

# Spectral investigation of the stability of a photopolymerizable composite material

M. CONSTANTINIUC<sup>a</sup>, M. MURESAN POP<sup>b</sup>, M. POTARA<sup>b</sup>, M. TODICA<sup>c,\*</sup>, A. ISPAS<sup>a,\*</sup>,  
M. E. BARBINTA-PATRASCU<sup>d</sup>, D. POPA<sup>a</sup>

<sup>a</sup>“Iuliu Hațieganu” University of Medicine and Pharmacy, Cluj-Napoca, Romania, 32, Clinicilor Street, RO-40047 Cluj-Napoca, Romania

<sup>b</sup>Nanostructured Materials and Bio-Nano-Interface Center, Interdisciplinary Research Institute on Bio-Nano-Sciences, Babes-Bolyai University, RO-400271 Cluj-Napoca, Romania

<sup>c</sup>Faculty of Physics, “Babes-Bolyai” University, 1 Kogalniceanu Street, RO-40047 Cluj-Napoca, Romania

<sup>d</sup>University of Bucharest, Faculty of Physics, 405 Atomistilor Street, PO Box MG-11, Bucharest-Magurele, 077125, Romania

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This work aims to investigate the structural stability of a photopolymerizable composite resin when subjected to the aggressive action of some substances, possible occurring in the oral cavity when drinking, regurgitating, or in gastroesophageal reflux disease. The material stability was assessed by XRD and Raman spectroscopy in two situations (in the warranty period specified by the manufacturer, and after this period) by immersing for different time intervals in some acidic media. A modification of the structural composition was observed after hydrochloric acid treatment.

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## 1. Introduction

Dental composite materials (e.g. acrylic resin-based polymer materials) constitute an important group of materials in modern restorative dentistry [1]. Lately improved qualities have recommended them to be used in fillings with any location on dental surfaces because they have good aesthetics, mechanical resistance, strong bond with hard dental tissue and easy handling.

These dental materials are subjected, in the oral cavity, to pH variations induced by ingested or regurgitated substances in the gastroesophageal reflux disease. Acidic pH has been shown to affect negatively wear resistance of composite resin materials [2].

To be clinically successful, restorative materials are required to have long-term continuousness, a quality which is strongly influenced not only by the intrinsic characteristics of the materials, but also by the environment to which they are exposed to [2-4].

Composite materials, like any other dental materials, should be used in accordance with the manufacturer's instructions without exceeding the expiration date. The longevity of dental restorations depends on the durability of the material and its properties. Some studies concluded that under acidic conditions, all dental restorative materials have shown degradation over time. However, composite materials have shown higher durability [5, 6].

The chemical wear caused by the exposure of the surfaces (material or tooth) to microorganisms, saliva, or chemicals from drinks and food, can undergo softening

and roughening, making their surfaces more susceptible to the physical forces occurring during mastication [7].

A World Health Organization (WHO) study in 2016 estimated that oral cavity diseases affect half of the world's population (i.e., 3.58 billion people), the dental caries of the permanent teeth being the most widespread disease. Dental caries are formed when microbial biofilm (plaque) formed on the tooth surface converts the free sugars contained in foods and drinks into acids that dissolve tooth enamel and dentine over time [8]. Statistics showed that the consumption of carbonated soft drinks has increased dramatically over the past 50 years, representing about 25% of the daily fluid intake. Consumption of acidic drinks can degrade the teeth and restorative materials [9].

Nowadays, light-cured resin-composites are the most commonly used direct dental restorative materials for treating tooth decay [10].

Resin-based composite materials are frequently used due to their favourable physical and mechanical properties, including high resistance to compression and wear, relatively low costs, and simple application [11].

Composites are essentially made of three basic components: resin-based organic matrix, inorganic filler particles or inorganic dispersed phases, and organic-inorganic bonding agent, silane [12].

Organic matrix is made of monomers which by polymerization lead to polymers, forming a three-dimensional network, which is filled with fillers, and in this way, the physical and mechanical properties of the

network are improved. Filler materials typically include glass or quartz particles, or fused glass particles [11].

As hard dental tissues, restorative materials are subject to aggressive factors in the mouth. Along with the thermal and mechanical agents that can damage the hard structures (dental tissues and restorative materials) in the oral cavity, chemical agents such as various acids can be enemies of dental treatments.

One of such dental restorative materials frequently used in dental practice is Herculite, a photo-polymerizable methacrylate-based composite resin (see Table 1) with improved mechanical and chemical resistance. The methacrylate-based compounds are also used to design materials with enhanced optoelectronic properties [13, 14].

The purpose of this study was to determine the effect of some acidic fluids (citric acid, acetic acid, and hydrochloric acid) that reach the oral cavity in various situations (when eating, drinking and regurgitating in gastroesophageal reflux disease) on Herculite dental acrylic composite resin used for fillings.

Sources of acids can be endogenous (hydrochloric acid) or exogenous (citric acid, acetic acid). Hydrochloric acid is an important gastric component, while acetic acid is a usual ingredient for salad dressing known as vinegar, and citric acid is an organic acid naturally occurring in vegetables and fruits, especially in the *Citrus* variety. Moreover, the citric acid is the most common preservative and flavouring additive in food, beverages or pharmacological products.

In this work, Raman and XRD investigations were performed in order to check the stability of the Herculite dental acrylic composite resin, to aggression of some usual endogenous and exogenous acids.

## 2. Experimental part

For the purpose of this study, an experimental model (Fig. 1) was duplicated using a duplicating silicone (Exaktosil N21, Bredent, Germany). This silicone mold was used to obtain 22 specimens fabricated from an acrylate composite resin (Herculite XR V Ultra, Kerr Dental) (see Table 1). In a cylindrical silicone mold with the height (H) of 1 mm and the diameter (D) of 100 mm (Fig. 1), the composite was condensed with the aid of a shutter. Subsequently, it was photopolymerized with a photo lamp (Mini LED OEM - Satelec Acteon Group) for 20 seconds on both sides.

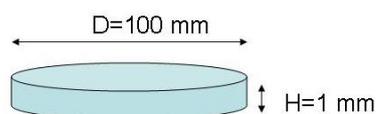


Fig. 1. Geometrical parameters of the obtained specimens

Table 1. The acrylate components of Herculite

Components of Herculite	Structural chemical formula
Hexamethylene diacrylate (C <sub>12</sub> H <sub>18</sub> O <sub>4</sub> )	
3-trimethoxy-silylpropyl methacrylate (C <sub>10</sub> H <sub>20</sub> O <sub>5</sub> Si)	
1,6-hexanediyl Bismethacrylate (C <sub>14</sub> H <sub>22</sub> O <sub>4</sub> )	
2,2'-ethylenedioxy-diethyl dimethacrylate (C <sub>14</sub> H <sub>22</sub> O <sub>6</sub> )	

Half of the specimens were made using composite resin within warranty period and the other half using composite resin out of expired date, 2 years ago. The reason of using different composite colours was to be able to differentiate easily the valid materials from the expired ones, which were additionally marked with an "x" made with the turbine bur on the face that was not examined (Fig. 2).



Fig. 2. The colour differentiation of the valid sample (left side) and the aged one (right side)

Both categories of specimens were placed in closed glass containers bearing acids (acetic acid pH 3.4, citric acid pH 2.4, and hydrochloric acid pH 2) provided by Alfa Aesar Chemicals, which were used without any further purification. Analysis of the experimental models was performed after 7 and 9 days of exposure to acids.

X-ray powder diffraction patterns were recorded with a Shimadzu XRD-6000 diffractometer equipped with graphite monochromator, operating at 40 kV and 30 mA. The samples in the form of discs with a height of about 1 mm were fixed on the glass sample holder and measured at room temperature, in 2θ range of 10–80°, with a CuKα radiation (λ = 1.54178 Å). X-ray diffraction data were processed with the software Shimadzu XRD-6000 and compared in Fullprof Suite software.

Raman spectra were performed on a portable Raman spectrometer (Raman Systems R3000CN from Ocean Optics) equipped with a 785 nm diode laser coupled to a

fiber optic probe of 100  $\mu\text{m}$  core diameter. The measurements were conducted at an integration time of 20 s for each spectrum. The laser power was set to 170 mW.

### 3. Results and discussion

The valid materials are denoted by the symbol “V”, and the expired ones, by the symbol “X”. Both kinds of

samples were investigated by XRD before and after exposure to different acids as presented in the Experimental section. Firstly, we analysed the unexpired reference sample (the polymerized composite material without any chemical degradation with acids) denoted by “V reference” in Fig. 3. The XRD pattern of this sample shows a crystalline structure with narrow and high intensity of diffraction peaks in the domain  $25^\circ\div 35^\circ$  (Fig. 3).

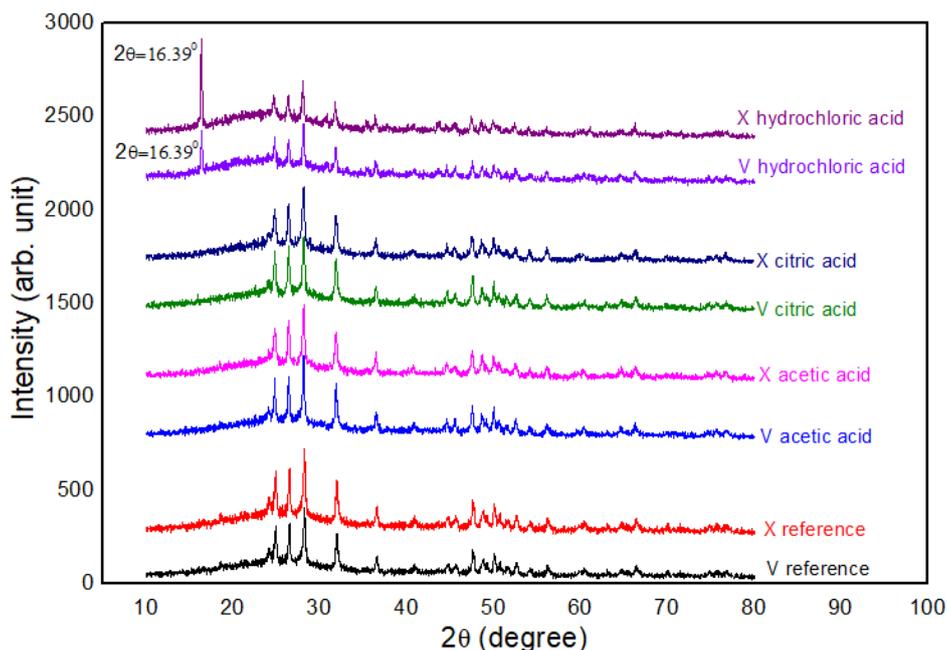


Fig. 3. The XRD patterns of the reference samples and of the samples exposed during 7 days to different acids

Other diffraction peaks with small intensity, can be seen in the domain  $40^\circ\div 60^\circ$  (Fig. 3). All these peaks are determined by the crystalline phase included into the composite material. The above-mentioned peaks are superposed over a large diffraction peak between  $15^\circ$  and  $40^\circ$ , assigned to the amorphous phase of the polymeric matrix. Such superposition is frequently observed in polymeric materials including crystalline phase [15-17]. The amorphous phase can be associated also to the broadening of the spectrum between  $40^\circ$  and  $80^\circ$ . Similar diffraction patterns were observed at the sample prepared from the expired materials (sample denoted by “X reference” in Fig. 3), before any degradation. The similitude of the spectra denotes insignificant modification of the structure of the materials after the period of warranty, if they are not submitted to the action of acids, meaning a good stability of the Herculite’s components.

The samples prepared from the unexpired materials do not present any modification of the XRD patterns under the action of citric and acetic acids (samples “V acetic” and “V citric”, in Fig. 3). Modifications can be seen for the samples exposed to hydrochloric acid (see “V hydrochloric” in Fig. 3). For these samples it could be observed a new intense peak at  $2\theta = 16.39^\circ$ , corresponding to a typical orthorhombic crystal [18] that means the apparition of a new structure with different inter-planar

distances compared with the “V reference” samples [19]. These structures could be determined by the inclusion of the chloride atoms into the structure of the crystalline component of the composite determined by the chemical reaction with the acid. The analysed samples show both crystalline phases characterized by diffraction peaks, as well as the amorphous phase characterized by a diffraction halo. The degree of crystallinity is defined as the ratio between the sum of the areas of the diffraction peaks, divided by the total area determined by the diffraction peaks and the characteristic halo of the amorphous phase. The degree of crystallinity increases from 31% for the reference sample, to 42% for the sample stored in hydrochloric acid.

In Fig. 3 it is observed that the crystalline phase characteristic of the reference sample is found in all the analysed samples. In the case of the sample stored 7 days in hydrochloric acid, it is observed a new peak at  $16.39^\circ$ , identified as belonging to  $\text{C}_{17}\text{H}_{25}\text{ClO}_3$  (taken from data base PDF2:53-1639).

The same analysis was made for the samples prepared from expired materials. The recorded XRD patterns are very similar with those of the unexpired samples. Again, the treatment with acetic and citric acids does not involve any significant modification of the diffraction peaks, and then on the structure of the samples “X acetic” and “X

citric" (Fig. 3). Only the hydrochloric acid ("X hydrochloric") give rise to the peak at  $2\theta=16.39^\circ$ , like in the case of the unexpired sample. However, the amplitude of this peak is higher than for the unexpired sample. Probably, the long-time conservation before use facilitates the apparition of some structural defaults, holes or fails in the crystalline phase of the initial composite material, which can be easily penetrated by the acid. This is equivalent with the increase of the contact surface between the material and the acid, enhancing the effect of the acid on the material structure. This explains the increase of the intensity of the peak  $2\theta=16.39^\circ$  observed for the expired sample. Due to the fact that the acetic and citric acids have insignificant effect on the structure of the samples, we continued only the investigation concerning the effect of the hydrochloric acid. We increased the time of immersion up to 9 days. The prolongation of the immersion time from

7 to 9 days has no supplementary effect. The XRD spectra after 9 days are similar with those recorded after 7 days, for both samples, expired and unexpired (Fig. 4). That means that the hydrochloric acid affects the structure of the composite material in the first days of immersion, after that the chemical reaction is almost completely consumed and the material reaches a new stable structure.

Our results show a good stability of the composite against acetic and citric acids for both unexpired and expired materials. However, the structure of these materials is affected by the hydrochloric acid, even in the period of validity.

For complementary information we further analysed the samples kept in hydrochloric acid by Raman method (Fig. 5). This investigation can indicate every modification of the molecular bond vibrations induced by different factors.

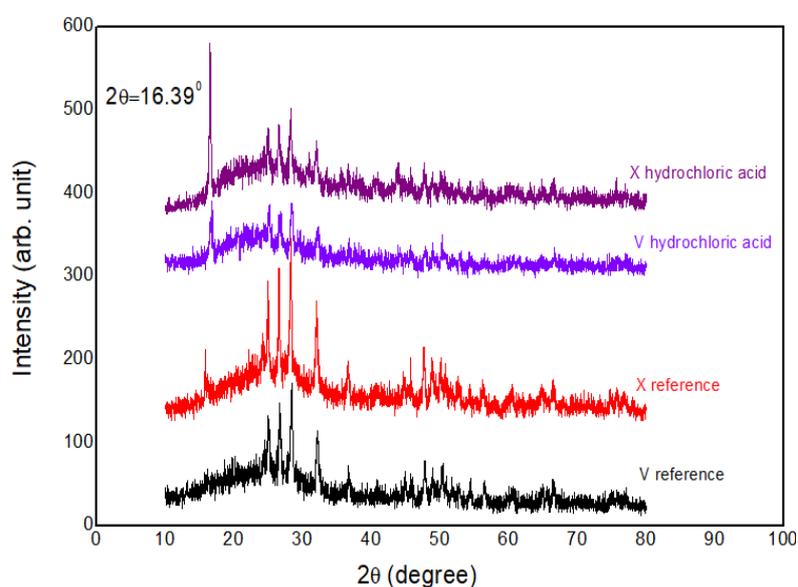


Fig. 4. The XRD spectra of the reference samples and of the samples exposed during 9 days to HCl

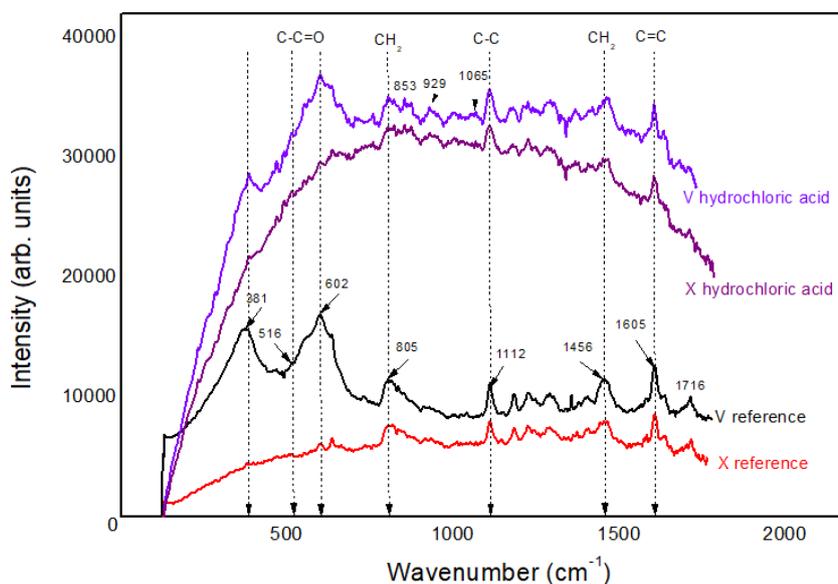


Fig. 5. Raman spectra of reference samples and of the samples kept in hydrochloric acid for 9 days

Both reference samples, the valid and expired one, exhibit the same vibration bands in the domain 800-1700  $\text{cm}^{-1}$ . The molecular vibrations assigned to these bands are not affected by the ageing of the initial material. The situation is completely different in the domain 350-650  $\text{cm}^{-1}$ . Here, we can observe two very intense vibration bands located at 381  $\text{cm}^{-1}$  (assigned to C-C aliphatic chain bend, [20]) and 602  $\text{cm}^{-1}$  (attributed to symmetric Si-O-CH<sub>3</sub> [21] from 3-trimethoxysilylpropyl methacrylate) for the unexpired material (Fig. 5). These bands vanish completely for the expired material. That means a dramatic modification of the vibrations of the chemical bonds designed by these bands. During long time of conservation, the polymeric chains are subject of slow diffusion or reptation process, which modifies the whole conformation of the polymeric network [22]. Due to this fact the surrounding vicinity of the components included into the polymeric matrix is affected. Modification of the relative position of the components, or the modification of the distance between them, can affect the vibration of some chemical bonds, especially the bending parts of the molecules. Other effect is the oxidation of the components of the composite material. New chemical bonds appear, leading to the modification of the vibration spectrum of the molecules [23].

For the samples immersed into hydrochloric acid, the Raman spectra of the samples prepared from the unexpired material is almost similar with the spectrum of the valid reference samples. The vibration bands in the domain 600-1700  $\text{cm}^{-1}$  appear unshifted with small reduction of the intensity, compared with the reference sample. Important difference is observed for the band 381  $\text{cm}^{-1}$  which has small intensity compared with the reference sample.

For the samples prepared from the expired material immersed in hydrochloric acid, we can observe only the bands in the domain 600-1700  $\text{cm}^{-1}$ , but the intensities of these bands are smaller than those of the reference sample. The bands at 381  $\text{cm}^{-1}$  and 602  $\text{cm}^{-1}$  vanishes. We suppose that the conformational modification of the polymeric matrix after a long-time conservation, as explained above, increases the surface of the component in contact with the hydrochloric acid, facilitating the chemical reaction. It is the reason for which the two bands at 381  $\text{cm}^{-1}$  and 602  $\text{cm}^{-1}$  vanishes in the Raman spectrum.

Significant modifications could be observed in the domain 800-1100  $\text{cm}^{-1}$  for the samples treated with HCl. Thus, some bands appeared at:

- 1) 853 & 929  $\text{cm}^{-1}$  originated from -C-O-C- groups [20] of acrylate components of Herculite,
- 2) 467 & 1065  $\text{cm}^{-1}$  assigned for Si-O-Si linkages formed during condensation,
- 3) 637  $\text{cm}^{-1}$  attributed to asymmetric Si-O-CH<sub>3</sub> [21] originated from 3-trimethoxysilylpropyl methacrylate component.

Clinical performance of filling materials is affected by erosion. Studies reported that acidic conditions degraded glass ionomer cements, polyacid modified resin composites, and restorative composites [24].

The increased risk of dental erosion due to the presence of dietary and gastric acids highlights the need of understanding the phenomena of restorative materials degradation, as well as their interaction with the adjacent enamel [6].

Rios et al. [6] highlighted the fact that 1-week period allows post-irradiation hardening of the composites and stabilization of the acid-base reaction of glass-ionomer cements. Because of that we chose various time intervals, including a one-week period. The greatest change in hardness of resin composites after conditioning with these solutions has been shown to occur within the first 7 days [25]. However, the immersion time of 7 days in the acid solutions is not sufficient for most composites, which is normally saturated within 7÷60 days [25].

More deep investigations of the stability of dental materials can be done only by methods involving the observation of the structure of the materials on the microscopic scale, nanometric or molecular size. It is the reason for which we chose to use X-Ray Diffraction (XRD) and Raman methods, which are suitable for investigation of physical properties of the materials in this domain [26].

In initial state, Herculite appears as a viscous material, with low mechanical stability, easy to be mould. This property is essential for the dental care, offering the possibility to fill holes or to build specific dental structures. As composite material, it contains a crystalline stuff inserted into a polymeric structure. Initially the polymer exists in monomeric state that confers the viscous character of the composite. Rigidity of the structure is obtained after photo-polymerization under the UV exposure. The hardness of the final structure is determined by the crystalline phase. The role of the polymer is to include the microcrystalline domains into a stable network. Usually the crystalline phase is very stable over time, but could react chemically with some aggressive agents, like acids, which may be present, usually or accidentally, in the oral cavity. Much susceptible to be influenced by the ageing is the polymeric matrix, not due to its chemical resistance, that it is known to be very high, but for the stability of the entangled structure [27].

Some factors affect this stability, the initial state of the polymer before polymerization and the defects of the matrix after polymerization. This behaviour is strongly influenced by the ageing of the initial product. Long-time conservation, exceeding the expiration time, can allow self-polymerization of some monomers into small structures, conducting to the apparition of local domains, with high rigidity [28]. These domains could not be again polymerized and play the role of network defaults. They will be included into the polymeric structure resulted after the polymerization under UV radiation, but their inclusion in this network will weaken the rigidity of the final solid stuff, and can facilitates the apparition of fails. The aggressive agents like acids, can easily penetrate these fails and react locally with the micro-crystals of the composite material. New ordered structures could appear there. The XRD investigation can reveal the apparition of

such structures. It is the reason for which two series of samples were prepared using a valid (unexpired) material, and expired composite material.

#### 4. Conclusions

The structural stability of some dental composite samples, prepared from Herculite material, in warranty and after expiration period, submitted different time periods to the action of acetic, citric and hydrochloric acids, was analysed by XRD and Raman methods.

XRD investigation cannot reveal significant structural modification of the samples prepared from expired and unexpired Herculite, before immersion in the acids. The structural organization of these samples, highlighted by XRD, is not affected after 7 days and 9 days of immersion in acetic and citric acids, demonstrating the good stability of the material against these aggressive factors.

Modification of the structural organization appeared under the action of the hydrochloric acid, for all samples, prepared from valid or expired materials, proved by the apparition of new diffraction peaks in the XRD spectra.

Raman investigation showed modification at molecular level of the samples prepared from the expired materials, before immersion in the acids. The chemical reaction with the hydrochloric acid modified the vibrational spectra. The effect is more pronounced for samples prepared from aged Herculite.

As a general conclusion, one can say that the unexpired Herculite is very stable against acetic and citric acids excepting the hydrochloric acid. The expired Herculite is not indicated for dental care due to its reduced structural stability.

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\*Corresponding authors: ana24ispas@yahoo.com  
mihai.todica@phys.ubbcluj.ro