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Effect Of Chlorine From Drinking Water On Denture Base Resin And Chemical Characterization Using Ultaviolet (UV) And Infrared (IR)Spectroscopy .

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Abstract: *Thegeneral instruction for the patients waering complete denture is to store the denture in water when not in use. Dentre in the mouth absorb the saliva, and when kept outtside the mouth the water will come out ,reapted absorption and desecation will reault in warpage of the polymer chain and resulting in illfitting denture.The reason for the water absorption is denture are made up of Poly Methy Meth Acrylate (PMMA), it is hydrophilic polmer with carboxyl group which has affinity towater.The water used to store the denture can be from ground water (well),Surface water (lakes ,river).The water available in the city are frequently disinfected with chlorine .Denture when stored in water containing chlorine along with the water molecule chloride ions enter in to the denture and can interact with the polmer chain of PMMA.The chloride ions when interact with the terminal double bond of PMMA ,further reapir will be difficult .This study is planned to find out the interaction of chloride with the PMMA using Ultraviolet (UV) and Infrared (IR) spectroscopy.*

Key words: *Waer absorption of dentures,PMMA, Chloride on PMMA ,UVspectroscopy ,IR spectroscopy.*

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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.

Aims and objectives:
The action of chlorine on the bonds of PMMA is assessed by ultra violet spectroscopy, Infrared spectroscopy.

II. 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 interaction of chlorine ions with the polymer chain is evaluated by ultraviolet spectroscopy (UV) and (IR) spectroscopic analysis. Scrapings were taken from one acrylic blocks in Group I, Group II, Group III representing one from the control group and the other from higher and intermediate concentration of chlorine and subjected to spectroscopic analysis.The spectroscopy has a light source and a separator to allow the particular wave length outside and to retain the remaning wave length .The specified wave length pass through the sample .The sample absorb the certain frequency according to the chemical structure and emit the reamning frequency .The frequency absorbed will be recorded in a graph and it will be assessed .The shematic diagram of spectroscopy is shown in (Fig 6).

Cary 5E is a high resolution ultra violet spectrophotometer available Regional Sophisticated Instrumentation center, IIT, Chennai (Fig 7) is used for this study. This is a double beam instrument controlled by a microprocessor. The frequency range is 3150-185 nm. Sample for ultraviolet spectroscopy were done by taking the sample in a container and ultraviolet rays were passed through the sample .The amount of reflectance

is recorded on a graph paper with percentage of reflectance in Y-axis and wavelength in nanometer on X-axis. This is done to verify the existence of conjugated bonds[13].

The Perkin Elmer Spectrum1 FT-IR instrument available in Regional Sophisticated Instrumentation center, IIT, Chennai is used for this study(Fig 8). It consists of globar and mercury vapor lamp as sources, an interferometer chamber comprising of KBr and mylar beam splitters followed by a sample chamber and detector. Entire region of 450-4000 cm^{-1} is covered by this instrument. Solid samples are dispersed in KBr or polyethylene pellets depending on the region of interest.50 mg of sample is dispersed in KBr pellet and IR rays were passed to assess the functional groups like -OH, -CN, -CO, -CH, $-NH_2$ .Sample for infrared spectroscopy (IR) was done by mixing the sample with potasiumbromide and made into pellet form and placed in the container and infrared rays were passed through the sample. The amount of transmittance on a graph with percentage of transmittance in Y-axis and wave number in X-axis.The spectrum of the reference sample is compared with the samples stored in chlorine water and the interaction of chlorine on the bonds of PMMA can be assessed.

III. Results

The UV-VIS spectrum is due to the electronic transitions of the molecule. This is characteristic of a compound. Qualitative and quantitative estimations of compounds are possible by this non destructive technique.50 mg of sample is taken and UV rays are passed into the sample the result are obtained on a graph with wavelength in nanometer on X axis and the percentage of reflectance on Y axis.

Interpretation of UV spectrum: If an organic compound absorb UV radiation it means that the compound contains carbonyl or conjugated double bonds[3]. since PMMA absorb UV rays the existence on this bonds are conformed.(graph 1,2,3).

Infrared spectroscopy : Infrared spectroscopy is one of the characterizing tool to assess the functional groups like -OH, -CN, -CO, -CH, $-NH_2$. Solid samples are dispersed in KBr or polyethylene pellets depending on the region of interest.50 mg of sample is dispersed in KBr pellet and IR rays were passed into the sample taken in a container.The results are obtained in a graph called spectrograph.

Interpretation of IR spectrum : An infrared spectrum consist of -1.The functional group region 4000-1300 cm^{-1}2.The finger print region 1300-667 $cm.^{-1}$ In the functional region ,functional groups present in a chemical compound can be assessed. In case PMMA the functional group present are carbonyl group and vinyl group . Finger print region is very complex with stretching and bending originating by interacting vibrational models of C-C, C-O, and C-N. The patterns of the spectra in finger print region are extremely sensitive and change with minor chemical or sterochemical alterations in a molecule. The frequency distribution of IR spectrum for the chemical groups present in poly methylmethacrrylate is given in the following table 2.

On comparing the spectrograph graph 4 (Group IControl) with graph 5 (Group IV) following changes are observed –

1.- CH = CH2 - vinyl group region Vinyl group is one the main functional group of PMMA it is responsible for addition of free radical to complete the polymerization process. The peak value obtained for GroupI(control) are 3000.1cm-1 ,2953.8cm-1 ,2930.0 cm-.1 .The values obtained for group IV (3ppm) are 3000.7 cm-1, 2955.0cm-1, 2844.5cm-1.

2. **C = O - carbonyl group region** - Carbonyl group is another functional group of PMMA. There is no change in this region for Group I & Group IV**.**
3. **-(CH2) –n region** -This is the main back bone of the polymer chain over which the methyl and carboxymethyl groups were arranged in alternative manner. There is no change in this region for Group I&Group IV.

On comparing the spectrograph graph 4 (Group I control) with graph 6 (group V) following changes are observed –

1. **- CH = CH2 - vinyl group region** - Vinyl group is one the main functional group of PMMA it is responsible for addition of free radical to complete the polymerization process The peak value obtained for GroupI(control) are 3000.1cm-1 ,2953.8cm-1 ,2930.0 cm-1 . .The values obtained for group V are (100 ppm) are 3000.2 cm-1 ,2954.4cm-1 ,2844.8cm-1
2. **C = O - carbonyl group region** - Carbonyl group is another functional group of PMMA. There is no change in this region for Group I & Group V**.**
3. **-(CH2) –n region** - This is the main back bone of the polymer chain over which the methyl and carboxymethyl groups were arranged in alternative manner. There is no change in this region for Group I&GroupV .

IV. 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 cavity[28]. 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 water[28].

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 group[28]. The terminal double bond is responsible for addition polymerization (Fig 7).[14,31,12]Chlorine 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 ions[19]. 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 denture[30,33].

Chlorine being highly electronegative and chemically reactive halogen will interact with the chemical structure of PMMA[31,33] .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 resin[23].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 important[14]. 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 process[31]. 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 bond[34]. 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.

Near infrared spectroscopy (NIR) to assess the double bond conversion in acrylic resins. The sample were mixed with potassium bromide pellet and subjected to analysis. NIR is a nondestructive analysis of products in a variety of fields including agricultural, medical, pharmaceutical, and in textile industry. NIR spectroscopy has been widely used in polymer industry for quality assurance and process control ,especially as a technique to monitor a epoxy curing reaction[34].In this study NIR was used to find out the reaction of chlorine on PMMA.The degree of double bond conversion in light cured composites using was assessed using micro attenuated total reflection infrared spectroscopy (Micro-ATR)[12].

The above references indicates IR, is an effective tool to characterize PMMA. Chlorine interact with PMMA and can alter the physicochemical property of the polymer .Chemical interaction of chlorine over the double bond of PMMA can be assessed by spectroscopy techniques.. Hence scrapings were taken from Group I,Group IV and Group V and subjected to spectroscopy analysis. UV spectroscopy gives idea about the conjugated double bonds only. Individual functional group can studied by IR spectroscopy.

IR spectroscopy confirms the chemical interaction of chlorine on PMMA. In the vinyl group region (terminal double bond) .Spectrograph of Group V shows good change when compared with Group I .G.B.Pariiskii - studied the effect of chlorine on PMMA and concludes chlorine can react with the terminal double bond ,carbonyl group and the methyl group. In the present study chlorine mainly adds to the terminal double bond and does not add to the methyl and carbonyl groups. From this study it is under stood that chlorine from chlorinated water interact chemically with PMMA over the terminal bonds and split the polymer chain at higher concentration .On the other hand at lower concentration the action of chlorine is negligible.

V. Conclusion

Within the limitation of the study it can be concluded that :
1.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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