CLINICAL STUDY

Evaluation of Chemical Properties of Polymethylmethacrylate in Two Different Media by Using Ultraviolet-Visible Spectroscopy

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ABSTRACT

Aim: This study aimed to evaluate the effect of concentration of chlorine on the polymethylmethacrylate and the influence of chemical properties of polymethylmethacrylate using ultraviolet-visible spectroscopy.

Materials and methods: A total of 30 acrylic blocks of dimensions 65X 13X 3 mm as per the specification of ASTM [American standard for testing materials] were made in heat cure denture base resin to evaluate the effect of chlorine on polymethylmethacrylate. 30 samples were divided into 3 groups of 10 samples in each. Group I was stored in artificial saliva which acts as a control group, Group II was stored in 3ppm concentration of chlorine and Group III was stored in 100ppm concentration of chlorine.

Results: Ultraviolet rays are passed into the sample, the results are obtained on a graph with a wavelength in nanometer on the X-axis and the percentage of reflectance on the Y-axis. If an organic compound absorbs ultraviolet radiation, it means that the compound contains carbonyl or conjugated double bonds3. Since polymethylmethacrylate absorbs ultraviolet rays, the existence of these bonds is confirmed in the graph.

Conclusion: Within the limitations of the study it was concluded that the effect of chlorine on polymethylmethacrylate can react over the conjugated bond or carbonyl group at higher concentration, whereas the action of chlorine is negligible at a lower concentration.

KEYWORDS: Polymethylmethacrylate, Ultraviolet Visible Spectroscopy, Denture Base Resins, Chlorine.

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INTRODUCTION

The polymethylmethacrylate (PMMA) was introduced in 1937 opened up a tremendous prospective for the manufacture of partial removable and complete dentures. Denture base resins are very much capable of absorbing water when immersed in liquid. This absorption is facilitated by the polar properties of PMMA macromolecules through a diffusion process [1]. PMMA is formed by polymerization of the monomer, methylmethacrylate by emulsion method of polymerization. It has a main carbon skeleton with pendant hydrogen (H), methyl (CH₃), and carboxymethyl (COOCH₃) arranged in an alternative manner. Chain termination and chain transfer limit the polymerization, this will create a terminal double bond in the polymer [2,3]. 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. Chlorine is
widespread use as a disinfectant for water in our country being more electronegative and highly reactive halogen, it can interact with the bonding site of the polymer chain [4,5].

Structure of PMMA has a terminal double bond and pendant methyl (\(\text{CH}_3\)) and carboxymethyl (\(\text{COOCH}_3\)) group which act as electron releasing and withdrawing groups respectively, which can create electron depletion in the terminal bond and can favor an electrophilic and nucleophilic attack [6]. The chemical structure of PMMA can favor the reaction of chlorine [6,7], considering this criteria study was conducted to evaluate the introduction of chlorine from chlorinated water on the bonds of PMMA and the action of this chlorine on the bonds of PMMA was assessed by ultraviolet-visible spectroscopy [8]. The aim and objectives of this study were to evaluate the effect of concentration of chlorine on the PMMA chemical structure and the influence of chemical properties of PMMA using ultraviolet-visible spectroscopy.

MATERIALS AND METHODS

This study was performed to find out and analyze the influence of different concentrations of chlorine on bonds of PMMA. A commercially available heat cure resin, Acrylyn-H, and self resin, Acrylyn-R manufactured by Asian acrylates, India were used to make samples (Table 1).

Table 1: Materials used to prepare the test samples

| S. No. | Material        | Manufacturer’s name | Chemical name          |
|-------|----------------|---------------------|------------------------|
| 1.    | Heat cure resin| Acrylyn-H           | Polymethylmethacrylate |
| 2.    | Self cure resin| Acrylyn-R           | Polymethylmethacrylate |

A total of 30 acrylic blocks of dimensions 65X13X3 mm as per the specificaion of ASTM [American standard for testing materials] were made in heat cure denture base resin to evaluate the effect of chlorine on PMMA. 30 samples were divided into 3 groups of 10 samples in each. Group I was stored in artificial saliva which acts as a control group, Group II was stored in 3ppm concentration of chlorine and Group III was stored in 100ppm concentration of chlorine (Table 2).

Table 2: Grouping of samples

| S. No. | Group | Media                     |
|-------|-------|---------------------------|
| 1.    | I     | Artificial saliva         |
| 2.    | II    | Prepared chlorine solution of 3ppm strength |
| 3.    | III   | Prepared chlorine solution of 100ppm strength |

Preparation of the test samples:

Preparation of the die: The die for making the resin pattern was made out of mild steel. The approximate composition: Fe-99%, C-0.25%(max), Mn-0.4-0.7%, Si-0.1-0.5%, sulphur and phosphorus residual. The rectangular die consist of three parts as i) Base die, ii) Middle die (or) Match plate, iii) Lid (Figure 1).

The 3 parts were mounted one above the other and locked tight. The middle part was split into 2 halves parallel to the long axis of the die to facilitate easy removal of the sample. Indexing marks were placed on the sides of all 3 parts to ensure correct alignment.

Figure 1: Parts of a die

Base part: This consisted of a flat base with four vertically aligned bars that served to lock the middle and the upper part.

Middle part: The middle part is 3mm thick and consists of a rectangular opening measuring 65mmX13mmX3mm. The dimensions were based on ASTM standards. There were four holes in the four corners for proper aligning of the die. The middle part was split in the middle parallel to the die’s long axis for easy retrieval of samples.

Lid: This consisted of a smooth lid with four holes that aligned into the vertical bars of the lower part. This served to lock the middle part after the resin was poured so that samples were obtained in flush with the metal die.

Preparation of acrylic blocks using the moulds: The second part of the die is assembled over the base and coated with petrolatum jelly; auto-polymerizing resin was mixed with the monomer in dough stage it was packed into the die. The third part of the die was placed over the second part and pressed well to get the required contour. After the self-cure resin sets the third part of the die was removed, the second part was removed in two halves and the blocks are recovered, trimmed to remove the excess, and now the blocks were ready for processing in heat cure resin.

Processing the test specimen: 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 boil over a period of 1 hour and keeping it in boiling water for an additional hour. After processing the flasks were bench cooled deflasked and excessive flash were trimmed. The dimension of the blocks was checked and found to be as per the ASTM standards and coded.

Preparation of chlorine solution: 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 an indicator for color change which indicates the termination of the reaction.

The known strength of sodiumthiosulphate is taken in the burette and the unknown chlorine solution is taken in a conical flask, iodine is added as an indicator. Sodiumthiosulphate is titrated against the chlorine solution and the point of the reaction is calculated by the change of color.

The normality of sodiumthiosulphate is known, the volume of sodiumthiosulphate consumed to react with a known volume of chlorine solution by using the following formula strength of chlorine solution is estimated.

\[ \frac{V_1 N_1}{V_1} = \frac{V_2 N_2}{V_1} \]

\[ N_1 = \text{Normality of chlorine solution not known.} \]
\[ V_2 = \text{Volume of sodiumthiosulphate consumed for the reaction} \]
\[ N_2 = \text{Normality of sodiumthiosulphate.} \]

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, India.

Characterization of PMMA: The interaction of chlorine ions with the polymer chain is evaluated by Ultraviolet Visible spectroscopic analysis. Scrapings were taken from one acrylic block in Group I, Group II, and Group III representing one from the control group, and the other from a lower and higher concentration of chlorine were subjected to spectroscopic analysis.

Ultraviolet Visible (UV-VIS) spectroscopy: Cary 5E is a high-resolution spectrophotometer available at Regional Sophisticated Instrumentation Center, IIT, Chennai, India was 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 was done by taking the sample in a container and ultraviolet rays were passed through the sample (Figure 2). The amount of reflectance is recorded on a graph paper with a percentage of reflectance in Y-axis and wavelength in the nanometer on X-axis. This was done to verify the existence of conjugated bonds.

RESULTS
UV-VIS spectroscopy: The UV-VIS spectrum is due to the electronic transitions of the molecule considered to be the main 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 results are obtained on a graph with wavelength in nanometer on X axis and the percentage of reflectance on Y axis.

Interpretation of UV-VIS spectrum: If an organic compound absorbs UV radiation, it means that the compound contains carbonyl or conjugated double bonds. Since PMMA absorb UV rays, the existence on these bonds is confirmed in graph 1, 2 & 3.
DISCUSSION

The structure of PMMA is formed by the repetition of methylmethacrylate which has the main carbon skeleton and pendant methyl and carboxymethyl group arranged in an alternating manner. PMMA has two double bonds one at the terminal region and the other in the carbonyl group [2]. The terminal double bond is responsible for addition polymerization [3,6,9].

Chlorine in water exists as hypochlorus acid and chloride ions. Hypochlorous acid in aqueous solution form chloride ions and hydrogen ions. Hence chlorinated water will have chloride ions and hypochlorous acid. Water along with chloride will diffuse into the denture and will interact with the structure of PMMA.

\[
\begin{align*}
\text{H}_2\text{O} + \text{Cl}_2 & \rightarrow \text{HClO} + \text{H}^+ + \text{Cl}^- \\
\text{HClO} & \rightarrow \text{H}^+ + \text{ClO}^- 
\end{align*}
\]

Chloride ions from water can interact with the double bonds of PMMA. It will form product1 & product2. Product1 blocks the terminal double bond which is important for further polymerization reaction, while product2 is formed by the reaction of chloride ions with the carbonyl group of PMMA.

\[
\begin{align*}
\text{Me} - \text{Me} - \text{Me} - \text{H} - \text{Me} & \rightarrow \text{C} - \text{C} - \text{C} - \text{C} = \text{C} \rightarrow \text{Cl}^- \\
\text{COMe} - \text{COMe} - \text{COMe} & \rightarrow \text{COMe} - \text{COMe} - \text{COMe} - \text{COMe} \\
\text{Me} - \text{Me} - \text{Me} - \text{H} - \text{Me} & \rightarrow \text{C} - \text{C} - \text{C} - \text{C} = \text{C} - \text{Cl}^- \\
\text{COMe} - \text{COMe} - \text{COMe} - \text{COMe} & \rightarrow \text{COMe} - \text{COMe} - \text{COMe} - \text{COCl} \\
\text{Me} - \text{Me} - \text{Me} - \text{H} - \text{Me} & \rightarrow \text{C} - \text{C} - \text{C} - \text{C} = \text{C} \\
\text{COMe} - \text{COMe} - \text{COMe} - \text{COMe} & \rightarrow \text{COMe} - \text{COMe} - \text{COMe} - \text{COCl}
\end{align*}
\]

Chlorine is one of the common disinfectant used for water purification, chlorine in water exists as hypochlorous acid and hypochlorite ions [4]. Water is a molecule with
2 atoms of hydrogen and one atom of oxygen. Chlorine is a single atom and the atomic radius is less and size is also small hence chlorine along with water can also enter into the denture. Chlorine being highly electronegative and chemically reactive halogen will interact with the chemical structure of PMMA [5,6,10].

G.B. Pariiskii et al [11] studied the effect of chlorine on PMMA and concludes chlorine can react with the terminal double bond, carbonyl group, and the methyl group, but in the present study, chlorine reacts with the carbonyl or conjugated bond and not over the other region of PMMA.

Chang K.H. Sharma et al [3] studied the polymerization kinetics of acrylic and concluded the existence of a terminal double bond. For further polymerization the existence of the double bond is important. J.W. Stansbury et al [12] determined the double bond conversion in dental resin by near infrared spectroscopy and concluded that after polymerization double bond gets converted to a single bond. The presence of carbonyl or conjugated double bond was confirmed by UV-VIS spectroscopy. Raj K. Bansali [4] depicted that a carbon double bond consists of a 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 hypochlorite ions. Blocking of the terminal double bond will inhibit the further polymerization process.

Central public health and environmental engineering organization (CPHEEO) Government of India, advocates the concentration of chlorine for effective disinfection should be 1.5 ppm at the tail ends in a water distribution system [4]. PMMA when stored in water containing chlorine it can interact chemically and can produce some changes in the structure of the polymer which can be assessed by spectroscopy [8].

J.W. Stansbury, S.H. Dickens [12] used the near infrared spectroscopy (NIR) to assess the double bond conversion in acrylic resins. The sample was mixed with potassium bromide pellets and subjected to analysis. NIR is a non-destructive analysis of products in a variety of fields including agricultural, medical, pharmaceutical, and textile industries. NIR spectroscopy has been widely used in the polymer industry for quality assurance and process control, especially as a technique to monitor epoxy curing reaction. Eliades et al [9] evaluated the degree of double bond conversion in light-cured composites using micro attenuated total reflection infrared spectroscopy (Micro-ATR).

V. Sankar et al [13] conducted a study to characterize photo initiated PMMA using IR techniques. Chlorine interacts 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. UV-VIS spectroscopy gives an idea about the carbonyl or conjugated double bonds only. The individual functional group can be studied by IR spectroscopy. IR spectroscopy confirms the chemical interaction of chlorine on PMMA. R.Nimma Elizabeth [14] characterized PMMA & PVC using infrared spectroscopy (IR). G.B. Pariiskii [11] studied the effect of chlorine on PMMA concludes chlorine can react with the terminal double bond, carbonyl group and the methyl group.

CONCLUSION

Within the limitations of the study, it was concluded that chlorine from chlorinated water interacts chemically with PMMA over the carbonyl or conjugated bonds and split the polymer chain at higher concentration. On the other hand, at lower concentrations the action of chlorine is negligible.

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