



Surface modification of E-glass fibers with radio frequency plasma polymerization and its effect on fatigue resistance of composites
by Dongrui Fang

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in
Chemical Engineering
Montana State University
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Abstract:

Today the steady increase in the consumption of reinforced composite materials indicates their value as competitive engineering materials, and they are successfully replacing more conventional materials in many applications. In the wind energy industry, glass fiber reinforced composite materials have been used to make wind turbine blades which require long service life under severe loading and unloading environments. Thus, the fatigue resistance of wind turbine blades is an important design consideration. In this study, a plasma reactor system was developed and plasma polymerization was used to modify the surface of E-glass fibers in an attempt to improve the fatigue resistance of composites.

An inductively coupled radio frequency glow discharge reactor was designed and constructed “in house” for the experiments. E-glass fiber strands and fabric cloth were used as the substrates. Ethylene and methane gases were used as the monomers. The effects of different reaction parameters, such as the discharge power, the reaction time, the gas flow rate and system pressures, were explored. The characteristics of plasma polymerized films were analyzed using x-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM). The mechanical properties of treated fiber strands and fabric cloth were tested by Jinhua Bian at Montana State University.

Plasma treatment of glass fibers is an effective method for modifying the fiber surface properties and allows for the most flexibility. The ethylene or methane plasma polymerized films on the glass fibers could not be washed off with acetone, and no degradation was observed after keeping the treated fibers in- the air for one week. For ethylene or methane plasma treated fiber strands and fabric, a better coating was obtained at higher discharge power and longer reaction time. However, the plasma deposition and plasma etching would reach an equilibrium state and no further plasma deposition could be observed after the equilibrium discharge power and reaction time level.

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RESISTANCE OF COMPOSITES

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APPROVAL

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This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style, and consistency, and is ready for submission to the College of Graduate Studies.

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ABSTRACT

Today the steady increase in the consumption of reinforced composite materials indicates their value as competitive engineering materials, and they are successfully replacing more conventional materials in many applications. In the wind energy industry, glass fiber reinforced composite materials have been used to make wind turbine blades which require long service life under severe loading and unloading environments. Thus, the fatigue resistance of wind turbine blades is an important design consideration. In this study, a plasma reactor system was developed and plasma polymerization was used to modify the surface of E-glass fibers in an attempt to improve the fatigue resistance of composites.

An inductively coupled radio frequency glow discharge reactor was designed and constructed "in house" for the experiments. E-glass fiber strands and fabric cloth were used as the substrates. Ethylene and methane gases were used as the monomers. The effects of different reaction parameters, such as the discharge power, the reaction time, the gas flow rate and system pressures, were explored. The characteristics of plasma polymerized films were analyzed using x-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM). The mechanical properties of treated fiber strands and fabric cloth were tested by Jinhua Bian at Montana State University.

Plasma treatment of glass fibers is an effective method for modifying the fiber surface properties and allows for the most flexibility. The ethylene or methane plasma polymerized films on the glass fibers could not be washed off with acetone, and no degradation was observed after keeping the treated fibers in the air for one week. For ethylene or methane plasma treated fiber strands and fabric, a better coating was obtained at higher discharge power and longer reaction time. However, the plasma deposition and plasma etching would reach an equilibrium state and no further plasma deposition could be observed after the equilibrium discharge power and reaction time level.

CHAPTER 1

INTRODUCTION

When an organic vapor is injected into a glow discharge of an inert gas or when a glow discharge of a pure organic vapor is created, the deposition of polymeric films onto an exposed surface is often observed. Polymer formation that occurs in such a process is generally referred to as plasma polymerization or glow discharge polymerization [1].

Although the recognition of thin film formation by plasma polymerization can be traced back to 1874, and of chemical reactions in electrical discharges to 1868, systematic investigation of plasma polymerization began only in the 1960s [2]. Once some of the advantageous features of plasma coating were recognized, much applied research on the use of the process was done.

Applications of plasma polymer films may conveniently be divided into two classes [3]. Firstly, alteration of the surface properties of a substrate may be the goal. An example of such applications includes modification of a polymer surface for the purpose of increasing (or decreasing) adhesion at the interface. Secondly, the

application may capitalize on the bulk properties of a thin, flawless, and /or highly adherent film. An example would be the use of the transport properties of such films as in membranes for gas separation or water purification.

Since the reactant gases are more reactive in the plasma state than the neutral state, plasma deposition can be carried out at much lower temperatures than those of chemical vapor deposition process. Plasma polymer films also have one or more of the following characteristics:

—Thin films can be easily formed with thicknesses of 500 Å to 1 μm .

—Flawless, uniform and highly crosslinked smooth films can be easily made by this process.

—Such films are often highly coherent and adherent to a variety of substrates including polymer, glass, and metal surfaces.

—Multilayer films or films with a gradation of chemical or physical characteristics are easily made by this process.

However, plasma polymerization process also has some disadvantages, such as, films are not always stoichiometric because of the complexity of the reaction and are often contaminated with by-products and incidental species. Films can be often deposited on the internal electrodes and the

walls of the reactor. The process can also create internal tensile and compressive stresses in the films.

Motivation and Objectives

Fiber reinforced composite materials are now an important class of engineering materials. They offer outstanding mechanical properties, unique flexibility in design capabilities, and ease of fabrication. Additional advantages include light weight, corrosion resistance, impact resistance, and excellent fatigue strength. In the wind energy industry, glass fiber reinforced composite materials have been used to make wind turbine blades utilizing their high strength to weight ratio and less expensive properties. The fatigue resistance of wind turbine blades is an important design consideration since these blades can experience as many as 10^8 to 10^9 significant fatigue loading cycles in their ten to thirty year lifetime [4]. In this research, a plasma reactor system was developed and plasma polymerization was used to modify the surface of E-glass fibers in an attempt to improve the fatigue resistance of composites.

Surface modification by plasma treatment has been employed to increase the adhesion and compatibility of dissimilar phases used in composites, but treatment to the surface of E-glass fibers to improve the fatigue resistance

has not been done previously and is studied in this research for the first time. Some published applications of plasma treatment include modification of the surface of polyamide fibers and weaves to increase adhesion to the epoxy matrix in a composite [5,6]. The adhesion of epoxy resins to films of polyethylene, poly(tetrafluoroethylene), and poly(vinyl chloride) has been improved by coating with acetylene plasma polymer [7]. It was found that plasma polymerization at low flow rates yielded the best results and that the plasma polymer coating led to both increased surface polarity and increased roughness.

Extensive research has been directed towards developing filament surface treatments to improve composite interfacial properties. The primary goal of those efforts has been to improve filament wettability, with chemical bond formation as a secondary objective. Filament wetting by the matrix resin is the essential first step in forming an interfacial bond. Good wetting is also required to attain the molecular level contact necessary to form chemical bonds. This approach was illustrated by the development of coupling agents for glass filaments [8] and oxidative surface treatments for graphite filaments [9,10,11]. Another method was used to improve the dry shear properties of the graphite epoxy composites by oxygen etching and polymerization with methylmethacrylate monomer [12].

The main purpose of this study is to develop a plasma treating system and use it to modify the surface of E-glass fiber strands and fabric cloth with plasma polymerization in an attempt to improve the fatigue resistance of composites. The different effects of plasma polymerization parameters (discharge power, reaction time, gas flow rate and system pressure) on the surface properties of coated fibers are studied. X-ray photoelectron spectroscopy and scanning electron microscopy are used to analyze the characteristics of thin films. The mechanical properties of treated glass fibers are tested by Jinhua Bian who is a graduate student at Montana State University.

CHAPTER 2

LITERATURE SURVEY

Glass Fibers

A great majority of materials are stronger and/or sometimes stiffer in the fibrous form than as a bulk material. A high fiber aspect ratio (length : diameter ratio) permits very effective transfer of load via matrix materials to the fibers, thus taking advantage of their excellent properties. Therefore, fibers are very effective and attractive reinforcement materials.

The most important reinforcement fiber is E-glass because of its relative low cost. However, boron, graphite, and the aramid polymer fibers are most exceptional because of their high stiffness value. The need for high-temperature reinforcing fibers has led to the development of ceramic fibers.

The first glass developed specifically for production of continuous fibers was a lime-alumina-borosilicate glass designed primarily for electrical applications [13]. Designated E glass, this glass was found adaptable and

highly effective in a great variety of processes and products ranging from decorative to structural applications and it has become known as the standard textile glass. By far the major portion of all continuous filament glass produced today is E glass.

E-glass fiber does not have a single composition but may vary in composition within the range given in Table 1 [13]. Changes within the indicated ranges do not significantly influence its electrical or mechanical properties.

Table 1. Compositions of E-glass Fibers

Material	Range (% by weight)
Silicon Oxide	52-56
Aluminum Oxide	12-16
Calcium Oxide	16-25
Magnesium Oxide	0-6
Boron Oxide	8-13
Sodium Oxide	0-3
Ferrous Oxide	0.05-0.4
Titanium Oxide	0-0.4
Miscellaneous	0-0.5

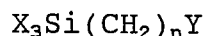
Silane Coupling Agents

The chemical treatments applied during the forming of glass fibers are called sizes [14]. These are of two general types: temporary sizes and compatible sizes (also called coupling agents).

The temporary sizes are applied to minimize the degradation of strength resulting from abrasion of fibers to one another and to bind the fibers together for easy handling in forming woven glass fiber products. These sizes must be removed and replaced by coupling agents before the fibers can be impregnated with resin.

The most common coupling agents are organofunctional silanes. The function of silane coupling agents is to provide a stable bond between two otherwise nonbonding surfaces and to reduce the destructive effects of water and other environmental forces on this bond. In reinforced and filled plastics, the improved bond between the fibrous or particulate inorganic component and the organic matrix polymer results in greater composite strength and longer service life.

Silane coupling agents are a family of organosilicon monomers which are characterized by the formula [14]:



where $n = 0-3$

Y = organofunctional group that is compatible with polymer matrix

X = hydrolyzable group on silicon converted to silanol group on hydrolysis.

The group Y may be very simple, for example chlorine, or may contain several chemical functional groups. The silanol functional group establishes hydrogen bonds with the glass

Plasma Polymerization

Glow discharge polymerization or plasma polymerization, like so many topics in science, is incompletely understood. It has its own sub-language of special terms, with names that are often misleading, and with meanings which can not be assumed to be constant from book to book. In some papers, plasma polymerization is used to describe a special kind of polymer formation mechanism in glow discharge, and glow discharge polymerization is used to refer to plasma polymerization in the wider meaning. In this study, no emphasis is put on the mechanism of glow discharge polymerization, so these two terms are used synonymously just like most applied scientists do, which plasma physicists may get into semantic discussions and arguments.

Another misleading terminology is "polymerization". Although the phenomenon of polymer formation in a glow discharge is referred to as glow discharge polymerization, the term of "polymerization" may not represent the actual process of forming a polymer. The conventional meaning of polymerization is that the molecular units (monomers) are linked together by the polymerization process. Therefore, the resultant polymer is conventionally named by "poly + (the monomer)". For instance, the polymer formed by the polymerization of ethylene is named polyethylene. In this

meaning, polymerization refers to molecular polymerization, i.e., the process of linking molecules of a monomer. In a strict sense, polymerization in the conventional context does not represent the process of polymer formation that occurs in a glow discharge which may be characterized as elemental or atomic polymerization, although molecular polymerization may play a role, depending on the chemical structure of a monomer and also on the conditions of the glow discharge [16].

In plasma deposition, reactive intermediates are formed in the gas phase which can result in the formation of non-volatile species that deposit on surfaces exposed to the plasma. Plasma deposition is a general term used to describe deposition of thin films from plasma sources; when dealing with organic species a term commonly used is plasma polymerization. Plasma polymerization can be carried out with a wide range of reactants including some which are not generally considered to be monomers, such as methane. This is possible due to the conversion of the initial reactant to polymer-forming intermediates in the discharge.

What Is a Plasma

A plasma is a partially ionized gas consisting of equal numbers of positive and negative particles, a variety of neutral species including atoms, molecules, free radicals,

and photons [17]. We can consider a simple plasma consisting of positive ions and negative electrons in a sea of neutral atoms as shown in Figure 1 [18]. Ion-electron pairs are continuously created by ionization and destroyed by recombination, and since these processes are always pairwise, the space occupied remains charge neutral. The electron impact process which leads to ionization is also likely to cause excitation and the subsequent relaxation of the atom leading to photon emission, which is another common feature of the plasma. For instance, an oxygen plasma appears a light blue to the eye.

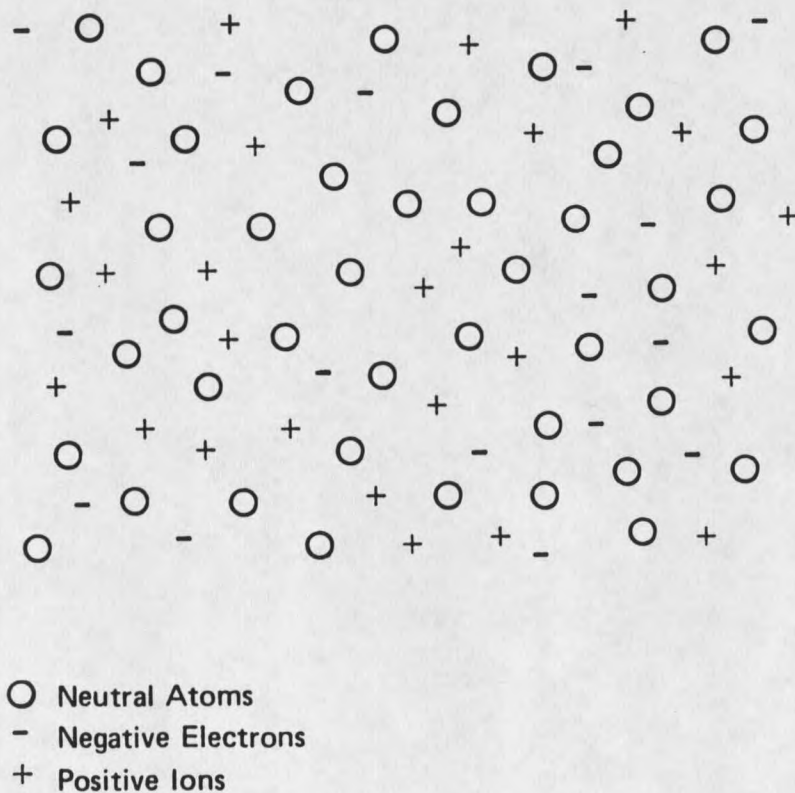


Figure 1. Illustration of plasma

The plasma is formed by exposing the gaseous monomer at low pressure to an electric field. Energy is transferred by the electric field to free electrons which collide with molecules, electrodes and other surfaces. Inelastic electron collisions with molecules generate more electrons as well as ions, free radicals, and molecules in excited states. Although the degree of ionization is low, typically about 10^{-5} - 10^{-7} , charged particles can play an important role in determining both the deposition rate and the chemical structure of the plasma polymer film. All fragments are very reactive with surfaces exposed to the plasma and with other fragments. Ion and neutral molecule temperatures remain near that of the reactor vessel ($<500^{\circ}\text{K}$), hence the designation of low-temperature plasma or cold plasma. Electrons, because of their high mobility, are rapidly accelerated by the applied field and have temperatures one to two orders of magnitude higher than the plasma gas molecules. The electron temperatures are usually over $20,000^{\circ}\text{K}$ [19].

The complexity of the chemistry which can take place in the glow discharge volume is increased when one considers the processes which may proceed at a surface above which a discharge is initiated and maintained. As such, plasma polymerization involves reactions between plasma species, between plasma and surface species and between surface species. Plasma-surface interactions are at least as important as interactions amongst plasma species in

determining the chemical and physical properties of a plasma polymer film. The general type of plasma-surface processes which may accompany exposure of a surface to fluxes of ions, reactive intermediates, low energy electrons and photons include: the deposition of material from the gas phase onto the surface; the etching of surface material via the production of volatile products and/or the alteration of the surface region by exposure to electronically excited neutrals, ions, electrons and photons emanating from the discharge above it.

Plasma Process Parameters

Characteristic polymer deposition by glow discharge polymerization occurs onto surfaces exposed to the glow. Some deposition of polymers occurs on surfaces in nonglow regions, but the deposition rate is orders of magnitude smaller. The surface on which a polymer deposits could be an electrode surface, a wall surface, or a substrate surface suspended in the glow region. Another important factor is that glow discharge polymerization is highly system dependent, which means it also depends on the reactor geometries, e.g., dimensions of reactor vessel and of electrodes, internal or external electrodes or coils, location of monomer inlet with respect to exciting electrodes or coils, location of plasma polymer deposition

with respect to monomer inlet and to exciting electrodes, etc. Therefore, other plasma process parameters such as monomer flow rate, system pressure, and discharge power, etc., representing a set of coating conditions to define the polymerization process carried out in a reactor system may not generally apply to that occurred in another reactor system having different configurations and sizes. This arises often because of the process not being compared at a comparable level of conditions and/or parameters. The system dependence of experimental parameters becomes more complicated in a flow system where plasma polymerization is normally carried out. As the reactor design varies from laboratory to laboratory, interlaboratory comparison of results is generally not straightforward. Consequently, plasma process parameters serve as empirical means of describing operational conditions of glow discharge polymerization in a particular system, but they should not be taken beyond this limitation [20].

The plasma process parameters include [20]: frequency of exciting potential, excitation power, monomer flow rate, system pressure, geometrical factors of reactor, and temperature of deposition site, etc. One thing we should remember is that all parameters influence glow discharge polymerization in an interrelated manner. Any single factor cannot be taken as an independent variable of the process.

Frequency of Exciting Potential Electric power sources with frequencies in the zero (dc) to gigahertz (microwave) range can be used for glow discharge polymerization. The use of a low frequency electric power source (up to about the audio frequency range) requires internal electrodes. With higher frequencies, external electrodes or coils also can be used [20].

The use of internal electrodes has the advantage that any frequency can be used, but polymer deposition often occurs onto the electrode surface under low frequency range. In order to restrict the glow to the space between the electrodes in the low pressure range, it is necessary to employ magnetic enhancement. With a high frequency (radio frequency range) power source, the glow tends to stray away from the space between the electrodes, and polymer deposition onto a substrate surface placed in between the electrodes increases. The microwave apparatus usually generates a plasma of fairly even intensity over a large area, as required for deposition of uniform thin films. In one paper [21], researchers used two different apparatus in which both rf and microwave deposition were carried out. It was demonstrated that the rate of plasma polymer deposition was five times greater using microwave (>100 MHz) than rf (<30 MHz), using identical power levels. In general it has been found that, with a.c. discharges on electrodes, the best results are obtained at higher frequencies. As the

frequency of the discharge is increased, more energy is transferred to the gas and less to the electrodes.

Excitation Power The excitation power or discharge power to describe glow discharge polymerization is a system-dependent parameter, not simply the power input into the system. In essence, the absolute value of discharge power itself cannot be considered as an independent variable of the operation, since a certain level of discharge power (e.g., 60 W) in a given set of discharge conditions for one starting material (e.g., ethylene) could not even initiate a glow discharge with another starting material (e.g., n-hexane) under otherwise identical conditions. In other words, a relative level of discharge power which varies according to the characteristics of starting materials is needed to describe the discharge power for glow discharge polymerization [20].

It is known that the discharge power necessary for glow discharge polymerization depends on both the molecular weight and chemical structure of the compounds. The best first-order approach to dealing with this situation is to use the parameter given by W/FM , where W is the power input, F the flow rate given in cubic centimeters (STP) per minute, and M the molecular weight of the starting material [22]. The parameter W/FM represents the power input per unit mass of the starting material. With this parameter, plasma

polymerization of various organic compounds can be compared at a more-or-less comparable level.

Although the composite parameter can be used as a comparable parameter to define the conditions of plasma polymerization occurred in two different reactor systems, it can only be applied in a relative sense. The absolute value of the parameter does not provide a meaningful basis for the comparison simply because it includes no parameter that accounts for the geometrical factor of and flow pattern within the reactor system. However, it is still a useful parameter to describe glow discharge polymerization of different starting materials in a polymerization reactor.

Monomer Flow Rate The flow rate describes the total number of gas molecules coming into a system per unit time, when it is expressed by the volume of gas in the standard state, e.g., cm^3 (STP)/min, which is the most commonly used unit for the flow rate. In steady-state flow, the monomer feed rate is equal to the pumping-out rate.

The flow rate in most cases of glow discharge polymerization simply refers to the feeding-in rate of the starting materials into the total vacuum system, and it does not necessarily mean the rate at which the starting material is fed to the region of the system where polymerization occurs since the flow rate is measured in the non-plasma

state and no knowledge of the plasma gas phase is generally available [20].

Another important factor to be considered in conjunction with flow rate is that the plasma polymerization predominantly occurs in the glow region; however, the volume of glow is not always the same as the volume of the reactor. Flow rate is usually measured and presented as the feed-in rate into the reactor volume, but not into the glow volume. For instance, in a bell-jar-type reactor the glow volume is only a few percent of the reactor volume. Therefore, the bypass ration of flow, which may be roughly proportional to the ratio of the reactor volume to the glow volume, should be taken into consideration. However, the bypass ratio itself is a variable under conditions of plasma polymerization, since effective plasma polymerization acts as a pump and sucks the monomer into the glow region from the surrounding volume [20].

System Pressure Two pressures in the reactor should be considered: the pressure before the glow discharge is initiated and the pressure in the steady state glow discharge [20].

The system pressure before glow discharge is a function of the flow rate and the pump (and trap) pumping rate for that particular monomer. At a given flow rate, the higher the pumping rate, the lower is the value of system

pressure. The pumping rate of a system is dependent on the nature of the gas and is particularly important when a liquid nitrogen trap or a turbomolecular pump is employed in a vacuum system. These are excellent pumps for most organic vapors and some gases; however, they offer virtually no pumping action for hydrogen, which is the main product gas when hydrogen-containing compounds are used as the starting material [20].

The pressure in the steady state glow discharge is different from the pressure before the glow discharge because a portion of the monomer is removed by the process of plasma polymerization (decreasing the pressure), but by-product gas is generated (increasing the pressure) if more than one mole of by-product gas is generated per mole of monomer or if the by-product gas is pumped less efficiently by the pump and trap. Consequently, the system pressure with the glow discharge on is largely determined by the pumping efficiency of the product gas, the efficiency of the polymerization, and the production rate of gases. In addition, a generally unrecognized factor affecting the pressure in the steady state glow discharge is the fact that the plasma will generally be at a slightly higher temperature than room temperature [23].

Geometrical Factors of Reactor Reactor design can be divided into bell-jar systems and tubular-flow systems. The

effects of location, at which plasma polymer is deposited within the reactor, is relative to the coil or plates giving rise to the electric field and relative to the monomer inlet. Plasma polymer properties tend to be fairly uniform in a capacitively coupled discharge using flat plate electrodes, and such an arrangement is favored for industrial processes. The effects of location tend to be much more pronounced for inductively coupled, cylindrical reactors [22].

The location where the starting material is introduced is very important for polymer deposition. The importance of flow pattern with respect to the location of energy input and of polymer deposition can be visualized in an example of glow discharge polymerization in a straight tube reactor with an external coil placed in the middle portion of the tube. In such a system, the volume of glow discharge is generally much larger than the volume of the portion of tube which is directly under the coil. Consequently, polymer deposition can occur at the downstream and upstream sides of the coil. This factor is less obvious in a system with internal electrodes.

In glow discharge polymerization which utilizes internal electrodes, either the substrate is placed directly on an electrode surface or in the space between the electrodes. With external electrodes or a coil, the location of substrate can be chosen in a variety of ways. Since the

polymer properties and the deposition rate are dependent on the location within a reactor, this is an extremely important factor in practical applications.

The effect of reactor design has raised considerable interest among researchers in the recent past[24,25]. There are lots of factors to consider when designing a reactor and all the geometrical factors of reactor are important to the properties of plasma polymerization. A generalized conclusion would be that reactor design should be considered relative to the desired application.

Temperature of Deposition Site It is known that substrate temperature has a negative effect on the polymerization rate since the reaction occurs through the adsorption of the radicals on the activated surface. The effect of substrate temperature on the polymerization kinetics and polymer structures has been reported for rf glow discharges fed with fluorocarbon monomers [26,27]. It was noted that increasing the substrate temperature resulted in decreasing the fluorine content of plasma polymerized films, thus the film structure became more crosslinked.

Polymer Deposition Rate

Polymer deposition rate is highly dependent on the chemical structure of the monomer, although some other

factors, such as plasma process parameters, also influence the polymer deposition rate.

In plasma polymerization of hydrocarbons, triple bond and/or aromatic structure (group I), double bond and/or cyclic structure (group II), and saturated structure (group III) are three functions which determine the rate of polymer formation and the properties of plasma polymers [28]. Group I compounds form polymers by utilizing the opening of triple bonds or aromatic structures with the least evolution of hydrogen. Group II compounds form polymers via both the opening of double bonds or cyclic structures and hydrogen abstraction. Production of hydrogen is considerably higher than formed by group I compounds. Group III compounds polymerize primarily by plasma polymerization based on hydrogen abstraction. Consequently, hydrogen production is much higher than in those for group II compounds [28].

The discharge power necessary for glow discharge polymerization of hydrocarbons is also dependent on the types of compound. Groups I and II compounds require approximately the same energy input. However, the dependence on flow rate is nearly zero for group I compounds, but an appreciable increase in the required energy input is observed for group II compounds for increasing flow. Group III compounds require the highest energy input and their dependence on flow rate is much greater than that for group II compounds.

Flow Rate The polymer deposition rate usually increases linearly with the flow rate of a starting material under ideal conditions where the conversion ratio of starting material to polymer is high or remains at a constant level. However, the change of flow rate is often associated with changes in flow pattern (affecting the bypass ratio of the flow) and/or the efficiency of discharge power input. Therefore, the apparent dependence of the polymer deposition rate on flow rate is often characterized by a decrease of the polymer deposition rate after passing a maximum or a narrow plateau, as shown in Figure 2 [28].

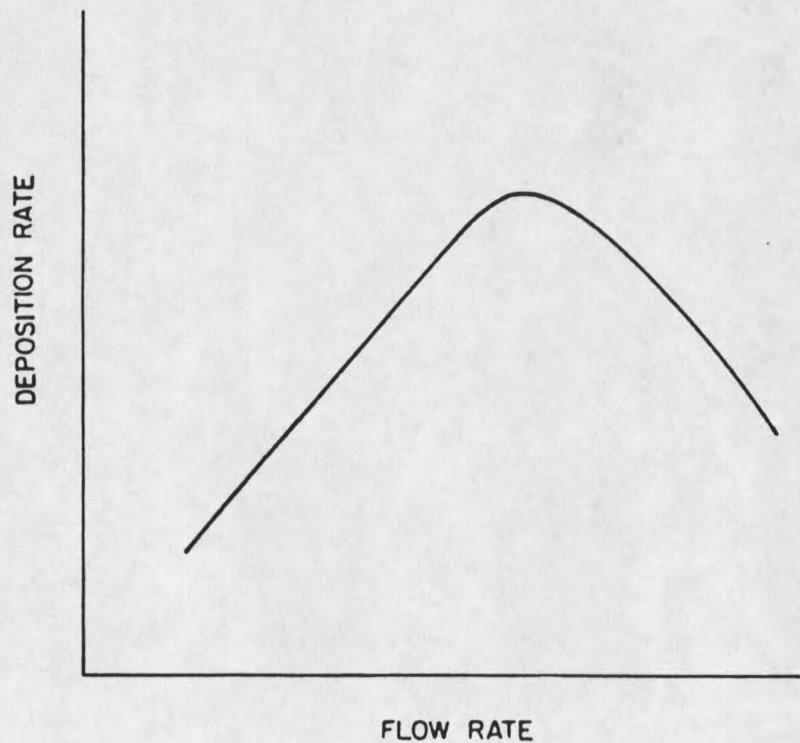


Figure 2. Schematic representation of the dependence of polymer deposition rate on flow rate of a starting material when a constant discharge power is used.

