CHAPTER 4

DISCUSSION

4.1 Discussion of part 1

In the first part of this study, for both FRC and DT posts, treatment with Ar, N_2, and He+N_2 plasma significantly improved the tensile-shear bond strength between the post and composite core build-up material when compared with the control group ($p<0.05$). However, the O_2 plasma treatment significantly improved the tensile-shear bond strength only for the FRC posts. Generally, with O_2 plasma treatment, polar functional groups can be induced on the surface of the polymer, resulting in higher surface wettability (Liston *et al.*, 1993; Wei *et al.*, 2005). Therefore, results of this study suggested that the induction of polar functional groups probably did not apply to the O_2-treated DT posts. Bond breaking or degradation may be difficult to achieve by O_2 treatment in the highly cross-linked networks of DT posts, which were composed of epoxy resin. On surface roughness, oxygen plasma treatment usually creates microroughness on the treated surface due to an etching effect (Cvelbar *et al.*, 2003; Wei *et al.*, 2005). However, in the present study, no significant increases in average surface roughness were observed on the surface of either the FRC or DT post when compared with the control groups. This was probably due to the low concentration of O_2 in this study.

Argon plasma treatment significantly enhanced the tensile-shear bond strength for both types of posts. This enhancement might be the result of polymer chain scission caused by the bombardment of energetic Ar particles, which were high-molecular-weight particles. Although inert gas plasma treatments (He, Ar) do not induce any new reactive functionalities on the polymer surface (Grace and Gerenser, 2003), treatment with inert gas can induce free radical formation on the polymer surface through ion bombardment and ultraviolet (UV) radiation (Boenig, 1982). These free radicals can react with other surface radicals or with other chains in the chain-transfer reactions of polymers.

By these reactions, chemical interaction between free radicals on the surface of the fiber-reinforced posts and the functional groups in the composite core build-up material may occur, thereby resulting in a significant increase in tensile-shear bond strength. It could be assumed that these chemical interactions, rather than micromechanical interlocking between the two surfaces, were the cause of higher tensile-shear bond strength in the FRC posts, because the average surface roughness of the FRC posts was not increased.

In N_2-treated groups, the tensile-shear bond strengths between the composite core build-up material and both types of posts were significantly increased. The increase in bond strength might be the result of functional groups induced on the surfaces of both types of posts. Grace and Gerenser (2003) demonstrated that the amine and imine carbon species were induced as functional groups on the surface of N_2-treated polystyrene. The majority of these functional groups usually contain a terminal nitrogen (primary amine or imine). Nitrogen plasma treatment also damaged the polymer surface through bond breaking of the phenyl ring in polystyrene. In the present study, it was hypothesized that the induced functional groups on the surfaces of both N_2-treated FRC and DT posts might contain a terminal nitrogen, which then reacted with the functional groups in the composite core build-up material. Moreover, these amine and imine functional groups might remain stable over time as compared to the oxygen functional groups; this speculation is well confirmed by a study on the aging effects of N_2-modified PET (Grace and Gerenser, 2003).

Amongst all the plasma treatment groups, the He+N_2 plasma treatment yielded the highest tensile-shear bond strength between the composite core build-up material and both types of posts, but it was not significantly different from that in the Ar group. Liston *et al.* (1993) reported that the helium plasma in this mixture strongly emitted VUV radiation, which could have introduced a subsurface cross-linking layer. This layer then acted as a barrier against diffusion of LMW species from the polymer bulk to the surface. On the other hand, this layer could have reduced the thermodynamically driven reorientation of polar moieties away from the surface into the subsurface (Grace and Gerenser, 2003), which meant that surface energy might still have remained. Moreover, as a result of surface bombardment by the energetic species of helium plasma, selective bond breaking could have occurred.

Subsequently, with N_2 plasma treatment in this study, the nitrogen functional groups could have been easily induced on the surface and become more stable over time. These findings were in agreement with those of Grace and Gerenser (2003), who pointed out that the degree of incorporation of new functional groups with reactive/inert gas mixtures, depended on the efficiency of the VUV radiation emitted by the gas.

With the FRC posts, the active sites on the polymer surface and the base monomer of the composite core build-up material were the same. Therefore, chemical interaction between the functional groups and/or free radicals in both materials occurred and resulted in high tensile-shear bond strength. This was reflected in the mixed adhesive/cohesive failure mode, resulting in exposure and delamination of fiber from the post. For the DT posts, the polymer matrix was epoxy resin which was completely different from the composite core build-up material. The epoxy resin is a highly cross-linked material, such that chemical interaction between the plasma-treated post and the composite core build-up material was difficult to achieve. It is interesting to observe that the mixed failure mode exhibited by this group demonstrated low tensile shear-bond strength. This might stem from the poor bond between the quartz fiber and the epoxy resin or surface topography of the post.

Based on the results obtained in this study, the null hypothesis that either the post or plasma treatment has no significant influence on the tensile-shear bond strength between the fiber-reinforced composite post and the composite core build-up material was rejected.

4.2 Discussion of part 2

In this part, three parameters, including the gas pressure, the discharge power, and the treatment time were evaluated since all of them directly had influences on the density and the energy of ions impinging on the post surfaces (Yun *et al.*, 2004) which subsequently involved in reaction of the free radicals (Liston *et al.*, 1993). Basically, gas pressure in this study represented the gas content of helium and nitrogen in the chamber. Obviously, it is expected that with the highest gas pressure and the highest discharge power, the highest intensity of energetic species should be induced and then resulted in the highest reaction of the free radicals. According to this condition; the highest tensile-shear bond strength should be obtained. However, in this study there were no significant differences in tensile-shear bond strength among all of the gas pressure groups and the discharge power groups. The possible reason is that the overall results of operating the plasma-generating system with different gas pressure may provide the same level of radical formation and functionalization. This assumption was in agreement with those of Yun *et al.* (2004) who demonstrated that at the lower chamber pressures, the mean free paths of the ions and electron are longer, and the ions can strike the surface with a relative low loss of kinetic energy, resulted in high generation of radical. At the high pressure, however, the intensity of collisions between the ions and the neutral molecules increases, with the particles losing kinetic energy before colliding with the surface, resulting in low generation of radicals. At too low gas pressure, the number of particles (neutral molecules) is low and the generation of ions is less, since ions are generated from the collision of electrons with neutral molecules. Even if the ions strike the surface of the polymer without loss of kinetic energy, the number of collisions between the ions and the surface is not high and there are not enough radicals formed on the surfaces (fig. 26). A radical can generate the reaction in several ways: by ejecting another radical to form a double bond; by adding a molecule to form a different radical, by termination with another radical, generally to form a crosslink; or by migration along the polymer chain to an unsaturated position to form a stable allyl radical (Hall *et al.*, 1972). In the present study, varying the discharge power at 25 W and 75 W did not significantly increase the tensile-shear bond strength for both types of posts when compared among
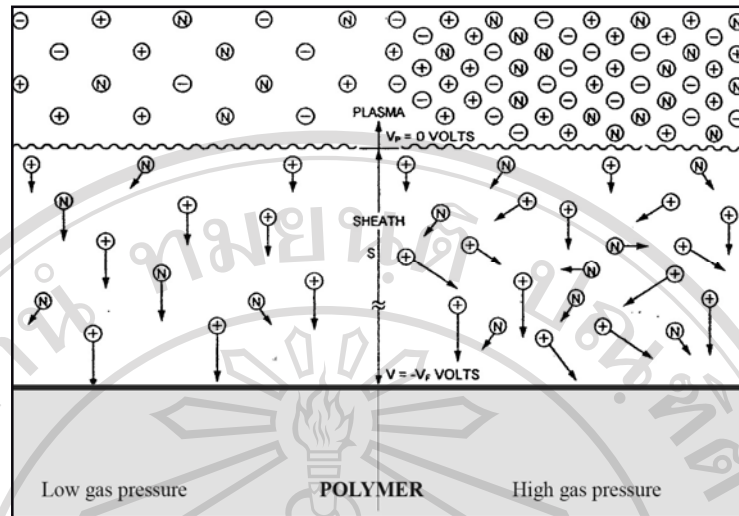
Figure 26 Ion collisions in a sheath between the plasma and a workpiece. The low-pressure regimen (left side), the mean free paths of ions are longer than the sheath thickness (S), and the high-pressure regimen (right side), the mean free paths of ions are shorter than the sheath thickness causing by the increasing in collisions between the ions and the neutral molecules (modified from Roth, 2001).

their treatment groups. The possible reason is that the maximum values of an incorporation of the reactive functional groups into the post surfaces for three different discharge powers would be the same within the treatment time for 10 minutes. The higher discharge power may need shorter exposure time to reach maximum uptake of functional group and then level off. In contrast, the lower discharge power need longer exposure time to reach maximum level, however in this study, 10 minutes of exposure time was adequate. This result was in line with Pittman *et al.* (1998) who pointed out that with different power level, the higher power level of plasma treatment consumed shorter exposure time for maximizing the acidic functional groups uptake on PAN-base carbon fiber and then the uptake went down slightly for longer exposure, whereas the lower power level need more exposure time in order to reach the maximum concentration of acidic functional groups. France and Short (1997) mentioned that exposure of the samples to the atmosphere after plasma treatment could initiate functionalization through the reaction of oxygen with free radicals. However, this process will reach a saturation level, which is the point at

which no more oxygen is incorporated on further treatment. The similar process may happen in the present study and the saturation of functionalization could be obtained with 10 minutes for each discharge power. However, for the DT posts, the discharge power at 50 W resulted in the highest tensile-shear bond strength probably due to the limited functionalization on the surface of the DT posts that was epoxy resin. Thereby, this level of discharge power was adequate for the DT posts.

For the FRC posts, the selected discharge power was 75 W due to the chemical structure of FRC itself. FRC post composed of TGDMA and UDMA which contained dimethacrylate at the chain end groups (fig. 27) whereas DT post contained oxirane structure (epoxy functionality) at the chain end groups (fig. 28). As mentioned earlier, plasma treatment is a modification process that is restricted at the top most layer of the surface of the treated material. Therefore, only polymer chains which located near the surface of the polymer materials take part in the plasma treatment, and polymer chains locating at deep layers from the surface never contribute to the modification (Inagaki, 2007). Inagaki (2007) demonstrated about the treatment of poly (oxybenzoate-co-oxynaphthoate) with different kinds of plasma and found that the concentration of the chain end groups had significantly influenced on the bond strength between this material and copper metal. Chain end groups are more mobile than the polymer chains, due to large free volume. As a result, the authors suggested that functional groups such as nitrogen-containing groups formed at the chain ends will contact and interact more tightly with copper metal at the film surfaces than the functional groups formed at the middle of the main chains. It was concluded that chain end groups could contribute effectively to the adhesion. In the present study, if the functional group at the chain ends plays a major role in bond strength of the post, the energy need to break bond at the chain ends for radical formation and functionalization must be considered. Bond energy of C–H at chain end of dimathacrylate group is around 414 KJ/mol, whereas bond energy of C–O in the chain end of oxirane structure is around 356 KJ/mol (ราณี, 2552). According to the difference in bond energy; bond breaking at the chain ends of FRC post should required more energy than in DT post, consequently, a higher discharge power for plasma treatment for FRC post than DT post was anticipated.
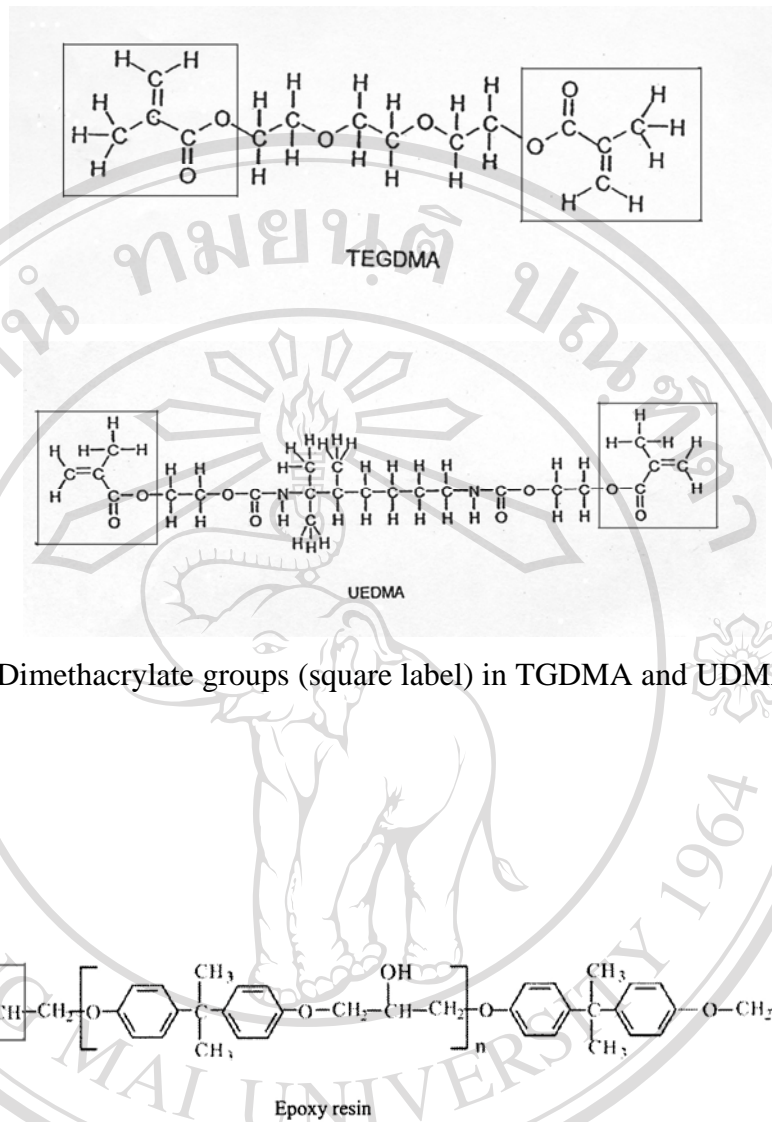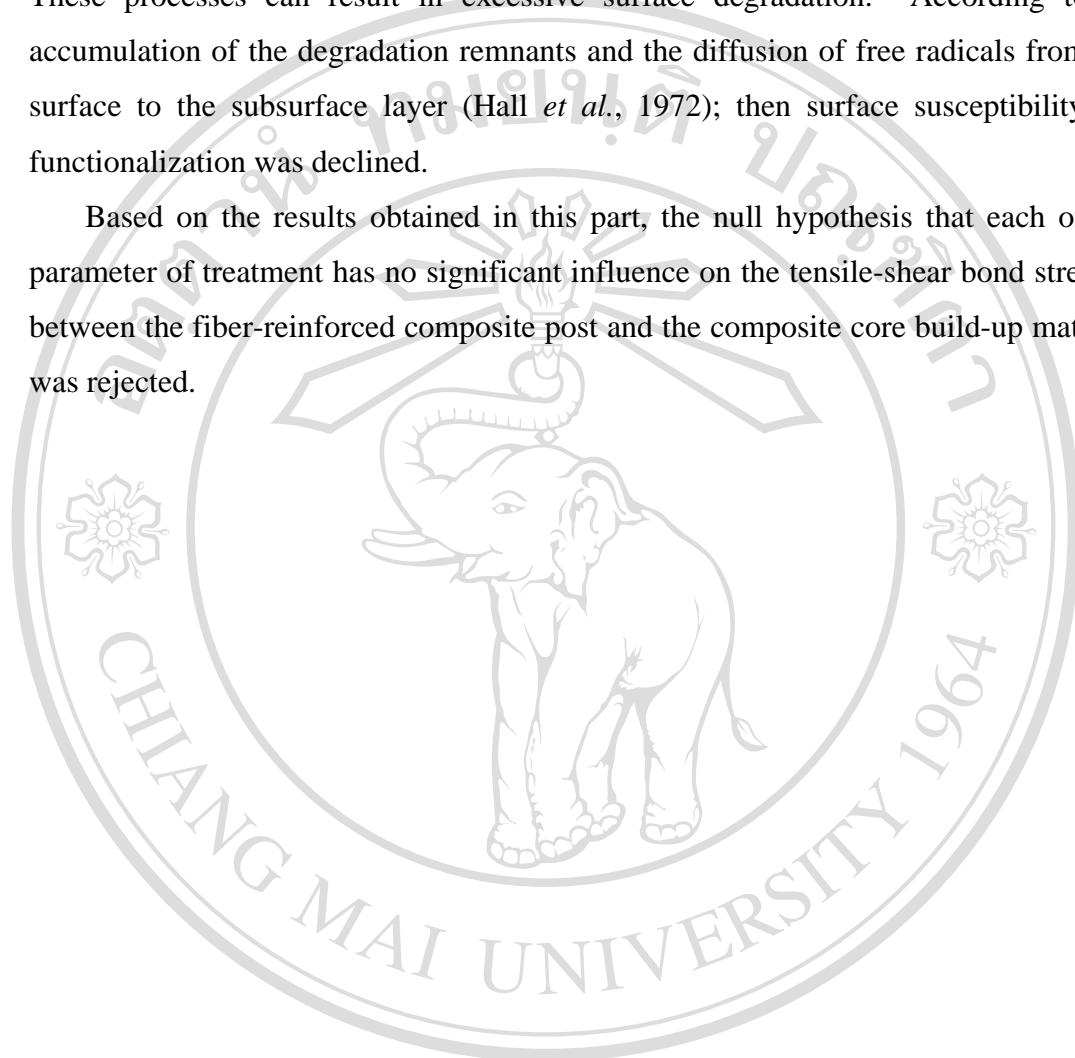
Figure 27 Dimethacrylate groups (square label) in TGDMA and UDMA of FRC post.

Figure 28 oxirane structure (square label) of epoxy resin of DT post.

In the third step of this study, gradually increase the treatment time influenced the tensile-shear bond strengths for both types of the posts, however the DT posts need more treatment time to maximize the tensile-shear bond strength than the FRC post may be due to the lower discharge power in the DT post groups. The increase in the tensile shear bond strength may cause by rapid introducing cross-linking subsurface layer on the polymer surface and the elimination of LMW fractions (Hall *et al.*, 1972). In contrast, longer treatment time tended to decrease the tensile-shear bond strength, probably due to an increase in chain scission and LMW species diffused to the surface. Generally, the dimension of the polymer chain which serves as a primary

nucleus is expected to be able to re-dissolve and reform repeatedly. The shorter chains than the primary polymer chain, can only be dissolved (Rusu *et al.*, 2007). These processes can result in excessive surface degradation. According to an accumulation of the degradation remnants and the diffusion of free radicals from the surface to the subsurface layer (Hall *et al.*, 1972); then surface susceptibility for functionalization was declined.

   Based on the results obtained in this part, the null hypothesis that each of the parameter of treatment has no significant influence on the tensile-shear bond strength between the fiber-reinforced composite post and the composite core build-up material was rejected.

4.3 Discussion of part 3

In this study, the storage condition of the specimens in water at 37 ^{o}C for 7 days was selected because this condition was closely matched to the oral environment. The results of the present study demonstrated that when the specimen was stored in room temperature, plasma treatment increased tensile-shear bond strength between the FRC post and the composite core build-up material as the treatment time increased. However, in hydrothermal condition, the tensile-shear bond strength was dramatically decreased, particularly in medium to long plasma treatment time (3-30 minutes). It was interesting that with the short plasma treatment time (30 seconds-1 minute), there was no significant different in bond strength between the posts that storage in room temperature and in hydrothermal storage condition and was not different from the control group. It may be implied that too short plasma treatment cannot enhance bonding efficiency of the FRC post, possess inadequate energy to generate energetic species for radical formation. In contrast, increasing treatment time also increase bond strength of the post, however, this bond strength was suppressed by hydrothermal condition of any plasma treatment times. Apparently, bonding efficiency of the FRC post was significantly influenced by plasma treatment time only in the room temperature condition but not for the hydrothermal storage condition.

For the DT posts, the bonding efficiency of the post increased with an increasing in treatment time even in room temperature condition or hydrothermal storage condition; however, their increasing rates were different. With the plasma treatment time between 30 seconds–3 minutes, there was no significantly different in bond strength of the post in room temperature condition and in hydrothermal storage condition and this bond strength was still higher than the control value. It may be that with this treatment time there is adequate energy for generating radical and functionalization for the subsequently reaction. At the same time, with this treatment time the degradation of the post may not so high, then bond strength was not interfered by hydrothermal storage condition. Whereas the bond strength of the post with plasma treatment time between 3-30 minutes was significantly decreased by hydrothermal storage condition. This can be assumed that for longer period of plasma treatment time, more degradation of the post may occurred, consequently, hydrolysis at the interface may play a role in decreasing bond strength. Regarding to these

results, bond strength of the DT post was significantly influenced by the plasma treatment time in both storage conditions. These findings were not the same as in the FRC posts since the composition of the polymer matrices of these two types of posts were absolutely different.

The result of section 1: thermal effect and section 2: hydration effect revealed that an increase in storage temperature from room temperature (25 ^{o}C) to 37 ^{o}C in both storage conditions significantly decreased the tensile shear-bond strength of the plasma-treated posts. Tensile-shear bond strength was not significantly influenced by the storage condition. In contrast, the non plasma-treated posts were not affected by an increasing temperature even in wet or dry storage conditions. Regarding to these results it can be assumed that the increasing in storage temperature probably be the main factor of hydrothermal instability that caused the decreased in bonding efficiency of plasma-treated fiber post. Increasing in temperature tended to deteriorate tensile-shear bond strength of the post probably due to the result of the mobility of the polymer chains. This finding was in agree with those of Yun *et al.* (2004), who point out that high temperature helps the polymer chain to move freely and accelerate the surface rearrangement. With plasma-induced nitrogen functional group on the surface of the posts, hydrogen bond between this functional group and the CH_3 groups in the composite core build-up material may occur (fig. 29). Mobility of polymer chains by increasing temperature tend to decrease the strength of the hydrogen bond that is not so stable and strong as covalent bond (Rosen, 1993), subsequently resulted in low tensile-shear bond strength. Pascual *et al.* (2008) demonstrated that temperature is one of the main influencing parameters in the aging of plasma-treated surfaces. Temperature promotes diffusion processes that control the rearrangement mechanism of polar groups and diffusion of LMW materials from the plasma-treated polymer surface toward the bulk material. They also mentioned that plasma treatment is not permanent; it is subjected to an important aging process related with a rearrangement of the polar groups generated during and immediately after plasma treatment. Although their studies involved only the aging mechanism of plasma-treated polymer surface that may or may not be happened at the interface between two materials. However, the present study had revealed that temperature took effect on bonding efficiency between the plasma treated post and composite core
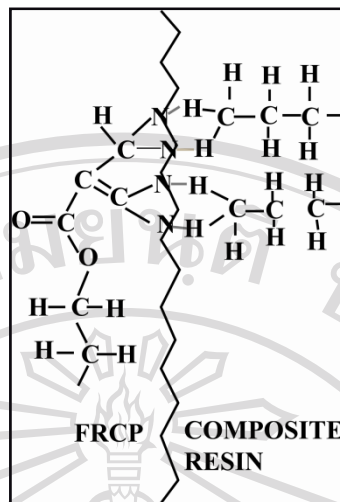
Figure 29 Schematic illustration of hydrogen bond between the induced-functional groups on the fiber-reinforced post and the CH_3 groups in the composite core build-up material.

build-up material. This may be the result of some energetic particles in plasma-treated surface that were not immediately reacted with the functional groups of the composite material took part with aging effect and accelerated the degradation of bond caused by temperature.

Increasing in temperature may also interfere with mechanical interlocking between these two interfaces due to creep and stress relaxation of polymeric materials. According to the method of the specimen preparation; polymerization shrinkage of composite core build-up material could compress this material to adapt to the surface of the post instead of expanding of the polymerization mass due to the rigidity of the metal mold. As the temperature is increased, materials under loads which caused no permanent deformation at room temperature start to creep. Creep is slow, continuous deformation with time. Polymers, too, creep; many of them do so at room temperature. Well above the glass transition temperature (T_g), the polymer is in leathery or rubbery state, and will creep under load (Ashby and Jones, 1980). An increasing in temperature may accelerate creep at the post's surface and then, micromechanical interlock between two surfaces was disrupted.

In this study, it could be pointed out that increasing in temperature had much reversal effect in tensile-shear bond strength in the FRC posts rather than in the DT posts. Difference in the chemical structure of these posts may play a major role in this effect. Polymer matrices of both types of posts can be classified by their reaction to heating and cooling as a thermosetting polymer (Rosen, 1993). Thermosetting polymers are usually amorphous because there is no possible ordering portion of the network structure due to the restriction imposed by the presence of cross-links (Pascault *et al.*, 2002). The polymer matrices of the FRC posts compose of UDMA and TGDMA that usually are linear chain structure whereas the DT posts composed of aromatic ring structure (Laurens *et al.*, 1999). Aromaticity within the polymer back-bone is usually being a structure that invulnerable attack by etching mechanism of the inert gas plasma (France and Short, 1997). Yun *et al.* (2004) reported about the aging that the surface rearrangement due to reorientation and diffusion at the surface can be reduced by limiting the mobility of the polymer chains. The chain mobility mainly occurs in an amorphous region and the mobility in a crystalline region is fairly limited because of an orderly packed structure. Similar mechanism may occur in the DT post that aromatic ring structure probably restrict the mobility of polymer chain when the temperature was raised, therefore the less decreasing in tensile-bond strength was obtained in DT post as compared with the FRC post.

At this juncture, it must be clarified that many important factors come into play in each plasma treatment when it is applied to optimize the adhesive properties of polymers. The present study evaluated the effect of plasma treatment time and hydrothermal effect on tensile shear bond strength between He+N$_2$ plasma-treated FRC and DT posts and composite core-build up material. Hence, further studies on the bonding efficiency between different types of posts with different types of plasma treatment bonded to composite core build-up material are encouraging. Using a more sensitive device such as XPS in detecting a new generated chemical bond in the near-surface of the plasma-treated surface is suggested, since with the FTIR, the probing depth may too deep for detecting chemical changes in the near-surface region (Loyaga-Rendon *et al.*, 2007).

Based on the results obtained in this study, the null hypothesis that either the plasma treatment time or the hydrothermal effect has no significant influence on the

tensile-shear bond strength between the fiber-reinforced composite post and the core build-up material was rejected.