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ANALYSIS OF THE DEGREE OF HYDRO-THERMAL FATIGUE DAMAGE OF THE SURFACE LAYER OF POLYMER-CERAMIC COMPOSITES INTENDED FOR OPERATION IN A BIOTRIBOLOGICAL NODE

ANALIZA STOPNIA USZKODZENIA ZMĘCZENIOWEGO HYDROTERMICZNEGO WARSTWY WIERZCHNIEJ KOMPOZYTÓW POLIMEROWO-CERAMICZNYCH PRZEZNACZONYCH DO EKSPLOATACJI W WĘŹLE BIOTRIBOLOGICZNYM

Key words: microhardness, PMCCs, hydro-thermal fatigue.

Abstract The paper addresses the problem of assessing the operational quality of the surface layer (SL) of polymer-ceramic composites. These materials are used in conservative dentistry to reproduce geometrical features of human lateral teeth carrying the largest biomechanical loads. The chewing process causes that applications of these materials partly work in sliding friction conditions. Their durability in the biotribological node depends on the mechanical contact loads and is related to the influence of oral environment factors.

In this study, we assessed the impact of cyclical hydro-thermal shocks, among others, related to the consumption of hot and cold food, on the condition of SL polymer-ceramic composites. In our own research, cyclic hydro-thermal shocks with cycle temperatures of 5–55°C were simulated. Evaluation of the remaining surface strength (after implementation of the hydro-thermal cycles) was made on the basis of microhardness measurements using the Vickers method. Calculations of the damage function value were made. It has been demonstrated that the durability curves depend on the number of fatigue cycles and the structure of the material. In addition, it has been shown that the phenomenological measure of SL damage, assuming accumulation of damage, is useful in the assessment of the operational quality of polymer-ceramic composites.

Słowa kluczowe: mikrotwardość, PMCCs, zmęczenie hydro-termiczne.

Streszczenie W pracy podjęto problem oceny jakości eksploatacyjnej warstwy wierzchniej (WW) kompozytów polimerowo-ceramicznych. Tworzywa te są stosowane w stomatologii zachowawczej do odtwarzania cech geometrycznych zębów ludzkich bocznych, przenoszących największe obciążenia biomechaniczne. Proces żucia pokarmów powoduje, że aplikacje z tych tworzyw pracują częściowo w warunkach tarcia ślizgowego. Ich trwałość w węźle biotribologicznym zależy od obciążeń mechanicznych kontaktowych oraz związana jest z oddziaływaniem czynników środowiska jamy ustnej.

W przedmiotowej pracy oceniono wpływ cyklicznych wstrząsów hydrotermicznych, związanych m.in. ze spożywaniem gorących i zimnych pokarmów, na stan WW kompozytów polimerowo-ceramicznych. W badaniach własnych symulowano cykliczne wstrząsy hydrocieplne o temperaturach cyklu 5–55°C. Oceny pozostałej wytrzymałości powierzchniowej (po realizacji cykli hydrotermicznych) dokonano na podstawie pomiarów mikrotwardości metodą Vickersa. Wykonano obliczenia wartości funkcji uszkodzenia. Wykazano, że krzywe trwałości zależą od liczby cykli zmęczeniowych oraz od struktury tworzywa. Ponadto wykazano, że fenomenologiczna miara uszkodzenia WW, zakładająca kumulację uszkodzeń, jest przydatna w ocenie jakości eksploatacyjnej kompozytów polimerowo-ceramicznych.

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INTRODUCTION

Polymer matrix ceramic composites (PMCCs) are used as biomaterials in conservative methods of restoring geometrical and mechanical features of teeth, structural reinforcement of the dental arch, and in orthopaedics for fixing knee and hip joint prostheses, bonding bone fragments and filling in cavities **[L. 1]**. Light-curing PMCCs are used in conservative dentistry. The matrix of these composites is made from acrylated epoxy and urethane resins and sometimes solvents. Fillers (50–80% by volume) are micro and nanoparticles based on silicon dioxide in the form of crystalline quartz, glass fillers, aluminium-silicon-sodium salts, boron salts, zirconium oxide, lithium, and heavy metal oxides **[L. 2]**. After adding a powdered filler, a consistency of high viscosity is obtained. Before curing, PMCCs have a consistency similar to adhesives – adhesive regenerative composites.

Curing PMCCs is a chemical process. This process can be initiated under the influence of visible light activation. In order to initiate the polymerization process, it is necessary to introduce a suitable initiator into the material. The initiator under certain conditions breaks down into active free radicals initiating polymerization **[1]**. Camphorquinone is a frequently used photoinitiator. Halogen lamps (HAL) used to be the most commonly applied for photopolymerization, recently diode lamps (LEDs) are currently used on a large scale. HAL lamps are slowly replaced by LEDs, among others, due to the filters used in HAL lamps, which cause that only 1% of the total energy of the lamp is used in the stream of blue light **[L. 3]**.

Exploitation of the tribological system involves the transformation of the technologically produced surface layer (SL) of materials into the exploitative surface layer **[L. 4]**. This also applies to biotribological systems **[L. 4]**. Elements made of composites with a polymer matrix are subjected to cyclic hydro-thermal loads in the process of exploitation **[L. 5]**. As a result of physiological processes, e.g., eating food (hot soups, cold and warm beverages), there is a change in temperature in the mouth. A typical temperature range on the tooth surface is in the range of 1–50°C **[L. 6–9]**. However, there often are also higher temperatures. A special case of transient temperature is thermal shock (the same terms – heat shock, thermal shock are also met).

There are two cases of thermal stresses. In the case of multiphase materials, including powder reinforced composites, the thermal expansion of individual filler particles is not the same, but the matrix extensibility is still different. This results in the first thermal stress in the structure of PMCCs **[L. 10–12]**. In the PMCCs described, the filler and the matrix have a different thermal expansion coefficient, e.g., the average value of the coefficient of linear thermal expansion (α) for PMCCS composite resins in the temperature range of 0–60°C is respectively: Bis-GMA – $120.3 \cdot 10^{-6}$/°C, TEGDMA – $110,1 \cdot 10^{-6}$/°C, UDMA – $118,3 \cdot 10^{-6}$/°C, and PCDMA – $173,8 \cdot 10^{-6}$/°C. However, for selected popular micro hybrid PMCCS composites, the α coefficient assumes the following values: Filtek-100 – $23,2 \cdot 10^{-6}$/°C, Filtek WITH-250 – $33,0 \cdot 10^{-6}$/°C, Alert – $29,1 \cdot 10^{-6}$/°C(13), and the α coefficient of the Filtek Supreme nano-hybrid composite is $50.8 \cdot 10^{-6}$/°C **[L. 14]**. The temperature gradient in the material resulting from the uneven temperature distribution in the volume causes stress of the second type. In the described case, the temperature gradient is created as a result of heating the surface element and the surface and core of the material remaining in the force interaction, inhibit the change of surface dimensions **[L. 10, 12]**.

In the case of alternating interactions, e.g., heating and cooling with liquid, the gradient is cyclically changed along with the distribution of stresses, which may lead to thermal fatigue of the material. Thermal fatigue is considered to be a low-cycle fatigue process **[L. 15–17]**. According to **[L. 16]**, three stages of the thermal fatigue process can be distinguished: thermo-cyclic strengthening (weakening), stabilization of deformation (repeated processes of strengthening and weakening), and destruction. It is the process of the formation and development of damage in materials, due to changes in internal energy, under the influence of multiple random or periodic temperature changes. It is possible that also the action of the fluid itself has an effect on the structure of the PMCCs and, in particular, on the surface layer. It is possible that thermal fatigue may lead to the thermo-diffusion of water molecules to SL, easily noticeable in the case of swelling and contraction of wood-based materials, polymers, and concretes **[L. 16]**. The thermo-diffusion process is irreversible.

Significant clinical criteria for the quality evaluation of PMCCs dental applications are based on the state of the surface (2012). For PMCCs manufacturers, it is important to look for quantitative measures that allow one to assess the durability of the material at the stage of pre-clinical laboratory tests. In connection with the above, the aim of the research is the analysis of the possibility to determine the degree of fatigue damage of the PMCCs hydro-thermal surface layer, intended for operation in the biotribological node, based on microhardness measurements.

RESEARCH METHOD

Commercial materials were selected for the study. Filtek Ultimate (3M ESPE) is a nano-hybrid composite (FUl designation) with 78.5% (weight) content of inorganic filler particles (SiO_2 20 nm, ZrO_2 4–11 nm,0.6–20 μm clusters), G-aenial (GC-Corporation, Japan) containing an inorganic filler in the form of pre-polymerized particles of strontium, fluorolentane glass – 17 μm and silicon – 16 μm, silicon glass – 850 nm, and fumed silica – 16 nm (composite is indicated by the letter G), Kalore (GC-Corporation, Japan) by 82% (weight) of the content of inorganic fillers in the form of prepolymerized particles – 17 μm, SiO_2 – 16 nm, strontium fluoro-alumino-silicate glass – 700 nm and silica – 16 nm (composite marked with the letter K). The samples of materials were made at the Medical University of Lublin at the Chair and Department of Conservative Dentistry with Endodontics. The samples had the shape of discs with a diameter of 14 mm and a thickness of 2 mm, and they were made in the form of a divided metal. Astralis 7 (Ivoclar-Vivadent) halogen lamps and Demetron 1. LED L.E. were used for curing samples. Exposure times were varied, i.e. 40 s were assumed (in the results ".") and 60 s (in the ":" results). In the case of exposure to the HAL lamp, the PUL polymerization program was used ("Pulse program") for applications performed with layered technique. In the PUL program, during 15 seconds, the power rises from 150 to 450 mW/cm^2, after, which for the next 25 seconds, the pulses vary from 400 to 750 mW/cm^2 (the total exposure time was 40 s). The second used lamp was a LED lamp of a light intensity between 20 and 800 mW/cm^2.

The following parameters of the thermal cycle (TC) were adopted in the presented tests: the maximum cycle temperature (t_{max}) of 65°C, the minimum cycle temperature (t) equal to 5°C, resistance time int_{max} and $t_{min,}$ respectively, marked with τ_{max} and τ_{min} were equal to 30 s, and heated/cooled liquid pumping times – τ_1 and τ_2 were set at the level of 10 s (**Fig. 1**).

One work cycle of the device for thermal shocks consisted in performing the operations in the following order: pumping liquid from the tank, closing the valve that cuts the flow of heated liquid and opening the cooled liquid valve, filling the sample vessel with cooled liquid, keeping the cooled liquid in the sample container, pumping the cooled liquid from the sample container, closing the valve that cuts the flow of cooled liquid and opening the heated liquid valve, filling the sample vessel with heated liquid, and keeping the heated liquid in the sample container for a specified period of time. Schematic operation of the device is presented in **Figure 2**. The procedure and device for hydro-thermal fatigue is described in more detail in **[L. 19, 20]**.

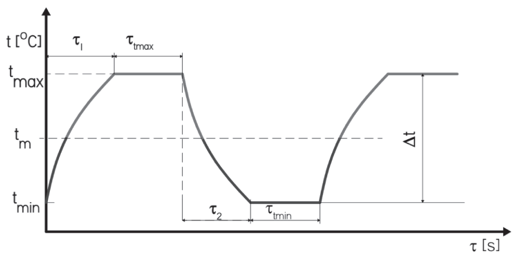

Fig. 1. Schematic presentation of the thermal cycle
Rys. 1. Schematyczna prezentacja przebiegu cyklu cieplnego

The Futertech FM 700 device was used for the tests of microhardness. The test applied a load of 50 g, and the indenter penetration time was set to 20 s. The coordinates of measurements were set to cover the entire surface area of the sample, and they were the same for all samples (**Fig. 3**). Hardness was tested on the surfaces of light-cured (LC) and not light-cured (NLC) samples. Five samples (n = 5) were examined from each group defined by the material, the type of lamp, and exposure time. The roughness of the samples (Ra parameter) was measured before and after the cyclic hydro-thermal shocks on a Bruker optical profilometer. A scanning electron microscope (SEM) Phenom Pro (Phenom-World B.V) was used for microscopic examination.

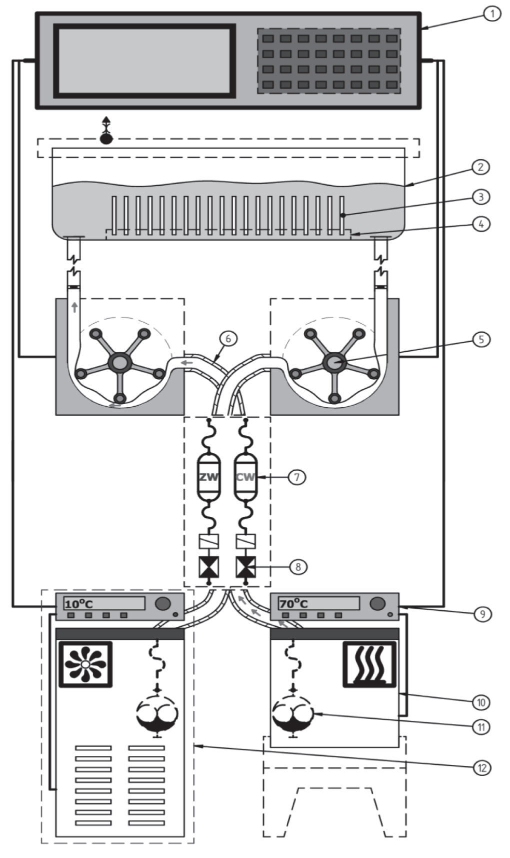

Fig. 2. The principle of operation of the device used in fatigue tests in the pumping phase of heated liquid: 1 – digital control system, 2 – working tank, 3 – samples subjected to fatigue process, 4 – perforated plate supporting samples, 5 – peristaltic pump, 6 – flexible wire insulation, 7 – hot water tank, 8 – solenoid valve, 9 – thermostat, 10 – tank with heated liquid, 11 – rotary pump, 12 – liquid cooling system

Rys. 2. Zasada działania urządzenia wykorzystanego w badaniach zmęczeniowych w fazie pompowania cieczy ogrzanej: 1 – cyfrowy układ sterujący, 2 – zbiornik roboczy, 3 – próbki poddane procesowi zmęczenia, 4 – płytka perforowana podtrzymująca próbki, 5 – pompa perystaltyczna, 6 – izolacja przewodu elastycznego, 7 – zasobnik ciepłej wody, 8 – elektrozawór, 9 – termostat, 10 – zbiornik z cieczą ogrzaną, 11 – pompa rotacyjna, 12 – układ chłodzenia cieczy

In this work, the modified equation by Kaczanow, presented in **[L. 21]**, was used to assess the degree of surface damage to the material:

$$D = 1 - \frac{H}{H^*} \tag{1}$$

The damage assessment was based on a comparison of the microhardness of the material with the load history in which the damage was assumed – H to the material without fatigue damage (virgin) – H^* **[L. 21]**.

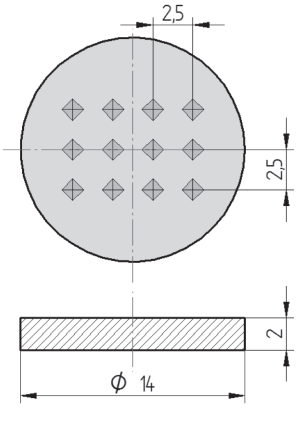

Fig. 3. The microhardness measurement system on PMCCs material samples

Rys. 3. Układ pomiaru mikrotwardości na próbkach tworzyw PMCCs

RESULTS AND ANALYSIS

In the case of LC PMCCs, the surface and volume fatigue of the composite is important. Paper **[L. 22]** shows the influence of thermal cycles on the fatigue degradation of the surface of LC PMCCs composites resulting in deterioration of wear resistance. In paper **[L. 23]**, the authors stated that softening the surface of polymers depends on the presence of water, the temperature of the polymer, and the difference between the glass transition temperature *Tg* and the operating temperature. They also noticed that a greater difference in these temperatures resulted in higher brittleness.

Our own study has shown that as a result of hydro-thermal fatigue on the surface of PMCCs surface damage to SL occurs; as demonstrated by optical observations and SEM presented in **Figure 2**, surface losses were observed (**Figures 4a** and **4b**). Observations carried out at higher magnifications revealed surface cracks, which presumably arise as a result of stretching hydro-thermal stresses (**Fig. 4d**). It is possible that the action of stretching thermal stresses results in the opening of micro-damage of SL and facilitates the penetration of water into it. It can be assumed that the water that penetrates into the fracture has a decomposing effect, causing damage to be increased (**Fig. 4d**). A humid environment determines the development and propagation of surface cracks. In paper **[L. 24]**, it was found that the PMCCs' crack resistance increases in the initial stages of exposure in a humid environment, but during the long exposure, it is reduced significantly (ΔK_{th} the threshold value of stress intensity factor). The formation of such cracks may depend on the temperature above the thermal stability of the material, which are lower than the melting point at which rapid relaxation of stress occurs **[L. 25]**. As shown in studies **[L. 26]**, crack propagation in composites containing pre-polymerized particles, referred to as hybrid, which were used in this work, occurs at a smaller range of WIN threshold values (ΔK_{th}) than in the case of materials containing large particles.

The degree of damage to the surface of the micro-hybrid G material after the implementation of cyclic thermal shocks was significant. It is possible that the phases of the composite underwent decohesion and the polymer phase was extracted from the surface of the polymer phase.

Surface damages also translate into surface roughness (**Fig. 5**). Probably as a result of the decohesion of the composite and decomposition of the polymer phase, filler particles, or prepolymerised aggregates have been uncovered, and some of them have been extracted. The tops of the exposed filler particles and the bottom of the defects in the polymer matrix of the composite form the highest and lowest points of the roughness profile. It is worth adding that the filler particles are much harder than the composite itself, and their hardness is from 3 to even 17 GPa (in the case of zirconium oxide).

Hardness testing is used by industrial manufacturers and PMCCs researchers, and it allows the assessment of mechanical properties of SL composite. It has been noticed that there is a significant correlation between PMCCs microhardness and the modulus of elasticity, the level of polymerization shrinkage, the depth of light polymerisation **[L. 27]**, and the degree of composite conversion **[L. 28]**. These properties have utility meaning and microhardness is to a certain extent representative for these quantities. What is more, **[L. 29]** demonstrated a close relationship between the microhardness of the composite and the level of wear. The microhardness test may also be used to assess the local photopolymerization gradient, i.e. the homogeneity of the composite properties in the area of the spectrum of the lamp's light impact **[L. 30]**, the effect of polymerization time, and the type of lamp light **[L. 31]**. It has also been demonstrated that the sorption of water by a polymeric material is inversely proportional to its hardness **[L. 32]**. The relation between the hardness of PMCCs and the hard tissues of the tooth is important. The hardness of most PMCCs ranges from 20 to 100 HV. The hardness of enamel is higher and amounts to ~ 330 HV **[L. 33]**.

In the microhardness tests of PMCCs, the Vickers and Knoop methods are most commonly used. There are many works in which the mechanical properties of SL PMCCs were tested using the Vickers method **[L. 31, 34–36]**.

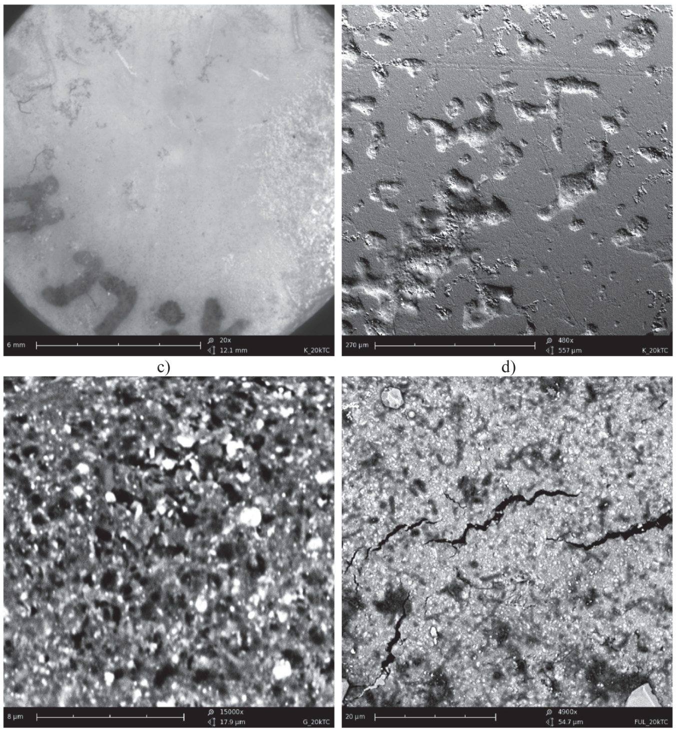

Fig. 4. Surface damage of LC PMCCs after implementation of 20 thousand. hydrothermal cycles: a) Filtek Utimate material (20x), b) Kalore material (480x), c) Gaenial material (15000x), d) Filtek Ultimate material (4900x)

Rys. 4. Uszkodzenia powierzchniowe LC PMCCs po realizacji 20 tys. cykli hydrotermicznych: a) materiał Filtek Utimate (pow. 20x), b) materiał Kalore (pow. 480x), c) materiał Gaenial (pow. 15000x), d) materiał Filtek Ultimate (pow. 4900x)

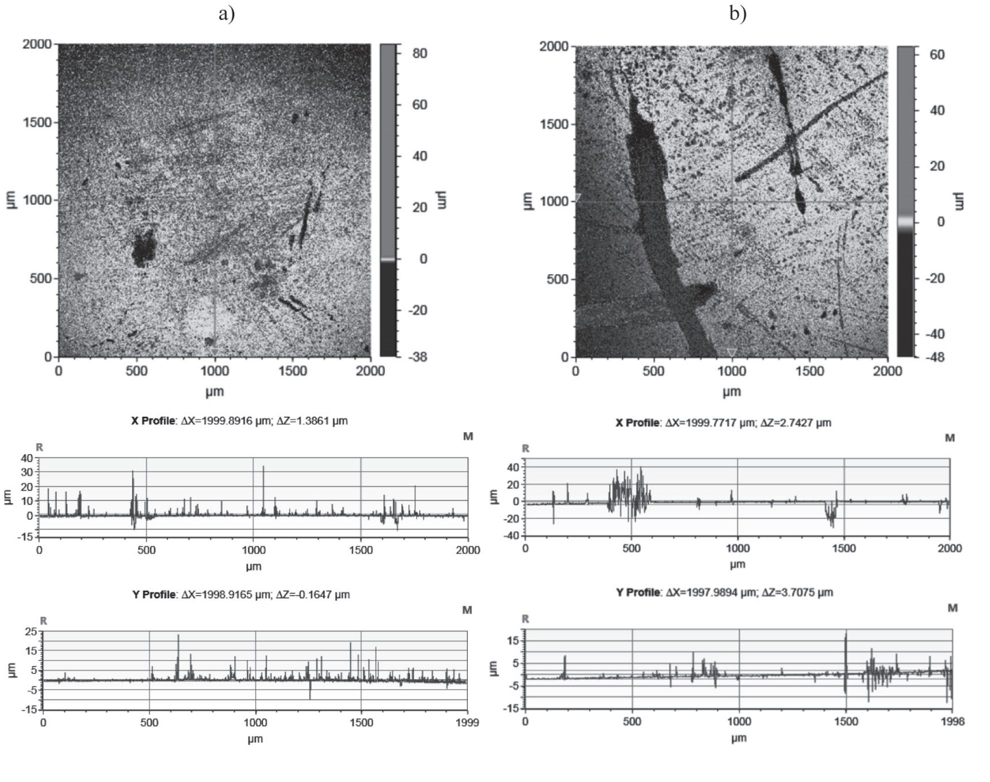

Fig. 5. 2D profilograms of the FUl composite surface: a) material sample without history of FUI hydro-thermal load (n_{TC} = 0), R_a = 0.865 µm, b) sample of FUl material after implementation of hydro-thermal cycles (n_{TC} = 20,000), R_a = 2.601 µm

Rys. 5. Profilogramy 2D powierzchni kompozytu FUl: a) próbka materiału bez historii obciążenia hydro-termicznego FUl (n_{TC} = 0), R_a = 0,865 µm, b) próbka materiału FUl po realizacji cykli hydrotermicznych (n_{TC} = 20000), R_a = 2,601 µm

The determination of fatigue life of composite material can be made on the basis of stiffness degradation **[L. 37]**. In our own research, Vickers microhardness was determined. The volume was used to calculate the degree of SL damage depending on the number of hydro-thermal cycles (TC). The initial microhardness and the remaining one after the hydro-thermal fatigue were used to compute the value of *D* function, which is assumed to reflect the degradation of the structure on the surface of the materials.

The results of own research indicate that the surface strength of materials changes under the influence of cyclic hydro-thermal shocks in various ways and depends on the material and the lamp used in the curing process.

There are a number of works concerning the influence of polymerization lamps on the mechanical properties of PMCCs **[L. 28, 38–42]**. In our own research, the LED lamp more than the HAL lamp influenced the microhardness stability of SL PMCCs than hydro-thermal load cycles. It is possible that the characteristics of the LED light spectrum are important. The LED lamp light has a higher intensity and shorter wavelength. Paper **[L. 43]** shows that LED polymerisation affects the higher conversion rate of monomers to polymers and reduces the thermal expansion of the composite. In own research, this dependence is particularly visible in the case of material K.

The negative values of the damage parameter (*D*) of material K are associated with an increase in microhardness in the first two load intervals. Strengthening of SL referred to a greater degree of samples cured for 60 seconds. After half of the intended number of cycles (n_{TC} = 10,000) of hydro-thermal load, the degree of damage increased, but still took negative values. Higher durability was characterized by samples of material K light-cured for 40 s.

The Kalore (K) nanocomposite is distinguished by a significant content (82% by weight) of the filler, including the nano-filler. In **[L. 44]**, the authors showed a beneficial effect of the high filler content on the Vickers hardness (HV0,2). The resin constituting the K-matrix contains particle-forming monomers with specific mechanical properties – DX-511 (DuPont). Both ends of the DX-511 monomer are flexible and the interior is stiff, which minimizes the polymerization shrinkage and thermal expansion coefficient. The rigid core of the molecular structure counteracts the change in volume and elastic arms increase the reactivity, usually reduced in structures with long monomer chains. The molecular weight of DX-511 is twice the molecular weight of Bis-GMA or UDMA, which are typical components of the PMCCs matrix.

In the literature, the decrease in microhardness of materials subjected to the influence of thermal loads has been noted, among others, in **[L. 45]** (cycle temperature range: 5–55°C, number of cycles: 10 thousand, exposure time in t_{max} and t_{min} amounted to 30 s). In many studies, however, the improvement of the surface properties of composites was observed under the influence of cyclic thermal loads. For example, in **[L. 46]**, an increase in the hardness of the material called Sinfony under the influence of hydro-thermal loads was noted (temperature range: 5–55°C, cycle number: 5 thousand, exposure time in t_{max} and t_{min} amounted to 30 s). The authors of the study **[L. 6]** observed an increase in the indentation hardness of composites due to hydro-thermal fatigue (temperature range: 5–55°C, cycles number: 2 thousand, exposure time: 30 s) and immersion of materials for 48 h in liquids at the temperature of 55±5°C.

The results of our own research on FUI nano-hybrid material indicate a deterioration of strength properties of SL. Interpolation with linear intervals of the damage function values has a total waveform similar to a linear one. In the case of this material, it seems that the theoretical waveforms of the damage function will be linear, and the most compatible with the linear model in the case of samples cured with the HAL lamp. Such waveforms indicate systematic fatigue degradation probably caused by the accumulation of micro-damages. In the case of FUl material, the highest values of the damage parameter were obtained. After the assumed number of cycles (N_{TC}), the value of parameter *D* was in the range from approx. 0.15 to approx. 0.3. In the worst case, this means that the remained strength has deteriorated by 30% compared to the initial one.

In the case of FUl material, the degree of damage *D* was shown to vary depending on the plane of the sample. The degree of damage was higher on the non-light-cured surface (NLC) of the samples. This indicates the possibility of the anisotropy of mechanical properties depending on photopolymerization. Paper **[L. 47]** presents the results of studies on the impact of photopolymerization on the variability of hardness on exposed (LC) and unexposed (NLC) sides. There, the influence of lamp type and exposure time on microhardness, bending strength, and the resilience of LC PMCCs was also demonstrated. The influence of photopolymerization parameters on the mechanical properties of composites is also described in **[L. 48–52]**. Higher intensity damage to the FUl composite was demonstrated on the surface (NLC) of the samples. Our study used samples with a thickness of 2 mm. According to ISO 4049 **[L. 53]**, the depth of curing one layer of PMCCs must not be less than 1.5 mm. However, most materials available on the market polymerize to a depth of 3 mm. Materials included in our research are included in this group.

In the case of composite G, as K, the course of the damage function indicates the existence of a threshold number of cycles (n_{TC} = 10,000). After the next load interval (n_{TC} = 15,000), a steady intense increase in the parameter *D* up to N_{TC} was observed. The highest value of the damage parameter was approx. 0.14, which means that the remaining surface strength of SL was 14% lower

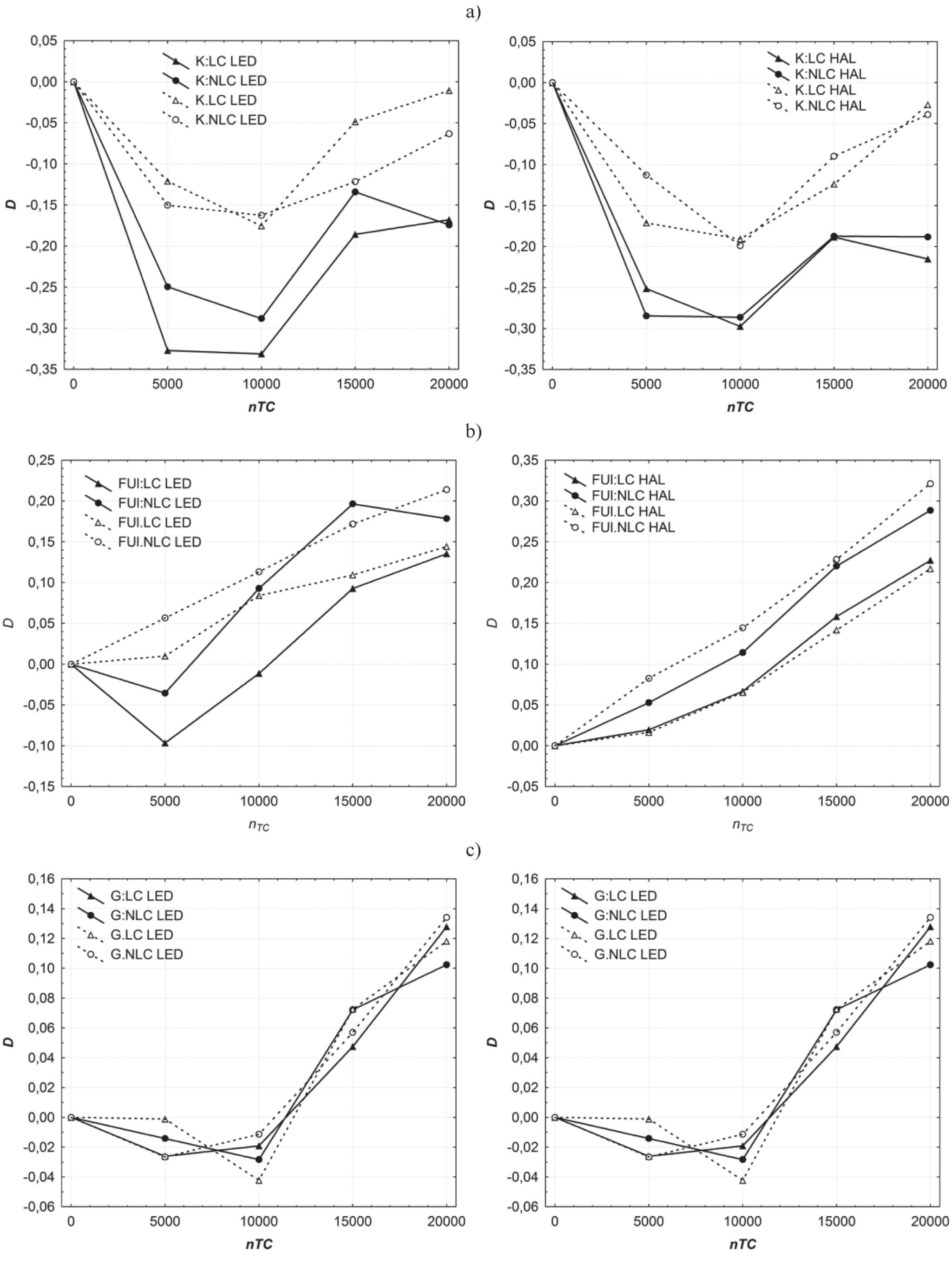

Fig. 6. Distribution of the damage parameter values in the function of number of hydro-thermal fatigue cycles: a) Kalore material, b) Filtek Ultimate material, c) Gaenial material

Rys. 6. Rozkład wartości parametru uszkodzenia w funkcji liczby cykli zmęczeniowych hydrotermicznych: a) materiał Kalore, b) materiał Filtek Ultimate, c) materiał Gaenial

than the initial one. Degradation of this material turned out to be smaller than FUl, despite the fact that damage to the surface of material G observed in microscopic studies was greater.

Specific impact on aging of LC PMCCs can have the humid environment. The absorption of water in the PMCCs LC structure occurs mainly through the matrix and by the “interphase” **[L. 54]**. Moisture absorption in materials of this type depends on matrix, exposure time, temperature, element shape, relative humidity, and lighting conditions **[L. 37]**. In general, the process of diffusion of water particles to multicomponent materials can be described by Fick's law, which depends on the degree of diffusion depending on time and temperature **[L. 55]**. The hydrolytic aging process of LC PMCCs is intensified in the case of cyclic load **[L. 24]**. Some believe that water in the structure of polymer matrix composite acts as a plasticizer, and its action leads to relaxation of stresses and reduction of stiffness **[L. 49]**. Degradation of the polymer network structure has an adverse effect, facilitates the propagation of defects in the structure, eliminating the positive effects associated with the relaxation of its own stresses. The mechanism of hydrolytic degradation is not well recognized. It is also likely that the chemical compounds in the aqueous solution cause decomposition of the polymer network by disintegration of the of ester bonds **[L. 56]**. It is also considered that moisture sorption depends on the amount and type of filler particles and the type of monomers used in the production of the matrix **[L. 57]**. In addition, the viscoelastic behaviour of PMCCs structures may also be reflected in the aging process **[L. 24]**.

The aging rate of polymer composites depends mainly on their physical and chemical properties. Amorphous polymers are more vulnerable to hydrolytic degradation than crystalline ones, and polymers with a linear structure are more vulnerable to hydrolytic degradation than branched ones, which are polymers of higher molecular weight. This can be indicated by the course of the damage function of composite K. Degradation depends on the presence of specific chemical groups in the molecule, e.g., ester, amide and urea groups. The intensity of degradation also depends on the condition of the surface of the material, its defects, and on the type and proportion of additional substances (e.g., filler particles, initiators) **[L. 58, 59]**. In addition, the kinetics of degradation of the polymer composite depends on the type, intensity, and duration of the impact of the factors leading to the degradation of the material **[L. 59]**, which are also indicated in the results of our research, in particular, composite G. Moreover, the process of thermal fatigue that occurs in the aquatic environment may lead to thermo-diffusion of water molecules, which easily noticeable in the case of swelling and contraction of wood-based materials, polymers, and concretes **[L. 16]**. The thermo-diffusion process is irreversible **[L. 16]**.

SUMMARY

The paper deals with the problem of surface degradation of polymer-ceramic composites (PMCCs). PMCCs designated for use in conservative dentistry were selected for the study. These materials are used to fill the cavities in the posterior teeth, which are involved to the greatest extent in the process of grinding and chewing food. The influence of one of the environmental factors of the operation, i.e. the cyclical interactions of cold and hot fluids (water), was assessed. Fatigue tests were carried out including hydro-thermal cycles with constant amplitude and frequency of follow-up. In particular, in the operating conditions of the PMCCs, contact strength is important; therefore, the degree of surface damage is determined based on Vickers microhardness measurements. The assumed method of assessing the degradation of SL PMCCs regarding the hydro-thermal factor has proved to be appropriate. Hydro-thermal softening, decomposition of the matrix, and decohesion of the composite phases translated into a change in the hardness of the tested composites. The increased number of TC cycles adopted in this study has allowed the disclosure of the strengthening of SL of some composites and the reduction of microhardness. On the basis of the conducted research, it can be concluded that the lower number of hydro-thermal cycles accepted by many researchers **[L. 60]** does not allow for inference about the durability of PMCCs in the range of expected periods of operation.

The degree of damage of both K and G materials is different, just as the structures of these materials are different. However, the degree of damage to both these materials changes adversely after exceeding 10,000 TC, wherein the degradation of the material G is greater. In the case of the FUl composite, the course of the damage function is different. The degradation of the mechanical properties of SL is progressing systematically in the subsequent hydro-thermal load intervals.

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