Predictive algorithms for determination of reflectance data from quantity of pigments within experimental dental resin composites

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Abstract. Being able to estimate (predict) the final spectrum of reflectance of a biomaterial, especially when the final color and appearance are fundamental for their clinical success (as is the case of dental resin composites), could be a very useful tool for the industrial development of these type of materials.. *Objective:* Development of predictive models which enable the determination of the reflectance spectrum of experimental dental resin composites based on type and quantity of pigments used in their chemical formulation. *Materials and Methods:* 49 types of experimental dental resin composites were formulated as a mixture of organic matrix, inorganic filler, photo activator and other components in minor quantities (accelerator, inhibitor, fluorescent agent and 4 types of pigments). All samples underwent an artificial chromatic aging, and their reflectance spectrum was measured using a spectroradiometer. A Multiple Nonlinear Regression Model (MNLR) was used to predict the values of the Reflectance Factors values in the visible range (380nm-780nm), before and after aging, from % Pigment (%P1, %P2, %P3 and %P4) within the formulation. *Results*. The average value of the prediction error of the model was 3.46% (SD: 1.82) across all wavelengths for samples before aging and 3.54% (SD: 1.17) for samples after aging. *Conclusion:* Within the framework of this pilot study, the nonlinear predictive models developed allow the prediction, with a high degree of accuracy, of the reflectance spectrum of the experimental dental resin composites.

Keywords: experimental dental resin composites, MNLR modelling, inorganic pigments, reflectance.

Introduction

It has been reported that the composite restorative materials are one of the many successes of modern biomaterials research due to their capability to replace biological tissue in both appearance and function1. In a recent review of treatment considerations for esthetic restorations Sadowsky and collaborators pointed out that at least half of the posterior direct restoration placement now rely on composite materials2. Currently, methacrylate resin formulations dominate both the commercial market and research studies. The resin phase is composed primarily of dimethacrylate monomers (typically selected from Bis-GMA, BisEMA, and/or UDMA or a mixture of them) usually mixed with a low-viscosity reactive diluents (most commonly TEGDMA). These base monomers result in restorative materials with excellent mechanical properties, rapid polymerization, and low shrinkage.

Several authors implemented the use of experimental dental composites, as a continuous effort to understand the interrelationships among composition, resin viscosity, degree of conversion, shrinkage, flexural strength, fracture toughness, water sorption and solubility, etc. This type of materials were used to study the physical and mechanical properties of a new methacrylate monomer through comparisons with a commonly used Bis-GMA monomer[3], the effects of ceramic and porous fillers on the mechanical properties[4], the influence of irradiant energy on the degree of conversion, polymerization rate and shrinkage stress[5], the effect of co-initiator ratio on the polymer properties[6] or the curing efficiency of dental resin composites[7]. Furthermore, Park and collaborators, in their study on the influence of the fluorescent whitening agent on the fluorescent emission of resin composites, incorporated the fluorescent agent to the experimental dental resin formulation[8].

Color prediction in dentistry is a research area that has barely been explored. So far, it has been proven that the polymerization dependent color changes in resin composites can be successfully predicted using multivariable linear models of statistical inference[9]. Also, Herrera and collaborators were able to predict the color change after tooth bleaching using a novel fuzzy logic model[10] while Wee and collaborators were able to predict the final color of 25 opaque feldspathic dental ceramic specimens fabricated by mixing six different pure shades in different concentrations[11].

The reflectance spectra is a physical characteristic of a sample, which provides valuable information with respect to the interaction of light (incident radiation) with the sample. Furthermore, based on the values of the reflectance factors for each wavelength of the visible spectrum, the final color of the sample under any available illuminant can be calculated. Therefore, being able to estimate (predict) the spectrum of reflectance of a biomaterial, especially in the case of materials whose color and appearance are fundamental for its clinical success (as it is the case of dental resin composite), could be a very useful tool for the industrial development of these type of materials. However, to the best of our knowledge, there is no available study on reflectance predictions for experimental dental resin composites.

Therefore, the main objective of this study is the development of predictive models which enable the determination of the reflectance spectrum in the visible range of experimental dental resin composites using as input data the type and quantity of pigments used in their chemical formulation.

Materials and Methods

Experimental Dental Resin Formulation

For the development of this study, 49 different types (147 specimens = 49 samples x 3 specimens/sample) of experimental dental resin composites (samples) were formulated as a mixture of organic matrix, inorganic filler, photo activator and other components in minor quantities: accelerator, inhibitor, fluorescent agent and four types of Pigments (in various mixtures) according to available standards and literature8, and following standard manufacturing procedures. The relative quantities of each chemical component within the experimental resin composites are listed in Table 1.

A total of 49 different mixtures of pigments were generated by varying the relative amount of each of the four pigments. All chemical components were weighted using a high precision digital scale (BL 60 S, Sartorius AG, Goettingen, Germany) and carefully hand-mixed until a homogeneous mixture was obtained. All specimens were cylinder shaped with a diameter of Φ=20mm and 1.5mm thickness. Each of the 147 specimens was carefully packed in a custom built silicon mold in a glass plate sandwich with a mylar strip on both sides. The specimens were light cured during 60 seconds on each side using a light curing unit (BluePhase, Ivoclar Vivadent AG, Schaan, Liechtenstein). In order to mimic a clinical situation and before storage, all samples were polished using a one-step diamond micro-polishing system (PoGo, Dentsply, USA), by applying light intermittent pressure at moderate speed during 40s.

All samples underwent an artificial chromatic aging. Specimens were placed inside an artificial aging chamber (Suntest XXL, ATLAS, USA) and subjected to artificial aging according to ISO 4892-2 A112 and ISO 749113 Standards.

Reflectance Measurements

The reflectance spectrum in the 380nm-780nm range of all specimens was measured inside a completely dark room using a spectroradiometer (PR 670, PhotoResearch, USA) and a spectrally calibrated reflectance standard (SRS-3, PhotoResearch, USA). Specimens were placed on a custom built sample holder, 40cm away from the spectroradiometer and illuminated using a Xe-Arc Light Source (Oriel Research, Newport Corporation, USA). The illuminating/measuring geometry corresponded to CIE 45°/0°. The aperture of the spectroradiometer was set to 1°, which allowed the measurement of a central spot (measuring field) of the specimen of approximately 0.7cm.

Table 1. Chemical components as well as the relative percentages within the total mixture (by weight w/t) used to formulate the resin composites used in this study.

Component		Chemical Name		% w/t
Organic Matrix	45% BisGMA	Bisphenol A glycerolate dimethacrylate		68.8% (Average)
	45% TEGDMA	Triethylene glycol dimethacrylate		
	10% UDMA	Diurethane Dimethacrylate		
Inorganic Filler		SiO_2 Glass Spheres [Φ: 9-13μm]		30%
Photo Activator		Camphorquinone		0.7%
Accelerator		2-(Dimethylamino)ethyl methacrylate		0.35%
Inhibitor		Butylated hydroxytoluene		0.05%
Fluorescent Agent		1.4-Bis(2-benzoxazolyl)naphthalene		0.04%
Pigment		Pigment 1 (P1)	$FeO \cdot OH$	0.06% (Average)
		Pigment 2 (P2)	FeO	
		Pigment 3 (P3)	TiO_2	
		Pigment 4 (P4)	Fe_2O_3	

Reflectance measurements were performed both before and after the chromatic artificial aging procedure was applied. Three repeated measurements were performed for each specimen and the results were averaged. The reflectance spectrum for each type of experimental resin composite (sample) corresponded to the mean value between the three specimens corresponding to the type. Color calculations (chromatic coordinates L*, a* and b*) were subsequently performed in base of the CIE D65 Standard Illuminant and the CIE Colorimetric 2° Standard Observer assumptions14.

Design of the Predictive Models

Samples were divided into a Training (Active) Group, which contained 44 samples (sample 1 to 44) from the total of 49 samples available, and a Testing (Validation) Group, which contained 5 samples from the total of 49 samples available (Sample 45 to 49). Samples in the Testing Group present a combination of the 4 pigments. In all cases, the Active (Training) Group was used to build the predictive model while the Validation Group was used exclusively for testing the appropriate functioning of the model as well as its accuracy.

A Multiple Nonlinear Regression Model (MNLR) was used to predict the values of the Reflectance Factors values in the visible range (380nm-780nm) before and after aging from % Pigment (%P1, %P2, %P3 and %P4) within the formulation.

The equation describing the model is a 4th Order Polynomial, as described by:

$$Y = pr1 + pr2 \cdot X_1 + pr3 \cdot X_2 + pr4 \cdot X_3 + pr5 \cdot X_4 + pr6 \cdot X_1^2 + pr7 \cdot X_2^2 + pr8 \cdot X_3^2 + pr9 \cdot X_4^2 + \\ + pr10 \cdot X_1^3 + pr11 \cdot X_2^3 + pr12 \cdot X_3^3 + pr13 \cdot X_4^3 + pr14 \cdot X_1^4 + pr15 \cdot X_2^4 + pr16 \cdot X_3^4 + pr17 \cdot X_4^4$$

where:

Y is the predicted variable: Reflectance Factors values in the visible range (380nm-780nm) at 2nm step the before and after aging;

X_i are the input variables: %P1, %P2, %P3 and %P4;

pr1 … pr17 are the parameters of the model.

The models were built using the Training Group and tested using the Validation Group. The model was considered to be accurate after 200 iterations were performed and/or a convergence of 0.00001 was achieved.

A total of 402 models (one for each Reflectance Factor before and after aging) were designed. All the Multiple Nonlinear Regression (MNLR) predictive models were designed using the XLSTAT-Pro commercial software (XLSTAT, Addinsoft, USA).

Results and Discussion

In dentistry, it would be ideal to achieve a restoration that has identical colors as the tooth structure under various illumination conditions, within at least acceptable limits, but more preferably within limits of perceived color difference15. Although the importance of the pigments on the final color and appearance of the dental resin composite is well known, there is no research study available which made use of coloring pigments when formulating the experimental dental resin composites. Therefore, in this study, the use of pigments was included in the chemical formulation of the resin composites.

The research in science and biomedical applications often involves using controllable and/or easy to measure variables (input factors) to explain, regulate or predict the behavior of other variables (output factors or dependent variables). When dealing with a reduced number of input factors which are not significantly redundant and have a strong relationship with the output variables, the Multiple Nonlinear Regression (MNLR) is one of the best options to take into account for modeling the data.

The correlation between the input variables of the model (in this case, the Reflectance Factors at 2nm steps in the 380nm-780nm interval before and after the artificial aging) and the output variables of the model (in this case, the percentage of each type of Pigment used - %P1, %P2, %P3 and %P4), was carried out as an initial step. The results obtained for the Pearson Correlation coefficient are graphically presented in Figure 1.

The correlation between variables, when biomaterials are studied, is considered to be strongly direct if the value of the Pearson Coefficient exceeds 0.7 and is considered to be strongly inverse if the value of the Pearson Coefficient is lower than -0.7. As it can be observed in Figure 1, for the 5 samples included in the testing group (validation group) before aging, there is a strong inverse correlation between the quantity of the fourth Pigment (%P4) and reflectance factors of wavelengths between 525nm-650nm. This implies that higher quantities of Pigment 4 within the mixture of the experimental resin composite will decrease the values of the reflectance factors between the specified interval, affecting the lightness value of the sample and generating an orange-reddish color shift. Also, a strong correlation usually is associated with increased performance of the predictive model, but no conclusion should be drawn before analyzing the other parameters of the quality of fit, such as goodness of fit or relative residuals.

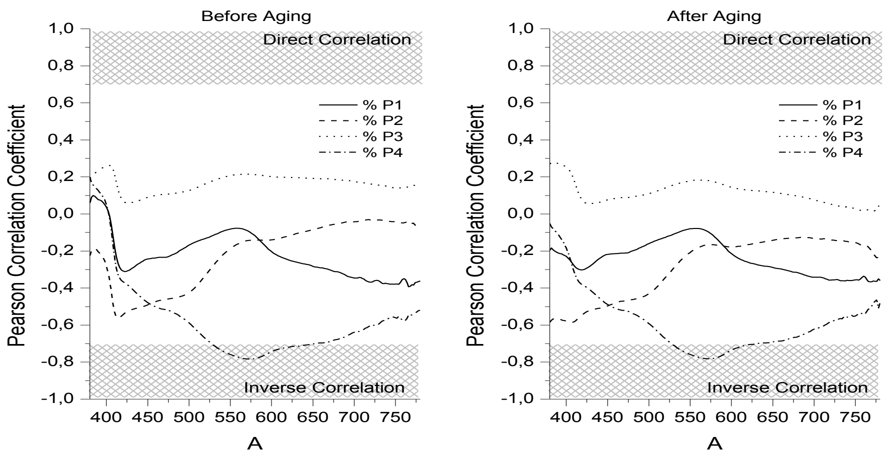

Fig. 1. Pearson Correlation Coefficients between 380nm-780nm Reflectance Factors before and after aging and % Pigment.

The goodness of fit, in terms of R2 and the Root Mean Square Error (RMSE) for the predictive models of the Reflectance Factors for wavelengths between 380nm-780nm, both before and after the artificial aging procedure was carried out, is displayed on Figure 2. Numerical measures of goodness of fit are divided into two type measures: measures of deviation from the real (measured) values and measures of how well the trend relative magnitudes are predicted. If only one type of these measurements is used, only one of these two types of information is being captured, and that it is why several researchers recommend the use of a combination of R2 for trend relative magnitude and RMSE for deviation from exact data location16. We found high values (>0.7) of the Coefficient of Determination for the predictive models of the Reflectance Factors for wavelengths higher than 425nm, both before and after aging. However, it seems that the predictive model works best for wavelengths between 425nm and 600nm, since in this interval the R2 values are higher than 0.9.

This mean that future works should be focused on improving the MNLR models in order to obtain better performance for large wavelengths. It should be noted that, if we assess the quality of the predictive model on the exclusive basis of the value of R2, the model performs better for aged samples, since the values obtained for the Coefficient of Determination are slightly higher. Both before and after aging, the RMSE values are very low, in accordance to the interval of the studied variable. All these results support the quality of the Multiple Nonlinear Regression Predictive model designed and serve to ensure the proper development of the method.

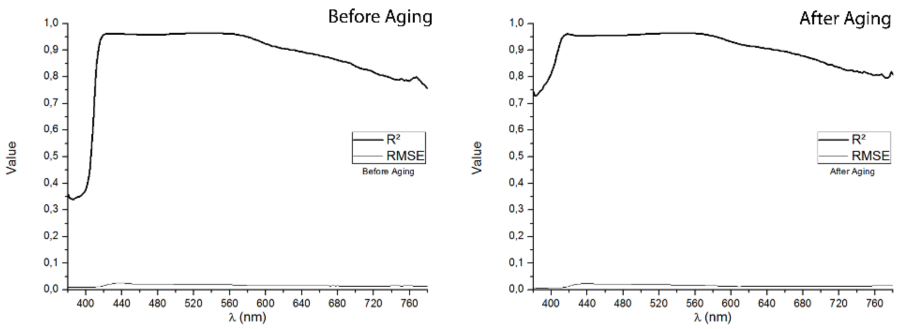

Fig. 2. Goodness of fit (in terms of R2 and RMSE) for the Reflectance Factors (380nm-780nm) for samples before aging (left) and after aging (right).

One of the best methods for assessing the accuracy of point predictions is to use overlay scatter plots and overlay line graphs. In these graphical forms, the model and data are overlaid on the same graph, allowing a direct comparison of the real (measured) data and the predicted values. The reflectance spectrum of the five samples included in the Validation Group, as measured with the PR-670 Spectrorradiometer and as predicted with the Multiple Nonlinear Regression model, both before and after aging, are presented in Figure 3– 7.

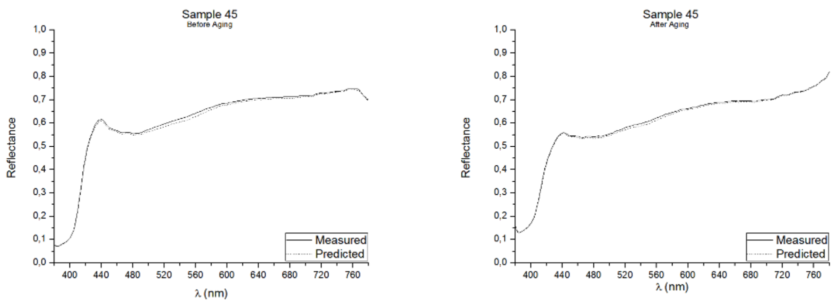

Fig. 3. Real (measured) and Predicted spectral reflectance of Sample 45 between 380nm-780nm before aging (left) and after aging (right).

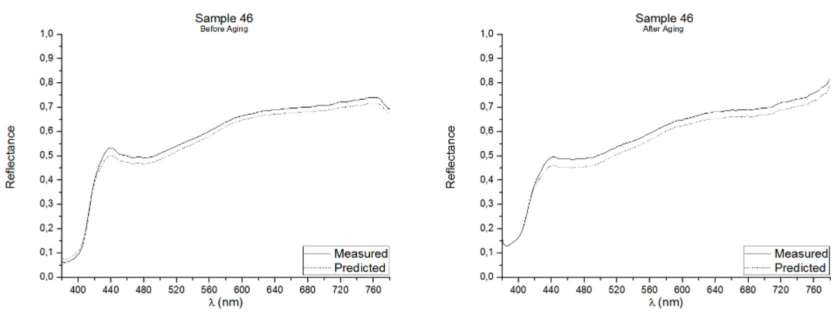

Fig. 4. Real (measured) and Predicted spectral reflectance of Sample 46 between 380nm-780nm before aging (left) and after aging (right).

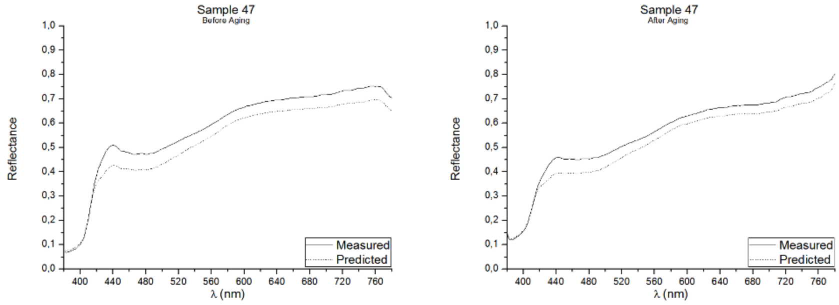

Fig. 5. Real (measured) and Predicted spectral reflectance of Sample 47 between 380nm-780nm before aging (left) and after aging (right).

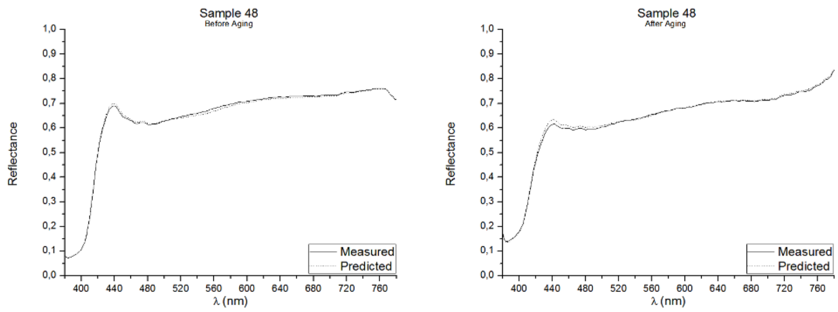

Fig. 6. Real (measured) and Predicted spectral reflectance of Sample 48 between 380nm-780nm before aging (left) and after aging (right).

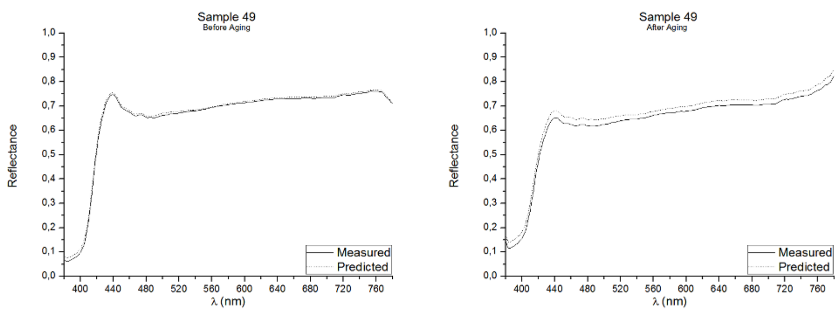

Fig. 7. Real (measured) and Predicted spectral reflectance of Sample 49 between 380nm-780nm before aging (left) and after aging (right).

Visual displays of goodness of fit are useful for a rough estimate of the degree of fit and for indicating where the fits are most problematic. Visual displays are also useful for diagnosing a variety of types of problems (e.g., systematic biases in model predictions). Noteworthy, the human visual system is not particularly accurate in assessing small to moderate differences in the fits of model to data.

Our visual system is also subject to many visual complications that can produce systematic distortions in the visual estimates of the quality of a fit16. However, as it can be observed in Figures 3-7, the quality of the fit is excellent for almost the entire spectrum, providing accurate estimates of the Reflectance Factors for all wavelengths.

In order to assess the overall quality of the prediction capacity of the proposed models, the mean value over the 5 samples (relative to the value of the variable – Reflectance Factor) along the 380nm-780nm interval was calculated. The results for samples before and after the aging procedure was applied are schematically shown in Figure 8. For samples before aging, the average value of the prediction error of the model was 3.46% (SD: 1.82), showing higher values for shorter wavelengths and considerably lower values for longer wavelengths In the case of the samples after aging, the average value of the prediction error was 3.54% (SD:1.17), exhibiting, as the case of samples before aging, lower error for longer wavelengths. The high errors obtained for short wavelengths are probably caused by the instability of the measuring system (the spectrorradiometer) which presents variability in the measured data for wavelengths lower than 400nm. This variability is expected to affect the quality of the predictive model, since no clear pattern in the input data can be established, so the provided output variables are distant from the measured ones.

Several Multiple Nonlinear Regression predictive models have been developed, which achieved to accurately predict the reflectance spectrum of the manufactured experimental dental resin composites. These models are very helpful when, in a laboratory situation, the chromatic behavior of the samples needs to be controlled. In this study, we considered the pigments as the main responsible (not exclusive) of the final color of the composites, and therefore we centered the study on the influence of the four types of pigments on the final color of the experimental dental resin composites.

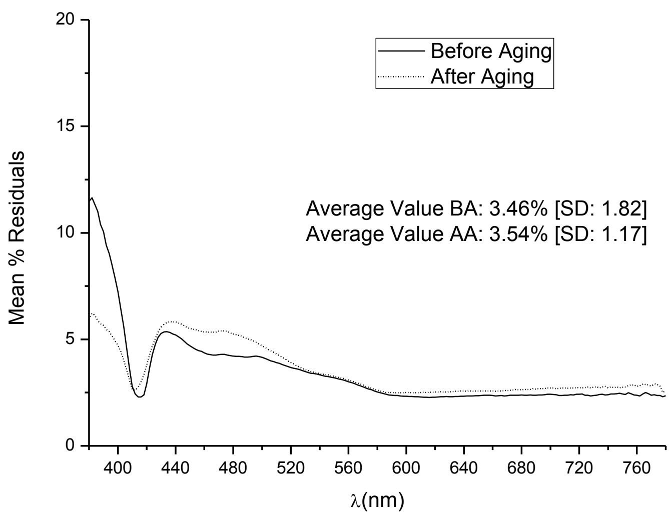

Fig. 8. Mean %Residuals of all samples of the Validation Group, before and after aging, in the 380nm-780nm interval

It has to be mentioned that the range of application of the proposed predictive models is limited, since they are designed to work exclusively with the experimental dental resins developed in this study. It is necessary to expand the present work with further studies on multiple areas, such as varying the materials used for the formulation, varying amounts of both the organic matrix and the inorganic filler as well as the quantities of the other components used in the chemical formulation.

It would also be interesting to study more carefully the behavior of the different pigments, through a wider range of combinations between them and, on the other hand, other pigments can be used for colorimetric formulations. Another development path for future studies is an improved experimental design, in terms of better coverage of the dental color space with the manufactured samples. A proper distribution of the samples within the area of interest of the color space will allow the use of newer, more accurate and reliable predictive methods, such as Fuzzy Logic.

Soft science applications involve so many variables that it is not practical to seek a model which explicitly relates them all. The Multiple Nonlinear Regression is one of the possible solutions and although it is continuously evolving as a statistical modeling technique, there are other fields which can provide also good results, such as principal components regression, maximum redundancy analysis, methods which handle the colinearity in regression, such as the ridge regression proposed by Banerjee and Carr[17], or newer methods such as the neural networks[18]. The neural networks are probably the strongest competitors for MNLR in terms of flexibility and robustness of the predictive models, but they do not explicitly incorporate a linear extraction of latent factors – that is dimension reduction[19].

Conclusions

Within the framework of this pilot study, the nonlinear predictive models developed allow the prediction, with a high degree of accuracy, of the reflectance spectrum of the experimental dental resin composites (average error <3.54% across all wavelengths of the visible spectrum). These results open the way for custom design of dental resin composites, with multiple direct and immediate clinical applications, such as the manufacture of dental shade guides, development of new dental materials, and finally, performing dental restorations that perfectly match the color of their surrounding dental structures. However, before bringing these materials to the clinic, the present study has to be complemented with studies on other physical and chemical properties of the material, such as polymerization shrinkage, hardness, wear resistance, degree of polymerization, temporal and thermo chromatic stability, etc.

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