

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

BRANISLAVA PETRONIJEVIC SARCEV¹, DANKA LABUS ZLATANOVIC^{2,3*}, MIROSLAV HADNADJEV⁴, BRANKA PILIC⁵, IVAN SARCEV¹, DUBRAVKA MARKOVIC¹, SEBASTIAN BALOS²

¹ Department of Dentistry, Medical Faculty, University of Novi Sad, Hajduk Veljkova 3, Novi Sad, Serbia

² Department of Production Engineering, Faculty of Technical Sciences, University of Novi Sad, Trg Dositeja Obradovica 6, Novi Sad, Serbia

³ Department of Production Technology, Technische Universität Ilmenau, Gustav-Kirchhoff-Platz 2, Ilmenau, Germany

⁴ Institute of food technology, University of Novi Sad, Bulevar Cara Lazara 1, Novi Sad, Serbia

⁵ Department of Material Engineering, Faculty of Technology, University of Novi Sad, Bulevar Cara Lazara 1, Novi Sad, Serbia

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.

*email: danlabus@uns.ac.rs

2. Materials and methods

In this paper, Vertise™ Flow composite resin material was used as a basis. This material was modified with two types of TiO₂ 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 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. %. To better describe various sample groups, a designation system was devised, as shown in Table 2. 15 samples per group per test were prepared by a standard light-curing method. The samples were then stored in dark light-proof containers at 37°C for 24 h.

Table 1. Materials as specified by manufacturers

| Materials | Manufacturers | Matrix type | Filler/particle type | Filler/particle diameter | Filler loading | Description |
|---------------|---------------|---|---|---|----------------|------------------------------------|
| Vertise™ Flow | Kerr | GPDM ¹ , HEMA ² , MEHQ ³ | Prepolymerized particles, Ba glass, colloidal SiO ₂ , YbF ₃ , ZnO | 1 μm for Ba glass; nanoscale SiO ₂ and YbF ₃ . Overall mean: 1 μm | not specified | Flowable composite |
| Aeroxide P25 | Evonik | - | TiO ₂ | 20 nm | - | Hydrophilic Fumed TiO ₂ |
| Aeroxide T805 | Evonik | - | TiO ₂ | 20 nm | - | Hydrophobic Fumed TiO ₂ |

¹ glycerol phosphate dimethacrylate, ² hydroxyethyl methacrylate, ³ monomethyl ether hydroquinone

Table 2. Sample group designation system

| Specimen group | Nanosilica content [%] | Designation |
|---------------------------------------|------------------------|-------------|
| Control | 0 | 0 |
| Hydrophilic TiO ₂ addition | 0.05 | 0.05 I |
| | 0.2 | 0.2 I |
| | 1 | 1 I |
| Hydrophobic TiO ₂ addition | 0.05 | 0.05 O |
| | 0.2 | 0.2 O |
| | 1 | 1 O |

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):

$$C = 4F_{max} / (\pi d^2) \quad (1)$$

where C is compressive strength [MPa], F_{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):

$$VHN = 1.8544F/d^2 \quad (2)$$

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 ($50 \text{ cm}^3/\text{min}$). 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 $10^\circ\text{C}/\text{min}$. 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 Fischer 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 (η^*) 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 statistic 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 insignificant 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.

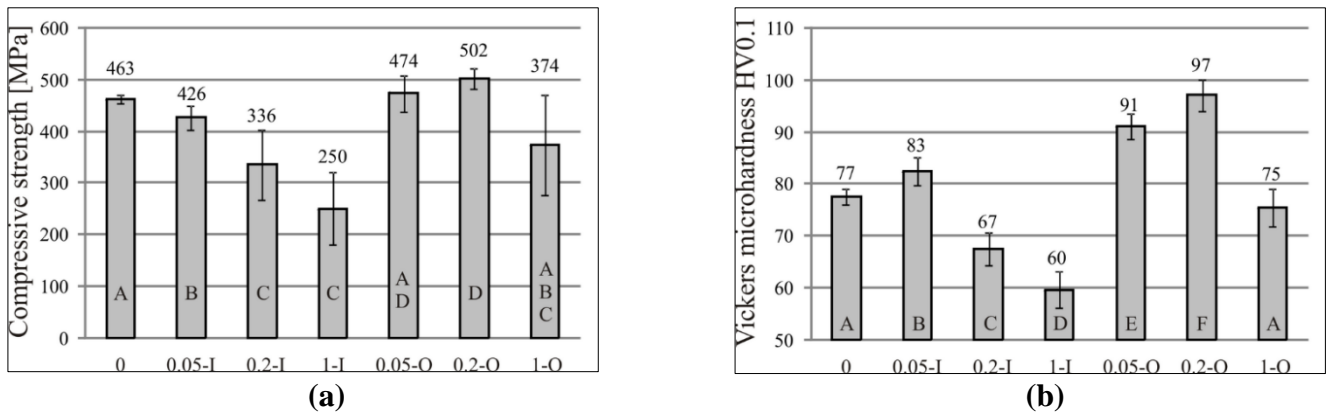


Figure 1. (a) Compressive strengths of tested materials; (b) Microhardnesses of tested materials. Different letters marked in bars indicate statistically significant differences between mechanical properties of various specimens at a level of 95 %

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 (YbF_3) particle [17], while Spectrum 2 indicates that it may be interpreted as barium silicate glass ($1\text{BaO} \cdot 2\text{SiO}_2$) [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 TiO_2 clustered nanoparticles.

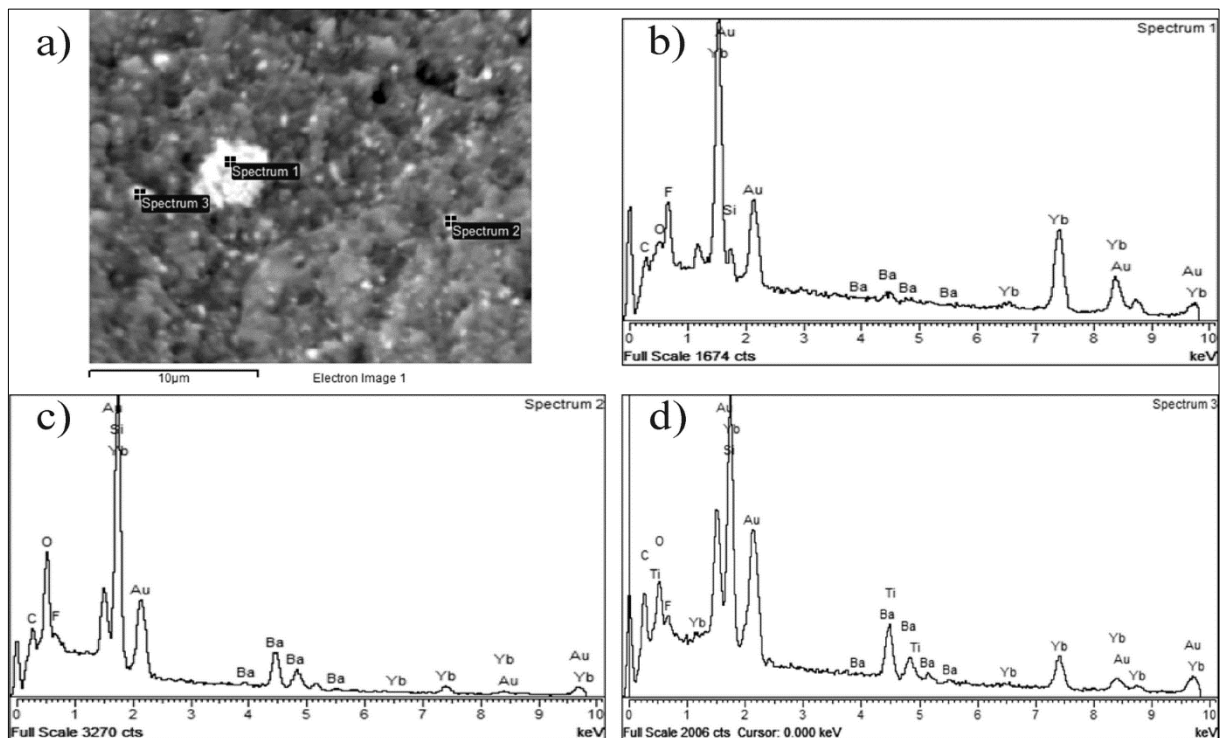


Figure 2. EDX analysis of the specimen 1 I

Table 3. Chemical composition and phase identification of spectra shown in Figure 2

| Spectrum No. | C | O | F | Si | Ti | Ba | Yb | Phase identification |
|--------------|-------|-------|-------|-------|-------|-------|-------|------------------------|
| Spectrum 1 | 15.56 | 4.38 | 17.17 | 1.87 | - | 2.17 | 58.85 | YbF ₃ |
| Spectrum 2 | 22.80 | 36.17 | 5.90 | 16.80 | - | 12.25 | 6.09 | 1BaO 2SiO ₂ |
| Spectrum 3 | 37.70 | 17.14 | 4.04 | 11.79 | 13.37 | 2.24 | 13.73 | TiO ₂ |

3.3.DSC analysis

Figures 3 and 4 show heat flow over the temperature chart for modified samples with hydrophobic and hydrophilic TiO₂, 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 TiO₂ 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.

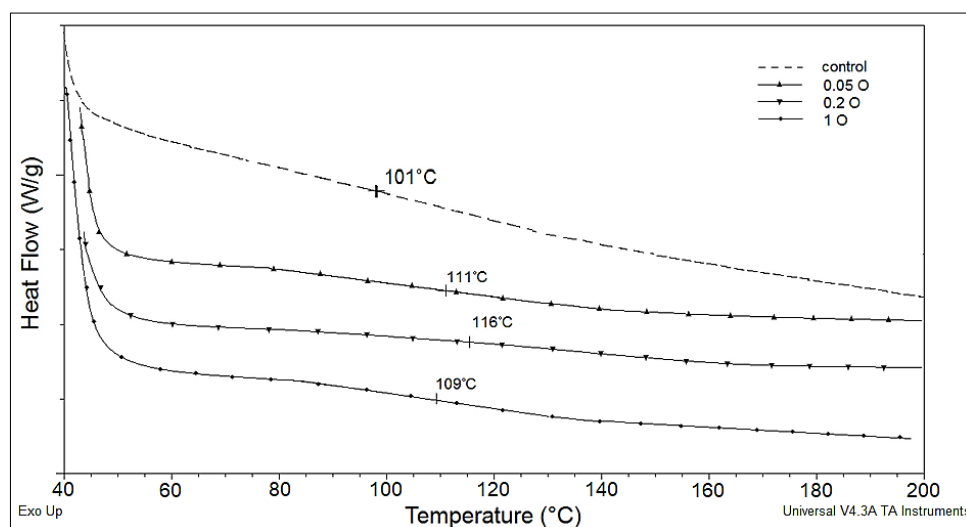


Figure 3. DSC curves of prepared samples with different hydrophobic TiO₂ content

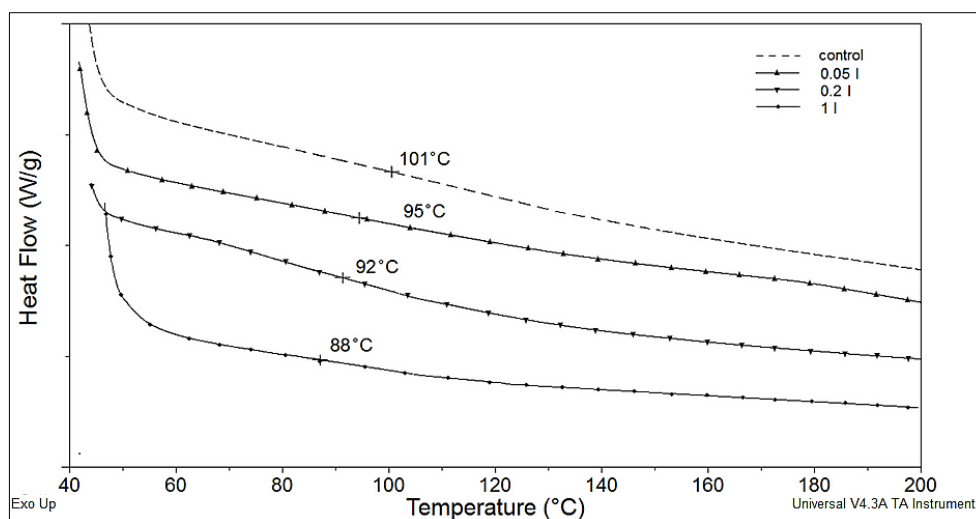


Figure 4. DSC curves of prepared samples with different hydrophilic TiO₂ content

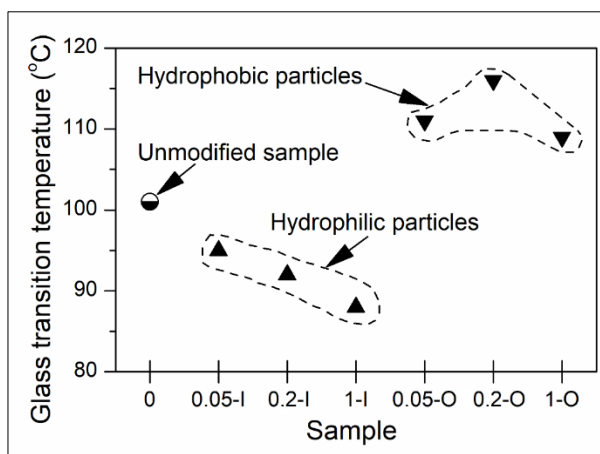


Figure 5. Glass transition temperatures of tested materials

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.

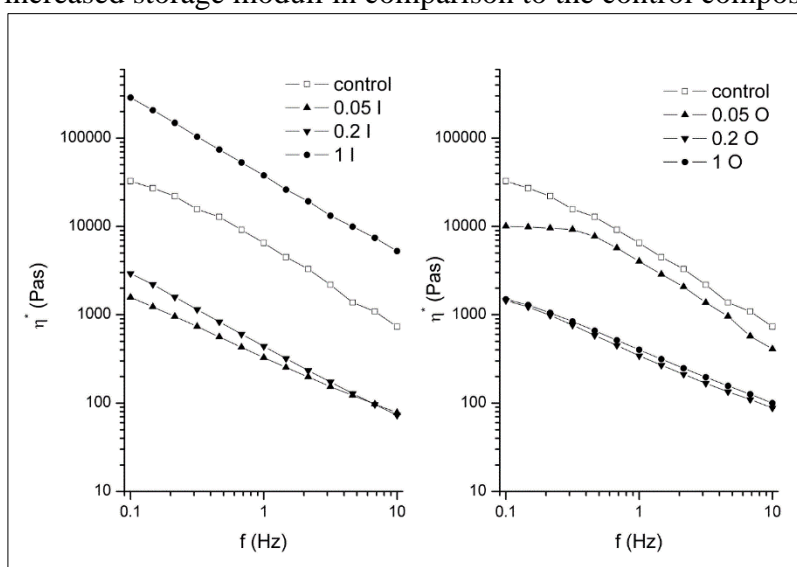


Figure 6. Complex viscosity vs. frequency of flowable composites with the addition of hydrophilic (I) TiO_2 and hydrophobic (O) TiO_2 particles

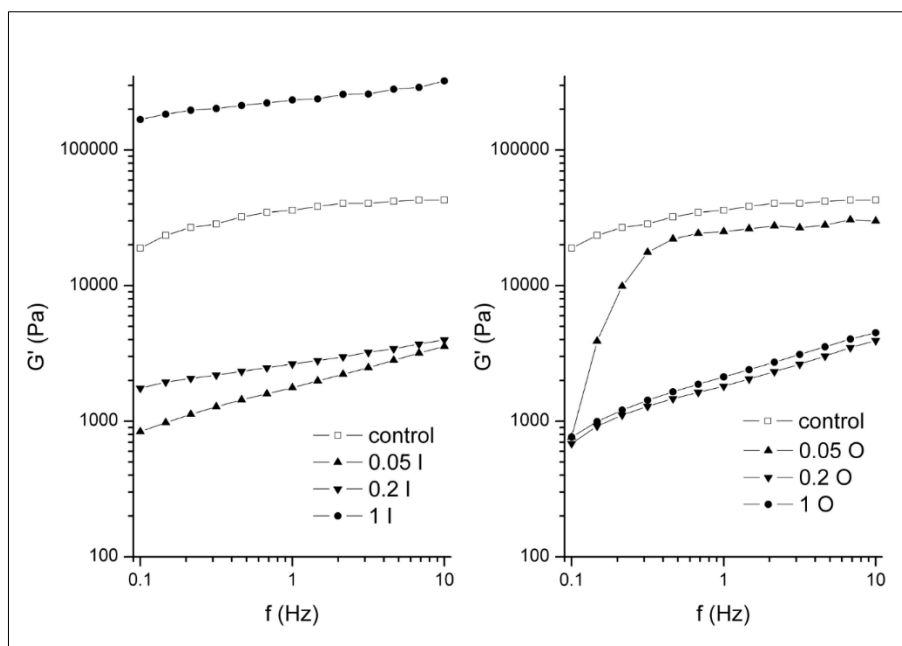


Figure 7. Storage moduli vs. frequency of flowable composites with the addition of hydrophilic (I) TiO_2 and hydrophobic (O) TiO_2 particles

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 nanocomposites 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 disproportionately 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.

Acknowledgments. This research was supported by the Department of Production Engineering, Faculty of Technical Sciences Novi Sad Serbia, entitled "Interdisciplinary technologies in production engineering".



References

1. SALERNO, M., DERCHI, G., THORAT, S., CESERACCIU, L., RUFFILLI, R., BARONE, A.C., Surface morphology and mechanical properties of new-generation flowable resin composites for dental restoration, *Dent Mater.*, **37**, 2011, 1221–1228. <https://doi.org/10.1016/j.dental.2011.08.596>
2. BAYNE, S.C., THOMPSON, J.Y., SWIFT JR, E.J., STAMATIADIS, P., WILKERSON, M., A characterization of first-generation flowable composites, *J Am Dent Assoc.*, **129**, 1998, 567–577. <https://doi.org/10.14219/jada.archive.1998.0274>
3. LEE, J.H., UM, C.M., LEE, I.B., Rheological properties of resin composites according to variations in monomer and filler composition, *Dent Mater.*, **22**, 2006, 515–526. <https://doi.org/10.1016/j.dental.2005.05.008>
4. LEEVAILOJ, C., COCHRAN, M.A., MATIS, B.A., MOORE, B.K., PLATT, J.A., Microleakage of posterior packable composites with and without flowable liners, *Oper Dent.*, **26**, 2001, 302–307. PMID: 11357574.
5. HELVATJOGLU-ANTONIADES, M., PAPADOGIANNIS, Y., LAKES, R.S., DIONYSOPOULOS, P., PAPADOGIANNIS D., Dynamic and static elastic moduli of packable and flowable composite resins and their development after initial photo curing, *Dent Mater.*, **22**, 2006, 450–459. <https://doi.org/10.1016/j.dental.2005.04.038>
6. FERRACANE, J.L., Resin composite - State of the art, *Dent Mater.*, **27**, 2011, 29–38.
7. LEE, I.B., MIN, S.H., KIM, S.Y., FERRACANE, J., Slumping tendency and rheological properties of flowable composites, *Dent Mater.*, **26**, 2010, 443–448. <https://doi.org/10.1016/j.dental.2010.01.003>
8. BONILLA, E.D., YASHAR, M. CAPUTO, A.A., Fracture toughness of nine flowable resin composites, *J Prosthet Dent.*, **89**, 2003, 261–267. <https://doi.org/10.1067/mpr.2003.33>
9. KARABELA, M.M., SIDERIDOU, I.D., Synthesis and study of properties of dental resin composites with different nanosilica particles size, *Dent Mater.*, **27**, 2011, 825–835. <https://doi.org/10.1016/j.dental.2011.04.008>
10. BALOS, S., PILIC, B., PETRONIJEVIC, B., MARKOVIC, D., MIRKOVIC, S., SARCEV I., Improving mechanical properties of flowable dental composite resin by adding silica nanoparticles, *Vojnosanit Pregl.*, **70**, 2013, 477–483. <https://doi.org/10.2298/VSP1305477B>
11. SUN, J., FORSTER, A.M., JOHNSON, P.M., EIDELMAN, N., QUINN, G., SCHUMACHER, G., ZHANG, X., WU, W.L., Improving performance of dental resins by adding titanium dioxide nanoparticles, *Dent Mater.*, **27**, 2011, 972–982. <https://doi.org/10.1016/j.dental.2011.06.003>
12. XIA, Y., ZHANG, F., XIE, H., GU N., Nanoparticle-reinforced resin-based dental composites, *J Dent.*, **36**, 2008, 450–455. <https://doi.org/10.1016/j.jdent.2008.03.001>
13. BALOS, S., PILIC, B., PETROVIC, DJ., PETRONIJEVIC, B., SARCEV, I., Flexural strength and modulus of autopolymerized poly(methyl methacrylate) with nanosilica, *Vojnosanit. Pregl.* **75**(6), 2018, 564–69. <https://doi.org/10.2298/VSP160203359B>
14. BALOS, S., PILIC, B., MARKOVIC, D., PAVLICEVIC, J., LUZANIN, O., Poly(methyl-methacrylate) nanocomposites with low silica addition, *J. Prosthet. Den.*, **111**, 2014, 327–34. <https://doi.org/10.1016/j.prosdent.2013.06.021>
15. BEUN, S., BAILLY, C., DEVAUX, J., LELOUP, G., Rheological properties of flowable resin composites and pit and fissure sealant, *Dent Mater.* **24**, 2008, 548–555. <https://doi.org/10.1016/j.dental.2007.05.019>
16. ZHANG, S.S., Y.J., WANG, H.W., Effect of particle size distributions on the rheology of Sn/Ag/Cu lead-free solder pastes, *Mater Des.*, **31**, 2010, 594–598. <https://doi.org/10.1016/j.matdes.2009.07.001>
17. SKUCHA-NOWAK, M., NOWAK-WACHOL, A., SKABA, D., WACHOL, K., KOTYTKOWSKA -WALACH; A., Use of Ytterbium Trifluoride in the Field of Microinvasive Dentistry-An In Vitro Preliminary Study, *Coatings* **10**, 2020, 915; <http://doi:10.3390/coatings10100915>
18. MCKENZIE, M.E., DENG, B., VAN HOESEN, D.C., XIA, X., BARKER, D.E. REZIKYAN, A., YOUNGMAN, R.E., KELTON, K.F., Nucleation pathways in barium silicate glasses, *Sci. Rep.*, **69**, 2021, <https://doi.org/10.1038/s41598-020-79749-2>



- 19.MOTA, E.G., HÖRLE, L., OSHIMA, H. M., MAYUMI HIRAKATA, L., Evaluation of inorganic particles of composite resins with nanofiller content, *Stomatologija*, **14**, 103-107, 2012
- 20.PERESSINI, D., SENSIDONI, A., POLLINI, C.M., DE CINDIO, B., Rheology of wheat doughs for fresh pasta blends and salt content production: influence of semolina-flour blends and salt content, *J Texture Stud.*, **31**, 2000, 163–182. <https://doi.org/10.1111/j.1745-4603.2000.tb01415.x>
- 21.SIVARAMAKRISHNAN, H.P., SENGE, B., CHATTOPADHYAY, P.K., Rheological properties of rice dough for making rice bread, *J Food Eng.*, **62**, 2004, 37–45. [https://doi.org/10.1016/S0260-8774\(03\)00169-9](https://doi.org/10.1016/S0260-8774(03)00169-9)
- 22.RONG, M.Z., ZHANG, M.Q., ZHENG, Y.X., ZENG, H.M., WALTER, R., FRIEDRICH, K., Structure property relationship of irradiation grafted nano-inorganic particle filled polypropylene composites, *Polymer.*, **42**, 2001, 167–183. [https://doi.org/10.1016/S0032-3861\(00\)00325-6](https://doi.org/10.1016/S0032-3861(00)00325-6)
- 23.THOSTENSON, E.T., LI, C.Y., CHOU, T.W., Nanocomposites in context, *Compos Sci Technol.*, **65**, 2005, 491–516. <https://doi.org/10.1016/j.compscitech.2004.11.003>
- 24.CONRADI, M., Nanosilica-reinforced polymer composites, *Mater and Tech*, **47**(3), 2013, 285-293.
- 25.GACITUA, W.E., BALLERINI, A.A., ZHANG, J., Polymer nanocomposites: Synthetic and natural fillers-A review, *Maderas Cienc y Tecnol*, **7**(3), 2005, 159–178 <http://dx.doi.org/10.4067/S0718-221X2005000300002>
- 26.NJUGUNA, J., PIELICHOWSKI, K., Polymer nanocomposites for aerospace applications: fabrication, *Adv Eng Mater.*, **6**, 2004, 193–203. <https://doi.org/10.1002/adem.200305111>
- 27.KHARE, H.S., BURRIS, D.L., A quantitative method for measuring nanocomposite dispersion, *Polymer*, **51**, 2010, 719–729. <https://doi.org/10.1016/j.polymer.2009.12.031>
- 28.BERA, O., PILIĆ, B., PAVLIČEVIĆ, J., JOVIČIĆ, M., HOLLO, B., MESAROS SZECSENYI, K., ŠPIRKOVA, M., Preparation and thermal properties of polystyrene/silica nanocomposites, *Thermochim Acta*, **515**, 2011, 1–5. <https://doi.org/10.1016/j.tca.2010.12.006>
- 29.ELSHEREKSI, N.W., MOHAMED, S.H., ARIFIN, A., MOHD ISHAK, Z.A., Effect of filler incorporation on the fracture toughness properties of denture base poly(methyl methacrylate), *J Phys Sci.*, **20**, 2009, 1–12.
- 30.BALOS, S., PILIC, B., MARKOVIC, D., PAVLICEVIC, J., LUZANIN, O., Poly(methyl-methacrylate) nanocomposites with low silica addition, *J Prosthet Den.*, **111**, 2014, 327–334. <https://doi.org/10.1016/j.prosdent.2013.06.021>
- 31.KOTSILKOVA, R., FRAGIADAKIS, D., PISSIS, P., Reinforcement effect of carbon nanofillers in an epoxy resin system: rheology, molecular dynamics, and mechanical studies, *J Polym Sci Pol Phys.*, **43**, 2005, 522–533. <https://doi.org/10.1002/polb.20352>
- 32.BERA, O., JOVIČIĆ, M., PAVLIČEVIĆ, J., PILIĆ, B., The influence of oxide nanoparticles on the kinetics of free radical methyl methacrylate polymerization in bulk, *Polym Compos.*, **34**, 2013, 1342–1348. <https://doi.org/10.1002/pc.22548>
- 33.ARRIGHI, V., MCEWEN, I.J., QIAN, H., SERRANO PRIETO, M.B., The glass transition and interfacial layer in styrene-butadiene rubber containing silica nanofiller, *Polymer*, **44**(20), 2003, 6259–6266. [https://doi.org/10.1016/S0032-3861\(03\)00667-0](https://doi.org/10.1016/S0032-3861(03)00667-0)
- 34.LESLEY, M.H., RUI, Q., PHILLIP B.M., BRINSON, L.C., Effects of dispersion and interfacial modification on the macroscale properties of TiO₂ polymer–matrix nanocomposites, *Compos Sci Technol.*, **69**, 2009, 1880–1886. <https://doi.org/10.1016/j.compscitech.2009.04.005>
- 35.LEE, I.B., CHO, B.H., SON, H.H., UM, C.M., Rheological characterization of composites using a vertical oscillation rheometer, *Dent Mater.*, **23**, 2007, 425–432. <https://doi.org/10.1016/j.dental.2006.02.013>
36. ELLAKWA, A., CHO, N., LEE, I.B., The effect of resin matrix composition on the polymerization shrinkage and rheological properties of experimental dental composites, *Dent Mater.*, **23**, 2007, 1229–1235. <https://doi.org/10.1016/j.dental.2006.11.004>



37.LEE, I.B., SON, H.H., UM, C.M., Rheologic properties of flowable, conventional hybrid, and condensable composite resins, *Dent Mater.*, **19**, 2003, 298–307.

[https://doi.org/10.1016/S0109-5641\(02\)00058-1](https://doi.org/10.1016/S0109-5641(02)00058-1)

38.NOACK, M.J., ROULET, J.F., BERGMANN, P., A new method to lute tooth colored inlays with highly filled composite resins, *J Dent Res.*, **70**, 1991, 457. Abstr No. 1528

39.MEERBEEK, B.V., INOKOSHI, S., DAVIDSON, C.L., DE GEE, A.J., Lambrechts, P, Braem, M, Vanherle, G., Dual cure luting composites-Part II: Clinically related properties, *J Oral Rehabil.*, **21**, 1994, 57–66. <https://doi.org/10.1111/j.1365-2842.1994.tb01124>

40.DIETSCHI, D., MAGNE, P., HOLZ, J., Recent trends in esthetic restorations for posterior teeth, *Quintessence Int.*, **25**, 1994, 659–677. PMID: 9161244.

41.PETRICCIONE, A., ZARRELLI, M., ANTONUCCI, V., GIORDANO, M., Aggregates of Chemically Functionalized Multiwalled Carbon Nanotubes as Viscosity Reducers, *Materials*, **7**, 2014, 3251-3261. <https://doi.org/10.3390/ma7043251>

Manuscript received: 15.12.2020