Effect of Hydrothermal Aging on the Thermo-Mechanical Properties of a Composite Dental Prosthetic Material

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The aim of this investigation was to evaluate the long-term effects of aging in water on the physical properties of a new class of commercially available dental polymer composites. The selected product consists of a bisphenol A glycidyl methacrylate (Bis-GMA) resin diluted with triethylene glycol dimethacrylate (TEGDMA) and reinforced with long E-glass fibers, specifically developed for prosthetic dental bridges. Samples were prepared according to a standard procedure suggested by the producer, and aged in water at 37°C and 70°C up to 32 weeks. Samples were periodically tested in order to assess their mass variation, static flexural modulus and strength, fatigue resistance, and dynamic mechanical thermal behavior. Experimental results evidenced that aging caused two simultaneous phenomena, having opposite effects on the specimen mass. In fact, composites absorbed a certain amount of water (up to 0.8 wt% at 37°C and 1.2 wt% at 70°C) but at the same time a mass loss was detected, which could be attributed to a release of unreacted monomeric species and fragments generated by polymer chain degradation (especially at 70°C). Flexural strength strongly decreased during aging in water, reaching 80% and 45% of the initial value for samples aged for 32 weeks at 37 and 70°C, respectively. Aging practically does not affect flexural modulus, while a sensible reduction of the material fatigue life was observed. Glass transition temperature and the relative activation energy were markedly influenced by the aging in water with effects related to the water uptake and mass loss phenomena.

1. INTRODUCTION

Fiber-reinforced polymer composites consist of high performance fibers (i.e. fibers with elevated strength and modulus) embedded in a polymer matrix with distinct interfaces between them (1, 2). They offer outstanding specific mechanical properties, corrosion resistance, impact strength, and excellent resistance under fatigue loads (3–6). An important feature of composites is that their properties can be tailored according to the particular application by varying the proportions and properties of the matrix and the reinforcement, the shape, size, orientation, and distribution of the reinforcement, and by controlling the fiber/matrix adhesion level.

During the last 30 years a number of polymer based composite formulations, reinforced with either short (7) or long (8–10) fibers, were developed to serve as structural components for various dental appliances, such as retainers (11, 12), splints (13, 14), fixed prostheses (15–18), endodontic posts (19–21), complete dentures (22–25), etc.... This wide subject has been recently reviewed by Vallittu (26), and Goldberg *et al.* (27). Main advantages offered by composite materials in dental applications are related to the absence of corrosion phenomena, to the possibility of making their modulus of elasticity to match that of dentine, to their superior aesthetic appearance in the final appliance and easy chairside fabrication due to the use of light-curable resins (28–31). Open questions still limiting a wide clinical acceptance of polymer composite materials are mainly related to their behavior during long term exposure in the oral environment, in terms of retention of adequate mechanical properties like rigidity, strength, and fatigue resistance (4–6). In order to shed some light on this critical aspect, a number of *in vitro* studies have been conducted on several types of dental composite materials (32–35).

For dental applications, namely, for the fabrication of bridges and crowns, quite recently two new products have been proposed (36–44). The first, named Vectris, is made by a Bis-GMA/TEGDMA based resin (45–49) reinforced with long glass fibers, and the second, Targis, is composed of the same resin filled with

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an inorganic micro-fine filler. These materials offer unique advantages in terms of aesthetic and mechanical properties, being in principle a valid alternative to metals or ceramic for the restoration of teeth and denture. Vectris is a continuous fiber-reinforced material specifically designed to fabricate metal-free, translucent frameworks for crowns and bridges; Targis is a highly filled veneering material that provides aesthetic properties similar to those of ceramics, while the organic matrix ensures the ease and accuracy of processing of the resin materials.

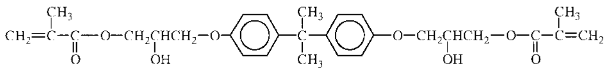
In the present study, aiming at testing the long term stability of Vectris and its capability to maintain its designed and wanted mechanical properties while in service, samples of the product named Vectris-Pontic were prepared according to the processing protocol suggested by the producer, and aged in water at 37 and 70°C. Aging effects on the composite material were monitored by measuring mass changes, and by a number of techniques including static and fatigue mechanical tests, dynamic mechanical thermal analyses, and differential scanning calorimetry.

2. EXPERIMENTAL

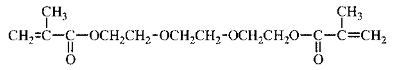
2.1. Materials

Vectris-Pontic uncured material was supplied by Ivoclar in the form of commercial packages of continuous-fiber pre-impregnated strands, whose composition is reported in *Table 1*.

The main components of the composite matrix are: 2,2-bis[4-(2-hydroxy-3-methacryloyloxypropoxy)-phenyl)-propane frequently denoted as bisphenol A glycidyl methacrylate (Bis-GMA):



and triethylene glycol dimethacrylate (TEGDMA):



$$\mathrm{CH_2{=}\overset{\displaystyle CH_3}{\overset{|}{C}}-\underset{\underset{\displaystyle O}{\|}}{C}-OCH_2CH_2\text{-}OCH_2CH_2\text{-}OCH_2CH_2O-\underset{\underset{\displaystyle O}{\|}}{C}-\overset{\displaystyle CH_3}{\overset{|}{C}}{=}CH_2}$$

Samples of Vectris-Pontic composite in the shape of 36-mm-long bars of rectangular cross section (nominal dimensions 4 mm × 1 mm) were prepared by using the devices Vectris/VS1 and Targis/Power, kindly provided by the material producer. According to the indications given by Ivoclar, the following processing steps were performed: i) each single sample was inserted in the Vectris VS1 apparatus and shaped under vacuum (150 mbar) in an open silicon mold covered by a rubber membrane; ii) a consolidation pressure (2.2 bar) was applied on the rubber membrane; iii) while under pressure the composite sample was irradiated for 6 min with a light of wavelength in the range 350–750 nm; iv) pressure was removed and the sample extracted from the Vectris VS1 device; v) sample was positioned in the Targis/Power apparatus, heated at 95°C for 10 min and simultaneously irradiated with a light of wavelength in the range 400–580 nm; vi) sample was cooled to room temperature and extracted from the Targis/Power device. Overall curing cycle, lasting about 25 min, is summarized in *Fig. 1*.

Table 1. Composition of Vectris-Pontic Composite; Data From the Producer's Technical Data Sheet.

Component	Weight percentage (%)
Glass fibers	65.0
Bis-GMA	24.5
Decandiol dimethacrylate	0.3
Triethyleneglycol dimethacrylate	6.2
Urethane dimethacrylate	0.1
High dispersed silica	3.5
Catalysts and stabilizers	< 0.3
Pigments	< 0.1

2.2. Aging

Hydrothermal aging was performed at 37 and 70°C in a great surplus of distilled water (~20 L for all studied specimens of total weight ~20 g). The aging process was followed up to 32 weeks. At each follow-up time, part of the samples were removed from the degradation baths, quickly wiped and weighted to assess the mass variation. The specimens used for fatigue and dynamic mechanical measurements were dried under vacuum at 50°C for 24 hours until a constant mass was achieved.

2.3. Testing

Differential Scanning Calorimetry (DSC) measurements were conducted using a Mettler DSC 30 calorimeter, covering 0 to 250°C at 10°C/min in nitrogen flushing at 100 ml/min.

The static mechanical properties of the samples were measured at room temperature by using an Instron tensile tester (model 4502) equipped with a 10 kN load cell, at a cross-head speed of 2 mm/min.

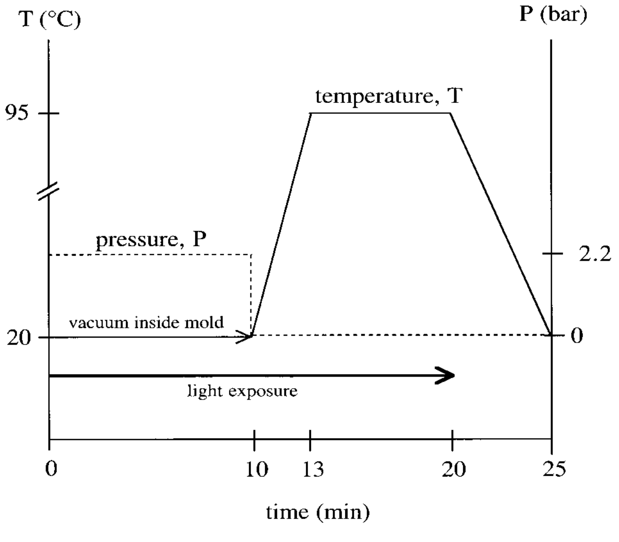


Fig. 1. Temperature, pressure, and light exposure conditions for a standard curing cycle.

Specimens with a span length of 25 mm (i.e. a span to depth ratio equal to about 25) were tested in the three point bending configuration as recommended by the ASTM standard D 790. All the reported flexural properties represent average values of at least five tests.

The flexural fatigue behavior of Vectris-Pontic samples was evaluated at room temperature by a closed loop servohydraulic MTS 858 Mini Bionix testing machine in the three point bending configuration. The sinusoidal load cyclic frequency was fixed at 1 Hz, and tests were performed under load control between a fixed minimum load of 10 N and various maximum applied loads in the range 35–150 N.

Dynamic Mechanical Thermal Analysis (DMTA) tests were conducted in the bending loading mode, by using a Polymer Laboratories dynamic mechanical thermal analyzer (model MkII) with a peak to peak displacement of 16 μm, in a temperature range from 25 to 250°C, and at a heating rate of 0.5°C/min at various frequencies (0.3, 1, 3, 10, 30, and 50 Hz)

3. RESULTS AND DISCUSSION

3.1. Differential Scanning Calorimetry

DSC thermograms of Vectris-Pontic samples are reported in *Fig. 2*. In particular, the upper line in *Fig. 2* is the result obtained on the as-received uncured system, which shows a well-defined curing exothermal peak having a maximum located at about 173°C and a specific area of 52.1 J/g. The second scan, performed on the same specimen after rapid cooling, evidences the complete curing of the resin (no residual exothermic peaks) and a clear glass transition temperature at about 207°C. On the other hand the DSC thermogram performed on a sample cured under standard curing conditions (see experimental), reveals the presence of an exothermal peak (area of about 9.3 J/g), thus indicating that polymerization is still not complete and that a residual amount of resin (about 18 wt%) completes its polymerization during the DSC scan. This uncompleted polymerization could, however, be purposely wanted in order to achieve a certain chemical bond between the Vectris-Pontic bridge and the veneering Targis material that is usually applied on it.

3.2. Mass Changes

Mass changes during aging in water at 37°C and 70°C are reported in *Fig. 3*. For both aging temperatures it can be observed that specimen mass initially increases and it reaches a maximum within the first 36 hours of immersion in water. The higher the aging temperature, the higher the extent of maximum mass increase. After this point the weight gradually decreases at a rate that increases as the aging temperature increases. This behavior can be explained under the hypothesis that two different phenomena, having opposite effects on the specimen mass, are simultaneously occurring during the in-water aging of Vectris-Pontic composite. The mass increase is surely related to the water uptake, while the mass loss could be attributed to a release of unreacted monomeric species and oligomers (especially at 70°C). As clearly evidenced in *Fig. 3*, the mass loss phenomena are strongly accelerated by the temperature. As summarized in *Fig. 4*, the separate contribution of the water uptake and mass loss can be assessed by carefully drying the samples removed from the degradation baths, thus allowing a direct measurement of their water content. As expected, both phenomena are accelerated as the temperature increases.

3.3. Static Mechanical Tests

Static mechanical properties were evaluated in a three point bending configuration. As shown in *Fig. 5*, unaged samples display an almost linear elastic load-deflection curve up to brittle fracture. Flexural modulus and strength resulted to be equal to 35 ± 1.7 GPa

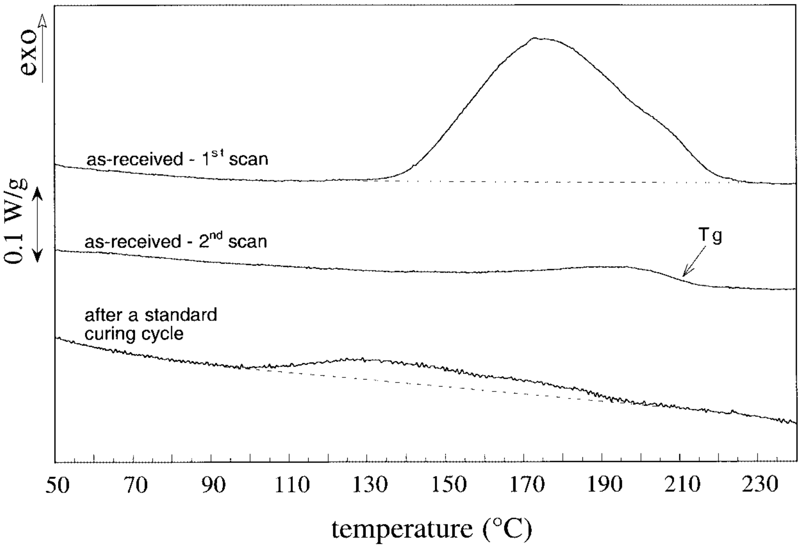


Fig. 2. DSC thermograms on Vectris-Pontic samples, as received (1st and 2nd scan) and after a standard curing cycle.

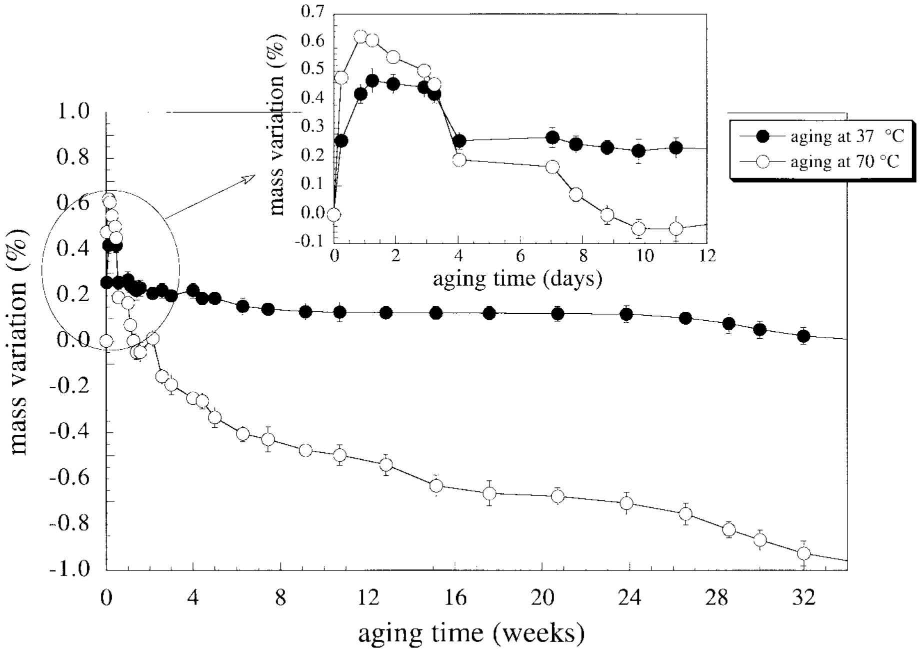


Fig. 3. Mass changes during in water aging at 37°C (●) and 70°C (○).

and 1376 ± 56 MPa, respectively, in good agreement with the values reported on the Vectris technical data sheet. As a consequence of the water exposure, a marked decrease of both maximum load and deflection occurs; by way of example the load-deflection curves of samples aged for 32 weeks at 37°C and 70°C are reported in *Fig. 5*. Flexural modulus and strength data for various aging times at 37°C and 70°C are shown in *Figs. 6* and *7*, respectively. In any case, modulus values are almost unaffected by the *in-vitro* aging, the variation being within ± 10% of the initial value. Vice versa, clear aging effect is observed on the flexural strength, which shows a large reduction only after a few weeks. The residual strength reduces to 80% of the initial value (i.e. 1100 ± 66 MPa) after 32 weeks of water immersion at 37°C, and becomes less than one half (i.e. 615 ± 66 MPa) after 32 weeks at 70°C. Similar results have been reported by Ferracane and co-workers for particle-filled Bis-GMA based composites (31). The experimental behavior can be tentatively explained by supposing a weakening of the polymer/matrix interface due to the hydrothermal

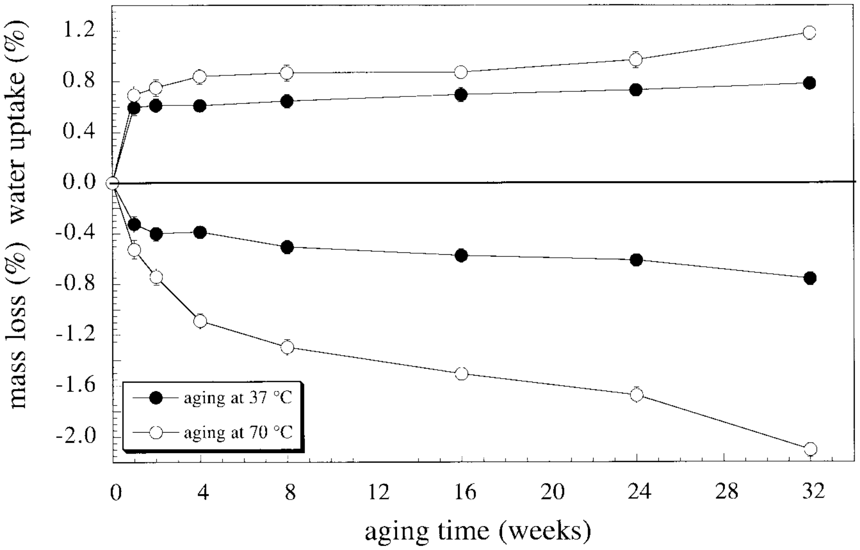


Fig. 4. Water uptake and mass loss during in water aging at 37°C (●) and 70°C (○).

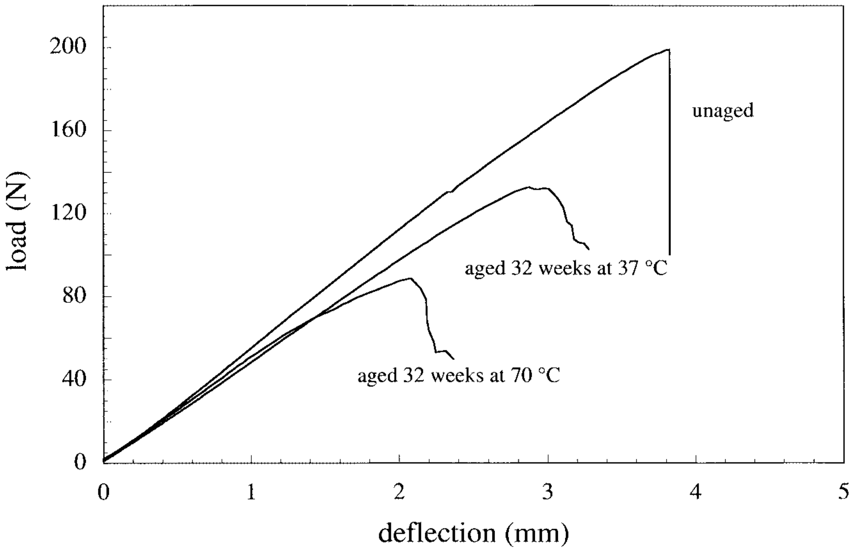


Fig. 5. Effect of the hydrothermal aging on the load-deflection curves evaluated in a three-point bending test configuration.

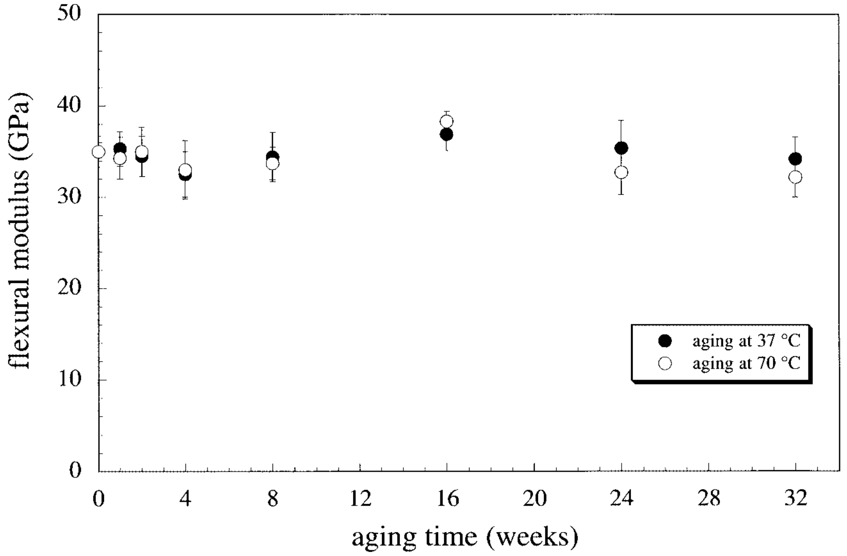


Fig. 6. Flexural elastic modulus during in water aging at 37°C (●) and 70°C (○).

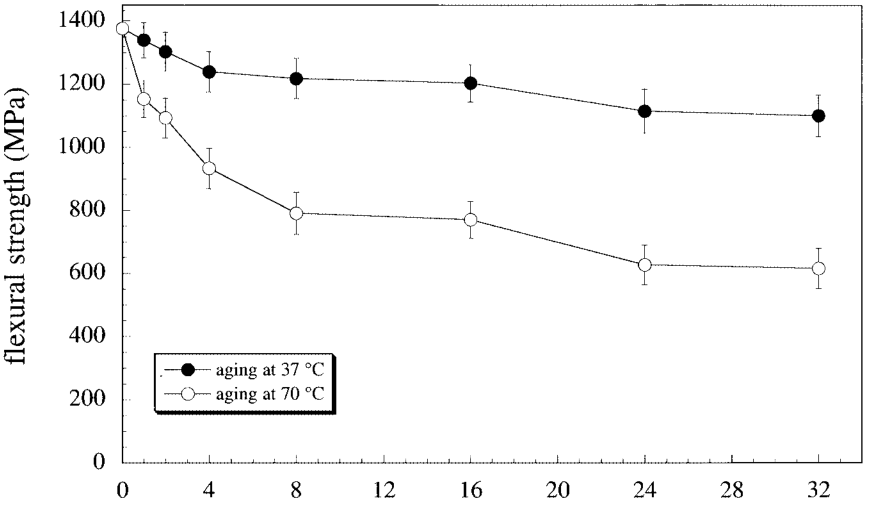


Fig. 7. Flexural strength during in water aging at 37°C (●) and 70°C (○).

aging (50–52). In fact, it is well known that for fiber-reinforced composites a decrease of the fiber/matrix adhesion mainly affects the ultimate properties, like strength and toughness, while elastic properties, evaluated at low deformations, are only slightly influenced (53–56).

3.4. Fatigue Life

The fatigue behavior of unaged Vectris-Pontic samples was first investigated by measuring the residual flexural strength of specimens subjected to 10^4 fatigue cycles at 1 Hz, under stress levels oscillating between a minimum value fixed at 70 MPa (i.e. applied load 10 N) and a maximum value varying from 895 to 1070 MPa (125–150 N). Results are reported in *Fig. 8*, which clearly shows how the unaged Vectris-Pontic composite manifests very little sensitivity to fatigue loading, at least up to maximum applied stresses of about 1036 MPa, i.e. about 75% of the initial stress at break. On the other hand, when the maximum applied load is modestly increased to 1070 MPa, the sample fails after 4036 cycles. The effect of hydrothermal aging on the fatigue resistance is summarized in *Figs. 9a* and *9b*, where the number of cycles to failure is reported as a function of the aging time. Specimens aged at 37°C up to four weeks do not fail even after 10^6 fatigue cycles, under a maximum applied stress of 1001 MPa, i.e. not exceeding 81% of the static residual strength. At longer aging times, the fatigue life dramatically decreases. At 8 weeks the fatigue life drops to 10,000 cycles, and longer aging provokes a marked decrease of the material's ability to resist fatigue. For samples aged at 70°C, a similar trend is observed, but with enhanced effects, since fatigue data are obtained at a markedly lower value of the maximum applied stress (i.e. 572 MPa).

3.5. Dynamic Mechanical Thermal Analysis

The effect of temperature on dynamic storage and loss modulus as measured with DMTA is reported in *Fig. 10* for unaged and aged samples. It can be observed that long term aging results in a slight decrease of the room-temperature storage modulus, as evidenced in static tests. Nevertheless, storage modulus variation with temperature is negatively influenced by aging to a marked extent. Loss modulus shows a wide transition peak with a maximum that can be considered as the glass transition temperature. It is observed that the effect of aging is to shift the peak toward lower temperature and to spread the peak to a wider temperature region. The variation of the glass transition temperature taken as the maximum of the loss factor peak (tanδ) during aging at 37°C is reported in *Fig. 11* for various testing frequencies. At any given frequency, the effect of aging on the Tg position is to cause an initial decrease followed by a gradual increase; this holds even for the higher aging temperature. This behavior can be attributed to the contrasting effects due to the water sorption (plasticizing effect) and to mass loss and/or a further crosslinking reaction (antiplasticizing effect). Because of the time-temperature equivalence in viscoelastic materials, the dynamic mechanical behavior may be tested against frequency as well as against temperature, wherein the effect of longer time (lower frequency) is equivalent to that of higher temperature. Thus, the α peak (Tg), evaluated as the maximum of the loss factor curves, is shifted to lower temperatures as the frequency is decreased (57). The frequency-temperature dependence is usually expressed by an Arrhenius type equation, as follows:

$$\omega = A \exp\left(\frac{-\Delta E}{RTg}\right) \tag{1}$$

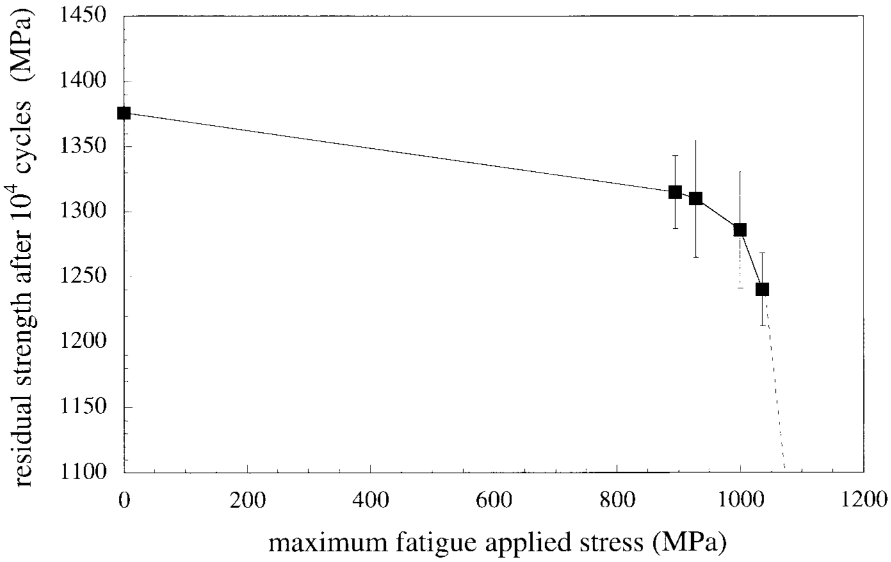


Fig. 8. Residual flexural strength of unaged samples after 10^4 fatigue cycles under various maximum stress values at 1 Hz frequency.

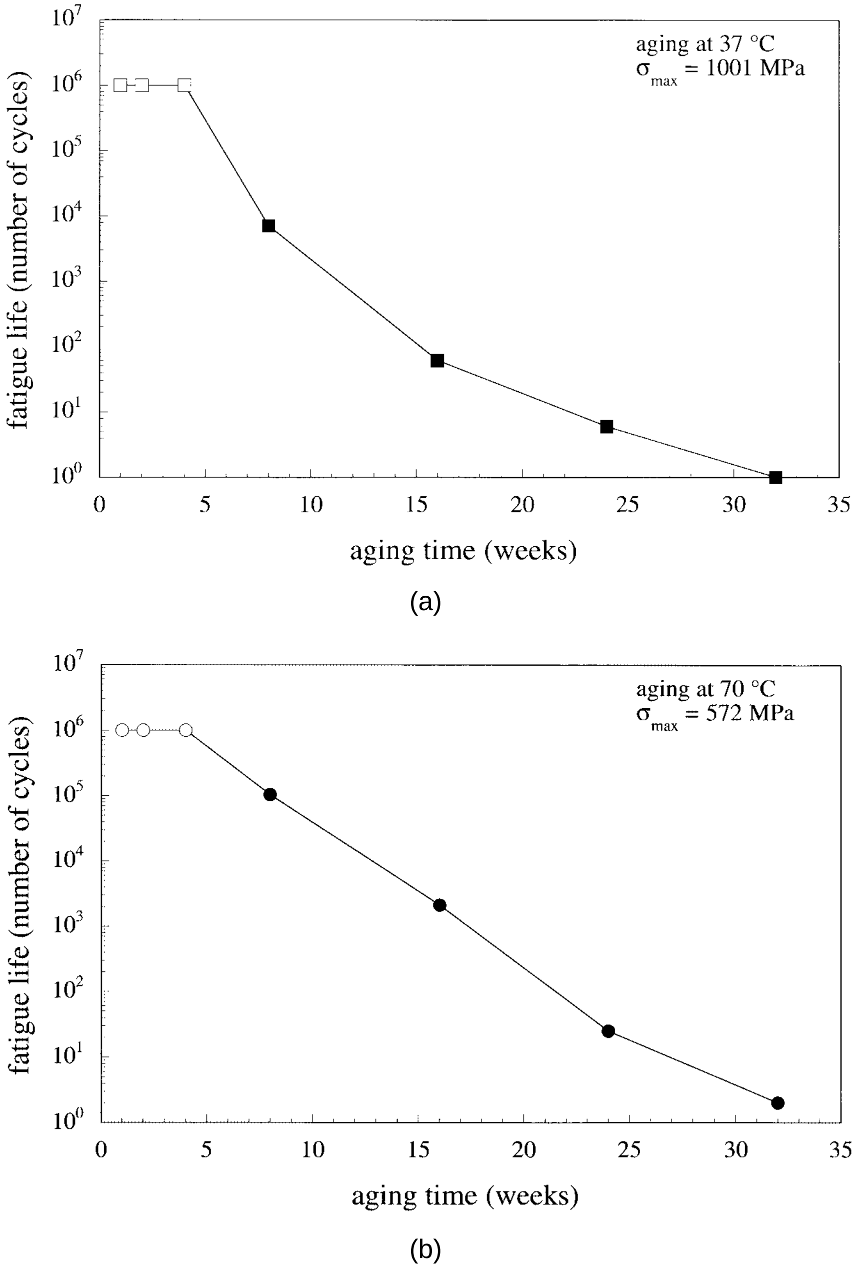


Fig. 9. Fatigue life at 1 Hz frequency vs. the aging time. Open symbols refer to samples still unbroken after 10^6 cycles. a) □ and ■ aging at 37°C, maximum stress equal to 1001 MPa; b) ○ and ● aging at 70°C, maximum stress equal to 572 MPa; In any case, minimum applied stress is equal to 70 MPa.

where ΔE is the activation energy for relaxation, corresponding to the energy barrier for polymer chain movement (58), ω is the frequency. Linear regression of the experimental frequency vs. $1/Tg$ data yields a line with a slope that produced the activation energy values presented in *Fig. 12*. It is interesting to observe how the activation energy for the glass transition temperature decreases during aging, reaching a minimum value after 4 weeks, and then steadily increases. This experimental evidence further supports the hypothesis of the contrasting effects played by the water uptake and mass loss during the sample degradation. For as concerns the glass transition activation energy values, no great difference is found between the two different aging temperatures.

4. CONCLUSIONS

This study was undertaken to investigate the effects of hydrothermal aging at 37°C and 70°C on the thermomechanical properties of a commercial composite dental prosthetic material consisting of a Bis-GMA/TEGDMA resin reinforced with long E-glass fibers.

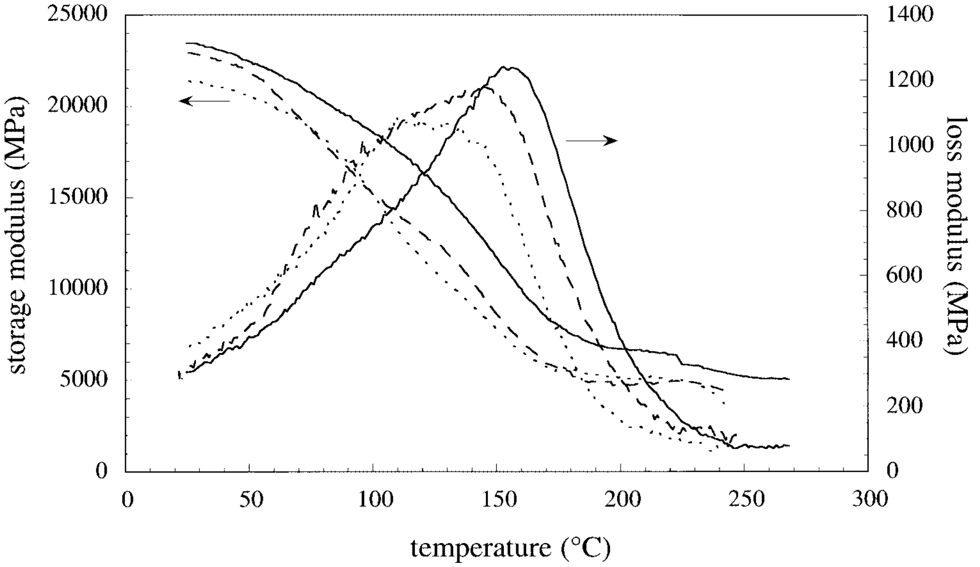


Fig. 10. Dynamic storage and loss moduli vs. temperature evaluated on samples unaged (continuous line), aged for 32 weeks at 37°C (dashed line), and aged for 32 weeks at 70°C (dotted line) measured at 1 Hz frequency.

Elastic flexural modulus was practically unaffected by long-term aging in water. On the other hand, the flexural strength strongly decreased during aging in water, reaching 80% and 45% of the initial value for samples aged for 32 weeks at 37 and 70°C, respectively. At the same time, flexural fatigue behavior was negatively influenced by aging, since a sensible reduction of the material fatigue life was observed for both aging conditions. The simultaneously occurring phenomena of water uptake and mass loss during aging influenced the glass transition temperature and the relative activation energy.

These results suggest that aging in water probably causes a weakening of the interface between glass fiber and matrix, due to the hydrolytic attack of water on the interface and/or the fiber itself.

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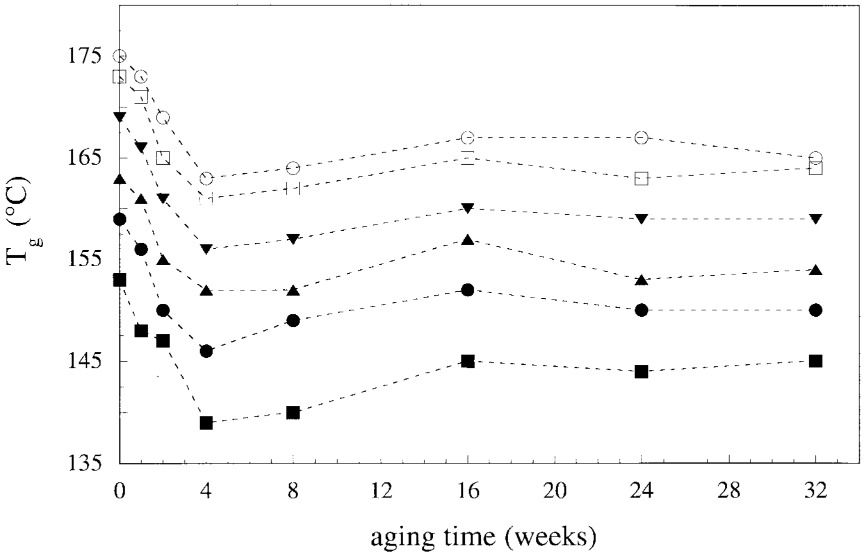

Fig. 11. Glass transition evaluated as the tanδ peak in DMTA at various frequencies (○ 50 Hz, □ 30 Hz, ▼ 10 Hz, ▲ 3 Hz, ● 1 Hz, ■ 0.3 Hz) during aging at 37°C.

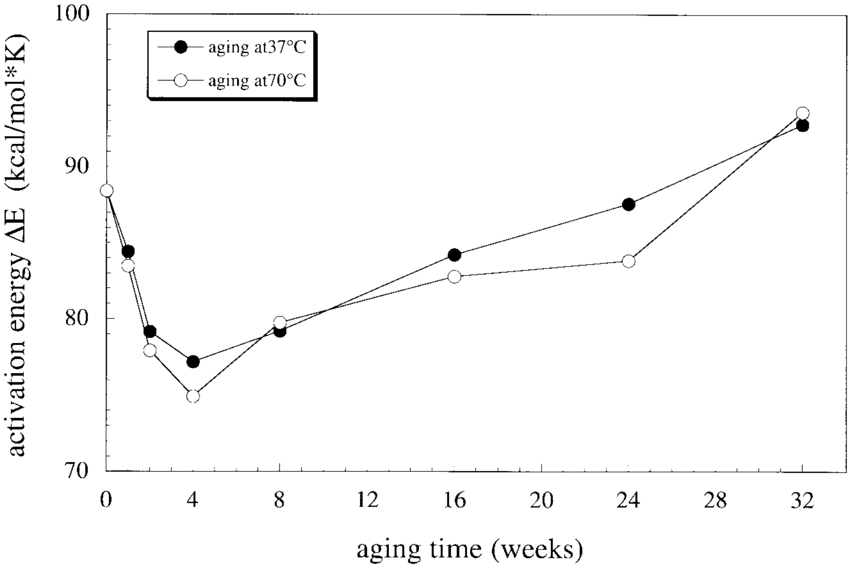

Fig. 12. Effect of in water aging at 37°C (●) and 70°C (○) on the activation energy for the glass transition.

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