Giant Dielectric Constant and Mechanical, Heat Conducting and Structural Properties of Dental Composites by Adding Ca Ions

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Abstract

It was investigated the micro-structural, mechanical, heat conducting and dielectric properties of composites by Ca addition. It was purposed the investigation of dielectric properties of the composites and the improvement of the mechanical strength and the decrease of the thermal conductivity. It is found that the Ca addition causes diffusion in the main matrix or accumulated in the inter-granular region of the composites. The thermal and mechanical properties showed a strong relationship between the type of composites and Ca content. It is concluded that the diffusion of Ca into the main matrix causes the improvement of the mechanical and thermal conducting properties which can be used in the commercial composite resins in the near future. The dielectric measurement of the composites showed giant values (10⁸-10⁹) depending on the Ca content and the composites which are promising results for electronic applications.

Keywords: Dental Composite; Mechanical Strength; Thermal Conductivity; Dielectric Constant

Introduction

Dental composite resins were started to use in the middle of 1960’s as a commercial dental restoration material [1,2]. It is well known that the composite resins consist of initiating agent, resin matrix (polymer matrix) and inorganic fillers [3,4]. Their mechanical, esthetic and biocompatible properties have made a major impact for using in the clinical studies and the manufacturer gives much attention for developing and finding of new dental composite materials.

The dental composites can be classified by the filler particles and their ingredients which can cause the change of their mechanical, heat conducting and the other properties [5-7]. So, the filler technology is particularly significant for improving their dental properties since the filler ingredients can cause the change of the mechanical, thermal, structural properties, etc [7-12]. The fabrication process of composite resins also has an importance for the dental properties of the composites. Furthermore, the inorganic fillers in the dental composites cause the protection of polymerization shrinkage during to light curing process and so the mechanical strength of the dental composites will be increased [13].

Some of the important properties expected from the dental composites can be given as high mechanical strength, low thermal conductivity and structural stability during to the aging [14,15]. These properties can be provided by improving or modifying the inorganic fillers of the composite resins. The manufacturers use the elements of Ti, Al, Ba, Mo, Zr, etc. for increasing the physical properties of the composites [16-21].

To improve, mechanical, thermal and structural stability of the inorganic fillers, scientist has been working to find new materials, new fabrication techniques and modification of the composites. For this reason, oxide materials such as SiO₂, ZrO₂, TiO₂, Al₂O₃ and B₂O₃ which can improve the mechanical strength, thermal conductivity or structural stability of the system are doped, added or substituted in the dental composites [22-24]. Generally, the doping of the elements or compounds in the composites are chosen to be between 5% to 30% ratio since the excess content in the main matrix causes the formation of defects which the mechanical and thermal properties exhibit worse behavior when compared by the pure materials [25-28].

The calcium ions have been mixed into resins to fabrication of the composites in literature [29-31]. It was mentioned by Skrtic et al. [32], that non-uniform mixing of the adding materials in the composite can cause formation of the defects for critical calcium content in the materials. In this case, the Ca ions can penetrate to inside of the cracks in the composites in the form of the clusters [33].

Dielectric properties are related to electrical nature of the materials. As well known, the materials including organic matrix have gained wider application in electronic devices especially as a dielectric components due to easier fabrication, flexibility, better resistance for chemical attacks [34]. Since the dielectric polymers with high or low dielectric constants are used in the electronic industry, new or existing composites including polymers which can be modified by structural change or by additives can be used for future technologies. The other important properties of applications of the composites including polymers in technology are the flexibility of these materials for wide range of temperatures [35].

In this study, it was investigated the mechanical, thermal, dielectric and structural properties of the Ca added and un-added composites in detail. It is found that G-aenial Universal Flo (GU) showed better mechanical properties and lower thermal conductivity which can be used for commercial production. The dielectric constants of the composites were found as a giant value of∼10⁸ which can be used in electronic applications.

Methods

Some of the commercial dental composites includes Arabesk Top (AT), Clearfil Majesty Esthetic (CM), G-aenial Universal Flo (GU) and Alpha core LC (AC), (table 1) which were used for the investigation of structural, mechanical, thermal and dielectric properties. The The CaCO₃ (alpha aesar cas no 471-34-1) was added and mixed to the systems at ratios of 3%, 6% and 9% at 10 minutes in a dark room due to the fast solidification of the materials from the gel form. After obtaining a homogeneous mixture, the pure and Ca-added composites were poured into the Teflon die which have 8 mm × 2 mm diameters and presses under 1 kN pressure.
Transparent band was placed both sides of the samples and they were polymerized under LED (Light Emitting Diode) which has a wavelength of 400 nm for 40 seconds.

The structural properties of the materials were performed by XRD pattern using CuKa radiation between 2-80° and Rad-B Dmax wavelength of 400 nm for 40 seconds. The micro-structural characterization was performed with Scanning electron microscope (SEM, Leo EVO- 40 VPX) with combined EDX unit (Bruker X flash detector 4010).

Optical microscope photographs of the samples were taken with Leica DM4000M microscope with 500x magnification. The micro-hardness of the samples were performed by a Vickers indenter hardness tester system [Shimadzu HMV-G21] using a pyramid on square base diamond indenter. It was applied a load of 10-25g/15s during to mechanical tests which the tests were repeated five different regions of the surface for each sample to calculated the average values. The micro hardness obtained by Vickers technique defined as the ratio of the load applied [in kg] to the projected area of the indentation [in mm²] as given by the following relation [36]:

$$H_v = \frac{1.854}{d^2} \cdot \frac{P}{d}$$

Where \( H_v \) value is the Vickers micro hardness value, \( P \) is the applied load in kg and \( d \) is the diagonal length of the impression.

The heat conductivity of the samples was analyzed by the home made thermal conductivity measurement system. We used two brass blocks which the first base has a heater inside it and the second is the heat sink and both of them have k-type thermocouple inserted the surface of the blocks. We calibrated the system using Al (alfa aerar cas no: 7429-90-5 which have thermal conductivity value 205 W/Km) [37]. It was used 120W power to obtain temperature gradient in both sides with PID temperature controller to reach 55°C temperatures which is the highest temperature that can be applied without decomposition of the biomaterials.

The dielectric measurement of the composites fabricated in this study were measured using Hioki 3520 LCR meter up to 200 kHz from 40 Hz in the chamber under 10⁻² bar. The sandwich configuration with active conduction is of 100 mm² were performed for the measurement using silver electrodes and paste.

### Results

We only present the XRD pattern of 9% Ca added samples in figure 1 since the effect of Ca can be seen in the highest adding level into the dental composites. It is easily seen from the XRD pattern that there are two solid phases, one is the organic binder such as bisphenol-A-glycidyl methacrylate that gives a broad halo in the XRD pattern between 20-30° and the second is the inorganic materials which give the peaks in the XRD pattern such as Luicide, \( \text{Al}_2\text{O}_3 \), \( \text{SiO}_2 \) etc. The detailed phase analysis of the materials was given the figure 1.

According to XRD analysis, the main phase of the samples were

<table>
<thead>
<tr>
<th>Material</th>
<th>Manufacturer</th>
<th>Type</th>
<th>Filler</th>
<th>Filler Size Range</th>
<th>Filler Weight (%)</th>
<th>Microhardness at room temperature</th>
<th>Ingredients Matrix System</th>
<th>Flexural Modulus (GPa)</th>
<th>Thermal Conductivity at room temperature (W/K-m)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arabesk Top (AT)</td>
<td>Cuxhaven, Germany</td>
<td>Microhybrid</td>
<td>Silica dioxide, Strontium glass</td>
<td>0.0-0.7 μm</td>
<td>77</td>
<td>23.5</td>
<td>Bis-GMA, UDMA, TEGDMA,</td>
<td>22.9</td>
<td>Not indicated</td>
<td>49-53</td>
</tr>
<tr>
<td>Clearfil Majesty Esthetic (CM)</td>
<td>Kuraray, Japan</td>
<td>Nanohybrid</td>
<td>Silanated barium, pre-polymerized glass, organic fillers</td>
<td>0.7 μm</td>
<td>66</td>
<td>57.7</td>
<td>Bis GMA, Hidrofohib Aromatik dimetakrilat Hidrofohib Alatifik dimetakrilat</td>
<td>10</td>
<td>Not indicated</td>
<td>54,55</td>
</tr>
<tr>
<td>G-aenial Universal Flo (GU)</td>
<td>GC Co., Milford, DE, USA</td>
<td>High-viscosity flowable composite</td>
<td>Silicon dioxide, Strontium glass</td>
<td>0.7-2 μm</td>
<td>69</td>
<td>48.54</td>
<td>UDMA, Bis-MEPP, TEGDMA,</td>
<td>7.95</td>
<td>Not indicated</td>
<td>56,57</td>
</tr>
<tr>
<td>Alpha core LC composite (AC)</td>
<td>US and Canada</td>
<td>Hybrid</td>
<td>Silanized quartz, barium glass, silica and aluminium oxide.</td>
<td>0.04-4.4 μm</td>
<td>62</td>
<td>Not Indicated</td>
<td>Bis GMA</td>
<td>105</td>
<td>Not indicated</td>
<td>58</td>
</tr>
</tbody>
</table>

Table 1: The general properties of the commercial dental composite resins.
found as SiO₂ with amorphous organic structure and the other inorganic phases are changed from one commercial composite to another. All composites have Ca peaks in the XRD pattern and it shows that the most part of Ca ions didn’t react by the dental composites. This results expected since it was not applied any process for the reaction of Ca with the composites such as temperature, pressure and etc. CM, AT and AC are same impurity phases such as Al₂O₃ and BaAl₂Si₂O₈ but GU have different multi impurity phases as seen in the figure 1. It is expected that minor phases in the samples may not be seen in the XRD pattern.

To understand the dispersion of Ca in the dental composites, we performed EDX-dot mapping as given in the figure 2a-d. The Ca added CM showed three phase regions and the elemental distributions of these regions were also given in the figure 2a. According to figure 2a, we can say that A regions are Si rich region, B regions consist of Ba, Al and Si, and the C regions are Ca rich compositions. The elemental dot analyses of these regions were also given in table 2. In figure 2b, the elemental distribution of GU was given and we observed four different regions that the main phase is named as B in the figure. It is seen that the A regions have Al, Ge, W and Si rich, B regions consist of Al, Si, Na, K, W. The C regions consist of Al, Si, K and W and the D region have Na, Al, Si, K, Ca elements. There are also some minor phases which are not seen in the XRD due to the detection limit of the XRD measurement system. AT composite have three different phase regions in the SEM images that A-regions indicate Si-rich compositions and the B-regions consist of Al, Si, Ba and C-regions have pure Ca as seen in the table 2. Meanwhile, AC has two different regions that A indicate the phases including Al, Si, Ca and Ba and the B regions have the phases of Al, Si, Ca and Ba. According to surface analysis we observed unsolved or accumulated phases during to light application which is unwanted state for dental treatment and the dental material named AC have almost homogeneous small grains with the lowest size when compared the others.

![Figure 2: EDX dot mapping of the materials of (a) CM, (b) GU, (c) AT and (d) AC.](image)

<table>
<thead>
<tr>
<th>Sample</th>
<th>A-regions</th>
<th>B-regions</th>
<th>C-regions</th>
<th>D-regions</th>
<th>Un-added sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>GU</td>
<td>36.18±0.6% Al</td>
<td>19.94±0.7% Si</td>
<td>0.79±0.1% Ge</td>
<td>20.58±1.4% W</td>
<td>Same with A, B and C region</td>
</tr>
<tr>
<td>AT</td>
<td>100.0% Si</td>
<td>14.95±0.2% Al</td>
<td>72.31±0.9% Si</td>
<td>12.74±0.5% Ba</td>
<td>Same with A and B region</td>
</tr>
<tr>
<td>AC</td>
<td>14.19±0.2% Al</td>
<td>66.97±1.0% Si</td>
<td>6.87±0.1% Ca</td>
<td>11.97±0.6% Ba</td>
<td>1.31±0.1 % Al</td>
</tr>
<tr>
<td>CM</td>
<td>2.14±0.1% Al</td>
<td>97.86±1.0% Si</td>
<td>11.68±0.2% Al</td>
<td>7.05±0.9% Si</td>
<td>3.21±0.1% Ca</td>
</tr>
</tbody>
</table>

Table 2: Elemental dot analysis of the surface of the materials in the Figure 2.
It has been seen that the chemical structure and compositions of the composites were changed from one composite to another [38]. Filler contents show also differences in composites and Si seem to be a common filler component in this study. So the filler contents of the composites can affect the thermal, mechanical and structural properties. Some filler can cause the reduction of mechanical strength and the others can improve. In this case there are no general rules about the filler content which can improve the dental properties.

Optical surface photographs of the un-added commercial materials and 9% Ca added materials were given in figure 3a-h. The EDX dot mapping analysis and optical microscope images showed that there are arbitrarily dispersed particles for the composite resins named CM and GU. The filler particle does not have a homogeneous size distribution in the matrix. The average particle size in the matrix of CM is about 1-30µm. The distribution of the size of filler particles in the matrix of GU is more uniform when compared to CM and the particle size distribution was changed from 1 to 60 µm. The filler particles dispersed into the resin matrix are almost homogeneous in the composite resin named as AT and the particle size was observed from 2 to 10µm. In the composite named AC, the filling particle was homogeneously dispersed in the matrix with the size of a few microns. The addition of Ca for all samples showed a particle size distribution of 5-10µm. The doping of Ca was caused the formation of more homogeneous main matrix since Ca may cause the degradation of the grains in the main matrix of the composite resins. We also observed an accumulation of Ca particles which is an undesirable case in this kind of materials.

The hardness properties of the dental composite resins are one of the important subjects in the clinical studies [39]. The filler particles which have a uniform distribution within the composite matrix (such as AT and AC) were displayed higher hardness value when compared with others. In contrast, non-uniform distribution of filler particles in the composites (such as CM and GU) may cause a decrease in the hardness value [40].

When the Ca content in dental composite resins was increased, the hardness values of AT and AC materials have also increased. The composites named as CM and GU with 3% and 6% Ca-adding the main matrix were showed lower hardness value when compared the pure samples as seen in figure 4.

However, the addition of Ca in the ratio of 9% can cause an increase in the hardness value of the composites in this study. The deviation range of the hardness value by adding Ca for AT and AC materials are less than the hardness of the other two materials. So we concluded that these particles in the resin matrix is believed to have a strong bond due to the increasing the hardness of Ca filler particles.

The measured micro hardness of the composites show a change in the range of 55-110 Hv depending on the starting material and Ca content in the structure as shown in figure 4. The micro hardness of CM was first showed a small decrease till 6 % Ca adding and then it was increased. This behavior can be explained with the small amount of Ca were settled the inter-grain region and then when it reaches a critical thresholds, the Ca ions were diffused into main matrix as seen in the table 1.

In this case, the hardness of the composite named CM is increased by the Ca addition. GU showed worse mechanical properties as seen in the figure 4 when compared the pure composite. After a critical level of Ca, AT showed an increase of the mechanical properties with increasing further Ca content which a promising results for clinical aspect. AC has also promising results for this area in which
the hardness were increased by a certain level of Ca as seen in the figure 4.

We found that after adding Ca to the composite resins, the particle size of the materials were increased as GU>CM>AL>AT. Meanwhile, micro-hardness values of AT which have the smallest particle size showed the strongest mechanical strength among the others. Although it is found that the particle size is not directly affected by the surface hardness, we found an inverse relation by micro-hardness value and particle size of the composite resins [41-44].

The heat conduction phenomena are one of the important subjects for the dental composites [40]. To simplify the determination of heat conduction coefficient, one dimensional heat equation can be considered [41]. When the heater was started to work, the temperature gradient between two surface of the sample were established as $\Delta T = T_2 - T_1$ which $T_1$ is the temperature of the sample at heater region and $T_2$ is the temperature of the sample at heat sink region so the equation for the relation of temperature gradient and thermal conductivity can be given as [41]:

$$Q = \kappa \frac{dT}{dx}$$

Where $Q$ is the heat flux, $T$ is the temperature in Kelvin and $\kappa$ is the thermal conductivity coefficient of the materials. So, we calibrated the system by using a piece of Al which the dimensions and thermal conductivity coefficient were known and the thermal conductivity of the pure and Ca doped samples are relatively measured. We calculated the steady state thermal conductivity values of the un-doped and Ca doped samples which are given in the figure 5. Although the $\kappa$ values of the commercial materials are low enough to use in dental treatment which it was expected have low enough to use in dental treatment which it was expected have the lowest thermal conduction of the heat from surface to dental pulp nerves, while the lowest $\kappa$ was obtained as 3.88 W/mK for GU, the highest value (= 4.76W/Km) belongs to CM among the other materials in this study.

The $\kappa$ values of AT and AC were increased by Ca addition in the sample. Although the $\kappa$ value of Ca added composite named AT is higher than that of the pure composite, a decrease with increasing Ca content was observed as seen in the figure 5. AC showed the lower values for 9% Ca addition. The lowest $\kappa$ values were obtained for the sample GU by 3-6% Ca addition. After a certain content of Ca, the $\kappa$ was started to increase as seen in the figure 5. CM also showed a similar behavior with GU.

The ac dielectric properties of the materials consist of real ($\epsilon'$) and imaginary ($\epsilon''$) part which real part is named as dielectric constant and the imaginary part is called dielectric loss [42]. The dielectric measurements of the compounds were performed at room temperature and the frequency range from 40 Hz to 200 kHz. The frequency dependence of $\epsilon'$ and $\epsilon''$ for the compounds fabricated was given in Figure 6a-d and inserts in the figure 6.

It is well known that the decrease of $\epsilon'$ and $\epsilon''$ with increasing frequency can be explained with the dielectric polarization in the compounds [43]. The dielectric polarization under ac-electrical field can be due to deformational and relaxation polarization [44]. Although the electrical dipoles in the compounds can be easily effect on applied electric fields, when the frequency of ac-electrical field is increased, the dipoles in the compounds cannot be rotate as performed at low frequency. After a certain frequency of applied field, the dipoles in the sample are unable to response the field and the dielectric constants of the compounds are not changed by increasing field. The field response of the dielectric materials is also related to polar or non-polar properties of the polymers [45]. While the dipoles of the polar molecules can align by applied field, the dielectric constant of non-polar molecules is independent of applied fields [46].

Figure 7 shows $\epsilon'$ value of composite resins by addition of Ca at low frequency region and it is seen that the $\epsilon'$ value of AT was started to decrease by Ca addition from 3 x $10^8$ to 0.6 x $10^8$ which Ca caused to decrease of $\epsilon''$. The CM has the value of 3 x $10^8$ and it was increased to 6 x $10^8$ by Ca addition and after 6% addition of Ca the $\epsilon''$ was decreased. Small addition of Ca for GU sample was caused to increase $\epsilon''$ and the increasing Ca content caused to decrease of $\epsilon''$ value. The $\epsilon'$ value of the resin named composite were increased by addition of Ca as seen in figure 7. So the $\epsilon''$ values of the commercial samples were high for using in the electronic application. The $\epsilon''$ values of the samples were given in the inserts of the figure 7 and they show similar results by $\epsilon'$ values.

**Discussion**

In this study, the Ca additions in the commercial composite resins were investigated in detail. The resin matrix which consists of the elements such as Al and Si were detected in all the materials with similar concentrations. In addition of this, AT and AC presented the highest concentration of Ca which can be related with an observation of the highest Vickers hardness value among the samples. The filler contents showed different elements such as Ge, W, K and Na which causes the change of the thermal conductivity and mechanical strength of the dental composite resin.

One of the most interesting results is the elemental content of the GU. According to EDX dot mapping analysis, Tungsten (W) was detected in the GU. Although tungsten improve the structural and mechanical strength of materials, micro hardness values of GU were found lower than pure composite resin and the other materials such as AT and AC since the particle size of GU was determined to be greater than other materials. When we compare the thermal conductivity data, it is seen that the composite resins including Ca show higher thermal conductivity than pure samples but thermal conductivity of Al's lower value than pure composite resin which is important for dental studies.

The addition of Ca in the composites causes two types of behavior; one is settling in the intergrain region without any chemical reaction. In this case, while the mechanical properties goes worse due to multiphase structure of the matrix, the heat conduction was increased since this region may behave as a heat reservoir which have higher heat storage properties and the thermal conductivity can increase as seen in the similar study of [47]. Second is the
Ca diffuse into the main matrix that the materials which have homogeneous phase formation with the multiphase structure have stronger bonding character than that of the un-added composition and so the mechanical properties can increase by Ca addition in the composite. The thermal conductivity of the commercial and Ca added samples showed different behavior depending on the composite as seen in figure 5. Generally the thermal conductivity were increased by Ca but, the composite named GU and CM interior showed promising results for small amount of Ca addition which can be used by next future in the clinical treatment.

The dielectric constant of the composite resins in this study was also investigated and it is found giant dielectric constant in the composite resins and it can be due to the polymer matrix in the resins. The value of the dielectric constant has the value of $10^6$-$10^8$ which is important for electrical applications.

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References


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