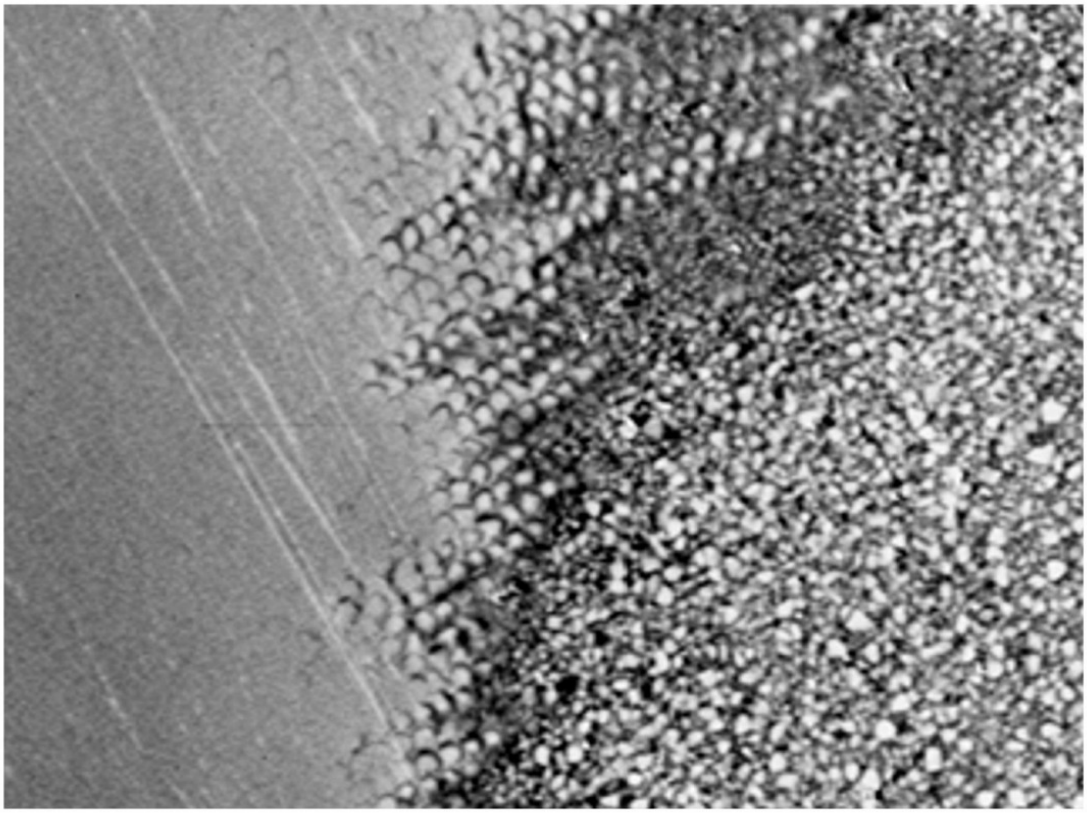
Dental Resins

Material Science & Technology

Advanced Level - 1st Edition

Ralf Janda



Cover picture: SEM picture enamel-hybrid composite interface

1st Edition

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In Memoriam

Queeny, Buffy, Vinny

Welcome

Shawny & Lenny

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Preface - 1st Ed. Advanced Version

The “Advanced Version” is the second book of the series “Dental Resins - Material Science & Technology”. It comprises around 670 manuscript pages, 253 figures and 57 tables. The Advanced Version presents a very comprehensive and detailed insight into the material science and technology of dental resin polymers and their application and thus enormously extended the knowledge base of the Basic Version. It mainly addresses very interested dentists, teachers of dental universities/schools, postgraduate students, PhD candidates, researchers, material scientists, industrial developers or experts of adjoining professional disciplines.

Many thanks for your interest and best regards

Ralf

January 2021

Preface - Book Series

Resin materials are broadly used in dentistry for almost all indications and they will gain even more importance in future. Especially the increasing performance and efficiency of CAD/CAM technology and 3D-printing open possibilities to use resins not used up to now for dental applications. Besides of dentists, dental technicians, dental students, teachers of dental universities/schools, postgraduate students and PhD candidates there are many other specialists such as researchers, material scientists, industrial developers or experts of adjoining professional disciplines who are technically engaged in dental resins. Mainly two reasons are responsible for this interest: a) many persons dealing with dentistry feel a large desire for deeper knowledge in dental resins, b) the knowledge of many different specialists is requested to develop, to investigate, to test and to evaluate dental resins; c) dental resins offer very sophisticated highly developed properties so that they are also used in other disciplines for other purposes or are the base to develop tailor-made products for other very special non-dental applications.

The idea of this e-Book is to present a three-level textbook dealing with material science and technology of dental resins. The Basic Level addresses students, dental technicians, teachers or all those interested in dental resins. The Basic Level gives a comprehensive insight into chemistry, physics and toxicology of dental resins and their technical application. The Advanced Level broadens the information of the Basic Level significantly and mainly addresses teachers of dental universities/schools, postgraduate students,

PhD candidates, researchers, material scientists, industrial developers or experts of adjoining professional disciplines. The Expert Level gives a very deep insight into the science of dental resins and mainly addresses scientists doing research on dental resins, industrial developers or scientists of adjoining professional disciplines who are very strongly interested to become also specialists in dental resin material science.

Contrarily to print books, it is the great advantage of e-Books that improvements, corrections, additions or enhancements can be done swiftly so that new improved editions can be produced and distributed rapidly and cheaply. Therefore, the e-Book is the ideal format to update the content immediately whenever errors or mistakes must be eliminated or the scientific progress makes it necessary. It is the desired and planned scenario that the content of this e-Book will not become obsolete as fast as it usually happens with conventional print books but will be refreshed in shorter periods of time.

Illustrations and tables will increase in number with each level. The information they give is - hopefully - clear and understandable but certainly they will not become prettier or colored. This is a low-cost book and everything is done keeping costs to a minimum.

The author is aware that there will be errors, inaccuracies and ambiguousness but hopefully no incorrect or even misleading information in the text despite of all the care taken. The honorable readership is kindly asked for understanding and the author will be very grateful for any hints and proposals to improve the content of the book or the book at all. Therefore, every type of constructive criticism will be highly appreciated.

Having said all this, I hope you will enjoy the book and you will get the information that is helpful and valuable for you and your work.

Many thanks and best regards

Ralf

Literature/Trademarks/Other

Not all the literature used to write this book is specifically cited. Common dental, chemical or material science knowledge taken from textbooks is not specifically cited in the text. Such textbooks are

- dentistry and dental materials [1-20]
- chemistry [21-46]
- adhesives and adhesive technology [47-50]
- material science [50-52]

Also information, figures or tables taken from the author's sole publications are not specifically cited; these are [53-79].

Information (terms, definitions, etc.) deriving from scientific organizations is not always specifically cited; these organizations are [80-83].

Specific information given is specifically cited.

Product names are not specifically marked as registered even if they are so. Principally brand names are only used when they are important in connection with the described subjects. This might be the case when only one product of a specific product category is available. Apart from that representatives of product categories presented in tables or graphics are anonymized.

Numbers of figures and tables indexed with “b” are part of the basic, advanced and expert level version. When they are indexed with “a” they are part of the advanced and expert level and when they are indexed “e” they are only part of the expert level version. In higher versions improved figures or tables of lower versions are indexed with “ba”, “ac” or “bac”.

Introduction

Besides of metals, alloys and ceramics plastics and composite resins have become to one of the most important material category in all areas of daily life such as engineering, electronics, building and construction industry, car industry and many other industries as well as in medicine and dentistry. In 1922 Hermann Staudinger discovered these high molecular compounds and called them macromolecules [84]. This was the start of a new until then unknown chemistry called polymer chemistry. The development of numerous polymeric materials and combinations thereof with other organic or inorganic substances or materials gave birth to a huge number of advanced materials with exceptional properties.

In the early years plastics were considered to be cheap and inferior materials but today composite resins and high performance plastics are very valuable and indispensable in all industries. The most important aspect for the resin materials' breakthrough is certainly the fact that for nearly every usage custom-made, often also called tailor-made, products can be developed and finally provided. For sure, more and more new, until now unknown, resins or resin composites will be tailor-made for further or today even unknown applications in future.

Resin materials (plastics, composite plastics, composite resins, resin composites) are high molecular mass products (polymers). They are manufactured by transformation of naturally occurring or by synthesis from low molecular mass substances (monomers). These low molecular mass

substances (monomers) are the smallest multiple recurring units building the high molecular mass substances (polymers). The properties of each of the resulting polymers depend on how the monomers are linked, on their chemical structure as well as on the spatial configuration of the formed macromolecules. Polymers or macromolecules do not have an exact but an average molecular mass because the single chains building the polymer/macromolecule are growing randomly and not in a well-defined manner.

Abbreviations

Abbreviations important in the context of this book or the dental literature are given in accordance with IUPAC [80-83]. Information given here is important for all versions of this book series.

Monomers

4-Met = 4-methacryloyloxypropyl trimellitic acid

4-Meta = 4-methacryloyloxypropyl trimellitic anhydride

AA = acrylic acid

BDMA = butanediol dimethacrylates

Bis-EDMA(2) = bis-EMA(2) = 2,2-bis[4(3'-methacryloyloxy)ethoxyphenyl)]propane

Bis-GMA = 2,2-bis[4(3'-methacryloyloxy-2'-hydroxy)propoxyphenyl]propane

EDMA = ethylene glycol dimethacrylate

EMA = ethyl methacrylate

GDM = glycerol dimethacrylate

GPDM = glycerol phosphate dimethacrylates

HEMA = hydroxyethyl methacrylate

HPMA = hydroxypropyl methacrylate

i-BuMA = iso-butyl methacrylate

MA = methyl acrylate

MDP = 10-methacryloyloxydecyl dihydrogen phosphate

MMA = methyl methacrylate

PENTA = dipentaerythritol pentaacrylate monophosphate

PMDM = pyromellitic dihydroxethyl methacrylate

TEGDMA = triethylene glycol dimethacrylate

TTEGDMA = tetraethylene glycol dimethacrylates

UDA = 7,7,9-trimethyl-4,13-dioxo-3,14-dioxa-5,12diazahexadecane-1,16-dioxy-diacrylate

UDMA = 7,7,9-trimethyl-4,13-dioxo-3,14-dioxa-5,12-diazahexadecane-1,16-dioxy-dimethacrylate

Thermoplastics/Duromers

ABS = acrylonitrile butadiene styrene copolymer

APE = aromatic polyester

CA = cellulose acetate

E/P = ethylene propylene copolymer

EP = epoxy polymer

EVA = ethylene vinyl acetate copolymer

HDPE = high density polyethylene

HMWPE = high molecular weight polyethylene

LDPE = low density polyethylene

LLDPE = linear low density polyethylene

PA = polyamide

PAA = polyacrylic acid

PAN = polyacrylonitrile

PBTP = polybutylene terephthalate

PC = polycarbonate

PDMS = polydimethylsiloxane

PE = polyethylene

PEEK = polyaryletheretherketone

PEMA = polyethyl methacrylate

PEO = polyethylene oxide

PES = polyethersulfone

PETP = polyethylene terephthalate

PF = phenol formaldehyde resin

PI = polyimide

PMMA = polymethyl methacrylate

POM = polyoxymethylene

PP = polypropylene

PS = polystyrene

PSU = polysulfone

PTFE = polytetrafluoroethylene

PU = polyurethane

PVAC = polyvinyl acetate

PVAL = polyvinyl alcohol

PVC = polyvinyl chloride

PVC-P = soft PVC - plasticized

PVC-U = hard PVC - unplasticized

SAN = styrene acrylonitrile copolymer

SB = styrene butadiene copolymer, high impact PS = HIPS

TPU = thermoplastic polyurethane

UF = urea-formaldehyde resin

UHMWPE = ultra high molecular weight polyethylene

UP = unsaturated polyester

VPE or XLPE = cross-linked polyethylene

Elastomers/Rubbers

ABR = acrylate butadiene rubber

AU = polyester urethane rubber

BR = butadiene rubber

EPR = ethylene propylene rubber

E-SBR = styrene-butadiene rubber

EU = polyether urethane rubber

FKM = fluoro rubber

IIR = isoprene isobutene rubber = butyl rubber

IR = cis-1,4-polyisoprene = synthetic rubber

NBR = acrylonitrile butadiene rubber = nitrile rubber

NCR = acrylonitrile chloroprene rubber

NIR = acrylonitrile isoprene rubber

NR = natural rubber

PBR = vinylpyridine butadiene

PDMS = polydimethylsiloxane

Composite Resins/Composite Plastics

AFP = asbestos fiber-reinforced plastic

BFK = boric fiber-reinforced plastic

CFK = carbon fiber-reinforced plastic

FK = fiber-reinforced plastic

GFK = glass fiber-reinforced plastic

MFK = metal fiber-reinforced plastic

MWK = metal whiskers fiber-reinforced plastic

SFK = synthetic fiber-reinforced plastic

UD = unidirectional fiber-reinforced plastic

Other

BPO = DBPO = dibenzoyl peroxide

CQ = camphorquinone

HQ = hydroquinone

HQME = hydroquinone monomethyl ether

M = molecular mass [g mol^{-1}]

mass% = percent by mass, often also called wt% = percent by weight

mol = molar mass [mol] is the mass of 1 mole of a given substance divided by the amount of the substance and is expressed in g mol^{-1}. Example: 100 g of water is about (100 g)/(18.015 g mol^{-1}) = 5.551 mol of water
mol% = percent of mole SEM = scanning electron microscopy

TEM = transmission electron microscopy

tert. arom. amine = tertiary aromatic amine

TPO = (2, 4, 6,-trimethylbenzoyl)diphenylphosphine oxide

vol% = percent by volume

Terms & Definitions

1 Chemistry/Polymer Chemistry

Terms and definitions important in the context of this ebook or the dental literature are explained in accordance with the IUPAC definitions [80-83] or with the literature [29-32, 85, 86].

Additive: Any type of substance that is added in very small quantities to a monomer, oligomer or polymer to improve, alter, and stabilize or to change its properties in any requested direction.

Antioxidant: A substance that inhibits or reduces the oxidation of other molecules or macromolecules, respectively. *Primary* and *secondary antioxidants* are differentiated. *Primary antioxidants* (mostly sterically hindered phenols or amine derivatives of higher molecular mass) are radical scavengers but *secondary* are not. *Secondary antioxidants* (sterically hindered phenols of lower molecular mass, organic phosphites or organic sulfides) decompose hydroperoxides to form stable alcohols and, thereby, chain branching can be avoided. It is the common purpose of all antioxidants to hinder or to diminish polymer degradation due to oxidative processes and to preserve the polymer's properties.

Catalyst: Atoms, molecules or ions which diminish the activation energy with the result that a specific chemical reaction can occur. The catalyst does

not participate in the reaction but exists before and after the reaction in the same chemical condition.

Comonomer: A second monomer added to the main monomer.

Constitutional unit: A species of atoms or atomic groups in a macromolecule, polymer or oligomer.

Composite resin/composite plastic: A resin/plastic that contains organic and/or inorganic fillers in all kinds of shapes (fibers, splinters, platelets, crystals, spheres, ligaments, etc.).

Copolymer: A polymer derived from more than one species of monomer.

Copolymerization: Polymerization of more than one species of monomer in which a copolymer is formed.

Cross-linkers: Cross-linkers are multifunctional monomers which form covalent chemical bonds between two separately growing polymeric chains to form a firm polymeric network. For polymerization reaction at least bifunctional monomers are requested, for polyaddition and polycondensation the monomers must be trifunctional at least.

Degree of crystallinity: The percentage of crystalline amount in a thermoplastic polymer.

Degree of conversion: The percentage of monomers that polymerize and form the polymer.

Degree of cross-linking: Relates to the number of groups that interconnect two materials. It is generally expressed in mole percent (mol%).

Degree of polymerization: The number of monomeric units/repeat units in a macromolecule, an oligomer or chain. For homopolymers the number of monomeric units corresponds with the number of repeat units. For copolymers this is not always true and sometimes the degree of polymerization is defined as the number of repeat units. Considering polyamide 66 (PA 66), for instance, the repeat unit consists of two monomeric units (-NH-(CH2)6-NH-OC-(CH2)4-CO-) with the result that a chain of two thousand monomeric units have only one thousand repeat units.

Functional group: A group of atoms in a molecule which significantly determines the reactivity or properties of the molecule (e.g. double bonds, triple bonds, aromatic compounds and hydroxyl or carboxyl groups).

Homopolymer: A polymer derived from only one specific monomer.

Inhibitor = Stabilizer: A molecule which deactivates radicals to inhibit a premature or unintended free radical polymerization. Inhibitors/stabilizers act similar to primary antioxidants.

Initiator: One or more molecules or ions forming radicals under the influence of energy and, thereby, start the free radical polymerization. The initiator takes part in the reaction and is consumed. In case the energy involved is light the initiator is called photoinitiator or light-initiator, in case it is heat it is called thermal or heat initiator, and in case it is “chemical” energy it is called redox initiator.

Ligand: Atom, molecule, ion or radical chemically bonded to a central atom.

Macromolecule/polymer molecule: A molecule of high relative molecular mass, the structure of which derives essentially of the multiple repetitions of molecule units with relative low molecular mass.

Macroradical: A macromolecule which is a radical.

Matrix resin: Unpolymerized monomer/oligomer blend or polymerized material that may contain different types of fillers (organic or inorganic), initiators, catalysts, stabilizers, pigments or various types of other additives.

Molecule: Two or more identical or different atoms chemically bonded to each other.

Monomer molecule, functionality: It is differentiated between mono-, bi-, tri-, tetra- or penta-functional monomer molecules. Monofunctional molecules have one reactive group, bifunctional have two, trifunctional have three and so on reactive groups to run a polyreaction. Monomers with more than one functional group are also called multifunctional or higher functional monomers; they function as cross-linkers.

Monomer molecule: A molecule which can polymerize and contributes a constitutional unit to the structure of a macromolecule. In other words: the smallest molecule which repeats oneself during a polymerization to form a polymer/macromolecule.