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Introduction to
DENTAL MATERIALS

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ELSEVIER

Introduction to
Dental Materials

Fifth Edition

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ELSEVIER Edinburgh London New York Oxford Philadelphia St Louis Sydney Toronto 2013

CONTENTS

SECTION 1: Basic Science for Dental Materials

SECTION 2: Clinical Dental Materials

SECTION 3: Laboratory and Related Dental Materials

PREFACE

There are very few dental restorative procedures that do not make use of a dental material in one way or another. The dental materials market is competitive and lucrative, and there are strong market forces for the development of new and augmented dental materials, meaning that the typical lifespan of a material before it is modified or replaced can be as little as 3 years. Consequently, many materials in use today will be superseded by new ones within the duration of a typical undergraduate dental degree, and as such dental and dental therapy students must be equipped not only with an understand of *today's* materials, but of the fundamental principles and concepts that *underpin* them, such that they can apply this understanding to new materials as they are developed. A rapid progression of new restorative materials and adhesive products prompted the fourth edition, and now in the fifth edition we again seek to bring the book up to date, still covering the more traditional (but still relevant) materials and supplementing this with coverage of some of the more novel products that clinicians encounter. With all the changes in dental materials since the first edition almost 30 years ago, one thing remains the same: the dentist has ultimate responsibility for what is placed in the patient's mouth and thus needs to have a sound knowledge of the materials used.

The book is set out in three sections, each covering a different aspect of dental materials science.

SECTION ONE: BASIC SCIENCE FOR DENTAL MATERIALS

This section describes the structure of materials, with chapters on atomic bonding, metals, ceramics and polymers. The first chapter has been revised to reflect the growing need to be aware of the safety aspects of dental materials and the care that has to be taken when sourcing materials from across the world. Further chapters explain the necessary terminology used in the description of the physical, chemical and mechanical behaviour of materials. A separate chapter is devoted to the principles of adhesion.

SECTION TWO: CLINICAL DENTAL MATERIALS

This section deals with those materials commonly used in the dental surgery, including dental amalgam, composite resin and compomers, glass–ionomer cements and resin-modified glass–ionomer cements. The composition, chemistry, handling characteristics and properties relevant to their clinical use are discussed. The chapter on lining and base materials considers issues relating to pulpal protection, which is also taken up in the chapter on endodontic materials. Resin bonding to enamel and dentine is covered in a separate chapter, reflecting the high importance of this subject in clinical dentistry. Impression materials are also covered in this section.

SECTION THREE: LABORATORY AND RELATED DENTAL MATERIALS

In this section, the student of dental materials science is introduced to the materials used by dental technicians in the construction of fixed and removable prostheses. A sound knowledge of the materials available and how they are used will help towards developing an understanding of the work of the dental technician and assist in communication with him or her. Also included in this section is a chapter on cementation, describing the wide variety of materials and procedures used in the dental surgery when providing patients with indirect restorations.

The philosophy in the earlier editions of this book was to make dental materials science readily accessible to the dental student, and we have sought in this edition to expand the audience to a growing professional group: the dental hygiene and therapy student. We have endeavored to retain the simplicity and clarity that we feel was the hallmark of the previous editions, but those who are familiar with the previous edition will notice that much has been added to reflect the changes in clinical dental materials. We have retained the comment boxes throughout the text in order to highlight issues of clinical significance, which we hope the reader will continue to find helpful.

It should be appreciated that this book was written on a need-to-know basis and is only the first step towards that process of independent learning and critical appraisal of dental materials. As the title suggests, the book represents only an introduction to dental materials and there is obviously much, much more that can be learnt. The list of suggested further reading at the end of each chapter has again been updated and the reader is urged to take advantage of the better knowledge and understanding that can be gained from reading widely around the subject.

The aim of this textbook is to guide readers down the long road to becoming informed practitioners who not only know what should be done and how it should be done, but also why it should be done. I believe that the student of dental materials science will find this book a useful first step in the right direction.

Michele Barbour and Ric van Noort, 2023

A HISTORICAL PERSPECTIVE

INTRODUCTION

Poor dentition is often thought of as being a modern-day problem, arising as a consequence of overindulgence in all things considered 'naughty, but nice'! At first glance, the diet of years gone by, consisting of raw meat, fish, rye bread and nuts, would be considered better for the dentition than the cooked food and high sugar intake foods consumed today. However, the food was not washed as diligently then as it is now, meaning that it contained grit in the form of sand, flint and shells, which had the effect of wearing away the grinding surfaces of the teeth. The surface protective layer of enamel is only thin, and the underlying dentine is worn away rapidly. Eventually, the pulp is exposed and will be invaded by bacteria, which, before long, will cause the formation of an abscess, leaving no other recourse than to have the offending tooth extracted. The problems this presented were formidable, and we will return to these at a later stage.

Thus, the loss of teeth is by no means a new problem, and has been with man for time for as long as can be remembered.

ETRUSCANS (1000–600 BC)

For some of the earliest records of the treatment of dental disease, one has to go back well before the time of Christ. While much is lost with the passage of time, the Etruscans did leave behind a legacy of some very high-quality dentistry.

The Etruscans were a people that came from the near East and established themselves in the leg of Italy. They were the forebears of the Romans (upon whom they had a great influence) and laid the basis for the formation of the Roman Empire. The quality of their craftsmanship was outstanding. Their skills were put to good use, as they fashioned artificial teeth from cadaver teeth using gold to hold the tooth in place. Gold had the two advantages of being aesthetically acceptable, and of being one of the few metals available to them with the necessary malleability for the production of intricate shapes.

The Romans must have inherited at least some of their interest in teeth, as made evident by one of their articles of law of the Twelve Tables, which states that:

To cause the loss of a tooth of a free man will result in a fine of 300 As.

More remarkable, perhaps, is the fact that the slaves too were offered some protection, but in their case the fine was only 100 As. Although no physical evidence remains that false teeth were worn, it may be inferred from the written records that this was the case. Horace (65 BC), wrote of 'witches being chased and running so fast that one lost her teeth', and later still Martial (AD 40–100), referred to ivory and wooden teeth.

THE DARK AGES

Little is known of what happened in dentistry from Martial's time until the 16th century, and this period must be considered as being the 'Dark Age of Dentistry'. We owe our patron saint of dental diseases, Saint Apollonia, to this period. She was 'encouraged' to speak ungodly words by having her teeth extracted or else be burnt on the pyre. She chose to burn! This did leave the church with somewhat of a dilemma, because suicide was not allowed, but in this case the problem was overcome by considering this as divine will.

There are odd records scattered about throughout this period showing that toothache was a persistent problem. For example, one important person was known to pad out her face with cloth in order to hide the loss of teeth, whenever there was an important function to attend. This was none other than Queen Elizabeth I. Then there was Louis XIV, the 'Sun King', who suffered terribly from toothache and had to make many momentous decisions, such as the revocation of the Edict of Nantes (in 1642), while suffering excruciating pain. Possibly this clouded his judgement.

THE FIRST DENTURES (18TH CENTURY)

In the 18th century, it became possible to produce reasonably accurate models of the mouth by the use of wax. These models were then used as templates from which ivory dentures were carved to the required shape. By the latter part of the 18th century, various craftsmen produced finely carved ivory teeth. They set up in business solely to supply false teeth to the rich. Of course, this type of dentistry was not available for the masses.

Lower dentures made of ivory and inset with cadaver teeth worked reasonably well and managed to stay in place without too much difficulty, especially if weighted with some lead. The difficulties really came to the fore with the upper denture, which refused to stay in place due both to the heavy weight and the poor fit. In order to overcome this problem, upper dentures were fashioned onto the lower denture by means of springs or hinges. This technique would ensure that the upper denture would always be pushed up against the roof of the mouth, but, as can be imagined, they were large, cumbersome and very heavy.

Clearly, the use of cadaver teeth could hardly have been hygienic. Similarly, ivory is slightly porous and thus presented an ideal substrate for the accumulation of bacteria. In fact, George Washington regularly soaked his dentures in port, ostensibly to overcome the bad taste and to mask the smell.

In 1728, Fauchard suggested that dentures should be made from porcelain instead of ivory inset with cadaver teeth, arguing that porcelain would be more attractive (as it could be coloured as required) and would be considerably more hygienic. What made this suggestion possible was the introduction into Europe of the secret of making porcelain by Father d'Entrecolle, a Jesuit priest who had spent many years in China. Given the problems of the high shrinkage of porcelain during firing, it is perhaps not surprising that we had to wait until 1744 for the first recorded case of a porcelain denture, made by a man called Duchateau.

THE VICTORIAN AGE

The Victorians frowned on the wearing of dentures as a terrible vanity, more so because all of these false teeth were absolutely useless for eating with! Nevertheless, false teeth were still worn extensively by the rich. The fact that they were non-functional, combined with Victorian prudishness, is said to lie behind the custom that developed during that time of eating in the bedroom just prior to going to dinner – a custom that insured against any possible disaster at the dinner table as well as making possible the romantic affectation that young ladies lived on air.

A number of important discoveries were made during the 19th century that had a profound effect on the treatment of dental disease. The first of these was made in about 1800 by a 'dentist' from Philadelphia by the name of James Gardette.

He had carved a full set of ivory dentures for a woman patient, and had delivered these to the woman saying that he did not have time to fit the springs there and then, but that he would return to do so as soon as he possibly could. (It was the custom in those days for the dentist to visit the patient!) As it turned out, it was some months before he returned to the woman patient, and he was astonished to find that on asking her to fetch the dentures, the woman replied that she had been wearing them ever since he had delivered them. She had found the dentures a little uncomfortable at first but had persevered, and, after a little while, had found them to be quite comfortable and had no need for the springs.

Upon examination of the dentures, he realized immediately that the retention of the dentures was due to a combination of a suction effect arising from the different pressure of the atmosphere and the fluid film, and the surface tension effects of the fluid. This retention was attained because of the close fit of the denture, so it was possible to do without springs altogether, if only the denture could be made to fit as closely as possible to the contours of the oral structures. Unfortunately, the production of close-fitting dentures still presented a serious problem, which we will return to in a moment.

At this time, the extraction of diseased teeth presented a formidable problem, because there was no painless means of accomplishing the extraction. This situation was to change dramatically in 1844 due to the astuteness of a young dentist called Horace Wells, who discovered the anaesthetic effects of nitrous oxide, more commonly known as 'laughing gas'. One evening, he found himself present at a public entertainment on the amusing effects of laughing gas. A friend who subjected himself to the gas became very violent while under the influence, and in the ensuing fracas stumbled and badly gashed his leg. He had no knowledge of this wound until Wells pointed to the blood-stained leg, upon which his friend responded that he had not felt a thing. Wells realized immediately the importance of this discovery, and the next day subjected himself to the removal of one of his own teeth with the aid of the gas. This turned out to be highly successful, and before long many sufferers of toothache had the offending teeth painlessly extracted.

Unfortunately, Wells did not live to see the benefit of his discovery for long, as he committed suicide 3 years later after becoming addicted to chloroform. As a consequence of Wells's discovery, there were many people who had their teeth painlessly extracted.

At that time, few were in the position of being able to afford dentures of either carved ivory or porcelain. Other techniques had been developed, whereby it was possible to obtain accurate impressions of the oral structures, and much of the ivory was replaced by swaged gold, beaten to a thin plate on a model. The fixing of the artificial teeth to the gold was a difficult and lengthy process, and, like dentures, was also expensive.

This situation was to change dramatically with the invention, by Charles Goodyear (in about 1850), of the process of vulcanization. In this process, rubber was hardened in the presence of sulphur to produce a material called vulcanite. This material was not only cheap but was also easy to work with; it could be moulded to provide an accurate fit to the model and hence to the oral structures. It did not take off as quickly as might have been expected however, because the Goodyear Rubber Company held all the patents on the process and charged dentists up to $100 a year to use it, with a royalty of $2 per denture on top of this. The situation changed when the patent expired in 1881, and cheap dentures could be made available to the masses of people in need of them.

Nowadays, vulcanite has been replaced by acrylic resins, which came with the discovery of synthetic polymers, first made between the two World Wars. Also, wax has been replaced by a wide range of oral impression materials with far superior qualities; this has made possible the construction of very close fitting, complex prostheses.

TOOTH CONSERVATION

If the 19th century was the time for tooth replacement, then the 20th century must be considered the time of tooth preservation. For example, in 1938, 60% of dental treatment was still concerned with the provision of dentures, but by 1976 this had dropped to 7%, with the rest consisting essentially of tooth preservation procedures.

Of course, the idea of preserving a decayed tooth was by no means new. As far back as the 11th century, Rhazes suggested that cavities in teeth could be filled with a mixture of alum, ground mastic and honey. Oil of cloves was promoted by Ambrose Pare (1562) to alleviate toothache, and Giovanni de Vigo (1460–1520) suggested the use of gold leaf to fill cavities. Pierre Fauchard (1728), considered by many to be the father of dentistry, discussed many aspects of dentistry, including operative and prosthetic procedures, and mentioned lead, tin and gold as possible filling materials.

However, there were a number of important gaps in the knowledge of the dentition that held back the development of conservative dental techniques.

There was a lack of understanding of the reasons for tooth decay, which was originally thought to be due to some evil spirit invading the tooth. Some thought it was due to a worm of sorts, and promoted various nasty tinctures with the objective of killing it.

The first serious conservative dental procedures did not come into use until the second half of the 19th century. By then, it was possible to work on people's teeth without causing severe pain and discomfort, thanks to the discovery of anaesthetics. This discovery made the use of the dental drill feasible.

The first such drill only became available in about 1870, but this is not too surprising, given that the drilling of teeth without an anaesthetic would have been unthinkable. Now that the preparation of teeth could be carried out, it was possible to undertake some more adventurous procedures than the wholesale extraction of decayed teeth.

CROWNS AND BRIDGES

By the turn of the century, some highly advanced dental work was carried out in which badly broken-down teeth were reconstructed with porcelain crowns. This procedure was aided by the invention of a cement that would set in the mouth (i.e. zinc phosphate cement), and which is still widely used to this day. That this could give a great deal of satisfaction can be illustrated from the letters of President Roosevelt of the United States of America to his parents when still a young man:

> ***After lunch I went to the dentist, and am now minus my front tooth. He cut it off very neatly and painlessly, took impressions of the root and space, and is having the porcelain tip baked. I hope to have it put in next Friday, and in the meantime I shall avoid all society, as I talk with a lithp and look a thight.***
>
> **May 19, 1902**

This was followed by a letter a week later in which he writes:

> ***My tooth is no longer a dream, it is an accomplished fact. It was put in on Friday and is perfect in form, colour, lustre, texture, etc. I feel like a new person and have already been proposed to by three girls.***

Obviously a delighted customer!

As is often the case with these rapid developments, there were to be some problems ahead. One of these was highlighted by an English physician, William Hunter, who accused what was then called 'American Dentistry' of contributing to the ill health of many of his patients. He had a number of patients with ailments he was at a loss to diagnose until he noticed the extensive restorative work in their mouths. These bridges and crowns appeared dirty, and were surrounded by unhealthy looking tissue, which would have been particularly bad, as oral hygiene was virtually non-existent. At that time, root canal treatment was unheard of, so the roots of teeth readily became infected. On many occasions, crowns and bridges would have been constructed on badly diseased teeth. He suggested that these crowns and bridges be removed and the teeth extracted, in response to which he received considerable objection from the patients because of the cost of the dental treatment. But, for those who agreed to have the bridgework removed, a significant number showed an immediate improvement in their health. This led Hunter to describe American Dentistry as 'mausoleums of gold over a mass of sepsis'. Consequently, teeth were blamed for all manner of illnesses that could not be readily diagnosed, and this led to many perfectly sound teeth being extracted unnecessarily.

Eventually, sanity prevailed with the introduction in 1913 of X-ray equipment by C. Edmund Kells. It could now be shown whether a tooth with a dead root was healthy or diseased. If healthy, it could be kept, and only if diseased would it be removed.

These days we take the provision of crowns and bridges for granted. Yet new developments can still excite us such as the introduction of ceramic veneers in the 1980s and the rapid developments in CAD–CAM technology that have opened up new opportunities with new materials such as pure alumina and zirconia, which give the promise of all-ceramic bridges.

FILLING MATERIALS

The middle of the 19th century saw the organization of dentistry into a profession, and many dental societies came into existence, as well as numerous dental journals. One of the first acts of the American Society of Dental Surgeons was to forbid its members to use silver amalgam, resulting in the 'amalgam war'.

Amalgam is a mixture of silver, tin and mercury, and was one of the first filling materials used by the dental profession. However, many problems arose with the use of this material because of a lack of understanding of its qualities. It was not until the work of G. V. Black that some order was created out of the chaos.

He published two volumes on operative dentistry in 1895, which became the world standard for restorative dentistry. Until he had

TABLE 1 **Milestones in the History of Dental Materials**

600 BC	Etruscan gold bridge work
AD1480	First authentic record of gold fillings in human teeth by Johannes Arculanus, University of Bologna
1500s	Ivory dentures began to be carved from wax models
1728	Fauchard proposed the use of porcelain
1744	Duchateau makes the first recorded porcelain denture
1826	Taveau of Paris suggests the use of silver and mercury to make a paste for filling teeth
1839	The first dental journal is published: *American Journal of Dental Science*
1840s	'Amalgam war' – the use of silver amalgam is forbidden
1850	Charles Goodyear invented vulcanite – sulphur-hardened rubber
1879	The first cement to set in the mouth, zinc phosphate, is introduced
1880s	Silicate cements developed
1895	G.V. Black publishes the first detailed study of the properties of amalgams
1907	W.H. Taggart of Chicago invented a practical method of casting gold inlays
1950s	Introduction of acrylic resin for fillings and dentures
1955	Buonacore discovered the acid-etch technique for bonding to enamel
1970	Composites began to replace silicate cements
1976	Glass ionomer cements are invented by A. Wilson
1978	Light-activated composites appear on the market
1983	Horn introduced the resin-bonded ceramic veneer
1985	Development of dentine-bonding agents
1988	Introduction of resin-modified glass–ionomer cements
1994	First compomer appears on the market

studied both the behaviour of amalgam in detail and how best to use it, amalgam did not have a very good reputation. Since then, however, and up until this very day, amalgam has become one of the most important restorative materials used by the dental profession.

It is a great credit to his intellect and ability that some of his philosophy is only now being challenged; especially in the light of what we know now compared to 1900. It is a lesson the dental profession will have to learn over and over again as new materials are brought onto the market (Table 1).

SUMMARY

As can be noted from the preceding discussion, there are numerous restorative techniques that the dentist needs to learn. In addition, dentists use a wide variety of different materials, some being hard and stiff and others being soft and flexible.

It is important that the dentist fully appreciates the various features of these materials, what it is that makes them so useful for dental applications, and what their limitations are. Only then will the dentist be able to select the most appropriate material for a particular application.

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SECTION 1

Basic Science for Dental Materials

1.1

Biomaterials, Safety and Biocompatibility

BIOMATERIALS

The dental restorative materials described in this textbook are a special sub-group of what are more generally known as biomaterials. When a material fulfills a function in, or in intimate contact with, the human body, it is referred to as a biomaterial. A biomaterial may be defined as a non-living material designed to interact with biological systems.

There are many different applications of biomaterials. In this book we are concerned with dental restorative materials, such as those used for fillings, fixed prosthetics (such as crowns, bridges, implants), removable prosthetics (such as full and partial dentures), and those materials used in the preparation of these (including impression materials, waxes, laboratory materials). There are many other applications of biomaterials, of course, including in orthopedics, cardiovascular materials and devices, limb prostheses, reconstructive materials following surgery or accidents, and even the humble contact lens, to name but a few.

The latter part of the 20th century saw a remarkable development in new dental materials and technologies. At the beginning of the century, the choice of dental materials on offer was virtually limited to amalgam for posterior teeth, silicate cements for anterior teeth, and vulcanite for dentures, which support the ceramic teeth. Since this time, the situation has evolved considerably, and there is now so much choice and such a vast range of materials available to the clinician that the process of selecting the best materials for a particular clinical situation has become much more complex.

To make matters yet more complicated, there is ever-growing pressure to abide by the principles of evidence-based dentistry and, by corollary, evidence-based dental material selection. However, it is not at all clear what constitutes evidence-based dental material selection, or even what constitutes evidence. If one were to start from the basis that only double-blind, randomized, controlled clinical trials constitute evidence, then with respect to dental materials, we have a serious problem, as such evidence simply does not exist. So the first thing we need to do is to explore our understanding of what constitutes evidence-based dentistry more fully.

EVIDENCE-BASED DENTISTRY

There are many potential definitions of evidence-based medicine, but the one we will use here is *the conscientious, explicit and judicious use of current best research evidence in making decisions about the care of individual patients, taking into account clinical expertise and patient choice.*

What is appealing about this definition is the fact that it encompasses all aspects of the delivery of health care: namely, the evidence of research, the evidence of clinical ability, and the evidence of patient need and choice. The value of clinical ability and patient choice are reasonably easy to understand, whereas the evidence of research requires a more in-depth exploration. This is provided in the supplementary parts of the definition, which state what best research evidence is:

Clinically relevant research, often from the basic sciences of medicine, but especially from patient-centered clinical research, into the accuracy and precision of diagnostic tests (including the clinical examination), the power of prognostic markers, and the efficacy and safety of therapeutic, rehabilitative, and preventive regimens.

New evidence from clinical research both invalidates previously accepted diagnostic tests and treatments and replaces them with new ones that are more powerful, more accurate, more efficacious, and safer.

The important thing to point out here is the recurring theme of safety. In this book we will concern ourselves with dental restorative materials, and a great deal of space is devoted to two important aspects of their use: their composition and their characteristic properties. However, as the evidence-based statement above clearly indicates, we must also consider the safety of patients and of the dental team when handling dental materials.

SAFETY

When a biomaterial is placed in contact with the tissues and fluids of the human body, there is invariably some form of interaction between the material and the biological environment. Thus it is quite reasonable for patients to ask their dental practitioner what evidence there is to show that the material about to be put in their mouth is safe. This does rather pose the question: 'How do we know if a material is safe to use?' Besides, what do we mean by 'safe'? The most straightforward definition of safety in this context is to suggest that dental materials should not cause any local or systemic adverse reactions, either in patients or in the dental personnel handling the materials. How we might seek evidence to support the contention that the dental materials we use will not cause any adverse reactions can be gleaned from two sources, namely:

- basic research using methods of premarket testing
- clinical research via post-market surveillance.

The first of these involves putting the material through a battery of laboratory experiments and testing it for cytotoxicity, mutagenicity, etc., according to well-established ISO 10993 guidelines. But that is not all, as it is important to remember that many materials have the potential to be toxic under unfavorable circumstances and at sufficient doses, and yet can also be beneficial when the appropriate circumstances prevail. Many chemicals used in dental materials in their raw state would be considered highly toxic but might have very different properties when processed and/or combined with other components.

It must be understood that safety testing is not about whether or not a material is toxic; rather, it is about *risk assessment*. Whether or not a material can be used depends on the risk it poses, relative to the benefit it brings. Many dental materials can be shown in the laboratory to be cytotoxic, yet this does not preclude them from being used. For example, zinc oxide–eugenol cements have been used for over 100 years, yet they display substantial cytotoxic and irritant properties. Nevertheless, what makes it effective as a temporary filling material is its ability to kill bacteria, providing its obtunding effect; if allowed to come in contact with the pulp, however, its effect can be highly deleterious. Thus this material carries the risk of killing the pulp but, if used correctly, can save many a pulp from dying by removing the bacterial antagonist and giving the pulp the opportunity to recover from the onslaught. 'Safe' requires careful consideration and definition.

The regulatory controls of dental materials, which are largely classified as medical devices, vary across the world. In Europe once materials have undergone a risk assessment and are considered to carry an acceptable risk, they are eligible for being awarded a CE ('European conformity') mark, assuming the material is also 'fit for purpose'. In the United Kingdom post-'Brexit', this is gradually being replaced by a UKCA (UK Conformity Assessed) certification. 'Fit for purpose' in this context indicates that the material is able to perform the functions for which it has been approved. In effect, all this means is that where a material has been approved for use as, say, an anterior filling material, then it must be able to perform that function. It should be clearly understood that this does not mean that the material is efficacious. Evidence of efficacy is not a requirement for the CE approval process. It also means that the material cannot and must not be employed in situations for which its use has not been approved.

There are many other potentially adverse reactions besides toxicity, such as:

- irritant contact dermatitis
  - acute toxic reaction
  - cumulative insult dermatitis
  - parasthesia
- allergic contact dermatitis
- oral lichenoid reactions
- anaphylactoid reactions
- contact urticaria
- intolerance reactions.

Biological reactions can take place either at a local level or far removed from the site of contact (i.e. systemically). The latter is a very important consideration because it may not always be readily apparent that clinical symptoms, such as dermatological, rheumatic, or neural reactions, could be associated with a biomaterial. Both the patient and the dental personnel are exposed to these interactions and the potential risks, with the patient being the recipient of the restorative materials and the dental personnel handling many of the materials on a daily basis.

There are therefore many aspects to risk assessment, such as making sure that any unnecessary contact with dental materials that may cause irritant contact dermatitis is avoided (Figure 1.1.1.), especially among members of the dental team who will be working with these materials every day. This is often just a matter of common sense, combined with sensible packaging of the materials to be handled. There is no doubt that manufacturers have become much more aware of these issues over the years, paying a lot more attention to how they present their materials and doing it in such a way as to minimize contact.

It is estimated that there are some 140 ingredients in dental materials that can cause an allergic adverse reaction. The question then is: 'How do we know if the materials used might cause any one of these adverse reactions?' Tests to assess the potential of a dental material to cause an allergic adverse reaction are very difficult since they involve the patient's immune system and we are all different in this respect. Some studies suggest that the frequency of adverse reactions to dental materials can be anything from 1:700 to 1:10 000. Experience tells us that some materials are particularly likely to cause an allergic adverse reaction; these include the poly(methyl methacrylate) used in dentures and latex rubber in surgical gloves. Much of this information is anecdotal, although a limited amount of knowledge has been acquired via post-market surveillance. Many countries and regions have systems in place for the reporting of adverse events associated with dental materials. In the UK and EU this is done via the competent national authority (e.g. the Medicines and Healthcare Products Regulatory Agency [MHRA] in the United Kingdom), while in the USA the reporting procedure is the responsibility of the US Food and Drug Administration (FDA) via the MedWatch program. Despite the wide use of dental materials, information on their clinical safety is not

Figure 1.1.1 Irritant contact dermatitis due to resin contact.

particularly abundant, although, from the little evidence that is available, it would appear that adverse reactions to dental materials are fairly rare and that severe adverse reactions are even more so. It should be noted that many compounds potentially cross-react, which means that an allergic sensitization induced by one compound will extend to one or more other similar compounds. Therefore one has to be aware that sensitized individuals are often multi-allergic to a range of compounds.

BIOCOMPATIBILITY

There is a subtle distinction between safety and biocompatibility. Safety is concerned primarily with the fact that materials in contact with the human body should not cause an adverse reaction. A material may be said to be *biocompatible* when it elicits an appropriate hose response, that is to say, that it has the quality of being non-deleterious in the biological environment but must also act or interact in such a way as to benefit the patient. It is important to appreciate that this interaction works both ways. That is, the material may be affected in some way by the biological environment, and equally, the biological environment may be affected by the material. A dental material need not necessarily be inert in order to be biocompatible; that is, it may interact with the environment, for instance, exchanging ions with the saliva; it is biocompatible if it does this to the patient's benefit.

For example, post-operative sensitivity is a local reaction to a restorative procedure. It is often associated with the placement of filling materials, where there is an adverse pulpal reaction following the operative procedure. Although at one time this was thought to be due to a lack of biocompatibility of the restorative material itself, it has now become well accepted that a significant role is played by the ingress of bacteria into the gap between the restorative material and the tooth tissues. If the restorative material were able to provide a hermetic seal, which would prevent bacterial ingress, then post-operative sensitivity from this source would be far less likely. A pulpal reaction could still arise if the restorative material itself were found to be toxic to the pulp. Prevention of bacterial invasion was an important consideration in the development of adhesive restorative materials. Some materials have a distinctly positive effect on the pulp: for example, calcium hydroxide induces tertiary dentine formation by the pulp. This illustrates the above point relating to bioactivity; for a biomaterial to be biocompatible does not mean that it is inert in the biological environment (i.e. that it elicits no reaction) but that it should, ideally, induce a response that is both appropriate and beneficial.

Corrosion is an unwanted interaction between the biological environment and the biomaterial. One of the better-known dental examples is the corrosion of dental amalgams. This corrosion causes discoloration of the tooth tissues and has been implicated in the common observation of marginal breakdown of amalgam restorations. Composite restorative materials can discolor in the mouth due to the corrosive action of the environment, and this causes many to be replaced when the aesthetics become unacceptable. The corrosive effects of the biological environment on the casting alloys used in the construction of fixed and removable intra-oral prostheses can also cause unwanted effects. When a material is susceptible to corrosion in the biological environment, it may release corrosion products into the local biological tissues; this may cause an adverse reaction either locally or systemically. Some patients can develop allergic or hypersensitive reactions to even very small quantities of metals, such as mercury, nickel, and cobalt, that may be released due to the corrosion process. Hence it is important that biomaterials have appropriate corrosion resistance.

From the above, it should be clear that it is very important for the dental clinician to know the composition and chemistry of the materials to be used in the oral cavity and how these materials may interact with the biological environment.

CLINICAL SIGNIFICANCE

Dental practitioners are ultimately responsible for the materials to which a patient will be exposed. They must have a knowledge and understanding of the composition of the materials to be used and how these might affect the patient.

SUMMARY

The main objective of good design in restorative dentistry is to avoid failure of the restoration. However, it is important to appreciate that failure can come in many guises. Some failures may be due to unacceptable aesthetics. A clear example of this is the discoloration of composite restorative materials, which might arise from a lack of chemical stability in the biological environment. A material may need to be removed because it elicits an allergic reaction or corrodes excessively. These are aspects of the biocompatibility of the material. Equally, a restoration may fail mechanically because it fractures or shows excessive wear, possibly because the design was poor or because the material was used in circumstances unsuited for its properties.

Thus the clinical performance of dental restorations depends on:

- appropriate material selection, based on a knowledge of each material's properties
- the optimum design of the restoration
- a knowledge of how the material will interact with the biological environment.

Aspects of the function of dental materials will be covered where appropriate.

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1.2

Atomic Building Blocks

INTRODUCTION

All materials are built up from atoms and molecules, so it is not really surprising that there is a close relationship between the atomic basis of a material and its properties. Important in this context are the nature of the atoms and the ways in which they are arranged. The atoms combine to determine the microstructure of the solid and, as a consequence, determine its properties. Therefore, if we are to understand the properties of materials, we need to have an understanding of the way atoms can combine to make solids.

JOINING ATOMS TOGETHER

When two atoms are brought together, they may link to form a molecule; any bonds that form are called *primary bonds*. Alternatively, they may move apart and so retain their individual identity. Depending on the degree of interaction between the atoms, one of three states can form, these being gases, liquids, or solids. These are referred to as the three main *phases* of matter, where a phase is defined as a structurally homogeneous part of the system and each phase will have its own distinct structure and associated properties. In the gaseous state there is little or no resistance to the relative movement of atoms or molecules, while in the liquid state the resistance to movement is considerably greater, but molecules can still flow past each other with ease. In solids the movement of atoms and molecules is mostly restricted to local vibrations, although some movement at the atomic level is possible through diffusion.

The controlling factor in bond formation is energy, and a bond will only form if it results in a lowering of the total energy of the atoms being joined. This means that the total energy of the molecule must be less than the sum of the energies of the separate atoms, irrespective of the type of bond being formed. A simple way of visualizing this is the energy-separation diagram, which considers what effect moving two atoms closer together will have on their total energy. A typical energy-separation curve is shown in Figure 1.2.1.

When the two atoms are far apart, the total energy is $2E_a$, where E_a is the total energy of one atom. As they are brought closer together, the total energy begins to fall until it reaches a minimum, E_m, at a distance a_o. Thereafter, as the atoms are brought more closely together, the total energy increases due to repulsion between their clouds of electrons. As the atoms are brought even closer together, their nuclei begin to repel each other as well, but such proximity is not usually achieved in normal circumstances. Thus we have attraction at long ranges and repulsion at short ranges.

The conditions under which two atoms will bond together depend on the atoms' electron configurations, which completely determine their chemical reactivity. The more stable the electron configuration, the less reactive the atom; the extremes of stability are the 'inert gases', such as argon, helium, and neon, which are almost totally non-reactive. Their near-inertness is caused by their having complete outermost electron orbitals, with no opportunity for more electrons to 'join' the atom, and no 'spare' or 'loose' electrons to leave the atom.

All atoms try to reach their lowest energy state, and this is tantamount to having a complete outermost electron orbital, as the inert gases have. The atoms of some elements have 'gaps' for electrons in their outermost orbits, whereas the atoms of other elements have 'spare' electrons in their outermost orbits. By combining with each other, these two different types of atoms can both achieve complete outermost orbitals. The formation of bonds therefore involves only the outermost *valence* electrons.

TYPES OF PRIMARY BONDS

There are three types of primary bonds: *covalent*, *ionic*, and *metallic*.

Covalent Bonds

The covalent bond is the simplest and strongest bond and arises when atoms share their electrons so that each electron shell achieves an inert gas structure. The formation of such a bond for two hydrogen atoms is shown in Figure 1.2.2.

As the two atoms approach one another and the orbitals of the electrons begin to overlap, a molecular orbital is formed where the two electrons are shared between the two nuclei. Since the electrons will spend most of their time in the region where the orbitals overlap, the bond is highly directional.

Ionic Bonds

An atom such as sodium is predisposed to donate its single valence electron, as this would result in a configuration similar to that of neon. Naturally, it cannot do so unless there is another atom to accept the electron.

Elements that can attain an inert gas structure by acquiring a single extra electron are fluorine, chlorine, bromine, and iodine, collectively known as the halogens. Thus, if a sodium

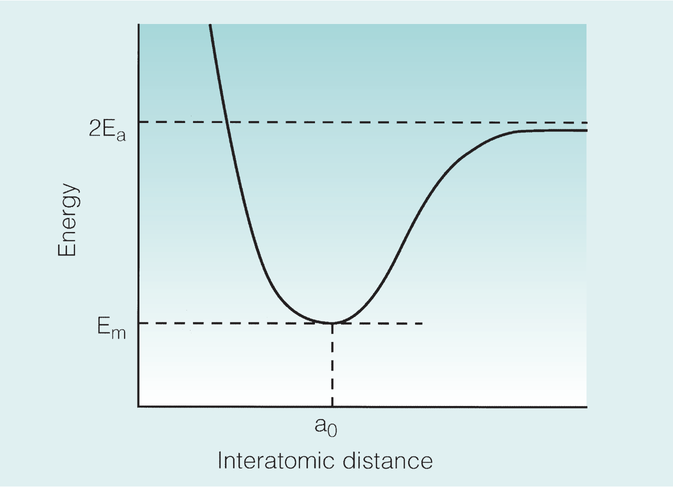

Figure 1.2.1 Energy separation curve for two atoms, each of energy E_a.

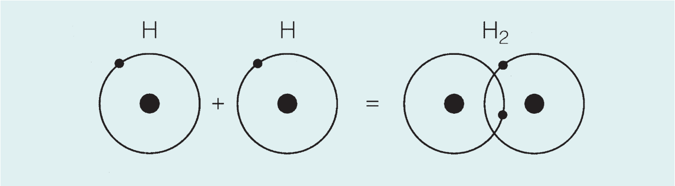

Figure 1.2.2 Two hydrogen atoms combine through covalent bonding to form hydrogen gas.

and a chlorine atom are allowed to interact, there is a complete transfer of the valence electron from the sodium atom to the chlorine atom. Both attain an inert gas structure, with sodium having a positive charge due to the loss of a negative electron and chlorine a negative charge due to its acquisition of the extra electron. These two ions will be attracted to one another because of their opposite electrical charges, and there is a reduction in the total energy of the pair as they approach. This is shown in the model in Figure 1.2.3; such bonds are called ionic bonds.

An important difference between the covalent bond and the ionic bond is that the latter is not directional. This is because ionic bonds are a result of the electrostatic fields that surround ions, and these fields will interact with any other ions in the vicinity.

Metallic Bonds

The third primary bond is the metallic bond. It occurs when there is a large aggregate of atoms, usually in a solid, which readily give up the electrons in their valence shells. In such a situation the electrons can move about quite freely through the solid, spending their time moving from atom to atom. The electron orbitals in the metallic bond have a lower energy than the electron orbitals of the individual atoms. This is because the valence electrons are always closer to one or another nucleus than would be the case in an isolated atom. A cloud of electrons, as shown in Figure 1.2.4, surrounds the atoms. Like the ionic bond, this bond is non-directional.

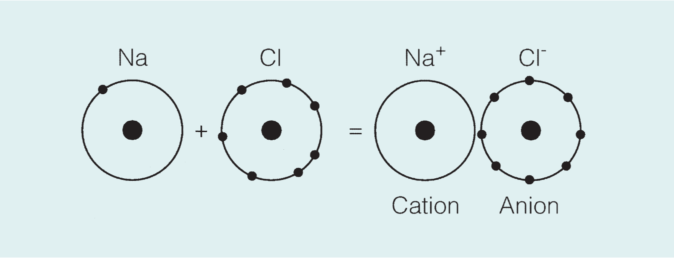

Figure 1.2.3 Formation of an ionic bond between sodium and chlorine.

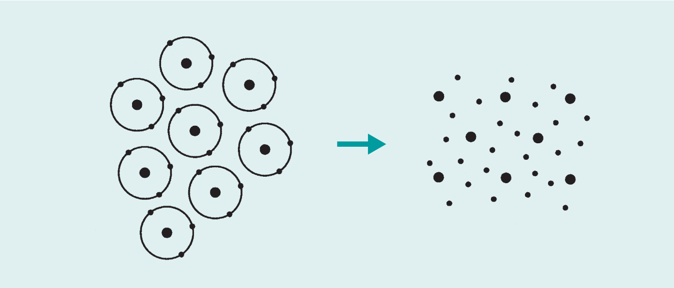

Figure 1.2.4 Formation of a metallic bond, showing a cloud of electrons surrounding the nuclei.

TABLE 1.2.1 Typical Bond Energies for the Three Bond Types

Atoms Bonded	Bond Type	Bond Energy (eV)
C–C	Covalent	6.3
C–F		5.6
H–H		4.5
H–O		4.4
C–Cl		4.0
Na–Cl	Ionic	4.2
K–Br		3.9
Na–I		3.2
Au–Au	Metallic	2.3
Cu–Cu		2.0
Ag–Ag		1.8
Pb–Pb		0.8
Hg–Hg		0.2

Bond Energies

An important feature of a bond is the *bond energy*. This is the amount of energy that has to be supplied to separate the two atoms and is equal to $2E_a - E_m$, as defined in Figure 1.2.1. Typical bond energies for each of the three types of bonds are given in Table 1.2.1.

A general feature that can be seen from the bond energies is that the covalent bonds tend to be the strongest, followed by the ionic bonds, and then finally the metallic bonds. For the metallic bonds, there is a wide range of bond energies, with some approaching that of ionic bonds, and some being very low.

Mercury has a very low bond energy, giving a bond that is not even strong enough to hold the atoms in place at room temperature, resulting in mercury's liquid state under ambient conditions.

THE FORMATION OF BULK SOLIDS

Ionic Solids

Ions are surrounded by non-directional electrostatic fields, and it is possible that the positively and negatively charged ions can find positional arrangements that are mutually beneficial from the point of view of reaching a lower energy. The ions can form a regular, three-dimensional network, with the example of sodium chloride being shown in Figure 1.2.5.

Ionic substances such as chlorides, nitrides, and oxides of metals are the basic building blocks of a group of materials known as *ceramics*, of which a rather special group are the *glasses* (see Chapter 1.3). These materials are very stable because of their high ionic bond strengths.

Metallic Solids

A similar arrangement to that of the ionic solids is possible with the metallic bond. In this case there is no strong electrostatic attraction between the individual atoms (as there was between the ions in the ionic solids), as they are held together by the cloud of electrons; this cloud forms the basis of the *metals*, which are discussed in Chapter 1.4.

Covalent Solids

There are only a few instances in which atoms of the same element join by covalent bonds to form a solid; these are carbon, silicon, and germanium. It is the directionality of the covalent bond that is the essential difference between it and the other two primary bonds. This directionality places severe constraints on the possible arrangements of the atoms.

An example of a covalently bonded solid is diamond, which is a form of carbon. Carbon has an arrangement of electrons in its outer shell such that it needs four more electrons to obtain a configuration similar to neon; in the case of diamond, it achieves this by sharing electrons with neighboring carbon atoms. The direction of these bonds is such that they are directed toward the four corners of a tetrahedron with the carbon atom's nucleus at its center. The three-dimensional structure of diamond can be built up as shown in Figure 1.2.6.

Covalent solids consisting of a single element tend to be very rare. Covalent bonds are more usually formed between dissimilar elements where each takes up an inert gas configuration. Once the elements have reacted to form these bonds, the created molecule becomes highly non-reactive toward molecules of the same type and does not provide a basis for the formation of a three-dimensional network.

The electron orbitals overlap and the electrons are shared, resulting in a filled orbital that is very stable. In this configuration there are no partially filled orbitals available for further bonding by primary bonding mechanisms. Thus covalently bonded elements result in stable molecules, and most elements, which join by covalent bonding, tend to be gases or liquids, for example, water, oxygen, and hydrogen. Of these examples, water will solidify at 0°C, and for this to be possible, there must be some additional attraction between the water molecules; something must hold these molecules together, but it is not primary bonding.

Secondary Bonding

A consequence of the sharing of electrons by two or more atomic nuclei is that the electrons will spend a disproportionately longer time in one particular position. The effect of this is that one end of the molecule may acquire a slight positive charge and the other end a slight negative charge, resulting in an electrical imbalance known as an *electric dipole*. These

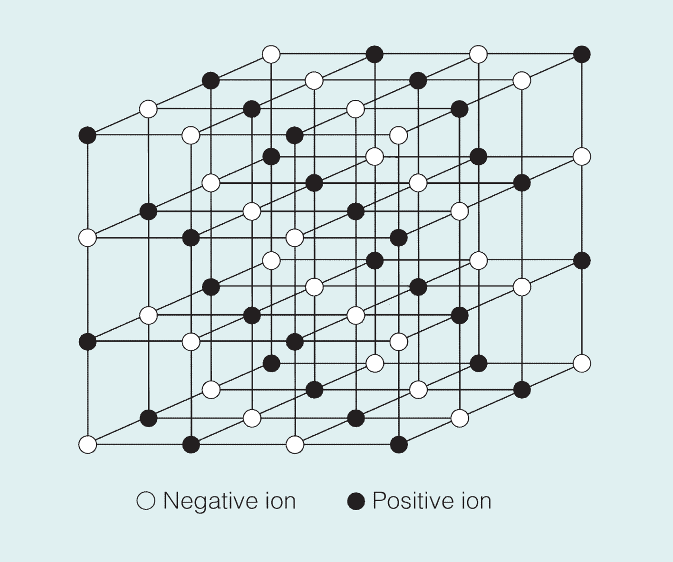

Figure 1.2.5 Formation of a bulk solid, through the ionic bonding of sodium (•) and chlorine ions (◦).

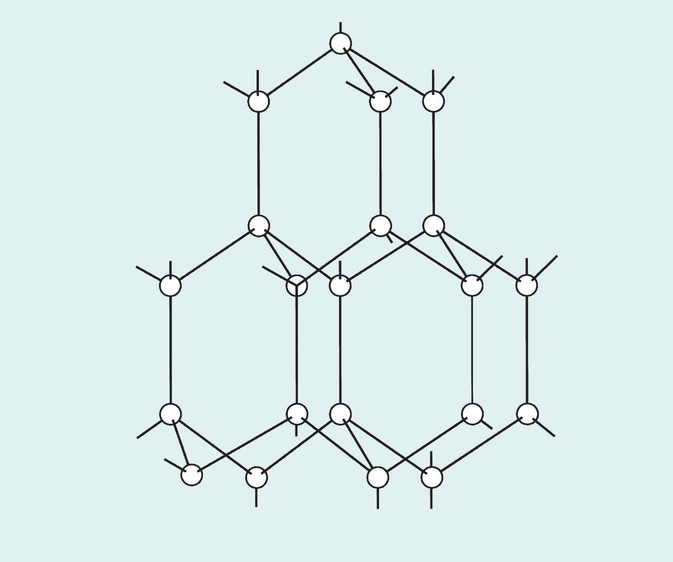

Figure 1.2.6 The structure of diamond, showing the three-dimensional network built up from the tetrahedral arrangement of the carbon bonds.