Chemical Corrosion of Nano-filled Composite Resins in Various Solutions

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The aim of the present paper was to investigate the chemical corrosion in various solutions, of a commercial resin based restorative nano-filled composite. 20 samples of a nanocomposite Filtek Supreme XT (3M ESPE) were immersed for 30 days in Ringer (physiological solution), Fusayama artificial saliva, and Afnor artificial saliva. After that, they were examined by scanning electron microscopy and energy-dispersive X-ray spectroscopy. It resulted that the corrosion is mainly due to the pitting, micrometric holes being observed. Also, preferred directions of corrosion resulted, as consequence of micro-scratches formation during the samples preparation. The oxygen content generally increased due to the oxides formation, while carbon, silicon and zirconium normalized atomic percents decreased, showing the corrosion both of the polymeric matrix and of the filler particles. Micro-holes size statistics revealed quantitatively the degree of corrosion and agrees well with the changes of chemical composition.

Keywords: nanofilled composite, pitting corrosion, artificial saliva

In recent years, resin based materials have been widely used in restorative dentistry. One of their limitations in long term clinical performance, however, is their inadequate resistance to wear. In the wear phenomenon four fundamental processes, either single or in combination, are involved [1,2]. Mechanical forces are involved in three of these: abrasive-wear, adhesive-wear and fatigue-wear. The fourth, corrosive-wear, is the result of joint action of chemical and mechanical forces, and is associated with the mechanical removal of corroded layers that form on the surface of a material as a reaction with its environment [1,3].

Restorative composites generally consist of an organic polymerizable matrix, inorganic fillers such as quartz, borosilicate, silica and silane-coupling agent, which connect the inorganic fillers to the organic matrix [3,4]. The latest development in the field has been the introduction of nanofilled materials, by combining nanometric particles and nanoclusters in a conventional resin matrix. Nanofilled materials offer excellent wear resistance, strength and ultimate esthetics due to their exceptional polishability and shinny appearance [5,6].

Saliva, the aqueous milieu of the mouth, is a potentially aggressive electrolyte. That is why corrosion plays an important role in the intraoral wear of resin composites [1]. Corrosion tests of dental materials are fundamental and they are often made in artificial solutions due to the instability and fluctuant characteristics of natural saliva. More than 60 formulae of artificial saliva were elaborated, a comprehensive presentation being given in [7,8]. Some of these solutions are simulating well the human saliva, especially regarding the electrochemical behaviour and they were often used in corrosion tests. The interactions of various salts with the substrate are complex [9]. The chlorides produce a slight inter-crystalline corrosion around attacking areas, as porosities. Adding HPO_4^{2-} reduces corrosion effect and the accumulation of corrosion products in those specific areas. Adding HCO_3^- to the system Cl^-/HPO_4^{2-} increases corrosion [10,11]. Contrarily, adding SCN^- to the previous system decreases the corrosion of the microstructure.

The aim of the present study is to investigate the corrosion process of a commercial nanocomposite restorative material after the immersion in various *p*H solutions, using scanning electron microscopy (SEM) for microstructure and energy-dispersive X-ray (EDX) spectroscopy for chemical composition.

Experimental part

The material used in this study was the nanocomposite resin Filtek Supreme XT (3M ESPE). 20 cylindrical samples (10.8 mm diameter and 2.5 mm thickness) were made, and they were photo-polymerized using a LED light source (Optilight LD MAX, Gnatus). The samples were immersed for 30 days in different closed chambers containing the following solutions: i) Ringer physiological solution (*p*H 5.1), Fusayama artificial saliva (*p*H 5.29), and Afnor artificial saliva (*p*H 7.1). Their chemical composition is given in table 1. After 30 days, the samples were cleaned with distilled water and dried with air. The surface topography and the chemical composition were assessed using SEM and EDX detector (VEGA II LSH TESCAN, Czech).

Table 1

CHEMICAL COMPOSITION OF THE SOLUTIONS USED FOR CORROSION

Solution	Chemical composition (g/l)		pH
RINGER (physiological solution)	NaCl	9,000	5,1
	$NaHCO_3$	0,200	
	$CaCl_2.6H_2O$	0,400	
	KCl	0,430	
FUSAYAMA (artificial saliva)	NaCl	0.400	5,29
	KCl	0.400	
	$CaCl_2 \cdot 2H_2O$	0.795	
	$NaH_2PO_4 \cdot H_2O$	0.690	
	$Na_2S \cdot 9H_2O$	0.005	
	Uree (CH_4ON_2)	1.000	
AFNOR	NaCl;	0,700	7,16
	$CaCl_2 \cdot 2H_2O$	1,200	
	KCl;	0,26	
	Na_2HPO_4 .H_2O	1,500	
	$NaHCO_3$	0,330	
	KSCN;	1,330	

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Table 2
RESTORATIVE MATERIAL USED IN THIS STUDY

Material	Matrix	Filler
Filtek Supreme XT	Bis-GMA, Bis-EMA(6), TEGDMA UDMA	Silica and zirconia 0.01-3.5 μm, average size 0.6 μm 60% volume

Bis-GMA: Bisphenol A diglycidylmethacrylate; Bis EMA(6): Bisphenol A polyethylene glycol diether dimethacrylate; UDMA: Urethane dimethacrylate; TEGDMA: Triethyleneglycoldimethacrylate.

In table 2 the composition of the studied composite is synthesised as given by the producer specifications. Filtek Supreme XT is a nano-filled composite, having non-agglomerated nanoparticles and clusters of agglomerated zirconia/silica.

Results and discussions

In figure 1 the typical microstructure of Filtek Supreme XT before (a,b) and after corrosion (c,d,e) is given for different magnifications. Firstly, the not-corroded surface reveals the existence of micrometric particle clusters (fig. 1a), while using a higher magnification the nanometric structure of the material can be observed (fig. 1b). The microstructures after corrosion in Ringer (fig. 1c), Fusayama (fig. 1d), and Afnor (fig. 1c) solutions show that, generally, the corrosion is given by pitting, but a non-uniform process on sample surface exists. For example, in figure 1e) two distinct areas corroded by pitting were observed: the first (I) is roughly characterized by 10-25 micro-holes per 100×100 μm^2, with diameters between 2 and 50 μm, and slightly corroded one (II) having about 2-5 micro-holes per 100×100 μm^2, with diameters less than 10 μm. We note that such evaluations are only qualitatively made, while a full statistical analysis of holes size distribution is given bellow. Specific directions of corrosion were recorded for all cases, due to the non-uniform application of the restorative material and micro-scratches formation during the sample preparation.

The chemical composition of Filtek Supreme Universal XT before and after chemical corrosion, as resulted from EDX measurements is presented in figure 2. An increase of the oxygen percentage can be generally observed as a consequence of the oxides formation on the sample surface. The carbon, silicon, and zirconium percentages decreased, showing the corrosion process both in the polymeric matrix and in the fillers. Also, small quantities (less than 1%) of calcium, potassium, and sodium were detected and they resulted from the chemical reaction products. The existence of these compounds is confirmed by the local peaks of atomic percentage (fig. 3a,b) along a line. For example in figure 3a, along a distance of 1500 μm, the local decrease of silicon and oxygen percentages reveal the corrosion of silica particle cluster by particle solving, while in figure 3b, along a distance of 310 μm, the local increase of sodium and chlorine percentages indicate the existence of NaCl compound on sample surface.

In order to make quantitative evaluations of the corrosion through pitting, the recorded images were processed using

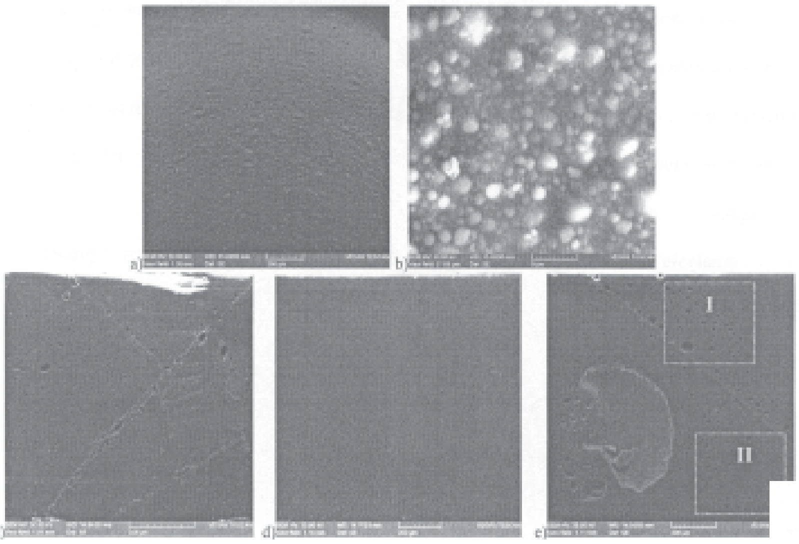

Fig. 1. Microstructure of Filtek Supreme XT before (a,b) and after the corrosion in various solutions: Ringer (c), Fusayama (d) and Afnor (e)

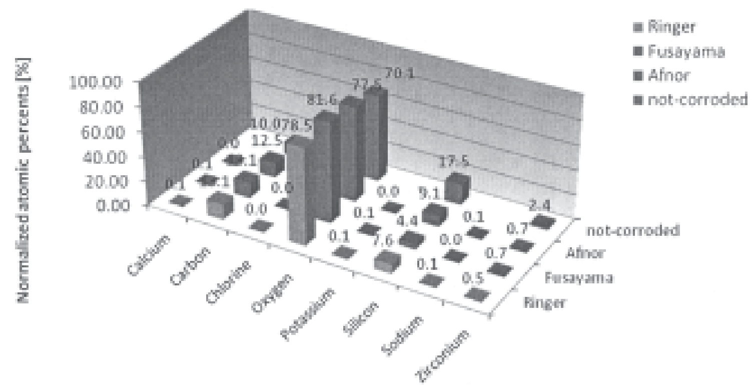

Fig. 2. Chemical composition of Filtek Supreme XT before and after the corrosion in various solutions on 2×2 mm^2 area

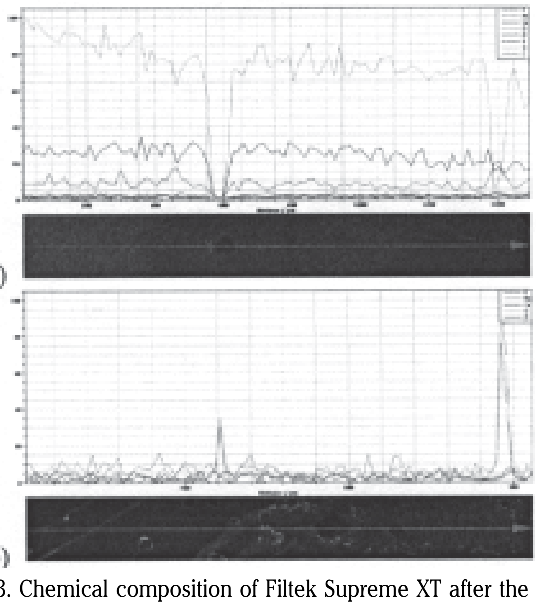

Fig. 3. Chemical composition of Filtek Supreme XT after the corrosion in Fusayama artificial saliva along various lines

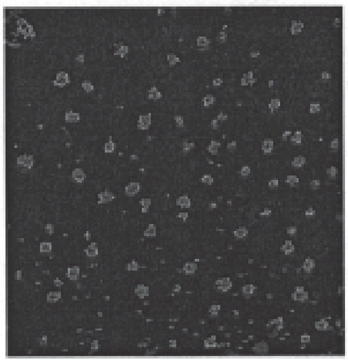

Fig. 4. Micro-hole identification on the corroded surface

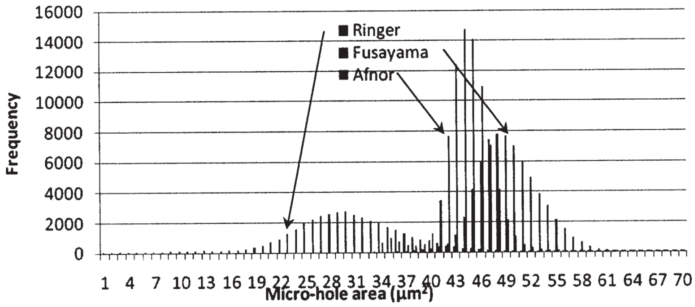

Fig. 5. Histogram of averaged micro-hole size distribution for tested dental composite in various corrosion environments

Table 3

AVERAGED SIZES, PERCENTS OF CORRODED AREA AND CIRCULARITY OF MICRO-HOLE RESULTED FROM PITTING CORROSION IN VARIOUS SOLUTIONS

Corroding solution	Averaged hole area (μm^2)	Standard deviation	% of corroded area	Circularity
Ringer	43.171	2.545	2.985	0.909
Fusayama	48.373	3.767	3.116	0.945
Afnor	29.385	3.856	2.629	0.833

the ImageJ software. This allowed us to obtain full estimations of the percentage of corroded surface, micro-hole sizes, circularity and size distribution. For example in figure 4 a typical holes identification is shown.

In table 3 the averaged statistical results over 20 samples immersed in each of the previous three solutions are given. Also, in figure 5 the histograms of micro-hole area-distribution were plotted. The following can be concluded: i) having in view the percentage of corroded area and averaged hole area, the most intense corrosion takes place in the case of Fusayama solution, while the lowest corrosion can be observed in the case of Afnor solution. These results are in a good agreement with the previous ones obtained by EDX measurements; ii) even the low number of tested corrosion environments, no correlation with the solution *p*H can be inferred; iii) a high circularity was obtained and it indicates an almost semi-spherical shape of the pits.

The monomer 2,2_-bis-[4-(methacryloxypropoxy)-phenyl]-propane (Bis-GMA) has been widely used as an important dental base monomer since it was invented in early 1960s [12]. Bis-GMA is a very viscous liquid. To improve the handling qualities, a low viscosity diluent monomer, such as tri (ethylene glycol) dimethacrylate (TEGDMA), is added to thin the resin. In Bis-GMA/TEGDMA dental resin, Bis-GMA functions to limit the photo-polymerization induced volumetric shrinkage and to enhance resin reactivity, while TEGDMA provides for the increased vinyl double bond conversion. In Filtek Supreme XT restorative material, the majority of TEGDMA has been replaced with a blend of UDMA (urethane dimethacrylate) and Bis-EMA(6)1 (Bisphenol A polyethylene glycol diether dimethacrylate) [13]. The filler consists in usual zirconia and silica particles, but it was discovered a way to modify the sintering process to produce loosely agglomerated nanoparticles, *i.e.* nanoclusters. Although structurally different from densified particles, these nanoclusters behave similarly to the densified particles found in other composites in terms of providing high filler loading. This resulted in a material with the strength and wear of hybrids with significantly improved polish retention and optical properties. The filler consists in a combination of a non-agglomerated/non-aggregated, 20 nm nanosilica filler, and loosely bound agglomerated zirconia/silica nanocluster, consisting of agglomerates of primary zirconia/silica particles with size of 5-20 nm fillers. The cluster particle size range is 0.6 to 1.4 microns. The filler loading is 78.5% by weight.

In wear phenomenon of resin-based materials multiple degradation processes, such us corrosive, abrasive, adhesive, fatigue are involved [14]. Corrosive wear results from the chemical reaction of the material with its environments and from the mechanical removal of corroded layers. The following steps are associated with the corrosive wear of resin composites [1,3]: i) the process of water absorption as the resin restoration is placed in the oral environment. The water-sorption leads mainly to hydrolytic corrosion of silane coupling and reinforcing fillers; ii) the internal diffusion of the water through resin matrix, filler interfaces, pores which dissolves the filler particles and alters their reinforcing effect. Such transport phenomena are well described by the theoretical and numerical models given in [15-18]. If the corroded layer is removed due to mastication or tooth brushing, a fresh surface is exposed, and the cycle of corrosion continues.

For laboratory studies, slightly low *p*H media best mimic *in vivo* conditions, but the effect is slow acting. Therefore, to produce quick microstructural damages high alkaline or very low acid media would be used [3]. Our results show that in slightly acid (Afnor) or in slightly alkaline solutions (Fusayama artificial saliva, Ringer solution) the chemical corrosion process can be microscopically evidenced, through micro-pores formation. Even macroscopically, mass looses cannot be measured, changes of the atomic percents were recorded through EDX.

Conclusions

The corrosion process in various solutions was studied for a nano-filled dental restorative composite, *i.e.* Filtek Supreme XT. The microstructures of the samples were analyzed by scanning electron microscopy, while the chemical composition through energy-dispersive X-ray spectroscopy. The corrosion is mainly due to the pitting, micrometric holes being observed for all corrosion environments. Also, preferred direction of corrosion resulted as consequence of micro-scratches formed during the samples preparation. The oxygen content is generally increasing due to the oxides formation, while carbon, silicon and zirconium normalized atomic percentages are decreasing, showing the corrosion both of the polymeric matrix and of the filler particles. Small amounts (less than 1%) of sodium, potassium, chlorine, and calcium were detected, originating from the artificial saliva. Even the immersion environments were slightly acid or alkaline, the chemical corrosion after 30 days was evidenced, but no correlation with the solution's *p*H could be inferred.

References

1. SARKAR, NK., J. Biomed. Mater. Res. (Appl. Biomater.), **53**, 2000, p. 371
2. MAIR, LH., STOLARSKI, TA., VOWLES, RW., LLOYD, CH., J. Dent., **24**, 1996, p. 141
3. PRAKKI, A., CILLI, R., MONDELLI, RFL., KALACHANDRA, S., PEREIRA, JC., Dent., **33**, 2005, p. 91
4. SODERHOLM, KJM., Scand. J. Dent. Res., **98**, 1990, p. 82
5. SILIKAS, N., KAVVADIA, K., ELIADES, G., Am. J. Dent. **18,** 2005, p. 95
6. ZHANG, X., KOLB, B., HANGGI, D., CRAIG, B., WO 01/30307 A1, 3M, 2001.
7. LEUNG, VW-H., DARVELL, BW., J. Dent., **25**(6), 1997, p. 475
8. GAL, JY., FOVET, Y., ADIB-YADZI, M., Talanta, **53**, 2001, p. 1103
9. DUFFO, GS., QUEZADA CASTILLO, E., Corrosion, **60**(6), 2004, p. 594
10. FUSAYAMA, T., KATAYORI, T., NOMOTO, S., J. Dent. Res., **42**, 1963, p. 1183
11. HOLLAND, RI., Dent. Mater., **8**, 1992, p. 241
12. BOWEN, RL., J. Am. Dent. Asoc., **66**, 1963, p. 57
13. 3M DENTAL PRODUCTS LABORATORY, Filtek Supreme XT: Technical Product Profile; U.S.A. 2005
14. FERRACANE, JL., Dent. Mater. **22**, 2006, p. 211
15. PAUN, V.-P., Mat. Plast., **44**, no. 4, 2007 , p. 393
16. PAUN, V.-P., Mat. Plast. **43**, no. 1, 2006 , p. 57
17. PAUN, V.-P., PAUN, M.-A., TOMA, A., CIUCU, C., POPENTIU, F., Mat. Plast., **45**, no. 1, 2005 , p. 57
18. PAUN, V. P., Cent. Eur. J. Phys., **7,** nr. 2, 2009, p. 264

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