Brazilian Dental Journal (2013) 24(6): 599-604
http://dx.doi.org/10.1590/0103-6440201302263
ISSN 0103-6440

Microstructure and Mechanical Properties of Composite Resins Subjected to Accelerated Artificial Aging

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The aim of this study was to investigate the influence of accelerated artificial aging (AAA) on the microstructure and mechanical properties of the Filtek Z250, Filtek Supreme, 4 Seasons, Herculite, P60, Tetric Ceram, Charisma and Filtek Z100. composite resins. The composites were characterized by Fourier-transform Infrared spectroscopy (FTIR) and thermal analyses (Differential Scanning Calorimetry - DSC and Thermogravimetry - TG). The microstructure of the materials was examined by scanning electron microscopy. Surface hardness and compressive strength data of the resins were recorded and the mean values were analyzed statistically by ANOVA and Tukey's test (α=0.05). The results showed significant differences among the commercial brands for surface hardness ($F=86.74$, $p<0.0001$) and compressive strength ($F=40.31$, $p<0.0001$), but AAA did not affect the properties (surface hardness: $F=0.39$, $p=0.53$; compressive strength: $F=2.82$, $p=0.09$) of any of the composite resins. FTIR, DSC and TG analyses showed that resin polymerization was complete, and there were no differences between the spectra and thermal curve profiles of the materials obtained before and after AAA. TG confirmed the absence of volatile compounds and evidenced good thermal stability up to 200 °C, and similar amounts of residues were found in all resins evaluated before and after AAA. The AAA treatment did not significantly affect resin surface. Therefore, regardless of the resin brand, AAA did not influence the microstructure or the mechanical properties.

Key Words: composite resins, aging, calorimetry.

Introduction

In order to minimize the problems related to polymer degradation, it is essential to know the surface and structural behavior of polymeric materials. This concern has been expressed by various authors (1,2) who highlighted the need for a deeper understanding about the polymeric matrix and clinical strength of the materials (3).

Mechanical properties are relevant to the durability of composite resins (3,4) and are related to the filling ratio, which includes such factors as the shape, type, number and distribution of charged particles (5). These properties also depend on the degree of polymerization (6). Persistence of residual monomers culminates in reduced strength and hardness and interferes on the final outcome of the restorative material (7).

Knowledge of the structure-property relationships in composite resins allows analyzing the factors that influence their behavior and act on them to improve performance and enables the improvement of performance. Infrared spectroscopy (IR) stands out as one of the main characterization techniques, allowing the structural identification and/or determination of the degree of polymerization (7-8). Information about the percent weight of inorganic particles, polymerization efficiency, thermal stability and composite crystallization can be obtained via thermal analyses (9). Morphological analysis conducted by scanning electron microscopy (SEM) provides insight into particle size and shape as well as surface and bulk morphology (5).

An accelerated artificial aging (AAA) system (10) that operates by pre-set UV-B light, moisture and heat cycles can be employed for short- and long-term analyses of the behavior of non-metallic materials (11). Changes such as color or brightness loss, opacity and adhesion, as well as the appearance of cracks are probably influenced by intrinsic chemical modifications in the material during the degradation process elicited by AAA (12).

For a better understanding of the events which are correlated with the mechanical and microstructural properties with aging effect, in the present study were employed characterization techniques such as IR, TG, DSC and SEM analyses as well as mechanical tests, in order to assess the stability of composite resins used in restorative procedures before and after AAA. The tested hypothesis was that the accelerated aging promotes changes in the structure and mechanical properties of composites.

Material and Methods

Specimens

Eight composite resins were used: Z250 (3M/ESPE,

St. Paul, MN, USA; microhybrid); Supreme (3M/ESPE; Nanoparticle); 4 Seasons (Ivoclar/Vivadent AG, Schaan, Liechtenstein; microhybrid with nanoparticles); Herculite (Kerr, Romulus, MI, USA; microhybrid); P 60 (3M/ESPE; Condensable); Tetric Ceram (Ivoclar/Vivadent; microhybrid); Z 100 (3M/ESPE; microhybrid); Charisma (Heraeus Kulzer, Dormagen, Germany; microhybrid). Teflon matrices were used for preparation of specimens with 9-mm diameter and 2-mm height, for the surface hardness tests, IR, TG and DSC analyses and SEM and, for the strength to compression assays, with 4-mm diameter and 8-mm height. The specimens were obtained using the incremental technique and light curing was carried out with a halogen lamp (Ultralux electronic; Dabi Atlante, Ribeirão Preto, SP, Brazil), followed by polishing with sandpaper discs (Sof-Lex; 3M, Sumaré, SP, Brazil). Eighty-four specimens were prepared for each resin and then divided in two groups: NA (non-aged) and A (aged). In each group, 30 specimens were used for the compression test and surface hardness (n=15 for each test), and 12 for SEM analysis, TG, DSC, and IR (n=3 for each test).

Accelerated Artificial Aging (AAA)

Group A specimens were stored in plastic containers with distilled water and kept in the absence of light, until their fixation in the AAA system (Comexim Materias Primas Ltda, São Paulo, SP, Brazil). The system operated under UV light, and condensation was successively and automatically performed during separate cycles. The UV-B light source consisted of 40 W fluorescent tubes with emission concentrated in the ultraviolet B region. The condensation process was carried out by exposing the specimens to a heated, saturated air-vapor mixture. The duration of the operation program included four hours of exposure to UV-B light with radiation concentrated between 280 and 320 nm, at 50 °C, followed by four hours of condensation at 50 °C and maximum aging time of 384 h, which corresponded to a ten-year aging. After this procedure, the samples belonging to group A were submitted to mechanical tests as well as thermal and SEM analyses. All procedures were conducted in accordance with the ASTM-G-53 standard (10).

Surface Hardness Assays

The surface hardness tests were accomplished on a microhardness tester (Shimadzu model HMV-2000; Shimadzu, Tokyo, Japan) with a 50 kgf load for 5 s. Three measurements were made on each specimens with Knoop type diamond indenter.

Compressive Strength Test

Strength to compression was measured in a universal testing machine (EMIC DL-2000; São José dos Pinhais, PR, Brazil) with 2000 kgf load at crosshead speed of 1 mm/min. Tesc version 2.0 (EMIC, São José dos Pinhais, PR, Brazil) software was employed for entering data.

Physical Characterization

Three techniques were selected for characterization: Fourier-transform Infrared spectroscopy (FT-IR), Differential Scanning Calorimetry (DSC), and Thermogravimetry (TG). The FTIR spectra were acquired by a Spectrum GX spectrometer (Perkin Elmer Inc., Wellesley, MA, USA) working in the transmission mode and using the sample pressed into KBr pellets. A total of 16 scans with a resolution of 4 cm^{-1} were recorded. TG was conducted in a thermal analyzer TGA V5 (TA Instruments, New Castle, DE, USA). The investigated parameters were heating from ambient temperature to 900 °C at a heating rate of 20 °C/min in an inert nitrogen atmosphere. DSC was carried out on the DSC Diamond (Perkin Elmer Inc.) equipment. The specimens were cut into pieces of approximately 10 mg, and were then placed in an aluminum crucible that was later transported to the calorimeter. Heating and cooling curves at 20 °C/min were utilized; after each cycle, the sample was annealed for three minutes, so as to erase the thermal history of the material.

The materials were also characterized in a scanning electron microscope (XL-30 FEG; Philips, Eindhoven, The Netherlands) at an accelerating voltage of 20kV.

Statistical Analysis

Surface hardness and strength to compression were measured before and after AAA. The data were submitted to the following statistical tests: normality test (Kolmogorov-Smirnov – $p>0.05$ = normality), parametric test (ANOVA) and multiple-comparison test (Tukey - $p<0.05$ = level of significance). The NCSS 2007 (NCSS, Kaysville, UT, USA) software was employed for the analyses.

Results

Mechanical Assays

The mean values obtained in the tests are presented in Table 1.

Comparing the same material, it was observed that there was no statistically significant difference in surface hardness ($F=0.39$, $p=0.53$) and compressive strength ($F=2.82$, $p=0.09$) before and after accelerated aging in any resin. However, aging caused a slight non-significant increase in the hardness of Charisma and Z250 microhybrid resins and P60 posterior resin; for the other resins a reduction in this property was noted. The compressive strength was slightly increased for the Tetric Ceram, Seasons, Herculite and Supreme resins, and decreased for others. An interaction was observed between the type

of composite resin and AAA factors (F=4.51, p<0.0002) (F=3.20, p<0.004). The factor analysis revealed significant differences between resin hardness (F=86.74, p<0.0001) and compressive strength (F=40.31, p<0.0001) among the brands. The resin Z100, before AAA showed hardness and compression higher than the other resins, and after AAA also showed higher hardness.

Morphological Analysis

The SEM micrographs showed that AAA had no significant influence on the surface of the tested composite resins. However, aging did elicit a more eroded appearance on the surface of the samples.

Physical Characterization

The TG curves recorded for the samples of the NA and A groups revealed a similar thermal behavior. There were no signs of volatile compounds or non-reticulated groups, which are generally eliminated up to approximately 100 °C. Mass loss was uniform and ranged between 20 and 30 wt% for all the samples, which resulted in inorganic around 70 to 80 wt% (Fig. 1).

DSC gave information about the light-curing efficiency, which is vital to structure-property relationships. Results attained for the NA and A resin samples of the same brand were similar. Figure 2 depicts the typical DSC curves achieved for NA and A samples for the resins Charisma and Z250. Results obtained for the other resins were similar.

The materials were not different in terms of the degree of polymerization, as already verified by FTIR spectroscopy. The only observation was that different brands displayed slightly different curves, which cannot be considered statistically significant or be attributed to the aging process. FTIR analyses (spectra not shown) indicated that NA and A specimens of the same brand exhibited similar spectral profile. New bands did not appear, and there were no alterations in the relative intensity of the detected bands. Therefore, the molecular structure of the composite resins remained unchanged after AAA.

Table 1. Mean values of surface hardness and compressive strength

Sample groups*	Surface hardness (HK)	Compressive strength (MPa)
Charisma NA	55.1	351.7
Charisma A	58.3	317.8
Tetric Ceram NA	63.9	296.5
Tetric Ceram A	60.1	302.8
Seasons NA	62.5	254.8
Seasons A	62.2	270.4
Herculite NA	72.8	294.8
Herculite A	69.1	308.4
Supreme NA	78.4	296.6
Supreme A	72.4	304.5
Z250 NA	77.3	362.4
Z250 A	88.5	351.4
P60 NA	77.9	399.6
P60 A	88.9	333.7
Z100 NA	107.3	399.6
Z100 A	101.5	333.7

NA: non-aged. A: aged.

Discussion

This study used microstructural characterization techniques such as infrared (8) and thermal analyses (13) and tests of surface hardness (14) and compressive strength (4), as well as scanning electron microscopy (SEM) to check the influence of AAA on the properties of composites. Numerous studies reported that artificial aging leads to a significant decrease in the mechanical properties of dental materials (15,16), but in this study the aging process did not cause significant changes in the properties of the aged resins and the study hypothesis was rejected.

The mechanical analyses were selected because compressive strengths are transmitted to the supporting tissues of the oral cavity and consequently to dental restorative materials. When parafunctions are present, this force is multiplied, often leading to fracture of the tooth and restoration (17), so laboratory testing of compressive strength allows observing *in vitro* fractures that may occur clinically (18). On the other hand, hardness is a mechanical characteristic used to forecast the wear behavior of the material (14).

To analyze the surface behavior of composite resin restorations after a long time, a result would be required for that period and then proceed to evaluate the results (11). However, a major problem is that the industrial evolution is very fast, and one needs to constantly know the composition to predict the behavior of materials, which justifies the AAA used in this study.

In dentistry, a material may be set to a safe temperature, so that it does not suffer any problems resulting from residual reactions related to a higher degree of polymerization. Before and after subjecting the samples to the artificial aging process, the maximum heating temperature without damaging the material was determined and compared to verify if the aging process would result in a loss of weight for thermogravimetry analysis (TGA) (19).

This test evaluated the possible changes in weight (loss

or gain), depending on the temperature and/or time. The weight loss started around 200 °C and increased near 300 °C. Above 600 °C the mass stabilized. This was observed both before and after aging. In the same way, the samples showed similar behavior showing mass loss in the temperature range from 250 to 450 °C. TG analysis did not reveal the presence of volatile materials, which have been disposed of up to approximately 100 °C. Mass loss was uniform, and the samples were 70 to 80% by weight of residue, which was not removed during the decomposition of the organic part. Thus, the samples belonging to the aged and non-aged groups exhibited similar behavior.

According Ferracane (20) there is a correlation between the degree of polymerization and the properties of the composites, which can be checked by infrared analysis. This technique was used since the degree of conversion of the polymer can affect the chemical stability of the composite. The hypothesis was that the presence of carbon double bonds could make the material more susceptible to degradation reactions (21). The results showed that the polymerization process was complete, and that there were no differences in FTIR spectra of the specimens before and after aging. Comparing the curves obtained for the various brands, no differences that would justify a change in the mechanical behavior after AAA were observed. The mechanical properties of different materials here investigated may be explained because the size and amount of inorganic filler dispersed in the composite was not due to lack of polymer conversion.

The continuous degree of conversion (DC) indicates the

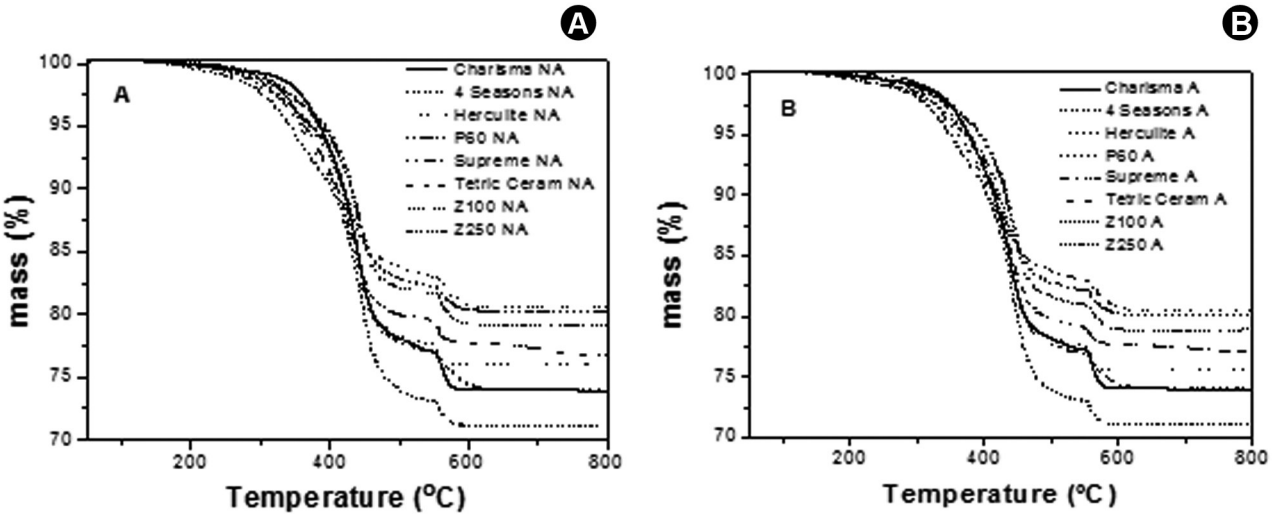

Figure 1. TG curves for the studied composite resins non-aged (NA) and aged (A).

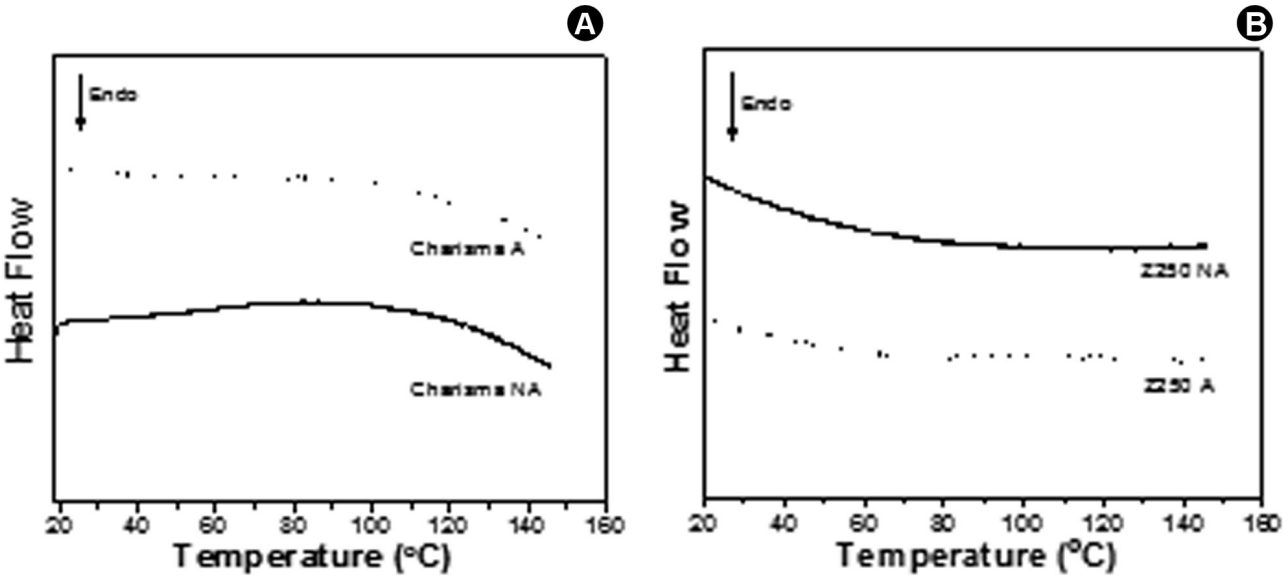

Figure 2. DSC curves obtained for Charisma and Z250 before and after aging.

percent conversion of monomer to polymer, and an index for the qualitative and quantitative analysis of the extent of polymerization and physical-mechanical characteristics. The composite clinical performance is compromised by a low DC, since residual monomers may act as plasticizer, reducing the mechanical properties and increasing swelling. Due to the crosslinked polymeric structure, the DC is associated with the surface hardness, flexural strength, tensile strength, flexural modulus, tensile strength and wear resistance (22).

The thermal energy of the reaction can be measured by differential scanning calorimetry. DSC is known as a highly sensitive and as one of the most direct methods for evaluating the thermal and physical characterization of materials, such as DC. The critical temperature of a resin can be determined, and information on the efficiency of light curing can be obtained. In this study there was no evidence of failure in the materials polymerization. The only observation was that there was little difference in the curves of different brands, which cannot be considered significant in terms of brand or the aging process. Thus, the accelerated artificial aging process does not influence the polymerization process of the resins (23).

The effect of aging on the surface of the composites was also evaluated in the present study by scanning electron microscopy which showed that this did not significantly affect the resin surface. Only a small erosion on the surface of the aged specimens was observed.

The properties of a composite resin also depend on the filler content, type of fillers and coupling efficiency of the particles (24). In the present study, although there was no statistical difference between the aged and not aged composites, such as mechanical properties, there was an interaction between the resin brands and the resin Z100, with higher amounts of inorganic particles, showed superior mechanical results. Studies show that better mechanical properties are observed for materials with smaller particles and hence a greater percentage, by volume, which results in a better distribution, since the distance between adjacent particles is smaller, thereby increasing the contact area (25). This condition justifies the results of this study where the resin with higher volume of zirconia and silica showed a better performance in terms of hardness and compressive strength.

The results showed that all the tested materials exhibited good mechanical properties and good long-term chemical stability. Although this analysis can not exactly mimic the fault mechanisms found in clinical practice, they are important to understand the relationship between structure and properties.

It may be concluded that the characterization and structure properties showed that the materials exhibited similar behavior in terms of thermal stability and polymerization before and after the aging procedure. A resin with better performance could not be indicated, because all composites subjected to AAA in this study behaved in a similar manner.

Resumo

A influência do sistema de envelhecimento artificial acelerado (EAA) na microestrutura e nas propriedades mecânicas das resinas compostas Z250, Filtek Supreme, 4 Seasons, Herculite, P60, Tetric Ceram, Charisma e Filtek Z100 foi investigada. Os compósitos foram caracterizados por espectroscopia de infravermelho com transformada de Fourier (FTIR) e análises térmicas (calorimetria exploratória diferencial - DSC e termogravimetria - TG). A microestrutura dos materiais foi analisada por microscopia eletrônica de varredura. Os dados de dureza superficial e resistência à compressão foram registados para as resinas e os valores médios foram submetidos ao teste de Kolmogorov-Smirnov ($p>0,05$), ANOVA e teste de Tukey ($\alpha=0,05$). Os resultados mostraram diferenças significativas entre as marcas comerciais em termos de dureza ($F=86,74$, $p<0,0001$) e resistência à compressão ($F=40,31$, $p<0,0001$), mas o EAA não afetou as propriedades (dureza superficial: $F=0,39$, $p=0,53$, resistência à compressão: $F=2,82$, $p=0,09$) de qualquer uma das resinas. FTIR, DSC e análise de TG revelou que a polimerização da resina foi completa, e não houve diferenças entre os espectros e os perfis de curva térmica dos materiais obtidos, antes e depois de EAA. TG mostrou a ausência de compostos voláteis e evidenciou uma boa estabilidade térmica até 200 °C, e quantidades similares de resíduos foram encontradas em todas as resinas avaliadas, antes e depois de EAA. O tratamento de EAA não afetou significativamente a superfície das resinas. Portanto, independentemente do tipo de resina, o EAA não influenciou a microestrutura e as propriedades mecânicas.

Acknowledgements

The authors thank CNPq , FAPESP, FAPEMIG and CAPES for the financial support.

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Received May 23, 2013
Accepted October 10, 2013