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DEGREE OF POLYMERIZATION OF DUAL CURE RESIN CEMENT MEASURED BY FTIR

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Abstract: Introduction: The degree of polymerization of dental resin cement materials is very important for the longevity and quality of the clinical success of the restorative procedure. Insufficiently effective polymerization reaction of dental resin cement materials may result in adverse effects on the mechanical and adhesive performance of the material. It is believed that the proportion of triethylene glycol dimethacrylate (TEGDMA) monomers in the chemical structure of the material significantly influences the polymerization reaction. With the increase in TEGDMA, the degree of conversion of monomers into the polymer increases.

Aim: The aim of this study has been to determine the degree of polymerization of dual cure dental resin cement.

Material and methods: For the analysis of the degree of polymerization, Fourier transform infrared (FTIR) spectroscopy was used. 10 samples of dual cure resin based cement Variolink II were prepared in accordance with the manufacturer's instructions. Analysis was performed 24 hours after polymerization procedure.

Results: Degree of polymerization of Variolink II resin based cement ranged from 69.2% to 98.7% with a mean value of 85.81%.

Conclusion: Variolink II dual cure resin cement contains a significant percentage of TEGDMA which can be the cause of high degree of polymerization. The minimum acceptable percentage of the degree of polymerization of dental resin cement has not yet been established.

Keywords: resin based cement, dual cure cement, degree of polymerization, FTIR.

1. INTRODUCTION

The general trend of aesthetic dentistry is the application of resin based cement in the cementation procedure of indirect restorations, owing to the establishment of an excellent bonding between materials and dental tissues, as well as the possibility of achieving superior aesthetics with the use of color cement comparable to the restoration color. Resin based cements as compared to a group of conventional cements show advantages such as color selection, adhesion to dental tissue, reduced solubility, improved mechanical properties and the possibility of light or light-chemical polymerization [1]. The free radical polymerization mechanism is a feature of most polymeric dental materials, as well as resin based products, and involves the conversion of organic monomers into the crosslinked polymer structure [2]. According to the mechanism of the polymerization reaction, the resin based cement materials are divided into light cure, self cure and dual cure materials [3,4,5]. Light cure cements show better properties for handling, but passing light, and consequently adequate polymerization in inaccessible regions of the tooth structure, such as the intraradicular space, can be a problem. Dual cure cements are designed to overcome all difficulties in working with light cure cement materials [6]. Today, the most widely used resin based cement materials are from the group of dual cure because of the ability to polymerize under light in a short time, while achieving adequate polymerization in regions that are not available or are hardly accessible to light polymerization [3,7]. Although this group of materials includes two mechanisms of polymerization, they are independent and supplementary [8]. Dual cure cements are different in their use characteristics, composition and properties such as the ability to

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polymerize, bending and hardness resistance [9]. The attractive application of self-adhesive dual cure cements is reflected in the fact that the entire cementation process is simplified, the handling of the material is easier, and the dentine is no longer present [3,10,11]. The polymerization of resin based cement depends on certain factors, of which the following are important: the type and percentage distribution of filler particles, the type of organic resin matrix, the concentration and type of polymerization initiator, the intensity of the light emitted and the exposure time [12,13,14,15]. In the literature, the polymerization efficiency or degree of conversion of monomers in the polymer is defined as the percentage of double carbon-carbon C = C bond of the monomers that cross into the single C-C bond of the polymer and counts as the ratio of double C = C bond in the polymerized and unpolymerized material [16]. To calculate the degree of polymerization efficiency, apply the following equation:

$$DC = [1-R_{polymerized}/R_{unpolymerized}] \times 100$$

DC=degree of conversion (in %)
R=ratio of peak area to 1638 cm^{-1} and 1608 cm^{-1} in polymerized and unpolymerized material

Theoretically, during the polymerization process, all monomer molecules are converted to polymers. However, dimethacrylate monomers exhibit a certain percentage of residual unreacted double C = C bonds in the polymer so that the degree of polymerization efficiency varies between 55 and 75% [17]. For composite materials currently available in the dental market, the conversion rate varies between 36 and 67% [18]. The conversion of monomers into polymer is an important determinant of the physical and mechanical strength of the newly formed polymer [16,19,20,21]. The degree of polymerization efficiency is determined by applying various methods such as micro-Raman spectroscopy, Fourier transform infrared spectroscopy (FTIR), Differential thermal analysis (DTA), Differential scanning calorimetry (DSC) [22,23,24,25].

2. MATERIAL AND METHODS

For the analysis of the degree of polymerization of resin based cement, 10 samples of dual cure cement were prepared (Variolink II, Ivoclar Vivadent AG Liechenstein, Table 1, Figure 1). Samples of cement material were prepared in accordance with the instructions of the manufacturer, using silicone molds of a circular shape measuring 6 mm in diameter and 2.5 mm in height. Light polymerization is enabled using the SmartLite PS (Dentsplay, USA) LED lamp at the same distance from the top surface of the mold. After the preparation of the samples, they were stored in closed mini tubes in a water bath at a temperature of 37 ° C for 24 hours. A method of infrared spectroscopy with Furie's transformation was used to analyze the degree of polymerization of dual cure resin based cement. The FT-IC spectra of the samples were recorded in potassium bromide (KBr) tablets (0.5 mg of sample with 150 mg KBr) in the wavelength range 400 to 4000 cm-1, on the FT-IC spectrometer (Bomem Hartmann & Braun MB-series, Figure 2). The analysis using an IC spectrometer was performed 24 hours after cementation procedure.

Figure 1. Resin based cement material Variolink II

Table 1. Resin based cement material (name, manufacturer and chemical composition of the test material).

Material	Manufacturer LOT N°	Type of polymerization	Composition
VARIOLINK II	Ivoclar Vivadent AG, Liechenstein LOT M36112 Base LOT M13215 Catalyst	Dual cure resin cement Application with Excite DSC	BisGMA, UDMA, TEGDMA Barium glass Ytterbiumtrifluoride Ba-Al fluorosilicate glass Dibenzoyl peroxide

Figure 2. Infrared spectrophotometer with Fourier transformation, Bomem Hartmann

3. RESULTS

Table 2. Minimum and maximum values of polymerization efficiency, mean values and standard deviation of tested material.

Material	*Number of samples*	*Degree of polymerization -minimum*	*Degree of polymerization -maximum*	*Mean value*	*Standard deviation*
VARIOLINK II	*10*	*0,69181*	*0,98749*	*0,8581615*	*0,9002248*

The values of the degree of polymerization efficiency for the dual cure resin cement Variolink II ranged from 69.2% to 98.7% with a mean value of 85.81%.

4. DISCUSSION

The degree of conversion of resin based cement materials during polymerization is of great importance for the longevity and quality of the clinical success of the restorative procedure [26]. Insufficiently effective reaction of polymerization of resin based cement materials can result in adverse effects on mechanical and adhesive performance [20]. The conversion of monomers into the polymer is rarely complete and it is generally accepted that it is low in composite materials and in adhesives [16]. The chemical structure, the degree of conversion of monomers, and the kinetics of the polymerization reaction are important parameters that determine mechanical performance and monomers in clinical situations [27]. Basically, the degree of conversion of monomers affects the structure of resin based materials in terms of mechanical characteristics as well as chemical stability and it has been determined that it never amounts to 100% [16,23]. A lower degree of polymerization efficiency may result in altered biomechanical properties of the material, in terms of reduced hardness, increased hydrolytic degradation, reduced resistance to fracture and wear, as well as significant release of residual monomers and consequently altered biocompatibility of materials [16,26]. In conditions of incomplete polymerization when the conversion level is far below the expected one, it is also possible to expect a weaker bond strength of the material and dental structure [28]. Dual polymerization combines light and chemical polymerization, owing to a catalyst that polymerizes dually. The polymerization reaction occurs only chemically or only in light or combination. It is recommended that the polymerization reaction be initiated in light for 10 seconds and then left for 5 minutes to complete the whole process by chemical means. Application of dual cure cements is indicated for situations where there is a possibility of insufficient light polymerization and adequate conversion of monomers, such as the procedure for cementing fiber posts [29]. With all the advantages, dual cure cement material reduces the need for mixing the two components and pronounced fluidity, which can cause air bubbles and pore formation in the material [18]. The polymerization of materials with the structure of composite resins depends on certain factors, of which the following are significant: the species and percentage representation of

inorganic particles, the organic component of the material, the concentration and type of polymerization initiator, the intensity of the light emitted and the exposure time [12,13,14]. The available literature data regarding the values of the degree of polymerization efficiency of resin based cement material suggest the following: the degree of monomer conversion in the polymer ranges from 59.3% to 75.0% for self-cure materials and 66.6% to 81, 4% for dual cure materials [26]. In this study, the range of the degree of polymerization efficiency for the tested material ranged from 69% to 98%. It is believed that the proportion of TEGDMA monomers in the chemical structure of the material significantly influences the polymerization reaction. With the increase in TEGDMA representation, the degree of conversion of monomers to the polymer [17] is also increasing. Variolink II possesses a significant percentage of TEGDMA which gives an explanation for the high degree of polymerization efficiency. The degree of conversion of resin based cement materials with BisGMA is dependent on the amount of TEGDMA in the sense that a higher proportion of TEGDMA increases the conversion rate due to the higher mobility and reagency of the TEGDMA molecules [30,31,32]. After activation, the light polymerization process continues for the next 24 hours and the reason for this is thought to be the TEGDMA molecule, in the sense that a higher concentration of TEGDMA gives less polymerization in the post-treatment period. The maximum degree of conversion of monomers is achieved 24 hours after light polymerization [33,34]. The data of degree of conversion for Variolink II cement in the current literature are not available.

5. CONCLUSION

The minimum acceptable percentage of degree of polymerization of resin based cement materials has not yet been established, nor there is a definitive recommendation on the selection of cementitious material of optimal clinical performance for a given prosthetic indication.

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СТЕПЕН ЕФИКАСНОСТИ ПОЛИМЕРИЗАЦИЈЕ ДВОЈНОПОЛИМЕРИЗУЈУЋЕГ ЦЕМЕНТА НА БАЗИ СМОЛА МЕРЕН ПРИМЕНОМ FTIR

Сажетак: Увод: степен конверзије денталних цементних материјала на бази смола током полимеризације од значаја је за дуготрајност и квалитет клиничког успеха рестауративне процедуре. Недовољно ефикасна реакција полимеризације цементних материјала на бази смола може резултовати неповољним ефектима на механичке и адхезивне перформансе материјала. Сматра се да удео TEGDMA мономера у хемијској структури материјала значајно утиче на полимеризациону реакцију. Са повећањем заступљености TEGDMA, повећава се и степен конверзије мономера у полимер.

Циљ рада: одређивање степена ефикасности полимеризације двојнополимеризујућег денталног цемента.

Материјал и методе: За анализу степена ефикасности полимеризације коришћена је метода инфрацрвене спектроскопије са Фуријеовом трансформацијом. Припремљено је десет узорака двојнополимеризујућег денталног цемента Вариолинк II у складу са упутством произвођача. Анализа применом IC спектрометра извршена је 24 сата након полимеризације цементног материјала.

Резултати: вредности степена ефикасности полимеризације Вариолинк II цемента биле су у опсегу од 69,2% до 98,7% са средњом вредности од 85,81%.

Закључак: Вариолинк II поседује значајан процентуални удео TEGDMA што и даје објашњење за висок степен ефикасности полимеризације. Још увек није утврђен минимум прихватљивог процента успешности полимеризације цемената на бази смола.

Кључне речи: цементи на бази смола, двојнополимеризујући цементи, ефикасност полимеризације, FTIR.

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