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Impact of artificial ageing process on the wear resistance of dental materials

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To Kristy (for everything)

and to my grandfather

Contents

1 Introduction

The application of materials used as amalgam alternative has risen during the last years due to the demand for aesthetic restorations and the concern about the possible adverse effects of amalgam. The materials mostly used as amalgam alternatives are either ceramic (in form of all ceramic or metal ceramic crones or ceramic inlays) or composite resins (in form of direct or indirect restorations). Although remarkable improvements have been achieved in the technology of these materials (more particularly of resin composites) clinical problems limit their application in certain indications. Failures of the resin restorations are still reported, particularly when resin composites are placed in stress-bearing areas (1). Several studies have demonstrated that a major component of a dentist's work is re-restoration of previously restored teeth (2).

Poor marginal adaptation particularly along the cervical margin, secondary caries and material fracture have been established as the common clinical problems of posterior resin composite restorations (3). Furthermore, inadequate wear resistance under masticatory attrition, which leads to a loss of anatomic form, limits the application of resin composites in relatively conservative posterior restorations (4). Annual failure rates up to 9 % for direct posterior composite restorations were reported (3). About 60 % of the operative work done has been attributed to the replacement of restorations (5). Surface stability of these materials in the challenging oral environment is a problem, which is not yet solved. Even though the colour stability of the dental composites in posterior region is not often considered as a failure reason, it is a problem that occupies the dental practitioner as well as the patients. As mentioned before, there is an increased demand for an aesthetic, which should not deviate from the real tooth substance. The surface texture and subsequently its physical characteristic, namely roughness plays an important role in the maintenance of the aesthetic aspect of the restorations. The restorations, which lose their gloss and become rough, disturb the patients and influence their quality of life. These problems result in relative frequent repair or even replacement (more often of the resin composite) of the restorations. This affects negatively the tooth hard substance as well as the patient itself in different aspects (physically, morally and financially). A new sort of composites introduced in the market during the last years promised a much better wear resistance combined with surface stability behaviour similar to dental hard substance.

Generally, the in vivo evaluation of restorative materials, besides ethical reasons, is very complicated, time-consuming, and expensive. Thus, in vitro methods simulating the oral conditions have been designed in order to predict the clinical performance and longevity of restorations. Most of the current in vitro set-ups are focusing in examining the behaviour of the materials solely under simulated occlusal forces, without taking account of the complexity of the oral environment, which imposes an additional form of degradation. Additionally, the most in vitro ageing models are examining solely the effect of water on the material properties. The dental materials must perform under very different situations in the oral cavity e.g. different pH and temperature (6). Thus, the combination of the impact of chemical as well biochemical agents of the oral cavity (i.e. soluble enzymes derived from saliva, bacteria) with the occlusal forces should be thoroughly examined.

1.1 Purpose of the study

Summarizing, as argued before the wear analysis is complicated and comprises various aspects of different weight. The wear resistance and in general the stability of new dental materials cannot be measured effectively in the oral cavity. Ethical problems as well as complicated and time consuming clinical study designs make such analyses very difficult to fulfil. A clinical research concerning the wear resistance of a material should last at least 3-5 years in order to achieve representative data for the clinical performance of a dental composite. It is clear that this process cannot initially respond to the needs of the dental industry, which introduces new materials every 2-3 years. Therefore, in vitro set-ups are preferred. However they should be precise, effective, reliable and fast in order to be in the position to meet the desired requirements. Most of the current wear experimental set-ups are focusing on the examination of the mechanical stability of the contacting materials without taking account of the ageing process and its impact on the mechanical strength of a material in the oral cavity. The chemical and biochemical interaction between the oral environment and the restorative materials is generally absent from wear analysis tests and surface stability tests. More precisely, is not yet examined the structural modifications of the materials because of the action of saliva or bacteria and their constituents (e.g. enzymes). The materials degradation provoked from the action of water has been intensively examined. Nevertheless, an increasing criticism has been exercised to the effectiveness of water storage to provoke degradation relevant to the one occurring in the oral cavity. Thus, this study aimed to investigate the suitability of distilled water compared to other ageing models for degradation's test of dental materials. Additionally, the study hypothesis of this study was that the enzymatic degradation was considerably more accentuated than the one provoked of the water storage.

2 Theoretical considerations about resin composite as restorative material - Literature Review

2.1 Composite

A composite material has been defined as a "three dimensional combination of at least two chemically different materials with a distinct interface separating the components (7). Dental composites consist of a polymer matrix (organic) part usually methacrylate-based and inorganic reinforcing filler particles, commonly glass, quartz or ceramic oxide, such as alumina or silica. Coupling agents such as silanes are widely used to improve the bonding at the filler/polymer-interface matrix (8). Dental composites also comprise chemical substances which initiate and promote the polymerization reaction (9).

Some of the properties of dental composites are mainly related to the filler and the coupling agent while other mainly stem from the resin matrix (4). The first group (i.e. related to the filler and the coupling agent) includes strength, stiffness, abrasion resistance and coefficient of thermal expansion, while colour stability and softening tendency can be found in the second group (10, 11, 12). However, the mechanical properties of composites are also highly influenced by the organic matrix (4).

2.2 Resin monomers

The resin component of a cured dental resin composite is a polymer matrix. A polymer is a large molecule built up by repetitively bonding together of many smaller units called monomers (4). The predominant dental resin monomers consist of complexed methacrylate resins. These were conceived as early as 1956, when Bowen described a hybrid molecule that was polymerised through methacrylate groups (13) coupled with Bis-phenol A derivatives via ester groups. An experimental dimethacrylate monomer was synthesized by the reaction of glycidyl methacrylate (14) and was later produced by the reaction of methacrylic acid and the diglycidyl ether of Bisphenol A. The monomer is commonly referred to as Bis-GMA, an acronym for 2,2-bis [4(2-hydroxy-3-methacryloxypropoxy)-phenyl]) propane. Polymerization of Bis-GMA occurs through the carbon-carbon double bonds of the two methacrylate groups (4).

Bis-GMA exhibited many potential advantages. The viscous, relatively non volatile monomer could incorporate high filler loading and hence provide the basis for reinforced composite resins (8). Furthermore, when compared to the methyl methacrylate that was previously used, Bis-GMA exhibited lower polymerization shrinkage and hardened rapidly under oral conditions (14). This introduced the possibility that the composites would be endowed with superior mechanical properties (15). Beside Bis-GMA, urethane dimethacrylate (UDMA) is also one of the most widely used monomers for dental composites (9).

These base monomers have molecular weights of 500-1000 g/mol, and some, such as Bis-GMA, are very viscous and need substantial dilution to be workable. They copolymerise with lower molecular weight diluents (100-300 g/mol) by a free radical addition reaction involving substantial cross-linking (9).

2.3 Fillers

The major constituent, by weight and volume, of the most composite resin materials has been the reinforcing filler particles. It is the element that has been mainly changed during the 50 years of composite existence as the resin monomer used for composites has been all these years the same. Fillers are used in dental composites to provide strengthening (16, 17), increased stiffness (18, 19), reduced dimensional change when heated and cooled (12), reduced setting contraction (20), radiopacity (21), enhanced aesthetics and improved handling. The fillers themselves are relatively inert inorganic materials; however, the coupling agents associated with them are themselves prone to hydrolysis via ester linkages within the molecules or siloxane links that are formed with the filler particle. Most commercial dental composites contain fillers such as quartz, colloidal silica, and silica glasses with barium or strontium and lithium aluminium silicate (22). In general, the physical and mechanical properties of the composites are improved in direct relation to the amount of added filler (23). Each type of filler endows the composite resins with specific advantages for selected applications (22). There has not been a definite study to prove the superiority of any specific filler. Several studies have identified and evaluated the elements leached from dental composites aged in vitro and have verified that the radiopaque glasses containing zinc, barium and strontium are more soluble than quartz or silica in aqueous solutions (24, 25, 26). The main concern has been related to the possibility that the filler matrix interface may become hydrolytically unstable due to the solubility of the fillers, leading to a more rapid erosion of the composite (23).

2.4 Coupling agent

The most common technique used to enhance the mechanical stability of the filler-matrix interface is the chemical bonding. The coupling agent γ-methacryloxypropyltrimethoxy silane has been one of the most commonly used filler treatment agents in dentistry. Silane coupling agents contain a silicon-containing compound linked to a reactive organic structure with a vinyl-group that can subsequently react with the resin matrix (Fig. 1). The methoxy groups on the silicon component can by hydrolysed by water to form silanol groups, which can then react on the filler surface in monomeric or oligomeric forms (22). It was proposed that coupling agent makes an effective load transfer between matrix and filler (27).

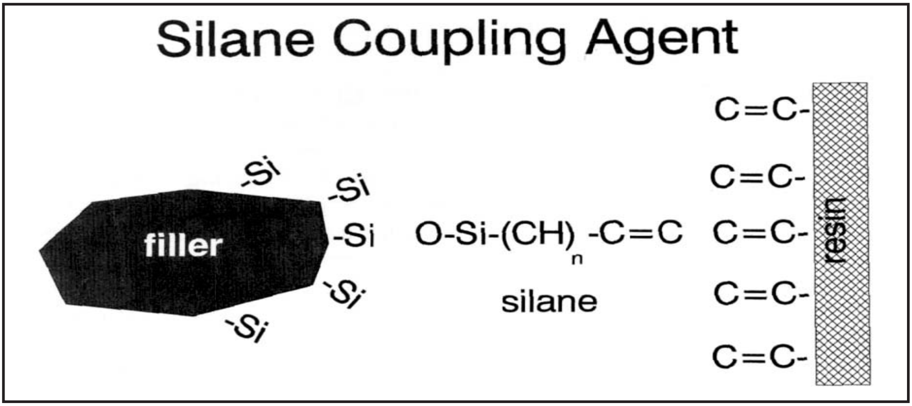


Fig. 1 Illustration of the bonding between inorganic filler and resin by the silane coupling agent [as depicted by (23)].

2.5 Other components

The polymerization of monomers to form the polymeric matrix is accomplished with the aid of chemicals such as benzoyl or laurryl peroxide, various tertiary amines, and camphoroquinone (9). In addition, small amounts of chemicals are added to inhibit the polymerization reaction, thus providing ample shelf-life or working time. Typical inhibitors used in dental composites include butylated hydroxytoluene and hydroquinone. Finally, because organic polymers can be degraded by ultraviolet light, UV stabilizers, such as benzophenone, are added to commercial products (28).

2.6 Conversion of Monomers

Dental composites are converted from a viscous resin to a rigid solid via a free radical polymerization of the methacrylate monomers, by either thermal, chemical, or photochemical means (29). Since the 1960s, photo polymerization of dimethacrylate resins has gained wide application in the dental field, including composite resins, adhesives and denture and impression materials (29).

In a free radical polymerization, each molecule grows by addition of a monomer to a terminal free radical reaction site. The diffusion rate of the propagating free radicals undergoes a drastic reduction as the polymerization proceeds (29). This has been attributed to the effect of steric hindrance as the molecules increase in size, and to the fact that the system's glass transition temperature approaches the polymerization temperature. The cross linking reaction produces a gel structure which severely reduces molecular mobility and greatly slows the rate of polymerization. At the termination of the polymerization process not all of the monomer's double bonds have reacted (Fig. 2).

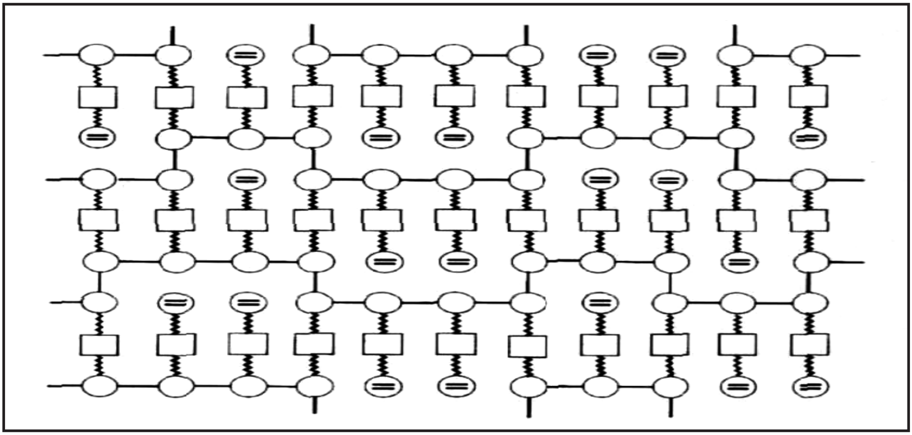


Fig. 2. A theoretical illustration of 70 % degree of conversion of a monomer [as depicted by (4)]. Notes: (=) carbon-carbon single bonds- (-) unreacted carbon-carbon double bonds.

Studies with infrared spectroscopy have indicated that significant percentage of the methacrylate groups (from 25 to 60 %) remains unreacted (30,31). Most of the unreacted carbon-carbon double bonds belong to molecules, which have reacted at one end and are thus bound to the polymer chain and are not free to elute (Fig. 3).

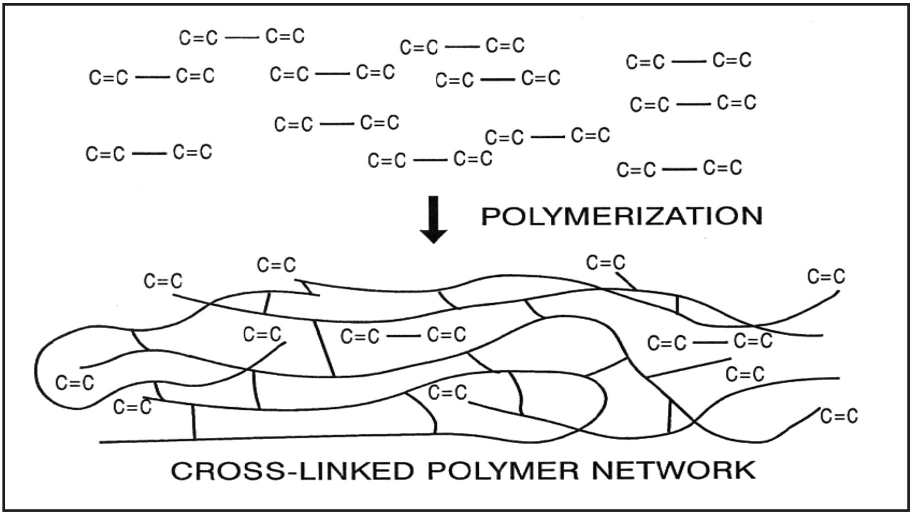


Fig. 3. A multi dimensional model of the conversion of dental monomers in polymer matrix [as depicted by (23)].

These species are referred to as pendant methacrylate groups. However, the polymer matrix also contains a small proportion of residual monomer (9). Unreacted pendant vinyl monomers which can be hydrolysed from the resin matrix (32) represent a relatively labile chemical group which can define the toxicity of resin monomers (33). Beside that, the presence of unreacted carbon-carbon double bonds has a plasticizing effect on the polymer (34).

The optimal conversion of vinyl groups in composite resins was found to be dependent on monomer composition. Materials with relatively large quantities of the rigid Bis-GMA monomer have exhibited relatively poor conversions (15). This has been attributed to the high viscosity of Bis-GMA, which restricts the mobility of reactive species and reduces the probability of their random encounters (16). In contrast, diluent monomers such as TEGDMA contribute to an increase in the number of crosslinks in the system, due to their ease of mobility in the polymer matrix (15). On the same basis, the substitution of a rigid urethanephenyl group in one oligomer by a flexible hexamethylene-di-urethane group in another oligomer produced an increase in the degree of conversion of the corresponding composites (15).

The quantity of remaining double bonds depends on the monomer mixture composition, the nature of the initiator system (30, 35) and the amount of activating light (36, 37). For a given monomer the degree of conversion is an important factor because it influences the mechanical properties of the polymer (34, 35) and the amount of free monomer that can be eluted from the polymer (9, 38). But, although optimal mechanical properties have been achieved with high degrees of conversion, it must be considered that excessive cross-linking can lead to clinically unfavourable conditions, such as polymerization contraction (39).

2.7 Classification of resin based dental composites

Although a number of classifications of dental composites was proposed (40, 41), the traditional classification of Lutz et al. (42) who divided composites into conventional, microfilled and hybrid, based on filler type and particle size, is considered still valid (43). It is well accepted that the average particle size of the inorganic fillers should range between 1 to 3 µm to provide good polishability and high abrasion resistance. Since all modern composites follow this requirement, the inorganic filler particle is no longer an issue. It is rather the filler type that influences the properties (43).

Five inorganic filler types should be considered regarding contemporary composites:

- Pyrogenic silicon dioxide, average particle size between 0,002 and 0,04 µm
- Microfine barium- or strontium-silicate glass
- Fine ground quartz
- Zirconium-dioxide glass
- Yttrium- or ytterbium-trifluoride.

Products containing only pyrogenic silicon dioxide are called microfilled composites. The microfilled composites are subdivided in Type I and Type II materials. Type I materials contain pyrogenic silicon dioxide in the resin matrix as well as in a splinter polymer. Type II materials contain pyrogenic silicon dioxide as well as larger agglomerates of pyrogenic silicon dioxide but no organic fillers in the resin matrix. The microfilled composite contain filler with an average particle size between 0,04 and 0,1 µm (23). Microfilled composites were introduced into dental composites in application areas requiring very smooth surfaces. Their mechanical properties, however, were weaker than those of some other types of dental resins. This deficiency results from physical limitations in the amount of filler (typically < 50%) that can be incorporated into the composite (23).

Products containing different types of inorganic fillers are called hybrid composites. The hybrid composites contain a mixture of small particles (average particle size of approximately 1 µm) and micro-particles (<0,1 µm) and provide a relatively smooth surface but a more durable physical character, due in part to the higher filler loading achieved (typically >75 % by weight) (39). The hybrid composites are also subdivided in Type I and Type II materials. Type I materials are filled with a blend of pyrogenic silicon dioxide (up to 15 per cent by weight) and microfine glass (barium strontium silicate or zirconia dioxide glass, up to 80 per cent by weight). Or they are filled with fine ground quartz (up to 60 per cent by weight). Type II materials contain a blend of pyrogenic silicon dioxide and of yttrium-or ytterbium trifluoride (up to 40 per cent by weight), but no microfine glass (43).

2.8 Stability: Definition, Changes of the mechanical and chemical properties of dental composites in the oral cavity (Biodegradation)

Polymers, especially those, which are used in biomedical applications, are undergoing degradation. This degradation may be rapid or slow or even controlled (44). Biodegradation is defined as the gradual breakdown of a material mediated by specific biological activity (45). In the oral cavity, degradation is a complex process as it includes disintegration and dissolution of materials in saliva and other types of chemical/physical degradation, such as wear and erosion caused by food, chewing and bacterial activity (46). The degradation can be roughly divided in physical, mechanical and chemical one.

2.8.1 Physical degradation

This process comprises physical reactions as sorption, dissolution and elution to which every material placed in the aqueous oral environment is exposed and physical changes as softening, swelling (47). The simplest form of interaction between dental composites and wet environment is the transfer of material across the composite-liquid interface (48).

Elution of unreacted components from dental composites is a diffusion-rate dependent process influenced by polymer type, surface treatment of the filler particles and the nature of the solvent used for elution (9). It has also been indicated that elution is linked to the degree of cure in the polymer network (49). Composite components are thought to elute in the oral cavity not only from the external surface but rather from most of surfaces, with the probable exception of those in contact with enamel, which should be fairly impermeable to resin and devoid of fluid (50). In the context of biocompatibility, the quantity of leachable components from composites may be clinically significant, since recent publications have reported that eluted TEGDMA stimulates the growth of bacteria such as Streptococcus and Lactobacillus (51), while Bis-phenol A dimethacrylate and unknown degradation products of Bis-GMA are suspected of being potentially estrogenic (52).

The leaching of monomers has a potential effect on the structural stability of dental composites. It was reported that only 10 % or less of the residual monomer could be eluted into water (53) and that 50 % of the leachable species are eluted into three hours in water (50).

2.8.2 Mechanical degradation

The mechanical degradation that a dental material undergoes in the oral cavity is mainly described from the different types of wear.

2.8.2.1 Wear

Wear is a progressive phenomenon, which takes places when 2 bodies are moving the one over the other. Wear in the oral cavity can result in loss of the anatomical structure of the tooth. The process may be a result of physiological or pathological conditions (54). Physiological wear is surface degradation that produces a progressive, but very slow loss of convexity of the cusps, which manifests as a flattening of cusp tips of the posterior teeth and incisal edges of mammelons on the anterior teeth. Excessive wear yields unacceptable damage to the occluding surfaces and alteration of the functional path of mastication movement. It may also destroy anterior tooth structure that is essential to acceptable anterior guidance function or aesthetics, resulting in increased horizontal stresses on the masticatory system and associated joint remodelling (55, 56). Time/age, gender, occlusal conditions, muscle hyperfunction, parafunction, gastrointestinal disturbances, environmental conditions and saliva were proposed to be some factors of importance for excessive tooth wear (57).

2.8.2.2 Wear mechanisms in the oral cavity

Clinical wear processes can be classified as they are material and patient dependent and comprise different wear mechanisms (58). There are four main types of wear (Fig.4). Three of them occur with sliding (abrasive, adhesive wear and fatigue) and one with occluding (corrosive wear) motion.

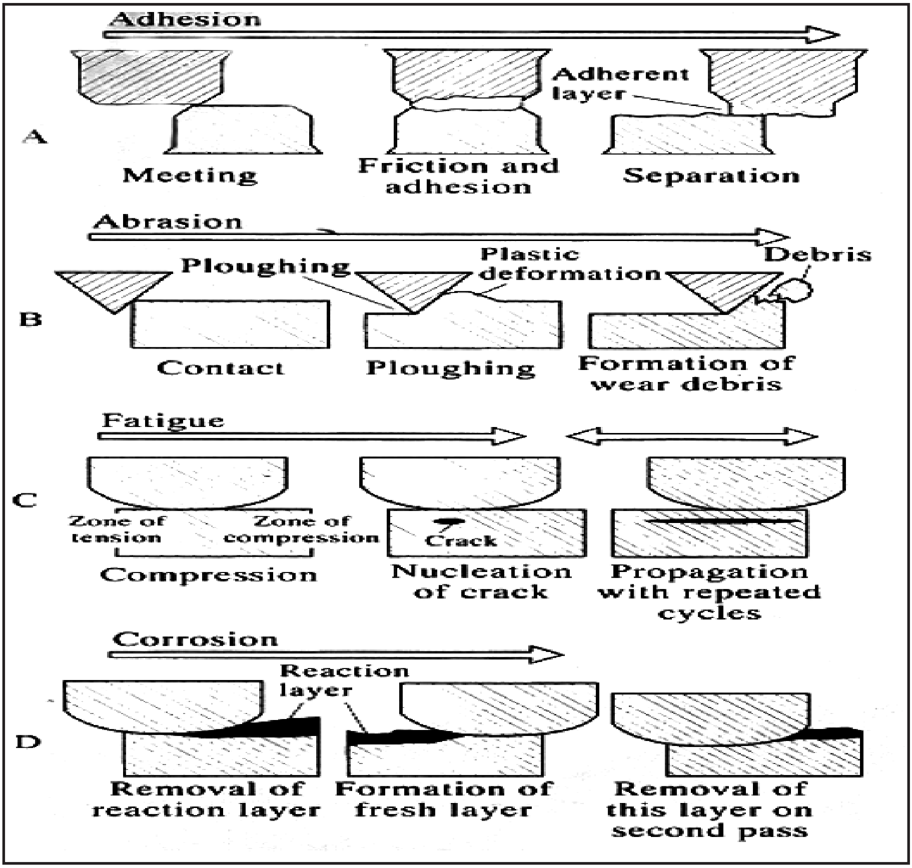


Fig. 4. The four fundamental mechanisms of wear according to (58).

Abrasive wear: It is the most common wear mechanism and the one the dentists are the most familiar with (59). It is generated when hard asperities plough into softer surfaces (58). These asperities may be an integral part of one surface (e.g. filler particles protruding from a dental composite). This type is known as 2-body abrasion and it occurs when there is a great dissimilarity in hardness between the two rubbing surfaces. It is proposed that the rough asperities under the applied normal load dig into the softer surface and literally plow up furrows that break loose as wear particles (59). The asperities may also be separate particle which are enmeshed between two surfaces, resulting in 3-body abrasion (58). Abrasion is proposed to be proportional to the hardness of the materials in contact, the geometry of the abrasive particles, the load and the sliding contact (58).

Comparing 2 and 3-body abrasion reveals that abrasive particles involved in two body abrasion move forward and hit and scratch any object in front of their moving path. This is possible because 2-body abrasion particles are firmly attached to one of the surfaces. 3- body abrasion particles however, change their sliding direction in an attempt to find the path of least resistance, and rotate and tumble in an attempt to reduce frictional resistance between the two surfaces. Consequently, 3-body abrasion targets the softer polymeric matrix of a composite, while two body abrasion cuts through both filler and matrix (59). It was suggested that the rate of material removal in 3-body abrasion can be only one order of magnitude lower than that for two body abrasion, because the loose abrasive particles abrade the solid surfaces between which they are situated only about 10 % of the time, while they spend about 90 % of the time rolling (60). Particle size, hardness and shape and volume fraction and distribution of the fillers, properties of the matrix and the interfacial bonding are thought to influence the abrasive resistance of a composite material (60). The hardness of the abrasive particles is obviously important and has a minimum value that must be significantly harder than the softer of the two rubbing surfaces. In addition, its hardness, relative to that of each of the two rubbing surfaces, will determine whether it will exist as a loose rolling particle between the two surfaces or whether it will become embedded in the softer of the two surfaces, and act on the other surface. The transition from low to high wear level of the multiphase material starts and ends when the hardness of the matrix and the hardness of the reinforcing phase are respectively exceeded by the hardness of the abrasive particles. At the high wear level, the wear loss of the multiphase material can be greater than that of a single phase material if the reinforcing phase can be detached from the matrix and acts abrasively on the matrix in addition (60).

Hard abrasive particles can easily dig out small phases and cut or crack larger ones. Soft abrasive particles are able to dig out small phases or produce large pits. The indentation depth of soft abrasive particles is substantially reduced by hard reinforcing phases if the mean free path between them is smaller than the size of the abrasive particles (60).

The shape or degree of angularity of the abrasive particles also has been shown to be important, as angular particles of a soft material produce more wear than rounded harder ones. Considering these aspects, one should expect that large variations exist among patients owing to large variation in abrasive food particles (59).

Something which is a very common finding among the in vivo studies of longevity of dental restorations (61).

Adhesive wear: The resulting wear from the sliding of two surfaces when they are displaced in relationship to each other is known as adhesive wear. The effects of friction cause the asperities on one surface to become cold yielded to the other surface. Material can be transferred from the one surface to the other as a result of this action. The volume of material transferred is proportional to the real area of contact and the sliding distance (58).

Fatigue wear: During the interaction between two surfaces, which slide the one over the other, a zone of compression in the material ahead of the motion is formed. Plastic deformation of the material causes a zone of tension behind the motion. Sub surface cracks are thought to nucleate and propagate during repeated cyclic loading at a depth governed by the materials properties (62). Finally these cracks may propagate to the surface and coalesce yielding material loss. This displaced material may itself form wear debris and cause 3-body abrasion (58). The term used to describe the substance loss either of natural teeth or of restorative materials because of fatigue wear in the oral cavity is attrition. The load-cycling chewing function is thought to be the main responsible for attrition although the mechanism of adhesive and abrasive wear have been proposed as co-responsible mechanism for its appearance (63). That is the reason why attrition cavities appear in occlusal points.

There are physiological and pathological forms of attrition. Physiological attrition is observed when the teeth come in contact (e.g. speaking, swallowing) whereas pathological attrition forms are often the results of parafunctional habits (e.g. Bruxism). It was estimated that the teeth are coming in contact in average 17,5 min/day during normal function (chewing, swallowing) (64). This value is no doubt vastly exceeded by most bruxers (57).

Corrosive wear: A chemical reaction between the oral fluids and the restorative materials can yield the formation of a surface layer, which is more prone to degradation because of cyclic contact with an antagonist. When this layer is removed a new fresh layer will be revealed and subjected to the same reaction (62). The removal can cause debris, which may agglomerate into larger particles and change the modus of abrasion e.g. to 3-body.

The uniqueness of the oral milieu as wear environment is that there is a continuous shift between the different wear mechanisms. In addition, they occur rather simultaneously than separately in different time periods. A characteristic sign of the etiologically multiplicity of wear in vivo is that the same restorative materials may show extensive wear in some patients with a particular environment while wear signs can be completely absent in other patients (2). As mentioned before, the properties of the contacting materials, the type of movement, the velocity, the load and duration of tooth contact, the diet, saliva consistency, the wear mechanism involved and the temperature were proposed to affect the wear process in the oral cavity (57). That makes the prediction of the performance of restorative materials based on in vitro wear analysis even more difficult.

2.8.2.3 Wear classification according to localization of the defects

OCA: Wear in the Occlusal Contact Areas. This kind of wear appears in contact and proximal points. The main responsible mechanism for this wear form is proposed to be the attrition caused by the repeated load cycling of chewing function. The pressure of chewing function is directly assigned from the antagonist to the restoration where it will be absorbed. The process results in deep but rather localized cavities on the contact points of a restoration. The action could possibly lead to the loss of occlusion height, which is of clinical value (65). Attrition could also lead to loss of essential anatomic form and possibly to change in mastication efficiency (66).

CFA: This kind of wear forms appears in non-contact areas or else Contact Free Areas (CFA's). In this case the cavities are not so deep but rather extended. The main responsible mechanism for this form is thought to be abrasive wear and chemical degradation (58). The wear at the CFA's affects also buccal and lingual grooves, which are the spill-ways for food abrasion (65). Although the resulted depth of the cavity is proposed to be about 2,5 times lower than the depth of the wear cavities in the occlusal contact areas (67), the generalized of the process often results in the replacement of the restoration. It was proposed that after a certain period of time macroprotection limits the degree of wear in contact free areas (68).

2.8.2.4 Wear and restorative materials

In vivo: Major discrepancies have been found between the in vivo and in vitro wear rates of posterior composites (69). Attempts to correlate in vitro results with a long term in vivo situation have not been very successful (70).

The multifactorial aspects of the wear process explain the wide variations in the observed wear, and are exemplified by large deviations in clinical wear measurements (2).

Results differ among evaluators, due to operator variations, patient variations, evaluated product, preparation designs among different clinics (61) as well as differences in finishing and polishing procedures and last but not least due to the wear evaluation method (61).

The wear of composites in the oral environment is primarily related to filler particle size and interparticle spacing (71). Because the matrix is softer and less wear resistant than the inorganic filler, it is preferentially abraded by food, toothpaste, etc. As the polymer matrix wears down, it exposes the filler particles, allowing them to be plucked from the surrounding matrix during the next abrasion cycle.

As a rule the submicron sized posterior composites are more resistant to generalized wear, but they are more prone to localized wear (72). Furthermore those composites consisting entirely of colloidal silica or filler particles averaging less than 1 µm generally exhibiting marginal fracturing or "ditching" (73). Such types of defects normally do not occur with materials containing larger-sized filler particles (74). Microfilled and small particle hybrid composite tend to display abrasion resistance competitive with amalgam, but their attrition wear sensitivity may predispose them to catastrophic failure (58).

Composite resin with fillers> 1 µm exhibit good resistance to attrition wear but unacceptable high abrasive wear rates resulting in a general loss of anatomical form (36).

As a rule the microfilled composites, as well as those in which the mean filler particle is less than 1 µm, exhibit a linear rate of generalized wear (75). Posterior composites containing supramicron sized filler particles on the other hand were proposed to exhibit decreasing rate of wear (76).

Conventional composites experienced an initial wear rate of about 100 µm per year (76) while newer formulations were proposed to exhibit a wear rate similar to this of enamel (77). The average wear rate on enamel occlusal contact areas has been reported to be about 29 µm per year for permanent molar teeth and about 15 µm per year for premolar teeth (78).

A steady mean enamel wear loss of 0,04 mm^3 by volume and 11 µm by depth per year in a small young population was reported. But large arithmetical variation as reflection of biologic variation was also reported (79).

For a bruxist volume loss value of 3,69 mm^3 for the mandibular first molar after a period of 8 years was reported. However, the corresponding depth of this cavity in the same time was relatively small i.e. 115 µm (80).

Premolars generally offer more favourable conditions for composites compared to molars (81, 82). No significant difference (statistically) has been reported between male and female wear rates. Bruxers exhibited significantly greater (statistically) wear measured by volume only after 2 years of observation (79).

But as outlined before many of the wear measurement methods (mainly the visual ones) tended to underestimate the extent of wear (61, 65, 83). An additional problem is that almost all of them were limited to reporting only the wear depth. But as the contacting area between two wearing surfaces is growing, it is expected that the pressure will be divided in larger area and consequently the wear depth development will be retarded. The volume loss is linear with time while the depth loss is not linear (65). The loss of contour can be the same problematic as deep cavities. While some methods suggest a non-linear progression of wear depth (84) some others propose a linear development of the wear values based on the assessment of loss of volume per occlusal area (65, 79). It has been suggested that it is misleading to calculate and describe wear levels of 3-dimensional cavities in terms of micrometer/year (84). The wear measured by volume is perceived to be occurring at a much faster rate than wear measured by depth. Besides that, reporting wear by volume and by mean depth is particularly useful because it describes the entire process of occlusal wear (79).

Wear is a phenomenon under control of the masticatory system, and all the teeth must be considered. As one area wears, it changes the relationship of the teeth, bringing other areas into contact. These other contacting areas can alter the functional path and thus the wear area on the tooth under consideration. A wear facet can express uneven activity, reduced activity, or become completely inactive (79).

In high-wearing situations a large increase in the area is consistent with a loss of contour and progress toward a flat cuspal morphologic structure. Therefore it might be said that, although facial height is conserved, the price to be paid is loss of cuspal structure in high-wearing occlusions. In a progressive situation, when all cuspal structure is gone and the teeth are relatively flat, wear loss by volume and depth will be more closely correlated again and facial height will be more quickly lost (79).

2.8.3 Chemical Degradation

2.8.3.1 Oxidation

Degradative reactions can result in formation and release of by-products such as formaldehyde (85). Investigation of different resin composites showed that all materials released small quantities of formaldehyde during water storage up to 115 days (85). The formaldehyde released was proposed to be the outcome of oxygen-inhibited surface layer the removal of which significantly reduced formaldehyde release. The release was initially greatest, but was still detectable after 115 days (85).

2.8.3.2 Hydrolysis

Salivary esterase and other oral enzymes have been shown to be able to degrade the dimethacrylate resin matrix, assumable the pendant methacrylate groups, resulting in the production and liberation of methacrylic acid (MAA) (86). Accompanying the liberation of methacrylic acid by the hydrolysis of the ester linkage in a pendant methacrylate group, the central part of the molecule turns into an alcohol or, in the case of Bis-GMA, a divalent alcohol (4).

2.9 Composite Surface Properties

Numerous properties are used in order to describe the surface of dental materials. Some of them will be described in the following:

2.9.1 Colour

Different colour describing systems are introduced in dentistry. The Munsell system is based on the description of Hue (i.e. the direction of the colour in the black-white axis), Chroma, which expresses the saturation of the colour, and Value, which terms the lightness. The CIE Lab-System describes the colour of a material based on three parameters: L*, a* and b*. The advantage of this colour system is that its arrangement is an approximately uniform three-dimensional colour space whose elements are equally spaced on the basis of visual colour perception. A unit change in each of the three colour parameters is approximately equally perceived (87). The colour element L* represents the lightness -it ranges between 0 (black) and 100 (white). The colour element a* represents the colour ton. The ton can be either red (positive a value) or green (negative a value). The colour saturation can be described with the colour element b*. Positive b* values indicate gold colour saturation, whereas negative values rather a blue saturation. The value of the colour elements L*, a* and b* compose the three-dimensional rectangular coordinate system for the colour location, which is described through the measured value E.

The change of colour at different time intervals can be calculated by ΔE*. This value is calculated according to the following equation:

$$\Delta E = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2}$$

A ΔE value that exceeds 2 is considered representative of a visually perceptible colour change for resins in the yellow to yellow red range of the colour spectrum (88). The tendency for the Bis-GMA resins to yellow seems to be accelerated also with heat (89). Only a minimal amount of unreacted methacrylate groups need to be present to cause a large colour change (89). The optical properties of dental materials in the oral cavity even if they are considered stable and unchangeable, are not. A discoloration may appear as a slight change in shade of the entire restoration or as a preferential staining of the margins (89). The colour change during a material lifetime period is a complicated phenomenon. It depends on a combination of the impact of intrinsic as well as extrinsic factors. Thus, colour change per se is not only a surface issue. The main responsible for this change over time are intrinsic factors of the composite such as chemical reaction of tertiary accelerators (90). The increasing polymerisation with time in the oral temperature of 37˚C and the respective increased carbon double bonds formation are proposed to play also a role in colour changes (50). Beside material related factors, the action of external variables such as the wide consume of soft drinks, wine, coffee or tea could lead to a discoloration. This could provoke aesthetical problems by staining which in extreme cases can result even in the replacement of the restoration.

In vivo: There are few reports concerning quantitative measurements of colour stability of composite materials in vivo. After 18 months of performance resin veneering materials became darker and more yellow, indicating that discoloration was partly affected by internal reactions (91). A similar tendency for veneering resin composites materials to become more yellow (that means a change of the value of b* variable) after 2 years of clinical function was reported (92). It should be regarded that most of those materials belonged to earlier generations of composites.

In vitro: It was demonstrated that discoloration is caused by distinct pigments that penetrate the structure of the resin (93). In vitro studies suggested that ΔE values of 2 units is visually perceptible (88) and a ΔE up to 3, 3 units is clinically acceptable (93, 94).

2.9.2 (Micro) hardness

The surface behaviour of a restoration is relevant to the ability to be polished, its long-term retention of that smooth surface, i.e. withstand scratching, as well as to withstand the stress due to an opposing cusp (95). Therefore different bulk material properties are measured in order to predict its behaviour against plastic deformation. One of these is (micro) hardness, which is determined by measuring the resistance of material surface to permanent deformation or penetration by an indenter (96). The measurement of hardness is based on the appliance of an indenter of specified geometry to the surface under predetermined load, and from a measurement of the width of the indentation (d) or its depth (t), its area is calculated. From this, is then the present stress is calculated. Hardness, expressed in stress units, is effectively a measure of strength. It corresponds to the stress that the material could just support at equilibrium without further deformation, that is to say, a kind of yield point (95). In other words, the smaller the indentation, the greater the hardness of the tested material.

The hardness of composite materials depends on the density of the organic matrix, the hardness of the reinforcing inorganic filler and the filler proportion in the composite (97).

In vivo: There are few reports concerning changes of hardness composites after their placement in the oral cavity. There is a general belief that materials placed in the oral cavity undergo some sort of superficial softening during their function lifetime, followed by intermittent mechanical abrasion. After 1 month immersion in the oral cavity the hardness of a light cured dental composite was considerably reduced (98).

In vitro: While most in vitro studies indicate a disintegration of hardness after storage in different ageing solutions (32, 99, 100, 101, 102), an increase of hardness after one week of water storage for dental composites was also reported (103).

2.9.3 Roughness

Surface texture is the combination of fairly short wavelength deviations of a surface from the nominal surface. Texture includes roughness, waviness and lay, that is all of the deviations that are shorter in wavelength than error form deviations.

Profile filters separate profiles into long wave and short wave components. The profile filter separates the roughness profile from longer wave components (e.g. waviness).

Thus small variations in profile called roughness are imagined as superimposed on what might be a more systematic waviness, itself superimposed on a general form error, which latter is thought of as the macroscopic departure from the designed shape of the piece (95).

The cut-off of a profile filter determines which wavelengths belong to roughness and which ones to waviness.

Roughness includes the finest (shortest wavelength) irregularities of a surface. Roughness generally results from a particular production process or material condition. Waviness includes the more widely spaced (longer wavelength) deviations of a surface from its nominal shape. Waviness errors are intermediate in wavelength between roughness and form error. The distinction between waviness and form error is not always clear.

Roughness is of significant interest in manufacturing because it is roughness (given reasonable waviness and form error) of a surface that determines its friction in contact with another surface. The roughness expresses the smoothness of a surface (95). For moving parts the roughness determines how the surface will wear, how well it will retain lubricant, and how well it will hold a load (104).

It was proposed that surface irregularities such as pits and grooves promote colonization because they shelter bacteria from clearance forces of salivary flow, chewing, swallowing and hygiene procedure (105). A rough surface is the ideal environment for the formation and development of dental plaque (106). The amount of early plaque colonization seems to be more related to the degree of roughness than to other factors (107). Preferential retention occurs on rough surfaces since bacteria on such surfaces are more protected against shear forces and can, thereby, have the necessary time to reach direct contact or to bridge the distance (107). A rough surface allows the staining of the restoration from extrinsic factors as coffee, wine or tea. Another important effect of roughness is the impact on the aesthetic appearance of the restoration. A rough restoration surface has an aged appearance, although it can be relatively recent, as restorations with higher roughness values lack on glossy.

The most widely used roughness parameter for the characterization of surfaces of dental materials is R_a, which expresses the arithmetic mean value of every profile of the tested area (Fig. 5). It is a height parameter, which demonstrates the distance of the profile from a middle line. It was proposed that R_a values greater than 0,2 µm allow the formation and growth of dental plaque on a dental restoration surface (107). This R_a score is supported by the theory of bacterial adhesion and retention. Physically, bacterial adhesion and retention occur in four phases: transport of the bacterium toward the surface, initial bacterial adhesion, attachment by specific interactions, and finally, colonization of the surface (108). Initial bacterial adhesion and retention are physico-chemically possible because a bacterium and a surface interact with each other from a certain distance (approximately 50 nm) through a combination of Van der Waal's attractive forces and electrostatic repulsive forces (107).

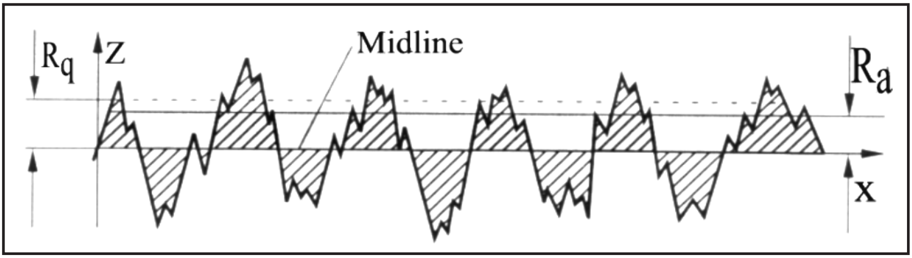


Fig. 5. Illustration of the mean arithmetic roughness R_a of a single profile

In vivo: The perception of roughness changes of composites materials for the patients was reported to lie between 0,25 and 0,5 µm (109).

In vitro: No considerable change of roughness was reported after immersion of dental composites in different ageing solutions (102). On the other hand, statistically significant changes of roughness were reported after immersion of experimental composites in water (110).

3 Biodegradation Simulation Models (chemical, biochemical, thermical and mechanical)

3.1 Chemical models

Numerous different chemical models were developed in order to evaluate the effect of the oral environment and its ingredients (saliva, bacteria, microorganisms) on the stability of dental materials. Each one of them was proposed to simulate different factors of the oral environment. The most of these models comprised a solution which was considered a) to simulate as close as possible the conditions in the oral cavity or b) to accelerate the degradation in order to meet a time effective answer whether the tested materials are resistant to degradation in vitro. Some of them intended to simulate the effect of the chemical conditions (different pH levels) found in the oral cavity, some others the impact of thermal fluctuations occurring in the oral environment and some others the solubility action of food elements. It was very often attempted to incorporate all these factors in a solution, which could simulate saliva. Therefore numerous artificial saliva models were developed. A newer more reasonable approach includes solutions, which comprise active ingredients of saliva (such as proteins). An effort will be made to present the most widely used and most effective (according to the literature) of these models. Nevertheless, it should be noticed that there are hundreds of them.

3.1.1 Artificial Saliva

It is clear that a solution, which simulates all chemical, thermical and biochemical elements would be ideal to reproduce the oral conditions and eventually predict certain characteristics of dental materials behaviour in vivo. The conception of the so called artificial saliva solution had begun as early as 1931 (111). It is also clear that duplicating exactly the properties of human saliva is impossible due to the inconsistent and unstable nature of natural saliva (112). This instability also makes natural saliva itself inappropriate for use in standardized in vitro studies. Although it has been a long history of artificial saliva compounds development, it is characterized by generally haphazard and ad hoc formulations (111). A large assortment of many different artificial saliva compounds is available. Very few of them were found to contain all major ionic components with concentrations in the physiological range (111). A main problem of many artificial compounds is their too high Ca content which is not bound by proteins as it happens with human saliva (111). Though the unreliability of the artificial saliva compounds, it was demonstrated that a certain compound was more capable to provoke filler leaching from experimental dental composites than distilled water (113). This imposes questions whether distilled water or artificial saliva or eventually another solution may lie closer to the clinical situation.

3.2 Food simulating liquids (FSL's)

It has been found that substances of food and drink having solubility parameters within a certain range induce a softening of restorative resins (114). Ethanol was found to be one such substance. FDA (Federal Drug Association, USA) proposed the ethanol water solution 75/25 as a medium which simulates the fatty food effect on dental materials and as clinical relevant (115, 116). Since then this solution has been used, in order to facilitate the extraction of not polymerised monomers, and to accelerate the in vitro degradation of dental materials, especially of composites. Generally, it is proposed that organic solvents are more efficient for extracting components from dental composites than water (9). The matching of the solubility coefficient of ethanol to the one of Bis-GMA (99) facilitates the easier entrance of ethanol in the polymer and the consequent elution of the unpolymerised monomers which are not firmly attached to the matrix. The result of this effect is the so-called plastization of the composite and subsequently degradation of the composite mechanical properties, either because of replacement of these monomers by water molecules or solely because of their elution of them. Numerous experiments demonstrated a degradation of dental materials after storage in ethanol solution (99, 117). The real oral environment is proposed to provoke a situation which lie between the one yielded after the incubation in water and ethanol, respectively (9).

3.3 Solutions simulating acidic environment

In human dental plaque a number of acids are produced by bacterial metabolism. The predominant acids are acetic, propionic, and lactic acid (118). Some of these acids can soften the resin composites as their solubility parameter is close to that of ethanol (118), while some other were proposed to hydrolyse the ester groups in the resin matrix (119). The reduction of hardness of composites after one year storage in lactate solution (pH=4) was reported (120) even though in another experiment storage in lactic acid did not produce any change in the hardness of composite materials (118). Low pH (due to cariogenic microorganisms) or acidic food ionic composition and ionic strength of the saliva may influence the quantity and quality of substances released from a restorative material as well as its properties (101). It was suggested that an acidic environment might increase the wear rate of composite restorations (121). The surface roughness of resin-based restoratives subjected to a pH-cycling model was significantly higher compared with both distilled deionised water and artificial saliva (122).

3.4 Solutions simulating basic environment

Saliva should be considered as a potential corrosive factor for the materials (123). Water is able to entry in the polymer matrix. The outcome of this entrance is thought to be a swelling of the matrix and the hydrolytical degradation of the silane bond between filler and matrix (124). This process is proposed to be long lasting in the oral cavity, but much longer in in vitro set-ups with either distilled water or artificial saliva (123). The solution of 0,1N NaOH (pH=13) contains 1 million hydrogen ions more than distilled water or artificial saliva with pH=7. Therefore it should intensively advance the whole degradation process (123). Reduced wear resistance of materials and increased degradations potential for NaOH were reported (123). Reduced hardness of cured and post-cured heat treated dental composites was reported after immersion in NaOH (125). Such an aggressive solution serves to test the limits of restorative materials and comparatively the effect of other incubation solutions (as worst case scenario).

3.5 Distilled Water

Water absorption is a diffuse controlled phenomenon (126). It is thought to be dependent upon the time and filler part (24, 26). Water diffusion causes elution of unpolymerised monomers (44). The degradation of dental composites is due to their interaction with OH^- and is associated with filler dissolution (24) and reaction with the coupling agent, resulting in the failure of the filler-matrix bond (124). This process depends on the size of the molecules: Smaller and more mobile molecules as those of the not polymerised TEGDMA (triethyleneglycol dimethacrylate) are primarily the ones that are identified by elution experiments for dental composites (101, 127). A much smaller portion of Bis-GMA molecules (2, 2-bis [4-(2-hydroxy-3-methacryloxypropoxy)-phenyl]-propane or UDMA (urethanedimethacrylate) were identified after water storage (128).

Polymers generated from polymerisation of a mixture of hydrophobic monomers are going to absorb less water than the polymers which contain more hydrophilic monomers (26).

3.6 Biochemical models

3.6.1 Enzymatic environment

The need of simulating the oral cavity, which is biochemically active environment, made the use of enzymatical solutions for degradations' analyses necessary. The reduction of mechanical properties (wear resistance, hardness) of composites, due to the hydrolytical action of different enzymes was reported (32, 127). The mechanism of the enzymatic action on dental materials is not yet fully understood. Similarly, the impact of enzymes on the wear resistance and the stability of dental materials are not thoroughly examined. The place where this hydrolysis occurs is proposed to be the steric bond between the dimethacrylates (monomers), which are the structural parts of the polymer. As outlined before in the Introduction chapter the polymer network contains unpolymerised monomers which do not at all react (residual) and others, which are only partly polymerised (pendant). It was reported that the hydrolysis of steric groups is dependent upon the pH: it is catalysed through the presence of acids (119).

3.7 Thermical models

Thermocycling was introduced in order to simulate the impact of different temperatures on the stability of dental materials. Intraoral temperature changes may be induced by routine eating, drinking and breathing (129). These temperature changes produce a hostile environment for restorative materials, as they have a different thermal expansion coefficient compared to natural teeth.

Thermal fluctuations encountered in vivo can induce surface stresses due to the high thermal gradients near the surface. Typically, the stresses developed at stress concentration have been calculated to be a minimum of 0,2-0,3 of the tensile strength for dental composites (130). Thermal stresses can be pathogenic in two ways. Firstly, mechanical stresses induced by differential thermal changes can directly induce crack propagation through bonded interfaces (129). Secondly, the changing gap dimensions are associated with gap volume changes which pump pathogenic oral fluids in and out of the gaps (129). Materials with low coefficients of thermal diffusion require long times to dissipate the thermal gradients developed at the surface. The duration of surface stresses can be relevant if the combination of stress and environment causes a time dependent growth of surface microcracks.

3.8 Mechanicals models: Simulators, 3-body machines

The idea of simulating the oral function in terms of chewing simulation is a very old one. Nevertheless, up to now there is no established and commonly accepted wear simulation method (131). ISO proposed eight different wear simulator machines (Table 1) which simulate either 2 or 3 body abrasion or both of them (131).

Table 1: the technical characteristics of the wear simulators as described in the ISO technical Specification (131).

System's Name	Antagonist	Medium	Movement	Reference	Measurement Method
DIN	Al_2O_3	H_2O	Sliding	PMMA sheet	Weight or profilometry
Acta	Steel or dental. material	Rice, husks of millet spray	Sliding	-	Profilometry
Zurich	Tooth enamel	H_2O	Impact+ Sliding	Last Test	Profilometry
Alabama	Polyacetal	PMMA beads	Sliding	-	REM
Freiburg	Al_2O_3	H_2O	Sliding	PMMA sheet	Weight or profilometry
Minnesota	Tooth	H_2O	Sliding	-	Profilometry
OHSU	Tooth Enamel	Poppy seed	Impact+ sliding	-	Profilometry+ videoimage
Newcastle	Steatite or tooth enamel	H_2O	Sliding	-	Profilometry

One should consider that the aforementioned machines are included in "a prospective standard for provisional application" in the field of assessment of wear for dental polymeric materials and not in an "International Standard" (131).

4 Materials and Methods

4.1 Materials

The materials tested as well as their characteristics can be seen in Table 2.

Table 2. The materials tested in this study (Data were provided by the manufacturers).

Material	Manufacturer	Charge/Shade	Classification/Filler	Monomer
Arabesk Top	Voco, Cuxhaven	008735 A3 (Enamel)	77 wt. % (56 Vol. % microfiller ca. 0,05 µm and very small particles with mean particle size 0,7 µm Bariumaluminiumsilicate glass Lithiumaluminiumsilicate glass ceramic Highly dispersed silicon dioxide	Bis-GMA, UDMA, TEDMA
Artglass	Heraeus-Kulzer, Hanau	030105/DA2 (Dentin)	68 wt. % inorganic filler (54 Vol. %) Diameter 1 µm (microfill) Bariumaluminium silicate glass (55 %) Specific silicon dioxide (14 %) (no pyrogenic)	Bis-GMA, TEGDMA, UDMA, hydroxypropylmethacrylat, oligoethertetraacrylat
Grandio	Voco, Cuxhaven	V21040/A2 (Enamel)	87 wt.% inorganic filler (71,4 vol. %) Nano-hybrid composite SiO_2 (20-60 nm) Glass ceramic	Bis-GMA, UDMA TEGDMA Initiator: camphoroquinone
Signum	Heraeus-Kulzer, Hanau	V21040 (Enamel)	73 wt. % inorganic filler SiO_2, SiO_2/ poly 12 methylendimathacrylate	(di) UDMATEGDMA12-dioldimethacrylate
Sinfony	3M ESPE, Seefeld	026/E3 (Enamel)	48 wt. %. inorganic filler Very fine particles Macrofiller Strontium-Aluminium Borosilicate Glass (40 %) Diameter: 0,5-0,7 µm Microfiller: pyrogenic silica (5%) Special glass ionomer (5 wt %.)- Silane: 1 wt %.	Combination of aliphatic and cycloaliphatic polyfunctional Monomers (no Bis-GMA or TEGDMA)

30 specimens from each material were manufactured. The specimens were polymerised in cylindrical forms (10,5 x 2,5 mm). The polymerisation was conducted according to the instructions of the manufacturer for every material, respectively.

Arabesk Top was placed in layers of 1 mm in standardised forms of a metal plate. It was polymerised with a halogen lamp (Douglas, Degussa Dental, Hanna: mean light intensity of 600-800 mW/cm^2-according to the manufacturer). Every layer was polymerised for 40 sec. The upper layer was covered with a Mylar strip in order to avoid the entrapment of an oxygen layer in the material bulk.

Artglass was placed in layers of 1 mm in standardised forms of a metal plate. It was polymerised in Dentacolor ® XS (Heraeus-Kulzer, Hanau: radiation spectrum 320-520 nm-according to the manufacturer). Every layer was for 90 sec polymerised. At the end the specimens were 180 sec final polymerised.

Grandio was placed in layers of 1 mm in standardised forms of a metal plate. It was polymerised with a halogen lamp (Degulux, Degussa Dental, Hanau: mean light intensity of 600-800 mW/cm^2-according to the manufacturer). Every layer was for 40 sec polymerised. The upper as well as the lower layer was covered with a mylar strip in order to avoid the entrapment of an oxygen layer in the material bulk.

Sinfony was placed in layers of 1 mm in standardised forms of a metal plate. Every layer was polymerised with ESPE Visio Alfa for 5 sec. At the end the final polymerisation was conducted in ESPE Visio Beta Device in the main program for 15 min.

Signum was placed in layers of 1 mm in standardised forms of a metal plate. It was polymerised in Dentacolor ® XS (Heraeus-Kulzer, Hanau: radiation spectrum 320-520 nm). Every layer was for 90 sec polymerised. At the end the specimens were 180 sec final polymerised.

4.2 Methods

The samples were embedded with a two component modelling resin (Palavit G, Heraeus Kulzer, Hanau) in respective forms for the later chewing simulation. After the end of polymerisation the specimens were incubated in distilled water in 37˚C for 48h in order to end the polymerisation process (9) and to allow the leaching of unpolymerised monomers. The specimens were then polished in a polishing machine (Metaserv, Buehler, Duesseldorf) with abrasive paper of increasing graining (300-1200 grit SiC under copious water-cooling (150 rpm) in order to achieve flat surfaces and to remove oxygen inhibition layer eventually trapped during the polymerisation process.

After polishing the specimens were ultrasonically cleaned in distilled water for 5 min. Subsequently colour, mean arithmetical roughness value R_a as well as microhardness was measured for the specimens.

Surface characterization: Surface degradation analysis was conducted at several time intervals: At the beginning, after the 3 months immersion period (0 cycles) 120000 cycles (simulating approx. 6 months), 240000 cycles (approx. 1 year), 640000 cycles (approx. 3, 5 years) und 1200000 cycles (approx. 5 years) (132).

Surface analysis was conducted with a mechanical contact profilometer (Perthometer 3D, Mahr, Goettingen), which was equipped with a special software (Concept 7.0) allowing assessing the volume and the depth (deepest point) of the wear cavity. The characteristics of the profilometric measurements can be seen in Table 3.

Table 3 Characteristics of the profilometer.

Lateral resolution	2 µm
Needle Radius	2 µm
Speed of the stylus	0,5 mm/sec
Angle	90°
Measured surface	3 x 4 mm
Cut-off filter (Gauss)	0,8 mm
Distance between profiles	20 µm

101 measurements equidistant to each other (20 µm) were made across each specimen. The measurements were conducted in the same direction, parallel to each other as the stylus was moving back and forward (Fig. 6).

Fig. 6. The profilometer used in the present study (Perthometer 3D, Mahr, Goettingen).

Microhardness Measurement: The Vickers hardness of the specimens was assessed before and after the ageing procedure (chemical, biochemical and thermical). It was measured with a respective measurement device (Leitz, Germany) as it can be seen in Fig. 7. The samples were loaded with 100 g for 30 sec, and then the length of the diagonals of the 136-degree diamond pyramid were measured with the help of an especially modified ocular. For every specimen five measurements were undertaken.

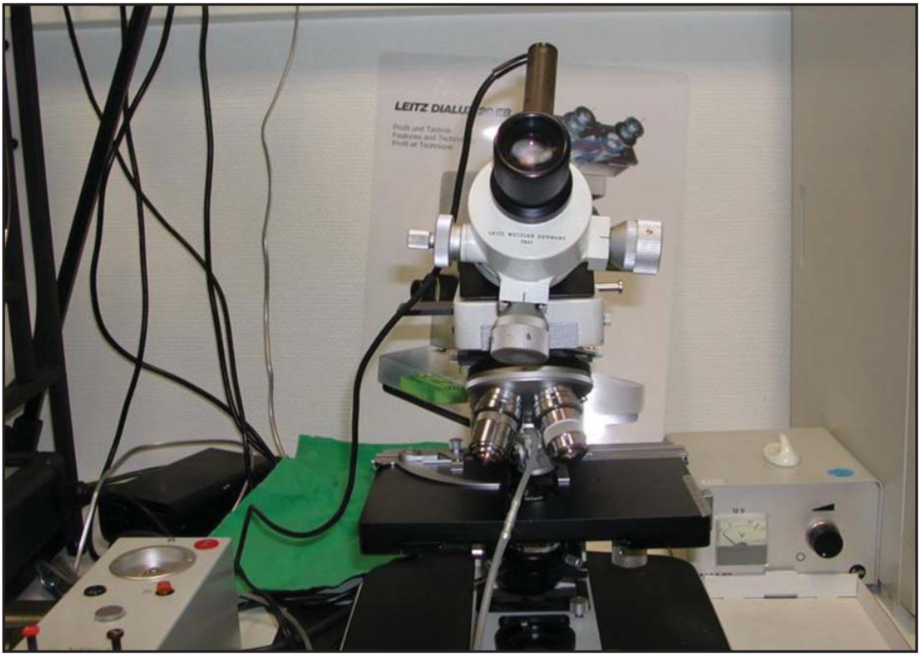


Fig. 7. The Vickers microhardness-measuring device used in the present study (Leitz, Frankfurt)

The resulted Vickers hardness was calculated according to the respective formula:

$$HV = \frac{0{,}189 \times F}{\left[(d1 + d2)/2 \times 0{,}001\right]^2} = \frac{0{,}189 \times B \times 9{,}81}{\left[(d1 + d2)/2 \times 0{,}001\right]^2}$$

B = Weight

d1, d2: the length of the diagonals produced after the loading

Colour Measurement: At the beginning and at the end of the ageing process a colour analysis of the specimens was performed. The analysis was conducted with

a spectrophotometer (Castor, Nordmeditech, Flensburg).
The colour elements of CIE* were assessed before as well as after the ageing procedure. The colour elements L* (Brightness), a* (Red-green amount of the specimen) und b* (gold blue amount of the specimen) were assessed five times for every sample tested. The mean value of the colour elements L*, a* und b* compose the three-dimensional rectangular coordinate system for the colour space, which is described through the measured value E. The colour difference between two situations (in this case the situation before and after the ageing process) can be assessed with the mathematical formula:

$$\Delta E = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2}$$

Before the colour measurement of every individual specimen, a colour alignment with the help of the white standard was performed. Because of the sensitivity of the colour device in the position of the specimen, a tripod was used in order to place the specimen exactly perpendicular to the emitting light as it can be seen in Fig. 8.

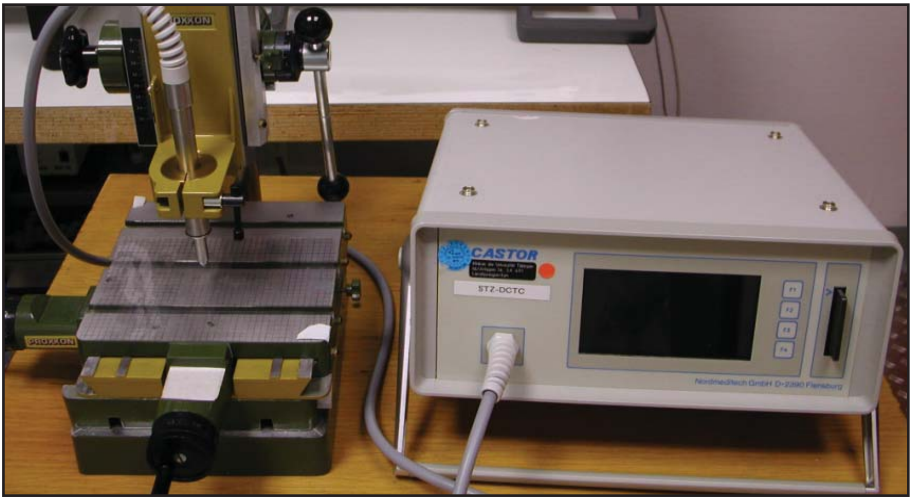


Fig. 8. The colour-measuring device used in the present study (Castor, Nordmeditech, Ellensburg).

Castor disposes a measuring field with a diameter of 0,7 mm. The specimens are illuminated with an optical fibre designed for lighting and measurement. The fibre emits light with wavelength between 380 und 780 nm. The reflected spectrum is analysed with photodiodes in 512 frequency bands (133).

The specimens were randomly divided in 6 subgroups. Each one comprised 5 specimens.

Afterwards the specimens (5 for each condition) were immersed in different solutions. The solutions were:

1) Ethanol/Water 75/25
2) Lactic acid (pH: 2,3)
3) 0,1N NaOH (pH: 13)
4) Enzymatic solution of Horse serum butyrylcholinesterase or else pseudo-cholinesterase (E.C no 3.1.1.8, LOT no 54H7175) with activity of 50 mU/ml. One unit will hydrolyse 1.0 µmole of butyrylcholine to choline and butyrate per min at pH 8 at 37˚C. The enzyme was provided from Sigma-Aldrich Chemie (Taufkirchen Munich). PCE was dissolved in phosphate buffer saline solution (Phosphate Buffer Solution DULBECCO'S without calcium, magnesium and sodium bicarbonate pH=7) with an activity of 1U/ml. Aliquots of the prepared solutions were stored at -20 ˚C.
5) Distilled Water
6) The 6th subgroup was thermally cyclic exposed in water tray (Haake W15, Thermo Haake GmbH, Karlsruhe). The specimens were immersed for 30 sec in 5/55˚C for 10000 cycles respectively. Between the two trays with different temperatures was a 5 sec pause. The temperature was controlled with a microprocessor (Haake DC 10, Thermo Haake GmbH, Karlsruhe).

The specimens were stored in darkness at 37˚C for 90 days. In order to avoid bacterial contamination during the incubation period sodium azide in concentration of 0,05 % was added to the solutions. The solutions were changed weekly, as a preliminary enzyme stability experiment revealed that the activity of PCE remains relatively stable during a week. The enzyme stability was assessed in enzymatic solutions of an activity of 50 and 100 mU/ml with and without composites, respectively. The enzymatic activity at 37˚C was determined every 24 h for a period of a week. It was measured according to the Ellman's modified reaction (134,135) using a spectrophotometer (SLT, Elisa Reader 340 ATC Laborinstruments, Germany, with a filter of 405 nm at 37 ˚C). The activity was measured with 50 µl 0, 1 M NaPO4, pH: 7, 2; + 1, 25 mM DTNB [(5-5'-dithio-bis (2-nitrobenzoic acid), Sigma-Aldrich Chemie) + 0, 1 mM EDTA (Ethalynediaminetetraacetic acid, Sigma-Aldrich Chemie). Following the addition of 150 µl of 0,2 M MOPS (4-Morpholinepropanesulfonic acid) +5 mM S-butyrylcholine iodide the volume was adjusted to 200 µl. At the end 150 µl of the enzymatic solution was added (50 and 100 mU/ml, respectively). The quantity every time assessed was 350 µl

During the experiment the ratio between the composite sample surfaces area and the incubation solution volume was 42,4 mm^2/ml (136).

After the chemical and thermical exposure the specimens were ultrasonically cleaned in distilled water for 5 min. Then they were placed into a chewing simulator load-cycling device (Willytec, Munich). The protocol used for this device comprised 1,2 x 10^6 cycles, a number of cycles which is thought to represent 5 years of clinical function (132).

The chewing simulator consists of 8 identical specimen chambers and two stepped motors which allow computer-controlled vertical and horizontal movements between two opposing specimen in each sample chamber.

Each of the eight chambers has a plastic sample holder, which is adjustably fixed by a butterfly nut to the base of the sample chamber and the underlying lower crossbeam. The samples were placed into the lower sample holder. The lower crossbeam is moved by one stepper motor and allows a horizontal, sliding motion of the samples. The antagonistic samples were embedded into the upper sampler holders, which were fixed at the lower end of the vertical guide rails. The load cycling was conducted in chambers full with distilled water in room temperature (22± 1 ˚C). Spheres of steatite (Ceramtec, Marktredwitz) with a radius of 3 mm were used as antagonists. The spheres were embedded with a two component modelling resin (Palavit G, Heraeus Kulzer, Hanau) in the respective forms and then mounted on the chewing machine (Fig. 9).

Fig. 9. Picture of the chewing simulator used in the present study (Willytec, Munich).

The guide rails are freely mounted within bearings in upper crossbeam and the adjustment screw on top of the upper crossbeam adjusts the vertical height of the antagonistic sample. The upper crossbeam is moved by the second stepper motor and moves the antagonistic samples vertically. When the upper crossbeam moves down and the antagonistic upper samples touch the lower samples, the upper crossbeam moves an additional 2 mm down. The characteristics of the chewing simulation can be seen in Table 4.

Table 4. Characteristics of the chewing simulator.

Number of cycles	1,2 x 10^6
Weight	5 Kg
Frequency	1, 6 Hz
Vertical movement	3 mm
Lateral movement	0,2 mm
Descending speed	30 mm/sec
Rising speed	70 mm/sec
Forward speed	40 mm/sec
Backward speed	40 mm/sec
Kinetic Energy	2250 J x 10^{-6}

Because the guide rails are freely mounted within bearings in the crossbeam, their individual weight is fully transferred to each lower sample. The chewing machine's computer unit calculates and displays the effective impact as kinetic energy (137). The scheme of the experimental design of the present study can be seen in Fig. 10.

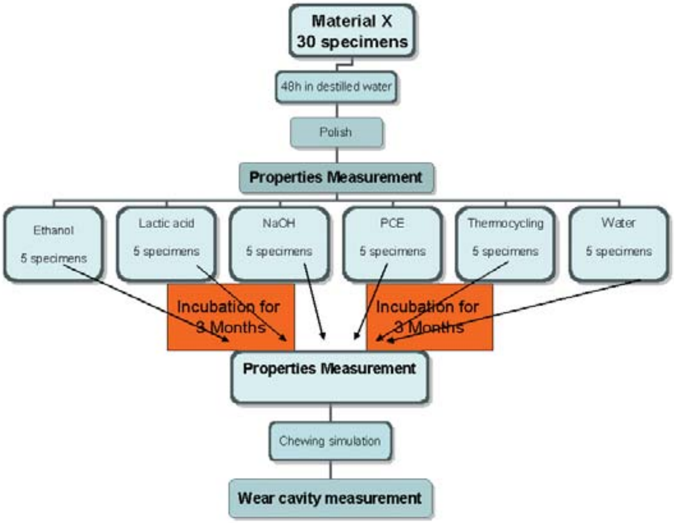


Fig. 10. The scheme of the present experimental set-up, considering as example material X.

Mean values of any examined property were calculated for each specimen. More precisely the differences ΔE (colour), ΔHV (microhardness), ΔR_a (roughness) and ΔW (wear) were calculated for each specimen separately. Each of these differences Δ referred to measured values of the corresponding material between the end and the beginning of the artificial ageing process: Δ end-beginning= [Mean (Property) end- Mean (Property) beginning]. In case of wear, of course, the value of wear in the beginning was zero. In case of hardness calculations were made in the opposite way: ΔHV= (Mean Value Hardness beginning- Mean Value Hardness end) because of the expected reduced hardness values after the immersion in the solutions and the desired positive sign.

4.3 Statistical analysis

Every experimental set up examines the effect of some independent variable on a dependent variable. For this purpose some specimens are allocated randomly into different groups. These groups then form samples from the same population. We apply different treatments (e.g. ageing procedures) to the samples. These treatments form the independent variable. If the treatments have the same effect, we still have samples from the same population (e.g. same degradation effect, the dependent variable); if not, the samples belong now to different populations (e.g. different degradation effect) [compare for (138)].

In order to check the above theoretical concept we used an appropriate statistical test, here a one-way analysis of variance. Any statistical test is based on a specific hypothesis called null hypothesis, in short H0. Here: H0 states (hypothetically) that no difference exists between the degradation effects of different samples. In other words the different samples belong to the same population (as before the ageing process). It was expected that the yielded degradation (in terms of ΔE, ΔHV, ΔR_a and ΔW) would be the same no matter what immersion solution was used. However, a statistical test comprises an alternative hypothesis H1 in case the null hypothesis has to be rejected. Here H1 states that the different samples belong to different population after the ageing process.

Some quantitative differences may be observed between randomly selected samples even when H0 is valid. Then, the statistical test (in this case one way analysis) computes the probability of the observed mean sample difference in view of H0. If this probability is less than the preselected test level $\alpha = 0{,}05$ then the observed mean difference is commonly considered as to be statistical significant at the test level of $\alpha = 0{,}05$.

The study hypothesis, usually opposed to the statistically null hypothesis, supports the assumption that the specimens immersed in enzymatic solution (PCE) supposed to suffer from a greater degradation compared to these immersed in distilled water.

The results were statistically evaluated employing the JMP statistical analysis program (JMP, Version 5.0.1a 1989-2002, SAS Institute). The analysis used was Fit Y by X to calculate a one-way analysis of variance. Pairewise multiple comparison of means used the Tukey-Kramer procedure.

The presentation of the results was given in form of box plots. These plots summarize the distribution of points at each treatment level. The ends of the box are the 25th and 75th quantiles. The lower quantile (25 %) indicates the value below which are the lower 25 % of all data. Similarly the upper quantile (75 %) indicates the value below, which is the 75 % of all data. The difference between those quantiles is the interquartile range. The line across the middle of the box identifies the median sample value. Each box has lines, sometimes called whiskers that extend from each end. The whiskers extend from the ends of the box to the outermost data point that falls within the distances computed as following: upper quartile + 1.5*(interquartile range) and lower quartile - 1.5*(interquartile range). Values above or below the range of the intervals defined from the end of the both whiskers are considered as "outliers".

The wear results were presented employing the Origin graphical program (Origin, Version 6.0 1991-1999, Microcal software) in the form of mean value mv + standard deviation (sd). The presentation of the data in this form is informative. Because, even if the distribution of the results were normal the range defined from mv - (sd) to mv - (sd) contains ca. 67 % of the data. In this case the assertion of the range defined of mv -2sd to mv +2sd would be more informative concerning the variance of the data, as it would include minimum 75 % of the data.

However, this way of presentation was chosen for demonstrative reasons.

5 Results

The results for every surface property tested for every ageing model separately for each material can be seen in the Tables 5-9, respectively.

Table 5. Mean values and 95% confidence intervals (in brackets) of the tested properties ΔE, ΔHV, ΔR_a and ΔW for the material Arabesk Top.

ARABESK TOP						
Solutions **Properties**	**Ethanol**	**Lactic acid**	**NaOH**	**PCE**	**Thermocycling**	**Water**
ΔE	**4,7** (3,6- 6)	**4,3** (3,18- 5,34)	**10,56** (9,85- 11,3)	**2,43** (2,05- 2,8)	**2,6** (2,2- 3)	**1,9** (1,5- 2,24)
ΔHV [VHN]	**13,05** 9,75- 16,35)	**17,8** (13,8- 21,7)	**50,73** (47,7- 54)	**12,61** (7,9- 17,4)	**5,4** (2,1- 8,65)	**5,74** (1,8- 9,7)
ΔR_a [µm]	**-0,05** (-0,13- 0,03)	**0,00** (-0,07- 0,1)	**0,75** (-0,14- 1,65)	**-0,04** (-0,14- 0,07)	**-0,03** (-0,05- 0,00)	**0,03** (-0,03- 0,1)
ΔW [mm^3]	**0,28** (0,1- 0,46)	**0,3** (-0,1- 0,7)	**0,4** (0,04- 0,73)	**0,5** (0,1- 1)	**0,32** (0,22- 0,42)	**0,2** (0,01- 0,4)
ΔW [µm]	**145,7** (99- 192,4)	**146,5** (71,85- 221)	**176,3** (104,8- 248)	**211** (160,3- 261,73)	**168,2** (148,4- 188)	**118** (51,5- 184)

Table 6. Mean values and 95% confidence intervals (in brackets) of the tested properties ΔE, ΔHV, ΔR_a and ΔW for the material Artglass.

ARTGLASS						
Solutions **Properties**	**Ethanol**	**Lactic acid**	**NaOH**	**PCE**	**Thermocycling**	**Water**
ΔE	**1,93** (1,6 - 2,3)	**7,44** (6,66 - 8,2)	**21,04** (16,54 - 25,54)	**1,4** (1,1 - 1,7)	**1,4** (1,13 - 1,7)	**2,44** (1,8 - 3,1)
ΔHV [VHN]	**6,65** (3,4 - 10)	**1,8** (-1,7 - 5,2)	**31,1** (28,4 - 33,7)	**0,8** (-1,2 - 2,8)	**2,16** (-4,26 - -0,1)	**0,7** (-2,4 - 3,73)
ΔR_a [µm]	**0,05** (-0,1 - 0,2)	**0,00** (0,00 - 0,01)	**0,37** (0,2 - 0,56)	**0,04** (-0,14 - 0,22)	**0,01** (-0,03 - 0,02)	**0,02** (0,00 - -0,04)
ΔW [mm^3]	**0,2** (0,04 - 0,4)	**0,06** (0,02 - 0,1)	**0,44** (0,13 - 0,7)	**0,35** (0,17 - 0,5)	**0,1** (0,04 - 0,2)	**0,1** (0,01 - 0,16)
ΔW [µm]	**131,4** (54,5 - 208,2)	**76,7** (53,7 - 99,64)	**181,64** (130,2 - 233)	**172,33** (118,6 - 226,1)	**103** (65,4 - 140,45)	**88,76** (59 - 118,7)

Table 7. Mean values and 95% confidence intervals (in brackets) of the tested properties ΔE, ΔHV, ΔRa and ΔW for the material Grandio.

GRANDIO						
Solutions **Properties**	**Ethanol**	**Lactic acid**	**NaOH**	**PCE**	**Thermocycling**	**Water**
ΔE	**3,6** (2,4 - 5)	**4,64** (4,1 - 5,23)	**11,7** (8,2 - 15)	**3** (2,3 - 3,75)	**2,6** (2,1 - 3,14)	**4,1** (3,5 - 4,73)
ΔHV [VHN]	**10,4** (3,35 - 17,44)	**47,5** (41,6 - 53,35)	**99,03** (96,2 - 102)	**7,1** (1,36 - 13)	**9** (3,7 - 14)	**16,5** (10,1 - 23)
ΔR_a [µm]	**0,02** (0,07 - 0,04)	**0,5** (0,14 - 1)	**1,6** (0,3 - 3)	**0,01** (0,03 - 0,02)	**0,00** (0,02 - 0,03)	**0,01** (0,1 - 0,12)
ΔW [mm^3]	**0,08** (0,03 - 0,1)	**0,22** (0,03 - 0,4)	**0,36** (0,2 - 0,5)	**0,25** (-0,04 - 0,5)	**0,23** (0,05 - 0,42)	**0,35** (0,1 - 0,6)
ΔW [µm]	**75** (46 - 104)	**118,5** (79,5 - 157,5)	**167,5** (124,3 - 211)	**135,3** (77,3 - 194)	**132,3** (58,3 - 206,4)	**153,4** (92,7 - 214)

Table 8. Mean values and 95% confidence intervals (in brackets) of the tested properties ΔE, ΔHV, ΔR_a and ΔW for the material Signum.

SIGNUM						
Solutions **Properties**	**Ethanol**	**Lactic acid**	**NaOH**	**PCE**	**Thermocycling**	**Water**
ΔE	**2,84** (2,4 - 3,3)	**2,34** (1,95 - 2,7)	**6,6** (4,7 - 8,5)	**1,75** (1,4 - 2,1)	**2,5** (2,14 - 3)	**1,5** (1,16 - 2)
ΔHV [VHN]	**11,8** (9,8 - 14)	**2,7** (0,2 - 5,6)	**21,6** (19,6 - 23,5)	**4,56** (2,8 - 6,3)	**0,8** (-0,23 - 2)	**9,45** (7,3 -11,6)
ΔR_a [µm]	**0,06** (0,05 - 0,16)	**0,02** (-0,04 - 0,1)	**0,26** (0,02 - 0,5)	**0,1** (-0,04 - 0,2)	**0,02** (-0,1 - 0,06)	**0,01** (0,06 - 0,05)
ΔW [mm^3]	**0,2** (0,05 - 0,4)	**0,2** (-0,02 - 0,4)	**0,2** (0,1 - 0,4)	**0,23** (0,1 - 0,4)	**0,15** (0,1 - 0,2)	**0,15** (-0,01 - 0,3)
ΔW [µm]	**127** (67,2 - 186,4)	**114,4** (39 - 190)	**147** (85,5 - 208,4)	**151** (88 - 216)	**113,3** (86,5 - 140)	**104,15** (43 - 165,35)

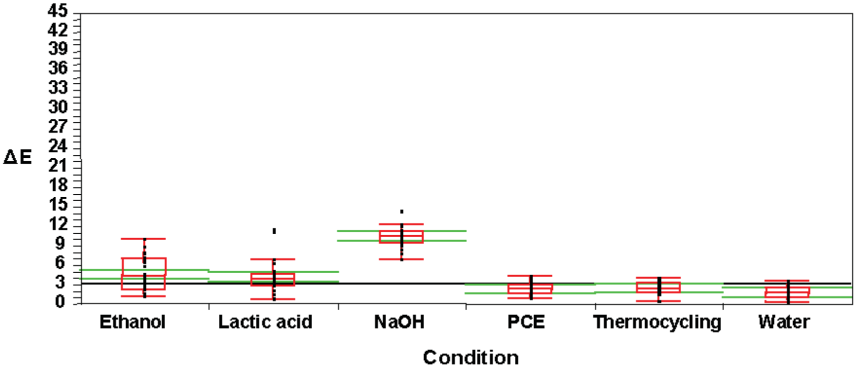
Table 9. Mean values and 95% confidence intervals (in brackets) of the tested properties ΔE, ΔHV, ΔR_a and ΔW for the material Sinfony.

SINFONY						
Solutions **Properties**	**Ethanol**	**Lactic acid**	**NaOH**	**PCE**	**Thermocycling**	**Water**
ΔE	**5,85** (5,04 - 6,7)	**3,1** (2,7 - 3,54)	**7,76** (6,73 - 9)	**3,76** (3,13 - 4,4)	**1,63** (1,3 - 2)	**3,57** (3 - 4,12)
ΔHV [VHN]	**8,9** (7,8 - 10)	**0,3** (1,35 - 2)	**11,55** (9,7 - 13,4)	**1,45** (-0,5 - 3,4)	**3** (1,5 - 4,5)	**1,93** (0,5 - 3,4)
ΔR_a [µm]	**0,03** (-0,1 - 0,16)	**0,02** (-0,1 - 0,15)	**0,04** (-0,01 - 0,1)	**-0,02** (-0,04 - 0,00)	**-0,05** (-0,1 - -0,01)	**0,00** (-0,05 - 0,05)
ΔW [mm^3]	**0,07** (0,04 - 0,1)	**0,1** (0,03 - 0,17)	**0,17** (0,1 - 0,23)	**0,24** (0,1 - 0,4)	**0,1** (0,03 - 0,2)	**0,1** (0,04 - 0,1)
ΔW [µm]	**73,04** (48 - 98,2)	**114,15** (58,5 - 170)	**118** (74,5 - 161,4)	**148** (100,2 - 196)	**101,7** (62,56 - 141)	**89,7** (59 - 120,5)

5.1 Arabesk Top

Colour: The observed effect of incubation in different solutions on colour stability of Arabesk Top can be divided into two main categories. The first one comprised the changes provoked by the immersion in the solutions (i.e. ΔE mean value) which are considered unacceptable [i.e. ΔE mean value > 3,3 (94)]. Specimens stored in ethanol and lactic acid exhibited this behaviour (Mean values of ΔE of 4,7 and 4,3, respectively). The specimens stored in NaOH were heavily damaged on the surface (Mean values of ΔE of 10,6). The second category comprised the ageing models which caused perceptible but acceptable surface degradation [2<ΔE <3,3 (88)]. Specimens stored in PCE as well as those, which were thermocycled, belong to this category (Mean values of ΔE of 2,43 and 2,57, respectively). The third category comprised the storage in water, which yielded no perceptible colour change (Mean values of ΔE of 1,87). According to Tukey's multiple analysis the effect of the immersion can be divided into 3 groups (see Diagram 11): a) NaOH produced the greatest surface degradation which was significantly greater (statistically) than any other. b) Ethanol and lactic acid caused changes which were in the middle of the scale c) the third group comprised specimens stored in water, enzymatic solution (PCE), and specimens which were thermocycled. These ageing models resulted in the less accentuated colour changes and showed no statistical significant difference between them.

It should be remarked that the scaling of the presentation of the results was purposely chosen for standardization's reasons.

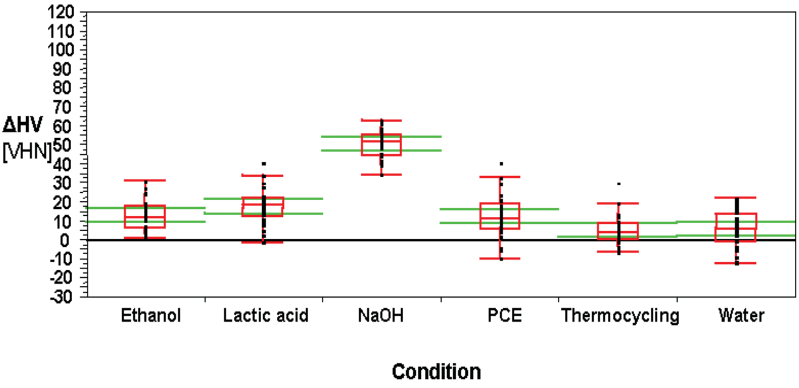


Conditions				Mean values
NaOH	A			10,56
Ethanol		B		4,7
Lactic acid		B		4,26
Thermocycling			C	2,57
PCE			C	2,42
Water			C	1,87

Conditions not connected by same letter are significantly different (statistically).

Diagram 11. Mean colour change ΔE for Arabesk after the ageing process. The mean values of ΔE are listed in the corresponding table. The black horizontal line indicates the borders beside which the colour change value (i.e. 3,3) is considered clinically unacceptable (94). The green horizontal lines indicate 95% confidence intervals. The red marked numbers indicate clinically unacceptable mean colour changes, while the blue marked numbers indicate acceptable but still perceptible colour changes. The black marked numbers indicate non-perceptible colour changes.

Hardness: A relatively similar pattern as the one of colour change was noticed for the hardness change (ΔHV) after the immersion in different solutions: Immersion in NaOH caused the most remarkable softening of the material. Lactic acid, ethanol and PCE composed the second group of incubation solutions, yielding significant hardness changes (mean ΔHV values) which were statistically lower than the effect of NaOH but more pronounced than the effect resulting from the remaining ageing models. Thermocycling caused no significant difference (statistically) compared to water. But this change was statistically the most negligible compared to NaOH, lactic acid and ethanol (see Diagram 12).

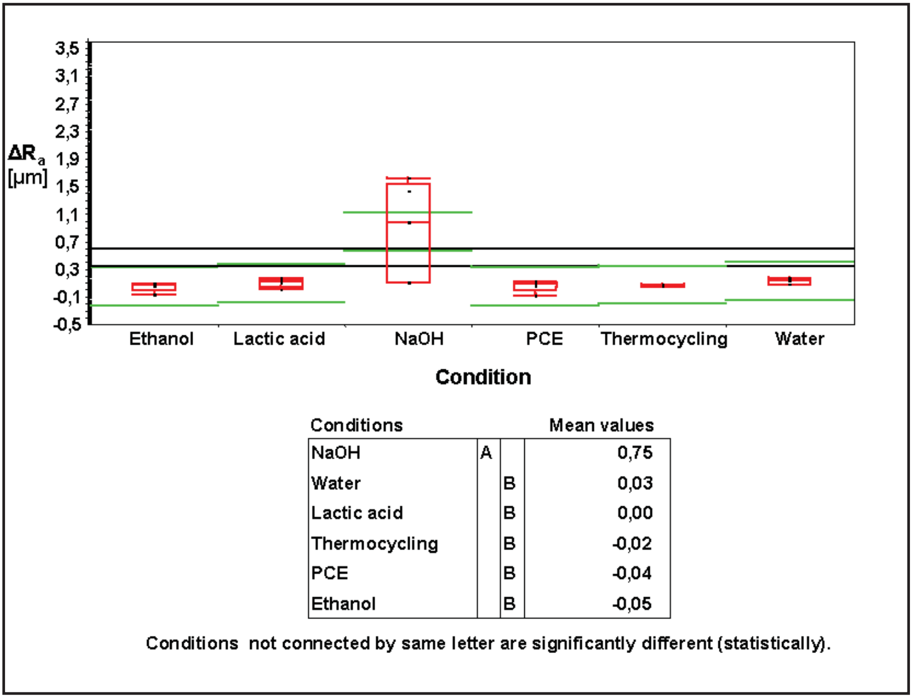


Conditions					Mean values
NaOH	A				50,73
Lactic acid		B			17,8
Ethanol		B	C		13,05
PCE			C		12,61
Water				D	5,74
Thermocycling				D	5,37

Conditions not connected by same letter are significantly different (statistically).

Diagram 12. Mean hardness change ΔHV [VHN] for Arabesk after the ageing process. The mean values of ΔHV are listed in the corresponding table. The black horizontal line indicates no hardness change (ΔHV= 0) while the green horizontal lines indicate 95 % confidence intervals.

Roughness: The ageing models (with the exception of NaOH) generated negligible roughness differences between the beginning and the end of the ageing process. There were no statistical differences (Diagram 13) between the roughness results of the diverse ageing models (always with the exception of NaOH). Mean values of ΔR_a of -0,05 µm (ethanol), of 0,004 µm (lactic acid), of -0,04 µm (PCE), of -0,02 µm (thermocycling) and 0,03 µm (water) were estimated, respectively. The only significant surface degradation was observed after the immersion in NaOH (mean ΔR_a of 0,75 µm).



Conditions			Mean values
NaOH	A		0,75
Water		B	0,03
Lactic acid		B	0,00
Thermocycling		B	-0,02
PCE		B	-0,04
Ethanol		B	-0,05

Conditions not connected by same letter are significantly different (statistically).

Diagram 13. Mean roughness change ΔR_a [µm] for Arabesk after the ageing process. The mean values of ΔR_a are listed in the corresponding table. The black horizontal lines indicate the range of roughness values change (0,25- 0,5) which is clinically perceptible (109) while the green horizontal lines indicate 95 % confidence intervals.

Wear: The storage in PCE yielded the generation of the largest cavities at the end of the chewing simulation, in the case of Arabesk Top (Diagram 14). But these were not significantly different (statistically) to the ones produced after the storage in ethanol, lactic acid, NaOH, water and thermocycling, respectively.

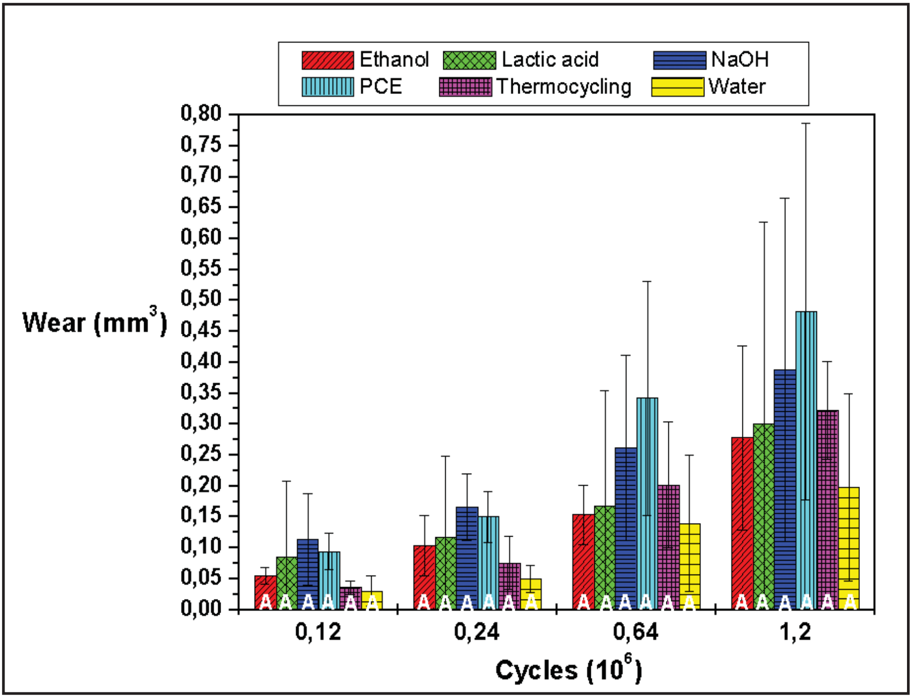
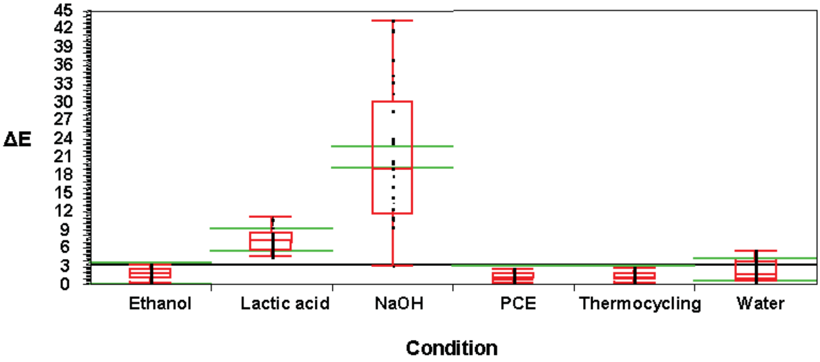


Diagram 14. Wear results for Arabesk at different time intervals. Data are presented as mean ± SD [mm³]. Conditions not connected by same letter are significantly different (statistically).

5.2 Artglass

Colour: The same distinction (visible and not acceptable or visible but acceptable for the colour change of the aged specimens) can be made also for Artglass. The first group comprises specimens stored in NaOH and lactic acid (with unacceptable values: mean value $\Delta E > 3,3$), whereas the second group comprises specimens stored in water (perceptible but acceptable; mean value $2 < \Delta E < 3,3$). The third group comprises specimens stored in ethanol, PCE as well as those, which were thermocycled (not perceptible, mean ΔE value <2). The specimens stored in NaOH were once again heavily damaged (mean ΔE values of 21). Statistically less accentuated degradation effect presented the specimens stored in lactic acid, nevertheless visible and not acceptable (mean ΔE value of 7,4). The use of Tukey's multiple analysis at a test level of $\alpha=0,05$ revealed that the ageing effect on colour can be once again divided into 3 groups: a) NaOH produced the greatest surface degradation which was significant greater (statistically) than any other. b) Immersion in lactic acid caused colour changes placed in the middle of the degradation's scale c) the last group comprised specimens stored in ethanol, water, enzymatic solution (PCE), and specimens which were thermocycled. These ageing models resulted in the less pronounced colour changes and showed no statistical significant difference between them (see Diagram 15).

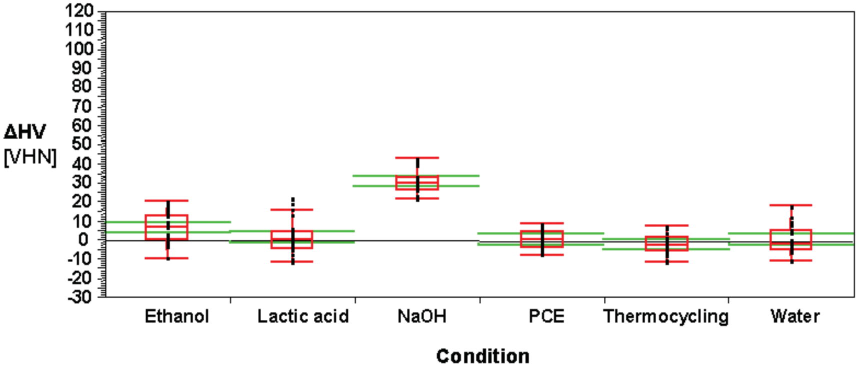


Conditions				Mean values
NaOH	A			21,04
Lactic acid		B		7,44
Water			C	2,44
Ethanol			C	1,93
PCE			C	1,40
Thermocycling			C	1,39

Conditions not connected by same letter are significantly different (statistically).

Diagram 15. Mean colour change ΔE for Artglass after the ageing process. The mean values of ΔE are listed in the corresponding table. The black horizontal line indicates the borders beside which the colour change value (i.e. 3,3) is considered clinically unacceptable while the green horizontal lines indicate 95% confidence intervals. The red marked numbers indicate clinically unacceptable mean colour changes, while the blue marked numbers indicate acceptable but still perceptible colour changes. The black marked numbers indicate non-perceptible colour changes.

Hardness: As was expected, the immersion in NaOH once again yielded the most remarkable softening of the material whereas this time storage in ethanol produced the second most pronounced softening (but always statistically lower than the one produced from NaOH). Lactic acid, PCE and water generated softening, which was statistically lower than the effect produced from NaOH and ethanol. Thermocycling resulted in statistically lower softening compared to lactic acid but not different compared to the effect of PCE and water (see Diagram 16).

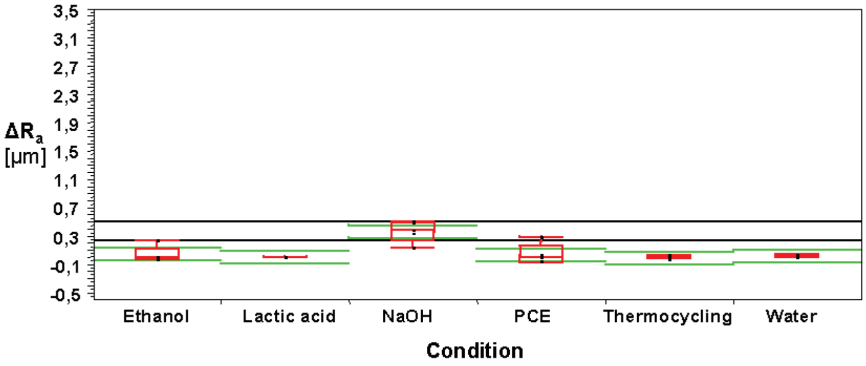


Conditions					Mean values
NaOH	A				31,1
Ethanol		B			6,65
Lactic acid			C		1,8
PCE			C	D	0,8
Water			C	D	0,7
Thermocycling				D	-2,16

Conditions not connected by same letter are significantly different (statistically) .

Diagram 16. Mean hardness change ΔHV [VHN] for Artglass after the ageing process. The mean values of ΔHV are listed in the corresponding table. The black horizontal line indicates no hardness change (ΔHV= 0) while the green horizontal lines indicate 95% confidence intervals.

Roughness: The ageing models produced the same situation as with Arabesk Top: Negligible roughness differences between the end and the beginning of the ageing process for all ageing solutions (with the exception of NaOH). There were no statistical differences between the roughness results of the diverse ageing models (always with the exception of NaOH) as can be seen in Diagram 17. Mean values of ΔR_a of 0,05 µm (ethanol), of 0 µm (lactic acid), of 0,04 µm (PCE), of -0,01 µm (thermocycling) and 0,02 µm (water) were estimated, respectively. As mentioned before the only significant surface degradation was observed after the immersion in NaOH (mean ΔR_a of 0,37 µm).



Condition			Mean values
NaOH	A		0,37
Ethanol		B	0,05
PCE		B	0,04
Water		B	0,02
Lactic acid		B	0,00
Thermocycling		B	-0,01

Conditions not connected by same letter are significantly different (statistically).

Diagram 17. Mean roughness change ΔR_a [µm] for Artglass after the ageing process. The mean values of ΔR_a are listed in the corresponding table. The black horizontal lines indicate the range of roughness values change (0,25- 0,5 µm), which is clinically perceptible while the green horizontal lines indicate 95% confidence intervals.

Wear: NaOH caused also in this case the greatest surface degradation at the end of the chewing simulation (1,2 x10^6 cycles). Remarkable is also the result of the storage in PCE, which produced also large wear cavities (not statistically significantly different from that of NaOH. The ranking of the resulted wear cavities after storage and chewing simulation is as follows: NaOH = PCE = Ethanol ≥ Thermocycling ≥ Lactic acid = Water. The development of the wear cavities sorted to cycles intervals can be seen in diagram 18.

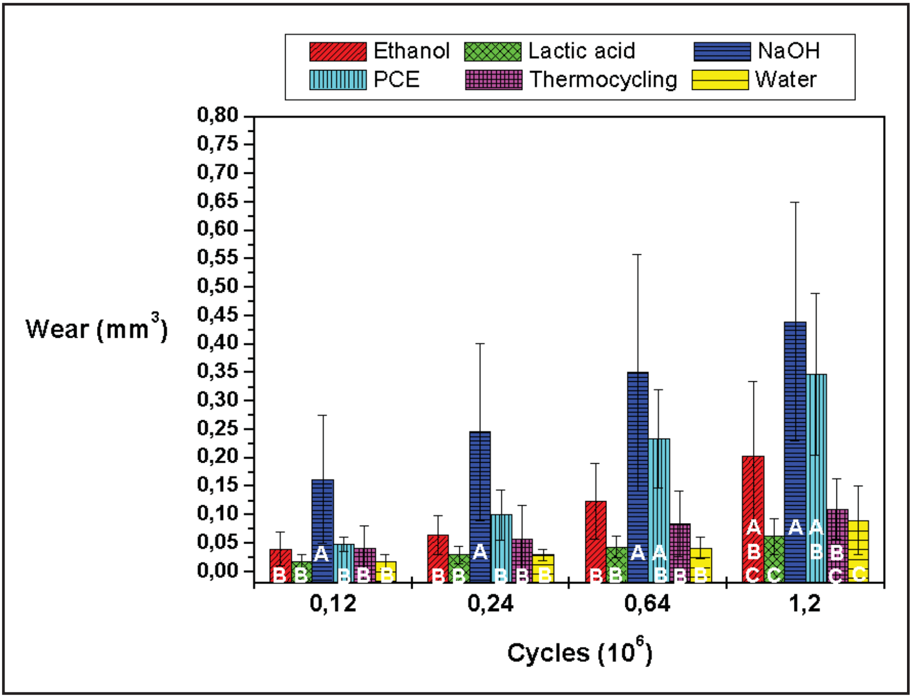
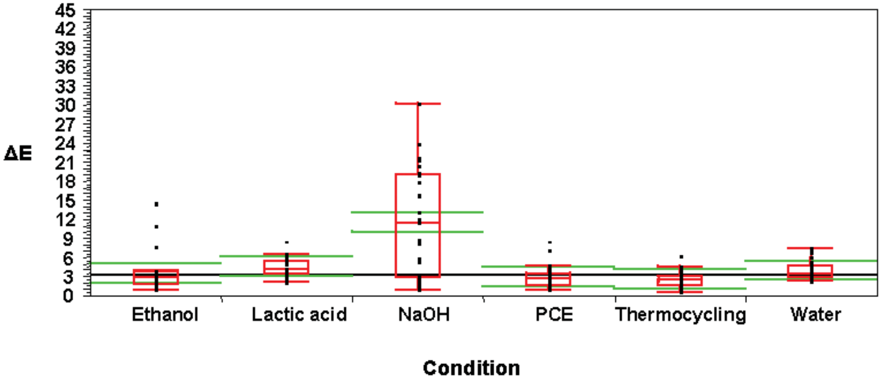


Diagram 18. Wear results for Artglass at different time intervals. Data are presented as mean ± SD [mm^3]. Conditions not connected by same letter are significantly different (statistically).

5.3 Grandio

Colour: Similar situation was observed also for Grandio. The only difference is that although NaOH, lactic acid, water and ethanol yielded unacceptable colour changes (mean ΔE value of 11,7; 4,64; 4,1 and 3,63, respectively) only the values for NaOH differed significantly compared to all others. That means that the mean ΔE values estimated for PCE and thermocycling though they were clinically acceptable were not statistically less pronounced than the colour changes produced after storage in lactic acid, water and ethanol consisting the second group of colour changes for Grandio (Diagram 19).

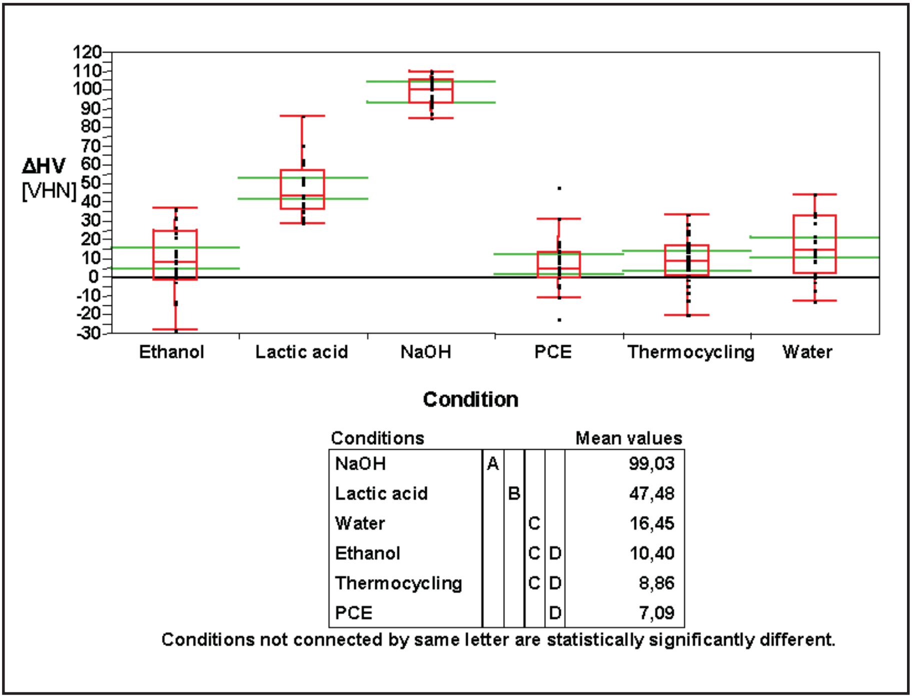


Conditions			Mean values
NaOH	A		11,68
Lactic acid		B	4,64
Water		B	4,11
Ethanol		B	3,64
PCE		B	3,01
Thermocycling		B	2,60

Conditions not connected by same letter are significantly different (statistically).

Diagram 19. Mean colour change ΔE for Grandio after the ageing process. The mean values of ΔE are listed in the corresponding table. The black horizontal line indicates the borders beside which the colour change value (i.e. 3,3) is considered clinically unacceptable while the green horizontal lines indicate 95% confidence intervals. The red marked numbers indicate clinically unacceptable mean colour changes, while the blue marked numbers indicate acceptable but still perceptible colour changes. The black marked numbers indicate non-perceptible colour changes.

Hardness: NaOH generated the most remarkable softening of Grandio whereas immersion in lactic acid produced the second most pronounced softening (but always statistically lower than the one produced from NaOH). Water, ethanol, thermocycling and PCE consisted the third group of significant change in hardness, which was statistically lower than the effect produced from NaOH and lactic acid. The effect of PCE was significantly lower (statistically) than that of water (see Diagram 20).

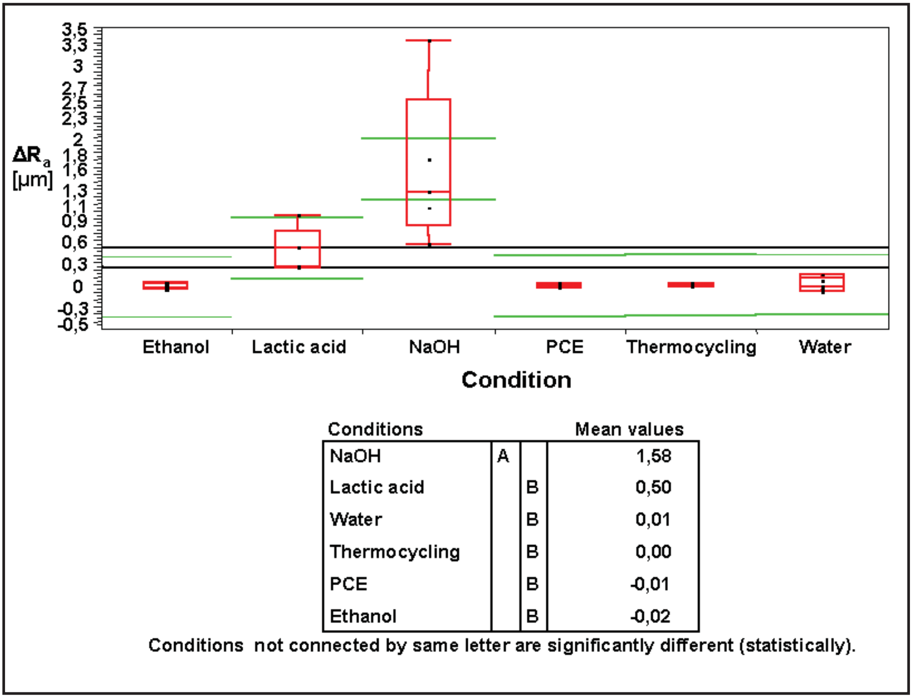


Conditions					Mean values
NaOH	A				99,03
Lactic acid		B			47,48
Water			C		16,45
Ethanol			C	D	10,40
Thermocycling			C	D	8,86
PCE				D	7,09

Conditions not connected by same letter are statistically significantly different.

Diagram 20. Mean hardness change ΔHV [VHN] for Grandio after the ageing process. The mean values of ΔHV (VHN) are listed in the corresponding table. The black horizontal line indicates no hardness change (ΔHV= 0) while the green horizontal lines indicate 95% confidence intervals.

Roughness: Once again the same classification: Specimens stored in NaOH suffered the most pronounced surface degradation in terms of roughening. The difference this time was that the surface degradation which occurred after the storage in lactic acid, even though it was not significant more pronounced (statistically) that the other ageing models was meaningful. That means that the mean roughness change ΔR_a of the specimens stored in lactic acid reached values of almost 0,5 μm which is considered to be the maximum limit of perception of intraorally roughness change concerning restorations (109). The other ageing models exhibited negligible roughness changes (with the exception of NaOH). Mean values of ΔR_a of -0,02 μm (ethanol), of -0,01 μm (PCE), of 0 μm (thermocycling) and 0,01 μm (water) were estimated, respectively (Diagram 21). As mentioned before the only significant surface degradation was observed after the immersion in NaOH (mean ΔR_a of 1,6 μm).



Conditions			Mean values
NaOH	A		1,58
Lactic acid		B	0,50
Water		B	0,01
Thermocycling		B	0,00
PCE		B	-0,01
Ethanol		B	-0,02

Conditions not connected by same letter are significantly different (statistically).

Diagram 21. Mean roughness change ΔR_a [µm] for Grandio after the ageing process. The mean values of ΔR_a are listed in the corresponding table. The black horizontal lines indicate the range (0,25- 0,5 µm) of roughness values change, which is clinically perceptible while the green horizontal lines indicate 95% confidence intervals.

Wear: The wear cavities at the end of the chewing simulation produced after the NaOH storage was the largest also for Grandio. Nevertheless, they were not significantly larger (statistically) than the ones produced after the storage in lactic acid, PCE, water and thermocycling, respectively. Ethanol produced the smallest cavities, which were also not significantly different (statistically) than the ones produced after the storage in lactic acid, PCE, water and thermocycling, respectively (Diagram 22).

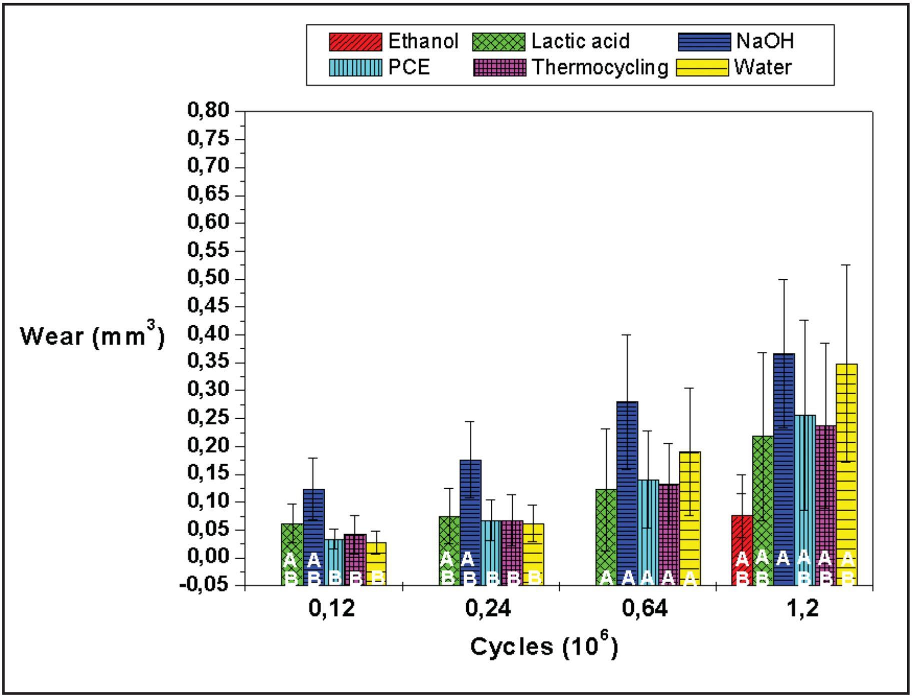
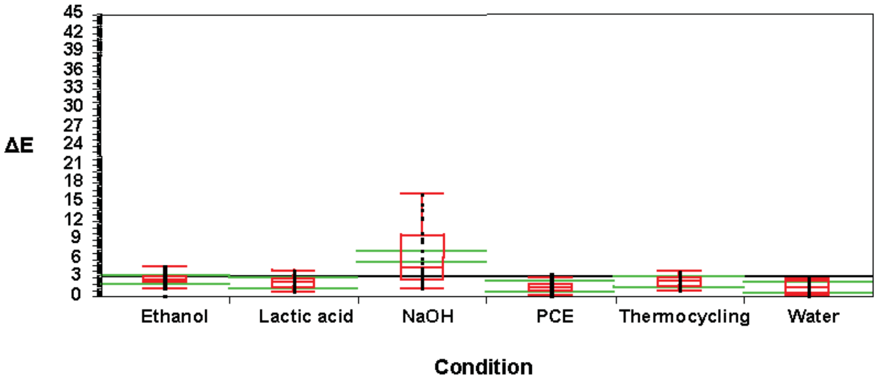


Diagram 22. Wear results for Grandio at different time intervals. Data are presented as mean ± SD [mm^3]. Conditions not connected by same letter are significantly different (statistically).

5.4 Signum

Colour: Once again the same distinction: unacceptable surface damage for NaOH (mean ΔE values of 6,6), which differed significantly from the other ageing models. The specimens stored in ethanol, lactic acid and those, which were thermocycled, consisted the second group (perceptible but acceptable, $2<\Delta E<3{,}3$), whereas the surface degradation produced after the immersion in PCE and water was not perceptible ($\Delta E< 2$).

Statistically, storage in NaOH generated the greatest colour degradation, while all the other ageing models resulted in statistically similar colour damage for the specimens. Water had a significantly lower effect compared to ethanol (Diagram 23).

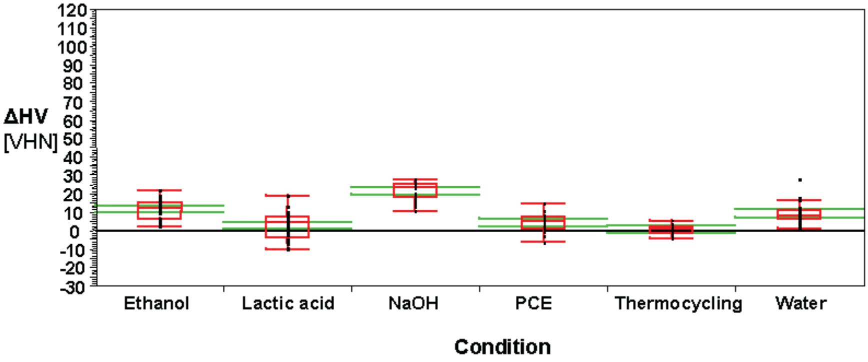


Conditions				Mean values
NaOH	A			6,57
Ethanol		B		2,84
Thermocycling		B	C	2,48
Lactic acid		B	C	2,34
PCE		B	C	1,75
Water			C	1,55

Conditions not connected by same letter are significantly different (statistically).

Diagram 23. Mean colour change ΔE for Signum after the ageing process. The mean values of ΔE are listed in the corresponding table. The black horizontal line indicates the borders beside which the colour change value (i.e. 3,3) is considered clinically unacceptable while the green horizontal lines indicate 95% confidence intervals. The red marked numbers indicate clinically unacceptable mean colour changes, while the blue marked numbers indicate acceptable but still perceptible colour changes. The black marked numbers indicate non-perceptible colour changes.

Hardness: The results of hardness after the artificial ageing was also for Signum similar to the ones of the other materials with small differentiations (Diagram 24): NaOH yielded the most remarkable softening of Signum whereas ethanol and water produced this time the second most pronounced softening (but always statistically lower than the one produced from NaOH). PCE, lactic acid belonged statistically to the third group of softening effect, whereas thermocycling to the last one (though not statistically different to the effect of lactic acid).

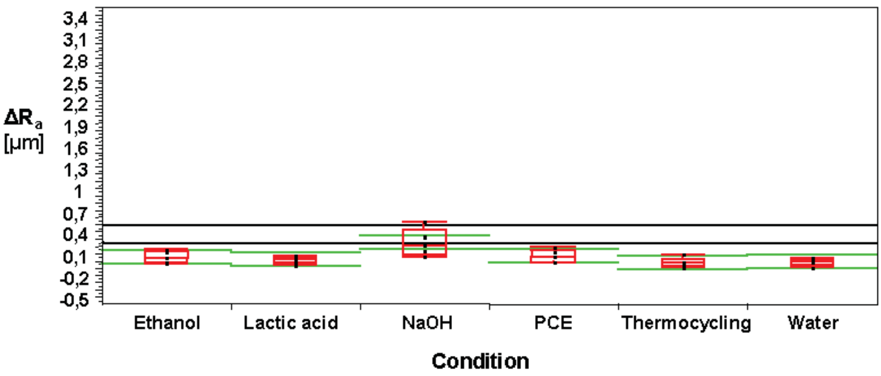


Conditions					Mean values
NaOH	A				21,60
Ethanol		B			11,83
Water		B			9,45
PCE			C		4,56
Lactic acid			C	D	2,69
Thermocycling				D	0,80

Conditions not connected by same letter are significantly different (statistically).

Diagram 24. Mean hardness change ΔHV [VHN] for Signum after the ageing process. The mean values of ΔHV are listed in the corresponding table. The black horizontal line indicates no hardness change (ΔHV= 0) unacceptable while the green horizontal lines indicate 95% confidence intervals.

Roughness: The same pattern (with a small difference) was noticed also for roughness changes for the Signum specimens: Specimens stored in NaOH suffered from the most pronounced surface degradation in terms of roughening (mean ΔR_a values of 0,26), which was not statistically significant different compared to the one produced from PCE (Mean ΔR_a values of 0,7). The other ageing models exhibited lower roughness changes (which were not statistically significantly lower compared to the ones produced from immersion in PCE). Mean values of ΔR_a of 0,06 µm (ethanol), of 0,02 µm (lactic acid), of -0,02 µm (thermocycling) and of -0,01 µm (water) were estimated, respectively (Diagram 25).



Conditions			Mean values
NaOH	A		0,26
PCE		B	0,07
Ethanol		B	0,06
Lactic acid		B	0,02
Water		B	-0,01
Thermocycling		B	-0,02

Conditions not connected by same letter are significantly different (statistically).

Diagram 25. Mean roughness change ΔR_a [µm] for Signum after the ageing process. The mean values of ΔR_a are listed in the corresponding table. The black horizontal lines indicate the range (0,25- 0,5 µm) of roughness values change, which is clinically perceptible while the green horizontal lines indicate 95% confidence intervals.

Wear: In the case of Signum, PCE caused the greatest wear cavities (mean wear volume: 0,23 mm^3) at the end of the chewing simulation (1,2 x10^6 cycles). Remarkable were also the wear cavities produced after the storage in ethanol (mean volume: 0,22 mm^3) and NaOH (mean wear volume: 0,21 mm^3), respectively (but not statistically significantly different from that of PCE). Because of the large variations no statistical difference could be pointed between the different ageing models for Signum. The development of the wear cavities at different time intervals can be seen in Diagram 26.

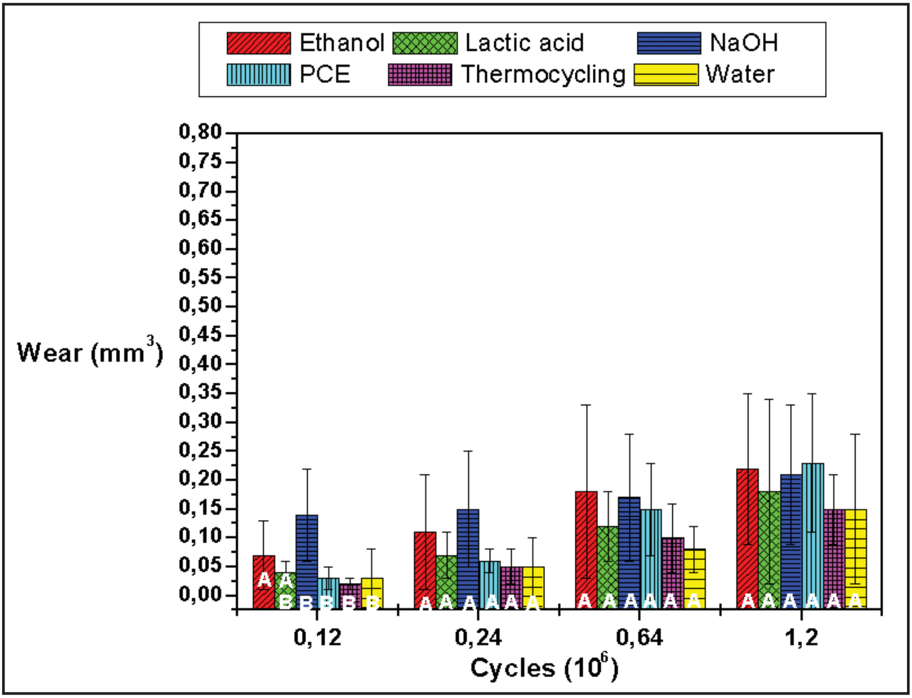
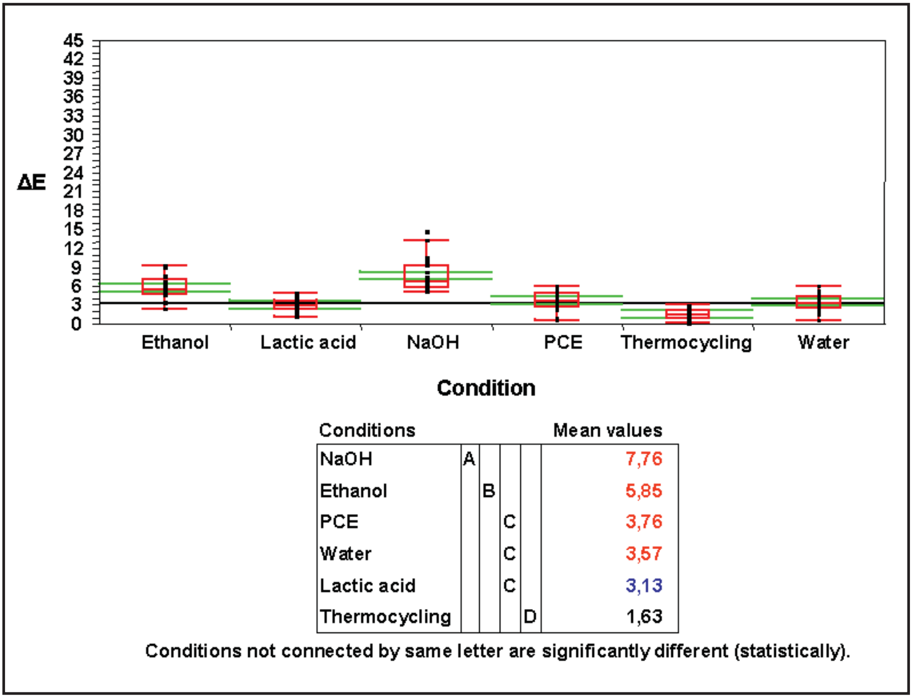


Diagram 26. Wear results for Signum at different time intervals. Data are presented as mean ± SD [mm^3]. Conditions not connected by same letter are significantly different (statistically).

5.5 Sinfony

Colour: Ethanol, NaOH, PCE, water resulted in unacceptable colour changes (mean ΔE value of 5,85; 7,75; 3,75 and 3,56, respectively), whereas lactic acid yielded changes that were perceptible but acceptable (mean ΔE value of 3,13). The thermocycled specimens exhibited a colour change which is considered as not perceptible (88) (mean ΔE value of 1,63). The Tukey's multiple analysis revealed four levels of colour change significance. NaOH generated the most pronounced colour change while ethanol resulted in the second most pronounced (statistically) colour change. The third group of colour change consisted of PCE, water and lactic acid, while the fourth group (the most negligible statistically colour change) consisted from thermocycling (Diagram 27).

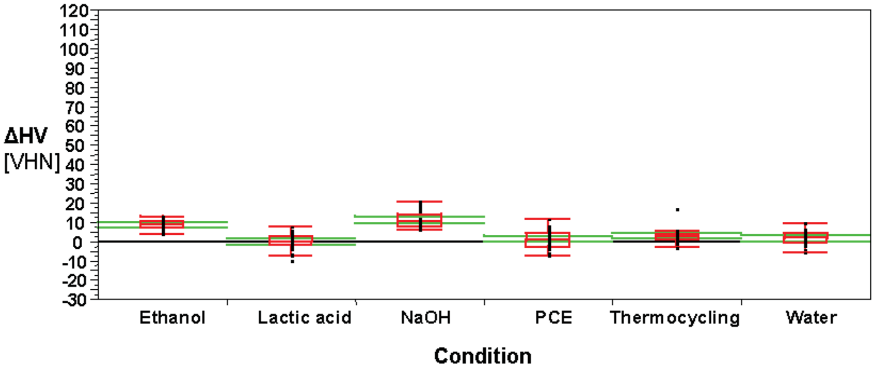


Conditions					Mean values
NaOH	A				7,76
Ethanol		B			5,85
PCE			C		3,76
Water			C		3,57
Lactic acid			C		3,13
Thermocycling				D	1,63

Conditions not connected by same letter are significantly different (statistically).

Diagram 27. Mean colour change ΔE for Sinfony after the ageing process. The mean values of ΔE are listed in the corresponding table. The black horizontal line indicates the borders beside which the colour change value (i.e. 3,3) is considered clinically unacceptable while the green horizontal lines indicate 95% confidence intervals. The red marked numbers indicate clinically unacceptable mean colour changes, while the blue marked numbers indicate acceptable but still perceptible colour changes. The black marked numbers indicate non-perceptible colour changes.

Hardness: The immersion in NaOH proved to be for Sinfony the one causing the most remarkable softening (statistically). The second group of statistically considerable hardness change consisted of the Sinfony specimens stored in ethanol. Specimens of Sinfony exposed to thermocycling, water and PCE immersion composed the third group of softening (Diagram 28). The immersion in lactic acid produced the (statistically) lowest softening of Sinfony (though not statistically different to the effect of water and PCE).

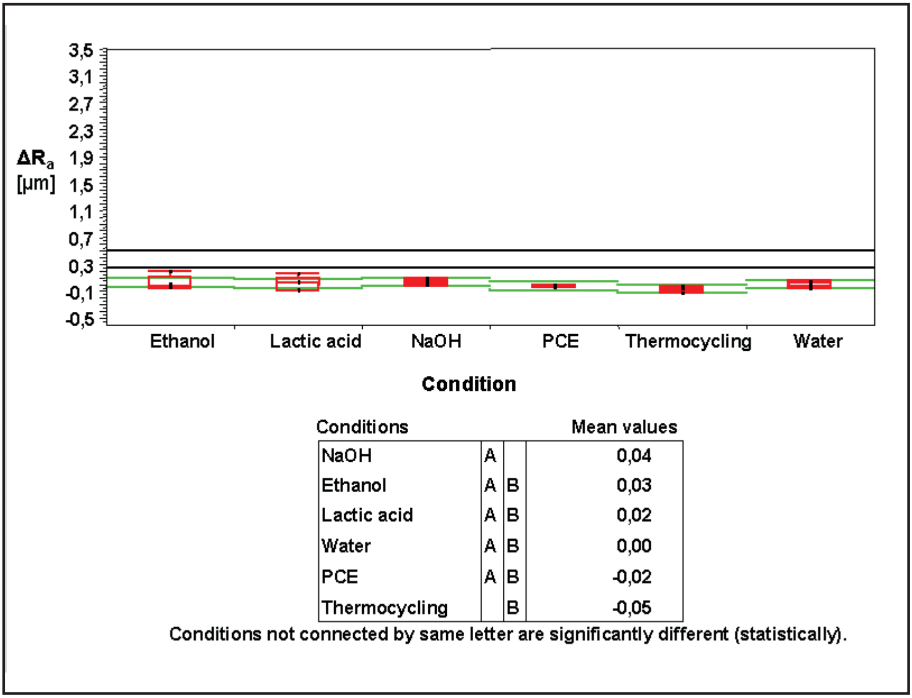


Conditions					Mean values
NaOH	A				11,55
Ethanol		B			8,88
Thermocycling			C		3,02
Water			C	D	1,93
PCE			C	D	1,45
Lactic acid				D	0,32

Conditions not connected by same letter are significantly different (statistically).

Diagram 28. Mean hardness change ΔHV [VHN] for Sinfony after the ageing process. The mean values of ΔHV are listed in the corresponding table. The black horizontal line indicates no hardness change (ΔHV= 0) while the green horizontal lines indicate 95% confidence intervals.

Roughness: Even though those specimens stored in NaOH suffered from the most pronounced surface degradation in terms of roughening (Mean ΔR_a values of 0,04), their roughness change did not differ (statistically) from the ones produced from the other ageing models (with the exception of thermocycling). Mean values of ΔR_a of 0,03 µm (ethanol), of 0,02 µm (lactic acid), of 0 µm (water), of -0,02 µm (PCE) and -0,05 µm (thermocycling) were estimated, respectively (see Diagram 29).



Conditions			Mean values
NaOH	A		0,04
Ethanol	A	B	0,03
Lactic acid	A	B	0,02
Water	A	B	0,00
PCE	A	B	-0,02
Thermocycling		B	-0,05

Conditions not connected by same letter are significantly different (statistically).

Diagram 29. Mean roughness change ΔR_a [μm] for Sinfony after the ageing process. The mean values of ΔR_a are listed in the corresponding table. The black horizontal lines indicate the range (0,25- 0,5 μm) of roughness values change, which is clinically perceptible (in this case only the line of 0,25 μm) while the green horizontal lines indicate 95% confidence intervals.

Wear: Sinfony presented at the end of the chewing simulation (1,2 x 10^6 cycles) larger wear cavities after storage in PCE (and subsequent chewing simulation) compared to the produced cavities after storage in NaOH (and subsequent chewing simulation). But this difference was not statistically significant (Diagram 30). The remaining ageing models resulted in significantly smaller (statistically) wear cavities (but not statistically different compared to the ones produced after the immersion in NaOH).

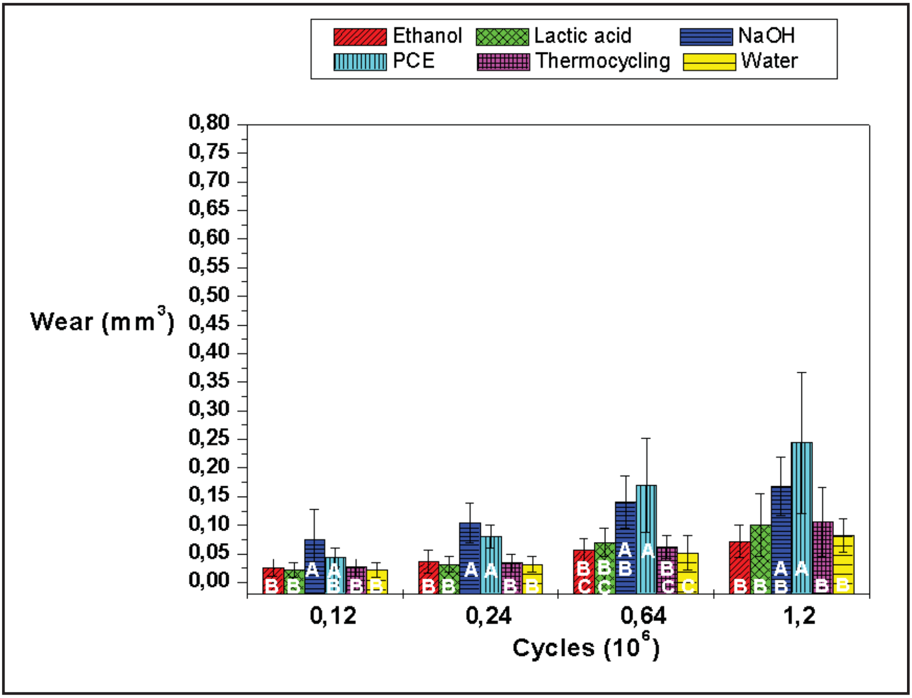


Diagram 30. Wear results for Sinfony at different time intervals. Data are presented as mean ± SD [mm³]. Conditions not connected by same letter are significantly different (statistically).

5.6 Ranking of mean relative changes of the tested properties

In order to get a general overview of the effect of the diverse ageing models on the amount of properties examined, the ranking of mean relative change was estimated. The ranking of mean relative change was calculated from the sum of the mean relative changes of the tested properties after the ageing process (storage for colour, hardness and roughness and chewing simulation for wear). In other words the ranking (Ran) was produced from the sum: Ran= rΔE+ $r\Delta R_a$+ rΔHV + rΔW. rΔE was defined as the mean relative colour change or else the colour difference observed between the end and the beginning of the ageing process (ΔE) divided through the value E, measured at the beginning (i.e. rΔE= ΔE/ EBeginning= ΔE/). In the case of EBeginning ΔL is equal to the mean L* value at the beginning. The Δa and Δb values are equal to the corresponding a* and b* values. Similarly, $r\Delta R_a$ defined as mean relative roughness was calculated according to the following formula: $r\Delta R_a$= R_aEnd- R_aBeginning/ R_aBeginning=

ΔR_a/ R_aBeginning, where ΔR_aBeginnig is the mean R_a values of the materials before storage. rΔHV which is defined as mean relative hardness change was estimated as the mean difference of hardness between the beginning and the end of the ageing process (as mentioned before in the case of hardness because of the expected negative sigh the calculations were made in the opposite way compared to the other properties) divided to the mean hardness value at the beginning of the ageing process (i.e. rΔHV= HVBeginning- HVEnd/ HVBeginning= ΔHV/ HVBeginning). The problem with rΔW was that there were no wear values at the beginning of the ageing process. Therefore the rΔW was estimated solely from the mean wear values (volume) produced at the end of the chewing simulation (Table 11).

Table 11: The results of the mean colour, mean hardness, and mean roughness change as well as those of wear volume (C: Colour, H: Hardness, R: Roughness, W: Wear).

	C	**H**	**R**	**W**	**C**	**H**	**R**	**W**	**C**	**H**	**R**	**W**	**C**	**H**	**R**	**W**	**C**	**H**	**R**	**W**
Material / **Solution**	**Arabesk**				**Artglass**				**Grandio**				**Signum**				**Sinfony**			
Ethanol	8	24	-19,4	0,28	2	15	24	0,2	8	9	-8	0,08	4	32	28	0,22	12	33	14	0,07
Lactic acid	7	32	2	0,3	10	4	2	0,06	11	44	206	0,22	3	8	12	0,18	6	1	9	0,10
NaOH	18	90	353	0,38	28	70	181	0,44	27	93	816	0,37	9	62	173	0,21	15	41	17	0,17
PCE	4	22	-14	0,48	2	2	2	0,35	7	6	-3	0,26	2	13	33	0,23	7	5	-9	0,24
Thermo-cycling	4	10	-12	0,32	2	-5	-2	0,11	6	8	1	0,24	3	2	-9	0,15	3	10	-26	0,11
Water	3	10	14,5	0,2	3	2	11	0,09	9	15	5	0,35	2	23	-4	0,15	7	7	1	0,08

The resulting mean relative ranking (Ran) was estimated separately primarily for every property under each condition and material tested. At the beginning the ranking was expressed with numbers (from 1 to 6: 1 for the most negligible effect and 6 for the most accentuated surface degradation)

By adding the rankings for the different properties for each solution and material, the final ranking of the effect of the different solutions on the entirety of properties of a material was produced (Table 12).

Table 12. The resulted relative ranking of surface properties (C: Colour, H: Hardness, R: Roughness, W: Wear).

	C	H	R	W	C	H	R	W	C	H	R	W	C	H	R	W	C	H	R	W
Material / Solution	**Arabesk**				**Artglass**				**Grandio**				**Signum**				**Sinfony**			
Ethanol	5	4	5	2	3	5	5	4	3	3	4	1	5	5	4	5	5	5	4	1
Lactic acid	4	5	1	3	5	3	1	1	5	5	5	2	4	2	3	3	3	1	2	3
NaOH	6	6	6	5	6	6	6	6	6	6	6	6	6	6	6	4	6	6	5	5
PCE	3	3	3	6	2	2	3	5	2	1	2	4	2	3	5	6	4	2	3	6
Thermo-cycling	2	2	2	4	1	4	2	3	1	2	1	3	3	1	2	2	1	4	6	3
Water	1	1	4	1	4	1	4	2	4	4	3	5	1	4	1	1	2	3	1	2

The overall ranking of the tested properties for every ageing model was estimated, by adding the mean relative changes of the tested materials. But this time it was expressed with letters of the Greek alphabet (Α, Β, Γ, Δ, Ε, Ζ: Α for the most negligible effect and Ζ for the most accentuated surface degradation). The first letters of the greek alphabet were chosen in order to avoid confusion with the letters used in the Results to indicate statistical significance (see Table 13).

Table 13. The relative ranking of the impact of the ageing models on the tested properties.

Solution	Colour	Hardness	Roughness	Wear
Ethanol	Δ (21)	Ε (22)	Ε (23)	Γ (13)
Lactic acid	Ε (21)	Δ (16)	Α (12)	Β (12)
NaOH	Ζ (30)	Ζ (30)	Ζ (29)	Ζ (26)
PCE	Γ (13)	Α (11)	Δ (16)	Ε (23)
Thermocycling	Α (8)	Β (13)	Β (13)	Δ (15)
Water	Β (12)	Γ (13)	Γ (13)	Α (11)

If the sum was the same for two or more properties or solutions then the ranking was decided according to the produced wear results. That means that the ageing model, which generated the greatest wear results, achieved the highest degradation ranking. Finally, the overall ranking of the degradation for every ageing model arranged to materials was estimated by adding the relative changes of all tested properties (see Table 14).

Table 14. Final relative ranking of the effect of ageing models on the tested materials.

Material / Solution	Arabesk	Artglass	Grandio	Signum	Sinfony
Ethanol	E (16)	E (17)	Γ (11)	E (19)	Δ (15)
Lactic acid	Γ (13)	A (10)	E (17)	Γ (12)	B (9)
NaOH	Z (23)	Z (24)	Z (24)	Z (22)	Z (22)
PCE	Δ (15)	Δ (12)	B (9)	Δ (16)	E (15)
Thermocycling	B (10)	B (10)	A (7)	B (8)	Γ (14)
Water	A (7)	Γ (11)	Δ (16)	A (7)	A (8)

5.7 Summary of the results after storage (Incubation effect)

Ethanol: Ethanol resulted in considerable degradation of every single tested property. It produced the second most accentuated change of hardness and roughness (Position E) and the third most accentuated colour change (Position Δ). The wear cavities produced after the immersion in ethanol were the fourth most pronounced (Position Γ in the ranking, see Table 13).

Lactic acid: Lactic acid resulted in the second most accentuated change of roughness (Position E) and the third most accentuated hardness change (Position Δ). The roughness change after immersion in lactic acid was relatively negligible (Position A) as well as the produced wear cavities (Position B, see Table 13).

NaOH: NaOH proved to be the most aggressive degradation model. It resulted in the most accentuated changes of each property for every material tested (Position Z in the ranking, see Table 13).

PCE: PCE proved to be an aggressive degradation solution though its effect concerning some tested properties was not pronounced. It resulted in the most negligible relative change of hardness (Position A) and the third most accentuated roughness change (Position Δ). The colour change after immersion in PCE was the fourth most accentuated (Position Γ). The produced wear cavities were the second most accentuated (Position E, see Table 13).

Thermocycling: Thermocycling proved to be the least aggressive degradation solution. It resulted in the most negligible (relatively) colour change (Position A). Slight were also the produced hardness and roughness changes (Position B). The produced wear cavities occupied the third ranking position (Position Δ, see Table 13).

Water: Water proved to be rather friendly to the composites compared to the other degradation models. It resulted in negligible relative changes regarding colour and wear (Position B and A, respectively). The immersion in water caused the fourth most pronounced hardness and roughness changes (Position Γ, see Table 13).

6 Discussion

The complicated in vivo oral condition can only be partially simulated in vitro at least for the time being. Clinically, restorations will be covered within a short time by an organic film, a pellicle (46). This film will probably change the diffusion on the surface of the composite (46). The model used in this experimental set up comprised the storage of the tested materials in different solutions in order to test their resistance in a combined (bio)chemical exposure and mechanical loading. The applied conditions represent extreme situations (e.g. 0,1N NaOH) in order to test the materials' stability thresholds. The use of very aggressive storage solutions is thought to accelerate effectively the degradation process and enlighten diverse degradation mechanisms.

From the results of this study, the null hypothesis, i.e. "The nature of the storage solutions has no influence on the tested properties", can be rejected: The specimens stored in water suffered significantly from less surface degradation (partly) compared to the specimens submitted to the other ageing models. Storage of the specimens in water did not produce any meaningful changes of the materials' properties tested (with the exception of Grandio). It seems that distilled water is no representative solution for the simulation of the condition in the oral cavity for such experimental set-ups. From this point of view one should consider the use of distilled water for short-term degradation experiments useful as reference storage modus. The effect of the other ageing models (with the exception of NaOH, which's impact was almost always the most accentuated) was more pronounced concerning wear resistance rather than colour, roughness and hardness (with some exceptions).

Due to the relatively high variance, [possibly because of inherent variation among the test specimens, fine differences in the mechanical operation of the chewing simulator from run to run, inhomogenity of the steatite antagonist, which has slightly porous structure (139)], the observed arithmetical wear values differences after storage in water and PCE could only partially prove statistical differences. Nevertheless, the mean degradation values for every property tested were higher for PCE than water (Table 14), though not always statistically different.

Although the storage conditions (ratio of solution quantity and surface of the specimens) have been kept constant, a different surface degradation cannot be excluded. It was demonstrated that soaking has the effect of increasing the variability of the strength of the materials (27, 140). This is the main reason why a mean relative change of at least 10 % will be considered as meaningful.

The examined properties (colour, hardness, roughness, wear) were selected in order to achieve a spherical overview of what is actually happening mainly on the surface and below it (as some of the properties, e.g. colour, hardness, wear involve also deeper layers of the composite) during an experimental ageing set-up. The use of only one variable was thought to provide insufficient information concerning the performance of the materials after the ageing process.

The fact that the examined surface properties were influenced in a different way from the same storage solution (see Table 11) confirmed our assumption that the information provided from the examination of only one property is insufficient. There was a different ranking for changes in colour, roughness, hardness and wear after the immersion of a material in the same solution.

A value of ΔE over 2 has been considered as clinically perceptible while a value of ΔE over 3,3 has been considered unacceptable (94). A ΔR_a range between 0,25 and 0,5 was proposed to be clinically perceptible for dental composites (109). In contrast to roughness and colour changes where clinical perceptible values have been cited, this is not the case with hardness. There are no values reported, which indicate an effect of the hardness change on the overall performance of the resin composite.

6.1 Choice of the conditions used in the experimental set-up

The choice of the antagonist material is a complicated and controversial subject. The enamel antagonists, even standardised, mainly in forms of enamel cusps exhibit morphological and physical differences which often lead to inhomogeneous results (141). In order to cope with this problem different enamel substitute materials were used: stainless steel (142), Al_2O_3 (143), steatite (144). All these substitute materials were used with the argument that their properties or at least some of them are very similar to that of enamel. Although the reports about steatite as enamel substitute are contradictory (139, 145) the similarity of its abrasive behaviour to that of enamel favours the use of this material, when 2-body wear is of primary concern (146). The form of the antagonist is also very important for this kind of experiments. Cylindrical antagonists may plough the tested specimens because of their shape (147) and finally result in a change of the wear mechanism and in acceleration of the wear ratio of the specimens. A sphere with a radius of 3 mm is thought to be in the midrange of cuspal radii (2-4 mm) (148).

The medium used during the load-cycling is also a controversial theme. Distilled water is the most widely used medium for this kind of experimental set-ups (2-body and attrition experiments). Nevertheless, salivary films may affect friction coefficients and wear rates (149). Although this problem is well known, distilled water was used in this experiment because it is considered as an inactive, reference solution, which does not chemically interact with the tested materials during the short period of the chewing simulation. Therefore, it was possible to monitor the results of the chemical exposure and those of load-cycling separately.

6.2 Properties changed after storage (Incubation effect)

6.2.1 Ethanol: Colour, Hardness, Roughness, Wear

According to the ranking of the impact of the ageing models (Table 14) on the tested properties of the materials, ethanol achieved the second most accentuated (Position E) degradation for Arabesk (77 wt. %), Artglass (70 wt. %), Signum (73 wt. %). The main reason for this result for Artglass and Signum were the changes in hardness (15 and 32 %, respectively), roughness (24 and 28 %, respectively) and wear (mean wear volume of 0,2 and 0,22 mm^3, respectively) while the change of colour is negligible (2 and 4 %, respectively). The relative colour, hardness and roughness change as well as mean wear value for Arabesk after immersion in ethanol were relatively high (8; 24 and -19,4 % and 0,19 mm^3, respectively). These were the factors that primarily caused the high-ranking position (Position E) that ethanol occupied in the impact ranking for Arabesk.

Wear did not play such a considerable role for Sinfony (0,07 mm^3). But in the case of Sinfony the relative colour change (12 %) as well as the relative hardness (33 %) and roughness changes (14 %) contributed to the high ranking (Position Δ) regarding the effect of ethanol (see Table 14). A more limited effect of ethanol (Position Γ) was observed for Grandio. The reason for that were the relative low mean changes of colour, hardness and roughness (8; 9 and 8 %, respectively) and mean wear volume (0,08 mm^3) for this material.

In general, the colour changes after storage in ethanol were not meaningful (<10 %). The only meaningful colour difference was observed for Sinfony (12 %). The main reasons for this are thought to be the oxidation reaction of unreacted C=C double bonds which can produce coloured peroxide products of the resin-rich polymer (50 wt. %) of Sinfony and the continuous polymerisation of camphorocinone (an a-Diketon) through the ageing process (89, 91, 150). The hydrolysis of the silane bond and the following detachment of filler might also play a role in colour changes. As the fillers possess a different refractive index compared to that of the matrix, their detachment after ageing will yield a colour change.

The high values of mean hardness change for Sinfony can be attributed to its relatively low filler content (50 wt. %). The resin-rich Sinfony may allow for an easier penetration of the organic solvent. It has been shown that the organic solvent disposes greater ability to penetrate and swell the polymer network than water and to facilitate the liberation of unreacted and leachable monomers (9). As the solvent penetrates the matrix and expands the openings between polymer chains, monomers which are not firmly attached to the polymer structure diffuse out (9). The resulting loss of these monomers and their substitution by water molecules may degrade the physical and mechanical properties of the materials. After ageing in ethanol, softening of the resin matrix as well as cracking within the resin and at the resin/matrix interface were reported (117). The reduction of the mechanical properties after storage in ethanol was reported several times (27, 100). Hardness after ethanol storage is dependent on several factors. A major factor is the monomer ratio of Bis-GMA/TEGDMA (118), which influences the degree of cross linking by changing the degree of conversion (30). Also, the content of non-functional monomer plays a significant role. This may be the explanation for the relatively high mean hardness change of Arabesk (24 %), although this material disposes greater content of filler (77 wt. %) than Sinfony. Softening has been correlated with reduced resistance to wear in vitro (99). Storing in ethanol reduced the fracture toughness and the elastic modulus of a composite material (117), properties which were proposed to influence the wear resistance of composites.

Although neither distilled water nor ethanol/water 75/25 can simulate the oral conditions 100 %, the real situation occurring in the oral cavity was proposed to be somewhere between the effect of these two solutions (9).

Ethanol seems to have also a considerable effect on roughness of the materials. Most of them exhibited a mean increase of 10 % and in some cases over 20 %, respectively. The materials, which exhibited the most pronounced roughness increase, were the resin richest materials (Artglass, Signum, Sinfony). The increased elution of molecules (9), the dissolution of the matrix and the subsequent exposure of fillers (102) after storage in ethanol are thought to be the reasons for the increase in roughness.

The reason for the mean reduction of roughness after immersion of Grandio and Arabesk in ethanol is unclear. One possible cause may be the high roughness values achieved for both of these materials at the beginning of the experiment. The surface roughness has been related to the filler particle size (151). As the materials were polished after manufacturing, a preferential resin abrasion took place and the filler phase was exposed (106, 110). It was proposed that mainly plucking out of filler leads to decreased roughness after ageing (110). Filler detaching can also occur due to the deterioration of the silane bond, reported after soaking in ethanol (27). The resulting porous surface was suggested to be smoother than the initial one (110).

6.2.2 Lactic acid: Colour, Hardness, Roughness, Wear

Lactic acid produced the second most accentuated (Position E) degradation for Grandio (see Table 14). In case of Grandio, the mean change of roughness was dramatically high (206 %). The produced mean roughness change of 0,5 µm is in the range of the perception of patients (109). Weak acids cause dissolution of glass fillers and the matrix of dental materials (152).

The mean change of hardness and colour were also considerable (44 and 11 %, respectively- see Table 11). These results confirm previous reports of reduction of hardness of composites after one year storage in lactate solution (pH=4) (120). The structure of resin composites is proposed to be disintegrated at low pH predominantly due to hydrolytic degradation (101, 120).

Similarly, the mean wear volume after immersion in lactic acid for Grandio was not negligible (0,22 mm^3). Organic acids produced from dental plaque proposed to have impact on the dental materials properties as hardness and wear resistance (118, 120).

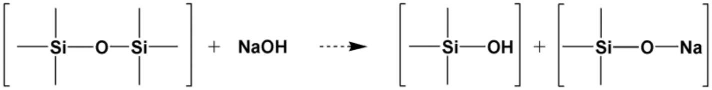
In the case of Arabesk, storage in lactic acid resulted in Position Γ of the degradation's ranking (Table 14). The main reason for this ranking was the relatively high mean hardness change (32 %), and the relatively high wear volume (0,3 mm^3) as it can be seen in Table 11. The colour change (7 %) is not considered meaningful.

In the case of Signum and Sinfony, lactic acid's effect is placed in the third position (Position Γ) and second place (Position B) regarding aggressiveness, respectively (see Table 14). The main reason for this ranking for both composites was the mean roughness change (12 % for Signum and 9 % for Sinfony). Degradation of the matrix could account for that, as signs of degradation of matrix or silane coupling agent of resin composites have been documented in a pH cycling experiment (122). The colour change for Sinfony (6 %) has also partly contributed to this position, while the corresponding colour change for Signum was negligible (3 %). The mean hardness change played also a role for Signum (8 %) whereas there was practically no mean change of hardness for Sinfony (1 %). Wear volume was also adapted to the general degradation behaviour for Sinfony (0,1 mm^3) and Signum (0,17 mm^3), as can be seen in Table 11. The effect of lactic acid on Artglass was the most negligible for this material (Position A). A negligible mean change of roughness (2 %) and hardness (4 %) as well as low mean wear volume (0,06 mm^3) contributed to this low ranking for Artglass- Table 11). On the other hand the mean colour change was considerable (10 %) but not able to influence the overall good degradation behaviour of Artglass after storage in lactic acid.

6.2.3 NaOH (Sodium hydroxide): Colour, Hardness, Roughness, Wear

Hardness, colour, roughness and wear resistance were severely affected (negatively) after immersion in NaOH. The changes induced from the storage in NaOH occupied the highest relative ranking among the ageing models for every material tested. The immersion in NaOH changed dramatically every property tested. The mean changes ranked from 9 % (mean colour change for Signum) up to 816 % (mean roughness change for Grandio). Even the mean wear volumes were representative for the highest degradation grade: from 0,17 mm^3 for Sinfony up to 0,44 mm^3 for Arabesk (Table 11). The mean roughness change for all materials stored in NaOH (with the only exception of Sinfony) are considered to be in the range of patient's perception [i.e. 0,25- 0,5 µm (109)].

When immersed in NaOH, the degradation of the siloxane bonds is expected to be accelerated due to an excess of OH- ions. The applicable reaction of the silica network in a glassy filler was proposed to be [according to (125)]:



The following observations were documented after storage of composites in NaOH: a) Filler debonding, b) Interface debonding, c) Resin matrix cracks and d) sub-surface damage layer (123). In accordance to our results a dramatic decrease in hardness of heated and unheated composites stored in 0, 1 N NaOH after 14 days has been also reported (125). An increase in pH of the medium increases the wear rate (153) and the solubility of composite resins (154). The aforementioned solution represents a very rare and aggressive situation. Nevertheless, it was used in order to test the stability thresholds of the materials and to obtain a so-called "worst case scenario" of the degradation's effect.

6.2.4 PCE: Colour, Hardness, Roughness, Wear

The effect of storage in PCE ranked in the position Δ (Table 14) for three of the five tested materials (Arabesk, Artglass, Signum) whereas it was placed in Position B for Grandio. The relative mean change of hardness (22 %) and roughness (-14 %) as well as the large wear cavities (mean volume of 0,48 mm^3), as can be seen in Table 11, caused the high relative ranking of PCE (Table 14). In the case of Artglass the mean roughness change was the same negligible as colour and hardness change. But it was the mean wear volume values (0,35 mm^3), which affected decisively the relative ranking of PCE for Artglass. In the case of Signum the mean roughness change (33 %) was the decisive factor for the high placement of PCE in the relative ranking. The mean wear value (0,23 mm^3) as well as the hardness change (13 %) played also a considerable role for this ranking, whereas the colour change was negligible (2 %). In the case of Grandio, the mean wear volume (0,25 mm^3) along with the relative not meaningful mean changes (Table 11) of hardness (6 %), colour (7 %) and roughness (-3 %), were not high enough to contribute to a higher placement of PCE in the relative ranking (Position B in Table 14). The effect of PCE achieved the highest position (Position E) in the case of Sinfony. The main reason for this placement was the high wear value (mean wear of 0,24 mm^3). Considerable was also the effect of the mean roughness change (-9 %) but not as decisive as the impact of reduced wear resistance of Sinfony after storage in PCE.

From the oral enzymes, the most important family in the study of biodegradation of dental composites is the one of esterases since resin composites dispose steric bonds. It was suggested that the enzymes attach at a specific molecular site, so that the electrostatic forces of nearby atoms sharply reduce the energy needed to cleave and re-form the appropriate chemical bonds (155). This specific molecular site has been proposed to be the site of the steric bond of the composites, which is located between the dimethacrylates (monomers), which are the components of the polymer (Fig. 27).

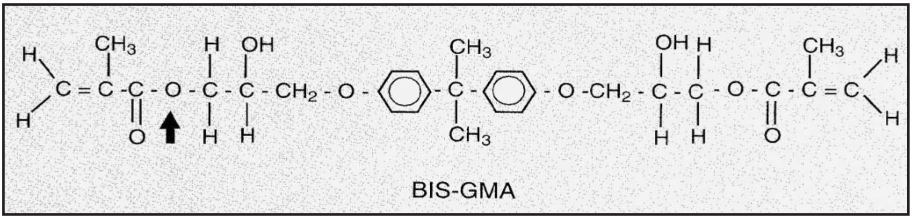


Fig. 27. Illustration of the proposed action of the esterase in the steric bond of a Bis-GMA molecule [according to (155)].

The action of esterase is proposed to affect the unreacted monomers (156,157), but also monomers of the matrix (156, 158, 159). It was proposed that mainly the pendant monomers of the matrix (partly polymerised and connected only via the one side to the polymer) are affected from the enzymatic action (158). The products of this degradation are the corresponding diols, along with MA (methacrylic acid). Beside the degradation of the polymeric form, esterases have been shown to be able to catalyse degradation of structural monomers of dental composites as TEGDMA, BISGMA, UEDMA (86). It has been shown that human saliva is capable of converting the dimethacrylate ester TEGDMA into methacrylic acid and the alcohol part of the ester (32). The production of MAA in the interior of the polymer due to hydrolysis can strongly affect the level of pH in the pores, a decisive factor for the degradation of composites (44). A self-sustained mechanism of the hydrolysis because due to formed MAA has been suggested (154). The liberated MAA and the increased water uptake caused by an increased hydrophilicity of the matrix may have a plasticizing effect on the surface (32).

Different salivary enzymes produced a reduction of the mechanical properties of composites because of their hydrolytical action (32, 127). The hydrolysis of (poly) methacrylates by esterases is proposed to be highly dependent upon the linkages of the polymer (157). Whether the hydrolytic enzymes have the capability to cleave interchain ester bonds is not clear (160).

Though the existing reports of SEM micrographs of rougher surfaces after incubation in salivary esterases or artificial equivalent enzymes (158), this could not be demonstrated in the present study. The roughness results after immersion in PCE of the present study confirm previous report of no significant change (statistically) of composites roughness after immersion in enzymatic solution up to a year (161). The only material, which was found to be considerably rougher after immersion in PCE, was Signum (33 %). The main reason for this seems to be the ability of PCE to degrade Signum (matrix consisted of UDMA, TEGDMA).

The decisive factor for the placement of PCE effect in Position Δ of the relative ranking is the mean wear values (volume). The reason for this increased mean wear values after immersion in PCE should lie in the structural changes that PCE causes in the composite polymer rather than in the effects that PCE had on superficial properties as hardness, colour and roughness. Two exceptions were the 22 % mean hardness reduction for Arabesk as well as the 33 % mean roughness increase for Signum.

As to wear resistance, the degradation of the polymer network around the reinforcing filler reduces the support of the filler. Finally, when the chewing load-cycling occurs, the already weakly supported filler will be easily and fast exfoliated (detached). The lost of the reinforcing filler yields a less wear resistant matrix and further substance loss. It was proposed that composites with less filler content are more susceptible to enzymatic degradation because of the sensitivity of the polymer, which is rich in organic compounds (156). There are no data available in the literature concerning the 2-body wear resistance of composites after immersion in enzymatic solution.

It was reported that butyrylcholinesterase or Pseudocholinesterase (PCE) represents 70 % of the activity of the cholinesteric activity in saliva (162). Although the different kinds of cholinesterases (and their respective activities) which are active in the oral cavity are not yet 100 % defined, similarities in character and action between PCE and human saliva esterase have been proposed (158). One might expect to find a variety of hydrolases in human saliva, derived from bacteria, the lingual glands and epithelial cells (163). In contrast to the in vitro model, composites in the oral cavity are continuously bathed in unprocessed human saliva and are influenced by dynamically changing human salivary enzyme concentrations that are specific for that environment as well as the renewal of the enzyme (esterase) activities, derived from oral microorganisms (158). Diverse materials possibly respond differently to human saliva. It is also likely that different individuals have different esterase activities, which vary in both stability and concentration. Furthermore, it is likely that some degradation products may be generated in different levels for one individual but not for another (158).

The enzymatic ageing model with PCE even though did not result, in general in considerable changes of hardness and roughness, produced considerable wear cavities after the chewing simulation. This reveals that a biochemically active environment could affect structural properties of composites in a way that is not yet investigated. It has been shown that the effect of PCE on unfilled and filled dimethacrylate dental resins represent a kind of an enzyme-driven depolymerisation mechanism which plays a potential role in vivo (159). The co-operation of different hydrolases in human saliva was reported to have a synergistic degradative effect (164). The model of synergistically acting enzymes seems to be a very promising one regarding degradation studies.

6.2.5 Thermocycling: Colour, Hardness, Roughness, Wear

Thermocycling proved to be the relatively least aggressive ageing model (position A) for one of the five tested materials. More precisely, Grandio exhibited the least degradation values after thermocycling. The low values of mean colour, hardness, and roughness change and wear volume contributed to this placement for Grandio. One common finding for the other materials (Arabesk, Artglass, Signum and Sinfony) was the reduced roughness values after thermocycling (ranging from -2 % up to -26 % mean relative change).

A peculiar finding was the decreased mean roughness value for Sinfony (-26 %). Thermocycling generated the second less accentuated (position B) degradation for Arabesk, Artglass and Signum (see Table 14). The reason for this position were once again low values of mean changes of colour, hardness, roughness as well as low wear volumes for these materials after thermocycling. The only exception was the relatively reduced wear resistance exhibited from Arabesk after thermocycling (mean wear volume: 0,32 mm^3).

The highest degradation ranking position after thermocycling was achieved for Sinfony. Responsible for this position was the 26 % relative mean change (negative) of roughness as well as the 10 % relative mean hardness change (Table 11). The contribution of the mean colour change as well as the wear cavity volume to this position was negligible for Sinfony. Failures of the filler/matrix interface were reported for thermocycled specimens after a toothbrush experiment (130).

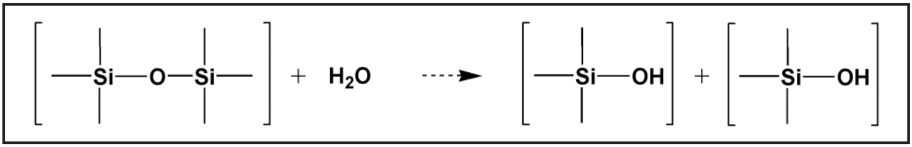
There are many different models of thermocycling concerning temperature spectrum, duration of the thermical loading, number of thermocycles etc. It was proposed that 10000 cycles of thermal loading should represent one year of clinical function (129). There are models which use only two temperatures (i.e. an upper of 50˚C and a lower of 5 ˚C, (130, 165) and other ones which use three temperatures (i.e. an upper of 50˚C a lower of 5˚C and an intermediate of 37˚C) to mention only some of them. The last one was proposed to better reflect the conditions encountered clinically because of the equilibration time at physiological temperature (166). Nevertheless, this model also failed to show degradation signs (especially reduction of abrasion resistance) of all materials tested after thermocycling (166). In another toothbrush abrasion experiment thermocycled specimens exhibited increased depth of surface degradation and initial wear and surface roughness (130). Nevertheless, it must be noted that in this experiment, chemically cured composites were tested and not all of them showed a difference to the degradation of the control (dry) specimens (130).

As thermocycling caused minor degradation concerning all tested materials, its use as an ageing model should be reconsidered. It was indicated that, confirming the results of this study, there is no concrete evidence that failures in clinical practise occur because of thermal stresses, notwithstanding the theoretical expectation (129).

6.2.6 Water: Colour, Hardness, Roughness, Wear

Water generated the least accentuated degradation effect (Position A) for Arabesk, Signum and Sinfony. The negligible change of colour (3 %), for Arabesk, the change of colour (2 %) and roughness (-4 %) for Signum and the change of roughness (1 %), and hardness (7 %) for Sinfony (Table 11) contributed to this placement of the water effect. Another contributor to this low ranking for water degradation was the low wear values (0,2; 0,14 and 0,08 mm3, respectively, in Table 11) after water storage. The mean hardness and roughness change for Arabesk (14,5 and 10 %, respectively) as well as the mean hardness change for Signum (23 %) and the mean colour change for Sinfony (7 %) were the most meaningful changed properties after water storage (Table 11). For Artglass, water storage resulted in position Γ (Table 14) in the degradation ranking. The reason for this placement was mainly the mean change in roughness (11 %). The mean colour and hardness change were negligible. The mean colour and hardness change (9 and 15 %, respectively) as well as the high wear values (0,35 mm^3) placed water in position Δ (Table 14) in the relative degradation ranking for Grandio. The considerable mean relative change for Grandio (15 %) as well as its high wear value though it’s very high filler content may indicate a hydrolysis of the filler-resin bond during the immersion in water.

Water exposure is considered to contribute to the degradation of dental composites because of degradation of fillers (24, 124, 167). Dental composites stored in distilled water leach filler components (168). Glass-modifying elements- such as sodium, barium, and strontium can increase the leaching rate (24). When water comes in contact with a silica surface, it breaks siloxane bonds to form silanol groups, according to the following equation (113):



It was proposed that water is able to degrade also the bond between the filler-matrix interface (117). This could be an explanation for the 15 % mean hardness reduction of Grandio after storage in water.

The polymer matrix is also considered degradable from water (167, 169, 170). It has been argued that water sorption is related to filler volume fraction (171) since it occurs predominantly in the resin (126). Soaking a composite in water results in both a rapid elution of unbound molecules and a much slower sorption of water that is controlled predominantly by diffusion into the polymer matrix (50). Plasticisation and stress relaxation by water can occur in the polymer and this may lead to a change in the wear resistance of the composite (172). Absorbed water causes sorption expansion, increasing the effective free volume and the ease of movement of chain segments, thus reducing the elastic modulus of the material (173). Most of the water molecules occupy free volume between the chains and crosslinks as microvoids are created during polymerization (174). Water is considered as a poor solvent for the resin, and therefore exerts a more limited effect compared to other solvents (117). On the other hand, gradual relaxation of polymerization contraction stresses in the matrix concentrated around the filler particles leads into a more homogenized distribution throughout the entire polymer matrix. The total stress in the matrix around and underneath the particles during mechanical loading may therefore decrease with time, reducing the formation of microcracks and consequently wear (175). In a similar storage experiment an increase of hardness of different composites was reported. This should indicate a progressive cross linking reaction that occurs following light activation of composite resin (103). It is expected that with increased storage time, the filler surface and the filler/matrix bond will be affected by the storage solution (154).

From the results of this study water is proposed to represent only a control storage solution. Most similar degradation analysis comprised storage of the specimens in distilled water as a test solution. However, the results of our study indicate that the compositional degradation that occurs after 3 months of water storage cannot be compared with the degradation occurring in other storage solutions. Limited degradation of composites after water storage was also previously reported (49, 161). Therefore, the use of distilled water for this kind of degradation tests as a storage solution, beside control or reference, should be questioned.

6.3 Impact of ageing on surface stability of composite resins

Traditionally wear of composites has been explained simply in terms of the effects of the amount of filler, the nature of the matrix or the coupling agent bond (59, 176). Jorgensen et al. proposed that decreasing the interparticle spacing, which is best achieved with the smallest filler particles, would be the key to improving the wear resistance of composites (177). Filler particles packed very closely protect the softer matrix from abrasives, thus reducing wear (178). Nevertheless, it was reported that the wear variability can be explained by the percent of the surface area occupied by the filler particles, while the number of filler particles and their mean size were not significant factors in predicting wear volumes (179). Even if the addition of particles increases the wear resistance of composites, the optimal enhancement of wear resistance can only be achieved if the particles are well bonded to the resin matrix (178). Abrasion is reduced through the protection hypothesis (177) while attrition is proposed to be reduced through increased fracture toughness (178). In addition to interparticle spacing, another key factor in wear of composites is good stress transfer ability at the resin/filler interface. The stress transfer can be enhanced by either improving the bond between the filler and the matrix or by increasing the filler surface area. Because filler particles have a much higher modulus of elasticity than the interdisposed resin matrix, filler particles were hypothesized to compress the intervening matrix during mastication and to produce localized cracks (58). During load cycling the surface is plastically deformed and microcracks are generated within the material. These microcracks eventually coalesce, causing a crack running parallel to the surface followed by the eventual loss of a wear particle (144).

6.3.1 Arabesk Top

According to the manufacturer Arabesk Top is a glass ceramic microhybrid composite with 77 wt. % microfiller approximately 0,05 µm in size and very fine particles. The glass ceramic structure should provide an optimal stability (180).

Colour: Arabesk exhibited considerable colour stability throughout the storage time (with the exception of NaOH). For every ageing model the mean colour difference was not higher than 10 %, a result that is considered not meaningful. Unfortunately, there are no reports in the literature concerning the colour stability of Arabesk Top after ageing. NaOH yielded a mean colour change of 18 % (Table 11). This meaningful colour change was observed for every single material. It’s the result of the aggressiveness of the 0,1N NaOH solution. As Arabesk Top is heavily filled, the outer surface should be predominantly occupied from filler particles, which’s bond to the resin is proposed to be intensively hydrolysed during the immersion in NaOH (123). Their subsequent detachment from resin will cause a surface with different refractive index and consequently in different colour. It has been also reported that rougher surface texture can affect colour by increasing the scattering of incident light (181).

Hardness: In case of hardness the generated mean hardness change after thermocycling and water was not considered as meaningful (10 %). But all other ageing models caused a meaningful softening (> 10 %) of Arabesk. The mean hardness changes ranged from 22 % (PCE) up to 90 % (NaOH), as can be seen in Table 11. Similarly to colour stability, there are no reports in the literature concerning the hardness stability of Arabesk Top after ageing. The difference between ethanol and water effect lies in the much closer matching of coefficient of solubility of ethanol and Bis-GMA compared to water. That means practically that the ethanol molecule is able to penetrate the polymer network easier and deeper and facilitate the elution of pendant methacrylate groups. The effect of PCE on hardness is caused possibly by the effect of PCE on pendant methacrylate groups and the polymer network (hydrolysis of steric bonds), the subsequent liberation of MAA and the increased water uptake (32). Hydrolysis is thought to be also the effect of lactic acid, which results in softening of the surface of Arabesk (32 %). Responsible for the considerable softening during NaOH storage may be the very intensive hydrolysis of the silane bond between resin and filler and the subsequent filler detachment. It was reported that glass fillers (Arabesk contains glass fillers) are hydrolytically more unstable than fillers containing silica (15, 24).

Roughness: The roughness remained practically the same after the immersion in lactic acid, whereas for some ageing models the final surface was smoother compared to the initial situation. As outlined before polishing, after manufacture caused a preferential resin abrasion and the exposure of filler phase. It was proposed that plucking out of filler is the main reason that leads to decreased roughness after ageing (110). Filler detaching can also occur because of the deterioration of the silane bond reported after soaking in ethanol (27). PCE and thermocycling resulted in smoother surfaces. The produced porous surface was suggested to be smoother than the initial one (110). Even if filler was detached after the storage in NaOH, the surface was in such a way damaged that a mean roughness difference of 306 % for Arabesk Top was documented. The surface stability (concerning roughness) of Arabesk is not yet examined. Thus, there are no results available to compare with.

Wear: The ageing in different solutions generated no statistical different wear cavities. The reason for this was the large variance of the results. The direct polymerisation as well as the viscous paste of the material makes the entrapment of oxygen and the creation of pores very likely. The existence of pores, which can act as weak links and increase fatigue wear contributes probably to large deviations. Beside that, soaking has the effect of increasing the variability of the strength of the materials (27, 140). Though the dissimilarity of the wear behaviour of the incubated specimens even in the same solution, the largest wear cavities (volume, mm^3) were documented after immersion in PCE and NaOH, respectively (mean values).

The dynamic elastic modulus of Arabesk was found to be relatively stable even after 6 months of water storage (182). As previously noticed, a composite with a high modulus of elasticity, if combined with high fracture parameters such as flexural strength; diametral tensile strength, and fracture toughness would be able to resist occlusal loads and provide support at the interface between the restorative material and the tooth (182). Arabesk exhibited similar wear resistance to other micro hybrid composites in a pin on block wear study (183).

6.3.2 Artglass

Artglass matrix is a combination of conventional dimethacrylate monomers and new multifunctional methacrylates monomers. The polymer network was proposed to be more flexible and absorb stress better compared to the conventional Bis-GMA (184). This new matrix resulted also in a lower elastic modulus and microhardness compared to a Bis-GMA based composite (184). This greater elasticity is considered to reduce problems like chipping and fractures.

Artglass contains over 70 % wt. inorganic filler with mean size of 1 µm (according to the manufacturer). It contains special rheological glass (silicate approx. 1 µm), which is thought to provide a more concrete consistence. Artglass dentine proposed to contain 66,8 % SiO_2; 25,3 % BaO and 7,9 % Al_2O_3 (185). SEM observations revealed that Artglass contained filler particles larger than 1 µm (186). Artglass had a fairly uniform distribution of fine filler particles with a particle size of about 1 µm. It showed several large round and irregular particles with dimensions ranging from 3 to 8 µm (186).

Artglass was reported to absorb water during the first week of water storage but the situation stabilizes afterwards. The water absorption and the solubility were proposed not to be influenced by changes of pH (187).

Colour: Artglass exhibited almost the same colour behaviour as Arabesk Top. The only difference was that the specimens stored in ethanol did not show colour deterioration over the so-called visible limit of acceptance of 3,3 (mean value of 1,93). Lactic acid produced also in the case of Artglass visible colour degradation (mean value of 7,43, mean colour change of 10 %) and NaOH proved to be surface detrimental for the Artglass specimen (mean values of 21,04, mean colour change of 28 %, in Table 11). The other ageing models caused practically no meaningful colour changes (< 10 %). In different artificial ageing experimental set ups the colour changes of Artglass were slight and difficult to assess with the eye (186, 188). The production of chromatic degradation products indicating an intrinsic source of colour change was reported for Artglass (188).

Hardness: In the case of Artglass only ethanol (15 %) and NaOH (70 %) generated meaningful mean changes. As stated before ethanol molecule is able to penetrate easier and deeper the polymer network and facilitate the elution of pendant methacrylate groups. Responsible for the considerable softening of NaOH storage is thought to be the very intensive hydrolysis of the silane bond between resin and filler and the subsequent filler detachment. Water storage up to 30 days did not significantly alter the hardness of Artglass (189). Artglass contains barium-glass filler, which is supposed to be hydrolytically less stable than quartz fillers (24).

Insufficient ageing resistance of Artglass silanization and subsequent superficially filler detachment was reported after an ageing experiment (186).

Roughness: Ethanol (24 %) and NaOH (181 %) yielded also meaningful mean changes concerning roughness for Artglass (Table 11). Meaningful roughness change was also observed after water storage (11 %). Surface disintegration, filler detaching, and matrix dissolution are considered to be the reasons for this degradation behaviour.

Roughness analyses of Artglass gave diverse results. Mean Ra values of 0,09 µm after the use of fluoride varnish and of 1,23 µm for Artglass dentine after toothbrush experiments were reported (185, 190).

Wear: The largest wear cavities in the case of Artglass were documented after the immersion in NaOH (0,44 mm^3), PCE (0,35 mm^3), and ethanol (0,2 mm^3), respectively (Table 11).

The filler detachment and the resin disintegration after NaOH, the elution of pendant methacrylate groups after ethanol storage and finally the hydrolysis of steric bonds of pendant methacrylate groups' polymer network are considered to be the main responsible mechanisms for this result. Confirming this suggestion, insufficient ageing resistance of Artglass silanization and subsequent superficial filler detachment was reported after an ageing experiment (186). Statistically, ethanol and PCE wear cavities did not differ from the ones produced after thermocycling.

Wear resistance of Artglass is thoroughly examined in many wear analyses: In a similar experimental set-up (without ageing process before) Artglass exhibited a relative good 2-body abrasion resistance (137). According to the manufacturer a substance loss to a depth of 40-70 µm is expected for Artglass after 5 years of clinical function (191). By an experiment with another chewing simulator (OHSU) attrition and abrasion depth values of 84 and 42 µm were reported, respectively (184). Compared to a predecessor direct resin composite (Charisma) of the same manufacturer Artglass exhibited significantly less wear resistance and it was more aggressive against enamel antagonist. The lower Young's modulus, as well as its reduced hardness were considered to be the main responsible for this behaviour (184).

Contradictory to the relatively good in vitro wear results for Artglass, in vivo studies report occlusal contact area wear depth values for molars of 105 µm (with standard deviation of 140 µm) for Artglass crones (192) and wear depth values between 37 and 72 µm after one year of clinical function (193), respectively.

It exhibited also less 2-body abrasion resistance compared to other direct composites, which contain a larger filler part (194). Artglass showed a correlation between higher wear values and less hardness values (191). The lower hardness and elastic modulus of Artglass were thought to be responsible for its lower wear resistance compared to another dental composite material, although the two materials disposed similar filler content (184).

6.3.3 Grandio

The relatively high degradation that Grandio exhibited can be explained partially by the high filler content of this material. According to its manufacturer, Grandio possesses filler content of about 90 wt. % (195). Although it was proposed that composites for posterior use should have a Young's modulus at least equal to the one of dentine (18,5 GPa) materials with such high filler content and respectively high elastic modulus are more brittle than less filled composites and they suffer more often from fractures during their function lifetime (18). This behaviour indicates a material which is overloaded beyond its elastic limit (2).

Grandio exhibited the highest hardness baseline values of all materials tested in the present study. Nevertheless, it exhibited also probably the greatest tendency for attrition wear compared to the other materials. Its higher elastic modulus may have caused a lower fracture resistance, which is thought to be the most important factor concerning deformation after cyclic fatigue (which was the dominant loading mechanism in this experiment).

Materials with high modulus of elasticity dissipate more energy in the ceramic filler than in the resin binder. Therefore mechanical properties of composites with higher filler fractions would deteriorate more rapidly than otherwise. Htang et al. showed that composites with considerably lower or higher filler content than certain amount of filler (<60% or >80% by weight) had reduced fatigue resistance (196).

It was reported that composite with average filler particles smaller than 1 µm in size have experienced accelerated occlusal contact wear ,due to their inadequate fracture resistance (18, 74).

Colour: NaOH (27 %) and lactic acid (11 %) generated the most pronounced and meaningful changes in colour for Grandio. The mean colour changes produced from the remaining ageing models cannot be considered as meaningful (<10 %), as can be seen in Table 11. This colour behaviour was a part of the general degradation behaviour of Grandio in NaOH and lactic acid. After storage in both of these solutions the specimens' surfaces were heavily disintegrated. Degradation of matrix or silane coupling agent may account for this behaviour after storage in lactic acid. The hydrolysis of the silane bond and the following detaching of filler should account mostly for this colour change. The main portion of filler in Grandio is pyrogenic silica. It was reported that elemental oxygen is lost when silica fillers are depleted in an ageing experiment, leaving more organic material on the surface (186). As the fillers possess a different refractive index compared to the one of matrix, their detachment after ageing will acuse a colour change. The same, but in a much larger scale must have happened in the case of NaOH.

Hardness: Storage in NaOH (44 %) and lactic acid (93 %) resulted in the most meaningful changes regarding hardness. The change of hardness after storage in water (15 %) was also considered meaningful (Table 11). The surface disintegration as well as the hydrolysis of the silane bond between resin-filler and the subsequent detaching of fillers is thought to be responsible for this softening after ageing. The changes induced after the storage of the specimens in other media was not considered meaningful.

Roughness: Storage in lactic acid (206 %) and NaOH (816 %) produced very considerable roughness changes. Surface disintegration, filler detaching and matrix dissolution are considered to be the reasons for this degradation behaviour.

Wear: The larger cavities (volume) were observed for the specimens stored in NaOH (0,36 mm^3) and water (0,35 mm^3). Nevertheless, they were not statistically different from the cavities produced after the storage in the other ageing media. The reason for this higher disintegration after storage in NaOH and water should be the hydrolysis of silane bond and the subsequent filler detachment. Storage in ethanol yielded the smallest cavities (mean volume 0,08 mm^3).

6.3.4 Signum

Signum contains 73 wt. % filler consisted mainly of pyrogenic silica. The main monomer is UDMA with the addition of the diluent TEGDMA (197).

Colour: The artificial ageing revealed no meaningful colour changes for Signum (i.e. <10 %). The most accentuated colour change was the one observed after storage in NaOH. Nevertheless, it was not meaningful (9 %). A colour change after 72h ageing process for Signum was reported (198). The colour change was attributed mainly to a change of b* factor (ΔE of 3,4). This yellowing of the material was explained through camphorocinone (an a-Diketon) continuous polymerisation through the ageing process. The most decisive factor regarding colour stability is the composition of matrix as well as its polymerisation grade (198). The structure of the material as well as the molecule dimensions influence the depth of the penetration of colour pigments (91). These pigments were proposed to attribute to an internal discoloration of the composite material (93).

Hardness: In the case of hardness a different behaviour compared to colour was documented for Signum. Storage in PCE (13 %), water (23 %), ethanol (32 %) and NaOH (62 %) caused meaningful changes of hardness (Table 11). As mentioned before, the most of these ageing models act in a similar way but with different intensity. In other words, water and ethanol practically act in the same way with the difference that an ethanol molecule is able to penetrate easier and deeper the polymer network and facilitate in greater extent the elution of pendant and unreacted methacrylate groups compared to water. The effect of PCE on hardness lies possibly to the enzymatic action on pendant methacrylate groups and polymer network (catalysis of hydrolysis of steric bonds) and the subsequently liberation of MAA. The main reason for the considerable softening of NaOH storage is thought to be the very intensive hydrolysis of the silane bond between resin and filler and the subsequent filler detachment.

Roughness: A slight difference was observed regarding the mean roughness change compared to the hardness change. Water storage produced no meaningful roughness change (-4 %) while after storage in lactic acid the roughness increased by 12 %. Additionally storage in ethanol (28 %), PCE (33 %), and NaOH (173 %) produced meaningful changes in roughness for Signum (Table 11). Surface disintegration, filler detaching and matrix dissolution are considered to be the reasons for this degradation behaviour.

Wear: The meaningful changes of hardness and roughness for Signum, to mention the structural changes, did not cause the corresponding wear results. There was no statistical difference between the wear results of the different ageing models. Nevertheless, the most pronounced wear cavities were documented after storage in PCE (mean volume 0,23 mm^3), in ethanol (mean volume: 0,22 mm^3), and NaOH (mean volume: 0,21 mm^3).

6.3.5 Sinfony

Sinfony was introduced as an indirect composite, the matrix of which contains a combination of aliphatic and cycloaliphatic monomers (97). Sinfony contains very fine particles of Strontium/ alumina and borosilicate glass as well as silicate dioxide (50 wt. %). The mean filler size is about 0,6 µm. Because of the vacuum polymerisation of this material the prevalence of pores is considered to be very small. This polymerisation seems to provide a very homogeneous surface without pores of air bubbles entrapment, which could provide weak links concerning wear resistance

Sinfony confirms the belief that also not heavily filled composites can provide effective protection of the resin matrix, showing good wear resistance. As outlined before, even if the addition of particles increases the wear resistance of composites, the optimal enhancement of wear resistance can only be achieved if the particles are well bonded to the resin matrix (178). In this context, very small filler fraction (about 30 wt. %) were suggested to ensure good wear resistance (178). The findings of the present study confirm other studies that state that rather the matrix composition as well as the degree of polymerisation are the most significant factors affecting wear rate (4, 61, 199, 200). Sinfony's polymerisations grade was found to be about 66 % (97).

Colour: The colour changes in Sinfony were practically invisible in the case of thermocycling. But in the cases of lactic acid, PCE, and water the colour changes were very close either above or below the visible limits of 3,3 (mean values of 3,12; 3,75 and 3,65, respectively- see Results). This result seems to contradict the good colour stability reported for Sinfony in an ageing study with the use of different ageing means (201). Storage in ethanol produced a clearly visible change of colour for Sinfony specimens (mean value of 5,85) and NaOH accentuated colour deterioration (mean value of 7,75).

Storage in ethanol (12 %) and NaOH (15 %) egnerated meaningful colour changes for Sinfony (Table 11). Filler detachment and surface degradation are thought to be the reasons for this behaviour, as mentioned before.

Hardness: The same behaviour was observed for hardness of Sinfony after artificial ageing. In other words, ethanol (33 %) and NaOH (41 %) caused meaningful softening (Table 11). The only exception this time is that thermocycling generated also a meaningful softening (10 %). Filler detachment and erosion of resin as well as elution of monomers are thought to be the main reasons for this behaviour.

Roughness: Sinfony did not behave differently concerning roughness compared to the other surface properties (colour, hardness). Thus, ethanol (14 %), NaOH (17 %) and thermocycling (-26 %) yielded meaningful changes, whereas the remaining ageing models did not (Table 11). Filler detachment and resin degradation may be the main reasons for this behaviour.

Wear: Sinfony was the material, which exhibited the most accentuated (also statistically) wear cavities after immersion in PCE. The reason for that should be the degradation of residual and pendant monomers of the resin rich material. The catalysed hydrolysis of the steric bond of these monomers and the subsequent (possibly) elution of methacrylic acid should attribute to an increased water uptake for Sinfony. Nevertheless, the proposed action mechanism did not result in a meaningful reduction of hardness (5 %), in the case of Sinfony. NaOH produced in cavities, which did not differ significantly from the ones produced after the immersion in PCE as a part of the general degradation produced after the storage in NaOH.

The other ageing models generated smaller cavities (but not significantly different from the ones produced after immersion in NaOH).

Sinfony has been shown to exhibit the best 2-body abrasion resistance results in a similar experimental set containing only mechanical loading. Sinfony behaved the best compared to other materials even though it was the softest of all (202).

7 Conclusions

The present study showed that dental composites widely used in the daily practice should be thoroughly tested not only for their mechanical but also for their biochemical, especially enzymatical, stability. The examination of the mechanical stability of the materials even comprising incubation for a certain period in water before is not considered enough to monitor and in a certain way to predict the behaviour of the materials in the oral cavity. Therefore, diverse ageing models should be used in vitro.

The manufacturers of dental products claim that their products are thoroughly tested before their introduction in the dental market. But very often a biochemical stability examination is absent. The integration of enzymatically degradation test helps to achieve a situation closer to the oral one. This will facilitate the better understanding of the interacting of dental materials and oral environment and the wear mechanisms in vivo and the respectively selective enhancement of the materials properties. Nevertheless, individual degradation behaviour of the materials was registered, indicating specificity between the enzymatic action and the monomer composition. The combination of different enzymes should be investigated in the future.

A very interesting finding of this study was that the different properties were influenced in a different way from the same storage solution. This implies that in order to describe the effect of a certain ageing model concerning the stability one should examine different properties (in macroscopic as well as in microscopic niveau). The examination of only one property (e.g. wear resistance) is very useful but does not necessarily describe the whole spectrum of the changes induced during the ageing of a material.

8 Summary

In this study the effect of different ageing models was examined concerning the surface stability of different composite materials. More precisely, 30 specimens of the tested material (Arabesk Top, Artglass, Grandio, Signum, Sinfony) were aged in 6 different ageing models (ethanol, lactic acid, NaOH, PCE, thermocycling and water). One aim of this study was to show that water is useful only as control ageing model, whereas other models succeed much faster and more intensive degradation. The study hypothesis was that PCE storage can cause greater surface degradation than water.

The colour, hardness and roughness of the specimens were analysed before the immersion in the ageing solutions. After 90 days of storage the same properties of the materials were analysed. Afterwards, the specimens were subjected to load-cycling in a chewing simulator for a period equivalent to 5 years of chewing function. The wear cavities were measured at the end of the chewing simulation. The difference of the mean values of the tested properties was calculated. The effect of the different ageing models was statistically analysed with the help of the Tukey Kramer test (test niveau: $\alpha = 0{,}05$).

In order to achieve on overview of the effect of the different ageing models the relative mean ranking for every solution was estimated (by adding all the individual rankings of every single property for each material).

The results of the present study indicate the unsuitability of water to produce a considerable degradation of dental composites. Therefore, the null hypothesis was rejected. The final ranking revealed that NaOH primarily, ethanol secondarily and PCE thirdly were able to produce a more intensive degradation than water. The study hypothesis could only partially be accepted. Even though the effect of PCE did not always exhibit a statistically significant difference compared to the one of water, the relative ranking of these two solutions revealed that PCE was in most cases (with the exception of Grandio) more destructive than water.

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