Journal of Applied Polymer Science

Characterization of light-cured, dental-resin-based biocomposites

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ABSTRACT: The dependence of the depth of cure (DOC) and degree of conversion (DC) on the depth of experimental and commercial materials were determined according to ISO 4049 procedure and with the use of Raman spectroscopy, respectively. Moreover, an attempt was made to find the correlation between the DOC and DC and the depth of the material. The hypothesis was that curing time recommended by the manufacturers is appropriate for curing both commercial and experimental materials to achieve comparable values of the examined properties. The impact of the filler characteristic was clearly observed. The longer curing time provides a deeper curing (DOC values) and higher reaction rate (DC); however, the dependence between the DC values and DOC values was not visible. Instead, a logarithmic trend in the relation of the DOC and curing time was clearly observed. The results of this study suggest that the experimental materials give some hope for potential clinical applications and should be further investigated.
 J. Appl. Polym. Sci. **2015**, *132*, 42812.

KEYWORDS: photopolymerization; properties and characterization; resins

Received 10 April 2015; accepted 5 August 2015
DOI: 10.1002/app.42812

INTRODUCTION

Photopolymerizable resin-based composites (RBCs) are the most popular materials applied in dentistry.[1–5] Their application includes many areas, for example, restorations[1–5] or prostheses.[2] The main advantage of these polymeric products is a high aesthetic level, enabling the imitation of the natural tooth appearance.[1,4–9] Other advantages of RBCs include their good longevity after application,[9] good mechanical properties,[1,7] biocompatibility, ease of use,[4] and good price.[10] These polyphase composites consist of two main parts: an organic resin matrix and inorganic filler particles.[5,6,9,11] The most popular organic matrixes consist of methacrylic resins and, in particular, bisphenol A glycidyl methacrylate (Bis-GMA; Bowen's resin: [4-2-hydroxyl-3-methacryloxypropoxy phenyl] propane).[5,6,9,12] According to the high viscosity of this compound, some low-viscosity comonomers are added to the matrix.[5,9,12] Hydroxyethyl methacrylate, triethylene glycol dimethacrylate, urethane dimethacrylate, and ethoxylated bisphenol A dimethacrylate are the most frequently used methacrylic comonomers.[5,6,9,12] The organic matrix acts as a continuous phase of the composite, whereas an inorganic filler is the dispersed phase, whose main task it is to improve the properties of the composite. The addition of the filler affects the mechanical, chemical, physical, and biological properties of the RBC and also reduces the cost of the final product.[9] One of the very important roles of the filler is to reduce the polymerization shrinkage, the main disadvantage of light-cured materials; this is the cause of gap formation, a reduction in the adhesion between the tooth and the restoration.[9,13,14] The most commonly used fillers are fluoroaluminosilicate glasses and ceramics.[5,6,9] A significant portion of the organic matrix is the photoinitiator system, which is generally 5% or less of the weight of the organic matrix. Most commercial solutions contain camphor quinone (CQ) as a main initiator combined with different aliphatic or aromatic amines, for example, 2-ethyl-dimethylbenzoate.[5,9,15–17] CQ absorbs blue light (maximum at 470 nm) and initiates the radical polymerization of the composite, whereas amine accelerates this process.[5,9,17] The source of visible blue light is light-emitting diodes in most cases. Formerly, halogen lamps were used; however, according to their better characteristics (less power, longer life, minimal heat generation, greater efficacy, etc.), light-emitting-diode lamps replaced them.[18–20] Photopolymerization is a more appropriate solution for curing composites than chemically activated polymerization according to its faster reaction rate; however, it influences the irradiated material properties.[21]

There are several requirements for composite materials for dental applications, such as a natural appearance,[14,22] longevity,[23] harmlessness, and lack of toxicity.[14] However, it is well known that no polymerized material could react with 100% efficiency. From incompletely polymerized composites, some amount of toxic or harmful compounds can be leached out in the moist

environment in the human mouth.[14,24–27] Also, some mechanical properties decrease with a lower degree of reaction.[24,26] A quantitative measure of the reaction efficiency is the *degree of conversion* (DC), which can be assessed as the number of double methacrylic bonds that are broken during polymerization before and after the reaction.[28]

One of the important properties of light-cured composites is the *depth of cure* (DOC); this is defined as the depth of which the material is adequately cured after exposition on blue light.[29] This parameter is affected by many factors, including the composition of the material and light absorption, scattering, and refraction in the depth of the material, filler characteristic (particle size, amount, and type of the filler), irradiation time (a longer irradiation provides a greater DOC), light source characteristics (intensity and spectral distribution), composite color, depth of which the light penetrates the cured material, the distance between the light source and the material, and so on.[15,18,22,29–34] The DOC influences other properties of the polymerized composite, for example, the mechanical properties (Vickers hardness, elastic modulus, etc.).[29]

The European Committee for Standardization recommends a scratching method for the determination of the value of DOC after some period of irradiation (as defined by the manufacturer for commercial materials). This method is described in ISO 4049. The scratching method involves the scraping of the uncured part of the polymerized material preceded by the irradiation of the material from the top. In that way, each subsequent soft part of the composite is removed, and the thickness of the hard residue is measured by a micrometer. The value divided by two is defined as the DOC of the material.[35] This method seems to be very subjective according to a different understanding of which part of the material should be removed, how much force should be applied to scraping, and whether two different people can get the same results. If not, which one is the proper one? Many authors determined the values of DOC for a large group of experimental[14,36] and commercial[10,20,21,30–33,37–39] light-cured dental materials by the ISO 4049 method. Other methods for assessing the curing depth are also in use. The application of a penetrometer as a tool for scratching the uncured part of the composite brings some benefits, including the elimination of human subjectivity and the difference in the applied scraping force.[37,40] Some of the methods are indirect and involve the determination of other parameters related to the depth of the examined material. Subsequently, the values of these parameters are compared with the DOC, and some correlations are defined. One of the most popular methods in this group is the determination of the hardness at various depths of the material.[18,20,24,34,39,41]

According to the fact that DC is strictly correlated with other crucial properties (chemical, mechanical, biological, and physical),[10,14,15,18,27,29,34,39,42] it also can be measured as a function of the material depth to estimate a suitable curing depth. Raman spectroscopy is a nondestructive method for determining DC. Recently, this method has been widely used as a tool to determine the various properties of biomaterials and biological materials.[43–47] Fourier transform infrared spectroscopy is other technique for calculating DC in dental resins.[48,49] The DC value is calculated as the ratio between the intensity of the band corresponding to double methacrylic bonds that are broken during the reaction ($C{=}C_{meth}$, at $1638\,cm^{-1}$) to the intensity of the band that does not change during the reaction (aromatic $C{=}C_{Ph}$ at $1608\,cm^{-1}$ or carbonyl C=O at $1712\,cm^{-1}$).[22,28,29,36,42,50–54]

Attempts are still being made to improve the final properties of resin-based dental fillings. The manipulation of the RBC composition is the main method for changing the properties. The main direction is the modification of the organic matrix or the introduction a new types of fillers. Some interest has been focused on new calcium phosphates fillers.[55–59] This group includes a very large spectrum of different compounds that can be applied in all fields of dentistry.[60] The main advantages of this type of materials are their properties, especially their chemical similarity to the inorganic phase of bone and tooth,[60–62] good biocompatibility,[60,62] bioactivity, osteoconductivity,[60,63] remineralization potential, and lower cost compared to other inorganic fillers.[60] Within this group of compounds, most popular in biomedical applications are hydroxyapatite (HA), fluorapatite, amorphous calcium phosphate, α-tricalcium phosphate, β-tricalcium phosphate, and tetracalcium phosphate.[60,64–71] Despite the many advantages, calcium phosphates have not been used in commercial restorative dental materials yet. However, our published and unpublished preliminary studies have shown that calcium phosphates containing RBC have some properties that are similar to commercially available dental fillings, so further investigations are justified.[54,72] These types of fillers can be promising alternative to the fillers that are currently in use.

The aim of this research was to investigate the new RBCs with potential use as restorative dental biomaterials. The DOC according to ISO 4049 and DC versus depth by Raman spectroscopy were determined. The properties of three experimental and two commercial materials were compared to each other. The relationships between DOC and DC and the depth of the studied restoratives were also observed. The final properties (DC and DOC) of new the dental biomaterials were comparable to or better than the properties of the commercial fillings. This would allow commercial use of the studied materials in the future. Furthermore, the obtained results facilitate an answer to whether the curing time recommended for commercial restorative materials is appropriate for the experimental ones.

EXPERIMENTAL

Materials

Three experimental and two commercial dental fillings were examined. Experimental materials were composed from an organic matrix and inorganic filler. The organic matrix was prepared with Bis-GMA (Sigma-Aldrich) and hydroxyethyl methacrylate (97%, Sigma-Aldrich, 60 : 40 w/w). Experimental composites differed in the type and content of filler. The HA composite contained 50 wt % of HA (p.a. $\geq$90%, Sigma-Aldrich). The tricalcium phosphate (TCP) composite was filled with 70 wt % TCP particles (p.a. $\geq$96%, Sigma-Aldrich). The bioglass (BG) composite contained 70 wt % commercial dental glass (GM35429, Schott) with the following composition: 30 wt % SiO_2, 10 wt % CaO, 30 wt % Al_2O_3, 15 wt % F, $<$10 wt %

P_2O_5, and <10 wt % Na_2O. This composite was created to compare the effect of calcium phosphate fillers with glass fillers when the same composition of the matrix was applied. The content of inorganic fillers in experimental materials was set on the maximum possible level to provide good mixing with the matrix. CQ (97%, Sigma-Aldrich) and 2-ethyl-dimethylbenzoate ($\geq$99%, Sigma-Aldrich) were used as an initiator and accelerator of polymerization, respectively, both in amount of 0.5 wt %.

The commercial dental fillings were Charisma (shade A3, Heraeus Kulzer) and Riva Light Cure (shade A3, SDI). The Charisma was composed from an organic matrix (Bis-GMA and triethylene glycol dimethacrylate), an inorganic filler (Ba–Al–B–F–Si glass, pyrogenic SiO_2), and an initiator (CQ). The content of the filler was 78 wt %. The Riva Light Cure consisted of a liquid [poly(acrylic acid), tertaric acid, 2-hydroxyethyl methacrylate, dimethacrylate crosslinker, acidic monomer: 15–25, 1–5, 20–30, 10–25, and 10–20 wt %, respectively] and a powder (95–100 wt % F–Al–Si glass). The powder was with the liquid in the proportion 3.1 : 1; this corresponded to a 76 wt % content of the filler. All of this information came from the manufacturers.

The average particle sizes of the examined materials were 13 μm (HA composite), 0.22 μm (TCP composite), 10 μm (50% of the BG composite), and 63 μm or less (99% of the BG composite), 0.7 μm (50% of the Ba–Al–B–F–Si glass in Charisma), less than 2 μm (99% of the Ba–Al–B–F–Si glass in Charisma), and 0.01–0.07 (pyrogenic SiO_2 in Charisma). No information about the filler particle size in the Riva Light Cure was given by the manufacturer.

Methods

DOC Determined by ISO 4049. The examined materials were placed in a cylindrical silicon mold that was 8 mm long and 4.5 mm in diameter. The mold was covered on both sides with poly(ethylene terephthalate) foil. The samples were irradiated by a dental curing lamp (Hilux Optimax, 81 W) that emitted blue light for 5, 10, 15, 20, 30, 60, 90, and 120 s (10 samples for each curing time). After curing, the specimens were removed from the mold, and the uncured part was scratched with the spatula. The height of the cylindrical samples was measured in four places with use of an electronic caliper. According to the ISO procedure, this value divided by two was considered the DOC.

We decided to conduct this test with two people (tests 1 and 2) to check the error resulting from the subjectivity of the test method. Each of these people scratched five samples for each curing time.

DC of the Depth by Raman Spectroscopy. The examined materials were placed in a rectangular polytetrafluoroethylene mold ($4 \times 4\,mm^2$, 3 mm in height), which was covered on both sides with poly(ethylene terephthalate) foil. The samples were irradiated by a dental curing lamp (Hilux Optimax, 81 W), which emitted blue light for 5, 10, 15, 20, 30, 60, 90, and 120 s (five samples for each curing time). After curing, the specimens were removed from the mold, and Raman spectra were collected along the side wall of the sample with a 100-μm measurement step. DC was calculated according to the following equation:

$$DC = \left(100 - \frac{R_{polymer}}{R_{monomer}} \times 100\right)(\%) \quad (1)$$

where

$$R = \frac{I_{C=Cmeth}}{I_{reference}} \quad (2)$$

where $R_{polymer}$ and $R_{monomer}$ is a ratio of the appropriate band intensities, $I_{C=Cmeth}$ is the intensity of the band corresponding to the double methacrylic bond (at 1638 cm^{-1}), $I_{reference}$ is the intensity of the band corresponding to the reference bond that remains unchanged during the reaction (aromatic at 1608 cm^{-1} for the experimental composites and Charisma and the carbonyl at 1712 cm^{-1} for Riva Light Cure), $R_{monomer}$ is calculated on the basis of the spectra for uncured materials, and $R_{polymer}$ is calculated with the spectra obtained after each curing time.

The spectroscopic measurements were carried out on a Renishaw inVia microscope with a diode-pumped laser, emitting a 785-nm near-infrared wavelength, and an argon laser, emitting green light at a 514.5-nm wavelength. Diffraction gratings of 1200 and 1800 mm^{-1} were used for the diode and argon laser, respectively. The laser beam was focused on the sample surface through the long working distance of a 50x/0.5NA microscope objective; this ensured an overall in-plane spatial resolution of about 2 μm. In the system, an air-cooled, charge-coupled device camera detector (Rencam) was used. Raman scattering spectra were acquired along a line on the side surface of the sample with steps of 100 μm and were recorded in the spectral ranges 1570–1800 cm^{-1}. The overall spectral resolution was better than 1 cm^{-1}. The time of exposure to obtain individual Raman spectra was 10 s; the spectra were recorded without accumulation. The integrated areas of the Raman bands were calculated by curve fitting. Cosmic ray artifacts were removed, and analyses of the spectra were performed in the same WiRE 3.4 software (Renishaw). The Rayleigh scattering background was subtracted manually from each raw spectrum with a polynomial curve.

RESULTS AND DISCUSSION

In Figure 1, the DOC values obtained by the ISO procedure are presented. The results allowed us to compare the DOC values obtained by the two tests. Furthermore, differences in the DOC values according to the curing time and type of material were also observed. First, it should be noted that this procedure was very subjective because there were clearly distinctive differences in the mean values of DOC obtained from tests 1 and 2. This was due to the fact that the two people conducting this experiment scratched the sample surface with different strengths. The stars indicate results with no statistical differences between these two tests. We observed that it occurred only in a few cases, and no dependence was found, so this similarity was rather random. Another observed fact was that the prolongation of the curing time resulted in an increase in the DOC value. This was a normal tendency, which was also observed by other authors.[30,38] However, this relationship was not linear. The dependence of the mean DOC values (calculated from both tests) on the curing time are presented in Figure 2. In the case of all of the examined materials, a logarithmic trend was clearly observed. The highest values of DOC were observed for the experimental materials with glass filler [Figure 1(a)] and commercial materials

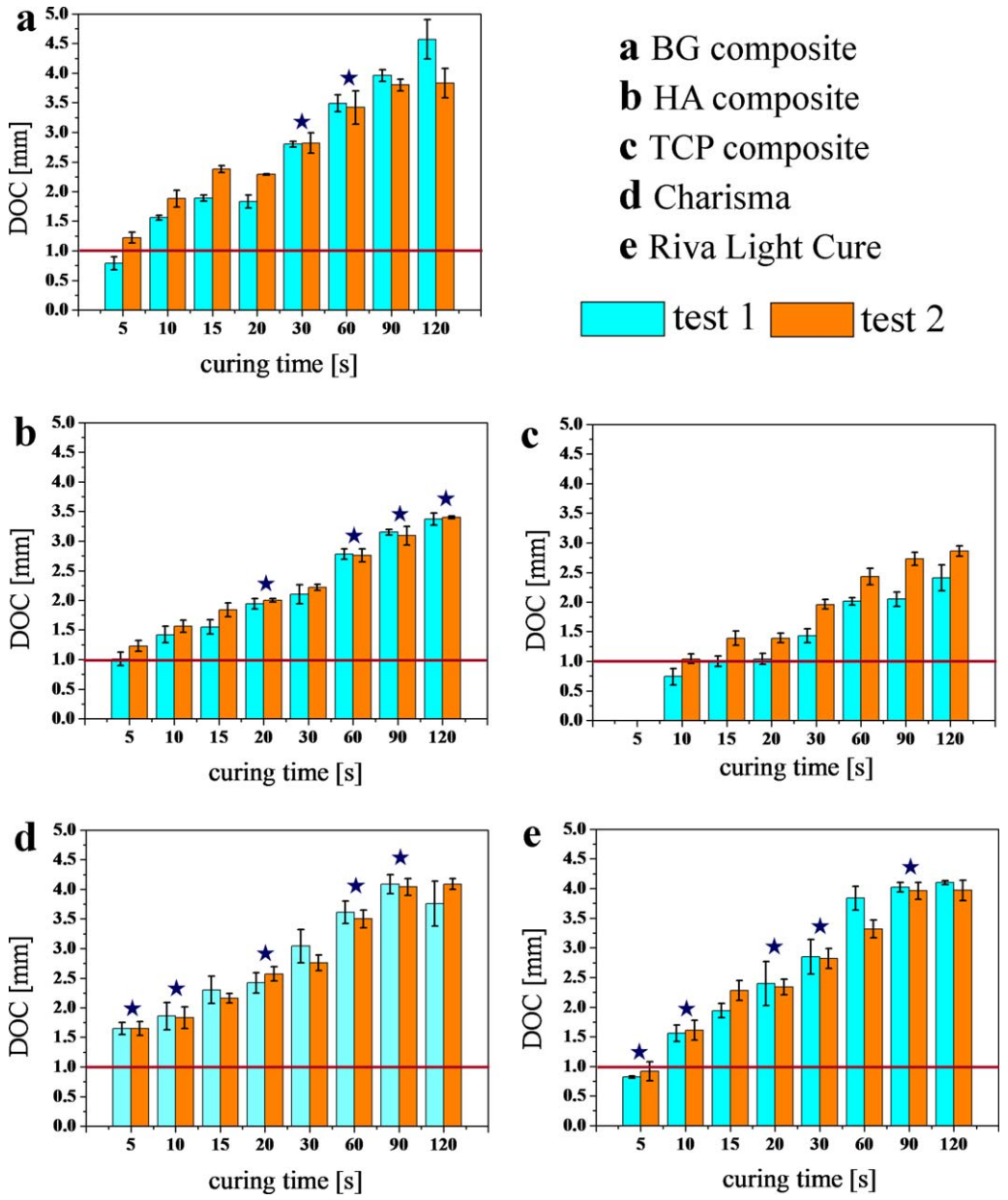

Figure 1. Dependence of DOC (examined by ISO 4049) on the curing time. The mean values and standard deviations are shown as error bars. The stars indicate insignificant statistical differences between the DOC values obtained with tests 1 and 2. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

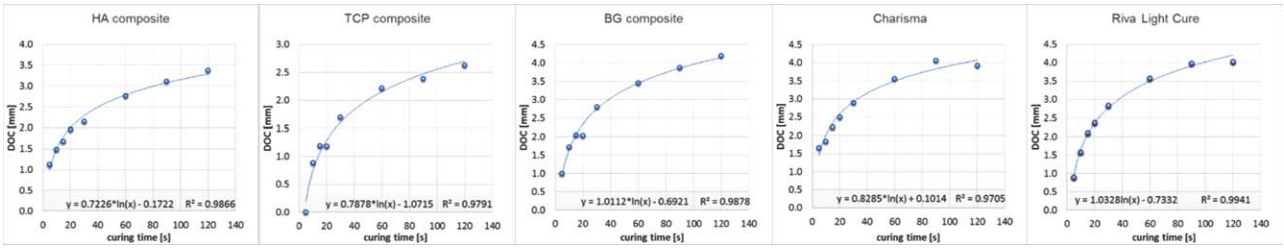

Figure 2. Logarithmic relationship between DOC and the curing time for all of the examined materials. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

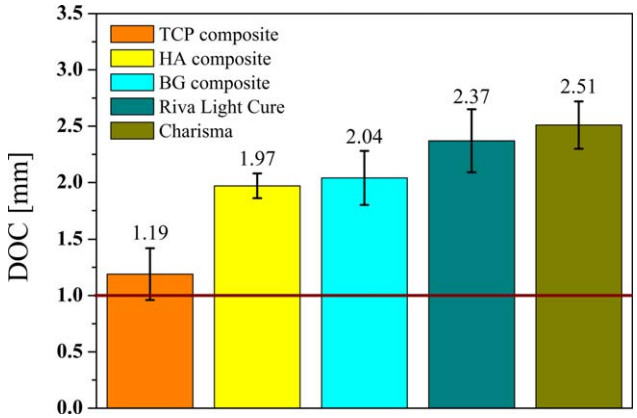

Figure 3. Comparison of the studied materials based on DOC examined by ISO 4049 after 20 s of curing. The mean values and standard deviations as error bars are shown. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

[Figure 1(d,e)]. The composites containing calcium phosphate filler [HA and TCP composites; Figure 1(b,c)] exhibited much lower DOC values than the glass-containing materials: the BG composite and commercial restoratives. This could have been due to the worse light transmittance of the calcium phosphate fillers in comparison with the glass fillers. It is well known that the transparency of the material influenced the DOC of the irradiated restorative material.[31,36,38] According to ISO 4049, the DOC of opaque restorative materials should be not less than 1 mm.[35] This minimal required value of the DOC is marked in Figure 1 by horizontal lines on each DOC versus the curing time graphs. On the basis of these results, we noticed that the examined materials did not reach these minimal values only in a few cases: the 5-s-cured TCP composite, BG composite (test 1), and Riva Light Cure (test 1) and the 10-s-cured TCP composite (test 1). All of the remaining examined materials were characterized by higher values of DOC after longer curing times. This means that even 10 or 15 s of curing was sufficient to achieve the ISO 4049 requirements.

In Figure 3, the mean values of DOC after 20 s of curing are presented. The mean values were calculated from both tests. The curing time was 20 s; this time was recommended by the manufacturers of both commercial materials examined in this study. The minimum required value of DOC (1 mm) is also marked by a horizontal line. According to the manufacturers, the DOC values of Charisma and Riva Light Cure after 20 s of curing were 2.0 and 1.8 mm, respectively. Our results show even higher values: 2.51 and 2.37 mm, respectively. However, these differences may have been caused by the mentioned subjectivity of the scratching method. The DOC values of all of the experimental materials were lower than those of the commercial ones. This means that these experimental materials needed to be cured longer to obtain comparable DOCs. The glass-containing experimental material (BG composite) showed the closest values of this parameter to Charisma and Riva Light Cure. All of them contained glass filler. Once again, the materials containing calcium phosphate fillers (HA and TCP composites) showed the lowest values of DOC. The smallest DOC was obtained in the case of the TCP composite; this could be explained by the greatest filler content in comparison with the HA composite. One-way analysis of the variance and post hoc Tukey's multiple comparison tests were applied to determine significant differences in the DOC values obtained from both tests. The significance level was set at 5% ($p > 0.05$). The analysis of variance results indicate that the HA and BG composites showed statistically insignificant differences in the DOC values after 20 s of curing. Statistical similarity was also found for both commercial materials. It is also well known that the particle size of the filler has an impact on the DOC values. The small-particle composites exhibited poorer curing than the larger particle composites.[40] The average particle size of HA was 13 μm, whereas that for TCP was only 0.22 μm. We also noted that the curing time was equal to 20 s, a time that is often recommended and was sufficient for curing of all of the experimental materials with depths of higher than 1 mm (required by ISO 4049).

The Raman scattering spectra for the Riva Light Cure and HA composite (as an exemplary experimental material) obtained in the region of Raman shifts between 1570 and 1800 cm^{-1} are given in Figure 4. The bands that served for the determination of DC in the depth of examined materials are marked by dotted lines. The progress of the reaction, understood as the value of DC, was estimated as a decrease in the number of double methacrylic bonds. The maximum intensity of the band corresponding to the double methacrylic bonds was observed at 1638 cm^{-1} in the case of all of the polymerized and unpolymerized materials. A sharp decline in the intensity of this band after curing was very clearly observable. The bands at 1712 and 1608 cm^{-1} corresponding to the carbonyl group (Riva Light Cure) and double aromatic bonds (all experimental materials and Charisma), respectively, were chosen as reference bands. The intensity of these bands remained unchanged during polymerization. This phenomenon is also presented in Figure 5. There were Raman scattering spectra obtained at different depths of the experimental HA composite in the direction from the cured surface after 20 s of curing. The reference band (at 1608 cm^{-1})

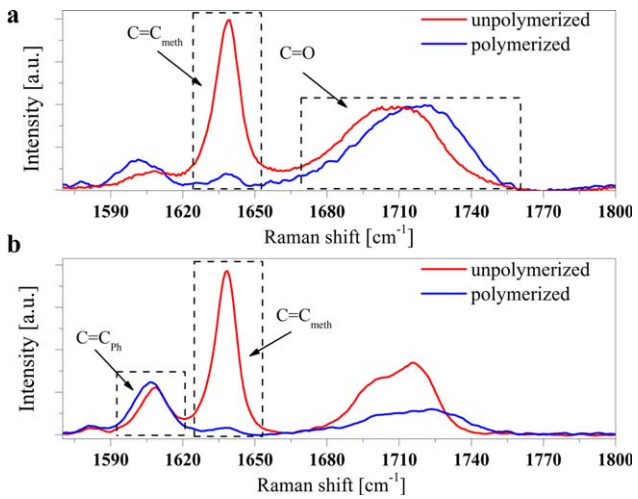

Figure 4. Raman spectra of (a) Riva Light Cure and (b) the HA composite in the Raman shift region between 1570 and 1800 cm^{-1} before and after 20 s of curing. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

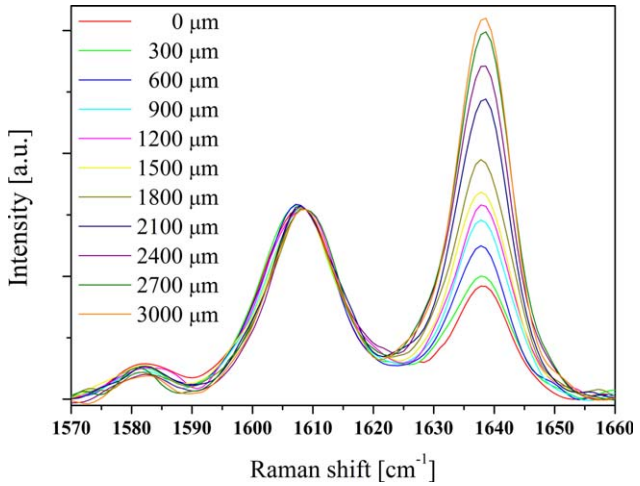

Figure 5. Intensity changes of the band corresponding to the double methacrylic bonds (at 1638 cm^{-1}) and the reference band corresponding to the double aromatic bonds (at 1608 cm^{-1}) as a function of the HA composite depth after 20 s of curing. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

did not change its intensity with the depth of the material. The intensity of the band corresponding to the double methacrylic bonds (at 1638 cm^{-1}) increased with the depth of the material. This means that the number of these bonds also increased with this depth and resulted in the decrease in the value of DC in depth. We envisaged that the DC value would decrease in the direction from the cured surface to the depth of the material. This was confirmed by the results presented in Figures 6–11. The values of DC and the depth after each curing time are given in Figures 6–10 for each of the examined materials separately. These figures show the dependence of DC on the depth of the material. The vertical lines indicate the DOC values; the solid line is the minimal value required by ISO 4049 DOC, whereas the dotted lines are the DOC values obtained after each curing time (highlighted on the graphs). Because DC was

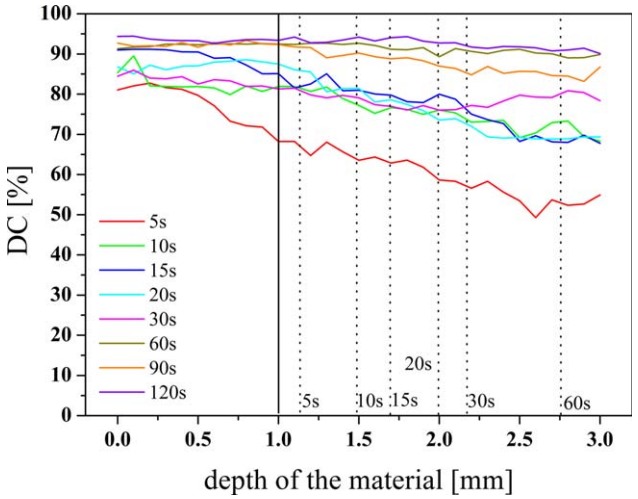

Figure 7. Dependence of DC on the material depth for different curing times for the HA composite. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

measured at a maximum depth of 3 mm, only the values of DOC ranging from 0 to 3 mm were placed on the graphs. The maximum depth of 3 mm was used because only thin layers of dental restorative materials were in use, also in deeper cavities (incremental technique of placement). Bulk fill is appropriate only in the case of shallow cavities,[73] so the thicker layers were not in use. A longer curing time produced a restorative layer cured at greater depths, but the temperature effect was also significant. A considerable temperature rise during polymerization may damage the pulp in the tooth structure, so the application of shorter curing times, which produces smaller temperature effects, is crucial.[74] In Figures 6–10, a visible decrease in DC with the depth of the material was observed in some cases. In the case of the BG composite (Figure 6), these significant changes in DC were observed for samples cured for 5 and 10 s. Curing this material for longer curing times provided a more stable course of this dependence; much lower changes in the

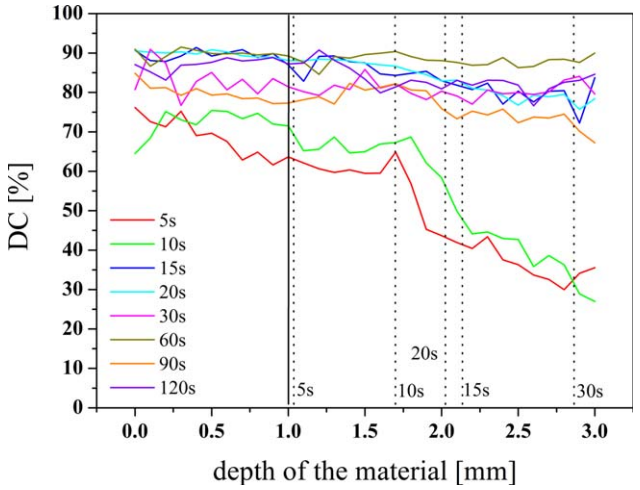

Figure 6. Dependence of DC on the material depth for different curing times for the BG composite. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

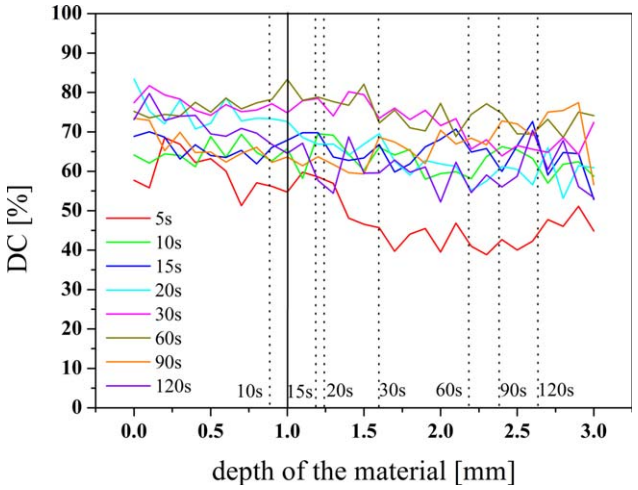

Figure 8. Dependence of DC on the material depth for different curing times for the TCP composite. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

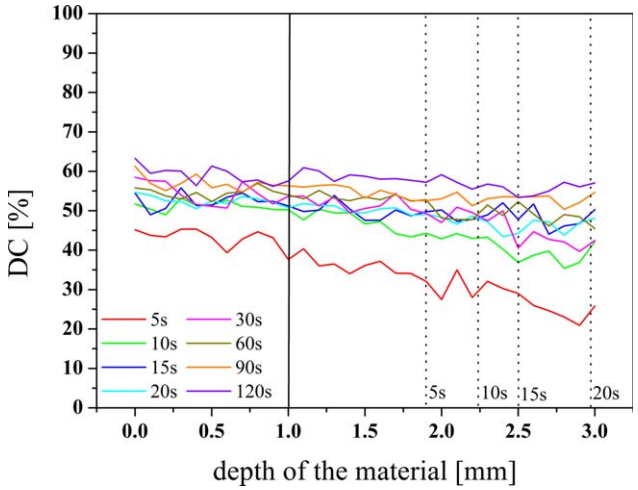

Figure 9. Dependence of DC on the material depth for different curing times for Charisma. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

DC values between different depths of the material were observed. DC demonstrated comparable values throughout the depth on quite a similar level for all of the remaining curing times (15, 20, 30, 60, 90, and 120 s). This means that the curing of the BG composite even at 15 s allowed us to obtain the material polymerized on a very high level in its whole depth. Figure 7 presents the DC changes with the depth of HA composite. We observed that the dynamic decrease in the DC values with depth of the material occurred for short curing times (5, 10, 15, and 20 s), whereas samples cured for 30 s showed a more stable curve course. Much higher DC values were observed after 60, 90, and 120 s of curing. After these curing times, DC changed it values with depth only slightly. As shown in Figure 8 (TCP composite), it was very difficult to observe any tendency of DC with depth. A large DC changed between every subsequent point was noticed. There were also decreases and increases in the DC values without any tendency. However, the overall level of DC could be considered kind of stable (with the exception of the samples cured for 5 s, for which a clear decrease in the DC values on depth was observed). DC changes with the depth of the commercial restorative material Charisma were rather small (Figure 9). The DC versus material depth dependency was most stable in all of examined materials for all curing times, with exception of those cured for 5 s. However, the DC values were much lower compared to those in all of the other materials. This could have been caused by the consistency of this material. Before the polymerization process, this material was the most dense. The migration of the radicals in that viscous environment could be difficult, so the DC was not very high when the material was cured. Among the two examined commercial materials, the Riva Light Cure exhibited higher values of DC (Figure 10). However, the DC changes with depth were higher for this material when compared with those for Charisma. A decrease in DC was observed in the case of nearly all of the applied curing times. Significant changes occurred after 5, 10, 15, 20, and 30 s of curing, whereas DC decreases after longer curing times were only slight. A comparison of the DC values versus the depth for the examined materials after 20 s of curing is shown in Figure 11. The greatest DC values was observed for the BG composite, whereas the smallest was observed for Charisma. These values obtained after the polymerization of the HA composite were also high, whereas in the case of the TCP composite and Riva Light Cure, the most dynamic changes were observed. The most stable DC seemed to occur in the case of the BG composite, the HA composite, and Charisma. It was somehow surprising because the glass fillers were characterized by a higher light transmission than the calcium phosphate fillers. The lowest DC values for Charisma were probably caused by the consistency of this material, as mentioned earlier. However, it did not explain the low DC values for Riva Light Cure because this material was liquid. It also should be noted that the filler loading of the TCP composite was 20 wt %; this was higher than that of the HA composite.

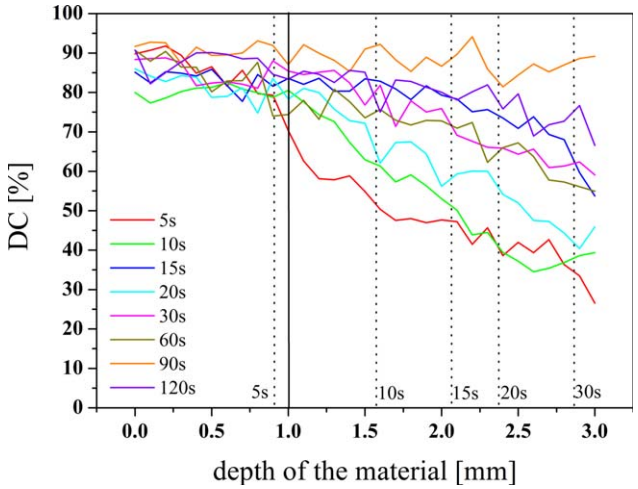

Figure 10. Dependence of DC on the material depth for different curing times for Riva Light Cure. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

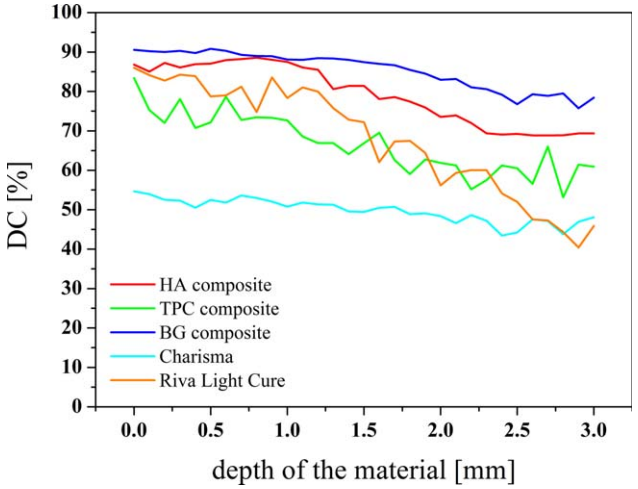

Figure 11. Comparison of the studied materials based on DC versus the depth after 20 s of curing. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table I. DOC of the Examined Materials and Corresponding DCs

Curing time (s)	Material											
	BG composite		HA composite		TCP composite		Charisma		Riva Light Cure			
	DOC ± SD (mm)	DC ± SD (%)	DOC ± SD (mm)	DC ± SD (%)	DOC ± SD (mm)	DC ± SD (%)	DOC ± SD (mm)	DC ± SD (%)	DOC ± SD (mm)	DC ± SD (%)
5	1.01 ± 0.25	63.62 ± 18.61	1.13 ± 0.20	68.24 ± 3.24	—	—	1.66 ± 0.18	37.17 ± 3.69	0.89 ± 0.17	79.31 ± 17.23
10	1.72 ± 0.21	67.27 ± 16.52	1.49 ± 0.16	77.19 ± 3.01	0.89 ± 0.25	62.63 ± 13.11	1.85 ± 0.28	44.25 ± 5.88	1.59 ± 0.20	61.31 ± 6.72
15	2.05 ± 0.24	82.95 ± 1.54	1.68 ± 0.22	79.74 ± 5.61	1.20 ± 0.28	69.79 ± 12.36	2.23 ± 0.22	47.78 ± 3.89	2.11 ± 0.24	78.32 ± 8.54
20	2.04 ± 0.24	82.93 ± 5.67	1.97 ± 0.11	73.56 ± 2.85	1.19 ± 0.23	66.88 ± 2.86	2.50 ± 0.21	44.2 ± 1.96	2.37 ± 0.28	54.14 ± 8.32
30	2.81 ± 0.14	83.13 ± 11.23	2.15 ± 0.19	77.21 ± 3.54	1.70 ± 0.34	76.04 ± 7.51	2.90 ± 0.27	39.67 ± 6.27	2.84 ± 0.25	61.32 ± 6.77
60	—	—	2.77 ± 0.16	89.01 ± 0.66	2.22 ± 0.31	74.44 ± 5.29	—	—	—	—
90	—	—	—	—	2.39 ± 0.40	84.17 ± 7.18	—	—	—	—
120	—	—	—	—	2.64 ± 0.35	85.45 ± 9.27	—	—	—	—

SD, standard deviation.

DOC and the corresponding DC values after each curing time are presented in Table I. These results were obtained for depths of 0–3 mm. In all cases, the DOC values increased with longer curing times. This corresponded to greater values of DC, but it was not a rule. Deviation from that rule was observed in case of Riva Light Cure, but the standard deviations were also significant. Generally, longer curing times provide deeper curing (DOC values) and a higher reaction rate (DC). A 20-s curing time, which is most frequently recommended by the manufacturers of commercial restorative materials, provided sufficient curing for all of the examined materials. After this time, all of them showed a higher than required DOC (>1 mm) and a high value of DC (>80% for the BG composite, >70% for the HA composite, >66% for the TCP composite, >44% for Charisma, and >54% for Riva Light Cure). The lowest DC values obtained after 20 s of curing were found for the commercial materials Charisma and Riva Light Cure: 44.2 (±1.96) and 54.14 (±8.32), respectively. This suggested that the experimental materials were characterized by DC values sufficient for clinical applications. However, further investigation of experimental restoratives are required. We also noted that a curing time of 20 s provided a higher degree of hardening (DOC values) for commercial materials with less progress of the reaction (DC values) in comparison to the experimental materials. For each of the examined materials, the DC values increased with increasing DOC value. However, some materials characterized by high DOC values showed low DC values (e.g., Charisma) and vice versa (e.g., TCP composite).

CONCLUSIONS

The results of this study show the subjectivity of the ISO 4049 method for examining DOC. We also observed that the prolongation of the curing time results in higher values of DOC. This trend proved to be logarithmic. The highest DOC values were observed in the case of glass-filler-containing materials in comparison to the calcium phosphate filled composites. This was probably caused by the characteristics of the applied fillers (transparency, filler content, and particle size). The minimal DOC value required by ISO was achieved for all of the examined materials after only 10 or 15 s of curing. The Raman bands corresponding to the double methacrylic bonds changed their intensity, depending on the progress of polymerization, so they could be used to monitor the reaction. DC decreased with the depth of the materials, especially those cured for shorter times. The highest DC values were obtained for the experimental materials. This means that these materials reacted to a greater degree than commercial ones. A curing time of 20 s was sufficient for achieving an appropriate DOC (minimum = 1 mm) and a high DC (greater than for the examined commercial restoratives) of the experimental materials. This suggests that experimental materials should be further investigated to give some hope for potential clinical applications. A longer curing time provided deeper curing (DOC values) and a higher reaction rate (DC), but the highest DC values were not correlated with the highest DOC values in this experimental group. Moreover, our results show also that Raman spectroscopy is a precise method that could be used to characterize this type of material.

ACKNOWLEDGMENTS

This article was produced with the financial support of the National Science Center (contract grant number 2012/05/N/ST8/03575), and this support is gratefully acknowledged.

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