

## **Polymerization of the Dental Adhesives**

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### **ABSTRACT**

**Objective:** The bonding adhesive holds the composite filling to the residual tooth, creating a chain cross—link during the photo polymerization process. In this article we will be discussing the polymerization process under a thermodynamic viewpoint between amorphous structures of the dental market adhesives, the hybrid layer of the residual tooth and the white polymers filling. The thermodynamic can explain the relationship between energy and the effects on the mechanical properties. These results will be the platform of the mechanical properties of these adhesives.

**Significance:** The main significance is that the amorphous structure is present in all six adhesive experiments, showing strong possibilities of bonding with another molecule. The amorphous structure of dental adhesive has intrinsic high entropy and high free Gibbs's energy, thus improving the possibility of bonding with the neighbor's molecules.

**Findings:** The bonding quality is related to the time delay of photopolymerization and it was controlled with the variable etching treatment water evaporation. In addition, it was found that different curing light wavelength sizes could obtain better molecular organization, avoiding internal stress and bonding defect.

### **1. INTRODUCTION**

Normally, the clinicians are not familiar with the variety of polymer materials. The selection of the dental adhesive is determined by the results and familiar brand names; however, the selection may not always be the best one to use in one restorative tooth. This selection can be made, more specifically, if we can clarify the mechanical properties of different dental adhesives. The main objective is to create strong bonds to the residual tooth and to the white composite filling, which is normally some other polymer.

The amorphous structure presented in these experiments creates an ideal molecular bonding environment. There is a thermodynamic relationship between the degree of atomic disorder given by the entropy and the Gibbs's free energy of the amorphous adhesive. This free energy governs the spontaneous chemical reaction of the photopolymerization process; it is not related to the bonding quality. The strength of the restoration will depend upon the bonding between the adhesive and the enamel-dentin surface. The strong ionic bond of the hybrid layer is at the level of the dentine.

Bouillaguet<sup>2</sup> studied the mechanism of the polymerization dependence on the water evaporation in the intertubular and peritubular dentine with the hybrid layer, which is a function of the solvent's presence. In addition, he studied the role of dental adhesive as a sealer. The best sealer represents the perfect bonding with a minimum of

structural defects. These requirements are related to the entropy of the adhesive and to the time delay to initiate the photopolymerization process, which can promote the manipulation of the bonding process.

According to Carvalho<sup>1</sup>, the bond strength with the ability of the primer is to maintain expansion of the collapsed demineralized dentine. This is an environment where the amorphous structure adhesive shows the capacity of diffusion without polymerization in the interfibril collagen spaces. To obtain maximum diffusion in the intertubular and peritubular dentine, the surfaces are required to be wet, resulting in a stronger chemical and mechanical bonding. The process is called self-expansion. The amorphous structure material is the key to control the bonding process.

J.T. Cheng<sup>3</sup> studied the efficiency of the one-step dental adhesive. His article explains the hybrid layer formation based on the amorphous adhesive and bonding mechanism into the intertubular dentine. The result is in favor of the old-fashioned three-step adhesive with etching acid application. The benefits of the three-step adhesive can be explained during the manipulation of the polymerization process with water-air removal from the dentine fibril. With the three-step adhesive, the etching produces more demineralized dentine and a strong bonding link. It allows the hybrid layer to obtain better organization and deeper diffusion, creating more uniform bonding against the tooth and avoiding internal defects and potential leakage. In contrast, one-step dental adhesive creates a weak hybrid layer causing a weak bonding link with low concentration. The variables that will imply time delay are the control of water evaporation and the wavelength size of the curing light before the photopolymerization process.

## 2. EXPERIMENTS, MATERIALS AND METHODS

Six pure bonding adhesive samples were prepared at the clinic of Dr. Michael Barnard, DDS, Fort Lauderdale, Florida, the X-R Diffraction was performed at the X-R Diffraction Lab of Florida Atlantic University, Boca Raton, Florida, under the supervision of Professor Dr. Th. Leventtore, Physics Department. The SEM- EDS experiments were performed at the University of Central of Florida, Orlando, Florida.

This material was selected from the clinical history requested by the office of Dr. Michael Barnard. Manufacturer's brand and assigned names are listed in Table 1:

**Table 1: Market Adhesives**

Assignment	Adhesive Names	Manufacturer
R1	1) One Coat Self-Etching	Coltene Whaledent
R2	2) Optibond Solo Plus	Csds Kerr Sybrom
R3	3) Prime and Bond	Dentply De Trey
R4	4) Adper Single Bond Plus	3M ESPE
R5	5) 1Bond Gluma inside	Heraeus
R6	6) Heliobond	Kulzer,GmbH,Wehrheim Germany

## 3. RESEARCH STAGES

The research first stage is the tooth morphological study, followed by the chemical composition background, environmental boundary condition, and state of decay. All dental restoration treatment variables were revised.

The second stage identifies the structure type and the six pure different adhesive composite fillings chemical composition. The X-R Diffraction, Energy Disperse Spectroscopy (EDS), Scanning Electron Microscopy (SEM) experiments were performed. The third stage was under the control of certain variables; the evaluation of these results was given a practical manipulation approach to the polymerization process. The fourth stage involves the mechanical test results. The fifth stage is the computer simulation. The sixth stage was the discussion and conclusion of the results of the Analysis of Variance (ANOVA).

It will be interesting to give a research results overview, showing some experiments and results were performed in different stages.

### 3.1 X-R DIFFRACTION EXPERIMENT RESULTS

The X-R Diffraction experiment starts with a glassy sample material. The experiments were a repetition of each sample adhesive and all of them showed an amorphous structure pattern curve, classified based on the conventional interpretation. The curve profile shows no relevant intensity peaks or absorption counts. It presents minor or non-linearity Bragg's reflection, poor background linearity, non-intensity periodicity, showed in Fig 1. The peaks of these patterns represent the elements of the chemical composition, showing the phases at the bottom of the different plots. The manufacturer specification shows that all of these adhesive compositions have methacrylate derivatives monomers in complete molecular disorder.

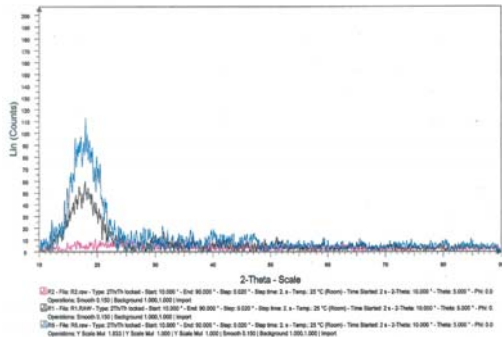


Fig.1 X-Diiffraction. Plot R1, R2, and R6

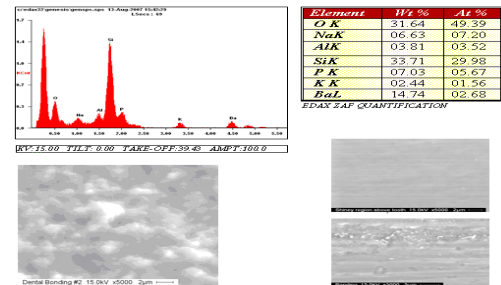


Fig 2. EDS- SEM of R3 adhesTooth and Bond.

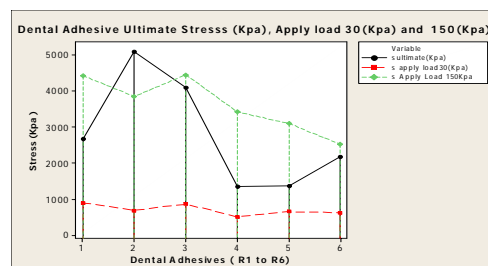
### 3.2 SCANNING ELECTRON MICROSCOPY (SEM) AND ENERGY DISPERSE SPECTROSCOPY(EDS)

The EDS-SEM is performed simultaneously. The SEM caption Fig 2; shows micro-disorder distribution and the topographical and morphological details of the adhesive R3 surface. It is the platform for the dental adhesive related to the entropy and the negative Gibbs's free energy, promoting the spontaneous polymerization bonding. The EDS Fig 2 graphic curves show the chemical composition and their weight percentage analysis. The six adhesives with EDS caption are the same basic methacrylate monomer elements. The relevant part of this monomer, it creates the free radical in the photo polymerization process.

The computation of free energy and constant K will be our sensors in the rate of photo-polymerization. This will be manipulated for the benefit of the bonding. The chemical element role is crucial to determine the energy, electronegative and affinity level, predicting the type of possible bond and time delay that we can apply, giving better atomic organization or distribution of the hybrid layer in the dentine tubules.

### 3.3 MECHANICAL TEST AND COMPUTER SIMULATION

The Mechanical Test Traction and Pure Shear were performed on a real tooth specimen at the Ocean Engineering Lab, Florida Atlantic University. The mechanical test shows the real meaning of the bond mechanical properties. It gives real data about maximum tensile and shear stress, obtaining the Young modulus, Shear modulus, Poisson Ratio, Strain, and Strain Energy for different adhesives, as shown in Fig 3. The direct impact test is very weak.



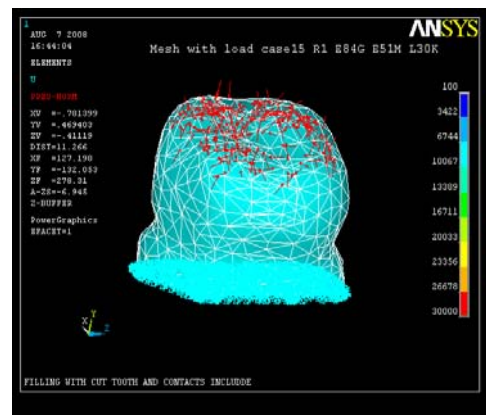
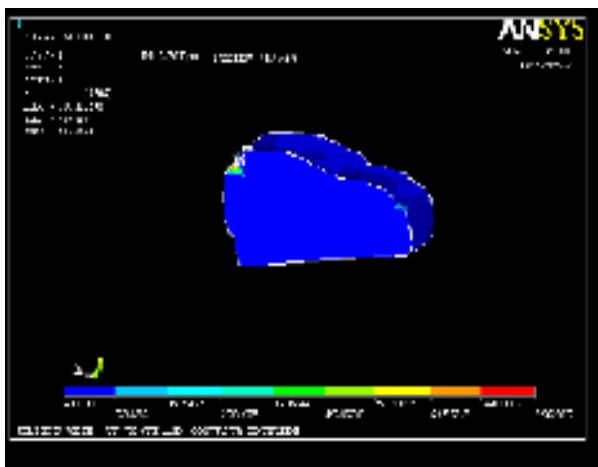
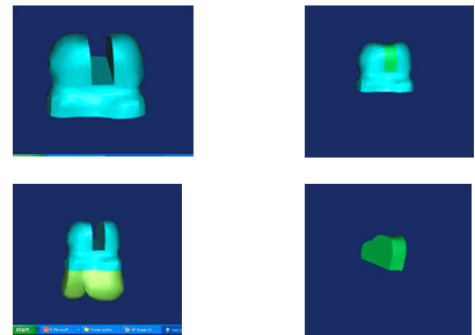
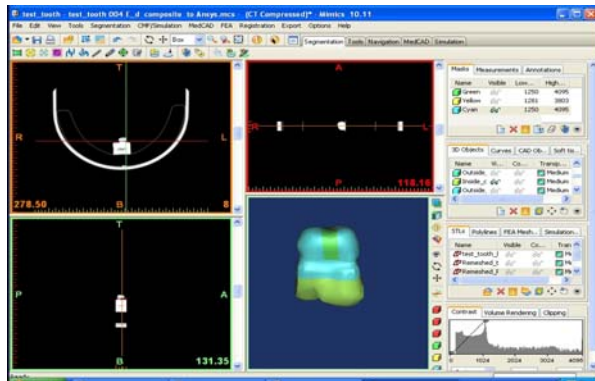
**Figure 3 Tensile Stress, Young modulus Rupture Stresses**

### 3.4 COMPUTER SIMULATION

The forth stage is the computer simulation. It starts with a CT tomography of the real tooth at the CT- MRI Well Center, Lantana, FL. The data image used in the Ansys computer simulation will be obtained from the Computer Tomography Scanner Image. This type of 3-D image works with DICOM medical files. These files need to be converted into engineering files using the Mimics and Magics program. as shown in the Fig 4.

Mimic and Magics, create the geometry. To obtain this simple geometry it is necessary to pass for all kinds of different ones. It tries to find the most critical geometry that represents the maximum stress and create the maximum risk to break the bond. Any volume that uses 90-degree angle in the geometry creates maximum stress concentration in boundary of this angle surfaces.

The geometry will be exported to the ANSYS program using Finite Elements Analysis to perform a general stress analysis. The following computer simulation information was obtained with the Finite Elements Analysis using the experimental data obtained from the mechanical test:



#### 4. ENERGY OF AMORPHOUS MATERIALS

The polymer chain in the dental adhesive is the repeating of many structural units called monomers. There can be a different configuration in function of the chemical bond. The change of the state of the matter is given by these three following equations:

Gibbs's free energy at constant temperature is given by

$$\Delta G = \Delta H - T \Delta S$$

Enthalpy at constant pressure and defined like heat content is given by

$$\Delta H = \Delta E + P \Delta V$$

Helmholtz free energy at constant temperature given by

$$\Delta A = \Delta E - T \Delta S.$$

All of these equations are state functions, which do not depend on the path of the process. The most important in polymers is the Gibbs's Free Energy equation at constant temperature that governs the general polymerization process, especially the thermo process and photopolymerization. The arguments explain the process from the thermodynamics viewpoint; this is exactly the information that we need to understand how favorable the amorphous material is in the dental adhesive restoration.

The solubility of one component in another is governed with Gibbs' equation

$$\Delta G_m = \Delta H_m - T \Delta S_m \quad (1)$$

$\Delta G_m$  = Change Gibbs's Free Energy of the mixed.

$\Delta H_m$  = Change in Enthalpy of the mixed

T = Absolute Temperature

$\Delta S_m$  = Change in Entropy of the mixed

The negative value of the free energy indicates that the process spontaneously changes. The change in Entropy by the temperature is positive. It is necessary to increase the entropy with the atomic or molecular disorder, that way the free energy Gibbs' is negative. If the Enthalpy, heat content of the mixing is small and positive, then being negative can depend on the component. The amorphous dental adhesive is in complete atomic disorder. If  $\Delta G$  is negative, the change is favorable, and in this case, bonding polymerization occurs spontaneously, but if it is positive, no change occurs, then large energy is needed to force change. If it is at zero then it is in equilibrium. If the  $\Delta H$  is negative, energy will release, positive energy to supply the system in order to force the change. If  $\Delta S = 0$ , there is no change in the molecular configuration,  $T \Delta S$  is related to the configuration in the space. If the Entropy is positive then the change occurs spontaneously in the molecular system. The change of the state produces changes in the value of G, H, S, and the properties.

The synthesis of the polymers is related to the thermodynamics conditions and kinetic of polymerization, which affects the molecular weight and the polydispersity index. The thermodynamic of the chain polymerization is governed by the Gibbs' free energy equation, function of the equilibrium constant of polymerization K. This is exactly what happens with polymerization in the intertubular and peritubular dentin, infiltrated with the collagen fibril, and the dental adhesive polymer. Therefore, a wet environment gives an advantage to manipulate the polymerization process. After the water has evaporated, the polymerization process starts having no time to organize in a uniform mix. This way this mixture has different concentration contraction gaps, shrinkage, internal stress, possible leakage and infections. The control of the polymerization in dental restoration is a challenge but it is directly related to the water presence and the negative Gibbs's Free Energy of bonding given by:

$$\Delta G = -R T \ln(K) \quad (2)$$

K = Equilibrium constant of polymerization or constant of polymerization

R =  $1.38 \times 10^{-23}$  J/deg-molecule, Boltmann's constant

T = Absolute Temperature

We can solve for K, constant of polymerization we have:

$$K = e^{-\Delta G/RT} \quad (3)$$

The Entropy is always positive in the Gibbs equation. When the Enthalpy is zero, the Gibbs' energy is equal to the Entropy change by the temperature. In the hybrid layer, the entropy is high. The Statistical thermodynamics of mixing, the Entropy is calculated by counting distinctive arrangement in the space  $\Omega$ .

The Boltmann's equation relate to the Entropy with the distinguishable arrangement in the space

$$S = k \ln(\Omega) \quad (4)$$

$\Omega$  = Distinguishable arrangement in the space.

$k$  = Boltmann's constant/Avogadro number, Boltmann's constant in the molar based,  $k=R/N_A$

Boltmann's equation can also define the variation of Entropy, in function of the constant of polymerization  $K$  and the Boltmann's constant  $R$  given by:

$$\Delta S = R \ln K \quad (5)$$

The calculation of Gibbs' free energy with zero enthalpy of the mixing in one ideal solution is the sum of the components free energy. The Gibbs' free energy equation coming from (1) is given by:

$$\Delta G = - T \Delta S \quad (6)$$

The Boltmann's relation also can reach the Entropy per unit volume, using the transformation to volume fraction, based in number of molecules and mole fraction. Solvent  $\phi_1$ , adhesive  $\phi_2$  and polymers volume fraction. Change to molar basis  $k=R/N_A$ , where  $N_A$  is the Avogadro's number,  $n_i$  is the number of moles,  $n_i = N_i/N_A$ , where  $N_i$  is number of molecules and the variation of Entropy given by :

$$\begin{aligned} \Delta S &= -k (N_1 \ln(\phi_1) + N_2 \ln(\phi_2)) \\ \Delta S &= -R (n_1 \ln(\phi_1) + n_2 \ln(\phi_2)) \end{aligned} \quad (7)$$

$n_i = N_i/N_A$

$k = R/N_A$

$R = 1.38 \times 10^{-23}$  J/deg-molecule, Boltmann's constant

$N_A = 6.022 \times 10^{23}$  mol<sup>-1</sup>

$\phi$  = Arrangement space term of solvent  $\phi_1$ ,  $\phi_2$  polymers, volume fractions

$N_i$  = Number of molecules solvent  $N_1$  and polymer  $N_2$

Replace the variation of Entropy (7) into the (6) the Gibbs's Free Energy is given by

$$\Delta G = RT (n_1 \ln(\phi_1) + n_2 \ln(\phi_2)) \quad (8)$$

Just to clarify and define the process of interface, the constant of polymerization  $K$  also represents the ratio of the rate forward and reverse of polymerization used in thermoprocess being in function of the ceiling temperature  $T_c$ , when it is reached, the monomers cannot be polymerized and start spontaneously de-polymerization. The dental adhesive photo polymerization is not dependent on the temperature, but if the temperature is lower polymerization is better, the photo-depolymerization process will not exist.

If we know the value of  $\Delta G$  from tables related to  $K$  value and solve for  $K$  with the equation  $K = e^{-\Delta G/RT}$  Example  $\Delta G = -1$  KJ/mol the value of  $K$  is 1.5, positive at 298 Kelvin, it means that there are more products polymerized adhesive than the reactive at equilibrium. The dental adhesive becomes stronger and has a high rate of bonding when the Constant of Polymerization ( $K$ ) is greater than one.

Almost all dental adhesives and primers the chemical composition is given by methacrylates derivatives, the scenario that shows the kinetics of the synthesis reactions under the free radical polymerization.

The equation that controls the polymers, which grow under the chain reaction of free radical of polymerization, is given by:

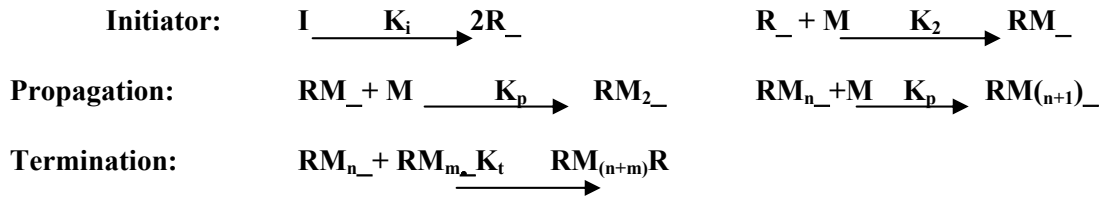
$$M_n + M = M_{(n+1)} \quad (9)$$

$M_n$  = Monomer with free radical.

$M$  = Molecule of Monomer or monomer unit in polymer chain

$M_{(n+1)}$  = Polymers

The notation with the little bar stands for “the end of the chain with a free radical polymerization”. The Kinetic of polymers change under the free radical three step polymerization with the Initiator (I), Propagation (p) and Termination (t), the chain link grow up and given by



$K_i, K_p, K_t$  stands for constant of initiator, propagation and termination of polymerization Use table value  
 $M_n$  and  $M_m$  stand for Polymer of degree of polymerization n and m.

$RM_{\bar{\cdot}}$  = Free radical Monomers

I = initiator element

R = Initiator radical

The brackets in the equations represent concentration. The rate of polymerization is given by:

$$R_p = K_p (K_i/K_t)[M][I]^{1/2} \quad (10)$$

[M] = The equilibrium monomer concentration or molecule of monomers in the polymers

The kinetic chain length change is given by

$$\nu = R_p/R_i = R_p/R_t = K_p [M]/2(fK_iK_t [I])^{1/2} \quad (11)$$

f = initiator efficiency factor, fraction of initiator molecules ~ 0.8

$R_p$  = Rate of propagation

$R_i$  = Rate of Initiation

$R_t$  = Rate of termination

The value of degree of polymerization  $DP_n$  is given by

$$DP_n = 2\nu \quad (12)$$

$DP_n$  = Degree of polymerization

$\nu$  = Kinetic chain length for termination by combination.

PDI = Polydispersity index value 1.5 -2

The Gibbs's energy,  $\Delta G$  needs to be < zero. In a condition, which lowers the enthalpy or raises the entropy in a particular specimen, it could cause the system to shift the equilibrium in favor of the specimen. Therefore, the polymers will grow creating the cross-link polymerization between the hybrid layer and the composite filling or residual tooth. Using the translational and rotational degree of freedom of the system, accompanied with the Entropy change, the polymerization is associated with the reaction where many molecules form one big molecule. This explains the link mechanism of the monomers with polymers and their behavior. Many polymers association reduced the entropy close to being < 0, negative. The polymerization has to do when the  $\Delta H$  is sufficiently negative that compensates for the entropy loss, which gives a negative  $\Delta G$ . The polymerization is better in low temperature, when the  $T\Delta S$  is small.

Observing the above chain-link polymerization and with a simple parallel, it will be easy to understand the photopolymerization process.



$R_{\bullet}$  = Free radical

I = molecular initiator

The Rate formation of active center has a factor 2 representing the number of chain are connected or the number of radicals formed from one molecule of initiator and given by:

$$R_i = 2f k_d [I] \quad (14)$$

$$R_i = d[R_{\bullet}]/dt = -d[M_{\bullet}]/dt \quad (15)$$

$k_d$  = Rate constants for initiator of disassociation.

f = initiator efficiency, it is the fraction of first free radical R•

R• = free radical.

Factor [R•] = concentration of free radical,

The rate of polymerization or rate of consumption of monomer for initiation by thermolysis is given by:

$$R_p = - [dM]/dt = K_p [M] (R_i/2k_t)^{1/2} \quad (16)$$

$$R_p = K_p (fK_d/K_t)^{1/2} [M] [I]^{1/2} \quad (17)$$

[M] = molecule of monomers in the polymers

R<sub>i</sub> = fraction of primary free radical R that initiates the polymerization, Rate of formation of active center

**Photolysis:** The hybrid layer and the all restoration normally use the cure light and the common method of initiation is the photoinitiation, given by:



The photochemistry deals with the interaction between the light and matter to induce chemical reaction. The dental adhesives chemical reaction is induced with the electromagnetic spectrum and wavelength range of the ultraviolet and visible light. Two molecules in special arrangement select this kind of initiation of polymerization, the absorption of the electromagnetic energy given in the equation (19) and (20) stimulate the molecules. The Photon Energy is given by:

$$h\nu = hc/\lambda \quad (19)$$

Where the photoinitiation energy or the electromagnetic energy absorbed and then temporally stored like stimulated electron and then move very fast along and among the chain ~100ps, creating the free radical or ions and initiate the photopolymerization, the energy is given by :

$$\Delta E = nh\nu = nhc/\lambda \quad (20)$$

h = 6.626 x 10<sup>-34</sup> Js Planck's constant n = integer

c = 2.99979 x 10<sup>8</sup> m/s Velocity of light

λ = Wavelength of the incident light. ~ 500nm in the dental adhesive light cure

Sometime appear the quenching phenomenon based in two molecular interactions, one is excited and the other is quenched or ground state, in an electronic relaxation system.

The monomer with photopolymerization absorbed light producing free radical or ions and the chain of propagation and termination is not affected, in this case can use the photosensitized to activate the polymerization. The most important advantages in the dental adhesives field are the initiation process can start in large range of temperature.

Two-photoinitiation light absorption with monomer molecule stimulated electron and give a free radical, photoinitiation rate of initiation of radical formation is independent of the temperature and proportional to the monomer concentration and given

$$R_i = 2 \Phi \epsilon I_0 [I] \quad (21)$$

$$R_p = K_p (\Phi \epsilon I_0 / K_t)^{1/2} [M] [I]^{1/2} \quad (22)$$

I<sub>0</sub> = Intensity of the incident light; Cure light

ε = molar absorption of the initiator

Φ = quantum yield in photochemical, it is the same of initiator efficiency f.

The quantum yields (Φ) are number of molecules of the product or reactant consumed divided by quantum of light absorbed. In photopolymerization the quantum yields for initiation is the number of chain or number monomers molecules divided by quantum light absorbed, given by the rate

$$\Phi_p = \text{Rate of chain initiation} / \text{Rate of light absorption} \quad (23)$$

The photo initiation absorption disassociate in two monoradicals Φ with values between 0 to 2, the polymers require long chain processes Φ<sub>p</sub> is order 10<sup>2</sup> to 10<sup>3</sup>. The Amorphous dental adhesives have favorable condition to propagate the bond with others substances with low temperature in dental restoration under photopolymerization processes even adding photosensitizers to help the photoinitiators start the polymerization.

The propagation in photopolymerization is related with the formation of σ bond in the new bonding restoration from a less stable π-Bond of the Hybrid layer, composite filling and residual tooth.

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## 5. DISCUSSION

The result of the X-R Diffraction experiments of dental bonding samples shows the pattern of amorphous structure, which means it has no form and is without a particular structure. The atoms or molecules have a random spatial arrangement. While in atomic disorder, they are closely packed. Normally, the amorphous material's property is similar to that of the transparent glass plate, acrylic (polymethacrylate), and Lexan (Polycarbonate). However, bonding occurs with a good elastic mechanical property; especially to the sheer stress.

The dental polymers material looks like liquid structure in the diffraction patterns, but it is really a solid. When entering into the solid state with the light curing, the liquids physical properties are changed with the photo polymerization process, even is better at lower temperature. The rate of photopolymerization is very high, similar to that of the thermoprocess; time is not allotted for the molecules to organize in order to create crystalline structure. The amorphous structure with atomic disorder with produces high entropy in the atomic level. This creates an ideal environment for bonding to occur with other neighbor's molecules.

Sometime the monomers need to add photosensitizers to absorb light with specific wavelength disassociate in free radical or give energy to the monomers. The photosensitizes produce radicals or ions when absorb ultraviolet and visible light, lower temperatures reaction the most important advantages in the dental adhesives field, the initiation process can start in large range of temperature.

The amorphous adhesives are an energy-loaded material with a disposition to create the convenient condition of free radical polymerization bonding. It attempts to get more stable at a lower energy level; especially with the covalent bond sharing electron, ionic bonding, Van der Waal's bond, and mechanical interlock.

Normally the covalent bonding is created with two no metals, they share electrons because both want to gain electron, trying to fill the valence shell. The dental adhesives are polymers molecules connected by the covalent bond; they are a large molecules mass composed with repeating monomers unit's structure.

The chain chemical reaction is based on the catalyst reactant represented by the free radical; this component with the free electron can form a covalent bond with other molecule, creating linear, branches or cross-linked polymers structures. The strongest chemical bonds or intramolecular forces are function of the number of the electrons involve in a bond orbital, typically is multiples of two, four or six, they loves to be paired showing lower energy; beside is function of the bond length normally given in pm or Armstrong and the bond Energy in KJ/mol. The elements with the electro-negativity difference, the smaller is difference, more covalent properties has the bond and the distribution of the orbital path available to the bonded atoms. The chemical composition, especially electronegativity-affinity, balance stoichiometry, and molar calculation represent practical monomers bonding possibilities

According to this theory, there are advantages in the mechanical properties of dental bonding adhesives, if the bonding system can be manipulated under kinetic of polymerization using the appropriate size of the wavelength, thermodynamics conditions and rate of water evaporation of the mixture of desmineralized collagen dentin, also called "the state of the hybrid layer".

## 6. CONCLUSION

One important inference is the dental adhesives use of the photopolymerization process and no dependence on temperature. At a low temperature, the rate of polymerization is high. Another important inference is about the possible manipulation of the initial polymerization process by controlling the etching vaporization of water of the hybrid layer, creating an ideal environment for bonding against the residual tooth and the white composite filling. This kind of inference can be present with advantages in the field of dental restoration. Some results we can be obtained with a mechanical test, showing mechanical properties of the six different adhesives that are related with the quality of the polymerization under load.

From an energy viewpoint, the value of  $\Delta G$  free energy is negative and can get numerical values from the tables. Therefore the constant polymerization  $K$ , given by the equation (3), must be a positive value, meaning that there are more products, polymerized adhesive, than reagents monomers from white composite filling, hybrid layer and residual tooth, without polymerization. In order to get strong bonding, the synthesis chemical reaction needs a positive value of the polymerization constant  $K$ , ideal  $K$  more than one.

Under this theory, the system can practically be manipulated by the kinetic chemical reaction with the rate in which water is evaporated throughout the mixture of desmineralized collagen dentin. Also the bonding case of the hybrid layer, the filling composite and residual tooth, is controlled by the curing light with the photoinitiators and photosynthesizers that give start to the photopolymerization in the chain –link photochemical reaction. Given this complex scenario the dentist would decide variable control or manipulation of the variables depending on the type of restoration. The dentist would also need to consider the molecular organization time in order to avoid shrinkage, internal stress, concentration contraction gaps, and possible infections that would produce a leakage. The control of polymerization in dental restoration is a challenge, but it is directly related to water presence and the negative Gibbs's Free Energy of bonding chain link polymerization.

The variables that will imply time delay are the control of water evaporation and the wavelength size of the curing light before the photopolymerization process. The element atomic number, Ionization energy and element atomic radii affect the density distribution. Normally, dental adhesives use stress absorbers, adding nanosized filler particles into the matrix to improve strength. Fillers are very small radii and need time delay to flow through the interfibril collagen spaces to create a hybrid layer. The fillers distribution is not uniform; and hybrid layer regions have different density distribution and mechanical properties. This no uniform distribution causes a weakness in the bonding link. Therefore, the fast chain-reaction photopolymerization affects atomic organization and is responsible for internal stress or failure restoration

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