Structure of Dental Adhesives

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ABSTRACT

This article discusses the results of the structure type of six market dental adhesives obtained from the X-R Diffraction, Energy Disperse Spectroscopy (EDS) and Scanning Electron Microscopy (SEM) experiments. The amorphous structure was one of the results in these experiments. In addition, it will be discussed the bonding advantages of this type of structure in dental restoration.

The significance of the amorphous structure of dental adhesive is the intrinsic high entropy and high free Gibbs's energy, thus improving the possibility of bonding with the neighbor's molecules. The thermodynamics can explain the relationship between these energies and the effects on the mechanical properties. This bonding adhesive holds the composite filling to the residual tooth, creating a chain cross-–link during the photo polymerization process. By controlling this process, shrinkage can be avoided and better strength is obtained in the bonding restoration. The dental adhesive creates bonding very quickly with a higher contraction gap and there is no time to organize the structure. The one-step production that

1. INTRODUCTION

The clinician normally is not familiar with the polymers terms and the market dental adhesives. The selection is determined by experience and brand name. Specific selection can be clarified by knowing the mechanical properties of dental adhesives. This is an advantage that it is reflected on the adhesive selection for specific class of the direct restoration. The goal of the adhesive is to create strong bond against the residual tooth, as well as the white composite filling. The amorphous structure of the dental adhesives presented in the 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 photopolymerization process, not related to the bonding quality. The strength of the restoration will depend on the bonding between the adhesive and the enamel- dentin surfaces; the strong ionic bond of the hybrid layer is at the level of dentine.

According to Bouillaguet[2], who studied the mechanism of the polymerization's dependence on the water evaporation in the intertubular and peritubular dentine with the hybrid layer; that is a function of the solvent's presence. In addition, he studied the role of dental adhesive as a sealer layer. The best sealer represents a perfect bonding with a minimum of structural defects. These requirements are related to the entropy of the adhesive, and the time delay to initiate the photopolymerization process, which can promote the control or manipulation of the bonding process. In this article the polymerization process describes the control of the presence of water. When the water is removed, the amorphous adhesive promotes the spontaneous polymerization.

According to Carvalho[1], 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, 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[3] 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. In contrast, one-step dental adhesive creates a weak hybrid layer and therefore a weak bonding link with low concentration.

This article discusses the effects of the polymerization time delay on the dental bonding quality. 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. The variables that will be discussed are the control of water evaporation and the wavelength size of the curing light before the photopolymerization process (implies time delay). The chemical composition, especially electronegativity–affinity, balance stichiometrie, and molar calculation represent practical monomers bonding possibilities.

The element atomic radii affects 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 distribution causes a weakness in the bonding link. The fast polymerization affects atomic organization and is responsible for internal stress or failure restoration.

In addition, this article discusses the following experimental results obtained from the X-R Diffraction, SEM and EDS experiments.

2. EXPERIMENTS, MATERIALS AND METHODS

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

This material was selected from the clinical history requested by the office of Dr. Michael Barnard. Manufacturer 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 Dental specialist
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. ENERGY OF AMORPHOUS MATERIALS

The experiment result shows an amorphous structure in dental adhesives, which is a favorable condition of the bonding adhesives. The Gibbs's free energy equation relates to the adhesive atomic disorder given by the entropy and energy that causes spontaneous bonding. It governs the polymerization of the dental adhesive based on the change of state of the matter at a constant temperature. The solubility of one component in another is given by the standard Gibbs equation; this is only the standard state condition.

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \tag{1}$$

ΔG^0 = Change standard Gibbs's Free Energy.
ΔH^0 = Change standard Enthalpy of mixed
T = Absolute Temperature
ΔS^0 = Change standard Entropy of mixed

The change in entropy is described by the structure atomic disorder. It can change with any chemical reaction. When the entropy of the amorphous dental adhesive increases, the free Gibbs's energy decreases; both are absolute value. The negative value of the Gibbs's free energy of the dental bonding system indicates a spontaneous chemical reaction. The state of ΔG^0 is controlled when:
- The enthalpy is negative and the entropy is positive: the reactants monomers structures are in atomic disorder, like in the amorphous dental bonding system. An exothermic and spontaneous chemical reaction occurs. The dentist takes advantage of this phenomenon when placing composite layers.
- The entropy and enthalpy are negative, an exothermic but non-spontaneous reaction occurs with high temperature.
- The entropy and enthalpy are positive, an endothermic spontaneous reaction occurs e.i. Depolymerization.
- The enthalpy is positive and the entropy is negative, an endothermic and no spontaneous reaction occurs.
When the free energy ΔG^0 is zero, the chemical reaction is at equilibrium; the forward and the reverse reaction occur at the same rate. Numerical computation of the reactants energy and the products are obtained from tables. Before any calculation, all chemical reaction equations need to apply the balance and stoichimetry principle. The computation of standard ΔH^0, ΔG^0 and ΔS^0 is analogous to the Hess Law , $\Delta S^0 = \Sigma \Delta S^0{}_{products} - \Sigma \Delta S^0{}_{reactants}$

$$\Delta G^0 = -2.303RT\log(K) \tag{2}$$

The kinetics and thermodynamics of spontaneous polymerization are governed by the standard Gibbs' free energy equation, a function of the constant of polymerization K, solving for K given with the equations.

$$K = e^{-\Delta G/RT} \tag{3}$$

R=1.38x10-23J/deg-molecule,Boltmann's const.
T= Absolute Temperature
The Boltmann's equation relates the variation of entropy with the space arrangement $\tilde{\varphi}$

$$\Delta S = k \ln (X) \tag{4}$$

X , Distinct arrangements of molecules in the space. Permutation (N_1+N_2) objects fall into two classes containing N1 objects of type 1 and N2 type objects; X_1 $_{-~.1}$ $\tilde{~}$ $_{.1} N_2!)$
Boltmann's constant in the molar based $k = R/N_A$ $N_A = 6.022 \times 10^{23}$ mol^{-1}
ni=number of moles polymer and solvent+ solute
Ni= Number of molecules solvent and polymer
X_i=Arrangement space term of solvent and polymer X_1, X_2, polymers mole fractions
The experimental hybrid layer entropy is at zero enthalpy; the Gibbs energy is given by:

$$\Delta G^0 = RT[n_1\ln(X_1) + n_2\ln(X_2)] \tag{5}$$

The value obtained from ΔG^0 is applied on "(3)"and the constant or rate polymerization K can be calculated, which is our numerical manipulation sensor. Manipulation means to make the photopolymerization process slower or faster. Thus, we have direct control of the moles or molecules of substrates and products.
The photopolymerization process is a synthesis chemical reaction, given by the free radical chain reaction of the methacrylates derivatives of primers and dental adhesive.
The free radical polymerization is given in three steps: Initiator (I), Propagation (p) and Termination (t). These three steps have individual rates of polymerization K, each step Ri,, R_P ,Rt.

$$K_p = R_p(R_i/R_t)[M][I]^{1/2} \tag{6}$$

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

The monomer grows to polymers under the free radical chain reaction of polymerization, given by the equation:

$$M_{fr} + M = M_{(fr+1)} \tag{7}$$
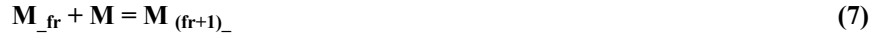
M_{fr} = Monomer with free radical.

M = Molecule of Monomer or monomer unit in polymer chain

$M_{(fr+1)}$ =Polymers.

The photochemistry explains the interaction between the light and matter to induce chemical reaction. The dental adhesive chemical reaction is induced with the curing light, which is an electromagnetic spectrum of a 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 is given in the equation (8) and (9) to stimulate the molecules. The photon energy is:

Photon Energy $$h\nu = hc/\lambda . \tag{8}$$

$$\Delta E = nh\nu = nhc/\lambda \tag{9}$$

Initiation. $$I \quad \xrightarrow{hc/\lambda} \quad 2R_- \tag{10}$$

R_- =Free radical

λ = Wavelength of the incident light curing, $\sim$ 550 nm in the dental adhesive.

h= 6.626 x 10-34 Js Planck's constant

n = Integer

c=2.99979x108 m/s Velocity of light

The electromagnetic initiator energy is absorbed and temporarily stored as excited electron, moving at very high-speed along the chain $\sim$110ps, creating the free radical or ions, initiating the photopolymerization with the energy given by equation (9). The photopolymerization initiation absorbs the light, induces the free radical or ion and is proportional to the monomer concentration. The light does not affect the chain of propagation and termination. An important advantage in the dental adhesive field is that the initiation starts at a large range of temperature.

The addition of photosensitizers to the monomers induces the absorption of light with specific wavelength, disassociating the free radical, giving energy to the monomers for the propagation and termination process. The rate of initiation is given by the equation:

$$Ki = 2\varphi I_0 [I] \tag{11}$$

$$Kp = Rp \, (\Phi \acute{\varepsilon} I_0 / Rt)^{1/2} [M] [I]^{1/2} \tag{12}$$

I_0=Intensity of the incident light; Cure light

$\acute{\varepsilon}$ =molar absorption of the initiator

φ =Quantum yields in photochemical.
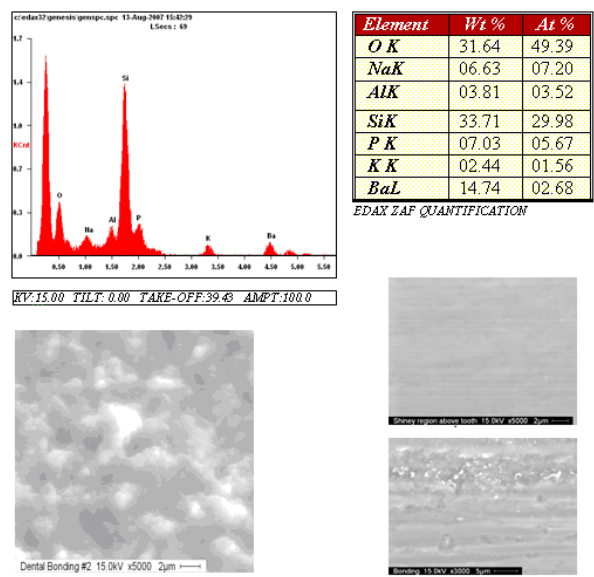
$$\varphi = \text{Rate-ini.chain/Rate-lightabsorption} \tag{13}$$

The propagation speed is based on the σ bond in the new bonding restoration, from the less stable π-Bond of the hybrid layer, composite filling, and residual tooth.
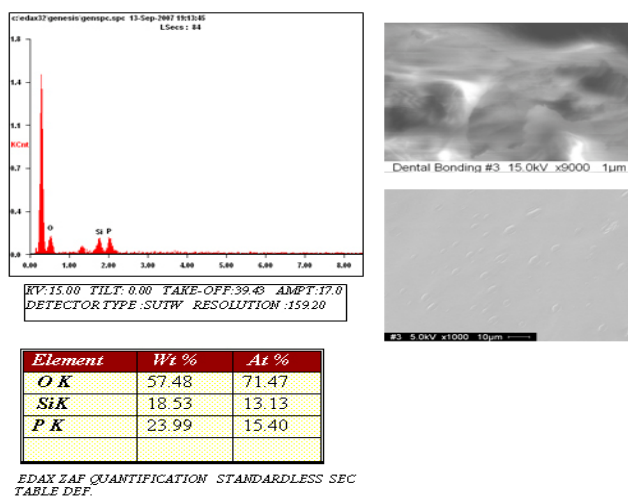
4.0 EXPERIMENT RESULTS

ENERGY DISPERSE SPECTROSCOPY (EDS)

The EDS experiment is a chemical composition microanalysis, performed simultaneously with SEM. The EDS is a collection of data from X-rays emitted from the specimen caused by the impact of electron emission and show the elements in EDS line profile analysis, detecting the chemical composition and their weight percentages Fig. 1. The EDS electron beam scans a selective line across the specimen. It detects the X-ray energy spectrum at each position, plotting the element concentration.

Element	Wt %	At %
O K	31.64	49.39
NaK	06.63	07.20
AlK	03.81	03.52
SiK	33.71	29.98
P K	07.03	05.67
K K	02.44	01.56
BaL	14.74	02.68

EDAX ZAF QUANTIFICATION

KV:15.00 TILT: 0.00 TAKE-OFF:39.43 AMPT:100.0

Fig 1. EDS- SEM of R3 adhesive, Real tooth and Bonding

KV:15.00 TILT: 0.00 TAKE-OFF:39.43 AMPT:17.0
DETECTOR TYPE :SUTW RESOLUTION :159.20

Element	Wt %	At %
O K	57.48	71.47
SiK	18.53	13.13
P K	23.99	15.40

EDAX ZAF QUANTIFICATION STANDARDLESS SEC
TABLE DEF.

Fig 2. EDS- SEM of R2 adhesive

The six different adhesives with EDS caption deviate in the distribution but are the same basic methacrylate monomer elements in the chemical composition. The relevant part of this monomer creates the free radical in the dental photopolymerization process. This monomer matched with the X-R diffraction elements chemical composition was obtained from the probable chemical elements of the manufacturer bonding adhesive. The chemical formulas are from the Sci-Finder Skolar and Chem.-Draw programs, which identify the manufacturer's composition. The relevant part of this EDS experiment was that it showed the real chemical composition of the material R3 in the Fig 1 with a typical micro disorder distribution of an amorphous structure showed in the SEM picture (all in one caption).

The significance of these experiments is to identify the elements chemical composition and their weight percentage. The information is based on the calculation of bond energy under standard condition. Some of the free energy conditions of the spontaneous chemical reaction are based on the standard state concentration of 1 mole at 25^0C (298K) of reactants and product. 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 the chance for better atomic organization or distribution of the hybrid layer in the dentine tubules.

X-R DIFFRACTION EXPERIMENT RESULTS

The X-R Diffraction experiment starts with a glassy sample material, and the results are amorphous structure. The experiments were a repetition of each sample adhesive and all of them showed an amorphous structure pattern curve, as shown in Fig 3.

The simultaneous Plot Corresponding Files of three curves profiles of different adhesives and colors obtained with the EVA program in one plot Fig 3. These results show amorphous structure in all the pattern curves of different samples, classified as amorphous structure material 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 linearity of the background and non-intensity periodicity, showed in Fig 3.

The meaning of this type of curve is a complete atomic disorder. It is favorable for the dental adhesives to have high entropy amorphous structure, creating an ideal environment for a spontaneous chemical reaction with the neighbor's molecules. The experimental results given in the plot of R2 Fig 5 and R5 were obtained after the pattern reduction. The peaks of these patterns represent the elements of the chemical composition, showing the phases at the bottom of the different plots and on Table 2 (Chem. Composition). We selected the most realistic ones. The manufacturer specification shows that all of these adhesive compositions have methacrylate derivatives monomers in complete molecular disorder. The profile line of the amorphous structure differs greatly from the crystalline structures, as shown in Fig 4.

The Powder Diffraction File, PDF cards obtained with the EVA program can identify possible phases of the sample creating a crystal symmetric lattice using the ATOMS program. The experiments' PDF data cards could create tiny spots of crystalline lattice; the cell symmetry is lost because of atomic disorder and the curve pattern changed immediately, with no physical representation.
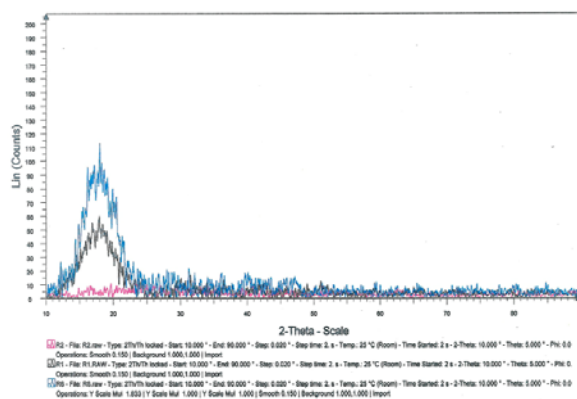

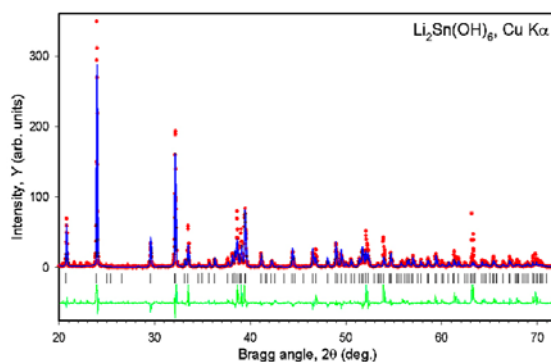**Fig.3 X-Diffraction. Plot Corresponding file of R1, R2 and R6 patterns adhesives**

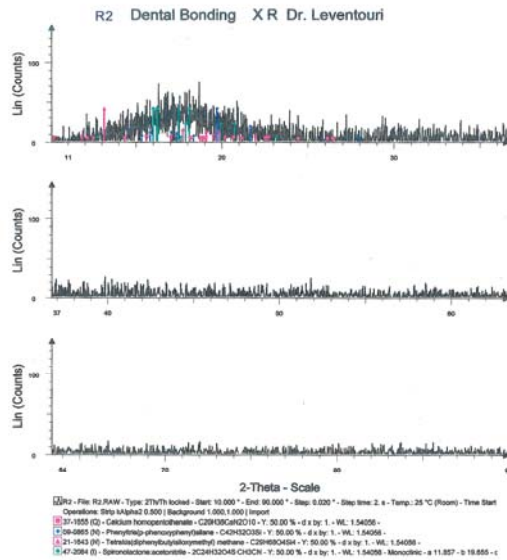**Fig4 X-R Diffraction curve of crystalline structure**

Fig.5 X-R Diffraction curve of R5 adhesive.

Table 2 Chemical composition

X-R Plot chem. Comp.	Formula
Calcium homopanthotenate	$C_{20}H_{36}CaN_2O_{10}$
Phenyltris(p-phenoxyphenyl) Silane	$C_{42}H_{32}O_3Si_4$
Tetrakis(difenilbutylsilo-xymethyl)methane	$C_{29}H_{68}O_4Si_4$
Spironolactone aventonitrile	$2C_{24}H_{32}O_4S-CH_3CN$

SCANNING ELECTRON MICROSCOPY (SEM).

The SEM is a high-resolution image of amorphous dental adhesive surface, which is created with the collection of electrons. The chemical composition analysis can be achieved by the EDS-SEM performed simultaneously.

A carbon coat was required on all samples in order to perform the SEM and EDS experiments using the Sputter Carbon Coater machine, so that the samples could achieve better conductivity surfaces for the Electron Beam attraction. The electron beam impacted the specimen that was placed over the metal plate which will be identified by the same sequence, assigned in Table 1.

We can see a significant difference in their morphology, given by the SEM picture. This is a real bonding distribution of the composite atomic disorder. The elements chemical composition is given by Fig 1 in the EDS caption. Fig 1 can display the amorphous structure of the white composite filling that is bonding to the adhesive R3 layer with size.

Fig.2. shows the composite filling, where we can see the different types of structures, although continuing being amorphous with micro molecular disorder and high entropy, attractive to any bonding with other composite layer

It is interesting to see in Fig. 1 the top of one real tooth with real enamel structure called ultra structure crystalline. The images displayed the EDS result in one caption. The graphic curves show the chemical composition, and the pictures show the topographical and morphological details of the adhesive surface, in Fig 1, 2, and 3 with the EDS caption. The SEM caption shows a microdisorder distribution typical of an amorphous material. Some spots show a uniform and clear structure but immediately can change to become dark with a different structure with morphological disorder. This kind of micro disorder identifies amorphous material. It is the platform for the dental bonding adhesive related to the entropy and the negative Gibbs's free energy, promoting the spontaneous polymerization bonding. The result comparison of the six different adhesives with SEM caption finds differences in the distribution but no structure organization. This microdisorder is present in all of them, proving the presence of amorphous structure and confirmed in the X-R with constant pattern change produced by molecular disorder.

7

The SEM caption is represented by the change of the color black and white. The relieves of the surface show agglutinate spot Fig 1, 2.

5. DISCUSSION

EDS-SEM

This experiment performs EDS and SEM simultaneously. The EDS experiment can determine and plot the chemical composition results of the dental adhesive as shown in Fig. 1. The X-R pattern can identify the type of structure of the sample. The EVA program requires inputting data of possible element components. Information is obtained from the manufacturer user manuals. These possible phase components result from one of the dental adhesives shown on Table 2. The X-R Diffraction and EDS chemical composition elements results were matched, based on the manufacturer's monomer elements specification, like methacrylate derivatives elements.

The calculation of K given in the thermodynamic topic shows a possible manipulation of the process as a function of the substrates entropy. Considering the monomers, components of dental adhesive have methacrylate derivatives. Therefore, all of them have Carbon, Hydrogen, and Oxygen, which combined become CH_2 and CH_3 monomers. With EDS and X-R experiment data we know the elements and their weight percentage belonging to the monomers (Fig.1, 2). With a simple transformation from mole or molecules to the atomic weight we know the percentage of the monomers and their elements. Identifying the monomers percentage of each adhesive, we can discern which adhesive has more possibilities to create cross-link bonding with the neighbor's molecules. The rate of formation manipulation or initiation of the free radical is a function of the energy absorption per unit volume. This is proportional to the intensity of the incident light and the monomers-photosentizers concentration. The incident light absorption can be controlled (manipulated) with the wavelength size of the curing light. The longer the wavelength is, the slower the response of the photopolymerization process. At this point, a better diffusion result and a uniform distribution can be achieved in the dental bonding. The idea is to achieve the best bonding result. For this, we need to use most of the adhesives that are already in the market that have the same monomers to create the free radical chain reaction, rather than having to make an entirely new adhesive.

X-R DIFFRACTION

The result of the X-R Diffraction experiments of dental bonding samples show the pattern of amorphous structure. In the six curves profiled, there are no relevant intensity peaks or absorption counts nor non-intensity periodicity. There is a minor non-linearity of the background. The physical meaning is that the atomic arrangement present is not crystalline nor without particular structure. While in atomic disorder with a continuously changing pattern, they are closely packed with beneficial elastic, mechanical property, and especially sheer stress. The density molecular distribution affects the X-R diffraction patterns; the electromagnetic waves are diffracted continuously, changing the pattern when hitting the atoms in disorder (Fig 4). The ATOMS computer program cannot create a symmetric crystal lattice with the experimental PDF cards. The program cannot give physical meaning with this continuing pattern change created by the atomic disorder. The crystalline material has different profile lines with clear periodicity and high intensity absorption, stable, chemical equilibrium (Fig 5).

The six dental adhesives exhibit a rapid photopolymerization, avoiding crystallization in the photochemical reaction. The adhesives photo-polymerization process is promoted by adding adequate photosynthesizers and camthoquinone photoinitiators. These promoters do not allow time for the monomers to organize before applying the cure light. The atomic disorder interferences destroy any pattern. This is the reason why the adhesive samples curve pattern has no linearity (Fig 5). These phenomena occur when a short electromagnetic wavelength interacts with the atoms and responds as intensity peaks.

The dental amorphous material looks like a liquid structure and the diffraction patterns are like liquid but are really a solid. When entering into the solid state with curing light, the liquid physical properties are changed under the photo-polymerization. The rate of photo-polymerization is fast; it has no time for the molecules to organize in order to create a crystalline structure.

Relevant results of these experiments appear in the plot of X-R Diffraction R2, Fig 3 and R3, Fig 5. The patterns are typical of amorphous materials: we can see the constant change; therefore the structure is an asymmetric crystal lattice. Other relevant information is that the chemical composition obtained by the X-R and EDS

experiments are close to the manufacturer specification monomer elements, which are methacrylate derivatives. In the experiment, the constant polymerization K all values were greater than one, so the products polymerized of dental bonding are more than the reactants at the equilibrium.

The final concentration of the hybrid layer is not uniform because it is affected by gravity; therefore the bond will be weak in direct relation to the lower density of the filler particles. The density distribution affects the entropy and the negative free Gibbs's energy of the hybrid layer before the polymerization. Both benefit the spontaneous dental bonding by layer.

From the energy viewpoint, the constant polymerization K, given by "(3)", must be a positive value greater than one in order to get strong bonding. Positive value of K means that there is more polymerized adhesive than reactant monomers. The photopolymerization is a synthesis chemical reaction.

The chemical reaction that makes the constant K represents the ratio of the rate forward (polymerization) or in reverse (depolymerization). In dental adhesives, the depolymerization is not applied. The polymerization is only forward with K always being greater than one. The control of value K, depends on manipulating the monomers weight and the wavelength size of the curing light.

The initiation of polymerization starts when the photoinitiator absorbs the light disassociating the monomers forming free radicals and energizing the monomers. These monomers absorb the light producing a free radical or ions, only affecting the initiation step; the propagation and termination are not affected. Sometimes monomers need photo-sensitizers to start the process.

This discussion concerns the area of intertubular and peritubular dentine. At this point, the photopolymerization can take advantage of a wet environment to manipulate the process. The photochemical reaction waits for water to be evaporated; the polymerization is very fast and starts after the water evaporates; normally the molecules have no time to be organized into a uniform mix, presenting different concentrations, contraction gaps, internal stress, leakage and infections. The water manipulation is located in the hybrid layer and is obtained from the etching treatment.

The photopolymerization control of dental adhesives is directly related to the presence of water, the constant K, wavelength size of the curing light, and the entropy represented by the monomers concentration in dental bonding. The results are the chain cross-link network with the structure of the amorphous material and can reach high strength with high elastic limits. The real numerical value of strength for each dental adhesive will be obtained through mechanical tests.

6. CONCLUSION

The results from the SEM and X-R Diffraction patterns of different dental adhesives have almost the same profile curves as the amorphous structure. In fact, all six dental market adhesives do have amorphous structure. Normally, the rate of photopolymerization is high; it allows no time for the molecules to organize and to create crystalline structure. For this reason, the amorphous structure has a high atomic disorder with high entropy in the glassy structure, as well as a negative Gibbs's free energy. This amorphous structure provides the energy necessary to create the spontaneous photopolymerization of dental bonding adhesive expressed in chain-cross-link polymer, controlled by the absorption of the photon light energy.

The manipulation of time delay is an advantage of the photopolymerization initiation process. Another conclusion obtained from the amorphous structure results from the SEM and X-R Diffraction experiments is that there exist the possibility to control the process, giving more time for the dental bonding to obtain the maximum molecular organization, thereby avoiding internal defects like shrinkage, internal stress etc. As we control the rate of water vaporization of the hybrid layer in intertubular and peritubular dentine, all photochemical reaction waits for the water to be evaporated. This event occurs simultaneously before applying the curing light: the restoration remains wet with the dental adhesive and the bonding surfaces with water from the etching treatment. There is time delay obtained by the natural water evaporation, which the dentist can use in controlling the photopolymerization

At the atomic level, the conclusion is that the energy photopolymerization is a variable, which can be manipulated by the curing light wavelength: the longer the wavelength, the slower the photopolymerization will be. This is another way to add more time delay for better atomic organization and avoid defects.

The curing light with a shorter wavelength close to the border of UV produces a fast and weak dental bonding, compared to the longer wavelength like visible light spectrum ~600 nm obtaining a uniform mix, and avoiding

defects. Thus, dentist can use specific wavelengths of curing light for different layers of a specific type of the restoration.

The best sealer is obtained with a perfect bonding with the minimum of structure defects. These requirements are represented by the entropy of the bonding, given by profile curves of the X-R diffraction experiment results. This entropy is a function of the monomers concentration and rate of photopolymerization. The rate is given by the wavelength size curing light and the water evaporated time delay explained above. Numerical results will be reflected in the mechanical test.

The EDS and X-R Diffraction elements chemical composition of the samples play an important role in the manipulation of the process (Table2). Some calculations explained in the discussion can determine an approximate value of the adhesive monomers. These results reflect the adhesive possible bonding and the rate of polymerization, based on the polymers as a chain of monomers and interconnection between monomers and a chain cross-link that can form a 3-D network. In addition, there is a possibility to predict the type of polymers bonding, based on competition of the electronegativity-affinity, atoms radii and hybridation of the monomers elements. Thus, for different levels of electronegativities, we can predict the type of bonding that should be applied. This example of atomic radii sizes can clarify this conclusion; the atoms radii of reactants can take a part in numerical evaluation of the photon energy that needs to remove or to add valence electrons from different energy orbital, creating the ions. Thus, these ions or free radical initiators have been created and take a part in the ionic bond. When the atomic radii of the adhesive elements is known, we can obtain the lattice energy or strength of ionic bond that is directly proportional to the charge of the ions divided by sum of two radii. In addition, the radii size affects inversely proportional to the flow in the hybrid layer, which promotes a uniform mix avoiding bonding defects.

The idea is to obtain the best uniform bonding with amorphous material existing in the market today, considering that they have the same monomers to create the free radical chain reaction.

The amorphous adhesive is an energy-loaded material with a disposition to create the free radical photopolymerization .It attempts to be more stable at a lower energy level, especially with the covalent, ionic and Van der Wall's bonds, adhering to residual tooth and the composite filling. Future articles can relate to the experiment structure, bonding mechanical test and computer simulation test, showing a deeper relationship between the experiment parameters and the real numerical value of mechanical properties, reflected by tension rupture stress, Young modulus, Poisson ratio, shear stress, strain and energy.

REFERENCES

[1] Lieng- Huang Lee, Polymer Science Technology vol 12A) Adhesion and Adsorption of Polymers .New York 1980

[2] Larry L. Hench, M R S Bulletin/May 1999, Medical Material for Next Millennium.

[3] Vitalij K. Pechasky, Peter Y Zavalij, Fundamentals of Powder Diffraction and Structural Characterization of Material, New York, 2005

[4] http://amtiac.alienscience.com/quartely

[5] http://amptiac.alionscience.com/quarterly. Material EASE

[6] http://www.icdd.com. File International Center for Diffraction Data

[7] Souheng Wu, Polymer Interface and Adhesion, New York, 1982

[8] D.R Morrow and Yu Chen, Advance in Polymers Science and Engineering, New York, 1972

[9] Wanpeng Cao & Larry Hench, Ceramics International 22(1996), Bioactive Material

[10] Serge Bouillaguet, Biological Risks of Resin-Base Materials to the Dentin –Pulp Complex, Critical Reviews in Oral Biology & Medicine, pp 2- 30.

[11] T.Cheng, K.Itoh, M Kusunoki,T Hasegawa, S. Wakumot & H. Hisamitsu,Effect of dentine conditioners on the bonding efficacy of one-bottle adhesives, Journal Oral Rehabilitation, pp 2-9