Acta Odontologica Scandinavica, 2013; 71: 215–222

informa
healthcare

ORIGINAL ARTICLE

Filler morphology of resin-based low-viscosity materials and surface properties after several photoactivation times

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Abstract

Aim. This study aimed to characterize the morphology of filler particles and to analyze the effect of shortened and extended photoactivation times on hardness (VHN) and cross-link density (CLD) of resin-based low-viscosity materials. ***Methods.*** Sixteen commercially available materials were tested: four fissure sealants (Alpha Seal, Fluroshield Yellowed, Bioseal and Fluroshield White) and 12 flowable composites (Opallis T, Permaflo T, Opallis A2, Natural Flow A2, Master Flow A2, Permaflo A2, Filtek Z350 A2, Natural Flow O, Master Flow OA2, Opallis OA3.5, Filtek Z350 OA3, Opallis OP) at six curing times (10 s, 20 s, 30 s, 40 s, 50 s and 60 s). Specimens were fabricated ($n = 5$), analyzed by Scanning Electron Microscopy, by VHN and by CLD. ***Results.*** Unimodal and multimodal filler particles sizes with spherical and irregular shapes were observed. Unfilled materials were also detected. There were no differences among curing times for either VHN or CLD. Opallis A2 and Opallis OA3.5 showed the highest VHN at all curing times, whereas Master Flow A2 and Master Flow OA2 presented the lowest VHN. Opallis A2 presented the highest CLD at all curing times and Alpha Seal showed the lowest CLD. ***Conclusions.*** Filler particle morphology differed among the resin-based low-viscosity materials tested. The shortest photoactivation time tested could yield similar VHN and CLD means to those provided by the most extended photoactivation time.

Key Words: *flowable hybrid composite, physical properties, pit and fissure sealants*

Introduction

Resin-based low-viscosity materials such as light-activated fissure sealants and flowable composites are routinely used in dentistry. The efficacy of these materials to prevent dental caries initiation [1] or even to arrest progression of pre-existent lesions [2,3] has been demonstrated. Resin-based low-viscosity materials can also be utilized in the repair of existing tooth restorations [4], in the restoration of non-carious cervical lesions [5] and as class II restoratives in primary molars [6]. Thus, ensuring the beneficial surface physical properties of resin-based low-viscosity materials might improve their performance in the oral environment.

Crucial physical properties of resin-based dental materials are hardness and cross-link density of monomers. Low hardness values are usually linked to poor wear resistance [7] and susceptibility to scratching [8]. In addition, insufficient cross-linking of the polymer matrix may make resin-based materials more sensitive to the plasticizing effect of exogenous substances that contain a variety of chemicals, e.g. acids, bases, salts, alcohols, oxygen, etc., which enter the oral environment during eating and drinking [9], compromising its clinical efficacy.

Factors such as material composition, opacity/shade and photoactivation time can interfere upon the characteristics of the polymer network generated after curing, affecting hardness and cross-link density

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(Received 24 October 2011; revised 2 December 2011; accepted 21 December 2011)

ISSN 0001-6357 print/ISSN 1502-3850 online
DOI: 10.3109/00016357.2012.654613

[10,11]. Resin-based low-viscosity materials with different monomers, filler content and opacities are commercially available. It has been shown that an extended curing time (60 s) can improve hardness and cross-link density of a yellowed flowable composite (Permaflo) in comparison with shortened curing time (20 s), although no positive influence was found for an opaque fissure sealant (Fluroshield) [11]. However, there is the need to evaluate a higher amount of commercial brands, including translucent materials, and a greater amount of shortened and extended photoactivation times. Moreover, the filler particles characteristics of dental materials, especially the morphology, play a significant role in their mechanical behavior [12,13]. Nevertheless, little else is known concerning filler particles shapes and cross-link density of contemporary commercially available resin-based low-viscosity materials.

Therefore, this study aimed: (1) to characterize the morphology of filler particles of 16 resin-based low-viscosity materials; and (2) to evaluate the hardness and cross-link density of 16 resin-based low-viscosity materials as influenced by shortened and extended photoactivation times. The null hypotheses tested were: (1) there is no difference in filler particles among the materials; and (2) there is no difference in hardness and cross-link density among the materials and photoactivation times.

Materials and methods

Experimental design

For hardness (VHN) and cross-link density (CLD) assessments, the factors under study were *materials* at 16 levels: four fissure sealants (Alpha Seal, Fluroshield Yellowed, Bioseal, and Fluroshield White) and 12 flowable composites (Opallis T, Permaflo T, Opallis A2, Natural Flow A2, Master Flow A2, Permaflo A2, Filtek Z350 A2, Natural Flow O, Master Flow OA2, Opallis OA3.5, Filtek Z350 OA3, Opallis OP); and *photoactivation time* at six levels: 10 s (12.6 J/cm^2), 20 s (25.2 J/cm^2), 30 s (37.9 J/cm^2), 40 s (50.5 J/cm^2), 50 s (63.2 J/cm^2) and 60 s (75.8 J/cm^2). For filler morphology, the factor under study was only *materials*. The materials' manufacturer, composition, opacities and batch numbers are shown in Table I.

Samples preparation

Cylinder Teflon molds (5 mm diameter × 1 mm height) (Ferramentas ALFA, São Paulo, Brazil) were

Table I. Resin-based low viscosity materials used in this study.

Commercial brand and manufacturer	Opacity/shade	Lot number	Composition
Alpha Seal (DFL, Rio de Janeiro, RJ, Brazil)	Translucent	10040530	TEGDMA (%)*; Bis-GMA (%)*; 2,6 Diurethan (%)*; benzyldimethyl ketal (%)*; canforquinone (%)*; quantacure EHA (%)*
Fluroshield (Dentsply Ind. Com., Rio de Janeiro, RJ, Brazil)	Yellowed Opaque	248206C 13307	Bis-GMA (<5%); UED-BisGMA (<40%); Resins (<10%); PENTA Phosphate (<5%); Glass filler (<30%); Silica amorphous (<2%) (load size: ns); TiO_2 (<3%); NaF (<5%)
Bioseal (Biodinâmica, Ibiporã, PR, Brazil)	Yellowed	04410	TEGDMA (%)*; Bis-GMA (35.6%); silicium dioxide (%)*; sodium fluoride (%)*; calcium fluoride (%)* and catalyst
Opallis (FGM, Joinville, SC, Brazil)	Translucent Yellowed (A2) Opaque (OA3,5) Extra-opaque	151009 140610 150210 290410	TEGDMA (5–10%); UDMA (5–10%); Bis-EMA (5–10%); silanized inorganic load Ba-Al-Si microparticles and SiO_2 in nanoparticles (0.05 and 5.0 μm) (72%)
Permaflo (Ultradent Products, South Jordan, UT)	Translucent Yellowed	B4GS B4CLX	TEGDMA (20%); Bis-GMA (8.5%); Sodium Monoflurophosphate (0.3%); Zirconium filler (68%) (load size: ns)
Natural Flow (DFL, Rio de Janeiro, RJ, Brazil)	Yellowed Opaque (O)	10060693 10020254	Bis-GMA (%)*; dimethacrylate resins (%)*; glass Bo-Al-Si and synthetic silica filler (43%) (load size: ns) and dyes
Master Flow (Biodinâmica, Ibiporã, PR, Brazil)	Yellowed (A2) Opaque	06810 06010	Bis-GMA (34.33%); UDMA (%)*; inorganic filler (35.7%) (load size: ns), pigments and catalysts
Filtek Z350 (3M ESPE, St Jordan, MN)	Yellowed Opaque (OA3)	N136410 N136844	TEGDMA (10–15%); Bis-GMA (10–15%); UDMA (1–5%); silane treated ceramic (52–60%); Silane treated silica (3–11%); silane treated zirconium oxide (3–11%); mean load size (0.01–6 μm); functionalized dimethacrylate polymer (1–5%)

Alpha Seal, Fluroshield and Bioseal are fissure sealants. Opallis, Permaflo, Natural Flow, Master Flow and Filtek Z350 are flowable composites.

TEGDMA, Triethylene Glycol Dimethacrilate; Bis-GMA, Bisphenol A-Glycidyl Methacrylate; UED-BisGMA, Urethane modified Bis-GMA dimethacrylate; UDMA, Urethane Dimethacrylate; Bis-EMA, Etoxilated Bisphenol-A Diglicidil Methacrylate. * The manufacturer did not provide the %; ns: not supplied by the manufacturer.

used to fabricate 480 specimens (n = 5 per group). The low-viscosity materials were injected into the center of the matrix using the disposable tip supplied by the manufacture. Materials surface was covered with a Mylar strip (K-Dent – Quimidrol, Joinville, Brazil) and then photoactivated with the light-emitting diode Coltolux (Coltène/Whaledent, Switzerland; 1264 mW/cm^2).

VHN and CLD assessment

After 24 h, the top surface of specimens were ground with #200-, 400- and 600-grit SiC abrasive (Carborundum, Saint-Gobain Abrasives, Recife, Brazil). Then, each specimen was mounted in an acrylic block and three initial Vickers indentations (MH_i) were made for each specimen with a load of 1 kg over a period of 20 s by means of a hardness tester (Pantec HSV 100A, Panambra, São Paulo, SP, Brazil). All specimens were immersed in absolute ethanol at room temperature and a second Vickers microhardness measurement (MH_f) was performed. Three Vickers measurements were made on the top surface of each specimen as previously described. The CLD was estimated based on the percentage of hardness decrease (%HD) that occurred on the sealant surface as a result of its exposure to ethanol [14,15]. The analysis of MH_i and MH_f was done by the same operator. The results were tabulated and the %HD was calculated using the following equation: $\%HD = 100 - [(MH_f \times 100)/MH_i)]$, where MH_f represents the final Vickers hardness number (VHN) value (after absolute ethanol storage) and MH_i represents the initial VHN value (before absolute ethanol storage).

Filler particle morphology

Five disk-shaped specimens of each material were prepared using cylinder Teflon molds (5 mm diameter × 1 mm height) (Ferramentas ALFA, São Paulo, Brazil) and light-cured for 5 s with the LED light-curing unit Coltolux. Each disk was immersed for 1 week in 2 mL acetone, which was changed daily [13]. Thereafter, the specimens were fixed in metallic stubs, sputter-coated with gold (MED 010; Baltec, Balzers, Leichtenstein) and observed with a scanning electron microscope (XL30, Philips, the Netherlands). Representative areas showing the filler particles were photographed at × 2500 magnifications.

Statistical analysis

The VHN and %HD data were submitted to two-way Analysis of Variance (ANOVA) and Tukey's test using the ASSISTAT Software (Federal University of Campina Grande, Campina Grande, Brazil) at the level of 5%. The filler particles were analyzed descriptively.

Results

VHN

There were no differences among the photoactivation times. For all photoactivation times, Opallis A2 and Opallis OA3.5 composites showed the highest VHN, whereas Master Flow A2 and Master Flow OA2 presented the lowest VHN (Figure 1).

%HD

There were no differences among polymerization times. Alpha Seal showed the highest %HD at all photoactivation times, the lowest CLD. On the other hand, Opallis A2 presented the lowest %HD at all photoactivation times, the highest CLD (Figure 2).

Filler particles

It could be observed that Alpha Seal and Bioseal are unfilled materials. Filtek Z350 A2 and Filtek Z350 OA3 contain multimodal spherical-shape particles. Opallis T, Permaflo T, Opallis A2, Natural Flow A2, Master Flow A2, Permaflo A2, Fluroshield Yellowed, Natural Flow O, Master Flow OA2, Opallis OA3.5, Opallis OP and Fluroshield White presented multimodal irregular-shape particles (Figure 3).

Discussion

Since there were differences among the filler particles morphology of the materials tested, the first null hypothesis was rejected. Despite the materials having shown statistically different VHN and CLD means, all photoactivation times tested provided statistically similar VHN and CLD means for the same material. Thus, the second null hypothesis tested was partially validated.

Filler shape of composite resins is related to other physical/mechanical properties such as Young's modulus and surface roughness. In general, composite resins containing spherical-shape particles can show lower Young's modulus [16], but lower surface roughness [17] than those composite resins with irregular-shape filler particles. Thus, although spherical particles may favor a decrease in composite resin roughness, they also may provide a decrease in Young's modulus. In fact, commercially available resin-based low-viscosity materials with different filler particle shapes and resin matrices were evaluated in this study. In this sense, lower Young's modulus and roughness for Filtek Z350 A2 and OA3.5, which present spherical-shape filler particles, might only be suggested by the present results. Further analyses are necessary to confirm this assumption.

In this study, although the filled materials presented different filler shapes, only multimodal materials were

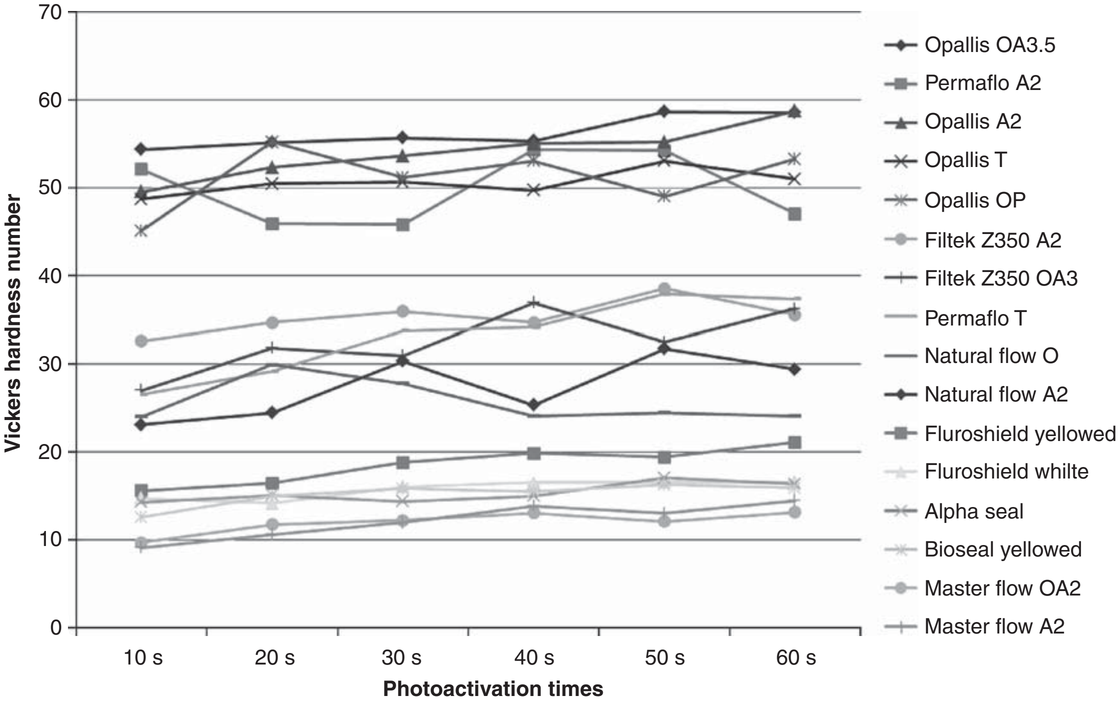

Figure 1. Hardness means of the resin-based low viscosity materials tested at different photoactivation times.

observed. It has been postulated elsewhere that it is uncommon to encounter commercially-available composite resins with just one filler size [16], corroborating the findings achieved in the present investigation. Manufacturers are attempted to include either spherical- or irregular-shape particles with different sizes in composite resins. The concept of multimodal fillers enables the composites to obtain high filler loading and allows a strong integration of small particles into the resin matrix that can be eroded by breaking off small individual particles rather than large ones [18]. In fact, the introduction of finer particles among larger ones will result in reduction of interparticle spacing and the amount of resin

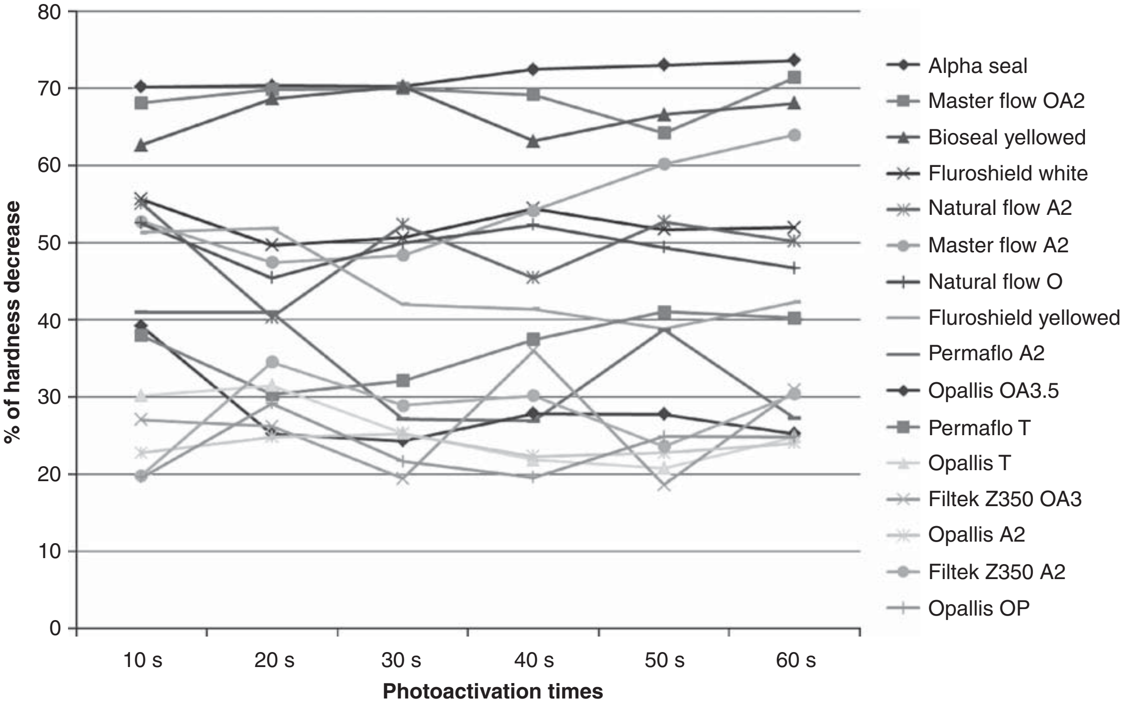

Figure 2. Hardness decrease means (%) of the resin-based low viscosity materials tested at different photoactivation times.

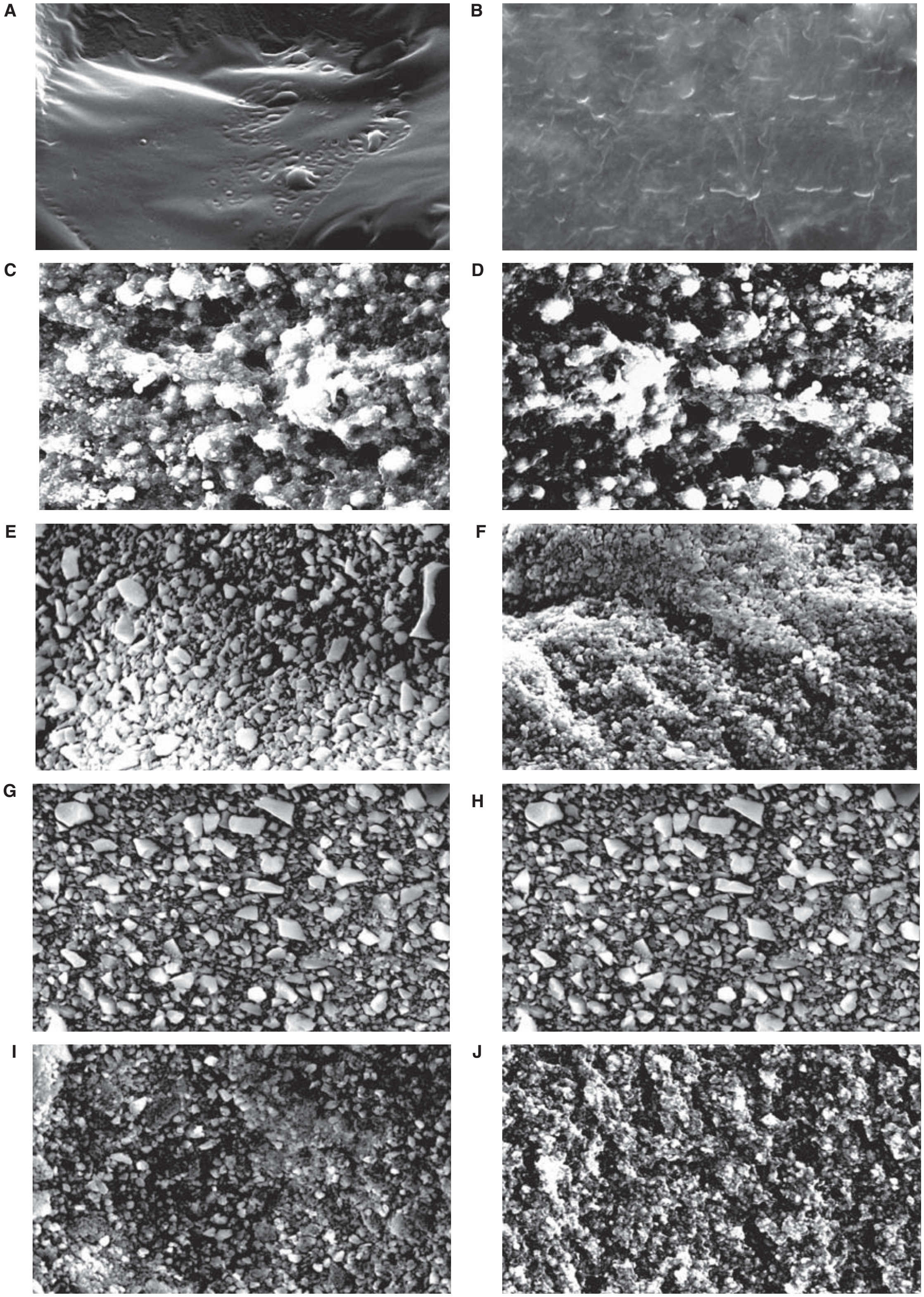

Figure 3. Filler morphology of the resin-based low viscosity materials: (A) Alpha Seal, an unfilled pit and fissure sealant; (B) Bioseal, an unfilled pit and fissure sealant; (C) Filtek Z350 A2, presenting spherical-shape multimodal filler particles; (D) Filtek Z350 OA3, presenting spherical-shape multimodal filler particles; (E) Opallis T, presenting irregular-shape multimodal filler particles; (F) Permaflo T, presenting irregular-shape multimodal filler particles; (G) Opallis A2, presenting irregular-shape multimodal filler particles; (H) Natural Flow A2, presenting irregular-shape multimodal filler particles; (I) Master Flow A2, presenting irregular-shape multimodal filler particles; (J) Permaflo A2, presenting irregular-shape multimodal filler particles; (K) Fluroshield Yellowed, presenting irregular-shape multimodal filler particles; (L) Natural Flow O, presenting irregular-shape multimodal filler particles; (M) Master Flow OA2, presenting irregular-shape multimodal filler particles; (N) Opallis OA3.5, presenting irregular-shape multimodal filler particles; (O) Opallis OP, presenting irregular-shape multimodal filler particles; (P) Fluroshield White, presenting irregular-shape multimodal filler particles.

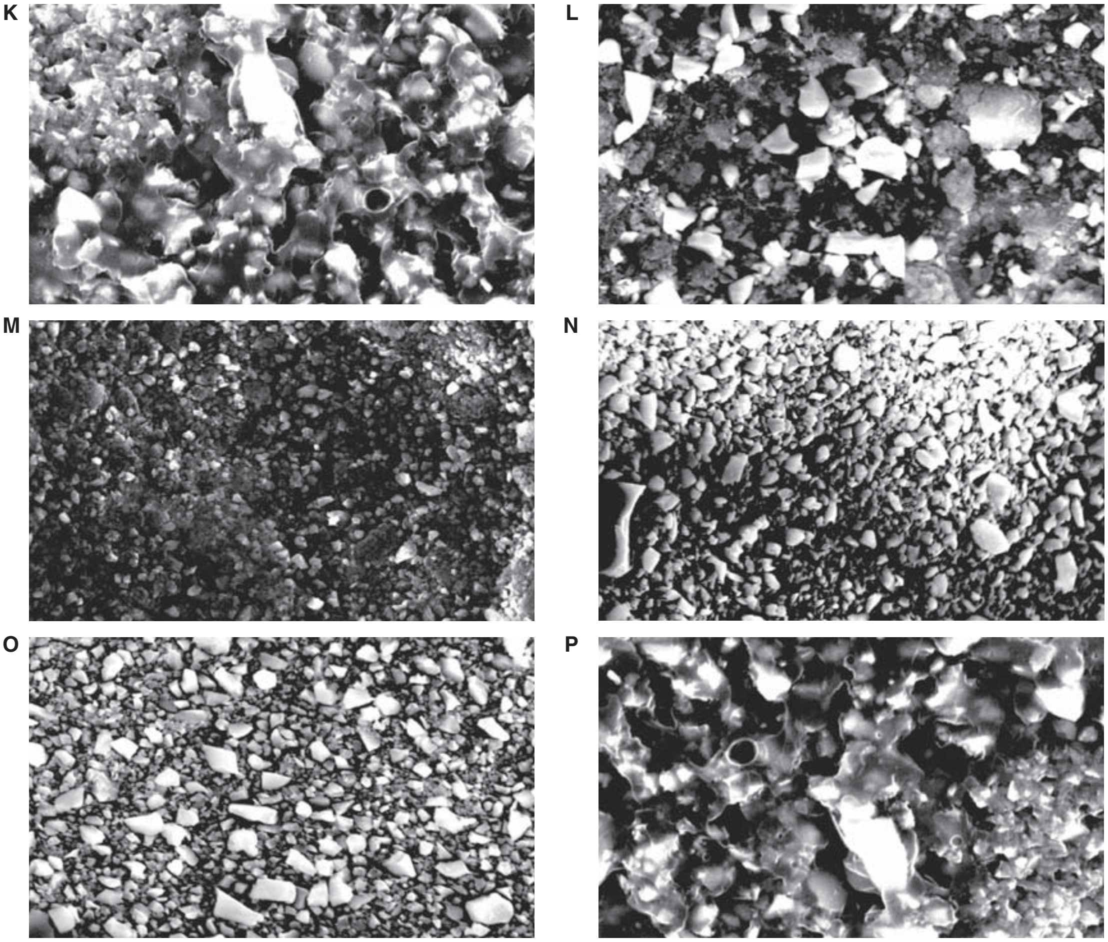

Figure 3. (*Continued*).

matrix, thus maximizing the overall properties of the material [19].

Hardness is a physical property that may be related to the degree of conversion [20] and to the amount of filler particles [21] in composite resins. Thus, a low degree of conversion as well as a relatively low amount of filler particles may have favored Master Flow A2 and OA2 to achieve the lowest VHN means. These resin-based low-viscosity materials present a polymeric matrix based on the Bis-GMA and UDMA monomers, which present high molecular weight and viscosity. It has been shown that, in the absence of low molecular weight and viscosity monomers such as TEGDMA, the mixture of Bis-GMA and UDMA achieves a low degree of conversion [22]. On the other hand, the highest amount of filler particles and a resin matrix based on high and low weigh monomers (UDMA, TEGDMA and Bis-EMA) were found in Opallis T, A2, OA3.5 and OP, justifying the highest VHN means. The fact that at the most experimental conditions Opallis OP showed lower VHN means than the other Opallis brands may be attributed to the presence of extra-opaque pigments in Opallis OP. In comparison with the pigments present in Opallis T, A2 and OA3.5, the extra-opaque pigments present in Opallis OP probably caused more substantial reflection, scattering and absorption of light, preventing more curing through the surface of the material [23].

The fact that hardness is dependent upon the association between the degree of conversion and the amount of filler particles present in resin-based materials could be confirmed by the results of the present study. Both unfilled materials (Alpha Seal and Bioseal) presented statistically higher VHN than the filled Master Flow A2 and OA2. It is likely that the relatively high degree of conversion of the Bis-GMA/TEGDMA resin matrix for Alpha Seal and Bioseal might have compensated for the absence of filler particles, slowly increasing VHN means. On the other hand, the softening test is based on repeated VHN measurements before and after the immersion of the samples in organic solvents such as absolute ethanol [15]. It is generally accepted that highly cross-linked polymers are more resistant to degradation and solvent uptake, whereas linear polymers present more space and pathways for solvent molecules to diffuse within their structure [24]. This could result in increased softening, which can be assessed by a hardness test [25]. Thus, a polymer containing only organic components without filler particles is more susceptible to degradation, especially when a poorly cross-linked network was obtained, justifying the findings that Alpha Seal and Opallis A2 presented, respectively, the highest and the lowest %HD. In this sense, Alpha Seal presented the lowest CLD, and may present a poor clinical performance in comparison with Opallis A2, that presented also the highest cross-link density, predicting a greater clinical performance.

Light energy densities from 12.6 J/cm^2 (10 s of photoactivation) to 75.8 J/cm^2 (60 s of photoactivation) were evaluated in this study using a high-radiance light emitting diode (Coltolux). Probably, 12 J/cm was already necessary to achieve the best conversion and CLD of the resin-based low-viscosity materials on the materials' top, providing similar VHN and CLD means for the materials, regardless of increased energy densities (photoactivation times). This find is of great concern, since it would be beneficial if the photoactivation time of restorative materials can be reduced without adverse consequences [26]. Although further tests to investigate the influence of shortened photoactivation times on other physical properties such as polymerization depth, hardness and CLD are important physical properties of dental materials since their adequate clinical performance is directly dependent on a high hardened and cross-linked polymer network. The results of this study also highlight the importance to evaluate several commercially available resin-based low-viscosity materials, since they present different behaviors due to differences in chemical compositions. Thus, clinicians should attempt to choose suitable materials.

Therefore, filler particle morphology differed among the resin-based low-viscosity materials tested. The shortest photoactivation time tested could yield similar hardness and cross-link density means to those provided by the most extended photoactivation time.

Acknowledgments

The authors thank Vigodent (Rio de Janeiro, RJ, Brazil), FGM (Joinville, SC, Brazil), DFL (Rio de Janeiro, RJ, Brazil) and Biodinâmica (Ibiporã, PR, Brazil) for providing some materials and the curing-light unit used in this study. The authors also show gratitude to NEPGN (Petroleum and Natural Gas Research Center) and to CTPETRO-INFRA I and FINEP/LIEM projects for SEM assistance.

Declaration of interest: The authors report no conflicts of interest. The authors alone are responsible for the content and writing of the paper.

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