



EVALUATION OF PHYSICAL PROPERTIES OF DENTURE BASE RESIN IN TWO DIFFERENT MEDIA BY USING THERMAL GRAVIMETRIC ANALYSIS AND DIFFERENTIAL THERMAL ANALYSIS.

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Conflicts of Interest: Nil

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Abstract:

Aim: The aim was to evaluate the physical properties of denture base resin in two different media such as artificial saliva and chlorinated water by using thermal gravimetric analysis (TGA) & differential thermal analysis (DTA).

Materials and Methods: 40 samples divided into 2 groups of 20 samples each. One group was stored in artificial saliva the other group was stored in chlorinated water of 3ppm concentration. Total number of 40 acrylic blocks was grouped as Group I & II. Scrapings were taken from the blocks of both the Group I & II. Samples of artificial saliva and chlorinated water were subjected to thermal behavior by TGA and DTA.

Results: TGA Thermograph of Group I shows broad endothermic peak at 282.9^oC to 357.7^oC and exothermic peak at 535.4^oC to 602.2^oC. TGA Thermograph of Group II shows broad endothermic peak at 336.2^oC to 362.2^oC and exothermic peak at 535.6^oC to 643.9^oC. The phase change corresponding to the weight change is shown in DTA thermograph. The thermograph of TGA/DTA shows changes in thermal behavior in both the medium.

Conclusion: Changes in the physical properties of denture base resin such as transition temperature and phase changes were evaluated by thermal analysis. Chlorine being highly reactive will react with the double bonds of polymethylmethacrylate (PMMA). Blocking of double bond can affect the physical properties of denture base resin.

Keywords: Polymethylmethacrylate, Differential thermal analysis, Thermal analysis, Denture base resin.

Introduction:

Polymethylmethacrylate (PMMA) is formed by polymerization of monomer (methylmethacrylate) by emulsion method of polymerization. It has a main carbon skeleton with pendant hydrogen (H), methyl (CH₃) and carboxymethyl (COOCH₃) arranged in alternative manner. Chain termination and chain transfer limits the polymerization, this will create a terminal double bond in the polymer.^[1] PMMA absorbs water slowly over a period of time. Absorption of water is facilitated by the polarity of PMMA molecule. The diffusion co-efficient of typical heat cure denture base resin is 1.08 X10m/sec at 37^oC. The diffusion occurs between the macromolecules which are forced apart by the diffusion of water and thereby relieving the inherent stress with constant relaxation, so possible changes occurs 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%. 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 widely used as a disinfectant for water being more electronegative and highly reactive halogen, it can interact with the bonding site of the polymer chain.^[2]

Pavarina AC et al^[3] reported that use of sodium hypochlorite 1% as a disinfectant of denture base resin decrease the transverse strength of acrylic resins. Neppelenbroek et al^[4] reported that use of sodium hypochlorite as a disinfectant effectively decreases the hardness of acrylic denture base resin. Chlorine effectively decreases the bond strength between tooth and denture base resin.^[3,4]

Structure of PMMA has a terminal double bond and pendant methyl (CH₃) and carboxymethyl (COOCH₃) group which are electron releasing and withdrawing groups respectively, which can create electron depletion in the terminal bond and can favor an electrophilic and nucleophilic attack .

The aim and objectives of this study was to evaluate the thermal behavior of the denture base resin by using DTA & TGA.^[5]

Materials and Methods:

This study was performed to analyze the thermal behavior of denture base resin was stored in artificial saliva and 3ppm concentration of chlorine. A commercially available

heat cure resin (Acralyn-H, Asian Acrylates 4, Vora House, Mumbai, India) was used to make samples. A total 40 acrylic blocks of dimensions 65 X 13 X 3 millimeter as per specification of American standard for testing materials (ASTM) were made in heat cure denture base resin. 40 samples were divided into 2 groups of 20 samples each. One group was stored in artificial saliva and the other group was stored in chlorinated water of 3ppm concentration.

Preparation of the test samples:

a) 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 consists of three parts as:

i) Base part ii) Middle part (or) Match plate, iii) Lid

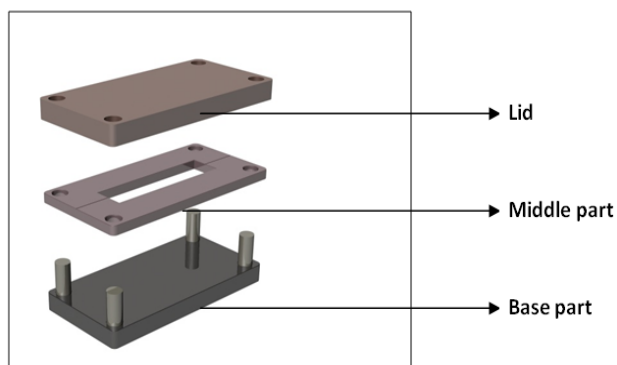


Figure 1: Parts of a die

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.

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 the 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.

b) 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 (Acralyn-R, Asian Acrylates 4, Vora House, Mumbai, India) was mixed with the monomer in dough stage it was packed into the die. 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 third part of the die was removed, 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.

c) 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 boiling over a period of 1 hour and keeping it in boiling water for additional hour. After processing the flasks were bench cooled, deflashed and excessive flash were trimmed. Dimension of the blocks were 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 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 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, the strength of chlorine solution is estimated.

$$V_1 N_1 = V_2 N_2$$

V_1 = Volume of chlorine solution.

N_1 = Normality of chlorine solution unknown.

V_2 = Volume of sodiumthiosulphate consumed for the reaction.

N_2 = Normality of sodiumthiosuphate.

$$N_1 \text{ (Normality of chlorine solution)} = \frac{V_2 N_2}{V_1}$$

Once the strength of chlorine solution is known, it can be diluted according to the needs. Preparation of chlorine solution was done at Chennai Metro water Quality control lab, Kilpauk, India.

Thermal analysis:

Scrapings were taken from the acrylic blocks in Group I & Group II were subjected to the following thermal analysis by TGA and DTA. Simultaneous Thermal Analyzer (Netzsch STA 409, Regional Sophisticated Instrumentation center, Indian Institute of Technology, Chennai, India) is used to study the samples. It records simultaneous TGA and DTA measurements. Temperature ranges from room temperature to 600°C. 5 mg of sample was placed in a pan and lid was crimped to maximize the contact between the sample and the pan. The sample was heated from room temp to 600°C at a constant heating rate of 20°C /minute under nitrogen purge and the results are obtained in a graph called thermograph.

TGA is a technique where by the weight of a substance in an environment heated or cooled at a controlled rate is recorded as function of time or temperature. The equipment has a thermo balance, heating and temperature measurement, sample cups, atmosphere control, recorder (Fig. 2). The sample is weighed in milligrams and placed in a sample cup which is connected to a thermo balance, air in the furnace is evacuated under nitrogen atmosphere, the sample is heated as a result with increase in temperature, the weight percentage of the sample decreases and it is recorded on a graph with percentage of weight loss in the Y-axis and temperature in the X-axis.

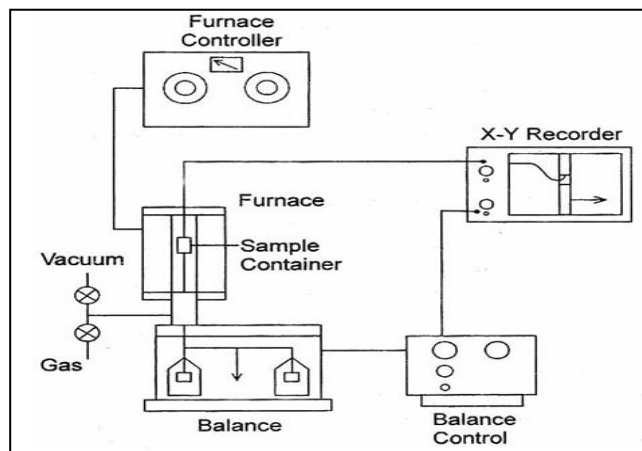


Figure 2: Schematic Diagram for Thermal Gravimetric Analysis

DTA is a technique in which the temperature difference (ΔT) between the samples and thermally inert reference material are continuously recorded as function of temperature. The apparatus consist of a furnace, sample holder, thermostat to control the furnace temperature and sensor to record the difference in the temperature between the sample and the reference material (Fig. 3). The sample and reference material (aluminum oxide) is taken in the sample holder and heated; the temperature difference (ΔT) between the two sample is recorded on graph with temperature on X-axis and (ΔT) on the Y axis. The thermograph of TGA & DTA of the reference material is compared with blocks stored in chlorinated water and artificial saliva, change in glass transition temperature and thermal behavior of the samples were assessed.

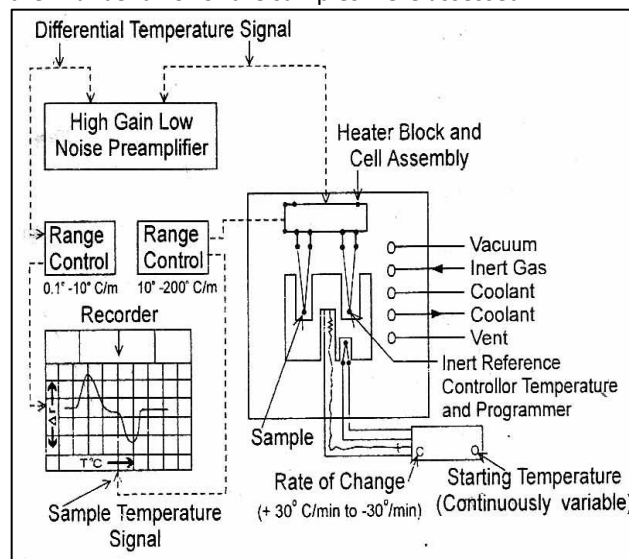


Figure 3: Schematic Diagram for Differential Thermal Analysis

Characterization of samples:

The samples were subjected to various physicochemical techniques to find out any changes in chemistry of PMMA such as addition of chlorine on the bonds of PMMA. Sample of Group I & Group II are assessed for the thermal analysis. Thermal analysis is a group of techniques in which the physical property of a substance is measured as a function of temperature, while the substance is subjected to a controlled temperature program. These includes change in weight as TGA and temperature difference as DTA.

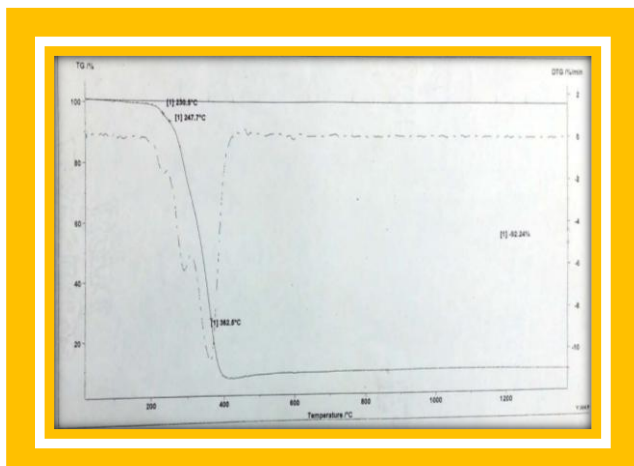
Results:

Interpretation of TGA/DTA thermograph:

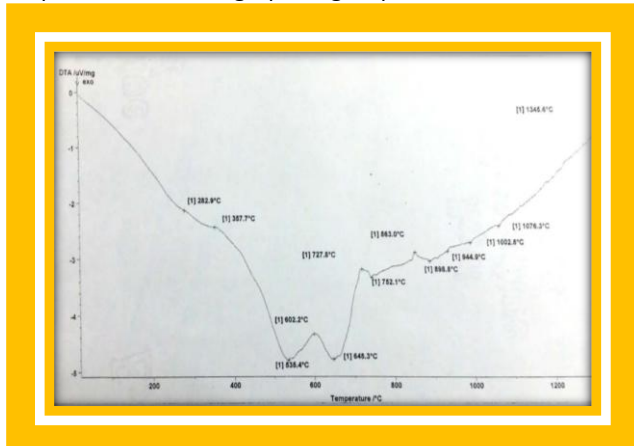
Group I:

The sample is taken in a crucible and heated from room temperature to 600°C. The thermal analyzer will record the

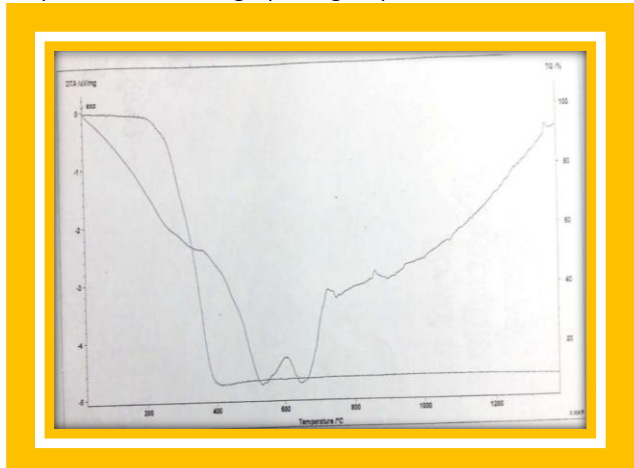
weight change and the phase change simultaneously. TGA shows first weight changes which occurs at 230.5°C to 247.7°C. The second change occurs at the temperature of 362.5°C (Graph 1). The phase change corresponding to the weight change is shown in DTA thermograph. The graph shows broad endothermic peak at 282.9°C to 357.7°C and exothermic peak at 535.4°C to 602.2°C (Graph 2). Graph 3 represents both TGA & DTA in a single graph.



Graph 1: TGA thermograph of group I

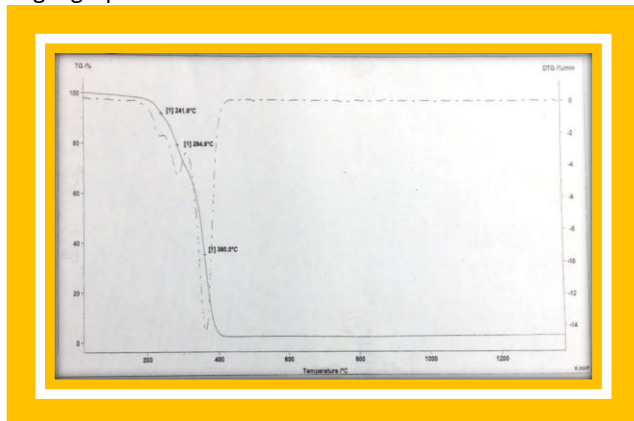


Graph 2: DTA thermograph of group I

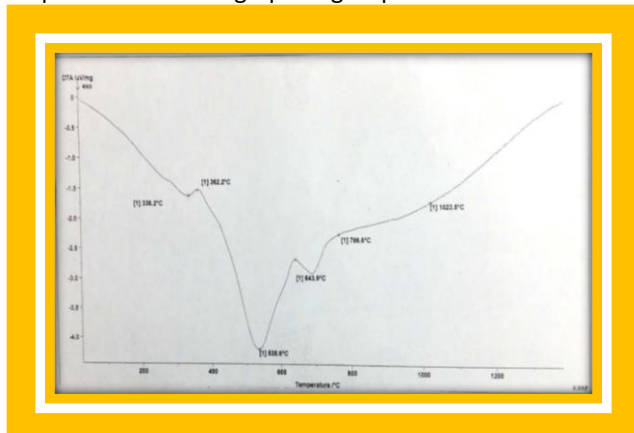


Graph 3: TGA/DTA thermograph of group I

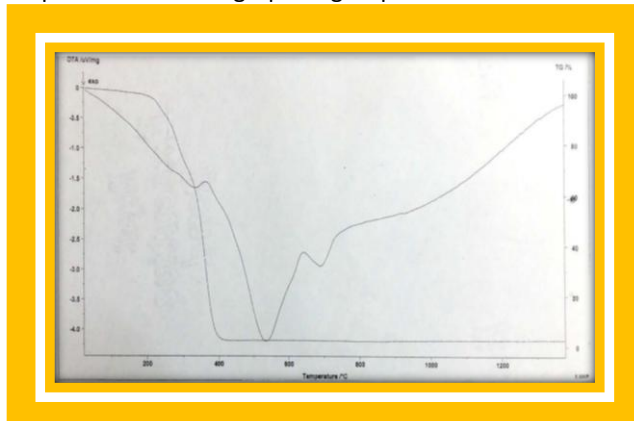
Group II:
The sample is taken in a crucible and heated from room temperature to 600°C. The thermal analyzer used will record the weight change and the phase change simultaneously. TGA shows first changes which occurs at 241.60°C to 284.9°C. The second change occurs at the temperature of 360°C (Graph 4). The phase change corresponding to the weight change is shown in DTA thermograph. The graph shows broad endothermic peak at 336.2°C to 362.2°C and exothermic peak at 535.6°C to 643.9°C (Graph 5). Graph 6 represents both TGA & DTA in a single graph.



Graph 4: TGA thermograph of group II



Graph 5: DTA thermograph of group II



Graph 6: TGA/DTA thermograph of group II

Discussion:

PMMA has earned a great popularity and widely used in dentistry because they can be processed easily using relatively simple technique, esthetic and more 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.^[6] 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. A typical denture base require a period of 17 days to become fully saturated with water.^[6] 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 and thermal analysis.^[5]

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 very important. If the bonding site is blocked, then repair will be difficult. Chlorine from chlorinated water and carbonated beverages significantly decrease the bond strength between the teeth and the denture base resin.

Nimma Elizabeth R et al^[7] characterized PMMA & Polyvinylchloride using infrared spectroscopy and TGA & DTA. Bing Zhang and Frank D. Blum^[8] conducted thermo gravimetric studies of PMMA on silica. Sankar V et al^[9] conducted a study to characterize photo initiated PMMA using TGA & DTA techniques. PMMA when subjected to thermal analysis two main degradation generally occurs. At lower temperature, monomer evolution is initiated at the unstable terminal double bonds present in some of the macromolecules as a consequence of disproportionate termination reaction. This occurs at 250°C - 320°C with a maximum peak of 310°C. At higher temperature, there is random bond scission of the polymer chain. These reaction have different energies of activation depending on the chain length and percentage of double bonded chains in the polymer. This occurs at 320°C- 420°C with a maximum rate at 380°C. The above reference indicates TGA & DTA are effective tool to characterize PMMA. Chlorine interact with PMMA and can alter the physicochemical property of the polymer. A change in the physical properties such as

glass transition temperature and phase changes was evaluated by thermal analysis.

Conclusion:

Patients are advised not to store the denture in water containing chlorine. Chlorine is one of the disinfectant used for disinfection of water. Hence, chlorine along with water can enter into the denture. Chlorine being highly reactive will react with the double bonds of PMMA. Blocking of double bond can affect the physical properties of PMMA. Thermal behavior of denture base resin was assessed by TGA & DTA analysis. Thermograph of TGA & DTA shows changes in thermal behavior which are stored in artificial saliva and 3ppm concentration of chlorine.

Acknowledgements:

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