EFFECT OF MICRO- AND NANO-FILLERS ON THE COEFFICIENT OF THERMAL EXPANSION OF COMPOSITE SYSTEMS WITH POTENTIAL APPLICATIONS IN STOMATOLOGY

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Abstract

This experimental study aims to assess the effect of selected filler types on the longitudinal thermal expansion of composite systems. The studied issue concerns the dimensional stability or durability of white dental fillings, composite systems of photo polymerizing polymer with particulate fillers of micrometer and nanometer dimensions, mainly based on silica and zirconia. ChS Epoxy 455 epoxy resin cured with P11 hardener was used as the matrix of the composite systems on which the effect of selected filler types was evaluated. The fillers were particulate and fibrous materials of different chemical compositions, sizes, and combinations. Synthetic silica nanoparticles, cellulose particles, hybrid fillers derived from modified rice husk, and cellulose nanocrystals were used as fillers. The longitudinal thermal expansion of the prepared composite systems was evaluated in the temperature range of 20 ° to 40 °C, which corresponds to the temperatures to which dental fillings are usually exposed. The selected fillers fracture surfaces of samples were analyzed on a scanning electron microscope, and the longitudinal thermal expansion was measured on a thermomechanical analyzer. Based on the dimensions and chemical compositions of fillers used, the quality of the interphase, and the arrangement of the fillers in the polymer matrix, the contribution of these reinforcing elements to the potential influence of the thermal expansion coefficient was evaluated. In view of results obtained, the following experiments will focus on the study of material combinations of particulate and fibrous fillers, the evaluation of the influence of the environment on materials, and machinability.

Keywords: Composite system, epoxy resin, micro-fillers, nano-fillers, dentistry

1. INTRODUCTION

Composite materials are currently widely used not only in technical applications but we can also find them in medical areas. A typical example is the composite materials used in dentistry as dental fillings. These fillings are a composite or nanocomposite system in which the matrix is a photopolymer, and the filler is a nanoparticle. Most often based on oxides - silicon dioxide, zirconium oxide, barium oxide, and aluminum oxide [1-4]. These fillers ensure the mechanical parameters of the filling, such as hardness, resistance to abrasion, toughness, and color, which is no less critical for these white fillings. Filtek, Ceram and Omnichrom are among the most widely used materials used as dental fillings. However, after a specific time, dental composite material ages. Even if the filling initially has good adhesion to the dentin or tooth enamel, it breaks off, and a micro gap forms between the tooth and the filling. The breaks are followed by the enlargement of the micro gap and the formation of secondary tooth decay. This process is observed over a long time and occurs approximately four to six years after applying a white filling. It is related to dental hygiene, diet, and immunity. The problem lies in the degradation of the composite system used, or instead in the shrinkage of the filling, as a result of which it will detach from the tooth [5-8].

From the theory of composite behavior, it is clear that the use of particle filler cannot provide the matrix with the same mechanical parameters as if fiber fillers were used. The use of fiber fillers in materials for dental

fillings is currently not adequately studied. Some undesirable phenomena could be avoided using suitable fiber fillers. Choosing the right fiber filler is also essential, as it is a material that comes into contact with humans [7-10].

The present work aims to analyze samples based on epoxy resin filled with selected particle and fiber fillers and their combinations. In the first step, this analysis is intended to provide insight into the behavior of selected hybrid structures in the epoxy matrix. In the second step, use the chosen fillers or their mixtures, optimize the composition and proportions and transform these fillers into a photo-polymerizing material.

1. EXPERIMENT

The two-component epoxy resin ChS Epoxy 455 cured with hardener P11 (Districhem, s.r.o.) was used as a matrix of composite samples for this work. As fillers, synthetic nanoparticles of fumed amorphous silica Cab-O-Sil LM-150 (CABOT, GmbH), cellulose particles known in practice as abrasive wood pulp (University Pardubice), purified rice husks (Cersum, s.r.o.), fibers from purified rice husks were used as fillers (Cersum, s.r.o.) and cellulose nanocrystals (TUL). Combinations of these materials have also been used. A scanning electron microscope TESCAN MIRA3 (TESCAN ORSAY HOLDING, a. s.) was used to evaluate the fracture surfaces, respectively, the interphase adhesion. A thermomechanical analyzer (Pragolab, s.r.o.) was used to determine the longitudinal thermal expansion.

Due to the existing experience with dental fillings, which are composite systems with particulate fillers, the evaluation of the effect of selected fillers was designed to use particulate, fibrous, and their combination. Synthetically produced silicon dioxide in the form of nanoparticles, used in dental fillings in Filtek, Ceram, and Omnichrom products, were chosen as an inorganic particle filler. The so-called abrasive wood pulp was selected as an organic particle filler based on cellulose. Another type of filler was modified rice husks, provided by Cersum, s.r.o. These are composed of both cellulose fibers and nanoparticles of biogenic silicon dioxide, placing them in the hybrid organic-inorganic fillers group [11]. Fibers separated from treated rice husks were also used, provided by the company Cersum, s.r.o. [12] The last filler was cellulose nanocrystals, characterized by width in units of nanometers and a length in hundreds of nanometers [13].

The filler added to the base epoxy resin was chosen so that the effect of the different behavior of particle filler, fiber filler, and their mixtures, consisting of both fibers and particles, was noticeable. From a chemical point of view, a filler analogous to the typical filler used for dental fillings, i.e., nanoparticles of silicon dioxide, was used. Silica is also contained in rice husks and fibers from treated rice husks. For that reason, combinations of cellulose fibers, particles, nanofibers, and silica were designed and tested, and mixtures were prepared in which fiber and particle fillers were combined **(Table 1).**

Mixtures were prepared by mixing epoxy resin with different fillers, and their combinations were cast into silicone molds and cured. Curing of the samples took place in a pressure vessel to remove inhomogeneities and bubbles at a pressure of 0.7 MPa, for 24 hours at a temperature of 23 °± 2 °C. The prepared samples were not further cured. Before the longitudinal thermal expansion determination, the samples were surface treated according to the requirements for measurement.

2. RESULTS

The results of the experiments were assessed both from the point of view of the measured values of the longitudinal thermal expansion (10 measured samples for every material composition) and from the point of view of the interphase of the designed composite systems **(Table 1). Table 1** shows the composition of hybrid systems and the average values of longitudinal thermal expansion for individual groups of samples for the temperature interval 20 °C to 40 °C. From the fracture surfaces, it can be seen whether the particles and fibers are homogeneously distributed in the polymer matrix and, above all, the quality of the interphase adhesion, which is an essential condition for ensuring the desired behavior in composite systems.

Table 1 Composition of individual samples with the corresponding coefficient of thermal expansion α

	Polymer matrix	Inorganic filler	Organic filler	α (10^{-6}·K^{-1})
1	10 g ChS Epoxy 455	-	-	72.93
2	10 g ChS Epoxy 455	1.0 g silicon dioxide nanoparticles	-	66.45
3	10 g ChS Epoxy 455	-	1.0 g cellulose particles	77.52
4	10 g ChS Epoxy 455	-	1.0 g modified rice husks	71.77
5	10 g ChS Epoxy 455	-	1.0 g fibers from modified rice husks	69.14
6	10 g ChS Epoxy 455	0.5 g silicon dioxide nanoparticles	0.3 g fibers from modified rice husks	67.48
7	10 g ChS Epoxy 455	-	1.0 g cellulose nanocrystals	77.53
8	10 g ChS Epoxy 455	1.0 g silicon dioxide nanoparticles	1.0 g cellulose nanocrystals	72.21

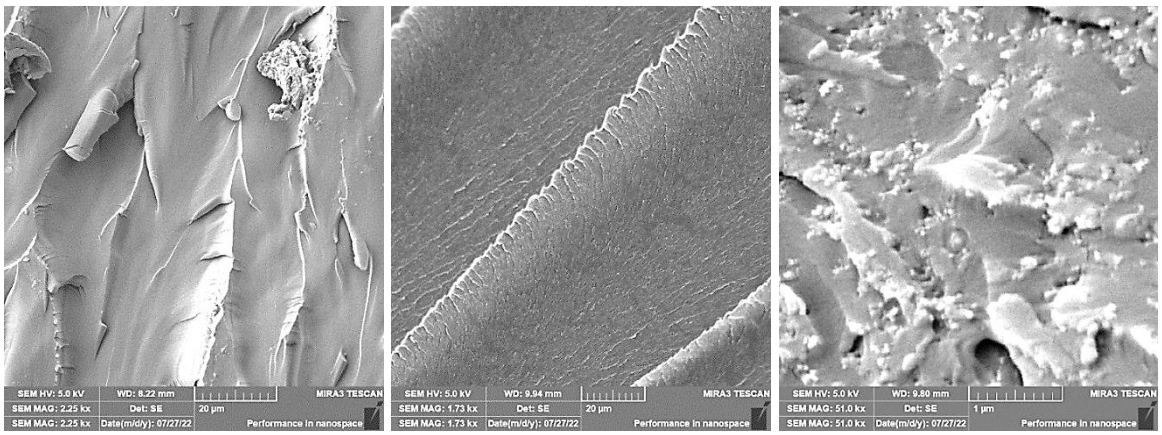

Figure 1 Epoxy resin without fillers (left), epoxy resin with silicon dioxide nanoparticles (middle), and a detailed picture with a visible distribution of silicon dioxide nanoparticles (right)

Figure 1 (left) shows the characteristic brittle fracture of epoxy resin without filler. In the other images of **Figure 1**, it is clear that there is a change after adding silicon dioxide nanoparticles, like the material's fracture. From the overview picture in **Figure 1** (middle), it can be seen that the filler is more or less evenly distributed in the epoxy matrix. When viewing **Figure 1** (right) in detail, it can be seen that the nanoparticles form larger or smaller clusters, and part of the matrix is not filled with them. Adhesion of nanoparticles can be considered reasonable. The measured values of the coefficient of longitudinal thermal expansion α are assigned to the mentioned images, which for a sample of pure epoxy resin reaches a value of $72.93 \cdot 10^{-6} \cdot K^{-1}$, while for a sample with a high content of silicon dioxide nanoparticles, the value is $66.45 \cdot 10^{-6} \cdot K^{-1}$ is the lowest average value measured in the entire series of prepared samples.

Epoxy resin filled with cellulose particles of irregular shape **(Figure 2 left)** does not show good adhesion, the fracture of the surrounding resin is brittle, and the value of the coefficient of longitudinal thermal expansion α is $77.52 \cdot 10^{-6} \cdot K^{-1}$ **(Table 1)**.

Purified rice husks **(Figure 2 middle, right**) are specific for their two-component structure **(Figure 2 right)**, where it can be seen that the outer part of the husk is made up of a few-micrometer layer of silicon dioxide nanoparticles. In contrast, the inner part is built up of organic fibers. Purified rice husks do not show sufficient adhesion in epoxy resin **(Figure 2 middle).** Moreover, these are relatively large particles with a length and width of hundreds of micrometers. As a result, a considerable amount of the epoxy matrix is not affected by their presence, and the fracture is then fragile in these polymer parts **(Figure 2 middle)**. The character of the particles and poor adhesion is also matched by the value of the coefficient of longitudinal thermal expansion of the prepared system, which is equal to the value of $71.77 \cdot 10^{-6} \cdot K^{-1}$ and is thus practically at the level of the value of longitudinal thermal expansion of unfilled epoxy resin **(Table 1)**.

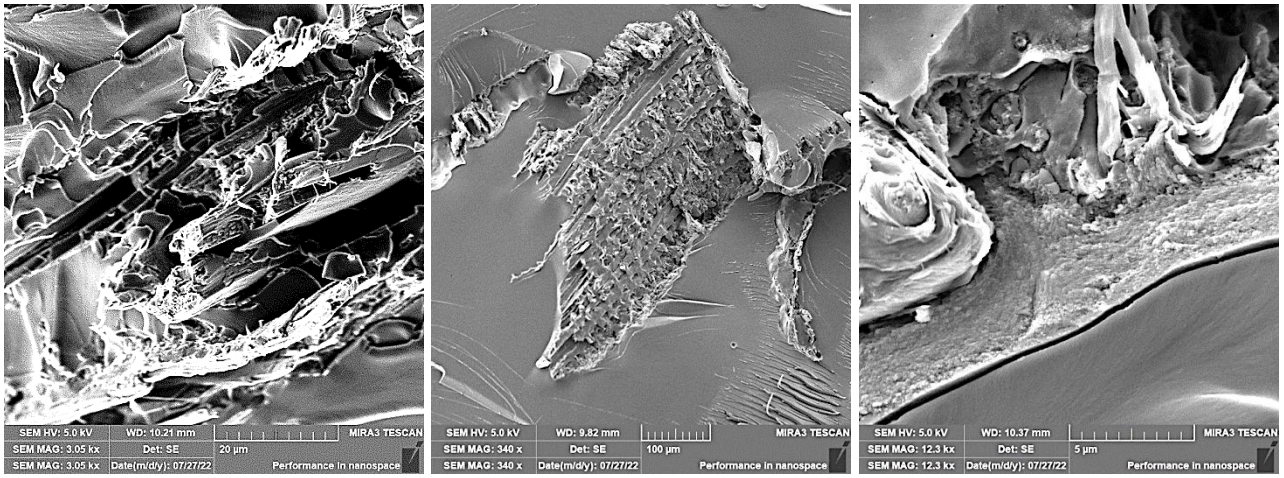

Figure 2 Epoxy resin with cellulose particles (left), epoxy resin with treated rice husk particles (middle), detailed pictures of rice husk particles interfacial adhesion with typical silicone dioxide part and cellulose part (right)

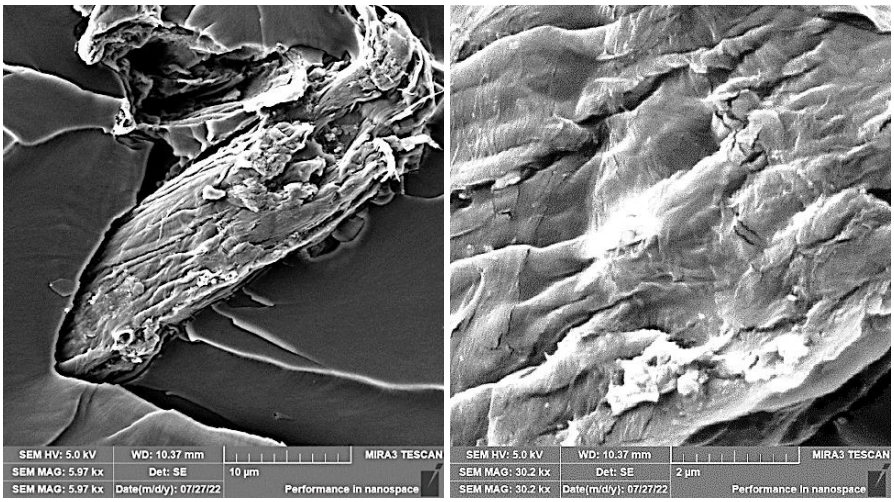

Figure 3 Epoxy resin with treated rice husk fibers in epoxy resin (left), detailed picture of fibers with silicon dioxide nanoparticles on the surface (right)

Cellulose fibers obtained from purified rice husks **(Figure 3)** have a diameter of about 10 micrometers. The length is usually many times greater [12]. On the surface of the fibers, there are residues of nanoparticles of biogenic silica **(Figure 3 right)**, which are primarily formed in rice husks during their growth, and which were not completely removed during their treatment. The surface of the fibers is finely structured. As seen from the picture **(Figure 3 left)**, the adhesion between the fibers and the matrix is not very good. The fracture of the surrounding epoxy resin is brittle. The value of the coefficient of longitudinal thermal expansion α of this composite system is $69.14 \cdot 10^{-6} \cdot K^{-1}$ **(Table 1)**.

Cellulose fibers obtained from purified rice husks and synthetic silica nanoparticles provide good adhesion to the epoxy matrix. The fibers are well coated with resin, the silicon dioxide nanoparticles are more or less homogeneously distributed **(Figure 4 left)**, and the fracture of the composite system is not fragile. Similar to the case of the epoxy resin-silica nanoparticles system, there are visible parts of the resin that is not filled with nanoparticles **(Figure 4 right)**. The value of the coefficient of longitudinal thermal expansion α of this hybrid organic-inorganic composite system is equal to the value of $67.48 \cdot 10^{-6} \cdot K^{-1}$ **(Table 1)**.

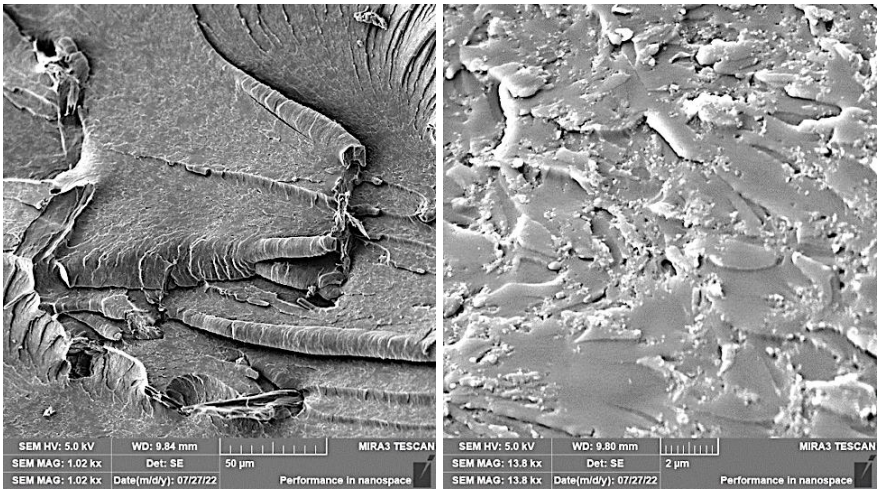

Figure 4 Epoxy resin with treated rice husk fibers and silicon dioxide nanoparticles - adhesion between fibers and epoxy resin (left), distribution of silicon dioxide nanoparticles in epoxy resin (right)

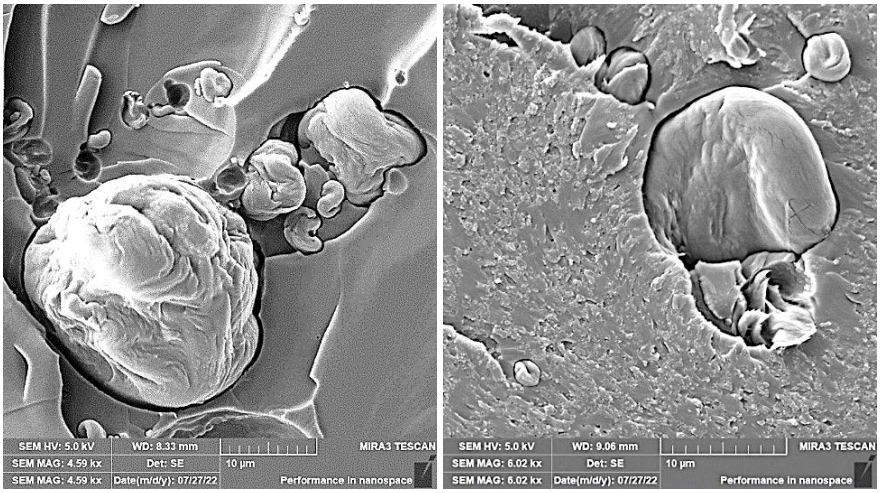

Figure 5 Epoxy resin with cellulose nanocrystals (left), epoxy resin with cellulose nanocrystals and silicon dioxide nanoparticles (right)

Due to their chemical composition, cellulose nanocrystals form spherical structures of larger or smaller dimensions **(Figure 5 left)**. These clusters of nanocrystals do not break down into smaller nanostructures in the epoxy resin, so this filler functions only as a particulate filler. The particles have inferior adhesion to the epoxy matrix, free spaces are visible in the electron microscope images where they are present, and the material shows a brittle fracture **(Figure 5 left)**. Bad adhesion corresponds to the highest ever average measured value of the coefficient of longitudinal thermal expansion α $77.53 \cdot 10^{-6} \cdot K^{-1}$, comparable to the value obtained using cellulose particles or abrasive wood **(Table 1)**. The cause is free spaces between the filler and the binder.

The epoxy resin system filled with cellulose nanocrystals and, at the same time, silicon dioxide nanoparticles **(Figure 5 right)** shows similar behavior as in the previous case, which corresponds to the coefficient of longitudinal thermal expansion α $72.21 \cdot 10^{-6} \cdot K^{-1}$ **(Table 1)**. However, there is a noticeable influence of the present nanofiller based on silicon dioxide, which stands against the non-functional particles of cellulose nanocrystals. As in all previous variants, the silicon dioxide nanoparticles are more or less well distributed in the matrix and change the character of the fracture from initially brittle to tough.

3. CONCLUSION

Based on the measurement of the values of the coefficient of longitudinal thermal expansion and comparison with the character of the fracture surfaces and the quality of interfacial adhesion, it is clear that particle fillers with micrometer dimensions - modified rice husks, cellulose particles, and at the same time also cellulose nanocrystals forming compact units - have a minimal effect on the longitudinal thermal expansion of the system, which has minimal adhesion to the epoxy matrix. The maximum impact leading to a reduction in the coefficient of longitudinal thermal expansion was achieved using nanoparticles of synthetic silicon dioxide. However, it is clear from the available literature and practical experience that particulate fillers will not ensure the functionality of the dental composite system for many years. The experiments showed a significant reduction in the coefficient of longitudinal thermal expansion occurs in the case of a combination of organic and inorganic filler-micrometer cellulose fibers from treated rice husks with residues of biogenic silicon dioxide nanoparticles on their surface and synthetic silicon dioxide nanoparticles. These organic-inorganic fibers are very well incorporated into the polymer matrix, and the value of the coefficient of longitudinal thermal expansion with its value is close to the lowest value achieved when using silicon dioxide nanoparticles. Because of the achieved results, a comprehensive evaluation of the longitudinal thermal expansion coefficients for other material ratios of organic fibers and silica nanoparticles in different polymer matrices will follow.

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