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LABORATORY STUDIES OF THE INFLUENCE OF THERMAL CYCLING ON ANTI-WEAR PROPERTIES OF COMPOSITES USED IN BIOTRIBOLOGICAL FRICTION PAIRS

LABORATORYJNE BADANIA WPŁYWU CYKLICZNIE ZMIENNEJ TEMPERATURY NA WŁAŚCIWOŚCI PRZECIWZUŻYCIOWE KOMPOZYTÓW STOSOWANYCH W BIOTRIBOLOGICZNYCH WĘZŁACH TARCIA

Key words: polymer-ceramic composites, indentation hardness, scratch test.

Abstract This paper presents the problems associated with changes in resistance to the tribological wear of light-cured polymer matrix ceramic composites (LC PMCCs) used in conservative dentistry and in dental prosthetics (fillings of carious cavities, dental bridges, structural reinforcements of the dental arch). Wear resistance of the surface layer of PMCCs depends on the time of exposure to the conditions of the oral environment, such as alternating temperatures and the exposure to liquids. The aim of the study was to assess changes in the mechanical properties of the surface layer under thermal cycling in liquid. Indentation hardness tests and scratch tests were performed before and after conditioning. Conditioning included 10,000 cycles of step temperature changes (10–70°C). The results of the scratch tests showed that universal composites that had relatively high filler contents were more resistant to scratching than flow type composites with lower filler contents. It was found that cyclic changes in ambient temperature reduced the wear resistance of universal composites but improved the resistance of flow type composites. In addition, in the case of flow type composites, the hardness of the surface layer was also increased.

Słowa kluczowe: kompozyty polimerowo-ceramiczne, twardość indentacyjna, test zarysowania.

Streszczenie W pracy zaprezentowano problematykę zmian odporności na zużycie tribologiczne światłoutwardzalnych kompozytów polimerowo-ceramicznych (LC PMCCs – light-cured polymer matrix ceramic composites) stosowanych w stomatologii zachowawczej oraz w protetyce stomatologicznej (wypełnienia ubytków próchnicowych w zębach, mosty stomatologiczne, wzmocnienia konstrukcyjne łuku zębowego). Odporność na zużycie warstwy wierzchniej PMCCs jest cechą zależną od czasu oddziaływania środowiska jamy ustnej, między innymi zmiennej temperatury i obecności płynów. Celem pracy była ocena zmian właściwości mechanicznych warstwy wierzchniej ze względu na cykliczne oddziaływanie płynów o zmiennej temperaturze. Badano twardość indentacyjną i ślad zarysowania przed i po kondycjonowaniu. Kondycjonowanie obejmowało 10 tys. cykli skokowej zmiany temperatury (10–70°C). Wyniki testu zarysowania wykazały, że materiały typu uniwersalnego o względnie dużej zawartości wypełniacza są bardziej odporne na zarysowania niż materiały typu flow o mniejszej zawartości wypełniacza. Stwierdzono, że cykliczne zmiany temperatury otoczenia zmniejszają odporność na zużycie kompozytów uniwersalnych, natomiast poprawiają odporność kompozytów typu flow. Ponadto w przypadku kompozytów typu flow obserwowano umocnienie warstwy wierzchniej polegające na wzroście twardości.

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INTRODUCTION

Polymer-ceramic composites used in dentistry are referred to as Polymer Matrix Ceramic Composites (PMCCs) **[L. 1]**. The matrix, the organic phase of these composites, is formed from acrylated Bis-GMA resins. The organic phase comprises about 20–30 wt% of the composite.

The inorganic phase consists of ceramic fillers in the form of powders dispersed evenly in the volume of the composite. Composites with a filler content of 70–80 wt% are ubiquitously used in conservative dentistry **[L. 2]**. A separate group are semi-liquid flow type composites. These materials contain much less filler: 52–68% (by weight) **[L. 3]**. They are usually characterized by poorer mechanical properties, but they are more effective in penetrating dental micro-cavities **[L. 4]**.

The success of dental hard tissue reconstruction depends, among others, on the restoration of physiological functions: the ability to transfer occlusive biomechanical loads and to masticate food. These functions cannot be performed without the surface layer having appropriate mechanical characteristics. Strength properties, including surface strength, depend largely on the structure of the PMCCs. On the other hand, maintenance of strength over time depends on operational loads and the impact of ageing factors. Usually, the properties of composites deteriorate as a result of exposure to fluids of varying temperatures. Hot and cold beverages produce thermal shock to the surface of a dental reconstruction. A typical range of temperatures on the tooth surface in the oral cavity is 1–50°C **[L. 5–8]**, but teeth can sometimes be exposed to higher temperatures.

Temperature changes in the oral cavity can be quite abrupt. In thermal shock conditions, there is a gradient of stresses and thermal deformations. When the surface of the tooth is heated, a thermal front moves into the core of the material's structure. The largest variation in temperature fields occurs on the surface. As a result of this variability, thermal fatigue may occur.

A negative impact on the condition of the surface layer of a PMCCs composite may also be exerted by a moist environment. Water is sorbed into the composite structure through the matrix and the "interphase.” According to Lohbauer and colleagues **[L. 9]**, hydrolytic ageing may intensify under cyclic loading. It can be assumed that the stretching effect of thermal stresses can initiate the formation of surface micro-defects. Water penetrating into the microcracks may have a debonding effect.

Long-term use in a temperature-varying moist environment can lead to thermal fatigue of the composite. The surface layer is particularly vulnerable to this type of fatigue, because it remains in direct contact with the medium and has the highest temperature gradient.

The condition of the surface layer also affects the clinical situation. One of the criteria for replacement of worn dental fillings is the smoothness of their surface, as assessed by a dentist **[L. 10]**.

The aim of the study reported in this paper was to assess the impact of cyclic hydro-thermal loading on the anti-wear properties of the surface layer of light-cured PMCCs used in dentistry.

MATERIALS

Two universal types and two flow type LC PMCCs mounted in an epoxy resin were used in the study. Two materials from the 3M ESPE company (Z500 and FFlow) and two experimental composites (Ex mhyb(P) and Ex Flow(P)) were selected. Measurements were carried out on the irradiated surface. Photopolymerization was performed using a light emitting diode device, and the exposure time was 40 s. The resin-mounted specimens were wet ground and mechanically polished. Details regarding the test materials are presented in **Table 1**.

METHODS

Hardness tests were carried out according to the Olivier and Pharr method using an Anton Paar Micro Combi Tester equipped with a Vickers indenter. The measurements were performed at a maximum load of

Table 1. Details of the polymer-ceramic composites
Tabela 1. Informacje o badanych kompozytach polimerowo-ceramicznych

Material	Z500	Ex mhyb(P)	FFlow	Ex Flow(P)
Type	Universal	Universal	flow	flow
Resin	Bis-GMA, UDMA, TEGDMA, Bis-EMA	Bis-GMA, TEGDMA, Bis-EMA	Bis-GMA, Bis-EMA, TEGDMA	Bis-GMA, UDMA, TEGDMA, Bis-EMA
Filler	SiO_2 particles (20nm) ZrO_2/SiO_2 (clusters 0.6–1.4 µm, particles 5–20 nm)	Bar-aluminum-fluoro-boro-silica glass particles, fire silica and titanium oxide (average size of 0.90 µm)	ZrO_2 / SiO_2 particles (0.01–6 µm)	Bar-aluminum-fluoro-boro-silica glass particles, fire silica and titanium oxide (average size of 0.76 µm)
Filler content in the composite in wt %	78.5	78	68	64

0.5 N and a loading/unloading rate of 2 µm/min. The holding time at maximum load was 15 s.

The scratch test was performed on the Anton Paar Micro Combi Tester using a Rockwell diamond cone stylus with a spherical tip. The instrument had a cone angle of 120° and a tip radius of 0.1 mm. In the scratch test, the indenter was drawn across the surface of a specimen under an increasing load. The following test parameters were adopted: initial load – 0.1 N, final load – 5 N, indenter speed – 1 mm/min, and scratch length – 2 mm.

A laboratory simulation of cyclic thermal loading of the specimens was run on a dedicated thermal shocks simulator **[L. 10]**. The specimens were placed in a plastic vessel, and a working liquid of a specified temperature was pumped into and out of the vessel at specified times. The temperature range was set between 10 and 70°C, and the time of exposure of specimens to the working liquid with the specified temperature was 30 s. Ten thousand thermal cycles were performed, each lasting 201 s. One cycle included pumping cooled liquid into the specimen vessel (35 s), holding the cooled liquid in the vessel (30 s), pumping out cooled liquid (35 s), a pause (0.5 s), pumping heated liquid into the specimen vessel (35 s), holding the heated liquid in the vessel (30 s), pumping out heated liquid (35 s), and a pause (0.5 s). The specimens in the vessel were mounted on a plastic frame to ensure maximum contact of the surface of the composite materials with the working liquid.

RESULTS

Tables 2 and **3** present the results of hardness tests of the investigated LC PMCCs. The following parameters were tested: H_{IT} – indentation hardness, HV_{IT} – Vickers hardness, E_{IT} – elastic modulus, E* – reduced elastic modulus, S – rigidity, W_{spr} – elastic deformation work, and $W_{plas.}$ – plastic deformation work. **Figures 1** and **2** show graphs of indenter load as a function of indenter tip displacement.

Table 2. Descriptive statistics of indentation hardness measurements of universal type composites with and without a history of thermal loading

Tabela 2. Statystyki opisowe wyników pomiaru twardości indentacyjnej kompozytów typu uniwersalnego, z historią i bez historii obciążenia cieplnego

		Z500	Z500 10kTC	Ex mhyb(P)	Ex mhyb(P) 10kTC
	Number of specimens	10	10	10	10
H_{IT} [MPa]	Mean	1204.18	1155.74	953.40	864.04
	Median	1046.40	1107.43	934.19	858.63
	Min	1016.09	1029.20	862.78	773.92
	Max	2572.72	1662.32	1253.29	918.80
	SD	481.59	181.55	111.67	40.76
	Var. Coeff.	39.99	15.71	11.71	4.72
HV_{IT} [Vickers]	Mean	113.66	109.09	89.99	81.55
	Median	98.77	104.53	88.18	81.04
	Min	95.91	97.14	81.43	73.05
	Max	242.83	156.90	118.29	86.72
	SD	45.46	17.14	10.54	3.85
	Var. Coeff.	39.99	15.71	11.71	4.72
E_{IT} [GPa]	Var. Coeff.	31.56	14.13	9.60	4.26
	Mean	18.45	18.08	17.53	16.45
	Median	17.41	17.55	17.24	16.33
	Min	16.90	16.64	16.86	15.37
	Max	28.24	23.72	19.85	17.20
	SD	3.45	2.03	0.85	0.52
E* [GPa]	Var. Coeff.	18.71	11.24	4.86	3.13
	Mean	20.28	19.87	19.26	18.08
	Median	19.14	19.29	18.95	17.94
	Min	18.57	18.28	18.53	16.89
	Max	31.04	26.06	21.81	18.90
	SD	3.79	2.23	0.94	0.57
S [mN/nm]	Var. Coeff.	18.71	11.24	4.86	3.13
	Mean	0.47	0.46	0.50	0.49
	Median	0.47	0.46	0.50	0.49
	Min	0.46	0.45	0.49	0.48
	Max	0.48	0.51	0.51	0.50
	SD	0.01	0.02	0.01	0.00
$W_{spr.}$ [pJ]	Var. Coeff.	1.92	3.45	1.41	0.82
	Mean	397930	401707	392434	398003
	Median	398530	402225	391704	396992
	Min	385117	390527	385579	394892
	Max	404107	406699	399368	403482
	SD	5308	4969	4770	2944
$W_{plas.}$ [pJ]	Var. Coeff.	1.33	1.24	1.22	0.74
	Mean	535583	527663	633737	649972
	Median	558856	544334	633385	650285
	Min	286819	329107	612849	640582
	Max	579170	576236	646258	656039
	SD	88557	70588	9516	4621

Table 3. Descriptive statistics of indentation hardness measurements of flow composites with and without a history of thermal loading

Tabela 3. Statystyki opisowe wyników pomiaru twardości indentacyjnej kompozytów typu flow, z historią i bez historii obciążenia cieplnego

		FFlow	FFlow 10kTC	Ex Flow(P)	Ex Flow(P) 10kTC
	Number of specimens	10	10	10	10
H_{IT} [MPa]	Mean	558.36	615.01	538.72	555.86
	Median	553.57	608.94	535.75	537.91
	Min	516.58	587.23	507.11	509.63
	Max	613.68	661.64	574.77	617.32
	SD	32.28	21.58	22.53	38.68
	Var. Coeff.	5.78	3.51	4.18	6.96
HV_{IT} [Vickers]	Mean	52.70	58.05	50.85	52.47
	Median	52.25	57.48	50.57	50.77
	Min	48.76	55.43	47.86	48.10
	Max	57.92	62.45	54.25	58.27
	SD.	3.05	2.04	2.13	3.65
	Var. Coeff.	5.78	3.51	4.18	6.96
E_{IT} [GPa]	Mean	10.97	10.13	11.27	11.27
	Median	11.03	10.04	11.28	11.24
	Min	10.12	9.93	10.59	10.71
	Max	11.70	10.50	11.54	11.92
	SD	0.59	0.20	0.29	0.39
	Var. Coeff.	5.37	2.01	2.60	3.46
E* [GPa]	Mean	12.05	11.13	12.38	12.38
	Median	12.12	11.03	12.40	12.35
	Min	11.12	10.92	11.64	11.77
	Max	12.85	11.54	12.69	13.10
	SD	0.65	0.22	0.32	0.43
	Var. Coeff.	5.37	2.01	2.60	3.46
S [mN/nm]	Mean	0.41	0.36	0.43	0.42
	Median	0.42	0.36	0.43	0.42
	Min	0.37	0.35	0.40	0.41
	Max	0.44	0.36	0.44	0.43
	SD	0.03	0.00	0.01	0.01
	Var. Coeff.	7.35	0.84	2.58	1.19
$W_{spr.}$ [pJ]	Mean	496164	551784	473383	478569
	Median	476143	552303	469139	479449
	Min	462171	542620	450696	468486
	Max	543282	560484	499596	486262
	SD	33042	5366	13223	6049
	Var. Coeff.	6.66	0.97	2.79	1.26
$W_{plas.}$ [pJ]	Mean	814680	716372	848941	837521
	Median	827293	707690	845328	825411
	Min	727932	679235	817724	810406
	Max	877805	752004	883416	895675
	SD	58793	21870	17213	30837
	Var. Coeff.	7.22	3.05	2.03	3.68

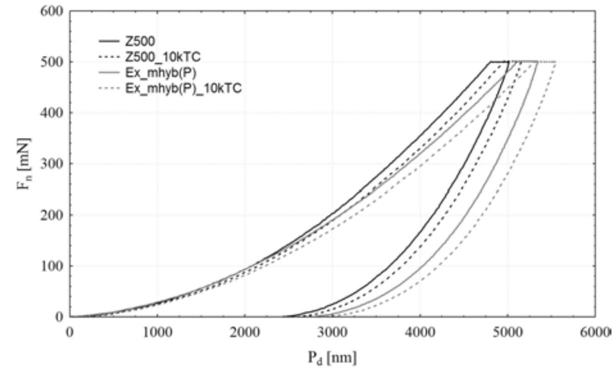

Fig. 1. Examples of curves of load as a function of indenter tip displacement for universal type composites with and without a thermal loading history

Rys. 1. Przykładowe krzywe obciążenia kompozytów typu uniwersalnego, z historią i bez historii obciążenia cieplnego, w funkcji przemieszczenia wgłębnika

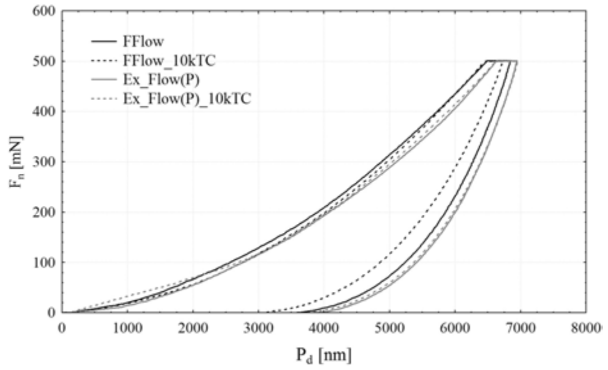

Fig. 2. Examples of curves of load as a function of indenter tip displacement for flow type composites with and without a thermal loading history

Rys. 2. Przykładowe krzywe obciążenia kompozytów typu flow, z historią i bez historii obciążenia cieplnego, w funkcji przemieszczenia wgłębnika

Figures 3 and **4** show the mean friction coefficients for the tested composites obtained in the scratch test. Mean permanent scratch depths are given in **Figures 5** and **6**.

DISCUSSION

It was established in the present study that the oral environment, and in particular hydrothermal loads occurring in it, significantly affect the anti-wear properties of the surface layer of both universal and flow type composites. The results reported in the literature are not unequivocal. According to different studies, cyclic thermal loading can lead to the degradation of the surface layer or improvement of its properties. Absorption of water by a composite can lead to plasticization and softening of the polymer matrix **[L. 13–15]**. Thermal stresses, on the other hand, may lead to secondary polymerization of the matrix and its curing **[L. 5]**. The properties of the surface layer of polymer-ceramic composites depend, among others, on the type of composite, and more specifically on the type, content, and dispersion of filler particles, and the monomers used in the production of the matrix. Moreover, the operating conditions are of no mean significance.

The properties of the surface layer of the investigated universal composites differed from the properties of the flow type materials. The universal composites were characterized by a higher indentation hardness, a higher elastic modulus, and a lower elastic and plastic deformation work. This was related to the content of ceramic filler particles. The same dependence was also found in publications by Kim et al. **[L. 16]**, McCabe and Wassell **[L. 17]**, Neves et al. **[L. 18]**, and Borba et al. **[L. 19]**.

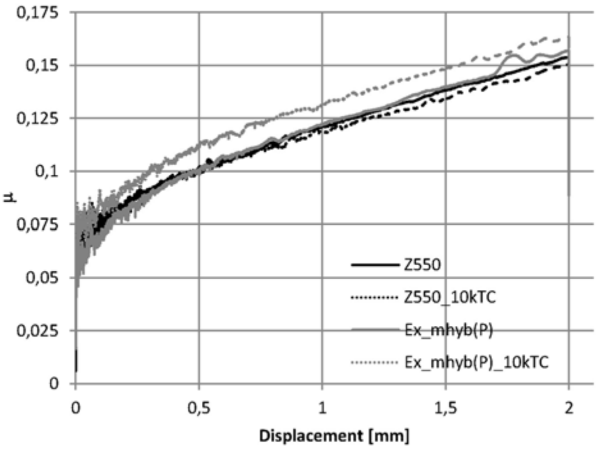

Fig. 3. Mean friction coefficient of universal type composites with and without a loading history

Rys. 3. Średni współczynnik tarcia kompozytów typu uniwersalnego, z historią i bez historii obciążenia

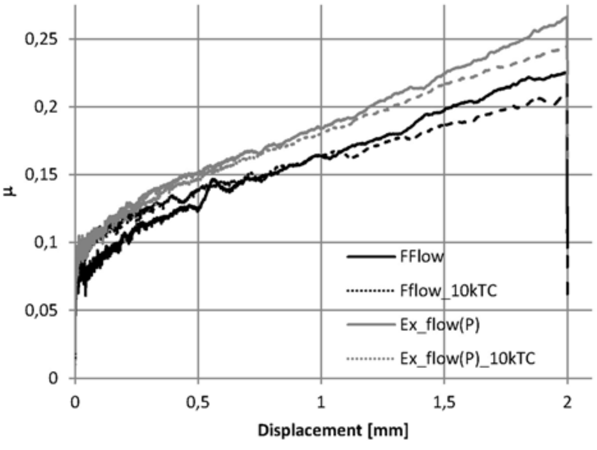

Fig. 4. Mean friction coefficient of flow type composites with and without a loading history

Rys. 4. Średni współczynnik tarcia kompozytów typu flow, z historią i bez historii obciążenia

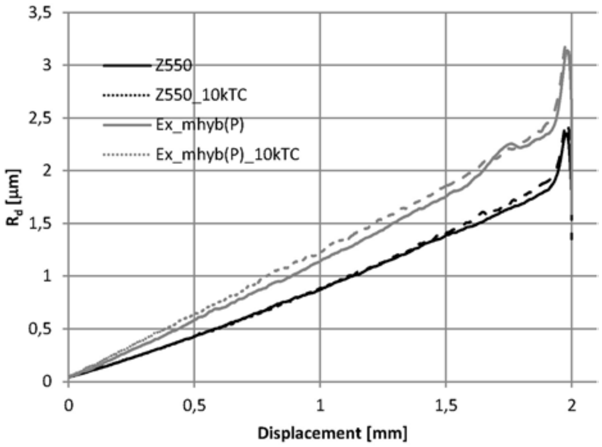

Fig. 5. Mean permanent scratch depth (R_d) for universal type composites with and without a loading history

Rys. 5. Średnia głębokość trwałego zarysowania (R_d) kompozytów typu uniwersalnego, z historią i bez historii obciążenia

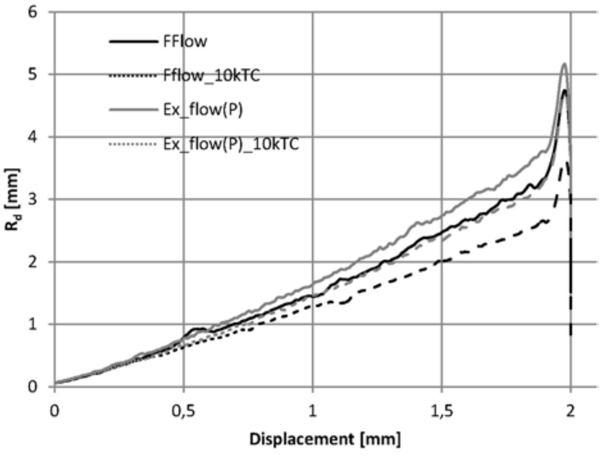

Fig. 6. Mean permanent scratch depth (R_d) for flow type composites with and without a loading history

Rys. 6. Średnia głębokość trwałego zarysowania (R_d) kompozytów typu flow, z historią i bez historii obciążenia

Studies conducted by Tornavoi et al. **[L. 20]** and dos Reis et al. **[L. 21]** demonstrated that the hardness of polymer-ceramic materials depends, to a large extent, on the type of filler particles. It was observed that the hardness of the materials increased along with an increasing content of zirconium and silica particles. The composites used in this present study all contained a similar type of filler. However, the hardness of the Z500 composite turned out to be significantly higher than that of Ex mhyb(P). This was probably related to the use of nanoscale particles. Studies conducted by Beun et al. **[L. 22]** also showed that particle size had an effect on the properties of the surface layer of the materials they tested. The results of the indentation hardness tests performed in the present study indicated that there was no significant difference between the properties of the SL of the flow composites.

Scratch resistance can be used to indirectly assess the resistance of light-cured polymer-ceramic composites to adhesive wear **[L. 23, 24]**. This type of resistance depends on many factors, including the size, dispersion, and content of filler particles in the matrix and the adhesion between the ceramic particles and the matrix **[L. 25]**.

In the scratch test, the flow type composites had higher friction coefficients and a greater permanent scratch depth than the universal ones. This was probably related to the content of hard filler particles. The universal type materials were characterized by similar friction coefficients, but Ex mhyb(P) had a smaller permanent scratch depth than Z500. This was possibly due to the fact that Z500 contained nanoscale particles, which increase friction in the kinematic node and enhance the scratch resistance of the material being scratched. In the case of flow type materials, Ex Flow(P) had a higher friction coefficient and a greater permanent scratch depth than FFlow.

In the present study, it was also found that the hardness and elastic modulus of universal type composites dropped under hydrothermal loading. This decrease was larger for Ex mhyb(P). The polymer matrix absorbs water, and the degree of absorption depends on the type of monomers used. According to Yu and colleagues **[L. 26]**, composites with UDMA monomers are more hydrophilic than materials containing Bis-GMA monomers. Among the composites analysed in the present study, Z500 and Ex Flow materials contained UDMA monomers. The decrease in hardness for Z500 was slight. It was lower than in the case of the composite that did not contain this monomer (Ex mhyb(P)). It seems that the hardness of universal type composites under hydrothermal loading may depend on the adhesion between filler and matrix particles.

It was found that the hardness of flow composites increased under the influence of cyclic thermal loading. A similar observation was made by Ayatollahi and colleagues **[L. 5]**. Those authors explained the improvement in surface properties by improved adhesion between filler particles and the matrix as well as by reduction of voids in the material due to thermal stresses. The experiments conducted in our study showed that changes in the properties of the surface layer of flow composites were larger for FFlow than for Ex Flow(P). In the case of the latter composite, only slight changes were observed. When Z500 was tested, an increase in hardness was observed with a simultaneous decrease in rigidity and resilient modulus under the influence of hydrothermal loading. The elastic deformation work increased substantially while plastic deformation work considerably decreased. This indicated that the structure of the composite changed under the influence of cyclic thermal loading.

In the scratch test, alternating thermal loads had a larger effect on the flow type composites than the universal ones. In the case of Ex mhyb(P), changes in the coefficient of friction and slight changes in the permanent scratch depth were observed. The properties of Z500 as determined by the scratch test did not change under thermal loading. By contrast, the properties of flow composites did change. The friction coefficient and the permanent scratch depth were reduced in both flow type materials. However, the changes were more pronounced for FFlow than for Ex Flow(P). It seems that the flow materials were strengthened and the strengthening depended on the type of matrix.

Both in the hardness and scratch tests, cyclic thermal loading caused larger changes in the properties of the surface layer of the flow type material manufactured by the 3M ESPE Company compared to the experimental composite. In the case of universal composites, the reverse was true, with the experimental material having undergone greater changes.

CONCLUSIONS

The following conclusions were formulated on the basis of the results obtained in the present study:

1. Anti-wear properties of the surface layer of composites depend on the type of composite (the content of filler particles in the matrix).
2. Universal type composites have a higher indentation hardness and a smaller permanent scratch depth than flow type materials.
3. Indentation hardness values of experimental material Ex mhyb(P) and reference material Z550 were different, although they both had similar contents of filler particles. Scratch test results show that Z550 composite is more resistant.
4. Cyclic thermal loading affects the properties of the surface layer of light-cured polymer-ceramic composites in a variety of ways. This influence depends on the type of composite and the type of matrix.
5. In case of universal type materials, the influence of thermal cycling on wear resistance was insignificant. In case of flow type composites, strengthening of the surface layer was observed.

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