

CHAPTER 1

INTRODUCTION

1.1 Statement and significant of the problem

Endodontically treated teeth (ETT) with a few remaining tooth structures resulted in less stiffness and usually present with the problems of coronal rehabilitation. Cast metal post and core has usually been advocated in gaining retention for coronal restorations (Sorensen and Engelman, 1990) (fig. 1). However, crack or root fracture could occur in ETT after bearing with masticatory forces (Assif and Gorfil, 1994), in some cases there were catastrophic fractures and unable to restore. Many studies demonstrated that fracture of the roots may be caused by post design (Goodacre and Spolnik, 1994; Sorensen and Engelman, 1990; Sorensen and Martinoff, 1984) or the difference in the modulus of elasticity between the metal post and the dentin. The mismatch in modulus of elasticity may result in interfacial stress at the wall of the root (Assif and Gorfil, 1994). Rengo (1999) and Torbjorner *et al.* (1996) demonstrated that the component with the higher modulus of elasticity will tend to transfer functional stresses to the component with lower modulus of elasticity. With a rigid and high modulus of elasticity of metal post, it may transfer functional stress to the tooth and root structure (Isidor *et al.*, 1996; Martinez-Insua *et al.*, 1998; Rengo, 1999; Dean *et al.*, 1998), especially in an uncontrolled area that may actually increase the potential for root fracture (Duret *et al.*, 1996). These studies corresponded to the study of Malferrari *et al.* (2003) who also found that metal post with high rigidity appeared to vibrate at high frequencies when loading with lateral forces and may cause root fracture or metal corrosion at the unpredictable areas (Goodacre and Spolnik, 1994). Corrosion caused by dissimilar metals first reported by Mateer and Reitz (1970) was implicated as a source of fracture potential in post-endodontic restorations (Glantz and Nilner, 1994; Silness *et al.*, 1979). Accumulation of metallic corrosion byproducts in the root has been significantly weakened the dentin and the interface between the post and the canal. These byproducts are also diffused into the root which cause irreversible discoloration and damage (Angmar-

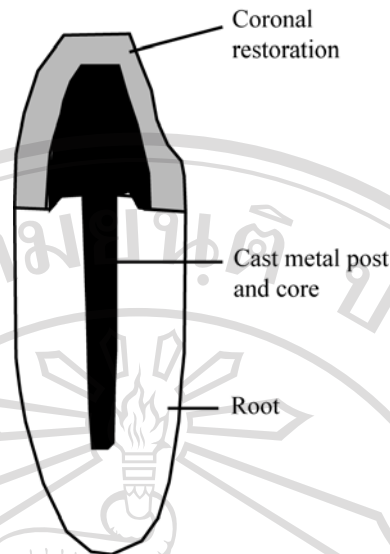


Figure 1 Schematic illustration of cast metal post used for gaining retention for coronal restoration.

Mansson *et al.*, 1990). With a metallic post, a “shine through” dark color which interfering natural light transmission through the tooth and gingival complex (Pitel and Hicks, 2003) may cause unpleasant results and were esthetically unaccepted by the patients.

Most research regarding post and core aimed to develop systems that are biocompatible, preservation of root dentin, less stress to the root, strong retentive with dental cements, corrosion resistant, and compatible with restorative materials (Purton and Payne, 1996). Carbon fiber-reinforced resins are considered as the viable alternative to metal in many fields, when strength, stiffness, lightness, and resistance to corrosion and fatigue are considered. Composipost (RTD Grenoble, France) is a system of root canal posts made from carbon fiber-reinforced epoxy resin that was first introduced by Duret *et al.* in 1990. These posts are fabricated from continuous, unidirectional carbon fibers, 8 micron in diameter, uniformly embedded in epoxy resin. The fibers constitute of 64% by weight of the post (Purton and Payne, 1996). In recent years, the use of these posts had gained popularity due to a number of advantages, including biocompatibility, resistance to corrosion and fatigue, mechanical properties that closely match to those of the tooth (Sorensen and Engelman, 1990; King and Setchell, 1990), and ease of post removal from the root

canal (Purton and Payne, 1996; Purton and Love, 1996). It also exhibited high fatigue and high tensile strength (Viguie *et al.*, 1994; Malquarti *et al.*, 1990; King and Setchell, 1990).

Carbon fiber-reinforced posts are intentionally manufactured to have a very similar modulus of elasticity to that of dentin (15 GPa to 40 GPa) (Pitel and Hicks, 2003; Viguie *et al.*, 1994; Malquarti *et al.*, 1990; King and Setchell, 1990) and closely match with composite resin (20 GPa) (Duret *et al.*, 1996). The reason was, when all of the reconstructive components have a very similar modulus of elasticity, a more uniform stress distribution throughout the restored tooth with lower interfacial stress and less chance for failure was obtained (Dietschi *et al.*, 1996; Rengo, 1999). This post can be bonded within root canal space with dentin bonding agents and resin cements of similar stiffness. This effectively reduces the stress between the post and the root structure, which causes less root fracture (Duret *et al.*, 1990; Asmussen *et al.*, 1999; Ferrari *et al.*, 2000). The condition of this phenomenon was named “a monobloc” (Pitel and Hicks, 2003). Semiprecious and precious alloys have modulus of elasticity that is significantly different from dentin (7-10 times higher). All ceramic posts are also much stiffer than dentin. Achieving a monobloc with any of these materials is impossible. Many clinical evaluations and retrospective studies revealed clinical success of fiber-reinforced epoxy resin posts in daily practice for restoring ETT (Ferrari *et al.*, 2000; Mannocci *et al.*, 2002; Fredriksson *et al.*, 1998).

Although the carbon fiber-reinforced composite post (carbon FRCP) presented with an interesting property but it possessed a black color and did not provide any significant esthetic over a similar sized prefabricated metal post (Pitel and Hicks, 2003). However, improved versions of the carbon fiber post were introduced with a white mineral coating/sheath surrounding a black carbon fiber core (AESTHETI-POST, Bisco Dental product, Schaumburg, IL). This white FRCP consists of quartz or glass fibers embedded in an epoxy or resin matrix. Unlike the earlier carbon FRCP, this post offers significant esthetic advantages without sacrificing the functional benefits. Because of their tooth-like colorations, most of these posts will not “shine through” a dark color through the tooth and gingival complex (Pitel and Hicks, 2003).

Generally, there are two major groups of white FRCs. The first group composed of unidirectional glass fiber (61.5% vol) embedded in a polymer matrix of triethylene-glycol-dimethacrylates (TEGDMA) and urethane-dimethacrylate (UDMA) monomers, in combination with highly dispersed silicon dioxide, for example FRC Postec Post (Ivoclar Vivadent, Schaan, Liechtenstein) (Goracci *et al.*, 2004). The second group composed of unidirectional prestress quartz fiber (60% vol), bound in an epoxy resin matrix, for example DT Light-Post (RTD, St. Egrevé, France) (Goracci *et al.*, 2004). Both resin matrices are highly cross-linked, and do not possess functional groups that can react with the methacrylate groups of the resins usually employed in dental composite, resulting in no chemical bonding between the surface of fiber post and composite resin (Purton and Payne, 1996).

However, to achieve a monobloc condition, each interface between the fiber post, dentin and composite resin foundation must have an ultimate bonding (Monticelli *et al.*, 2003; Goracci *et al.*, 2004; Aksornmuang *et al.*, 2004) (fig. 2). In order to improve the bond strength between the post and the composite resin, many kinds of surface treatments of the post were studied. This can be achieved via mechanical treatment (Sahafi *et al.*, 2004; Balbosh and Kern, 2006) or chemical treatment (Goracci *et al.*, 2005; Aksornmuang *et al.*, 2004; Monticelli *et al.*, 2006; Vano *et al.*, 2006). Therefore, by mechanical technique the surface may be too rough and their effects are limited, or in some cases with aggressive treatment there may be perceptible volume loss of the post (Sahafi *et al.*, 2004). On the other hand, by chemical techniques the surface may have a non uniform roughness and non reproducible effect and also may be hazardous to the environment (Yang and Gupta, 2004).

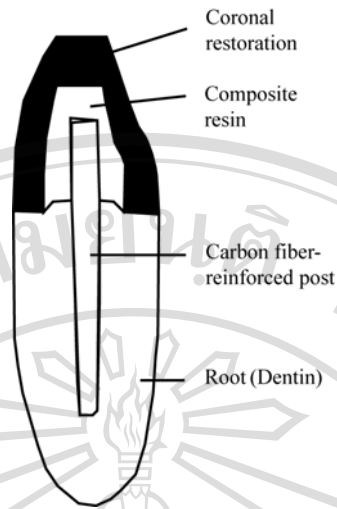


Figure 2 Schematic illustration of each interface between the fiber post, dentin and composite resin foundation must have an ultimate bonding to achieve a monobloc condition.

ลิขสิทธิ์มหาวิทยาลัยเชียงใหม่
Copyright© by Chiang Mai University
All rights reserved

1.2 Rationale

In modern industry, cold gas plasma has become a technique widely used for treating the surface of polymer (Cvelbar *et al.*, 2003). Since bonding and finishing of many polymers present a problem due to the low hydrophilicity of their surfaces. Plasma treatment is a very effective way in providing the hydrophilicity to a polymer surface. The improving of surface hydrophilicity was induced by forming of new oxygen-containing groups on the surface, such as -OH, -OOH etc., which are hydrophilic (Lai *et al.*, 2006). With plasma, there are energetic-free electrons produced at the ambient temperatures, which can collide with polymer surfaces and gas molecules around to form active species both in the gas phase and on the substrate surfaces (Morosoff *et al.*, 1976). When plasma particles react with the surface of polymers, the following effects can be occurred: surface cleaning, degradation of the polymeric chains, removal of material from the surface, formation of radicals on the surface, and changing of tacticity of the polymer chains (Kinloch, 1987). The combined effects of these processes result in an improvement of the adhesion properties of the surface. Recently, plasma treatment has been considered as a way of avoiding the need for adhesive primer (Nishigawa *et al.*, 2003; Vassilakos *et al.*, 1993). Cold gas plasma treatment also provides a clean and environmentally friendly approach to modify the surface of polymer nanofibers without affecting the bulk properties of the treated nanofibers (Wei *et al.*, 2005). Until now, there were not any experiments employing plasma treatment for white FRCP, since the matrix part of white FRCP was a polymer; we expect that this treatment should improve the bonding properties of the white FRCP to the composite resin.

1.3 Literature review

1.3.1 Surface treatment of fiber-reinforced post

1.3.1.1 Mechanical treatments

According to highly cross-linked of polymer matrix of FRCP as above-mentioned, Sahafi *et al.* (2004) used sandblasting technique and Cojet system (3M, ESPE) for roughening the surface of glass fiber post. Sandblasting was performed at 4 bar for 15 seconds using alumina particles of 50 μm in diameter with an extraoral sandblasting device held perpendicular to the post surface at distance of 20 mm whereas Cojet treatment consists of sandblasting with an intraoral sandblasting device at 4 bar for 15 seconds using 30 μm silicate-coated particles followed by silane coating. According to a diametral tensile strength (DTS) test, it was not allow for the determination of the effect of surface treatment on the bonding of resin cement to glass FRCPs. Since in the DTS test, the load was applied in a direction perpendicular to the orientation of the fibers and resulted in splitting of the fiber post, indicating that the diametral strength of the post in this direction was surpassed. Thus, the load at fracture was limited by the diametral strength of the post itself, implying that any differences between the surface treatments were obscured by premature fracture of the post. However, they found that sandblasting, including Cojet treatment, resulted in perceptible volume loss of the posts. As their observation, sandblasting in combination with Cojet treatment may have a weakening effect, which was not recommended for glass fiber post. Conversely, Balbosh and Kern (2006) also used sandblasting technique to treat surface of glass fiber post compared with ED-Primer (Kurarey, Osaka, Japan) before cementation with Panavia F (Kurarey, Osaka, Japan). They found that sandblasting provided significantly higher bond strength between post and resin cement when compared with ED-Primer. Since sandblasting was performed with 50 μm alumina particles at 2.5 bar for only 5 seconds from a distance of 30 mm, this regimen did not produce visible changes on the post. This result is consistent with those of previous studies refer that reported airborne-particle abrasion with alumina particles increased the surface area and enhanced the mechanical interlocking between the cement and the roughened surface of post (Sahafi *et al.*, 2003).

1.3.1.2 Chemical treatments

Goracci *et al.* (2005) applied chemical agents, silane (Monobond-S, Ivoclar-Vivadent) on the FRCP surface before built up with flowable composite resin. They demonstrated the enhancement of the interfacial bond strength between the post and composite resin. Since the highly cross-linked polymers of the matrix in FRCP have no functional group (-OH group) available for reaction, their reaction with silane is impossible. The increase in interfacial bond may be due to the improvement in post surface wettability following silane coating. The chemical bond at the fiber post-composite core interface is possible only when the exposed glass or quartz fiber directly contact with silane coupling agent (Aksornmuang *et al.*, 2004; Goracci *et al.*, 2005). Monticelli *et al.* (2006) and Vano *et al.* (2006) have shown that 24% of hydrogen peroxide for 10 minutes or 10% for 20 minutes was able to dissolve the epoxy resin matrix, breaking epoxide and exposing the surface of fibers for silanization. This method was found in enhancing the retention between epoxy resin based, conventional fiber post systems and core materials. They demonstrated significantly increasing bond strength between these treated fiber posts and composite core compared with silanization group. Monticelli *et al.* (2006) also demonstrated that etching DT Light-Post with alkaline potassium permanganate solution (20% vol in deionized water; pH 12-13) for 10 minutes at 70-80 °C can dissolve the epoxy matrix resulted in the exposed quartz fiber component of these posts. Likewise, the simultaneous increase in surface roughness of the post and the surface area of the quartz fibers also provide additional friction resistance and sites for silanization, further enhancing the bonding of the fiber posts to the methacrylate-based composites. However almost of these methods had the similar mechanisms of treatment by removing of the outer surface of the post and/or roughened the surface. The depth of treated surfaces was unpredictable by these treatments which may affect to the bulk properties of the post. In contrast with plasma treatments, the reactive surface was affected only the very outward layer of the plasma exposed surfaces approximately 1-10 nm, leaving the bulk properties of the substrates unchanged (Grace and Gerenser, 2003).

1.3.2 Definition of plasma

Plasma can be defined as a partially or wholly ionized gas with a roughly equal number of positively and negatively charged particles. It has been dubbed as the “fourth state of matter” because of its general properties which are similar to both a gas and a liquid (Nickerson, 2000). In gas plasma, it composed of the energetic species including ions, electrons, radicals, metastables, and photons in the short-wave ultraviolet (UV) range (Loh, 1999). To enable the gas to be ionized in a controlled and qualitative manner, the process is carried out under vacuum conditions. A high-frequency generator, which can be the kilohertz, megahertz or microwave range, is then used to ionize the gas into plasma (Derand *et al.*, 2005). When a gas is raised to a sufficiently high temperature, the atoms and molecules of the gas become ionized, electron being stripped off by the violent collision as the consequence of the thermal agitation of the particles. When this happens, the dynamic behavior of the gas may be dominated by the electromagnetic forces acting on the free ions and electrons (Thompson, 1962). Surfaces in contact with gas plasma are bombarded by these energetic species and their energy is transferred from the plasma to the solid (fig. 3). These energy transferred are dissipated within the solid by variety of chemical and physical processes such as cross-linking, etching (degradation), deposition (grafting) and functionalization resulting in the surface modification (Loh, 1999) (fig 4).

1.3.3 Classification of plasma

Plasma states can be divided in two main categories: hot plasma (near-equilibrium plasma) and cold plasma (non-equilibrium plasma). Hot plasma is characterized by very high temperature of electrons and heavy particles, both charged and neutral. They are closed to maximal degrees of ionization (100%) for example electrical arcs, plasma jets of rocket engines, thermonuclear reaction generate plasma, etc. Cold plasma (non-equilibrium plasma) composed of low temperature particles (charged and neutral molecular and atomic species) and relatively high temperature electrons. They are associated with low degrees of ionization (10^{-4} -10%). Cold plasma includes low-pressure direct current (DC), radio frequency (RF) discharges (silent discharges), and discharges from fluorescent (neon) illuminating tubes, etc. (Denes and Manolache, 2004). Since cold plasma chemistry takes place at near

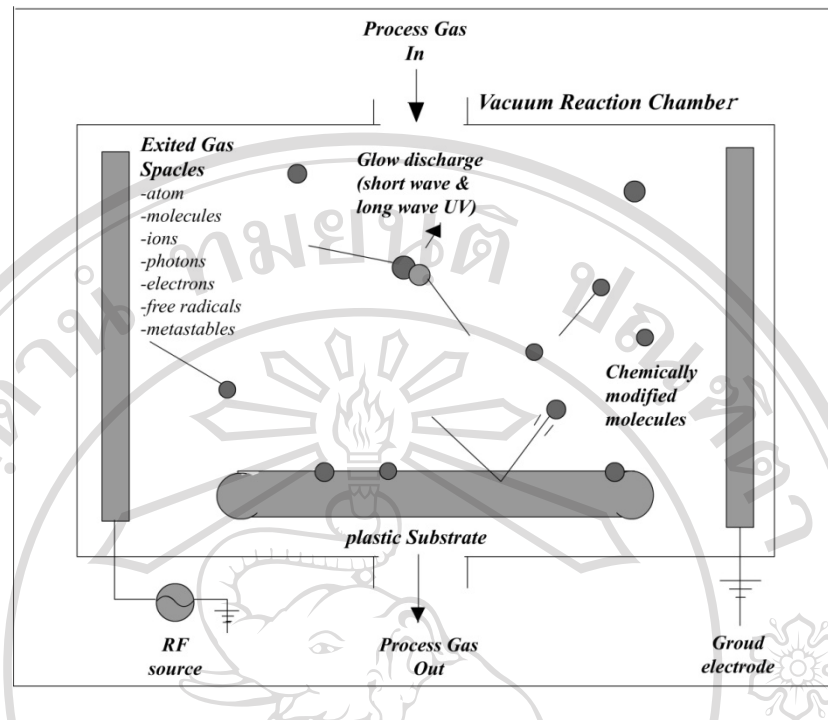


Figure 3 Schematic illustration of plasma modification within the plasma reactor (modified from Loh, 1999).

ambient temperature, it is well suited for processing thermally sensitive material such as semiconductors, textile and polymer (Liston *et al.*, 1993). Basically, this kind of plasma is obtained at low pressure so it was necessary to generate under vacuum chamber. To overcome this limitation, an atmospheric pressure (AP) plasma treatment system can be used, which not only avoids the need for vacuum equipment but also permits both the treatment of large objects and production line continuous treatment. Typical AP plasma systems are corona discharges and dielectric barrier discharges (Kusano *et al.*, 2007). A special type of AP plasma is a plasma jet where the plasma constituents are expelled through an orifice of a nozzle (Noeske *et al.*, 2004). One problem with corona treatment is that the modification effects decay quickly, and the treated surfaces needed to be retreated before being used (Yang and Gupta, 2004). Characteristics of plasmas used in different technologies depend on the nature of the material treated. Many applications require plasma with a high degree of ionization, while some are proven to be better if weakly ionized plasma is used (Cvelbar *et al.*, 2003).

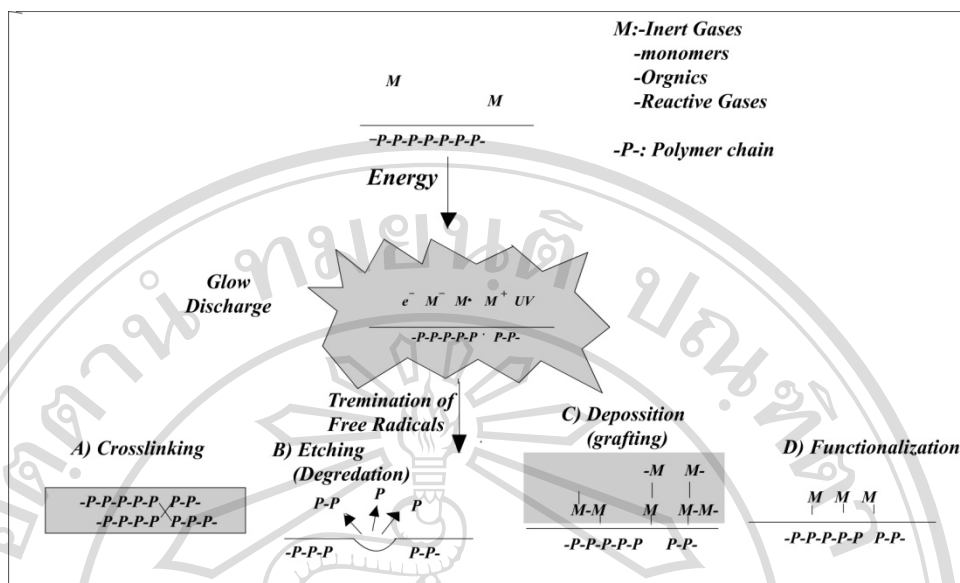


Figure 4 Schematic illustration of the reaction mechanisms of plasma surface modifications (modified from Loh, 1999).

1.3.4 Effect of plasma gas

The effect of plasma treatment on polymer surface is influenced by the gas chemistry associated with the plasma, as well as the chemical structure of the polymer surface (Grace and Gerenser, 2003). The plasma treatment process for each gas is optimized by varying the time, power, pressure and gas flow rate to the substrate. For example, argon plasma treatment induces the cross-linking between substrate and polymer, while fluorine plasma treatment decreases the surface energy of the polymer. In addition, it was reported that hydrogen-argon plasma gas mixtures can effectively remove oxide from metallic substrates (Noh *et al.*, 2007). In order to improve adhesive properties of polymers, the selection of gas to produce plasma which properly matched with polymer chemistry would be a crucial factor. However, it is also important to stress that there are no 'standard' in plasma process. There are normal starting processes for various polymers that are learned through experience, but it is usually necessary to optimize the best processing condition for each application (Liston *et al.*, 1993).

According to non-equilibrium plasma, plasma energy is often transferred solely by the electrons. The faster electrons mainly initiate the chemical reactions in the

plasma by colliding with gas molecule and excite them to high energy levels, thereby losing part of their energy which is replenished by the electric field. The excited molecule can now, either dissociate or initiate other reactions due to its high internal energy. In plasma chemistry, it is very importance that the transfer of energy via electrons to the species which take part in the reactions is very efficient. This is accomplished easily by a short electron pulse. However, not only electrons, ions, atoms and molecules, but also photons are found. If the photons have adequate energy, they can also initiate chemical reactions. The photon is an energy carrier, but with somewhat different characteristics from electron. It has no mass and moves at the speed of light, whereas the electron can be pictured as a bullet traveling at a certain speed determined by its kinetic energy (Eliasson and Kogelschatz, 1991). Especially, low pressure plasma generated by inert gas (He, Ar) usually emits vacuum ultraviolet (VUV) photons. VUV radiation in plasma reactors can break any organic bond and initiate rapid free-radical chemistry. Within these free radicals, they can react with other surface radicals or with other chains in chain-transfer reaction of polymer; therefore, they tend to be very stable. If the polymer chain is flexible, or if the radical can migrate along it, this can give rise to recombination, unsaturation, branching, or cross-linking. The latter may improve the heat resistance and bond strength of the surface by forming very cohesive skin (Liston *et al.*, 1993). In addition, energetic ions are believed to contribute to cross-linking of polymer chain in the surface region of polymer. This effect is known as cross-linking by activated species of inert gases (CASING). Cross-linking was suggested as a barrier that can mitigate the reorientation effects of the modified polymer surface (Grace and Gerenser, 2003), resulting in more stable of plasma-treated surface.

1.3.5 Bonding enhancement through plasma treatment

The various effects of the plasma-surface interactions contribute to the different mechanisms of adhesion. Bonding enhancement can be regarded as a result from the following overlap of effects: (a) removal of organic contamination and of weak boundary layers by cleaning and ablation; (b) cohesive strengthening of the polymeric surface by the formation of a thin cross-linking layer that mechanically stabilizes the surface and serves as a barrier against the diffusion of low-molecular-weight (LMW)

species (caused by bond breaking or polymer chain scission) to the interface; and (c) creation of chemical groups on the stabilized surface that result in acid-base interactions and in covalent linkages believed to yield the strongest bonds (Liston *et al.*, 1993).

For polymer-polymer bonding, plasma treatment can improve the bonding properties by increasing wettability of the treated polymer by the adhesive and modifying the surface chemistry of the polymer. The changed surface chemistry facilitates reaction of the adhesive with surface species during curing, to form covalent bonds with the plasma interphase (Liston *et al.*, 1993). The highest adhesion force appears when the surface is mechanically stabilized by cross-linking and the effect of a weak boundary layer due to excessive LMW oxidized molecules is minimal. Another type of chemical bonding mechanism might be acid-base interaction caused by the acidity of a strongly oxidized surface interact with Lewis base of adhesive or vice versa (Liston *et al.*, 1993).

Plasma treatment typically modifies outer 1-10 nm of a polymer surface, so it needs the surface-sensitive techniques to characterize the plasma-induced chemistry. According to surface sensitivity, combined with quantitative and chemical state identification capability have made x-ray photoelectron spectroscopy (XPS) the most broadly applicable polymer surface technique. In XPS, monoenergetic soft x-ray is used to irradiate a sample material in high vacuum (typically $\leq 10^{-9}$ Torr) producing photoionization and ejected free electron. These photoelectrons are collected with an electron lens assembly, energy analyzed, and counted. The resulting spectrum consists of peaks that correspond to the electronic energy states of the sample materials. By integrating the area under a given peak and correcting for its ionization cross section, quantitative element analysis of the material can be made (Grace and Gerenser, 2003). Base on the study of Noeske *et al.* (2004), they revealed the AP plasma treatment improves the adhesive bonding of polyethyleneterephthalate (PET), polyamide 6 (PA6), polyvinylidene fluoride (PVDF), high density-polyethylene (HD-PE), and polypropylene (PP). XPS had shown a strong increase (up to 22 at % point) of oxygen concentration and a much smaller increase (0.3-3 at %) of nitrogen for all polymers. For more detailed analysis of the XPS of the non-treated and the plasma-treated HD-PE surface indicated the formation of the oxygen functional groups such

as carboxyl, carbonyl, and alkoxy groups. Epoxy groups have also been formed. Similar results have also been observed for the other polymers. Probably the formation of additional functional groups at the surface is the most significant contribution to the adhesion improvements by the AP plasma jet treatment. In addition, with the study of Nishigawa *et al.* (2003), they demonstrated that AP plasma treatment is effective in increasing shear bond strength between heat cured acrylic resin and self-curing acrylic resin [polymethylmethacrylate (PMMA)] compared with control group. With plasma treatment, the surface of PMMA could be washed and degreased; thereby the wettability of the surface would be raised. It has been assumed that the hydroxyl group (-OH) is brought to the surface of the plasma irradiated polymer. This action also leads to the improvement of surface wettability. In a similar way, Ozden *et al.* (1999) reported that exposure of glow discharge (cold plasma) both in air and argon atmosphere improved the wettability of acrylic resin. Decreasing of contact angle of distilled water on the surface of treated acrylic resin was achieved compared with untreated groups. XPS measurements indicated that glow discharge altered the acrylic resin surface. The improvement in surface wettability of acrylic resin materials might be attributed to the formation of the hydroxyl group bonded to the carbon atom (-COH) group. Also, plasma treatment seemed to offer a durable wettability (at least up to 60 days) of the treated acrylic resin both in air and in distilled water storage. Whereas, Chai *et al.* (2004) reported that the formation of the carboxyl, carbonyl, and carbonate groups on the surface of PMMA by a DC pulsed oxygen plasma treatment could be occurred in many possible oxidation schemes. The reasons were that there were at least three potential sites for initiating the oxidation reaction by a C-H rupture and different oxidation reactive reactions take place simultaneously while competing with each other (fig. 5). These induced polar functional groups led to improve the surface wettability of PMMA.

For other type of polymers and gases, Wei *et al.* (2005) treated the surface of PA6 nanofibers with oxygen plasma (cold gas plasma) and they revealed that oxygen plasma treatment created additional oxidized functional groups on the nanofiber surface. XPS has been shown the formation of many hydroxyl and carboxylic functional groups. These groups mainly replace the hydrocarbon or carbonyl groups in the PA6. They also found that oxygen plasma treatment considerably reduced the

contact angle on the fiber surface. Reactive plasma (such as oxygen and nitrogen) can probably produce the polar functional groups, which can dramatically increase the surface energy of the polymer result in increasing surface wettability (Liston *et al.*, 1993). Atomic force microscopy (AFM) image revealed nanosize pores aggregated on the fiber surfaces after treated with oxygen plasma for 60 seconds. This observation can be attributed to the etching effect of the oxygen plasma treatment. This microroughness may enhance adhesive properties between the surface of polymer and adhesive material by micro-mechanical interlocking at the interfaces instead of only chemical interaction of functional groups. Corresponding to the study of Cvelbar *et al.* (2003) who showed that the exposure of graphite/PPS polymer (p-phenylene sulfide) to oxygen plasma for 180 seconds causes etching of polymer. At the same time, oxidation causes a formation of oxygen rich functional groups as well as low mass volatile molecules. Apparently, the plasma interacts with the surface both chemically and physically. The distribution of functional groups is produced by reactive gas plasma treatment. However, some of the functional groups may not be important and some may have detrimental effects on adhesion improvement. Thus it is desirable to determine which of the functional groups is important for a given application and attempt to shift the distribution in favor of the desired functional group or groups. The distribution can be shifted in favor of a specific functionality by changing the plasma gas or other plasma parameters (Grace and Gerenser, 2003).

To understand the effects of different plasma gases on the surface chemistry of treated-polymers, the best way was to use a structurally simple polymer such as polystyrene (PS). After exposure of the PS to Ar, O₂ and N₂ plasma gas, XPS has shown different results. Ar plasma treatment could demonstrate the damage of the polymer surface involving bond breaking of the phenyl ring and possibly chain scission of the PS backbone suggested by XPS result. Similar results were observed for the other inert gases and demonstrated that treatments with inert gases did not induce new reactive functionalities into the polymer surface (Grace and Gerenser, 2003). However, treatment with inert gas can induce radical formation on the polymer surface through ion bombardment and UV radiation (Boenig, 1982). The radicals formed on the surface of treated polymers are very stable in vacuum but will react rapidly on exposure to reactive gas such as oxygen. The UV radiation can also

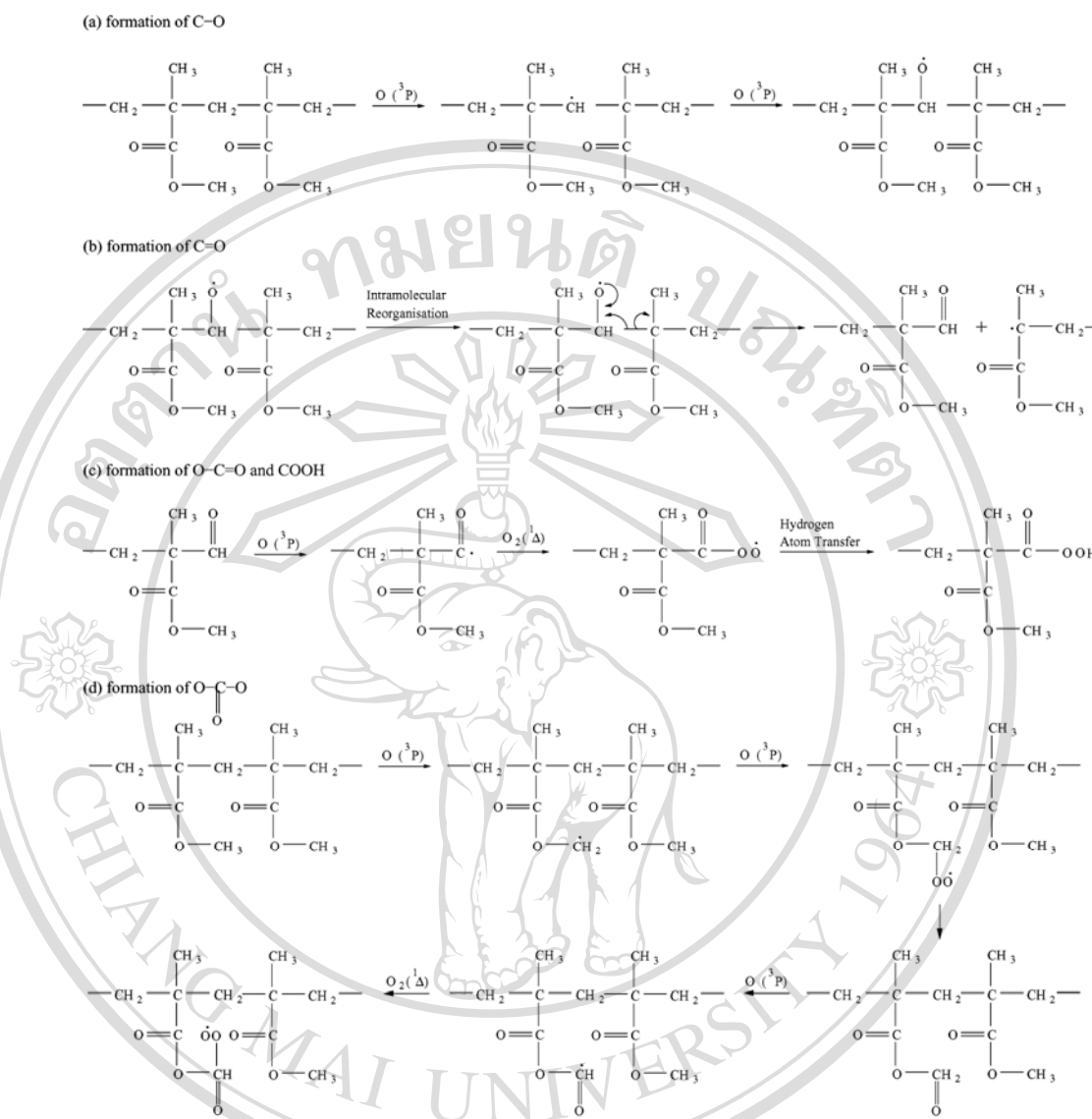


Figure 5 A possible oxidation scheme of O_2 plasma treated PMMA (from Chai *et al.*, 2004).

induce cross-linking of the polymer surface, which can affect the cohesive strength of the polymer (Grace and Gerenser, 2003). Arefi-Khonsari and Tatoulian (2008) demonstrated the formation of cross-linking of isotactic PP after exposed to plasma of inert gases such as Ar, He, and Ne, by the free radicals interactions which were formed readily due to the tertiary carbon bearing a methyl group (fig. 6).

In contrast to Ar plasma treatment, XPS analysis has shown a high binding energy at the C 1s spectra for the O_2 and N_2 of plasma-treated PS, indicating the formation of new chemical functionalities. By interpretation of XPS images, both of

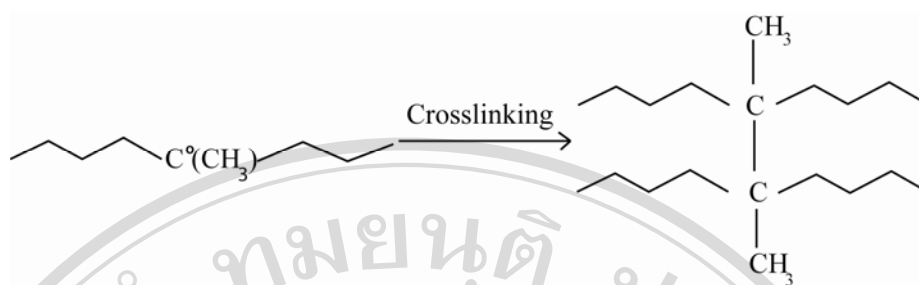
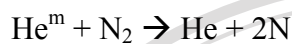
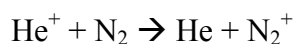


Figure 6 Formation of cross-linking due to free radicals interactions (from Arefi-Khonsari and Tatoulian, 2008).

these plasma treatments cause damage to the polymer surface involving bond breaking of the phenyl ring, but the O_2 plasma induce the formation of three distinct carbon-oxygen species, C-O (ether, hydroxyl, or epoxy), C=O (carbonyl as an aldehyde or ketone) and O-C=O (carboxyl or ester). In comparison with the N_2 plasma, the functional group was distinctly different. For the N_2 plasma-treated PS, the amine and imine carbon species were induced and were presented in a 3:1 ratio and the majority of them usually contained a terminal nitrogen (primary amine or imine). Similar results were found for N_2 plasma-treated PE (Grace and Gerenser, 2003).

Although inert gas plasma treatment does not incorporate new chemical species into polymer such as PE, PS, or PP, selective bond breakage, and desorption of various short chain species can occur. On the other hands, plasma treatments done with small amounts of a reactive gas mixed with the inert gas can introduce reactive functional groups into the polymer surface. It should be pointed out that the degree of incorporation of new functional groups with reactive/inert gas mixtures may depend on the efficiency of the VUV radiation emitted by the gas (Grace and Gerenser, 2003). The efficiency roughly follows the sequence $He > Ne > H_2 > Ar > O_2 > N_2$ (Liston *et al.*, 1993). Therefore, mixtures of reactive gases with He may be more effective at incorporating oxygen compared to mixtures of reactive gases with Ar. In the case that nitrogen was added in the gaseous mixture with helium, the reactions can give rise to ionization or dissociation according to the following reactions which induced N_2^+ excited species in the discharge (Arefi-Khonsari and Tatoulian, 2008).



However, the chemical structure of a polymer can also play a major role in the surface chemistry obtained by plasma treatment. For instant, the rate of incorporation of new chemical species by either O₂ or N₂ plasma treatment under identical conditions was found to be greater for PS compared to PE or PP. In the case of N₂ plasma treatment, the rate of nitrogen incorporation was roughly a factor of two. This may be the π system in the phenyl ring of PS and/or differences in crystallinity between the polymers. The π system in PS may have a good responsibility for UV absorbance, leading to significantly more radical formation, which can then react with plasma gas species. In addition, the induction rate of functional groups in PS after O₂ plasma treatment also different from PE due to more composition of ether and/or epoxy groups in PE (> 75%) than in PS (< 50%) (Grace and Gerenser, 2003).

1.3.6 Aging effects (stability)

Although the functional groups on the surface of polymer play an importance role in adhesive properties of the polymer. The stability of the plasma-treated polymer surface also plays a key role for these properties too. Since in practical application, the plasma-treated polymer cannot be stored in a controlled environment at all the time, or coated immediately after treatment. One of the most common examples of the aging effect is usually a revert to a less wettable state within time (Morra *et al.*, 1990). This process may result from a combination of four effects: (1) the thermodynamically driven reorientation of polar moieties away from the surface into the subsurface; (2) the diffusion of mobile additives or oligomers from the polymer bulk to the surface, (3) the formation of LMW species in the subsurface and their subsequent migration to the surface; and, finally, (4) the reaction of residual free radicals, i.e. chemical change (Liston *et al.*, 1993). However, the stability of a modified surface depends on several factors including the chemical structure of the

polymer treated, the treatment level, the plasma gas, and the storage environment (Grace and Gerenser, 2003).

The effects of air exposure of plasma treated surface can be shown in plasma-treated PE. The smallest change was found for the Ar plasma while air exposure resulted in a 2% oxygen uptake. Contrarily, the O₂ plasma-treated PE surface appears to be depleted in oxygen with correspond to the increase in the level of carbon and small amount of nitrogen after air exposure. Whereas the N₂ plasma-treated PE surface exhibits the most interesting changes after air exposure: adsorption of 5% oxygen and a small amount of carbon accompanied by loss of approximately 40% of plasma-induced nitrogen. It was found that PET treated with N₂ and O₂ plasma showed similar result. However, after initial rapid decrease of the incorporated surface species (nitrogen or oxygen), the nitrogen plasma-modified surface remains stable with time, but the oxygen plasma-modified surface continues to lose surface oxygen with time. Since the oxygen plasma-modified PET undergoes surface reorganization even at low doses. That may be due to more bond breaking and chain scission with oxygen-plasma even at the short treatment times, thus producing more LMW oxidized material. The amount of cross-linking in the near-surface region may be different of the two gases and may have an effect on the mobility of LMW oxidized material (Grace and Gerenser, 2003).

According to aging effect, an optimum plasma treatment should yield two simultaneous effects: surface cross-linking and the formation of the requisite chemical functionalities. The cross-linking process not only leads to mechanical strengthening of the surface, but also simultaneously provides a barrier against diffusion of LMW species from the polymer bulk. In practice, the control of cross-linking can be achieved by using plasma gases which strongly emit VUV radiation (Liston *et al.*, 1993) as mentioned earlier.

In conclusion, for optimal adhesive properties of the polymer surface by cold gas plasma treatments, the following criteria should be considered: (a) the selection of plasma-gas must be correctly match with the chemical structure of the modified polymer, creating the functional groups; (b) the parameters of plasma treatments such as treatment time, power and gas pressure etc. must be calibrated for each polymer;

and finally (c) the selection of plasma gases either pure or mixture which strongly emit VUV radiation in order to reduce ageing effect.

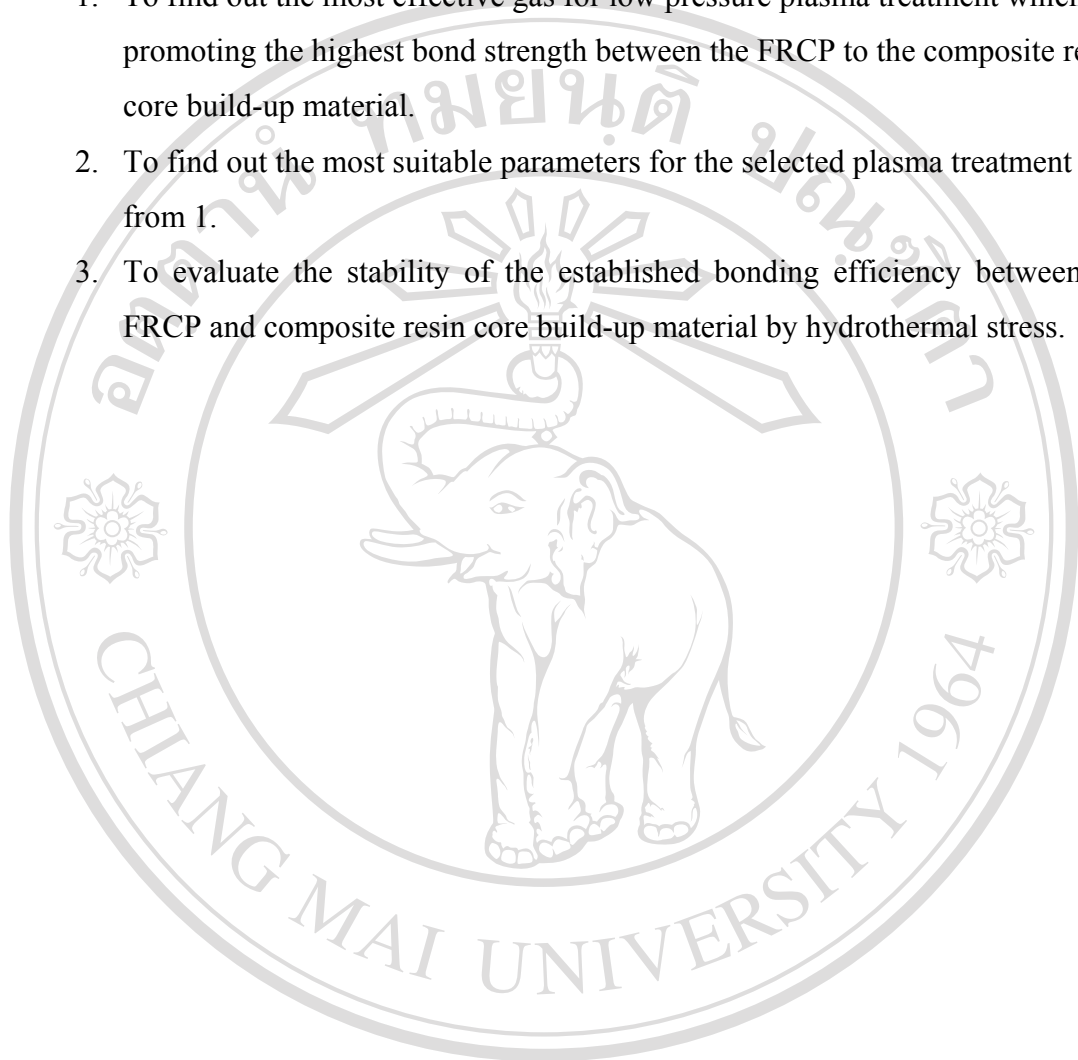


ลิขสิทธิ์มหาวิทยาลัยเชียงใหม่
Copyright© by Chiang Mai University
All rights reserved

1.4 Purpose of the study

The objectives of this research were:

1. To find out the most effective gas for low pressure plasma treatment which promoting the highest bond strength between the FRCP to the composite resin core build-up material.
2. To find out the most suitable parameters for the selected plasma treatment from 1.
3. To evaluate the stability of the established bonding efficiency between the FRCP and composite resin core build-up material by hydrothermal stress.



ลิขสิทธิ์มหาวิทยาลัยเชียงใหม่
Copyright© by Chiang Mai University
All rights reserved