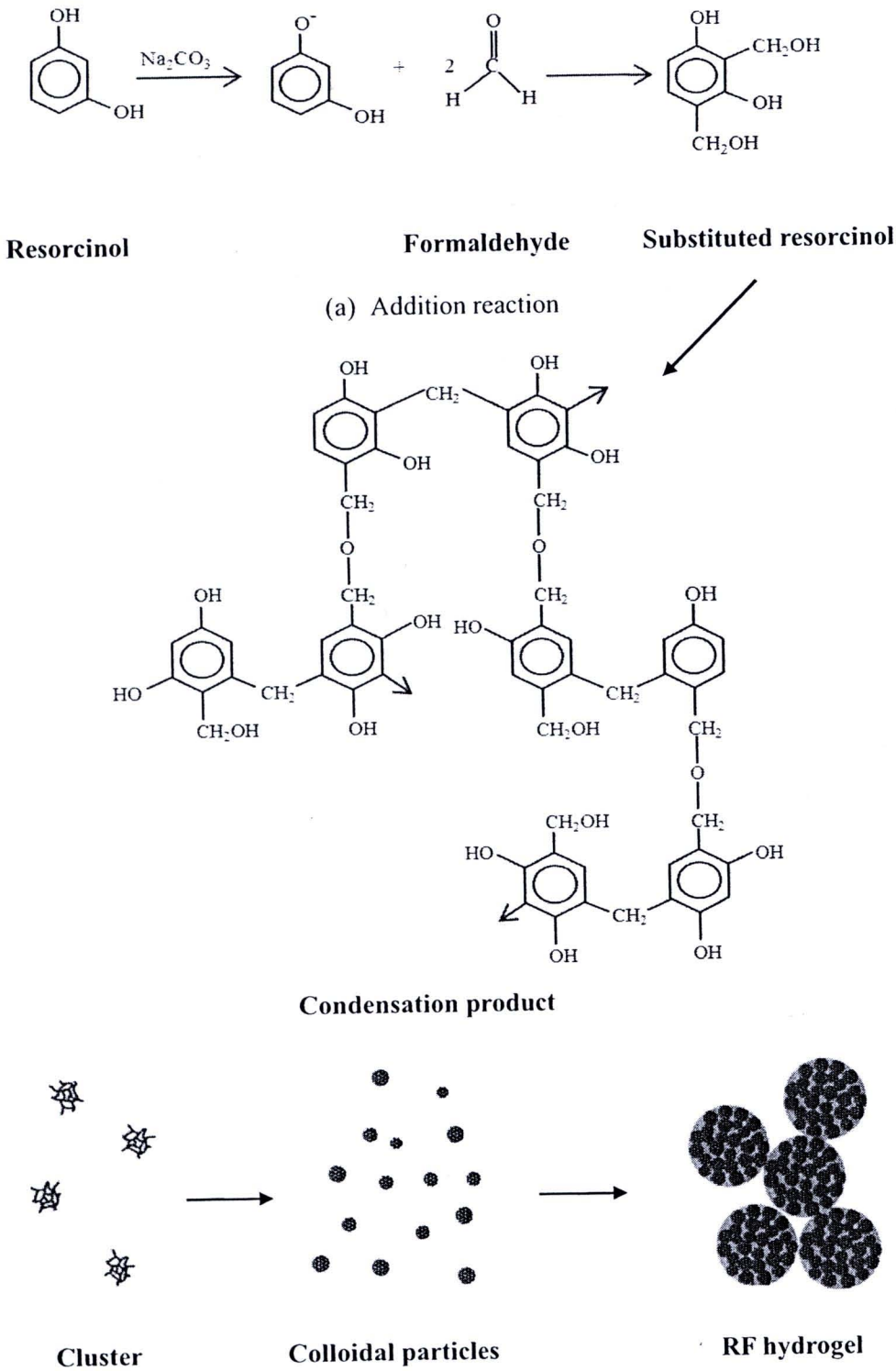

Figure 2.3: Schematic diagram of the sol-gel polycondensation of RF solution (a) addition reaction, (b) condensation reaction [12].

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.

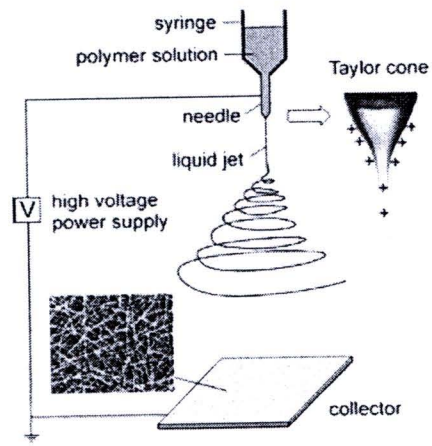

Figure 2.4: Schematic representation the electrospinning process.

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].