Clinical Control of Denture Base Acrylics Polymerization for the Quality Assurance: Pilot Study of Spectroscopic Approach

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Abstract
Objective of the research was to verify the validity of spectroscopic approach for clinical control of denture base acrylics polymerization during quality assurance check-up after laboratory manufacturing phase. 15 samples with 1 mm thickness 5 mm width and 10 mm length of four different denture acrylic resins were prepared due to the manufacturer's protocols of polymerization. Spectroscopic analysis was held with the use of Monochromator MDR-204 supplied with the light filters, sample holder, optosensor and gage system of signal intensity on the photodetector. During the comparison of the light transmission spectrums among all the tested acrylic resins after their complete polymerization specific regions were noted with practically stable transmittance values, that could serve not only for the identification of material used for denture base manufacturing, but also for the evaluation of polymerization process completeness. These intervals for “Florax” and “Villacryl H plus” correspond to the wavelength range of 530-685 nm, and for “Sinma-M” and “Redont-colir” to the wavelength range of 560-680 nm. Absorption curves of tested acrylic resins after 45 minutes of polymerization differed significantly, especially in the wavelength range of 400-570 nm (p<0.05). Due to the obtained results and registered statistical relationships it can be resumed that proposed approach of spectroscopic analysis could be effectively used for clinical control of denture base acrylics polymerization during quality assurance check-up. But such quality assessment could be provided only in the means of correspondence to the specific spectral dependencies and patterns of transmission and absorption coefficients, such as linearity trend sections, extremums at discriminant wavelength ranges, distinctive fluctuations after different polymerization time periods at targeted wavelengths.

Keywords: Acrylic resin, denture base, polymerization, spectroscopy, quality assurance.

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Introduction
Even though acrylic dentures have been widely used for dental rehabilitation purposes, especially in the low-budget patient’s conditions, there are still unsolved problems, considering their far from ideal mechanical and biocompatible properties.¹,²,³,⁴,⁵,⁶ Some of the treatment nonconformances during the use of acrylic dentures caused by specifics of prosthetic designs, chemical nature of resins and non-compliant treatment planning, while others are associated with the problems occurred during the laboratorial stages of denture manufacturing.¹,³,⁴,⁷,⁸,⁹ Clinically related issues of denture fitting or denture structure defects could be easily recognized or at least prognosed by dentist, who can correct them and discuss all the aspects of denture maintenance and exploitation with the patient.⁸,⁹,¹⁰,¹¹ Such approach of predictive treatment with periodic control visits, long-lasting monitoring of dental changes and total informational support of the patients oriented towards high quality of dental care in general. On the other hand, occurrence of laboratory-associated issues could not be fully tracked by the dental clinician, and in the most cases such problems related to the inconsistencies of acrylic resins polymerization protocol recommended by manufacturer in the terms of time, temperature and heat increase/decrease pattern.

Experience of University of Louisville

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School of Dentistry had shown that incorporation of Laboratory Quality Assurance Program helped to minimize the amount of remake cases in laboratory practice and improved overall treatment results by quality and efficiency criteria. Improvements in acrylic dentures fabrication process could be accomplished with the use of novel and adopted scientific approaches aimed at enhancement of their mechanical and physical properties, but overall increase of dental care quality regarding acrylic dentures could not be fully realized without the controlling results of laboratorial output in clinical conditions. The challenge of adequate clinical control for denture base acrylics polymerization is fraught with practical deficiency of adapted, fast and easy-to-use methods, which could provide reliable and valid results of quality assurance proceedings. Moreover, development of such methods is also argumented by the forensic dental aims, which include comparative and reconstructive person’s identification and dental treatment quality evaluation during legal precedents.

Spectroscopic and spectrometric analytical methods have been widely used in different kinds of dental studies considering changes and stability parameters of various dental materials, such as metals, composites, resins and acrylics used for dental prostheses, crowns and fillings. In most of published spectroscopic/spectrometric dental studies implementation of such approaches were widely described in laboratorial (in vitro) conditions, while only few have highlighted perspective of their technological transition into clinical employment framework. Nevertheless, development or adaptation of highly validated physical methods of investigation with its further incorporation into clinical dental practice remains relevant, considering the wide range of its possible quality-oriented application.

In respect to the above-mentioned background, the objective of the research was to verify the validity of spectroscopic approach for clinical control of denture base acrylics polymerization during quality assurance check-up after laboratory manufacturing phase.

**Materials and methods**

Protocol for pilot study of spectroscopic approach used for clinical control of denture base acrylics polymerization consisted of next phases: 1) preparation of acrylic resins samples; 2) analysis of prepared samples with spectroscopic device; 3) validation of outcome results though iteration of measurements; 4) statistical analysis of obtained data.

Four different dental acrylic resins have been used in the study: “Sinma-M” (hot cured acrylic resin, JSC “CTOMA”, Ukraine), “Ftorax” (hot cured acrylic resin, JSC “CTOMA”, Ukraine), “Redont-colir” (cold cured acrylic resin, JSC “CTOMA”, Ukraine), “Villacryl H plus” (hot cured acrylic resin, Zhermack Dental, Poland), characteristics of which represented at the official manufacturers sites. 15 samples with 1 mm thickness 5 mm width and 10 mm length of each above-mentioned acrylic resins were prepared due to the manufacturer’s protocols of polymerization.

Spectroscopic analysis was held with the use of Monochromator MDR-204 device supplied with the light filters, sample holder, optosensor and gage system of signal intensity on the photodetector. Analysis was provided in the wavelength of 400-800 nm. Each acrylic resin sample was tested at 15, 25, 35 and 45 minutes of polymerization for 5 times to calculate the average value for each timepoint. Such timepoints were used due to the polymerization instructions provided for different kinds of acrylic resins by manufacturer. Coefficients of light transmission and absorption were used as target values, analysis of which was held by spectral curves formed with the obtained spectral datasets. Considering that both of above-mentioned coefficients are dimensionless, their absolute values were represented in the form of conditional units (c.u.).

Systematization and categorization of numerical data was provided in Microsoft Excel 2016 software (Microsoft Office, 2016), in which all absolute values were prepared for further statistical analysis via IBM SPSS Statistics 22 (SPSS). Posttest analysis was provided to estimate the deviation mode of absorption and transmission coefficients during repetitive registration of spectroscopic results. Relationship between absorption and transmission coefficients due to the used different polymerization time modes was processed with regression analysis methods. Pearson product-moment correlation coefficient (PPMCC) with corresponding p-value (p<0.05) were employed to estimate the
dependence between income values of analytical wavelength changes and nett results of absorption and transmission coefficients. Graph plotting and tabulation of data were held in Microsoft Excel software (Microsoft Office 2019, Microsoft).24,25,26

Results

Experimental studies have shown that tested acrylic resins samples are different from each other in the means of light absorption and transmission coefficients. The results of the spectral analysis provided for “Ftorax” acrylic resin in the wavelength range of 400-800 nm indicated the increasing pattern of light transmission coefficient associated with the longer polymerization time (up to 45 minutes). The rate of transmission curves for different polymerization time modes was similar, but statistically different in means of absolute values for each of them (p<0.05). Each of “Ftorax” transmission curve demonstrated slight increase from the 695 nm to the 705 nm with beginning of the sharp rise at the 705 nm and maximum at 770 nm. The maximum values of transmission coefficient for each time mode of polymerization were 0.38 c.u., 0.43 c.u., 0.44 c.u. and 0.54 c.u. for the periods of 15, 25, 35 and 45 minutes of polymerization respectively.

The nature of the spectral curve of the investigated acrylic resin "Villacryl H plus" was similar to the curve of "Ftorax". The maximum values of light transmittance were noted at 760-770 nm of wavelength, which differed insignificantly between each other with next absolute values of 0.32 c.u., 0.35 c.u., 0.37 c.u. and 0.39 c.u. for the polymerization time of 15, 25, 35 and 45 minutes respectively. However, the greatest deviations (p<0.05) of the linearity pattern was noted in the short-wavelength regions of the spectrum at the wavelength intervals of 400-480 nm and 400-520 nm for 15 and 25 minutes of polymerization respectively, and 400-510 nm for curves corresponding to the polymerization time of 35 and 45 minutes (Fig. 2).

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were 0.54 c.u., 0.45 c.u., 0.33 c.u. and 0.31 c.u. for the periods of 15, 25, 35 and 45 minutes of polymerization respectively (Fig. 3).

A similar dependence was observed for acrylic resin “Redont-colir”: practically horizontal graph line sections were noted after 15 and 25 minutes of polymerization in the wavelength range of 440-520 nm, and after 35 and 45 minutes in the range of 570-680 nm. Nevertheless, pattern of transmission coefficient values was statistically different between 15, 25- and 35-minutes polymerization modes (p<0.05), while no statistical difference was noted between 35- and 45-minutes polymerization modes until 750 nm of wavelength (p>0.05). The maximum values of transmission coefficient for each time-mode of polymerization were 0.71 c.u., 0.58 c.u., 0.40 c.u. and 0.38 c.u. for the periods of 15, 25, 35 and 45 minutes of polymerization respectively (Fig. 4).

Both acrylic resins “Redont-colir” and “Sinma-M” were featured by the relatively transmission coefficient constancy at the polymerization time modes of 35 and 45 minutes, by which it can be concluded that critical changes of transmission coefficient corresponded to the interval of 15-25 minutes of polymerization time.

During the comparison of the light transmission spectrums of all tested acrylic resins after their complete polymerization specific regions were noted with practically stable transmittance values, that could serve not only for the identification of material used for denture base manufacturing, but also for the evaluation of polymerization process completeness. These intervals for “Ftorax” and “Villacryl H plus” correspond to the wavelength interval of 530-685 nm and for "Sinma-M" and "Redont-colir" to the wavelength interval of 560-680 nm, while light transmission coefficients for “Ftorax” were within 0.3-0.35 c.u., for "Villacryl H plus" – 0.23-0.25 c.u., for "Sinma-M" – 0.12-0.14 c.u., for plastic "Redont-colir" – 0.11-0.12 c.u.

Absorption curves of tested acrylic resins after 45 minutes of polymerization differed significantly, especially in the 400-570 nm wavelength range (p<0.05). The minimum values were noted in the wavelength range of 750-770 nm, while in visible spectrum of 610-670 nm changes of absorption coefficients were statistically insignificant (p>0.05). Maximum values of absorption coefficient for “Ftorax” and “Villacryl H plus” were registered at 400 nm of wavelength, while for “Sinma-M” and “Redont-colir” such maximal extremums were noted at 470 nm of wavelength (Fig. 5).
The correlation levels between wavelength changes and corresponding fluctuations of transmission and absorption coefficients varied from 0.977 to 0.995 for “Ftorax” acrylic resin, in the range of 0.988-0.991 for "Villacryl H plus" acrylic resin, in the range of 0.977-0.989 for “Sinma-M” acrylic resin, and in the range of 0.985-0.992 for “Redont-colir” acrylic resin. Such consistency of correlation levels among different acrylic resins indirectly indicated about validity of used approach considering multifarious changes of transmission and absorption coefficients during iteration of measurements with retained statistically approved dependencies.

Discussion

Use of spectral characteristics have been widely accepted during quality evaluation of dental materials and for other purposes related to the verification of such in the means of correspondence to the original manufacturer’s or laboratorial assured features.16,17,18,19,20,21 Obtained results of spectral analysis provided for four tested different acrylic resins used for denture base manufacturing had shown that each of them differs by the absorption and transmission coefficients at various wavelength ranges. Considering presence of specific spectral dependencies and patterns, such as linearity trend sections, extremums at discriminant wavelength ranges, distinctive fluctuations after different polymerization time periods at targeted wavelengths, it could be resumed, that those parameters associated with each of tested material could be successfully used for the next two goals: 1) evaluation of polymerization protocol realization accuracy (polymerization quality assurance); 2) identification of each material or denture made from it during complex forensic dental investigations related to person’s identification or dental care quality assessment.

Evidence-based guidelines for care and maintenance of complete dentures published by the American College of Prosthodontists includes aspects of denture quality assurance during their functioning with the use of different “specific denture-cleaning components”.27 But considering relatively low price of such prosthetics and its accessibility as a socially oriented rehabilitation option for patients with partial or full edentulism, it has been found that quality problems could be identified not only during prolonged denture functioning, but right after denture arrival from the dental laboratory. There is a deficiency of control phase in the acrylic denture fabrication process, which could play the role of transitional step between its’ laboratorial manufacturing and clinical delivery stages.

Due to the Dental Appliance Manufacturers Audit Scheme fabrication of custom dental devices should follows such requirements, as general ones considering “Quality Management System, human resources, facilities, equipment and the manufacturing environment” and also requirements for “manufacturing the products or providing services”.28 Evaluation of acrylic dentures quality could be provided with classical method developed by Sato et al.,29 but such is oriented mostly on clinical criteria of assessment, while not considering importance of interim stage of denture delivery from the lab to the dentist. Some authors even have stated that quality assurance of dental protheses could be organized and controlled by the third party not dependent on laboratorial or clinical management or supervision.28 On our opinion optimization of acrylic dentures performance in the system of dental care could be reached by the dichotomic approach, which includes next two aspects: improvement of denture manufacturing process and clinical control of denture quality.

Use of LC-QTOF-MS (liquid chromatography coupled to quadrupole time of flight mass spectrometry) method helped to found out that material’s safety data sheets of different dental materials are not fully representing exact components of those, while investigators were able to identify different forms of oligomers, impurities and isomers.30 Even though such research was mostly dedicated to the evaluation of composites and sealants, but question of exact chemical composition also remains relevant for acrylic resins used for denture bases manufacturing.

Alteration of acrylic resin polymerization process associated with risk of allergy development because of residual monomer effect. Number of reviews and meta-analytical studies have shown different levels of cytotoxic effects caused by the acrylic materials used for denture base manufacturing.4,31,32,33,34 In the Goiato et al. review authors have highlighted that considering the fact that most of acrylic resins characterized
by the toxicity influence, there is a need of future studies aimed to this topic with the use of different evaluation methods.\textsuperscript{4} In the systematic review it was noted that in the most of analyzed studies influence of residual monomer was evaluated over the incubation process in culture media, but no information was provided about possibilities of clinical quality assessment of acrylic denture bases due to the fact of probable monomer excess presence cause by divergences in polymerization protocol.\textsuperscript{31} In Ardelean et al. study in vivo results have indicated the presence of allergic inverse reaction associated with dental acrylic resins, while in vitro results have not identified any significant amount of residual monomer.\textsuperscript{1} Such outcome authors have interpreted as accurate polymerization protocol performance. Even though in our study identification of denture-related allergic reactions or calculation of remaining monomer amount were not considered by the originally formulated objective, but we can resume that proposed protocol of spectroscopic control for denture base polymerization indirectly can verify the fact of improper changes in monomer conversion process. Theoretically we can suspect that spectroscopic controlling of denture base polymerization characterized with a high level of sensitivity to evaluate cases with prognostic improper value of residual monomer, which could be identify by the registration of inadequate levels of absorption and transmission coefficients in specific wavelength range. On the other hand, we cannot make the same theoretical conclusion considering parameter of this method specificity due to the absence of excessive amount of unconverted monomer. There is a need of further studies related to the statistical evaluation of proposed spectrometric protocol's sensitivity and specificity values due to the presence or absence of residual monomer and its’ exact redundant count. These aspects could be esteem as further research perspectives depended on the validity of spectroscopic method, used to define the quality of acrylic resins polymerization.

Urban V.M. et al. have developed high performance liquid chromatography approach for estimation of residual monomer amount in the dental acrylic resins with specific algorithm of extraction procedure.\textsuperscript{35} Analogical advanced method of denture base materials evaluation was described with the use of Fourier transform infra-red spectroscopic analysis.\textsuperscript{36} Due to the obtained results it was resumed that amount of residual monomer in CAD/CAD denture base materials was quantitatively low and not statistically different of such in the heat polymerized materials used for denture base manufacturing. Analogical approach was used in research, dedicated to the assessment of newly proposed auto-polymerized acrylic resin.\textsuperscript{37} Proposed methods were characterized with high levels of precision and accuracy, but realization of such assumes the use of different laboratory test equipment and ingredients, while the aim of our study was to develop and validate the easy-to-use method, which dentists can incorporate in fully clinical conditions with minimal need of additional supplies.

Systematic review and meta-analysis on monomer modification of denture base acrylic resins have found that assessment of dimensional stability/accuracy of the denture could be categorized as a focus question in further research.\textsuperscript{34} In our study we have proposed algorithm which could help to evaluate the completeness of acrylic resin polymerization considering the thickness parameter of used material, since we tested samples only with 1 mm thickness. So, such approach partially helping to solve the above-mentioned focus question noted in systematic review by comparing spectroscopic values of study sample and referent sample with primary known thickness of the same acrylic resin.

It is interesting to note that renewal of removable dentures showing statistically significant increase in the patient’s satisfaction due to the “Oral condition” criteria estimated by Geriatric Oral Health Assessment Index (GOHAI), even though the functional domain of GOHAI index was not significantly increased.\textsuperscript{38} It appears probable that increase of “Oral condition” parameter could be associated with manufacturing new dentures of better quality. This way initial fabrication of high-grade acrylic denture with full correspondence to the polymerization protocol could positively influence patient-oriented treatment outcome, and precise control of such correspondence could minimize the risk of possible toxic-associated side effects development.

Proposed approach of spectroscopic parameters evaluation for each acrylic denture could be used also in forensic dental practice.
Previously there have been proposed several methods of denture marking and labeling (metal bands, QR-codes, leadfoil plates, bar-codes), which characterized with specific disadvantages.\textsuperscript{13,14,15} Basically, spectroscopic parameters of some specific region of denture base could be easily used as an “electronic spectroscopic label”, which is consistent with all requirements of Council on Prosthetic Services and Dental Laboratory Relations: it’s not altering strength or esthetics of the denture, it is cost-effective to use, the marking is “spectroscopically”-visual and biologically non-active.\textsuperscript{39} The disadvantage is that “spectroscopic label” could change over the long period of time because of general acryl exploitation changes, but further research need to be provided for such issue investigation. Other limitation is that such “spectroscopic label” is not resistant to the fire. Nevertheless, both above mentioned limitations are associated not only with the “spectroscopic label”, but with the most of possible denture markings, so such approach could not be categorized as comparatively less effective than others.

Limitations of this study are related to the several methodological aspects, which in fact could be interpreted as perspectives of future research. Objective of present research was related to the validation of spectroscopic approach for clinical control of denture base acrylics polymerization during quality assurance check-up after laboratory manufacturing phase. Spectral parameters of each material after 45 minutes polymerization mode were used as referent, because such time was identified by manufacturers as indicative for complete polymerization. But in future we need to find out the level of correspondence not between spectral parameters at different time modes to 45 minutes polymerization regime as benchmark, but between exact levels of monomer conversion after each polymerization time mode and concordant values of absorption and transmission coefficients. Moreover, in this experimental study we have tested samples with specific width, length and thickness parameters, while designs of dentures are diverse and could not be specified to some absolute geometrical or volumetrical values. It would be reasonable to provide future study dedicated to the evaluation of average spectral parameters right on the denture constructions delivered from laboratory, but not on preformed acrylic resin samples to overcome this issue. Above-mentioned aspects are not critical considering pilot design of study and initially formulated objective of this research, but they should be considered during future investigations related to the topic of spectroscopic evaluation of denture acrylic materials.

Conclusions

Due to the obtained results and registered statistical relationships it can be resumed that proposed approach of spectroscopic analysis could be effectively used for clinical control of denture base acrylics polymerization during quality assurance check-up after laboratory manufacturing phase. But such quality assessment could be provided only in the means of correspondence to the specific spectral dependencies and patterns of transmission and absorption coefficients, such as linearity trend sections, extremums at discriminant wavelength ranges, distinctive fluctuations after different polymerization time periods at targeted wavelengths. Nevertheless, such analysis of denture base acrylic resins will help to control the completeness and accuracy of laboratorial stage of denture manufacturing as additive transitional testing step in full complex of prosthetics delivery. Moreover, such approach also could be implemented in forensic dental practice during dental care quality evaluation trials and person’s identification by the changes of dental status.

Declaration of interest.

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References


