A Narrative Review of Different Types and Processing Methods of Acrylic Denture Base Material

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Abstract

Acrylic resin is commonly used to fabricate removable prostheses due to its adequate physical, mechanical properties and cost effectiveness. There has been continuous development of the materials to improve their properties and to widen their applications in different clinical settings. This study aimed to provide a historical development of the acrylic resin and elaborate on the properties of different types and the processing methods of acrylic resins used to fabricate denture base which are commercially available in the market. This would help dental clinicians to choose the best material of choice in the market. The authors have summarized the history, development and classification of different types of acrylic resins used in fabricating dentures and processing methods based on published research available on this topic using published materials available in the Dental Library, University of Malaya and the database (Science Direct, PubMed). Every type of acrylic denture base material has its pros and cons. Therefore, careful selection of the material and processing method is crucial to ensure patients are receiving the best outcome in prosthodontic treatment hence upholding the patients' best interest and improving their quality of life.

Introduction

Acrylic resin polymer was first introduced in mid-1940s. It is commonly used to make removable prostheses due to its favorable working characteristics, excellent aesthetics, adequate mechanical strength and inexpensive [1, 2]. In order to fabricate a comfortable and fitting denture, the base should be dimensionally stable with good adaptation and border seal [3]. However, the shrinkage and expansion properties of the material during processing procedures are virtually inevitable, leading to the development of new processing methods such as rapid heat-cured, injection molding and microwave activated technique [4-6].

History of Denture Base Material

Earliest denture base material was documented

before the year 1900. Prior to the development of plastic material, replacement of missing tooth was dependent on natural resins or exudates and tissues from plants, animals and insects [7]. The most notable resin was shellac material which was derived from resin products by tiny insects (*Coccus Lacca*). Furthermore, Guerini mentioned that the dentures were carved from hardwood, ivory or bone and fastened to natural teeth by screws or other means before 1800 [8]. However, the dentures were functionally ineffective, easily stained, pitted, and foul from decay [2].

In 1839, Charles Goodyear discovered a method of producing a mixture of sulfur with caoutchouc (natural rubber) with greater flexibility [7]. A harder rubber or known as vulcanite was invented by Charles' brother, Nelson Goodyear in 1851. It was further developed and introduced as a denture base material in 1855 [9]. Vulcanite had many advantages over all other materials available during that period. It was cheap, adaptable to a master cast and insoluble in saliva. Although porcelain teeth mounted in vulcanite was the

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standard in denture making for the next seventy-five years, the main drawback of this material was its poorly controlled color. Furthermore, dyes and pigments added to obviate the natural dark brown color have weaken the final properties of vulcanite denture [10].

A more aesthetically pleasing color material known as celluloid was introduced in 1868 by Hyatt. It was used as a denture base in 1890 [11]. Nevertheless, the disadvantage of this material was it stained easily due to the porous structure. Furthermore, the plasticizer added to facilitate molding produced an unpleasant taste and odor [12]. In order to improve the properties of denture base material at that time, vulcanized rubber was used as the denture base and celluloid as the gingiva around porcelain teeth. This denture was flexible, easy to fabricate and mimicked gingival tissues well. Unfortunately, celluloid absorbed stains, gradually became grossly discolored, produced odors and easily flammable. Hence, further improvements in both its appearance and functional durability were needed [1].

During early 20th century, the period from 1910 to 1950 was referred as the age of thermoplastic as wide variety of synthetic elastomers were developed. Some examples were phenol-formaldehyde or commonly known as Bakelite, polystyrene, epoxy resin, polyvinylchloride (PVC), vinyl acetate and other synthetic polymers [13]. But none of these materials was able to produce a dimensionally stable and accurate denture until the introduction of a heat processed thermosetting material, polymethyl-methacrylate (PMMA) in 1936 [2, 14].

It was estimated that by 1946, 96.0% of dentures had been made from PMMA because of its favorable working characteristics, inexpensive and, easy to manipulate. Furthermore, it has adequate strength with biocompatible property with better aesthetic [2, 15]. Despite all the excellent properties of PMMA, one of the drawbacks is dimensional changes due to shrinkage and expansion during processing [16]. This has led to the improvisation of PMMA compositions, manipulation techniques as well as processing methods.

Criteria for an Ideal Denture Base Material

In order to fabricate a retentive and comfortable denture, the material of which the denture base is constructed must have met certain requirements in order to perform satisfactorily. From the perspective of both the dentist and technician, the material should be of adequate strength to withstand occlusal loading, easy to manipulate, low toxicity during processing, biocompatible with oral cavity, dimensionally stable, radiopaque and easy to repair [17].

On the other hand, from the patient's point of view the denture should fit well, feel comfortable, does not traumatize the tissues, easy to clean, aesthetically pleasing both immediately on placement and in the longer term, allow good heat diffusion to retain normal perception of thermal stimuli and permit food to be tested normally so that food can be appealing [17].

Despite the continuous improvisation of the current denture base materials, none of the material fulfil all the ideal criteria. The materials which fulfilled most of these criteria are the resin polymers, namely polymethyl methacrylate (PMMA). For this reason, many research has been focusing on the properties and development in every aspect of acrylic resin since early 20th century till now.

Physical and Mechanical Properties of Acrylic Resins

The physical and mechanical properties of acrylic resins are important to produce a fitting, comfortable and functional removable partial denture. Some of the minimal requirements are set out in ISO specification 20795-1:2013 as shown in (Table 1).

Classification of Denture Base Material

According to International Organization for Standardization (ISO) 20795-1:2013, denture base can be classified according to their composition and processing technique as shown in Table 2 [18]. Different types of denture base material are developed based on different clinical application. Acrylic resin or more specifically polymethyl methacrylate (PMMA) is a polymer formed from the addition reaction of the monomer methylmethacrylate (MMA). Even though PMMA is available as gel, sheet or blank, the powder/liquid presentation is most widely used [17, 19].

Table 1: Requirements of denture base polymers as given in ISO 20795-1:2013

Type	Ultimate Flexural Strength MPa (minimum)	Flexural Modulus MPa (minimum)	Residual methyl methacrylate monomer % mass fraction (maximum)	Water sorption µg/mm³ (maximum)	Solubility µg/mm³ (maximum)
1,3,4,5	65	2000	2.2	32	1.6
2*	60	1500	4.5	32	8
* auto-polymerize					

Table 2. Classification of denture base material based on ISO 20795-1:2013 (ISO, 2013)

Type	Class	Descriptions
1	1	Heat-polymerizable materials (Powder and liquid)
1	2	Heat-polymerizable materials (Plastic cake)
2	1	Autopolymerizable materials (Powder and liquid)
2	2	Autopolymerizable materials (Powder and liquid for pour-type resins)
3	-	Thermoplastic blank or powder
4	-	Light-activated materials
5	-	Microwave-cured material

PMMA powder is composed mainly of small spheres called beads or pearls that may have to be modified with small amounts of ethyl methacrylate or ethyl acrylate to produce a softer final product. The size of these particles is approximately 150 µm in those resin which are processed by heat. Benzyl peroxide is coated at the surface of polymer beads for the initiation of polymerization. As only a small amount of polymer is required to start the reaction, it is important that these beads are not contaminated to prevent premature initiation of polymerization reaction. PMMA is a clear, glass like polymer to which pigments and opacifiers have been incorporated in order to produce a more natural colored denture base [20, 21].

The liquid is predominantly non-polymerized methyl methacrylate monomer. It is a clear colorless, low viscosity liquid with a boiling point of 100.3ºC, melting point of -48ºC, highly inflammable and very susceptible to free radical addition polymerization. Therefore, with small amount of hydroquinone which is an inhibitor, it prevents undesirable polymerization or "setting" of the liquid during storage, hence prolonging its shelf life. Another way of reducing unwanted radicals is to store the liquid in a can or a dark brown bottle. On the other hand, glycol methacrylate which is a commonly used cross linking agent can be added to liquid at a concentration of 1-2% by volume to improve denture base's physical properties [22, 23].

PMMA is formed by addition polymerization of multiple methyl methacrylate molecules in three stages which is initiation, propagation and termination [24]. In the presence of heat or chemical activation, benzyl peroxide as the initiator breaks down to free radicals. They act upon the vinyl group of methyl methacrylate, opening the π bond causing formation of a new б-bond to one carbon, leads to the creation of a lone unpaired electron on the central carbon atom [25]. This process is known as a free radical addition polymerization chain reaction resulting in the shift of the unshared electron to the end of the monomer and the formation of activated monomer molecules [1, 26].

The activated monomers attack the double bonds of additional available monomers, resulting in the rapid addition of monomer molecules to the free radical. The second stage, propagation, continued as the chain grows in length. Chain termination could occur at any time and is dependent upon the concentration of available free radicals resulting from the mutual reaction of two free radicals [24, 26]. (Figure 1) shows the stages of addition polymerization of methyl methacrylate.
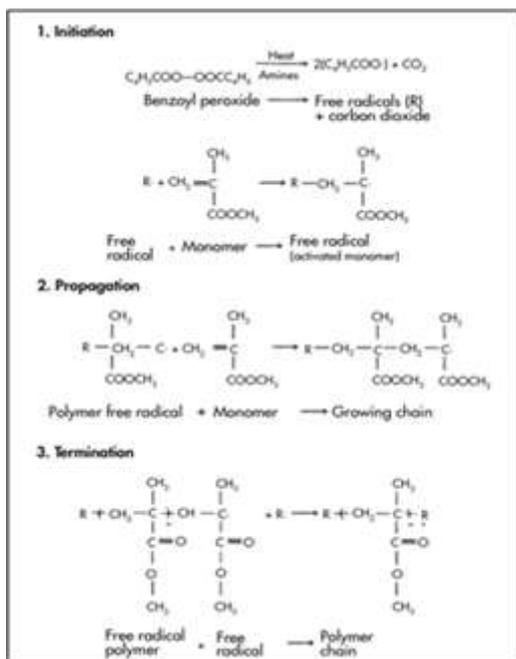
Figure 1. Three stages of addition polymerization of methyl methacrylate [26].

Heat Curing Polymers

The energy required for polymerization of heat-activated PMMA is most commonly provided in the form of water bath, or less frequently a microwave oven [27]. Benzoyl peroxide is commonly used as the initiator due to its low cost, when heated above 60°C, molecules of benzoyl peroxide decompose, producing pairs of free radicals which rapidly attacks the double bond in methyl methacrylate, initiating chain reaction [28]. Even though benzoyl peroxide does dissociate at room temperature, it is too slow to be of practical use and therefore heat must be utilized to produce radicals at a higher rate that the polymerization occurs within a suitably short time [29].

Clinically, monomer and polymer are mixed together in a ratio of 1:3 by volume and goes through five distinct stages. During the first stage, also known as sandy stage, little or no interaction occurs at the molecular level, polymer beads are merely wet but remained unaltered [25]. Next is sticky stage, the monomer begins to penetrate the surface of individual particles causing the polymer chains to uncoil thereby increasing viscosity of the mix. Subsequently, the mass enters a dough-like stage where monomer and dissolved polymer are formed. However, it is important to note that a large quantity of swollen but undissolved polymer remains. It is best to introduce the material into mold cavity at the latter phases of dough-like stage

when it is no longer tacky or stick to spatula. Following the dough-like stage, the mixture enters rubbery or elastic stage. At this stage, monomer is dissipated by evaporation and by further penetration into remaining polymer beads. The mass rebounds and no longer flows freely hence cannot be molded by conventional compress techniques [1, 30].

Auto-polymerized Polymer

Chemical activators that initiated polymerization at room temperature were developed in 1947. Such acrylic resins are known as self-cured, chemically cured, cold cured or auto-polymerized. They do not rely on heat to initiate polymerization. Tertiary amine such as N,N dimethyl-para-toludine or sulphinic acid are commonly added to the monomer and decomposes benzoyl peroxide to produce sufficient free radicals on initiating polymerization [5, 17].

The main difference between heat-cured polymer and auto-polymerized polymer is the method by which benzoyl peroxide is divided to produce free radicals. Otherwise all factors in the process such as the initiator and reactants remain the same [22]. The degree of polymerization achieved in auto-polymerized polymer is usually less than heat-cured resins [31]. This shows that there is a greater amount of unreacted monomer in denture bases fabricated via chemical activation which may lower the tensile strength, hardness, stiffness and fatigue resistance, mainly due to the plasticizing effect of the monomers [32, 33]. Furthermore, resin polymerization via chemical activation generally displayed 3-5% free monomer, whereas heat activated resin exhibited 0.2-0.5% free monomer [1, 17]. In relation to the previous statement, several literature reported that this high level of residual monomers was responsible for mucosal irritation, thereby compromising the biocompatibility of the denture base [34-36].

As a result of less conversion of the monomer to polymer, auto-polymerized polymer displayed slightly less shrinkage than heat-cured polymer [31]. This imparts less dimensional change on setting with only 0.1% dimensional change seen on polymerization [17]. On the other hand, auto-polymerized polymer generally was inferior to the color stability of heat-cured polymer owing to the presence of tertiary amines which were susceptible to oxidation. Nonetheless, discoloration of these resins could be minimized by the addition of stabilizing agents that prevent oxidation [37].

There was another kind of chemical activated resins which are known as pourable resins. The chemical composition of this pour-type denture resins was similar to the conventional auto-polymerized resins. The main difference is the pourable resins consist of smaller polymer beads. These materials are mixed to a very fluid consistency using a low powder/liquid ratio, poured into a hydrocolloid mold and allowed to cure at just above the room temperature with centrifugal casting and injection molding techniques [38].

Light Activated Material

The first light activated material was developed in 1985 by Dentsply International Company under the name "Triad" [39]. It is supplied in sheet and rope forms in a light proof pouches. This material is composed of urethane dimethacrylate, microfine silica and high molecular weight acrylic resin monomer. The filler consists of varying sizes of acrylic-resin beads. Photosensitizing agents such as camphorquinone serves as the initiator for polymerization while visible light acts as the activator [1].

The latest generation of light activated denture base resin consists of a base forming resin, tooth setting resin and a contouring resin. Gohlke Wehre reported in a randomized clinical study that light activated material could be recommended to patients with hypersensitivity to PMMA [40]. However, although visible-light cured resin exhibited comparable transverse strength, hardness, rigidity, non-toxicity as compared to heat-cured acrylic resins, its susceptibility to staining and brittleness and its low impact resistance has limited its use [39, 41].

Microwave Cured Material

Microwave cured denture base material was first introduced in 1968. Kimura and friends reported that it was possible to cure acrylic resins in a shorter time compared to the conventional heat technique [42]. Microwaves are electromagnetic waves produced by a magnetron which cause the methyl methacrylate molecules within the acrylic resin to orient themselves in the electromagnetic field at a frequency of 2450MHz. Numerous polarized molecules are flipped over, leading to molecular fiction and produced heat which breaks down the benzoyl peroxide molecules into free radicals, initiating chain reactions [43]. Therefore, microwave activated polymerization is independent of thermal conductivity with curing cycles involving the application of rapid heat may be conducted without development of high exothermic temperature [27].

The main advantages of microwave heating over conventional heating are shorter curing time and substitution of the heavy brass flask and water-bath curing tank by the lighter plastic flask and microwave oven [44]. Saunders claimed microwave cured acrylic has reduced porosity, but other studies by Al-Doori and Reitz showed that this material continued to encounter the problem of porosity when the sections were around 2.5-3.0 mm thick. In 1991, Balfie et al., reported a reduced mean porosity of microwave-cured resin by processing with Micro Liquid whereas Barbosa suggested frequency and size of porosity in thick specimens could be reduced to 30 percent by a longer polymerization time at a lower wattage [45, 46].

Based on both classic and recent studies, there are no significant differences in the physical and mechanical properties between heat-cured and microwave cured resins. Nevertheless the choice of a suitable power and polymerization time in microwave curing process reduces porosity and dimensional changes to a minimum level [27, 43, 47, 48].

Processing Methods for Acrylic Resins

Compression-moulding Technique

Heat-cured denture bases are most commonly processed by the compression molding, also known as conventional pressure packing technique. To allow processing of the acrylic, it is important to have an accurate wax trial denture prepared, subsequently sealed into master cast and flaked [1]. By using boiling water and a detergent, the wax is completely removed from flask investment. Next, the master cast is coated with a thin layer of separating medium such as sodium alginate or ammonium alginate to prevent adherence of investment [24, 49].

The packing and adaptation of denture base resin within the mold cavity are termed packing. It is important that the mold cavity is adequately filled to avoid excessive thickness associated with tooth movement or noticeable voids [1]. Furthermore, in order to prevent faults during packing, it should be carried out in a number of stages with gradual incremental pressure application. Application of a polythene separating sheet, trial closure, removal of excessive resin until no more flash is evident upon opening the denture flask. When flash is no longer apparent, the mold is closed for the last time with no polyethylene sheet placed. After that,

the mold is properly aligned, placed in flask press and followed by flask carrier to maintain pressure on flask during denture base processing [50].

The polymerization reaction is activated by immersing packed flask in hot water bath. As the reaction is very exothermic, and because the thermal conductivity of acrylic material is lower compared to gypsum mold, there comes a point when more heat is being produced by the reaction than can be dissipated. As shown in (Figure 2), during the early stage, the flask and the dough are at lower temperature compared to external water bath.
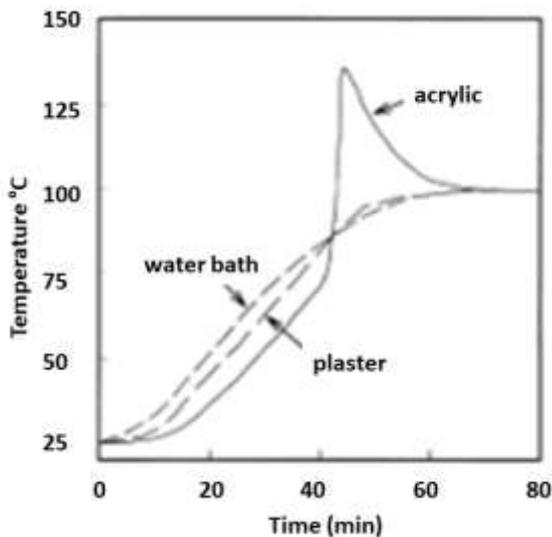

Figure 2. Changes of temperature observed in water bath, plaster and acrylic resins when a denture base is processed by raising the water bath continously to 100 °C [51].

However, when it is around 70°C, the reaction rate increased whereby internal temperature of acrylic may reach 130°C or more, especially if the material is thick. As monomer has a boiling point only just over 100°C, this might cause porosity and affects the strength of the produced denture base [51]. In short, this can be overcome by controlling the heat of the flask, proper clamping during flaking or increases boiling point by increasing pressure during processing [52]. Figure 3 shows the relationship between the rate of heating and temperature rise within the denture base.

As the boiling point of monomer is 100.8°C, polymerization represented by curve *C* probably would produce porosity in thick portions of acrylic denture since the temperature is way above the boiling point. On the other hand, curve *A* represents a slow rate of heating which fails to reach the boiling temperature of the monomer, resulting in a higher level of unreacted monomer.

Hence, an optimum polymerization cycle lies somewhere between curves A and C which is well represented by curve B [1, 51].
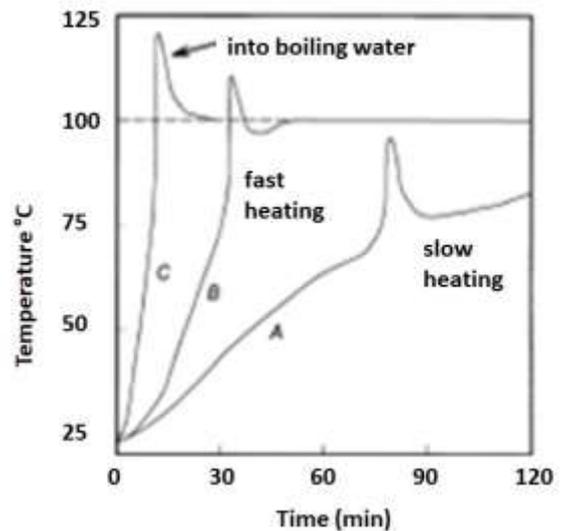

Figure 3. Temperature changes observed in acrylic resins when subjected to various curing schedules at ambient pressure. **A:** gradually to 70°C **B:** gradually to 100 °C **C:** flask placed in water at 100 °C [51].

Long Curing Cycle without Terminal Boil

As low curing temperature prevents boiling of the monomer during exothermic reaction, a long curing cycle of 7 to 14 hours around 70°C is used to cure the acrylic. Longer curing time would be needed to achieve a higher degree of polymerization since lesser radicals are produced in this decreased heating rate [53]. However, Vallitu and colleagues mentioned 70°C is below the glass transition temperature of the polymer. Consequently, it does not only produce fewer radicals but also lower molecular motion for polymerization [54]. On top of that, with the increased levels of residual monomers which act as plasticizers, decreased transverse bond strength and surface hardness were reported in acrylic resins which underwent this curing cycle [55].

Long Curing Cycle with Terminal Boil

In order to produce the best surface hardness and tensile strength, a second technique which involved processing the denture base resin in a 74°C water bath for 8 hours and then increasing the temperature to 100°C for 1 hour [56]. This cycle allowed higher degree of polymerization and removed most of the residual monomers at 100°C [53].

Short Cycle

Some manufacturers introduce a shorter cycle whereby it involves processing the resin at 74°C for approximately 2 hours, then increasing the temperature of the water bath to 100°C and further processes it for 1 hour [1]. However some authors claimed that a short cycle has a potential risk of porosity especially at thick sections of denture bases, owing to a possible high exothermic reaction [53]. Jerolimov and colleague suggested polymer powder with a specific initiator content and particle size can be used to overcome this problem. Besides that, if very thick sections are present, a slightly longer rapid cure is preferred [57].

Over the years, there has been a development of new resin with shorter heat-cured polymerization time ranging from 15 to 20 minutes. Only Axcent 15 minute (Garreco, USA) permits 15 minutes heat-cured in boiling water whereas other brands suggested a 20minute cycle. Although most manufacturers did not disclose details regarding the material's composition, it is believed that the monomer was modified by the addition of 0.025% dimethyl-p-toluidine (DMPT) as an initiation activator and 5% of ethylene glycol dimethacrylate (EGDM) as a cross-linking agent. Hence, modification of hybrid material of cold and heat cure enables the material to be cured using 20 minutes period in boiling water [47]. With the addition of a cold cure initiator, it reduces heat spike shown in conventional heat cure by dissipating some of the heat of reaction before water bath heating process is started [25, 47]. However, it should be appreciated in this system, polymerization begins at the time of mixing the polymer and monomer, thereby increases the rubbery nature of dough during packing, possibly making it more prone to error. Thus, manufacturer instructions should be followed to ensure complete polymerization with less processing error [25].

The first research related to 20 minutes heat-cured resin was done by Firtell and colleagues in the year 1981. They concluded that the special acrylic resin designed to process acrylic at 100°C for 20 minutes showed less distortion than conventional acrylic resin [58].This is in accordance with studies reported by Nick Polychronakis and Negreiros [59, 60]. A five-year clinical study was conducted to determine the dimensional changes that occurred in maxillary dentures made of conventional and rapid heat-cured acrylic resins. There were no significant dimensional changes observed between

these two groups upon 5 years follow up [60]. Furthermore, Bartoloni mentioned that conversion values for rapid cure technique were similar to other polymerization techniques, thus unlikely to induce adverse tissue responses [61]. Overall, with proper manipulation during denture processing, the end product of this rapid cure system is comparable to the conventional heat-cured technique.

Injection-molding Technique

A specially designed task is needed for the injection molding technique. Thermoplastic resin such as low molecular weight PMMA with no cross-linking, polycarbonate, nylon or polyamide is softened by heat and injected into the mold. This resin is allowed to cool and solidify. The injection-molding technique is applicable for heat-cured or auto-polymerized polymers [26].

Although available data and general information showed denture base fabricated using injection molding could provide a slightly improved clinical accuracy, its smaller polymer to monomer ratio subjects the denture to an increased curing shrinkage, thereby affecting its palatal fit [1, 53, 62]. However, it can be improved by greater preparation of the post palatal seal area to ensure contact of the polymerized denture base with patient's palatal tissue [1].

Pour Resin Technique

The fluid resin technique employs a pourable, chemically activated resin for the fabrication of denture bases. It was first developed in 1955 by The Austenal company and generally accomplished using auto-polymerized polymer and hydrocolloid moulds [63]. After mixing in the proper proportions, low viscosity resin is poured into mold cavity, subjected to increased atmospheric pressure and allowed to polymerize at ambient pressure for around 30 to 45 minutes [1].

The main advantages for this pour resin technique including improved adaptation to underlying soft tissue, decreased probability damage to prosthetic teeth and denture base during deflasking and simplification of the processing procedures. However, Antomopoulos (1978) found fluid resin complete dentures underwent larger dimensional changes than the conventionally processed heat-cured denture [64]. Furthermore, shifting of the prosthetic teeth occasionally occurs during processing, presence of voids or porosity in the resin due to air entrapment, poor bonding between denture base material and acrylic teeth [65]. In short, pour resin technique is rather

technique sensitive, denture bases fabricated in this matter exhibited physical properties somewhat inferior than those conventional heat-cured resin.

Microwave Curing Cycle

In this processing technique, a 2450MHz frequency (12cm wavelength), and 550 W outlet power microwave is often used [66]. As microwaves are reflected by metal surfaces, flasks used in the microwave cannot be of metal. A Teflon flask made of polytetrafluoroethylene is used instead. Continuous pressure is applied by tightening the Teflon screws of the flask [43] (De Clerck, 1987; Kimura et al., 1983)

Kimura reported the best result of polymerization obtained in 3 minutes of curing at 500W, similar to Ilbay's research which stated curing occurs in 3 minutes at 550W [66, 67]. On the other hand, Reitz and colleagues found curing was achieved in 13 minutes at 90w. However Patil and friends stated maximum flexural strength and minimal residual monomer content were offered with the irradiation at 650W for 5 minutes [44, 68]. Despite that, in 2015, Spartalis et al., noted microwave cycle of lower power and irradiation time (550W for 3 min) promoted higher values of flexural strength and modulus of elasticity as compared to the other polymerization cycle [48].

In conclusion, choice of a suitable acrylic resin, current power and polymerization time is important to improve the physical properties of a microwave-cured resin which is comparable to a conventional heat-cured resin.

Light Curing

The curing unit for light cured resin emits high intensity collimated shielded light from quartz halogen lamps. First, the base forming resin is adapted to the dental cast and placed into a high intensity light chamber to induce polymerization. Then the tooth setting resin is used to attach the prosthetic teeth to the polymerized base. Subsequently, a high intensity light source is used to polymerize the tooth setting resin to maintain the prosthetic teeth in desired position. Finally contouring resin is used to generate the desired final surface form and coated with barrier chemical such as boxymethylcellulose before placing into the light chamber to complete the denture base fabrication process [1, 17].

This type of resin usually used to construct orthodontic appliances, gum work portion of metal based partial dentures, repair of fractured acrylic dentures, hard relines and special trays [17].

Conclusion

This review discussed about the properties of different types of acrylic denture base material with different processing methods. As none of the material is able to fulfil all the ideal criteria, careful selection of material should be based on good understanding of the strength and limitations of each material to provide the best treatment for patients. More clinical studies which look into material selections should be conducted in order to help clinicians in choosing the best treatment plan for patients. This will lead to a better quality of life for patients.

Declaration of Interest

The review paper is part of the literature review of the MClinDent dissertation report. The authors report no conflict of interest. Authors are totally responsible with the content and writing of paper.

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