Selected Properties of Core-Buildup Materials for Prosthetic Restorations

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Direktor: Prof. Dr. Wöstmann

Gutachter: Prof. Dr. Wöstmann

Gutachter: Prof. Dr. Frankenberger

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1. Introduction

A lot of teeth often show considerable coronal hard tissue defects, frequently requiring a core-buildup as a preprosthetic treatment [103, 111] before fabrication of the subsequent extra-coronal prosthesis [35, 93] providing retention and support [111, 127] to restore lost functions and esthetics. This problem is even greater when the restoration has to be placed on an endodontically treated tooth.[111]

A lot of skill in selecting the most appropriate material and technique is required, [129] as the strength demanded of such a foundation varies according to the amount of tooth structure lost, as well as its location. [127]

As a core-buildup has to support and preserve the residual tooth structure, as well as to offer sufficient resistance to displacement and retention of the final restoration, [93, 127] it should also possess adequate mechanical and physical properties, surely influencing its longevity in service.

Flexure strength (FS), flexural modulus (FM) as well as degree of conversion (DC) were among the most famous parameters used to determine the mechanical properties [44, 47, 51, 52, 64, 65, 74, 112] for restorative materials to be successful in service, with differences in these properties occurring according to type and composition of each material, as well as the type of bonds participating in its structure.

With increasing esthetic demands in restorative dentistry over the past few years, [3, 33, 79] tooth-colored restorative materials specifically formulated to restore esthetic dental defects, [3, 79] are nowadays preferred, even over traditionally famous non-esthetic restorative materials, for restoring badly damaged teeth, serving as cores. These materials possess mechanical and physical properties, making them suitable for both situations. [127]

Nowadays, four chemically different groups of alloplastic materials are used for this purpose, replacing traditional core-buildup materials, comprising glass ionomer cements (GIC), resin modified glass ionomer cements (RMGIC), compomers (Compo), and composite resins (CR). [36, 72, 127, 128] Therefore, it is of clinical interest to establish which of these materials are most suitable to form a base for the subsequent long term stable tooth-colored restoration.

2. General on tooth-colored core-buildup materials

2.1. Core-buildup materials

Due to increased esthetic demands in restorative dentistry during the past few years, [3, 6, 36, 127] the use of tooth-colored restorative materials has even been extended to the construction of cores, as a means of building-up badly broken-down teeth, [127] restoring lost resistance and retention, required for proper seating the future prosthesis. [111] These include composite resins, glass- ionomers, resin–modified glass ionomer formulations and polyacid modified composite resins.[8, 34]

2.1.1. Definition

Core- buildup materials are used for restoring badly broken down vital or non-vital teeth [35, 93, 111, 128] that are to be used as abutments [103, 127] under subsequent restorations [35, 93] trying to stabilize its weakened part, providing a foundation for the tooth, that allows the clinician to create a favorable retention and resistance form for the overlying prosthesis. [111]

2.1.2. Requirements of core- buildup materials

A material used for a core-buildup should possess satisfactory mechanical and physical properties, including compressive and flexural strength (FS), to resist intraoral forces which could result in core fracture or displacement during service. The materials used should also be biocompatible, easy to apply, with an ability to bond to tooth structure, and to pins or posts, if applied.[127] Core materials should be independently retentive, having a stable connection with the remaining tooth structure and properties similar to those of the tooth structure to be replaced.

These systems usually have a contrasting color to the tooth structure [6, 127], most commonly being blue-white, or opaque. [36]

2.1.3. Materials available for core-buildups

A core material could either be metallic, resinous or ceramic, being directly or indirectly constructed. Gold alloys and ceramics, which were placed as indirect core materials, and the directly placed amalgam, were the most common core materials used until relatively recently. Within the past few years, directly placed tooth-colored restorative materials, were introduced for use as core-buildups, as opposed to the most famous

metallic dental amalgam. These include resin composites, reinforced glass-ionomer cements, resin-modified glass-ionomers and compomers (polyacid-modified composites), providing the possibility of core-buildup and tooth preparation to be done in the same appointment. [36, 72, 127, 128]

Cores could be retained in place through several methods, including cavity modifications, as well as application of resin or cement bonding agents. Pins could also be used, either single or in combination. [128] In case of endodontically treated teeth, cores are either in cast forms as one unit with the post, or are built-up on ready-made posts seated in the root-canal.[111]

2.2. Composite resins (CR)

2.2.1. Composition and setting reaction

Resin composites are widely used in restorative dentistry, since their introduction in 1960, with several improvements undertaken since. [75] These materials are mainly composed of 3 components, the organic polymer matrix, the inorganic fillers, and the coupling agent (organosilane) that bonds the filler to the matrix. [6, 123]

The polymer matrices most commonly used are the highly viscous diacrylate resin matrices Bis-glycidyl dimethacrylate (Bis-GMA) or Urethane dimethacrylate (UDMA), [57, 76, 122] requiring the addition of a low molecular weight 'co-monomer' to dilute their viscosity, [57] with Methyl-methacrylate (MMA), Ethylene-dimethacrylate (EDMA), Triethylenegycol- dimethacrylate (TEGDMA) being the most commonly used diluents.

Improvements carried out since their introduction were mainly based on the development of new monomers, [11, 29] while for fillers, the developments concentrated on filler loading, particle size, silanization and on developing new filler particles. [59, 104] According to the type, size, shape, and distribution of its fillers, dental composites were classified into traditional macrofilled composites with larger glass filler particles, [36] microfilled resins introduced in the late 1970s containing colloidal silica particles ranging between 0.01-0.05 μm., followed by microfine particles (0.04-0.2 μm), fine particles (0.4-3 μm), and finally microhybrid blends of fine particles and some microfine particles. [36]

In regard to the setting reaction, it is via a free-radical addition polymerization process, [102, 122] chemically linking monomer units together, rendering high-molecular-weight molecules. [36]

2.2.2.   *Presentation and properties*

Early composites were introduced as two chemically–setting pastes, to be hand-mixed, with an activator, such as a tertiary amine in one paste, and an initiator, usually a benzoyl-peroxide (BPO) in the other. [57, 123] With the introduction of light-activated composites as a single paste in the early 1970s, the problems of chemically-cured systems, of increased air incorporation during mixing, and the inability to control working time of the mix were overcome, [6] allowing a controlled working time as well as less air incorporation into the mix, with less resultant discoloration and increased strength of the material. [6] At the beginning, these were ultra-violet (UV) - activated, to be   replaced by visible light-cured (VLC) types, in 1976 [43, 102, 123], with camphorquione (CQ) being the most commonly used photo-initiator, having an absorption maximum of around 470 nm. [57] Dual-cured resins, formed of two light-curable pastes were then introduced, with a combination of both chemically and visible light-curing components to overcome the problems of limited curing depths, as these composite resins set by light as well as a chemical reaction. [6] To ensure complete polymerization of composites, and to reduce the inherently occurring polymerization-shrinkage, [1, 6, 108] they are to be incrementally placed, [36, 93] except for specifically light-activated core composites, offering depths of cure up to 8 mm, [127] or indirectly constructed inlays. [6]

Composite core materials are often two-paste chemically-cured systems, designed for bulk placement, [36, 93] as well as light - cured and dual - cured products, [36] usually having a contrasting color to the tooth structure. [6, 127]

For tooth-colored restorative materials being placed directly into the cavity, [6, 36] they also show chemical bonding to the tooth structure by the use of bonding agents under provided moisture control. Additionally the rapid command set of the material allows immediate tooth preparation for the fitting of a crown, therefore saving time.[34, 93, 127] Due to their high mechanical properties, including tensile and flexure strengths, [35, 70] their acceptance as a core-buildup restorative material has increased tremendously.[93]

Unfortunately, these materials are not easy to handle, displaying technique sensitivity and therefore being more time consuming, due to their incremental placement technique, [6, 76] as well as inadequate degree of conversion (DC) and inherent polymerization-shrinkage, [116] with a resulting breakdown at the interface and consequent gap formation with microleakage. [93] The huge potential for water-uptake and the high coefficient of thermal expansion are other shortcomings of these materials. [127]

2.3. Glass-ionomer cements (GIC)

Glass-ionomer cements (GIC), also known as glass-polyalkenoate cements, were introduced by Wilson and Kent in 1971. [123]

2.3.1. Composition and setting reaction

Glass-ionomer cements are formed mainly of an inorganic fluoroaluminosilicate (FAS) glass powder, the polyacid, water and tartaric acid, [57, 123] with an acid-base reaction taking place upon mixing to form the set cement. [122] Its slowly developed final structure [36] consists of unreacted glass particles, each of which is surrounded by silica gel, embedded in a matrix of cross-linked polyacrylic acid, [53, 123] showing increasing properties with the progress of the setting reaction.[99]

2.3.2. Presentation and properties

Glass-ionomer cements are available in 3 formulations, namely the traditional powder/liquid systems with the polyacid in an aqueous solution, the anhydrous systems formed of a freeze-dried acid incorporated in the powder, and finally the encapsulated versions. [123]

All commercial glass-ionomers have been categorized as either conventional glass-ionomer cements or resin-modified glass-ionomers (RMGIs), [131] to be used mainly for the restoration of abrasion/erosion lesions and as luting agents for crown and bridge restorations. [123]

Glass-ionomer cements possess several unique properties, including their ability to bond to tooth structure, their anticariogenic property due to Fluoride-release, thermal compatibility due to their coefficient of thermal conductivity being similar to tooth structure, their biocompatibility, [133] as well as their translucency. [6] Due to the lower shrinkage with acid-base–mediated cross-linking reactions in case of glass-ionomer cements, better bond strength and retention in low-stress areas [6, 36] is

achieved, as compared to composite resins, which show higher polymerization-stresses.[123]

On the other hand, traditional glass-ionomers show mechanical properties, being much more unfavorable than those of other restorative materials, such as their brittle nature with minimal deformation when subjected to force fracturing, [57, 84, 93, 129] restricting their use to low-stress sites. [57, 133] Also, the short available working time and long setting time of glass-ionomers, as well as their relative brittleness, cracking easily on desiccation, and their poor resistance to acid attack, add to their major disadvantages. [123, 129]

2.4. Metal-modified glass ionomers (MMGI)

2.4.1. Composition and setting reaction

As an attempt to reinforce glass-ionomer cements, and to render them sufficiently radiopaque as well, [123] silver-tin metal alloys were either physically incorporated with glass powder, resulting in a silver alloy admix, or were sintered with glass, producing a glass cermet material. [6, 93] The idea of the silver cermet was to increase the toughness of the material, by acting as a stress-absorber, to improve its wear characteristics, and to render the restoration sufficiently opaque.[123] Regarding their setting reaction, it is by the conventional acid-base reaction known for glass-ionomers.[6, 36, 123]

2.4.2. Presentation and properties

An incorporation of metallic fillers, as admixed types or cermets, in the form of capsules, have provided no advantages over conventional glass-ionomers, [6, 87, 123, 127] limiting their use as core-buildups to situations where the cement constitutes less than 40% of the total remaining tooth structure.[6, 7]

These products have also shown poor adhesion to tooth structure, [127] initially releasing appreciable amounts of fluoride (F), with a decrease over time. A lower F amount is released from the cermet cement, because a portion of the glass particle is metal-coated.[6]

2.5. Resin-modified glass-ionomers (RMGI):

2.5.1. Composition and setting reaction

A modification of glass-ionomer cement by the incorporation of polymerizable functional groups, in the product known as resin-modified glass-ionomer, was undertaken recently. These products are hybrids between conventional glass-ionomers and chemically- or light-cured resin restorations, [79, 93] typically consisting of a powder similar to that of glass-ionomers, [36] a chemically- or light-curable monomer in the liquid, such as hydroxyethylmethacrylate (HEMA), an ion-leachable glass, and water. [67, 89] As some of the water in resin-modified glass-ionomer system has been replaced by HEMA, the initial setting of these materials is due to the free radical addition polymerization of HEMA. [131] Subsequently, the acid-base reaction typical of conventional glass-ionomer takes place, [89] serving to harden and strengthen the already created polymer matrix, [131] allowing a considerable working time, with ease of manipulation and maintained fluoride-release [123]. Chemical bonding to tooth structure without a bonding agent is maintained as well. [36] Finally, a metal polyacrylate salt matrix as well as a polymer matrix is formed. [131]

2.5.2. Presentation and properties

Resin-modified glass-ionomers are presented in powder/liquid (P/L) form for hand mixing, or in the form of capsules to be mixed mechanically. [36] Depending on the formulation of the material, and P/L ratios, resin-modified glass-ionomers may be used as liners, fissure sealants, bases, core-buildups, restoratives as well as for several other purposes. [6]

These hybrid ionomers set rapidly, after chemical- or light initiation, allowing for an immediate finishing of the restoration [36] with better mechanical properties. [6, 36, 84, 131] Also, improved resistance to desiccation and acid attack is obvious, [78, 92] compared to conventional glass-ionomer cements. Its coefficient of thermal expansion and contraction is close to ideal, minimizing the microleakage typical of conventional glass-ionomers. [123]

However, their greater degree of shrinkage upon polymerization compared to conventional glass-ionomers, [6] their lower rigidity compared to that of composites, [20] and a strength being lower than that of the tooth structure, hybrid ionomers should

only be used as fillers.[28, 127] Resin-modified glass-ionomers also lacked translucency. [131]

Additionally, due to the presence of the hydrophilic HEMA in the formulation, resin-modified glass-ionomers absorb water easily, [24] with accompanying degradation. [67] Also, a retardation of the acid-base reaction [89] and a reduced ability to wet the tooth structure with increased microleakage and less ionic activity were noticed, [6] due to the reduced carboxylic acid and water quantity in the liquid. [6, 36, 123]

2.6. Polyacid-modified composite resins (Compomers)

These were introduced in 1995, [36] also referred to as compomers (Compo).

2.6.1. Composition and setting reaction

Compomers are composed of fluoroaluminosilicate (FAS) glass particles and a polyacid-modified monomer without any water [6, 123] Compomers have a volume filler % ranging from 42-67% [36] with their glass particles partially silanized, and its matrix being formed mainly during the light activation, through a free-radical polymerization reaction of its monomers, [82] being the driving force for the setting process of these materials. The acid-base reaction that also takes place provides further cross-linking to the matrix, ionic diffusion, [25, 82] and a slow but continuous fluoride-release. [123]

2.6.2. Presentation and properties

Compomers are usually packaged as single paste formulations in compules and syringes for restorative applications, protecting them from humidity, and facilitating their application. [6, 36] They show the fluoride-releasing capability of conventional glass-ionomers, the structure, physical properties, durability and improved handling, as well as esthetic properties of composites. [3, 6, 57] These properties have made them suitable for applications in class V cavities in permanent teeth and as filling materials in primary dentition [115] resembling popular alternatives to glass-ionomers and resin-modified glass-ionomers. [123]

In contrast to the slow rate of water-uptake shown by composites, compomers show a more rapid rate of water sorption, provided by its hydrophilic resin matrix. [6, 36, 123] The rapid water sorption helps a rapid compensation for polymerization-shrinkage of the resin matrix, with a reduction of marginal gapping. [123]

Compomers show mechanical properties being somewhat inferior to those of composite resins, but better than those of glass-ionomer and resin-modified glass-ionomer cements, which show a higher Fluoride-release. An excessive hygroscopic expansion was also recorded for compomers. [123] Because of the absence of water in the formulation of compomers, the cement is not self-adhesive, requiring an adhesive to bond to the tooth structure. [6, 123]

2.7. Testing the mechanical properties of tooth-colored restorative materials

The fracture-related material properties under stress have usually been evaluated by choosing the material parameters flexure strength (FS), flexural modulus (FM) and fracture toughness (FT), [36] where for brittle materials, flexural tests are preferred to other mechanical tests. This is because these properties more closely simulate the stress distribution in the restoration during service.[6]

Flexural strength of a material represents the maximum stress it withstands before failure when subjected to bending loads [113], whereas the elastic modulus of a material describes its stiffness. This is measured by the slope of the elastic portion of the stress-strain curve, [6] as the interatomic and intermolecular forces of the material are responsible for its elastic properties. [36] Early achievement of high physical-mechanical performance of a restoration minimizes the possibility of early damage, [99] since the greatest increase in strength or in shrinkage occurs at the time of polymerization. [137]

2.8. Degree of conversion (DC) and its measurement

Degree of conversion (DC) is a measure of the percentage of methacrylate double bonds converted to single bonds during formation of a polymeric resin. [6, 36] It was proven to play an important role in determining the ultimate success of the restorative, as it affects several properties of the resin system [44, 47, 51, 52, 64, 65, 74, 112], such as flexural properties, solubility, dimensional and color stability as well as their biocompatibility. [114] Due to the positive correlation found to exist between the increased conversion and the improved mechanical properties of dental resins, their degree of cure was indirectly evaluated by means of measuring the mechanical properties of resin materials.[44] However, no correlation between DC and the

diametral tensile strength, compressive strength, hardness, or fracture toughness of composite resin materials was detected. [30, 31, 48]

Several authors proved a correlation between DC and mechanical properties to be dependent on the material, and further being significantly influenced by variables of depth from the surface, light source and energy level. [15, 31, 44, 136]

Moreover, Ferracane [44] has stated that the mechanical properties of resins proved to be much dependent upon network formation, which is not equivalent to the DC of these materials. [31, 44, 52]

Besides the beneficial effects of higher DC, it also results in larger amounts of polymerization-shrinkage in materials based on resin/filler systems.[43]

Several techniques have been used to determine the DC of resins, with the Fourier Transformation Infra Red Spectroscopy (FTIR) being widely used as a reliable method, detecting the carbon double-bond stretching vibrations directly before and after curing of the material. [41, 75, 105] The FTIR spectroscopy is based on the fact that molecules absorb electromagnetic radiation in the IR region (750 nm to 0.5 nm), triggering vibrations and rotations in the system.[32, 130] The attenuated total reflection (ATR) FTIR type of spectroscopy, utilizes the physical phenomena of light reflection at an interface of two media of different refractive indices. [130] The % DC of each material is determined from the ratio of the absorbance intensities of C=C aliphatic peak (at 1638 cm^{-1}) / C..C aromatic ring peak (at 1608 cm^{-1}) before and after curing [30, 38, 105, 118] , as shown in the following equation:

DC% = 100 x [1-R polymerized / R unpolymerized]

Where R represents the rates between peak heights, representing recorded aliphatic: aromatic ratio of the individual samples. [6, 36, 42]

3. Review of the Literature

Effects of different storage conditions and various factors related to type of material and composition on flexural properties as well as DC of tooth-colored core-buildup materials:

3.1. Flexure Strength (FS)

3.1.1. *Effect of storage environment and storage time on Flexure Strength*

The storage environment significantly influences FS of tooth-colored restorative materials. The composite resins, glass-ionomers, resin-modified glass-ionomers, compomers tested, have shown a higher dry strength compared to their wet ones, with most of conventional glass-ionomers, metal-modified glass-ionomers and resin-modified glass-ionomers tested, showing little decrease in their FS and softer surfaces after aging in distilled water . [13, 18, 23-26, 46, 62, 63, 82-84, 86, 96]

Flexural strength of various glass-ionomer cements (luting, esthetic, reinforced cements and liners or bases) are lower compared to those of amalgams or composite resins. Compared to conventional glass-ionomers and cermets tested after 24 h or 1w storage in distilled water, resin-modified glass-ionomers show higher dry and wet FS, and more water sensitivity, absorbing higher amounts of water during the first 24 h. [24, 26, 84, 121, 133]

Light-cured microfilled composite resins show a reduction in FS with time of wet storage, and Dyract, the compomer tested, shows a decline from its peak in FS with time of storage in artificial saliva. On the other hand, all resin-modified glass-ionomer cements and conventional glass-ionomer cements tested show an increase in FS with maturation in distilled water, with the values for resin-modified glass-ionomers being higher than for conventional glass-ionomers. [18, 62, 67, 86]

Flexural strength of conventional glass-ionomers and resin-modified glass-ionomer specimens (Vitremer) either stored in an acidic medium (Coca-Cola) or in neutral media, were not significantly different. In contrast to this, storage of specimens in acidic beverages (orange and apple juices), has resulted in the loss of strength, with the conventional glass-ionomers undergoing severe erosion. Also, FS of glass-ionomers and

the compomer tested were lower when stored in artificial saliva than when stored in saturated water vapor. [81, 86]

Compared to resin-modified glass-ionomers and microfilled composite resins, compomers (inclusive Dyract and Compoglass) show higher flexural properties when tested dry, immediately after light activation, as well as after 1w water storage. [63]

Flexural strength of composite resins tested, shows a great sensitivity to increased testing conditions (temperature and cross-head speed) with significant softening and a small decline in FS under wet immersion at different temperatures (12, 24 and 37°C), with the visible light-cured composite resin showing limited variation. On the other hand, FS of composite resins was unaffected by preparation temperatures, or thermocycling, with differences occurring as a function of material. The hybrid, packable and flowable composite resins tested, perform well before as well as after thermocycling, with the packable composite resin showing highest FS values. [66, 76, 85, 124, 126]

A positive effect of water storage on FS and mechanical properties of glass-ionomer, resin-modified glass-ionomer and composite resin tested is also noticed, with glass-ionomers showing a slow rise in FS with maturation within the first 24 h, maintaining a constant value afterwards, with no effect of storage time on the properties. Resin-modified glass-ionomers have shown higher FS values compared to conventional glass-ionomers with maturation in distilled water. The flowable and hybrid composite resin show a significant increase in FS after 24 h water storage, but a decrease in strength was obvious for the microfilled composites, revealing the lowest FS besides other mechanical properties, when tested after (7d) storage in water at 37°C. [2, 18, 62, 67, 98]

Other authors are of the opinion, that storage environment has no effect on FS of glass-ionomers, resin-modified glass-ionomers, and composite resins, showing similar values when either stored in dry air with 22% relative humidity (RH), water vapor with 100 % relative humidity (RH), and artificial saliva or in distilled water, while storage time had an effect on their FS. [2, 53, 67, 81, 86]

Regarding setting and storage times, some authors were of the opinion, that these properties influence the mechanical performance of composite resins, compomers and glass-ionomers tested, with the FS of glass-ionomers being lower than those of self-

cured composite resins and compomers [2, 53, 67, 81, 103], or having little or no influence on the mechanical properties of materials tested. [24, 25, 27, 35, 46, 82-84, 99, 121]

Little influence of long term aging on composite resins is proven, only showing limited degradation and increased water sorption, with visible light-cured composite resins being significantly stronger than chemically-cured types, and Ketac Silver, the metal-modified glass-ionomer, being the weakest. [120] Light-cured glass-ionomers and polyacid-modified composites (Compo) tested, have shown similar FS values throughout their storage in water for different time periods (1d, 1w, 2w, 1 mth, 2 mths), with their values being inferior to those of composite resins tested. [120]

The compomers (Dyract AP and Compoglass F), a conventional glass-ionomer cement (Ketac Molar) and a self-cured composite resin tested show an increase in their FS at the times between 15 minutes and 24 h, of storage in distilled water for different time periods. [103] Compomers have shown significantly higher FS values compared to light-cured glass-ionomers after 1 d and 6 mths, but not after 1 year of water storage, with the conventional glass-ionomers showing lowest values. [121] It was also stated that the FS of the compomer tested (Dyract) sharply declines from its 1 mth peak after storage in artificial saliva (AS) for different time periods. [86, 103, 121]

Flexural strength of metal-modified glass-ionomer materials tested have shown a significant increase after water storage for 1 w, staying unchanged after 1 mth. The FS values of metal-modified glass-ionomers were not significantly affected by a changing storage environment, (distilled water or artificial saliva) for different time periods, maintaining their early strength over extended storage periods. [6] Also, prolonged aging in water of commercial glass-ionomers of types I, II, and III tested, resulted neither in a continuous increase nor a decrease in FS. However, most of them have kept rather constant mechanical strengths, with records of 24 h and 12 mths usually being similar. [6, 27]

As composite resins have shown higher FS compared to resin-modified glass-ionomers, compomers and conventional glass-ionomers, which have all shown similar values, [12, 72, 103, 120] composite resins turned out to be more suitable as a core material for the restoration of mutilated posterior as well as for anterior teeth. [18, 26, 132]

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All types of current glass-ionomers (conventional-, resin-modified-, metal-modified-glass-ionomers, and Cermets) are proven unsuitable as core-buildups for anterior or posterior teeth, and should only be used as fillers for defect elimination, being limited to areas subject to low stresses [82, 132], whereas the mechanical properties of light-cured glass-ionomers could be suitable for core foundations. [72, 82, 132]

3.1.2. Effect of composition on Flexure Strength

The existence of an important relationship between the composition, microstructure and mechanical properties of glass-ionomers (filling cermets, resin-modified glass-ionomers, base cements and filling cements) and composite resins has been proven. [10, 18, 47, 59, 62, 125, 133, 138]

Metal or resin addition to glass-ionomer cements tested, had little or no effect on their strength, as metal-modified glass-ionomers were only significantly stronger than resin-modified glass-ionomer cements at 7d of wet storage, with no significant differences between the conventional glass-ionomer, metal-modified glass-ionomer, or resin-modified glass-ionomer materials at any other time. [13, 87, 95, 119]

An increased FS of experimental composite resins was achieved by replacing bisphenol-A-glycidyl methacrylate (Bis-GMA) or TEGDMA by urethane dimethacrylate (UDMA), whilst replacing Bis-GMA with TEGDMA has resulted in a reduction of the FS of experimental composite resins stored in water for 1 w. [10]

Increased inhibitor, initiator and activator concentrations have negatively affected FS of composite resins tested after storage in water for 24h, obtaining its highest FS with a 2.5 wt% initiator and 1 wt % activator concentration. [47, 125]

The FS of composite resin has been proven to generally increase with the degree of cure, to a lesser extent with increased filler volume, and the percentage of silane-treated fillers. [46, 59, 69, 138] Also, filler silanization, shape and loading are proven to be determining factors for materials' strength, with higher filler volume amount and filler silanization being associated with increased strength of the experimental composite resin tested. Also, composite resin containing stronger and more porous fillers has shown better FS values. [46, 138]

Glass-ionomer materials based on polyacrylic acid alone have shown a more rapid rise and higher FS values as compared to materials based on polymaleic/polyacrylic acid copolymers (Ketac Fil and Ketac Silver), which have a slower increase in FS over 24h

after mixing, keeping a relatively constant value for up to 3 mths of water storage. [6, 98]

The results of the storage environment, time and composition on FS of tooth-colored restorative materials are summarized in the following table. (Table 3.1)

Tab. 3.1 Investigations on flexure strength of tooth-colored restorative materials after different storage periods and conditions

Materials Tested	Test Method	Results	Authors
GI, Compo, CR	3-point bending	CR showed higher FS compared to RMGI, Compo and conventional GI, showing similar values	12, 72, 103, 120
Experimental CR	3-point bending	Higher FS was achieved by replacing Bis GMA or TEGDMA by UDMA	10, 19
GI	Biaxial and 4-point flexure	GI show slower rise in FS within the first 24h of water storage maintaining a constant value afterwards.	6, 98
GI, CR	4-point flexure	Dry FS values for different GI-based materials and CR are higher than wet values, with storage time having no effect on FS of CR.	13, 23
GI, Compo, CR	3-point bending	Storage time had little influence on the mechanical properties and FS of GI, Compo and CR investigated.	24, 25, 27, 35, 46, 82-84, 99, 121
Compo, RMGIC, CR	3-point bending	Storage environment has influenced FS of tested materials, with the dry strength being higher than wet values	18, 24-26, 46, 62, 63, 82, 86, 96
CR	3-point bending	FS of CR generally increases with degree of cure, increased filler volume, % of silane treated fillers.	46, 59, 69, 138
Experimental CR	3-point bending	Increased inhibitor, initiator and activator concentrations resulted in a decreased FS of CR	47, 125
GI, CR	Biaxial and 4-point flexure	Storage environment had no effect on FS of RMGIC, GI and CR tested, while storage time reveals an effect.	53, 67, 81
GI	3-point bending	RMGIC showed higher dry and wet FS compared to conventional GI.	84, 121, 133
CR, Compo, GI	3-point bending	Setting time influenced mechanical properties of CR, Compo and GIs investigated	103
GI	3-point bending	No improvement of mechanical properties of GI due to addition of metal particles.	87, 95, 119
Experimental CR	3-point bending	With 2.5 wt% initiator and 1 wt % activator concentrations, the highest FS could be obtained.	125
CR	3-point bending	FS of CR were unaffected by preparation temperatures or thermocycling, with differences occurring as function of material, showing great sensitivity to testing conditions of temperature and cross-head speed.	66, 76, 85, 124, 126
GI, CR	3-point bending	Important relationship exists between composition, microstructure and mechanical properties of GI and CR	10, 18, 47, 59, 62, 125, 133, 138
Experimental CR	3-point bending	Stronger and more porous fillers have a significant positive effect on FS.	138
GI	4-point flexure	GI based on polymaleic/polyacrylic acid show lower FS than those based on polyacrylic acid alone.	98

Abbreviations: **FS**= Flexure strength, **CR**= Composite resin, **GIC**= Glass ionomer cement, **Conv GIC**= Conventional glass-ionomer cement, **RMGI** = Resin-modified Glass- ionomer, **Compo**= Compomer (Polyacid-modified composite resin), **Bis-GMA**= Bis-glycidyl- dimethacrylate, **UDMA**= Urethane dimethacrylate, **TEGDMA**= Triethylenegycol - dimethacrylate.

3.2. Flexural Modulus (FM)

3.2.1. Effect of storage environment and storage time on Flexural Modulus

The storage environment influences FM of tooth-colored restorative materials tested. Conventional glass-ionomers, resin-modified glass-ionomers, composite resins, compomers under investigation have shown higher dry strength values compared to samples stored in water, or those dried after storage in water. The FM of conventional glass-ionomer cement and resin-modified glass-ionomer proved to be more affected in comparison with CR, which has shown significant softening. [18, 24, 25, 46, 82, 86, 96, 124]

Composite resin materials showed higher FM values compared to those of resin-modified glass-ionomer cements, compomers and conventional glass-ionomers, showing similar values. The resin-modified glass-ionomer cement tested showed higher dry, (30 min after mixing) as well as wet FM values, compared to conventional glass-ionomers tested after storage in distilled water for different time periods (24h and 3 mths). [12, 84]

It is proven, that the type of composite resin is a determining factor in the materials performance in a wet environment, as flowable and hybrid composite resins have shown a significant increase in FM after 24h water storage , whilst microfilled composite resins have shown the lowest values after 7d aging in water. [18, 62]

It was also stated that FM of composite resins proved to be unaffected by preparation temperatures, nor to be significantly changed by thermocycling. [66, 126] However, they proved to be highly influenced by testing conditions of temperature and cross-head speed. [85] Similar FM values were shown when prepared under temperatures either simulating intraoral or ambient laboratory conditions, with differences having only occurred as function of the material tested. [85] Visible light-cured (VLC) composite resin tested has shown a marked decline in FM when the temperature and cross-head speed were increased, whilst by solely increasing the cross-head speed, a steady increase in FM at all temperatures was noticed, except at 0°C, as the specimens were stored for 7d in artificial saliva at temperatures of 12, 24, and 37°C. [66, 76, 85, 126]

The compomer tested has shown a slight decline in its FM when stored in dry air with 22% relative humidity, saturated water vapor with 100% relative humidity, or in artificial saliva for different storage periods, whilst that of composite resin and glass-

ionomer were relatively stable, showing higher dry, as well as wet FM values, compared to resin-modified glass-ionomers and microfilled composite resins. [46, 63, 86]

The storage time has influenced FM of the glass-ionomer, composite resin and compomer tested, increasing with time of storage, either being dry or wet (in distilled water) for longer periods. The FM of visible light-cured, a chemically-cured composite resin and a metal-modified glass-ionomer have shown less difference throughout all storage periods, whilst compomers and resins-modified glass-ionomers tested have shown significantly higher FM values when aged in (distilled) water for longer periods compared to those aged for shorter periods. [25, 35]

Other authors were of the opinion that wet storage (in artificial saliva) for longer periods has negatively affected FM of Dyract, the compomer tested, resulting in a slight decline from its 1 mth peak, whilst that of composite resin and glass-ionomer were relatively stable. [46, 86]

3.2.2. *Effect of composition on Flexural Modulus*
With increasing initiator and activator concentrations, a decrease in FM was noticed, whilst with 1 wt% initiator and activator concentrations, the highest value of FM was reached. [47, 125]

Also, filler shape, loading and silanization have influenced the mechanical properties of composite resins tested, after being stored in distilled water for 24h, showing higher FM with silanized fillers incorporated, compared to composites with unsilanized fillers and with a higher filler volume percentage. [59, 69]

On the other hand, replacing Bis GMA or TEGDMA by UDMA has increased the FM of experimental composite resins tested after storage in water for 1w. [10]

Regarding the types of composite resin, nanofilled types have shown a higher FM compared to hybrid and microfilled types, except for one which was tested after 7d of water storage. [18]

The results of storage environment, time and composition on flexure modulus of tooth-colored restorative materials are summarized in the following table.(Table 3.2)

Tab. 3.2 Investigations on flexural modulus of tooth-colored restorative materials after different storage periods and conditions

Materials Tested	Test Method	Results	Authors
GI, Compo, CR	3-point bending	CR show FM higher to that of RMGIC and Compo, which show FM similar to conventional GIC	12, 84
Experimental CR	3-point bending	Replacing Bis GMA or TEGDMA by UDMA increased FM.	10, 19
Compo, RMGI, GI, CR	3-point bending	Storage environment has influenced FM of materials tested, showing higher dry strength values.	18, 24, 25, 46, 82, 86, 96, 124
Compo, GI, CR	3-point bending	Storage time, has influenced FM of the materials tested, showing an increase with time.	25, 35
Experimental CR	3-point bending	Increased inhibitor, activator and initiator concentration decreased the FM of CR.	47, 125
Experimental CR	3-point bending	Filler silanization is a determining factor for a higher FM of CR.	59
CR	3-point bending	Type of CR determines the materials performance in wet environment.	18, 62
CR, RMGI, Compo	3-point bending	Compomers have shown higher dry as well as wet FM compared to RMGI and microfilled CR	63
CR	3-point bending	Filler shape, loading and silanization influenced mechanical properties of CR	59, 69
CR, Ormocers	3-point bending	FM of CR is unaffected by preparation temperatures, or thermocycling, with differences occurring as function of material, showing high sensitivity to testing conditions of temperature and cross-head speed.	66, 76, 85, 126
CR, Compo, GI	3-point bending	Longer storage time resulted in a slight decline in FM of Compo from its peak, while that of CR and GI has been relatively stable.	46, 86
Experimental CR	3-point bending	With 1 wt% initiator and activator concentrations, the highest value of FM was reached.	125
Experimental CR	3-point bending	No difference in FM between composites with porous and non-porous fillers.	138

Abbreviations: FM= Flexure Modulus, **CR**= Composite Resin, **GIC**= Glass-Ionomer Cement, **Compo**= Compomer, **Bis-GMA**= Bis-glycidyl-methacrylate, **UDMA**= Urethane dimethacrylate, **TEGDMA** = Triethylene-gycol - dimethacrylate.

3.3. Material and Degree of Conversion (DC)

A positive correlation was found to exist between the increased conversion and the improved mechanical properties of dental resins. [44, 47, 51, 52, 64, 65, 74, 112]

3.3.1. Effect of storage environment and storage time on Degree of Conversion

Storage in different drinks, such as sports drink, yoghurt, and soft drinks based on cola and red wine or in distilled water, for different time periods, had no effect on the degree of conversion (DC) of composite resin materials tested. [75]

3.3.2. *Effect of composition and curing mode on Degree of Conversion*

Several factors, such as resin composition, light transmission through the material, concentration of sensitizer, initiator and inhibitor affected the monomer to polymer conversion. Additionally, curing time, power of the curing unit as well as changing the baseline technique played a significant role in the degree of monomer conversion of composite resins. [6, 46, 47, 61, 94, 97, 105, 112, 117, 123, 125, 136] Also, the type of composite polymerization, time of testing and the curing style applied significantly influenced the DC of composite resin materials. Whereas different curing modes did not result in conversion differences, as long as the same monomer formulations and adequate light-curing was employed, [6, 51] depending for optimal conversion on the monomer composition.[106] It was stated that dual-cured composite resins have shown higher values of monomer conversion when tested after 24h, than when tested immediately, while that of light-cured composite resins was not significantly affected by the testing time, [97] where the DC at 24h could be referred to as the maximum DC, showing an approximately linear increase with time through 24h, with no further increase at 48h. [44]

A higher DC was noticed with higher diluents (e.g. TEGDMA), initiator and activator concentrations in dental resins, as well as lower inhibitor and filler concentrations, less filler silanization, lighter shades and longer irradiation. [46, 47, 55, 61, 93, 117, 125, 136, 138] It was also proven, that the use of multifunctional monomers having more than two reactive double bonds per molecule allows higher reaction rates with more cross-links, but reduced DC. [5]

Increased TEGDMA amounts in Bis-GMA/ TEGDMA mixtures have shown higher polymerization rates due to the higher accelerating and plasticizing effect of TEGDMA on Bis-GMA compared to UDMA and Bis-EMA, [112] whereas UEDMA-based resins were declared to be even more reactive than Bis-GMA-based resins. [42]

Moreover, longer irradiation resulted in higher DC due to improved mobility of reactive groups during curing, allowing for enhanced diffusion of reactive groups. [51, 61] However, as the polymerization of composite resins further continues at slower rates after exposure, a termination point at approximately one day is reached, with no further significant increase of the final degree of conversion with extended exposure time. [71, 138] That is because the diffusion rates of the propagating free radicals, the unreacted dimethacrylate molecules and the pendant methacrylate groups are reduced as the

polymerization reaction proceeds. [50] Most probably a decay of the radicals is the main cause for the great loss in the post-curing efficiency of the remaining unpolymerized bonds observed 24h after irradiation. [41]

Actually, TEGDMA is considered to be the main contributor to post-irradiation of polymerization of Bis-GMA based composites, with higher amounts of TEGDMA resulting in increased DC, however being accompanied by a decrease in post-irradiation polymerization. [118] Contribution of TEGDMA is most probably related to its chemical nature, specifically its ether linkages and the lack of hydroxyl groups, as well as its lower molecular weight being about half that of Bis-GMA, rendering the molecule more flexible, of lower viscosity and thus significantly higher DC. [31, 118]

It was also declared that different amounts of residual methacrylate groups in polymerized materials were related to different resin formulations, and that an increased TEGDMA content in the mixture resulted in decreased amounts of TEGDMA molecules remaining unreacted during post-irradiation. [107, 118]

Regarding the filler content, it is assumed that the filler concentration and the nature of bonding between filler particles and resinous matrix play an important role in determining the properties of dental composites. [30, 31] Halvorson et al [55] have stated that the conversion progressively decreased with increased filler loading, independent of the filler being silane-treated or not, with the suggestion, that most of the methacrylate functionality within the silane layer is in a non-reactive environment. Several authors have proven flowable composite resins to demonstrate higher DC than universal types, followed by packable composites, at a 1 mm distance from the surface. [46, 61, 117, 136, 138]

The higher the filler fraction and the smaller the particle size, the lower the stability of the radicals, denoting a catalytic effect of the filler surface on the decomposition of radicals, the effect being reduced by silane-treatment of the fillers. [22]

Ferracane et al [49] had proven that DC showed a tendency to increase when the volume of silane treated fillers was reduced, being in accordance with the opinion that composite resins showed higher DC with lower filler volume amount, less silanization, and lighter shades. [46, 61, 117, 136, 138]

Depth of cure and hardness of composite resins tested, extended with increased inorganic loading, [41] As long as the selected light-curable dental composite resin of a

certain thickness receives a fixed light energy amount, the same degree of cure is produced independent of light-irradiance. [43, 108, 136] Additionally, it was affirmed, that the chemistry of photo-initiator and co-initiators incorporated, markedly influenced the light transmission and DC of experimental composite resins. [94, 117]

On the other hand, Luiz et al [75]denied any change in DC at different specimen depths, and significant differences being only observed either when materials compared or when top and bottom surfaces of single specimens were studied. [43]

Investigations undertaken on the DC of tooth-colored restorative materials are summarized in the following table (Table 3.3).

Tab. 3.3 Investigations on Degree of Conversion of tooth-colored restorative materials

Materials tested	Test Method	Results	Authors
Experimental CR	FTIR Spectroscopy	Higher diluents, initiator, activator and lower inhibitor concentrations, resulted in higher DC, with highest values obtained with 2.5 wt% of initiator and activator concentrations.	47, 61, 94, 125
Experimental CR	FTIR Spectroscopy	Type, amount and silanization of fillers as well as shade of composites significantly affected DC of CR tested, showing higher DC with lower filler volume amount, less silanization, and lighter shades.	46, 61, 117, 136, 138
CR	Raman Spectroscopy	Storage environment had no effect on DC of CR with any detectable change in DC at different specimen depths.	75
CR	FTIR Specroscopy	Variation of light source, type of composite polymerization, time of testing and curing style affected DC of CR.	9, 97
CR	FTIR Spectroscopy	DC CR have shown higher DC compared to LC CR when tested after passage of 24h, proving to be significantly more influenced by testing time.	97
CR	FTIR Spectroscopy	Monomer conversion was highly influenced by changing baseline techniques applied for interpretation of IR-graphs.	105
CR	FTIR Spectroscopy	Curing depth, LCU and light energy applied, significantly affect DC of CR.	94, 117, 136
CR	FTIR Spectroscopy	No difference in DC between chemically-activated and light-activated composites of the same monomer formulations with adequate light-curing.	6, 51
CR	FTIR Spectroscopy	Optimal conversion in chemically and light-activated composites depends on their monomer composition.	106
CR	FTIR Spectroscopy	Lacking hydroxyl groups in side-chains of molecular structure results in lower viscosity of the material and higher DC.	31
CR	FTIR Spectroscopy	Filler silanization reduces catalytic effect of filler surfaces on the decomposition of radicals.	22
CR		The use of multifunctional monomers, allows higher reaction rates with more cross-links, but reduced DC.	5
CR	MIR Spectroscopy	Increased aromatic monomer concentration, results in increased amount of unreacted methacrylate groups.	107
CR	FTIR Spectroscopy	Higher TEGDMA amounts increase DC but result in less post-irradiation polymerization.	61, 118
CR	FTIR Spectroscopy	Same degree of cure results, if a fixed light energy amount is received, being independent of light irradiance.	43, 108, 136
CR	FTIR Spectroscopy	DC increases by post-curing'' dark-cure''	44, 56, 73, 118, 138

Abbreviations: **CR**= Composite resin, **FTIR**= Fourier transform infrared spectroscopy, **DC**= Degree of conversion, **LCU**= Light-curing unit**, IR**= Infrared, **TEGDMA** = Triethyleneglycol - dimethacrylate.

4. Aim of the Study

The following study aimed to test 4 hypotheses:

The first hypothesis was that material types as well as storage condition have no influence on the flexural properties of 4 different groups of tooth-colored filling materials, tested in a 3-point bending test following storage for different time periods under different storage conditions.

The second hypothesis tested was that for 4 dual-cured materials, no difference in flexural properties exists within the same material when either dual-cured or when tested after omission of the light-curing step.

The third hypothesis tested was the absence of any correlation between the degree of conversion and the flexural properties of 7 composite resins investigated.

And finally, the hypothesis that storage conditions have no influence on the degree of conversion of the composite resins investigated was tested.

5. Materials and Methods

5.1. Test conditions

All tests were conducted under ambient laboratory conditions at 50 % relative humidity and a room temperature of $23 \pm 1°C$. All materials were used according to their manufacturers' instructions.

5.2. Materials

5.2.1. *Flexure Strength and Flexural Modulus*

Fourteen different materials comprising the following material groups were investigated in this study:

1) Glass-Ionomers (GI)　　　　a- conventional glass –ionomers (GI)

　　　　　　　　　　　　　　　b- metal-modified glass-ionomers (mmGI)

2) Resin-modified glass-ionomers (RMGI)

3) Composite resins　　　　a- self-cured (SC)

　　　　　　　　　　　　　　b- light-cured (LC)

　　　　　　　　　　　　　　c- dual-cured (DC)

4) Polyacid-modified composite resins (Compomers)

Table 5.1 represents the materials under investigation.

Tab. 5.1 Materials under investigation

Nº	Material	Type of Material	Shade	Manufacturer
1.	Luxa Core Automix	SC composite	A3	DMG
2.	Clearfil Core New Bond	SC composite	Neutral	Kuraray
3.	Rebilda SC	SC composite	Dentin	Voco
4.	Clearfi Photo Core	LC composite	Translucent	Kuraray
5.	Charisma	LC composite	A3	Heraeus Kulzer
6.	Rebilda DC	DC composite	Dentin	Voco
7.	Luxa Core Automix Dual	DC composite	A3	DMG
8.	Ketac Molar Applicap	GI	A3	3M ESPE
9.	Fuji IX GP	GI	A3	GC
10.	Ketac Silver	mm GI		3M ESPE
11.	Vitremer	RMGI	A3	3M ESPE
12.	Fuji II LC	RMGI	A3	GC
13.	Dyract Extra	Compomer	A3	Dentsply
14.	F2000	Compomer	A3	3M ESPE

Abbreviations: **SC=** **S**elf-cured, **LC** = Light-cured, **DC** = Dual-cured, **mm** = Metal-modified, **GI** = Glass- ionomer, **RMGI** = Resin-modified glass-ionomer

5.2.2. Degree of Conversion

Seven composite resins were separately investigated for their degree of conversion in this study. Table 5.2 represents the composite resins under investigation.

Tab. 5.2 Composite resins under investigation

Nº	Material	Type of Material	Shade	Manufacturer
1.	Luxa Core Automix	SC composite	A3	DMG
2.	Clearfil Core New Bond	SC composite	Neutral	Kuraray
3.	Rebilda SC	SC composite	Dentin	Voco
4.	Clearfi Photo Core	LC composite	Translucent	Kuraray
5.	Charisma	LC composite	A3	Heraeus Kulzer
6.	Rebilda DC	DC composite	Dentin	Voco
7.	Luxa Core Automix Dual	DC composite	A3	DMG

Abbreviations: **SC** = Self-cured, **LC** = Light-cured, **DC** = Dual-cured

5.3. Methods

5.3.1. Flexure Strength and Flexural Modulus

A split stainless steel mold, consisting of a frame, six inlets and two side frames (Figure 5.1) was used to prepare bar-shaped specimens of 25 mm x 2 mm x 2 mm in dimension, according to EN ISO 4049. (Figure 5.2)

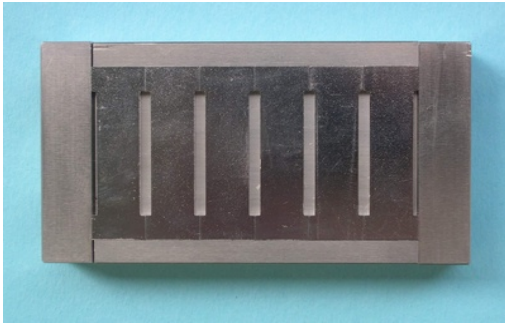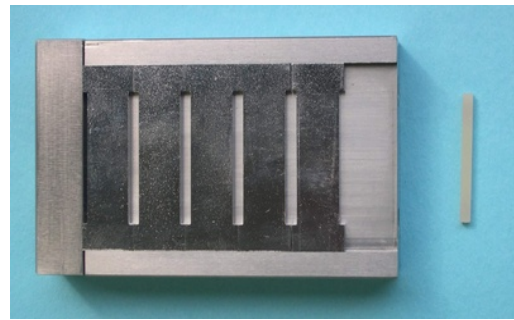Fig. 5.1 Stainless steel split mold .

Fig. 5.2 Open stainless steel mold; with the first inlet removed; to the right: a specimen of the dimensions: 25 mm x 2 mm x 2mm.

All specimens were prepared according to a standardized protocol (10 specimens / material and storage condition). Table 5.3 represents the delivery form, mixing ratio and mixing procedure for all materials under investigation.

Tab. 5.3 Delivery forms, mixing ratios and mixing procedures of materials under investigation

Material	Presentation	Mixing Ratio	Mixing Procedure
Luxa Core Automix Luxa Core Automix Dual Rebilda SC Rebilda DC	Paste/paste forms in 50g automix dual cartridges		Prior to specimen preparation, a small amount of the material was dispensed on a mixing pad with the mixing tip positioned to ensure proper mixing.
Charisma F2000 Clearfil Photo Core	4g, 4g and 4.4 g single syringes respectively		Prior to specimen preparation, a small amount of the material was dispensed on a mixing pad to clean the orifices, and the pastes were directly injected into the molds.
Fuji IX GP Fuji II LC Ketac Molar Applicap Ketac Silver Maxicap	Capsules	0.4g:0.11g 0.33g:0.10g 0.1 ml 0.45 ml	Capsules were activated in a special activator, then mixed in an amalgamator (CapMIX, ESPE, Seefeld, Germany) for the time period required (10s or 15s) according to their manufacturers' instructions. Using a special applicator a small amount of the material was dispensed onto a mixing pad to ensure opened orifice.
Dyract Extra	Compules	0.2g	Compules were directly injected into the molds using a special gun applicator. (Compules Tips Gun, Dentsply, DeTrey, Germany)
Clearfil Core New Bond	Base and Catalyst pastes in two jars.	1:1	Pastes were hand mixed on a mixing pad using a plastic spatula, until a uniform color was seen. Afterwards, the paste was filled into a Ramitec syringe (3M ESPE, Seefeld, Germany) to facilitate its injection into the mold.
Vitremer	Powder: Liquid	2.5:1 by wt	Powder and liquid were hand mixed on a mixing pad using a plastic spatula. The paste was then placed into a Ramitec syringe, to be injected into the mold.

After a polyethylene strip (Hostaphan, Pfütz, Taunusstein, Germany) was placed into the frame underneath the inlets, the mixed paste was injected into the molds in excess. The filled molds were covered by a second polyethylene strip placed on the free surface of the injected material and were adapted tightly. Finally, a metal plate was

placed on top, and the assembly was placed under a hydraulic press for five seconds, to extrude excess material. For LC and DC materials, the metal plate was removed and the assembly was inserted into the incubator with the polyethylene strip tightly adapted, to allow for light-curing.

After removal from underneath the hydraulic press, self-curing materials were immediately placed with the assembly into an incubator (Ehret, Emmendingen, Germany) for 10 min at 37°C, whereas LC and DC materials were first light-cured inside their molds from one side in a Uni XS laboratory light-curing unit (Heraeus Kulzer, Hanau Germany) for 90 s, then on the other side after removal from their molds for the same time period. The Uni XS unit is equipped with two Xenon bulbs, having a power input of 270 W, a flash frequency of 20 Hz, and a wavelength of 320-520 nm. Afterwards, the materials were placed into the incubator for 10 min. Prior to light-curing; the light-output of the light-curing unit was checked using a Translux Tester (Heraeus Kulzer, Hanau, Germany). The metal plate on top of the self-cured materials was removed, the screws opened, and the polyethylene strip removed in order to remove the specimens from the molds.

Additionally, 4 dual-cured materials, namely 2 resin-modified glass-ionomers (Fuji II LC and Vitremer) and 2 composite resins (Luxa Core Automix Dual and Rebilda DC) were tested after omitting the light-curing step, depending only on their chemically-initiated polymerization.

5.3.1.1 Storage of specimens

Prior to testing, all materials were subjected to five different storage conditions, in distilled water at 37°C: 2h, 24h, 7d and 7d thermocycling, after their dry storage for 10 min (baseline) in an incubator at 37°C, resulting in a total of 850 specimens (Table 5.4).

Tab.5.4 Storage conditions before testing flexural properties

Storage Time	Explanation
10 min	10 min dry storage at 37°C (Baseline)
2h	10 min dry storage at 37°C + 2h in distilled water
24h	10 min dry storage at 37°C +24h in distilled water
7d	10 min dry storage at 37°C + 7d in distilled water
7d thermocycling	10 min dry storage at 37°C + 5000 thermocyles at 5-55°C, with a 50s keeping time / temperature and 4 s transfer time.

5.3.1.2 3-Point bending test

Excess material was removed by wet grinding on SiC paper (grit 2400) immediately before testing, the specimens were then dried and their height and width was measured using a digimatic screw micrometer (Mitutoyo, Kawasaki, Japan) at an accuracy of ± 0.001 mm. Specimens were also inspected for cracks or bubbles. If any defect was found, the specimen was discarded.

Flexural strength testing was performed in a universal testing Zwick machine 1454 (Zwick/Roell, Ulm, Germany). The specimens were centrally placed on 2 supports (distance between the supports: 20 mm) to be tested at a crosshead speed of 1 mm/min (Figure 5.3). The maximum force registered prior to fracture was determined. Also, the modulus of elasticity of each individual specimen was analyzed and calculated directly from the linear portion of the stress-strain curve in the graph between 0.1-0.3 % deflections. Table 5.5 represents the parameters of the Zwick 1454 universal testing machine.
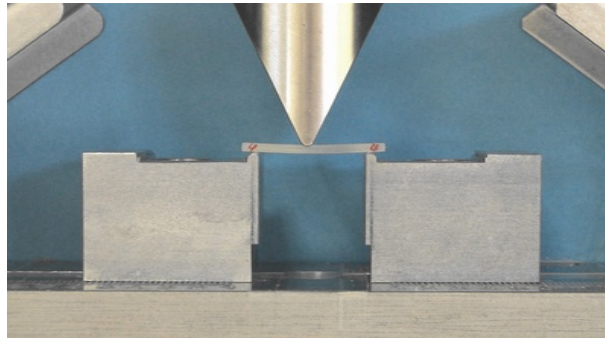

Fig.5.3   3-point bending test design in the Zwick 1454 machine.

Tab.5.5 Parameters of the Zwick 1454 universal testing machine

Load cell	0.5 kN
Crosshead speed	1 mm/min
Distance between supports	20 mm
Diameter of supports	2 mm
Diameter of the chisel	2 mm
Calculated parameters	Flexural Strength in MPa; Flexural modulus in MPa
Software	Test Xpert 10.1
Test manuscript	3-point bending test- lower part-0,5 kN-2 mm ZPV.

The FS and FM were calculated using the following equations (1) and (2):

$$FS = \frac{3 Fl}{2bh^2} \quad (1)$$

AND

$$FM = \frac{F_{lin} l^3}{4d_{lin} b h^3} \quad (2)$$

Where F = ultimate force [N], l = distance between supports [mm], b = width [mm] of the specimen, h = height [mm] of the specimen, F_{lin} = force in the linear part of the stress / strain curve [N] and d_{lin} = corresponding deflection at F_{lin} [mm].

After testing, the area of fracture was inspected for any defects (bubbles or cracks). If defects were detected, the specimens were discarded, and the experiment had to be repeated with new specimens.

5.3.2. Degree of Conversion

Seven composite resins were prepared for flexure properties test in the same manner as described before. All specimens were prepared according to a standardized protocol (5 specimens / material and storage condition). Degree of conversion was determined by

calculating the percentage of reacted C=C double bonds using FTIR analysis (baseline method) [14, 21, 32, 101] on the fractured bar-shaped specimens after recording the flexural properties. Table 5.6 represents the delivery form, presentation, mixing ratio and mixing procedure of the composite resins investigated.

Tab.5.6 Delivery form, presentation, mixing ratio and mixing procedure of composite resins investigated for degree of conversion testing

Material	Presentation	Mixing Ratio	Mixing Procedure
Luxa Core Automix Luxa Core Automix Dual Rebilda SC Rebilda DC	In paste/ paste forms in 50g automix dual cartridge		Prior to specimen preparation, a small amount of the material was dispensed on a mixing pad with the mixing tip positioned to ensure proper mixing.
Charisma Clearfil Photo Core	4g and 4.4 g single syringes respectively		Prior to specimen preparation, a small amount of the material was dispensed on a mixing pad to clean the orifices, and the pastes were directly injected into the molds.
Clearfil Core New Bond	Base and Catalyst pastes in two jars.	1:1	Pastes were hand mixed on a mixing pad using a plastic spatula, until a uniform color was seen. Afterwards, the paste was filled into a Ramitec syringe (3M ESPE, Seefeld, Germany) to facilitate its injection into the mold.

5.3.2.1   *Storage of specimens*

Prior to testing, the 7 composite resin materials were subjected to 8 different storage conditions: 5 min and 10 min dry storage in an incubator at 37°C, in distilled water at 37°C: 1h, 4h, 24h, 2d, 7d and 7d thermocycling after their dry storage for 10 min (baseline) in an incubator at 37°C, resulting in a total of 280 specimens. Table 5.7 represents the storage conditions of composite resins before testing their flexural properties in a 3-point bending test, to be followed by testing their degree of conversion.

Tab.5.7 Storage conditions of composite resins before testing their degree of conversion after fracture in a 3-point bending test

Storage time	Explanation
5 min	5 min dry storage at 37°C
10 min	10 min dry storage at 37°C (baseline)
1h	10 min dry storage at 37°C + 1h in distilled water
4h	10 min dry storage at 37°C + 4h in distilled water
24h	10 min dry storage at 37°C +24h in distilled water
2d	10 min dry storage at 37°C + 2d in distilled water
7d	10 min dry storage at 37°C + 7d in distilled water
7d thermocycling	10 min dry storage at 37°C + 5000 thermocycles at 5-55°C, with a 50s keeping time / temperature and 4s transfer time.

5.3.2.2   Degree of Conversion test

All composite resins were tested in a 3-point bending test following the same procedures mentioned before, to determine their flexural properties. Afterwards, fractured specimens were immediately placed on an ATR diamond crystal of a Spectrum[TM] 100 FTIR device (Perkin Elmer, Shelton, USA) to determine their degree of conversion. The machine was equipped with a universal diamond ATR unit (spectral range: 4000-650 cm^{-1}; operating at a spectral resolution of 4 cm^{-1}) [30, 65]. Moreover, the amount of unreacted double bonds inside the material prior to polymerization was determined, by directly dispensing a small amount of freshly mixed material (0.2 ml) on the ATR crystal (n = 5 per material), to record a spectrum immediately (16 scans / spot). [30, 65] Figure 5.4 illustrates the uncured paste dispensed on the ATR crystal of the Spectrum 100[TM] FTIR testing device. As a reference, the mean spectrum of the uncured samples was calculated.

For calculation of the degree of conversion, spectra of the cured bar-shaped specimens (n = 5 / material and storage condition) were recorded after fracture, by placing the specimens onto the ATR crystal, fixing them with the ATR unit's movable arm to achieve the closest contact possible at a maximum force of 150 units for optimal documentation (Figure 5.5). On each specimen, spectra were recorded at 3 different points, requiring 64s scan-time per spot. Mean spectrum of all 15 measurements was

calculated (Spectrum^{TM} software; release: 6.0.1, Perkin-Elmer, Shelton, USA). FTIR spectra were recorded after 5 min, 10 min, 1h, 4h, 24h, 2d, 7d and 7d thermocycling, determining a baseline for each composite resin (range: 1670 and 1580 cm^{-1}) in both, the uncured as well as the cured (tested after flexure testing following various storage conditions). The relative peak height of absorbance intensity of the aliphatic peak (1638 cm^{-1}) as well as the aromatic peak (1609 cm^{-1}) was determined in reference to the baseline [14, 21, 32, 101]. Table 5.8 represents the parameters of the Spectrum 100^{TM} FTIR testing machine.

Tab.5.8 Parameters of the Spectrum^{TM} 100 FTIR testing machine.

Operating unit	ATR diamond crystal
Spectral resolution	4 cm^{-1}
Spectral range	4000-650 cm^{-1}
Units	% T
Apodisation	Strong
N^{o} of scans	16
Scan speed	0.20 cm/s
Software	Spectrum^{TM} ; release 6.0.1.

The DC % was calculated as the quotient of the relative peak heights of the cured versus uncured materials according to the following equation:

$$DC\,(\%) = 100 \times \left(1 - \frac{\text{cured (rph aliphatic C=C / rph aromatic C...C)}}{\text{uncured (rph aliphatic C=C/rph aromatic C...C)}} \right)$$

Where: rph = relative peak height

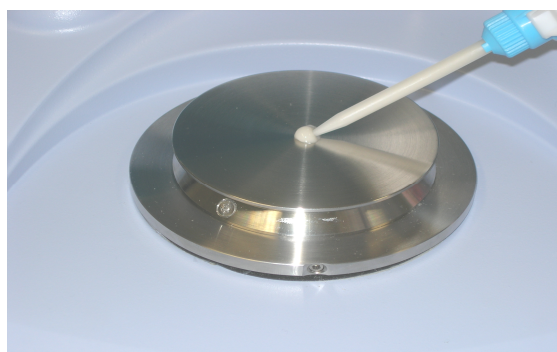Mean values and standard deviations of the DC data were calculated.

Fig.5.4 Uncured paste dispensed on the ATR crystal of the Spectrum 100^{TM} FTIR testing machine.
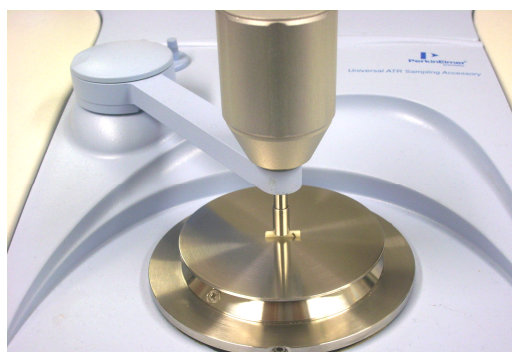
Fig.5.5 Fractured bar-shaped specimen placed onto the ATR crystal of the Spectrum^{TM} 100 FTIR testing machine.

5.4. Statistical Methods

5.4.1. Flexure Strength and Flexural Modulus

Within the framework of this study, the influence of several variables on both flexural properties (FS and FM) was investigated. For test groups with a balanced design, a test for normal distribution was not performed, while for groups with different specimen numbers, a test for normal distribution was mandatory, using the Kolmogorov-Smirnov-Test or the Shapiro-Wilk-Test.

Given a normal distribution, parametric tests were applied (Analysis of Variance), in case of materials showing deviation from normal distribution, distribution-free (non-parametric) tests (Mann-Whitney U-Test or Kruskal-Wallis H-Test) were required giving more precise conclusions.

As the specimen groups were of limited sizes all over the analysis, the Levene-Test for testing variance homogeneity had to be undertaken for all test series. In case of variance homogeneity, the F-Test was applied, while in case of significantly different variances, more robust tests (Brown-Forsythe- or Welch- Test) were used.

For more precise determination of the effects of different parameters on both flexural properties (being significant or not), paired comparisons were carried out between various parameters investigated using Post-Hoc-Tests (Tukey-Test or Games-Howell-Test).

All results were depicted in box-and-whiskers plots to inform about the distribution of values in respect to the median.

5.4.2. Degree of Conversion

Within the framework of this study, the influence of the degree of conversion on both FS and FM as well as the influence of different storage conditions on the degree of conversion of different composite resin materials was investigated. A bivariate correlation-analysis was carried out to test the correlation statistics for significance. If a relationship between two characteristics proved to be statistically significant; there was no need for any further analysis of the link. The results were depicted in graphs, indicating the type (squared) and the course (rising or falling) of the correlation, as well as its reliability: the higher r^2, the more accurate the prediction and the stronger the correlation.

6. Results

The results illustrated in table 6.1 show the mean values of FS and FM of all materials tested according to manufacturer's instructions.

6.1. Flexure Strength

A gradual increase in FS for the first 24h was noticed for all materials tested, to show a decline following the 7d storage period, except for F2000, the polyacid-modified composite resin, which showed a decrease in FS with increased storage time from the very beginning (Figure 6.1).

The developmental pattern of FS obviously differed according to the type of material as well as the storage condition. Hence, glass-ionomer cements as well as resin-modified glass-ionomers revealed continuous increase in FS following the 24h storage period ($p > 0.05$), while composite resins showed an insignificant and compomers a significant reduction in FS values following the 7d storage periods.

On the one hand, glass-ionomer materials showed significantly lower FS values and brittleness (with abrupt fracture and minimal deformation) throughout all storage conditions compared to the rest of the materials tested, with the resin-modified types showing significantly higher FS values (Fuji II LC > Vitremer) compared to the conventional and metal-modified types ($p < 0.05$).

On the other hand, composite resins showed the highest FS values, with the self-cured types presenting significantly lower values compared to both the light-and dual-cured types, while polyacid-modified composite resins (compomers) showed FS values between those of the glass-ionomer materials and composite resins (Dyract Extra > F2000). While compomer materials revealed insignificant differences in FS for all storage conditions, the rest of materials revealed significant differences between most storage conditions ($p < 0.05$).

For the composite resins, significant differences between the 3 curing modes (self-cured, light-cured and dual-cured) when stored under different conditions were discovered, with the light-cured and dual–cured types showing the highest FS throughout all storage conditions, and the self-cured types demonstrating the least FS values. A significant difference between self-cured and light-cured materials on one

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hand as well as self-cured and dual-cured materials on the other hand was noticed for all storage conditions, except after 2h, where an insignificant difference in FS values (α = 0.285) was determined. However, insignificant differences between light-cured and dual-cured composite resin types were detected.

Regarding the 7d storage conditions, some materials showed minimal further increase in FS compared to their 24h values (Ketac Molar Applicap, Ketac Silver Maxicap, Fuji II LC, and Vitremer). While some materials showed insignificantly different values from their 24h FS values (Fuji IX GP, Dyract Extra, Clearfil Core New Bond, Clearfil Photo Core and Luxa Core Automix Dual), other materials showed a decrease in FS values from their 24h values (F2000, Rebilda SC and Luxa Core Automix). Insignificant differences in FS between both conditions (7d WB versus 7d TC) ($p > 0.05$) were noticed for all materials tested, except for Fuji II LC, a resin-modified glass-ionomer, which showed significant differences in FS after thermocycling ($p < 0.05$). (Figure 6.2)
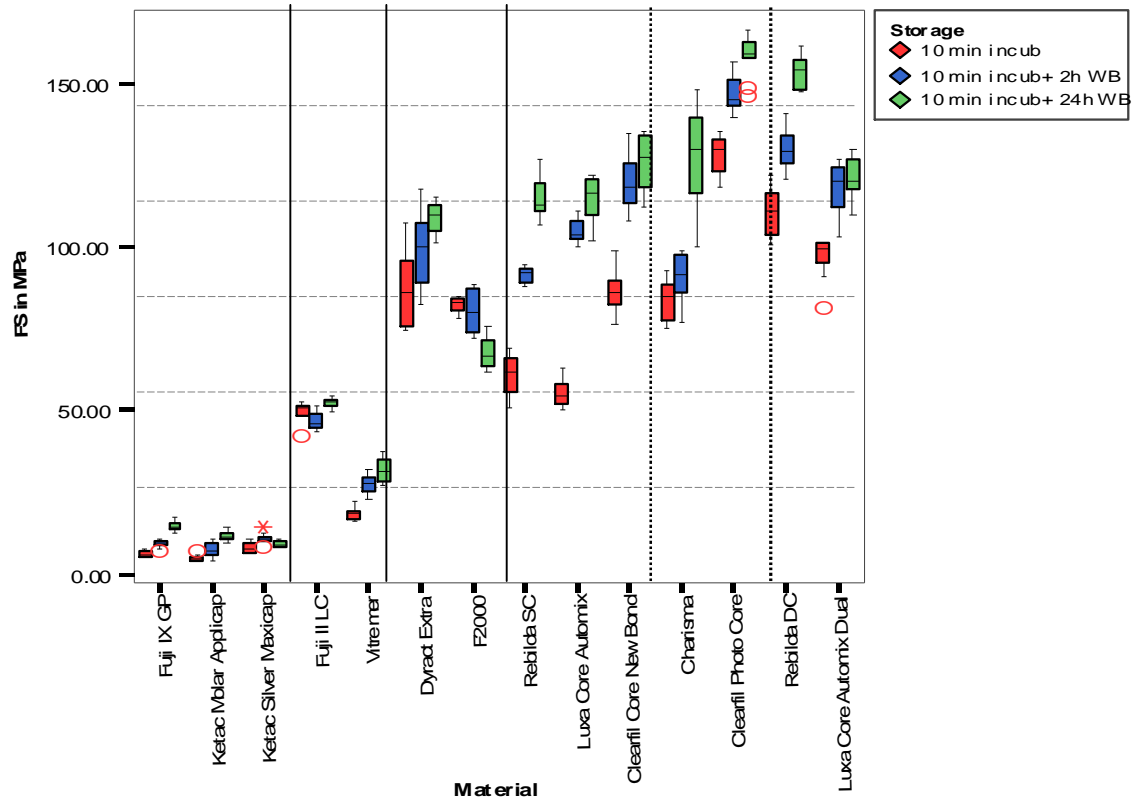
Fig.6.1 FS of materials tested after storage under different storage conditions for storage times up to 24h.
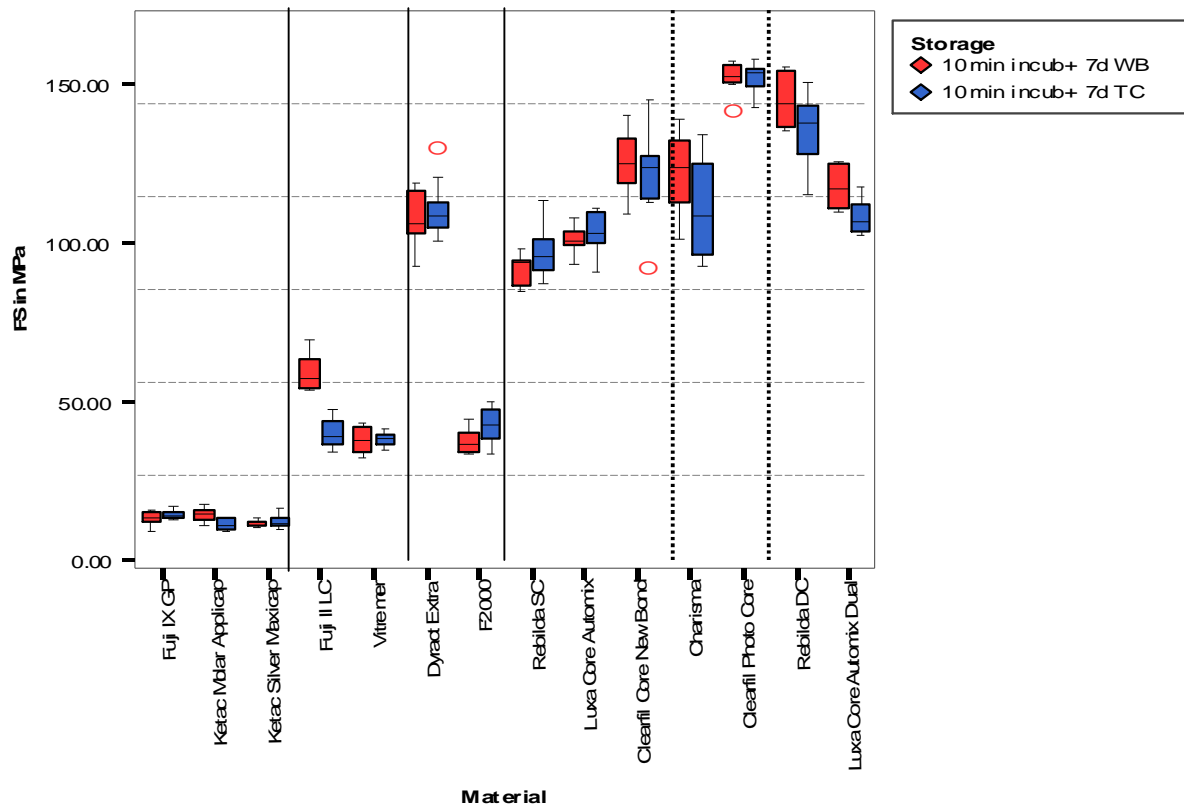

Fig.6.2 FS of materials tested after storage for 7d (WBvs.TC).

6.2. Flexural Modulus

A gradual increase in FM for all materials until 24h was noticed ($p<0.05$), to show insignificant differences afterwards, being almost similar ($p>0.05$). Moreover, insignificant differences between the 4 material groups for most storage periods were recorded, with their least values confirmed after the 10 min storage period. For all storage times and conditions a significant difference in FM between materials existed, whereas for the first 24h, glass-ionomer cements and resin-modified glass-ionomers on one hand as well as composite resins and compomers on the other hand revealed almost similar FM values. (Figure 6.3)

Concerning the glass-ionomer materials, their FM increased significantly until 24h, with insignificant differences in FM between 24h and 7d storage periods ($p > 0.05$). Fuji IX GP, the highly viscous conventional glass-ionomer material, revealed significantly higher values after 24h and 7d thermocycling period, compared to the rest of glass-ionomers, while Ketac Molar Applicap revealed the highest value for the 7d WB period, compared to the rest of glass-ionomer materials tested.

Throughout all storage conditions, Fuji II LC, the resin-modified glass-ionomer material, showed significantly higher FM values compared to Vitremer, the other resin-modified glass-ionomer material.

For the compomer materials, they showed some insignificant increase in FM with increased storage time, having their FM values existing inbetween those of glass-ionomers and composite resins; with F2000 showing higher FM values compared to Dyract Extra, being insignificantly different from those of Clearfil Core New Bond, the self-cured composite resin, throughout all storage conditions.

Concerning the composite resins tested, FM values raised significantly from the beginning until 2h, to stagnate afterwards. In regards to the different curing modes of composite resins, FM was significantly different between self-cured and light-cured specimens throughout all storage conditions. Moreover, significantly different FM values were recorded between self-cured and dual-cured specimens for all storage conditions, except after 24h ($p > 0.05$). Likewise, FM was insignificantly different between light-cured and dual-cured specimens (for 10 min, 2h and 7d TC), but significantly different for the 24h and 7d WB storage conditions.

The light-cured composite resin, Clearfil Photo Core, and the self-cured Clearfil Core New Bond, revealed the highest FM values compared to the rest of composite materials tested (Clearfil Photo Core > Clearfil Core New Bond). Insignificantly different FM values were recorded between Charisma, a light-cured composite resin and both dual-cured composite resins, Rebilda DC and Luxa Core Automix Dual, except for the 10 min storage period (Charisma < Rebilda DC< Luxa Core Automix Dual), as well as between both self-cured composite resin materials, Rebilda SC and Luxa Core Automix.

On the other hand, self-cured types, Rebilda SC and Luxa Core Automix, demonstrated lowest FM values among all composite resins tested, with Rebilda SC showing FM values, being insignificantly different from those for Luxa Core Automix for all storage conditions, except for the 2h and 7d WB storage periods (Luxa Core Automix > Rebilda SC).

Following a 7d storage period, only resin-modified glass-ionomers and compomers differed significantly in FM from one another following a storage for 7d WB. Regarding the 7d thermocycling period, compomers showed FM values being significantly different to the rest of materials tested, and resin-modified glass-ionomer materials revealed FM values that were significantly different to those of composite resins. Only Ketac Molar Applicap and Fuji II LC (7 d WB > 7d TC) revealed a decrease, while Luxa Core Automix Dual showed increased FM after thermocycling.

All materials showed FM values being insignificantly different from their 24h peak values (Fuji IX GP, Dyract Extra, F2000, Luxa Core Automix, Clearfil Core New Bond, Charisma, Clearfil Photo Core, Rebilda DC, Luxa Core Automix Dual), except for Ketac Silver Maxicap and Vitremer showing higher values, as well as Fuji II LC and Ketac Molar Applicap demonstrating increased FM values for the 7d WB storage condition, followed by a significant drop after thermocycling. On the other hand, Rebilda SC demonstrated a decrease from its 24h peak value. Lowest values were presented by self-cured composite resins, Rebilda SC and Luxa Core Automix (Rebilda SC < Luxa Core Automix), with no significant differences in FM between the resin-modified glass-ionomer Fuji II LC and the compomer material Dyract Extra, or between the glass-ionomer Ketac Silver Maxicap and the resin-modified glass-ionomer Vitremer (Figure 6.4).
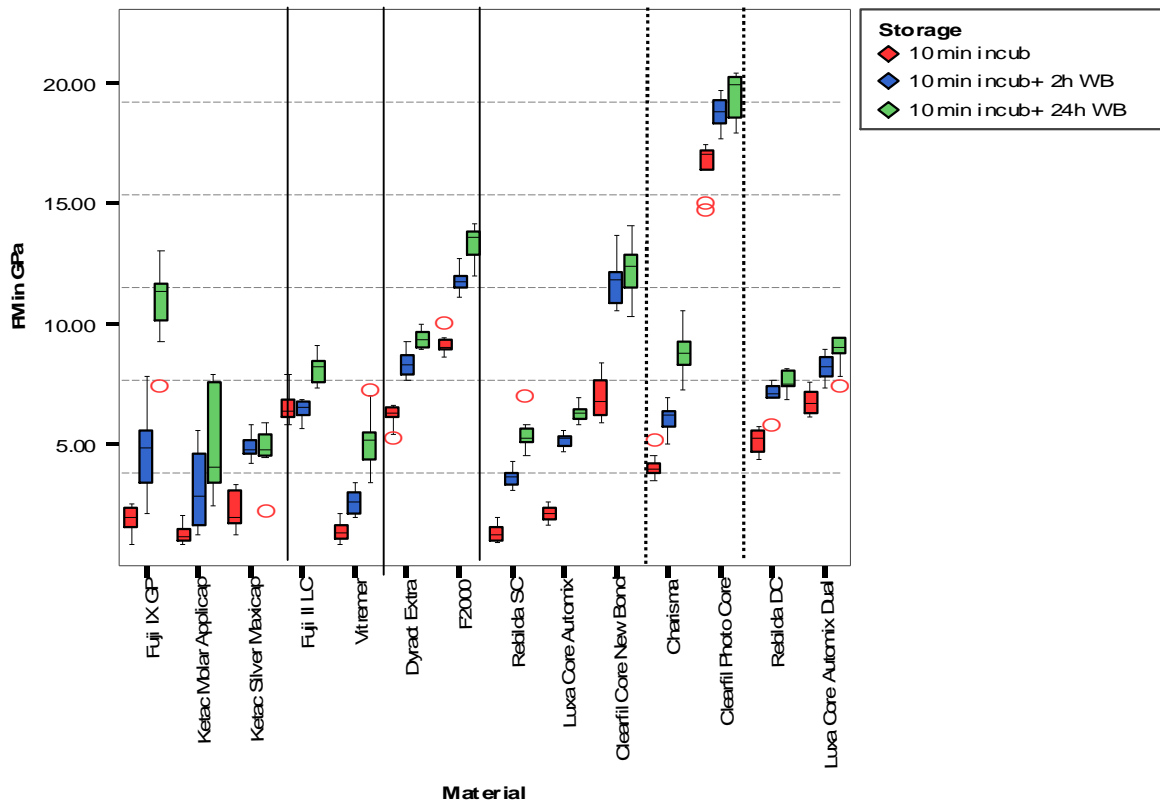
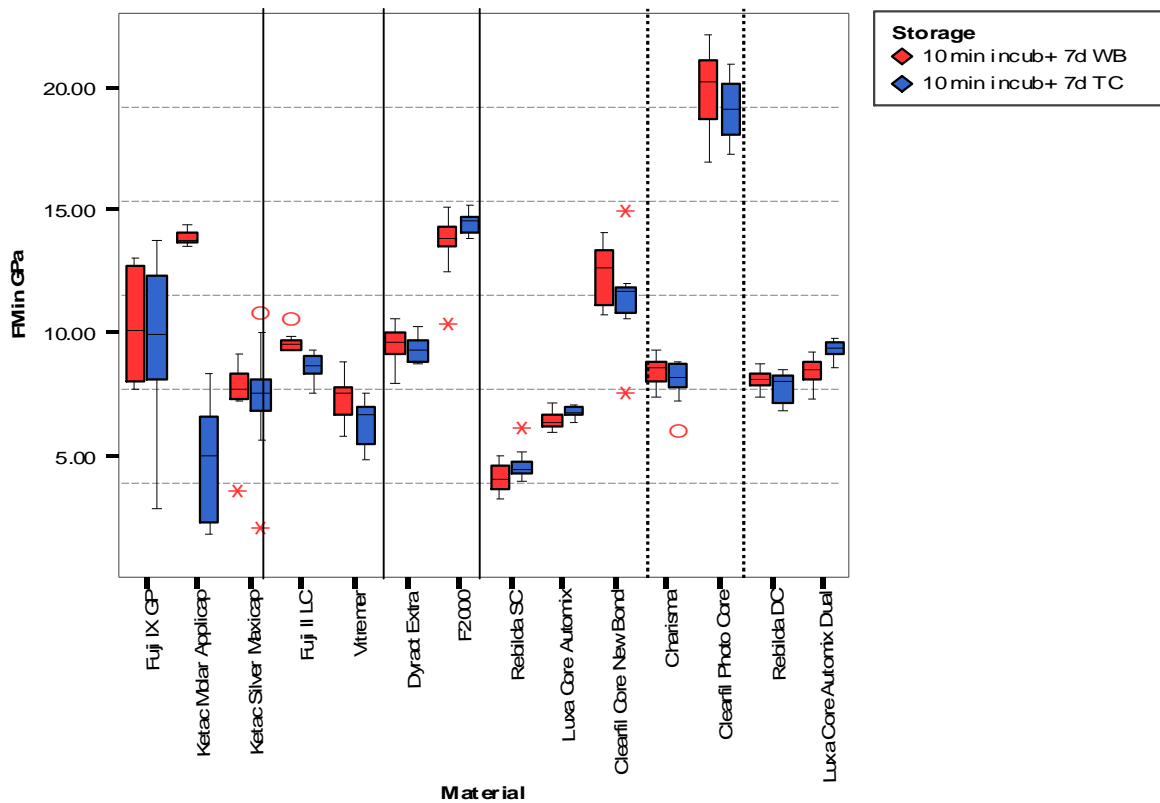Fig.6.3 FM of materials tested after storage under different storage conditions, for storage times up to 24h.

Fig.6.4 FM of materials tested after storage for 7d (WB versus TC).

6.3. Omission of the light-curing step

Four dual-cured materials were chosen to be tested without being light-cured after storage under different storage conditions. However, tests could only be performed on 3 materials, namely Fuji II LC, Luxa Core Automix Dual and Rebilda DC, as the resin-modified glass-ionomer, Vitremer, was too brittle to be removed from the molds after skipping the light-curing step. (Table 6.2)

6.3.1. Flexure Strength

Materials tested showed an elevation of the FS values with increased storage periods until 7d WB, except Luxa Core Automix Dual (24h < 2h). All 3 materials recorded significantly different FS values for all storage conditions until 7d WB, showing higher FS values for light-cured specimens compared to specimens without light-curing, and their highest values after the 7d storage periods. Insignificantly different FS values between 7d TC and 7d WB were recorded for all 3 materials, except for Fuji II LC, which demonstrated significantly higher FS values for the 7d WB storage period. For the dual-cured materials tested, FS reached its maximum value after 24h, to remain constant afterwards. (Figures 6.5-6.7)

Fuji II LC, the resin-modified glass-ionomer, showed a gradual increase in FS until the 7d WB storage period, with significantly higher values for the light-cured specimens compared to the chemically initiated ones (without light-curing). A significant drop in FS values was noticed after the thermocycling period, showing insignificant differences between both curing modes for the 7d storage specimens, but a significant affection by thermocycling. The lowest FS values were recorded for Fuji II LC compared to the rest of materials tested throughout all storage conditions for both curing modes.

Luxa Core Automix Dual, the composite resin tested, revealed significantly higher FS values for the light-cured specimens throughout all storage conditions, except for both 7d storage periods (WB versus TC), showing insignificant differences, with lower strength value for the thermocycled specimens. Throughout all storage conditions, Luxa Core Automix Dual showed significantly lower FS values compared to those of Rebilda DC for both curing modes, except after 10 min storage period, showing insignificantly different values from those of Rebilda DC for the chemical initiation (without light-curing).

Rebilda DC, the second composite resin tested, showed significantly higher FS values for the light-cured specimens after 10 min as well as 24h storage conditions, while insignificant differences between both curing modes were noticed for the other storage conditions. Throughout all storage conditions, Rebilda DC showed highest FS values compared to other materials tested (Luxa Core Automix Dual, Fuji II LC), except for the 10 min storage period, showing insignificantly different FS values compared to Luxa Core Automix Dual, for the chemical initiation (without light-curing).
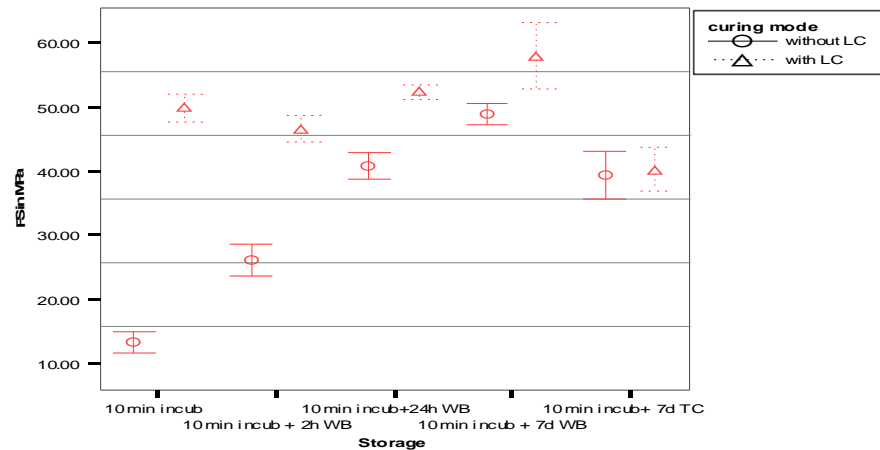

Fig.6.5 FS of Fuji II LC tested after different storage conditions with and without light-curing. Error bars show 95% CI of means
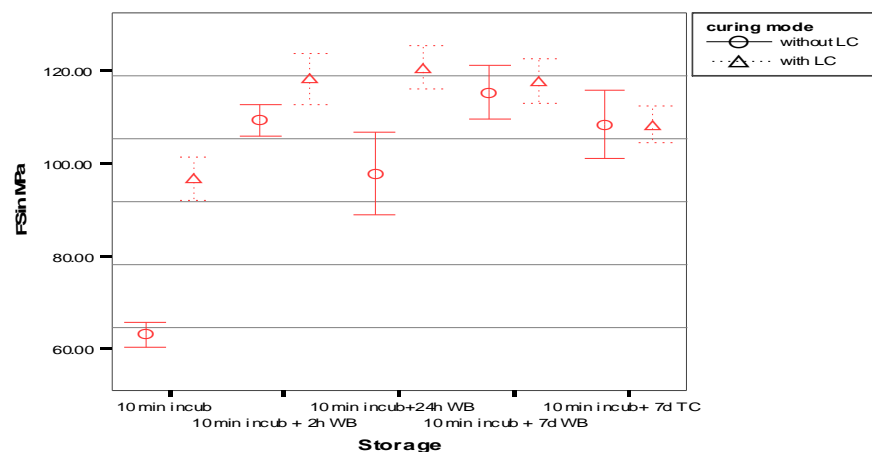

Fig.6.6 FS of Luxa Core Automix Dual tested after different storage conditions with and without light-curing. Error bars show 95% CI of means.
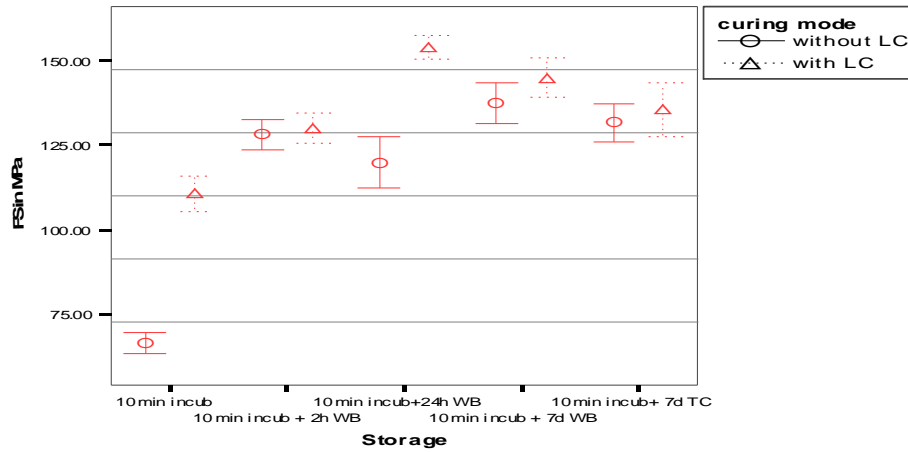
Fig.6.7 FS of Rebilda DC tested after different storage
conditions with and without light-curing. Error bars
show 95% CI of means.

6.3.2. *Flexural Modulus*

All 3 materials showed higher values for light-cured specimens compared to the chemically-cured specimens (without light-curing) for most storage conditions (Figures 6.8-6.10).

Fuji II LC showed a gradual increase in FM with time of storage, recording its highest values after 7d WB. Only for the 10 min and 2h storage periods, significantly higher FM values were noticed for the light-cured specimens compared to the chemically-cured types (without light-curing), with insignificant differences between both curing modes for the rest of storage conditions noticed.

Luxa Core Automix Dual showed significantly higher values for the light-cured specimens throughout all storage conditions ($p < 0.001$).

Rebilda DC showed a gradual increase in FM with time of storage for both curing modes, showing significantly different values between them for the 10 min, 2h and 7d WB storage conditions. On the other hand, insignificant differences between both curing modes were recorded for the 24h and 7d TC storage conditions, the highest FM values recorded for the 7d storage periods.

For the chemical initiation (without light- application): Fuji II LC showed FM values being insignificantly different to those of Rebilda DC for the 10 min (Fuji II LC = Rebilda DC < Luxa Core Automix Dual) and for the thermocycling period (Fuji II LC = Rebilda DC > Luxa Core Automix Dual). Furthermore, Fuji II LC showed least values after 2h (Fuji II LC < Luxa Core Automix Dual = Rebilda DC), highest values after 24h

(Fuji II LC > Rebilda DC > Automix Dual) and 7d WB (Fuji II LC > Rebilda DC = Luxa Core Automix Dual) storage conditions for non light-cured specimens.

For the light-curing mode: Fuji II LC showed FM values insignificantly different to those of Luxa Core Auto mix Dual, being higher than those of Rebilda DC after 10 min storage period (Fuji II LC= Luxa Core Automix Dual > Rebilda DC), least FM values for the 2h storage condition (Fuji II LC< Rebilda DC< Luxa Core Automix Dual). For the 24h storage period, Fuji II LC showed FM values being insignificantly different to those of Rebilda DC and less than those of Luxa Core Automix Dual (Fuji II LC = Rebilda DC < Luxa Core Automix Dual). Regarding the 7d storage conditions, Fuji II LC revealed highest FM values for the 7d WB storage condition (Fuji II LC > Rebilda DC= Luxa Core Automix Dual), while for the thermocycling period, Luxa Core Automix Dual showed highest FM values (Luxa Core Automix Dual > Fuji II LC > Rebilda DC).
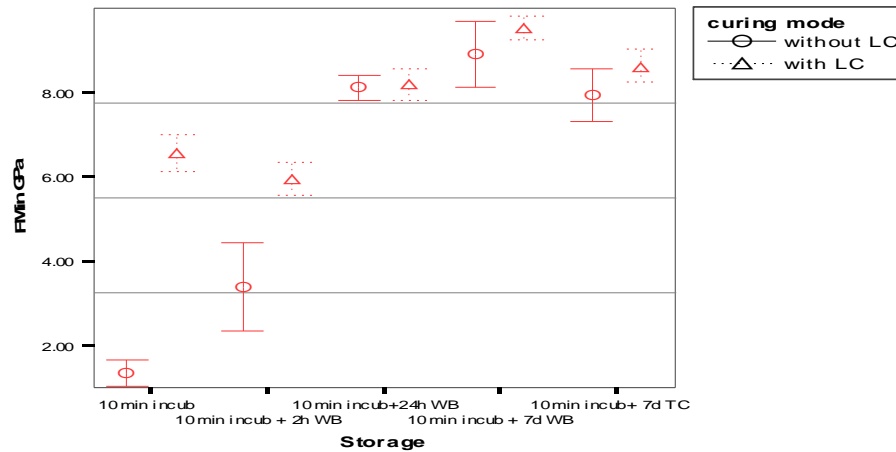

Fig.6.8 FM of Fuji II LC tested after different storage conditions with and without light-curing. Error bars show 95% CI of means.
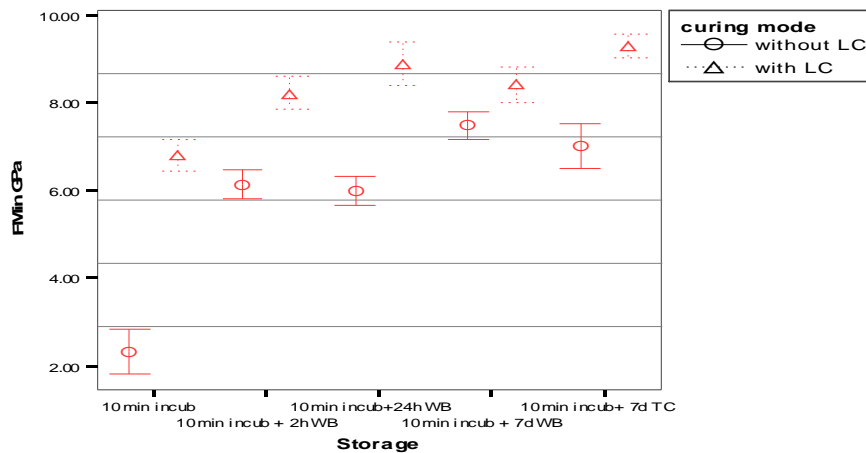

Fig.6.9 FM of Luxa Core Automix Dual tested after different storage conditions with and without light-curing. Error bars show 95% CI of means.
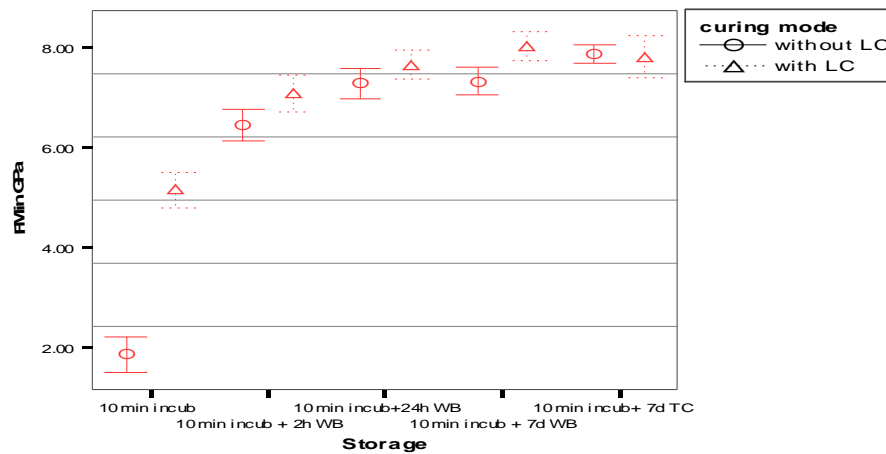
Fig.6.10 FM of Rebilda DC tested after different storage
conditions with and without light-curing. Error bars show
95% CI of means.

6.4.   Degree of Conversion

The results presented in Table 6.3 show the mean values of FS, FM and % DC of seven
composite resins tested after different storage conditions, assessing the relation between
their flexural properties and % DC.

6.4.1. Correlation between Flexure Strength and Degree of Conversion

The squared model turned out to be the most representative for each separate composite
resin.

The bivariate correlation analysis revealed a significant correlation ($p<0.05$) between
the conversion grade (%DC) and the FS properties, ranging from weak to average
(25.6% and 45.2%) for 2 self-cured (Luxa Core Automix-$r^2 = 0.292$, Clearfil Core New
Bond- $r^2 = 0.452$) as well as a dual-cured composite resin (Rebilda DC- $r^2 = 0.256$).
Those three composite resins with an increased % DC also showed an increase in FS
values.

A monotonic increase in FS values was noticed for Rebilda DC throughout the entire
observation period, whereas the FS data decreased slightly for both Luxa Core Automix
as well as Clearfil Core New Bond at a specific % DC value (60%-65%).

The bivariate correlation analysis for the rest of the composite resins revealed no
influence of the % DC on their FS ($p > 0.05$). Figures 6.12, 6.13 and 6.16 illustrate
significant correlations between FS and DC for the 3 materials (Rebilda DC, Luxa Core

Automix and Clearfil Core New Bond) graphically, while Figures 6.11, 6.14, 6.15 and 6.17 illustrate the remaining composite resins showing no correlation between both parameters.

$r^2 = 0.023$
$p > 0.05$

Fig.6.11 No correlation between FS and %DC of Rebilda SC tested after storage under different conditions was detected.

$r^2 = 0.292$
$p < 0.000$

Fig.6.12 A squared correlation between FS and %DC of Luxa Core Automix tested after storage under different conditions was detected.

$r^2 = 0.452$
$p < 0.000$

Fig.6.13 A squared correlation between FS and %DC of Clearfil
Core New Bond tested after storage under different conditions was
detected.

$r^2 = 0.004$
$p > 0.05$

Fig.6.14 No correlation between FS and % DC of Clearfil Photo Core
tested after storage under different conditions was detected.
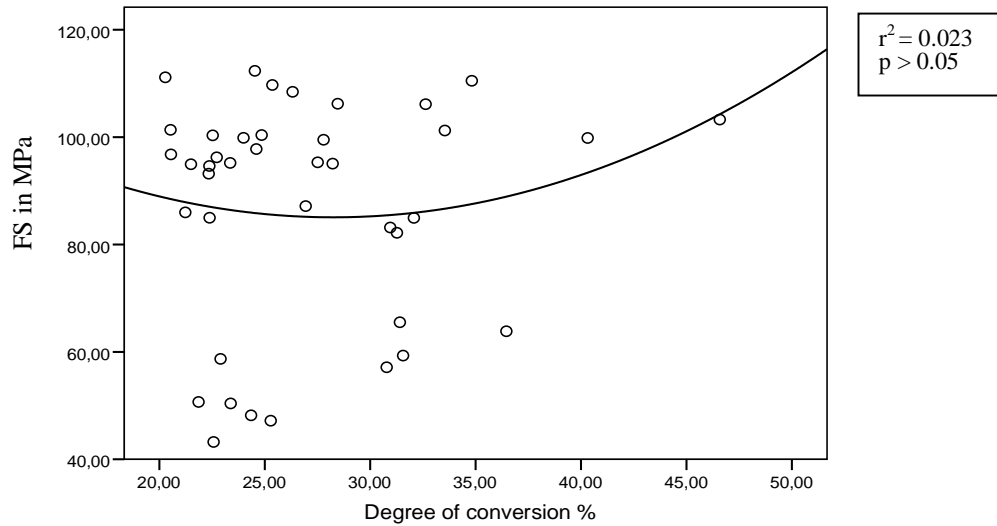

$r^2 = 0.012$
$p > 0.05$
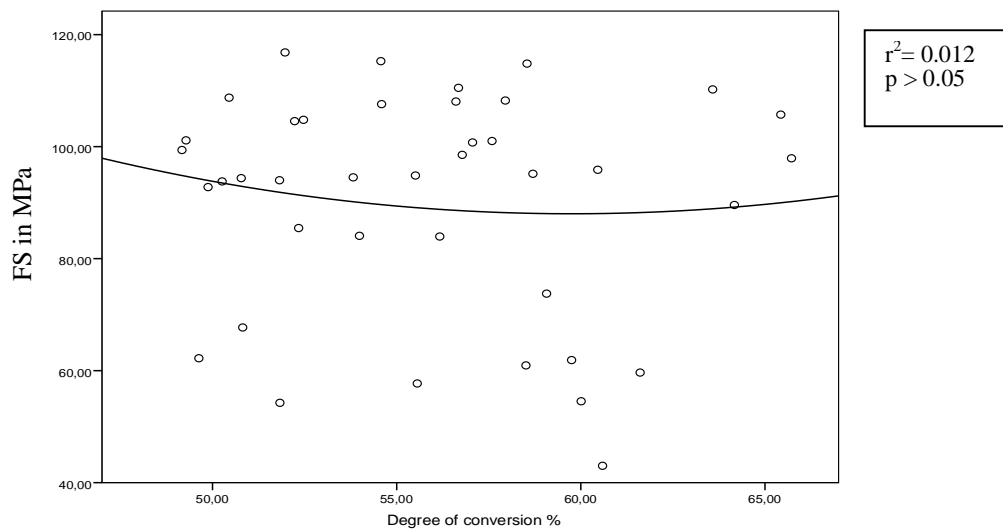
Fig.6.15 No correlation between FS and % DC of Charisma tested after
storage under different conditions was detected.

Fig.6.16 A squared correlation between FS and %DC of Rebilda DC
tested after storage under different conditions was detected.
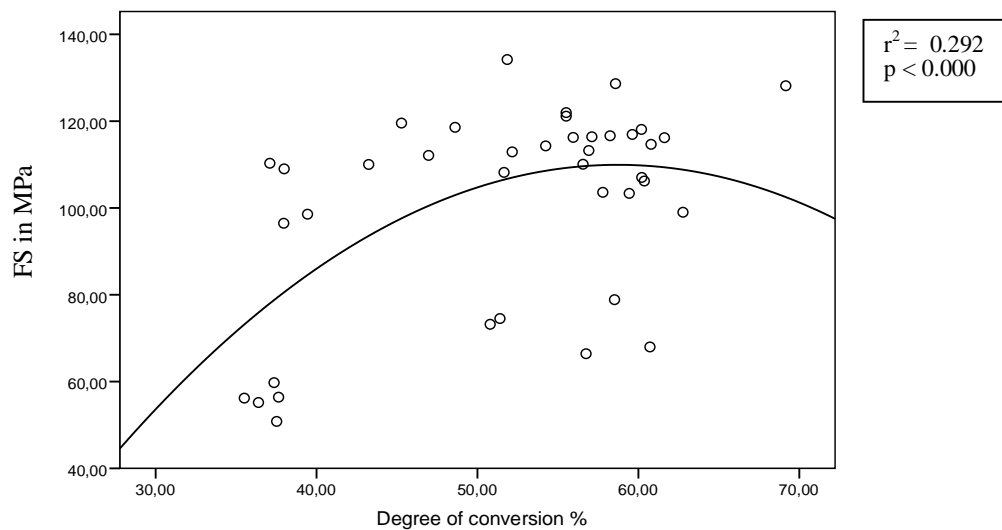

Fig. 6.17 No correlation between FS and %DC of Luxa Core Automix
Dual tested after storage under different conditions was detected.

6.4.2. *Correlation between Flexural Modulus and Degree of Conversion*

The squared model turned out to be the most representative for each separate composite resin.

The bivariate correlation analysis revealed a significant correlation ($p < 0.05$) between the conversion grade (% DC) and the FM properties, ranging from weak to average (18.7 % and 52.5 %) for 2 self-cured (Luxa Core Automix- $r^2 = 0.406$, Clearfil Core New Bond- $r^2 = 0.525$) as well as a dual-cured composite resin (Rebilda DC- $r^2 = 0.187$). Those 3 composite resins with an increased % DC also showed an increase in FM values.

A monotonic increase in FM values was noticed for Rebilda DC throughout the entire observation period, whereas the FM data decreased slightly for both Luxa Core Automix as well as Clearfil Core New Bond at a specific % DC value (60%- 65%).

The bivariate correlation analysis for the rest of composite resins, revealed no influence of the % DC on their FM ($p > 0.05$). Figures 6.20, 6.21 and 6.24 illustrate significant correlations between FM and % DC for the 3 materials (Rebilda DC, Luxa Core Automix and Clearfil Core New Bond) graphically, while Figures 6.19, 6.22, 6.23 and 6.25 illustrate the remaining composite resins showing no correlation between both parameters.
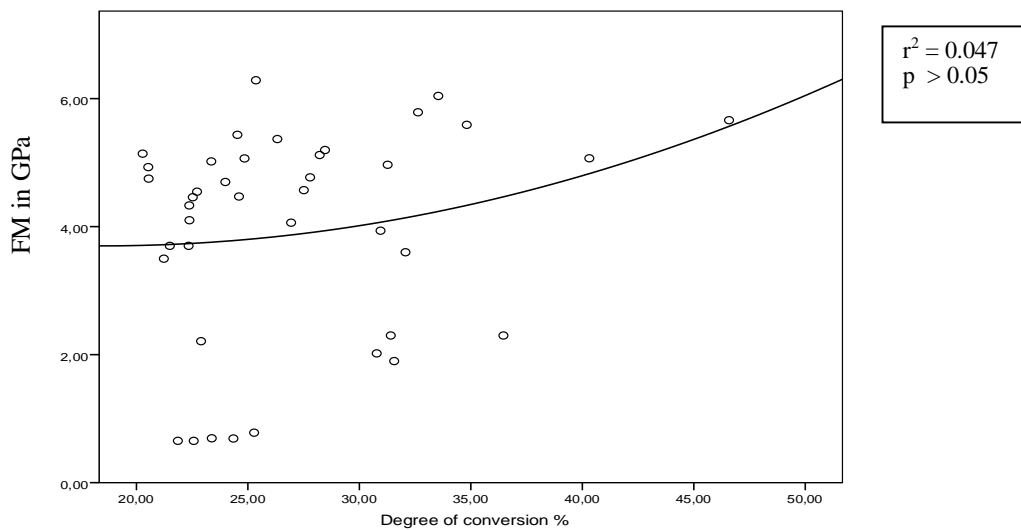
Fig.6.19 No correlation between FM and % DC of Rebilda SC, tested after storage under different conditions, was detected.

Fig.6.20 A squared correlation between FM and % DC of Luxa Core Automix, tested after storage under different conditions, was detected.
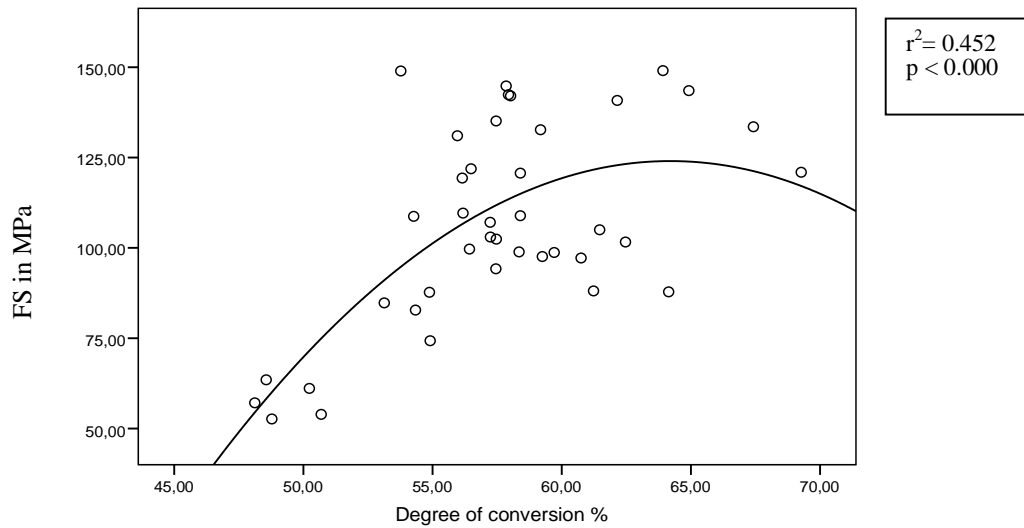
r² = 0.525
p < 0.00

Fig.6.21 A squared correlation between FM and % DC of Clearfil Core New Bond, tested after storage under different conditions, was detected.
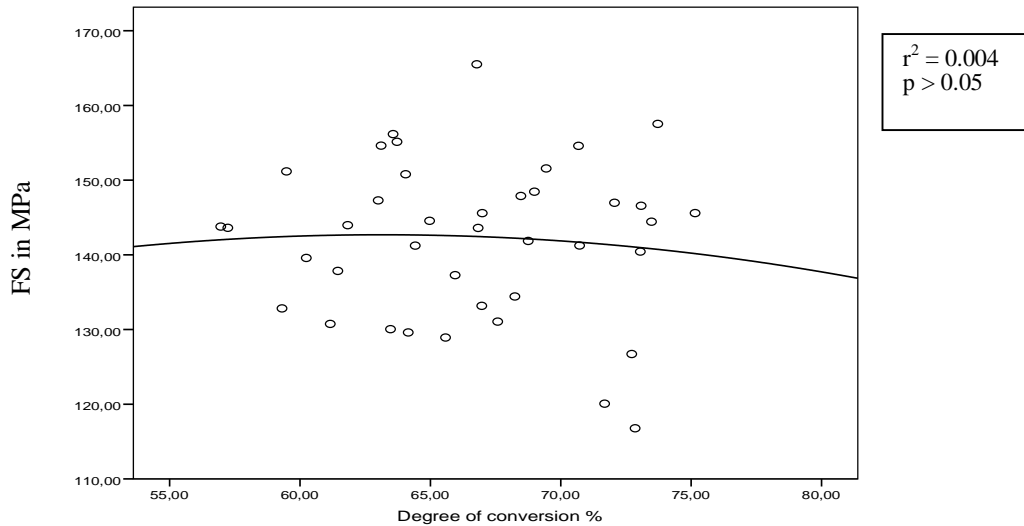

r² = 0.037
p > 0.05

Fig.6.22 No correlation between FM and % DC of Clearfil Photo Core, tested after storage under different conditions, was detected.

r² = 0.008
p > 0.05

Fig.6.23 No correlation between FM and % DC of Charisma, tested after storage under different conditions, was detected.
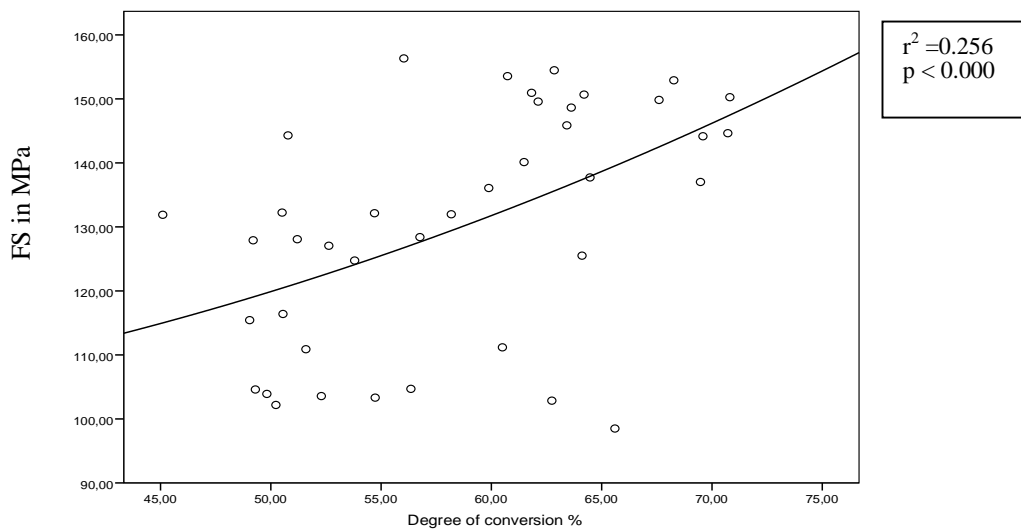
Fig.6.24 A squared correlation between FM and % DC of Rebilda DC, tested after storage under different conditions, was detected.
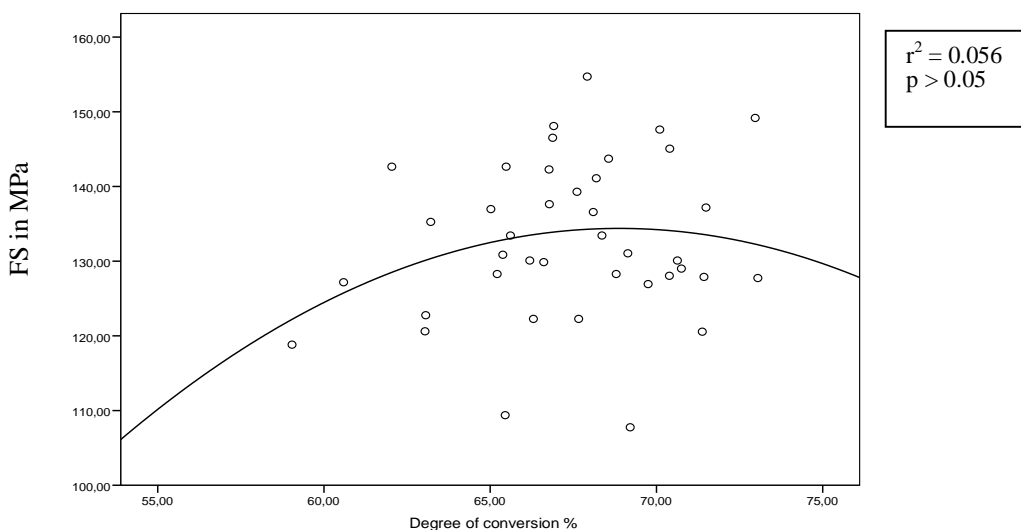

Fig.6.25 No correlation between FM and % DC of Luxa Core Automix Dual, tested after storage under different conditions, was detected.

6.4.3. Correlation between Storage condition and Degree of Conversion

Examination of the interrelation between storage and % DC for each separate material showed the squared function model to be the most suitable, providing the best balance between data fit, degrees of freedom and interpretability.

A significant ($p < 0.05$) yet weak ($r^2 < 0.25$) correlation between % DC and storage condition was noticed for all composite resins, with the exception of Luxa Core Automix Dual, which revealed no correlation between both parameters ($p > 0.05$).

Moreover, 2 composite resins demonstrated a relatively strong influence of storage condition on the % DC values, namely Luxa Core Automix, the self-cured composite resin ($r^2 = 0.459$) and Rebilda DC, the dual-cured composite resin ($r^2 = 0.428$), as represented in the Figures 6.27 and 6.31 respectively.

The % DC increased during the first 90 to 100 h, to decline within the next 4 days for the majority of materials (Luxa Core Automix, Clearfil Core New Bond, Charisma, Rebilda DC) on one hand, whereas some materials demonstrated a divergent pattern on the other: the % DC for Rebilda SC, the self-cured composite resin, rose slowly during the first 96 h, to increase rapidly afterwards (Figure 6.26), whereas the % DC for Clearfil Photo Core, the light-cured composite resin, had already declined after about 50h (Figure 6.29). Finally, the % DC for Luxa Core Automix Dual, the dual-cured composite resin, revealed a steady development during the first 96h, to decrease thereafter, showing no influence of storage condition on its DC. (Figure 6.32)

Furthermore, the squared function model showed the data in the best possible way as far as the 7d storage conditions (WB versus TC) were concerned.

A highly significant (p< 0.000) strong correlation between the % DC and the FS ($r^2 = 0.662$) and also between % DC and FM ($r^2 = 0.289$) was demonstrated under 7d WB storage condition. However, an insignificant correlation (p > 0.05) between these parameters was recorded for both the FS ($r^2 = 0.098$) as well as the FM ($r^2 = 0.126$) of composite resins, investigated following a 7d TC storage condition (Figures 6.33 and 6.34)
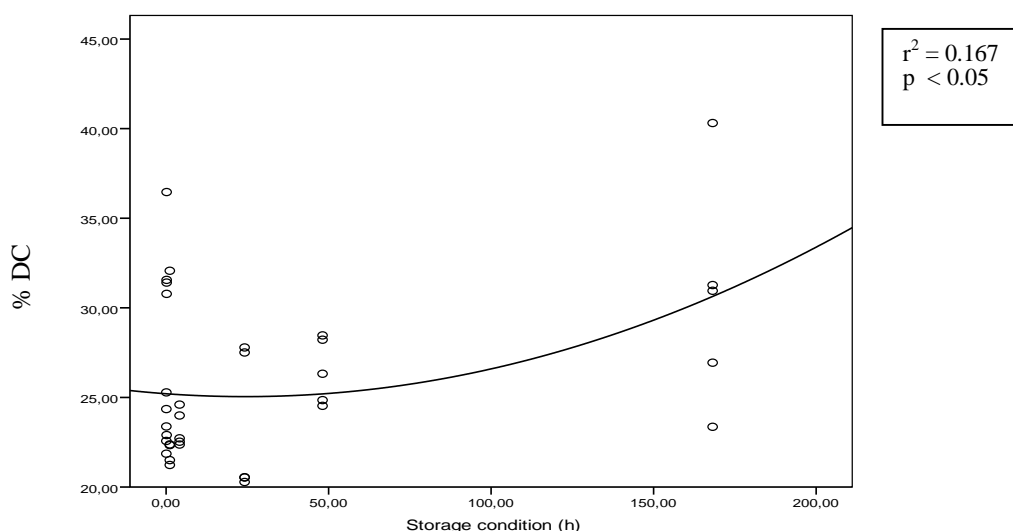
Fig.6.26 A squared correlation between storage and % DC of Rebilda SC, tested after storage under different conditions was detected.
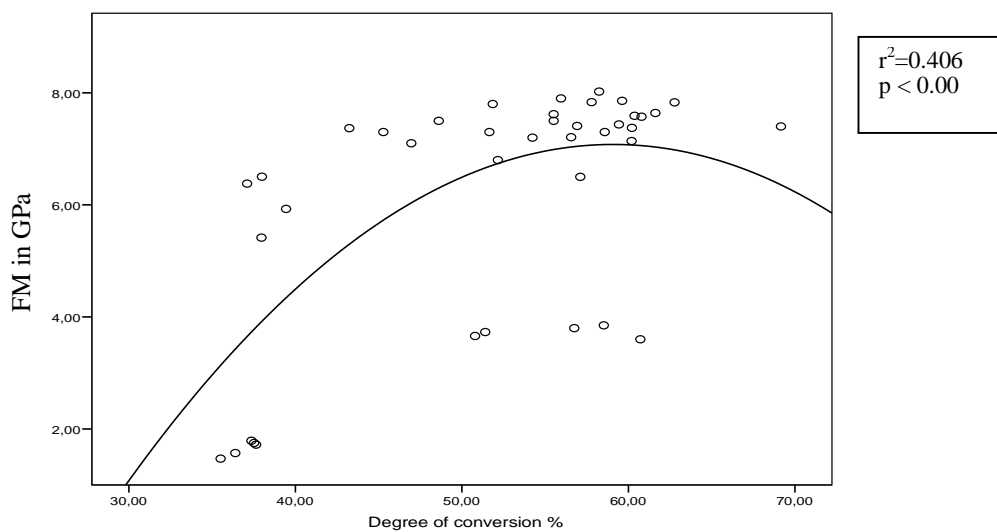
r² = 0.459
p < 0.000
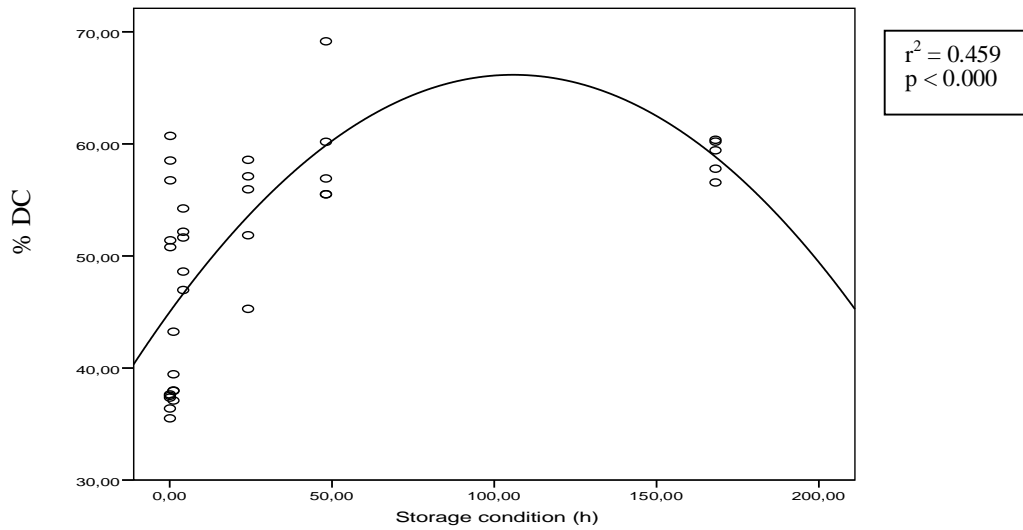
Fig.6.27 A squared correlation between storage and %DC of Luxa Core Automix, tested after storage under different conditions, was detected.
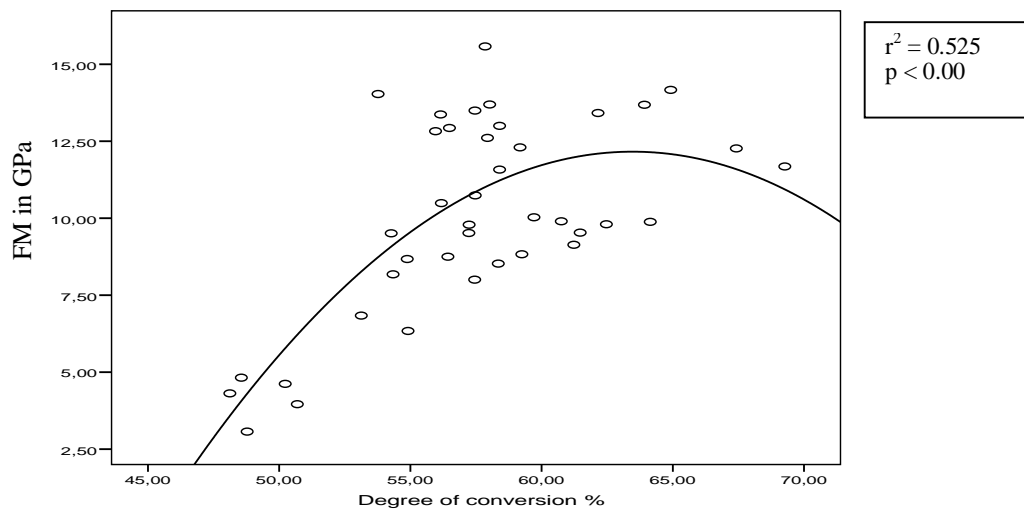

r² = 0.372
P < 0.001
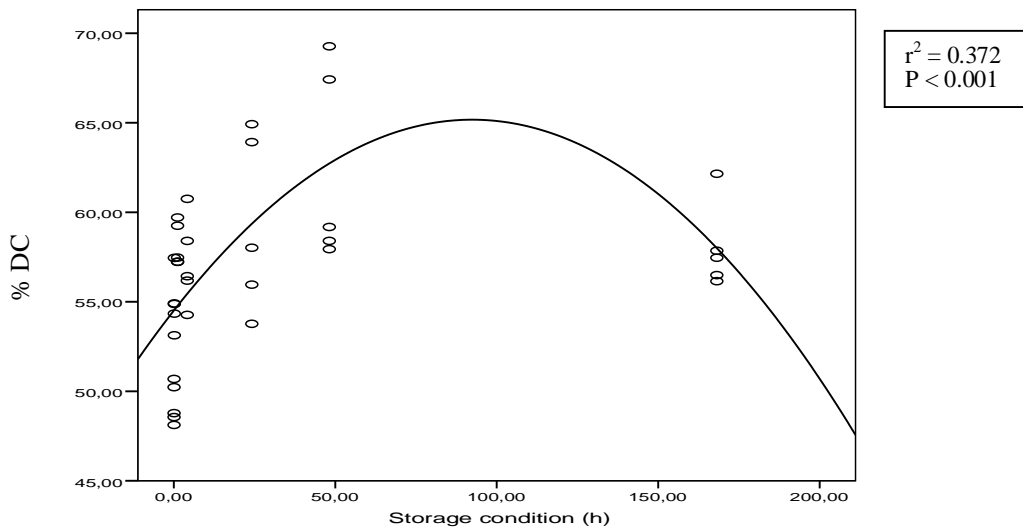
Fig.6.28 A squared correlation between storage and % DC of Clearfil Core New Bond, tested after storage under different conditions, was detected.
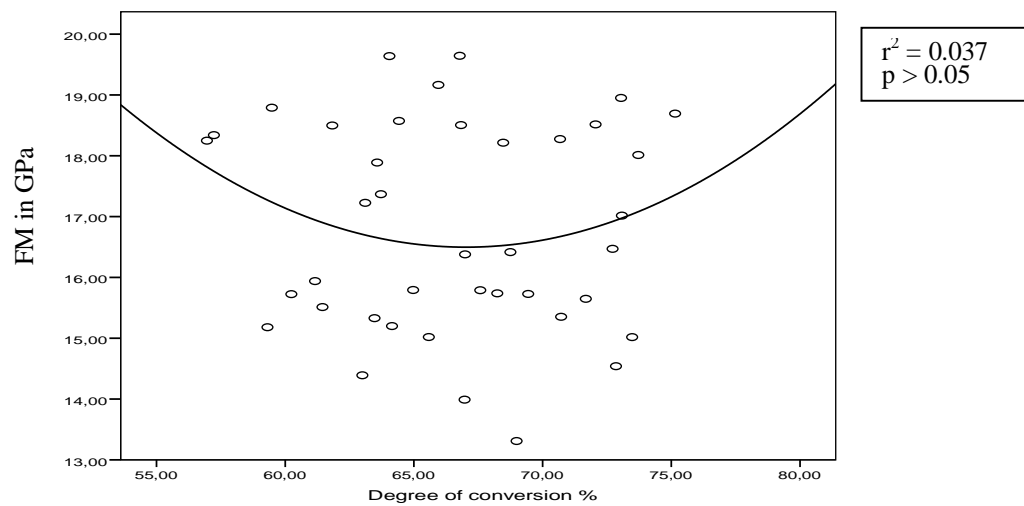

r² = 0.185
p < 0.05
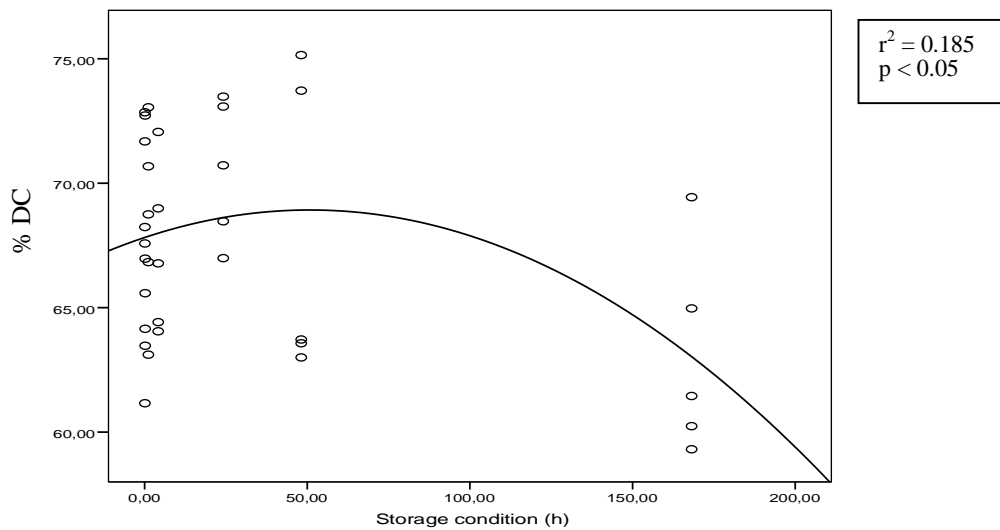
Fig.6.29 A squared correlation between storage and % DC of Clearfil Photo Core, tested after storage under different conditions, was detected.
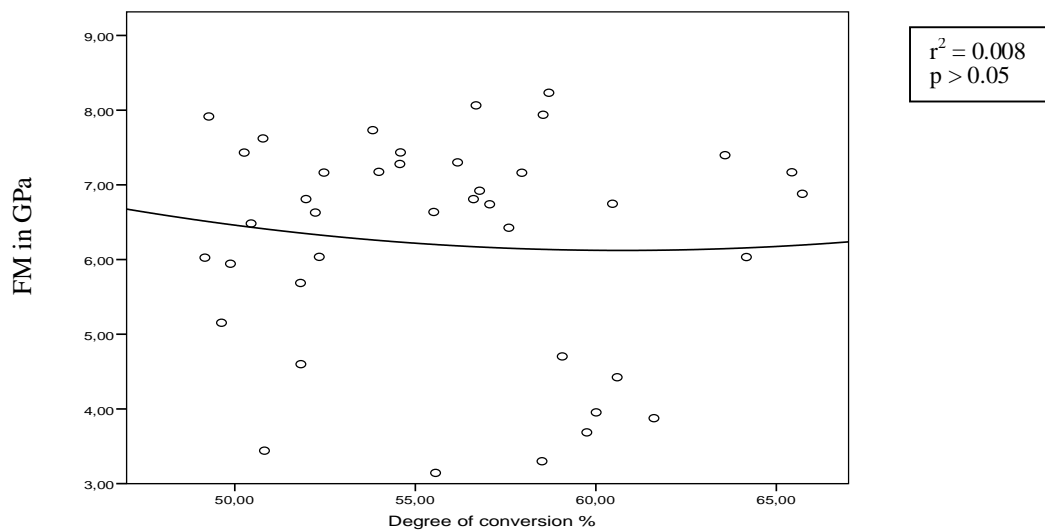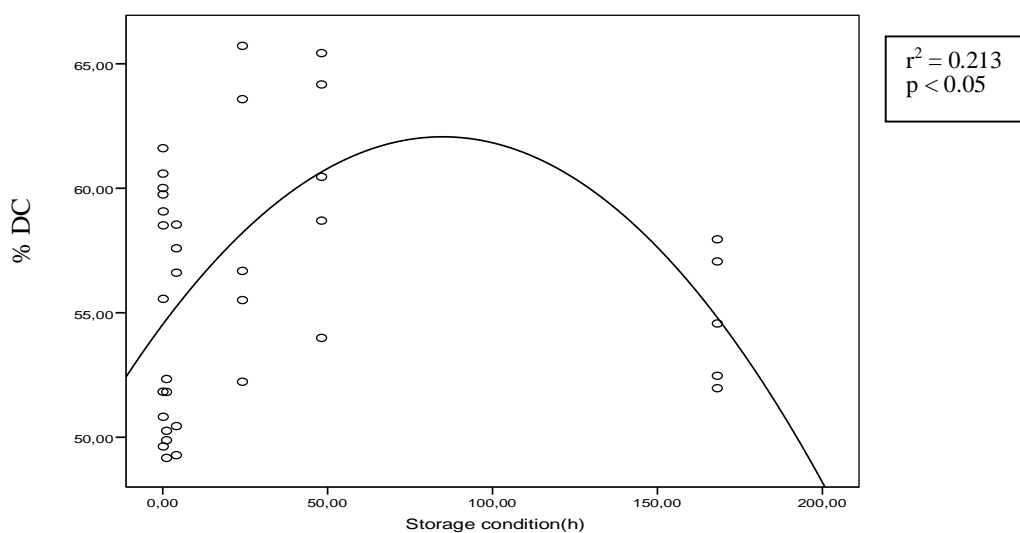
Fig.6.30 A squared correlation between storage and % DC of Charisma, tested after storage under different conditions, was detected.
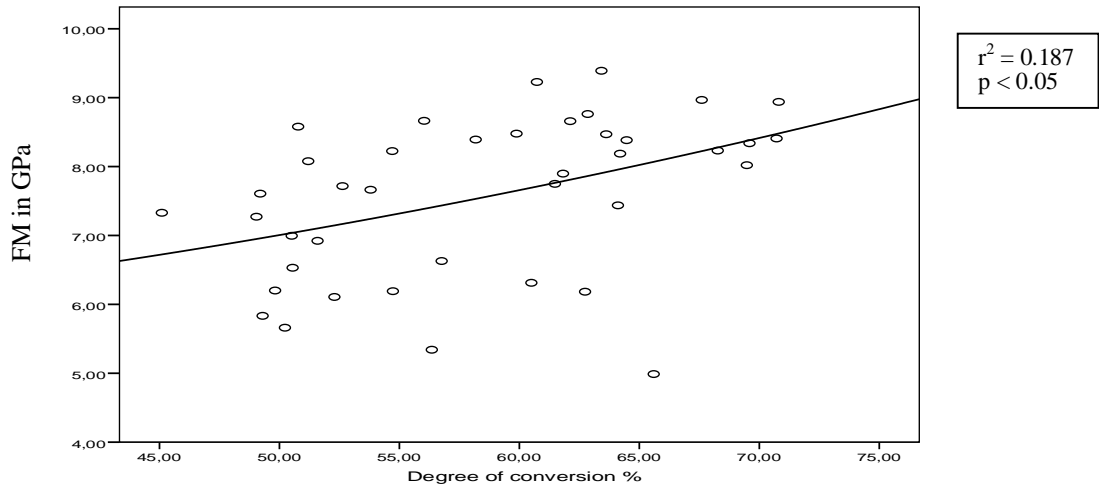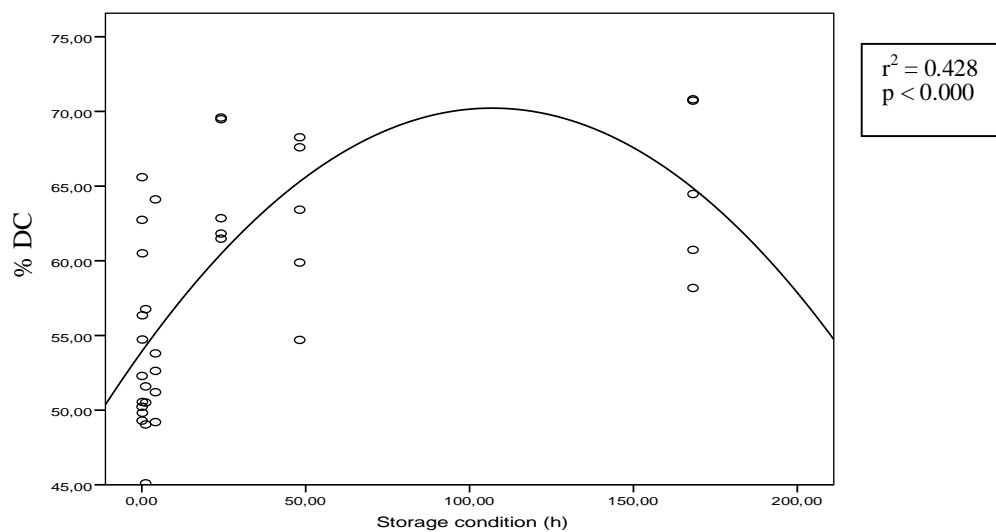

Fig.6.31 A squared correlation between storage and %DC of Rebilda DC, tested after storage under different conditions, was detected.
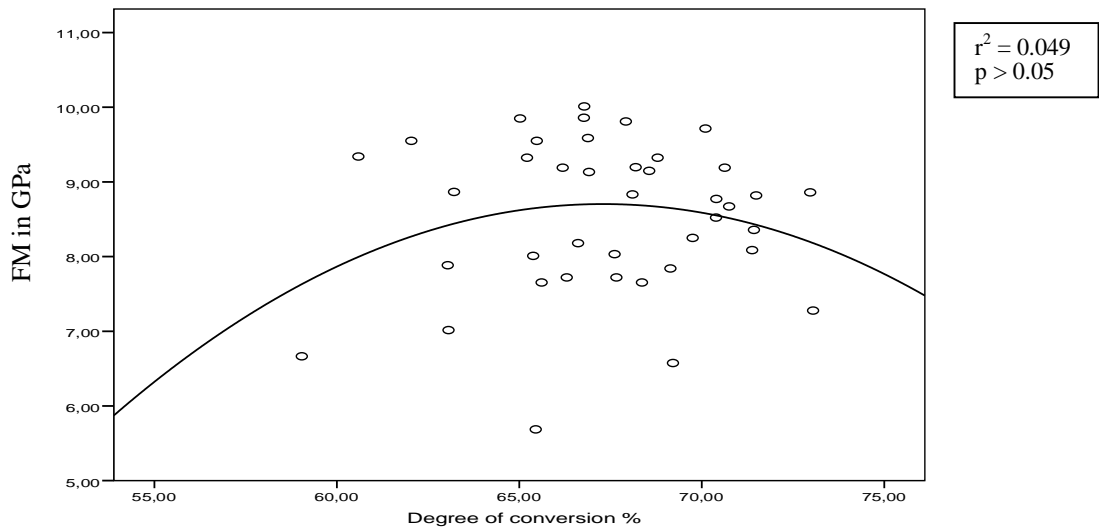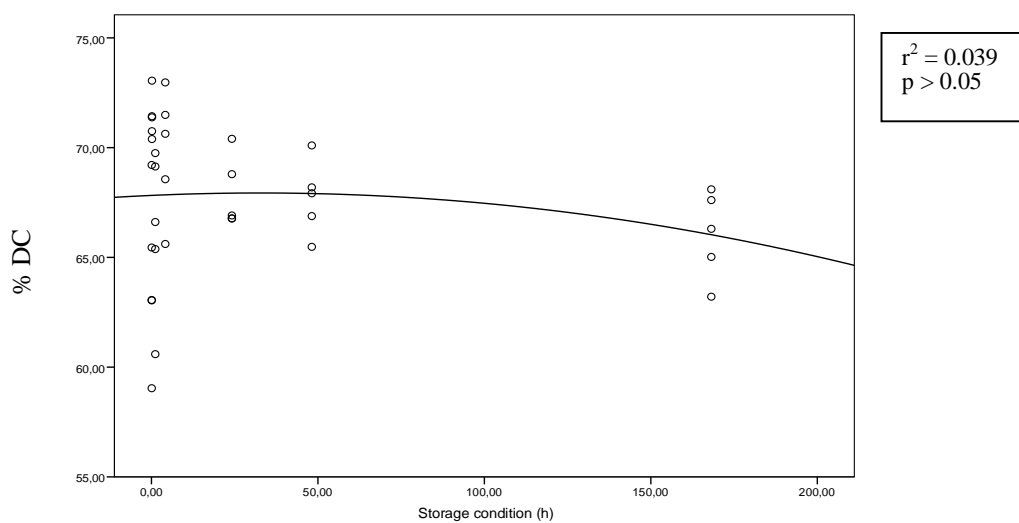

Fig.6.32 No correlation between storage and % DC of Luxa Core Automix Dual, tested after storage under different conditions, was detected.

(a)

(b)

Fig.6.33 Composite resins revealed a squared correlation between % DC and FS after a 7d WB storage period **(a),** while no correlation between % DC and FS was detected after a 7d TC storage period **(b).**

(a)

(**b**)
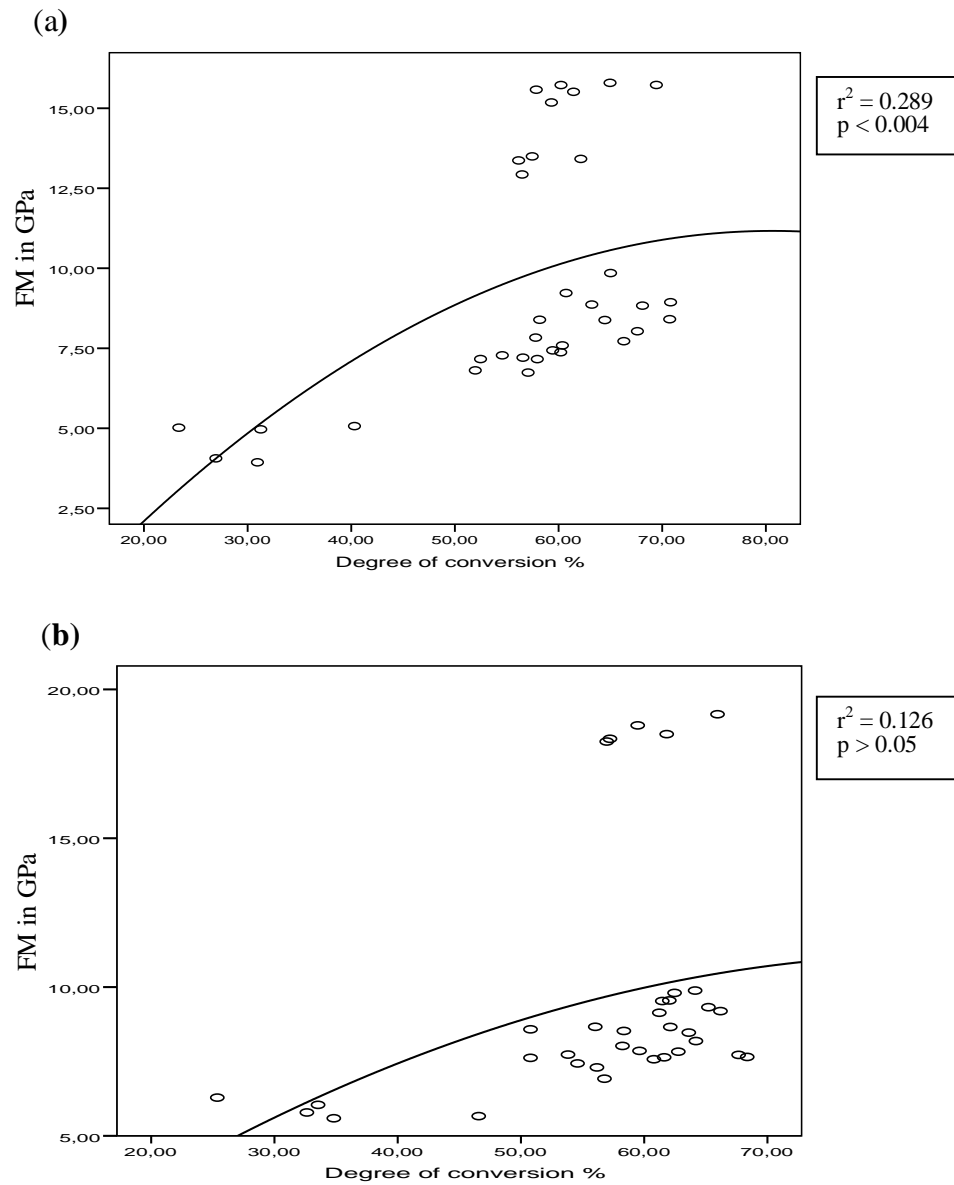
Fig.6.34 Composite resins revealed a squared correlation between % DC and FM after a 7d WB storage period **(a),** while no correlation between % DC and FM was detected after a 7d TC storage period **(b).**

Tab.6.1 FS (MPa) and FM (GPa) of all materials tested after different storage conditions, prepared according to manufacturers' instructions (Mean and SD) n=10.

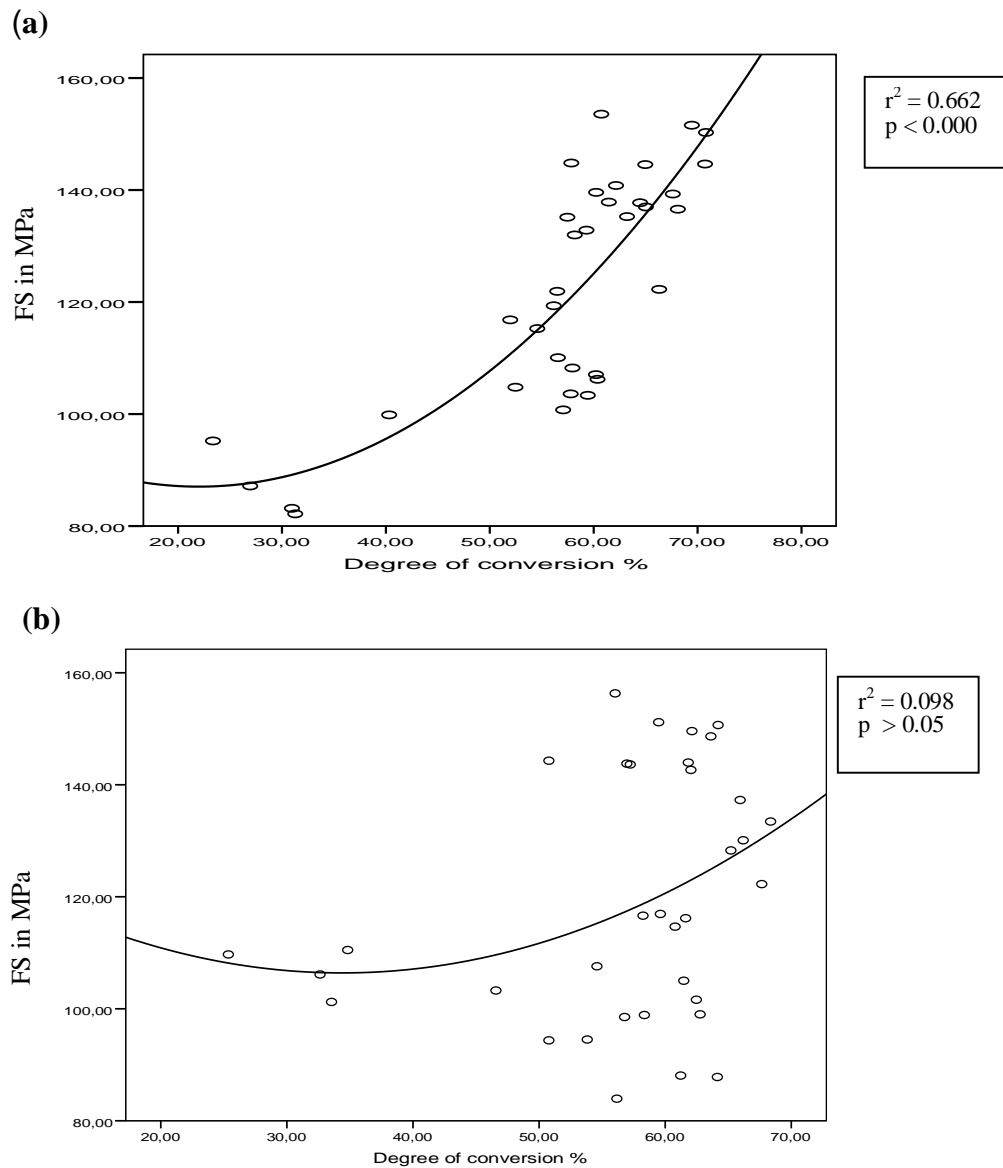| Material type	Material	Setting mode	Storage time /Storage condition	FS in MPa	FM in GPa
GIC	Fuji IX GP	SC	10 min incub	6.1 ± 1.0	2.0 ± 0.6
			10 min incub+2h WB	9.2 ± 1.1	4.8± 1.8
			10 min incub+24h WB	14.7± 1.3	10.8± 1.6
			10 min incub+7d WB	13.3± 2.1	10.3± 2.3
			10 min incub+7d TC	14.4± 1.4	9.5 ± 3.9
GIC	Ketac Molar Applicap	SC	10 min incub	4.9 ± 1.0	1.3 ± 0.4
			10 min incub+2h WB	7.2 ± 2.2	3.2 ± 1.9
			10 min incub+24h WB	11.5± 1.5	5.1 ± 2.5
			10 min incub+7d WB	14.4± 1.9	13.9 ± 0.4
			10 min incub+7d TC	11.3± 1.6	4.8 ± 2.8
GIC	Ketac Silver Maxicap	SC	10 min incub	8.1 ±1.6	2.3 ± 0.8
			10 min incub+2h WB	10.9 ±1.6	4.9 ± 0.5
			10 min incub+24h WB	9.2 ±1.0	4.7 ± 1.1
			10 min incub+7d WB	11.6±1.2	7.5 ± 1.5
			10 min incub+7d TC	12.3 ± 2.0	7.3 ± 2.4
RMGI	Fuji II LC	DC	10 min incub	49.8 ±3.0	6.6 ± 0.6
			10 min incub+2h WB	46.6 ± 2.8	6.5 ± 0.4
			10 min incub+24h WB	52.3 ± 1.6	8.2 ± 0.5
			10 min incub+7d WB	59.6 ± 5.8	9.6 ± 0.4
			10 min incub+7d TC	40.2 ± 4.8	8.6 ± 0.5
RMGI	Vitremer	TC	10 min incub	18.6 ± 1.9	1.4 ±0.4
			10 min incub+2h WB	27.7 ± 2.8	2.7 ± 0.5
			10 min incub+24h WB	31.8 ± 3.6	5.2 ± 1.2
			10 min incub+7d WB	38.3 ± 4.1	7.3 ± 0.9
			10 min incub+7d TC	38.1 ± 2.3	6.4 ± 0.9
COMPO	Dyract Extra	LC	10 min incub	88.4±12.1	6.2 ± 0.5
			10 min incub+2h WB	99.9±12.5	8.3 ± 0.5
			10 min incub+24h WB	108.9±4.7	9.4 ± 0.4
			10 min incub+7d WB	107.2±8.9	9.5 ± 0.7
			10 min incub+7d TC	110.4±8.7	9.3 ± 0.5
COMPO	F2000	LC	10 min incub	82.3± 2.3	9.1 ± 0.4
			10 min incub+2h WB	80.5± 6.3	11.8±0.5
			10 min incub+24h WB	67.4± 4.8	13.3± 0.7
			10 min incub+7d WB	37.5± 3.8	13.6± 1.3
			10 min incub+7d TC	42.5± 5.6	14.5± 0.5
CR	Rebilda SC	SC	10 min incub	60.8 ± 6.2	1.4 ± 0.4
			10 min incub+2h WB	91.7± 2.4	3.7 ± 0.4
			10 min incub+24h WB	115.3± 6.1	5.4 ± 0.7
			10 min incub+7d WB	91.7± 4.5	4.0 ± 0.6
			10 min incub+7d TC	97.8 ± 9.1	4.6 ± 0.6
CR	Luxa Core Automix	SC	10 min incub	55.3 ± 4.2	2.2 ± 0.3
			10 min incub+2h WB	104.8± 3.6	5.2 ± 0.3
			10 min incub+24h WB	114.7± 6.8	6.3 ± 0.3
			10 min incub+7d WB	100.9± 4.3	6.4 ± 0.4
			10 min incub+7d TC	102.9± 6.5	6.7 ± 0.3
CR	Clearfil Core New Bond	SC	10 min incub	86.2 ± 6.6	7.0 ± 0.9
			10 min incub+2h WB	119.7 ± 7.9	11.7 ±1.0
			10 min incub+24h WB	125.7 ± 8.1	12.2 ±1.0
			10 min incub+7d WB	125.2 ± 8.4	12.4 ±1.2
			10 min incub+7d TC	121.2 ± 9.9	11.4 ±1.8
CR	Charisma	LC	10 min incub	83.7 ± 6.1	4.1 ± 0.5
			10 min incub+2h WB	90.9 ±7.2	6.2 ± 0.5
			10 min incub+24h WB	127.4 ±9.5	8.8 ± 0.9
			10 min incub+7d WB	121.5 ±9.0	8.5 ± 0.6
			10 min incub+7d TC	109.7 ±8.5	8.0 ± 0.8
CR	Clearfil Photo Core	LC	10 min incub	127.9 ±5.8	16.6± 1.0
			10 min incub+2h WB	147.3 ±5.5	18.7± 0.7
			10 min incub+24h WB	158.7 ±6.5	19.5± 1.0
			10 min incub+7d WB	152.3 ±4.7	20.0± 1.6
			10 min incub+7d TC	151.7 ±5.0	19.2± 1.2
CR	Rebilda DC	DC	10 min incub	110.6 ± 7.4	5.2 ± 0.5
			10 min incub+2h WB	130.0 ± 6.3	7.1 ± 0.5
			10 min incub+24h WB	153.7 ± 5.1	7.7 ± 0.4
			10 min incub+7d WB	144.9 ± 8.3	8.0 ± 0.4
			10min incub+7d TC	135.3 ± 9.2	7.8 ± 0.6

CR	Luxa Core Automix Dual	DC	10 min incub	96.8 ± 6.6	6.8 ± 0.5
			10 min incub+2h WB	118.3± 7.8	8.2 ± 0.5
			10 min incub+24h WB	120.6± 6.5	8.9 ± 0.7
			10 min incub+7d WB	117.8± 6.6	8.4 ± 0.6
			10 min incub+7d TC	108.3± 5.5	9.3 ± 0.4

Abbreviations: **GIC**= Glass-ionomer cement, **mm GIC**= Metal-modified glass-ionomer, **RMGI**= Resin-modified glass-ionomer, **Compo**= Compomer, **CR**= Composite resin, **SC CR**= Self-cured composite resin, **LC CR**= Light-cured composite resin, **DC CR**= Dual-cured composite resin, **incub**= incubator, **WB**= Water bath at 37°C, **TC**= Thermocycling at 5-55°C.

Tab.6.2 FS (MPa) and FM (GPa) of all materials tested after different storage conditions with omission of the light-curing step (Mean and SD); n=10

Material type	Material	Setting mode	Storage time /Storage condition	FS in MPa	FM in GPa
RMGI	Fuji II LC	SC	10 min incub	13.3 ± 2.4	1.3 ± 0.4
			10 min incub+2h WB	26.2 ± 3.5	3.4 ± 1.5
			10 min incub +24h WB	40.8 ± 2.8	8.1 ± 0.4
			10 min incub +7d WB	48.1 ± 3.1	8.9 ± 1.0
			10 min incub+7d TC	39.4 ± 5.2	7.9 ± 0.9
CR	Rebilda DC	SC	10 min incub	66.6 ± 4.4	1.9 ± 0.5
			10 min incub+2h WB	128.1± 6.2	6.5 ± 0.4
			10 min incub+24h WB	119.8±9.8	7.3 ± 0.4
			10 min incub+7d WB	137.3±8.3	7.3 ± 0.4
			10 min incub+7d TC	131.5 ±6.6	7.9 ± 0.3
CR	Luxa Core Automix Dual	SC	10 min incub	63.2 ± 3.7	2.3 ± 0.7
			10 min incub+2h WB	109.2± 4.7	6.2 ± 0.4
			10 min incub+24h WB	97.7 ± 9.4	6.0 ± 0.5
			10 min incub+7d WB	115.3±8.2	7.5 ± 0.4
			10 min incub+7d TC	108.4±9.1	7.0 ± 0.7

Abbreviations: **RMGI**= Resin-modified glass-ionomer, **CR**= Composite resin, **SC** = Self-cured, **incub**= incubator at 37°C, **WB**= Water bath at 37°C, **TC**= Thermocycling at 5-55°C.

Tab.6.3 FS (in MPa), FM (in GPa) and % DC of different composite resin materials tested after different storage conditions (Means and SD in parentheses); n= 5

Material	Setting mode	Storage time/condition	FS in MPa	FM in GPa	% DC
Rebilda SC	SC	5 min incub	47.9 ± 3.0	0.7 ± 0.1	23.5 ± 1.4
		10 min incub	60.9 ± 3.6	2.2 ± 0.2	30.6 ± 0.9
		10 min incub + 1h WB	88.8 ± 4.9	3.7 ± 0.2	23.7 ± 4.9
		10 min incub + 4h WB	97.8 ± 2.4	4.5 ± 0.1	23.2 ± 1.0
		10 min incub + 24hWB	100.8± 6.2	4.8 ± 0.2	23.3 ± 3.9
		10 min incub + 2 d WB	104.5± 6.8	5.2 ± 0.2	26.5 ± 1.8
		10 min incub + 7d WB	89.5 ± 7.7	4.6 ± 0.6	30.6 ± 4.3
		10 min incub +7d TC	106.2± 4.0	5.9 ± 0.3	34.6 ± 5.7
Luxa Core Automix	SC	5 min incub	55.7 ± 3.2	1.7 ± 0.1	36.9 ± 0.9
		10 min incub	72.2 ± 5.1	3.7 ± 0.1	55.6 ± 4.4
		10 min incub + 1h WB	104.9±6.8	6.3 ± 0.7	39.2 ± 2.4
		10 min incub + 4h WB	113.2±3.8	7.2 ± 0.3	50.7 ± 2.9
		10 min incub + 24hWB	123.0 ± 6.0	7.4 ± 0.6	53.8 ± 5.4
		10 min incub + 2d WB	120.5 ± 5.5	7.4 ± 0.2	59.5 ± 5.8
		10 min incub + 7d WB	106.1 ± 2.8	7.5 ± 0.2	58.9 ± 1.7
		10 min incub + 7d TC	112.7 ± 2.7	7.8 ± 0.2	60.6± 1.8
Clearfil Core New Bond	SC	5 min incub	57.7 ± 4.6	4.2± 0.7	49.3 ± 1.1
		10 min incub	84.8 ± 5.3	7.6 ± 1.0	54.9 ± 1.6
		10 min incub + 1h WB	101.8± 3.8	9.8 ± 0.7	58.2 ± 1.2
		10 min incub + 4h WB	104.8± 4.6	10.1± 1.1	57.3 ± 2.5
		10 min incub + 24hWB	142.9± 5.4	13.7± 0.5	59.3 ± 4.9
		10 min incub + 2 d WB	130.1± 4.3	12.4± 0.5	62.8 ± 5.5
		10 min incub + 7d WB	135.4 ± 3.5	13.8 ± 1.0	58.0 ± 2.4
		10 min incub +7d TC	96.3 ± 7.9	9.4 ± 0.6	61.5± 2.1
Charisma	LC	5 min incub	54.7 ± 5.3	4.1 ± 0.4	58.8 ± 3.9
		10 min incub	64.5 ± 3.3	4.0 ± 0.9	54.3 ± 4.3
		10 min incub + 1h WB	93.1 ± 5.0	6.2 ± 0.7	50.1 ± 1.3
		10 min incub + 4h WB	106.8± 5.8	7.1 ± 0.8	54.5 ± 4.3
		10 min incub + 24hWB	103.6 ± 3.1	7.1 ± 0.6	58.7 ± 5.7
		10 min incub+ 2 d WB	94.1 ± 5.3	7.1 ± 0.8	59.4 ± 5.7
		10 min incub+ 7d WB	109.2 ± 4.8	7.0 ± 0.2	54.8 ± 2.7
		10 min incub + 7d TC	95.8 ± 3.1	7.4 ± 0.3	51.4 ± 2.7
Clearfil Photo Core	LC	5 min incub	126.6 ± 5.7	15.5± 0.6	68.3 ± 4.6
		10 min incub	129.7 ± 2.3	15.2± 0.9	66.6 ± 3.7
		10 min incub + 1h WB	147.0 ± 3.0	17.9± 1.0	68.5 ± 3.8
		10 min incub + 4h WB	150.6 ± 4.9	17.9± 2.6	67.3 ± 3.3
		10 min incub + 24hWB	145.1 ± 2.5	16.4± 1.3	70.6 ± 5.3
		10 min incub + 2 d WB	152.3 ± 5.5	17.3± 1.7	67.8 ± 6.1
		10 min incub + 7d WB	141.3 ± 5.1	15.6± 0.3	63.1 ± 4.2
		10 min incub + 7d TC	144.0 ± 4.9	18.6± 0.4	60.3 ± 3.7
Rebilda DC	DC	5 min incub	102.3 ± 2.3	5.8 ± 0.5	55.8± 4.7
		10 min incub	107.9 ± 5.7	6.1 ± 0.5	54.6 ± 3.5
		10 min incub + 1h WB	123.8 ± 3.9	7.0 ± 0.3	50.6 ± 2.5
		10 min incub + 4h WB	126.7 ± 1.5	7.7 ± 0.2	54.2 ± 3.8
		10 min incub +24hWB	145.4 ± 5.3	8.2 ± 0.4	65.8 ± 4.1
		10 min incub +2 d WB	143.4 ± 5.8	8.7 ± 0.5	62.8 ± 2.7
		10 min incub + 7d WB	143.6 ± 4.9	8.7 ± 0.4	65.0 ± 3.7
		10 min incub +7d TC	149.9 ± 4.3	8.5 ± 0.2	59.4 ± 5.8
Luxa Core Automix Dual	DC	5 min incub	115.9± 4.8	6.8 ± 0.8	63.6 ± 3.7
		10 min incub	126.7± 3.4	8.2 ± 0.6	71.2 ± 1.0
		10 min incub + 1h WB	129.2± 2.0	8.3 ± 0.6	66.3 ± 3.6
		10 min incub + 4h WB	138.7± 5.7	8.7 ± 0.6	73.3 ± 2.8
		10 min incub + 24hWB	140.3± 5.7	9.4 ± 0.5	67.9± 1.6
		10 min incub + 2 d WB	146.5± 3.3	9.6 ± 0.2	67.7± 1.7
		10 min incub + 7d WB	134.1± 4.7	8.7 ± 0.8	66.1± 2.0
		10 min incub + 7d TC	131.4± 4.2	8.7 ± 0.9	65.9± 2.5

Abbreviations: **SC**= Self-cured, **LC**=Light-cured, **DC**= Dual-cured, incub = incubator, **WB** = Water bath, **TC** = Thermocycling, **d**= days, **FS** = Flexure strength, **FM**= Flexure modulus, **DC** = Degree of conversion.

7. Discussion

As the aim of this study was to find out which of the restorative materials, belonging to 4 different groups, are most suitable to form a base for a long term stable tooth-colored consecutive restoration, both the FS and FM of these materials, as well as the degree of conversion of the group of composite resins were investigated. These parameters were chosen for testing, as for brittle materials, flexural tests are preferred to other mechanical tests, due to the fact that these properties more closely simulate the stress-dispersal in the restoration during service, [6] and the % DC was proven to play an important role in determining the mechanical properties and longevity of these materials. [47, 51, 52, 64, 65, 74, 112].

7.1. Flexural Strength

From the previously illustrated results, the noticed increase in FS for the first 24h for all materials (except for F2000) might be a result of an ongoing setting reaction of the materials after initial polymerization, accompanied by continuous cross-linking of the polymer chains with time of storage . [2, 18, 62, 67, 98]

Since FS shows more sensitivity to surface imperfections, high FS values might reflect better resistance to surface erosion caused by contact with water, with less tendency for the cement to craze.[26, 110]

Also, an important relationship exists between composition, and mechanical properties of materials tested, as previously confirmed. [10, 18, 47, 59, 62, 125, 133, 138]

7.1.1. Conventional Glass-ionomers

Glass-ionomers showed a slow rise in FS within the first 24h of water storage, [2, 98] with the conventional glass-ionomers demonstrating mechanical properties being much worse compared to those of other restorative materials tested [57, 133], showing a brittle nature with an abrupt fracture and minimal deformation when subjected to force.[57, 84, 93, 129] This increase in strength is thought to result from continued formation of polysalt complexes relating several ionic types, slow additional cross-linking and the buildup of a silica-gel phase accompanying the ongoing acid-base reaction due to hydration of the cross-linked matrix. [27, 53] However, these findings are in contrast to the opinions of some authors who denied any difference between conventional and resin-modified glass-ionomer materials, also demonstrating adverse   affection of

conventional, metal-modified and resin-modified glass-ionomer materials by storage in aqueous media.[13] The metal-modified glass-ionomer material, Ketac Silver Maxicap, demonstrated lower FS values after 24h storage period, compared to both viscous conventional glass-ionomer materials, Fuji IX GP and Ketac Molar Applicap, [103] probably as a result of a different acid base incorporation: the glass-ionomer material based on polymaleic / polyacrylic acid (Ketac Silver Maxicap) showed lower FS values than those based on polyacrylic acid alone (Fuji IX GP and Ketac Molar Applicap), with the latter showing greater stabilities.[98] A lower FS observed for polymaleic-based materials can be attributed to the copolymer and to the different type of glass used, whereas the increase in FS of conventional glass-ionomers with time of storage, can be attributed to the presence of water, allowing slow-setting glass-ionomers to complete the acid-base reaction or possibly to minimize the surface cracks. [16, 98]

Most of the glass-ionomer cements did not reach their maximum strength after 24h, [26] due to the slow rate of the preceding acid-base reaction, the strength increasing further with longer times of storage. FS values of the conventional glass-ionomer materials investigated were very close to each other showing insignificant differences throughout all storage conditions.

On the other hand slight weakening that occurred for the glass-ionomer material, Ketac Silver Maxicap, following 24 h water storage, may result from the plasticizing effect of water diffusion through the specimen, resulting in a reduction of their FS. The contacting water partly dissolves material components with a consequently altered network of the glass-ionomer cement.[24] Authors have attributed the decreased strength of conventional glass-ionomers to increased solubility of glass-ionomer materials, and the hydrogel phase increasing water sorption of the set materials, with the higher degree of hydration resulting in lower mechanical properties. [16, 89, 123]

In accordance with the relevant literature, metal-modified glass-ionomers showed properties not different to those of the other conventional glass-ionomers tested, with no improvement in flexural properties, as stated by several authors.[87, 95, 103, 119, 129]

7.1.2. *Resin-modified Glass-ionomers*

Resin-modified glass-ionomers showed significantly higher FS values compared to the conventional glass-ionomers throughout all storage conditions. A positive influence of resin incorporation [78, 83, 84, 133] was noted, allowing an initial setting reaction due

to hydroxyethyl methacrylate (HEMA) polymerization, subsequently followed by the slowly proceeding acid-base reaction typical of conventional glass-ionomers. The latter reaction served only to harden and strengthen the already created matrix.[89, 131]

In resin-modified glass-ionomer materials, several polymerizations take place:[131]

1-HEMA polymerization to poly HEMA

2-Modified polyacrylic acid (PAA), that contains unsaturated groups, will copolymerize with HEMA, so that HEMA will be chemically-linked to the polyacrylate matrix, preventing an occurrence of phase separation.

3-Modified PAA will further polymerize to form a cross-linked PAA, increasing strength of the cement.

Fuji II LC and Vitremer, the resin-modified glass-ionomers, have shown significantly higher FS values (Fuji II LC > Vitremer) throughout all storage conditions compared to the rest of glass-ionomers tested. The higher FS might be a result of a different composition, as an additional photocurable monomer in the liquid, such as HEMA, was incorporated to the glass-ionomer cement [36], enabling an additional light-cured polymerization to occur, with a resultant structure reinforcement, having a polymeric network containing both ionic and covalent cross-links. [24, 25, 63, 67, 89, 131]

Fuji II LC and Vitremer reached their maximum FS within 7d. [67] This might be a result of the acid-base reaction being much slower in water/HEMA mixtures than in water alone, the case with conventional glass-ionomers [131]. As some of the water in conventional glass-ionomers was replaced by HEMA, the initial set of these materials is due to the polymerization of HEMA , the chemically- or photocurable monomer[131] with the acid-base reaction further continuing for some days thereafter. Fuji II LC demonstrated significantly lower FS values following the 7d thermocycling period.

The reason for Fuji II LC showing higher FS values compared to Vitremer might be due to a different composition, as Fuji II LC contains urethane dimethacrylate (UDMA) monomers as compared to Vitremer which does not contain that component, proving increased FS values with replacement of Bis-GMA or TEGDMA by UDMA, as has been declared by some authors.[10, 19] Moreover, a more integrated microstructure (i.e. better glass particle-polymer matrix bonding) [133] with UDMA and dimethacrylate (DMA) oligomers added to the liquid, might be a result for higher FS values compared to Vitremer material, imparting more cross-linking with increased stiffness.

Another reason for the lower FS values for Vitremer compared to those of Fuji II LC, could be a result of the mixing mode, being hand-mixed for Vitremer, and in the form of automixed capsules for Fuji II LC. As Vitremer is hand-mixed, the increased possibility of air-bubble incorporation may cause a negative effect on the material's properties, hindering a more integrated microstructure.[27, 133]

Remarkable weakening in Fuji II LC following the thermocycling period may appear due to the plasticizing effect of water diffusion through the specimens, resulting in reduced FS. The contacting water partly dissolves material components with a consequently altered network of the glass-ionomer cement.[18] For Fuji II, the resin-modified glass-ionomer, showed hydrophilicity, readily absorbing water, due to its content of poly/HEMA, as well as its behavior like a hydrogel in presence of water. [19]

With regards to the 7d storage condition, some materials tested showed minimal further increase in FS with time of storage, (Ketac Molar Applicap, Ketac Silver Maxicap, Fuji II LC) indicating an ongoing acid-base reaction with further cross-linking and silica–gel phase buildup. It was stated that further setting during storage was dependent on the capacity of the cement setting reaction to continue after initial polymerization.[84]

The resin component in resin-modified glass ionomers slows down the ionic cure (acid-base) reaction and increases water sorption reversibly, most probably interfering with the ion-transport required for the acid-base reaction, hindering the formation of the ionic matrix.[13, 88] On the contrary, other authors were of the opinion that resin addition to materials increases their mechanical properties and flexure strength compared to those with limited or no resin content, demonstrating less water solubility and decreased moisture sensitivity. [53, 78, 84, 121, 133]

7.1.3. *Polyacid-modified composite resins*

Compomer materials showed FS values between those of glass-ionomers and composite resin restorative materials, [40, 82, 103, 121] depending on the resin content of the matrix phase of the set material[53], with properties determined by its composite character, [25] having less filler amount compared to hybrid composite resins.[60] Initial setting of compomers is by light-activation to be followed by acid-base reaction.[91] Moreover, compomer materials, which are partially silanized,[82, 90, 91] actually set only by polymerization, due to the insufficient amount of carboxylic acid functional groups to confer water-solubility on the molecule, without starting a neutralization reaction.[90]

Furthermore, silanization of reactive ionomer glass reduces rate of undergoing acid-base reaction for compomers and the water/HEMA mixtures in the resin-modified glass-ionomers, with a consequent reduction in FS.[4]

Both the brand of material and storage time significantly affected FS of compomers tested,[58] with Dyract Extra showing a gradual increase in FS with significantly higher values compared to those of F2000 throughout all storage conditions.

F2000 showed a reduction in FS despite of its high filler content (84 wt %) with increased time of water storage (least values after 7d storage (7d WB< 7d TC)]. This might be due to its hydrophilic polymer content of CDMA (a methacrylated polycarboxylic acid), [134] increasing water sorption of the material, or due to the use of fluoroaluminosilicate (FAS) glass fillers with a resultant decrease in strength due to the plasticizing effect of water partially dissolving material components [27] or degrading the filler matrix interface.[113]

Dyract Extra, the other compomer material, which has lower filler content (75 wt %) does not contain that hydrophilic component, but rather a mixture of methacrylate resins. No deteriorating effect of water storage was noticed. [58] Also the incorporated TCB- resin, the carboxylic-acid modified dimethacrylate, did serve to provide high cohesion to the resin mixture, imparting increased strength.

Another cause for lower FS of Dyract Extra, the compomer material, compared to composite resins, might be due to the incorporation of an ethoxylated dimethacrylate (Bis-EMA) that imparts less hydrophilicity into the compomer (due to the absence of hydroxyl groups) with reduced viscosity [68] and increased conversion [52], but with an absence of strong secondary molecular interactions, with a consequently decreased strength.[101]

Storage time in water proved to have an effect on FS of conventional glass-ionomers, resin-modified glass-ionomers and compomers, [2, 52, 66, 81, 103] contradicting the finding of some authors who proved little or no influence of storage time on the FS of these materials, being only influenced by the difference in material type.[24, 25, 27, 35, 46, 82-84, 99, 121]

7.1.4. *Composite resins*
Compared to composite resins which show a slower rate of water-uptake, lower FS values of compomers may be partially attributed to the more rapid uptake of water,

which is necessary for the activation of the acid-base reaction with the polymer matrix.[135]

Composite resin materials showed the highest FS values compared to the rest of the materials tested, throughout all storage conditions.[25, 28, 33, 59, 60] Clearfil Photo Core, the microhybrid light-cured composite resin, demonstrated the highest FS values throughout all storage conditions. [24] This might be due to its highest filler content (83 wt %), resulting an increased strength.[46, 59, 69, 138] The self-cured composite resin, filled with fine particles, Luxa Core Automix (72 wt%) and the flowable Rebilda SC (68.5 wt%), showed lower FS values compared to Clearfil Core New Bond, the microhybrid self-cured composite resin of higher filler amount (78 wt%) in its formulation., proving a trend for the FS to increase with increased filler content up to a specific level. [28, 33, 46, 59]

Charisma, the microglass-filled (78 wt%), light-cured composite resin showed FS values that were similar to Clearfil Core New Bond, a self-cured composite resin, but higher than those of the other self-cured types, for all storage conditions. FS values of Charisma were also higher than for the dual-cured composite resin Luxa Core Automix Dual (72 wt % microhybrid filler) for the 24h storage period, but not as high as those of the light-cured material Clearfil Photo Core, and the dual cured material, Rebilda DC (flowable, having 70 wt% fine dispersion fillers). Having lower FS values compared to the other light-cured and dual-cured materials might be due to its additional microsized silica content of increased surface area, favoring water sorption with accompanied degradation and a reduction of its FS.[18, 62, 67, 86] This finding contradicts the statement of some authors, who propose that a higher filler volume percentage of composite resins leads to higher flexural properties. [69, 109]

Also, the dual-cured material Rebilda DC, has its monomer system additionally based on di-UDMA monomers, providing more cross-linking and significantly higher strengths. [19, 35, 52] This is because the kinked bisphenol A core (in Bis-GMA), present in other composite resins, imparts stiffness and strength to the dimethacrylate, hindering polymerization, finally resulting in a higher amount of residual double bonds and a higher potentially leachable monomer, compared to the aliphatic UDMA.[73]

Lowered mechanical properties of composite resins when stored in water, could be attributed to a softened resin matrix and / or bond failures in the outer layer of fillers,

either placed in the silane coating or at the silane/matrix interface as a negative water effect.[113]

The brittleness of dimethacrylate-based networks (Bis-GMA, UDMA and TEGDMA) may be due to a specific structure-buildup by the formation and agglomeration of microgels.[17]

Regarding the 7d storage conditions (7d WB versus 7d TC), all materials tested showed insignificant differences between both storage periods. Storage environment has influenced the FS of some materials; Ketac Molar Applicap (a conventional glass-ionomer), Fuji II LC (a resin-modified glass-ionomer) and Luxa Core Automix Dual (a dual-curing composite resin), which showed decreased strength after thermocycling, supporting the opinion that composite resins are less influenced by storage environment, whilst glass-ionomers materials are influenced by temperature change.[25, 82] This may be due to the higher resin content in composite resins (compared to compomers and resin-modified composite resins) and the total absence of fillers in conventional glass-ionomer materials.[6, 36, 88, 95]

7.2. Flexural Modulus

Elastic modulus is a material's constant, completely dependent on its composition, not being influenced by the amount of elastic- or plastic-stress to which the material is subjected, but rather the interatomic forces of the materials, which are responsible for their elastic properties. [6, 36]

A gradual increase in FM of all materials was noticed for all storage conditions, with fewer differences between materials as previously declared by some authors,[25, 35, 66, 110] contradicting the opinions of other authors, announcing a negative effect of wet storage on resin-based and acid-based materials.[20, 77]

Water sorption has been associated with a change in the nature of the material from brittle to plastic, as absorbed water acts as plasticizer. [67, 96]

Increasing strength supposes a continuing setting reaction with increased cross-linking, where highly cross-linked polymers are expected to reveal high elastic modulus, but increased brittleness.[101]

7.2.1.   Conventional Glass-ionomers

Conventional glass-ionomers showed FM values that were either insignificantly different or significantly higher than Vitremer, the resin-modified glass-ionomer,

Rebilda SC as well as Luxa Core Automix, the self-cured composite resins. This is most probably due to the more flexible nature of the glass-ionomer matrix, being in accordance with the literature. [84, 133]

All glass-ionomer materials showed highest FM values after 7d storage periods, being insignificantly different from their 24h storage time, which might result from the slow acid-base reaction, rendering the FM values constant thereafter. [6, 27, 98]

Fuji IX GP, the highly viscous, fast-setting glass-ionomer cement,[36, 103] revealed its highest FM values after the 24h and 7d thermocycling periods, most probably due to its composition, which is different, as it is based on polyacrylic acid alone.[80, 98] Additionally Fuji IX GP contains fine glass particles, anhydrous polyacrylic acid of high molecular weight and a high powder–to-liquid mixing ratio.[36] On the other hand, Ketac Molar Applicap showed the highest FM values only for the 7d WB storage period, [103] most probably resulting from its slower acid-base reaction, with a slower setting and cross-linking, due to its type of acid base (polymaleic/polyacrylic acid) and its lower powder-to-liquid mixing ratio. Ketac Silver Maxicap showed significantly higher FM values for both 7d storage conditions compared to the rest of storage conditions, which may be related to its slower acid-base reaction with a resulting matrix formation.

7.2.2. Resin-modified Glass-ionomers

Throughout all storage conditions, Fuji II LC showed higher FM values compared to Vitremer. This might be due to different backbones of both materials. The incorporation of UDMA into the liquid of Fuji II LC, having its hydroxyl groups enabling formation of strong hydrogen bonds, resulted in increased FM of the material[10, 16, 17], while only HEMA monomer as well as pendant methacrylate groups were present in the Vitremer.[133] For the direct correlation between water-uptake and decreased FM that was recognized, the absorbed water partially dissolves material components with a subsequently altered network.[24] An increased bond strength within the material (in Fuji II LC), may also result in an increased resistance to the plasticizing effect of water.[10, 16, 17]

7.2.3. Polyacid-modified composite resins

F2000, the compomer material, showed higher FM values compared to Dyract Extra throughout all storage conditions, which may be due to its higher filler content (84 wt%)

compared to 75 wt% for Dyract Extra, with a resultant increased stiffness of the material, as well as due to the smaller filler size in Dyract Extra (0.35 μm, 1.5 μm), having increased surface area,[60] favoring plasticizing effect of water, weakening bond strength in the materials network. [36, 123]

F2000 materials have shown FM values being higher compared to resin-modified glass-ionomers and self-cured composite resins tested [63], most probably due to its higher resin amount, compared to resin-modified glass-ionomers, as properties of compomers are determined by their composite character [25], as well as their filler silanization, an important property for optimal physical properties. [4] Also, a greater strength of dimethacrylate-based networks (as for Dyract Extra, Rebilda SC and Rebilda DC) due to stronger hydrogen bonds, results in the formation of larger heterogeneities, being accompanied by increased brittleness of poly-dimethacrylates. [17] This brittleness results most probably from the formation and agglomeration of microgels.[17]

7.2.4. *Composite resins*

The light-cured Clearfil Photo Core and the self-cured Clearfil Core New Bond revealed highest FM values compared to the rest of composite resins tested (Clearfil Photo Core > Clearfil Core New Bond), both hybrid composite resins with higher filler amount (83 wt% and 78 wt% respectively) This might result from the higher filler volume fraction of the material, [59] while the lowest FM values were presented by the flowable self-cured Rebilda SC, in accordance with the literature, for the flowable type to show lower FM values.[66]

The microglass-filled universal composite resin, Charisma, showed lower FM values compared to the highly-packed hybrid composite resins, Clearfil Core New Bond and Clearfil Photo Core, and similar values to the dual-cured types (Rebilda DC and Luxa Core Automix Dual) for the 24h storage period, supporting the statement that hybrid composite resins possess better mechanical properties as compared to microfilled types.[18]

Rebilda SC and Rebilda DC, the flowable composite resins with lower filler content (68.5 wt% and 70 wt% respectively), although UDMA monomers added, still showed lower FM values. This may be due to its setting mechanism, which is only chemically-initiated (for Rebilda SC), lower filler content and size (fine dispersion fillers), the incorporation of HEDMA, favoring water sorption with increased plasticizing effect of water, which consequently results in bond deterioration.[13, 17] Also, the incorporation

of Bis-GMA in the material, containing pendant hydroxyl groups, renders the materials more hydrophilic with increased water sorption.[68]

Both dual-cured composite resins (Rebilda DC and Luxa Core Automix Dual) proved to be changed insignificantly by thermocycling, with the differences occurring as a function of material,[66, 76, 85, 126] as the type of composite resin material determines the materials' performance in wet environment.[18, 62]

Amongst self-cured composite resins, Clearfil Core New Bond revealed the highest FM values throughout all storage conditions, compared to the other 2 materials, Rebilda SC and Luxa Core Automix, both showing insignificant differences except at 2h and 7d WB storage conditions. This might be a result of the TEGDMA content of Clearfil Core New Bond, with the molecule behaving as a cross-linking agent with antiplasticiant effect.[101] Additionally, Clearfil Core New Bond is a microhybrid composite resin, with a higher filler content (78 wt %) and filler distribution, compared to the other self-cured composite resins, with Rebilda SC being of the flowable type (68 wt %) and Luxa Core Automix a fine particle size composite resin (72 wt%). These results support the statement that FM increases with increased filler volume fraction. [59]

Lower FM properties for self-cured composite resins could also result from the intense effect of the composite's component degradation following water storage.[8]

Some composite resins showed FM higher to that of resin-modified glass-ionomers and Compomers, which showed FM values similar to conventional glass-ionomers, possibly due to increased resin content in composite resins and their fillers being silanized. [12, 37]

Both self-cured composite resins, Rebilda SC and Luxa Core Automix showed FM values lower than that of compomers tested, contradicting the statement that composite resins show higher FM values.[33]

7.3. Omission of light-curing step

All 3 materials tested (Fuji II LC, Rebilda DC and Luxa Core Automix Dual), showed higher flexural properties for the light-cured specimens compared to the non light-cured specimens. A positive effect of water storage was recorded, with a gradual increase with time of storage, proving the continuing setting reaction with increased strength as a result of increased cross-linking with time. [2, 18, 62, 67, 98]

7.3.1. Flexure Strength

The lowest FS values were recorded for Fuji II LC, the highest for Rebilda DC, compared to both the other materials tested throughout all storage conditions for both curing modes. This could most probably be due to the fact, that the resin-modified glass-ionomer have limited resin content [53, 79], as well as an absence of filler silanization, [4, 37] as the case with composite resins tested.

The presence of HEMA in Fuji II LC may be a factor in its' increased water sorption, with an accompanying plasticizing effect on the matrix.[24, 27, 77]

Fuji II LC showed higher FS values for the light-cured specimen, and was significantly affected by the omission of the light-curing step, decreasing the integrity of the material with lower mechanical properties, contradicting the statement of de Gee et al, 1998 who stated that Fuji II LC is not affected by omission of the light-curing step, with a proved decrease in the integrity of Vitremer, the resin-modified glass-ionomer with delayed light-activation and further decline with light omission.[39] As the structural integrity of resin-modified glass-ionomers benefits from a chemical integration of the polyalkenoate /poly HEMA networks, which is most probably enabled with light-curing, these types of materials are greatly affected by skipping the light-curing step for polymerization of the HEMA component.[39]So, this material would only be dependent on the slow acid-base reaction, showing its complete strength after 7d storage in distilled water, followed by a significant drop after thermocycling, most probably due to erosion and plasticizing effect of water on the matrix.[27]

For the composite resin materials tested, filler silanization enhances damage tolerance, improving their clinical performance, as stated by Curtis et al 2009 [37] and several other authors [46, 59, 69, 138]

Rebilda DC, the flowable hybrid composite resin showed higher FS values compared to Luxa Core Automix Dual for both the light-cured as well as the chemically-cured specimens (without light-curing) throughout all storage conditions. The difference in FS was most probably due to incorporation of UDMA in Rebilda DC material [19] which enabled more cross-linking , flexibility and weaker intermolecular bonds [52], as well as less hydrophilicity, [25] compared to Bis-GMA oligomer available in Luxa Core Automix Dual. The Bis-GMA oligomer was proven to be more rigid, showing higher water sorption as well as less cross-linking and lower strength. [52]

7.3.2. Flexural Modulus

Amongst the non light-cured materials, Fuji II LC showed the lowest FM values after 10 min and for both modes after 2h storage conditions. This could be attributed to it depending for its setting only on the slowly progressing acid-base reaction, with a resultant slow additional cross-linking and buildup of a silica gel phase.[27]

On the other hand, Luxa Core Automix Dual recorded the lowest FM values after 24h and 7d thermocycling, for non light-cured specimens, showing insignificantly different values from those of Rebilda DC for the rest of storage conditions.

Higher cross-linking, with accompanying embrittlement and weaker intermolecular bonds in Rebilda DC material due to the incorporated UDMA,[52, 101] could be a result of a decreased FM, as increased strength of hydrogen bonds in dimethacrylates results in occurrence of larger heterogeneities increasing the materials' embrittlement.[17]

Rebilda DC, containing lower amount of fine dispersion fillers(70 wt%) compared to the microfine particles in Luxa Core Automix Dual (72 wt%), both depending in their setting only on the self-cured mechanism, most probably taking longer time, may be due to increased amount of residual monomers, that act as plasticizers with resulting structure alteration and weakness. [6, 123]

7.4. Degree of Conversion

7.4.1. Correlation between flexural properties and Degree of Conversion

The previously illustrated results showed a significant correlation between flexural properties (FS and FM) and % DC for 2 self-cured composite resins (Luxa Core Automix and Clearfil Core New Bond) and a dual-cured composite resin (Rebilda DC). Those three composite resins demonstrated with increased conversion, an apparent increase in FS as well as FM values, both rising gradually with increased storage time and % DC, being in accordance with several authors affirming the presence of a significant correlation between % DC and flexural properties. [44, 47, 51, 52, 64, 65, 74, 112]

However, there was no remarkable influence of DC on the development of flexural properties of the rest of composite resins investigated (Rebilda SC, Charisma, Clearfil Photo Core and Luxa Core Automix Dual), revealing a more rapid rise in %DC compared to their mechanical properties. The faster rise in DC noticed for these

materials compared to their flexural properties, can be explained by the continuous growth of polymer chains after mixing, resulting in higher molecular oligomers, most probably consuming higher amounts of double bonds during the very early stages of the reaction.[5] As the cross-linking density between the created oligomers required for a mechanical stability of a material has not yet been established at these early stages of polymerization, it seems the mechanical stability of a material to be inequivalent to its DC.[44] Though, with additional cross-linking over time, more molecular oligomers get linked together into a rigid polymer, with a considerable increase in mechanical properties.[5]

It has been reported, that the use of multifunctional monomers, of more than 2 reactive double bonds per molecule, apparently lead to higher reaction rates with more cross links, but a simultaneous reduction in DC.[5] That is because on polymerization of multifunctional monomers, pendant double bonds can react intramolecularly with the radical on its propagating chain to form a loop in a 1ry cyclization, resulting merely in microgel formation and heterogeneity of the matrix.[74]

This disparity between DC on one hand and the flexural properties (FS and FM) on the other, depends most probably on the material itself, with the mechanical properties being much dependent upon network formation, [31, 44] with more cross-linking, which is considered to be of greater importance for good network formation and better physical properties.[52] Differences in % DC values could accordingly be ascribed to dissimilarity in monomer systems used amongst materials, or the different chemical structure of the spacer group connecting the methacrylate groups.[42, 106, 112]

It has also been stated that dimethacrylate monomers polymerize to highly cross-linked, three-dimensional networks, within which polymerization has been found to occur at different rates, being higher in so-called ''microgel'' regions because of a local gel effect.[107] As polymerization proceeds, diffusion rates of propagating free radicals and unreacted dimethacrylate molecules are considerably reduced, hindering complete conversion of methacrylate double bonds. Therefore, about 25 to 55% of the methacrylate groups remain unreacted. [9, 106, 107]

Other parameters, such as inhibitor- and diluent concentrations influenced the DC, achieving higher DC with higher diluent- and lower inhibitor concentrations. [32, 47] Composite resins with higher DC are thought to develop more rigid networks than materials with lower conversion.[118]

Most composite resins in this investigation showed % DC varying between 55-73%, most probably due to limitations in conversion caused by vitrification of the polymer network during polymerization. [45, 51, 106]

The lowest flexural properties, accompanied by the lowest % DC were recorded for Rebilda SC, the flowable self-cured material, remaining at lower levels when compared to the rest of composite resins investigated. The poor performance of Rebilda SC, can be explained by its self-curing setting mechanism, since setting of dimethacrylates at room temperature may be the reason for creating glassy resins with an incomplete double bond conversion.[74, 112] Since the matrix of Rebilda SC is based on Bis-GMA monomer, relatively strong intermolecular interactions with higher viscosities are created, as a result of the available OH groups, finally causing slow diffusion of radicals within the network and a lower % DC. [31, 61, 101, 118] Increased viscosity of Bis-GMA monomers always results in incomplete and considerable concentration of unreacted C=C double bonds, which may be a reason for loss of mobility,[31, 74] and decreased reactivity of polymer radicals in highly viscous networks. Such mobility restrictions are thought to result in lower DC in polymer systems, [9, 31, 47, 52, 100, 106] with the diffusion-controlled kinetics and unreacted radical population limiting the final conversion.[74] Moreover, as nearly 25 to 55 % of methacrylate groups remain unreacted, [9, 106, 107] the plasticizing effect of residual unreacted monomers or unreacted C=C bonds on the polymer matrix renders them more susceptible to degradative reactions.

As the resin matrix of Clearfil Photo Core, Charisma and Clearfil Core New Bond is based on a Bis-GMA/TEGDMA mixture; an autoacceleration takes place with a rapid highly cross-linked network formation over comparatively shorter curing times due to a buildup of radicals. [74, 112] This is due to increased diluent monomer concentration (such as TEGDMA) reportedly improving the mobility of monomer molecules with enhanced reactivity of the components and increased diffusion of reactive groups. [51, 52, 61, 101, 112, 118] Triethyleneglycol- dimethacrylate (TEGDMA) also acts as a cross-linking agent with an antiplasticiant effect,[101] and is considered to be the main contributor towards post-irradiation of Bis-GMA-based composite resins, due to their ether linkages which render the molecule highly flexible.[73, 107, 118] Still, the TEGDMA-rich resin mixtures could develop lower strength as a result of cyclizaton, rendering the materials heterogeneous with higher conversion but lower strength.

Embitterment of TEGDMA-containing materials is the result of the formation of a glassy network.[52, 101]

The highest % DC was observed for dual-cured composite resins (Luxa Core Automix Dual and Rebilda DC) as well as a light-cured composite resin (Clearfil Photo Core), all showing higher flexural properties and higher % DC. [47, 51, 52, 64, 65, 74, 112]. These 3 materials were of different polymer matrix composition:

Luxa Core Automix Dual has its polymer matrix based only on Bis-GMA, that of Rebilda DC is based on both Bis-GMA and UDMA dimethacrylates, and finally that of Clearfil Photo Core is based on a Bis-GMA/TGDMA mixture.

The literature states that UDMA mixtures show a significantly higher conversion compared to Bis-GMA which shows more cross-linking. The increased reactivity of UDMA is most probably due to greater flexibility, weaker intermolecular bonding and chain transfer reactions caused by NH-groups present in UDMA, allowing for increased mobility of the radical sites in the network.[52, 112]

The network formation decreases the mobility of the monomer and the diffusion rates of proliferating free radicals and the pendant methacrylate groups as polymerization progresses, trapping unreacted monomers because of a rapid rise in viscosity, rendering these materials less resistant to degradation.[22, 32, 38, 52, 107, 112, 118]

The continuously increasing DC with time of storage, is most probably due to post-curing, resulting in increased DC, FS and FM; a phenomenon known as'' dark post-cure.'' [44, 56, 73, 118, 138]

For post-polymerization, sufficient mobility of remaining free radicals is required to increase DC, especially occurring at higher temperatures.[118] That is because new radicals are formed by stimulating residual catalysts or by splitting residual C=C groups, resulting in increased DC.[50, 65]

It was also established that higher amounts of stress are created inside the polymeric network during polymerization, due to further development of the elastic modulus, rendering the material susceptible to fracture.[116] A relief of such stresses could be achieved during storage at elevated temperatures (37°C, TC), due to relaxation processes occurring within the material, through reconfiguration and rearrangement of polymer chains with increased fracture resistance. [6]

From the obtained results, it could be seen, that materials differ in many aspects besides their differences in monomer base, with respect to type, amount and silanization of filler particles incorporated, as well as the differences in initiators and inhibitors added. [9, 30-32, 116, 138]

The type of filler, its concentration, as well as the nature of its bonding to the resinous matrix clearly affected the DC of composite resin materials investigated,[30, 31, 138] as far as the incorporated fillers are concerned, where microhybrid composite resins show a more reliable % DC. [38, 64] Several authors have proven that flowable composite resins demonstrate a higher DC than universal types, followed by packable composites of higher filler content. [46, 61, 117, 136, 138]

The difference in % DC between materials may be related to the fillers incorporated: Whilst Rebilda DC, the flowable composite resin with the least filler amount (70 wt % fine silica particles, average diameter: 2μm), followed by Luxa Core Automix (72 wt% microfine Ba-glass / pyrogenic silica, average diameter: 0.02- 4 μm), revealed the weakest correlation between % DC and FS (Rebilda DC: r^2 = 0.256, Luxa Core Automix: r^2: 0.292), as well as between % DC and FM (Rebilda DC: r^2 = 0.187, Luxa Core Automix: r^2 = 0.406), the hybrid self-cured Clearfil Core New Bond (78 wt% colloidal silica, average diameter: 4 μm) showed the highest correlation (FS: r^2 = 0.452, FM: r^2 = 0.525).

Clearfil Core New Bond revealed the highest correlation between flexural properties and % DC, most probably as a result of its higher silanized microhybrid filler concentration. This can be explained by the fact, that filler silanization reduces the catalytic effect of the filler surface on the decomposition of free radicals. [22] However, Clearfil Photo Core, the light-cured composite resin, of a much higher content of hybrid silane treated fillers (83 wt %) did in fact show no correlation between gradually increasing flexural properties and more rapidly increasing % DC, contradicting the opinion of authors stating a reduction in % DC with increased amount of silanized fillers. [46, 61, 117, 136, 138]

The influence of increased % DC on FS and FM was obvious for Rebilda DC throughout the entire observation period, whereas both self-cured composite resins (Luxa Core Automix and Clearfil Core New Bond) showed a slight reduction in their flexural properties starting at a 60-65% DC.

The weak correlation between flexural properties and % DC recorded for Luxa Core Automix and Rebilda DC may be explained by the smaller filler size and less filler amount of these materials. According to relevant literature, as a result of the light-scattering phenomena with reduced light transmission through the material, microfilled composite resins do present smaller depth of cure and higher amount of remaining C=C [41] as well as lower % DC. [64]

In conclusion, DC does not allow conclusions to be equally made across the mechanical properties for all composite resins.[14]

7.4.2. *Correlation between storage condition and Degree of Conversion*

All composite resin materials investigated, revealed a significant ($p < 0.05$) yet weak ($r^2 < 0.25$) correlation between % DC and storage condition, except for Luxa Core Automix Dual, which revealed no correlation between both parameters ($p > 0.05$).

The relatively strong influence of storage on % DC, demonstrated for Luxa Core Automix ($r^2 = 0.459$) and Rebilda DC ($r^2 = 0.428$), may be due to the diluting water effect on the mixtures, resulting in lower viscosity, thus enhancing diffusion and C=C double bond conversion.[54] As an improved mobility of reactive molecular groups is inevitable for an enhanced diffusion of reactive groups.[51]

The observed increase in % DC for the first 90 to 100 h, declining over the next 4 days for most composite resins investigated, largely depends on the monomer system incorporated, [31, 44] since the increased availability of unreacted molecular groups containing free radicals at the beginning of the polymerization process allows for substantial increase in DC.[50, 116, 118] Whereas the decline in % DC over 4 days is most probably the result of a decay of free radicals.[41, 50]

However, some materials demonstrated a divergent pattern of correlation on the other hand: Rebilda SC, the self-cured composite resin, showed a slow rise in its % DC during the first 96 h, which might possibly be explained by its lower filler content (68.5 wt%) of fine dispersion silica and its monomer system being based on both Bis-GMA and UDMA, rendering it more hydrophilic. Moreover, the hydroxyethyl-dimethacrylate (HEDMA) content of the material makes it more susceptible to water sorption, rendering the unreacted free radicals sufficiently mobile to contact other reactive molecular groups, with a resultant increased DC. [118,50, 65]

For Clearfil Photo Core, the light-cured composite resin, on the other hand, its % DC already declined after about 50h, which could possibly be explained by the autoacceleration process (gel effect) taking place, to demonstrate a highly cross-linked network formation over a comparatively short time, attributable to a buildup of free radicals in the system.[74, 112] However, a restriction of mobility of polymeric radicals (diffusion-controlled termination rate coefficient) with decreased % DC occurs with polymerization proceeding over time to develop a more rigid network.

Finally, the % DC for Luxa Core Automix Dual, the dual-cured composite resin, revealed an almost constant development during the first 96h, to decrease afterwards. This behavior may be explained by the free radical termination being a diffusion-controlled process, with the rate coefficient termination in the reaction being controlled by the time constant for diffusion to form radical-radical meeting pairs, rather than on the chemical reaction itself. [5] The decrease in % DC after 96h could be related to the depletion of free radicals in the monomer structure. [46, 61, 117, 136, 138]

Regarding the 7d storage conditions (WB versus TC), only the WB storage condition seemed to have a highly significant influence ($p < 0.000$) on the % DC. A strong correlation was demonstrated between % DC and flexural properties (FS: $r^2 = 0.662$, FM: $r^2 = 0.289$). This strong influence could be developed by the prolonged storage period (7d at a 37°C), thus increasing the availability of free radicals remaining in the composite resin after 7d to result in a significant increase in DC.[50]

On the contrary, following a 7d TC storage condition, no correlation ($p > 0.05$) between DC and flexural properties was recorded (FS: $r^2 = 0.098$, FM: $r^2 = 0.126$) for composite resins investigated. The reason for this behavior could be explained by the existence of a logarithmic relationship between the half-life of the radicals and the storage temp,[22] since it was proven, that an increased post-cure temperature of a composite resin severely reduced the half-life of radicals. Moreover, the type, size and filler coating affect the half-life of the radicals as well. [22]

Hydrohilicity and hydrophobicity of photo-initiators significantly affected both the DC as well as polymerization rate in presence of water. Since the addition of photo-initiator types improving radical efficiency, positively affects both the final DC and conversion rate. [54]

8.   Summary

 The aim of this study was to test four hypotheses, divided into two parts:

In the **1st Part** of the study, the flexural properties (flexure- strength (FS) and flexural-modulus (FM)) of 4 different groups of tooth-colored core-buildup materials (glass-ionomers: conventional-and metal-modified, resin-modified glass-ionomers, polyacid-modified composite resins (compomers) and composite resins: self-, light- and dual-cured, were investigated, testing the effect of different variables (material type, storage time and condition, and the curing mode) on flexural properties. Moreover, the effect of the light-curing step on 3 dual-cured materials (a resin-modified glass-ionomer and 2 composite resins) was investigated, comparing their flexural properties with and without light-curing.

A total of 850 bar-shaped specimens (25 mm x 2mm x 2mm) were tested in a 3-point-bending test device, after storage under 5 different conditions (10 min dry in an incubator (baseline) to be additionally stored for either 2h,24h and 7d in deionized water (37°C/7d thermocycling with 5000 cycles at 5-55°C).

From the results it can be concluded that several variables influence the flexural properties of the 4 groups of tooth-colored core-buildup materials. The type of material (glass-ionomer or resin-based), storage condition, as well as light-curing, significantly influences flexural properties of the 4 groups of tooth-colored restorative materials, showing higher flexural properties (FS and FM) for resin-based materials and light-cured-types compared to chemically-cured types.

In the **2nd Part** of the study the relationship between the flexural properties (FS and FM) and the degree of conversion as well as the influence of storage condition on the degree of conversion of 7 different composite resin materials were assessed.

A total of 280 bar-shaped specimens were tested. The degree of conversion was determined by calculating the percentage of reacted C=C bonds using an FTIR analysis (baseline method) on the fractured bar-shaped specimens immediately after recording the flexural properties. Prior to testing, the specimens were subjected to 8 different storage conditions (5 min and 10 min dry storage in an incubator at 37°C, in distilled water at

37°C for 1h, 4h, 24h, 2d, 7d and 7d thermocycling after being stored for 10 min as baseline in an incubator at 37°C).

The bivariate correlation analysis revealed a significant relationship (p<0.05) between % DC and flexural properties (FS and FM) for 3 materials: 2 self-cured composite resins (Luxa Core Automix and Clearfil Core New Bond) as well as Rebilda DC, the dual-cured composite resin, while the rest of composite resins revealed no correlation between both parameters.

For the influence of storage condition on the degree of conversion, a significant (p < 0.05) yet weak ($r^2 < 0.25$) correlation between both parameters was recorded for all composite resins, except for Luxa Core Automix Dual, the dual-cured composite resin, which revealed no correlation between both parameters (p > 0.05).

From the results it can be concluded that degree of conversion does not reflect the mechanical properties for all composite resins equally, and that in contrast to the 7 day storage period in distilled water, which obviously influenced both flexural properties, the thermocycling period revealed no influence on the DC values for all composite resins tested.

9. Zusammenfassung

Das Ziel dieser Studie war es, vier Hypothesen, unterteilt in zwei Teile, zu untersuchen:

Im 1.Teil der Studie, wurden die Biegeeigenschaften (Biegefestigkeit (FS) und Biegemodul (FM) von 4 verschiedener Gruppen zahnfarbener Kernaufbau-Materialien (Glas-Ionomere: konventionell-und Metall-modifiziert, Harz-Glas-Ionomere, Polysäure-modifizierte Komposite (Kompomere) und Komposit-Harze: selbst-, Licht- und dualhärtend) untersucht. Der Effekt verschiedener Variablen (Materialart, Lagerzeit und Zustand, und das Härtungsverfahren) auf die Biegeigenschaften wurde getestet. Darüber hinaus, wurde die Wirkung des Lichthärtungsverfahrens auf 3 dual-gehärtete Materialien untersucht (ein hazmodifiziertes Glasionomerzement und 2 Komposit-Harze), wobei deren Biegeeigenschaften (FS und FM) mit- und ohne Lichthärtung verglichen wurden.

Insgesamt wurden 850 stabförmige Proben (25 mm x 2mm x 2mm) in einem 3-Punkt-Biegeversuch getestet, nachdem diese einer Lagerung unter 5 verschiedenen Bedingungen (10 min trocken in einem Brutschrank (Basislinie), und dann eine zusätzliche Lagerung entweder für 2h, 24h und 7d in deionisiertem Wasser (37 ° C/7d Thermocycling mit 5000 Zyklen bei 5-55 ° C) ausgesetzt waren.

Aus den Ergebnissen lässt sich schließen, dass mehrere Variablen die Biegeeigenschaften der 4 Gruppen von zahnfarbenen Kern-Aufbau Materialien beeinflussen. Die Art des Materials (Glasionomer oder Harz-basiert), Lagerungsbedingungen sowie das Härtungsverfahren, beeinflusst die Biegeeigenschaften der 4 Gruppen maßgeblich, wobei Harz-basierte Werkstoffe sowie Lichthärtende - Materialien höhere Biegeeigenschaften (FS und FM) im Vergleich zu den chemischhärtenden Materialien zeigten.

Im 2. Teil der Studie wurden die Beziehung zwischen der Biegeeigenschaften (FS und FM) und dem Umsetzungsgrad (%DC), sowie der Einfluss der Lagerungsbedingungen auf den Umsatzungsgrad (%DC) 7 verschiedener Komposit Materialien bewertet.

Insgesamt wurden 280 stabförmige Proben getestet. Der Grad der Umsetzung wurde als Anteil (Prozent) der umgesetzten C=C- Bindungen mit Hilfe einer FTIR - Analyse (Baseline-Methode) der gebrochenen stabförmigen Proben sofort nach der Aufnahme der Biegeeigenschaften bestimmt. Vor der Prüfung wurden die Proben 8 verschiedenen Lagerbedingungen (5 min und 10 min trockene Lagerung in einem Brutschrank bei 37 °

C, in destilliertem Wasser bei 37 ° C für 1h, 4h, 24h, 2d, 7d und 7d Thermocycling nach einer Lagerung in einem Brutschrank bei 37 ° C als Basislinie) ausgesetzt. Die bivariate Korrelationsanalyse ergab eine signifikante Beziehung (p<0,05) zwischen % DC und Biegeeigenschaften (FS und FM) für 3 Materialien: 2 selbsthärtende Komposit-Harzen (Luxa Core Automix und Clearfil Core New Bond) sowie das dualhärtende Rebilda DC, während die anderen Komposit Materialien keine Korrelation zwischen beiden Parametern zeigte.

Bezüglich des Einflusses der Lagerungsbedingungen auf den Umsetzungsgrad, war eine signifikante ($p < 0,05$) doch schwache ($r^2 < 0,25$) Korrelation zwischen beiden Parametern für alle Komposit - Harze festzustellen. (Ausnahme: Luxa Core Automix Dual)

Aus den Ergebnissen lässt sich schließen, dass der Umsetzungsgrad nicht die mechanischen Eigenschaften für alle Komposit Materialien gleichermaßen widerspiegelt, und dass im Gegensatz zu einer 7 Tagen Lagerungszeit in destilliertem Wasser, welche die % DC-Werte aller untersuchten Komposit-Harzen beeinflusste, zeigte Thermocycling keinen Einfluss auf die % DC-Werte der Komposit Materialien.

10. Conclusions

Within the limitations of this study, the following conclusions were drawn:

1-Non of the investigated tooth-colored core-buildup material fulfills all requirements of sufficient flexural properties and degree of conversion under different storage conditions.

2- The mechanical properties proved to be more network-dependent, while the influence of % DC on the mechanical properties proved to be material-dependent.

3- Degree of conversion does not permit drawing conclusions about the mechanical properties equally for all composite resins.

4- Monomer composition, filler amount, size and distribution as well as particle content interaction, influence the flexural properties as well as % DC of materials tested.

5- Light-curing is mandatory for resin-based materials to achieve adequate flexural properties, as a result of the additional cross-linking reactions of the resin components occurring.

6- Storage time, material type and curing mode significantly influenced flexural properties of tooth-colored restorative materials.

7- Thermocycling negatively affects flexural properties of almost all restorative materials significantly, while having no influence on the degree of conversion of composite resins investigated.

8- Dentists should be informed about the early strength of resin-based and glass-ionomer core-buildup materials, trying to restrict their use to low-stress bearing areas.

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12. Declaration

¨I declare that I have written the submitted dissertation independently, without unauthorized outside help and only with the aids that I have stated in the dissertation. All text passages which I have quoted word-for word or which I have quoted in an analogous form have been taken from published or unpublished documents and all details which are given orally have been identified accordingly. I have followed the basic principles of good scientific practice as defined in the ¨Statute of the Justus Liebig University Gießen to secure good scientific practice¨.

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