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Effect of Chlorine from Drinking Water on Denture Base Resin and Evaluation of the Flexural Strength of Denture Base Resin.

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Abstract: *Acrylic resins were introduced to dentistry in 1937 and for decades no materials has been found that matches the appearance of the oral tissues. Its overall performance is regarded as satisfactory and widely used for the construction of complete and partial dentures. Poly methylmethacrylate (PMMA) absorbs water slowly over a period of time. It has been estimated that for each 1 percent increase in weight due to the absorbed water acrylic resin expands linearly by 0.23%. Chemicals present in the water will also diffuse along with the water molecule and can even interact with the polymer chain. Fracture of the denture is very common in practice, to repair the broken denture a new material is added to existing old material. Studies shown that chlorine from chlorinated water and carbonated beverages significantly decrease the bond strength between the teeth and the denture base resins. The aim of the study is to evaluate the flexural strength of the denture base resin and its effect of chlorine from chlorinated water on denture base resin.*

Key words: *Poly methylmethacrylate (PMMA), Flexural strength, Denture base resin, Chlorinated water.*

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I. Introduction

The dental prosthesis is found to be the most acceptable appliance to the individuals with impaired masticatory function. Although many newer material have been introduced periodically the popularity of poly methylmethacrylate (PMMA) still remains in the top position as far as complete denture, partial denture, maxillo-facial prosthesis are concerned. Poly methylmethacrylate absorbs water slowly over a period of time. Absorption of water is facilitated by the polarity of poly -methylmethacrylate molecule. The diffusion co-efficient of typical heat cure denture acrylic resin is 1.08 X10 m/sec at 37ºC. The diffusion occurs between the macromolecules, which are forced apart by the diffusion of water there by they are rendered more mobile with the result that inherent stress can be relieved with constant relaxation and possible change in the shape of the denture. It has been estimated that for each 1 percent increase in weight due to the absorbed water acrylic resin expands linearly by 0.23 percent[28].In modern days it has become a routine to use hard water, chlorinated water due to insufficient water supply, especially in countries like India. Chemicals present in the water will also diffuse along with the water molecule and can even interact with the polymer chain.

Fracture of the denture is very common in practice, to repair the broken denture a new material is added to existing old material. For effective repair the patency of the bonding site is important. If the bonding site is blocked then repair will be difficult. Studies have shown that chlorine from chlorinated water and carbonated beverages significantly decrease the bond strength between the teeth and the denture base resins[38].

Chlorine is widely used as disinfectant for water in our country being more electronegative and highly reactive halogen it can interact with the bonding site of the polymer chain[19,33]. Pavarina. Ac etal reported that

use of sodium hypochlorite 1% as a disinfectant of denture base resin decrease the transverse strength of acrylic resins[27]. Neppelenbroeketal reported that use of sodium hypochlorite as a disinfectant effectively decreases the hardness of acrylic denture base resin[23].

Poly methylmethacrylate (PMMA) is formed by polymerization of monomer (methyl methacrylate) by emulsion method of polymerization . It has a main carbon skeleton with pendant hydrogen (H), methyl (CH_3) and carboxymethyl ($COOCH_3$) arranged in alternative manner. Chain termination and chain transfer limits the polymerization, this will create a terminal double bond in the polymer[28,14].Structure of polymethylmethacrylate shows it has a terminal double bond and pendant methyl (CH_3) and carboxymethyl ($COOCH_3$) group which are election releasing and withdrawing groups, respectively, which can create election depletion in the terminal bond and can favor an electrophilic and nucleophilic attack [31].

Chlorine effectively decreases the bond strength between tooth and denture base. Sodium hypochlorite as a disinfectant decrease the flexural strength and hardness of denture base resin[27,23]. Chemical structure of poly methlmethacrylate can favor reaction of chlorine[3,31], considering this criteria study was conducted to evaluate the introduction of chlorine from chlorinated water on the bonds of polymethylmethacrylate (PMMA) and its effected on repair of denture base resin. The aim and objectives of this study is-To evaluate the effect of different concentration of chlorine on the poly methylmethacrylate chemical structure.

II. Aims and objectives

1.Flexural strength of intact samples was assessed which was stored in chlorinated water
2.Flexural strength of repaired blocks was evaluated to assess the bond strength between the old material and the added new material.
3.The action of this chlorine on the bonds of PMMA is assessed by ultra violet spectroscopy, Infrared spectroscopy[15].

III. Materials and Methods

This study was performed to find out and analyze the influence of different concentrations of chlorine on bonds of poly methyl methacrylate (PMMA). A commercially available heat cure resin Acrylyn-H and an autopolymerizing resin Acrylyn- R manufactured by Asian acrylates India was used to make samples.A total 40 acrylic blocks of dimensions 65X 13X 3 mm as per specification of ASTM [American standard for testing materials] were made in heat cure denture base resin to evaluate the effect of chlorine in polymethyl methacrylate .To fabricate the sample a die fabricated in mild steel shown in fig 1.The rectangular die consist of three parts – i) Bottom plate ii) Middle plate with slot for making sample iii) Top plate. The die parts lubricated with petrolatum jelly and self-cure was Mixed and placed on the middle part of the die with top and bottom part of the diein between (Fig 2).The acrylic block was allowed to set and removed from the die .Five acrylic blocks was made like this and used to make template for heat cure acrylic blocks .

The acrylic blocks were coated with petrolatum jelly and invested using gypsum type II dental plaster in a conventional dental flask. After the gypsum sets the acrylic blocks were removed from the flask. The gypsum mould surface was coated with cold mould seal, now the mould was ready to pack with heat cure resin.Heat cure acrylic polymer material was mixed with monomer and at the dough stage packed into the mould cavity and processed for by placing the flask in cold water and raising the temperature to boiling over a period of 1 hour and keeping it in boiling water for additional hour.After processing the flasks were bench cooled deflasked and excessive flash were trimmed. Dimension of the blocks were checked and found to be as per the ASTM standards and coded.Total number of 40 intact blocks (Fig 3) was grouped into Group I, II, III, IV, &V with eight samples in each group and the details are shown in table 1 . The Group I act as the control group and stored in artificial saliva ,Group II,III, IV,and V was stored in chlorine water with strength of 1.5ppm,2ppm,3ppm,100ppm respectively (Fig 4, 5) .

Chlorine gas from a cylinder was passed through a conical flask containing distilled water until the solution turns to dark yellow; this solution is of highly concentrated strength. Estimation of the strength of chlorine is done by titrating against known concentration of sodiumthiosulphate and iodine is used as a indicator for color change which indicate the termination of reaction.The known strength of sodiumthiosulphate is taken in burette and the unknown chlorine solution is taken in conical flask, iodine is added as indicator. Sodiumthiosulphate is titrated against the chlorine solution the and point of the reaction is calculated by change of color.

The normality of sodiumthiosulphate is known, the volume of sodiumthiosulphate consumed to react with known volume of chlorine solution by using the following formula strength of chlorine solution is estimated. $V_1N_1 = V2\ N2$. V_1= Volume of chlorine solutionN_1 = Normality of chlorine solution not known.V2 =Volume of sodiumthiosulphate consumed for the reaction, N2 = Normality of sodiumthiosuphate.N_1 (Normality of chlorine solution N 1) = V2N2/V1.Once the strength of chlorine solution is

known it can be diluted according to the needs.Preparation of chlorine solution was done at Chennai Metrowater Quality control lab, Kilpauk.

The acrylic blocks which were stored in Artificial saliva & chlorine solution were subjected to 3-point bend test to evaluate the flexural strength. An universal testing machine (Instron 4301T, England) (Fig 6)with static load cell of 5KN in the department of composite Technology (IIT),Chennai, was used to evaluate the flexural strength.Cross head speed of 5mm/min was used to transmit force to the samples. The variation in the breadth ,length and the width of each individual sample was calculated and noted this is to calculate the flexural strength of each sample accurately. The samples of all the Groups were subjected to the load until the fracture and the load was recorded in Newton shown in Table 2 to 6 . The flexural strength was calculated using the formula. Flexural strength $=3/2\ xFL/BD^2 N/mm^2$.F = Maximum load before fracture (N)L = Distance between the supports in (mm),B = Width of the samples in (mm),D = Thickness of the samples in (mm).

The fractured blocks were placed in the die at and the fit was verified, one mm of acrylic were removed on both the sides on the fractured segments total of 2mm of space were provided for addition of self cure resin. A trapezoidal groove was cut the length of the groove was 11mm from the center and breadth measured 2mm at the fractured site & 5mm at the end. The prepared blocks were placed on the mould; auto-polymerizing resin was mixed and added between the fractured segments all the fractured blocks were repaired in this manner. The repaired blocks were fractured in the universal testing machine to evaluate the strength of the repaired acrylic blocks. The flexural strength values of the repaired blocks are shown in Table 7 to 11. by comparing the values of before repair and after repair, the influence of chlorine on the bond strength were evaluated.

IV. Results

The flexural strength of samples before is given in table 2 to 6 . Table 1 represent the flexural strength of intact sample stored artificial saliva. Table 2 to 5 represent flexural strength of intact samples stored in chlorine solution of varied concentration such as 1.5, 2.3.&100 ppm. The flexural strength of intact specimen Group I is highest and in the remaining group the strength is in decreasing order which are represented in table 2 to 6 .Group V exhibited the lowest flexural strength. Group II, III, IV were in between the group I & V. The flexural strength of repaired specimen Repaired Group I is highest and in the remaining group the strength is in decreasing order which are represented in table 6 to 10 . Repaired Group V exhibited the lowest flexural strength. Repaired Group II, Repaired III, Repaired IV were in between the Repaired Group I & Repaired Group V.

Statistical analysis : The flexural strength of intact samples and repaired are subjected to the following test for statistical analysis. i. One way ANOVA analysis ,ii.Tukey multiple comparison tests. When the means of three or more independent groups have to be compared, the one way ANOVA test is employed to evaluate the significance .In this study the one-way ANOVA was used to determine the statistical differences in the flexural strength between the groups. In this study, since significant differences within the group were determined using ANOVA ,the results were further analyzed using Tukey-HSD test at significant level of 5%.This was done to determine where the differences between the groups and within each group .The difference in the flexural strength between the Groups of intact samples stored in artificial saliva and various concentration of chlorine solution was highly statistically significant at the 0.001 level.Group I had the highest strength while Group V possessed the least strength .Group III,GroupIV,GroupV had strength value intermediate between I &V.The differences were significant at a significance level of 0.050.The details shown in table 13.The difference in the flexural strength between the Groups of repaired samples stored in artificial saliva and various concentration of chlorine solution was highly statistically significant at the 0.001 level . Group IR had the highest strength .Repaired Group III,RepairedIV,Repaired V had strength value intermediate between Repaired Group I &Repaired GroupV.The differences were significant at a significance level of 0.050.The details shown in Table 14 .The difference in flexural strength between the intact samples and repaired samples were compared by paired students T test and was highly statistically significant at the level of 0.001 %..The details shown in table 15.

V. Discussion

Poly methyl methacrylate has earned a great popularity and widely used in dentistry because they can be processed easily using relatively simple technique ,they are esthetic and are also economical .The resin possess adequate strength and resilience as well as resistance to biting force or chewing forces ,impact forces excessive wear which occur in the oral cavity28. Advancement in polymer technology has contributed lot to the processing technology and PMMA still remains as the material of choice.Patients are advised to store denture in water after the use because water acts as plasticizer and residual monomer are released .Dentures when stored in water are capable of absorbing water mainly by polar properties of the resin .The process by which the resin

absorb water is diffusion 28 .A typical denture base require a period of 17 days to become fully saturated with water28.

Structure of Poly methylmethacrylate is formed by repetition of methyl methacrylate it has a main carbon skeleton and pendant methyl and carboxymethyl group arranged in alternating manner .PMMA has two double bond one at the terminal region and the other in the carbonyl group28. The terminal double bond is responsible for addition polymerization (Fig 7).14,31,12Chlorine in water exists as hypochlorus acid and chloride ions. Hypochlorus acid in aqueous solution form chloride ions and hydrogen (Fig 8).Hence chlorinated water will have chloride ions and hypochlorus acid. Water along with chloride will diffuse into the denture and will interact with structure of PMMA .

Chlorine is one of the common disinfectant used for water purification, chlorine in water exists as hypochlorus acid and hypo chlorite ions19. Water is a molecule with 2 atoms of hydrogen and one atom of oxygen. Chlorine is an single atom and atomic radius is less and size is also small hence chlorine along with water can also enter into the denture30,33.

Chlorine being highly electronegative and chemically reactive halogen will interact with the chemical structure of PMMA31,33 .The chloride can form two products 1 and 2 shown in (Fig 9).The product 2 does not have much clinical significance whereas the product 1has much clinical significance because it blocks the terminal double bond which is important for repair for the broken denture .

Studies on the effect of chlorine on PMMA concludes chlorine can effectively react with the terminal double bond ,carbonyl group and the methyl group 26.Sodium hypo chlorite as a disinfectant for denture effectively reduce the transverse strength 27.

Sodium hypo chlorite as a disinfectant effectively decrease the hardness of heat polymerized acrylic resin23.The effect of chlorine on denture base resin and alteration in the physical property may be due to the above chemical reactions on the polymer chain. The action of chlorine on the denture base resin is crucial and the aim of the study is justified .

The polymerization kinetics of acrylic concluded the existence of terminal double bond and for further polymerization the existence of the double bond is important14. A carbon carbon double bond consist of strong sigma bond and a weak pi bond . The pair of electrons in the pi bond is less firmly held between the two carbon nuclei and is capable of being easily reacted by hypo chlorite ions .Blocking of the terminal double bond will inhibit the further polymerization process31. The denture base resin on polymerization converts unsaturated double bonds to single bond by addition polymerization reaction .The near infrared spectroscopy concludes conversion of double bond to single bond and also the presence of terminal carbon double bond34. Considering the above aspects the effect of hypo chlorite ions and chloride ions on the terminal bond of PMMA and its effect on repair is assessed.

A typical denture may require a period of 17 days to become fully saturated with water. Hence all the samples for the study were stored for 17 days[28]. **Central public health and environmental engineering organization (CPHEEO) Government of India**, advocates the concentration of chlorine for effective disinfections should be1.5 ppm at the tail ends in a water distribution system[19]. So 1.5ppm, 2ppm & 3ppm were taken for the study .Higher concentration of 100ppm was also taken to evaluate the interaction of chlorine at higher level.

In the oral cavity compressive and tensile stress does not operate separately, combination of all this stress only occurs. Hence a test where in which all these stress acts together will be more suitable to evaluate the strength of the sample. Three point bend test is where in which combination of tensile, compressive strength and modulus of elasticity can be evaluated. This stress occurs in most of the prosthesis in the oral cavity[28]. Hence samples were subjected to three point bend test to evaluate the flexural strength. The samples were supported on 2 jigs that were 50mm apart and load was applied through the center of the sample using a loading lever. The breaking load was recorded and flexural strength was calculated and the results were assessed. From the result it was found that mean flexural strength of intact Group V was 84.90 N/mm^2 .Flexural strength of intact Group II, Group III, Group IV were 90.70 N/mm^2, 89.65 N/mm^2, 89.42 N/mm^2 respectively .Strength of intact Group I is 94.02 N/mm^2 .From this it can be inferred that chlorine effectively decreases the flexural strength in group V and the in remaining group is marginal.

Durable bond between the auto polymerizing resin to denture base resin is required when repair is performed using auto polymerizing resin[21]. The success of repair of acrylic resin depends on the design given. There are various designs for repairing such as butt joint (90 degree),45 degree angle joint, tapered ,rounded and joints with mechanical retention. Round joint appear to be most convenient in practice since it is easiest to produce[37]. Hence round joint were given for repairing the fractured samples. Fractured blocks were repaired by removing 1mm of acrylic on both and the corners were rounded on the sides. The gap was limited to this amount as it small gap minimizes the bulk of repair material which will further decrease the degree of setting shrinkage and dimensional change. Trapezoidal groove was given on either side for mechanical retention.

Autopolymerizing resin was used to repair the fractured blocks and subjected to three point bend test. Fracture load was calculated and the result was assessed.

From the result it was found that mean flexural strength of repaired group V was 42.07 N/mm ^{2}. Flexural strength of repaired Group II, Group III, Group IV were 58.17 N/mm ^{2}, 57.07 N/mm ^{2} ,57.74 N/mm ^{2} respectively. Strength of repaired Group I is 58.99 N/mm ^{2} from this it can be inferred that chlorine effectively decrease the flexural strength of repaired group V and the effect on the other group is marginal**.** The decrease of the flexural strength is due to the chemical interaction of chlorine with PMMA .

VI. Summary

Fracture of denture is one of the common occurrence in clinical practice. Repair of denture is done by adding new material between the fractured site .The bonding of new material with the old material depends on the various factors such as the patency of double bond for further polymerization ,design of the fracture site for repair .Patients are advised to store denture in water after the use. Denture absorb water by the process called diffusion .Chlorine is one of the disinfectant used for disinfection of water .Patients when store denture in water containing chlorine as a disinfectant ,chlorine along with water can enter into the denture. Chlorine being highly reactive will react with the double bonds and other regions of PMMA. Blocking of double bond can affect the repair process.To verify the action of chlorine an in vitro study was conducted. 40 acrylic blocks were made in heat cure resin .one group was stored in artificial saliva and the remaining groups were stored in chlorine solution of various concentration for period of 17 days .The blocks were subjected to 3 point bend test to assess the flexural strength. The fracture blocks were repaired using auto polymerizing resin and again subjected to 3 point bend test to assess the flexural strength after repair .The results were subjected to one way ANOVA and turkey HSD test to analyze the statistical significance.The result of the study showed that there is decrease of flexural strength of blocks stored in higher concentration of chlorine, for intermediate concentration of chlorine the flexural strength is not much when compared with the control group both for before repair after repair.

VII. Comclusion

Within the limitation of the study it can be concluded that :

1.Chlorine from chlorinated water effectively decrease the flexural strength for higher concentration. In lower concentration of chlorine there is decrease in flexural strength but not clinically significant.

2. Chlorine interact chemically with the terminal double bond of PMMA.

3.Higher concentration of chlorine there is break in polymer chain.

4.Patients are advised not to store the denture in water containing chlorine.

5.Chlorine based disinfectant for denture is avoided.

6.Sodium hypochlorite based denture cleansers are not advisible.

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