The Origins of Acrylates and Adhesive Technologies in Dentistry

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Purpose: To examine the origins of acrylates and adhesive dentistry up to 1955.

Materials and Methods: A search of MEDLINE database and a manual literature search were conducted to find relevant articles.

Results: Acrylic acid was discovered in 1843, methacrylic acid in 1865. In 1880, light polymerization of acrylate compounds using glass prisms was introduced. In 1928, polymethyl methacrylate (PMMA) was industrially produced from methyl methacrylate (MMA). In 1930, PMMA moldings that could be adapted under heat and pressure were introduced into dentistry. The process was improved in 1936 by mixing pulverized PMMA and liquid MMA. In 1940, the intraoral polymerization of dental resins using UV light or catalysts was discovered. In the same year, the combined procedure (dual-curing) and addition of inorganic fillers to improve the material properties (precursors of composites) were proposed. Effects on the oxygen inhibition layer and intraoral bonding between several resin portions were also described. In 1942, direct restorations with self-curing resins (combined with a precursory version of cavity sealing) were described. These new resins were marketed in the late 1940s. Intraoral repair of restorations and cementation of crowns and bridges with resins were also described in 1942. In 1949, a glycerophosphoric acid-based sealer was marketed. In the same year, it was discovered that etching of the enamel (with nitric acid) caused an adhesion to thin layers of acrylic-based materials. In 1955, phosphoric acid etching of enamel was shown to improve adhesion.

Conclusion: In the first half of the 20th century, important but little or unknown discoveries took place. These discoveries can improve our understanding of how adhesive dentistry evolved.

Keywords: history of dental acrylates, history of adhesive dentistry, origins of composites, redox cure, dual cure, photocure, origins of acid etching of enamel, beginnings of acrylic-based cementation of crowns and bridges, beginnings of acrylic-based restorations.

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Adhesive Dentistry began in 1955 with Buonocore's pioneering acid-etch technique[74] when Michael G. Buonocore reported clinical trials that showed significantly increased adhesion of acrylic-based resins on acid-etched enamel via micromechanical interlocking mechanisms.[12] Around this time, Rafael L. Bowen was developing new acrylic-based dental restorative materials[9] – also a milestone in dentistry. However, adhesive dentistry using acrylic-based compounds was not completely new at this time;[42] there had been discoveries and descriptions before, but these earlier observations are not well known. In this paper, we describe the early developments of acrylic-based adhesive technologies in dentistry leading up to and including 1955.

MATERIALS AND METHODS

The MEDLINE database was searched for articles on the origins of dental resins, adhesive techniques, and light polymerization. Original literature published up to 1955 and historical studies published later were included. The search terms are presented in Tables 1a and 1b. We also searched the

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Table 1a MEDLINE search via OVID of original research before 1955

#	Searches
1	exp Dentistry/
2	limit 1 to yr="1860-1954"
3	acrylate.mp. or Acrylates/
4	filling.mp.
5	Resins, Synthetic/ or Acrylic Resins/ or Composite Resins/ or Resin Cements/ or Dental Bonding/ or resin.mp. or Dental Restoration, Permanent/
6	resin sealer.mp.
7	plastic filling.mp.
8	adhesive.mp. or Adhesives/
9	"light-curing of dental adhesives"/ or "self-curing of dental resins"/
10	self-polymeri*ation.mp.
11	auto-polymeri*ation.mp.
12	cold-polymeri*ation. mp.
13	photo-polymeri*ation.mp.
14	light-curing.mp.
15	Dental Etching/ or Acid Etching, Dental/ or etching.mp.
16	1 and 2
17	3 or4 or 5 or 6 or 7 or8 or 9 or 10 or 11 or 12 or 13 or 14 or 15
18	16 and 17
19	limit 18 to (english or german)

Table 1b MEDLINE search via OVID for historical work

#	Searches
1	dental materials/ or resins, synthetic/
2	Dental Restoration, Permanent/ or Composite Resins/ or dental restoration.mp.
3	adhesive.mp. or Adhesives/
4	Polymerization/
5	"light-curing of dental adhesives"/ or "self-curing of dental resins"/
6	dental bonding.mp. or Dental Bonding/
7	1 or 2 or 3 or 4 or 5 or 6
8	history.mp.
9	exp "History of Dentistry"/
10	exp Dentistry/
11	8 and 10
12	9 or 11
13	7 and 12
14	limit 13 to (english or german)

reference list of the identified studies for additional relevant studies. Additional documents, including patent specifications, dissertations, company information, textbooks, and articles and reviews from other media (eg, military reports) were searched manually. All work that included information relevant to the abovementioned research question was included. Inclusion was restricted to articles published in English or German. All types of article and all settings were included. Titles and abstracts were screened for eligibility and the full texts of eligible articles were retrieved.

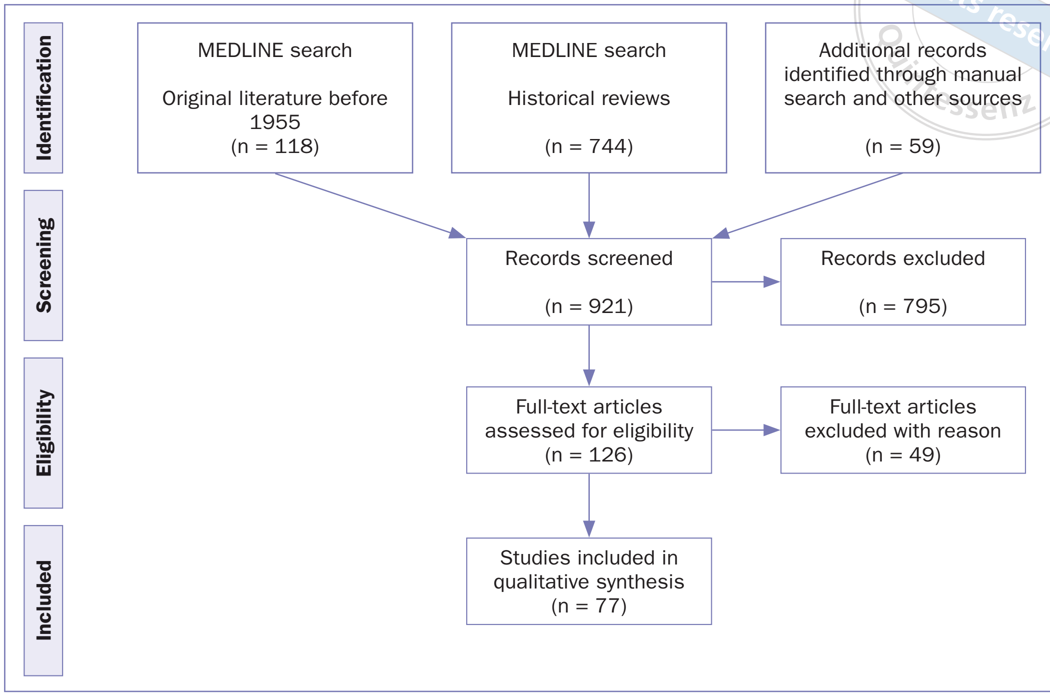
RESULTS

The results of the literature search are shown in Fig 1, which outlines the literature selection according to the PRISMA statement.[45]. The initial search strategy identified 862 articles; 67 of these were deemed relevant and the full text was obtained. Eighteen articles met the inclusion criteria.[5,11,14,16,26,37,39,42,44,46,51,53,54,60,61,65,73,77] Our manual search revealed 59 further relevant articles, giving a total of 77 sources.

Origins of Acryl-based Resins for General Purposes

Acrylic acid was discovered in 1843 by the chemist Josef Redtenbacher,[55] and methacrylic acid was described in 1865 by the chemists Edward Frankland and Baldwin Francis Duppa.[22] The conversion of liquid methacrylic acid to a solid resinous substance was reported in 1877 by the chemists Rudolph Fittig und Ludwig Paul.[21] In 1880, the chemist Georg Wilhelm August Kahlbaum produced the polymeric acrylic acid methyl ester for the first time.[4] He discovered that this liquid ester, which took on a gelatinous form after several months of storage, could be solidified by heat and light. When the liquid was exposed to direct sunlight using a glass prism, it solidified within a few hours and became completely hard within a few days.[31,75] In 1901, chemist Otto Röhm presented his dissertation, which described the solidification of acrylic acid esters in more detail.[59] These processes were better understood after the chemist Hermann Staudinger introduced the concept of polymer chemistry.[71] These early developments regarding acryl-based resins were initiated by academics, since there was little chemical industry at the time. In the 1920s and 1930s, various industrial uses for acrylates were developed. Among other things, this involved the synthesis of methacrylic acid and its esterification with methanol to produce the colorless liquid methyl methacrylate (MMA), which was used in large quantities as a starting material for the production of solids such as polymethyl methacrylate (PMMA). The development was driven by researchers in various countries, including Walter Bauer and Otto Röhm at Röhm & Haas Darmstadt, Hans Fikentscher at I. G. Ludwigshafen (BASF), Claus Heuck at I.G. Leverkusen, and John William Croom Crawford at Imperial Chemical Industries Ltd London; there was conflict over authorships and patents.[4,75] Walter Bauer, a chemist employed by Röhm & Haas, patented the results of his acrylate research, includ-

Fig 1 PRISMA 2009 flow diagram.



ing the synthesis of PMMA from MMA, which was later marketed as Plexiglas (called Perspex, Lucite, and Acrylite by other manufacturers). His company, Röhm & Haas, received the industrial property rights for this in 1928, and Bauer was named as the inventor.[2,4] Otto Röhm, the head of Röhm & Haas, cast the material into the first acrylic glass pane in 1933 and patented this process in his own name.[58] These events are summarized in Table 2. Acrylic-based plastics went on to be used in numerous applications, including dentistry.

Origins of Acryl-based Resins in Dental Prosthetics

In 1930 and 1935, Walter Bauer patented the use of PMMA for dental purposes,[3,57] thereby introducing PMMA-based plastics to dentistry. At first, polymerized, already cured moldings were produced (for dentures, artificial palates, artificial teeth, etc) that could be molded by heat and pressure similar to rubber or celluloid (known as dry processing).[76] In 1935, a PMMA resin with an injection device from a heatable container was offered in England under the trade name Kallodent (Imperial Chemical Industries Ltd).[54] A similar compound (colorless or in gingival shading) was offered in Germany under the name “Gingivist and Heliodon”.[4] In 1936, the dry processing technique was replaced by the wet processing technique invented by the dental technician Gottfried Roth.[48] Here, PMMA polymer (powder) and MMA monomer (liquid) were used together with catalysts (eg, benzoyl peroxide). These malleable compounds were pressed into a mold and cured in boiling water for at least 30 minutes (hot polymerization). These compounds were patented for use in dentistry by Kulzer in 1936 under the names Paladon (for prostheses) and Palapont (for crowns and bridges).[35] In the USA, it was distributed under the name Vernonite (Vernon-Benshoff Co).[4,52,60,66] Because liquid MMA tended to polymerize upon exposure to light or slight heating, albeit very slowly, stabilizers were added.

Origins of Acrylic-based Resins in Conservative Dentistry

The first steps toward the development of light-curing, self-curing, and dual-curing resins in conservative dentistry started with the work of the dentist Ernst Schnebel in the late 1930s. In 1940, Schnebel patented the following uses of these resins in the oral cavity.[63]

Introduction of UV light polymerization to dentistry

Schnebel designed a shielded UV-light device with special metal mirrors that could cure acrylic-based dental fillings directly in the oral cavity. He also produced infrared radiators for use in case heat was needed for polymerization. The chemical and physical effect of UV rays on synthetic resins had already been described, but treatment of resins directly in the mouth with UV rays or a mixture of UV rays and heat to produce dental restorations was novel at the time.

Compositions of resins and fillers (precursors of composites)

In his 1940 patent, Schnebel mentioned the addition of “hard mineral substances” to acrylate-based resins to increase “hardness” and “abrasion resistance”.

Table 2 Stages of development and application of acrylate-based resins for general use between 1843 and 1933

Year	Process	Name and source
1843	Discovery of acrylic acid	Josef Redtenbacher, chemist[55]
1865	Discovery of methacrylic acid	Edward Frankland und Baldwin Francis Duppa, chemists[22]
1877	Discovery of conversion of liquid methacrylic acid to a hard resinous substance	Rudolf Fittig und Ludwig Paul, chemists[21]
1880	Studies on the solidification of acrylic acid methyl ester and discovery of light polymerization	Wilhelm August Kahlbaum, chemist[4,31,75]
1901	Studies on the solidification of acrylic acid methyl and acrylic acid ethyl esters	Otto Röhm, chemist[59]
1920	Foundation of polymer chemistry	Hermann Staudinger, chemist[71]
1928	Synthesis of polymethylmethacrylate (PMMA) from methyl methacrylate (MMA)	Walter Bauer, chemist[2]
1933	Production of PMMA disks	Otto Röhm, chemist[58]

Introduction of special amine compounds for polymerization at lower temperatures

Schnebel succeeded for the first time in polymerizing acrylate-based resins in the oral cavity at reduced temperatures (even without UV light) by introducing tertiary amines.

Dual curing

In his patent, Schnebel suggested that acrylate-based resins could be polymerized by both chemical substances and UV light. This was the first description of dual curing.

Influencing the oxygen inhibition layer

Schnebel also described how to place and cure resin fillings and recommended, among other things, covering them with a protective film of transparent resin. He reasoned that this protected the still soft filling from moisture and atmospheric oxygen; keeping the atmospheric oxygen away accelerated polymerization.

Intraoral bonding of different acrylic materials

In his patent, Schnebel introduced the intraoral bonding of different acrylic materials, which could be used to cement inlay fillings and crowns. Thus, he not only introduced the idea of luting agents but also laid the foundation for the intraoral repair of restorations with acrylic-based resins, which he described in more detail in 1942.[64]

In 1941, Schnebel, together with Erich Czapp and Anna Gölz, used tertiary amines to accelerate polymerization in another patent.[17] In the same year, Karl Helbig paid tribute to Schnebel's experiments with UV light irradiation, heat exposure, and addition of chemical substances.[29] He pointed out that the limited number of UV-light devices had restricted the use of this polymerization process in clinical practice. In 1949, Max Stocklin wrote in the *Swiss Monthly Journal of Dentistry*, "Schnebel thus attempted to harden the normal acrylics by means of UV rays. For this purpose, he constructed a miniature quartz burner built into the head of a finger-thick, curved glass tube. In this way, he wanted to make the ultraviolet light accessible to all parts of the mouth."[72] According to Stocklin, however, the method was not optimal for clinical application at first because polymerization still took too long, and "hardening did not occur within the useful time period." Attempts to accelerate curing in the mouth at elevated temperatures (eg, with "heat matrices") also proved impractical. Therefore, Schnebel searched for chemical catalysts that would initiate polymerization at oral cavity temperature. However, the new additives used for this purpose (tertiary aromatic amines) had not yet been sufficiently tested for potential toxicity, discoloration, etc. Schnebel's work was taken up by the company Kulzer in the 1930s. Stocklin wrote: "Kulzer performed experiments using tissue from dogs, rabbits, and frogs, and Büche performed experiments on patients. Unfortunately, most of the files were lost during the war. The rest was taken to Switzerland, and the experiments had to be started all over again with this limited material. Many experiments, both in vitro and on patients, showed initial success, but severe discolorations appeared later. The surface of the fillings also became porous over time".[72] In the second half of the 1930s, many attempts were made to polymerize plastics intraorally. This was primarily derived from secondary literature; very little primary literature is available. Schnebel did not publish his research in scientific journals and archived material seems to have been lost during and after the Second World War. Ultimately, however, it should be noted that Schnebel invented the first fast-curing "autopolymer" or "cold polymer" based on PMMA, by adding benzoyl peroxide to PMMA powder and by adding tertiary aromatic amines to liquid MMA. In 1942, Alfred Deppe reported on the clinical application of these new materials (see below). According to S. A. Leader, the decisive factor in Schnebel's discovery was not the already known addition of benzoyl peroxide to the powder, but the addition of tertiary aromatic amines to the liquid, because this allowed cold polymerization for the first time.[36]

According to S. A. Leader (1948),[36] John W. McClean (1950),[39] WM. L. McCracken (1951),[38] Björn Hedegard (1955),[28] Floyd A. Peyton (1981),[52] and John F. Glenn (1982),[23] these discoveries were not internationally known until 1947. They were announced, not through the dental literature, but by L.M. Blumenthal from the Office of Military Government for Germany (US), the highest administrative institution of the American occupation zone of Germany.[7] This report, entitled "Recent German Developments in the Field of Dental Resins (field information agency, technical united states group control council for Germany)" is historically interesting to the field of dentistry. After the Second World War, Blumenthal visited Degussa (Frankfurt) and its subsidiary Kulzer (Friedrichsort im Taunus). He pointed out that the production of the first self-hardening acrylate (Palapont S. H.) was based on Schnebel's discovery. He stated, "Very little has been published on the subject except for the information contained in war time patent applications and the patents granted to Kulzer & Co. on the basis of those applications (cf. D.R.P. applications D. 85578-IV c/39 C, 7/29/41; French 88, 3679, 3/19/43; Swiss G 74, 466, 7/25/42; Swedish 3.896, 6/7/42; etc.). The product has never been manufactured except on an experimental scale." Whereas attempts had previously been made to polymerize the resin with heat, eg, using an electrically heated spatula, a heated air blower, or an infrared lamp, the addition of tertiary amines made polymerization possible at much lower temperatures. The adhesion of Palapont S. H. to dentin was mechanical and had to be improved by creating furrows. At that time, it had also been considered to make acrylic resins more resistant by adding inorganic fillers such as quartz powder and glass fibers, but this had not been investigated. A study to investigate how fillers affected the mechanical properties of the material had been planned, but never carried out.[7] Thomas M. Schulein, citing a 1957 paper by H. D. Coy,[15] pointed out that acrylate-based resins for direct fillings had only become known in the USA in 1947.[65] In 1949, the Rapid-Palodont compound was launched on the market by Kulzer. It was among the first of this group of materials. Stocklin reported on other similar compounds, including Filcryl (Portland Plastics Ltd.) and Hesacryl (Schönenwerd) in 1949.[72] Hedegard additionally named (for both conservative and prosthetic applications) numerous preparations such as Athermoplast V 10 (Athermoplast Products, Inc.), Simplex Pentocryl (no company named), Palavit (Kulzer), Palatex (Rockland Dental Co.), Swebond (Svedia Dentalidustri AB), Dentafil (Dental Fillings, Lts.), Autodent (no company named), Polyplast (no company named), Swedon (Svedia Dental-Industri), Kadon (L. D. Caulk Co.), Plastofilling (Plastodent, Inc.), Fastcrown (Acralite Company, Inc.), and Replica (Cosmos Dental Products, Inc.).[28] McCracken added the names Coldpac (Motloid Company, Inc.), NuSet (J. Yates Dental Mfg. Co.), Acralite 88 (Acralite Company, Inc.), and DuzAll (Coralite Dental Products Co.) to the list of self-curing resins developed for prosthetic purposes.[38] Leinfelder and Talyor also named Ames (The W. V-B Ames Co.), Texton (S.S. White dental Mfg. Co.), and Vitafilling (Vitaliner Co.).[37] Sevriton (Amalgamated Dental Company/DeTrey) contained a new polymerization catalyst based on sulfinic acid that was developed by Oskar Hagger,[24] and also came onto the market at this time.[26] In total, well over 20 cold-curing polymers for various dental applications were offered in a very short time.

Acrylate-based Dental Fillings

In 1941, Helmut Haußmann and others reported on indirect acrylate inlay fillings made from Hekodent.[27] In February 1942, Alfred Deppe published a paper on directly placed acrylate fillings that set quickly in the mouth and were made of a self-polymerizing compound produced by Kulzer that had only been used for experimental purposes until then. Deppe stated in his publication, "It is thanks to the pioneering work of Mr. Schnebel that self-curing acrylates such as Paladon and Palapont can now be produced using Kulzer's wet processing technique, which no longer discolor". Initial practical experience with direct acrylic fillings was described by Deppe as promising. Deppe stated that after tooth preparation, the cavity walls should first be "sealed" with monomer acrylate liquid and "lightly wiped". Next to disinfection, this allowed the tooth structure to adapt "particularly well" to the fast-curing resin to be applied. Even though adhesion was not achieved with this approach, he was the first to promote touching up the cavity to improve adaptation. Deppe's publication does not mention how many teeth or which cavity classes were treated. He simply wrote: "However, my practical experience to date and the control experiments I have carried out for this purpose have not shown any clinical irritation of the pulp. The vitality of the pulp was fully preserved in all tests during the short four-month observation period. An advantage of using the new resins in molar teeth rather than the usual amalgams is that they do not show pulp toxicity or wash out and discolor in the anterior region like the silicate cements do." Even though he admitted that he had only a few months of experience (ie, since 1941), he wrote: "My experiments and experiences with non-staining and self-curing acrylates have shown that these new materials, which for the time being cannot be manufactured and are therefore not yet available in the dental trade, have quite significant advantages over all previous resins, which will enable their widest application in the most diverse fields of our profession. Let us hope that the present difficulties of the industry can be overcome in the foreseeable future, so that this new material will soon be available to dentistry."[19] Deppe was thus also the first to describe the production of directly placed, fast-curing resin fillings in addition to acrylate-based "sealing" (for better adaptation of the interface between resin and hard-tissue substrates). The dentist Fred A. Slack, still mentioned by Ernst Sauerwein in 1985, already had experience with acrylic-based fillings in 1939.[62] Slack published on this subject in 1943.[67] His publication is particularly relevant from a historical and ethical point of view. Slack had also used the acrylate-based denture resins commonly used at the time for direct fillings. He mixed powder and liquid to form a "cement-like" workable mass, which solidified extremely slowly in the oral cavity because of insufficient exposure to pressure and heat. This did not result in true, continuous polymerization. Slack first reported these fillings in May 1939 in a 17-year-old patient who showed signs of a physical and mental illness that had manifested as high blood pressure, nervousness, anxiety, and lack of cooperation. The patient's teeth were all vital but decayed. The wish of the family, her doctor, her fiancé and the patient (please note the order) was that all teeth be extracted and replaced with complete dentures. The patient was offered fillings made of different materials including acrylic resins not previously used for such purposes. After consent had been obtained, dental fillings were placed under local and general anesthesia in the same month, including six direct fillings made of acrylic resin (the publication does not indicate which teeth were treated). Slack wrote that this experiment did not go well. Some fillings had already become loose during the (long) curing period and some had to be replaced immediately, but two were successful. Pain that would have indicated pulp damage was not reported by the patient. Six months later, it was decided to extract all teeth, including the two with successful fillings because of the patient's "mental state". Slack did not report on the condition of the fillings at the time of extraction. He merely pointed out that no peculiarities were observed in the roots. In 1941, he conducted the same experiment in a different patient.[67] These experiments were thus performed before the Second World War but were only described later.

In 1946, Stanley D. Tylman was still skeptical about the future of direct acrylic fillings.[73] However, once the cold polymerization process became known in 1947, numerous reports on these restorations were published. These reports addressed various questions, including color changes, surface properties, dimensional behavior, and processing techniques.[1,14,16,34,39,41,46,47,50,68]

First attempts to improve wear resistance by mixing the organic matrix with inorganic fillers to form composites were discussed in the 1940s as described in Schnebel's patent[63] and the abovementioned military report.[7] Improvements were refined from 1951 by adding fillers[32] and modifying the resin components. Rafael L. Bowen played a major role in these developments in the mid-1950s.[8-11] Bowen said, "The era of dental composites began in 1954 when silicate cements and unfilled methyl methacrylate resins were the only direct filling materials. Adhesive epoxy resins became available and were used to bind a maximum volume of small, fused silica particles. The slow hardening of epoxy formulations led to the synthesis of BIS-GMA in 1965."[43]

Adhesion Between Acrylate-based Resins and Hard-tissue Substrates

The first acrylate-based "sealing" was described by Alfred Deppe in 1942 (see above). In a 2007 publication, Karl-Johan M. Söderholm described how in 1949 Oskar Hagger developed a resin sealer from glycerolphosphoric acid dimethacrylate to create a chemical bond between acrylate and dentin. According to Söderholm, the sealer was marketed in 1949 under the name Sevriton Cavitiy Seal by the Amalgamated Dental Company/De Trey. Although this compound was not clinically successful, it made important contributions to the field of dentistry because mixing resins with acid monomers creates an etching effect and allows the composite to interact with tooth surfaces. This approach combines physical and chemical effects and was later used to form dental adhesives. Because of this, Hagger is now considered the "father of modern dental adhesives". In addition, the use of dental cements that harden during acid-base reaction has always been associated with acid on the tooth surface.[69] In 1996, John W. McLean wrote, "A great deal of work continued in the 1950s on dentin adhesives, and Hagger (1951) developed and patented Sevriton Cavity Seal based on glycerophosphoric acid dimethacrylate, the first dentin and enamel adhesive to use acid etching."[40] McLean supported his statements by citing studies by a 1951 patent from Hagger[25] and a research paper by Kramer und McLean from 1952.[33]

Historically, however, adhesive dentistry initially followed a different path, namely direct acid etching of enamel, which was separate from the subsequent application of the resin. The result was a physical bond between plastic and enamel. In 1949, the dentist Günter Staehle investigated the remineralization of tooth enamel using replicas of enamel surfaces that had been artificially demineralized by nitric acid (a common procedure for remineralization studies at the time). Staehle used the liquid methyl methacrylate plastic Paladon from the Kulzer company because of technical difficulties with the celluloid processes used to produce the replicas. Paladon hardened after application to tooth enamel and formed a thin film. In his dissertation, Staehle reported that the crystal-clear, stable and sharply defined structure of the plastic, which had previously not been used for replica production, was very suitable. However, he reported that acid etching sometimes increased adhesion of the resin film to the enamel surfaces. Staehle treated the enamel with 5% nitric acid for three minutes before rinsing with water, air drying, and then applying the acrylic resin. The strength of the adhesion was not consistent for reasons Staehle could not explain. He suggested that the increased adhesion was caused by mechanical retention of the plastic film due to acid-induced roughening of the surface. He wrote, "Various difficulties in removing the film arose later, especially in etched areas, whose roughness favors adhesion to the tooth surface."[70] Staehle was not only the first to describe the adhesion of acrylate-based resin to etched enamel but also correctly interpreted adhesion strengthening as a physical rather than a chemical process. However, he did not realize that acid etching to improve adhesion between enamel and acrylic resin could be useful for multiple dental purposes.

Instead, he viewed the enhanced adhesion between acrylate and enamel as a methodological problem in his experiments and did not realize the full potential for other applications. Some of Staehle's findings on remineralization were

Table 3 Stages of development and application of adhesively anchored acrylate-based resins for dental use between 1930 and 1955

Year	Process	Name and source
1930	First patent for use of polymethylmethacrylate (PMMA) in dentistry as a thermally adaptable molding for making dental prostheses, marketed by Röhm & Haas and other companies. Second patent in 1935.	Walter Bauer, chemist[3,57]
1936	Combination of PMMA powder with MMA liquid into a malleable compound that can be hardened by pressure and heat (also for various prosthetics), marketed by Kulzer under the names Paladon und Palapont; internationally produced and distributed as Vernonite (Vernon-Benshoff Co).	Gottfried Roth, dental technician[48]
1939	Experiments with direct, slow-hardening dental fillings (with acrylic-based dental resins).	Fred A. Slack, dentist[67]
1940	Patent for intraoral polymerization of acrylate-based dental resins at oral cavity temperature using UV light, chemical catalysts (eg, tertiary amines), or a combination of both (dual curing). Improvement of material properties by addition of mineral substances (precursors of "composites"), influence on the oxygen inhibition layer, and chemical combination of different dental resins (for cementations, repairs).	Ernst Schnebel, dentist,[63] see also[29,72]
1942	First description of an acrylate-based "sealing" and first description of acrylic fillings hardened directly in the mouth using rapidly polymerizing test products produced by Kulzer (this was before the market launch of corresponding preparations, which did not take place until after the Second World War in the late 1940s).	Alfred Deppe, dentist[19]
1949	Development of a resin sealer based on glycerophosphoric acid to create a bond between acrylic-based resins and dentin by primarily chemical means (marketed by Amalgamated Dental Company/De Trey under the name Sevriton Cavity Seal; patented 1951).	Oskar Hagger, chemist[40,69]
1949	Discovery and description of the physical adhesion of thin acrylic plastic films to enamel after etching with nitric acid.	Günter Staehle, dentist[70]
1955	Examination of physical adhesion of thicker acrylic resin samples to enamel after etching with phosphoric acid.	Michael G. Buonocore, chemist/dentist[12]
Mid-1950s	Further development of dental resins for subsequent production of composites.	Rafael L. Bowen, dentist[9,10]

published in 1949.[56] In this paper, Staehle did not refer to his novel finding that acid etching increased the adhesion between enamel and resin, considering this to be unimportant.

It was the chemist and dentist Michael G. Buonocore who realized the clinical potential of acid etching six years later, forming the basis of adhesive dentistry. Buonocore knew that etching metal surfaces with phosphoric acid improved their adhesion to plastics, but it was not clear to him whether this phenomenon was physical or chemical. He tested two etching methods on enamel surfaces. In the first experiment, he carried out a 30-second pretreatment with 50% phosphorus molybdenum and 10% oxalic acid. After rinsing with water and air drying, he applied a self-curing acrylic filling. In the second experiment, he treated the enamel with 85% phosphoric acid for 30 seconds before rinsing, drying, and applying the resin. He observed that phosphoric acid etching was clearly superior and interpreted the improvement in adhesion as a purely physical phenomenon.[12] It took several years for Buonocore's findings to be put into clinical practice. Nevertheless, acid etching of enamel played a dominant role in adhesive dentistry for awhile.[77] It was only later on that the early work of Hagger described above was used to develop enamel-dentin adhesives. These events from 1930 to 1955 are summarized in Table 3.

DISCUSSION

The milestones of acrylic-based resin use are described differently in the adhesive dentistry literature. Remarkably, pioneering work of the 19th and 20th century has partially been forgotten in the 21st century literature. Only a few of these pioneers continue to be acknowledged today.

Early Pioneers

The discovery of acrylic acid

The discovery of acrylic acid by Josef Redtenbacher in 1843 was mentioned in a 1997 review by Anne Peutzfeld.[51] However, Redtenbacher's name is rarely mentioned in more recent dentistry textbooks and publications.[53]

Discovery of light polymerization of acrylic compounds

Dental textbooks and articles have not attributed the discovery of light polymerization of acrylic compounds to the work of Georg Wilhelm August Kahlbaum back in 1880.[31,75]

Introduction of acrylate-based resins to dentistry

Walter Bauer, who introduced PMMA-based resins to dentistry in 1930, was still cited in the literature in the 1950s, eg, by Paffenbarger et al.[50] His name is also mentioned in a 1988 textbook on dental materials.[48] However, mention of Walter Bauer was removed from later editions of the book[30] and this is also true in the recent dental literature.

Development of light-, self-, and dual-curing acrylic resins

In her 1997 review, Anne Peutzfeld recalled the development of self-curing, rapidly polymerizing acrylate-based plastics by Erich Schnebel in 1940.[51] However, she did not refer to his work on UV light and dual curing. Schnebel's name is also not mentioned in more recent dental literature. This pioneering work on UV light curing and dual curing may be unknown because it took three decades before these discoveries were put to practical use through photoinitiators. In 1970, Buonocore wrote, "Just before use, 2.0% benzoinmethylether is dissolved in the adhesive liquid to form a UV-sensitive composition that is painted onto the tooth surface with a fine camel's hair brush".[13] McLean[40] cited 1971 as the starting point of this development and refers to authors Dart and Nemcock.[18] However, in 1982, John F. Glenn recalled that the photopolymerization of acrylate resins was not a new discovery and had, in fact, been available for a long time outside the field of dentistry.[23] Frederick A. Rueggeberg confirmed this in 2010: "Like many advances in dentistry, the technology for using light to polymerize resin-based materials did not originate within the profession, but instead was an existing technology that was adapted for dental use."[61]

The first direct resin fillings

Names of pioneers like F. A. Slack and A. Deppe were still known in the 1950s.[28] Deppe's work on fast-curing resins in 1942 was last referred to in a 1994 book by Rolf Nolden.[49] Since then, Deppe has not been mentioned in the dental literature. The work of Slack[67] on the first direct resin fillings has also been forgotten in the recent literature.

Luting resins and intraoral repair restorations

There is no mention of Schnebel's early work on luting resins and intraoral repair restorations[63,64] in the dentistry literature.

Development of composites

In the literature, the addition of fillers to acrylic resins ("reinforced" resins) has so far mostly been dated to the early 1950s.[6,20,32,44] However, composite materials had already been discussed earlier (with additives such as quartz and glass fibers), as shown in Schnebel's patent from 1940[63] and the FIAT's military report from 1947.[7] However, dental composites as we know them today (with a consideration of the interface between the resin matrix and the fillers) were created later.[5]

Adhesion and adaptation between acrylate-based resins and hard-tissue substrates

The first description by Deppe in 1942 of an acrylate-based "sealing" test to improve adaptation between acrylics and hard dental tissues has not yet been mentioned in the literature. John W. McLean (1996) and Karl-Johan M. Söderholm (2007) referred to the development of a plastic sealer based on glycerophosphoric acid in 1949 by Hagger and called him the "father of modern dental adhesives."[69] Günter Staehle discovered that acrylate-based resins adhere to nitric acid-etched enamel in 1949, but only reported these findings in his dissertation;[70] they were not published in a dental journal or patent.[70] This probably explains why his work has remained unknown. The importance of acid etching was first introduced to the technical world through the famous study by Michael G. Buonocore in 1955, which demonstrated an improvement in adhesion between acrylate-based plastics and phosphoric acid-etched enamel.[12,74]

Limitations of the Literature Search

Some important stages of acrylic-based resin development in adhesive dentistry are either inaccurately or incompletely described in the current literature. The present study highlights important work in this field, particularly that carried out between approximately 1930 and 1950, which has been largely unknown until now.

The study of digital media or data banks as well as manual reviews of the literature were limited. A search of the dental literature for work by pioneers such as Kahlbaum, Bauer, Schnebel, Deppe, or Slack will uncover very few articles. There are several reasons for this:

- Some research was industrially exploited, and the company owners were determined to keep the information secret rather than share it.
- A lot of work was done between approximately 1930 and 1950, the precarious era before, during, and after the Second World War, which further limited dissemination of research results. Some important findings may have been lost during the war, while others were not published in the dental scientific literature after the war, but rather by the Office of Military Government for Germany (US), and access to these data may have been restricted.
- Some discoveries, such as light polymerization, were initially more relevant to other industries and did not attract much attention in the field of dentistry.
- Some important pioneers were not trained scientists, but rather practicing dentists without an academic degree. With this background, they were not in an ideal position to publish their findings.

- Results that later turned out to be important were only published in small local journals, books, patents, and dissertations and were thus not internationally distributed.
- Other relevant publications were not published in English, the universal technical/scientific language, and thus could not be read by everyone.
- Dental literature published before 1955 has not been completely recorded digitally in online medical libraries. As described by Vesna Miletic in 2018, "early research papers are not readily available through today's medical libraries making it more difficult for today's researchers to get a glimpse into history of dental composites."[43]
- Manually searching primary and secondary sources proved to be more productive than digital research in some cases. However, not all relevant literature could be retrieved and searched, and some sources were only found by chance.
- The most important research up to 1955 was either the personal initiative of individual pioneers or industrially initiated. Public third-party funding was not of primary importance, which may explain why some information has not been made public.

CONCLUSION

Taken together, these points suggest that the results presented here cannot be considered exhaustive. Today, acrylic resins are one of the most important dental materials; therefore, it seems appropriate to increase our knowledge of how these materials were discovered, developed, tested, and adapted for use in dentistry, also with regard to failures and aberrations.

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Clinical relevance: Because acrylic resins are one of the most important dental materials, it seems appropriate to increase our knowledge of how these materials were discovered, developed, tested, and adapted for use in dentistry, also with regard to failures and aberrations.