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THE SIZE EFFECTS OF MICRON PARTICLES ON THE PHYSICO-MECHANICAL PROPERTIES OF RESINOUS COMPOSITES CONTAINING INORGANIC-ORGANIC DUAL FILLERS

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ABSTRACT

In this study, thermal polymerized resinous composites containing inorganic-organic dual fillers were developed. The size effects of micron particles on the physico-mechanical properties of composites were investigated. According to the standard BS EN ISO 4049, the degree of conversion, hardness, three-point flexural strength, water sorption and water solubility of the prepared composite materials were determined. Contrary to expectations, the degrees of conversion of the composites decreased as the micron particle size increased. It has been deduced that this increase is directly related to the varying surface areas depending on the particle sizes and the modification ratios that can vary depending on the surface areas. The hardness values did not show a general trend with increasing particle size. When the flexural strengths of composites containing varying micron size particles were examined, their strengths differed in relation to the degree of conversion and the ratio of modification, which is also effective in hardness. As with other properties, the effects of competing particle size and ratio of modification had an effect on the sorption behavior. When the resolutions of the composites are examined, the values of all are positive. It was concluded that this situation may be due to the absence of polar groups in the main monomer structure other than ester, hydroxyl and urethane groups, which will keep the absorbed water in the structure, and the release of unreacted monomers with the absorbed water.

Key Words: Dual filler, inorganic-organic, PMMA, resinous composite

1. INTRODUCTION

Since the beginning of the industrial era, various studies have been carried out on organic-inorganic hybrid materials in various fields. The combination of organic and inorganic materials improves the properties of each component while reducing the specific limitations of each material. These functional hybrid materials usually contain two or more different components, which are inorganic (inorganic particles, metal ions, salts, oxides, etc.) and organic groups (organic groups or molecules, organic ligands, organic polymers, etc.). Moreover, they are combined by various methods such as self-assembly, electrostatic interaction, intermolecular interactions and bonding in molecular structural units to enhance the synergistic effect of their functional properties. The chemical and physical bond between organic and inorganic components can be achieved by ionic bond, covalent bond, hydrogen bond or van der Waals bond. These organic-inorganic hybrid functional materials find widespread use in a variety of industries including catalysts, pharmaceuticals, optics, energy storage, environmental remediation, cosmetics and dental (1). Resin composites, which are widely used especially in aesthetic restorative dentistry, are an important member of organic-inorganic hybrid material applications (2). Recent advances in resinous restorative materials, as well as increasing demand for aesthetics, have led to a large increase in the use of these resin-based composites in dental restorations (3). The popularity of composites is increasing day by day due to their excellent biocompatibility, lack of taste-odor-tissue irritation and toxicity, insolubility in body fluids, excellent aesthetic properties, stable colors, optical properties, easy pigmentation, low cost and repairability (2). Thanks to these superior properties, they have found their place in various dental materials, including synthetic teeth, temporary and permanent fixed dentures, sealants, dentin adhesives, bonding agents for crowns and fixed partial dentures, and tooth-colored restorative materials. A number of properties have been identified as the determining factors of the ultimate success of these materials: mechanical properties (flexural strength, compressive strength, hardness, etc.), ease of application, water sorption, solubility, biofilm formation and aesthetics (3). Studies confirm that these properties are directly and/or indirectly affected by the matrix, filler components and matrix-filler interface interaction that forms the resin composite (4). These three elements are very important in obtaining optimal properties and satisfactory clinical performance in resin composite materials. In dental composites, the matrix (continuous phase) typically consists of acrylate-based monomer systems containing a free radical initiation system (5). Filler surfaces are coated with organosilane compounds with difunctional properties in order to strengthen their bonding to the matrix and increase the service life of the composite. At the same time, this silane-based agent allows better dispersion of surface-modified fillers throughout the matrix (6). The second important component of the composite is fillers, which reduces the unit volume ratio of the matrix while minimizing polymerization shrinkage that may occur during polymerization (7, 8). It is possible to divide the fillers, which are also used in order to improve the mechanical properties, into two classes as inorganic and organic (3). Commonly used inorganic based fillers are oxides, mainly silica, alumina, titania and zirconia with a chemical composition of MxOy. Among these filling materials, silicon dioxide particles are the most preferred particles in the dental field due to their osteoconductivity and biocompatibility properties. Dimensionally micron and nano scale silica particles, which are the first filling materials used in dentistry; geometrically granular, fibrous and newly formed; amorphous and crystalline according to their crystallinity; and it is possible to classify them as mesoporous and nanoporous according to their pore sizes (8). Organic bases are fillers that are candidates for polymer class members are not widely used. Powdered poly methyl methacrylates have started to be used as organic fillers in the dental field (3).

Our motivation in the study was to examine the size effects of micron particles on the degree of conversion of resinous composites containing inorganic-organic dual fillers. In addition to the degree of conversion observed with the changing size, the ternary physicomechanical properties of the obtained composites including flexural strength, water sorption and solubility values were correlated. In the last step, the hardness of composites containing fillers with varying micron sizes was determined and compared with the degree of conversion-flexural strength pair was discussed.

2. MATERIALS AND METHODS

2.1 Materials

While forming the organic matrix, which is one of the main components of the composite, Bisphenol A glycidyl dimethacrylate (BISGMA, Esschem) and Urethane dimethacrylate (UDMA, Esschem) are the main monomers; Triethylene glycol dimethacrylate (TEGDMA, Esschem) was used as the diluting/crosslinking monomer. Polymethyl methacrylate-A (PMMA-A, Aldrich) was preferred as organic filler, and Benzoyl peroxide (BOP, Merck) was preferred as initiator. 3-methacryloxy propyl trimethoxy silane (MPTS, Abcr) difunctional organosilane compound was used as the coupling agent holding the organic matrix and inorganic particles together. Hydrophobic fumed silica Aerosil R709 (40 nm, Evonik) and high-purity silica M8000 (1.8 µm, Sibelco), M6000 (4 µm, Sibelco), M4000 (6 µm, Sibelco), M3500 (10 µm, Sibelco), M3000 (17 µm, Sibelco) were used for the formation of silica particle pairs in nano and micron sizes, respectively.

2.2. Methods

2.2.1. Prepared of resinous composites containing inorganic-organic dual fillers

All mixtures were prepared in the same procedure, provided that the nano particle size and doping ratio (M8000-%1.5; other micron particles-%1.0) remained constant. For this, 60 wt% [R709:M8000 (1:1)] particle mixture and 30 wt% [(40:40:20]) [(UDMA:BISGMA):TEGDMA ternary monomer was used. The preparation of 5 g of composite is as follows: After 0,031 g of BOP was completely dissolved in 0.31 g of TEGDMA, 1.24 g (UDMA:BISGMA) was added and mixed for 15 seconds in a mixer with a rotation speed of 3600 rpm. 0.45 g of PMMA-A followed by 3.0 g of [R709-M8000] particle mixture was added to the prepared organic matrix, respectively (Figure 1). After the mixture was injected into the molds, it was polymerized in a hot press at a certain temperature and time. The mold was transferred to the cold press to terminate the polymerization (8).

Table 1. Codes of resinous composites containing inorganic-organic dual fillers and [nm/µm] particle pairs

Composite code	[nm/µm] particle pairs
KO-1	R709/M8000
KO-2	R709/M6000
KO-3	R709/M4000
KO-4	R709/M3500
KO-5	R709/M3000

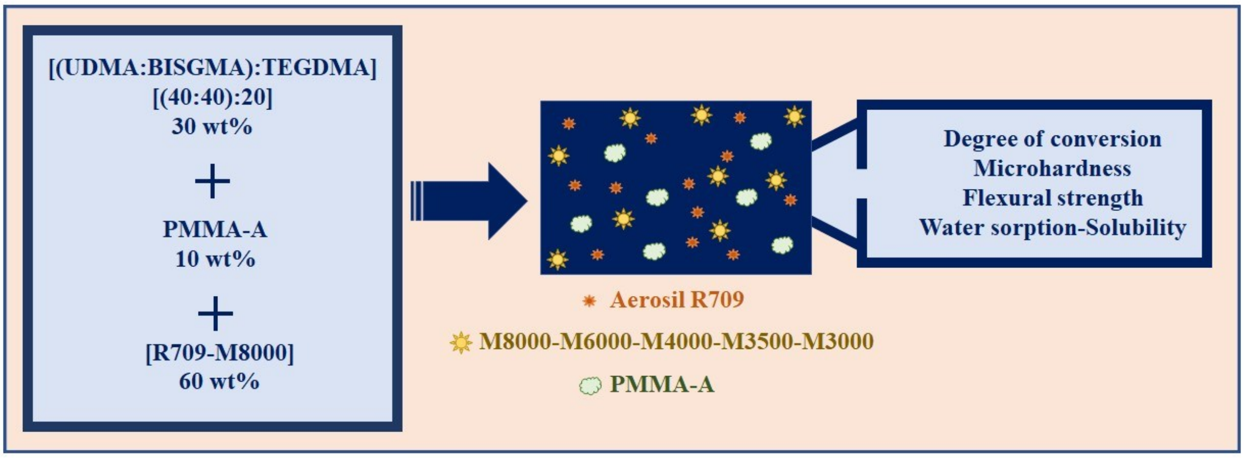

Figure 1. The schematic visual of preparation and characterization of resinous composites

2.2.2. Characterization techniques

2.2.2.1. Degree of conversion (DC%)

For resinous composites, although it is desirable to convert all monomers into polymers during the polymerization reaction, residual monomers from the inhomogeneous polymerization process can be seen. For the determination of these monomers, the degree of conversion (DC) calculation is made by determining the amount of carbon double bonds (C = C) converted to carbon single bonds (C - C). It is possible to obtain composites with desired mechanical properties by converting the double bond to C-C with more single bonds. Therefore, it is expected that the mechanical properties of the material such as hardness, flexural and compression strength are expected to be affected by the degree of conversion. If the conversion is insufficient, it may trigger hydrolytic cleavage at the matrix-particle interface. Parameters such as initiator used, quantity of particles, polymerization method and time can affect the degree of conversion. In this study, DC% values were determined in order to observe the effect of the addition of particles of varying micron sizes added to the composite on the degree of conversion depending on the polymerization with temperature. The widely used Fourier Transform Infrared Spectroscopy (FT-IR, Perkin Elmer Spectrum Two) was used for DC measurement. First, samples were prepared in disc-shaped stainless steel molds with a diameter of (15±0.1) mm and a thickness of (2±0.1) mm. After the molds were filled with the composite, it was polymerized by applying a hot press process. Then, the samples, which were brought to room conditions in cold press, were placed in water and kept in an oven at (37±2) ˚C for 1 day. DC measurement was measured from the bottom and top surfaces of the samples (n=5) and averaged.

The measurement conditions for the results to be obtained from the absorbance graphs are as follows: 32 scans, 4 cm^{-1}, resolution and wavelength range of 4000 to 400 cm^{-1}. The degree of conversion was determined by estimating the changes in the peak height ratio of the absorbance intensities of the aliphatic C=C peak at 1638 cm^{-1} and the internal standard peak of aromatic C=C at 1608 cm^{-1} during polymerization relative to the uncured material. The % DC for each sample was calculated using the following Equation 1:

$$\mathrm{DC}(\%) = \left(1 - \frac{(1638\ \mathrm{cm}^{-1}/1608\ \mathrm{cm}^{-1})_{cured}}{(1638\ \mathrm{cm}^{-1}/1608\ \mathrm{cm}^{-1})_{uncured}}\right) * 100\% \quad (1)$$

2.2.2.2. Microhardness measurement

The microhardness measurement of the composites was carried out with a Vickers microhardness tester with 50 grams of loading for 10 seconds. Samples were prepared as described in 2.2.1 and measurements were taken from the top and bottom surfaces of each sample. In order for the results to be reliable, measurements were taken by selecting 3 points with the same distance from the center of each sample (n=5). The mean and standard deviation of the obtained Hv values were calculated and used as a result.

2.2.2.3. Flexural strength

The flexural strength behavior of the composites was carried out according to the BS EN ISO 4049 standard, which has become the test protocol for the evaluation of dental composites, and it was performed on the Shimadzu brand AGS-X model universal test device. Samples were prepared in stainless steel molds with a length of 25 mm, a width of 2 mm and a thickness of 2 mm. After being polymerized in a hot press, the samples were placed in water and kept at (37±1) ˚C for 24 hours. Width (b) and height (h) measurements were made with a caliper with an accuracy of 0.01 mm. The distance between the supports was set to 20 mm according to the standard, and the maximum load (F) was applied to the specimen at a speed of 0.75 mm per minute until it reached yield point or fractured (9). Results were calculated in MPa using Equation 2.

$$\sigma = \frac{3xFxl}{2xbx\,h^2} \quad (2)$$

σ = flexural strength, F = maximum force (N), L = distance between supports (mm), b = width (mm), h = height (mm).

At least five samples were studied in this study to have meaningful and reliable test results. The evaluation was made on the average of the test results. In this study, and according to the relevant test standard, systems with flexural strength values of ≥50 MPa for composites were accepted as successful.

2.2.2.4. Water sorption-solubility

According to ISO 4049 standard, five samples of each composite with a diameter of 15 mm and a thickness of 1 mm were prepared. The samples were placed in a desiccator and kept in an oven at (37±2) ˚C for 22 hours and then in an oven at (23±1) ˚C for 2 hours. Then, the dry weight (M1) was measured with an accuracy of 0.1 mg using a precision balance. This process was repeated until M1 was <0.1 mg. The average values calculated by measuring the diameter from two regions and the thickness from five regions of the samples, which were weighed with a precision of 0.01 mm, were used. The volumes of the cylindrical samples were calculated in mm^3. The samples were placed vertically in the water with a distance of 3 mm between them. They were then kept at (37 ± 2) ˚C for 7 days. At the end of the 7th day, the water remaining on the sample surface was removed. The samples were kept in a dessicator until a constant mass to an accuracy 0.1 mg was obtained (M2). Weight measurements were taken again when the cycle was completed (M3). Water sorption results were calculated in $\mu g/mm^3$ with Equation 3.

$$WS = \frac{M_2 - M_3}{V} \quad (3)$$

For the reliability of the results, at least five samples were studied, and an evaluation was made on the average of the test results. Systems with test values of ≤40 µg/mm³, according to the relevant standard, were considered successful. Solubility values of the same samples were calculated with the help of Equation 4 in µg/mm³.

$$S = \frac{M_1 - M_3}{V} \quad (4)$$

For the reliability of the results, at least five samples were studied and evaluated on the average of the test results. Systems with test values of ≤7.5 µg/mm³, according to the relevant standard, were considered successful.

3. RESULT AND DISCUSSION

The size effects of micron particles on the degree of conversion, microhardness, flexural strength, water sorption-solubility of resinous composites containing inorganic-organic dual fillers were investigated.

3.1. Degree of conversion

The degree of conversion is an important property in determining the mechanical performance, degradation properties and biocompatibility of resinous composites (10). The degrees of conversion of nano\micron SiO2-PMMA-based dual filler-containing resinous composites determined using the direct method FT-IR are shown in Figure 2.

Studies in the literature have revealed that the monomer mobility increases and the degree of conversion increases in relation to the increasing flowability of the composite (11). Particle size and modification ratio are important parameters that determine the flowability of the composite. The surface area, which increases proportionally with the decrease in particle size, leads to a decrease in the amount of matrix per unit area and a decrease in the flowability of the composite. When the degrees of conversion are evaluated; as expected, the degrees of conversion of composites decreased with increasing micron particle size. This result is directly related to the varying surface areas depending on the particle sizes and the modification ratios. These two parameters are effective on the flowability of composites. In general, the flowability of the composite decreases with decreasing particle size and decreasing quantity of modifying agent (8).

M8000 (smallest micron size filler-1.5% MPTS), M6000 (1% MPTS), and M4000 (1% MPTS) fillers have smaller particle size than M3500 (1% MPTS) and M3000 (biggest micron size filler, 1% MPTS). Contrary to expectations, the degrees of conversion of composites (KO-1, KO-2, KO-3) containing M8000, M6000 and M4000 were found to be high due to the increased monomer mobility as a result of the modification ratio of the fillers. Similarly, the flowability and monomer mobility caused by the relatively bigger particles sizes of M3500 and M3000 in the composite were screened by the viscosity increase provided by the modification and exhibited low degrees of conversion (KO-4 and KO-5) (8). The result obtained here is that the modification ratio should be in an optimum range depending on the surface area that the particle has directly related to its size.

The microhardness of composite materials is often used to estimate wear resistance when used as restorations in functional areas (11). Materials with lower hardness are susceptible to surface defects and breakage. In contrast, high microhardness shows increased wear resistance and there is a relationship between the mechanical properties of materials and clinical longevity. long-lasting aesthetic restorations can be achieved by the physical properties of resin composites such as crosslink density or degree of conversion (12).

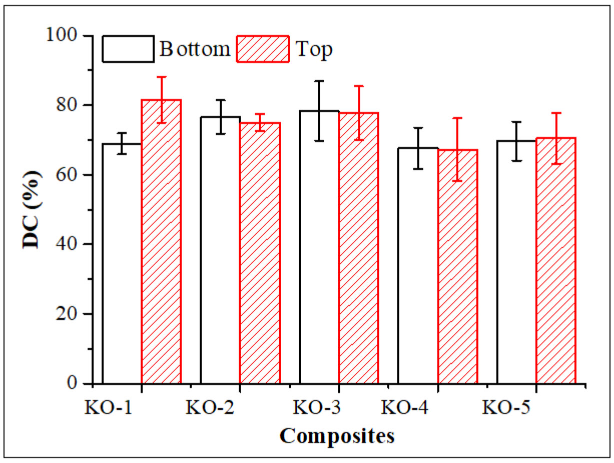

Figure 2. The degrees of conversion of nano\micron SiO2-PMMA based dual filler resinous composites

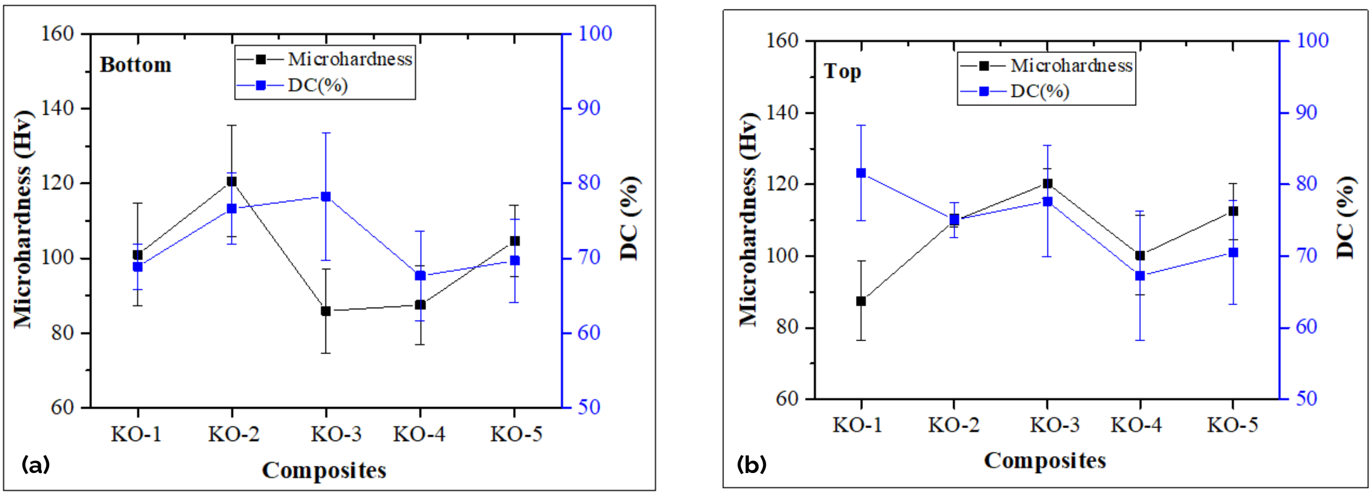

Figure 3. Transformation degree-microhardness values of the bottom region of nano\micron SiO2-PMMA-based dual filler-containing resinous composites (a), transformation degree-microhardness values of the top region (b)

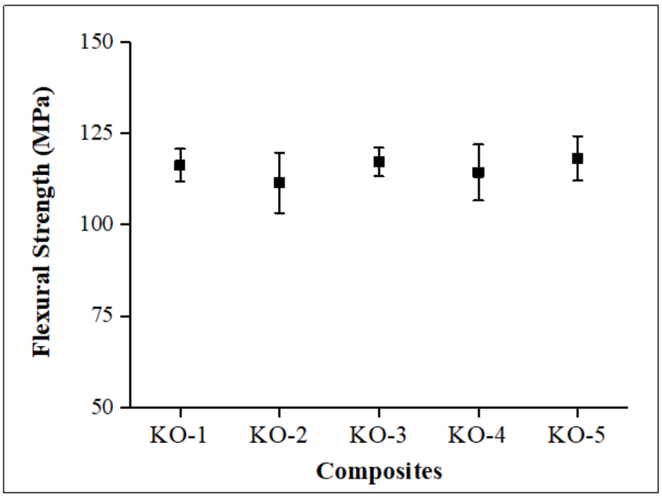

Figure 4. Flexural strength values of nano\micron SiO2-PMMA-based dual filler-containing resinous composites

The microhardness of nano\micron SiO2-PMMA-based dual filler-containing resinous composites is given in Figure 3 in comparison with their degrees of conversion.

The Vickers microhardness test is one of the most suitable tests to evaluate the mechanical properties of composites in terms of reliability and accuracy. When the hardnesses obtained from the bottom and top regions of the prepared test specimens were evaluated, it did not show a general trend with respect to the increasing micron particle size. The main factors affecting the hardness of composites are: particle type (I), particle size (II), strong particle-matrix interface between modified particle and matrix (III), particle distribution and optimum distance between particles (IV), particle hardness (V) (2). High hardness values may be related to the optimum inter-particle spacing and effective particle-matrix interface. It also leads to an increase in surface resistance to indentation as particle loading in the matrix increases (13). In the light of this information, an increased behavior in hardness, which was expected, was not observed in composites prepared using fillers with decreasing micron size. This result reveals that the particle size and the ratio of agent used in the modification of the particle surfaces are in competition. There is no correlation between the hardness values of the top and bottom regions of the nano\micron SiO2-PMMA-based dual filler-containing resinous composites and the degree of transformation. It is possible to come across studies with similar results in the literature (10).

Flexural strength is an important criterion in determining the durability and longevity of composites (14). It is a mechanical property that tensile and compressive forces exist, and which force will be effective depends on many factors, especially particle size and particle-matrix interface. The flexural strength behaviors of nano\micron SiO2 -PMMA-based dual filler-containing resinous composites are shown in Figure 4.

It is well known that the initial fracture of resin composites occurs at the particle-matrix interphase, as the stiffnesses of the silica-based fillers and the resins that make up the matrix are different. This intermediate phase contributes to the improved stress distribution under loading. As the size of the filler particles decreases, their surface area increases with respect to their volume, and accordingly, higher surface energy is observed in the interphase (15). Therefore, the stress concentration in the particle-matrix interphase decreases as the particle size of the filaments gets smaller, and as a result, the corresponding composites are expected to have higher flexural strength values. However, the flexural strength of the composites in the study has a different behavior than expected. It is thought that this situation is caused by the use of the modification ratio, which has an active role in the formation of the particle-matrix interface as well as the size, without changing it according to the changing surface area/ volume in micron particles (except for M8000).

Inorganic fillers are used to provide material reinforcement and strength in resin-based dental composites. Various types, shapes, sizes, volume fractions and distributions of filler particles are used in commercial products, and all these factors affect the properties of the material such as hardness, thermal stability, radio-opacity, gloss retention, roughness, water absorption and solubility (16). In the study, the water sorption and solubility of nano\micron SiO2-PMMA-based dual filler-containing resinous composites were determined (Figure 5 and Figure 6), and the variation of the absorptions and solubility of the composites prepared using particles of varying micron size were discussed.

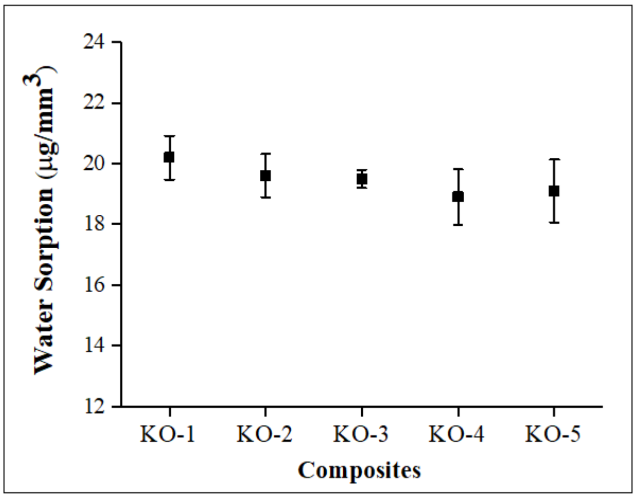

Figure 5. Water sorption values of nano\micron SiO2 -PMMA-based dual filler-containing resinous composites

The water sorption values decreased as the micron SiO2 particle size increased, and the standard deviation increased. As with other features, size and ratio of modification in competition with one another had an effect on sorption behavior.

When the resolutions of the composites are examined, the values of all are positive. The amount of water taken up is a function of the sorption and solubility between the polymer matrix and water molecules. Positive solubility value may be due to the absence of polar groups in the structure of the main monomer, apart from the ester, hydroxyl and urethane groups, to keep the absorbed water in the structure, and the release of unreacted monomers with the absorbed water (17). In this case, the residual unconverted methacrylate groups that can be found in the lower parts of the poorly polymerized composites not only pose cytotoxic and genotoxic risks, but their solubility can cause cavities and secondary caries formation (11).

4. CONCLUSION

The size effects of micron particles on the physicomechanical properties of resinous composites containing inorganic-organic dual fillers were investigated. The particle-matrix interface is an effective factor rather than varying micron-sized particles in the properties of the obtained composites. As is known, the resin-based dental composites are a multi-component mixture: monomers, polymerization initiator, particles, accelerators, inhibitors. The properties of the composite are directly related to the composite components. It was concluded that the final physicomechanical properties change may be in competition with the other basic parameters as well

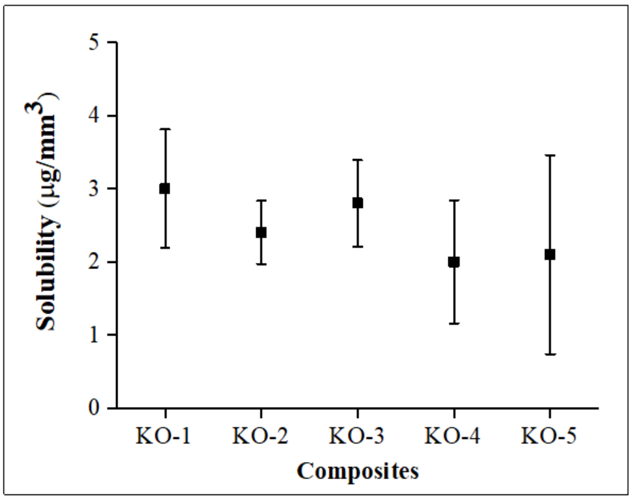

Figure 6. Solubility values of nano\micron SiO2-PMMA based resin composites containing dual fillers

as the monitored variables and may affect these properties. In addition, this study revealed the idea that if organic-based fillers, which can act synergistically with inorganic based fillers, are used in composites, they can be effective in the properties of the composite materials.

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