

Analysis of dentistry cements using FTIR spectroscopy

Agata Lada*

University of Applied Sciences in Tarnow, Faculty of Mathematics and Natural Sciences, ul. Mickiewicza 8, 33-100 Tarnów, Poland

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Abstract

The aim of this study was to evaluate the influence of artificial saliva on dental materials. Dental cements of various compositions and applications were analyzed. Five types of cements were selected for the study: ionomer glass, carboxylic glass and cements used for temporary fillings: zinc-sulphate cement and cement containing calcium hydroxide.

Dental materials were prepared in accordance with the manufacturer's instructions. In the first stage, the cements were examined using the transmission technique in the range of 400–4000 cm^{-1} . Dental cements were incubated in saliva at pH 5 for 21 days. After this time, the FTIR spectra for the cements were measured again and placed in artificial saliva. It was found that the FTIR spectra of dentistry cements after contact with artificial saliva differ from those corresponding to the starting materials.

Spectroscopic analysis was also performed on saliva before and after incubating dental cements and materials used as temporary fillings. FTIR results indicate that under these conditions changes occur on the surface of dental materials due to their incubation in artificial saliva. The composition of saliva changes after the incubation of dental materials in it. Urea present in artificial saliva is degraded. Carbonates and phosphates are formed on the surface of dental materials. The disappearance of some bands in the spectra of the cements and their appearance in the spectra of the artificial saliva indicates the transfer of some components from the cements to the artificial saliva. The environment of the artificial saliva affects the dental materials. Analogous changes in the spectra of all tested dental materials are observed. These changes are limited to their area.

Keywords: FTIR, artificial saliva, dentistry cements, biomaterials

Introduction

In recent years a great attention has been paid to dental prevention. This stimulates development of dentistry materials market which constantly offers modified dental materials. Hence, this development is closely connected with intense investigations on dental materials [1, 2].

Cements constitute large group of dental materials [3, 4]. They are divided into two groups: temporary and final cements. Final cements are categorised into connecting and fixing cements [5]. They are characterized by a different composition and various uses. There are many factors to consider when choosing a cement [5, 6]. Zinc-sulphate cements, brittle, not very resistant to friction, used as a temporary filling, are being replaced by new generation materials. Calcium hydroxide cements are used as temporary restorations as they have a bactericidal and odontropic effect.

Among them, there are chemically cured and light-cured cements (reinforced with resins), which are used for temporary cementation of crowns and bridges. Zinc-eugenol cements are used for the deposition of temporary restorations because they have poor mechanical properties, and also eugenol interferes with the bonding of cements containing resins. They are also characterized by bactericidal and odontotropic properties [6]. Carboxylic cements are another group of cements used as temporary cements. They have high biocompatibility resulting from the possibility of creating chemical bonds by carboxyl groups of cement with calcium ions present in the tooth tissues [6]. These were the first cements that showed the possibility of chemical bonding with the tooth structure [5]. These cements are thixotropic and have low compressive and tensile strength [5, 6]. Zinc phosphate cement was introduced in the 1980s. Although their use has decreased significantly, they are still available on the market. These cements do not bind to the tooth structure, they are characterized by moderate compressive strength, and they are weakly stretchable [5]. Glass-ionomer cements are

Corresponding Author: qwe66@wp.pl

a combination of two cements: silicate cement and polycarboxylate cements. They are characterized by low bond strength with the tooth structure, moderate compressive strength, and low tensile strength. They should be prepared in accordance with the manufacturer's instructions, because even slight changes in the amount of mixed powder and liquid significantly affect the properties of this cement. This cement is highly soluble, sensitive to moisture, little resistant to acid environment and tooth whitening. Resin-modified glass-ionomer cements are characterized by better adhesion to the tooth structure, greater solubility and strength than glass-ionomer cement [5]. Composite cements are used for the temporary deposition of crowns and veneers. Due to its color, it is recommended for use in the anterior segment of the dentition. Silicone cements are counted as temporary cements, it is a polyvinyl siloxane-based cement. It is used to embed temporary crowns [5, 6].

Various analytical techniques have been applied in the studies. Jukka P. Matinlinna et al. have used Scanning Electron Microscopy (SEM), Fourier Transform Infrared Spectrometry (FTIR) and Energy Dispersive X-ray Analysis (EDXA) to study organic resins applied as adhesives that bond a luting cement to silica-coated titanium surfaces [4, 7, 8]. G. Eliades et al. have investigated *in situ* the effect of dentin primers on the morphology, molecular composition and collagen conformation of acid-demined dentin using Atomic Force Microscopy and FTIR surface analysis [9]. Formation of hydrolyzed surface-layer on Duceram LFC and its effect on cytotoxicity of the porcelain as measured by cellular activity and concentrations of leached ionic species has been verified by Jason A. Griggs et al. by Atomic Force Microscopy (AFM) and FTIR methods [10]. Efficiency

of the novel amphiphilic copolymeric polyalkenoic acid based on acrylic acid and methacrylic macromonomer of Triton X-100 in the formation of glass-ionomer cements has been studied by FTIR and SEM methods [11]. FTIR spectroscopy has been also applied to evaluate the setting reaction of various endodontic sealers [12] as well as the effect of filler content on the shrinkage-strain kinetics and degree of conversion of dental composites [13]. Bonding mechanism and ultrastructural interfacial analysis of dentin has been evaluated by Kunio Ikemura et al. using ATR-FTIR and transmission electron microscopy (TEM) [14]. Residual double bonds in resin-dentin interface have been determined by M. Miyazaki et al. with the aid of Raman spectroscopy [15].

Analysis of the influence of various factors on dental materials is a very important aspect of investigations. Physical-mechanical properties of dental cements have been often tested as the function of either monomer conversion/polymerization degree [16–19] or filler surface modification [20]. Research has been conducted to assess whether the cement base isolates the pulp from the electric current generated in the metallic reconstruction in the oral cavity [21].

Considerable attention has been paid to behavior of dental cements in saliva. H. K. Yip and W. M. To have used FTIR to study the changes in physical characteristics of glass-ionomer cements upon action of artificial saliva and bacteria [22, 23]. Corrosion behavior of dental alloys in artificial saliva containing various concentrations of hydrogen peroxide, carbamide peroxide and fluoride ions has been examined using electrochemical techniques [24]. FTIR analysis has been applied in investigation of a liquid simulating food and an artificial saliva following exposure to dental resin composites [25].

Table 1. Dental materials studied

Cement symbol	Type	Cement components	Applications
Cement 1	Zinc – sulphate cement	Zinc oxide, zinc sulphate, model gypsum, yellow dextrin, red pigment, china clay, distilled water	Filling of losses during treatment of tooth decay, cambium and gums
Cement 2	cement containing calcium hydroxide	Di – and trisilicic resin, methyl salicylate, calcium hydroxide, zinc oxide	As the material protecting cambium, as an underlayer for composite materials
Cement 3	Oxide – zinc – eugenol cement	Zinc oxide, eugenol	Underlayers for gum dressings, temporary fillings
Cement 4	Carboxylic cement	Zinc oxide, magnesium oxide, acrylic acid	Underlayers, sealing of constant fillings
Cement 5	Glass – ionomer cement	Silicon oxide, aluminum oxide, aluminum fluoride, calcium fluoride, sodium fluoride, aluminum phosphate(V), acrylic acid – itaconic acid – maleic acid copolymer	Underlayers, sealing of constant fillings

The aim of the present work has been to establish the influence of artificial saliva of pH = 5 on five selected dental cements differing in composition and application. Artificial saliva which can undergo changes upon contact with a dental material, has been also studied. It should be stressed that no investigations on artificial saliva transformations upon action of dental cement have been carried out so far.

Materials and Methods

The Materials studied in the research are collected in Tab. 1. All the cement samples have been prepared according to the procedure recommended by the producer. Each package of the tested dental materials contained powder and liquid, which were mixed in the appropriate ratio: cement 1 – 2.8 g powder: 1 cm³ of liquid; cement 2 and cement 3 – powder and liquid in proportions ensuring non-sticky consistency; cement 4 – 3 g of powder: 1 g of liquid; cement 5 – 3.2 g: 1 drop of liquid. Dental materials have been shaped into cubes 3mm x 3mm x 3mm in size. Then they have been incubated in artificial saliva at pH = 5 for 21 days. Polypropylene containers with the studied samples have been placed in a water bath at the temperature of 37 °C.

Artificial saliva of pH = 5 has been prepared according to the procedure presented by H. Li and Z. R. Zhou [21]. It has contained 0.4 g NaCl, 0.4 g KCl, 0.795 g CaCl₂ · 2H₂O, 0.78 g NaH₂PO₄ · 2H₂O, 0.005 g Na₂S · 9H₂O, 1.0 g NH₂CONH₂ in 1 liter of distilled water.

In the studies of dental materials IR spectroscopy has been applied. The experiments have been performed in the middle infrared range, i.e. between 400 and 4000 cm⁻¹. Spectra have been recorded using fixed parameters: resolution of 4 cm⁻¹, number of scans equal to 256. BioRad FTS 60 spectrometer with DTGS detector has been used. The measurements have been performed in a vacuum, which maximizes the signal to noise ratio. Transmission technique has been applied.

Samples of dental materials for IR studies have been mixed with KBr (400 mg) and pressed into pellets using SPECAC 241 press at 10 T load. Pellets have been prepared from dental cements before and after incubation in artificial saliva. Artificial saliva has been placed on thallium pellets and then dried.

Results and Discussion

In the work, FTIR spectra of powders, liquids, hardened cements before and after incubation in artificial saliva as well as that of artificial itself have been measured. In Fig. 1 the spectra of cements containing various chemical components are collected.

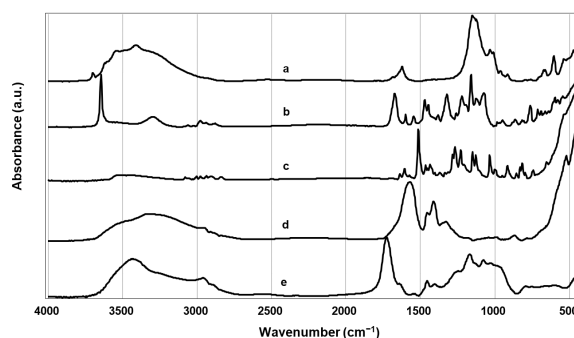


Figure 1. FTIR spectra of dental cements studied: a – cement 1, b – cement 2, c – cement 3, d – cement 4, e – cement 5

Characteristic bands corresponding to the main cements components can be distinguished in all the spectra. Zinc sulphate (VI) has been the major component in cement 1 which is confirmed by the presence of the band at 1120 cm⁻¹ originating from stretching SO₄²⁻ vibrations and the doublet in the range of 570–680 cm⁻¹ due to SO₄²⁻ deformations [24, 25]. Cement 2 has been based on calcium hydroxide and salicylic resins. Due to the organic component, it shows a very rich spectrum in the range of 500–1700 cm⁻¹ [29]. The presence of calcium hydroxide is confirmed by the intensive band at 3640 cm⁻¹ characteristic for stretching symmetric vibrations of OH group [10, 27, 28].

Zinc eugenolate has been the main component of cement 3. In its spectrum numerous bands in the range of 600–1600 cm⁻¹ originating from eugenol as well as the intensive band in the range of 420–550 cm⁻¹ characteristic for stretching Zn–O bond vibrations are visible [27–29]. Zinc polyacrylate has been the main component of cement 4. In the range of 420–550 cm⁻¹ two bands characteristic for Zn–O are present, whereas the bands originating from the bonds present in polyacrylic acid appear in the range of 1250–1700 cm⁻¹ [14, 27–29]. Intensive, broad band in the range of 1500–1600 cm⁻¹ due to stretching C=O vibrations is visible in particular [14, 29]. Cement 5 has been a glass-ionomer. It has been formed in 70–80% by calcium-aluminosilicate glass, which surrounds silica gel. In the FTIR spectrum of this cement the bands can be observed due to its organic component: at 1720 cm⁻¹ the intensive band due to C=O stretching vibrations [8, 14]. In the range of 1000–1250 cm⁻¹ the bands originating from stretching Si–O–Si vibrations, in the range of 700–800 cm⁻¹ the one due to Si–O–Si deformations appear [22, 27, 30].

Figures 2–6 show the spectra of dental cements before and after incubation in artificial saliva in the ranges where changes are visible. In the case of cement 1 (zinc-sulphate cement) (Fig. 2) three bands in the spectrum after material incubation in saliva are seen: at 1513 cm⁻¹, 1386 cm⁻¹, 831 cm⁻¹.

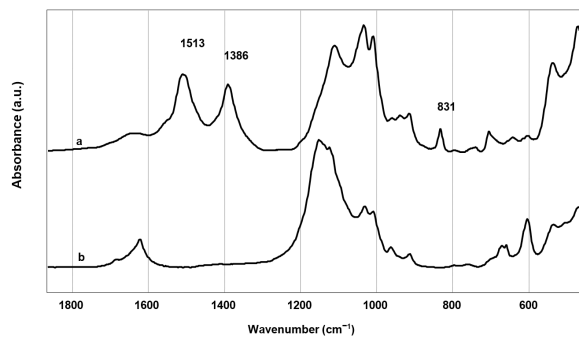


Figure 2. FTIR spectra of cement 1: a – after incubation in artificial saliva; b – before incubation in artificial saliva in the range of 400–1800 cm^{-1}

These bands can result from surface formation of carbonates with metals contained in cement 1 (zinc-sulphate cement) [30]. Appearance of carbonates in the systems may be due to the degradation of urea present in artificial saliva. In the range of 1000–1200 cm^{-1} band intensity ratios change. These bands are ascribed to SO_4^{2-} groups [27, 28]. Most probably, sulfates from the cement transfer to saliva. In the spectrum corresponding to the cement after incubation in saliva, the bands characteristic for china clay are visible. Similarity of these changes is visible in the spectrum corresponding to cement 3 (oxide-zinc-eugenol acid cement) (Fig. 3).

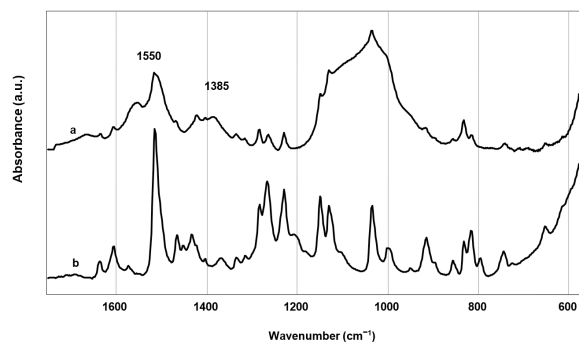


Figure 3. FTIR spectra of cement 3: a – after incubation in artificial saliva; b – before incubation in artificial saliva in the range of 400–1800 cm^{-1}

In the spectrum of this cement incubated in artificial saliva a broad band in the range of 900–1150 cm^{-1} appears. Most probably, this band originates from PO_4^{3-} groups stretching vibrations which have been present in saliva and formed a salt layer on cement surface.

In Fig. 4 the spectra of cement 4 (carboxylic cement) are collected. In the spectrum of the cement after incubation in artificial saliva changes are seen at 1036 cm^{-1} . It is possible that this band is due to stretching PO_4^{3-} vibrations originating from saliva similarly to cement 3 (oxide-zinc-eugenol acid cement).

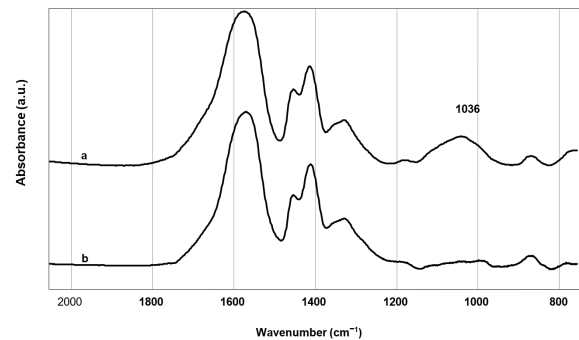


Figure 4. FTIR spectra of cement 4: a – after incubation in artificial saliva; b – before incubation in artificial saliva in the range of 400–1800 cm^{-1}

In the spectrum of cement 5 (glass-ionomer cement) recorded after incubation in saliva the band at 1565 cm^{-1} is seen (Fig. 5).

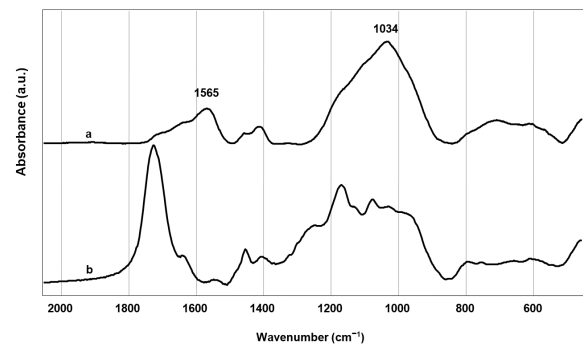


Figure 5. FTIR spectra of cement 5: a – after incubation in artificial saliva; b – before incubation in artificial saliva in the range of 400–1800 cm^{-1}

It may be connected with the formation of carbonates on the cement surface [27]. A broad band located at 1034 cm^{-1} may result from the deposition of phosphates from saliva on the cement surface [18, 24, 25, 27]. Disappearance of the bands due to organic cement components should be noted.

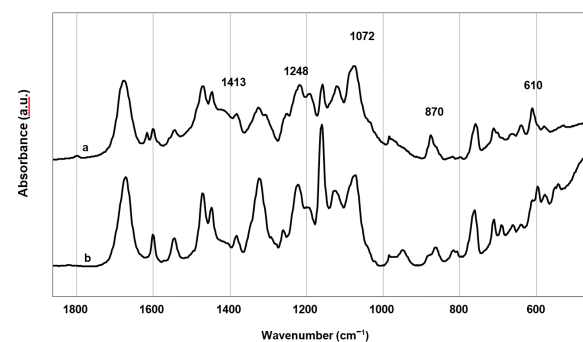


Figure 6. FTIR spectra of cement 2: a – after incubation in artificial saliva; b – before incubation in artificial saliva in the range of 400–1800 cm^{-1}

In the spectrum of cement 2 (cement containing calcium hydroxide) (Fig. 6) the band at 1413 cm^{-1} appears and that at 870 cm^{-1} grows which can be related to the formation of carbonate groups on the biomaterial surface, similarly to cements 1 (zinc-sulphate cement) and 3 (oxide-zinc-eugenol acid cement) [27]. Intensities of the bands at 1072 cm^{-1} assigned to stretching PO_4^{3-} vibrations and the band at 610 cm^{-1} originating from bending PO_4^{3-} vibrations also increase. This may be due to the deposition of saliva degradation products on the cement surface.

In Fig. 7 and 8 four spectra are collected: cement spectra before and after incubation in artificial saliva, the spectrum of artificial saliva after cement incubation and the spectrum of artificial saliva before cement incubation recorded for cements 1 (zinc-sulphate cement) and 2 (cement containing calcium hydroxide).

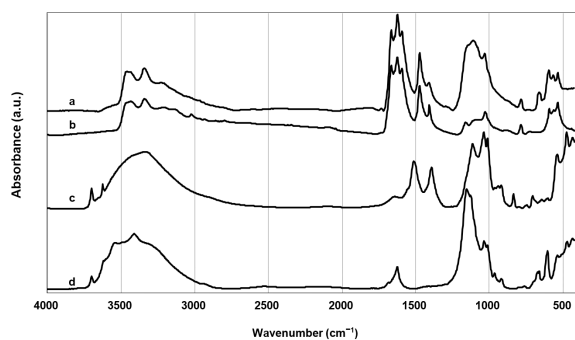


Figure 7. FTIR spectra of cement 1: a – artificial saliva after this cement incubation, b – artificial saliva, c – cement after incubation in artificial saliva, d – cement before incubation in artificial saliva

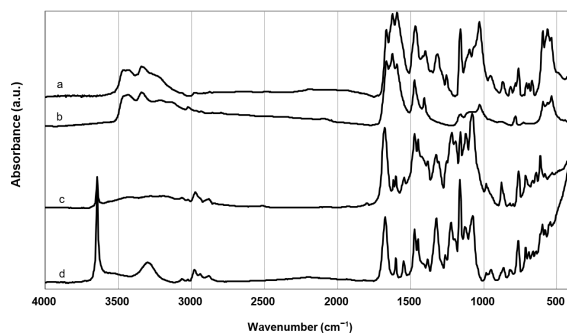


Figure 8. FTIR spectra of cement 2: a – artificial saliva after cement incubation, b – artificial saliva, c – cement after incubation in artificial saliva, d – cement before incubation in artificial saliva

In the spectrum of saliva (Fig. 7) after incubation of cement 1 (zinc-sulphate cement) the appearance of a broad band in the range

of $1000\text{--}1200\text{ cm}^{-1}$ as well as that at 660 cm^{-1} should be noted. These bands are most probably related to the transfer of sulfates, cement main components, from the cement to saliva [24, 25]. In the spectrum of artificial saliva recorded after cement 2 (cement containing calcium hydroxide) incubation (Fig. 8) the appearance of numerous bands in the range of $500\text{--}1800\text{ cm}^{-1}$ originating from organic cement components which most probably transfer into saliva should be noted [26].

Conclusions

From the studies carried out in the present work it follows that on the surface of dental cements changes resulting from their incubation in artificial saliva occur. Similarities in these changes have been established which indicates that urea present in saliva undergoes degradation and carbonates are formed on cement surfaces.

Incubation of cements in artificial saliva causes that phosphates present in saliva deposit on the cement surface as salts. Results of the investigations also suggest that the changes of saliva upon incubation of certain dental cements can result from the transfer of some cements components into saliva. This is proved by the disappearance of some bands in the spectra of cements and their appearance in the spectra of saliva.

To summarize, the experimental technique applied in the studies makes it possible to observe the changes which occur upon contact of dental cements with artificial saliva environment. Dental cements are not resistant to artificial saliva. Changes in its composition, however, are not significant and limited to its surface. In spite of various compositions of the cements studied, analogous changes in their spectra have been observed.

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