Analysis of the Anaerobic Conversion Efficiency of Various Group Composite Material

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Abstract

Tooth restoration involves the use of various types of materials. In modern reality, light-curing composite materials are used for this purpose. Also, polymer cements of various types of polymerization are used to fix indirect structures in highly aesthetic areas. All dental composites are polymerized according to the free radical type. The formation of free radicals and curing occur as a result of a thermal, chemical, or photochemical reaction. Polymerization of composites never occurs at 100%; upon contact with air, the surface of the material interacts with oxygen, which leads to the termination (inhibition) of the polymerization reaction. To prevent the formation of an oxy-gen-inhibited layer (OIL) on the surface of the composite, chemically inert, oxygen-impermeable protective glycerol gels are used.

To evaluate the feasibility and effectiveness of glycerol in preventing the oxygen-inhibited layer formation and to determine the relationship between the group of the composite and its qualitative composition during the formation of an oxygen-inhibited layer during polymerization.

This study was carried out using an Infralum FT-801 IR Fourier spectrometer in KBr tablets. 135 samples of 12 various composite materials were studied; each was subjected to IR spectrometry, cured in glycerol or without glycerol. 15 specimens of Enamel plus UE composite material underwent pre-polymerization heat in a special oven (Micerium; Avegno, Italy) to 55°C before one heating cycle.

The obtained results allowed us to conclude that the type of composite material does not significantly affect the process of oxygen inhibited layer formation.

Regardless of the composite material group, under aerobic conditions, an incomplete conversion occurs, and an oxygen inhibited layer is formed. Anaerobic conditions do the conversion completely, which leads to the absence of oil, which was confirmed by infrared spectroscopy data.

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Introduction

Tooth filling, as a process of closing a defect of tooth hard tissues, involves the use of various materials. The purpose of filling is to hermetically fill and isolate the internal structures of the tooth from the external environment, restore the shape, function, and, if possible, the color of the tooth and other aesthetic characteristics. Currently, composite polymeric materials are widespread in dentistry and are used not only for filling carious and non-carious lesions cavities but also for creating artificial coatings on the surface of teeth (direct veneering), luting artificial structures to tooth hard tissues.[1-5]

The composite polymer filling materials were developed in the USA in the late 1950s by Dr. Rafatl L. Bowen and were first used in

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dentistry about 40 years ago.[2] All composites polymerize according to the free radical type. The formation of free radicals and curing occur as a result of a thermal, chemical, or photochemical reaction. Composites of chemical and photo(light)-activation are the most widespread in practice.[1,2,3,6-16] In today's dentistry, a prevailing number of doctors use photopolymerizable (light-curing) composite materials for the manufacture of direct restorations and luting of thick veneers, dual-curing composite cements for "build-up" and cementation of some indirect prosthetic restorations. Also, practitioners rarely use chemically cured cements.

Each of the above-mentioned types of composite materials has certain features of the polymerization reaction, therefore, it is necessary to detail the processes occurring during polymerization.

The polymerization reaction of light-curing composites leads to the formation of highly reactive free radicals capable of attaching and creating new radicals until the entire volume of the monomer is converted into a polymer form or the reaction is completed. The organic matrix, which is mostly represented by dimethacrylates but also includes other monomers, is the primary mediator of polymerization in light-curing composites. The functional groups of monomers possess double bonds C=C, which have 2 pairs of electrons shared by two carbon atoms. During the initiation and course of the reaction, an extensive three-dimensional polymer network is formed with the formation of single C-C bonds in place of the double bonds.[17-19]

For the reaction to start, it needs to be initiated, which is achieved by including photoinitiation systems in the composite material that absorb light and drive the molecules to excited states, from there, free radicals or other initiator species form and initiate the conversion of monomers into a polymeric network. There are two types of photoinitiators: 1-type are trimethylbenzoyl-diphenylphosphine oxide (TPO), benzoyl peroxide (BPO) and 2-type are camphorquinone (CQ), phenanthrenequinone (PQ), benzophenone (BP), and 1-phenyl-1,2 propanodione (PPD) which combine two ways of polymerization. This division is caused by the different ways in which these photoinitiators produce free radicals. The polymerization process can be initiated by α-cleavage (type-1 photosensitizer) or H-abstraction (type-2 initiators).[21,22]

Both types lead to the formation of free radicals, i.e., highly reactive molecules with an unpaired electron. They trigger a photochemical process that initiates free radical-added polymerization reactions. The propagation of the polymerization reaction involves the interaction of chains with radical ends with successive monomer molecules.[21]

Self-cured materials are based on a little different mechanism of polymerization. There are always two components in self-curing luting composites. To avoid any early reactions, the initiators that are in charge of the curing are maintained apart. Benzoyl peroxide (BPO) and a tertiary aromatic amine component, such as DABA (diethyla-mine-3,5-di-tert-butylaniline), make up the initiator system of many of these compounds. The traditional fillers and the initiators combine to create a paste after being dissolved in the monomer matrix. Since amines have basic qualities, the BPO-containing paste is typically referred to as the catalyst and the amine-containing paste as the base. The curing process begins as soon as the two pastes are mixed to a homogenous consistency.

Dual-curing cements, as the name implies, combine two polymerization mechanisms - through a blue light source and a chemical reaction.[23]

Atmospheric oxygen has a high affinity for free radicals and can oxidize them to peroxides, which have low reactivity with respect to the monomer. This leads to a slowdown or inhibition of free radical polymerization.[17,23,24,25] Polymerization of composites never occurs at 100%, which provides a layer-by-layer connection as well as the possibility of restoring old restorations.[1] Upon contact with air, the surface of the material interacts with oxygen, which leads to the termination (inhibition) of the polymerization reaction.[8] Thus, the surface of all composites cured in air is covered with an oxygen-inhibited layer (OIL). This layer promotes better bonding of the compo-site layers to each other[6], acting by analogy with the adhesive system. The oxygen-inhibited layer (OIL) is a sticky, resin-rich, unpolymerized layer with a spent or reduced amount of photoinitiator.[24,25,26]

The OIL thickness depends on the type of composite used and ranges from 10 to 200 μm.[26] In both light-cured and self-cured dual-cured composites, free radicals come in contact with

atmospheric oxygen for a period of time. It is not a secret that the self-curing process is slower than the light-curing process, and therefore the free radicals in chemically cured restoratives have more time to react with oxygen. The above leads to the conclusion that a thicker OIL is formed on the surface of self-cured composites. It is worth noting that the oxygen-inhibited layer of a composite filling has in-creased permeability to food dyes, is subject to increased abrasive wear, is easily dam-aged by a tool, and, according to the requirements of standard composite application technique, must be removed.[10]

Chemically inert, oxygen-impermeable protective glycerin gels are used to pre-vent the formation of OIL.[2] The main hypothesis of this study is that a glycerin gel applied to the surface of a composite material during polymerization can prevent the formation of OIL.

The purpose of the present study was to evaluate the feasibility and effectiveness of glycerol in preventing the oxygen-inhibited layer formation and to determine the relationship between the group of the composite and its qualitative composition during the formation of an oxygen-inhibited layer during polymerization.

Materials and methods

Specimen selection
12 dental composite materials were used in presented study. Different types of composite materials and composite cements by curing type and inorganic particle size were included in the study to determine the effect of the above two parameters on the formation of the OIL (Table 1, Table 2).
Division of samples by type of polymerization reaction:
• light-cured composites (Estelite Sigma Quick, Esthet X HD WO, Enamel plus UE, Spectrum TPH3, Filtek Z550, Ceram-x duo, Variolink Esthetic LC Base, Relyx U200).
• dual-cured composites (Variolink Duo N Base, Dual Core Natural, Max-Cem Elite, U-Cem Premium).
  Division of samples by inorganic particle size:
• macrofilled composites (Relyx U200).
• microfilled composites (Estelite Sigma Quick, Esthet X HD WO, Variolink Esthetic LC Base, MaxCem Elite).
• microhybrid composites (Enamel plus UE,

Spectrum TPH3, U-Cem Premium).
• nanohybrid composites (Filtek Z550, Variolink Duo N Base, Variolink Es-thetic LC Base).
• nanofilled composites (Ceram-x duo).

Specimen preparation
5 samples were prepared from all composite materials (except for Enamel plus UE – 25 samples) and all the specimens were divided into two groups:
Group 1. Specimens polymerized without glycerol coating (70 samples).
Group 2. Specimens polymerized under a layer of glycerol (65 samples).
As a result, 135 samples were examined.

	Composite material	Manufacturer	Material group
1.	Estelite Sigma Quic	Tokuyama Dental, Tokyo, Japan	light-cured micro-filled composite filling material
2.	Esthet X HD WO	Dentsply Sirona, Charlotte, North Carolina, U.S.	light-cured micro-filled composite filling material
3.	Enamel plus UE	Micerium SpA, Via Guglielmo Marconi, Avegno GE, Italy	light-cured micro-hybrid composite filling material
4.	Spectrum TPH3	Dentsply Sirona, Charlotte, North Carolina, U.S.	light-cured micro-hybrid composite filling material
5.	Filtek Z550	3M ESPE St. Paul, MN, USA	light-cured nano-hybrid composite filling material

Table 1. Investigated light-curing composite filling materials.

1.	Ceram-x duo	Dentsply Sirona, Charlotte, North Carolina, U.S.	light-cured nano-filled composite cement
2.	Variolink Duo N Base without glycerol	Ivoclar Vivadent AG, Schaan, Liechtenstein	dual cured hybrid composite cement
3.	Variolink Duo N Base	Ivoclar Vivadent AG, Schaan, Liechtenstein	dual cured hybrid composite cement
4.	Variolink Esthetic LC	Ivoclar Vivadent AG, Schaan, Liechtenstein	light-cured hybrid composite cement
5.	Dual Core Natural	Vericom Co. Ltd., Toegyegongdan1-gil, Chuncheon-si, Gangwon-do, Korea	Dual cured Composite Cement
6.	MaxCem Elite	KaVo Kerr, Brea, California, U.S.	Dual cured Composite Cement
7.	U-Cem Premium	Vericom Co. Ltd., Toegyegongdan1-gil, Chuncheon-si, Gangwon-do, Korea	Dual cured Composite Cement
8.	Relyx U200 light cure	3M ESPE St. Paul, MN, USA	light-cured macro-filled cement

Table 2. Investigated composite cements of various curing types.

Glycerin-free samples (small portions of the composite material in the form of a ball - 10 mm in diameter) were polymerized in 4 points (top, bottom, medial and distal points) for 15 seconds for each, using an ultraviolet LED lamp - VALO LED (Ultradent Products, South Jordan, UT, USA) with a 430–480 nm wavelength at a light intensity of 900 mW/cm2. For all samples, the stationary distance between the tip and the

specimen was maintained at 1 mm.

Glycerin-coated samples were completely immersed in a glycerol-containing solu-tion (Mediagel, manufacturer Geltek, Russia) for samples 1–10, 12–13 for light-curing composite filling materials, and all samples (1–15) of composite cements, material 11 - glycerol-containing solution (LIQUID STRIP, manufacturer Ivoclar Vivadent AG, Schaan, Liechtenstein). All samples were cured in 4 points (top, bottom, medial and distal points) for 15 seconds for each, using a UV LED lamp - VALO LED (Ultradent Products, South Jordan, UT, USA) with a 430–480 nm wavelength at a light intensity of 900 mW/cm2. For all samples, the stationary distance between the tip and the specimen was maintained at 1 mm.

	Composite material	C=C, cm⁻¹	C=O, cm⁻¹	C-H, cm⁻¹
1.	Estelite Sigma Quick without glycerol	1647.6	1752	2874
2.	Estelite Sigma Quick with glycerol		1752.3	2856.7-3000.4
3.	Esthet X HDWO without glycerol	1639	1736	2857 – 2961
4.	Esthet X HD WO with glycerol	1637.9	1719.4	2879.5 – 2962
5.	Enamel plus UE without glycerol	1637.6	1719.2	2870.4-2978.4
6.	Enamel plus UE with glycerol	1639	1712.2	2876-2959.5
7.	Spectrum TPH3 without glycerol		1729.8	2811-2963
8.	Spectrum TPH3 with glycerol		1730.5	2660-3035
9.	Filtek Z550 without glycerol	1637.6	1719.5	2877.7-2979.5
10.	Filtek Z550 with glycerol		1736.3	2685-2980
11.	Enamel plus UE heated with glycerol of Ivoclar Vivadent		1708-1752	2862-2957
12.	Enamel plus UE heated without glycerol	1638.5	1730.5	2878.8-2960.6
13.	Enamel plus UE heated with glycerol		1719-1751	2860-3157

Table 3. Distribution of detected groups and peaks of their spectra for samples of light curing filling materials.

15 specimens of Enamel plus UE composite material underwent pre-polymerization heat in a special oven (Micerium; Avegno, Italy) to 55°C before one heating cycle.

Testing method

The IR spectrometry of the samples was carried out for 28 samples on an Infralum FT-801 IR Fourier spectrometer in KBr pellets (a standard 13-mm diameter pellet is prepared by pressing a 1-2 mg sample in 350 mg of KBr in an evacuated die), with a wavenumber range of 500–4000 cm⁻¹ (MIR - mid spectral region).

Statistical analysis

The one-way ANOVA test was provided with StatPlus 6 (AnalystSoft, CA, USA) for the average data obtained in each testing group, followed by a post hoc Tukey's test. The correlation test was applied to assess the correlation of OIL presence. The significance level was set at $p < 0.05$.

	Composite material	C=C, cm⁻¹	C=O, cm⁻¹	C-H, cm⁻¹
1.	Ceram-x duo without glycerol	1637.9	1720	2878.8-297
2.	Ceram-x duo with glycerol	1634.3	1731.6	2886.6-2954.6
3.	Variolink Duo N Base without glycerol	1638	1708-1720	2881.5-295
4.	Variolink Duo N Base with glycerol	1638.1	1736	2876-2955
5.	Variolink Esthetic LC Base without glycerol	1638.8	1730	2862-2976.
6.	Variolink Esthetic LC with glycerol	1638.2	1730	2857-2974
7.	Dual Core Natural without glycerol		1713-1730	2730-2894
8.	Dual Core Natural with glycerol		1730	2849-2953
9.	MaxCem Elite without glycerol			
10.	MaxCem Elite with glycerol			2930-3010
11.	U-Cem Premium without glycerol	1642.9	1730	2870-2974
12.	U-Cem Premium with glycerol		1730	
13.	Relyx U200 light-cure without glycerol			2739-2922
14.	Relyx U200 light-cure with glycerol			2751-2940

Table 4. Distribution of detected groups and peaks of their spectra for samples of polymer cements of various types of curing.

Results

Absorption bands corresponding to the groups C=C, C=O, C-H, – NH2, – COOH, hydrogen bonds were obtained in the course of Fournier spectroscopy in the mid spectral region of 135 samples. The distribution of the detected groups by materials is described in Table 3 for light-curing filling materials, in Table 4 for polymer cements of various types of curing.

In the following, some graphs of every composite material infrared spectral analysis of the mid-region will be presented to better understand the distribution of various groups over samples polymerized with or without glycerol.
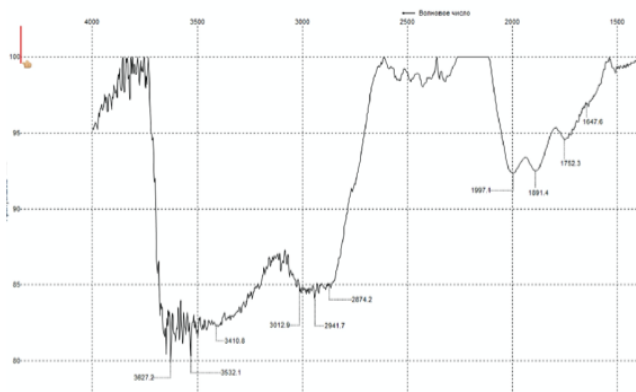
Figure 1. Sample 1. Estelite Sigma Quick without glycerol.
1647.6 - double C=C bond in alkenes
1752.3 - double C=O bond
2874.2, 2941.7 - C-H bonds in aliphatic compounds
3410.8 - NH2 group in primary amines or amides
3532.1-3627.2 - hydrogen bonds in alcohols
This sample has a high content of propylene glycol. Most likely there is an COOH group.
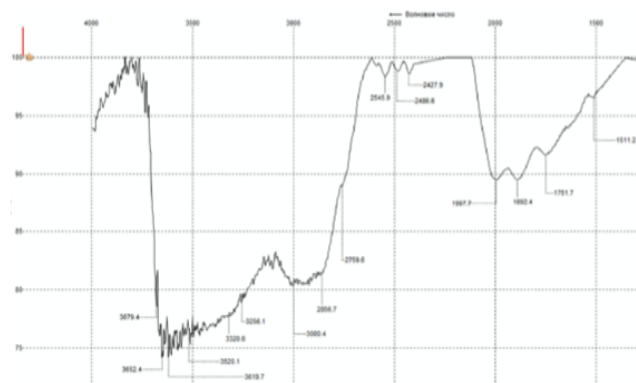

Figure 2. Sample 7. Estelite Sigma Quick with glycerol.
1752.3 - double C=O bond
2856.7 - 3000.4 - C-H bonds in aliphatic compounds
3520.6-3653.4 - hydrogen bonds in alcohols
This sample also has a high content of propylene glycol. Most likely there is a COOH-group.
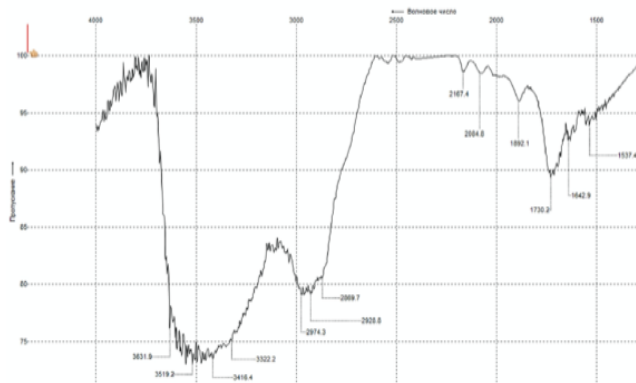

Figure 3. Sample 101. U-Cem Premium without glycerol.
1642.9 - double C=C bond
1730 - double C=O bond

2870 - 2974 - C-H bonds in aliphatic compounds
3322 -3632 - hydrogen bonds in alcohols
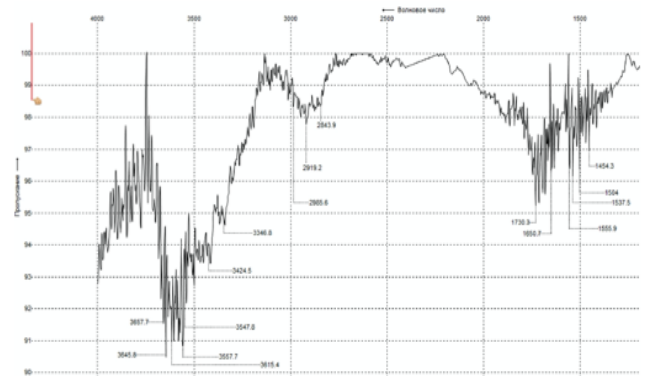This sample has a high content of multi-atomic alcohols, with less water. There is a COOH group.

Figure 4. Sample 106. U-Cem Premium with glycerol.
1730 - double C=O bond
3425 -3660 - hydrogen bonds in alcohols, amines
This sample has a high content of polyatomic alcohols, with less water. There is a COOH group.

Discussion

Light-curing dental composites are widely used materials in the field of therapeutic and prosthetic dentistry as filling materials and cements for fixation of fixed structures, respectively. The classic composition of this type of material is a mixture of an organic matrix, an inorganic filler, a silane, and a photoinitiator. A commonly used monomer is Bisphenol A-Glycidyl Methacrylate (Bis-GMA). Due to its large molecular size and rigid structure, qBis-GMA has a high viscosity, which mediates less polymerization shrinkage. To achieve a better degree of conversion, low-viscosity monomers, such as triethylene glycol dimethacrylate (TEGDMA) and urethane dimethacrylate (UDMA), are introduced into the composition of the organic matrix, since BISGMA has a high viscosity, which may limit the achievement of optimal DC during polymerization.[4,27-32,37]

The high degree of composite material conversion is one of the factors that pro-vides predictable treatment outcomes. DC can be examined by various methods, one of which is infrared spectroscopy. It seems possible to determine the concentration of C=C double bonds in a polymerized composite in relation to the total number of C–C bonds in an unpolymerized material using this method. Mid-(MIR) or near-infrared regions (NIR) are more

commonly used for organic matrices based on methacrylate monomers; MIR was used in the present study. The MIR absorption band for the aliphatic group C = C is, on average, 1630–1650 cm^{-1} is the standard value. [30,32,33,36] The aromatic peak C=C at about 1608 cm^{-1} arises from the aromatic bonds of the benzene rings in the monomer molecules, and its intensity remains unchanged during the polymerization reaction. [34,35]

Glycerin is a polyhydric alcohol with the molecular formula C3H8O3. [25] Glycerol obviously performs a protective function by creating an oxygen-free environment and thereby increasing the efficiency of all conversion steps since it prevents the oxidation of acrylic acid derivatives directly during polymerization. The absence of an oxygen inhibited layer (OIL) ensures a more complete conversion (curing of the composite) and complete adherence of the material. In some works, a decrease in the degree of oxygen inhibited layer formation on the composite surface was shown with glycerol usage in the course of finishing polymerization. [28,29]

This study demonstrated statistically higher OIL reduction after glycerin application (p<0.05), decrease in C=C bundles (p<0.05), respectively. In the IR spectrum of 1 composite samples (Estelite Sigma Quick), there was an absorption band at 1647.6 cm^{-1}, which corresponds to the absorption band of the double C=C bond in alkenes, which means that during polymerization, part of the composite was oxidized under the action of atmospheric oxygen and did not enter polymerization, while in the spectrum of 2 composite samples (Estelite Sigma Quick), there was no absorption band at 1647.6 cm^{-1}.

Double C=C bonds with characteristic absorption bands in the region of 1630–1650 cm^{-1} were present in the initial carbomer; during polymerization through a layer of glycerol, one of the bonds (π-bond) in the monomer (one molecule of acrylate, in our case) was broken, followed by the combination of a large number of monomers with each other and the formation of a polymer, respectively. Thus, in the IR spectrum of the polymer, no absorption bands should be observed in this region since there are no more double bonds; this is exactly what we observed, for example, in samples of composites 1 and 2 (Estelite Sigma Quick). If the polymerization was carried out without glycerol, then the acrylate

molecules, which were close to the surface, could be oxidized by atmospheric oxygen with the formation of an oxygen-inhibited layer, which means that with a high degree of prob-ability they would not be involved in the polymerization process and absorption bands characteristic of C–C bonds would be present in the IR spectra of the polymer.

Also, it is worth to note the fact that microfilled, nanofilled light-cured composite restorative materials, as well as various luting cements, included in this study, showed pronounced absorption bands in the 1630-1650 cm^{-1} zone, which indicates the presence of C=C double bonds and determines the presence of OIL while polymerization without glycerin layer.

Lim, J et al. investigated the effect of glycerol on the polymerization of methyl methacrylate-based dental polymers used in removable prosthetics with the help of Fourier transform infrared spectroscopy to measure monomer conversion rates. Thus, the data of the authors are comparable with those obtained by us in the course of this study: the use of glycerol as an oxygen-impervious agent had a positive effect on the degree of monomer to polymer conversion. The mechanism of the preventive activity of glycerol against OIL was due to the fact that an aqueous solution of glycerol pre-vents the diffusion of oxygen from the environment to the outer surface of the polymerizable composite. [34]

Similar data were demonstrated by Borges, M. G. In the study, higher DC was observed for glycerol surface treatment groups compared to different surface polishing protocols, regardless of the tested materials. During polymerization, oxygen reacts rapidly with free oxidized radicals, and its presence slows down the polymerization reaction. Inhibition of oxygen access by applying a glycerol gel to the sample surface improved the polymerization of the outer layer. [38]

A number of spectra also contain absorption bands in 1712–1752 cm^{-1} which correspond to the absorption bands of double C=O bonds. Their presence may be due to a high amount of EDTA disodium salt in the initial composite, which is necessary for softening the surface dentin, or to the occurrence of competing processes involving carboxyl groups in the initial carbomer.

The spectrum of composites, covered

with glycerin contains hydroxyl groups; hence, it can be concluded that the manufacturer (Mediagel or Ivoclar Vivadent) of glycerol does not affect the polymerization process in our study. It is obvious that the polymerization through a layer of glycerol is important, but the manufacturer and brand of glycerol do not matter.

In a number of spectra, hydrogen bonds H-O-H were observed, which may be due to one of the following factors:

1. In the sample glycerin was not completely removed after polymerization.

2. High content of water, propylene glycol, or pentaerythritol in the original composite.

3. Partial hydrolysis of the disodium salt of ethylenediaminetetraacetic acid (EDTA), since in addition to the EDTA salt itself, water and potassium hydroxide are also present in the composition of the starting materials.

It should be noted that the oxygen-inhibited layer of the composite material has increased permeability for food dyes, therefore, over time, various food pigments can be deposited in the filling area, tooth tissue-indirect restoration boarding zone. The above indicates a decrease in the aesthetic characteristics of direct and indirect restorations.[10,39]

Conclusion

Regardless of the composite material group, under aerobic conditions, an incomplete conversion occurs, and an oxygen inhibited layer is formed. Anaerobic conditions do the conversion completely, which leads to the absence of oil, which was confirmed by infrared spectroscopy data.

The use of glycerin at the final stages of work with composite materials for restorations and fixation of non-removable aesthetic structures improves the quality of their polymerization and prolongs the long-term perspective of direct and indirect restorations.

Acknowledgements

Declaration of Interest

The authors have no conflicts of interest.

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