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POLIMERY

Optical properties of polyetherketoneketone based indirect dental restorations veneered with composite

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Abstract: In this study, the optical properties of indirect dental restorations based on polyetherketoneketone (PEKK), zirconia (YZ), and nickel-chromium (Ni-Cr) veneered with composite were compared. Based on the spectral reflectance, the CIE L*a*b* color coordinates, the color difference (ΔE), the opacity and the translucency parameter (TP) were determined using a spectrophotometer equipped with a D65 illuminant. The PEKK and Ni-Cr groups demonstrated similar CIE L*a*b* color values on white and black backgrounds. However, the zirconia group on a white backgrounds showed a slight shift in values towards red-yellow shades. The highest recorded ΔE values were 1.3 and 1.61 between PEKK and YZ groups, and Ni-Cr and YZ groups respectively. The opacity and translucency (TP) parameters were consistent with the spectral reflectance data, with the Ni-Cr and PEKK groups being completely opaque (100% and 0 TP). It has been shown that the use of the same indirect light-cured composite veneer with different substructure materials has no clinical effect on the esthetics of the final restoration.

Keywords: PEKK, optical properties; zirconia, composite veneer, spectral reflectance, bi-layered crowns.

Właściwości optyczne pośrednich uzupełnień protetycznych na bazie polieteroketonoketonu licowanych kompozytem

Streszczenie: Porównano właściwości optyczne pośrednich uzupełnień protetycznych na bazie polieteroketonoketonu (PEKK), tlenku cyrkonu (YZ) i niklu-chromu (Ni-Cr) licowanych kompozytem. Na podstawie współczynnika odbicia spektralnego określono współrzędne koloru CIE L*a*b*, różnicę koloru (ΔE), nieprzezroczystość i parametr przezierności (TP). Współrzędne koloru grupy PEKK i Ni-Cr wykazywały podobne wartości koloru CIE L*a*b* na białym i czarnym tle. Natomiast w przypadku YZ na białym tle stwierdzono niewielkie przesunięcie wartości w kierunku odcieni czerwono-żółtych. Najwyższe odnotowane wartości ΔE wyniosły 1,3 i 1,61 odpowiednio dla grup PEKK i YZ oraz Ni-Cr i YZ. Parametry nieprzezroczystości i przezierności były zgodne z danymi spektralnego współczynnika odbicia, przy czym grupy Ni-Cr i PEKK były całkowicie nieprzezroczyste (100% i 0 TP). Wykazano, że zastosowanie tej samej pośredniej światłoutwardzalnej licówki kompozytowej z różnymi materiałami podbudowy nie ma klinicznego wpływu na estetykę ostatecznego uzupełnienia.

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Słowa kluczowe: PEKK, właściwości optyczne, cyrkon, okleina kompozytowa, odbicie widmowe, korony dwuwarstwowe.

Esthetics is of fundamental importance when it comes to restoring teeth, therefore, any restorative material is judged on its ability to produce a restoration that seems to match the surrounding natural teeth. Dental restorations are complex, multilayered structures with varying dimensions and optical properties in each. The quality of the restorations is determined by various factors such as the optical properties of the material used, the background color of the tooth or substructure material and the ambient light [1]. The veneering material plays an essential esthetic role in the successful restoration of teeth, especially in the anterior region where it may be necessary to mask the opacity of the natural underlying tooth or the restoration substructure, as they dramatically influence the final shape. The materials used for substructures are continually changing; the advent of advanced manufacturing has enabled the use of a broader range of materials, including high-strength ceramics and high-performance polymers, in addition to the more conventional metal alloys [2, 3].

Advances in polymeric materials and the simultaneous development of advanced manufacturing have extended their applications to the medical field, replacing known implant materials such as titanium and zirconia [4]. For instance, polyaryletherketone (PAEK), high-performance thermoplastic polymers, benefit from being able to be modified during manufacturing to adapt to the purpose of their application [5]. The most known PAEK materials are polyetheretherketone (PEEK) and polyetherketoneketone (PEKK), and both of them have been successfully applied in different medical and dental applications with the latter recently being introduced to dentistry as a restorative material [6–8]. These polymers could be considered as promising restorative materials due to their properties such as high fatigue resistance, tensile and flexural strength, low elastic modulus close to that of dentine, dimensional stability at high temperature, and high wear resistance [8]. Furthermore, they are easily adapted in both dental clinics and laboratories as they are processed using well-established techniques such as hot-pressing and CAD/CAM milling [9].

The PEKK based restorative material Pekkton® ivory (Cendres+Métaux SA) is indicated for fabricating fixed substructures veneered with indirect composite resin, although a full ceramic contour may be bonded onto the polymer substructure [10]. Pekkton® ivory consists of an implantable grade PEKK and titanium dioxide pigments to improve appearance resulting in a beige colored polymer. Similarly, PEEK based dental polymers also use titanium oxide to improve color and both PEKK and PEEK based restorative materials can be considered as opaque restorative materials [11, 12]. This opacity is due to PEEK polymers being linear, aromatic and semi-crystalline materials [4, 10]. As a result of the opacity, the polymeric substructures require veneering with resin composite for esthetic purposes [6, 13, 14].

Colored pigments and fillers in current dental composite resins gave them shades mimicking natural teeth. Along with that, being curable at oral temperature extended their use to indirect/direct restorations and for veneering alloy, polymer and ceramic substructures. Dental composites resins have been used in the field for roughly six decades [15]. Early acrylic resins with shades close to natural teeth were based on polymethylmethacrylate (PMMA) and suffered a few shortcomings such as limited wear resistance and shrinkage after curing, and later, newer composite resins were produced based on bisphenol A glycidyl methacrylate (bis-GMA), dimethacrylate resin and organic silane coupling agents to create the bond between the filler particles and the resin matrix. The ease of handling and repairing both in the clinic and laboratory, being less abrasive to natural teeth, aesthetics and biocompatibility to surrounding tissue are some of the using composite resin for veneering substructures benefits [16, 17].

Composite resins can be used as a laboratory based veneering material to produce indirect restorations thereby masking the restorative materials such as acrylics, amalgam, alloys and zirconia [18–20]. The advantages of using composite resin as a veneering material for substructures are well reported [21, 22]. Bonding composite veneer is a standard procedure associated with PAEK based restorations and they usually require surface roughening by shot-blasting using alumina oxide particles before the application of a universal and/or resin bonding primer [6, 23–26]. However, the opacity and color of the polymer present a challenge to the dental technologist in a fact that the surface color must be 'modified' before the veneering materials are applied in the same way as a metal substructure [27].

Consequently, this study aimed to evaluate the optical properties of polyetherketoneketone (PEKK) based indirect restorations veneered with light cured composite and compared these with that of a conventional zirconia and nickel-chromium (Ni-Cr) based restorations. The optical properties include: CIELab (Commision Internationale de l'Eclairage, L*, a*, b*) coordinates, color difference (ΔE), opacity (%) and translucency parameter (TP). The study hypothesis was that PEKK material would demonstrate similar optical properties compared to zirconia and nickel-chromium based restorations.

EXPERIMENTAL PART

Materials and methods

All tested substructure materials were fabricated as per the manufacturer's recommendation. The substruc-

Table 1. Materials used in the study

Material	Composition	Manufacturer
Composite (VITA VM LC)	Urethane dimethacrylate, triethylene glycol dimethacrylate, silica, primary particle (40–50 nm)	VITA Zahnfabrik H. Rauter GmbH & Co. KG, Germany
Zirconia (VITA In-Ceram® YZ)	Zirconium dioxide (ZrO_2), yttrium oxide (Y_2O_3) 5%, hafnium oxide (HfO_2) < 3%, aluminum oxide (Al_2O_3) and silicon dioxide (SiO_2) <1% (weight-%)	VITA Zahnfabrik H. Rauter GmbH & Co. KG, Germany
Ni-Cr (Talladium Tilite V)	Non-precious medical ceramic alloy containing nickel, chromium, and molybdenum.	Talladium, Inc, OH, USA
PEKK (Pekkton® Ivory)	OXPEKK® IG (implant grade PEKK) and titanium dioxide for coloring and optimization of mechanical properties	Cendres+Métaux SA, Biel, Switzerland
Primer for PEKK (Visio.link®)	Methylmethacrylate (MMA) and pentaerythritol triacrylate	Bredent GmbH & Co. KG, Germany.
Zirconia primer (Monobond® Plus)	Ethanol, 3-(trimethoxysilyl)propyl methacrylate, methacrylated phosphoric acid ester	Ivoclar Vivadent AG, Liechtenstein.
Alloy Primer (Kuraray Alloy primer®)	10-methacryloyloxydecyl dihydrogen phosphate (MDP) and 6-(4-vinylbenzyl-n-propyl) amino-1,3,5-triazine 2,4-dithione (VBATDT)	Kuraray Co., LTD, Japan

ture material included polyetherketoneketone (PEKK), zirconia (YZ), and nickel-chromium (Ni-Cr). The veneering composite was of A2 shade. The composition of the materials used in the present study is listed in Table 1.

The PEKK and Ni-Cr substructure were fabricated using the lost wax technique. The wax pattern was sprued and invested using investment material. The wax burnout was carried out by placing the set molds in a burnout furnace at 850°C for approximately 45 minutes. For PEKK, Pekkton® ivory was supplied in the form of ingots, which were hot-pressed using pressing furnace (365°C standby and holding temp and 10 minutes' press time).

Full details of pressing PEKK procedure can be found in a previously published study [9]. As for processing Ni-Cr samples, the alloy was cast at 1329°C and the molds were allowed to cool before alloy discs were de-vested. The samples were removed from the sprues using a cutting disc and finished using a diamond bur. The obtained discs samples were shot-blasted using aluminum oxide particles (Al_2O_3) as per: 110 μm, 2 bar and 10 seconds.

The zirconia samples were prepared using CAD/CAM blocks. The blocks were sectioned using a diamond blade in a precision saw to a thickness bigger than the final desired thickness by 20% to compensate for the shrinkage that occurs during firing. The acquired blocks were stained in light YZ coloring liquid for 2 min to match the blocks to that of 2M2 shade. The stained samples were fired in a vacuum furnace at 700°C for 5 minutes to eliminate excess liquid. The samples were then sintered at 1530°C for two hours in a high-temperature furnace. The obtained discs samples were shot-blasted using aluminum oxide particles (Al_2O_3) as per: 50 μm, 2 bar and 10 seconds[28]. The final finished samples of all substructure materials PEKK, Ni-Cr and YZ were 0.8 mm thick and were confirmed by a digital caliper (PK-0505, Mitutoyo Corporation, Japan). Prior to composite veneering, a single thin coat of primer was applied using a disposable brush. For the same purpose, three different primers were used according to the substructure materials; PEKK (Visio.link®, Bredent GmbH & Co. KG, Germany), zirconia (Monobond® Plus, Ivoclar Vivadent AG, Liechtenstein), and Ni-Cr (Kuraray Alloy primer®, Kuraray Co., LTD, Japan).

For composite veneering, a thin coating of VITA VM light-cured opaque paste was applied evenly on the primed surface and light-cured for 60 seconds using calibrated halogen light curing unit (Coltolux75, Coltène Whaledent Group, Switzerland). This was followed by the application of composite resin dentine paste on to the opaque layer using a plastic spatula and VITA VM LC modeling liquid. The disc was placed in a silicone mold to facilitate the shaping of the veneer and was light-cured for 60 seconds. The sample was then removed from the mold and light-cured again for 60 seconds to ensure optimum polymerization of the composite resin. The composite resin veneer was then polished under running water using waterproof carbide abrasive paper P400 and P600, respectively in a rotating disc polisher (Metaserv Buehler, UK).

The optical parameters were recorded using a spectrophotometer (CM-2600d Konica Minolta Sensing, Inc., Japan) equipped with a color data software (Spectra Magic NX, Konica Minolta Sensing, Inc., Japan). The spectral reflectance of the samples between wavelengths 360 to 740 nm at 10 nm intervals on black and white backgrounds were recorded to calculate:

CIE L*a*b* color coordinates

The color difference, ΔE of the study groups based on the equation (Eq.1):

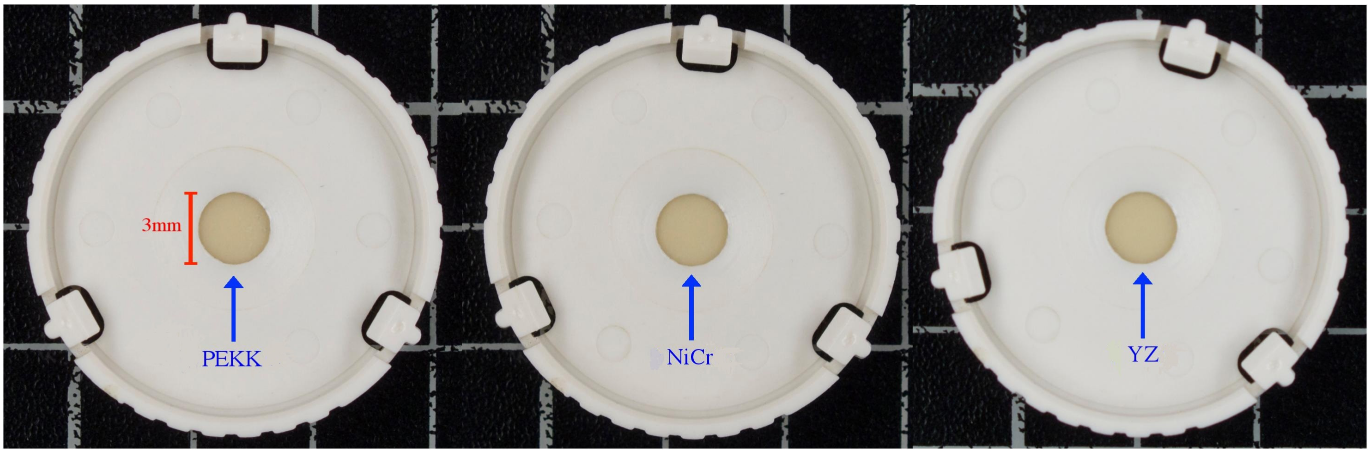

Fig. 1. Veneered samples placed over the spectrophotometer's target mask

$$\Delta E = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{½} \qquad (1)$$

(L^* represents light (0-black and 100-white), a^* represents redness (a^*+) or greenness (a^*-), and b^* represents yellowness (b^*+) or blueness (b^*-))

Opacity (%) was determined using the following equation (Eq.2): [29]

$$\text{Opacity}\,(\%) = \frac{R_b}{R_w} \cdot 100 \qquad \textbf{(2)}$$

(R_b – average reflectance when tested with a black background, and R_w – average reflectance when tested with a white background. The average reflectance is derived by dividing the total reflection at each wavelength from the number of wavelength points).

Translucency Parameter (TP) was determined using the equation below (Eq.3) [29]:

$$\text{TP} = \sqrt{\left(L_w^* - L_b^*\right)^2 + \left(a_w^* - a_b^*\right)^2 + \left(b_w^* - b_b^*\right)^2} \qquad \textbf{(3)}$$

A total of three spectral reflectance readings were recorded for each sample up to nine individual recordings for each group. The readings were taken at different areas so as to avoid overlapping of the readings. All measurements were carried out with a white background (L^*= 99.9, a^*=0.1 and b^*= -0.26) and a black background (L^*= 22.7, a^*= 0.2 and b^*= -0.35) under D65 illuminate (day light) and 3mm target mask opening of the spectrophotometer (Figure 1).

The data obtained was analyzed using statistical data analyzing software, Minitab 15 for Windows XP (Minitab Ltd., UK). One-way ANOVA followed by paired t-test were applied to analyze the data. A *'P'* value of ≤ 0.05 was considered statistically significant.

RESULTS

The CIE L*a*b* coordinates of the substructure samples veneered with A2 shade composite tested with black and white backgrounds is presented in Table 2. All the composite veneered groups displayed a very similar L*a*b* values with no significant difference.

The PEKK and Ni-Cr groups displayed the same reported values of reflectance with white and black backgrounds. The values of zirconia based veneers with white background showed a slight shift in values towards red-yellow shades.

Figure 2 shows the spectral reflectance of the groups with a black background. All the three composite veneered groups demonstrated the same light reflectance across the wavelength range from 360 nm to 740 nm with two increasing slopes in 380 nm and 480 nm wavelengths.

Figure 3 shows the spectral reflectance of the groups on a white background. The groups with an opaque substructure material (PEKK and Ni-Cr) remained the same whereas the zirconia group showed a difference in reflectance at the longer wavelengths.

The color difference, ΔE of the substructure materials is presented in Table 3. The zirconia group (YZ) demonstrated increased values on both white and black background compared to other two groups (PEKK and Ni-Cr).

The color difference, ΔE between the tested groups is presented in Table 4. The least ΔE difference was observed between the groups PEKK and Ni-Cr on a black (0.28) and

Table 2. CIE L*a*b* values of the veneered samples under black and white background

Group	L*		a*		b*	
	Black	White	Black	White	Black	White
PEKK	74.33 ± 0.15^{a}	74.31 ± 0.11^{a}	2.13 ± 0.26^{a}	$2.16\pm0.3^{a,b}$	18.17 ± 0.56^{a}	18.47 ± 0.71^{a}
Ni-Cr	74.49 ± 0.27^{a}	74.5 ± 0.22^{a}	1.9 ± 0.22^{a}	1.93 ± 0.18^{a}	18.2 ± 0.46^{a}	18.2 ± 0.45^{a}
YZ	74.1 ± 0.27^{a}	74.67 ± 0.35^{a}	2.4 ± 0.14^{a}	3.17 ± 0.72^{b}	18.65 ± 0.65^{a}	19.21 ± 0.69^{a}

For the same coordinates and background, groups with different superscript letters indicate significant differences ($P<0.05$).

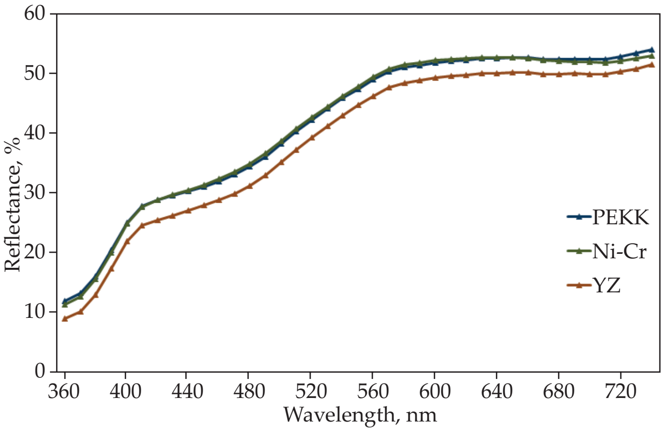

Fig. 2. Spectral reflectance data curve of the tested groups on a black background

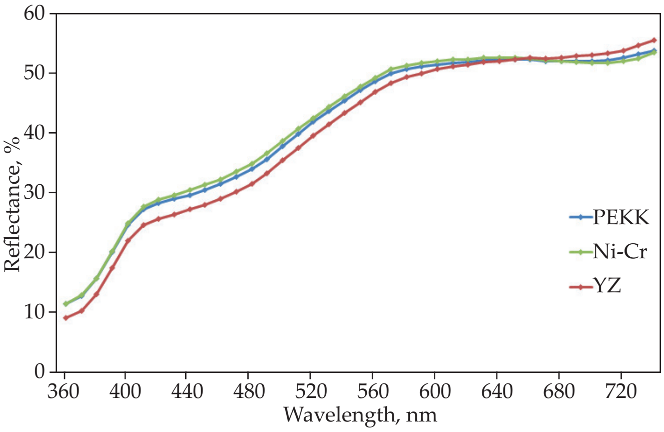

Fig. 3. Spectral reflectance data curve of the tested groups on a white background

Table 3. Color difference (ΔE) of the substructure materials

Groups	Background	ΔL*	Δa*	Δb*	ΔE
PEKK	White	-0.94	0.06	0.08	0.95[a]
	Black	-0.81	0.06	-0.02	0.81[b]
YZ	White	-2.44	0.15	1.12	2.69[c]
	Black	-2.43	0.11	1.08	2.69[c]
Ni-Cr	White	-0.69	0.09	-0.01	0.70[d]
	Black	-0.72	0.08	-0.01	0.70[d]

Same superscript letters denote significant difference ($P<0.05$)

white (0.4) backgrounds respectively. The highest ΔE difference was observed between the groups, Ni-Cr and YZ (1.61) and, PEKK and YZ (1.31) on a white background.

The opacity and TP results are in accordance with the spectral reflectance data with the groups Ni-Cr and PEKK being completely opaque (100% and 0 TP), and the group YZ group showing opacity of 97% and 1 TP value.

DISCUSSION

Polyetherketoneketone has been successfully applied in different medical and dental applications, and was recently introduced as a restorative material [13, 14, 27]. PEKK is considered to have favorable properties such as high strength, low elastic modulus, high temperature, and wear resistance to be used as a restorative material [11, 12]. A clinical pilot study (3–5 months) by Keul *et al.* [23], aimed to test the biocompatibility, stability, and comfort of temporary crowns made from PEKK and Co-Cr veneered with composite has shown that PEKK crowns showed better esthetics over Co-Cr crowns. This is, to the best of authors' knowledge, the first study to evaluate the optical properties of composite veneered PEKK. The optical properties of PEKK based indirect restorations veneered with composite was compared with that of a conventional zirconia and nickel-chromium (Ni-Cr) based restorations.

Although, the PEKK polymer is processed either by hot pressing or milling, the current study used samples that were hot pressed as no significant difference in the color values has been reported with both processing techniques [9]. The application of the outer indirect composite resin veneer was carried out following standard dental laboratory procedures according to the manufactur-

Table 4. Color difference (ΔE) between the groups

Compared groups		ΔE	
		Black	White
PEKK	Compared to Ni-Cr	0.28	0.4
	Compared to YZ	0.6	1.3
Ni-Cr	Compared to YZ	0.78	1.61

er's guidelines for each substructure material to closely match the real-case scenario of fabricating dental prostheses in a dental laboratory. Hence, the tested groups in this study appeared very similar after finishing the outer composite resin veneer even though the backgrounds of the three substructure materials were different in color. There was no significant difference in the CIE Lab color values between the tested groups and the spectral reflectance was very similar when tested on white or black backgrounds. The ΔE values ranging from 1 to 3 are perceptible to the naked eye and ΔE values greater than 3.3 are a critical value and are clinically unacceptable. It means that the values obtained in the current study had no clinical significance since all the test materials had values below 3.3 [30]. The YZ group in the current study showed opacity of 97% and 1 TP value. This could be explained by the fact that a small amount of light is transmitted through the zirconia, and the opaque composite does not fully cover the substructure of the zirconia and thus allow some translucency through the substructure.

For aesthetic composite veneers, several factors can have an effect on the appearance of composite resin veneers such as the degree of polymerization, layer thickness, color of abutment or substructure, and the bond between the substructure material and resin composite [31–35]. The inconsistency between different studies could be attributed to various reasons such as different test configuration, different sample finish and sample thickness and layer-to-layer thickness ratio. It was found in other studies that different restorative materials of the same color had different CIE L*a*b* color values when evaluated under the same configurations [30, 36-39]. The outcome of the previous studies varies in the L*a*b* values of VITA A2 shade of different materials [40–42]. Therefore, in studies with identical and consistent test configuration and procedures, direct comparison should be considered with caution.

Various alloys have been used as substructures including high gold, nickel chromium (Ni-Cr), cobalt chromium (Co-Cr), gold (Au) and palladium (Pd) alloys, for fixed prosthodontics. In a review by Stevenson and Ibbetson [43], many studies have shown variations in the values of L* and b* indicating difference between them in lightness and yellowness-blueness. In general, they found that most studies showed higher L* and b* values of gold alloy against other alloys, such as Ni-Cr and Pd alloys. On the contrary, in a study by Stavridakis *et al*. [44], lower L* and b* values have been observed with gold alloys as compared to other Pd alloys. However, in a study by Ozcellik *et al*.[45], inconsistent results were obtained between different dental alloys. The authors observed significant difference in values of a* and b* of Ni-Cr and Co-Cr alloys when compared to gold.

Polymers such as resin composite have been the topic of concern because of their inferior color stability properties after being in service due to different causes such as aging [36, 46–50]. This could be related to the materials composition and filler particle size allowing the water to penetrate the matrix or filler- matrix interface [51]. On the contrary, high performance polymers such as PEEK have been known to be a color-stable restorative material [52]. This was further confirmed in a study by Heimer et al.[53], who demonstrated that PEEK had significantly better color stability compared to composite and PMMA materials after 1-week storage in different media. Similarly, Stawarczyk *et al*.[30], evaluated the optical properties of PEEK, zirconia, Co-Cr-Mo alloy and titanium oxide with different veneers such as VITA Mark 2, IPS e.max CAD, LAVA Ultimate and VITA Enamic, The authors found that PEEK as a substructure material was comparable with other substructure materials and different veneering materials of the same shade were actually different in the L*a*b* color values. However, the major limitation in their study was not bonding the veneer to the substructure materials, but simply placing on top of each other. For clinical applications, PEKK and PEEK substructures usually requires further surface modification before bonding to resin cement and composite veneer. A few studies can be found in the literature testing the effect on the quality of bond of different pre-treatment procedures [6, 23–26, 54–59].

The major limitation of the study is the *in-vitro* design as the study did not simulate a clinical situation. The effects of saliva, dietary factors, and aging of the materials may influence the outcome in actual clinical conditions. Therefore, further studies should be directed towards the optical properties of materials in the clinical environment. In addition, future studies should also evaluate fatigue behavior, biocompatibility, and aging.

CONCLUSIONS

This study concludes that using the same indirect light cured composite veneer on different substructure materials has no clinical impact on the esthetics of the final restoration. The zirconia substructure provided better translucency with composite veneer in comparison with composite veneered PEKK and Ni-Cr substructures. Furthermore, different substructure material did not cause any significant difference in the L*a*b* color values when veneered with the same resin composite veneer.

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