DENTAL POLYMERS

B. David Halpern
Polysciences, Inc.
Rydal, Pa.

Dental polymers are primarily used in restorative dentistry and must serve both cosmetic and functional purposes. They must be adaptable for easy forming and final cure by simple techniques and equipment available in a dental laboratory or dentist's office. The final prosthetic device must fit exactly in spite of shrinkage due to polymerization and high coefficients of expansion. The plastic must withstand the occasional high shock loads of severe biting as well as the constant low loads that prevail in the mouth. Dental polymer materials must be free from toxicity, esthetically pleasing, and stable in the fluid environment of the mouth. The first practical dental polymer application took place in 1839 when Goodyear invented the vulcanization of rubber and this material was used to make a denture base. It was not long afterwards, in 1868, that Hyatt's invention of celluloid was likewise adapted for use in the production of denture-base resins. Almost every subsequent polymer material of any commercial significance has received at least research consideration by dental investigators. Some resins such as glyptals, phenol-formaldehydes, vinyl chloride copolymers, polystyrene, and epoxies have had varying periods of popularity. It was not until 1937, when acrylic resins were introduced, that a truly universal dental polymer appeared on the scene. Acceptance was immediate, and now acrylic resins and their modifications constitute the largest volume dental resin used. They have low water absorption and are dimensionally stable. The ease of fabrication and inherent attractiveness of acrylics made it possible for the dentist to provide his patient with plastic dentures which are very difficult to distinguish from natural teeth. Acrylics still have deficiencies. The severe shrinkage which they undergo on polymerization can cause high internal stress of as much as 3,000 psi in an upper denture.[1] The abrasion resistance of plastic teeth is not as good as that of porcelain teeth. Acrylic resins used in restoration show poor adhesion to wet tooth substance and they discolor when used with amine-peroxide room-temperature initiators. New polymer materials must overcome these deficiencies without any sacrifice of the many advantages of acrylics.

The market for dental materials is small when measured by current industrial standards of pounds consumed. The total resin market amounts to somewhat more than 600,000 pounds of finished products per year. Of this, almost 95% are acrylic and related resins since they provide the best combination of physical, chemical, and cosmetic properties for applications to denture-base and tooth materials. The actual purchase requirements for dental resins in 1964 were closer to 1,000,000 pounds since the molding operations and fabrication techniques require a considerable amount of over-mixture. Many other polymers are currently used in smaller amounts in order to achieve special effects. These include polystyrenes, polyesters, vinyls, nylons, natural polymers, silicones, polycarbonates, epoxides, and a variety of very special copolymers. Several surveys based on American Dental Association figures have been evaluated in order to arrive at the figures given in TABLE 1 for the resin consumption in 1964.[2,3] Specifications which cover the use of plastic materials in dentistry are set forth by the American Dental Association.[4] This group is assisted by the National Bureau of Standards where the Dental Association maintains a number of re-

TABLE 1

RESIN USAGE OF DENTAL MATERIALS IN 1964

Usage	Millions of Units/Year	Grams per Unit	Pounds of Resin
Full dentures	6.3	30	416,000
Partial dentures	4.4	6	58,000
Acrylic teeth*	40.0	1.25†	110,000
Denture reliners	3.3	5	36,000
Fillings‡	2.0	0.5	2,200
Miscellaneous			2,500
			624,700

* 33% of all teeth used, remainder porcelain.
† Allowing for mold flash and sprue.
‡ 1.2% of all fillings, remainder silicate, amalgam, and gold.

search fellowships. The Association keeps a list of approved manufacturers of dental materials[4,5] and has a rigid program of certification and quality control to insure continued high performance standards by manufacturers.

A consideration of specific types of application will give some insight into the types of plastics and the conditions of their usage.

DENTURE-BASE MATERIALS

The denture base is that portion of a denture in which the false teeth are invested. It is usually compression-molded from a monomer-polymer gel in a plaster mold which is a replica of the gums and palate of the mouth. Acrylic resins are the most important resin for this application. The advantages of acrylic resins over many other resins are their superior color characteristics, excellent light stability, low water absorption, dimensional stability, easy grindability in the dental laboratory, and adaptability to simple cure techniques. Finely divided acrylic suspension polymer is formed into a gel by mixing with methyl methacrylate monomer and a lesser amount of ethylene glycol dimethacrylate or allyl methacrylate for crosslinking. The crosslinker does not have much effect on the final tensile or fatigue strength.[6] This gel or dough is molded to the contours of the individual patient's mouth and accuracy of investment is critical. The dough mixtures are usually cured at 160°F in a plaster of paris mold by a lost-wax method. Where greater mold accuracy is required, a room-temperature cure may be used. Residual monomer is always present in the finished denture and more monomer is present in the case of cold-cure dentures. The monomer is easily leached by water or saliva without ill effects.[7]

Three molding systems are used in the formation of the denture-base resin. The first and by far the most popular is a plastic monomer–polymer gel cake of the type described which is made just prior to molding. The dough is hand-packed into a simple mold and clamped in position during cure. A second system employs a gel already preformed at the factory. A vinyl chloride copolymer with methyl methacrylate monomer is an example of this type. This specific gel is relatively stiff and a modified injection press is needed to fill the plaster mold. The vinyl-acrylic denture-base materials do not yield true copolymers but rather physical mixtures of methyl methacrylate monomer polymerized in the presence of a vinyl-chloride copolymer. The preformed gel cake may also be all acrylic. Because of residual catalyst in the polymer and "locked-in" free radicals, these gels must be refrigerated if long-term storage is required before use. A third

TABLE 2

PHYSICAL PROPERTIES OF SEVERAL DENTURE-BASE RESINS[9,10]

Property	Methyl Polymethacrylate	Polyvinyl Polymethacrylate	Polystyrene
Tensile strength, psi	7000–9000	7500	60000
Compressive strength, psi	11,000	10,000–11,000	15,000
Elastic modulus, psi	5.5×10^5	3.3×10^5	5.3×10^5
Impact strength, lb.	60	180	50–60
Transverse strength, psi	6000–8000	6000–8000	8000
Knoop hardness	16–22	14–20	14–20
Thermal coefficient of expansion per °C	81×10^{-6}	71×10^{-6}	$60–80 \times 10^{-6}$
Heat distortion temperature, °C	160–195	130–170	160–210
Polymerization shrinkage, vol %	6	6	–
24-hour H_2O absorption, %	0.3–0.4	0.07–0.4	0.05–0.3

molding method invests the already fully polymerized resin by a standard injection molding technique. Polystyrene and polycarbonates[8] have been used for injection molding. Shrinkage is very high and the method is not well accepted. The physical properties of the three denture resin systems are listed in TABLE 2. Numerous other systems, such as nylons[11,12] and epoxies,[12,13] have been tried in denture base, but they have never really gained acceptance. Epoxy resins absorb an appreciable amount of water, and have neither dimensional nor color stability, while the nylons tend to discolor and become foul in the mouth,[11] probably due to enzymatic and hydrolytic degradation. Polystyrene and vinyl-acrylic combinations have outstandingly low water absorption. They require more complicated molding procedures and therefore are not as popular as acrylics. Vinyl-acrylics also have very high impact strength.

Acrylic resins for denture base are manufactured by the suspension technique. This provides a finely divided polymer which will readily mix with methacrylate monomer to give an easily molded dough gel. The residual peroxide in the acrylic beads helps to catalyze the reaction in the gel stage. A typical procedure used to prepare a suitable suspension dental polymer is as follows:

Recipe for suspension polymer useful in dentistry

	parts by weight
Methyl methacrylate monomer	450
H_2O, deionized	800
Na_2HPO_4 buffer	4.75
Polymethacrylic acid suspending agent	4–7
Benzoyl peroxide catalyst	2.3

The batch is changed to a pressure vessel, usually stainless or glass-lined, and heated to 75°C and then allowed to exotherm at 103°C under the autogenous pressure of the reaction. The suspending agent is washed free of the finely divided polymers by repeated decantation with deionized water.

Reduction of the thermal shrinkage in denture base materials has been attempted by the incorporation of many mineral fillers. Addition of a glass filler can drop the coefficient of expansion of a methacrylate resin from 98.3×10^{-6} to 42.7×10^{-6}.[10] Fibrous fillers improve the impact strength appreciably but they are clinically unsatisfactory.[6] Some medical grade silicone rubbers have been considered for denture base.[14]

Impression and Duplicating Materials

An impression material is used by the dentist to accurately establish the relationship of the teeth to oral tissue. The impression material may be a rigid type such as plaster of paris, or a semirigid natural polymer gel such as agar-agar[15] and alginates.[16] Synthetics of low durometer such as thiokols[17] and silicones[18] are also used. A typical composition for a polysulfide rubber base impression material is as follows:[19]

Recipe for polysulfide impression material

	Weight %
Base	
Polysulfide polymer	79.7
ZnO	4.9
$CaSO_4$	15.4
Accelerator	
PbO_2	77.7
Sulfur	3.5
Castor oil	16.8
Other	2.0

Plastic Teeth

Plastic teeth are primarily made in this country from crosslinked acrylic resins. Their poor abrasion resistance and poor chewing efficiency have kept them from displacing porcelain teeth. When plastic teeth are opposed by porcelain teeth, the wear factor is improved.[20] Plastic teeth avoid the embarrassing click that occurs with complete porcelain dentures. Their popularity has been increasing steadily and they now represent about one-third of the market for prosthetic teeth. Crosslinking agents are routinely used by every tooth manufacturer to avoid crazing and staining by foods and fluids.[21] Premium quality teeth are made by several successive injections in a transfer molding procedure. The body of the tooth, where solvent resistance is less important, is less crosslinked than the enamel to permit bonding of the tooth to the denture base. The use of partially crosslinked teeth which are fully cured during molding to the denture base has been suggested as a way of overcoming the bonding problem of the solvent-resistant fully crosslinked teeth.[22] This is not necessary if one uses good commercial quality teeth. Teeth are all individually hand-characterized to avoid the unnatural appearance that comes from identically molded teeth. Plastic teeth require the addition of a fluorescing agent in order to give lifelike appearance. The cost of development, mold investment, and inventory for a single line of teeth can easily approach a million dollars before a single tooth is sold.

Restoration and Filling Materials

Plastic filling materials for teeth are based on very finely divided methyl polymethacrylate resins. They are used almost solely for anterior—i.e., front—teeth, where cosmetic considerations are more crucial than physical properties. The strength properties of restoration plastics are so poor that they are not used in posterior teeth. Resin fillings are far less soluble and less brittle than the conventional silicate fillings used in anterior teeth, but resin fillings lack adhesion to dentin and dimensional stability. Continued hot and cold cycling which comes with normal eating and drinking results in marginal separation due to the high coefficient of thermal expansion of the filling. Subsequent reinfection of the cavity can occur by percolation of fluid at the filling margins. As a result, only about 1.2% of all the fillings used are based on plastics. The necessity for cure at body temperature requires an amine-peroxide redox polymerization system.[23,24] Severe discoloration results over a period of years due to the amine. There is also some tendency toward pulp irritation due to residual monomer or amines. The yellowing which is attendant on these systems can be overcome by using reducing compounds such as sulfinic acid[25] and its derivatives; but because of their insolubility and lack of oxidation stability, they are difficult to use. Many studies of fillers have been made to reduce the shrinkage, but the adhesion of the resin to the filler has always been deficient. Bowen[26,27] has found that vinyl silane treatments on glass spheres or silica filler will permit better adhesion of the methacrylate resins to the filler, resulting in a more stable and less shrinking type of filling. A comparison of the coefficients of expansion of various dental filling materials in TABLE 3 will show the problem that unfilled acrylics pose (see reference 4, page 42). A reduction in the coefficient of thermal expansion to 45×10^{-6} has been achieved by using silane-treated glass bead fillers.[29]

The problem of adhesion to the dentin can be easily appreciated if it is remembered that when tooth structure is cut away to prepare the filling, the dentist cuts into viable tooth material which always has a veneer of moisture on it. In an attempt to modify the shrinkage problem, some investigators have resorted to direct filling by injection of molten polystyrene, polyamide,[29] and polycarbonate.[30] The complicated injection procedure and the resultant heat trauma (150°C) to the tooth have prevented acceptance of these methods. Various cavity liners have been studied as a means of promoting primary adhesion to the dentin. The dimethacrylate of glycerophosphoric acid[31] has been investigated with the hope that good bonding to dentin will result, but this has not been the case. The use of the addition product of N-phenylglycine and glycidyl methacrylate as a coupling agent is reported to significantly improve the water resistance of the resultant acrylic-to-tooth bond. An excellent review of some of the problems involved in dental adhesive restorative materials is contained in a recent symposium on this subject.[33]

TABLE 3

COEFFICIENT OF THERMAL EXPANSION OF VARIOUS DENTAL METHODS

Material	Range °C	Coefficient of Thermal Expansion $\times 10^{-6}$/°C
Porcelain	20–600	7.9
Silicate cement	20–50	8.1
Tooth	18–60	10
Gold (24 carat)	35	14.4
Amalgam	20–50	25
Acrylic (cold cure, no pressure)	37–70	127

Miscellaneous Applications

There are a number of miscellaneous applications of polymer materials in the dental field. Methyl alpha-cyanoacrylate is used for the fixation of braces and other orthodontic devices to the teeth.[34] The cyanoacrylates have been employed as incipient crack fillers in the enamel to prevent caries formation. Soft acrylics and other elastomers have been used for mouth guards for athletic applications.[35] Easily molded silicones and vinyls are also used. Techniques for endodonture or root canal work have utilized small amounts of highly filled polyethylene, polypropylene, or polystyrene. The fillers are usually radio opaque in order to permit x-ray examination.[36] Dental modeling waxes are in some cases polymer-modified in order to increase toughness. Misfit of dentures is often corrected by the use of a resilient liner made of silicone or higher alkyl acrylate materials. They maintain their resiliency over long periods of time, have good oral stability, and are nontoxic. They have a tendency to swell and to lose adhesion to the denture base after long usage. Highly plasticized polyvinyl chloride[37] and polyvinyl acetate have been used but the plasticizer is leached and the lining stiffens. The toxicity of dental resins has been studied and, while there are isolated cases of severe reaction, generally speaking, the acrylics are considered inert. The tumor-genicity of polymer materials is thought to be very low. The criticisms leveled against resins implanted in the body do not strictly apply to dental materials because they are not implanted in the surgical sense. The only exception might be the use of filling materials for root canals or possibly for cavities. The Food and Drug Administration has accepted most prosthetic materials in dentistry on the "grandfather clause" basis. Current indications are that many standby resins may be challenged and certainly new ones will be required to offer proof of safety.

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