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## DEGRADATION PROCESSES IN DENTAL CERAMIC-POLYMER COMPOSITES

The paper describes the degradation processes that proceed in dental ceramic/polymer composites as a result of the action of environment, polymerization shrinkage and tribological wear. The results are analyzed in terms of the perspectives for application of these composites. In the present study the composites based on the bis-GMA resin reinforced with (i) a ceramic glass microfiller (average particle size of 5  $\mu\text{m}$ ) and (ii) ceramic glass microfiller combined with nanosilica (average particle size of 40 nm) were investigated. Samples of composites in the form of 2 x 2 x 25 were exposed to solutions with varied pH, including 0.1M NaOH (pH = 13), 0.1M CH<sub>3</sub>COOH (pH = 3) and distilled water (pH = 7) in order to compare the stability of their properties. The microstructure (Figs. 1, 2) and the mechanical parameters (such a flexural strength and microhardness) (Fig. 3) of the materials before and after the exposure were examined for the exposure time of 15 h. In order to reduce polymerization shrinkage, two approaches were considered: (a) a modification of bis-GMA resin and (b) the use of a nanofiller. The results have shown that addition of hyperbranched macromonomer of metacrylate to bis-GMA resin decreases the shrinkage by 30% (Fig. 4). The polymerization shrinkage can further be reduced by adding ceramic microfiller and nanofiller (Figs. 5, 6). One of the parameters, which can be used to characterize the tribological properties of the materials, is the coefficient of friction  $\mu$ . The influence of nanosilica content on the coefficient  $\mu$  is shown in Figure 7 for different testing loads.

**Keywords:** dental materials, ceramic - polymer composites, degradation, polymerization shrinkage

### PROCESY DEGRADACYJNE W KOMPOZYTACH CERAMICZNO-POLIMEROWYCH

Opisano procesy degradacji występujące w kompozytach ceramiczno-polimerowych stosowanych na wypełnienia stomatologiczne. Degradację tych materiałów powodują: działanie środowiska, skurcz polimeryzacyjny i zużycie ściernie. Wyniki badań analizowano w kontekście perspektyw zastosowania tych kompozytów. Do badań użyto kompozytów na osnowie żywicy bis-GMA, wzmocnionej (i) mikrowypełniaczem w postaci szkła ceramicznego (średnia wielkość cząstek 5  $\mu\text{m}$ ) oraz (ii) mikrowypełniaczem w połączeniu z nanokrzemionką (o średniej wielkości cząstek 40 nm). Próbki o wymiarach 2 x 2 x 25 mm umieszczono w roztworach o różnym pH: 0,1M NaOH (pH = 13), 0,1M CH<sub>3</sub>COOH (pH = 3) i wodzie destylowanej (pH = 7) w celu określenia stabilności właściwości mechanicznych tych kompozytów (wytrzymałość na zginanie, mikrotwardość HV<sub>0,2</sub>). Pomiar przeprowadzono przed i po 15 h przetrzymywania w roztworach (rys. 3). Mikrostrukturę wytworzonych kompozytów obserwowano za pomocą SEM (rys. rys. 1 i 2). W pracy analizowano dwa sposoby redukcji skurczu polimeryzacyjnego: (a) poprzez modyfikację żywicy bis-GMS, (b) za pomocą dodatku nanowypełniacza. Żywicę bis-GMA modyfikowano za pomocą hiperrozgałęzionego makromonomeru metakrylowego, co spowodowało zmniejszenie skurczu o 30% (rys. 4). Dalsze obniżanie skurczu polimeryzacyjnego uzyskiwano dzięki dodatkowi wypełniaczy ceramicznych, w tym nanowypełniacza (rys. rys. 5 i 6). Odporność na zużycie ściernie badanych kompozytów charakteryzowano poprzez pomiar współczynnika tarcia  $\mu$ . Wpływ zawartości nanokrzemionki na współczynnik tarcia przy różnych obciążeniach przedstawiono na rysunku 7.

**Słowa kluczowe:** materiały na wypełnienia stomatologiczne, kompozyty ceramiczno-polimerowe, degradacja, skurcz polimeryzacyjny

## INTRODUCTION

In the past, the basic materials used for dental fillings were amalgamates. Although amalgamates have many advantageous properties, such as good mechanical strength and a high wear resistance, they contain mercury widely regarded as hazardous elements, show a high heat conductivity and an unpleasant metallic

color. Recently amalgamates are gradually replaced by a new group of materials, polymer matrix ceramic composites (PMCCs). Although the mechanical properties of these composites are worse than those of amalgamates, they can be improved by selecting a proper size, shape and dispersion of the ceramic particles. Another disad-

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vantage of PMCCs is a polymerization shrinkage, which can lead to cleavage at the tissue/filling interface. Despite these shortcomings, which are possible to overcome as the technology advances, the ceramic - polymer composites are used for dental fillings on the growing scale. On the other hand an expansion of the market for PMCC dental fillings requires optimizing their structure and long term evaluation of their properties. In particular, the stability of their properties in the environment typical at human mouth is of prime interest. In the present paper such stability has been investigated on a series of specimens of PMCC developed at the Material Science and Engineering of Warsaw University of Technology in collaboration with Technical University of Białystok and Glass and Ceramic Institute.

An important factor that will influence a wider use of dental fillings is their durability and the stability of properties in oral environment. The aim of the present paper is to analyze factors which affect degradation processes of these materials. The analysis is divided into:

- degradation resulted from the influence of environment,
- degradation due to polymerization shrinkage,
- degradation caused by tribological wear.

## INFLUENCE OF ENVIRONMENT

In the oral environment, the degradation processes consist of polymer chains breaking and the formation of oligomers and, subsequently, monomers, with different groups [1]. Water can enter the bulk polymer, which may be accompanied by swelling. The intrusion of water triggers chemical polymer degradation, leading to the formation of oligomers and monomers. This in turn changes the microstructure due to the formation of pores, through which the degradable components are released [1].

The rate of the reactions in polymer based dental fillings depend on the type of chemical bond, pH, copolymers compositions, water uptake and hydrophilicity of the polymer matrix [2]. The organic acids produced by bacterial metabolism in the oral environment include acetic, propionic and lactic acids [3, 4]. The acetic and propionic acids have a softening effect on the polymers, whereas the lactic acid has no effect on their properties [5]. Hosoda et al. [6, 7] report that, in alkaline environments, the surface of the composite resins undergoes structural changes. The composites immersed in a 0.1M NaOH solution at 60°C for one week exhibited accelerated degradation of the composite resin, with filler dissolution, resin exfoliation and destruction.

In the present study the composites based on the bis-GMA resin reinforced with (i) a ceramic glass microfiller (average particle size of 5  $\mu\text{m}$ ) and (ii) ceramic glass microfiller combined with nanosilica (aver-

age particle size of 40 nm) were investigated. As a result two types of specimens were used called respectively micro- and nanocomposites. The microfiller used for fabrication of the composites was provided by Glass and Ceramic Institute. The nanofiller was commercial material (R - 709), made by Degussa. The filler was silanized in order to improve its bonding with the polymer matrix, using gamma - methacryloyloxy - propyltrimethoxysilane.

Table 1 shows the compositions of the as - fabricated ceramic - polymer composites. The total volumetric percentage of the fillers amounted to 51%.

TABLE 1. **Composition of the materials**  
TABELA 1. **Skład badanych materiałów**

Polymer matrix weight %	Bis-GMA - 58,81 TEGDMA - 40 Photoinitiator - 0,16 Activator - 0,49 Inhibitor - 0,05	
Ceramic glass filler composition	BaO - SiO <sub>2</sub> - Al <sub>2</sub> O <sub>3</sub> - SrO - F - P <sub>2</sub> O <sub>5</sub> - Na <sub>2</sub> O	
Average size of filler particles, $\mu\text{m}$	5.113	
Volume percentage of nanosilica, %	0	10
Designation of fabricated material	microcomposite	nanocomposite

Samples of composites in the form of 2 x 2 x 25 were exposed to solutions with varied pH, including 0.1M NaOH (pH = 13), 0.1M CH<sub>3</sub>COOH (pH = 3) and distilled H<sub>2</sub>O (pH = 7) in order to compare the stability of their properties. The mechanical parameters (such a flexural strength and microhardness) and the microstructure of the materials before and after the exposure were examined for the exposure time of 15 h.

Figures 1 and 2 show the microstructures of the samples before and after the exposure to various solutions. It can be noted that acetic acid has the strongest influence on the samples. SEM microstructure observations give evidence of the dissolution of the phase which bonds the polymer matrix with the ceramic fillers. As a result the filler particles fall out. An exposure in a NaOH solution leads to a dissolution of the resin and ceramic particles protrude above the resin surface. After exposure in distilled water, the microstructure of the composites remains unchanged (Fig. 1).

Figure 3 shows the values of mechanical parameters for the samples before and after exposure to various solutions. In general, the changes in microhardness are more pronounced than those in flexural strength. This would suggest that microstructure changes and properties degrade only in the near surface zone. The results also show that the presence of nanoparticles improves the mechanical parameters and increases the resistance

to environmental degradation. The later is well visible in the  $R_f = f(\text{pH})$  plot.

Rys. 1. Mikrostruktura mikrokompozytów w stanie wyjściowym i po ekspozycji w różnych środowiskach (SEM)

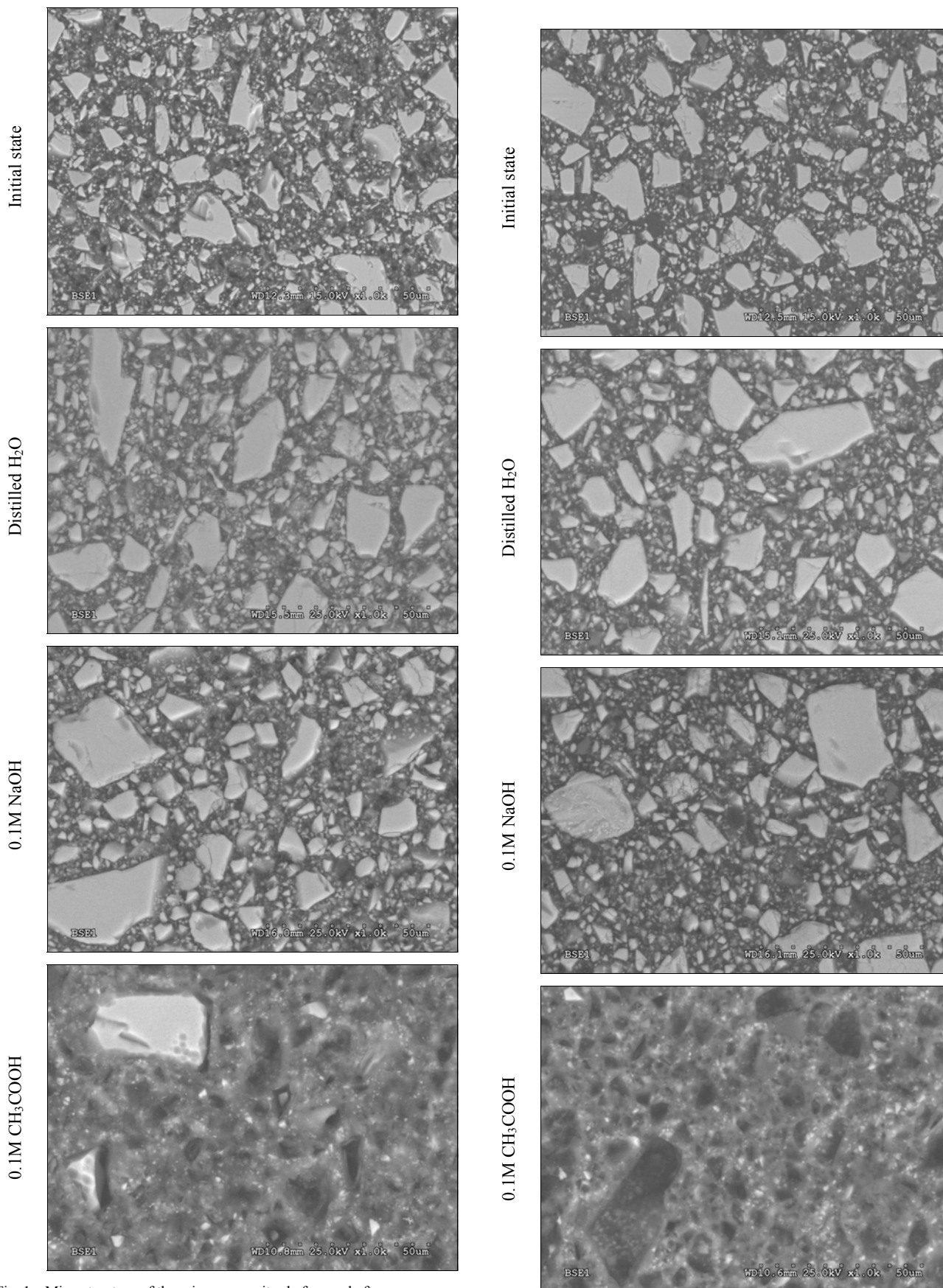


Fig. 1. Microstructure of the microcomposites before and after an exposure to various environments (SEM)

Fig. 2. Microstructure of the nanocomposites (with 10% vol. nanosilica) before and after an exposure to various environments (SEM)

Rys. 2. Mikrostruktura nanokompozytów (10% obj. nanokrzemionki) w stanie wyjściowym i po ekspozycji w różnych środowiskach (SEM)

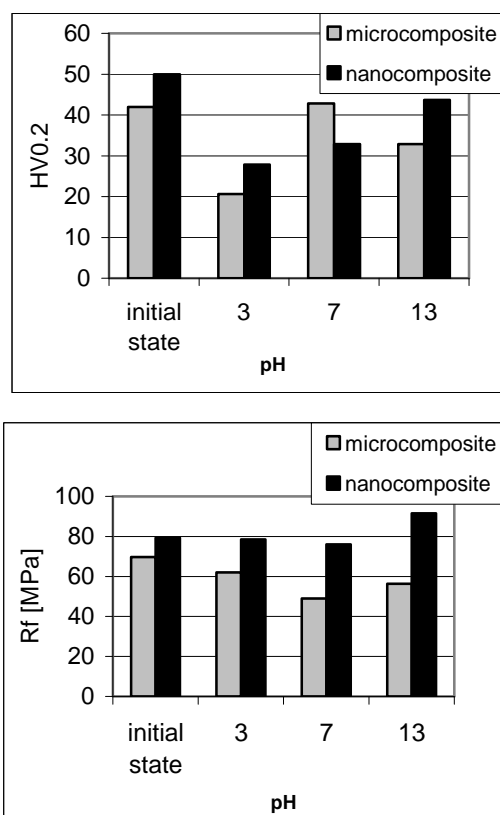


Fig. 3. Mechanical properties in the initial state and after a 15 h exposure in various environments

Rys. 3. Właściwości mechaniczne w stanie wyjściowym i po 15 h ekspozycji w różnych środowiskach

## POLYMERIZATION SHRINKAGE

Further development PMCCs for restorative dentistry depends on the quality of the tissue/ filling material bonding. If the bonding is poor it can result in cleavage, displacement at the tissue-filling interface and in secondary caries. The marginal integrity of stomatology materials depends on several factors. During restorative procedures, cavity size [8], placement technique [9], and dentine pretreatment [10] may have a significant influence. After placement, the material properties such as polymerization shrinkage [11], Young's modulus [12], and water sorption [13] can affect the integrity.

The main factor that affects the marginal integrity is the polymerization shrinkage. This shrinkage in a ceramic-polymer composite depends on the volume fraction of inorganic filler, the molecular weight of monomer system, and the degree of conversion of the monomer system [14]. In the study carried out at Warsaw University of Technology, two approaches were

considered for shrinkage reduction: (a) a modification of bis-GMA resin and (b) the use of a nano-filler.

In order to reduce the shrinkage of bis-GMA resin hyperbranched macromonomer of metacrylane was used as an additive. This configuration of macromolecules inhibits the reduction of the volume during polymerization. The obtained results indicate that such modification of the bis-GMA resin reduces polymerization shrinkage by 30% (Fig. 4).

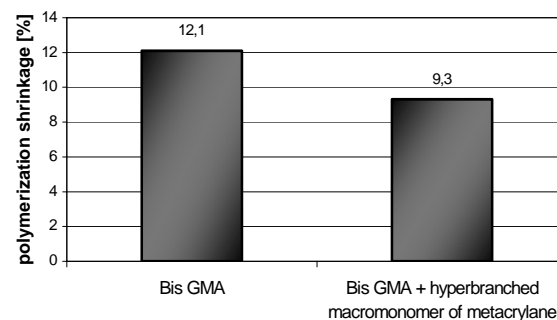


Fig. 4. Polymerization shrinkage in an unmodified and modified bis-GMA resin

Rys. 4. Skurcz polimeracyjny niemodyfikowanej oraz modyfikowanej żywicy bis-GMA

The polymerization shrinkage can further be reduced by adding ceramic fillers. Figures 5 and 6 show the result obtained in the present investigations. It can be noted that the addition of a microfiller reduces the polymerization shrinkage of the ceramic-polymer composites from 8 to below 2%. Further reduction of the polymerization shrinkage can be obtained by the nanofiller addition. It decreases twice as the nanofiller content increase to 15% (Fig. 6).

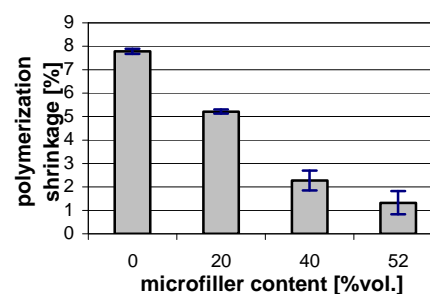


Fig. 5. Influence of the microfiller content on the polymerization shrinkage

Rys. 5. Wpływ zawartości mikrowypełniacza na skurcz polimeracyjny

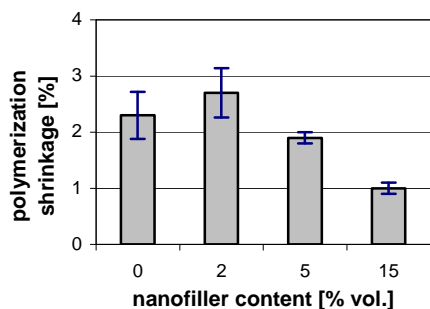


Fig. 6. Influence of the nanofiller content on the polymerization shrinkage of the composite containing 40% of ceramic phase

Rys. 6. Wpływ zawartości nanowypełniacza na skurcz polimeracyjny kompozytu zawierającego 40% fazy ceramicznej

## TRIBOLOGICAL PROPERTIES

The wear of dental composites in the oral environment is a complex phenomenon. The fundamental wear mechanisms involve adhesion, abrasion, attrition, fatigue and corrosion [15]. These processes may take place independently or in combination, intensifying the wear process in the oral cavity. One of the parameters, which can be used to characterize the tribological properties of the materials, is the coefficient of friction  $\mu$ . The influence of nanosilica content on the coefficient  $\mu$  is shown in Figure 7 for different testing loads. From data shown in Figure 7 one can conclude that an addition of the nanofiller decreases the friction coefficient  $\mu$ . This may result in a reduction of wear degradation of the nanocomposites.

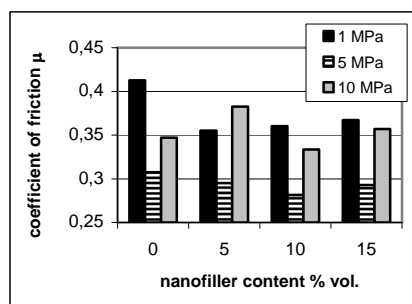


Fig. 7. Influence of the nanosilica content on the coefficient of friction  $\mu$  examined materials under various loads

Rys. 7. Wpływ zawartości nanowypełniacza na współczynnik tarcia badanych materiałów przy różnych obciążeniach

## SUMMARY

PMCCs developed at by Warsaw University of Technology exhibit good mechanical properties. They are characterized by a quite good stability of their properties in inert and alkaline environments. The acetic acid has a softening effect on the PMCCs. This probably results from the dissolution of the phase cementing the resin with the ceramic fillers. An addition of nanosilica improves the stability of mechanical parameters as well as the wear resistance of composites. It has also a positive influence on the reduction of polymerization shrinkage.

## REFERENCES

- [1] Prakki A., Cilli R., Lia Mondelli R.F., Kalachandra S., Pereira J.C., *Journal of Dentistry* 2005, 33, 91.
- [2] Gopferich A., *Biomaterials* 1996, 17, 103.
- [3] Geddes D.A.M., *Caries Research* 1975, 9, 98.
- [4] Margolis H.C., Moreno E.C., *J. Dent. Res.* 1992, 71, 1776.
- [5] Asmussen E., *Scandinavian J. of Dent. Res.*, 92, 257.
- [6] Hosoda H., Yamada T., Horie K., *Japanese Journal of Conservative Dentistry* 1987, 30, 863.
- [7] Hosoda H., Yamada T., Inokoshi S., *Japanese Journal of Conservative Dentistry* 1987, 30, 1251.
- [8] Hansen, E.K., *Scand. J. Dent. Res.* 1984, 92, 14.
- [9] Crim G.A., Chapman K.W., *Quintessence Int.* 1986, 17, 21.
- [10] Van Dijken J.W., Hörstedt P., *J. Prosthet. Dent.* 1986, 56, 677.
- [11] Davidson C.L., *J. Prosthet. Dent.* 1986, 55, 446.
- [12] Törstenson B., Brännström H., *Oper. Dent.* 1988, 13, 24.
- [13] Feilzer A.J., Dee Gee A.J., Davidson C.L., *J. Dent. Res.* 1990, 69, 36.
- [14] Suliman A.H., Boyer D.B., Lakes R.S., *J. Prosthet. Dent.* 1994, 71.
- [15] Palin W.M., Fleming G.J.P., Burke F.J.T., Marquis P.M., Pintado M.R., Randall R.C., Douglas W.H., *Dental Mater.* 2005, 21, 1112

Recenzent  
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