Mechanical and Rheological Properties of Flowable Resin Composites Modified with Low Addition of Hydrophilic and Hydrophobic TiO₂ Nanoparticles

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Abstract: The aim of this work was to find the influence of the addition of low amount of hydrophilic and hydrophobic TiO₂ nanoparticles on compressive strength, microhardness and rheological properties of flowable dental composite material. Specimens were prepared by adding 0.05; 0.2 and 1 wt. % of hydrophilic and hydrophobic 20 nm TiO₂ nanoparticles. These specimens were compared to non-modified control specimens in compressive strength and microhardness. Furthermore, their rheological properties were determined. The optimal nanoparticle loading was 0.2 % hydrophobic TiO₂, resulting in significantly higher compressive strength and microhardness than those of the control specimen group. Mechanical properties of flowable composites reinforced with hydrophilic and hydrophobic TiO₂ at higher loadings are lower than those of control specimens, which is the result of nanoparticle agglomeration. TiO₂ nanoparticles addition resulted in the decrease in viscosity in all specimens except for the specimen with 1% hydrophilic TiO₂ nanoparticles. In accordance to the obtained results, hydrophobic nanoparticle addition results in a more resistant and durable material, combined with an increased flowability compared to a non-modified composite.

Keywords: flow composite, TiO₂ nanoparticles, mechanical properties, rheological properties

1. Introduction

Recently, a new trend of the widespread use of flowable composites in dental restorations was reported [1]. The first generation of flowable resin composites was introduced in 1996, in response to requests for easy handling properties [2,3]. These properties allowed flowable resin composites to be used as liners in areas of difficult access, fissure sealants and restorations of small cavities [4-6]. However, their application is restricted to non-stress-bearing areas, because of their lower mechanical properties compared to conventional resin composites with a higher viscosity [7]. Mechanical properties of flowable resin composites are generally about 60–90% lower than those of conventional composites [2,8]. Efforts have been made to improve the mechanical properties of flowable composite resins by adding a small amount of nanoparticles [9-14]. On the other hand, the impact of nanoparticles on the viscosity of a resin composite is strongly influenced by the amount, shape, size and surface treatment of the filler particles added [7,10,15,16]. The viscosity of the unset composite resin is directly related to the handling characteristics of the material. Handling properties of flowable resin composites have included their malleability, ease of placement and shaping on the restored site, adherence to the tooth surface and not to an instrument and its holding shape or resistance to slumping [2,7]

In this work, the mechanical and rheological properties of a commercial flowable resin, modified with low amounts of hydrophilic and hydrophobic TiO₂ nanoparticles was tested.

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2. Materials and methods

In this paper, Vertise\textsuperscript{TM} Flow composite resin material was used as a basis. This material was modified with two types of TiO\textsubscript{2} nanoparticles: Aeroxide P25 and Aeroxide T805 (Evonik, Essen, Germany) with hydrophilic and hydrophobic surface properties, respectively. The properties of the materials used in this study are given in Table 1.

Before the sample preparation, nanopowders were dried in a vacuum at 110°C for 24 h. The proper amount of nanofiller weighed in a Ohaus\textsuperscript{TM} Adventurer Pro (Adventurer Pro Ohaus, Parsippany, NJ) analytic balance, was dispersed in flowable composite and homogenized. Homogenization was done for 10 min in a pre-darkened glass vial, placed in an ultrasonic bath Codyson PS-20 (Sherzhen Codyson, Shenzhen, China). The following nanoparticle loadings were used: 0.05, 0.2 and 1 wt.%.

Table 1. Materials as specified by manufacturers

<table>
<thead>
<tr>
<th>Materials</th>
<th>Manufacturers</th>
<th>Matrix type</th>
<th>Filler/particle type</th>
<th>Filler/particle diameter</th>
<th>Filler loading</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vertise\textsuperscript{TM} Flow</td>
<td>Kerr</td>
<td>GPDM\textsuperscript{1}, HEMA\textsuperscript{2}, MEHQ\textsuperscript{3}</td>
<td>Prepolymerized particles, Ba glass, colloidal SiO\textsubscript{2}, YbF\textsubscript{3}, ZnO</td>
<td>1 µm for Ba glass; nanoscale SiO\textsubscript{2} and YbF\textsubscript{3}; Overall mean: 1 µm</td>
<td>not specified</td>
<td>Flowable composite</td>
</tr>
<tr>
<td>Aeroxide P25</td>
<td>Evonik</td>
<td>-</td>
<td>TiO\textsubscript{2}</td>
<td>20 nm</td>
<td>-</td>
<td>Hydrophilic Fumed TiO\textsubscript{2}</td>
</tr>
<tr>
<td>Aeroxide T805</td>
<td>Evonik</td>
<td>-</td>
<td>TiO\textsubscript{2}</td>
<td>20 nm</td>
<td>-</td>
<td>Hydrophobic Fumed TiO\textsubscript{2}</td>
</tr>
</tbody>
</table>

\textsuperscript{1} glycerol phosphate dimethacrylate, \textsuperscript{2} hydroxyethyl methacrylate, \textsuperscript{3} monomethyl ether hydroquinone

For compressive strength and microhardness testing, cylindrical specimens 5 mm in diameter and 2 mm thick were prepared using standardized molds. Compressive strength was tested using a WPM ZDM 5/91 (WPM, Leipzig, Germany) universal testing machine and calculated according to Equation (1):

\[ C = \frac{4F_{\text{max}}}{\pi d^2} \]  \hspace{1cm} (1)

where \( C \) is compressive strength [MPa], \( F_{\text{max}} \) is maximum load [N] and \( d \) is specimen diameter [mm]. For determining compressive strength, ten specimens were tested.

Microhardness was measured using a Wilson Tukon 1102 (Uzwil, Switzerland) Vickers microhardness tester and the following parameters: 100 g load (0.9807 N) and 15 s dwell time. Ten indentations were made on the top specimen surface and microhardness was determined as an average value. Microhardness was calculated using Equation (2):

\[ VHN = 1.8544F/d^2 \]  \hspace{1cm} (2)

Table 2. Sample group designation system

<table>
<thead>
<tr>
<th>Specimen group</th>
<th>Nanosilica content [%]</th>
<th>Designation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Hydrophilic TiO\textsubscript{2} addition</td>
<td>0.05</td>
<td>0.05 I</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>0.2 I</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>1 I</td>
</tr>
<tr>
<td>Hydrophobic TiO\textsubscript{2} addition</td>
<td>0.05</td>
<td>0.05 O</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>0.2 O</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>1 O</td>
</tr>
</tbody>
</table>
where \( VHN \) is the Vickers hardness number, \( F \) is the load [kg] which was constant and \( d \) is the average size of two indentation diagonals [mm], a variable. Microhardness was designated as HV0.01 (Hardness Vickers 0.1 kg loading).

Fractured specimens were examined by a JEOL JSM-6460LV scanning electron microscope (SEM) operating at 25 kV. The specimens were previously coated with gold with Bal/Tec Leica SCD-005 (Leica – Leitz, Wetzlar, Germany). Furthermore, energy dispersive X-ray analysis (EDX) was performed to examine the agglomerated nanoparticles, using an Oxford Instruments INCA Microanalysis system.

DSC measurements were carried out using a TA Instruments Q20 (TA Instruments, New Castle, Del) DSC device equipment in a nitrogen atmosphere (50 cm\(^3\)/min). In order to erase the previous thermal history, samples with masses of about 10 mg were kept as melts at 200°C for 5 min and cooled down to 40°C. Finally, the samples were heated up to 200°C with a scan rate of 10°C/min. The glass transition temperatures \( (T_g) \) were determined on the basis of the second heating. The values of \( T_g \) were obtained using the middle point method.

Rheological measurements on all tested materials were performed in triplicates using HAAKE MARS (Thermo Fisher Scientific, Waltham, MA) rheometer, equipped with PP 20 Ti parallel plate measuring geometry (20 mm – diameter, 1 mm gap) at 23°C.

In amplitude sweep tests linear viscoelastic region was determined by increasing shear stress from 0.01 to 50 Pa at a constant frequency (1 Hz). Consequently, a frequency sweep test was conducted from 0.1 to 10 Hz in order to determine the changes of the complex viscosity \( (\eta^*) \) and storage \( G' \) (elastic) modulus as a function of applied frequency.

For a better assessment of the significance of the observed differences in the mechanical properties of the tested materials, the statistical analysis was performed. The compressive strength data were analyzed using Welch ANOVA (one-way analysis of variance) with Games – Howell post-hoc test. The microhardness data were analyzed using ANOVA with Tukey’s post-hoc test. Both statistical analyses were done by means of the SPSS v.20 software. The significance level was set at \( \alpha=0.05 \). The results of statistical analysis was represented by letter designations in charts. Different letters indicate statistically significant differences at a level of 95 %, while equal letters in bar charts depicting mechanical properties of various specimens indicate statistically unsignificant properties.

3. Results and discussions

3.1. Mechanical properties

The compressive strength and microhardness results of control and modified samples with hydrophilic and hydrophobic TiO\(_2\) are shown in Figures 1a and 1b. In Figure 1a, all results from the hydrophilic modified group show the negative influence of hydrophilic nanoparticles on compressive strength, with statistically significant differences in relation to control specimens (unmodified). On the other hand, the addition of hydrophobic TiO\(_2\) nanoparticles resulted in an increased compressive strength compared to the control samples in the case of samples 0.05-O and 0.2-O, while sample 1-O suffered the drop of the compressive strength. Sample 0.05-O is not significantly different compared to control sample 0, while sample 0.2-O is, resulting in the maximum value of compressive strength. HV0.1 microhardness results for control and modified samples with hydrophilic and hydrophobic TiO\(_2\) are shown in Figure 1b. Sample 0.05-I with hydrophilic particles experienced a rise in microhardness that is statistically significant compared to control sample 0, unlike samples 0.2-I and 1-I which suffered a statistically significant drop of microhardness. The samples 0.05-O and 0.2-O modified with hydrophobic TiO\(_2\) exhibited increased microhardness compared to control sample 0 which is statistically significant. However, sample 1-O does not show a significant drop in microhardness compared to the unmodified specimen group.
Figure 1. (a) Compressive strengths of tested materials; (b) Microhardnesses of tested materials. Different letters marked in bars indicate statistically significant differences between mechanical properties of various specimens at a level of 95%.

3.2. EDX analysis

EDX analysis results are shown in Figure 2 and Table 3. On this representative image, which refers to the specimen modified with 1% hydrophilic nanoparticles (fracture surface), three spectra were examined. Spectrum 1 reveals that the analyzed particle may be interpreted as ytterbium trifluoride (YbF₃) particle [17], while Spectrum 2 indicates that it may be interpreted as barium silicate glass (1BaO 2SiO₂) [18,19]. Both ytterbium trifluoride and barium silicate glass are most likely used as fillers in base flowable composite material. In both Spectrum 1 and 2, no Ti was detected, which is in contrast to Spectrum 3, where a considerable amount of Ti was found. The particle examined in Spectrum 3 analysis can be interpreted as an agglomerate consisted of TiO₂ clustered nanoparticles.

Figure 2. EDX analysis of the specimen 1 I
### Table 3. Chemical composition and phase identification of spectra shown in Figure 2

<table>
<thead>
<tr>
<th>Spectrum No.</th>
<th>C</th>
<th>O</th>
<th>F</th>
<th>Si</th>
<th>Ti</th>
<th>Ba</th>
<th>Yb</th>
<th>Phase identification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spectrum 1</td>
<td>15.56</td>
<td>4.38</td>
<td>17.17</td>
<td>1.87</td>
<td>-</td>
<td>2.17</td>
<td>58.85</td>
<td>YbF$_3$</td>
</tr>
<tr>
<td>Spectrum 2</td>
<td>22.80</td>
<td>36.17</td>
<td>5.90</td>
<td>16.80</td>
<td>-</td>
<td>12.25</td>
<td>6.09</td>
<td>1BaO 2SiO$_2$</td>
</tr>
<tr>
<td>Spectrum 3</td>
<td>37.70</td>
<td>17.14</td>
<td>4.04</td>
<td>11.79</td>
<td>13.37</td>
<td>2.24</td>
<td>13.73</td>
<td>TiO$_2$</td>
</tr>
</tbody>
</table>

#### 3.3. DSC analysis

Figures 3 and 4 show heat flow over the temperature chart for modified samples with hydrophobic and hydrophilic TiO$_2$, respectively. Figure 5 shows glass transition temperatures obtained from Figures 3 and 4. The glass transition temperatures are significantly higher in the presence of hydrophobic particles. Also, it can be noticed that samples filled with hydrophilic particles have a lower $T_g$ compared to control samples, while samples with hydrophobic particles show the opposite effect. With the increase of hydrophilic TiO$_2$ content, the glass transition temperature decreases from 95°C (for sample 0.05-I) to 88°C (for sample 1-I). On the other hand, the addition of hydrophobic nanoparticles increases $T_g$ in samples 0.05-O and 0.2-O in relation to the unmodified sample, while $T_g$ of sample 1-O slightly decreases.

![Figure 3. DSC curves of prepared samples with different hydrophobic TiO$_2$ content](image3)

![Figure 4. DSC curves of prepared samples with different hydrophilic TiO$_2$ content](image4)
3.4. Rheology

The complex viscosity versus applied frequency range of tested flowable composite samples is presented in Figure 6. According to obtained results, all samples exhibited pseudoplastic behaviour, i.e. their complex viscosity ($|\eta^*|$) decrease with frequency increase. Most of the composites expressed strong non-Newtonian behaviour and no hint of a Newtonian plateau even at the lowest frequencies was observed. Only, hydrophobic TiO$_2$ composites 0.05-O exhibited a small Newtonian plateau between 0.1-0.4 Hz indicating the Newtonian behaviour at applied low frequencies. The hydrophilic TiO$_2$ composites 0.05-I and 0.2-I TiO$_2$ showed a significant decrease in complex viscosity in comparison to the control sample, whereas a further increase in hydrophilic TiO$_2$ content resulted in a pronounced increase in $|\eta^*|$. However, all composite samples containing hydrophobic TiO$_2$ particles expressed a significant decrease in complex viscosity in comparison to the control sample. Additionally, it can be observed that higher content of hydrophobic TiO$_2$ particles (samples 0.2-O and 1-O) resulted in no significant changes in complex viscosity. Storage moduli of all flowable composites increase as the frequency increase, Figure 7. The control sample and the samples 0.2-I and 1-I exhibited lower slopes of storage modulus curves at the applied frequency range in comparison to most of the other samples indicating that they express stronger elasticity. However, the curve of the sample 0.05-O can be divided into two parts. The first part, at low frequencies (0.1-0.3 Hz) showing high-frequency dependence and pronounced viscous behaviour and the second part of the curve at higher frequency range (0.3-10 Hz) where very small frequency dependence of storage moduli can be observed i.e. more elastic behaviour [15,16,20,21] The values of storage moduli at the applied frequency range were lower than of the control sample for most of the tested composites containing both hydrophilic and hydrophobic TiO$_2$ particles. The sample 1-I obtained increased storage moduli in comparison to the control composite sample.
3.5. Mechanical properties, EDX and DSC analyses

The compressive strength and microhardness results suggest that hydrophobic TiO$_2$ nanoparticles offer superior properties compared to hydrophilic TiO$_2$ nanoparticles. By increasing the hydrophilic nanoparticle loading, both compressive strength and microhardness values gradually drop. A possible explanation relates to nanoparticle distribution, as well as the formation of agglomerates and their behaviour under load. Nanoparticles tend to join or to ‘stick’ to one another due to high specific area and energy. Furthermore, by interacting together, they are less interacting with the matrix, causing an uneven reinforcing field throughout the material [22-26]. Furthermore, as agglomerates have little cohesive strength due to the presence of relatively weak secondary bonds (Van der Waals forces, hydrogen, capillary, or by adsorption of foreign substances) between individual nanoparticles, their behaviour under load may further lower the mechanical properties of the nanocomposite [27,28]. After the nanofiller agglomerate fractures, the stress is transmitted to the matrix, whilst the crack propagates to adjacent filler particles. Subsequently, the stress in the surrounding filler particles or agglomerates suddenly increases, causing matrix overload and premature failure [29,30]. The presence of agglomerates is confirmed by SEM and EDX analyses. TiO$_2$ agglomerates were observed and identified in 1-O and 0.05-I; 0.2-I and 1-I samples. This indicates that hydrophilic TiO$_2$ nanoparticles are more prone to agglomeration than hydrophobic TiO$_2$, resulting in lower mechanical properties at corresponding loadings. The EDX analysis of the specimen containing 1% hydrophilic TiO$_2$ nanoparticles revealed the presence of an elevated Ti content that corresponds to clustered and agglomerated TiO$_2$ nanoparticles. Furthermore, the pronounced influence of agglomeration in specimens tested until fracture (compressive strength), compared to the locally deformed specimens (microhardness) is supported by median and inter-quartile ranges shown in Figures 1 and 2. Wider median and inter-quartile ranges in compressive strength test prevent the application of regular ANOVA and non-parametric post-hoc test (Tukey), leading to the application of the unconventional Welch ANOVA followed by Games – Howell post-hoc test. The wide median and inter-quartile ranges suggest a measure of stochastic behaviour that might be caused by agglomeration, which is most pronounced in specimen groups that failed at lower mean compressive strength tests, such as 0.2-I, 1-I and 1-O.

The influence of the nanoparticles in polymer composites on $T_g$ is controversial since $T_g$ of nanocomposites depends on a variety of factors such as degree of polymerization, polymer chemical
structure, filler size, filler loading, dispersion conditions, etc. [28]. In some cases, polymer nano-composites show an increase of the $T_g$, but in other cases, a decrease in $T_g$ is observed [30-33]. In specimens 0.05-I, 0.2-I and 1-I, the hydrophilic TiO$_2$ nanoparticles have a repulsive/dewetting interaction with the surrounding polymer, leading to an increase in free volume and chain mobility near the particles. As a result, the $T_g$ of the bulk material shifts to lower temperatures. On the other hand, specimens 0.05-O, 0.2-O and 1-O have an increased $T_g$, which may be attributed to the attractive/wetting interaction with the surrounding polymer, which was observed by Lesley et al. as well [34].

3.6. Rheology

All tested flowable composites were viscoelastic materials. They all expressed non-Newtonian pseudoplastic, shear-thinning behavior with complex viscosity decreasing disproportionally as frequency increased. The obtained results are in accordance with Beun et al., Lee et al. and Ellakwa et al. who also proved pseudoplastic, shear-thinning behavior of flowable resin composites [13,35,36]. Moreover, the viscosity of flowable composite materials is influenced by many factors such as resin matrix formulation, size, shape and content of filler particles, interlocking between the used filler particles and the interfacial interaction between those added particles and the resin matrix [3,37]. High-frequency agitation was used to increase flowability of composites used as a luting agents. These luting agents are used to secure dental restoration and provide the proper seating of the dental inlay [38-40]. According to performed rheological measurements, the addition of hydrophilic and hydrophobic TiO$_2$ particles resulted in different viscoelastic behaviour of flowable composites. There were no direct relationships between filler content and complex viscosity as well as storage modulus values as was in the case of Lee et al., who suggested that it could be explained by the multifactorial determination of composite consistency [37]. Moreover, the obtained rheological properties of investigated composites could probably be much more related to the type of filler and surface treatment than the content of used filler particles. According to obtained results of storage modulus and complex viscosity, investigated materials could be observed in two groups. The first one is characterized with lower complex viscosity, storage modulus and lower slopes of storage moduli curve (0.05-I, 0.2-I, 0.2-O and 1-O) and the second one (1-I, 0.05-O) is characterized with higher previously mentioned parameters. Therefore, the first group expressed less solid-like behaviour than the materials included in the second group. The main mechanism that enables the addition of nanoparticles to increase the flowability is polymer chain separation, which was found in the study of Petriccione et al. [41].

4. Conclusions

According to the presented results, and within the limitations of the study, the following conclusions can be drawn:

- Mechanical properties of nanocomposites with TiO$_2$ are highly dependent on nanoparticle type and loading.
- Hydrophobic nanoparticles proved to be more effective in increasing the mechanical properties of flowable composite material, whilst the optimum loading is 0.2% 20 nm nanoparticles.
- At higher loadings of hydrophobic nanoparticles and with hydrophilic nanoparticles added, agglomeration was found to degrade mechanical properties.
- The optimal addition of hydrophobic TiO$_2$ nanoparticles is 0.2%. This hydrophobic nanoparticle loading also decreases the complex viscosity and storage moduli of the nanocomposite material.
- All materials modified with nanoparticles exhibited a decreased complex viscosity and storage moduli versus the unmodified material, except for 1% hydrophilic nanoparticle loading.

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