Aus der Universitätsklinik
Für Zahn-, Mund-, und Kieferheilkunde Tübingen
Abteilung Poliklinik für Zahnärztliche Prothetik mit Propädeutik
Ärztlicher Direktor: Professor Dr. H. Weber

Sektion für Medizinische Werkstoffkunde und Technologie
Leiter: Professor Dr. J. Geis-Gerstorfer

# Dynamic mechanical analysis of direct and indirect dental composite resins

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Renata Vidal Mesquita aus Natal/Brasilien
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Dekan: Professor Dr. C. D. Claussen

1. Berichterstatter: Professor Dr. J. Geis-Gerstorfer
2. Berichterstatter: Prof. Dr. C. Löst

To my husband Adriano and
to my parents Vicente and Sônia.

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# 1 Introduction

## 1.1 Dental composite resins

### 1.1.1 Definition

Dental composite resins are complex, tooth-coloured filling materials composed of synthetic polymers, particulate ceramic reinforcing fillers, molecules which promote or modify the polymerization reaction that produces the cross-linked polymer matrix from the dimethacrylate resin monomers, silane coupling agents which enhance the adhesion of the reinforcing fillers to the polymer matrix (1), and other minor additions including polymerization inhibitors, stabilizers and colouring pigments.

### 1.1.2 Main components

**- Organic resin matrix**: Many of today's commercially available dental resin composite materials utilize Bisphenol-A-glycidyl dimethacrylate (BisGMA) or Urethane dimethacrylate (UDMA) as major monomer (2).

The BisGMA is the reaction product of Bisphenol-A and glycidyl ester methacrylate (GMA). This bulky bifunctional monomer has a high reactivity, high molecular weight, undergoes low polymerization shrinkage, and produces a cross-linked, three-dimensional resin network (3). Its main disadvantage remains the high viscosity attributed to the hydrogen bonding interactions between the two pendant hydroxyl groups, (1) which restricts the use of high amounts of filler (4). Thus, BisGMA must be diluted with a more fluid resin such as ethylene glycol dimethacrylate (EGDMA) or triethylene glycol dimethacrylate (TEGDMA) to achieve a viscosity suitable for incorporating fillers (2).

UDMA is the most commonly used urethane dimethacrylate in commercial visible-light-curable dental resin composites. This monomer has been used alone or in combination with other monomers such as BisGMA and TEGDMA. The advantages of UDMA have been reported to be lower viscosity and a greater flexibility of the urethane linkage, which may improve the toughness of resin composites based on this monomer (5).

**- Inorganic fillers**: Within practical limits, mechanical and physical properties of composite materials improve in proportion to the volume of filler added (1). Generally, increased filler leads to greater stiffness, higher elastic limits, better fracture resistance, and improved wear characteristics (6). The elastic modulus for the unfilled resin is lower than that of enamel (83 GPa) and dentine (18.6 GPa). However, the presence of an appropriate quantity of filler may raise this to approximately that of dentine. On the other hand, the rigidity of enamel is rather more difficult to emulate, and could only be achieved with a very rigid filler.

A wide variety of inorganic particulates have been used to improve the quality of the dental composites resins. These include: colloidal silica, barium silicate, strontium/borosilicate glass, quartz, zinc silicate, or lithium aluminium silicate. In addition, most microfill composites contain pre-polymerized resin fillers which are composed of dimethacrylate polymers filled with sub-microscopic silicon dioxide particles (7). Each of these groups has its own distinctive characteristics. Colloidal silica particles, for example, have a diameter less than 0.1 µm, are inert, have low coefficients of thermal expansion, and improve condensability and polishability. Barium silicate has medium hardness and is very radiopaque, while quartz is very stable but is hard to polish and can wear the opposing dentition.

### 1.1.3 Classification of resin composites

During the 1970s and 1980s the development of new resin composites focused mainly on the size and amount of filler particles. Resin composites were classified in three main groups concerning filler content: macrofilled, microfilled and hybrid composites (1).

**- Macrofilled** or conventional resin composites had filler particles with a size of 10-40 µm and their disadvantages were poor finish and relatively high wear. The most common used fillers in these composites were quartz and strontium or barium glass. Quartz filler had good aesthetics and durability but suffered from absence of radiopacity and high wear of antagonist teeth. Barium and strontium glass particles are radiopaque, but are less stable than quartz (8).

- **Microfilled** resin composites were introduced in the late 1970s to satisfy the need for a polishable composite. These materials contain a very fine particle size of colloidal silica that ranges between 0.01-0.05 µm. However, the very large surface area of the particles significantly limits the volume of filler that can be incorporated. Compared to macrofilled resin composites, the microfilled have lower mechanical properties due to the large volume of resin (8; 9).
- **Hybrid** resin composites were introduced to solve the mechanical and the shrinkage problems. The first introduced hybrid resin composites contained large filler particles of a size of 15-20 µm as well as colloidal silica of a particle size of 0.01-0.05 µm.
- **Modern hybrid** composites contain reduced submicron fillers. These composites are supposed to combine the advantages of macrofilled and microfilled composites, but they do not have the final finish and translucency of microfilled resin composites.
- **Nano-composites** are a recent development on the market. They contain filler particles with sizes less than 10 nm (0.01 µm) and are claimed to provide increased aesthetics, strength and durability (8).

**Table 1** Filler sizes and materials in dental composite materials.

| Composite type | Filler size (µm) | Filler material |
|---|---|---|
| Macrofilled | 10-40 | Quartz or glass |
| Microfilled | 0.01-0.1 | Colloidal silica |
| Hybrid | 15-20 and 0.01-0.05 | Glass and colloidal silica |
| Modern Hybrid | 0.5-1 and 0.01-0.05 | Glass, Zirconia and colloidal silica |
| Nanofiller | < 0.01 (10 nm) | Silica or Zirconia |

## 1.2 Elastic modulus

Recent dental research has focused on making the physical properties of dental composite resins similar to those founded in tooth structure. However, variations still exist between composites and teeth, despite tremendous advances since the first generation of macrofilled composites. Basically, there are three main differences between the physical properties of tooth and composite: polymerization shrinkage, coefficient of thermal expansion and elastic modulus (10).

The elastic modulus is a very sensitive parameter for evaluating and ranking particle reinforced dental composites (11). These restorative materials are being increasingly used in load-bearing areas of the posterior dentition (12) and are therefore inevitably subject to masticatory forces. When these forces stress the material below its elastic limit no plastic or permanent deformation occurs. However, when the elastic limit is exceeded, permanent damage starts.

Typically, dental composites with low modulus will more readily elastically deform under functional stresses. Excessive elastic deformation of dental restorative material under functional stresses may result in catastrophic fracture of the surrounding brittle tooth structures, or alternatively, increased microleakage may result (9; 13). In such cases, enamel and dentin will be forced to carry more forces than originally intended, increasing the risk of cusp fracture. Additionally, the occlusal stresses generated during clinical service, whether intermittent or otherwise, also tend to disrupt the interfacial bonding between the deformed resin restoration and the restored teeth (14). It may lead to interfacial gap formation and can contribute to microleakage, secondary caries and post-operative sensibility.

Conversely, composite materials with extremely high elastic modulus are unable to absorb occlusal vertical loading stresses. Consequently, masticatory stresses will be almost totally transmitted to the cavity walls, which can have a potential destructive effect on the prepared brittle tooth structure. Ausiello et al. showed that 90 GPa inlay ceramic restorations were unable to absorb occlusal vertical loading stresses that we totally transmitted to the cavity walls. On the other side, 50 GPa composite inlays partially absorbed and partially transferred the stresses to the cavity walls. This indicates a greater stress-dissipating effect of the material with greater compliance, in this case the composite, thus minimizing the risks of tooth catastrophic fracture (15).

Moreover, extremely rigid materials cannot flow and compensate for the volumetric contraction stresses developed during polymerization, putting at risk the integrity of the adhesive interface between the composite and the tooth, and also increasing the risk of cusp fracture (16; 17). A possible solution to this problem may be the application of restorative materials that render the restoration sufficiently flexible to compensate for that part of the shrinkage that challenges the bond. As a result, the adhesive bond will remain intact, and marginal integrity will be preserved.

Ideally, the elastic properties of dental composites should be matched to those of the dental tissue they are supposed to replace (13; 18). It would minimize the differential movement between the restoration and the tooth during mastication, thus avoiding catastrophic failures. However, since enamel and dentin have distinct elastic properties and generally must be simultaneously replaced, two distinct restorative materials should be combined. Then, a more realistic concept would be choosing one of either, enamel or dentin, as a standard.

Many dental materials are visco-elastic, including the wide range of polymeric-based materials (19). Logically, therefore, dental composite resins should be expected to exhibit some visco-elastic response. This gives a mismatch with the behaviour of enamel at body temperature, but a closer match to that of dentine that has been shown to exhibit visco-elastic properties (20; 21). Consequently, the dental tissue to be chosen as standard should be preferably the dentine. Thus, in order to survive in stress bearing areas in the oral environment, the elastic modulus of dental composites should be at least as high as dentin modulus (18), which is about 18 GPa (22), and preferably higher (23). This corresponds to an imaginary volume percentage of filler of 60% (24). Such composites would then be able to provide support at the interface with the tooth enamel, protecting the enamel rods at the margin from fracturing.

### 1.3 Elastic, viscous and visco-elastic materials

Ideally, materials would behave either entirely elastic and obey Hooke’s Law, which states the stress in the sample is a function of deformation only and not a function of time, or entirely viscous and obey Newton’s law of viscosity, which states the stress in the sample is a function of the rate of deformation (25). Although these basic concepts exist theoretically and in some very simple materials, such as steel and water, most materials such as polymers do not behave entirely as one of these two ideal classes of materials (25). Such materials that behave neither as perfectly elastic solids, nor as completely viscous materials are described as visco-elastic materials (26).

In essence visco-elasticity defines how a material responds gradually to an applied stress reaching an ultimate value after a time lag. The phenomenon is caused by the chains of molecules within a polymer requiring time to fully adjust to the applied stress. Thus the more rapidly a stress is applied the shorter the time available for the molecules to relax and accommodate that stress.

A purely elastic material such as a spring retracts to its original position when stretched and released, whereas a viscous fluid retains its extended shape when pulled. A visco-elastic material combines these two properties - it returns to its original shape after being stressed, but does it slowly enough to oppose the next cycle of vibration.

We could also say purely elastic materials are able to store all the energy applied during loading that is used for them to return to their original shape, while purely viscous materials do not return any of the energy applied during loading that is completely lost. On the other hand, visco-elastic materials, when deformed, store part of the loading energy within the material (elastic response), while some of the energy is dissipated as heat (viscous response). Once the load is removed, part of the material, corresponding to its elastic portion, returns to its original shape, while the other part, corresponding to material's viscous portion, undergoes permanent deformation.

The degree to which a material behaves either viscously or elastically depends on environmental temperature, vibration frequency, dynamic strain rate, static pre-load, time effects such as creep and relaxation, aging, and other irreversible effects. The most important parameters are temperature and frequency effects.

## 1.4 Static and dynamic tests

The laboratory assessment of the mechanical properties of composite restorative materials presents considerable difficulty. This might be attributed to the high stiffness of the materials, the visco-elastic nature of the resin base, and the need to use clinically realistic specimen sizes (27).

Traditionally, the mechanical properties of dental composites have been investigated using static tests. While valuable for determining ultimate strength, these methods are not well suited to measuring elastic properties. They provide limited information on material structure and their destructive nature excludes the possibility of the samples to be re-tested (28). The use of these tests has also led to difficulties in assessing and comparing materials which show visco-elastic behaviour under load (27), since they focus only on the elastic component of the material. Another common problem is the difficult to relate the physical properties to the structure of the material.

It is now common in materials science to use dynamic methods to assess the mechanical properties of polymeric materials (29). Dynamic tests such as dynamic mechanical analysis (DMA) are particularly well suited for visco-elastic materials, since they can determine both the elastic and viscous responses of a sample in one experiment (25). This test works basically in the linear visco-elastic range, revealing fundamental properties over time, temperature and strain rate. This technique also allows the re-examination of the samples following particular treatments (28), which can be a valuable tool specially when monitoring the efficiency of polymerization during curing studies.

Since dental composites are exposed to dynamic loading rather than static loading, dynamic tests have become increasingly relevant (30). While static tests obtain data related to a longer time scale than that of mastication (31), which can be a source of misleading results; dynamic tests better mimic the cyclic masticatory loading to which dental composites are clinically subjected (26). This might be extremely valuable to predict the clinical performance of biomaterials when working under the cyclic solicitations generated by the human body physiological movements.

### 1.5 Theory about Dynamic Mechanical Analysis (DMA)

Dynamic Mechanical Analysis (DMA) is a method that has been used to acquire useful information about visco-elastic properties of dental composite resins as a function of time, temperature, and frequency.

With this technique a sample with well-defined dimensions is exposed to a sinusoidal mechanical deformation (strain) at fixed frequency or range of frequencies over a specific temperature range and also isothermically as a function of time and the corresponding forces measured (44). This can be done in tensile, compression, shear, flexural and bending modes of operation. In an opposite way, the sample can be subjected to a pre-selected force amplitude and the resulting deformation (strain) is measured. The more delayed the response, the more viscous the material while less delayed responses are characteristic of more elastic materials (45).

Briefly, the strain is a measure of the change in length of a material after a force is applied, and the stress is an internal force in a material equal and opposite to the applied load (44). When a sinusoidal stress is applied to a perfectly elastic solid the deformation occurs exactly in phase with the applied stress, hence the modulus is not time dependent. A completely viscous material will respond with the deformation lagging 90° behind the applied stress. However, when the stress is applied to a visco-elastic material, it will behave neither as a perfectly elastic nor as a perfectly viscous body and the resultant strain will lag behind the stress by some angle *s,* where $s < 90°$ (28; 40). The magnitude of the loss angle is dependent upon the amount of internal motion occurring in the same frequency range as the imposed stress (34; 35).

The stress that is in phase with the applied strain is used to determine the elastic or storage modulus (E'), which is an indicator of elastic behaviour and reveals the ability of the material to store elastic energy associated with recoverable elastic deformation. The stress that is out of phase with the applied strain is used to calculate the viscous or loss modulus (E''). It is an indication of energy absorbed by the resin that is not returned elastically. Instead, this energy is used to increase segmental molecular vibration or to translate chain positions (33).

The loss tangent (tan δ) or mechanical damping is the phase angle between the dynamic strain and stress in the oscillating experiment. It is dimensionless and is given by the ratio of the viscous modulus to the elastic modulus (40). This visco-elastic property is a measure of the mechanical energy dissipation or “loss” within the material in the form of heat. A perfectly elastic solid has tan δ = 0 (26). Characteristically, the loss tangent reaches a maximum, or peak value, at the condition of temperature and/or frequency where the internal rate of molecular motion corresponds to the external driving frequency applied to the bulk specimen. The maximum of the loss tangent is frequently associated to the glass transition temperature ($T_g$) and the location of such “loss peaks” provides information about internal molecular mobility. The lower the loss tangent the quicker the material will respond to load (more elastic like), returning faster to its original shape, whereas the higher it is the higher the amount of energy lost as heat (more viscous like) (44).

### 1.6 DMA and dental polymers

There are several reports on examining the dynamic mechanical properties of dental polymeric materials.

Many DMA studies have been used to characterize both the rate and extent of polymerization of dental composite resins; as such processes are associated with time-dependent changes in the elastic modulus (32). Tamareselvy and Rueggeberg investigated the dynamic mechanical properties of two model dental restorative copolymers to elucidate the influence of pendent group length and addition of cross-linking agent (33). Harris et al. examined the dynamic modulus of elasticity of two composite materials cured by three light intensities at 37°C and 60°C using a dynamic thermal and mechanical analyser (34). Dionysopoulos and Watts studied a visible light-cured composite resin (Brilliant DI) over a wide range of temperature and frequency by a dynamic mechanical flexural method (35). Jacobsen and Darr tested a series of polymeric composite restorative materials cured by primary and secondary methods by static and dynamic testing (28). Lee et al. evaluated the changes in visco-elastic property of a UDMA-based dental resin as a function of time after initial light exposure (36). Jancar et al. reported the effect of BisGMA content varying from 0 to 100% on the degree of conversion and morphology of the cured resin. Dynamic scanning calorimetry (DSC), Fourier transform infrared spectroscopy (FTIR) and dynamic mechanical analysis were performed in order to determine the nature and location of unreacted unsaturations in relation to BisGMA concentration (37).

The dynamic mechanical properties of commercially available denture base resins and soft lining materials have also been reported. Phoenix et al. evaluated and compared the mechanical and thermal properties of six commonly used polymethyl methacrylate denture base resins using differential scanning calorimetry (DSC) and dynamic mechanical analysis (38). Saber-Sheikh et al. investigated the time dependent, visco-elastic characteristics of a number of dental soft liners using a dynamic mechanical analyser. The materials consisted in eight commercial products including methacrylate, silicone and phosphazine-based soft polymers as well as two experimental formulations (26). Fraunhofer and Sichina characterized the physical and visco-elastic properties of two resilient denture liners, the polyphosphazine-based Novus and silicone-based Molloplast b (39). Waters et al. investigated the deformation properties of a range of long-term denture soft-lining materials using dynamic mechanical analysis (40).

Other studies have also been performed using dynamic mechanical analysis. Vaidyanathan and Vaidyanathan investigated the deformation under stress and recovery after stress removal of three different popular composite resin systems for dental restorative applications (microfilled, minifilled and midifilled types) (41). Wilson and Turner characterized, by dynamic mechanical analysis, the polymeric materials used to restore teeth and, in particular, their glass transition temperatures (42). At last, Braem et al. compared the elastic modulus obtained with different tests that impose static, low-frequency, or high-frequency elastic deformations on dental composite systems (43).

### 1.7 Environmental challenge

The long-term exposure of polymeric composite materials to extreme-use environments, such as pressure, temperature, moisture, and load cycles, results in changes in the original properties of the materials. These changes in materials properties translate to structural changes that can have a potentially catastrophic effect on load-bearing composite structures (46).

Dental composite restorations must withstand a harsh environment that varies from patient to patient. Mastication forces, occlusal habits, abrasive foods, chemically active foods and liquids, large temperature fluctuations, pH and humidity variation, bacterial products, and salivary enzymes all contribute uncontrollable factors that affect composite restoration longevity (47-52).

Degradation of composites has already been reported even in the absence of loading and abrasive forces (53). Therefore, the limited durability of particulate filled polymer dental restorative materials in the oral environment (54) should not be exclusively attributed to the complex stress situation, but involves chemical degradation as well (55). Dental composites are intermittently or continuously exposed to chemical agents found in saliva, food and beverages. Intermittent exposure occurs during eating or drinking until teeth are cleaned. Continuous exposure may, however occur as chemical agents can be absorbed by adherent debris (such as calculus and food particles) at the margins of the restorations or be produced by bacterial decomposition debris (56). Hence, dental composite restorative materials should be able to withstand dental masticatory stresses and to resist to chemical degradation in the oral environment as well.

The oral environment is susceptible to larger temperature variations than any other structure in the human body. These intraoral temperature changes may be induced by routine eating, drinking and breathing, so that dental restorative materials can be exposed to a wide variety of temperatures typically ranging from 5 to 55°C. These extreme temperatures can produce a hostile environment for restorative materials and compromise their long-term stability.

## 1.8 Objectives of this study

In order to resist to intraoral mechanical deformation, the physical and mechanical properties of dental composite resins should be comparable to those of the natural dental tissues being replaced. However, as a consequence of their visco-elastic nature, the dynamic behaviour of dental composites, including their capacity to resist to deformational change under load, is significantly dependent on frequency and temperature, especially under conditions of moisture, such as observed in the oral cavity.

Therefore, the first objective of this study was to obtain a satisfactory understanding of the approximate visco-elastic behaviour of two direct and two indirect dental composites under conditions that simulate the oral environment. With this objective their visco-elastic properties were monitored using a dynamic mechanical analyser over the narrow range of temperature changes which can be found in the mouth and at variable frequencies, including an approximate masticatory frequency (1 Hz), after stored for up to 3 months in air or distilled water. The wet condition simulated the moisture in the oral environment, while the dry condition was taken for comparison to reveal changes in the properties due to water sorption.

Since the oral environment is subjected to larger temperature variations than any other part of the human body, it is wiser to choose a restorative material whose glass transition temperature ($T_g$) lies above its average service temperature. The glass transition temperature represents the temperature at which the material softens. No amount of filler or reinforcement can prevent this from occurring, and when it does take place the material rapidly drops in modulus. Therefore, information about the glass transition temperature of the composites can be useful in preventing us from choosing a composite material that would undergo sudden changes in its mechanical properties, in the form of plastic deformation, or a decrease in its elastic modulus, whilst it is in clinical service (42). Based on this assumption, our second objective was to find out the temperature sensibility of the four tested composites. With this purpose, their visco-elastic properties were scanned using a dynamic mechanical analyser over a large temperature range that would cover mouth temperature and composites' likely glass transition temperature, at an approximate masticatory frequency of 1 Hz. The influence of moisture on the visco-elastic properties of the composites was also assessed during this second test.

# 2 Materials and methods

## 2.1 Materials

Four commercial light-activated dental composite resins were investigated in this study. Two materials (DiamondLite and Grandio) were direct composites and two (Artglass and Vita Zeta LC) were indirect composites. All tested composites are one-paste systems.

Information regarding their classification, indication, monomer composition, type and size of reinforcing filler particles, percentage of filler by weight and occasionally (when available) by volume, batch number, selected shade and the respective manufacturer are summarized in the four following tables. Data were provided by the manufacturer.

### 2.1.1 Direct composites

#### 2.1.1.1 DiamondLite

**Table 2** Characteristics of Diamond Lite.

| | |
|---|---|
| **Classification:** | Microhybrid direct composite filling material |
| **Indication:** | Filling material for posterior and anterior areas |
| **Monomer:** | PEX (Phenol-Epoxy-Monomer) |
| **Filler:** | Barium borosilicate glass |
| **Filler particle size:** | 0.8 – 2.0 µm |
| **Percentage of filler:** | 78-84 wt. % |
| **Batch:** | 900050-1 |
| **Shade:** | B3 |
| **Manufacturer:** | DRM Laboratories, Branford, USA |

### 2.1.1.2 Grandio

**Table 3** Characteristics of Grandio.

| | |
|---|---|
| **Classification:** | Nano-hybrid direct composite filling material |
| **Indication:** | Filling material for anterior and posterior areas |
| **Monomer:** | BisGMA, TEGDMA and UDMA |
| **Filler:** | Glass ceramic particles and silicone dioxide |
| **Filler particle size:** | Glass ceramic particles (~1 μm) and silicone dioxide (20-60 nm) |
| **Percentage of filler:** | 87 wt. % and 71.4 vol. % |
| **Batch:** | V21513 |
| **Shade:** | - |
| **Manufacturer:** | Voco, Cuxhaven, Germany |

## 2.1.2 Indirect composites

### 2.1.2.1 Artglass

**Table 4** Characteristics of Artglass.

| | |
|---|---|
| **Classification:** | Fine particle hybrid composite veneering material |
| **Indication:** | Metal-free veneers, inlays/onlays, crowns and bridges; or veneering of metal frameworks. |
| **Monomer:** | Multifunctional methacrylic acid ester |
| **Filler:** | Barium alumina silica glass and silicone dioxide |
| **Filler particle size:** | 0.7- 2.0 μm |
| **Percentage of filler:** | 68 wt. % and 54 vol. % |
| **Batch:** | 040110 |
| **Shade:** | B3 |
| **Manufacturer:** | Heraeus Kulzer, Wehrheim, Germany |

### 2.1.2.2 Vita Zeta LC

**Table 5** Characteristics of Vita Zeta LC.

| | |
|---|---|
| **Classification:** | Fine particle hybrid composite veneering material |
| **Indication:** | Metal-free veneers and crowns in the anterior area; or veneering of metal crowns, bridges and telescopic crown; |
| **Monomer:** | BisGMA, TEGDMA and UDMA |
| **Filler:** | Multiphase feldspar frits and silicone dioxide |
| **Filler particle size:** | 0.04 – 1.5 µm |
| **Percentage of filler:** | 44.3 wt. % - 27 vol. % |
| **Batch:** | 6698 |
| **Shade:** | 2M2 |
| **Manufacturer:** | Vita Zahnfabrik, Bad Säckingen, Germany |

## 2.2 Preparation of the samples

A total of 45 bar shape specimens from each composite were prepared using a four-piece Teflon mold of internal dimensions 30 x 2.5 x 2 mm. The mold was lubricated with a thin layer of Vaseline and filled to excess, the material surface covered with a Mylar sheet and a glass slide. Moderate digital pressure was applied to the slide to extrude excess material. The glass slide was removed and the sample polymerized.

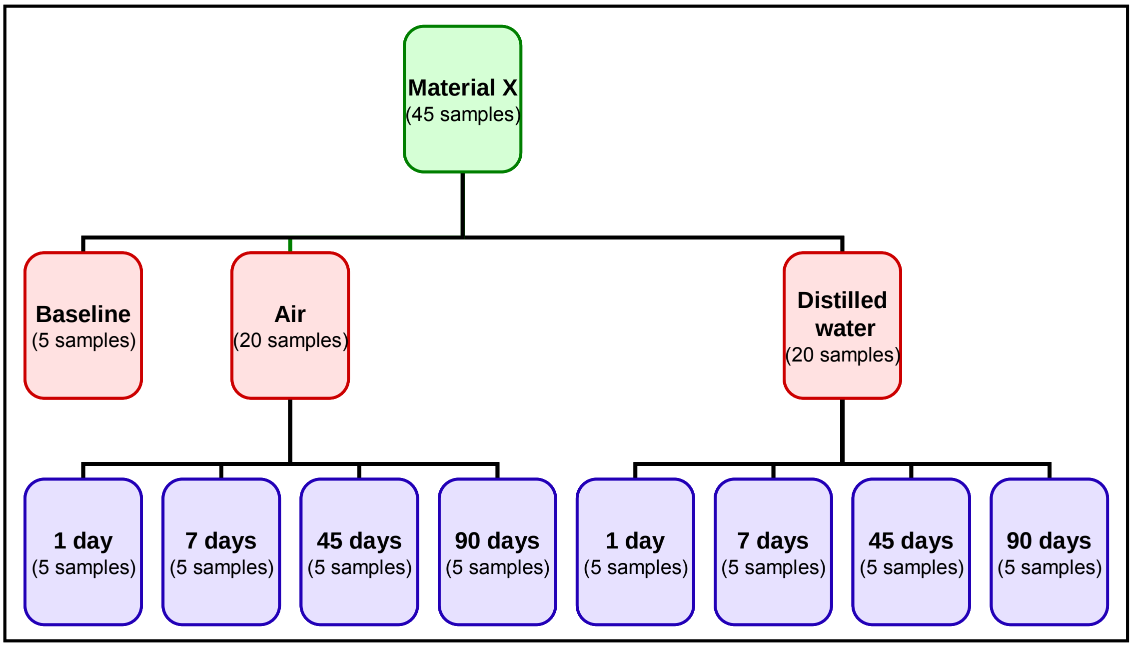
DiamondLite and Grandio samples were cured at room temperature (22 ± 1°C) for 60 seconds by placing the tip (9 mm spot diameter) of the hand light curing unit (Elipar® Trilight, 3M/Espe, USA) in direct contact with the Mylar sheet at the upper surface of the mold. The light tip was then moved, and a section overlapping the previous section was irradiated. The procedure was repeated until the whole sample was irradiated (4 exposures per sample). In this study, a stepped cure was performed, initially with a period of low-intensity (200 mW/cm$^2$) succeeded by a period of high intensity irradiance (900 mW/cm$^2$).

For the indirect composites Artglass and Vita Zeta LC the mold was placed in a light curing unit (Dentacolor®XS, Heraeus-Kulzer, Germany) and exposed at 40°C from the top for 3 min. The mold was disassembled, allowing free retrieval of the sample that was irradiated from the reverse side for another 3 min Following polymerization, the samples were visually inspected for superficial and bulk defects such as bubble and cracks. Defective specimens were discarded and satisfactory specimens were ground flat on 600 grit emery paper under water with a polishing machine (TG 200, Jean Wirtz, Düsseldorf, Germany). The final dimensions of the samples and the parallelism between their opposite surfaces were verified with digital callipers, whose precision was controlled with a metal bar of known dimensions. Samples to be tested with DMA require careful preparation to make sure that all the edges are straight and parallel (45). Error in parallelism or dimensions will translate into a similar size error in the elastic modulus calculated by the instrument's software.

### 2.3 Experimental groups

The 45 specimens made from each tested composite were equally distributed into 9 experimental groups (Figure 1):

**Figure 1** Scheme of the experimental groups formed, considering material X as example.



- **Group 1** Samples were tested immediately after preparation (baseline).
- **Group 2** Samples were stored in air for 1 day before testing.
- **Group 3** Samples were stored in air for 7 days before testing.
- **Group 4** Samples were stored in air for 45 days before testing.
- **Group 5** Samples were stored in air for 90 days before testing.
- **Group 6** Samples were tested after soaking in distilled water for 1 day.
- **Group 7** Samples were tested after soaking in distilled water for 7 days.
- **Group 8** Samples were tested after soaking in distilled water for 45 days.
- **Group 9** Samples were tested after soaking in distilled water for 90 days.

### 2.4 Storage medium

- **Air**: Immediately after fabricated, each air-stored experimental group was separately conditioned in a sealed plastic receptacle and kept in darkness at 37°C for either 1 day, 7, 45 or 90 days before being tested.
- **Distilled water:** Each water-stored experimental group was separately conditioned in a sealed plastic receptacle containing 20 ml of distilled water and kept in darkness at 37°C for either 1 day, 7, 45 or 90 days prior to testing. The solution was weekly exchanged during the whole storage period.

### 2.5 DMA Q800

In the present study, the dynamic mechanical analysis of the composite materials was carried out using a DMA Q800 (TA Instruments, New Castle, USA) (Figure 2, left) linked to a Dell computer. The DMA Q800 consists of a temperature–controlled mechanical testing chamber that includes a furnace, a specimen holder, a motor-driven mechanical testing apparatus and a displacement measuring system. The computer is responsible for controlling experimental parameters and recording results.

The DMA was set up for single cantilever mode (Figure 2, right) of flexural loading. This non-tensioning clamp contains two arms, a fixed and a moveable one which provides an oscillatory force using a non-contact direct driver motor, deforming the sample material. This instrument is designed to apply a reproducible force in the range of 0.0001-18 N, over a temperature range of

-145 to 600°C, using nitrogen as coolant. The oscillation amplitudes that can be selected by the operator in a dynamic experiment range from ± 0.5 to 10.000 µm. Due to instrument limitations the stiffness of the material must be considered during the selection of the test amplitude, since high amplitudes may not be accessible due to the high forces required to attain them.

The possible cooling rates range from 0.1 to 10°C/min and the heating rates from 0.1 to 50°C/min, although temperature ramp rates of more than 5°C/min are not recommended for DMA experiments. This concern avoids the sample to lag the actual temperature and the transitions to be pushed to higher temperatures. However, the choice of ramp rate will depend on sample size, desired degree of accuracy in transitions and frequency or frequencies of interest, which can range from 0.01 to 200 Hz. This is the frequency range that the instrument's motor is capable of driving; however, the upper frequency that can be applied is dependent on the stiffness of the sample. The higher the sample stiffness the easier it will be to drive the sample at higher frequencies

**Figure 2** DMA Q800 (left) and single/double cantilever (right) simulating sample deformation.

## 2.6 DMA calibration

The calibration of DMA is accomplished through the use of the Thermal Advantage Instrument control software and should be performed at least once a month. The types of calibration that are available for the DMA are:

**- Clamp calibration:** calibrates the properties of a DMA sample clamp.

**- Position calibration**: calibrates the absolute position of the drive shaft (and slide) as read by the optical encoder.

**- Instrument calibration**: calibrates the instrument electronics, drive force, and dynamic performance.

**- Temperature calibration**: calibrates the temperature of the DMA furnace. The instrument was calibrated using indium and ice, which melting points are respectively 156.4°C and 0°C.

### 2.7 Linear visco-elastic region

In order to use DMA to accurately determine mechanical properties and develop morphological relationships (cristallinity, molecular weight, cross-linking, etc) the material must be deformed at an amplitude that is within its linear visco-elastic region. When tested within this region, the material's response is independent of the magnitude of deformation and material's structure is maintained intact.

In order to determine the linear visco-elastic range of each material a strain sweep was performed at 1 Hz. During this test the strain amplitude ranged from 5 to 100 μm, at 37°C. The slope of the resulting stress-strain curve is equal to the elastic modulus. Thus, the end of the linear visco-elastic region was taken as the amplitude at which the initial value of the modulus changed by 5%.

After finding the linear region, subsequent scans, such as temperature ramps and frequency sweeps, should be conducted at amplitudes within the linear visco-elastic region. In the present study, the common value of 35 μm was selected for all studied composite materials, which allowed comparisons between the composites. During the whole experiment, constant amplitude was ensured by the machine that continuously adjusted the dynamic force applied to the sample.

### 2.8 Poisson's ratio

When a material is under axial loading as tensile or compression tests, it is stated that the stress provokes strain in an axial direction. However, lateral strain also occurs. Then, tensile force results in material elongation in the axial direction and a reduction of the cross-section. Brittle materials show little permanent reduction in cross-section during tensile test situations than more ductile materials.

On the other hand, compressive force leads material to increase in the cross-section and reduction of original length. If these reactions occur in the elastic limit, the ratio between lateral and axial strain is denominated Poisson's ratio. This property depends on the material itself but varies between 0.25 and 0.35 for dental composites. A constant value of 0.3 was chosen for all the materials in this study, since it was found that a variation of this value by ± 0.05 resulted in changes in elastic modulus considerably smaller than the standard deviation.

## 2.9 Glass transition temperature

In its glassy state, the mechanical behaviour of the polymer is relatively stable. The material is very stiff and brittle, and the properties do not change significantly with temperature, since the main-chain motion is frozen out and only side-chain motion and main-chain vibration are possible (25). However, as temperature rises, there will be a point where enough vibrational (thermal) energy is available in the system to create sufficient free volume to permit sequences of 6-10 main-chain carbons to move together as a unit. At this moment the behaviour of the polymer will fairly rapidly change from the glassy to a very tough and leathery behaviour. This change in behaviour is evidenced by a sharp decline in its elastic modulus. This region is termed the glass transition region and the temperature at the midpoint of this transition is defined as glass transition temperature, $T_g$.

There are multiple methods of determining the glass transition temperature, depending on the chosen one the value can differ up to 25°C from each other on the same run. It can be estimated from the graphic representations of either modulus; on the storage modulus plot, $T_g$ appears as a sharp drop. Conversely, it appears as a peak or maximum on the loss modulus curves (57). It can also be determined as the temperature at maximum in loss tangent.

Since the determination of glass transition for linear polymers is usually facilitated for the sudden changes in various physical properties, taking the elastic or viscous modulus to determine the glass transition would not be a problem (42). On the other side, with increasing degrees of cross-linking the changes on properties become less abrupt and the definition of glass transition is more difficult. For this reason, many authors prefer taking the glass transition temperature to be the maximum of the loss tangent versus temperature curves (42). For the same reason, also in the present study the glass transition temperatures are taken from the peak of the loss tangent curves.

Another challenging situation is determining the $T_g$ of undercured composite samples. Their glass transition region can be disturbed during the DMA experiment due to recommencement of polymerization at higher temperatures. The possible results are an increase in the $T_g$, a broadened transition region or even the presence of two different glass transitions. Since the glass transition temperature of the composites can be strongly influenced by its degree of cure, it is frequently used in curing studies to give a good indication as to the presence of unreacted methacrylate units in the polymerized network.

In highly cross-linked polymers, on the other hand, the glass transition does not take place at a unique temperature, but over a wide range of temperatures, which results in broad glass transition peaks. This can be mainly attributed to the fact that the polymerization of multifunctional monomers produces network polymers with highly heterogeneous environments as they contain highly cross-linked regions as well as less densely connecting cross-linked regions (58).

## 2.10 Experimental method

After the sample was clamped with a pressure of 8 cNm between the moveable and stationary fixtures, the length between both fixtures was recorded using digital callipers. Then, the sample was enclosed inside the environmental chamber and submitted to two consecutive testing conditions: 1) Frequency scan and 2) Thermal scan. During the tests the material’s response was continuously measured and material’s constants were determined as a function of temperature, which was controlled within the oven with calibrated thermocouples. The measurements during both DMA runs were plotted as elastic modulus, viscous modulus and loss tangent.

## 2.11 Frequency scan

During the frequency scan the visco-elastic response of the composite sample was measured under a nitrogen atmosphere, used to cool the sample as well as to provide an inert atmosphere. Initially the sample was cooled down to 5°C, and then the temperature was ramped from 5 to 55°C in 5°C increments. At each temperature step the visco-elastic response of the composite was measured at frequencies of 0.1, 1 and 10 Hz. A five-minute soak time was used at each test temperature to ensure isothermal conditions. On completion of the measurement at 55°C the composite sample was cooled down under a nitrogen atmosphere in the instrument. Afterwards, the thermal scan was performed.

The low frequency measurement (0.1 Hz) was responsible for making this procedure much slower than a more common constant heating experiment. On the other side, this method has several advantages: It generates more data than any other experiments; it eliminates the temperature lag between the furnace and the sample; and it also avoids the concern about changing two variables at the same time that would result in inaccurate data.

**Table 6** Test parameters selected for the frequency scan.

| | |
|---|---|
| **Test mode:** | Multi-frequency-strain mode |
| **Test:** | Temperature step/ Frequency sweep |
| **Clamp:** | Single Cantilever |
| **Sample shape:** | Rectangular |
| **Deformation amplitude:** | 35 µm |
| **Initial temperature:** | 5°C |
| **Final temperature:** | 55°C |
| **Temperature increment:** | 5°C/min. |
| **Isothermal soak time:** | 5 min. |
| **Frequency:** | Discrete (0.1, 1 and 10 Hz) |
| **Poisson ratio:** | 0.3 |

### 2.12 Thermal scan

After the sample was cooled down to 25°C the thermal scan was initiated. During this test the sample was scanned from 0 to 200°C at a fixed frequency of 1 Hz and a heating rate of 3°C/min under a nitrogen atmosphere.

**Table 7** Test parameters selected for the temperature scan.

| | |
|---|---|
| **Test mode:** | Multi-frequency-strain mode |
| **Test:** | Custom |
| **Clamp:** | Single Cantilever |
| **Sample shape:** | Rectangular |
| **Deformation amplitude:** | 35 μm |
| **Initial temperature:** | 0°C |
| **Final temperature:** | 200°C |
| **Temperature increment:** | 3°C/min. |
| **Frequency:** | Single (1 Hz) |
| **Poisson ratio:** | 0.3 |

### 2.13 Data Analysis

Thermal advantage software (TA instruments) was used for computer controlled experimental procedures and data collection. Data were analyzed using the TA Instruments Universal Analysis software package.

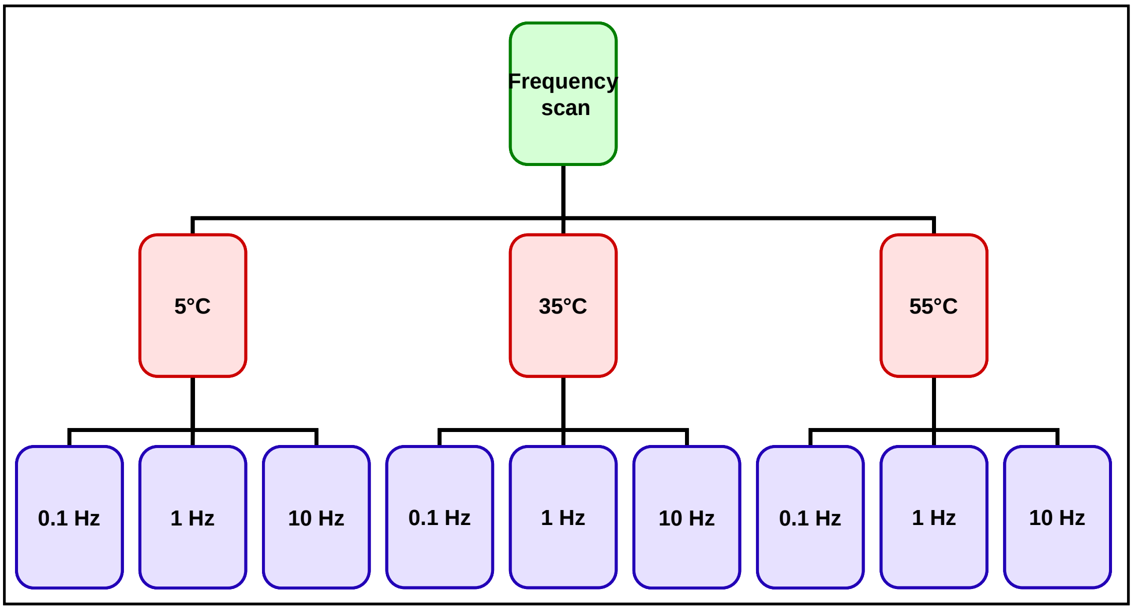
### 2.14 Statistical analysis

Diverse statistical analyses (analysis 1-8) were performed in order to properly analyse the results obtained during the frequency and temperature scans.

#### 2.14.1 Frequency scan

Although the three testing frequencies were scanned over 11 different temperatures between 5 and 55°C, three representative temperatures (5, 35 and 55°C) were selected for statistical analysis in the present work. Therefore, for each experimental group there were nine different testing conditions (Figure 3).

**Figure 3** Scheme of the nine testing conditions selected for statistical analysis.



### 2.14.1.1 Comparisons between composites

- **Analysis 1**: In order to assess their differences, direct and indirect composites are initially considered in the Results section as two main groups, each containing two different composites. DiamondLite and Grandio are part of the direct composites, represented as the left-sided green points in the Figure 4, while Artglass and Vita Zeta LC form the group of the indirect composites, represented in the same figure as the right-sided red points.

Each main group contains 162 different points. Each point corresponds to the mean elastic modulus of the five samples in one experimental group at a certain testing condition. Therefore, the 162 are respective to: 2 materials x 2 storage media (air and distilled water) x 4 storage periods (1, 7, 45 and 90 days) x 3 temperatures (5, 35 and 55°C) x 3 frequencies (0.1, 1 and 10 Hz); and additionally 2 materials x 1 baseline x 3 temperatures (5, 35 and 55°C) x 3 frequencies (0.1, 1 and 10 Hz). The mean value for all the mean points in each main group is represented by a horizontal mean line.

The same procedure was repeated for the viscous modulus and loss tangent results, represented respectively in the Figures 10 and 16.

**- Analysis 2**: In order to assess the individual contribution of the materials to the differences between direct and indirect composites, they are presented and analyzed separately. This time four main groups are formed. The first group situated on the extreme left side in the Figure 5 is DiamondLite, represented by green points. The second and third groups from the left to the right, represented by red and blue points, are respectively Grandio and Artglass. The last group is Vita Zeta LC, comprised of orange points.

Each of the four groups contains 81 points. Each point corresponds to the mean elastic modulus of the five samples in one experimental group of the composite at a certain testing condition. Therefore, the 81 points are respective to 2 storage media (air and distilled water) x 4 storage periods (1, 7, 45 and 90 days) x 3 temperatures (5, 35 and 55°C) x 3 frequencies (0.1, 1 and 10 Hz); and additionally 1 baseline x 3 temperatures (5, 35 and 55°C) x 3 frequencies (0.1, 1 and 10 Hz). The mean value for all the mean points in each group is represented by a horizontal mean line.

The corresponding viscous modulus and loss tangent results are presented in the Figures 11 and 17, respectively.

**- Analysis 3**: The elastic moduli of the four composites are compared across the nine experimental groups and nine testing conditions using one-way analysis of variance (ANOVA) followed by Tukey's pairwise multiple comparisons test to determine whether statistically significant differences existed between the composites. All results were considered statistically significant if $p < 0.05$.

### 2.14.1.2 Individual results

**- Analysis 4**: The elastic modulus values measured for all experimental groups of each tested composite at the nine different testing conditions are condensed in tables to means and standard deviations (Tables 8, 10, 12 and 14). The corresponding viscous modulus (Tables 16, 18, 20 and 22) and loss tangent (Tables 24, 26, 28 and 30) results are also illustrated.

- **Analysis 5**: The elastic moduli presented in those tables are analyzed with one-way analysis of variance (ANOVA) and compared with Tukey's test to determine whether statistically differences in this property existed between the two storage medium, the four storage periods, the three temperatures and also between the three frequencies.
- **Analysis 6**: The 95% upper, lower and mean elastic modulus confidence intervals measured at 1 Hz for all experimental groups of each composite at 5, 35 and 55°C are additionally presented in Tables 9, 11, 13, and 15, and Figures 6-9. This frequency was selected because it most closely approximated with the masticatory frequency.

The corresponding viscous modulus are presented in Tables 17, 19, 21 and 23 and Figures 12-15, while the loss tangent results are illustrated in Tables 25, 27, 29 and 31, and in Figures 18-21.

### 2.14.2 Temperature scan

- **Analysis 7**: The elastic modulus versus temperature curves obtained during the DMA thermal scan are presented for each tested composite as a function of temperature. For each tested material (DiamondLite, Grandio, Artglass and Vita Zeta LC) one double figure is presented (Figures 22-25). The left-sided figure in every double figure reproduces the elastic modulus curves of the experimental groups stored in air, while the right-sided figure the curves of those groups stored in distilled water. Every figure contains five different curves respective to the four storage periods of 1 day, 7, 45 and 90 days, and the baseline group, used as reference. Each curve was generated via statistical averaging of the multiple data sets for that experimental group of five samples.

The corresponding viscous modulus and loss tangent results are presented in Figures 26-29 and Figures 30-33, respectively.

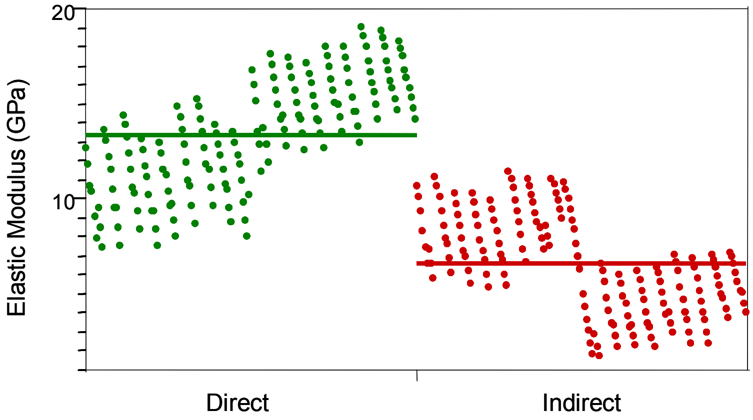
- **Analysis 8**: Since in the present study the glass transition temperature was taken from the maximum of the loss tangent versus temperature curves, Tables (32-35) containing the $T_g$ of all tested composites immediately after fabricated (baseline) and after 1 day, 7, 45 and 90 days storage in air and distilled water are presented exclusively for this property.

# 3 Results

## 3.1 Frequency Scan – Elastic Modulus

### 3.1.1 Comparisons between composites (Analysis 1)

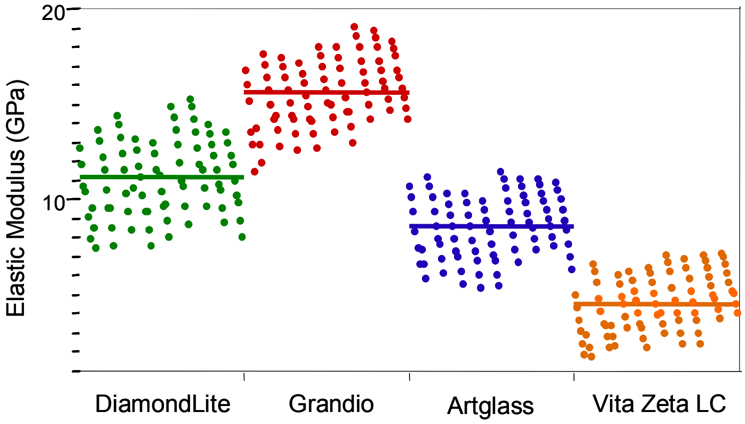
**Figure 4** Mean elastic modulus (GPa) of direct and indirect composites experimental groups at all testing conditions.



A qualitative analysis of the results in Figure 4 showed an overall trend of higher elastic modulus in favor of the direct composites, although some mean points seemed to be superposed. The different height levels of the mean lines, disposed horizontally among the points, confirmed this trend.

### 3.1.2 Comparisons between composites (Analysis 2 and 3)

**Figure 5** Mean elastic modulus (GPa) of DiamondLite, Grandio, Artglass and Vita Zeta LC experimental groups at all testing conditions.



Based on the height levels of the mean elastic modulus lines in Figure 5, it is reasonable to affirm that differences existed not only between direct and indirect materials, but also between materials in the same group. ANOVA and Tukey's test confirmed these observations, revealing statistically significant differences in modulus between the composites for all experimental groups and testing conditions, with the highest value in all cases being for Grandio, the lowest for Vita Zeta LC, and the intermediate values for DiamondLite and Artglass.

### 3.1.3 Individual results (Analysis 4, 5 and 6)

#### 3.1.3.1 DiamondLite

**Table 8** Mean (standard deviation) elastic modulus (GPa) of all DiamondLite experimental groups at 5, 35 and 55°C, and 0.1, 1 and 10 Hz.

| **Storage Medium** | **Storage Time** | **Temperature** | **Elastic Modulus (GPa)** | | |
|---|---|---|---|---|---|
| | | | **0.1 Hz** | **1 Hz** | **10 Hz** |
| Baseline | - | 5°C | 10.78 (0.28) | 11.84 (0.26) | 12.73 (0.25) |
| | | 35°C | 8.00 (0.37) | 9.13 (0.42) | 10.49 (0.26) |
| | | 55°C | 7.51 (0.21) | 8.51 (0.21) | 9.62 (0.22) |
| Water | 1 day | 5°C | 12.26 (0.36) | 13.09 (0.39) | 13.69 (0.43) |
| | | 35°C | 9.57 (0.31) | 10.56 (0.35) | 11.56 (0.40) |
| | | 55°C | 7.58 (0.24) | 8.54 (0.26) | 9.59 (0.30) |
| | 7 days | 5°C | 13.29 (0.33) | 13.98 (0.35) | 14.46 (0.36) |
| | | 35°C | 10.65 (0.32) | 11.59 (0.33) | 12.47 (0.35) |
| | | 55°C | 8.49 (0.25) | 9.39 (0.26) | 10.40 (0.26) |
| | 45 days | 5°C | 11.78 (0.15) | 12.63 (0.15) | 13.25 (0.16) |
| | | 35°C | 9.44 (0.33) | 10.26 (0.31) | 11.19 (0.30) |
| | | 55°C | 7.56 (0.30) | 8.44 (0.13) | 9.40 (0.31) |
| | 90 days | 5°C | 11.60 (0.20) | 12.43 (0.21) | 13.05 (0.24) |
| | | 35°C | 9.64 (0.23) | 10.44 (0.25) | 11.32 (0.27) |
| | | 55°C | 8.07 (0.19) | 8.89 (0.21) | 9.80 (0.23) |
| Air | 1 day | 5°C | 13.64 (0.33) | 14.39 (0.33) | 14.93 (0.33) |
| | | 35°C | 11.07 (0.42) | 12.01 (0.43) | 12.94 (0.44) |
| | | 55°C | 8.71 (0.48) | 9.71 (0.46) | 10.76 (0.45) |
| | 7 days | 5°C | 14.29 (0.43) | 14.91 (0.45) | 15.33 (0.47) |
| | | 35°C | 11.91 (0.48) | 12.76 (0.43) | 13.57 (0.42) |
| | | 55°C | 9.74 (0.57) | 10.61 (0.53) | 11.55 (0.49) |
| | 45 days | 5°C | 12.91 (0.23) | 13.54 (0.20) | 14.01 (0.18) |
| | | 35°C | 10.80 (0.17) | 11.56 (0.13) | 12.34 (0.11) |
| | | 55°C | 8.82 (0.17) | 9.63 (0.16) | 10.51 (0.15) |
| | 90 days | 5°C | 12.31 (0.27) | 13.02 (0.28) | 13.61 (0.27) |
| | | 35°C | 10.25 (0.23) | 11.04 (0.22) | 11.88 (0.22) |
| | | 55°C | 8.07 (0.21) | 8.97 (0.20) | 9.91 (0.19) |

**- Storage medium**: DiamondLite samples stored during the same time and tested under identical conditions showed higher elastic modulus when stored in air than in distilled water. Differences were statistically significant for all experimental groups and testing conditions but 90 days/55°C (all frequencies).

**- Storage period:** The highest elastic modulus increasing rates between baseline and 1 day storage were measured for the air-stored samples (12-38%), which were statistically significantly higher than that of the water-stored samples at all testing conditions. The lowest increasing rates (0-20%) were observed for the water-stored samples, which were only statistically significant at 5 and 35°C (all frequencies).

Between 1 day and 7 days storage the elastic modulus statistically significantly increased in both storage media at all testing conditions but air/5°C (1 and 10 Hz). Thereafter, between 7 and 45 days, the elastic modulus significantly dropped in air and in distilled water, especially in the later, at all testing conditions. Between 45 and 90 days, air and water-stored samples tended to decrease and increase their modulus, respectively. However, changes in modulus during this period were only significant for air/55°C/0.1 Hz and water/55°C/0.1 Hz.

**- Temperature**: The elastic modulus of all experimental groups statistically dropped as temperature was raised from 5 to 35°C. The highest decreasing rates were measured for the baseline group (18-26%), followed by the water-stored (13-22%) and finally by the air-stored groups (12-19%).

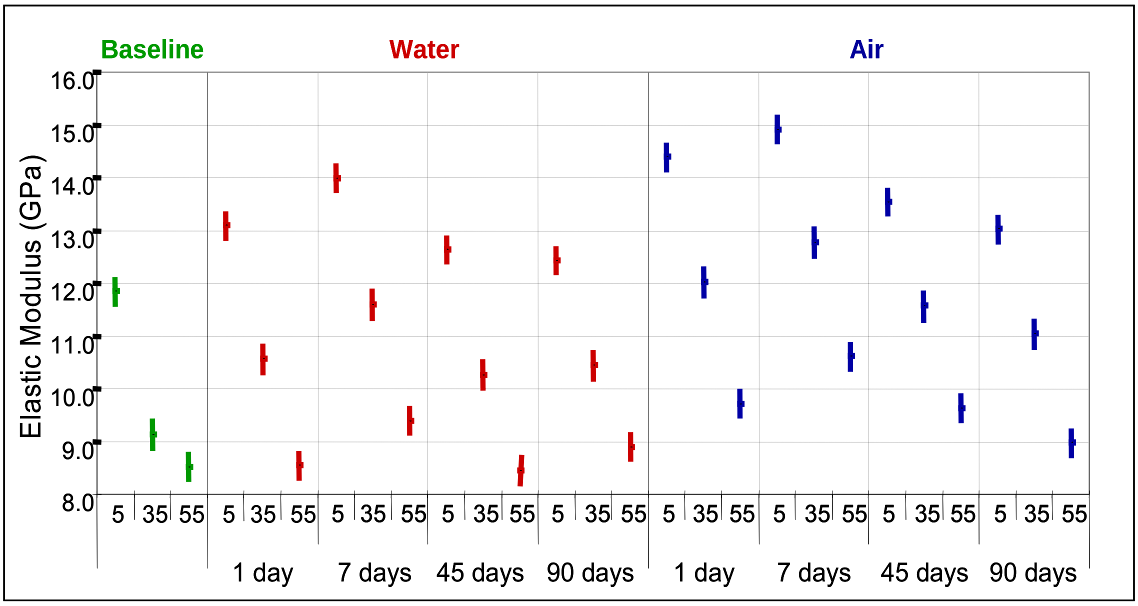
Between 35 and 55°C all experimental groups dropped their modulus at all tested frequencies, except for the baseline group at 0.1 Hz. Groups stored in distilled water had the highest modulus decreasing rates (13-26%), followed by the air-stored groups (15-21%) and the baseline group (6-8%).

**- Frequency**: Higher testing frequencies enhanced the elastic modulus of all DiamondLite experimental groups, at all temperatures. However, these results were not always statistically relevant. Non-significant changes in elastic modulus between 0.1 and 1 Hz were observed for air/7 days at 5 and 55°C. Between 1 and 10 Hz all non-significant groups were exclusively found at 5°C and they were water/1 day, water/7 days, air/1 day and air/7 days.

**Table 9** Upper, lower and mean 95% elastic modulus (GPa) confidence intervals of the DiamondLite experimental groups at 5, 35 and 55°C, and 1 Hz.

| Storage medium | Storage Time | Temperature | upper 95% | lower 95% | mean |
|---|---|---|---|---|---|
| Baseline | - | 5°C | 12.12 | 11.56 | 11.84 |
| | | 35°C | 9.44 | 8.83 | 9.13 |
| | | 55°C | 8.80 | 8.23 | 8.51 |
| Water | 1 day | 5°C | 13.36 | 12.81 | 13.09 |
| | | 35°C | 10.86 | 10.26 | 10.56 |
| | | 55°C | 8.82 | 8.26 | 8.54 |
| | 7 days | 5°C | 14.26 | 13.70 | 13.98 |
| | | 35°C | 11.89 | 11.28 | 11.59 |
| | | 55°C | 9.68 | 9.11 | 9.39 |
| | 45 days | 5°C | 12.91 | 12.35 | 12.63 |
| | | 35°C | 10.57 | 9.96 | 10.26 |
| | | 55°C | 8.73 | 8.16 | 8.44 |
| | 90 days | 5°C | 12.71 | 12.15 | 12.43 |
| | | 35°C | 10.74 | 10.13 | 10.44 |
| | | 55°C | 9.18 | 8.61 | 8.90 |
| Air | 1 day | 5°C | 14.66 | 14.11 | 14.39 |
| | | 35°C | 12.32 | 11.71 | 12.01 |
| | | 55°C | 9.99 | 9.43 | 9.71 |
| | 7 days | 5°C | 15.19 | 14.64 | 14.91 |
| | | 35°C | 13.07 | 12.47 | 12.77 |
| | | 55°C | 10.90 | 10.33 | 10.61 |
| | 45 days | 5°C | 13.81 | 13.26 | 13.54 |
| | | 35°C | 11.86 | 11.25 | 11.56 |
| | | 55°C | 9.91 | 9.35 | 9.63 |
| | 90 days | 5°C | 13.30 | 12.74 | 13.02 |
| | | 35°C | 11.34 | 10.73 | 11.04 |
| | | 55°C | 9.25 | 8.68 | 8.97 |

**Figure 6** Same as Table 9.



### 3.1.3.2 Grandio

**Table 10** Mean (standard deviation) elastic modulus (GPa) of all Grandio experimental groups at 5, 35 and 55°C, and 0.1, 1 and 10 Hz.

| Storage medium | Storage time | Temperature | Elastic Modulus (GPa) | | |
|---|---|---|---|---|---|
| | | | 0.1 Hz | 1 Hz | 10 Hz |
| Baseline | - | 5°C | 15.18 (0.20) | 16.05 (0.17) | 16.86 (0.18) |
| | | 35°C | 11.47 (0.74) | 13.01 (0.67) | 13.99 (0.29) |
| | | 55°C | 11.90 (0.82) | 12.93 (0.77) | 13.80 (0.74) |
| Water | 1 day | 5°C | 16.44 (0.11) | 17.07 (0.09) | 17.66 (0.11) |
| | | 35°C | 14.22 (0.18) | 14.99 (0.19) | 15.73 (0.19) |
| | | 55°C | 12.82 (0.26) | 13.65 (0.25) | 14.42 (0.25) |
| | 7 days | 5°C | 16.44 (0.11) | 16.99 (0.15) | 17.49 (0.20) |
| | | 35°C | 14.41 (0.08) | 15.11 (0.12) | 15.75 (0.17) |
| | | 55°C | 12.68 (0.17) | 13.47 (0.21) | 14.22 (0.25) |
| | 45 days | 5°C | 16.12 (0.41) | 16.66 (0.42) | 17.20 (0.43) |
| | | 35°C | 14.26 (0.42) | 14.89 (0.42) | 15.48 (0.43) |
| | | 55°C | 12.72 (0.47) | 13.46 (0.47) | 14.14 (0.46) |
| | 90 days | 5°C | 17.01 (0.37) | 17.57 (0.37) | 18.08 (0.38) |
| | | 35°C | 15.11 (0.45) | 15.76 (0.44) | 16.37 (0.44) |
| | | 55°C | 13.58 (0.52) | 14.31 (0.51) | 15.00 (0.50) |
| Air | 1 day | 5°C | 16.92 (0.21) | 17.51 (0.20) | 18.04 (0.18) |
| | | 35°C | 14.67 (0.23) | 15.43 (0.21) | 16.11 (0.20) |
| | | 55°C | 12.99 (0.21) | 13.84 (0.37) | 14.62 (0.34) |
| | 7 days | 5°C | 18.09 (0.21) | 18.61 (0.22) | 19.07 (0.24) |
| | | 35°C | 16.11 (0.25) | 16.75 (0.27) | 17.33 (0.29) |
| | | 55°C | 14.23 (0.21) | 15.00 (0.23) | 15.71 (0.24) |
| | 45 days | 5°C | 18.09 (0.53) | 18.52 (0.50) | 18.89 (0.48) |
| | | 35°C | 16.28 (0.79) | 16.83 (0.71) | 17.31 (0.63) |
| | | 55°C | 14.69 (1.00) | 15.31 (0.89) | 15.89 (0.80) |
| | 90 days | 5°C | 17.54 (0.26) | 17.94 (0.24) | 18.30 (0.25) |
| | | 35°C | 15.90 (0.30) | 16.40 (0.29) | 16.86 (0.29) |
| | | 55°C | 14.22 (0.28) | 14.84 (0.28) | 15.42 (0.27) |

**- Storage medium**: Most air-stored experimental groups showed statistically significant higher elastic modulus values than the corresponding groups stored in distilled water. Exceptions were 1 day/55°C (all frequencies), 90 days/5°C (1 and 10 Hz), 90 days/35°C/10 Hz and 90 days/55°C (1 and 10 Hz) that showed no statistically significant difference when stored in air and in distilled water.

**- Storage period**: Grandio samples significantly improved their elastic modulus between baseline and 1 day in both storage media. The highest increasing rates were observed for the air-stored (6-28%), and the lowest for the water-stored experimental groups (4-24%). This assumption was only relevant at 5 and 35°C. At 55°C no statistically significant differences were found between groups stored in air and water for 1 day.

No significant changes in modulus were observed between 1 day and 7 days for water-stored samples. On the other hand, air-stored samples significantly improved their modulus during this period.

Between 7 and 45 days neither air nor water-stored samples significantly changed their modulus. Between 45 and 90 days samples stored in distilled water significantly improved their modulus, while those stored in air did not change this property at all testing conditions but 5°C (1 and 10 Hz).

**- Temperature**: Rising temperatures significantly dropped the elastic modulus of all Grandio experimental groups in both temperature intervals, except for the baseline group that showed no change in modulus between 35 and 55°C (all frequencies).

The highest decreasing rates between 5 and 35°C were observed for the baseline samples (19-25%), followed by the water-stored (9-14%) and finally by the air-stored samples (8-13%).

In the second temperature interval, between 35 and 55°C, the highest decreasing rates were noticed for the water-stored samples (9-21%), while the intermediate and lowest increasing rates were measured, respectively, for the air-stored (8-12%) and baseline samples (0-5%).

**- Frequency**: The effect of frequency on elastic modulus was greatly influenced by the storage period. The elastic modulus of the 1 day and 7 days stored groups was greatly dependent on frequency, while the elastic modulus of 45 days air and water-stored groups, and 90 days water-stored groups was independent of changes in frequency.

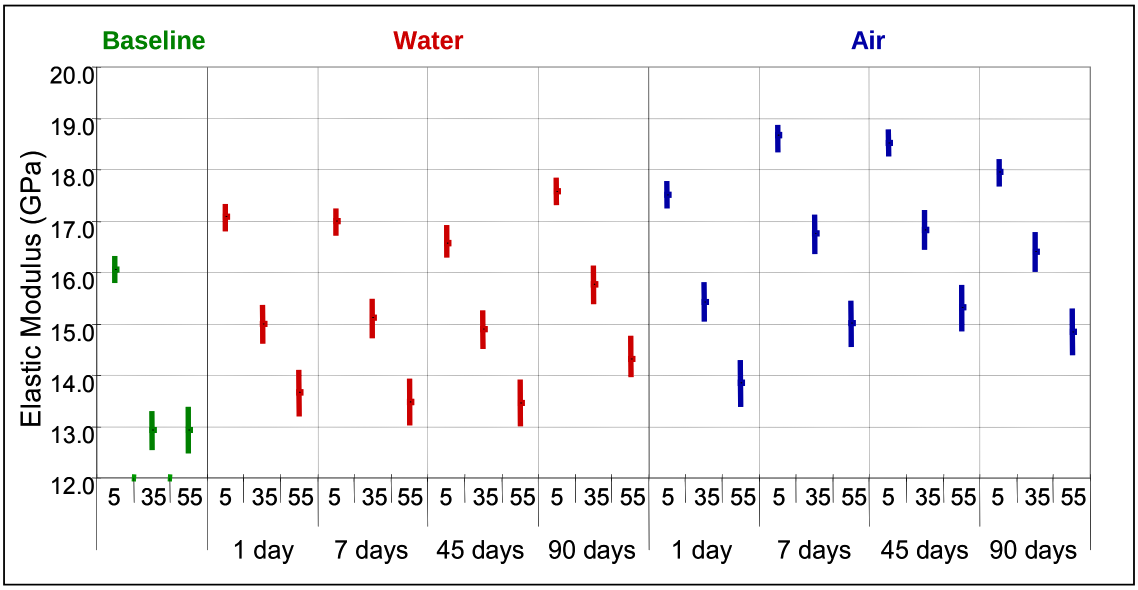
Additionally, no frequency dependence of elastic modulus was noticed for the baseline group at 35 and 55°C and for air/90 days /5°C in both frequency intervals.

The last non-significant experimental group was air/90 days/35°C, whose elastic modulus significantly increased between 0.1 and 1 Hz, but remained practically unchanged between 1 and 10 Hz.

**Table 11** Upper, lower and mean 95% elastic modulus (GPa) confidence intervals of the Grandio experimental groups at 5, 35 and 55°C, and 1 Hz.

| Storage medium | Storage Time | Temperature | upper 95% | lower 95% | mean |
|---|---|---|---|---|---|
| Baseline | - | 5°C | 16.32 | 15.79 | 16.05 |
| | | 35°C | 13.31 | 12.55 | 12.93 |
| | | 55°C | 13.38 | 12.48 | 12.93 |
| Water | 1 day | 5°C | 17.34 | 16.81 | 17.07 |
| | | 35°C | 15.37 | 14.61 | 14.99 |
| | | 55°C | 14.10 | 13.20 | 13.65 |
| | 7 days | 5°C | 17.26 | 16.73 | 16.99 |
| | | 35°C | 15.49 | 14.73 | 15.11 |
| | | 55°C | 13.93 | 13.03 | 13.48 |
| | 45 days | 5°C | 16.93 | 16.40 | 16.66 |
| | | 35°C | 15.27 | 14.51 | 14.89 |
| | | 55°C | 13.91 | 13.01 | 13.46 |
| | 90 days | 5°C | 17.84 | 17.31 | 17.57 |
| | | 35°C | 16.14 | 15.38 | 15.76 |
| | | 55°C | 14.76 | 13.96 | 14.31 |
| Air | 1 day | 5°C | 17.77 | 17.24 | 17.51 |
| | | 35°C | 15.81 | 15.05 | 15.43 |
| | | 55°C | 14.29 | 13.39 | 13.84 |
| | 7 days | 5°C | 18.88 | 18.35 | 18.61 |
| | | 35°C | 17.13 | 16.37 | 16.75 |
| | | 55°C | 15.45 | 14.55 | 15.00 |
| | 45 days | 5°C | 18.79 | 18.26 | 18.52 |
| | | 35°C | 17.21 | 16.45 | 16.83 |
| | | 55°C | 15.77 | 14.86 | 15.31 |
| | 90 days | 5°C | 18.21 | 17.68 | 17.94 |
| | | 35°C | 16.78 | 16.02 | 16.40 |
| | | 55°C | 15.30 | 14.39 | 14.84 |

**Figure 7** Same as Table 11.



### 3.1.3.3 Artglass

**Table 12** Mean (standard deviation) elastic modulus (GPa) of all Artglass experimental groups at 5, 35 and 55°C, and 0.1, 1 and 10 Hz.

| Storage medium | Storage time | Temperature | Elastic Modulus (GPa) | | |
|---|---|---|---|---|---|
| | | | **0.1 Hz** | **1 Hz** | **10 Hz** |
| Baseline | - | 5°C | 9.45 (0.13) | 10.14 (0.11) | 10.71 (0.10) |
| | | 35°C | 6.66 (0.03) | 7.49 (0.30) | 8.33 (0.27) |
| | | 55°C | 5.94 (0.13) | 6.66 (0.11) | 7.42 (0.10) |
| Water | 1 day | 5°C | 10.17 (0.24) | 10.76 (0.20) | 11.18 (0.17) |
| | | 35°C | 7.98 (0.21) | 8.65 (0.20) | 9.40 (0.23) |
| | | 55°C | 6.22 (0.18) | 6.93 (0.17) | 7.68 (0.16) |
| | 7 days | 5°C | 9.20 (0.47) | 9.82 (0.47) | 10.33 (0.47) |
| | | 35°C | 7.33 (0.45) | 7.95 (0.46) | 8.66 (0.47) |
| | | 55°C | 5.61 (0.38) | 6.30 (0.39) | 7.02 (0.40) |
| | 45 days | 5°C | 9.21 (0.12) | 9.87 (0.12) | 10.33 (0.44) |
| | | 35°C | 7.28 (0.13) | 7.89 (0.11) | 8.60 (0.11) |
| | | 55°C | 5.43 (0.13) | 6.12 (0.13) | 6.86 (0.12) |
| | 90 days | 5°C | 8.97 (0.26) | 9.54 (0.21) | 9.97 (0.15) |
| | | 35°C | 7.14 (0.33) | 7.71 (0.32) | 8.34 (0.28) |
| | | 55°C | 5.52 (0.63) | 6.13 (0.56) | 6.79 (0.53) |
| Air | 1 day | 5°C | 10.65 (0.11) | 11.14 (0.12) | 11.49 (0.14) |
| | | 35°C | 8.80 (0.09) | 9.39 (0.08) | 10.00 (0.09) |
| | | 55°C | 6.75 (0.09) | 7.43 (0.07) | 8.14 (0.05) |
| | 7 days | 5°C | 10.26 (0.49) | 10.74 (0.46) | 11.11 (0.42) |
| | | 35°C | 8.87 (0.58) | 9.33 (0.56) | 9.86 (0.53) |
| | | 55°C | 7.40 (0.82) | 7.94 (0.73) | 8.51 (0.67) |
| | 45 days | 5°C | 10.39 (0.24) | 10.83 (0.26) | 11.16 (0.28) |
| | | 35°C | 9.06 (0.25) | 9.49 (0.25) | 9.99 (0.25) |
| | | 55°C | 7.57 (0.32) | 8.08 (0.30) | 8.63 (0.29) |
| | 90 days | 5°C | 10.07 (0.29) | 10.54 (0.31) | 10.92 (0.31) |
| | | 35°C | 8.44 (0.27) | 8.95 (0.25) | 9.51 (0.25) |
| | | 55°C | 6.36 (0.19) | 7.03 (0.19) | 7.70 (0.19) |

**- Storage medium**: Artglass was more extensively affected by moisture than any other tested composite. Invariably, experimental groups stored in air had significantly higher elastic modulus than the corresponding groups stored in distilled water during the same period.

**- Storage period**: Significant increases in elastic modulus between baseline and 1 day were observed for the air-stored samples at all testing conditions but 55°C/0.1 Hz. This increase in modulus was less evident for water-stored samples and was not significant at 5°C/10 Hz and 55°C (all frequencies). Therefore, the highest increasing rates between baseline and 1 day were measured for the air-stored samples (7–32%) and the lowest, for the water-stored samples (4–20%).

Between 1 day and 7 days storage no statistically significant change in elastic modulus was found for the samples stored in air. On the other hand, samples stored in water underwent statistically relevant drops in elastic modulus at all testing conditions but 55°C (0.1 and 1 Hz).

Changes in modulus between 7 and 45 days were not statistically significant in both storage media at all testing conditions. The same happened between 45 and 90 days, except for air/55°C that dropped its modulus at all tested frequencies.

**- Temperature**: Artglass showed a great temperature dependence of elastic modulus, which significantly dropped for all experimental groups in both temperature intervals at the three frequencies.

Between 5 and 35°C the highest elastic modulus decreasing rates were measured for the baseline group (22-30%), followed by water-stored (16-22%) and air-stored groups (11-17%).

Between 35 and 55°C, the groups stored in distilled water showed the highest decreasing rates (18-25%). The second and third positions had respectively the air-stored (14-25 %) and baseline groups (11%).

**- Frequency**: Higher testing frequencies invariably enhanced the elastic modulus of the Artglass experimental groups at all testing temperatures, but not always significantly. The greatest frequency dependence was noticed for baseline samples, followed by water-stored and finally, by the air-stored samples.

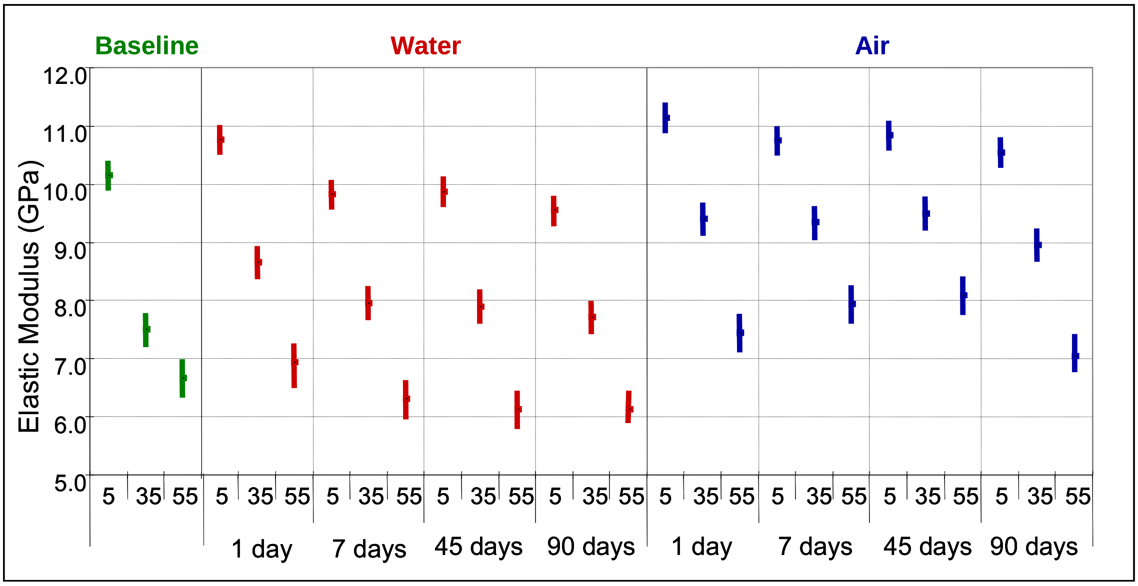
Between 0.1 and 1 Hz no significant change in elastic modulus was observed for air/7days (all temperatures), air/45 days (5 and 55°C), air/90 days/5°C, water/7days (5 and 35°C) and water/90 days/55°C.

Between 1 and 10 Hz the non-significant groups were air/7days (all temperatures), air/45 days/5°C, air/90 days/5°C, water/7days (5 and 35°C) and water/90 days/55°C.

**Table 13** Upper, lower and mean 95% elastic modulus (GPa) confidence intervals of the Artglass experimental groups at 5, 35 and 55°C, and 1 Hz.

| Storage medium | Storage Time | Temperature | upper 95% | lower 95% | mean |
|---|---|---|---|---|---|
| Baseline | - | 5°C | 10.40 | 9.88 | 10.14 |
| | | 35°C | 7.78 | 7.21 | 7.49 |
| | | 55°C | 6.99 | 6.33 | 6.66 |
| Water | 1 day | 5°C | 11.02 | 10.50 | 10.76 |
| | | 35°C | 8.94 | 8.36 | 8.65 |
| | | 55°C | 7.26 | 6.50 | 6.93 |
| | 7 days | 5°C | 10.08 | 9.56 | 9.82 |
| | | 35°C | 8.24 | 7.67 | 7.95 |
| | | 55°C | 6.63 | 5.96 | 6.30 |
| | 45 days | 5°C | 10.12 | 9.61 | 9.87 |
| | | 35°C | 8.18 | 7.61 | 7.89 |
| | | 55°C | 6.45 | 5.79 | 6.12 |
| | 90 days | 5°C | 9.80 | 9.28 | 9.54 |
| | | 35°C | 7.99 | 7.42 | 7.71 |
| | | 55°C | 6.46 | 5.79 | 6.13 |
| Air | 1 day | 5°C | 11.40 | 10.88 | 11.14 |
| | | 35°C | 9.68 | 9.11 | 9.39 |
| | | 55°C | 7.76 | 7.10 | 7.43 |
| | 7 days | 5°C | 11.00 | 10.49 | 10.74 |
| | | 35°C | 9.62 | 9.04 | 9.33 |
| | | 55°C | 8.27 | 7.60 | 7.94 |
| | 45 days | 5°C | 11.09 | 10.57 | 10.83 |
| | | 35°C | 9.78 | 9.21 | 9.49 |
| | | 55°C | 8.41 | 7.75 | 8.08 |
| | 90 days | 5°C | 10.80 | 10.28 | 10.54 |
| | | 35°C | 9.23 | 8.66 | 8.95 |
| | | 55°C | 7.36 | 6.70 | 7.03 |

**Figure 8** Same as Table 13.



### 3.1.3.4 Vita Zeta LC

**Table 14** Mean (standard deviation) elastic modulus (GPa) of all Vita Zeta LC experimental groups at 5, 35 and 55°C, and 0.1, 1 and 10 Hz.

| Storage Medium | Storage Time | Temperature | Elastic Modulus (GPa) | | |
|---|---|---|---|---|---|
| | | | 0.1 Hz | 1 Hz | 10 Hz |
| Baseline | - | 5°C | 3.68 (0.16) | 4.39 (0.14) | 5.00 (0.10) |
| | | 35°C | 1.87 (0.07) | 2.45 (0.07) | 3.14 (0.05) |
| | | 55°C | 1.80 (0.02) | 2.31 (0.04) | 2.90 (0.06) |
| Water | 1 day | 5°C | 5.68 (0.18) | 6.27 (0.20) | 6.67 (0.21) |
| | | 35°C | 3.51 (0.16) | 4.14 (0.18) | 4.82 (0.20) |
| | | 55°C | 2.32 (0.10) | 2.85 (0.10) | 3.47 (0.11) |
| | 7 days | 5°C | 4.95 (0.19) | 5.60 (0.18) | 6.13 (0.19) |
| | | 35°C | 3.33 (0.13) | 3.88 (0.16) | 4.55 (0.19) |
| | | 55°C | 2.38 (0.16) | 2.87 (0.16) | 3.44 (0.18) |
| | 45 days | 5°C | 5.21 (0.14) | 5.83 (0.15) | 6.30 (0.15) |
| | | 35°C | 3.51 (0.07) | 4.06 (0.09) | 4.72 (0.11) |
| | | 55°C | 2.29 (0.07) | 2.78 (0.08) | 3.36 (0.09) |
| | 90 days | 5°C | 5.68 (0.24) | 6.14 (0.26) | 6.42 (0.27) |
| | | 35°C | 4.02 (0.15) | 4.56 (0.18) | 5.11 (0.21) |
| | | 55°C | 3.07 (0.11) | 3.50 (0.13) | 4.05 (0.16) |
| Air | 1 day | 5°C | 6.24 (0.27) | 6.78 (0.21) | 7.15 (0.14) |
| | | 35°C | 4.09 (0.25) | 4.72 (0.25) | 5.38 (0.23) |
| | | 55°C | 2.49 (0.10) | 3.08 (0.10) | 3.74 (0.11) |
| | 7 days | 5°C | 5.91 (0.31) | 6.46 (0.30) | 6.90 (0.29) |
| | | 35°C | 4.08 (0.30) | 4.64 (0.30) | 5.26 (0.31) |
| | | 55°C | 2.50 (0.20) | 3.07 (0.22) | 3.70 (0.23) |
| | 45 days | 5°C | 6.50 (0.18) | 6.88 (0.20) | 7.12 (0.21) |
| | | 35°C | 5.00 (0.12) | 5.52 (0.14) | 6.02 (0.15) |
| | | 55°C | 3.80 (0.07) | 4.27 (0.08) | 4.84 (0.09) |
| | 90 days | 5°C | 6.63 (0.03) | 7.02 (0.04) | 7.27 (0.04) |
| | | 35°C | 5.20 (0.05) | 5.71 (0.05) | 6.20 (0.05) |
| | | 55°C | 4.13 (0.07) | 4.57 (0.06) | 5.12 (0.06) |

**- Storage medium**: The negative effect of moisture on elastic modulus was also perceptible for Vita Zeta LC. When stored during the same period, groups conditioned in air had higher elastic modulus values than those stored in distilled water. These results were statistically significant for all experimental groups and testing conditions but 7 days/55°C (all frequencies).

**- Storage period**: Vita Zeta LC showed the highest elastic modulus increasing rates between baseline and 1 day storage. The increase in elastic modulus during this time interval was statistically significant at all testing conditions, regardless of the storage medium. However, the highest increasing rates were measured for the air-stored samples (29–119%), while the lowest were observed for the samples stored in distilled water (20–88%).

Between 1 day and 7 days storage the elastic modulus of Vita Zeta LC samples did not significantly change in both storage media, except for water/5°C that significantly dropped its modulus at all frequencies. Similarly, no statistically relevant change in elastic modulus was observed for the water-stored samples between 7 and 45 days, while the air-stored samples improved their modulus during this period at all testing conditions but 5°C/10 Hz.

Between 45 and 90 days the water-stored samples increased their modulus at most testing conditions but 5°C (1 and 10 Hz). During the same period, the air-stored samples did not significantly change their elastic modulus, except when tested at 55°C (all frequencies), when their modulus increased.

**- Temperature**: Among all tested composites, Vita Zeta LC showed the greatest temperature dependence of elastic modulus.

Between 5 and 35°C all experimental groups significantly dropped their elastic modulus at all testing frequencies. The highest decreasing rates were measured for baseline samples (37-49%), followed by the water-stored (20-38%) and finally, by the air-stored samples (15-35%).

In the second temperature interval, between 35 and 55°C, significant drops in modulus were observed for all experimental groups at the three testing frequencies, except for the baseline group when tested at 0.1 and 1 Hz. The greatest drops in elastic modulus were seen for the water-stored samples (21-44%), followed by the air-stored (17-39%), and at last, by the baseline samples (3-8%).

**- Frequency**: Higher testing frequencies positively affected the elastic modulus of Vita Zeta LC that showed the greatest frequency dependence of elastic modulus among the four tested composites.

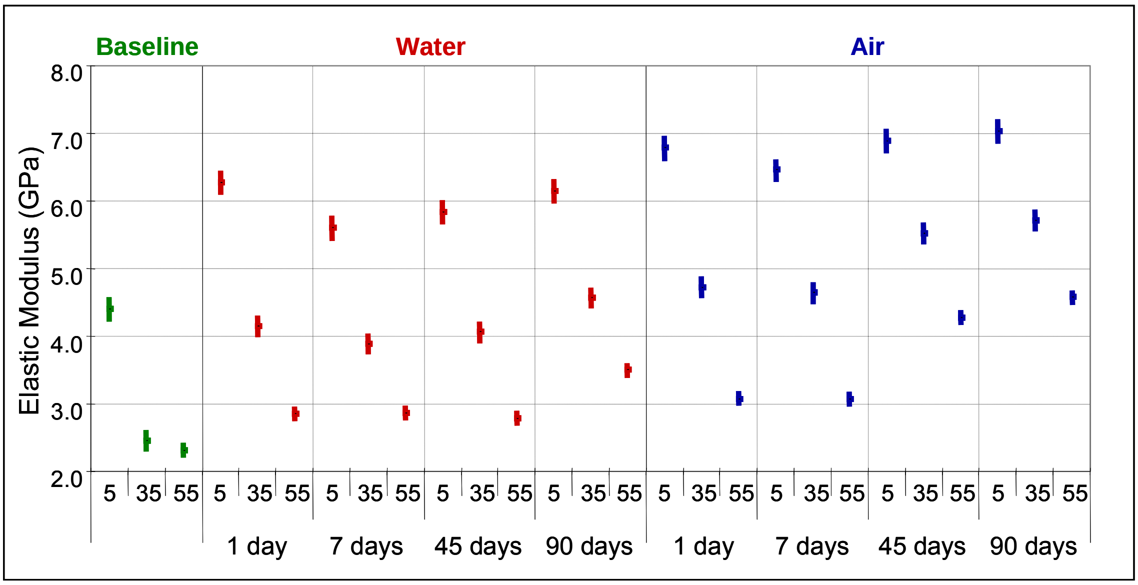
Between 0.1 and 1 Hz all experimental groups significantly raised their elastic modulus at all testing temperatures.

Statistically significant increases in elastic modulus were also found between 1 and 10 Hz for all experimental groups, except for water/90 days, air/7 days and air/45 days, all at 5°C.

**Table 15** Upper, lower and mean 95% elastic modulus (GPa) confidence intervals of the Vita Zeta LC experimental groups at 5, 35 and 55°C, and 1 Hz.

| Storage medium | Storage Time | Temperature | upper 95% | lower 95% | mean |
|---|---|---|---|---|---|
| Baseline | - | 5°C | 4.57 | 4.21 | 4.39 |
| | | 35°C | 2.61 | 2.29 | 2.45 |
| | | 55°C | 2.42 | 2.20 | 2.31 |
| Water | 1 day | 5°C | 6.45 | 6.09 | 6.27 |
| | | 35°C | 4.30 | 3.98 | 4.14 |
| | | 55°C | 2.96 | 2.74 | 2.85 |
| | 7 days | 5°C | 5.78 | 5.42 | 5.60 |
| | | 35°C | 4.04 | 3.72 | 3.88 |
| | | 55°C | 2.97 | 2.76 | 2.87 |
| | 45 days | 5°C | 6.01 | 5.65 | 5.83 |
| | | 35°C | 4.22 | 3.90 | 4.06 |
| | | 55°C | 2.89 | 2.67 | 2.78 |
| | 90 days | 5°C | 6.32 | 5.96 | 6.14 |
| | | 35°C | 4.72 | 4.40 | 4.56 |
| | | 55°C | 3.61 | 3.39 | 3.50 |
| Air | 1 day | 5°C | 6.96 | 6.60 | 6.78 |
| | | 35°C | 4.88 | 4.56 | 4.72 |
| | | 55°C | 3.19 | 2.97 | 3.08 |
| | 7 days | 5°C | 6.64 | 6.28 | 6.46 |
| | | 35°C | 4.79 | 4.48 | 4.64 |
| | | 55°C | 3.18 | 2.96 | 3.07 |
| | 45 days | 5°C | 7.06 | 6.70 | 6.88 |
| | | 35°C | 5.68 | 5.36 | 5.52 |
| | | 55°C | 4.38 | 4.16 | 4.27 |
| | 90 days | 5°C | 7.21 | 6.85 | 7.03 |
| | | 35°C | 5.87 | 5.55 | 5.71 |
| | | 55°C | 4.68 | 4.46 | 4.57 |

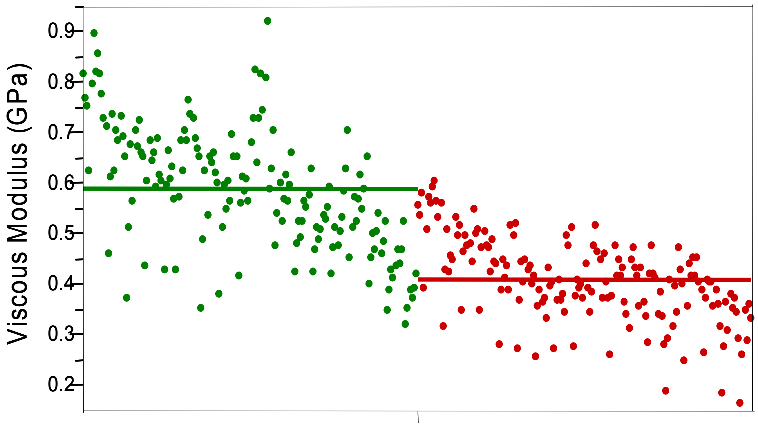
**Figure 9** Same as Table 15.



## 3.2 Frequency Scan – Viscous Modulus

### 3.2.1 Comparisons between composites (Analysis 1)

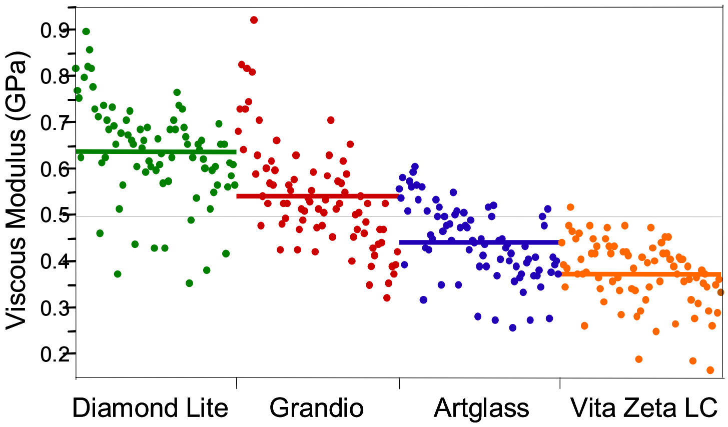
**Figure 10** Mean viscous modulus (GPa) of direct and indirect composites experimental groups at all testing conditions.



The irregular distribution of the points in Figure 10 made it extremely difficult to distinguish the two composites inside each main group. Another difference when compared to the elastic modulus results was the distance between the main groups' mean lines, much smaller for viscous modulus. Then, although direct and indirect materials differed in both properties, the viscous modulus seemed to be a less important factor to differentiate both groups of materials.

### 3.2.2 Comparisons between composites (Analysis 2 and 3)

**Figure 11** Mean viscous modulus (GPa) of DiamondLite, Grandio, Artglass and Vita Zeta LC experimental groups at all testing conditions.



The proximity of the mean lines in the Figure 11 suggested non-significant results, especially when materials in the same main group (direct or indirect) were compared. ANOVA and Tukey's test confirmed these observations. Significant differences in viscous modulus were only observed for all experimental groups and testing conditions when Diamond Lite and Vita Zeta LC were compared. Other comparisons resulted in significant differences in viscous modulus between the materials, but not always.

### 3.2.3 Individual results (Analysis 4, 5 and 6)

#### 3.2.3.1 DiamondLite

**Table 16** Mean (standard deviation) viscous modulus of all DiamondLite experimental groups at 5, 35 and 55°C, and 0.1, 1 and 10 Hz.

| Storage Medium | Storage Time | Temperature | Viscous Modulus (GPa) | | |
|---|---|---|---|---|---|
| | | | 0.1 Hz | 1 Hz | 10 Hz |
| Baseline | - | 5°C | 0.90 (0.04) | 0.80 (0.03) | 0.63 (0.03) |
| | | 35°C | 0.82 (0.01) | 0.86 (0.02) | 0.82 (0.03) |
| | | 55°C | 0.76 (0.01) | 0.77 (0.02) | 0.82 (0.02) |
| Water | 1 day | 5°C | 0.74 (0.06) | 0.62 (0.07) | 0.46 (0.06) |
| | | 35°C | 0.69 (0.04) | 0.71 (0.03) | 0.63 (0.03) |
| | | 55°C | 0.72 (0.04) | 0.73 (0.03) | 0.78 (0.04) |
| | 7 days | 5°C | 0.68 (0.01) | 0.52 (0.01) | 0.37 (0.01) |
| | | 35°C | 0.67 (0.02) | 0.71 (0.01) | 0.57 (0.01) |
| | | 55°C | 0.65 (0.01) | 0.70 (0.01) | 0.74 (0.01) |
| | 45 days | 5°C | 0.69 (0.03) | 0.61 (0.03) | 0.44 (0.03) |
| | | 35°C | 0.60 (0.01) | 0.66 (0.01) | 0.65 (0.01) |
| | | 55°C | 0.66 (0.01) | 0.66 (0.01) | 0.73 (0.01) |
| | 90 days | 5°C | 0.67 (0.02) | 0.60 (0.03) | 0.43 (0.03) |
| | | 35°C | 0.57 (0.02) | 0.64 (0.02) | 0.61 (0.02) |
| | | 55°C | 0.61 (0.03) | 0.62 (0.03) | 0.69 (0.03) |
| Air | 1 day | 5°C | 0.69 (0.03) | 0.58 (0.04) | 0.43 (0.03) |
| | | 35°C | 0.69 (0.04) | 0.71 (0.03) | 0.63 (0.03) |
| | | 55°C | 0.73 (0.02) | 0.74 (0.02) | 0.77 (0.03) |
| | 7 days | 5°C | 0.63 (0.06) | 0.49 (0.05) | 0.36 (0.04) |
| | | 35°C | 0.64 (0.07) | 0.66 (0.06) | 0.54 (0.06) |
| | | 55°C | 0.66 (0.04) | 0.67 (0.05) | 0.69 (0.05) |
| | 45 days | 5°C | 0.60 (0.03) | 0.52 (0.01) | 0.38 (0.02) |
| | | 35°C | 0.57 (0.05) | 0.61 (0.04) | 0.55 (0.02) |
| | | 55°C | 0.60 (0.02) | 0.62 (0.03) | 0.66 (0.02) |
| | 90 days | 5°C | 0.61 (0.03) | 0.56 (0.04) | 0.42 (0.03) |
| | | 35°C | 0.57 (0.04) | 0.61 (0.03) | 0.59 (0.02) |
| | | 55°C | 0.65 (0.03) | 0.66 (0.03) | 0.70 (0.03) |

**- Storage medium**: No relevant difference in modulus was found between air and water-stored groups after 1 day or 7 days storage. The same was true after 90 days, except at 5°C/0.1 Hz and 55°C/0.1 Hz. After 45 days, samples stored in water had the highest modulus at all testing conditions but 35°C/0.1 Hz.

**- Storage period**: The viscous modulus dropped between baseline and 1 day in both storage media at all testing conditions but 55°C (all frequencies). The same was true between 1 day and 7 days, except when air and water-stored samples were tested at 5°C/0.1 Hz and 35°C (0.1 and 1 Hz), and also when water-stored samples were tested at 55°C/1 Hz. Between 7 and 45 days, air-stored samples had no relevant change in modulus, while water-stored samples significantly increased (water/5°C at 1 and 10 Hz, and water/35°C/10 Hz), decreased (water/35°C at 0.1 and 1 Hz) or did not change it (water/5°C/0.1 Hz and water/55°C at all frequencies). Between 45 and 90 days relevant changes in modulus were only found for water/55°C (0.1 and 1 Hz) that dropped it.

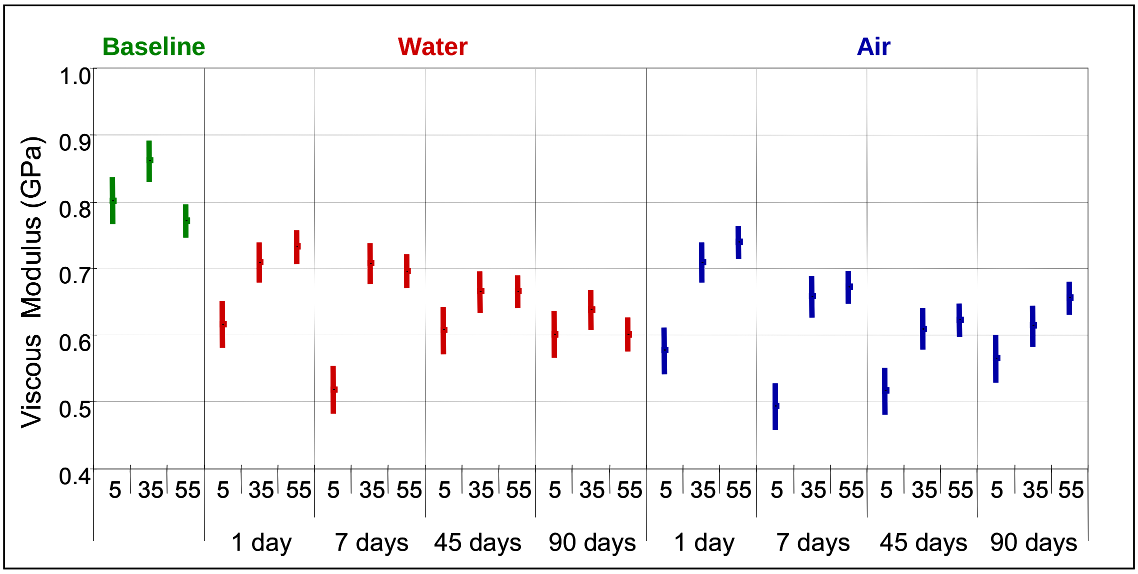
**- Temperature**: The baseline group dropped its modulus at 0.1 Hz between 5 and 55°C. At 1 Hz the modulus first increased from 5 to 35°C then decreased from 35 to 55°C. At 10 Hz it just increased from 5 to 35°C, thereafter no change was found. Between 5 and 35°C all air-stored and two water-stored groups (45 and 90 days) significantly dropped their modulus at 0.1 Hz. At 1 Hz, all groups but water/90 days and air/90 days considerably improved their viscous modulus. The same was observed at 10 Hz. Between 35 and 55°C no relevant change in modulus occurred at 0.1 Hz, except for water/45 days and air/90 days that increased their modulus. The same trend was observed at 1 Hz, while at 10 Hz all groups significantly improved their viscous modulus.

**- Frequency**: At 5°C all groups but air/90 days dropped their modulus between 0.1 to 1 Hz. At 35 and 55°C the air-stored groups had no significant change in modulus. However, all water-stored groups but water/1 day improved their modulus at 35°C between 0.1 and 1 Hz. On the other hand, only water/7 days improved its modulus at 55°C. Between 1 and 10 Hz all groups significantly dropped their modulus at 5°C. At 35°C the same was observed, except for baseline, 45 and 90 days stored groups. At 55°C all groups but water/1day, air/1 day and air/7 days significantly improved their viscous modulus.

**Table 17** Upper, lower and mean 95% viscous modulus (GPa) confidence intervals of the DiamondLite experimental groups at 5, 35 and 55°C, and 1 Hz.

| Storage medium | Storage Time | Temperature | upper 95% | lower 95% | mean |
|---|---|---|---|---|---|
| Baseline | - | 5°C | 0.84 | 0.77 | 0.80 |
| | | 35°C | 0.89 | 0.83 | 0.86 |
| | | 55°C | 0.80 | 0.75 | 0.77 |
| Water | 1 day | 5°C | 0.65 | 0.58 | 0.62 |
| | | 35°C | 0.74 | 0.68 | 0.71 |
| | | 55°C | 0.76 | 0.71 | 0.73 |
| | 7 days | 5°C | 0.55 | 0.48 | 0.52 |
| | | 35°C | 0.74 | 0.68 | 0.71 |
| | | 55°C | 0.72 | 0.67 | 0.70 |
| | 45 days | 5°C | 0.64 | 0.57 | 0.61 |
| | | 35°C | 0.70 | 0.63 | 0.66 |
| | | 55°C | 0.69 | 0.64 | 0.66 |
| | 90 days | 5°C | 0.64 | 0.57 | 0.60 |
| | | 35°C | 0.67 | 0.61 | 0.64 |
| | | 55°C | 0.65 | 0.58 | 0.60 |
| Air | 1 day | 5°C | 0.61 | 0.54 | 0.58 |
| | | 35°C | 0.74 | 0.68 | 0.71 |
| | | 55°C | 0.76 | 0.71 | 0.74 |
| | 7 days | 5°C | 0.53 | 0.46 | 0.49 |
| | | 35°C | 0.69 | 0.63 | 0.66 |
| | | 55°C | 0.70 | 0.65 | 0.67 |
| | 45 days | 5°C | 0.55 | 0.48 | 0.52 |
| | | 35°C | 0.64 | 0.58 | 0.61 |
| | | 55°C | 0.65 | 0.60 | 0.62 |
| | 90 days | 5°C | 0.60 | 0.53 | 0.56 |
| | | 35°C | 0.64 | 0.58 | 0.61 |
| | | 55°C | 0.68 | 0.63 | 0.66 |

**Figure 12** Same as Table 17.



### 3.2.3.2 Grandio

**Table 18** Mean (standard deviation) viscous modulus (GPa) of all Grandio experimental groups at 5, 35 and 55°C, and 0.1, 1 and 10 Hz.

| Storage Medium | Storage Time | Temperature | Viscous Modulus (GPa) | | |
|---|---|---|---|---|---|
| | | | 0.1 Hz | 1 Hz | 10 Hz |
| Baseline | - | 5°C | 0.82 (0.04) | 0.73 (0.04) | 0.64 (0.04) |
| | | 35°C | 0.92 (0.05) | 0.81 (0.04) | 0.75 (0.03) |
| | | 55°C | 0.83 (0.03) | 0.73 (0.03) | 0.69 (0.02) |
| Water | 1 day | 5°C | 0.60 (0.05) | 0.54 (0.05) | 0.48 (0.05) |
| | | 35°C | 0.62 (0.01) | 0.57 (0.01) | 0.53 (0.01) |
| | | 55°C | 0.71 (0.03) | 0.63 (0.02) | 0.59 (0.03) |
| | 7 days | 5°C | 0.53 (0.05) | 0.48 (0.05) | 0.43 (0.05) |
| | | 35°C | 0.57 (0.04) | 0.53 (0.04) | 0.50 (0.04) |
| | | 55°C | 0.66 (0.03) | 0.60 (0.03) | 0.57 (0.03) |
| | 45 days | 5°C | 0.52 (0.03) | 0.47 (0.03) | 0.43 (0.03) |
| | | 35°C | 0.54 (0.02) | 0.51 (0.02) | 0.49 (0.02) |
| | | 55°C | 0.63 (0.02) | 0.58 (0.02) | 0.56 (0.02) |
| | 90 days | 5°C | 0.52 (0.02) | 0.47 (0.02) | 0.42 (0.02) |
| | | 35°C | 0.54 (0.03) | 0.51 (0.02) | 0.48 (0.02) |
| | | 55°C | 0.69 (0.02) | 0.55 (0.02) | 0.53 (0.02) |
| Air | 1 day | 5°C | 0.58 (0.02) | 0.51 (0.02) | 0.46 (0.01) |
| | | 35°C | 0.62 (0.01) | 0.57 (0.01) | 0.53 (0.01) |
| | | 55°C | 0.71 (0.03) | 0.63 (0.02) | 0.59 (0.02) |
| | 7 days | 5°C | 0.51 (0.05) | 0.46 (0.04) | 0.40 (0.04) |
| | | 35°C | 0.54 (0.04) | 0.51 (0.03) | 0.47 (0.03) |
| | | 55°C | 0.65 (0.03) | 0.59 (0.03) | 0.55 (0.03) |
| | 45 days | 5°C | 0.43 (0.04) | 0.39 (0.03) | 0.35 (0.03) |
| | | 35°C | 0.47 (0.07) | 0.44 (0.06) | 0.42 (0.05) |
| | | 55°C | 0.53 (0.07) | 0.49 (0.06) | 0.47 (0.05) |
| | 90 days | 5°C | 0.39 (0.02) | 0.36 (0.02) | 0.32 (0.02) |
| | | 35°C | 0.43 (0.02) | 0.40 (0.02) | 0.37 (0.02) |
| | | 55°C | 0.53 (0.02) | 0.47 (0.02) | 0.45 (0.02) |

**- Storage medium**: The storage medium only played an important role in viscous modulus results of 45 and 90 days stored groups that showed significantly higher modulus when conditioned in distilled water than in air at all testing conditions but 35°C/0.1 Hz. No statistically significant differences were observed between air and water-stored samples after 1 day and 7 days storage.

**- Storage period**: The viscous modulus values significantly dropped between baseline and 1 day in both storage media at all testing conditions. However, there was no statistically relevant change in modulus between 1 day and 7 days, except for air/5°C and air/35°C both at all frequencies, and water/35°C and water/55°C both at 0.1 Hz that dropped their modulus.

Between 7 and 45 days no statistically significant change in modulus was measured for the samples stored in distilled water, while the air-stored samples significantly decreased their modulus at all testing conditions but 35°C/0.1 Hz. In the last time interval, between 45 and 90 days, relevant changes in viscous modulus were noticed neither for air nor for water-stored samples.

**- Temperature**: The temperature dependence of viscous modulus was also strongly influenced by the testing frequency. The baseline group significantly increased and decreased its viscous modulus at all frequencies in the first and second temperature intervals, respectively.

Regarding the water-stored groups, no significant change in modulus was found between 5 and 35°C at 0.1 Hz. Except for two groups (1 day and 90 days) that increased their modulus the same was true for the air-stored samples. At 1 Hz only three groups significantly improved their viscous modulus: water/45 days, air/1 day and air/ 90 days, while at 10 Hz most groups improved this property: water/45 days, water/90 days, air/1 day, air/ 7 days and air/90 days.

Between 35 and 55°C all experimental groups but air/45 days significantly improved their viscous modulus at all testing frequencies.

**- Frequency**: Independent on the temperature, the viscous modulus dropped for all experimental groups between 0.1 and 10 Hz, but not always significantly.

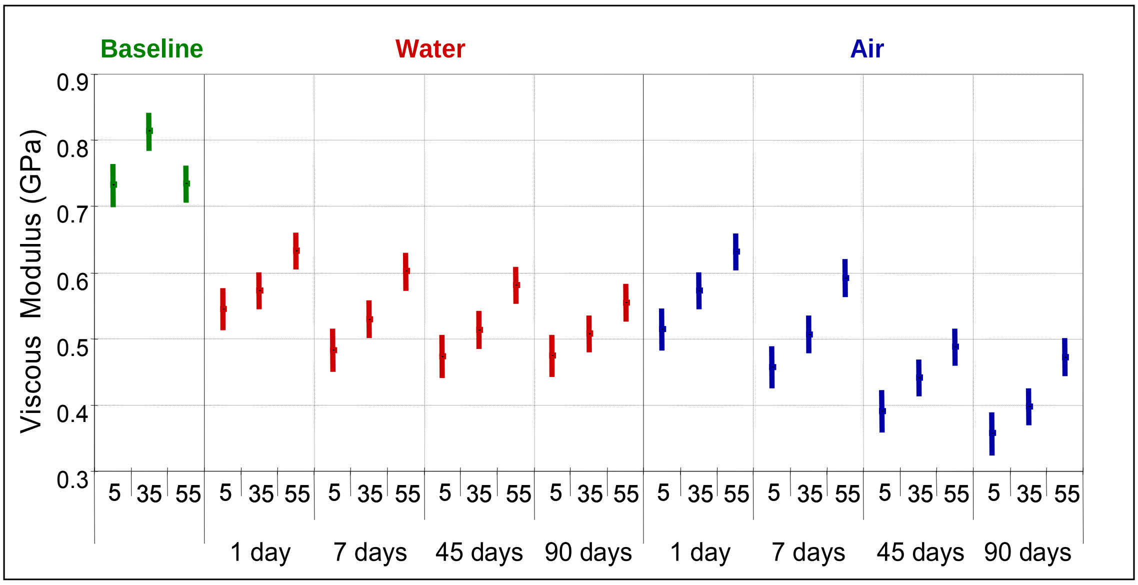
The baseline group significantly decreased its modulus between 0.1 and 1 Hz at all temperatures. Between 1 and 10 Hz significant drops in viscous modulus only existed for that group at 5°C.

At 5°C all groups kept their modulus constant in both frequency intervals, except for water/90 days and air/1 day that dropped their modulus between 0.1 and 1 Hz, and also between 1 and 10 Hz. At 35°C the same trend was observed, except for water/1 day and air/1 day that significantly dropped their modulus in both frequency intervals. At 55°C all groups but air/45 days underwent relevant drops in modulus between 0.1 and 1 Hz, while between 1 and 10 Hz no significant changes in modulus were seen, except for air/1 day and air/90 days that dropped this property.

**Table 19** Upper, lower and mean 95% viscous modulus (GPa) confidence intervals of the Grandio experimental groups at 5, 35 and 55°C, and 1 Hz.

| Storage medium | Storage Time | Temperature | upper 95% | lower 95% | mean |
|---|---|---|---|---|---|
| Baseline | - | 5°C | 0.76 | 0.70 | 0.73 |
| | | 35°C | 0.84 | 0.78 | 0.81 |
| | | 55°C | 0.76 | 0.71 | 0.73 |
| Water | 1 day | 5°C | 0.58 | 0.51 | 0.54 |
| | | 35°C | 0.60 | 0.54 | 0.57 |
| | | 55°C | 0.66 | 0.60 | 0.63 |
| | 7 days | 5°C | 0.51 | 0.45 | 0.48 |
| | | 35°C | 0.56 | 0.50 | 0.53 |
| | | 55°C | 0.63 | 0.57 | 0.60 |
| | 45 days | 5°C | 0.51 | 0.44 | 0.47 |
| | | 35°C | 0.54 | 0.49 | 0.51 |
| | | 55°C | 0.61 | 0.55 | 0.58 |
| | 90 days | 5°C | 0.51 | 0.44 | 0.47 |
| | | 35°C | 0.54 | 0.48 | 0.51 |
| | | 55°C | 0.58 | 0.53 | 0.55 |
| Air | 1 day | 5°C | 0.55 | 0.48 | 0.51 |
| | | 35°C | 0.60 | 0.54 | 0.57 |
| | | 55°C | 0.66 | 0.60 | 0.63 |
| | 7 days | 5°C | 0.49 | 0.42 | 0.46 |
| | | 35°C | 0.53 | 0.48 | 0.51 |
| | | 55°C | 0.62 | 0.56 | 0.59 |
| | 45 days | 5°C | 0.42 | 0.36 | 0.39 |
| | | 35°C | 0.47 | 0.41 | 0.44 |
| | | 55°C | 0.52 | 0.46 | 0.49 |
| | 90 days | 5°C | 0.39 | 0.32 | 0.36 |
| | | 35°C | 0.43 | 0.37 | 0.40 |
| | | 55°C | 0.50 | 0.44 | 0.47 |

**Figure 13** Same as Table 19.



### 3.2.3.3 Artglass

**Table 20** Mean (standard deviation) viscous modulus (GPa) of all Artglass experimental groups at 5, 35 and 55°C, and 0.1, 1 and 10 Hz.

| Storage Medium | Storage Time | Temperature | Viscous Modulus (GPa) | | |
|---|---|---|---|---|---|
| | | | 0.1 Hz | 1 Hz | 10 Hz |
| Baseline | - | 5°C | 0.58 (0.05) | 0.51 (0.04) | 0.39 (0.05) |
| | | 35°C | 0.61 (0.05) | 0.60 (0.04) | 0.56 (0.04) |
| | | 55°C | 0.58 (0.04) | 0.54 (0.03) | 0.56 (0.03) |
| Water | 1 day | 5°C | 0.51 (0.02) | 0.43 (0.03) | 0.32 (0.02) |
| | | 35°C | 0.45 (0.05) | 0.46 (0.04) | 0.43 (0.05) |
| | | 55°C | 0.56 (0.03) | 0.54 (0.02) | 0.57 (0.02) |
| | 7 days | 5°C | 0.50 (0.04) | 0.47 (0.05) | 0.35 (0.04) |
| | | 35°C | 0.45 (0.02) | 0.48 (0.02) | 0.48 (0.02) |
| | | 55°C | 0.52 (0.01) | 0.50 (0.01) | 0.54 (0.01) |
| | 45 days | 5°C | 0.51 (0.02) | 0.48 (0.03) | 0.35 (0.02) |
| | | 35°C | 0.43 (0.02) | 0.48 (0.02) | 0.48 (0.02) |
| | | 55°C | 0.51 (0.01) | 0.50 (0.01) | 0.55 (0.01) |
| | 90 days | 5°C | 0.45 (0.02) | 0.39 (0.05) | 0.29 (0.04) |
| | | 35°C | 0.39 (0.01) | 0.44 (0.01) | 0.42 (0.05) |
| | | 55°C | 0.45 (0.05) | 0.45 (0.04) | 0.49 (0.04) |
| Air | 1 day | 5°C | 0.45 (0.05) | 0.37 (0.04) | 0.27 (0.04) |
| | | 35°C | 0.43 (0.04) | 0.45 (0.04) | 0.41 (0.03) |
| | | 55°C | 0.53 (0.02) | 0.50 (0.03) | 0.52 (0.03) |
| | 7 days | 5°C | 0.39 (0.01) | 0.36 (0.03) | 0.26 (0.02) |
| | | 35°C | 0.34 (0.03) | 0.38 (0.02) | 0.37 (0.02) |
| | | 55°C | 0.42 (0.07) | 0.41 (0.05) | 0.44 (0.04) |
| | 45 days | 5°C | 0.41 (0.03) | 0.37 (0.04) | 0.28 (0.03) |
| | | 35°C | 0.35 (0.02) | 0.39 (0.02) | 0.37 (0.04) |
| | | 55°C | 0.41 (0.05) | 0.40 (0.03) | 0.44 (0.04) |
| | 90 days | 5°C | 0.41 (0.04) | 0.38 (0.03) | 0.28 (0.02) |
| | | 35°C | 0.38 (0.04) | 0.40 (0.03) | 0.40 (0.03) |
| | | 55°C | 0.52 (0.01) | 0.48 (0.01) | 0.50 (0.02) |

**- Storage medium**: Air-stored samples showed lower viscous modulus values than water-stored samples conditioned during the same period. However, these differences were only relevant for 7 and 45 days storage at all testing conditions, 1 day/5°C (all frequencies), 1 day/55°C/10 Hz and 90 days/55°C/0.1 Hz.

**- Storage period**: Drops in modulus between baseline and 1 day were relevant in both storage media at all testing conditions but 5°C/0.1 Hz and 55°C (all frequencies). Significant changes in modulus between 1 day and 7 days were observed neither for air-stored nor for water-stored samples, except for air-stored samples tested at 35°C (0.1 and 1 Hz), and 55°C (all frequencies) that dropped their modulus.

Similarly, no statistically relevant change in modulus occurred between 7 and 45 days. The same happened to the air-stored samples between 45 and 90 days at all testing conditions, except at 55°C (all frequencies) when they significantly dropped their modulus. On the other side, samples stored in water dropped their modulus at all testing conditions but 35°C (all frequencies).

**- Temperature**: When tested at 0.1 Hz the viscous modulus values of the baseline group remained constant between 5 and 55°C. At 1 and 10 Hz the viscous modulus of this group just improved between 5 and 35°C, remaining constant in the second temperature interval.

Between 5 and 35°C all water-stored experimental groups significantly dropped their modulus at 0.1 Hz, while the air-stored groups kept their modulus constant at all storage periods but 45 days, when their modulus dropped. At 1 Hz the modulus remained unchanged for all experimental groups but air/1 day that improved its modulus. On the other hand, all groups significantly increased their modulus at 10 Hz.

Between 35 and 55°C, all experimental groups but water/90 days significantly improved their modulus at 0.1 Hz. The same happened at 1 Hz for water/1 day and air/90 days. At 10 Hz all groups significantly improved their modulus.

**- Frequency**: The baseline group showed no relevant change in modulus at 35 and 55°C when frequency was raised from 0.1 to 10 Hz. At 5°C this trend was observed in the first, but not in the second frequency interval, when the modulus finally increased.

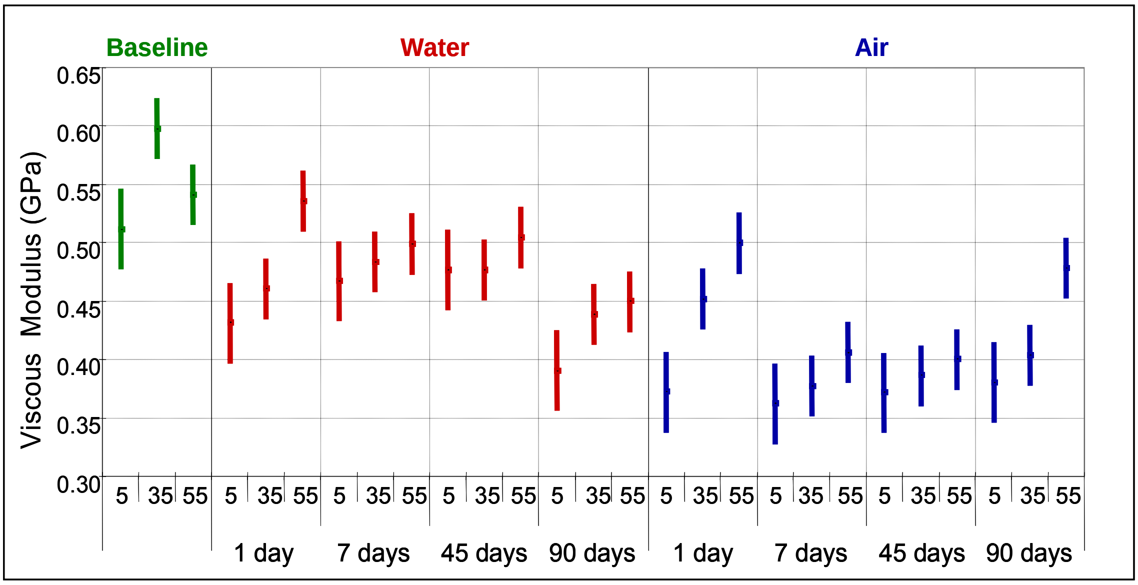
Between 0.1 and 1 Hz relevant changes in viscous modulus at 5°C were only observed after 1 day storage, when the modulus dropped. At 35°C, increases in modulus were only relevant for water/45 days, water/90 days and air/7 days. At 55°C no relevant differences were measured for most experimental groups except water/7 days and air/90 days that dropped their modulus.

Between 1 and 10 Hz all groups showed relevant drops in modulus when tested at 5°C. No significant changes in modulus were observed at 35°C. At 55°C only water/7 days and water/45 days significantly improved their viscous modulus.

**Table 21** Upper, lower and mean 95% viscous modulus (GPa) confidence intervals of the Artglass experimental groups at 5, 35 and 55°C, and 1 Hz.

| Storage medium | Storage Time | Temperature | upper 95% | lower 95% | mean |
|---|---|---|---|---|---|
| Baseline | - | 5°C | 0.55 | 0.48 | 0.51 |
| | | 35°C | 0.62 | 0.57 | 0.60 |
| | | 55°C | 0.57 | 0.51 | 0.54 |
| Water | 1 day | 5°C | 0.47 | 0.40 | 0.43 |
| | | 35°C | 0.49 | 0.43 | 0.46 |
| | | 55°C | 0.56 | 0.51 | 0.54 |
| | 7 days | 5°C | 0.50 | 0.43 | 0.47 |
| | | 35°C | 0.51 | 0.46 | 0.48 |
| | | 55°C | 0.52 | 0.47 | 0.50 |
| | 45 days | 5°C | 0.51 | 0.44 | 0.48 |
| | | 35°C | 0.50 | 0.45 | 0.48 |
| | | 55°C | 0.53 | 0.48 | 0.50 |
| | 90 days | 5°C | 0.42 | 0.36 | 0.39 |
| | | 35°C | 0.46 | 0.41 | 0.44 |
| | | 55°C | 0.48 | 0.42 | 0.45 |
| Air | 1 day | 5°C | 0.41 | 0.34 | 0.37 |
| | | 35°C | 0.48 | 0.43 | 0.45 |
| | | 55°C | 0.53 | 0.47 | 0.50 |
| | 7 days | 5°C | 0.40 | 0.33 | 0.36 |
| | | 35°C | 0.40 | 0.35 | 0.38 |
| | | 55°C | 0.43 | 0.38 | 0.41 |
| | 45 days | 5°C | 0.41 | 0.34 | 0.37 |
| | | 35°C | 0.41 | 0.36 | 0.39 |
| | | 55°C | 0.43 | 0.37 | 0.40 |
| | 90 days | 5°C | 0.41 | 0.35 | 0.38 |
| | | 35°C | 0.43 | 0.38 | 0.40 |
| | | 55°C | 0.50 | 0.45 | 0.48 |

**Figure 14** Same as Table 21.



### 3.2.3.4 Vita Zeta LC

**Table 22** Mean (standard deviation) viscous modulus (GPa) of all Vita Zeta LC experimental groups at 5, 35 and 55°C, and 0.1, 1 and 10 Hz.

| Storage Medium | Storage Time | Temperature | Viscous Modulus (GPa) | | |
|---|---|---|---|---|---|
| | | | 0.1 Hz | 1 Hz | 10 Hz |
| Baseline | - | 5°C | 0.52 (0.03) | 0.48 (0.04) | 0.39 (0.04) |
| | | 35°C | 0.38 (0.00) | 0.45 (0.01) | 0.47 (0.02) |
| | | 55°C | 0.35 (0.01) | 0.40 (0.01) | 0.44 (0.02) |
| Water | 1 day | 5°C | 0.48 (0.02) | 0.38 (0.02) | 0.26 (0.01) |
| | | 35°C | 0.42 (0.02) | 0.45 (0.02) | 0.42 (0.02) |
| | | 55°C | 0.38 (0.01) | 0.41 (0.01) | 0.46 (0.01) |
| | 7 days | 5°C | 0.48 (0.01) | 0.45 (0.02) | 0.32 (0.02) |
| | | 35°C | 0.36 (0.01) | 0.42 (0.01) | 0.44 (0.01) |
| | | 55°C | 0.34 (0.01) | 0.37 (0.01) | 0.43 (0.01) |
| | 45 days | 5°C | 0.48 (0.03) | 0.43 (0.03) | 0.29 (0.03) |
| | | 35°C | 0.34 (0.02) | 0.41 (0.02) | 0.42 (0.02) |
| | | 55°C | 0.34 (0.01) | 0.37 (0.01) | 0.44 (0.01) |
| | 90 days | 5°C | 0.41 (0.03) | 0.30 (0.02) | 0.19 (0.02) |
| | | 35°C | 0.35 (0.02) | 0.40 (0.02) | 0.32 (0.02) |
| | | 55°C | 0.28 (0.01) | 0.34 (0.02) | 0.39 (0.02) |
| Air | 1 day | 5°C | 0.44 (0.02) | 0.36 (0.05) | 0.25 (0.03) |
| | | 35°C | 0.42 (0.01) | 0.45 (0.01) | 0.42 (0.02) |
| | | 55°C | 0.40 (0.01) | 0.43 (0.01) | 0.48 (0.01) |
| | 7 days | 5°C | 0.41 (0.02) | 0.38 (0.02) | 0.27 (0.02) |
| | | 35°C | 0.36 (0.01) | 0.41 (0.01) | 0.41 (0.01) |
| | | 55°C | 0.39 (0.01) | 0.41 (0.01) | 0.46 (0.01) |
| | 45 days | 5°C | 0.37 (0.02) | 0.28 (0.02) | 0.19 (0.01) |
| | | 35°C | 0.36 (0.02) | 0.38 (0.02) | 0.31 (0.02) |
| | | 55°C | 0.32 (0.01) | 0.37 (0.01) | 0.39 (0.01) |
| | 90 days | 5°C | 0.35 (0.01) | 0.26 (0.01) | 0.17 (0.01) |
| | | 35°C | 0.34 (0.01) | 0.37 (0.01) | 0.29 (0.01) |
| | | 55°C | 0.30 (0.01) | 0.35 (0.01) | 0.38 (0.01) |

**- Storage medium**: When stored during the same period, water-stored samples had higher viscous modulus than air-stored samples for most storage periods and testing conditions, although some results were not statistically significant.

**- Storage period**: Between baseline and 1 day, samples significantly dropped their viscous modulus at 5°C in both storage media at all frequencies but water/0.1 Hz. At 35°C they increased their modulus at 0.1 Hz, did not change it at 1 Hz and significantly dropped their viscous modulus at 10 Hz. At 55°C, air-stored samples improved their modulus at all frequencies, while water-stored samples only did it at 0.1 Hz.

Between 1 day and 7 days storage most samples had no relevant change in modulus or they significantly dropped it, although relevant increases in modulus were observed for water-stored samples at 5°C (1 and 10 Hz). Between 7 and 45 days storage, water-stored samples had no significant change in modulus, while air-stored samples decreased it at all testing conditions but 35°C/0.1 Hz.

While water-stored samples significantly dropped their modulus between 45 and 90 days storage at all testing conditions but 35°C (0.1 and 1 Hz), air-stored samples did not change their modulus except at 55°C (all frequencies) when the modulus dropped.

**- Temperature**: Water-stored and baseline groups significantly dropped their modulus at 0.1 Hz when the temperature ranged from 5 to 35°C. Air-stored groups, however, had no relevant change in modulus in this temperature interval, except for air/7 days that dropped its modulus. At 1 Hz most experimental groups significantly improved their modulus between 5 and 35°C. Exceptions were baseline, water/7 days, water/45 days and air/7 days that did not change this property. At 10 Hz all groups significantly improved their modulus between 5 and 35°C.

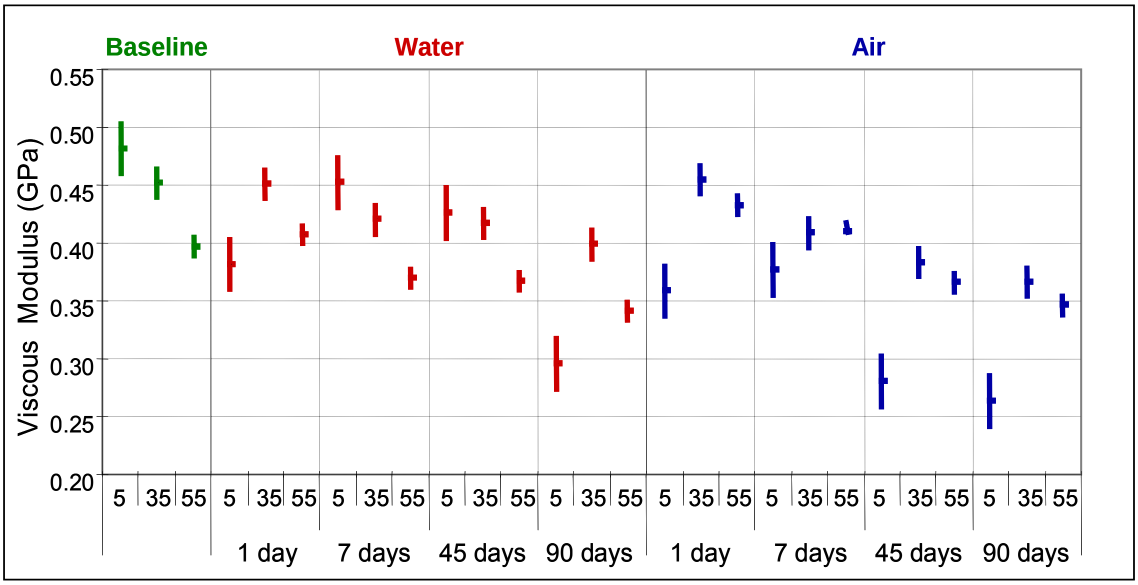
When temperature was raised from 35 to 55°C, most groups significantly dropped their modulus at 0.1 Hz. Exceptions were water/7 days, water/45 days and air/1 day that did not change this property, and air/7 days that improved it. At 1 Hz all water-stored, baseline and one air-stored group (90 days) significantly dropped their modulus. At 10 Hz, all groups significantly improved their viscous modulus except baseline, water/7 days and water/45 days.

**- Frequency**: When frequency was raised from 0.1 to 1 Hz, the baseline group decreased and increased its modulus at the lowest and the two highest temperatures, respectively. All water-stored groups but that stored for 7 days significantly dropped their modulus at 5°C between 0.1 and 1 Hz. The opposite was observed at 35 and 55°C, except for air/45 days/35°C that kept its modulus constant. Between 1 and 10 Hz all groups significantly dropped and improved their modulus at 5°C and 55°C, respectively. At 35°C either the experimental groups did not change their modulus or they significantly dropped it. To the latter group belong water/90 days, air/1 day, air/45 days and air/90 days.

**Table 23** Upper, lower and mean 95% viscous modulus (GPa) confidence intervals of the Vita Zeta LC experimental groups at 5, 35 and 55°C, and 1 Hz.

| Storage medium | Storage Time | Temperature | upper 95% | lower 95% | mean |
|---|---|---|---|---|---|
| Baseline | - | 5°C | 0.51 | 0.46 | 0.48 |
| | | 35°C | 0.47 | 0.44 | 0.45 |
| | | 55°C | 0.41 | 0.39 | 0.40 |
| Water | 1 day | 5°C | 0.41 | 0.36 | 0.38 |
| | | 35°C | 0.47 | 0.44 | 0.45 |
| | | 55°C | 0.42 | 0.40 | 0.41 |
| | 7 days | 5°C | 0.48 | 0.43 | 0.45 |
| | | 35°C | 0.43 | 0.41 | 0.42 |
| | | 55°C | 0.38 | 0.36 | 0.37 |
| | 45 days | 5°C | 0.45 | 0.40 | 0.43 |
| | | 35°C | 0.43 | 0.40 | 0.42 |
| | | 55°C | 0.38 | 0.36 | 0.37 |
| | 90 days | 5°C | 0.32 | 0.27 | 0.30 |
| | | 35°C | 0.41 | 0.38 | 0.40 |
| | | 55°C | 0.35 | 0.33 | 0.34 |
| Air | 1 day | 5°C | 0.38 | 0.33 | 0.36 |
| | | 35°C | 0.47 | 0.44 | 0.45 |
| | | 55°C | 0.44 | 0.42 | 0.43 |
| | 7 days | 5°C | 0.40 | 0.35 | 0.38 |
| | | 35°C | 0.42 | 0.39 | 0.41 |
| | | 55°C | 0.42 | 0.40 | 0.41 |
| | 45 days | 5°C | 0.30 | 0.26 | 0.28 |
| | | 35°C | 0.40 | 0.37 | 0.38 |
| | | 55°C | 0.38 | 0.36 | 0.37 |
| | 90 days | 5°C | 0.29 | 0.24 | 0.26 |
| | | 35°C | 0.38 | 0.35 | 0.37 |
| | | 55°C | 0.36 | 0.34 | 0.35 |

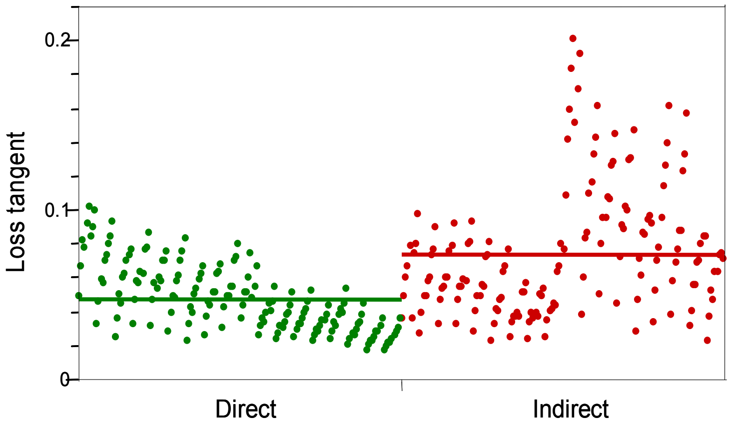
**Figure 15** Same as Table 23.



### 3.3 Frequency Scan – Loss tangent

### 3.3.1 Comparisons between composites (Analysis 1)

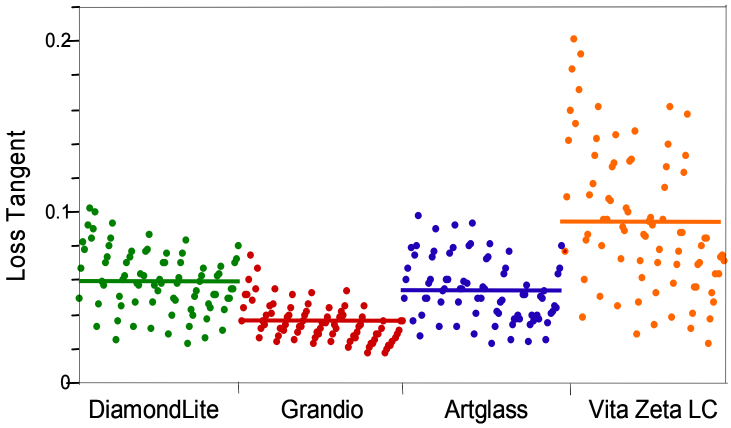
**Figure 16** Mean loss tangent of direct and indirect composites experimental groups at all testing conditions.



At first glance we recognize in Figure 16 a great discrepancy in the proximity of the mean points between both main groups, thus suggesting that the loss tangent of the direct composites was less extensively affected by the diverse storage and testing conditions than did that of the indirect composites. We could also say that the indirect composites, as a whole, showed qualitatively higher loss tangent values than the direct composites tested.

### 3.3.2 Comparisons between composites (Analysis 2 and 3)

**Figure 17** Mean loss tangent of DiamondLite, Grandio, Artglass and Vita Zeta LC experimental groups at all testing conditions.



Three qualitatively different groups were found in Figure 17. Vita Zeta LC showed the highest loss tangent values. DiamondLite and Artglass showed intermediary values, while Grandio had the lowest loss tangent values. Other interesting aspect in this figure was that Vita Zeta LC was responsible for the discrepancy in the points observed in this group. ANOVA and Tukey's test showed no significant differences in loss tangent between the composites for all the experimental groups and testing conditions. However, relevant differences between pairs of composites were observed for some experimental groups.

### 3.3.3 Individual results (Analysis 4, 5 and 6)

#### 3.3.3.1 DiamondLite

**Table 24** Mean (standard deviation) loss tangent of all DiamondLite experimental groups at 5, 35 and 55°C, and 0.1, 1 and 10 Hz.

| Storage Medium | Storage Time | Temperature | Loss Tangent | | |
|---|---|---|---|---|---|
| | | | 0.1 Hz | 1 Hz | 10 Hz |
| Baseline | - | 5°C | 0.083 (0.005) | 0.068 (0.003) | 0.049 (0.003) |
| | | 35°C | 0.102 (0.005) | 0.093 (0.004) | 0.079 (0.004) |
| | | 55°C | 0.101 (0.004) | 0.091 (0.003) | 0.085 (0.004) |
| Water | 1 day | 5°C | 0.060 (0.004) | 0.047 (0.005) | 0.034 (0.004) |
| | | 35°C | 0.074 (0.002) | 0.071 (0.002) | 0.058 (0.002) |
| | | 55°C | 0.094 (0.003) | 0.086 (0.003) | 0.081 (0.003) |
| | 7 days | 5°C | 0.051 (0.001) | 0.037 (0.001) | 0.026 (0.001) |
| | | 35°C | 0.063 (0.002) | 0.061 (0.002) | 0.046 (0.001) |
| | | 55°C | 0.077 (0.003) | 0.074 (0.002) | 0.071 (0.002) |
| | 45 days | 5°C | 0.058 (0.002) | 0.048 (0.002) | 0.033 (0.002) |
| | | 35°C | 0.063 (0.003) | 0.065 (0.002) | 0.058 (0.001) |
| | | 55°C | 0.087 (0.003) | 0.079 (0.003) | 0.078 (0.002) |
| | 90 days | 5°C | 0.058 (0.002) | 0.048 (0.002) | 0.033 (0.002) |
| | | 35°C | 0.059 (0.002) | 0.061 (0.002) | 0.054 (0.002) |
| | | 55°C | 0.076 (0.002) | 0.071 (0.002) | 0.071 (0.002) |
| Air | 1 day | 5°C | 0.051 (0.003) | 0.040 (0.003) | 0.029 (0.002) |
| | | 35°C | 0.062 (0.004) | 0.059 (0.003) | 0.049 (0.003) |
| | | 55°C | 0.084 (0.006) | 0.076 (0.005) | 0.071 (0.005) |
| | 7 days | 5°C | 0.044 (0.004) | 0.033 (0.003) | 0.023 (0.003) |
| | | 35°C | 0.054 (0.007) | 0.052 (0.006) | 0.040 (0.005) |
| | | 55°C | 0.068 (0.008) | 0.064 (0.007) | 0.060 (0.006) |
| | 45 days | 5°C | 0.046 (0.002) | 0.038 (0.001) | 0.027 (0.001) |
| | | 35°C | 0.053 (0.005) | 0.053 (0.004) | 0.045 (0.001) |
| | | 55°C | 0.068 (0.003) | 0.065 (0.003) | 0.063 (0.002) |
| | 90 days | 5°C | 0.050 (0.003) | 0.043 (0.003) | 0.031 (0.002) |
| | | 35°C | 0.055 (0.004) | 0.056 (0.003) | 0.050 (0.002) |
| | | 55°C | 0.081 (0.005) | 0.073 (0.004) | 0.071 (0.003) |

**- Storage medium**: Water-stored samples had higher loss tangent than the corresponding samples stored in air for most storage periods and testing conditions. Exceptions were 7 days/5°C/10 Hz, 90 days/5°C/10 Hz, 90 days/35°C/0.1 Hz and 90 days/55°C (all frequencies) that showed no relevant differences in loss tangent between air and water-stored samples.

**- Storage period**: The impact of conditioning the samples for 1 day in air or in water was decreasing their loss tangent. Changes in loss tangent between baseline and 1 day were significant at all temperatures when the samples were stored in air. For the water-stored samples, statistically relevant drops in loss tangent where only found at the two lowest temperatures, at all frequencies.

Significant drops in loss tangent were measured between 1 day and 7 days in both storage media at all testing conditions, except air/35°C (0.1 and 1 Hz). Between 7 and 45 days, water-stored samples significantly improved their loss tangent at all testing conditions but 35°C/0.1 Hz, while air-stored samples kept this property constant in this temperature interval at all testing conditions but 5°C (1 and 10 Hz). Between 45 and 90 days, air-stored samples did not change their loss tangent at any testing condition but 5°C/1 Hz and 55°C/0.1 Hz, when this property increased. The same happened to the water-stored samples, except at 5°C (all frequencies) and 35°C/0.1 Hz when the loss tangent dropped.

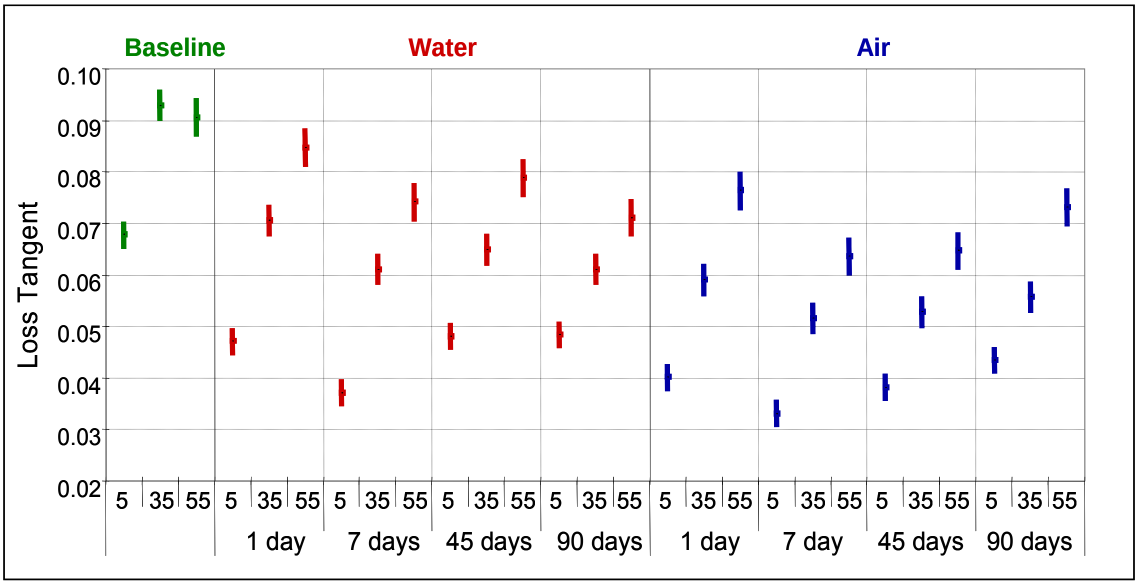
**- Temperature**: When temperature was raised from 5 to 35°C all experimental groups significantly improved their loss tangent at 1 and 10 Hz. At 0.1 Hz the same trend was observed, except for water/90 days, air/7 days and air/90 days. Between 35 and 55°C all groups but baseline at 0.1 and 1 Hz significantly increased their loss tangent at all frequencies.

**- Frequency**: All groups significantly dropped their loss tangent at 5°C in both frequency intervals. At 35°C there were no relevant changes in loss tangent between 0.1 and 1 Hz, except for baseline that dropped it. However, all groups significantly dropped this property at 35°C between 1 and 10 Hz. When tested at 55°C either the groups significantly dropped their loss tangent between 0.1 and 1 Hz, or they did not change it. The non-significant groups were water/7 days, air/1 day, air/7 days and air/45 days. No relevant change in loss tangent was observed at 55°C when the frequency was raised from 1 to 10 Hz.

**Table 25** Upper, lower and mean 95% loss confidence intervals of the DiamondLite experimental groups at 5, 35 and 55°C, and 1 Hz.

| Storage medium | Storage Time | Temperature | upper 95% | lower 95% | mean |
|---|---|---|---|---|---|
| Baseline | - | 5°C | 0.070 | 0.065 | 0.068 |
| | | 35°C | 0.096 | 0.090 | 0.093 |
| | | 55°C | 0.094 | 0.087 | 0.091 |
| Water | 1 day | 5°C | 0.050 | 0.044 | 0.047 |
| | | 35°C | 0.074 | 0.067 | 0.071 |
| | | 55°C | 0.089 | 0.082 | 0.086 |
| | 7 days | 5°C | 0.040 | 0.034 | 0.037 |
| | | 35°C | 0.064 | 0.058 | 0.061 |
| | | 55°C | 0.078 | 0.070 | 0.074 |
| | 45 days | 5°C | 0.051 | 0.045 | 0.048 |
| | | 35°C | 0.068 | 0.062 | 0.065 |
| | | 55°C | 0.082 | 0.075 | 0.079 |
| | 90 days | 5°C | 0.051 | 0.046 | 0.048 |
| | | 35°C | 0.064 | 0.058 | 0.061 |
| | | 55°C | 0.075 | 0.068 | 0.071 |
| Air | 1 day | 5°C | 0.043 | 0.037 | 0.040 |
| | | 35°C | 0.062 | 0.056 | 0.059 |
| | | 55°C | 0.080 | 0.073 | 0.076 |
| | 7 days | 5°C | 0.036 | 0.030 | 0.033 |
| | | 35°C | 0.055 | 0.048 | 0.052 |
| | | 55°C | 0.067 | 0.060 | 0.064 |
| | 45 days | 5°C | 0.041 | 0.036 | 0.038 |
| | | 35°C | 0.056 | 0.050 | 0.053 |
| | | 55°C | 0.068 | 0.061 | 0.065 |
| | 90 days | 5°C | 0.046 | 0.041 | 0.043 |
| | | 35°C | 0.059 | 0.053 | 0.056 |
| | | 55°C | 0.077 | 0.070 | 0.073 |

**Figure 18** Same as Table 25.



### 3.3.3.2 Grandio

**Table 26** Mean (standard deviation) loss tangent of all Grandio experimental groups at 5, 35 and 55°C, and 0.1, 1 and 10 Hz.

| Storage Medium | Storage Time | Temperature | Loss Tangent | | |
|---|---|---|---|---|---|
| | | | 0.1 Hz | 1 Hz | 10 Hz |
| Baseline | - | 5°C | 0.052 (0.003) | 0.044 (0.002) | 0.037 (0.002) |
| | | 35°C | 0.075 (0.012) | 0.061 (0.052) | 0.052 (0.006) |
| | | 55°C | 0.068 (0.008) | [c] 0.056 (0.006) | 0.049 (0.004) |
| Water | 1 day | 5°C | 0.037 (0.003) | 0.032 (0.003) | 0.027 (0.003) |
| | | 35°C | 0.046 (0.003) | 0.040 (0.002) | 0.035 (0.002) |
| | | 55°C | 0.055 (0.003) | 0.046 (0.002) | 0.041 (0.002) |
| | 7 days | 5°C | [f] 0.032 (0.003) | 0.028 (0.003) | 0.025 (0.003) |
| | | 35°C | 0.039 (0.003) | [h] 0.035 (0.002) | 0.031 (0.002) |
| | | 55°C | 0.052 (0.002) | 0.045 (0.002) | 0.040 (0.001) |
| | 45 days | 5°C | 0.034 (0.002) | 0.030 (0.002) | 0.026 (0.002) |
| | | 35°C | 0.040 (0.002) | 0.036 (0.001) | 0.033 (0.001) |
| | | 55°C | 0.053 (0.001) | 0.046 (0.001) | 0.042 (0.001) |
| | 90 days | 5°C | 0.030 (0.001) | 0.027 (0.001) | 0.023 (0.001) |
| | | 35°C | 0.036 (0.003) | 0.032 (0.002) | 0.030 (0.002) |
| | | 55°C | 0.044 (0.003) | [k] 0.039 (0.002) | 0.036 (0.002) |
| Air | 1 day | 5°C | 0.034 (0.001) | 0.029 (0.001) | 0.025 (0.001) |
| | | 35°C | 0.042 (0.001) | 0.039 (0.003) | 0.032 (0.001) |
| | | 55°C | 0.055 (0.003) | 0.046 (0.003) | 0.040 (0.002) |
| | 7 days | 5°C | 0.028 (0.002) | 0.025 (0.002) | 0.021 (0.002) |
| | | 35°C | 0.034 (0.002) | 0.030 (0.002) | 0.027 (0.002) |
| | | 55°C | 0.046 (0.002) | 0.039 (0.002) | 0.035 (0.002) |
| | 45 days | 5°C | 0.023 (0.003) | 0.021 (0.002) | 0.019 (0.002) |
| | | 35°C | 0.029 (0.006) | 0.026 (0.004) | 0.024 (0.003) |
| | | 55°C | 0.036 (0.007) | 0.032 (0.006) | 0.029 (0.005) |
| | 90 days | 5°C | 0.022 (0.001) | 0.020 (0.001) | 0.018 (0.001) |
| | | 35°C | 0.027 (0.001) | 0.024 (0.001) | 0.022 (0.001) |
| | | 55°C | 0.037 (0.001) | 0.032 (0.001) | 0.029 (0.001) |

**- Storage medium**: Loss tangent differences between air and water-stored groups conditioned during the same period were statistically significant after 7, 45 and 90 days storage at all testing conditions but 7 days/5°C/10 Hz. For all these groups the water-stored samples showed significantly higher loss tangent values than the corresponding samples stored in air.

**- Storage period**: Between baseline and 1 day the loss tangent of all Grandio samples significantly dropped in both storage media at all testing conditions. Between 1 day and 7 days the loss tangent of air and water-stored samples dropped at all testing conditions and only at 35°C (all frequencies), respectively.

No relevant change in loss tangent was seen between 7 and 45 days for water-stored samples at any testing condition and for air-stored samples at 5°C/10 Hz and 35°C at all frequencies. Samples stored in air during this period significantly dropped their loss tangent at 5°C (0.1 and 1 Hz) and 55°C (all frequencies).

Significant drops in this property between 45 and 90 days were only found for water-stored samples when tested at 35°C (1 and 10 Hz) and 55°C (all frequencies).

**- Temperature**: Higher temperatures positively affected the loss tangent of Grandio samples that visibly jumped in both temperature intervals.

Between 5 and 35°C all experimental groups significantly improved their loss tangent at all testing frequencies except for air/45 days.

Similarly, when the temperature was raised from 35 to 55°C all experimental groups except baseline and air/45 days underwent significant increases in loss tangent at all testing frequencies.

**- Frequency**: Rising frequencies dropped the loss tangent of all Grandio experimental groups in both frequency intervals. However, these results were often not statistically significant, especially in the second frequency interval.

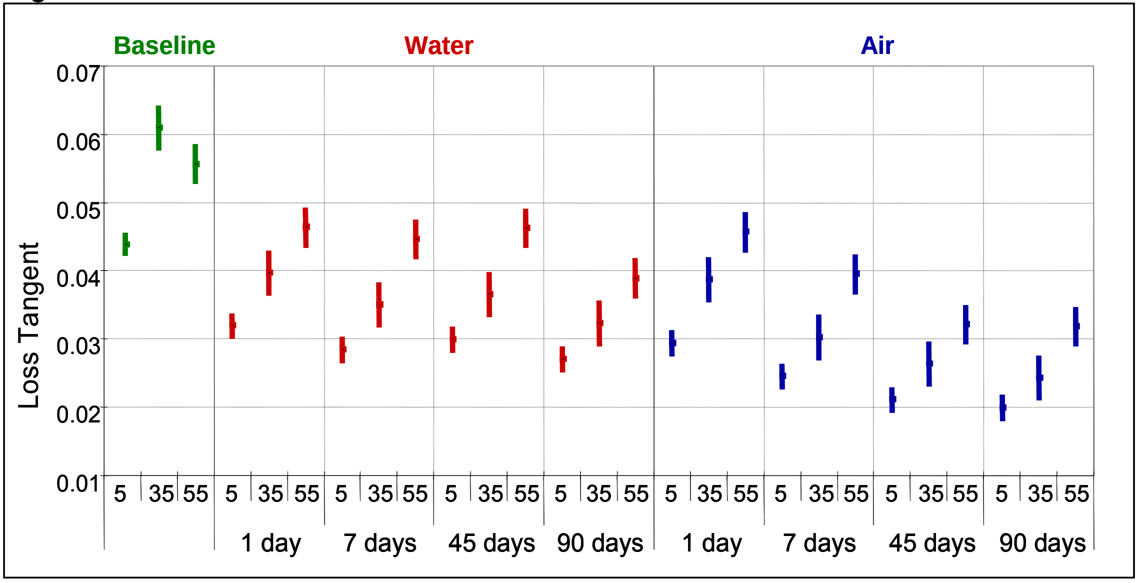
When the frequency was raised from 0.1 to 1 Hz most experimental groups significantly dropped their loss tangent at all temperatures. Nevertheless, non-significant results were found at 5°C for water/1 day, water/7 days, air/7 days and air/45 days; at 35°C for baseline, water/90 days and air/45 days; and at 55°C for baseline and air/45 days.

In the second temperature interval, between 1 and 10 Hz, the number of experimental groups that significantly dropped their loss tangent decreased. The non-significant groups at 5°C were water/1 day, water/7 days, air/7 days, air/45 days and air/90 days. When tested at 35°C the non-significant groups were baseline, water/7 days, water/90 days, air/7 days, air/45 days and air/90 days. At 55°C they were baseline, water/90 days and air/45 days.

**Table 27** Upper, lower and mean 95% loss confidence intervals of the Grandio experimental groups at 5, 35 and 55°C, and 1 Hz.

| Storage medium | Storage Time | Temperature | upper 95% | lower 95% | mean |
|---|---|---|---|---|---|
| Baseline | - | 5°C | 0.046 | 0.042 | 0.044 |
| | | 35°C | 0.064 | 0.058 | 0.061 |
| | | 55°C | 0.059 | 0.053 | 0.056 |
| Water | 1 day | 5°C | 0.034 | 0.030 | 0.032 |
| | | 35°C | 0.043 | 0.036 | 0.040 |
| | | 55°C | 0.049 | 0.043 | 0.046 |
| | 7 days | 5°C | 0.030 | 0.027 | 0.028 |
| | | 35°C | 0.038 | 0.032 | 0.035 |
| | | 55°C | 0.048 | 0.042 | 0.045 |
| | 45 days | 5°C | 0.032 | 0.028 | 0.032 |
| | | 35°C | 0.068 | 0.061 | 0.065 |
| | | 55°C | 0.082 | 0.076 | 0.079 |
| | 90 days | 5°C | 0.029 | 0.025 | 0.027 |
| | | 35°C | 0.036 | 0.029 | 0.032 |
| | | 55°C | 0.042 | 0.036 | 0.039 |
| Air | 1 day | 5°C | 0.031 | 0.028 | 0.029 |
| | | 35°C | 0.042 | 0.035 | 0.039 |
| | | 55°C | 0.049 | 0.043 | 0.046 |
| | 7 days | 5°C | 0.026 | 0.023 | 0.025 |
| | | 35°C | 0.034 | 0.027 | 0.030 |
| | | 55°C | 0.042 | 0.036 | 0.039 |
| | 45 days | 5°C | 0.023 | 0.019 | 0.021 |
| | | 35°C | 0.030 | 0.023 | 0.026 |
| | | 55°C | 0.035 | 0.029 | 0.032 |
| | 90 days | 5°C | 0.022 | 0.018 | 0.020 |
| | | 35°C | 0.028 | 0.021 | 0.024 |
| | | 55°C | 0.035 | 0.029 | 0.032 |

**Figure 19** Same as Table 27.



### 3.3.3.3 Artglass

**Table 28** Mean (standard deviation) loss tangent of all Artglass experimental groups at 5, 35 and 55°C, and 0.1, 1 and 10 Hz.

| Storage Medium | Storage Time | Temperature | Loss Tangent | | |
|---|---|---|---|---|---|
| | | | 0.1 Hz | 1 Hz | 10 Hz |
| Baseline | - | 5°C | 0.061 (0.006) | 0.050 (0.005) | 0.037 (0.004) |
| | | 35°C | 0.092 (0.011) | 0.080 (0.008) | 0.068 (0.006) |
| | | 55°C | 0.098 (0.008) | 0.081 (0.006) | 0.076 (0.005) |
| Water | 1 day | 5°C | 0.050 (0.002) | 0.040 (0.003) | 0.029 (0.002) |
| | | 35°C | 0.061 (0.004) | 0.059 (0.003) | 0.050 (0.003) |
| | | 55°C | 0.091 (0.007) | 0.077 (0.005) | 0.074 (0.004) |
| | 7 days | 5°C | 0.054 (0.004) | 0.048 (0.006) | 0.034 (0.004) |
| | | 35°C | 0.061 (0.004) | 0.061 (0.003) | 0.055 (0.004) |
| | | 55°C | 0.093 (0.007) | 0.079 (0.005) | 0.076 (0.003) |
| | 45 days | 5°C | 0.055 (0.002) | 0.048 (0.003) | 0.034 (0.002) |
| | | 35°C | 0.059 (0.004) | 0.060 (0.003) | 0.056 (0.002) |
| | | 55°C | 0.094 (0.003) | 0.082 (0.002) | 0.080 (0.001) |
| | 90 days | 5°C | 0.050 (0.004) | 0.041 (0.006) | 0.029 (0.004) |
| | | 35°C | 0.055 (0.003) | 0.057 (0.003) | 0.050 (0.007) |
| | | 55°C | 0.082 (0.018) | 0.074 (0.012) | 0.073 (0.011) |
| Air | 1 day | 5°C | 0.042 (0.004) | 0.033 (0.003) | 0.024 (0.003) |
| | | 35°C | 0.049 (0.004) | 0.048 (0.004) | 0.041 (0.003) |
| | | 55°C | 0.078 (0.005) | 0.067 (0.004) | 0.064 (0.003) |
| | 7 days | 5°C | 0.038 (0.003) | 0.035 (0.004) | 0.026 (0.006) |
| | | 35°C | 0.038 (0.005) | 0.041 (0.004) | 0.037 (0.004) |
| | | 55°C | 0.058 (0.016) | 0.052 (0.011) | 0.052 (0.009) |
| | 45 days | 5°C | 0.040 (0.003) | 0.034 (0.003) | 0.025 (0.003) |
| | | 35°C | 0.038 (0.003) | 0.041(0.003) | 0.037 (0.004) |
| | | 55°C | 0.054 (0.008) | 0.050 (0.005) | 0.051 (0.005) |
| | 90 days | 5°C | 0.041 (0.004) | 0.036 (0.003) | 0.026 (0.002) |
| | | 35°C | 0.045 (0.006) | 0.045 (0.005) | 0.042 (0.003) |
| | | 55°C | 0.081 (0.003) | 0.068 (0.003) | 0.065 (0.002) |

**- Storage medium**: When stored during the same period, water-stored groups showed higher loss tangent than air-stored experimental groups at all testing conditions but 90 days/5°C (1 and 10 Hz), and 90 days/55°C (all frequencies).

**- Storage period**: Between baseline and 1 day storage in distilled water the samples significantly dropped their loss tangent at the two lowest temperatures, but not at 55°C (all frequencies). Regarding the air-stored samples, they considerably dropped their loss tangent at all testing conditions but 55°C/10 Hz. After 1 day, the storage period played no important role in the results of water-stored samples that kept their loss tangent unchanged up to 90 days.

The air-stored samples, on the other hand, significantly dropped their loss tangent between 1 day and 7 days at all testing conditions but 5°C (all frequencies) and 35°C/10 Hz.

Between 7 and 45 days storage the loss tangent showed no statistically relevant change. The same was true between 45 and 90 days at all testing conditions but 55°C (all frequencies), when the loss tangent increased.

**- Temperature**: Rising temperatures enhanced the loss tangent of all Artglass experimental groups, but not always significantly.

When temperature was raised from 5 to 35°C none of the experimental groups showed relevant changes in loss tangent at 0.1 Hz, except for baseline and water/1 day that improved this property. When tested at 1 Hz all groups significantly improved their loss tangent in this temperature interval, except air/7 days and air/45 days. At 10 Hz all groups improved their loss tangent.

Raising the temperature from 35 to 55°C resulted in significantly higher loss tangent for all experimental groups at 0.1 Hz, except for baseline. When the frequency was raised to 1 Hz, all groups significantly improved their loss tangent at all testing conditions, except baseline and air/7 days. At 10 Hz the same was observed for all groups, except for baseline.

**- Frequency**: Artglass samples were barely sensitive to frequency variations. Even though, all experimental groups tended to drop their loss tangent as frequency was raised.

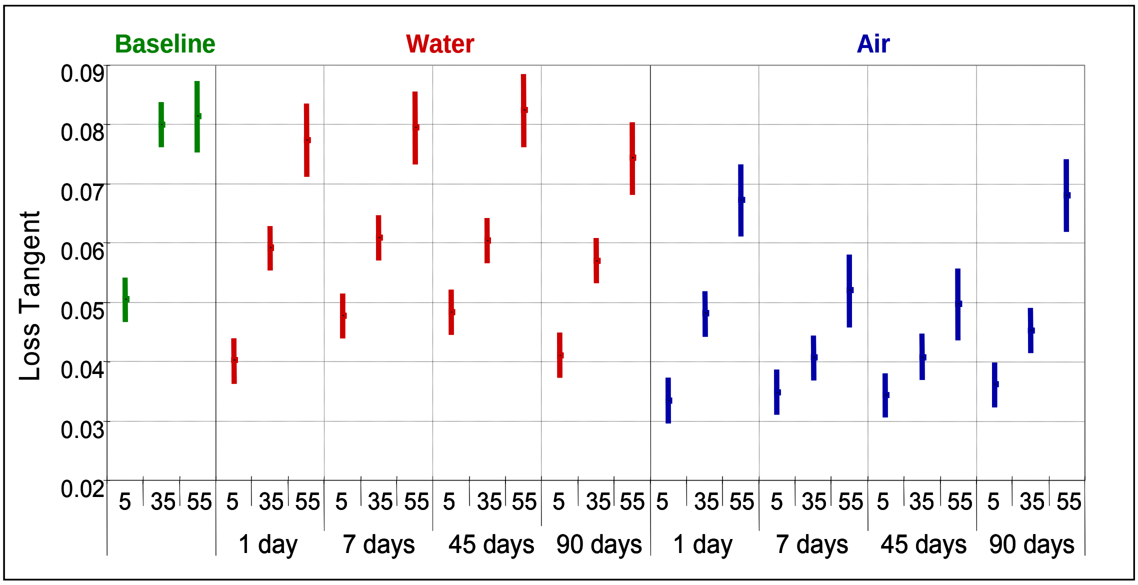
At 5°C, the loss tangent of all experimental groups statistically significantly dropped between 0.1 and 1 Hz, except for water/7 days, air/7 days and air/90 days. At 35°C no relevant change in loss tangent was observed for any experimental group. When tested at 55°C all groups but water/90 days, air/7 days and air/45 days statistically significantly decreased their loss tangent in the first frequency interval.

When the frequency was raised from 1 to 10 Hz all groups statistically significantly dropped their loss tangent at 5°C. When tested at 35°C, only two groups dropped their loss tangent: water/1 day and air/1 day. At 55°C there were no relevant differences in the loss tangent results for all experimental groups between 1 and 10 Hz.

**Table 29** Upper, lower and mean 95% loss confidence intervals of the Artglass experimental groups at 5, 35 and 55°C, and 1 Hz.

| Storage medium | Storage Time | Temperature | upper 95% | lower 95% | mean |
|---|---|---|---|---|---|
| Baseline | - | 5°C | 0.054 | 0.047 | 0.050 |
| | | 35°C | 0.084 | 0.076 | 0.080 |
| | | 55°C | 0.087 | 0.075 | 0.081 |
| Water | 1 day | 5°C | 0.044 | 0.036 | 0.040 |
| | | 35°C | 0.063 | 0.055 | 0.059 |
| | | 55°C | 0.083 | 0.071 | 0.077 |
| | 7 days | 5°C | 0.051 | 0.044 | 0.048 |
| | | 35°C | 0.065 | 0.057 | 0.061 |
| | | 55°C | 0.086 | 0.073 | 0.079 |
| | 45 days | 5°C | 0.052 | 0.045 | 0.048 |
| | | 35°C | 0.064 | 0.057 | 0.060 |
| | | 55°C | 0.088 | 0.076 | 0.082 |
| | 90 days | 5°C | 0.045 | 0.037 | 0.041 |
| | | 35°C | 0.061 | 0.053 | 0.057 |
| | | 55°C | 0.080 | 0.068 | 0.074 |
| Air | 1 day | 5°C | 0.037 | 0.030 | 0.033 |
| | | 35°C | 0.052 | 0.044 | 0.048 |
| | | 55°C | 0.073 | 0.061 | 0.067 |
| | 7 days | 5°C | 0.039 | 0.031 | 0.035 |
| | | 35°C | 0.044 | 0.037 | 0.041 |
| | | 55°C | 0.058 | 0.046 | 0.052 |
| | 45 days | 5°C | 0.038 | 0.030 | 0.034 |
| | | 35°C | 0.045 | 0.037 | 0.041 |
| | | 55°C | 0.056 | 0.044 | 0.050 |
| | 90 days | 5°C | 0.040 | 0.032 | 0.036 |
| | | 35°C | 0.049 | 0.041 | 0.045 |
| | | 55°C | 0.074 | 0.062 | 0.068 |

**Figure 20** Same as Table 29.



### 3.3.3.4 Vita Zeta LC

**Table 30** Mean (standard deviation) loss tangent of all Vita Zeta LC experimental groups at 5, 35 and 55°C, and 0.1, 1 and 10 Hz.

| Storage Medium | Storage Time | Temperature | Loss Tangent | | |
|---|---|---|---|---|---|
| | | | 0.1 Hz | 1 Hz | 10 Hz |
| Baseline | - | 5°C | 0.142 (0.013) | 0.110 (0.011) | 0.078 (0.009) |
| | | 35°C | 0.202 (0.008) | 0.184 (0.009) | 0.160 (0.021) |
| | | 55°C | 0.193 (0.003) | 0.172 (0.003) | 0.153 (0.002) |
| Water | 1 day | 5°C | 0.084 (0.002) | 0.061 (0.003) | 0.040 (0.001) |
| | | 35°C | 0.117 (0.006) | 0.111 (0.004) | 0.088 (0.003) |
| | | 55°C | 0.163 (0.005) | 0.143 (0.005) | 0.134 (0.004) |
| | 7 days | 5°C | 0.097 (0.002) | 0.081 (0.003) | 0.052 (0.002) |
| | | 35°C | 0.107 (0.003) | 0.108 (0.002) | 0.096 (0.002) |
| | | 55°C | 0.145 (0.011) | 0.129 (0.007) | 0.127 (0.005) |
| | 45 days | 5°C | 0.092 (0.005) | 0.073 (0.005) | 0.046 (0.004) |
| | | 35°C | 0.100 (0.008) | 0.103 (0.004) | 0.090 (0.003) |
| | | 55°C | 0.148 (0.003) | 0.132 (0.002) | 0.130 (0.002) |
| | 90 days | 5°C | 0.072 (0.002) | 0.048 (0.002) | 0.030 (0.002) |
| | | 35°C | $^{f}$ 0.087 (0.002) | $^{f}$ 0.087 (0.002) | 0.063 (0.002) |
| | | 55°C | 0.093 (0.002) | 0.097 (0.002) | 0.096 (0.002) |
| Air | 1 day | 5°C | 0.071 (0.007) | 0.053 (0.008) | 0.035 (0.005) |
| | | 35°C | 0.115 (0.030) | 0.096 (0.007) | 0.079 (0.008) |
| | | 55°C | 0.162 (0.006) | 0.140 (0.005) | 0.128 (0.004) |
| | 7 days | 5°C | 0.070 (0.004) | 0.058 (0.004) | 0.039 (0.003) |
| | | 35°C | 0.089 (0.007) | 0.088 (0.006) | 0.078 (0.006) |
| | | 55°C | 0.158 (0.009) | 0.134 (0.008) | 0.124 (0.007) |
| | 45 days | 5°C | 0.057 (0.003) | 0.041 (0.002) | 0.032 (0.012) |
| | | 35°C | 0.071 (0.004) | 0.069 (0.003) | 0.057 (0.010) |
| | | 55°C | 0.085 (0.003) | 0.086 (0.002) | 0.081 (0.002) |
| | 90 days | 5°C | 0.053 (0.002) | 0.037 (0.002) | 0.023 (0.002) |
| | | 35°C | 0.065 (0.002) | 0.064 (0.001) | 0.047 (0.001) |
| | | 55°C | $^{r}$ 0.072 (0.003) | 0.076 (0.002) | 0.074 (0.001) |

**- Storage medium**: When experimental groups stored during the same period in air or distilled water were compared, the latter showed statistically significant higher loss tangent values for 45 and 90 days storage at all testing conditions, 1 day/5°C/0.1 Hz, 1 day/35°C (1 and 10 Hz), 1 day/55°C/10 Hz, 7 days/5°C (all frequencies) and 7 days/35°C (all frequencies).

**- Storage period**: Drops in loss tangent between baseline and 1 day were significant at all testing conditions in both storage media. Between 1 day and 7 days storage there were no significant changes in loss tangent for the Vita Zeta LC samples stored in air. For samples stored in water the loss tangent increased for water/35°C/0.1 Hz and water/55°C (all frequencies). It decreased for water/5°C (all frequencies) and water/35°C/10 Hz, and showed no change for water/35°C/1 Hz.

All experimental groups tended to decrease their loss tangent between 7 and 45 days storage, although these drops were not statistically significant for water/5°C/0.1 Hz, water/35°C/0.1 Hz, water/55°C (all frequencies), air/5°C/10 Hz and air/35°C/0.1 Hz.

Between 45 and 90 days the water-stored samples significantly dropped their loss tangent at all testing conditions, while the air-stored samples showed no relevant change in loss tangent at any testing condition but 55°C (0.1 and 1 Hz), when this property dropped.

- **Temperature**: The loss tangent results of Vita Zeta LC samples were not exempted from the benefits of rising testing temperatures.

Their loss tangent significantly increased for all experimental groups when temperature was raised from 5 to 35°C, except for water/7 days and water/45 days both at 0.1 Hz.

The same was observed when the temperature was raised from 35 to 55°C, except for the baseline group (all frequencies).

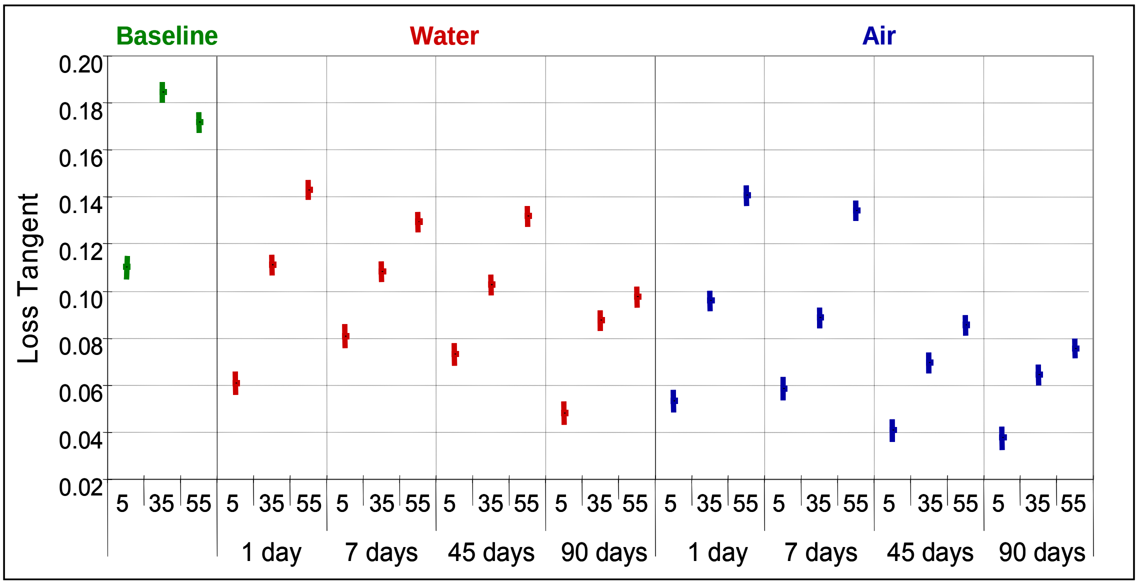
- **Frequency**: When the frequency was raised from 0.1 to 1 Hz all experimental groups significantly dropped their loss tangent at 5°C. On the other hand, no relevant change in this property was observed at 35°C. At 55°C, all water-stored groups but water/90 days significantly dropped their loss tangent. The same was true for the air-stored groups except air/45 days that showed no relevant change in loss tangent and air/90 days that significantly improved it.

Raising the frequency from 1 to 10 Hz lowered the loss tangent of all Vita Zeta LC experimental groups at 5°C, except for air/45 days. At 35°C the same was observed for all groups but air/1 day and air/ 7 days. When the temperature was raised to 55°C most experimental groups showed no relevant change in loss tangent. Exceptions were baseline, water/1 day, air/1 day and air/45 days that significantly dropped this property.

**Table 31** Upper, lower and mean 95% loss confidence intervals of the Vita Zeta LC experimental groups at 5, 35 and 55°C, and 1 Hz.

| Storage medium | Storage Time | Temperature | upper 95% | lower 95% | mean |
|---|---|---|---|---|---|
| Baseline | - | 5°C | 0.115 | 0.105 | 0.110 |
| | | 35°C | 0.189 | 0.180 | 0.184 |
| | | 55°C | 0.176 | 0.167 | 0.172 |
| Water | 1 day | 5°C | 0.066 | 0.056 | 0.061 |
| | | 35°C | 0.115 | 0.107 | 0.111 |
| | | 55°C | 0.147 | 0.139 | 0.143 |
| | 7 days | 5°C | 0.086 | 0.076 | 0.081 |
| | | 35°C | 0.113 | 0.104 | 0.108 |
| | | 55°C | 0.134 | 0.125 | 0.129 |
| | 45 days | 5°C | 0.078 | 0.068 | 0.073 |
| | | 35°C | 0.107 | 0.098 | 0.103 |
| | | 55°C | 0.136 | 0.127 | 0.132 |
| | 90 days | 5°C | 0.053 | 0.043 | 0.048 |
| | | 35°C | 0.092 | 0.083 | 0.087 |
| | | 55°C | 0.102 | 0.093 | 0.097 |
| Air | 1 day | 5°C | 0.058 | 0.048 | 0.053 |
| | | 35°C | 0.100 | 0.091 | 0.096 |
| | | 55°C | 0.145 | 0.136 | 0.140 |
| | 7 days | 5°C | 0.063 | 0.054 | 0.058 |
| | | 35°C | 0.093 | 0.084 | 0.088 |
| | | 55°C | 0.138 | 0.130 | 0.134 |
| | 45 days | 5°C | 0.046 | 0.036 | 0.041 |
| | | 35°C | 0.074 | 0.065 | 0.069 |
| | | 55°C | 0.090 | 0.081 | 0.086 |
| | 90 days | 5°C | 0.042 | 0.033 | 0.037 |
| | | 35°C | 0.069 | 0.060 | 0.064 |
| | | 55°C | 0.080 | 0.071 | 0.076 |

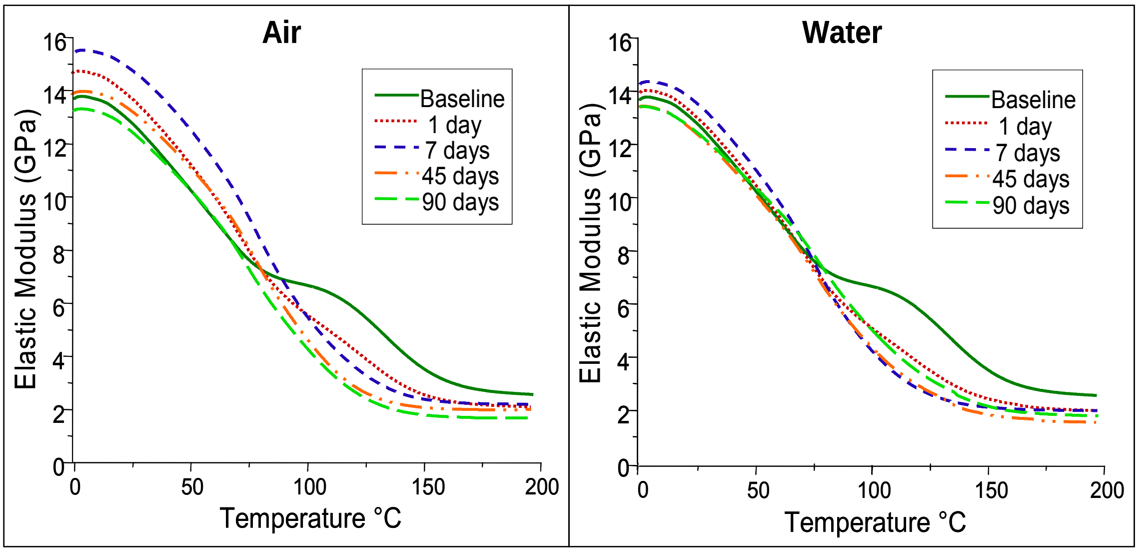
**Figure 21** Same as table 31.



## 3.4 Temperature scan - Elastic Modulus (Analysis 7)

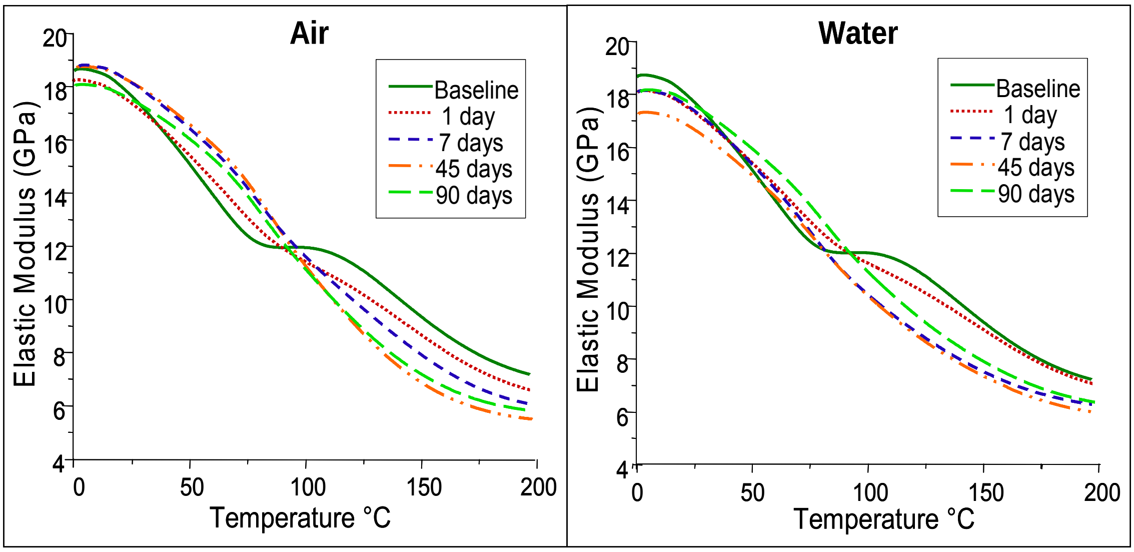
### 3.4.1 DiamondLite

**Figure 22** Plot of elastic modulus as a function of temperature for DiamondLite baseline and air (left) or water-stored (right) groups at 1 Hz.



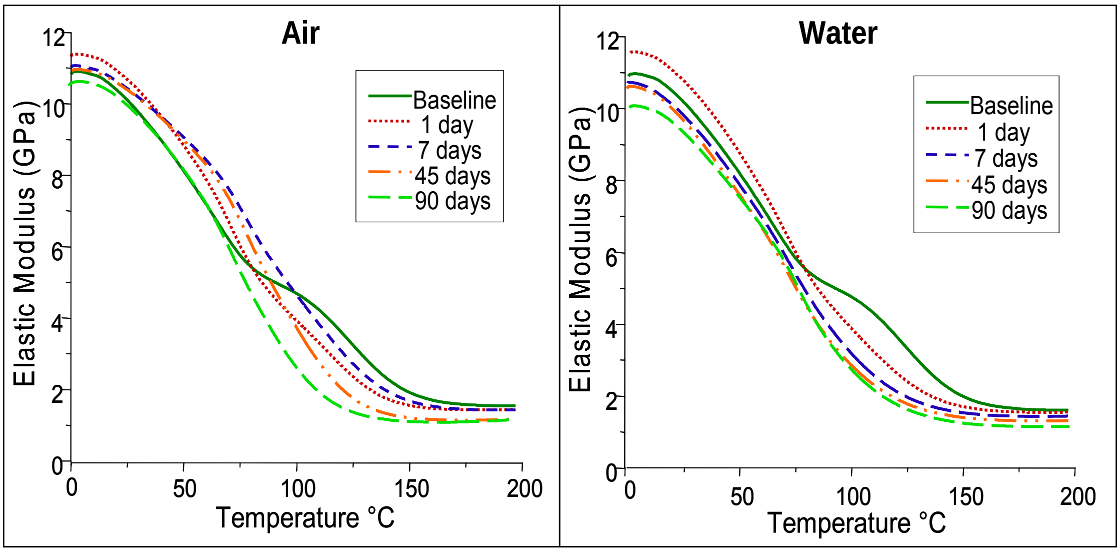
### 3.4.2 Grandio

**Figure 23** Plot of elastic modulus as a function of temperature for Grandio baseline and air (left) or water-stored (right) groups at 1 Hz.



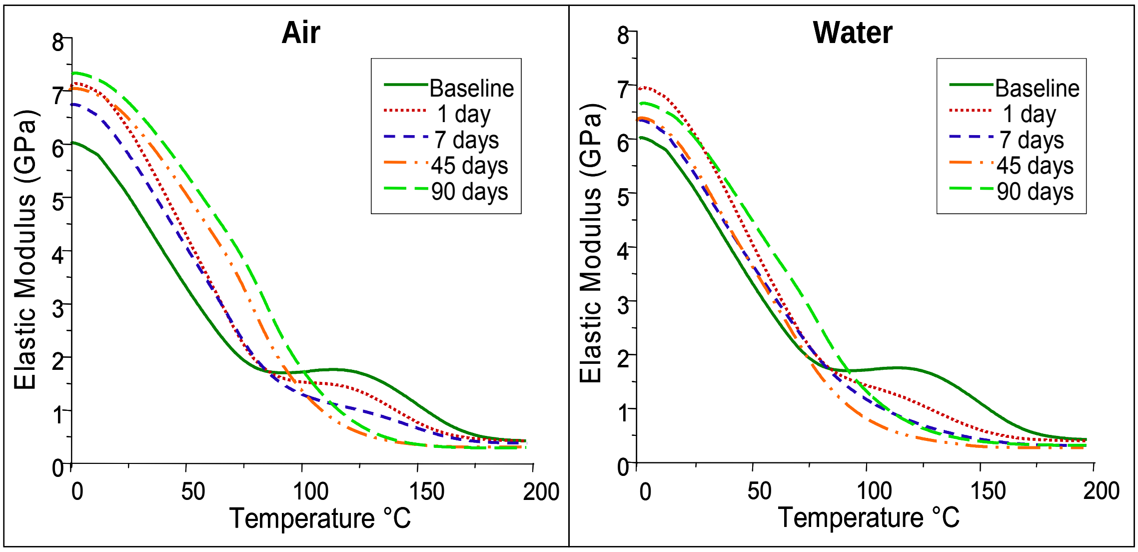
### 3.4.3 Artglass

**Figure 24** Plot of elastic modulus as a function of temperature for Artglass baseline and air (left) or water-stored (right) groups at 1 Hz.



### 3.4.4 Vita Zeta LC

**Figure 25** Plot of elastic modulus as a function of temperature for Vita Zeta LC baseline and air (left) or water-stored (right) groups at 1 Hz.



### 3.4.5 Interpretation of the results

All tested composites sharply dropped their elastic modulus when temperature was raised from 0 to 200°C. Nevertheless, the elastic modulus versus temperature curves qualitatively differed between stored and baseline groups (Figures 22-25).

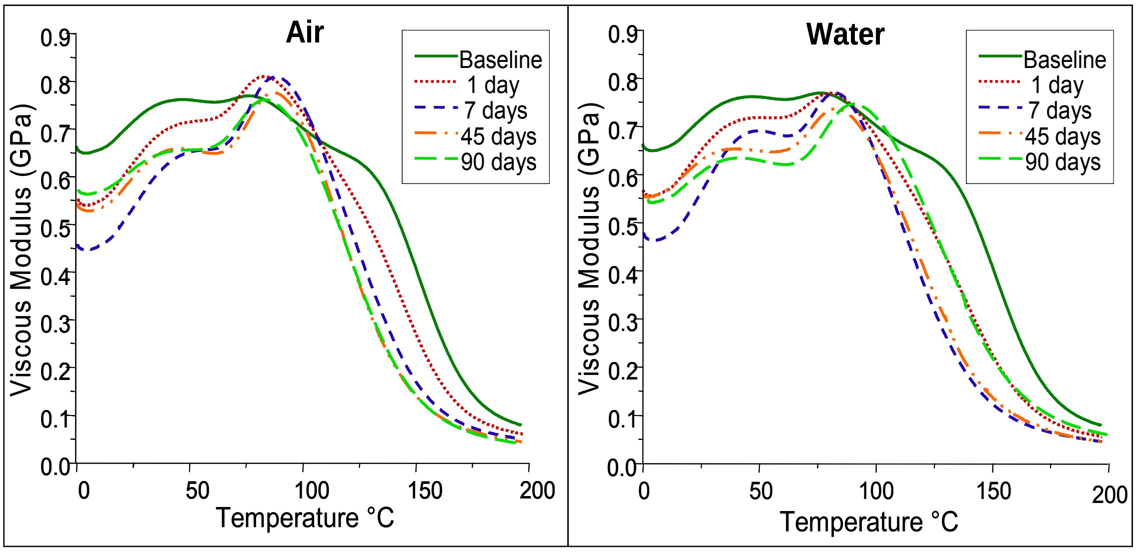
At very low temperatures, both stored and baseline groups either did not change their elastic modulus or did this very slowly. As temperature was further raised reaching the glass transition region, their elastic modulus drastically dropped. As heating continued, DiamondLite, Artglass and Vita Zeta LC stored groups left the glass transition region reaching the rubbery plateau region, where their modulus stopped dropping. The same was not true for Grandio stored groups that did not leave the glass transition region even when temperature reached 200°C.

Instead of sharply dropping their elastic modulus along the whole glass transition region, the baseline groups stopped dropping their modulus or did it quite slowly over a certain temperature range (region of thermal reaction). The same was observed for Vita Zeta LC after 1 day in both storage media and after 7 days storage in air. For the other materials and storage periods, no qualitative differences in the curves were observed between air and water-stored groups.

## 3.5 Temperature scan - Viscous Modulus (Analysis 7)

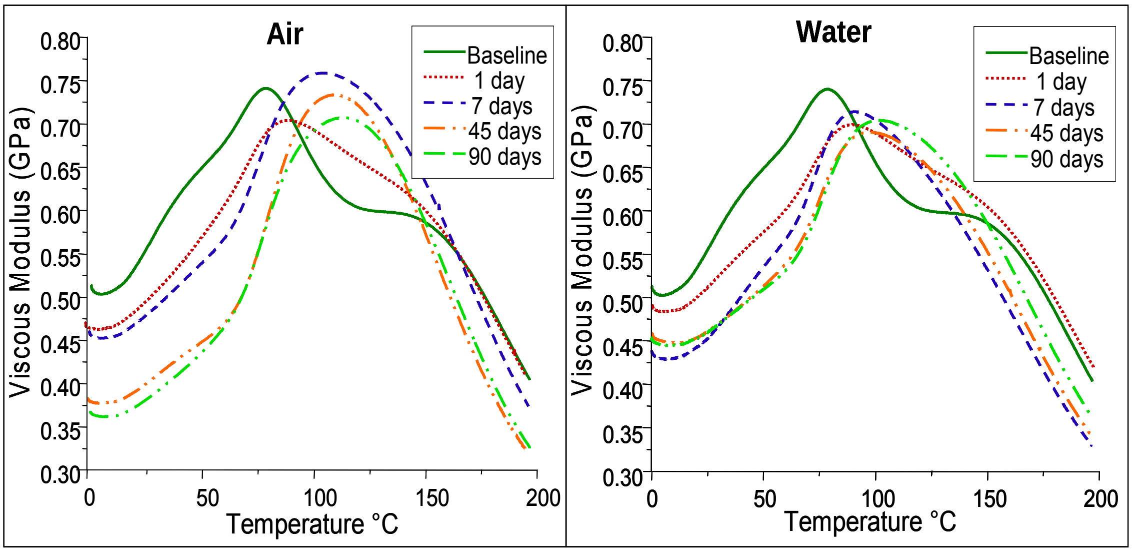
### 3.5.1 DiamondLite

**Figure 26** Plot of viscous modulus as a function of temperature for DiamondLite baseline and air (left) or water-stored (right) groups at 1 Hz.



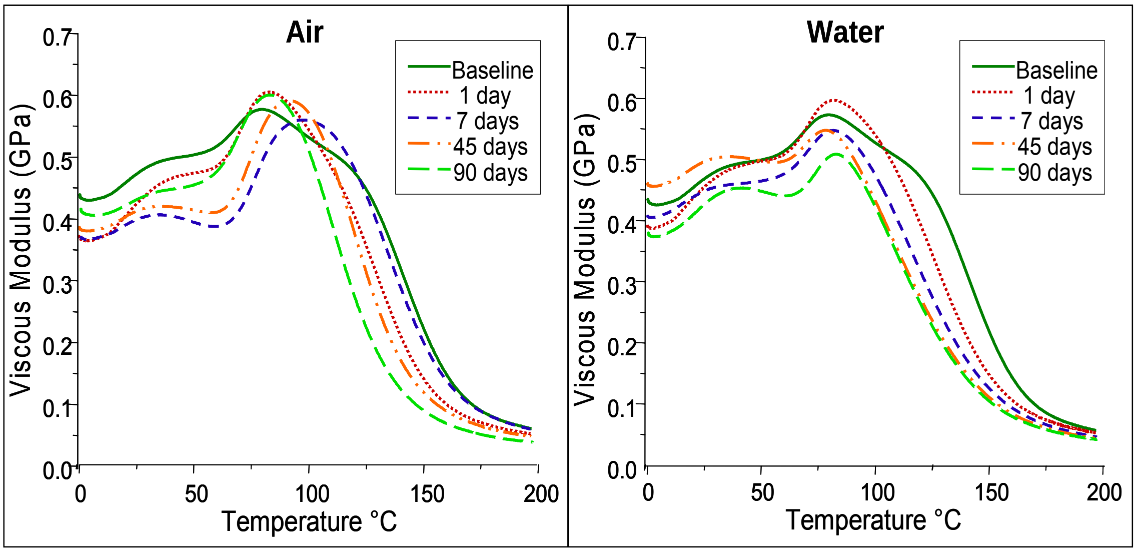
### 3.5.2 Grandio

**Figure 27** Plot of viscous modulus as a function of temperature for Grandio baseline and air (left) or water-stored (right) groups at 1 Hz.



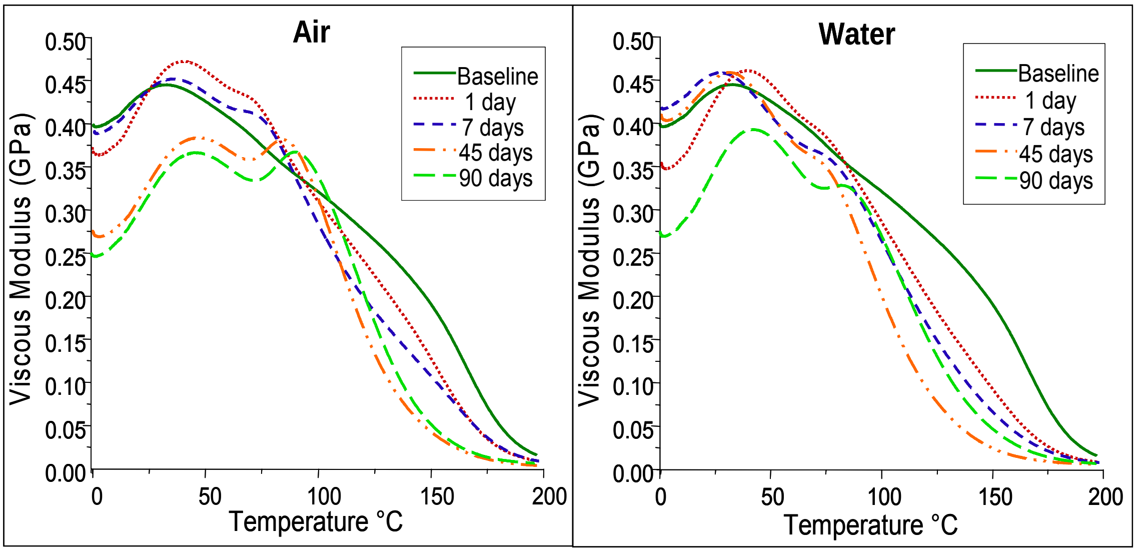
### 3.5.3 Artglass

**Figure 28** Plot of viscous modulus as a function of temperature for Artglass baseline and air (left) or water-stored (right) groups.



### 3.5.4 Vita Zeta LC

**Figure 29** Plot of viscous modulus as a function of temperature for Vita Zeta LC baseline and air (left) or water-stored (right) groups.



### 3.5.5 Interpretation of the results

When temperature was raised the viscous modulus of all tested composites increased until it reached its maximum (s) in the glass transition region (Figures 26-29). Thereafter, this property continuously decreased when temperature was further raised. However, the four composites showed in general distinct viscous modulus versus temperature curves.

The viscous moduli of DiamondLite and Artglass had similar responses to temperature. When temperature was raised the viscous modulus of their baseline groups continuously increased, reaching the first of three maximums at approximately 31°C for Artglass and 36°C for DiamondLite. Afterwards the viscous modulus slightly decreased before it increased again to reach the second maximum around 80°C for both materials. The third maximum was observed at approximately 123°C for Artglass and 132°C for DiamondLite.

The first and second maximums observed in the baseline curves of DiamondLite and Artglass respectively decreased and increased their height in the curves of the stored groups, while the third maximum vanished. For Artglass air-stored groups, the first and second maximums were found between 31-36°C and 83-97°C, respectively. Artglass water-stored groups showed their first maximum between 29-36°C and the second one, 78-82°C. The first maximum of DiamondLite air-stored groups was observed between 34-39°C, whereas the second one appeared between 83-88°C. The first maximum of DiamondLite water-stored groups was found between 30-41°C, compared with the second maximum observed between 80-88°C.

Instead of three, the curves of baseline Grandio samples showed only two maximums before it drastically dropped. The first one was found at approximately 75°C, while the second around 150°C. In the curves of the stored groups the two maximums observed in the curves of the baseline group merged into a single one that was found between 91-112°C for the air-stored and 93-101°C for the water-stored groups.

The curves of the Vita Zeta LC baseline group showed one maximum around 33°C before it dropped with two different decreasing regimes: the first with a smaller and the second with a greater slope. The stored groups showed two distinct maximums. The first maximum of the air-stored groups was observed between 36-47°C, whereas the second appeared between 73-90°C. For the water-stored groups, the first maximum was observed between 26-42°C and the second between 76-87°C.

The area under the viscous modulus versus temperature curves seemed to decrease for all composites as the storage period increased, either in air or in distilled water. However, a small difference was observed between air and water-stored groups: taking the baseline curves as reference, the global maximum point is smaller for water than for air-stored groups. Nevertheless, differences were not always statistically significant.

## 3.6 Temperature scan - Loss tangent (Analysis 7)

### 3.6.1 DiamondLite

**Figure 30** Plot of loss tangent as a function of temperature for DiamondLite baseline and air (left) or water-stored (right) groups.

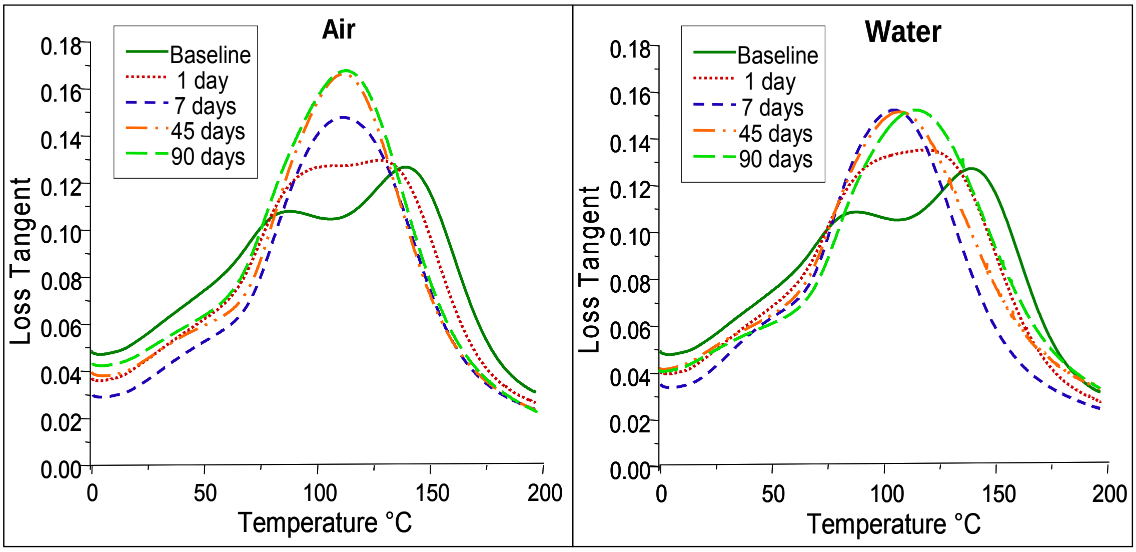


**Table 32** Glass transition temperatures (standard deviation) of DiamondLite experimental groups, taking baseline group as reference ($T_g$: glass transition; $T_{gLow}$: glass transition at low temperature; and $T_{gHigh}$: glass transition at high temperature).

| | **Baseline** | | **1 day** | | **7 days** | **45 days** | **90 days** |
|---|---|---|---|---|---|---|---|
| | **$T_{gLow}$** | **$T_{gHigh}$** | **$T_{gLow}$** | **$T_{gHigh}$** | **$T_g$** | **$T_g$** | **$T_g$** |
| **Air** | 82.3<br>(1.0) | 139.6<br>(4.6) | 91.1<br>(4.2) | 129.4<br>(2.7) | 111.3<br>(3.6) | 114.3<br>(3.7) | 112.5<br>(1.7) |
| **Water** | 82.3<br>(1.0) | 139.6<br>(4.6) | 87.8<br>(1.0) | 119.8<br>(1.4) | 104.3<br>(0.7) | 107.5<br>(2.9) | 115.0<br>(1.0) |

## 3.6.2 Grandio

**Figure 31** Plot of loss tangent as a function of temperature for Grandio baseline and air (left) or water-stored (right) groups.

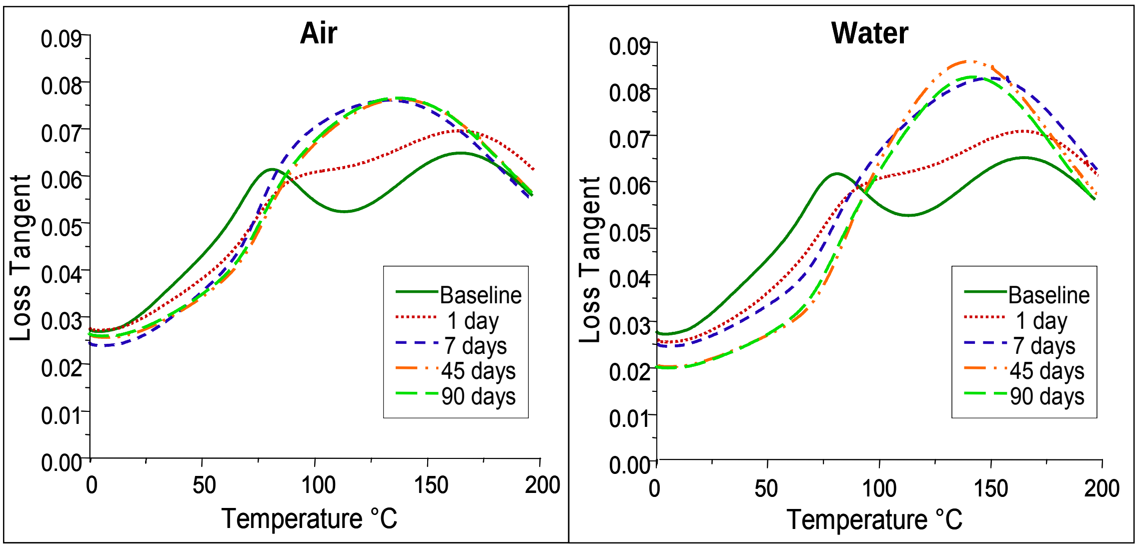


**Table 33** Glass transition temperatures (standard deviation) of Grandio experimental groups, taking the baseline group as reference ($T_g$: glass transition; $T_{gLow}$: glass transition at low temperature; and $T_{gHigh}$: glass transition at high temperature).

| | **Baseline** | | **1 day** | | **7 days** | **45 days** | **90 days** |
|---|---|---|---|---|---|---|---|
| | **$T_{gLow}$** | **$T_{gHigh}$** | **$T_{gLow}$** | **$T_{gHigh}$** | **$T_g$** | **$T_g$** | **$T_g$** |
| **Air** | 82.1<br>(2.9) | 164.7<br>(7.8) | 88.6<br>(2.3) | 164.0<br>(5.9) | 149.4<br>(3.3) | 141.5<br>(8.6) | 142.2<br>(2.0) |
| **Water** | 82.1<br>(2.9) | 164.7<br>(7.8) | 87.7<br>(1.3) | 163.9<br>(5.0) | 140.0<br>(10.1) | 138.8<br>(11.1) | 140.4<br>(5.4) |

### 3.6.3 Artglass

**Figure 32** Plot of loss tangent as a function of temperature for Artglass baseline and air (left) or water-stored (right) groups.

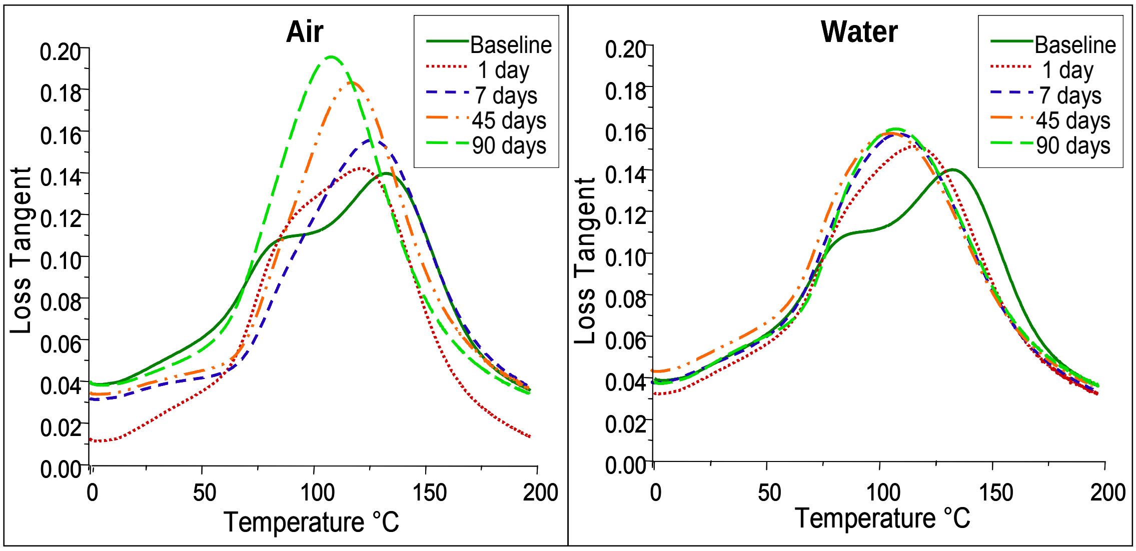


**Table 34** Glass transition temperatures (standard deviation) of Artglass experimental groups, taking the baseline group as reference ($T_g$: glass transition; $T_{gLow}$: glass transition at low temperature; and $T_{gHigh}$: glass transition at high temperature).

| | **Baseline** | | **1 day** | | **7 days** | **45 days** | **90 days** |
|---|---|---|---|---|---|---|---|
| | $T_{gLow}$ | $T_{gHigh}$ | $T_{gLow}$ | $T_{gHigh}$ | $T_g$ | $T_g$ | $T_g$ |
| **Air** | 81.2<br>(1.4) | 133.2<br>(4.7) | 85.5<br>(1.0) | 121.3<br>(1.3) | 126.6<br>(4.4) | 116.8<br>(4.0) | 107.8<br>(0.9) |
| **Water** | 81.2<br>(1.4) | 133.2<br>(4.7) | 116.6<br>(3.2) | | 110.1<br>(5.2) | 106.4<br>(2.1) | 105.6<br>(4.4) |

### 3.6.4 Vita Zeta LC

**Figure 33** Plot of loss tangent as a function of temperature for Vita Zeta LC baseline and air (left) or water-stored (right) groups.

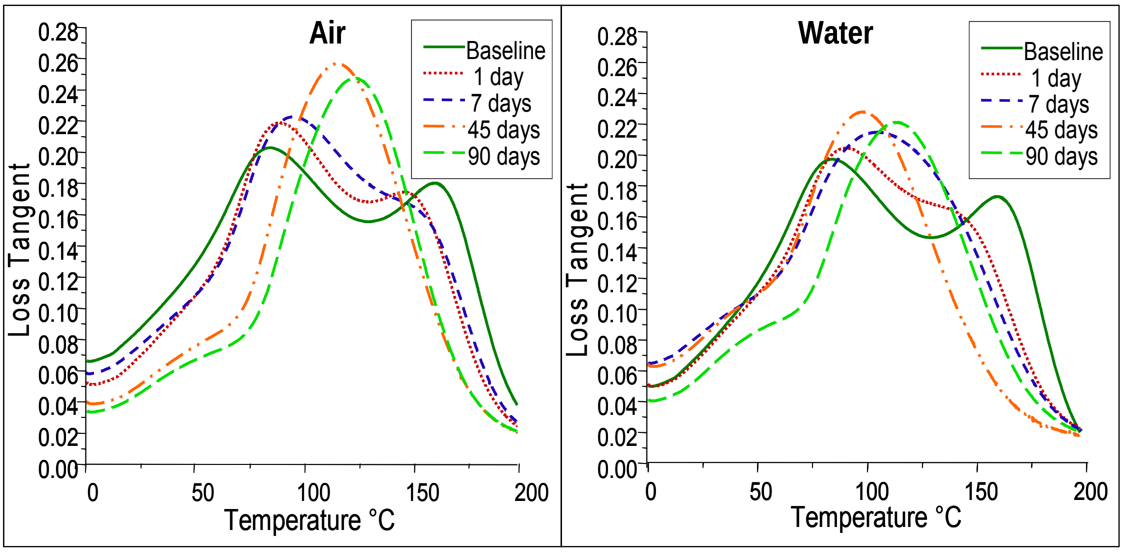


**Table 35** Glass transition temperatures (standard deviation) of Vita Zeta LC experimental groups, taking the baseline group as reference. ($T_g$: glass transition; $T_{gLow}$: glass transition at low temperature; and $T_{gHigh}$: glass transition at high temperature).

| | **Baseline** | | **1 day** | | **7 days** | | **45 days** | **90 days** |
|---|---|---|---|---|---|---|---|---|
| | $T_{gLow}$ | $T_{gHigh}$ | $T_{gLow}$ | $T_{gHigh}$ | $T_{gLow}$ | $T_{gHigh}$ | $T_g$ | $T_g$ |
| **Air** | 84.1 (0.7) | 162.6 (0.2) | 88.7 (0.4) | 152.1 (5.1) | 95.4 (2.5) | 156.2 (5.0) | 115.3 (0.9) | 123.1 (2.0) |
| **Water** | 84.1 (0.7) | 162.6 (0.2) | 90.7 (2.2) | 147.9 (1.8) | 107.5 (4.3) | | 97.7 (1.0) | 113.0 (1.9) |

### 3.6.5 Interpretation of the results

As observed for the viscous modulus, the loss tangent gradually increased for all tested composites when temperature was raised, reaching also its maximum (s) in the glass transition region (Figures 30-33), before it definitively dropped.

All baseline groups, all 1 day-stored groups (except for the Artglass water-stored group) and the Vita Zeta LC group stored for 7 days in air showed two maximums in the loss tangent versus temperature curves. The other groups presented only one maximum (Tables 32-35, Figures 30-33), that was generally higher for air than for water-stored samples, although these differences were often not significant.

It seems that conditioning the samples in air or distilled water for increasing time periods narrowed the peak of the loss tangent versus temperature curves and increased its amplitude. The widest loss tangent peaks were observed for Grandio, which also showed the lowest loss tangent values and highest glass transition temperatures among the tested composites.

# 4. Discussion

## 4.1 Frequency scan

### 4.1.1 Comparisons between composites

The visco-elastic properties of dental composite resins are reported to be affected by the choice of monomers, diluents, and fillers used in their formulation. It has been suggested that composites with high concentrations of more rigid monomers, such as BisGMA, and low concentrations of diluents containing flexible ether linkages, such as TEGDMA, undergo less deformation than do composites with higher diluents concentrations. A higher degree of deformation, when compared to BisGMA, is also attributed to UDMA due to the long aliphatic segment in the repeated unit that leads to greater chain flexibility (59).

Although the resin phase is the component susceptible to visco-elastic deformation in the composite (60), the presence of organic filler particles (pre-polymerized blocks of resin containing high loads of silica particle) might afford an additional visco-elastic component in the material. Thus, the deformation in composites containing this type of filler may probably be attributed to the deformation of both resin matrix and organic resin filler particles. By contrast, it is evident that composite resins with very hard, rigid fillers, such as glass or quartz filler particles are not expected to undergo visco-elastic deformation. Thus, the continuous resin phase alone will be the source of visco-elastic response in these materials (61).

#### - Elastic modulus

In this study it was often difficult to know what caused the observed differences in material properties, since the tested composites are different in several aspects and more specific information regarding their composition was frequently not available. Even though, a positive association between elastic modulus and percentage of filler by weight was found. This finding is not new to the literature (62; 63) and suggests that the filler themselves had a greater effect on elastic modulus than did the composition of the organic matrix, since more energy is dissipated in the filler and less in the resin matrix.

Presumably, differences in filler content were the main reason why the more heavily filled direct composites showed higher elastic modulus than the indirect composites studied; and also why Grandio showed higher modulus than DiamondLite, while Artglass exhibited higher elastic modulus than Vita Zeta LC. Regarding the size and morphology of the filler particles, they are expected to affect indirectly the elastic modulus of the composites, since they greatly influence filler loading (64).

Despite their small differences in the percentages of filler by weight, Grandio had significantly higher elastic modulus than DiamondLite for all experimental groups and testing conditions. In this case, differences in degree of conversion and cross-linking might have played an important role in the results. Other possibility is that the BisGMA (due to the high rigidity provided by the bisphenol-A backbone) (65) and UDMA resin matrices provide more rigidity than the PEX monomer. Other hypothesis is that information provided by the manufacturer regarding percentage of filler by weight was not accurate.

An optimum elastic modulus is an important pre-requisite for posterior composites that should be capable of retaining their shapes without deformational changes under functional loads, and a wide range of intraoral temperatures (90). Therefore, preferably, their elastic modulus should lie between dentin and enamel modulus. Then composites with high modulus, if combined with high fracture parameters such as flexural strength, diametral tensile strength and fracture toughness, would better survive in high stress-bearing areas (66).

In this study, Grandio showed the greatest resistance to elastic deformation that could be predominantly attributed to its high filler content of a combination of different filler sizes and types, which, in turn, minimize the amount of polymeric resin component. Although Grandio was the only material that approached the rigidity of dentine, its elastic modulus represents only one-fifth the rigidity of enamel. Hence, a conservative preparation is preferred, so that the tooth rather than the composite absorbs most of the stress.

For instance, DiamondLite may cause the restorations to deform and bend excessively under masticatory stresses, which limits its indications. However, it could be very satisfactorily used for the restoration of anterior teeth, subjected to lower functional stresses when normal occlusion is considered. DiamondLite could also be indicated for Class V restorations. Cervical cavities demand low modulus composites to allow the restoration to flex with the tooth during the masticatory stresses, thus avoiding the restoration to fail by debonding at the restoration-cavity margins. Another limitation of low modulus direct composites is their use as core materials of full-ceramic restorations. Since these composite resins can under functional fatigue undergo distortion in shape from masticatory forces, it can lead to catastrophic failure of the friable crown under normal function (67).

Regarding the tested indirect composite resins, when indicated as inlays or onlays they might work as direct composites, requiring a high elastic modulus to withstand the masticatory stresses. The use of low modulus materials in such cases might stress the tooth/restoration interface over time, which can result in marginal breakdown and loss of marginal seal (68-70). In the present study, the elastic modulus values measured for Artglass and especially for Vita Zeta LC make the decision to restore large carious lesions in stressed posterior teeth with these materials rather questionable unless the results of clinical data show more promising data.

On the other hand, a low elastic modulus can be advantageous when indirect composites are used for aesthetic veneering of partial dentures. In such cases, a flexible composite is needed due to the inevitable low deformability of the metallic framework. Instead of transmitting the masticatory stresses to the metal/composite interface, the flexible composite deforms and dissipates the stresses itself. Thus, the use of low elastic modulus composites would allow the material to be stressed or deformed without the veneer flaking off. In considering the elastic modulus of both indirect composites tested, Vita Zeta LC veneers seem to have greater chances to survive without flaking off than Artglass veneers.

### - Viscous modulus

Direct composites also showed the highest viscous modulus values, thus suggesting their greater ability to relieve excess energy build up through moderate viscous flow during tooth function. This can be mainly attributed to their higher filler content, since friction between the particles and the polymer matrix has been suggested as an important source of viscous energy dissipation during deformation under stress (71; 72).

Although the viscous modulus results also tended to be higher for composites containing greater amounts of reinforcing filler, DiamondLite showed higher modulus values than Grandio. This fact can be probably attributed to their differences in monomer composition. According to DiamondLite's manufacturer the polymerization of a glassy monomer as BisGMA leads to an amorphous random array of monomeric chain entanglements, which lacks the ability to dissipate cyclic masticatory stresses. On the other hand, the PEX matrix would be a semi-crystalline network of organized micro-morphological features, displaying an interesting profile of nuclei, in a liquid state of matter, bearing the seeds for proliferation of future lamellar projections which upon growth and expansion consequential to the polymerization process, both occupy greater volume than their neighbouring interstitial amorphous co-polymerization agents, as well as generate a micro-shock absorber feature.

From one side, the viscous or visco-elastic flow may dissipate or retard elastic energy build-up during tooth function, and consequently less energy is available to trigger and promote fracture, wear, debonding and other such catastrophic failure processes (14; 73). From the other side, materials with high viscous modulus tend towards soft and rubbery behaviour that can result in some permanent dimensional change, which may not be desirable. Therefore, the combination of high elastic modulus along with optimum energy dissipation characteristics would make the composite material potentially resistant to different types of failure.

The fact that differences in viscous modulus between composites inside each main group, direct or indirect, were not statistically significant for all experimental groups and testing conditions suggests that the filler content was a less important factor in determining the viscous modulus than the elastic modulus results.

**- Loss tangent**

The loss tangent gives an indication of the energy loss in the material during deformation and is important in the evaluation of the visco-elastic properties of materials. Higher values of tan δ indicate higher energy loss and more viscous behaviour, while lower loss tangent values indicate increasingly elastic behaviour (74).

The low loss tangent values presented by all composite materials ranged from 0.018 to 0.142 at 5°C, from 0.022 to 0.202 at 35°C and 0.029 to 0.193 at 55°C. The fact that the loss tangent approached “0” means the materials had a small viscous component over the temperature and frequency ranges investigated, which is suggestive of more elastic-like materials that do not absorb much energy as a result of deformation.

In this study Grandio was the stiffest material (high elastic modulus) with the quickest response to load (low loss tangent), therefore it had the greatest elastic response to deforming forces. This would suggest a quick return to its original shape after deformation, which would seem desirable. On the other side, Vita Zeta LC was the softest material. However, it had the highest loss tangent, indicating a slow response to deforming loads, which would seem to be undesirable in attempting to reproduce the properties of the dental tissues.

### 4.1.2 Influence of storage conditions

The influence of the storage conditions (medium and period) on the visco-elastic properties of the tested dental composite resins might result from the interaction of three main processes: water sorption, material loss and post-curing.

The precise behaviour of each composite during the three months in air or in distilled water depended upon its composition and original conversion, which generated conflicting trends of increase, no change or decrease in the elastic modulus, viscous modulus and loss tangent over time.

#### 4.1.2.1 Water sorption and material loss

Water sorption may alter the visco-elastic properties due to plasticizing and degradational effects – two distinctly different mechanisms (75). First, the matrix take up moisture and water enters the specimen from the surface. Then, water molecules diffuse into the composite through microflaws such as pores and cracks. Since the polymer network is composed of cross-linked molecules within which the unreacted monomers reside, as the solvent penetrates the matrix and expands the openings between polymer chains, soluble components and/or unreacted low-molecular-weight matters diffuse out (7; 76).

The loss of components is rapid during the initial period of soaking and slows substantially within hours (7). In fact, about 75% of the elutable species are extracted within several hours (77). On the other side, a complete saturation of the composite network with water requires weeks or months (78). At this time, the composite reaches equilibrium and no extra deterioration of the materials' properties occurs (79).

A simple mechanism of plasticization consists that every water molecule, when creating an H-bond with hydroxyl and other polar groups, weakens intermolecular interactions (80). Thereby, the water reduces the inner viscosity and lowers the height of a potential barrier that limits the segment's mobility. The increase in water content in this case, is equivalent to the increase in temperature (80). In other words, the absorbed water causes sorption expansion, increasing the effective free volume, defined as the space the molecules have to move, and the ease of movement of chain segments (75). This implies that slippage between molecules becomes easier, facilitating the flow of polymer when an external force is applied (63), thus reducing the elastic modulus and increasing the viscous modulus and loss tangent.

The ability of the dental composite resins to take up water is related to the availability of molecular-sized free volume holes in the polymer network and polymer-water interactions. The availability of holes depends on the polymer structure, morphology and crosslink density. Furthermore, polymer-water interaction depends on the polymer composition, particularly to the quantity of hydrophilic functional groups present in the network (81). The hydroxyl groups of BisGMA and the ethylene oxide elements of TEGDMA contribute to the relatively high water sorption of the resulting copolymers (82). The percentage of filler by volume is also an important compositional factor. Since water sorption is a diffusion-controlled process and occurs mainly in the resin matrix (83), the larger the volume percent of resin matrix, the higher the water uptake.

Although air-storage seems to be a stable condition when compared to distilled water and was used as reference in this study, it should not be considered so. According to Musange and Darvell, it appears that there is no zero-effect storage condition that can be relied on to give an adequate control for any experiment involving composite resins (75). On exposure to air, freshly prepared composite resins would be expected to lose volatile compounds (in particular, low molecular weight monomers). However, polar polymers in general absorb water from the surroundings depending on their hydrophilicity and the humidity of the environment (75). Thus, although the detrimental influence of distilled water is expected to be greater for water-stored samples, some effect should not be excluded on air-stored samples. Therefore, the variation of the elastic modulus of samples immersed in distilled water relative to the elastic modulus of samples kept in a dry environment is a function of the quantity of water absorbed by the samples.

### - Elastic Modulus

Water storage played an important role in the elastic modulus results of the experimental groups of all tested composites at most testing conditions, although the amount of sorbed water probably varied within the tested materials. The less impressive effects of water storage were observed at 55°C. At this temperature the expanded free volume might have facilitated molecular motion independently of the presence of water, thus decreasing the elastic modulus of the composites.

Between all tested composites, Grandio showed the highest incidence of non-significant differences in elastic modulus between air and water-stored samples. The main reason for this might have been the high filler content in this material (59). Another possible reason could be the presence of different sizes of fillers that reduce the spaces in between giving rise to strongly interlocked particles that reduce the space to entrap water, which should have a plasticizing and weakening effect. The low water penetration may also result of a highly cross-linked resin matrix of Grandio samples, especially after longer periods of storage.

On the other hand, Artglass was the most susceptible material to the softening effect of distilled water. The elastic modulus of all Artglass experimental groups decreased due to water sorption at all testing conditions. One possible explanation for this is the low water resistance of composite resins containing barium glass fillers. According to Tarumi et al. the surface of these fillers is damaged by water that would be retained in the interface between the barium glass filler and the matrix resin (84). Additionally, Ruyter and Oysaed have showed that elements were more readily leached into water from composites containing zinc, barium and strontium glasses than they were from composites which incorporated particles of silicon dioxide (85). Although DiamondLite also contain barium glass fillers, it was less affected by water storage. This can be probably attributed to the PEX monomer, whose characteristics are explained in the next subsection.

### - Viscous Modulus

The viscous modulus of DiamondLite was the least affected by water storage. According to its manufacturer, the polymer resin matrix comprises of a medical grade phenolic epoxy monomer (PEX), whose superhydrophobic nature would reduce by 1/3 its potential long-term sorption in comparison to traditional BisGMA or UDMA monomers. These results imply that DiamondLite’s viscous modulus results were less affected by the content of water than the elastic modulus results did. The second least affected composite by water storage was Grandio, also probably due to its high filler composition and cross-link density.

For both direct composites the few significant groups where the viscous modulus increased in water, were only found after 45 and 90 days storage. These results suggest the slow nature of the diffusion of water into the cross-linked resin matrix of Diamond Lite and Grandio samples, thus requiring a longer period for complete saturation. This agrees with the results of Ferracane et al., who showed that the slow uptake of water correlates with the fact than for the majority of the composites the properties were not reduced until the polymer matrix was essentially saturated with water (79).

Regarding the indirect composites, both materials were similarly affected by water storage that largely improved the viscous modulus for most storage periods and testing conditions. The significant groups were distributed at all storage periods, thus indicating great water sensitivity, even when the samples were stored for shorter periods. Probably, the sorbed water increased the free volume, thereby facilitating molecular mobility and improving material's energy dissipating capacity.

#### - Loss Tangent

With respect to the loss tangent, all materials showed higher values when stored in distilled water, compared to when stored in air, although this trend was not always supported statistically. This might be simply because of the plasticizing effect of the water that weakens intermolecular interactions facilitating molecular movement and consequently improving material's energy dissipating capacity.

The number of non-significant groups did not significantly vary between the tested composites, thus showing that their loss tangent values were uniformly affected by water-storage.

### 4.1.2.2 Post-curing

It would be desirable for a dental composite to convert all of its monomer to polymer during the polymerization reaction. Adequate polymerization is a crucial factor in obtaining optimal physical properties and clinical performance of resin composite restorative materials. Nevertheless, with high molecular-weight monomers such as BisGMA or UDMA, there is always an incomplete cure and significant concentration of unreacted carbon double bonds remaining within resin when it is cured with visible light at the oral temperature (86). This is mainly attributed to loss of mobility and decreased reactivity of the remaining monomers or growing polymers chains in the highly viscous polymeric network formed as polymerization proceeds (87). Therefore, the final network contains between 25 and 50% unreacted methacrylate groups (7), which may act as plasticizers, thereby altering the physical and mechanical properties of the composite resin (27; 88; 89).

Molecules inside the composite resin repel each other when they are too close; therefore, there is always some empty space between them. This empty space is called free volume. As liquids, small molecules can easily exchange places with nearest neighbours because the holes between them are similar in size to the molecules themselves. On the other hand, polymers are much larger than the empty spaces around them, and therefore cannot move as a single unit (36).

Molecules in partially cured composite resins have high mobility because they have a lower molecular weight and there are few cross-links. Such networks also have higher concentrations of reactive groups and more free volume, since there is not enough time for the molecules to be relaxed in the amorphous state by entering into the vitreous state (36). These features enable the remaining functional groups, residual monomers, and unreacted pendant groups with excess free volume to move with fewer constraints, more like small molecules, and do more easily find a reaction partner with which to form new cross-links, even at body temperature (36; 45).

By increasing polymer temperature above body temperature, the material warms up, expanding its free volume. Consequently, a greater segmental mobility of pendant groups is possible, increasing the chances of neighbour free-radicals to collide with unreacted methacrylate units, which leads to further bonding of these groups (27).

The progressive chain growth and cross-linking improve the rigidity of the composite network (27; 90; 91) by restricting the movement of large molecular segments and the microscopic movement of polymer segments, thereby minimizing the amount of permanent deformation (27; 90). This is reflected in the higher elastic modulus and lower viscous modulus and loss tangent of the material (27), since as the polymer network develops, the composite's capacity for viscous flow decreases (92).

Some authors have reported that incomplete conversion may be improved by the normal temperature of the mouth, as well as by the elevated temperatures found during the ingestion of hot food and beverages (28; 34). Lovell et al. found that the difference between the cure temperature and the storage temperature had a dramatic effect on the extent of post-cure of dental composites. The highest amounts of post-cure were seen in samples that were cured at temperatures less than or equal to the storage temperature (93). These samples exhibited similar or higher mobilities after irradiation so the radicals continued to propagate "in the dark" and significant amounts of post-cure were measured before trapped radicals were terminated. When cured at elevated temperatures the mobility of the forming network dramatically decreased effectively stopping the propagation reaction, thereby no additional cure was observed (93).

In the present study direct and indirect composites were polymerized at 22°C and 40°C, approximately. Since all composites were stored at 37°C, some degree of post-curing was expected, especially for the direct composites. Instead of assessing the degree of conversion and post-curing rates by using traditional direct and quantitative test methods, we have opted for dynamic mechanical analysis. This qualitative method may be used to characterize both the rate and extent of polymerization; as such processes are associated with time-dependent changes in the elastic modulus (32).

### - Elastic Modulus

Between baseline and 1 day storage, the increase in elastic modulus can be attributed to the higher cross-linking density in the samples following post-curing that can make the resin more rigid and less susceptible to deformation. Regarding the storage medium, the highest modulus increasing rates between baseline and 1 day were measured for the air-stored samples, although the samples stored in distilled water were expected to undergo a higher degree of post-curing due to the ability of the sorbed water to facilitate molecular motion.

This finding probably means that the plasticizing and degradational effects of water sorption outweighed the benefits of post-curing during this period.

The lowest elastic modulus increasing rates after 1 day storage were measured for Grandio, closely followed by Artglass. Vita Zeta LC clearly revealed the highest elastic modulus increasing rates in this period, followed by DiamondLite. According to Ruyter and Svendsen, commercially available composite restorative resin materials have different amounts of remaining unreacted methacrylate groups 1 day after start of polymerization (94). Since the amount of post-cure depends on the extent of initial cure, composites that showed the lowest elastic modulus increasing rates in the present study probably underwent the highest initial degrees of conversion. The different amounts of residual methacrylate groups in the polymerized materials tested are probably related to differences in their resin formulations and filler characteristics.

Between 1 day and 90 days storage, the elastic modulus results were found to vary to different extents with time when the samples were stored at 37°C, in air or distilled water. Regarding DiamondLite, its elastic modulus continued to improve up to 7 days, thus suggesting that appreciable residual concentration of free radicals were still available in the samples in this time interval. This finding agrees with that published by other authors who reported that the lifetime of residual free radical at room temperature could reach several days or months, depending on cross-linking density and storage temperature (76; 95; 96). Afterwards, the elastic modulus decreased. It is likely that this drop resulted of the negative influence of the storage conditions that finally outweighed the benefits of the decelerating post-curing process.

Grandio also improved its elastic modulus between 1 day and 7 days, but only when stored in air. It is possible that the plasticizing effect of water neutralized the benefits of the post-curing effect, so that the elastic modulus of water-stored samples remained constant during that period. After 7 days the modulus levelled off for the air-stored samples but increased between 45 and 90 days for the water-stored samples. Possibly the water molecules needed more time to swell the cross-linked network of this material, and therefore, to promote conversion by facilitating the movement of the molecules.

The elastic modulus of Artglass was found to behave significantly constant through the period between 1 day and 90 days when stored in air. Apart the drop in modulus between 1 day and 7 days, the same could be said about the water-stored samples. Based on these results, on the limited post-curing reaction between 35 and 55°C during the frequency scan of the baseline group and on the low elastic modulus increasing rates between baseline and 1 day storage, we could say that Artglass disposed of less reactive methacrylate units after light polymerization than the other three composites tested. According to its manufacturer, this result might be due to the multifunctional methacrylate monomers contained in this material that undergo higher initial degrees of conversion and result in a highly cross-linked polymer.

After the great increase in elastic modulus between baseline and 1 day storage, most Vita Zeta LC samples showed no important change in modulus between 1 day and 7 days. Exceptions were only found for water-stored samples tested at 5°C that significantly dropped their modulus. At this temperature, where the free volume is small, water saturation might have played an important role facilitating the movement of the molecules, thereby dropping the elastic modulus of the samples. Between 7 and 45 days only samples stored in air improved their modulus, thus confirming the availability of reactive free radicals. The stability of the modulus between 45 and 90 days for the air-stored samples suggests that all reactive radicals available were consumed before this period. On the other hand, samples stored in water increased their modulus between 45 and 90 days, confirming the ability of the sorbed water to promote post-curing in saturated samples.

### - Viscous Modulus

A higher degree of conversion of the resin matrix results in a more rigid material. The rigid matrix behaves like a hard elastic component that restricts polymer chain mobility, thereby minimizing the amount of permanent deformation under such a condition. Probably for this reason the viscous modulus of the baseline samples stopped to increase and started to decrease as post-curing started during the frequency scan in the second temperature interval.

Between baseline and 1 day and also between 1 day and 7 days the viscous modulus of both DiamondLite air and water-stored samples tended to decrease at most testing conditions. This event can be attributed to the post-curing reaction that improved the elastic modulus of the material in the same period. After 7 days storage no changes in viscous modulus were observed for the air-stored samples and most water-stored samples, showing that this property was less affected by the storage conditions than the elastic modulus.

All Grandio samples decreased their viscous modulus between baseline and 1 day as the result of post-curing. Between 1 day and 7 days and also between 7 and 45 days most air-stored samples decreased their viscous modulus, while most water-stored samples did not change their modulus. The decrease of the modulus in air can be also attributed to the post-curing reaction that improved the elastic modulus of the material in this period. On the other side, the stability of the modulus in water might result of the equilibrium of two processes with opposite effects: plasticizing effect of the water and post-curing. After 45 days no change in modulus was observed. Probably, the samples became saturated with water and the available unreacted methacrylate units were finished.

Between baseline and 1 day storage the Artglass experimental groups decreased their viscous modulus at most, but not all testing conditions. This might be due to the low number of unreacted methacrylate units available in the polymerized material, resulting in lower degrees of post-curing. Between 1 day and 7 days most air-stored samples decreased their modulus. No change in modulus was observed for the samples stored in water. This might be also the result of the opposite effects of plasticizing (water) and post-curing. After 7 days no change in viscous modulus was observed. Therefore, the viscous modulus results also confirmed the stability of Artglass along storage periods.

Regarding Vita Zeta LC, samples stored in air only decreased their viscous modulus between 7 and 45 days, while those stored in water just dropped this property between 45 and 90 days. These drops in viscous modulus are in agreement with increases in elastic modulus observed during the same period and are attributed to post-curing.

**- Loss Tangent**

The drops in loss tangent between baseline and 1 day were significant in both storage media for DiamondLite samples, except for water-stored samples at 55°C. In this case, the increased free volume at 55°C and the plasticizing effect of the water might have improved the loss tangent, while the post-curing process had the opposite effect. As a result, the loss tangent remained unchanged. The drops in this property between 1 day and 7 days can be also attributed to the post-curing reaction during storage. Thereafter, samples stored in air maintained their loss tangent constant, while those stored in distilled water only increased this property between 7 and 45 days, probably as a result of the plasticizing effect of the water.

Grandio samples continuously dropped their loss tangent up to 45 days when stored in air, thus showing that the material assumed a more elastic behaviour as a result of storage. When stored in water no changes in loss tangent were observed up to 45 days. Also in this case the opposite effects of plasticizing (water) and post-curing might have contributed to the equilibrium in loss tangent. Between 45 and 90 days this property significantly decreased, which coincided with an increase in elastic modulus.

The same was observed for DiamondLite, the drops in loss tangent between baseline and 1 day were significant in both storage media for Artglass samples, except for water-stored samples at 55°C. Also in this case, the increased free volume at 55°C and the plasticizing effect of the water might have improved the loss tangent, while the post-curing process had the opposite effect. After 1 day, the only change in loss tangent was observed for the air-stored samples between 1 and 7 days that dropped at the two highest testing temperatures. Probably, post-curing at 5°C did not significantly reduce molecular motion, since at this temperature the polymer was probably in a glassy state.

Post-curing also dropped the loss tangent of Vita Zeta LC between baseline and 1 day, in both storage media. Changes in loss tangent between 1 day and 90 days were identical to those observed to viscous modulus, and might also result of post-curing and water plasticizing effects.

### 4.1.3 Influence of testing conditions

#### 4.1.3.1 Frequency

When forced at high frequencies, a material reacts rigidly. Deformations are small and all energy introduced into the system can be regained upon releasing the strain. The elastic modulus is large and the viscous modulus vanishing small. At intermediate frequencies, deformations become large enough for structural elements to be permanently removed from their original equilibrium position. Such displacements dissipate energy because of atomic collisions and at the same time reduce the system's elastic storage capacity. Toward low frequencies, the loss modulus decreases again. The fluid flows effortlessly, resulting in large irreversible deformations, indicating that the elastic modulus is small as well (97).

Cycling the materials at a loading frequency close to that of chewing is an important requirement for visco-elastic materials. Clinically, dental composites are rather exposed to dynamic loading than static loading. The frequency of the loads range from rapidly applied forces caused by mastication and long-term, low level forces applied during resting. For this reason, instead of selecting one single frequency, we have tested the samples across a frequency range of two decades, including 0.1, 1 and 10 Hz.

**- Elastic modulus**

In the present study, the elastic modulus of all composites sloped upward towards higher frequency. This indicates the development of some elastic behaviour within the material at higher frequency, since the more rapidly a stress is applied the shorter the time available for the molecules to relax and accommodate that stress.

Very strong frequency dependence was measured for DiamondLite, and especially for Vita Zeta LC. On the contrary, the elastic modulus results of

Grandio and especially of Artglass were much less affected by rising testing frequencies.

Regarding Vita Zeta LC, the physical explanation of the strong frequency dependence of elastic modulus might be related to the low filler content in this material. The silicone dioxide responds purely elastically, which implies a negligible frequency dependence of elastic modulus. However, the matrix phase, abundant in this material, exhibits much more pronounced frequency dependence because of its visco-elastic nature (43).

In highly filled composites, such as Grandio, the filler phase predominates over the visco-elastic matrix phase, and one may expect smaller differences between the results obtained at different frequencies than when the low-filled composites are considered (43). However, the additional post-curing reaction occurred during the storage periods at 37°C seemed to play an even more important role in the results, since most non-significant differences in elastic modulus between the frequencies were measured after 45 and 90 days storage. At this time the cross-linked network in the samples was probably able to reduce material’s flow, even at lower frequencies.

The low frequency dependence of modulus observed for Artglass might also be attributed to a higher degree of conversion due to the incorporation of multifunctional monomers. This might be the main reason why DiamondLite showed a stronger frequency dependence of elastic modulus than Artglass, although the latter material contains a lower percentage of reinforcing fillers by weight.

Only when tested at 5°C, a few Vita Zeta LC experimental groups showed no frequency dependence of elastic modulus. The same was true for DiamondLite, except for one experimental group. At this low temperature the molecular movement was probably restrained due to the lack of free volume. Consequently, the material acted more elastic-like and was less susceptible to frequency changes. At 35°C and 55°C, on the other hand, chain motion was possibly facilitated by an expanded free volume; thereby the materials acted more viscous-like and became more frequency dependent. The fact that some Grandio and Artglass experimental groups showed no frequency dependence even when tested at these two temperatures reflects the elastic character of their network structure.

**- Viscous modulus**

As the frequency of measurement is increased, less time is allowed for the molecules to reorient. Therefore, a greater fraction of molecules is unable to relax or reorient and greater energy is stored in the system. Consequently, the viscous modulus of the composites tends to decrease.

Grandio also showed a very limited frequency dependence of viscous modulus. Either the experimental groups did not change their viscous modulus or they significantly dropped it at all temperatures in both frequency intervals. However, when the frequency was changed from 0.1 to 1 Hz at 55°C, most experimental groups dropped their modulus. At this temperature the free volume of the composite expanded, facilitating molecular motion even at 0.1 Hz. When the frequency was raised to 1 Hz, the ability of the molecules to move and consequently to dissipate energy significantly decreased, dropping the viscous modulus. The fact that no change in modulus was observed between 1 and 10 Hz at 55°C indicates a more elastic-like behaviour of this material at higher frequencies. Based on these results we can say that the cross-links and reinforcing fillers in this composite showed a great ability to restrain molecular motion, especially at the two lowest testing frequencies.

Artglass was less effective than Grandio in restraining molecular motion. This might be due to its lower filler content. Although most experimental groups showed no important change in viscous modulus or decreased this property in both frequency intervals at all temperatures, some groups considerably improved their modulus when tested at 35°C between 0.1 and 1 Hz, and at 55°C between 1 and 10 Hz. This might also be due to an expanded free volume in the material at these temperatures that facilitated molecular motion.

DiamondLite also reduced its ability to limit molecular motion when temperature was raised. At 5°C most experimental groups managed to drop their viscous modulus in both frequency intervals. At 35°C the experimental groups stored in water tended to increase their viscous modulus between 0.1 and 1 Hz, while those stored in air did not change it. The sorbed water modifies the behaviour of the composite by acting as a plasticizer. As a result, the contribution of the material's viscous component to the results increases. Between 1 and 10 Hz, either the experimental groups reduced their viscous modulus or they did not change it, confirming that at higher frequencies the material tends to show a more elastic-like behaviour. At 55°C most experimental groups increased their viscous modulus in both frequency intervals. This result can be also attributed to changes in free volume. Therefore, the effect of water, or water and high temperatures had an important effect on the viscous modulus of this composite material.

Vita Zeta LC showed the greatest frequency dependence of viscous modulus. At 5°C and 55°C, the modulus tended to decrease and increase, respectively, probably due to the same reasons cited above for the other materials. At 35°C changes in modulus varied according to the frequency interval. Between 0.1 and 1 Hz the modulus tended to increase, while between 1 and 10 Hz it either decreased or had no important change. This difference also shows that this material acted more elastic-like at higher frequencies.

Based on these findings we can affirm that, in general, the incidence of increases in viscous modulus when frequency was raised was higher in the first than in the second frequency interval.

### - Loss tangent

In general, at low frequencies polymeric materials flow more, acting in a similar fashion to flow at elevated temperature, thus showing a larger damping. As the frequency increases, the materials behave more elastically, thus decreasing the loss tangent values of the composites. This decrease is related to restrictions of chain motions in polymer at higher frequencies, thus decreasing material's energy absorption capacity (98).

Grandio experimental groups either dropped their loss tangent or they did not change this property when frequency was raised in both frequency intervals. The number of groups that significantly dropped this property increased when the temperature was raised. At 5°C, the small free volume and the highly loaded cross-linked network structure of this material were effective in restraining the molecular motion at 0.1 Hz. For this reason, most experimental groups showed no important change in loss tangent when frequency was raised to 1 Hz. The same might be true between 1 and 10 Hz. At 35°C, the free volume in the sample expanded facilitating molecular movement. Consequently, raising the frequency at this temperature strongly influenced molecular movement, thereby limiting the ability of the material to flow and dissipate energy. Therefore, the number of experimental groups that dropped their loss tangent increased at this temperature in both intervals. At 55°C chain mobility became even greater. Accordingly, increasing the frequency at this temperature had an even more dramatic effect in reducing the ability of the molecules to move. As a result, most experimental groups dropped their loss tangent in both frequency intervals at this temperature.

A greater frequency dependence of loss tangent was observed for the DiamondLite experimental groups. Instead of keeping their loss tangent constant at 5°C, as observed for Grandio, all groups dropped this property when the frequency was raised in both intervals. It is possible that despite of the low temperature, cross-links and reinforcing fillers were not able to restrain molecular motion at 5°C. Consequently, increasing the frequency decreased the ability of the molecules to move, thus slowing the rate of material’s response to load and increasing the energy absorption capacity of the material. At 35°C most groups did not change their loss tangent between 0.1 and 1 Hz, but they dropped it between 1 and 10 Hz. It shows that the network structure of this material was only able to reduce molecular motion when the frequency was increased by two orders of magnitude. At 55°C most of the groups stored in distilled water reduced their loss tangent between 0.1 and 1 Hz, while air-stored samples showed no important change in this property. The simultaneous effect of water and temperature might have facilitated chain motion in a larger scale at 0.1 Hz than temperature alone in the air-stored samples did. Consequently, increasing the frequency to 1 Hz had more dramatic effects in restraining molecular motion in the water than in the air-stored samples.

Most Artglass experimental groups also reduced their loss tangent in both frequency intervals at 5°C, probably, due to the same reasons presented above for DiamondLite. At 35°C, however, this property was basically independent on the testing frequency. While the higher temperature probably expanded the free volume, thereby facilitating chain motion and increasing the loss tangent, the higher testing frequency produced the opposite effect. As a result, the loss tangent values remained unchanged. When tested at 55°C most experimental groups dropped their loss tangent in the first, but not in the second frequency interval. It shows that increasing the frequency from 0.1 to 1 Hz restricted more efficiently chain motion for this material at 55°C than from 1 to 10 Hz.

Most Vita Zeta LC experimental groups also dropped their loss tangent when tested at 5°C. At 35°C, this property showed no important change in the first frequency interval, but it significantly dropped in the second. This finding also suggests that this material behaved more elastic-like at this temperature at higher testing frequencies. At 55°C the opposite effect was observed: the loss tangent decreased in the first frequency interval and remained constant for most experimental groups in the second. Again, increasing the frequency from 0.1 to 1 Hz restricted more efficiently chain motion for this material at 55°C than from 1 to 10 Hz.

#### 4.1.3.2 Temperature

The changes in the visco-elastic properties observed when the temperature was raised are due to changes in material’s free volume. At lower temperatures the molecular motion of the chains is impeded due to the lack of free volume. Under heating, the free volume expands, thus increasing the available space for the molecules to slip between each other. Consequently, the material will more easily flow under external forces, what decreases its elastic modulus and increases viscous modulus and loss tangent.

#### - Elastic modulus

The highest elastic modulus decreasing rates between 5 and 35°C were measured for the baseline groups. The samples in these groups probably had a low degree of conversion and a low cross-link density that might have reduced the ability of the materials to restrain molecular motion, especially at higher temperatures when the free volume expanded.

On the contrary, the baseline group showed the lowest elastic modulus decreasing rates in the second temperature interval. Between 35 and 55°C either the composites slightly dropped their modulus or they did not change it. Grandio showed no change in modulus at all frequencies, while Vita Zeta LC and DiamondLite either dropped their modulus or did not change it, depending on the frequency. Artglass was the only material that kept dropping its modulus at all frequencies. These results suggest that all four composites underwent some degree of post-curing during the frequency scan due to the expanded free volume between 35 and 55°C. Therefore, we can say that the frequency scan itself caused irreversible changes in samples.

All air and water-stored experimental groups substantially dropped their elastic modulus during the frequency scan in both temperature intervals. The drop in elastic modulus between 35 and 55°C suggests absence or just low post-curing during this part of the test. Probably, during their storage period at 37°C the samples underwent further polymerization, which enhanced their degree of cross-linking and consequently the amount of heat necessary to expand their free volume and induce post-curing during the frequency scan. This might justify why the elastic modulus of baseline samples remained almost unchanged between 35 and 55°C, while air and water-stored samples greatly reduced their modulus values in this temperature range. On the other hand, the higher elastic modulus decreasing rates observed for the samples stored in distilled water, in comparison to those stored in air, can be attributed to the plasticizing effect of the water that weakens intermolecular interactions facilitating the molecular movement, especially at higher temperatures

The temperature dependence of elastic modulus between 5 and 55°C varied according to the composite and seemed to be related to their percentages of filler by weight. This effect was already reported by other authors, who found that the incorporation of reinforcing particles changed the temperature dependence of elastic modulus that decreased at a slower rate than would be expected for unfilled and noncrosslinked polymers (54; 99).

In the present study Vita Zeta LC, the least filled composite tested, showed the highest elastic modulus decreasing rates between 5 and 55°C, while Grandio, the heaviest filled composite studied, showed the lowest modulus decreasing rates in this temperature interval. In other words, the heaviest filled composites were less negatively affected by rising temperatures than those with lower reinforcing filler's concentrations.

Although the temperature trial indicated no phase transition, a fairly rapid drop in elastic modulus did occur. This might be due to the high load of fillers and degree of cross-linking (27) in the polymeric phase of the materials, which are responsible for the shift of the transitions to higher temperatures.

It is possible that the polymer chains nearest to the filler particles are tightly bonded and are so highly restricted in mobility. Regarding the cross-links, they might act as anchors between the molecules restraining their motion, thereby positively affecting the ability of the material to resist to flow.

**- Viscous modulus**

The temperature dependence of viscous modulus was lower than that observed for elastic modulus and was noticed to be strongly influenced by the testing frequency. In general, the viscous modulus tended to increase when the temperature was raised, however, the number of experimental groups that improved this property in both temperature intervals gradually increased when the frequency was raised. Presumably, when tested at 5°C the materials experienced low internal friction and energy dissipation that produced low viscous modulus values. At this temperature the cross-links and reinforcing fillers might have restrained molecular motion. On the other hand, when the temperature was raised the free volume might have expanded enough to facilitate molecular motion and promote internal friction, thus increasing viscous modulus values.

At 0.1 Hz the molecules had more time to move and molecular motion was less dependent on temperature. For this reason most experimental groups did not increase their viscous modulus when the temperature was raised in both intervals. When the frequency was raised to 1 Hz, the ability of the molecules to flow was limited and became more dependent on the temperature. This might explain why the number of experimental groups that improved their viscous modulus increased at this temperature. At 10 Hz the movement of the molecules was dramatically restrained, becoming even more dependent on higher testing temperatures. Consequently, the number of groups that increased their viscous modulus was higher at this frequency than at the other two.

**- Loss tangent**

The loss tangent results were more affected by increasing testing temperatures than the viscous modulus results. All tested composites tended to increase their loss tangent when the temperature was raised between 5 and 55°C. The temperature dependence of loss tangent can be attributed to the facts that at higher temperatures materials behave more viscous-like, responding slower to deforming forces.

The highest incidence of non-significant differences in loss tangent was observed between 5 and 35°C at 0.1 Hz, for the same reasons explained above for viscous modulus results. Artglass showed the highest number of non-significant groups in this temperature interval, suggesting the more elastic-like behaviour of this material.

Vita Zeta LC showed the highest loss tangent increasing rates in the tested temperature intervals. Probably, its degree of cross-linking and lower filler content did not offer enough resistance to viscous flow at higher temperatures; the opposite might be true for the high-filled Grandio that showed the lowest loss modulus increasing rates between 5 and 55°C.

The absence of peaks in the loss tangent response over the experimental temperature range suggests the composites could have limited energy absorbing characteristics clinically.

## 4.2 Temperature scan

Temperature is perhaps the most important environmental factor affecting the dynamic properties of damping materials (100). At different temperatures polymers can dramatically change their visco-elastic properties, assuming more elastic or viscous-like characteristics.

In general, the elastic modulus versus temperature curves of polymers exhibit qualitatively five regions of visco-elastic behaviour. The first region is called the glassy region. In this state the polymer has a relatively high modulus and is very hard since the polymer chains are rigidly ordered and crystalline in nature, showing a high resistance to flow. The next phase is the glass transition region. This region is characterized by a sharp decrease in the elastic modulus of the material, since here the polymer chains obtain full segmental mobility and their state changes from glassy to rubbery.

In the rubbery plateau region the elastic modulus versus temperature curve reaches a lower plateau. In this region the polymer chains have full mobility and the properties are determined by the entangled network. Upon further heating, the polymer starts to disentangle and the elastic modulus decays further out of the measurable range. It corresponds to the fourth phase of visco-elastic behaviour in polymers called the rubbery flow region. Finally, the liquid flow region shows a sharper reduction in stress relaxation modulus because of the onset of viscous flow in the polymer.

The number of visco-elastic regions can vary according to the state of the polymer and its thermal history. Undercured polymeric samples, for example, have one more temperature region in their elastic modulus versus temperature curves. This extra region is called region of thermal reaction, which consists in a plateau inside the glass transition region that is split into two. It can be easily observed by analyzing the temperature at which the elastic modulus stopped decreasing inside the glass transition region of undercured samples.

In the present study, the number of temperature regions observed between 0°C and 200°C varied according to the material and the storage conditions of the experimental groups. All baseline samples, 1 day-stored samples (except for Artglass water-stored samples) and Vita Zeta LC samples stored in air for 7 days showed a region of thermal reaction with a more or less evident plateau region in the elastic modulus versus temperature curves. Therefore, samples inside these experimental groups were considered to be undercured. The samples in the remaining experimental groups, which did not exhibit any sign of thermal reaction during the temperature scan, were classified as fully cured.

### 4.2.1 Undercured experimental groups

#### - Elastic modulus

Between 0 and 200°C, the elastic modulus versus temperature curves of the undercured samples showed four different regions: glassy region, glass transition region, region of thermal reaction and rubbery plateau region. The exception was Grandio that showed no rubbery plateau region. The glass transition region of the undercured samples was characterized by two abrupt decreases in elastic modulus connected to each other by the region of thermal reaction that indicates a post-curing reaction during the thermal scan.

During the temperature scan the samples were initially cooled to 0°C. At this temperature the elastic modulus was high, since the methacrylate groups that remained inside the cured composite samples were trapped in a glassy, rigid state where no slippage was allowed. As temperature was gradually increased the material warmed up and expanded, increasing its free volume. Then localized bond movements and side chain movements occurred resulting in a greater compliance of the molecule and reducing the elastic modulus of the composites.

As temperature was raised further, reaching the glass transition temperature, the chains in the amorphous regions began to coordinate large-scale motions, promoting the further reaction of trapped radicals and unreacted double bonds. The additional post-curing reaction and cross-linking reduced the mobility of the molecular segments, thus increasing the elastic modulus of the composites. However, instead of this property to improve, a dynamic equilibrium was established. The positive effect of post-curing might have neutralized the negative influence of increasing testing temperatures, so that the elastic modulus remained approximately constant (plateau region) or failed slower until the additional cure was complete. The end of the post-curing process disturbed the dynamic equilibrium. Consequently, the elastic modulus rapidly restarted to decrease with temperature.

Above approximately 150°C the elastic modulus of DiamondLite, Artglass and Vita Zeta LC samples stopped to decrease forming a new plateau region, the so called rubbery plateau region. At this temperature the polymer matrix was completely softened and the elastic modulus was restrained from falling by the stable cross-linked network formed during polymerization. For this reason the elastic modulus at the rubbery plateau region is often used to relate the concentration of cross-links existing in a resin network. In this region, the modulus is a measure of the tightness and stability of the network (101). Therefore, the higher the elastic modulus at this region, the higher it is the degree of cure.

DiamondLite showed the highest elastic modulus values at the rubbery region, followed by Artglass and finally Vita Zeta LC. Grandio, on the other side, was even more resistant to temperature, since its elastic modulus did not level off to the rubbery plateau even when temperature reached 200°C. It means its elastic modulus would continue to fall if the temperature were further increased before it achieved a constant value. A high percentage of fillers, the combination of different filler sizes and a high cross-link density might have played an important role on the results for this material.

The presence of a thermal reaction region suggests that although the second DMA run followed another thermal analysis, the frequency scan clearly did not induce a full post-cure of the samples. This fact might be attributed to the low temperature range used during the first heating cycle (5-55°C), which lies considerably bellow the glass transition temperature of the composites. At lower temperatures the freedom of movement of the unreacted methacrylate units is relatively restricted, thus limiting the amount of post-curing.

### - Viscous Modulus

When the temperature was raised, the viscous modulus increased, reflecting that the polymer chains improved their ability to absorb energy due to the free volume created. However, after it reached its maximum (s) this property drastically decreased, since the material flowed effortlessly, resulting in large irreversible deformation.

DiamondLite and Artglass showed three different maximums in the viscous modulus versus temperature curves of baseline samples. The first and second maximums probably represented the relaxation processes of the unreacted methacrylate units and the polymerized resin matrix with a low cross-link density, respectively. The third maximum, however, might have resulted of further post-curing during the temperature scan thus representing the relaxation process of the thermally reacted material.

Grandio, on the other hand, showed only two maximums in the viscous modulus curves of baseline samples. The first point was probably the result of the relaxation process of the irradiated specimen containing unreacted and reacted methacrylate units. The presence of this maximum suggested a high degree of conversion that resulted in low number of unreacted units. The second maximum consisted in the relaxation process of the thermally reacted material, thus suggesting a low degree of post-curing for the baseline group during the temperature scan.

Vita Zeta LC showed a single maximum in the viscous modulus versus temperature curves of baseline samples. This finding suggests a very immature network containing low cross-link density and high number of unreacted methacrylate units.

### - Loss Tangent

Each of the drops in the elastic modulus curves corresponded to one of two maximums in the loss tangent versus temperature curves, due to two glass transitions, one at low ($T_{gLow}$) and the other at high temperature ($T_{gHigh}$). The mechanism of the split in the glass transition is considered to be additional thermal cure in the light-cured composite, which is responsible for the increase of the elastic modulus inside the glass transition region (32).

Therefore, the maximum at lower temperature in loss tangent curves might indicate the glass transition of the irradiated specimen still containing an uncured phase within the vitrified resin, whereas the maximum at higher temperature is more nearly characteristic of the glass transition of the thermally reacted material. For instance, the $T_g$ obtained from the low temperature maximum is an underestimated of actual $T_g$ of the irradiated specimen. The depression between the two loss tangent maximums, on the other side, represents the region of thermal reaction observed in the elastic modulus curves. Above the glass transition region the loss tangent curves decreased definitively, since the polymer segments at higher temperatures provide less resistance and are free to move (102).

No appreciable depression was observed between both maximums for Artglass undercured samples. It probably means that the post-curing reaction over higher testing temperatures was less extensive for this material than for the other tested composites. Other evidence that supports this theory is that its $T_{gLow}$ was much lower than that of the other tested composites. Since this maximum indicates the glass transition of the irradiated sample, as described above, this finding suggests the material contained a small amount of unreacted methacrylate units available to react when it was tested. The opposite was observed for Vita Zeta LC that showed the highest $T_{gLow}$ among the composites.

### 4.2.2 Fully cured experimental groups

**- Elastic Modulus**

In the tested temperature interval (0-200°C), it has been shown that fully cured dental composite samples underwent only three of the five temperature regions described for polymeric materials: glassy, glass transition and rubbery region. Therefore, the unique drop in the elastic modulus curves can be taken as the glass transition temperature.

Already after 1 day or 7 days storage the two inflexion points observed in the elastic modulus versus temperature curves of undercured samples converged to a single inflexion point and the region of thermal reaction (plateau) almost disappeared. The main explanation for this is the residual post-curing reaction that proceeded after irradiation when samples were stored for increasing time periods at 37°C. This reaction decreased the amount of “dormant” reactive methacrylate units available and consequently the amount of additional thermal reaction during the temperature scan. Therefore, no thermal reaction region appeared and the curves became flat. This finding supported the theory that the initial conversion rates of dental composites may be improved by the normal temperature of the mouth, especially during the ingestion of hot food and beverage (28; 34).

The elastic modulus curves of Vita Zeta LC samples stored in water for 7 days seemed to show a faster transition from the plateau to the flat-curve situation than the air-stored ones. The absorbed water is a peculiar catalyst of the post-curing chemical reaction, since it weakens polar physical bonds, thus increasing the intensity of molecular motion. The greater mobility of the molecules increases the probability of contact between the groups that have not reacted, and therefore, of creating chemical bonds. The embrittlement effect of water on the mechanical properties of composite materials was already showed by Bastioli et al. (103).

However, the plasticizing effect of distilled water reducing the elastic modulus was less noticeable during the temperature scan than during the frequency scan. It seems that the latter might have caused the materials to dehydrate. Probably, the part of absorbed water identified as free water evaporated, minimizing the negative influence of water during the temperature scan. This might have influenced the inconclusive results concerning the effect of water on the visco-elastic properties of the tested samples after this DMA run.

### - Viscous modulus

When the samples were stored for at least 1 day, the third maximum in the viscous modulus versus temperature curves of DiamondLite and Artglass disappeared. This fact can be attributed to the absence of a post-curing process during the temperature scan. On the other side, the first and second maximums decreased and increased their intensity, respectively. These events might be the result of a post-curing at 37°C during storage in air or distilled water, which reduced the number of unreacted methacrylate units (first maximum), thereby improving the degree of conversion and cross-linking (second maximum).

Already after 1 day storage, Grandio samples showed one single lower maximum in the viscous modulus versus temperature curves. This might also be attributed to the absence of post-curing during the test, resulting in one relaxation process for this material.

Vita Zeta LC showed the opposite trend observed for the other three composites and increased the number of maximums to two when the samples were stored for at least 1 day. The first maximum represented the relaxation peak of the irradiated material, while the second maximum was the relaxation of the thermally reacted material.

The viscous modulus is directly proportional to the heat dissipated per cycle and the area under the linear viscous modulus versus temperature curves is a quantitative measurement of the damping behaviour of the material. The fact that this area decreased with storage time suggests that the composite materials became more elastic and decreased their ability to dissipate energy. To the decrease of viscous modulus also contributes reduction of internal friction. The presence of pendant groups may have a plasticizing effect, explaining the greatest viscous flow observed at baseline and the initial periods of storage.

The maximums in the viscous modulus versus temperature curves of water-stored samples were lower that those of air-stored samples. This probably results of the effect of water as catalyst of the post-curing reaction. The higher degree of conversion and cross-link density restricted the ability of the molecules to flow, thus decreasing the viscous modulus values.

Materials with large secondary transitions located at temperatures below the end-use temperature will possess superior impact energy to those without such a relaxation mechanism (25). In the present study, all composites but Grandio showed a relaxation process in the oral temperature range. The high viscous modulus maximum showed by Vita Zeta LC suggests good impact properties that seem to be desirable for a veneer material.

**- Loss Tangent**

Over increasing storage periods, the two narrow loss tangent peaks observed for the undercured samples gradually shifted toward each other until a single broader and higher appeared at an intermediary temperature.

The single broad peak is characteristic of highly cross-linked polymers, whose $T_g$ does not take place at a unique temperature but over a wide range of temperatures. Therefore, the $T_g$ reported should be considered an average value, not a point at which the whole polymer changes from a glassy to a rubbery state (93). It happens because the polymerization of multifunctional monomers produces network polymers with highly heterogeneous environments as they contain very highly cross-linked regions as well as less densely cross-linked regions connecting those ones. Such an inhomogeneous distribution of environments results in a broad distribution of mobilities or relaxation times.

The height of loss tangent maximum or peak reflects the cross-link density and amount of filler, expected to cause a decrease in loss tangent and increase in peak width. Therefore, the reason why the loss tangent maximums increased their height over increasing storage periods in this study remain unclear and deserve further investigation, since the peaks were expected to decrease with time, as the materials developed a higher cross-linking density, changing from viscous to elastic behaviour (36).

The increase in height was even greater for samples stored in air, except for Grandio, where the plasticizing effect of the water might have outweighed its positive influence on post-curing. This finding is other evidence that the sorbed water increased the effective free volume, facilitating the movement of molecular chains, thus promoting a greater embrittlement of the composite materials that decreased the loss tangent. This result agrees with the study of Bastioli et al. (103)

Grandio showed a very high transition temperature with a low loss tangent even at its maximum, and remarkably low temperature sensitivity. All this characteristics added to its broad glass transition region suggest a highly cross-linked polymer with great amount of filler. Vita Zeta LC, on the other hand, showed a narrow and intense peak indicating more energy absorbed that can be attributed to lesser degree of cross-linking and lower filler content.

The lower glass transition temperatures obtained for samples conditioned in distilled water are to be expected, because sorbed water may act as plasticizer in the composite materials (80). The absorbed water expands the free volume facilitating the slippage between the molecules and consequently their flow. This finding is also not new in the literature (42; 63; 104).

Based on these findings we can say that the loss tangent results are affected by many factors including the degree of conversion and moisture content of the material. These findings are also not new in the literature (38).

# 5 Conclusions

Most of the living tissues, including dentine, have visco-elastic properties. Thus, besides the conventional quasi-static mechanical properties new composite resins to be used as dental restoratives should have compatible visco-elastic features with the tissues they will contact with. Tests such as DMA experiments in simulated physiological conditions, as presented in this work, may constitute a valuable tool for this evaluation. This method is potentially very accurate; the tests are simple to perform, and the measurements may be made rapidly.

Although the DMA is considered a non-destructive method, thus leading to considerable economy both in time and in use of materials, when assessing the frequency and especially the thermal DMA scan applied to the samples in this study, it must be recognized that they are in one sense destructive. Following the programmed frequency and temperature scans the samples were in a changed thermal condition. For this reason we could not store groups of samples that were tested and retest them after a new storage period was complete.

The visco-elastic properties of room-temperature polymerized composite resins were highly informative on their chemical composition and structure, as well as on the influence of free monomer content, internal plasticization, and degree of cure. The ranking of the elastic and viscous modulus reflects the composition of the materials. Those with high filler content have the highest moduli. However, the differences in the visco-elastic properties between the composites do not necessarily mean that one material is better than the other, but that each material would better suit a certain clinical indication. Depending on the intended use, resin composites of different elastic and viscous moduli may be desirable. For some purposes the materials should be stiff and strong, in other situations flexibility is more important. Undoubtedly, the ideal polymer for any given application will have a blend of these characteristics resulting in the optimal properties required.

Although the elastic modulus of the tested composites tended to decrease, while their viscous modulus and loss tangent tended to increased during the diverse storage periods in distilled water, the results were not uniform for all experimental groups and testing conditions. This fact can be mainly attributed to the highly crosslinked nature of the network of the composites, more difficult to swell. Another possible explanation is that for these composites the filler level was the most important factor in determining rigidity, and that variables affecting the polymer matrix played a less significant role. It should be noted, however, that the effect of other solvents and esterases present in the oral cavity may have even a more detrimental and sustained effect than water on the mechanical properties of composites (105; 106), thus playing an important role in the long-term stability of the composites.

The decrease in elastic modulus and increase in viscous modulus and loss tangent over the mouth temperature range suggests the composite networks formed did not offer enough resistance to material flow. This fact could be ascribed to an incomplete degree of conversion that typically affects the final concentration on cross-links in light-polymerized dental composite samples. However, the negative clinical consequences of this temperature dependence of the visco-elastic properties are difficult to interpret from one type of test. On the other side, since materials are basically equilibrated at 37°C in the mouth and are not thermal conductors, temperature changes from 37°C are expected to be small and should lead to only modest changes in both moduli. Therefore, no phase transition is expected.

Based on our findings we could say that light-cured dental composite restorations will contain a phase of uncured material during the initial hours and days. However, induced by the normal mouth temperature and higher temperatures due to the ingestion of hot food and beverages, the number of unreacted methacrylate units will decrease with time. In other words, considerable maturation of the composite materials will occur at mouth temperature. The clinical significance of these results is that dental resins will continue to stiffen after initial light activation and polymerization at oral temperature, which can have positive and negative effects to the restoration, such as greater rigidity and additional micro-leakage, respectively.

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## 8 Curriculum Vitae

Renata Vidal Mesquita, D.D.S.
Born on 11.07.1978 in Natal, Brazil
Family status: Married

**Education**

| | |
|---|---|
| 1995 - 1999 | Study of Dentistry, Federal University of Rio Grande do Norte (UFRN), Brazil |
| 27.08.1999 | Zahnärztliche Prüfung |
| 2000 - 2001 | Specialization in Prosthodontics, State University of São Paulo (UNESP), Brazil |
| 2002 - 2006 | Doctoral studies, Tübingen University, Germany |